

**UTILIZATION OF ZEOLITE INDUSTRIAL WASTEWATER
FOR REMOVAL OF COPPER AND ZINC
FROM COPPER-BRASS PIPE INDUSTRIAL WASTEWATER**

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THUNYALUK MUANGSUWAN

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT
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ABSTRACT

The feasibility of using zeolite industrial wastewater (ZIW) as a sorbent and/or precipitant in removing Cu, Zn, and other pollutants in copper-brass pipe industrial wastewater (CIW) was investigated. The ZIW and CIW were sampled and determined for pH, Temperature, Biochemical Oxygen Demand (BOD₅), Chemical Oxygen Demand (COD), Total solids (TS), Total dissolved solids (TDS), Total suspended solids (TSS) and heavy metals. Sorption isotherms of Cu and Zn in CIW onto solid of ZIW at various dilutions of CIW were explored. The relationship between Cu and Zn concentrations and their removal efficiencies under different conditions of wastewater pH, contact times, and ratios of CIW to ZIW was examined. Optimum treatment condition was selected and used for observation of their influence on the efficiency of treatment of other pollutants.

ZIW contained various carbonate compounds which contributed to high pH and TDS values, and low heavy metals contamination whereas CIW had low pH value and was enriched with heavy metals especially Cu and Zn. Application of ZIW significantly increased the pH of CIW and remove heavy metals. The higher pH of the mixture enhanced metal removal. The Langmuir equation described sorption isotherms of heavy metals by solid of ZIW at neutral pH (6-7) while the Freundlich equation did well at pH values over 12. The maximum Cu (97-98%) and Zn (92-96%) removal efficiencies occurred at non-adjusted pH condition (12.8) of ZIW, ratio of CIW to ZIW 3:1 (vol.:vol.) and 30 minutes of contact time. The efficiency of treatment under these treatment conditions of the pollutants, COD, TS, TDS and TSS was 40%, 2%, 2% and 23%, respectively.

Further study should put an emphasis on increasing the treatment efficiency of TS and TDS. The economic feasibility of using ZIW should also be reviewed together with other significant circumstances.

KEY WORDS: ZEOLITE INDUSTRIAL WASTEWATER/
COPPER-BRASS PIPE INDUSTRIAL WASTEWATER/
HEAVY METALS/COPPER AND ZINC

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การใช้ประโยชน์น้ำเสียจากขบวนการผลิตสารซีโอไลต์ในการบำบัดน้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลือง
(UTILIZATION OF ZEOLITE INDUSTRIAL WASTEWATER FOR REMOVAL OF
COPPER AND ZINC FROM COPPER-BRASS PIPE INDUSTRIAL
WASTEWATER)

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บทคัดย่อ

ศึกษาความเป็นไปได้ในการใช้น้ำเสียจากขบวนการผลิตสารซีโอไลต์เพื่อเป็นวัสดุดูดซับและ/หรือวัสดุตกตะกอนสำหรับการกำจัดทองแดง สังกะสี และมลสารอื่นๆในน้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลือง โดยทำการเก็บตัวอย่างน้ำเสียทั้งสองโรงงานมาวิเคราะห์หาค่าลักษณะสมบัติของน้ำเสีย ศึกษาถึงไอโซเทอมการดูดซับของอนุภาคของแข็งในน้ำเสียจากขบวนการผลิตสารซีโอไลต์ที่ความเข้มข้นของทองแดง และสังกะสีต่างๆ ตามการเจือจางน้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลือง ศึกษาความสัมพันธ์ระหว่างความเข้มข้นของโลหะหนัก และ ประสิทธิภาพการกำจัดที่สภาวะต่างๆ คือความเป็นกรด-ด่าง ระยะเวลาทำปฏิกิริยา และอัตราส่วนระหว่างน้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลืองต่อน้ำเสียจากขบวนการผลิตสารซีโอไลต์ โดยปริมาตร ผลของการศึกษาประสิทธิภาพการกำจัดทองแดง และสังกะสี ที่สภาวะต่างๆนี้จะนำไปใช้เพื่อทราบถึงประสิทธิภาพของการบำบัดมลสารอื่นๆอีกต่อไป

น้ำเสียจากขบวนการผลิตสารซีโอไลต์มีองค์ประกอบของคาร์บอนที่ทำให้ค่าความเป็นกรด-ด่าง ค่าของแข็งละลายทั้งหมดมีค่าสูง และโลหะหนักมีค่าต่ำ น้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลืองมีค่าความเป็นกรด-ด่างค่อนข้างต่ำ และโลหะหนักมีค่าสูง โดยเฉพาะค่าทองแดง และสังกะสี การประยุกต์ใช้น้ำเสียจากขบวนการผลิตสารซีโอไลต์มีผลต่อค่าความเป็นกรด-ด่างของน้ำเสียจากโรงงานผลิตท่อทองแดงทองเหลือง และประสิทธิภาพการกำจัดสารโลหะหนักเพิ่มสูงขึ้นอย่างมีนัยสำคัญ ค่าความเป็นกรด-ด่างของสารละลายผสมที่สูงขึ้นจะทำให้มีการกำจัดโลหะหนักมากขึ้น ไอโซเทอมของการดูดซับสำหรับอนุภาคของแข็งของน้ำเสียจากขบวนการผลิตสารซีโอไลต์อธิบายได้ด้วยสมการของ Langmuir ที่สภาวะความเป็นกรด-ด่างอยู่ช่วงเป็นกลาง (6-7) ในขณะที่สภาวะความเป็นกรด-ด่างที่มากกว่า 12 อธิบายได้ด้วยสมการของ Freundlich โดยประสิทธิภาพในการกำจัดทองแดง และสังกะสีสูงสุด คือ ร้อยละ 97-98 และ ร้อยละ 92-96 ตามลำดับ ที่สภาวะค่าความเป็นกรด-ด่าง ของน้ำเสียจากขบวนการผลิตสารซีโอไลต์ที่ไม่มีการปรับ อัตราส่วน 3:1 โดยปริมาตร ณ. เวลาทำปฏิกิริยา 30 นาที และประสิทธิภาพการกำจัดมลสารอื่นๆที่สภาวะนี้พบว่า การลดค่าซีโอดี ของแข็งทั้งหมด ของแข็งละลายทั้งหมด และของแข็งแขวนลอยทั้งหมด มีค่าร้อยละ 40 2 2 และ 23 ตามลำดับ

การศึกษาในครั้งนี้ต่อไปควรศึกษาการเพิ่มประสิทธิภาพการกำจัดค่าของแข็งทั้งหมด และของแข็งละลายทั้งหมด และควรทำการศึกษาทบทวนความเป็นไปได้ทางเศรษฐศาสตร์ควบคู่กับสภาวะแวดล้อมอื่นๆที่มีผลต่อการใช้ประโยชน์น้ำเสียจากขบวนการผลิตสารซีโอไลต์

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CHAPTER I

INTRODUCTION

1.1 Rational and background

The copper and brass industrial produces plate, sheets, and strips by rolling operations, rods and wire by extrusion and drawing operations, and tubes or pipes by piercing or extrusion and drawing. Among the principal alloys used in these processes is what is called normal brass (2/3 copper and 1/3 zinc, with small amounts of tin and lead). (1) The copper is widely used in the production of wire copper and brass, boiler pipe, cooking utensil, iron and steel industries, rinses and manufacturing of printed circuit. (1) Annealing is done in oil-fired furnaces; the alternate heating and cooling causes a rather heavy oxide scale to form on the surface of the metal. This scale must be removed before the rods, wire, pipe and tube are drawn, to prevent damage to the dies and sheets and so that the scale is not embedded in the final product. This is done by pickling in a bath of 5 to 10 percent H_2SO_4 by volume. Stains, particularly on the finished product, are removed in a bright-dip. (1) The copper-brass pipe production leaving the pickling bath and bright dip tank is washed with fresh water, which eventually overflows to wastewater. These released metallic pollutants together with acidic water quality, which tend to existing in environment, circulating and eventually accumulating throughout the food chain thus posing a serious threat to animals and human. Therefore, the effluent discharged from copper-brass pipe industrial must also comply with the stringent standards of heavy metals and pH. For water quality control, the Effluent Standard of Thailand for the copper-brass pipe industrial was copper not more than 2 mg/L, zinc not more than 5 mg/L and pH 5.5-9. (10)

Typically, it is necessary to pre-treat the wastewater in order to remove some substances such as TDS, TSS and precipitate heavy metal. Many separation and concentration processes are applicable for removing metal from industrial wastewater. The methods commonly used are sorption, chemical precipitation, evaporation, ion-

exchange, reverse osmosis, chemical oxidation-reduction, electrodialysis, electrolytic recovery and evaporation. (3)

Sorption and precipitation techniques are feasible alternatives, where removal of heavy metal cation from solutions is considered attractive because of the relative simplicity of the application. The sorption process is used especially in the water treatment field and investigation has been made to determine good, inexpensive sorbent. Attention has been focused on the various sorbents, which have metal binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost and local availability. Natural materials such as chitosan, zeolites, clay or certain waste products from industrial operations such as fly ash, coal and oxides are classified as low cost and local availability sorbents. (4) Beside this, the precipitation technique is the process, which converts a soluble substance to an insoluble form through the addition of chemicals (precipitant) to a point of supersaturation and results in the formation of an insoluble compound containing the contaminant. The precipitate can then be separated from the wastewater by some physical separation process, such as sedimentation and/ or filtration. The precipitation is also the most widely used process for removal of heavy metals from wastewater. (21)

Zeolites are naturally occurring structure and phyllosilicate minerals, with high cation exchange and ion sorption capacity. (5) Utilization of zeolite in pollution control, including effluent polluted with heavy metals ions has increased recently. Zeolites represent an appropriate material for removing heavy metals ions from wastewater because of their relatively low price coupled with the fact that their exchangeable ions (Na^+ , Ca^{2+} and K^+) are relatively harmless. (6)

There are increasing opportunity to use zeolite as a substitute of phosphate, which has adverse impact on environment for detergent industrial. The zeolite or crystalline aluminosilicate, which composed of silica and alumina, is safe for environment because it degrades to natural substances after being used. To produce zeolite, water is used in the production process and some amount is discharged as wastewater, which its pH is in the alkalinity range (pH 12-13). (Appendix A) The COD and BOD are low but fluoride and TDS are higher than the effluent standard and may cause impacts to environment. However, Sorption and precipitation by using wastewater from zeolite industrial offers certain advantages when compares with other

existing technologies. Thus, measures to deal with this wastewater should put emphasis on reuse it according to a beneficial property of zeolite.

Clean Technology as a strategy to reduce waste from the origin and/or to manage resources effectively, would reduce production cost as well as conserve the environment. Thus, the feasibility of using wastewater from zeolite production process for removing heavy metals from copper-brass pipe industrial wastewater by using sorption and precipitation techniques are aim to investigate. The study explored the sorption isotherm. In addition, heavy metals removal efficiencies from copper-brass pipe industrial wastewater at different pH conditions, contact times and ratios of wastewater from copper-brass pipe industrial to zeolite industrial also studied. Results from this research will enable management approach to reduce the waste effectively and provide wastewater-recycling options by utilizing as a sorbent and/or precipitant for heavy metals contained wastewater.

1.2 Objectives of study

1.2.1 General objective

To determine treatment efficiency of using zeolite industrial wastewater for removal certain pollutants from copper-brass pipe industrial wastewater.

1.2.2 Specific objectives

(1) To study zeolite industrial wastewater and copper-brass pipe industrial wastewater characteristics pH, Temperature, BOD₅, COD, TS, TDS, TSS, Cu, Zn, Cd, Cr, Fe, Hg, Ni, and Pb.

(2) To study heavy metals removal efficiency of copper-brass pipe industrial wastewater by zeolite industrial wastewater at different pH conditions of zeolite industrial wastewater.

(3) To study heavy metals removal efficiency of copper-brass pipe industrial wastewater by zeolite industrial wastewater at different contact times.

(4) To study heavy metals removal efficiency of copper-brass pipe industrial wastewater by using different ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater at selected pH condition and contact time.

(5) To study other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction conditions.

1.3 Hypothesis of study

(1) The heavy metals removal efficiencies would increase with the decreasing pH conditions of zeolite industrial wastewater.

(2) The heavy metals removal efficiencies would increase with the increasing of contact time between zeolite industrial wastewater and copper-brass pipe industrial wastewater.

(3) The heavy metals removal efficiencies would increase with the increasing of ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater.

1.4 Variables of study

1.4.1 Independent variables

1. pH conditions of zeolite industrial wastewater
2. Contact times
3. Ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater.

1.4.2 Dependent variables

1. Heavy metals (copper and zinc) removal efficiencies.

1.4.3 Control variables

1. Temperature (room temperature)
2. Concentration of copper and zinc
3. Speed of reciprocal shaking

1.5 Definition of Terms

1.5.1 **Synthetic wastewater:** The synthetic wastewater, which was prepared from a standard solution of copper concentration 1,000 mg/L and diluted with deionized water.

1.5.2 **Copper-brass pipe industrial wastewater:** The grab sample of wastewater from copper-brass pipe industrial. It produces copper and brass pipes. Major wastewater volume comes from the process of pickling in sulfuric acid and the metals were washed with water. The wastewater contained metals pollutant, copper and zinc, around 491 mg/L and 184 mg/L, respectively.

1.5.3 **Zeolite industrial wastewater:** The grab sample of influent wastewater from zeolite production processes. It is a detergent grade zeolite (zeolite A), producer. The zeolite A is used as a detergent builder for phosphate replacing in detergent formulation.

1.5.4 **pH conditions:** The pH of zeolite industrial wastewater, which was adjusted from 3 to 9 by conc. nitric acid or 1N NaOH and pH 12.8 from the real wastewater of zeolite industrial.

1.5.5 **Contact time:** A reaction time that copper-brass pipe industrial wastewater is contacted with zeolite industrial wastewater by continuous reciprocal shaking at 120 rpm. The studied contact times were 0, 15, 30, 60 and 120 minutes, respectively.

1.5.6 **Ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater:** Ratios between copper-brass pipe industrial wastewater and zeolite industrial wastewater were studied at 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol), respectively.

1.5.7 **Heavy metals removal efficiencies:** The efficiency of zeolite industrial wastewater to remove heavy metals (copper and zinc) from copper-brass pipe industrial wastewater.

$$\text{Heavy metals removal efficiency (\%)} = \frac{[C_i - C_f] \times 100}{C_i} \quad (1)$$

Where: C_i = The initial concentration of heavy metals (mg/L)

C_f = The final concentration of heavy metals (mg/L)

1.5.8 Other pollutants removal efficiencies: The efficiency of zeolite industrial wastewater to remove other pollutants. The studied pollutants were COD, TS, TDS, and TSS.

$$\text{Other pollutants removal efficiency (\%)} = \frac{[C_i - C_f] \times 100}{C_i} \quad (2)$$

Where: C_i = The initial concentration of other pollutants (mg/L)

C_f = The final concentration of other pollutants (mg/L)

1.5.9 Selected reaction condition: The reaction condition (pH, contact time and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater) was selected from the experimental result part 4.3 and 4.4 which gave a highest metals removing efficiency.

1.6 Scope of study

1.6.1 This experiment was conducted at laboratory scale in the laboratory room condition at Department of Environmental Health Science, Faculty of Public Health, Mahidol University.

1.6.2 Zeolite industrial wastewater was collected from zeolite industrial at outlet point of collection tank from production process. The random grab sampling was done 5 times at only period of time. They were fixed with conc. nitric acid for preservation and kept in the refrigerator at 4°C.

1.6.3 Copper-brass pipe industrial wastewater was collected from copper-brass pipe production industrial at outlet point of collection tank from production process. The random grab sampling was done 5 times at only period of time. The samples were fixed with conc. nitric acid for preservation and kept in the refrigerator at 4°C.

1.6.4 Heavy metal removal efficiency was studied for only two metals, copper and zinc.

1.7 Limitation of study

This research used the real wastewater from zeolite industrial and copper-brass pipe industrial. The random sampling would represent characteristics at only period of time. They may not represent the whole wastewater characteristics.

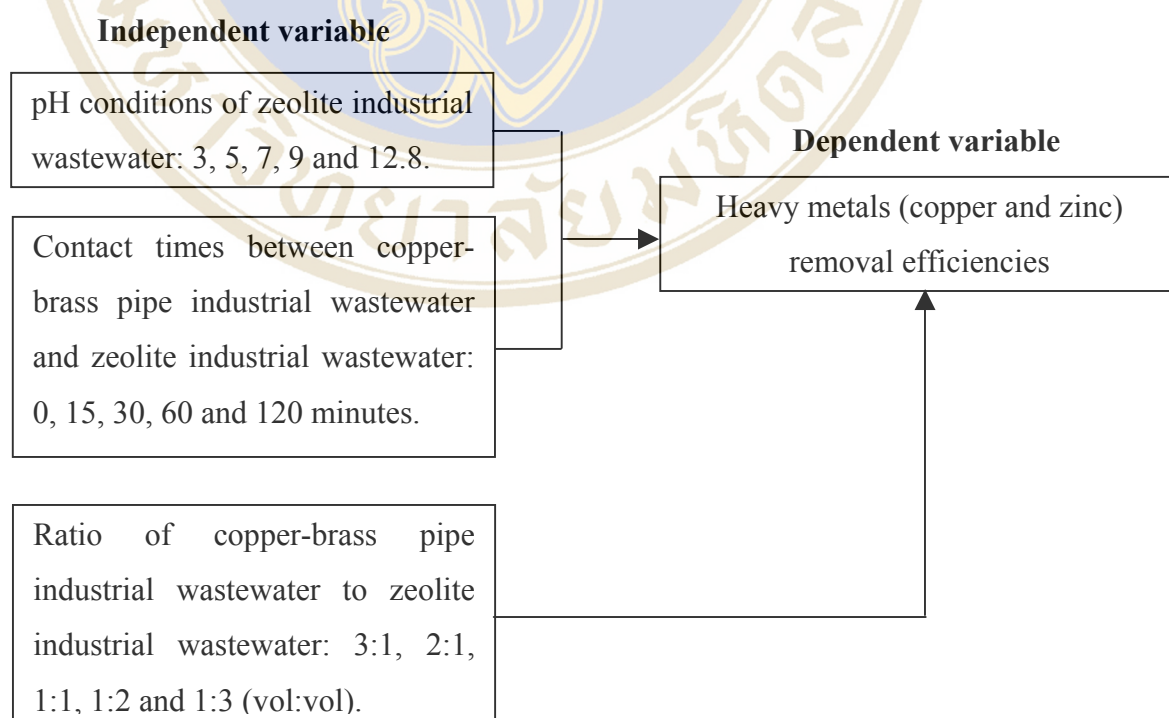
1.8 Expected outcome of study

1.8.1 Acquire basic information for the application of zeolite industrial wastewater in pre - treatment the wastewater containing heavy metals.

1.8.2 If application of this waste minimization technique could significantly reduce heavy metals, thus the cost of heavy metals treatment will properly be reduced.

1.9 Conceptual framework

Determination the appropriate pH, contact times and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater.



CHAPTER II

LITERATURE REVIEW

2.1 Copper-brass pipe industrial

2.1.1 Characteristic of copper-brass pipe industrial wastewater.

In copper-brass pipe industrial operations both chemical and mechanical treatment are conducted on raw materials to produce finished products. Unwanted by-products arise from the working of copper, brass, and other alloys of copper, occur in the process of pickling and washing the metal after hot working and annealing. (2) Annealing is done in oil-fired furnaces; the alternate heating and cooling causes a rather heavy oxide scale to form on the surface of the metal. This scale must be removed before the rods, wire, pipe and tube are drawn, to prevent damage to the dies and sheets and so that the scale is not embedded in the final product. This is done by pickling in a bath of 5 to 10 percent H_2SO_4 by volume. Stains, particularly on the finished product, are removed in a bright-dip. The copper-brass pipe production leaving the pickling bath and bright dip tank is washed with fresh water, which eventually overflows to wastewater. (1)

Major wastewater volume of these industries comes from the process of pickling in sulfuric acid and the metals are washed with water. Characteristics of copper-brass pipe industrial wastewater depend on the use of sulfuric acid and other metals (such as copper, brass and finishing chemicals). It contributes pH value ranged from 1-2, high concentration of heavy metals (copper and zinc) and high TS and TDS. The typical characteristics of wastewater from copper-brass pipe industrial are shown in the Table 1. (Appendix A)

2.1.2 Pollution effects of copper-brass pipe industrial wastewater.

The pollution effects of the wastewater from the washing of copper after pickling in sulfuric acid, besides being acidic in reaction, contain directly poisonous

copper salts; zinc salts and salts of most of the other metals with which copper is alloyed are also poisonous. (2) These released metallic pollutants tend to persist indefinitely in the environment, circulating and eventually accumulating throughout the food chain thus posing a serious threat to animals and man.

Table 1 Typical characteristics of wastewater from copper-brass pipe industrial.

Parameters	Wastewater Characteristic
pH	2
Temperature ($^{\circ}\text{C}$)	33
BOD ₅ (mg/L)	9
COD (mg/L)	21
TS (mg/L)	4,546
SS (mg/L)	10
TDS (mg/L)	4,462
Heavy metals	
- Cu (mg/L)	491.2
- Zn (mg/L)	184.2
- Hg (mg/L)	0.001
- Ni (mg/L)	0.040
- Pb (mg/L)	0.514
- Cr (mg/L)	0.030
- Fe (mg/L)	6.175
- Cd (mg/L)	ND

Remark: ND was not detectable.

Source: (Appendix A)

2.2 Zeolite

2.2.1 Structure and properties (7)

Zeolites are a well-defined class of crystalline naturally occurring aluminosilicate minerals. They have three-dimensional structures arising from a

framework of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ coordination polyhedra (Figure 1) linked by all their corners. The frameworks generally are very open and contain channels and cavities in which are located cations and water molecules (Figure 2). The cations often have a high degree of mobility giving rise to facile ion exchange and the water molecules are readily lost and regained; this accounts for the well known desiccant properties of zeolite.

The word “zeolite” has Greek roots and means “boiling stones”, an allusion to the visible loss of water notes when the natural zeolite are heated. This property illustrates their easy water loss. Easy water loss has been recognized in other materials and many hydrates have been described as having “zeolitic” water.

Many of the natural zeolite can be produced synthetically and several crystalline aluminosilicates with framework structures with no known natural counterpart have been made in the laboratory. The best known example of a synthetic zeolite is zeolite A, which can be related structurally to naturally occurring zeolites and so justify its inclusion as a zeolite mineral. It, like other synthetic zeolites, exhibits the definitive zeolitic properties of ion exchange and reversible water loss.

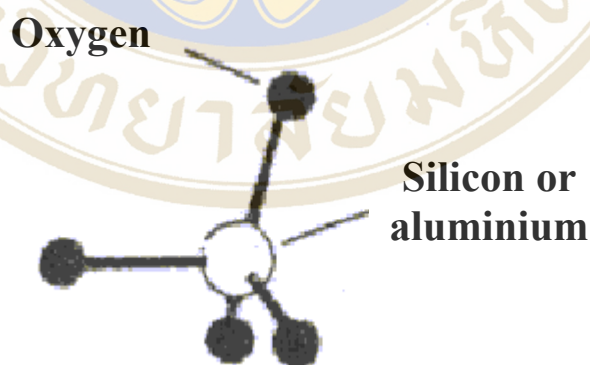


Figure 1 Representations of $[\text{SiO}_4]^{4-}$ and $[\text{AlO}_4]^{5-}$ tetrahedral (7)

Another characteristic zeolite property arises from their molecular framework structures in that the assemblages of tetrahedral creating their porous structure happen to create regular arrays of apertures. These apertures are of such a

size as to be able to selectively take up some molecules into their porous structure, whilst rejecting others on the basis of their larger effective molecular dimensions. This is the property of “molecular sieving”, largely unique to zeolite and responsible for their first commercial success. (7)

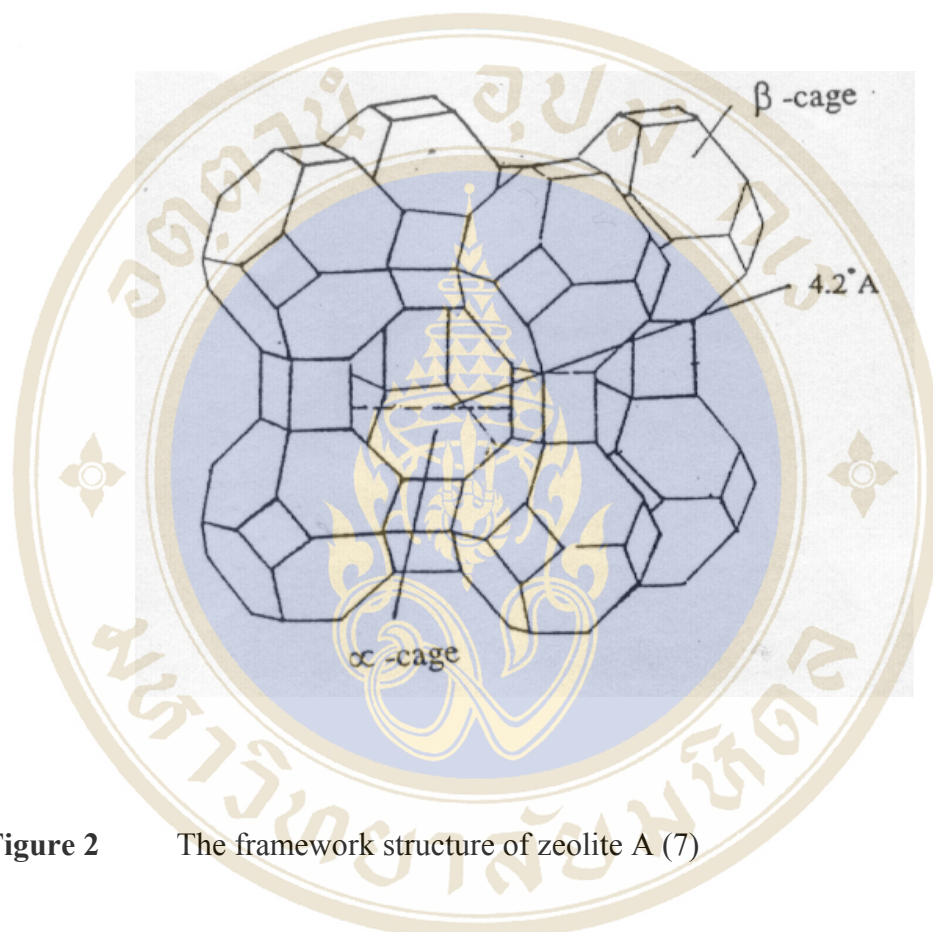
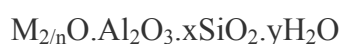


Figure 2 The framework structure of zeolite A (7)

For the definitions of zeolites, zeolites are crystalline framework aluminosilicates based on a three-dimensional network of SiO₄ tetrahedra, with all four oxygens shared by adjacent tetrahedra. Zeolite may be represented by the empirical formular



M is an alkali or alkaline earth cation of n valence, x is a number between 2 and 10, y is a number between 2 and 7. The principle cations are sodium, potassium, magnesium, calcium, strontium, and barium. The cations are loosely bound in the

structure and may be exchanged, to varying degrees, by each other. The framework contains channels and interconnected voids occupied by cation and water molecules. Most zeolites can be reversibly dehydrated. (8)

Zeolites are characterized by the following properties (7):

1. High degree of hydration.
2. Low density and large void volume when dehydrated.
3. Stability of the crystal structure of many zeolites when dehydrated.
4. Cation exchange properties.
5. Uniform molecular-sized channels in dehydrated crystals.
6. Various physical properties such as electrical conductivity.
7. Adsorption of gases and vapors.
8. Catalytic properties.

- Natural Zeolites (7)

Zeolite minerals have been used in many investigations of zeolite structure and properties (adsorption, ion exchange, etc.). The occurrence of zeolites is somewhat paradoxical. Some minerals that occur extensively are not suitable for most known commercial applications (for example, analcime and philipsite). Some synthetic zeolites, which have extensive commercial use, do not have mineral relatives. Other zeolite minerals occur in miniscale quantities.

- Synthetic Zeolites (7)

The synthetic of zeolites was first reported by St. Clair Deville in 1862. By heating aqueous solutions of potassium silicate and sodium aluminate in a glass tube at 170 °C. Deville produced the zeolite levynite. In 1882, De Schulten reported the synthesis of analcime. However, data are not available to substantiate these and other experiments, and much of the early work cannot be duplicated in the laboratory. The first substantiated synthesis of zeolites was not performed until the 1940's when x-ray diffraction was used to identify phases. Prior to this time, light microscopy was used for phase identification, and the fine-grained nature of synthesized zeolites made identification difficult.

2.2.2 Zeolites as components in commercial detergent composition (7)

Some 20 years ago a growing awareness of the environmental damage created by the use of polyphosphates in detergents caused detergent manufacturers to seek less hazardous replacements. The function of the polyphosphate was to ‘build’, i.e. enhance the cleaning efficiency of detergents primarily by removing Ca^{2+} and Mg^{2+} ions from washing water to prevent their precipitation by surfactant molecules. The use of zeolites as builders was suggested in the 1970s and since then it has been demonstrated that they can effectively carry out the water softening exercise needed for successful laundering. All readily available zeolites (natural and synthetic) have been screened as “builders” but the detergent industrial has chosen zeolite A as being the most effective. At present the chemical turnover for A as a builder runs in hundreds of millions of pounds and to date at least two plants have been purpose built to cater for an annual demand estimated at over 500 million tons per annum in 1989.

○ Certainly Zeolite A as synthesized in its sodium form has the appropriate selectivity for Ca^{2+} hardness removal, coupled with the fast exchange kinetics needed to function at normal washing temperatures and cycles. Zeolite A has less success in removing Mg^{2+} , as it has a poor selectivity (over Na and Ca) and unfavourable kinetics for the reasons stated earlier. Usually manufacturers add other “builders” to remove Mg^{2+} - often the undesirable sodium tripolyphosphate – but the sodium form of zeolite X can provide a satisfactory alternative. Some detergent formulations include mixtures of NaA and NaX as builders.

Two interesting side-issues have evolved from zeolite detergent use. Firstly, manufacturers have developed A crystals within tight particle size specifications having a special crystal morphology. In this morphology the more usual cubic habit of A with “salt-like” acute edges and corners has been modified to one with bevelled edges so that it is more readily lost from fabrics during rinse cycles. The second consequence of the use of “builders” is that it has demonstrated that zeolite A has no harmful environmental or human health effects.

2.2.3 Applications of zeolite

By 1980's, 40 natural zeolites had been identified over 100 zeolites had been synthesized. Approximately 163,000 standard of natural and synthetic zeolites

were consumed in the United States in 1980. While synthetic zeolite has been used extensively in commercial applications, demand for natural zeolites has been limited. Their primary use is in areas where the use of synthetic zeolites would be uneconomical. Several uses, both commercial and experimental, include ammonium-ion removal for aquaculture and uranium mine wastewater, odor control for chicken farming and cat litter, and removal of heavy metal ions from nuclear, mine, and industrial wastewater. (8)

2.2.3.1 Industrial uses

Zeolite applications are summarized as follow (8):

Adsorption:

Regenerative processes: Separations based on sieving
Separations based on sieving selectivity.

Purification

Bulk separations

Nonregenerative process: Drying

Windows

Refrigerants

Cryosorption

Ion exchange:

Regenerative processes: NH_4^+ removal

Metal separations,
removal from wastewater.

Nonregenerative process: Radioisotope removal and storage

Detergent builder

Artificial kidney dialysate regeneration

Aquaculture - NH_4^+ removal

Ruminant feeding of nonprotein-nitrogen (NPN)

Ion exchange fertilizers

Catalysis:

Hydrocarbon conversion: Alkylation
 Cracking
 Hydrocracking
 Isomerization

Hydrogenation and dehydrogenation

Hydrodealkylation

Methanation

Shape – selective reforming

Dehydration

Methanol to gasoline

Organic catalysis

Inorganic: Hydrogen sulfide oxidation
 Ammonia reduction of nitric oxide
 Carbon monoxide oxidation

2.2.3.2 Wastewater Treatment (7)

There is a constant need to remove protein breakdown products from water. In regions of the world where clinoptilolite, mordenite, phillipsite and chabazite are available as cheap, relatively pure commodities, they have been much used for the removal of ammonia and ammonium ions from municipal wastewater.

In early studies of the use of ion exchange for wastewater ammonia removal, a permutite type exchanger and various organic resin ion exchange were found to have poor selectivity for ammonia ions resulting in unacceptably low ammonium loadings and low regeneration efficiency, corresponding high costs, and problems of brine disposal. (9)

Clinoptilolite is the most often used – again demonstrating a particular zeolite use relying on a critical specificity for one ion over several more abundant ones. The scale of its use can be large and several designs of wastewater treatment plants using zeolite columns have been produced.

2.2.3.3 Metal Removal, Recovery, and Separations (9)

Many zeolite exhibit high selectivity for various heavy metals and are under consideration for use in recovery of precious and semi – precious metals and for removal of heavy metals from industrial and metals processing wastewater

Because of their availability the zeolites clinoptilolite and mordenite have been studied for heavy metals (especially Cd, Cu, Pb, and Zn) removal from wastewater. The high selectivities of several zeolite ion exchange for Ag^+ also suggests their use for the recovery of silver from wastewater.

Separations and purification of non-ferrous metals may also be accomplished by zeolite ion exchange. For example the unique separation of Co^{++} and Ni^{++} and LINDE Type A zeolite. Many other separations of non-ferrous metals are also possible. Separations of both free and complexed ions may be accomplished, suggesting that zeolite ion exchangers may provide unique new separations and purification in the processing of non-ferrous metals.

2.2.4 Zeolite industrial

In zeolite industrial is producer of detergent grade zeolite (zeolite A), supplying for the detergent manufacturers. Zeolite A was first used to replace phosphate as a detergent builder in detergent formulation.

The zeolite or crystalline aluminosilicate, which composed of silica and alumina, is safe for environment because it degrades to natural substances after being used. To produce zeolite, water is used in the production process and some amount is discharged as wastewater, which its pH is in the alkalinity range. The COD and BOD are low but fluoride and TDS are higher than the effluent standard (10) and may cause impacts to environment.

Major wastewater volume of these industries comes from the zeolite production process. The Characteristics of zeolite industrial wastewater are shown in the Table 2. (Appendix A)

Table 2 Typical characteristics of wastewater from zeolite industrial.

Parameters	Wastewater Characteristic
pH	12.8
Temperature ($^{\circ}\text{C}$)	32
BOD ₅ (mg/L)	68
COD (mg/L)	193
TS (mg/L)	12,571
SS (mg/L)	110
TDS (mg/L)	12,082
Heavy metals	
- Cu (mg/L)	0.070
- Zn (mg/L)	0.121
- Hg (mg/L)	0.001
- Ni (mg/L)	ND
- Pb (mg/L)	0.228
- Cr (mg/L)	0.052
- Fe (mg/L)	0.850
- Cd (mg/L)	ND

Remark: ND was not detectable.

Source: (Appendix A)

2.3 Heavy Metals

2.3.1 Heavy metals

Trace quantities of many metals, such as Nickel (Ni), Manganese (Mn), lead (Pb), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Copper (Cu), Iron (Fe), and Mercury (Hg), are important constituents of most waters. Some of these metals are necessary for growth of biological life, and absence of sufficient quantities of them could limit growth of algae, for example. The presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water because of

their toxicity; therefore, it is frequently desirable to measure and control the concentrations of these substances. (11)

These heavy metals have toxicity both in ions and complex forms. Different metals will be discharge from difference kind of industries. (12) Although conventional treatment technologies for most inorganic pollutants are well established, unusual treatment requirements or wastewater constituents may require unconventional applications. Advanced technologies such as ion exchange, adsorption, and reverse osmosis can be appropriate, but must consider the presence of fouling substances or high background salt levels. (13)

2.3.2 Copper

Copper has been known since early times. It is used to make utensils, electrical conductors, and alloys such as bronze, brass and other copper alloys. (2)

The primary sources of copper in industrial wastewater are metal – process pickling baths and plating baths. Copper may also be present in wastewater from a variety of chemical manufacturing processes employing copper salts or a copper catalyst. (14)

Copper is an essential element, which occurs in all body tissues. However, abnormally high copper levels in liver are characteristic of certain disease state in man, Wilson's disease, or hepatolenticular degeneration comes to mind first of all. Other condition, which manifests increased copper content in liver, includes thalassemia, hemachromatosis, cirrhosis and carcinomas. In addition, too much copper can inhibit growth of bones, reproduction and blood formation. (15) Thus copper concentration in discharge wastewater is not allowed over 2 mg/L. (10)

2.3.3 Zinc

Zinc is an ingredient in alloys such as brass, bronze and German silver. It is used as a protective coating to prevent corrosion of other metals, for galvanizing sheet iron, in gold extraction, in utensils, in dry cell batteries, and as a reducing agent in organic synthesis. Zinc is present in wastewater streams from steelworks, rayon yarn and fiber manufacture, ground wood-pulp production, and recirculating cooling

water systems employing cathodic treatment. Zinc is also present in wastewater from the plating and metal-processing industrial. (14)

Exposure to zinc dust can cause irritation, coughing, sweating, and dyspnea. Toxic effects from inhalation of its fumes include weakness, dryness of throat, chills, aching, fever, nausea and vomiting. Many zinc salts, such as zinc chloride and zinc oxide can produce metal fume fever when the fumes are inhaled. (NIOSH 1986) Thus zinc concentration in discharge wastewater is not allowed over 5 mg/L. (10)

2.3.4 Heavy Metals Removal (3)

Treatment of wastewater may involve the removal of soluble or particulate heavy metals such as lead, copper, zinc, mercury, and chromium. These materials are used in a large variety of industries and are hazardous to the environment because they do not naturally degrade and are toxic even at relatively low concentrations. Fortunately, heavy metals are generally not very soluble in water (depending on the pH, specific metal, such as settling or filtration. The major processes used to treat metal contaminated water include the use of ion exchange resins and the addition of lime to precipitate metal ions. Other, methods include adsorption, electrodialysis, and reverse osmosis are less frequently used. Each process can be summarizing as follows: (3, 32)

2.3.4.1 Precipitation techniques

Precipitation is the treatment process most often employed to remove heavy metals from metal-finishing waste streams. This method is used by a vast majority if the electroplating facilities which treat aqueous metal bearing wastes. The precipitation process is governed by the law of mass action, which affects the equilibrium that exists between crystal of a metal salt compound in the solid state and its ions in solution. Precipitation techniques practiced on aqueous metal wastes include hydroxide (e.g., lime), sulfide (soluble and insoluble), and carbonate precipitation processes. Although most precipitate applications use alkali metal hydroxides or alkaline earth metal oxides as precipitating agents, other metal salts such as $\text{Al}_2(\text{SO}_4)_3$, CaCl_2 or FeSO_4 can be used to coagulate colloidal particles to form diverse ions. However, the process requires excessive amounts of chemicals and the more chemical

use, the more expensive cost. Another disadvantage of the process is poor setting and filtering properties of the sludge.

2.3.4.2 Ion exchange

This is primary use to recover valuable or rare metals and widely applied in the photographic and electronic industries. Another principle application is to trap and prevent the discharge of prohibited element. This is effective process however, when the resin bed is exhausted, it is either regenerated for recovery the resin, or the whole resin column is exchanged for a fresh one. The latter is the more common method, being more convenient for many operators. Moreover, the limitation of this method depends on type of wastewater. If there are calcium or magnesium ions present in water, the metal removal capacity of resins will be affected since the resins can be fouled by precipitates. Besides, ion exchange resins are often high expensive cost and require skills for operation as well.

2.3.4.3 Adsorption

Adsorption (or sorption) is a process that involves the contact of a free aqueous phase with a rigid particulate phase, which has the propensity selectively to remove or store one or more solute (e.g., metal species) present in the solution (wastewater). Usually, the sorbent has a fixed total uptake whereby one solute been fulfilled, back washing or regeneration becomes necessary, since desorption will occur leaching potential pollutants back into solution.

2.3.4.4 Reverse osmosis

Process known as reverse osmosis (RO), in general, be characterized as material separation process. This method is an advanced unit operation in water treatment. RO has also been used by industrial as a pretreatment for ion exchange demineralization. This make used of special membranes. By application of an appropriate pressure, mostly higher than 100 atm, pure water molecules may be made to flow through the membranes while metals are retained.

2.3.4.5 Chemical oxidation-reduction

Chemical oxidation-reduction has been used to treat complex metals such as hexavalent chromium, mercury, copper, soluble lead, and silver. The overall reaction can be defined as a ion exchange in oxidation states where the oxidizing or reducing agent donate an electron in a oxidation-reduction (redox)

reaction. Redox reaction typically occurs in aqueous metal wastes that are relatively devoid of organic compounds. And disadvantages are associated with the use of this process. Cost of the agents depend on the type of wastewater which be treated.

2.3.4.6 Electrodialysis

Electrodialysis is a process in which ions are conveyed through ion-selective membranes from one solution to another under the action of a direct current electrical potential. However, its main advantage is selection of metal to remove but disadvantages of this process include an expensive pretreatment that is needed because the method is sensitive to organic macromolecules and ions, troublesome from high sulfate waters. In addition, the process is a sophisticated one since it requires skilled maintenance, supervision, high construction and operation costs.

2.3.4.7 Electrolytic recovery

This method is electrochemical process to win metals from solutions that plated onto the cathode in a pure form that is periodically removed. Metal recovery better than 99% can be achieved and the cell will recover from metal solutions as low as 20 mg/L (the rate of metal recovery depends on operating condition). Although the recovery of valuable metals, non generation of toxic hydroxide sludge and associated disposal costs, their main disadvantages are electrolytic cells have a high capital cost, energy running and skills are required.

2.3.4.8 Evaporation techniques

This technique may be economically feasible for on-site recycling of metals if there is sufficient metal to recover. The evaporation is a simple process by concentration metals at atmospheric pressure or vacuum pressure. The wastewaters, which are high in metal concentration, are good candidates for volume reduction by evaporation. Thus, the disadvantages of this technique are using large amount of area and high operation cost.

Table 3 Advantages and disadvantages of heavy metals removal technologies.

Advantages	Disadvantages
• Chemical precipitation - Low cost for high volume - Often improve by high ionic strength • Ion exchange - Operates on demand - Relatively insensitive to flow variation - Essentially zero level of effluent contamination possible - Large variety of specific resin available • Adsorption - Operates on demand - Insensitive to flow and total dissolved solids background - Low effluent contaminant level possible • Reverse osmosis - All contaminant ions and must dissolved non-ion are removed - Relatively insensitive to flow and total dissolved solids level - Low effluent concentration possible - Bacteria and particles are removed as well	• Chemical precipitation - Reliable process well suited to osmotic control - Stoichiometric chemical additions required - High-water-content sludge must be disposed off - Part per billion effluent contaminant levels may require two-stage precipitation - Not readily applied to small and intermittent flows - Coprecipitation efficiency depends on initial contaminant concentration and surface area of primary floc • Ion exchange - Spent regenerant must be disposed of - Variable effluent quality with respect to background ions - Usually not feasible at high levels of total dissolved solid - Beneficial selectivity reversal commonly occurs upon regeneration - Potential for chromatographic effluent peaking • Adsorption - Both acid and base are required for regeneration - Slow adsorption kinetics - Spent regenerant must be disposed of • Reverse osmosis - High capital and operating costs - High level of pretreatment required - Membranes are prone to fouling - Reject stream is 20-90 % of feed flow

Source: Clifford et. al., 1986. (3)

However, these traditional technologies are often ineffective as mentioned above. Thus, new technologies are required to decrease metal ion concentrations to environmentally acceptable levels at affordable costs.

Sorption and precipitation by using wastewater from zeolite industrial offers certain advantages when compared with these existing technologies. Especially, as zeolite is rich in this wastewater, which its pH is in the alkalinity range (pH 12-13). This may be valuable to be used as a sorbent and precipitant for heavy metals in copper-brass pipe industrial wastewater. In the wastewater of copper-brass pipe industrial was pH acidity range (pH 1-2) and high concentration of copper and zinc, which several metal ions are sorbed and precipitated with hydrous oxides (22). In addition wastewater of copper-brass pipe industrial treated by hydroxide precipitation. The use of NaOH as the precipitant to remove metals and pH adjustment. Therefore, zeolite industrial wastewater as the precipitant to remove metals. And from properties as a sorbent and a precipitant, it makes the reaction practical and an economically feasible.

2.4 Theory of sorption

2.4.1 Introduction

Sorption processes are very important to the fate and transport of contaminants in the environment and for the removal of contaminants in engineered reactors. *Sorption* is most often defined as the concentration or movement of contaminants from one phase to another phase. *Absorption* involves the partitioning of a contaminant from one phase into another phase. *Adsorption or sorption* can occur between any two surfaces – a liquid and a solid, a gas and a solid, a liquid with another liquid, or a gas and a gas and a solid. Several sorption processes devised by humans including activated carbon sorption for the removal of contaminants from air and water, and ion exchange for removal of contaminants from water have applications in environmental engineering. (16, 17)

The material being concentrated is the *adsorbate* or *sorbate*, and the adsorbing solid is termed the *adsorbent* or *sorbent*. There are three general types of sorption, *physical*, *chemical*, and *exchange* sorption. (17)

- *Physical sorption* is relatively nonspecific and is due to the operation of weak forces of attraction or van der Waals' forces between molecules. Here, the sorbed molecule is not affixed to a particular site on the solid surface but is free to move about over the surface. In addition, the sorbed material may condense and form several superimposed layers on the surface of the sorbent. Physical sorption is generally quite reversible; i.e. with a decrease in concentration the material is desorbed to the same extent that it was originally sorbed.

- *Chemical sorption* (sometimes called chemisorption), on the other hand, is the result of much stronger forces, comparable with those leading to the formation of chemical compounds. Normally the sorbed material forms a layer over the surface, which is only one molecule thick, and the molecules are not considered free to move from one surface site to another. When the surface is covered by the monomolecular layer, the capacity of the sorbent is essentially exhausted. Also, chemical sorption is seldom reversible. The sorbent must generally be heated to higher temperatures to remove the sorbed materials.

- *Exchange sorption* is used to describe sorption characterized by electrical attraction between the sorbate and the surface. Ion exchange is included in this class. Here, ions of a substance concentrate at the surface as a result of electrostatic attraction to sites of opposite charge on the surface. In general, ions with greater charge, such as trivalent ions, are attracted more strongly toward a site of opposite charge than are molecules with lesser charge, such as monovalent ions. Also, the smaller the size of the ion (hydrated radius), the greater the attraction. Although there are significant differences among the three types of sorption, there are instances in which it is difficult to assign a given sorption to a single type.

The most important sorbents for technical application are activated carbon, zeolite molecular sieves, silica gel, activated alumina, activated bauxite, bleaching and decolouring clay, and bone char. The choice of the most suitable sorbent for any specific purpose depends on many circumstances - for example, the total capacity of the sorbent, the sorbent's kinetic properties with respect to sorption, sorbate concentration, the type and degree of the required sorption selectivity, the temperature at which the sorption process is to take place, the magnitude of the heat of sorption and heat conductivity of the sorbent, the sorbent's resistance to temperature, acidic

and basic media, water and mechanical wear, the sorbent's weight – to – volume ratio, possibility and degree of difficulty of regeneration, price and availability of the sorbent, etc. (18)

2.4.2 Sorption equilibrium

Sorption from aqueous solutions involves concentration of the solute on the solid surface. As the sorption process proceeds, the sorbed solute tends to desorb into the solution. Equal amounts of solute eventually are being sorbed and desorbed simultaneously. Consequently, the rates of sorption and desorption will attain an equilibrium state. At equilibrium, no change can be observed in the concentration of the solute on the solid surface or in the bulk solution. The position of equilibrium is characteristic of the entire system, the solute, sorbent, solvent, temperature, pH and so on. Sorbed quantities at equilibrium usually increase with an increase in the solute concentration. (19)

2.4.3 Sorption isotherm

The presentation of the amount of solute sorbed per unit of sorbent as a function of the equilibrium concentration in bulk solution at constant temperature. (19)

The quantity of sorbate that can be taken up by a sorbent is a function of both the characteristic and concentration of sorbate and the temperature. Generally, the amount of material sorbed is determined as a function of the concentration at a constant temperature, and the resulting function is called a sorption isotherm. Equations that are often used to describe the experimental isotherm data were developed by Freundlich, by Langmuir, and by Brunauer, Emmet and Teller (BET isotherm). (11)

Several mathematical models (commonly called isotherm) have been developed to predict the mass of solute removed per mass of sorbent used versus concentration. Two commonly used forms are the Freundlich isotherm and the Langmuir isotherm. Both will be presented here

- **Freundlich Isotherm (16)**

This model, which depicts an empirical relationship, is expressed as

$$q_e = X/m = KC_e^{1/n} \quad (3)$$

where

q_e = mass of solute sorbed per mass of sorbent used [mg sorbed / mg solid]

X = mass of solute sorbed [mg or mol]

m = mass of sorbent [mg]

C_e = equilibrium concentration of solute [mg / L or M]

K = experimental constant

n = experimental constant

The Freundlich equation can be linearized so that a plot of experimental data can be used to determine the parameters K and n . Taking the logarithm of both sides of the equation yields.

$$\log (X/m) = \log K + 1/n \log (C_e) \quad (4)$$

If $\log (X/m)$ is plotted versus $\log (C_e)$, the data should fit a straight line. Otherwise, the Freundlich isotherm is not applicable. If the data generates a straight line, the y-intercept is $\log K$, and the slope of the line is $1/n$.

Data determining sorption characteristics of a contaminant can be obtained by placing a known volume and concentration of the contaminant into several flasks with different amounts of adsorbent. The flasks are then mixed for several days until equilibrium is reached. The final concentration of contaminant in the liquid phase is the measured.

- **Langmuir isotherm (19)**

The basic assumptions underlying Langmuir's model, which is also called the ideal localized monolayer model, are:

- The molecules are sorbed on definite sites on the surface of the sorbent.
- Each site can accommodate only one molecule (monolayer).

- The area of each site is a fixed quantity determined solely by the geometry of the surface.

- The sorption energy is the same at all sites.

In addition, the sorbed molecules cannot migrate across the surface or interact with neighboring molecules. The Langmuir equation was originally derived from kinetic considerations. Later, it was derived on the basis of statistical mechanics, thermodynamics, the law of mass action, theory of absolute reaction rates, and the Maxwell-Boltzmann distribution law. Derived from rational considerations, the Langmuir sorption isotherm is defined as;

$$\frac{x}{m} = \frac{q_{\max} b C_e}{1 + b C_e} \quad (5)$$

Where

x/m = amount sorbate sorbed per unit weight of sorbent (mg/g)

C_e = equilibrium concentration of sorbate in solution after sorption

$q_{\max}$ = the maximum possible amount of solute sorbed per unit weight of sorbent for monolayer coverage of the surface, also called monolayer capacity (mg/g)

b = a constant related to the affinity between the sorbent and sorbate (L/mg)

Equilibrium is reached when the rate of sorption of molecules onto the surface is the same as the rates of desorption of molecules from the surface. The rate at which sorption proceeds, then, is proportional to the driving force, which is the difference between the amount sorbed at a particular concentration and the amount that can be sorbed at that concentration. At the equilibrium concentration, this difference is zero.

Correspondence of experiment data to the Langmuir equation does not mean that the stated assumptions are valid for the particular system being studied because departures from the assumption can have a canceling effect. The constants in the Langmuir isotherm can be determined by plotting $C_e/(x/m)$ versus C_e and making use of equation (5) rewritten as;

$$\frac{Ce}{(x/m)} = \frac{1}{q_{max} b} + \frac{Ce}{q_{max}} \quad (6)$$

The Langmuir equation often does not describe sorption data as accurately as the Freundlich equation. The experimentally determined value of a and b often are not constant over the concentration range of interest, possibly because of the heterogeneous nature of the sorbent surface (a homogeneous surface was assumed in the model development), interaction between sorbed molecules (all interaction was neglected in the model development), and other factors.

The isotherm shape can be used to predict whether a sorption system is favorable or unfavorable in batch process. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by the following relationship (20, 23, 24):

$$R_L = \frac{1}{1 + b C_o} \quad (7)$$

Where R_L is a dimensionless separation factor, C_o is initial concentration (mg/L) and b is the Langmuir constant. The parameter R_L indicates the shape of the isotherm as following;

<i>Values of R_L</i>	<i>Type of isotherm</i>
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

2.4.4 Sorption kinetics (25)

Transport mechanisms. Removal of organic compounds by physical sorption on porous sorbents involves a number of steps, each of which can affect the rate of removal:

- *Bulk solution transport*: Sorbates must be transported from bulk solution to the boundary layer of water surrounding the sorbent particle. The transport occurs by diffusion if the sorbent is suspended in quiescent water, such as in a sedimentation basin, or by turbulent mixing, such as during turbulent flow through a packed bed of GAC, or when PAC is being mixed in a rapid mix or flocculator.
- *Film diffusion transport*: Sorbates must be transported by molecular diffusion through the stationary layer of water (hydrodynamic boundary layer) that surrounds sorbent particles when water is flowing past them. The distance of transport, and thus the time for this step, is determined by the rate of flow past the particle: the higher the rate of flow, the shorter the distance.
- *Pore transport*: After passing through the hydrodynamic boundary layer, sorbates must be transported through the sorbent's pores to available sorption sites. Intraparticle transport may occur by molecular diffusion through the solution in the pores (pore diffusion) or by diffusion along the sorbent surface (surface diffusion) after sorption takes place.
- *Sorption*: After transport to an available site, the sorption bond is formed between the sorbate and sorbent. This step is very rapid for physical sorption, and as a result one of the preceding diffusion steps will control the rate at which molecules are removed from solution. If sorption is accompanied by a chemical reaction that changes the nature of the molecule, the chemical reaction may be slower than the diffusion step and thereby control the rate of compound removal.

The rate at which a solute is removed from solution depends upon the rate coefficients, and upon the departure of the system from equilibrium. Once equilibrium is attained, the transfer of solute from solution to the solid stops. Many works have been completed dealing with the rate controlling mechanism as well as empirical mass transfer kinetics.

2.4.5 Factors which influence sorption testing (26)

2.4.5.1 Characteristic of the sorbate

The chemical character of the sorbate is important for a number of reasons. It is this character which determines the size as well as the configuration of the particular molecule to be sorbed. Molecular size is important for two reasons. First, for any homologous series of organic molecules, as size increase solubility generally decreases. A material, which has low solubility in water, will have a higher affinity for solid surfaces than for the water and will therefore have a tendency to concentrate on those surfaces, i.e., to sorb. Molecular size is also important for the perspective that all sorbents depend upon internal surface area for the full use of their sorption capabilities. If the molecular size is too large, sorption will be hindered and sorption capacity will decrease as very large molecules block or cannot penetrate pores or pathways within the sorbent. One further aspect of molecular size is that larger molecules will tend to diffuse more slowly from solution and therefore will require longer times for full equilibrium sorption capacity to be realized.

The molecular form of the particular sorbate is also of significance. Whether the molecule is in an ionic or neutral state, whether it is a branched isomer or straight chain can have significant effect on the removal of this material from solution by sorption. The molecular form can have consequences affecting the solubility of the sorbate and it can also determine the energy of sorption, i.e., the force with which the particular molecule is held on the sorbent. Further, these characteristics can affect the rate of diffusion of the molecule through the liquid. The rate of diffusion is usually a function of both molecular size and form for a given solvent.

2.4.5.2 Characteristic of the sorbent

The chemical and physical properties of the sorbent used to remove a material from solution are quite important. Chemical properties include the degree of ionization of the surface of the sorbent, the types of functional groups that are present on the sorbent, and the degree to which these properties may be changed by contact with the solution. The presence of ionized or otherwise active functional groups on the sorbent surface allow chemical interactions of “chemisorption” which usually produces effects different from and less reversible than physical sorption. This

effect may be advantageous or not, depending on a particular application. Further, the general ability of the chemical nature of the sorbent to change the chemical characteristics of the solution to be treated can also have either beneficial or adverse effects on the sorption process. This is particularly important where the treated solution is to be reused, or is for human consumption.

The physical properties of the sorbent are like-wise important. The sorbent can be in the form of granules or particles, which may have a density near or very different from the solution to be treated or the sorbent may be in very fine powdered form which may be easily suspended in the solution to be treated. These physical properties have most effect on the selection of the mode of application of the sorption process using that particular sorbent.

Some physical properties such as surface area, size and distribution of pores in the particles directly affect sorption performance by determining the amount of sorbent capacity available and the molecular sizes which can be sorbed.

2.4.5.3 Characteristic of the solution

The three major waste solution characteristics, which have particular impact on sorption, are the solution pH, its temperature and the presence of other competing sorbate compounds.

The pH of a solution is of significance for its effect on the sorbent, as well as on the sorbate. Both sorbate and sorbent may have chemical characteristics, which are affected by the concentration of hydrogen ions (H^+) in the solution. Some sorbents have affinity for H^+ or OH^- ions and can directly affect the solution pH and therefore solubility and sorption capacity. This effect must be considered during test design where large quantities of virgin sorbent may be used per volume of solution. The pH change may not be quite so evident in full-scale operation where large volumes of solution are treated. Thus significant differences between laboratory and full-scale results can be realized. Sorption from solution can be highly pH sensitive in aqueous systems where a sorbate exhibits an isoelectric point or neutral point on the pH scale. It is at this point where maximum sorption can be achieved since solubility is minimized and the non-polar sorbent has greatest affinity for non-ionic materials. In many cases solution pH change is possible in full-scale,

and it is a relatively simple effect to simulate in laboratory testing; it should not be overlooked.

The temperature of a solution has two major effects on sorption. First, the rate of sorption is usually increased at higher temperatures. This is due primarily to the increased rate of diffusion of sorbate molecules through the solution to the sorbent. Further, since solubility and sorption are inversely related, as temperature affects solubility it will therefore affect the extent of sorption or capacity of the sorbent for the particular sorbate. Temperature effects should be simulated carefully in the laboratory to reproduce expected full-scale conditions. In cases where change of process temperature is possible, it should be evaluated for possible beneficial effects.

A major influence of the solution character on sorption is the presence of competing sorbate compounds. Few sorbents demonstrate controllable selectivity for specific compounds and therefore all sorbable compounds present will compete for sorption sites. Further, since physical sorption is a reversible phenomenon, the presence of materials with a particularly high affinity for the sorbent will, under continued application, tend to displace from the sorbent materials of lesser affinity. This effect can result in what is known as a chromatographic effect. For the sorbent system operated in a fixed bed mode, this effect can have particularly dramatic consequences for the quality of an effluent.

2.5 Theory of chemical precipitation

2.5.1 Introduction

Chemical precipitation is the process whereby soluble-phase species are removed from solution by adding a chemical, which converts the contaminant to an insoluble form that can be removed by one of the previously described processes. Precipitation is most commonly used for removal of heavy metals from wastewaters from copper brass pipe industrial, metal plating, the steel and nonferrous industries, the inorganic pigments industry, mining, and the electronics industry. Precipitation is based on altering the chemical equilibrium of the system by exceeding the solubility product for the species. In most cases, this is accomplished by converting the metal to its hydroxide form by the addition of lime or caustic soda, increasing the pH to the point where the metal hydroxide has its minimum solubility.

The minimum solubility pH varies from metal to metal, as can be seen in Figure 3. Many metals have a minimum point, rising in soluble concentration both above and below the minimum pH. This is particularly true for metal hydroxides. Wastewaters with these *amphoteric* compounds often require careful pH control during precipitation to ensure effective removal of the metals. Treatment of wastes containing several metals is difficult because of the varying minimum solubility pH values. A system designed to provide a pH of 9.2, the approximate minimum solubility point for lead and zinc, will allow substantial quantities of cadmium to escape as soluble species. Conversely, a pH of 11 will allow most cadmium species to be precipitated, but lead and zinc will have solubilities in excess of 5 mg/L at this pH.

A solids separation process, such as sedimentation, filtration, or centrifugation, then removes the precipitate. Because metals are conservative, precipitation serves as a concentration process rather than a method of destruction. The product (for example, sludge) formed during the process may be reclaimed if the metals content is sufficient. Otherwise, sludge from the precipitation of a hazardous waste stream must be further treated, such as by solidification, or be disposed as a hazardous waste. (21, 27)

Chemical precipitation is the standard procedure for removal of metals from water and wastewater. Removal is primarily dependent upon two factors: (13)

1. The theoretical solubility of the most soluble solid species formed, which is a function of the solid species (solubility equilibrium constant), pH, and the concentration of the precipitating agent (common ion effect)
2. Separation of the solids from aqueous solution

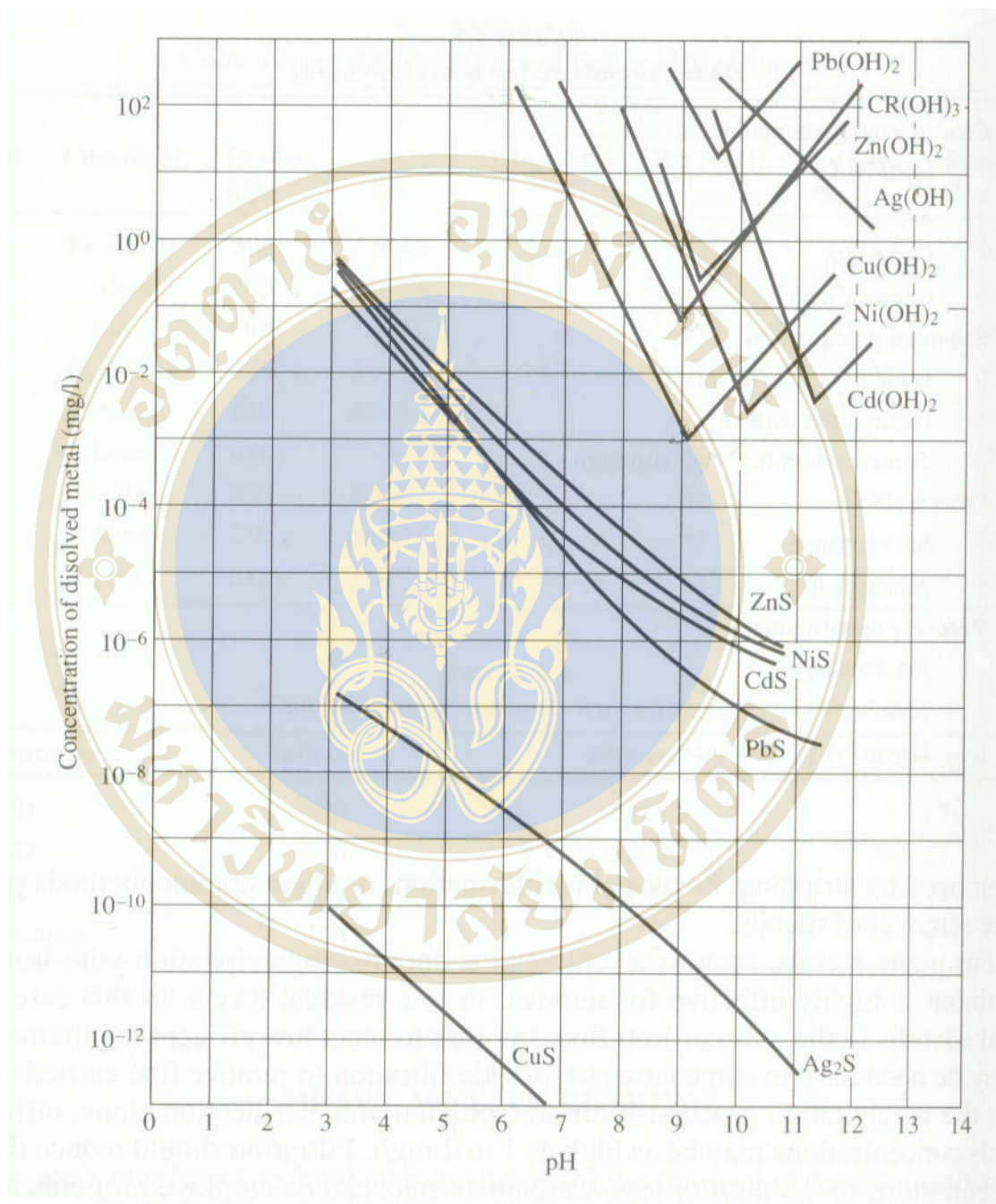


Figure 3 Solubility of metal hydroxides and sulfides as a function of pH. (14)

2.5.2 Factors that influence the solubility of metal ions and precipitates (35)

2.5.2.1 Complex formation

Complex formation in wastewater must be considered to make realistic solubility calculations. Reactions of the cations or anions with water to form hydroxide complexes or protonated anion species are common. In addition, the cations or anions may form complexes with other materials in solution, thus reducing their effective concentration. Soluble molecules or ions, which can act to form complexes with metals, are called ligands. Common ligands include OH^- , CO_3^{2-} , NH_3 , F^- , CN^- , $\text{S}_2\text{O}_3^{2-}$, as well as numerous other inorganic and organic species.

2.5.2.2 Chelating agents

The solubility of metal ions is also increased by the presence of chelating agents. A chelating forms multiple bonds with the metal ion. These bonds essentially form a ring in which the metal ions is held, so that it is not free to form an insoluble salt. Common chelating agents are ethylenediamine tetra acetic acid, citrate, and tartrate.

2.5.2.3 Temperature

Solubility depends on temperature; solubilities of inorganic and metal precipitate generally increase with increasing solution temperatures.

2.5.2.4 Coprecipitation

The actual solubilities of metal precipitates are lower than the theoretical solubilities if coprecipitation occurs. When the presence and precipitation of other metals in solution aid in the removal of target metals through surface sorption, it is called coprecipitation.

2.5.2.5 Oxidation and reduction

Certain metals may require oxidation (e.g., Fe^{2+} to Fe^{3+}) or chemical reduction (e.g., Cr^{6+} to Cr^{3+}) to change the valence state, so that a particular precipitation method can be effective.

2.5.3 Types of chemical precipitation

Applications of chemical precipitation generally focus on the removal of dissolved inorganic ions, particularly heavy metals. It can be used to treat industrial

wastewater and contaminated groundwater. Chemical precipitation can also be used as a pre-treatment technique to remove heavy metals from solution before biodegradation of hazardous organic compounds or metals recovery proposes (if single metal is present in the waste). The following precipitation processes are addressed: (28, 29, 30, 31)

2.5.3.1 Hydroxide precipitation

Hydroxide precipitation involves the use of calcium hydroxide, lime, $[\text{Ca}(\text{OH})_2]$ or sodium hydroxide, caustic, $[\text{NaOH}]$ as the precipitant to remove metals as insoluble metal hydroxides. The reaction is illustrated by the following equation for precipitation of divalent and trivalent metal using lime;



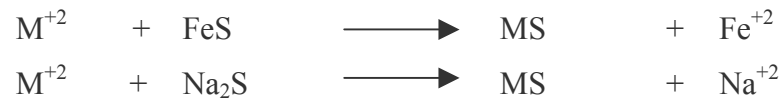
Among the divalent metal ions, which precipitate, as hydroxides are cadmium, copper, iron, lead, mercury, nickel, tin, and zinc. Ions, which precipitate as trivalent hydroxides, are aluminium, chromium, bismuth, gold, iron, antimony and titanium. Silver I, copper I and thallium IV can also be precipitated as hydroxides.

The solubility of metal hydroxides is sensitive to pH, because of its amphoteric property. That is, they can act as either bases or acids. The metal serves as cation in the bases and as part of anion in the acids. In the presence of sufficiently strong base at high pH, the metal hydroxides may dissolve, thus eliminating the hydroxide precipitate. Figure 3 shows how the metal hydroxide solubility varies with pH for a variety of metals. Each metal has its own optimum pH for precipitation, i.e., the minimum in its solubility curve.

2.5.3.2 Sulfide precipitation

Sulfide precipitation has several advantages as an alternative to hydroxide precipitation. It is used to remove lead, copper, silver, cadmium, zinc, mercury, nickel, thallium, arsenic, antimony and vanadium from wastewater. Several source of sulfide have been used including sodium sulfide (Na_2S) or sodium hydrogensulfide (NaHS), which are soluble, and ferrous sulfide (FeS), which is only

slightly soluble. The precipitation of divalent metal ions by ferrous sulfide and sodium sulfide are illustrated by the following equation;



The solubility of metal sulfides, shown in figure 3, are lower than those of corresponding metal hydroxide; the metals sulfides are not amphoteric and hexavalent chromium can be accomplished through reduction and precipitation of the chromium as chromic hydroxide in a single step as follows;



In the soluble sulfide process, either sodium sulfide or sodium hydrogen sulfide, both highly soluble, is added in high concentration either as a liquid reagent or from rapid mixing tanks using solid reagents. This high concentration of soluble sulfide results in rapid precipitation of metals, which results in the generation of fine precipitate particles and hydrate colloidal particles. These fine particles do not settle or filter well without the addition of coagulating and flocculating to aid in the formation of large, fast-settling floc. The high concentration of soluble sulfide may also lead to the generation of highly toxic and odorous hydrogen sulfide gas. To control this problem, the treatment facility must carefully control the dosage e.g. by the use of a specific ion electrode to measure free sulfide. And excess of 0.5 mg/L free sulfide can be successfully maintained by this method and/or the process vessels must be done in closed system with adequate ventilation.

Ferrous sulfide has been found practically as a sulfide precipitant because it is soluble enough to precipitate other heavy metals yet its own solubility is low enough to maintain a very low free sulfide concentration, virtually eliminating the problem of hydrogen sulfide evolution in the reaction tank, and assuring a low concentration of soluble sulfide in the effluent. Because of ferrous sulfide is reactive and therefore unstable. However, it is necessary to generate ferrous sulfide on site. This is accomplished by reacting ferrous sulfate, a soluble sulfide such as sodium

hydrogen sulfide and lime. There is therefore still a potential for hydrogen sulfide generation. Other disadvantages of the insoluble sulfide process include considerably higher than stoichiometric reagent consumption and significantly higher sludge generation than either the hydroxide or soluble sulfide process.

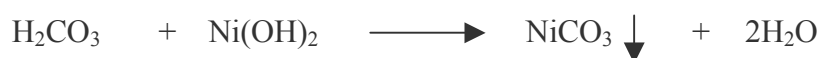
2.5.3.3 Carbonate precipitation

Carbonate precipitation with soda ash (sodium carbonate, Na_2CO_3) or calcium carbonate has proven to be an effective process for removal of cadmium, lead, nickel and zinc. (30, 33, 34) Precipitation as insoluble carbonates tends to occur at more neutral pH condition than with hydroxide precipitation. Carbonate-based reaction mechanism, however, proceeds at a slower pace than the hydroxide-based system. The solubility of soda ash also limits its use because a chemical feed of only 20 percent by weight can be maintained at room temperature without recrystallization. An advantage of soda ash is low sludge generation than hydroxide precipitation. However, this sludge can be difficult to filter. Calcium carbonate sludges show much better filtration properties. The precipitation of metals by sodium carbonate is accomplished as illustrated by the following example, where the M represents a divalent metal:



The process is not effective for all metals. Tests conducted by Patterson et.al. (35) indicated no improvement in effluent quality, operating pH, or sludge characteristics over hydroxide precipitation for zinc and nickel.

Carbon dioxide has also been used to treat metal – containing waste streams. Carbon dioxide gas is injected into the wastewater and upon hydration will form carbonic acid. The carbonic acid will then react with available hydroxides to form the less soluble carbonates as show in the equation:



High reagent cost associated with CO_2 systems make this treatment technique less attractive than conventional systems. Carbonate has proven to

be more effective at removing lead than hydroxide and it is the method of choice if nickel reclamation is deemed appropriate.

2.5.3.4 Sodium borohydride precipitation

Sodium borohydride is an extremely strong reducing agent that can be used to precipitate metals from solution as the insoluble element metal and can be reduced both chelated and non-chelated metals. (30) The pH-dependent reaction for a divalent metal is illustrated by the following simplified equation:



The process is usually carried out in the pH range 8 to 11 to assure efficient utilization of borohydride. At pH below 8, borohydride consumption increases as a result of hydrolysis of the borohydride, while at pH greater than 11 the rate of reaction decreases. The optimum pH is determined by testing to balance borohydride using against reaction time and effluent quality.

Sodium borohydride may be especially advantageous for recovery of metals from waste solutions and effective for removing lead, mercury, nickel, copper, cadmium and precious metals as gold, silver and platinum. Sludge volume reduction of 50 % or more has been reported for the sodium borohydride process over lime precipitation. Sodium borohydride is available as a free flowing active powder or as stabilized water solution of 12 percent sodium borohydride in caustic soda. The caustic soda is generally used because it is easy to handle with standard chemical metering and storage equipment. Sodium borohydride is capable of reducing chromate to the trivalent state before deposition as chromium hydroxide. A major disadvantage is that unless the liquid is removed from the sludge immediately, metals tend to go back into solution with water. Another problem is that pH control is critical. Explosive hydrogen gas is evolved at acidic pH values. The high cost of this reagent currently limits its use in industrial metal-bearing wastewater.

2.5.3.5 Xanthate precipitation

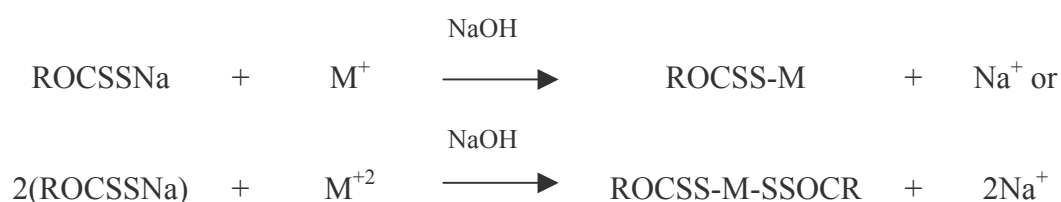
Another approach also effective in precipitating heavy metals from their soluble complexes, involves the use of starch xanthates. (34) Starch that has

treated with cross - linking agents such as epichlorhydrin, POCl_3 , sodium trimetaphosphate, formaldehyde and others is xanthated with carbondisulfide in alkaline conditions and reacted to form an insoluble alkali metal-magnesium starch xanthate. This type of product gives extremely insoluble heavy metal products in the presence of a cation polymer and has shown effectiveness in completing with complexing materials such as NH_3 , EDTA and tartrate, particularly after preliminary acidification of the metal solution to pH 3 to break the complex.

In xanthate treatment, metal contaminants exchange with sodium ions contained in the xanthate material to form an insoluble complex. The xanthate acts as an ion exchange material, removing heavy metals and replacement them with sodium and magnesium. The heavy metals-laden material can be removed from solution by sedimentation and filtration. Compared with metal hydroxide precipitation, xanthate treatment offers the following advantages:

- A higher degree of metal removal,
- Less sensitivity to fluctuations in pH (metal xanthates do not exhibit amphoteric solubilities,
- Less sensitivity to the presence of complexing agents,
- Improved sludge dewatering properties, and
- The capability of selectively removing metals.

This process will probably not be economical for initials metal concentrations exceeding 100 mg/L, although xanthate treatment could be used as a secondary treatment to further lower the metal concentration to below discharge limits. Xanthates are sulfonated organic compounds. The xanthate-metal precipitation process can be represented as follows:



Where M^+ or M^{+2} are the metal ions and NaOH indicates that the reaction occurs at high pH.

CHAPTER III

MATERIALS AND METHODS

3.1 Research Design

This study was laboratory experimental research design. Research models were multiple comparison groups with multiple independent variables. The experimental study was as follow;

3.1.1 Characterization of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

This section was study zeolite industrial wastewater and copper-brass pipe industrial wastewater characteristics. Samples were analyzed for determination of pH, Temperature, BOD₅, COD, TS, TDS, TSS, Cu, Zn, Cd, Cr, Fe, Hg, Ni, and Pb.

3.1.2 Heavy metal removal efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

There were 12 concentrations of copper and zinc in copper-brass pipe industrial wastewater reacted with zeolite industrial wastewater. Experimental conditions were pH of 7 from the adjusted pH of zeolite industrial wastewater and pH of 12.8 from the real wastewater of zeolite industrial at 30 minutes of contact time and ratio 1:1 (vol:vol) of copper-brass pipe industrial wastewater to zeolite industrial wastewater. Each experimental unit was done 3 replications. Thus, total units (12 x 2 x 3) were 72 units.

3.1.3 Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies.

There was one ratio (1:1) volume by volume of copper-brass pipe industrial wastewater reacted with zeolite industrial wastewater at 5 pH conditions (3, 5, 7, 9 and 12.8) and 5 contact times (0, 15, 30, 60 and 120 minute), respectively. Each

experimental unit was done 3 replications. Thus, total units (5x5x3) are 75 units. The detail of experimental units was as following diagram in Figure 4.

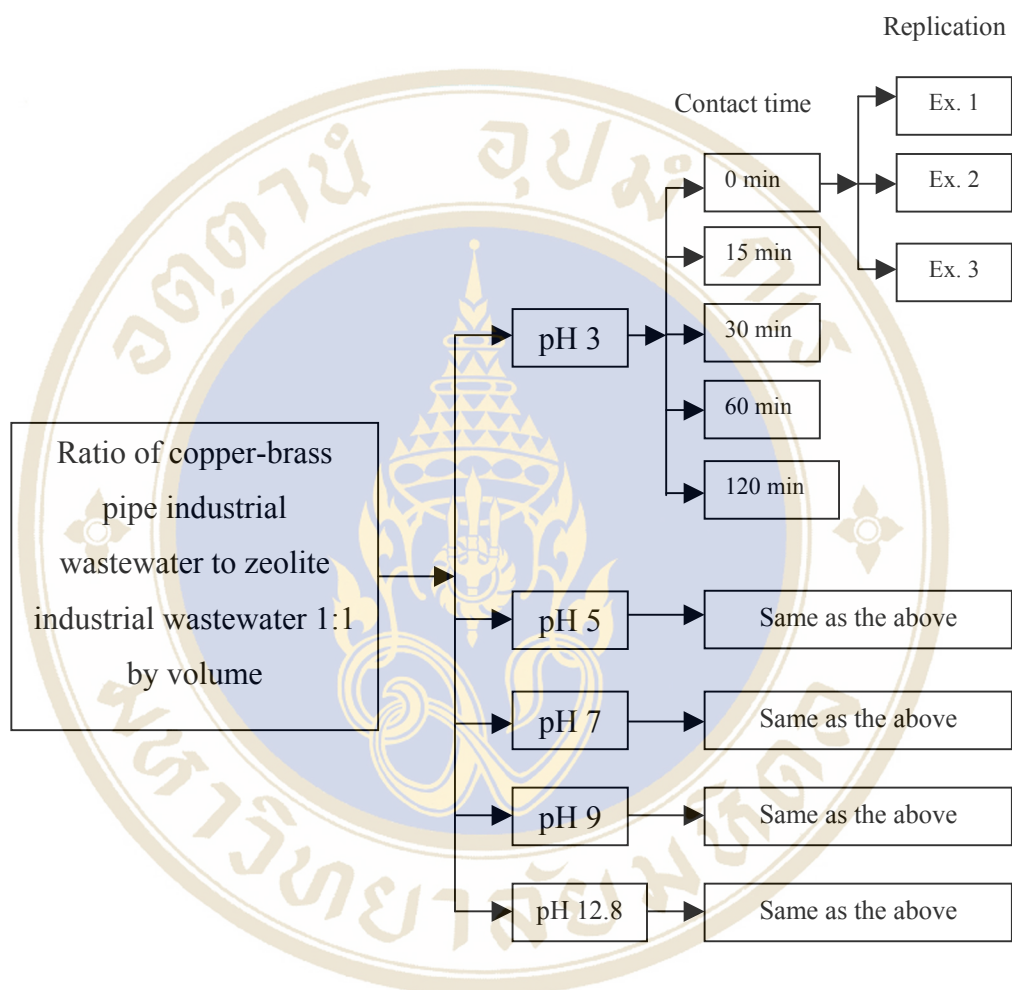


Figure 4 Detail experimental unit diagram of research design 3.1.3.

3.1.4 Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiency.

This section aimed to determine a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for removing heavy metals at chosen pH condition and contact time that gave the highest heavy metals removal efficiencies (from previous study section 3.1.3).

There were five designed ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (3:1, 2:1, 1:1, 1:2, and 1:3 (vol:vol)) reacted at selected

experimental conditions that gave the highest heavy metals removal efficiencies. Each experimental unit was done 3 replications. Thus, total experimental units (5x3) were 15 units. The detail of experimental units was as following diagram in Figure 5.

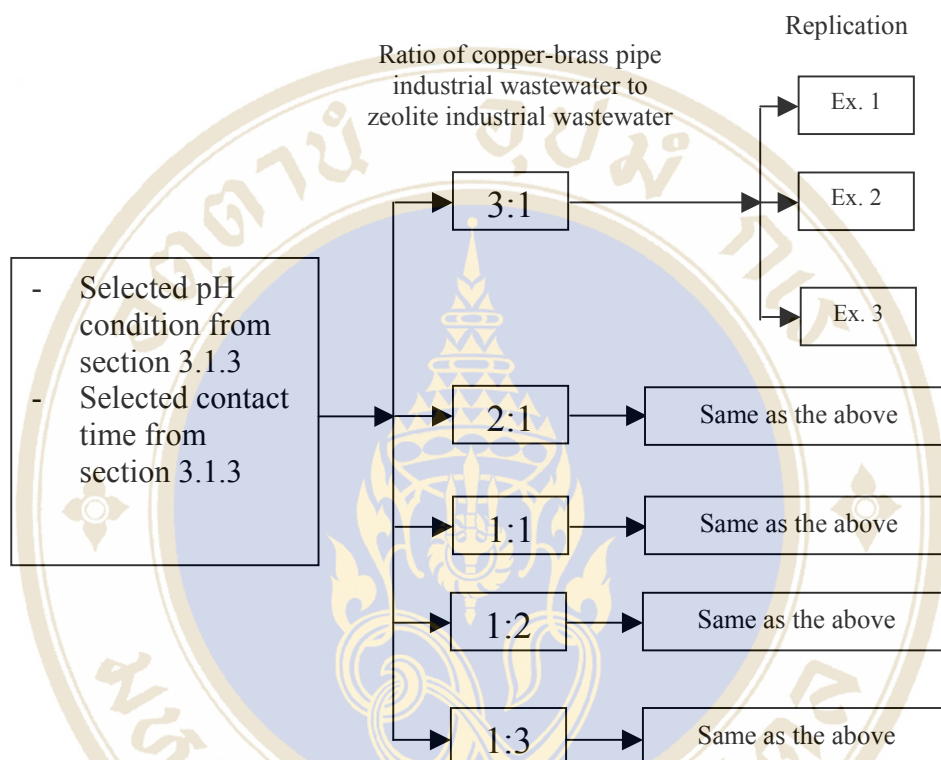


Figure 5 Detail experimental unit diagram of research design 3.1.4.

3.1.5 Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition.

The treatment that has the highest heavy metals removal efficiency from the previous study in 3.1.3 and 3.1.4 was selected as an experimental condition in this study. The other pollutants (COD, TS, TDS and TSS) removal efficiencies of copper-brass pipe industrial wastewater were studied. The detail of treatment was as following diagram in Figure 6.

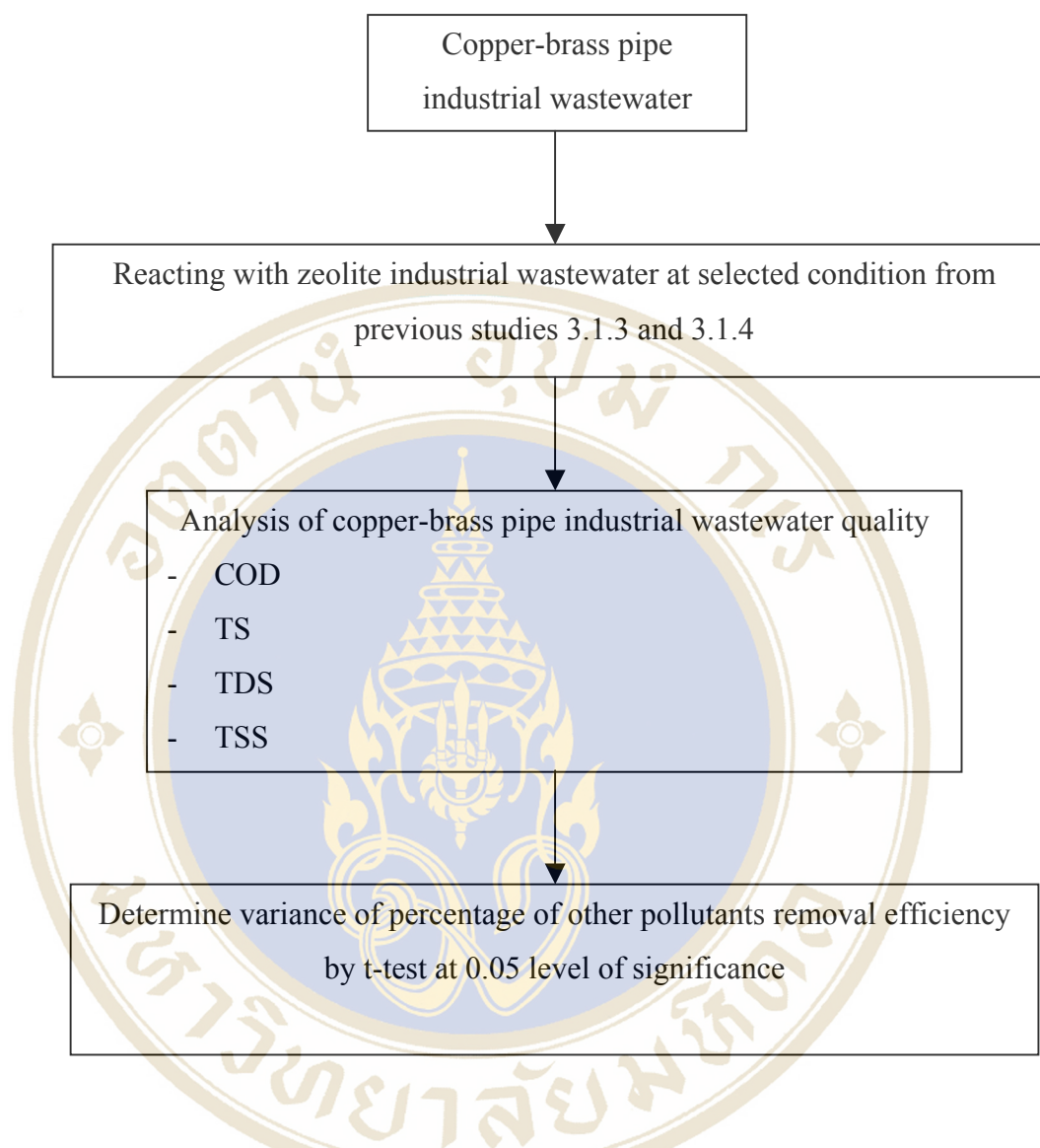


Figure 6 Detail experimental unit diagram of research design 3.1.5

3.2 Place of study

This experiment was conducted in laboratory of Department of Environmental Health Science, Faculty of Public Health, Mahidol University, Bangkok, Thailand.

3.3 Materials, Equipments and Chemical used.

3.3.1 Materials

- Zeolite industrial wastewater
- Copper-brass pipe industrial wastewater
- Distilled water
- Filtering paper GF/C, 47 mm Ø

3.3.2 Equipments

- pH meter (Hanna instruments Model HI8424, Singapore)
- Hot air oven (Memmert Model U30, Western Germany)
- Electrical balance (Mettler B5, Switzerland)
- Analytical balance (Overtling Model RB 153)
- Auto desicator (Sanpla Dry Keeper D-Box and Auto C-series)
- Jar Test Equipment (Phipps & Bird PB-700TM Jartester)
- Reciprocal shaker
- Suction pump
- Syringe 10 mL
- Experimental Glassware
 - BOD bottles and ground joint
 - Beaker size 100, 500 and 1,000 mL
 - Erlenmeyer flask size 250, 500 and 1,000 mL
 - Volumetric flask size 100, 500 and 1,000 mL
 - Burette size 25 and 50 mL
 - Pipette size 1, 5 and 10 mL
 - Cylinder size 25, 50, 100 and 1,000 mL
- Plastic bottles size 120 mL

3.3.3 Chemical used

- Chemical used for Chemical Oxygen Demand (COD) analysis
 - Standard potassium dichromate digestion solution, 0.1 N
 - Conc. Sulfuric acid reagent

- Ferroin indicator solution
- Standard ferrous ammonium sulfate titrant (FAS)
- Chemical used for Biochemical Oxygen Demand (BOD) analysis
 - Manganese sulphate solution
 - Alkaline-iodide azide reagent
 - Conc. Sulfuric acid reagent
 - Soluble starch reagent
 - Sodium thiosulphate solution, 0.025 N
- Chemical used for pH adjustment
 - Nitric acid (HNO_3) 69%
 - Sodium hydroxide (NaOH)
- Chemical used for wastewater digestion
 - Nitric acid (HNO_3) 69%
- Chemical used for synthetic wastewater
 - Copper standard solution

3.4 Research Methodology

3.4.1 Characterization of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

The grab samples of zeolite industrial wastewater and copper-brass pipe industrial wastewater were examined immediately after sampling. In case of time limitation, the samples were fixing with nitric acid for preservation and kept in the refrigerator ($4\text{ }^{\circ}\text{C}$). The selected experimental parameters and their analytical methods are described in Table 4.

3.4.2 Heavy metal removal efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

The study was determined the heavy metals (copper and zinc) removal efficiencies by using solids in zeolite industrial wastewater. There was 2 studied pH condition, which was one pH (12.8) from the real wastewater of zeolite industrial and

pH 7 from the adjusted wastewater pH. The chemical used for pH adjusting was Nitric acid (HNO_3) or Sodium hydroxide (NaOH).

The various concentrations of copper and zinc in copper-brass pipe industrial wastewater were prepared from copper-brass pipe industrial wastewater 1, 5, 10, 20, ... 100 mL and adjusted volume with deionized water to 100 mL. They were then made up to a concentration of copper and zinc solution as showed in Table 5.

Table 4 Parameters and analytical methods.

Parameter	Method of analytical
pH	Electrometric method
Temperature	Thermometer
BOD ₅	Azid modification of the Winkler method
COD	Closed reflux method
TS	Evaporation, then oven dried at 103 – 105 °C
TDS	Filtrate through GF/C, evaporate filtrated water to dryness and then oven dried at 103 – 105 °C
TSS	Filtrate through GF/C, then oven dried at 103 – 105 °C
Heavy metals	Digesting with Conc. HNO_3 , filtering through filter paper No.42 and analyzing by Atomic Absorption Spectrophotometer method (AAS)

Source: Franson MAH, et al. and American Public Health Association (36, 37)

Table 5 The copper and zinc concentrations at various dilutions of copper-brass pipe industrial wastewater.

Copper-brass pipe industrial wastewater (mL)	Copper concentration (mg/L)	Zinc concentration (mg/L)
1	4.91	1.84
5	24.56	9.21
10	49.12	18.42
20	98.24	36.84
30	147.36	55.26
40	196.48	73.68
50	245.60	92.10
60	294.72	110.52
70	343.84	128.94
80	392.96	147.36
90	442.08	165.78
100	491.20	184.20

Zeolite industrial wastewater 100 mL (after adjusted pH) and 100 mL of copper-brass pipe industrial wastewater (various concentrations of copper and zinc in copper-brass pipe industrial wastewater) were reacted in the 500 mL Erlenmeyer flasks then reciprocal shaken at 120 rpm at room temperature. After shaking, they were sampled, filtered by filter paper GF/C with 47 mm Ø and digested by nitric acid for determine heavy metals remaining in solution by Atomic Absorption Spectrophotometer (AAS).

3.4.3 Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies.

The study was determined the effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies. There were 5

studied pH conditions, which was one pH (12.8) from the real wastewater of zeolite industrial and 4 pH values (3, 5, 7 and 9) from the adjusted wastewater pH. The chemical used for pH adjusting was Nitric acid (HNO_3) or Sodium hydroxide (NaOH). Zeolite industrial wastewater 250 mL (after adjusted pH) and 250 mL of copper-brass pipe industrial wastewater were reacted in the 1,000-mL Erlenmeyer flasks then reciprocal shaken at 120 rpm at room temperature. They were sampled at 0, 15, 30, 60 and 120 minutes after shaking, respectively. After that all samples were filtered by filter paper GF/C with 47 mm $\varnothing$ and digested by nitric acid for determine heavy metals remaining in solution by Atomic Absorption Spectrophotometer (AAS).

3.4.4 Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiency.

The ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater was varied to 3:1, 2:1, 1:1, 1:2 and 1:3 volume by volume, respectively. The experimental condition was the selected pH and contact time from the previous study 3.4.3, which gave the highest heavy metals removal efficiency. All units were contained in the 1,000-mL Erlenmeyer flasks and reciprocal shaken at 120 rpm at room temperature. After shaking, they were sampled, filtered by filter paper GF/C with 47 mm $\varnothing$ and digested by nitric acid for determine heavy metals remaining in solution by Atomic Absorption Spectrophotometer (AAS).

3.4.5 Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition.

Zeolite industrial wastewater was used as a sorbent/precipitant for study of other pollutants (COD, TS, TDS and TSS) treating efficiency from copper-brass pipe industrial wastewater. The conditions from previous study part 3.4.3 and 3.4.4 were selected. After shaking, all samples were filtered by filter paper GF/C with 47 mm $\varnothing$ and determined for COD, TS, TDS and TSS.

3.5 Statistical Analysis

The statistical analyses for testing the research hypothesis are as follow;

- Mean, standard deviation and percentage were used for explain heavy metals removal efficiencies and other pollutants (COD, TS, TDS and TSS) removal efficiencies.
- The linear regression at 0.05 level of significance was used to find out the relationship between the initial copper and zinc concentration in copper-brass pipe industrial wastewater and copper and zinc removal efficiencies.
- The Two-way ANOVA at 0.05 level of significant was used to compare percentage of heavy metals removal efficiencies at different pH conditions of zeolite industrial wastewater, contact times and different ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater.
- The t-test at 0.05 level of significant was used to compare percentage of COD, TS, TDS and TSS removal efficiencies between before and after treating with the selected conditions.

CHAPTER IV

RESULTS

4.1 Characterization of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

Zeolite industrial wastewater and copper-brass pipe industrial wastewater were collected and characterized. The characteristics of zeolite industrial wastewater and copper-brass pipe industrial wastewater are showed in Table 6 and 7, respectively.

Table 6 Characteristics of zeolite industrial wastewater.

Parameters	Wastewater Characteristic
pH	12-13
Temperature ($^{\circ}\text{C}$)	30-32
BOD ₅ (mg/L)	54-82
COD (mg/L)	182-207
TS (mg/L)	12,437 – 12,705
SS (mg/L)	97-122
TDS (mg/L)	11,745-12,418
Heavy metals	
- Cu (mg/L)	0.070
- Zn (mg/L)	0.121
- Hg (mg/L)	0.001
- Ni (mg/L)	ND
- Pb (mg/L)	0.228
- Cr (mg/L)	0.052
- Fe (mg/L)	0.850
- Cd (mg/L)	ND

Table 7 Characteristics of copper-brass pipe industrial wastewater.

Parameters	Wastewater Characteristic
pH	1-2
Temperature ($^{\circ}\text{C}$)	31-34
BOD ₅ (mg/L)	6-15
COD (mg/L)	11-28
TS (mg/L)	4,528-4,563
SS (mg/L)	8-12
TDS (mg/L)	4,428-4,495
Heavy metals	
- Cu (mg/L)	491.200
- Zn (mg/L)	184.200
- Hg (mg/L)	0.001
- Ni (mg/L)	0.040
- Pb (mg/L)	0.514
- Cr (mg/L)	0.030
- Fe (mg/L)	6.175
- Cd (mg/L)	ND

The characterization of the zeolite A and the solids of zeolite industrial wastewater were examined by X-ray diffraction (XRD) analysis. The characterization of the zeolite A and the solids of zeolite industrial wastewater are shown in Figure 7 and 8, respectively.

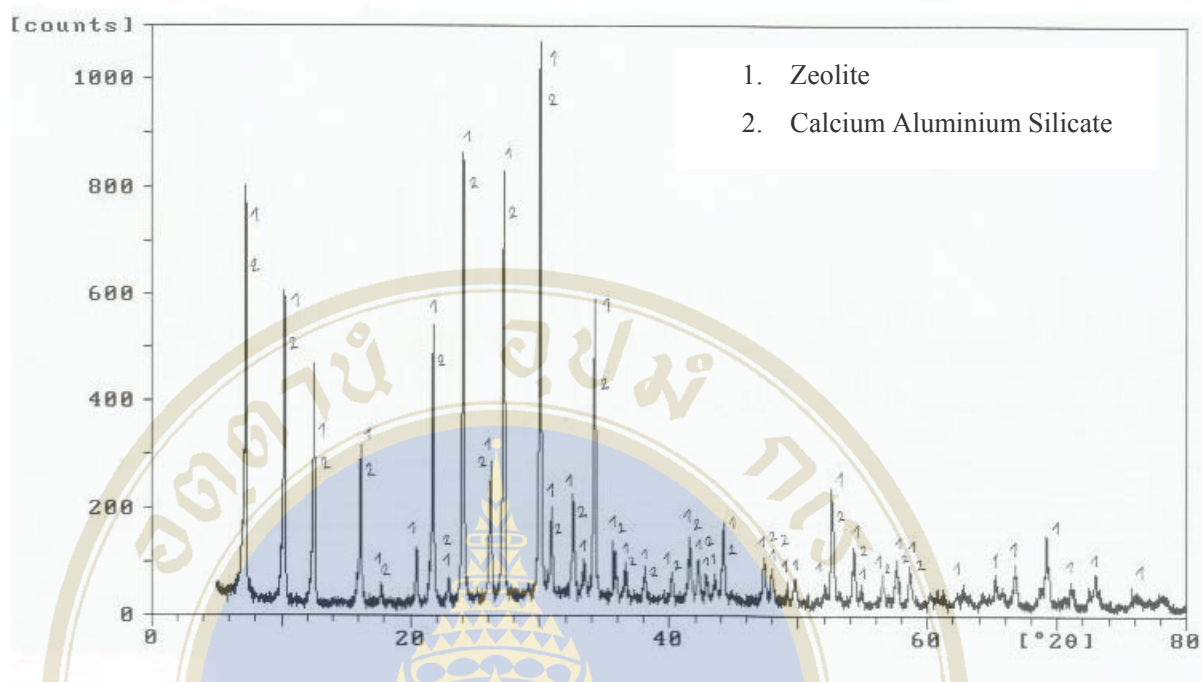


Figure 7 X-ray diffraction analysis of Zeolite A

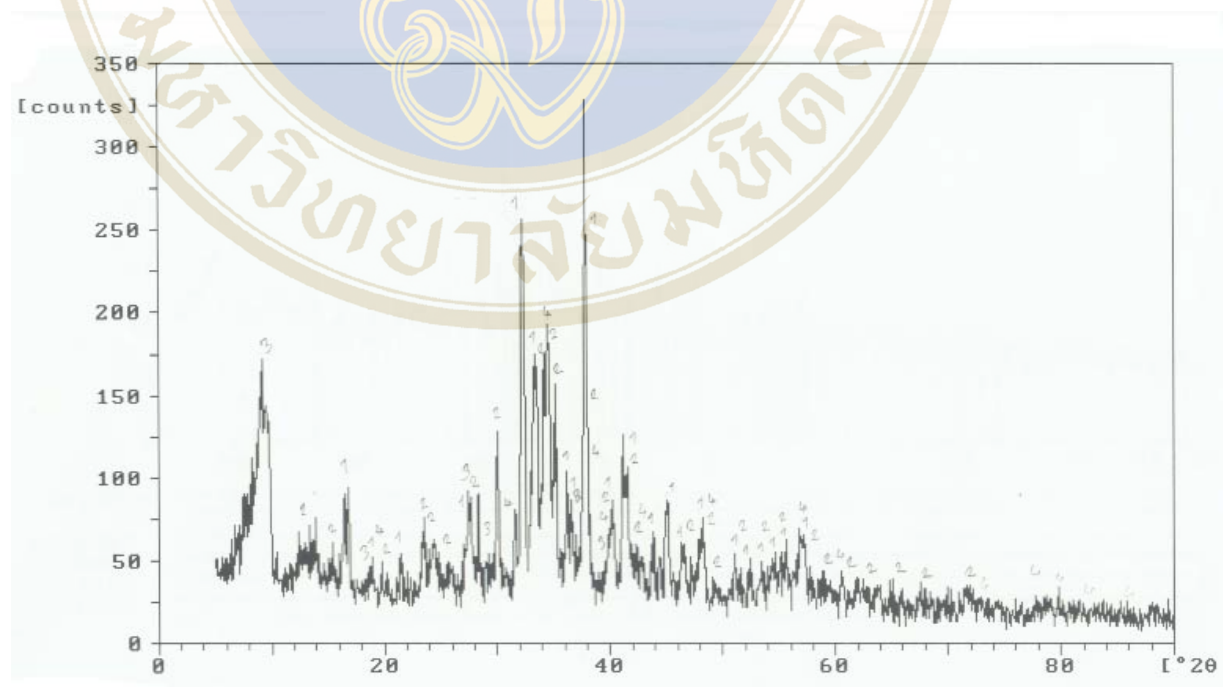


Figure 8 X-ray diffraction analysis of the solid of zeolite industrial wastewater

These diagnostic patterns in Figure 7 and 8 can provide an identification of the crystal structure and the mineral identity of the zeolite A and the solids of zeolite industrial wastewater. These were facilitated by using of a schematic chart, showing the characteristic XRD peaks for the relevant mineral species, furnished by the database of International Zeolite Association. (38) The analysis results of zeolite are given in Figure 7, which shows the characterization of zeolite A and Calcium Aluminum Silicate. At the same time, the analysis results of the solids of zeolite industrial wastewater are shown the characterization of Sodium Carbonate Hydrate, Sodium Carbonate, Calcium, Magnesium, Aluminum, Fluoride Silicate and Iron Manganese Aluminum Silicate.

4.2 Heavy metal removal efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

Zeolite industrial wastewater had been used for reacting with various dilutions of copper-brass pipe industrial wastewater. Experimental conditions were selected from Appendix D, which gave the maximum efficiency of heavy metals removal. Experimental conditions were pH of 7 from the adjusted pH of zeolite industrial wastewater and pH 12.8 from the real wastewater of zeolite industrial at 30 minutes of contact time. The experiments were conducted in order to determine the relationship between heavy metals (copper and zinc) concentration and its (copper and zinc) removal efficiencies.

After mixing, all experiments had different pH values and heavy metals concentrations. The results of initial and final copper and zinc concentrations and pH of the mixed solutions in each treatment of pH conditions are showed in Table 8 and appendix C.

Table 8 The initial and final copper and zinc concentrations and pH of the mixed solution of pH 7 and pH 12.8 of zeolite industrial wastewater and copper-brass pipe industrial wastewater (CIW)

pH conditions	pH of the mixed solution	Copper conc. (mg/L)			Zinc conc. (mg/L)		
		Copper conc. in CIW	Copper conc. in the mixture		Zinc conc. in CIW	Zinc conc. in the mixture	
			Initial	Final		Initial	Final
pH 7	6.8	4.91	2.46	0.44	1.84	0.92	0.14
	6.8	24.56	12.28	2.23	9.21	4.61	0.91
	6.8	49.12	24.56	4.58	18.42	9.21	3.20
	6.8	98.24	49.12	10.10	36.84	18.42	10.85
	6.5	147.36	73.68	17.83	55.26	27.63	18.73
	5.7	196.48	98.24	65.08	73.68	36.84	28.43
	2.5	245.60	122.80	101.93	92.10	46.05	37.08
	2.5	294.72	147.36	126.22	110.52	55.26	45.32
	2.5	343.84	171.92	144.18	128.94	64.47	56.08
	2.5	392.96	196.48	161.25	147.36	73.68	66.38
	2.5	442.08	221.04	183.15	165.78	82.89	72.98
	2.5	491.20	245.60	202.10	184.20	92.10	80.97
pH 12.8	12.2	4.91	2.46	0.85	1.84	0.92	0.15
	12.2	24.56	12.28	1.85	9.21	4.61	0.72
	12.2	49.12	24.56	3.75	18.42	9.21	1.36
	12.4	98.24	49.12	4.03	36.84	18.42	1.97
	12.6	147.36	73.68	4.93	55.26	27.63	2.56
	12.4	196.48	98.24	5.05	73.68	36.84	3.01
	12.4	245.60	122.80	5.53	92.10	46.05	3.34
	12.4	294.72	147.36	5.95	110.52	55.26	3.43
	12.4	343.84	171.92	6.03	128.94	64.47	3.46
	12.4	392.96	196.48	6.13	147.36	73.68	3.59
	12.4	442.08	221.04	6.15	165.78	82.89	3.66
	12.4	491.20	245.60	6.34	184.20	92.10	4.12

The copper and zinc containing in copper-brass pipe industrial wastewater had been treated by zeolite industrial wastewater. The initial copper and zinc concentrations in the mixture were effected by dilution. After treating, they had been

changed to final concentrations as shown in Table 8. For the adjusted pH 7 of zeolite industrial wastewater, the pH of mixed solutions was varied from neutral to acidity range (pH 6.8–2.5). On opposite, the mixture of real zeolite industrial wastewater had pH in the alkalinity range (pH 12.2–12.6). Beside this, the heavy metals (copper and zinc) removal efficiencies are as follow;

- Copper removal efficiency;

The solids of zeolite industrial wastewater were used to sorb various concentrations of copper. The experimental results had been calculated to a percentage of copper removal efficiency for pH 7 and pH 12.8 as showed in Figure 9 and Figure 10, respectively and appendix C.

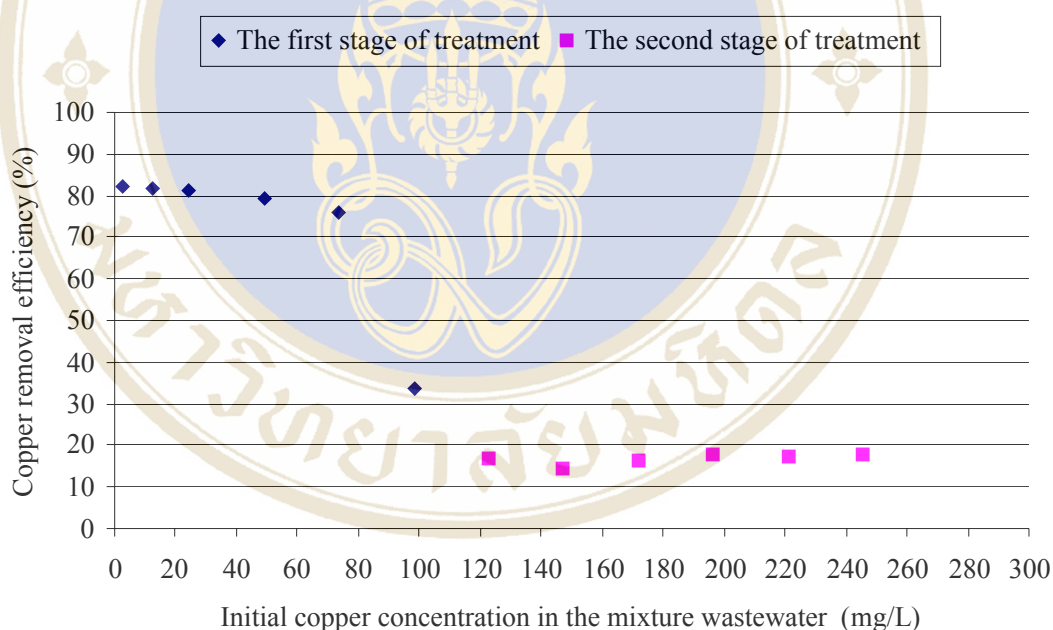


Figure 9 Removal of copper from copper-brass pipe industrial wastewater at various initial concentrations of copper by using zeolite industrial wastewater at pH 7 condition.

From results shown in Figure 9 of treatment of pH 7, the copper removal efficiency was 82.08% for the initial copper concentrations of 2.46 mg/L and it was slightly decreasing to 75.80% at 73.68 mg/L of the initial copper concentration. After

this, when increased more copper concentration, the copper removal efficiency was rapidly decreasing to 33.75% and 17% at copper concentration 98.24 and 122.80 mg/L, respectively. Afterward, the copper removal efficiencies were not greater than 17% until the end of experiment.

The trend of copper removal efficiency of treatment pH 7 could generally be divided into two stages as showed in Figure 9. In the first stage, the copper removal efficiencies were decreased when giving more initial copper concentration from 2.46 to 98.24 mg/L. In the second stage, after varying the initial copper concentration from 122.80 to 245.60 mg/L, the copper removal efficiencies were slightly change whether increased the initial copper concentration. Therefore, the maximum and minimum copper removal efficiencies for these two stages were 82.08% and 14.35%, respectively.

The relationship between the initial copper concentration in copper-brass pipe industrial wastewater and copper removal efficiency had been statistical analyzed by using simple linear regression analysis at 0.05 level of significance. It was found that the initial copper concentration had relationship with copper removal efficiency in term of linear regression ($p\text{-value} < 0.05$, see appendix G). The relationship of these two parameters for treatment of pH 7 could be divided into two equations. They are as the following equation (8) and equation (9) for the first stage (from the initial copper concentration 2.46 to 98.24 mg/L) and the second stage (from the initial copper concentration 122.80 to 245.60 mg/L), respectively.

$$\begin{array}{lcl} \text{Copper removal efficiency for the} & & 90.008 - 0.407 \text{ the initial copper} \\ \text{first stage of treatment pH 7} & = & \text{concentration} \quad \dots (8) \end{array}$$

$$\begin{array}{lcl} \text{Copper removal efficiency for the} & & 13.765 + 0.016 \text{ the initial copper} \\ \text{second stage of treatment pH 7} & = & \text{concentration} \quad \dots (9) \end{array}$$

These equations were used for explained a sorption of copper in copper-brass pipe industrial wastewater onto solids of zeolite industrial wastewater.

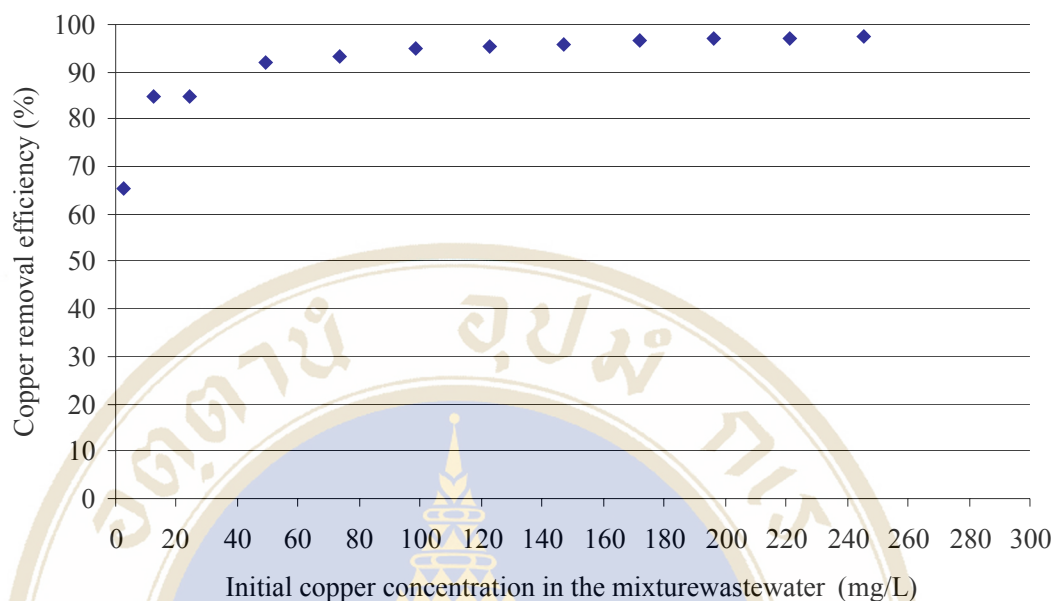


Figure 10 Removal of copper from copper-brass pipe industrial wastewater at various initial concentrations of copper by using zeolite industrial wastewater at pH 12.8 condition.

From results shown in Figure 10, the copper removal efficiency of treatments pH 12.8 was rapidly increasing from 65.39 % to 91.80 % during increasing the initial copper concentration from 2.46 to 49.12 mg/L. Afterward, they were slightly increased again from 93.31% to 97.42% of the initial copper concentration 73.68 mg/L until the end of experiment where the initial copper concentration was 245.60 mg/L.

The trend of copper removal efficiency of treatment pH 12.8 was increased when giving more the initial copper concentration. The maximum and minimum copper removal efficiencies were 97.42% and 65.39%, respectively.

The relationship between the initial copper concentration in copper-brass pipe industrial wastewater and copper removal efficiency had been statistical analyzed by using simple linear regression analysis at 0.05 level of significance. It was found that the initial copper concentration had relationship with copper removal efficiency in term of linear regression ($p\text{-value} < 0.05$, see appendix G). The equation showed a

relationship between these two parameters for treatment of pH 12.8 is as the following equation (10).

$$\text{Copper removal efficiency for the treatment pH 12.8} = 81.835 + 0.082 \text{ the initial copper concentration} \quad \dots (10)$$

This equation was used for explained a sorption of copper in copper-brass pipe industrial wastewater onto solid of zeolite industrial wastewater.

The amount of sorbate that can be taken up by a sorbent is a function of both the characteristic and concentration of sorbate. Generally, the amount of material sorbed is determined as a function of the concentration and the resulting function is called a sorption isotherm. The distribution of sorbate molecules between the liquid phase and the solid phase can be described by several mathematical model (isotherm) equations. All experimental results, then had been analyzed and used to predict the amount of sorbed copper from copper-brass pipe industrial wastewater (X) per the solids of zeolite industrial wastewater (m , mg/L) versus the copper equilibrium concentration solution (C_e).

The relationships of them are showed in Table 9, Figure 11 and Figure 12 for the first stage and the second stage of treatment pH 7, respectively and Table 10 and Figure 13 for the treatment of pH 12.8.

Table 9 The initial copper concentration in the mixture (C_0), the final copper concentration in the mixture (C_e) and the amount of copper in copper-brass pipe industrial wastewater loading on the zeolite industrial wastewater (X/m) for treatment of pH 7.

C_0 (mg/L)	C_e (mg/L)	X/m (mg/g)
2.46	0.44	0.167
12.28	2.23	0.832
24.56	4.58	1.654
49.12	10.10	3.230
73.68	17.83	4.623
98.24	65.08	2.745
122.80	101.93	1.728
147.36	126.22	1.750
171.92	144.18	2.296
196.48	161.25	2.916
221.04	183.15	3.137
245.60	202.10	3.601

According to the sorption isotherms of treatment pH 7, it could generally be divided to two stages as showed in Figure 11 and 12. In the first stage as shown in Figure 11, the rate of copper in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater were increased with increasing the final copper concentration in the mixture to 17.83 mg/L. Afterward, it was rapidly decreasing to 2.745 mg/g at the final copper concentration in the mixture 65.08 mg/L. In the second stage as shown in Figure 12, the rate of copper in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater was increased again after decreased from the first stage. It was increased during the final copper concentration in the mixture was increasing from 101.93 mg/L to 202.10 mg/L of the end of experiments.

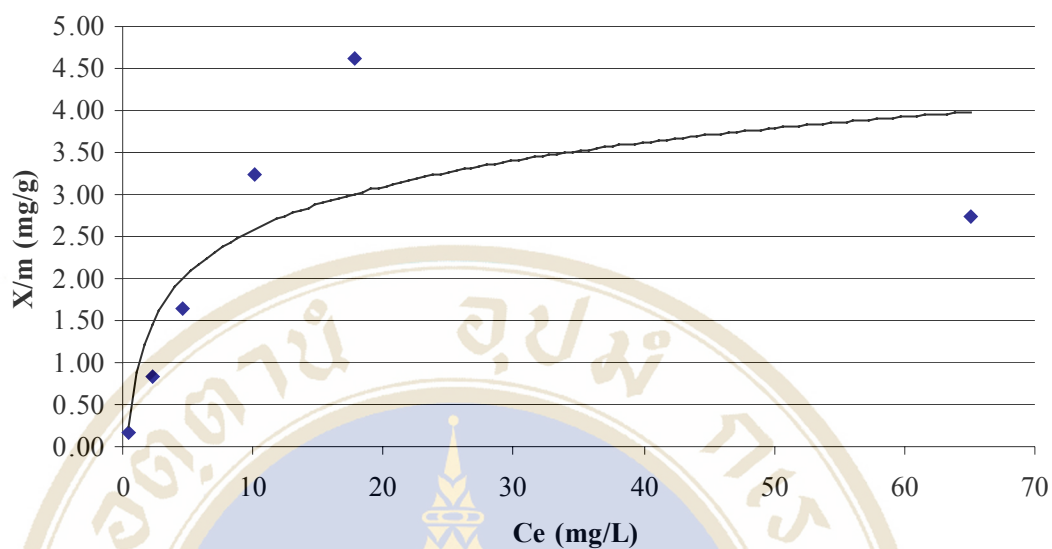


Figure 11 Sorption isotherms for copper concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the first stage of treatment pH 7.

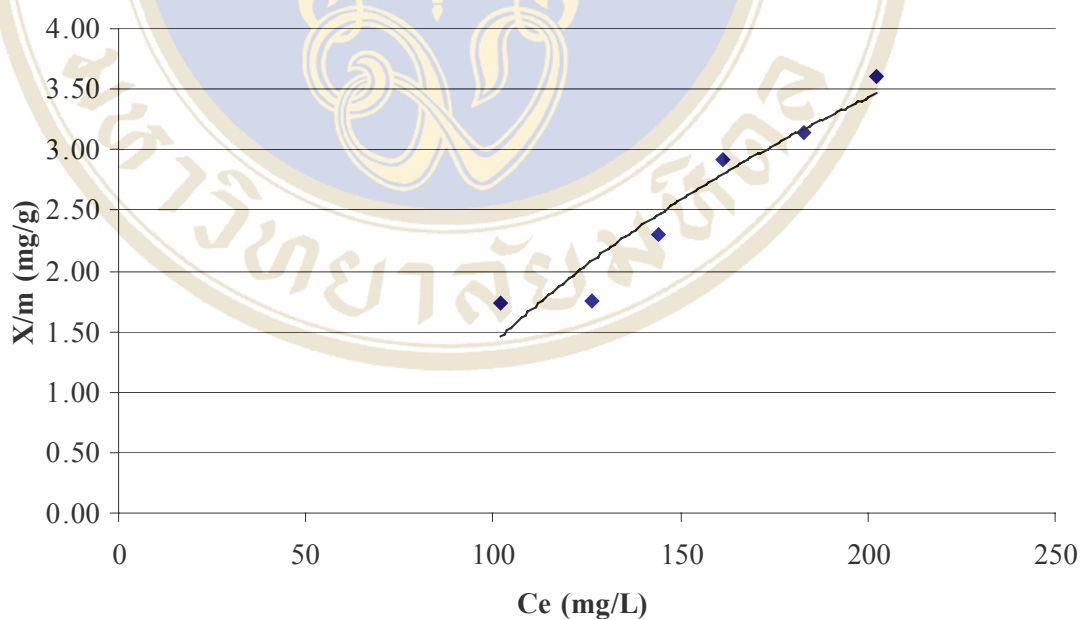


Figure 12 Sorption isotherms for copper concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the second stage of treatment pH 7.

Table 10 The initial copper concentration in the mixture (C_0), the final copper concentration in the mixture (C_e) and the amount of copper in copper-brass pipe industrial wastewater loading on the zeolite industrial wastewater (X/m) for treatment of pH 12.8.

C_0 (mg/L)	C_e (mg/L)	X/m (mg/g)
2.46	0.85	0.13
12.28	1.85	0.86
24.56	3.75	1.72
49.12	4.03	3.73
73.68	4.93	5.69
98.24	5.05	7.71
122.80	5.53	9.71
147.36	5.95	11.71
171.92	6.03	13.73
196.48	6.13	15.76
221.04	6.15	17.79
245.60	6.34	19.81

According to the sorption isotherms of treatment pH 12.8, the rate of copper in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater was slightly increased from 0.13 to 19.81 mg/g with the increasing of final copper concentration in the mixture until the concentration was 6.34 mg/L of the end of experiments.

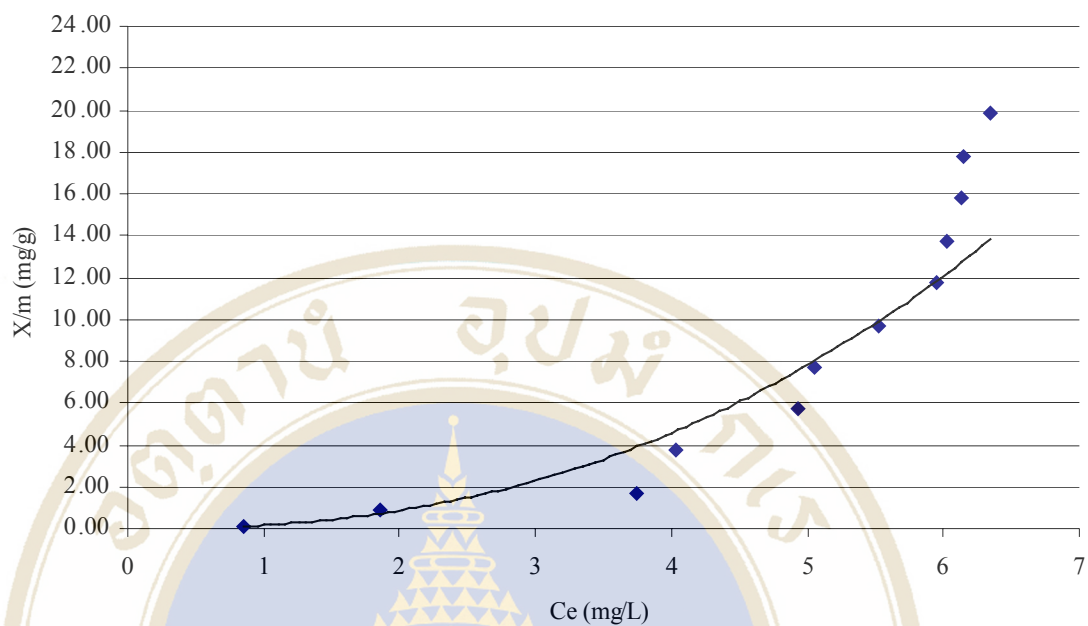


Figure 13 Sorption isotherms for copper concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the treatment of pH 12.8.

- Zinc removal efficiency;

The solids of zeolite industrial wastewater were used to sorb various concentration of zinc. The experimental results had been calculated to a percentage of zinc removal efficiency for pH 7 and pH 12.8 as showed in Figure 14 and appendix C.

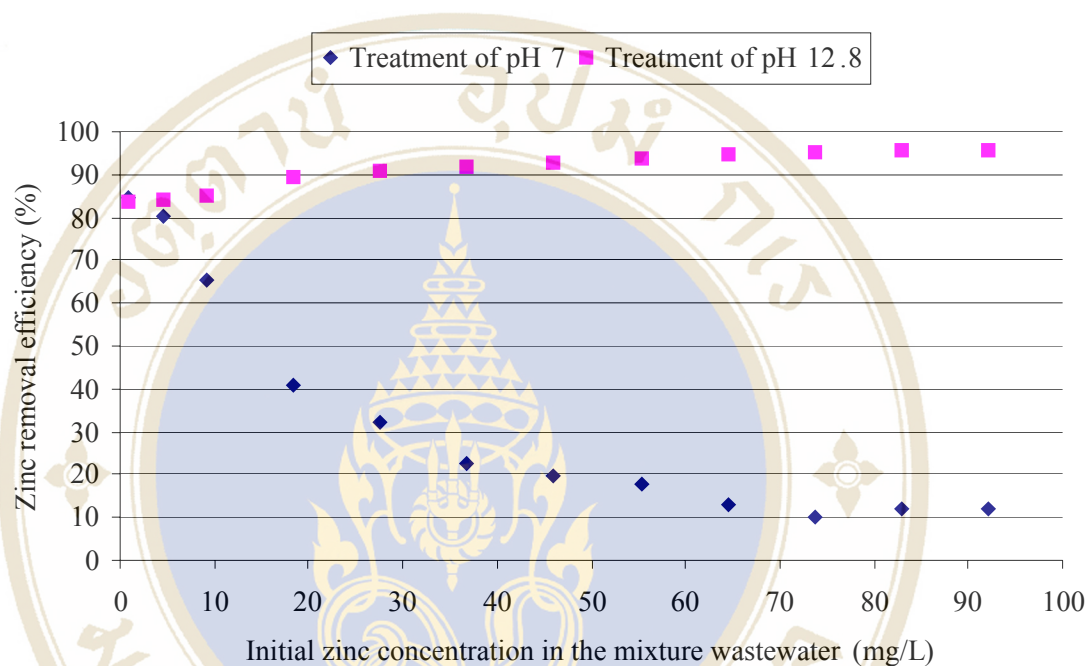


Figure 14 Removal of zinc from copper-brass pipe industrial wastewater at various initial concentrations of zinc by using zeolite industrial wastewater at pH 7 and pH 12.8 conditions.

For pH 7, the zinc removal efficiency was 84.80% for the initial zinc concentrations of 0.92 mg/L and it was slightly decreasing to 80.24% at 4.61 mg/L of the initial zinc concentration. After this, when increased the zinc concentration, it was rapidly decreasing to 65.26% and 41.10% at the initial zinc concentration 9.21 and 18.42 mg/L, respectively. Afterward, it was slightly decreased again from 32.21% to 9.91% of the initial zinc concentration 27.63 to 73.68 mg/L and then slightly increased to 11.96 % and 12.08% until the end of experiment where the initial zinc concentration was 82.89 and 92.10 mg/L, respectively. At the same time, for the results of treatment pH 12.8 as shown in Figure 14, the zinc removal efficiency was slightly increasing

from 83.71% to 95.53% during increasing the initial zinc concentration from 0.92 mg/L until the end of experiment where the concentration was 92.10 mg/L.

The trend of zinc removal efficiency of treatment pH 7 was decreased when giving more the initial zinc concentration from 0.92 to 73.68 mg/L. Afterward, they were slightly changed whether increased the initial zinc concentration from 82.89 to 92.10 mg/L. Therefore, the maximum and minimum zinc removal efficiencies were 84.80 % and 9.91 %, respectively. On opposite, the trend of zinc removal efficiency of treatment pH 12.8 was slightly increased when giving more the initial zinc concentrations. The maximum and minimum zinc removal efficiencies were 95.58 % and 83.71 %, respectively.

The relationship between the initial zinc concentration in copper-brass pipe industrial wastewater and zinc removal efficiency had been statistical analyzed by using simple linear regression analysis at 0.05 level of significance. It was found that the initial zinc concentration had relationship with zinc removal efficiency in term of linear regression ($p\text{-value} < 0.05$, see appendix G). The equation showed a relationship between these two parameters for treatment of pH 7 and pH 12.8 are as the following equation (11) and (12), respectively.

$$\begin{array}{lcl} \text{Zinc removal efficiency for the} & = & 67.469 - 0.779 \text{ the initial zinc} \\ \text{treatment pH 7} & & \text{concentration} \end{array} \quad \dots (11)$$

$$\begin{array}{lcl} \text{Zinc removal efficiency for the} & = & 85.444 + 0.132 \text{ the initial zinc} \\ \text{treatment pH 12.8} & & \text{concentration} \end{array} \quad \dots (12)$$

These equations were used for explained a sorption of zinc in copper-brass pipe industrial wastewater onto solids of zeolite industrial wastewater.

The amount of sorbate that can be taken up by a sorbent is a function of both the characteristic and concentration of sorbate. Generally, the amount of material sorbed is determined as a function of the concentration and the resulting function is called a sorption isotherm. The distribution of sorbate molecules between the liquid phase and the solid phase can be described by several mathematical model (isotherm)

equations. All experimental results, then had been analyzed and used to predict the amount of sorbed zinc from copper-brass pipe industrial wastewater (X) per the solids of zeolite industrial wastewater (m , mg/L) versus the zinc equilibrium concentration solution (C_e).

The relationships of them are showed in Table 11, Figure 15 for the treatment of pH 7 and Table 12 and Figure 16 for the treatment of pH 12.8.

Table 11 The initial zinc concentration in the mixture (C_0), the final zinc concentration in the mixture (C_e) and the amount of zinc in copper-brass pipe industrial wastewater loading on the zeolite industrial wastewater (X/m) for treatment of pH 7.

C_0 (mg/L)	C_e (mg/L)	X/m (mg/g)
0.92	0.14	0.065
4.61	0.91	0.306
9.21	3.20	0.498
18.42	10.85	0.627
27.63	18.73	0.737
36.84	28.43	0.696
46.05	37.08	0.743
55.26	45.32	0.823
64.47	56.08	0.695
73.68	66.38	0.604
82.89	72.98	0.820
92.10	80.97	0.921

According to the sorption isotherm of treatment pH 7 as shown in Figure 15, the rate of zinc in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater were rapidly increased from 0.065 to 0.737 mg/g with the increasing of final zinc concentration in the mixture from 0.14 to 18.73 mg/L. Subsequently, it was slightly decreased to 0.696 mg/g at the final zinc concentration in the mixture 28.43 mg/L and they were then increased from 0.696 to 0.823 mg/g during

increasing the final zinc concentration in the mixture from 28.43 to 45.32 mg/L. After ward, it was rapidly decreased again from 0.695 to 0.604 mg/g while the final zinc concentration in the mixture was increased from 56.08 to 66.38 mg/L. Finally, the rate of zinc in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater was rapidly increasing again from 0.820 to 0.92 mg/g of the final zinc concentration in the mixture 72.98 mg/L until the end of experiment where the final zinc concentration was 80.97 mg/L.

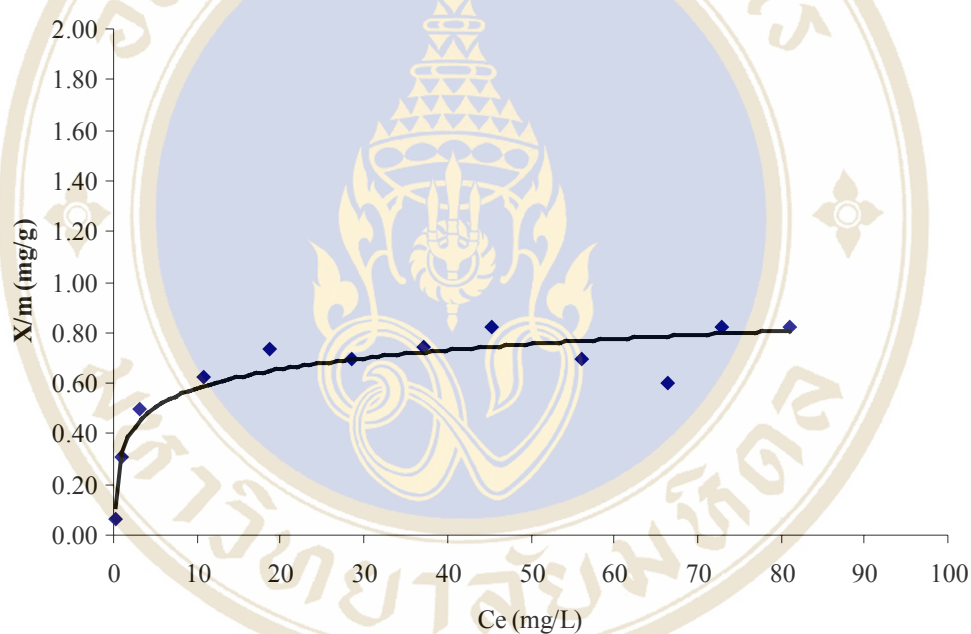


Figure 15 Sorption isotherms for zinc concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the treatment of pH 7.

Table 12 The initial zinc concentration in the mixture (C_0), the final zinc concentration in the mixture (C_e) and the amount of zinc in copper-brass pipe industrial wastewater loading on the zeolite industrial wastewater (X/m) for treatment of pH 12.8.

C_0 (mg/L)	C_e (mg/L)	X/m (mg/g)
0.92	0.15	0.064
4.61	0.72	0.322
9.21	1.36	0.650
18.42	1.97	1.362
27.63	2.56	2.075
36.84	3.01	2.800
46.05	3.34	3.536
55.26	3.43	4.291
64.47	3.46	5.050
73.68	3.59	5.802
82.89	3.66	6.559
92.10	4.12	7.283

According to the sorption isotherm of treatment pH 12.8 as shown in Figure 16, the rate of zinc in copper-brass pipe industrial wastewater sorption onto the solids of zeolite industrial wastewater was slightly increased from 0.064 to 7.283 mg/g with the increasing of final zinc concentration in the mixture 0.15 mg/L. until the end of experiment where the final zinc concentration 4.12 mg/L.

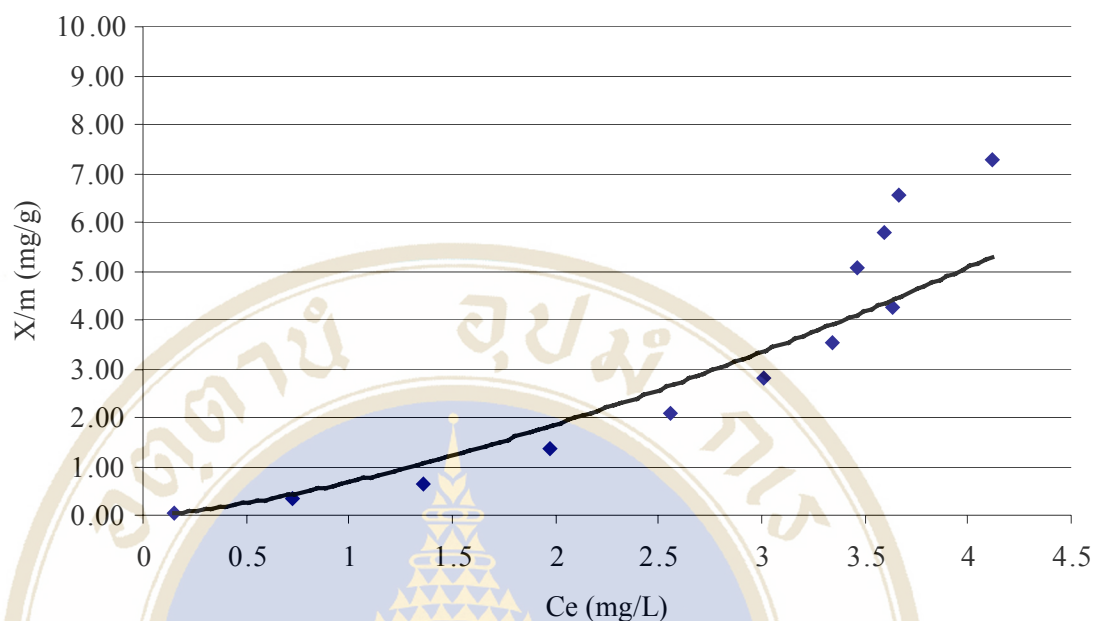


Figure 16 Sorption isotherms for zinc concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the treatment of pH 12.8.

4.3 Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies.

There were 5 studied pH conditions, which was one pH (12.8) from the real zeolite industrial wastewater and four adjusted pH conditions (3, 5, 7 and 9). The experiment was done at 5 contact times (0, 15, 30, 60 and 120 minutes) between zeolite industrial wastewater and copper-brass pipe industrial wastewater.

All experimental units were done at ratio 1:1 (vol:vol) of copper-brass pipe industrial wastewater to zeolite industrial wastewater. These were resulted in different pH values of the mixed solution. For these adjusted pH of zeolite industrial wastewater, the pH of mixed solution were in acidity range. There were pH 2, 2.3, 2.5 and 2.8 for the pH of the adjusted zeolite industrial wastewater 3, 5, 7 and 9, respectively. On opposite, the real zeolite industrial wastewater had pH of mixed solution in alkalinity range (12.4).

The heavy metals (copper and zinc) removal efficiencies at each condition are as follows;

- **Copper removal efficiency:** The amount of copper removal at each treatment condition is showed in Figure 17 and appendix D.

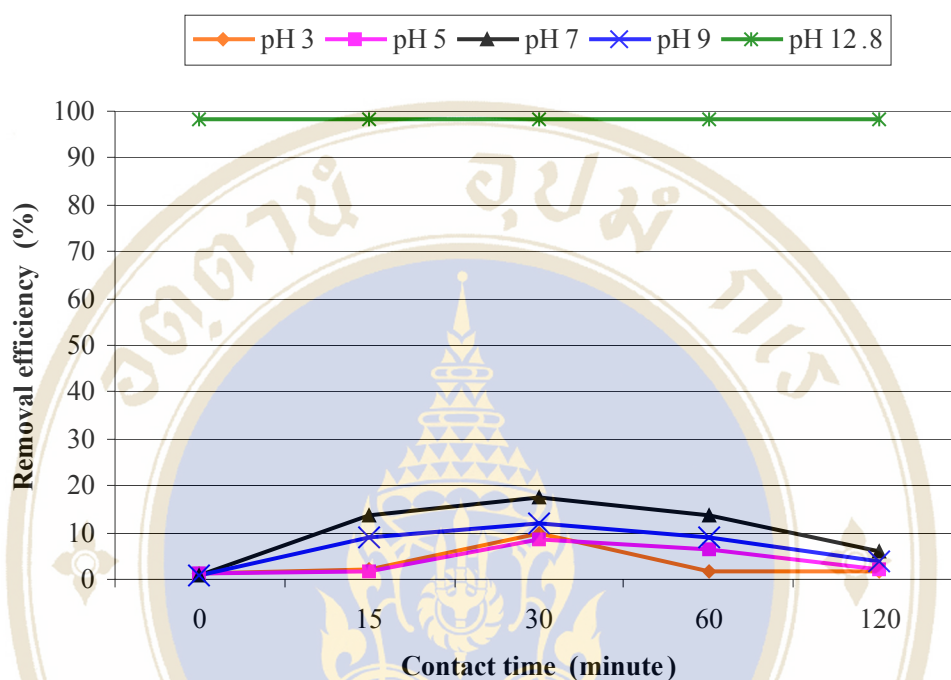


Figure 17 Copper removal efficiency of copper-brass pipe industrial wastewater at different pH conditions and contact times.

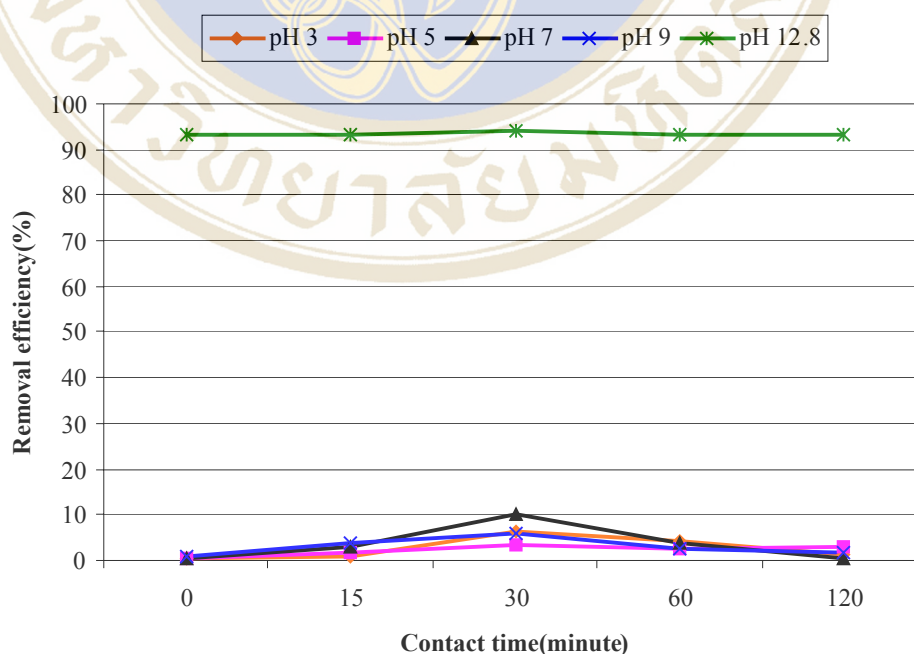
Regarding to a real zeolite industrial wastewater, copper had been highly removed than those other treatments. The Figure showed that varying contact time could result in changing the amount of copper removed for only a treatment of pH adjusted. Most of copper was removed more when increasing contact time from 0 to 30 minutes. They were then decreased during increasing a contact time from 30 minutes to 120 minutes for every pH conditions. These results had been calculated to a percentage of copper removal efficiency at each condition. Then, the maximum copper removal efficiency at pH 3, 5, 7, 9 and 12.8 were found at 30 minutes of contact time, which are indicated in Table 13.

Table 13 Copper removal efficiency (%) of zeolite industrial wastewater at 30 minutes of contact time.

pH condition	% copper removal efficiency at 30 minutes		
	MEAN	SD	RANGE
pH 3	9.82	0.21	9.60-10.02
pH 5	8.46	0.50	8.00-8.99
pH 7	17.35	1.50	15.64-18.45
pH 9	12.15	0.20	11.92-12.30
pH 12.8	98.47	0.17	98.28-98.61

From Table 13, the real zeolite industrial wastewater gave highest copper removal efficiency than the treatment of adjusted pH conditions. The maximum copper removal efficiency for the adjusted wastewater pH was found at pH 7.

- **Zinc removal efficiency:** The amount of zinc removal at each condition is showed in Figure 18 and appendix D.

**Figure 18** Zinc removal efficiency from copper-brass pipe industrial wastewater at different pH conditions and contact times.

Regarding to a real zeolite industrial wastewater, zinc had been highly removed than those other treatments. The Figure showed that varying contact time could result in changing the amount of zinc removed for only a treatment of pH adjusted. Most of zinc was removed more when increasing contact time from 0 to 30 minutes. They were then decreased during increasing a contact time from 30 minutes to 120 minutes for every pH conditions. These results had been calculated to a percentage of zinc removal efficiency at each condition. Then, the maximum zinc removal efficiency at pH 3, 5, 7, 9 and 12.8 were found at 30 minutes of contact time, which are indicated in Table 14.

Table 14 Zinc removal efficiency (%) of zeolite industrial wastewater at 30 minutes of contact time.

pH condition	% zinc removal efficiency at 30 minutes		
	MEAN	SD	RANGE
pH 3	6.35	0.60	5.91-7.04
pH 5	3.47	0.33	3.09-3.66
pH 7	9.94	0.58	9.42-10.56
pH 9	5.71	0.86	4.96-6.66
pH 12.8	94.21	0.17	94.03-94.38

From Table 14, the real zeolite industrial wastewater gave highest zinc removal efficiency than the treatment of adjusted pH conditions. The maximum zinc removal efficiency for the adjusted wastewater pH was found at pH 7.

The heavy metals removal efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater, at various pH and contact times, had been statistical analyzed by using Two-way ANOVA at 0.05 level of significance. It was found that pH of zeolite industrial wastewater could affect the heavy metals removal efficiency (p-value < 0.05, see appendix G). This result was not agreed with the hypothesis of the study part 1, which stated that the heavy metals removal efficiencies would increase with the decreasing pH conditions of zeolite industrial wastewater. Regarding to pH condition, from statistical analysis the pH 7 gave significantly copper and zinc removal efficiencies more than the other adjusted pH

conditions. Therefore, pH 7 was selected from the adjusted wastewater pH for further experiment. At the same time, pH 12.8 from the real wastewater also selected since it gave the highest heavy metals removal efficiencies. From the results, contact times could affect the heavy metals removal efficiency ($p\text{-value} < 0.05$, see appendix G). This result was not agreed with the hypothesis of the study part 2, which stated that heavy metals removal efficiency would increase with the increasing of contact time. From statistical analysis of the heavy metals removal efficiency at different contact time, 30 minutes of contact time gave the highest efficiency of heavy metals removal then it was selected for further experiment.

4.4 Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiencies.

Zeolite industrial wastewater had been used for reacting with copper-brass pipe industrial wastewater at various pH conditions and contact times. From these results, the pH 7 from the adjusted pH of zeolite industrial wastewater and pH 12.8 from the real wastewater of zeolite industrial, and 30 minutes of contact time were selected. The experiment was continued in order to determine the optimum treatment condition for remove copper and zinc from copper-brass pipe industrial wastewater at suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater. The ratios were varied as 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol), respectively.

After mixing, all experiments had different pH values. The results of copper and zinc removal efficiencies, pH of the mixed solution and amount of heavy metals sludge in each ratio are showed in Table 15 and appendix E.

Table 15 Copper and zinc removal efficiencies (%), pH of the mixed solution and amount of heavy metals sludge of pH 7 and pH 12.8 of zeolite industrial wastewater at 30 minutes of contact time.

pH conditions	Ratio (vol:vol)	pH of the mixed solution	Copper removal efficiency (%)	Zinc removal efficiency (%)	Amount of heavy metals sludge (mg/L)
pH 7	3:1	2.0	12.17	8.67	149.33
	2:1	2.2	8.22	6.96	132.00
	1:1	2.5	17.35	9.94	104.00
	1:2	4.7	11.63	5.75	194.00
	1:3	5.7	15.81	9.58	194.33
pH 12.8	3:1	7.0	98.27	92.06	1322.67
	2:1	11.4	94.93	93.11	1453.33
	1:1	12.4	98.47	94.21	1130.67
	1:2	12.6	94.40	82.86	872.00
	1:3	12.7	87.80	66.46	701.33

From Table 15, for this adjusted pH of zeolite industrial wastewater, the pH of mixed solutions were in an acidity range (pH 2.0-5.7). On opposite, the mixing of real zeolite industrial wastewater had pH in the alkalinity range (pH 7.0-12.7). By these results, especially for the ratio of 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol), it was found that the treatments of real zeolite industrial wastewater had higher amount of heavy metals sludge than these treatments of pH adjusted.

The heavy metals (copper and zinc) removal efficiencies at ratio 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol) are as follows;

- **Copper removal efficiency:** The amounts of copper removal at five different ratios are showed in Table 16 and appendix E.

Table 16 The amounts of copper removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol)

pH conditions	Ratio (vol:vol)	The amount of copper concentration (mg/L)		
		The initial conc.	The final conc.	The amount of copper removal
pH 7	3:1	368.40	323.57	44.83
	2:1	327.47	300.55	26.92
	1:1	245.60	202.98	42.62
	1:2	163.73	144.69	19.04
	1:3	122.80	103.39	19.41
pH 12.8	3:1	368.40	6.37	362.03
	2:1	327.47	16.61	310.86
	1:1	245.60	3.76	241.84
	1:2	163.73	9.17	154.56
	1:3	122.80	14.98	107.82

Regarding to a real zeolite industrial wastewater, copper had been highly removed than the treatment of pH adjusted. Considering the treatments of real zeolite industrial wastewater, the highest percentage of copper removal efficiency was 98.47% at ratio 1:1 following by 98.27%, 94.93%, 94.40% and 87.80% for ratio 3:1, 2:1, 1:2 and 1:3, respectively. The Table 16 showed that varying the mixing ratios could result in dramatically changing the amount of copper removal for a treatment of non-pH adjusted zeolite industrial wastewater. Most of copper was removed more when increasing concentrations of copper-brass pipe industrial wastewater from ratio 1:1 to 3:1 (vol:vol) and decreased when giving more concentration of zeolite industrial wastewater from ratio 1:1 to 1:3 (vol:vol). These results had been calculated to a percentage of copper removal efficiency at five different ratios as showed in Table 15 and appendix E.

- **Zinc removal efficiency:** The amounts of zinc removal at five different ratios are showed in Table 17 and appendix E.

Table 17 The amounts of zinc removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol)

pH conditions	Ratio (vol:vol)	The amount of zinc concentration (mg/L)		
		The initial conc.	The final conc.	The amount of zinc removal
pH 7	3:1	138.15	126.17	11.98
	2:1	122.80	114.25	8.55
	1:1	92.10	82.95	9.15
	1:2	61.40	57.87	3.53
	1:3	46.05	41.64	4.41
pH 12.8	3:1	138.15	10.96	127.19
	2:1	122.80	8.46	114.34
	1:1	92.10	5.34	86.76
	1:2	61.40	10.53	50.87
	1:3	46.05	15.45	30.60

Regarding to a real zeolite industrial wastewater, zinc had been highly removed than the treatment of pH adjusted. Considering the treatments of real zeolite industrial wastewater, the highest percentage of zinc removal efficiency was 94.21% at ratio 1:1 following by 93.11%, 92.06%, 82.86% and 66.46% for ratio 2:1, 3:1, 1:2 and 1:3, respectively. The Table 17 showed that varying the mixing ratios could result in dramatically changing the amount of zinc removal for a treatment of non-pH adjusted zeolite industrial wastewater. Most of zinc was removed more when increasing concentrations of copper-brass pipe industrial wastewater from ratio 1:1 to 3:1 (vol:vol) and decreased when giving more concentration of zeolite industrial wastewater from ratio 1:1 to 1:3 (vol:vol). These results had been calculated to a percentage of zinc removal efficiency at five different ratios as showed in Table 15 and appendix E.

Considering the pH of mixed solution, it was found that a mixture of the real zeolite industrial wastewater at ratio 3:1 and that of the pH adjusted of zeolite industrial wastewater at ratio 1:3 had pH range in the standard requirement. Nevertheless, the treatment of real zeolite industrial wastewater at ratio 3:1 had higher percentage of heavy metals removal efficiencies than that of the pH adjusted zeolite industrial wastewater at ratio 1:3 (vol:vol). Therefore, the treatment of real zeolite industrial wastewater at ratio 3:1 was selected for further experiment.

The heavy metals removal efficiencies at different ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater for two pH conditions of zeolite industrial wastewater at 30 minutes of contact time were statistical analyzed by using Two-way ANOVA at 0.05 level of significance. It was found that the ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater condition could affect the heavy metals removal efficiency (p-value < 0.01 for copper and zinc removal efficiencies, see appendix G). The ratio 1:1 of real zeolite industrial wastewater gave the highest heavy metals removal efficiencies. These results were not agreed with the hypothesis of the study part 3, which stated that the heavy metals removal efficiencies would increase with the increasing of ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater. From the analysis of this part, the highest efficiency of heavy metals removal at the ratio 1:1 of real zeolite industrial wastewater was not much higher than those of the ratio 3:1 of real zeolite industrial wastewater. Moreover, mixture of treatment of the real zeolite industrial wastewater at ratio 3:1 had a pH range in the standard requirement. Therefore, the ratio 3:1 of copper-brass pipe industrial wastewater to zeolite industrial wastewater was selected. It was used for further experiment as an experimental condition for a study of other pollutants (COD, TS, TDS and TSS) treating efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

4.5 Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition.

From previous experiments, various design reaction criteria such as pH, contact times and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater had been determined. All selected conditions, pH 12.8 (the real pH of zeolite industrial wastewater), 30 minutes of contact time and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater 3:1 (vol:vol) were used for observation of their influence to other pollutants treating efficiency.

The amount of other pollutants removal and their removal efficiencies are showed in Table 18 and appendix F.

Table 18 The amount of other pollutants removal and their removal efficiencies.

Other pollutants	Amount of other pollutants in the mixture (mg/L)			Removal efficiencies (%)
	Before Treatment	After Treatment	Amount of removal	
COD	48.28	29.60	18.68	38.71
TS	4,587.67	4,479.33	108.34	2.36
TDS	4,383.33	4,293.33	90.00	2.05
TSS	64.00	48.67	15.33	23.86

- **COD removal efficiency:** The COD of copper-brass pipe industrial wastewater, which has not been treated by selected conditions, was around 48 mg/L. After treated by using the selected conditions, the amount of COD of mixed solution was around 30 mg/L. Therefore, mean amount of COD removal was 19 mg/L and mean COD removal efficiency was 38.71%. (See appendix F)

The COD removal efficiency of treatment before and after treating with the selected conditions had been statistical analyzed by using pair t-test analysis at

0.05 level of significance. It was found that selected treatment conditions could affect the COD removal efficiency ($p\text{-value} < 0.05$, see appendix G).

- **Total Solids (TS) removal efficiency:** The TS of copper-brass pipe industrial wastewater, which has not been treated by selected conditions, was around 4,588 mg/L. After treated by using selected conditions, the amount of TS of mixed solution was around 4,479 mg/L. Therefore, mean changing the amount of TS concentration was around 109 mg/L. (See appendix F)

The TS removal efficiency of treatment before and after treating with the selected conditions had been statistical analyzed by using pair t-test analysis at 0.05 level of significance. It was found that selected treatment conditions could not affect to change the TS concentration ($p\text{-value} = 0.176$, see appendix G).

- **Total Dissolved Solids (TDS) removal efficiency:** The TDS of copper-brass pipe industrial wastewater, which has not been treated by selected conditions, was around 4,383 mg/L. After treated by using selected conditions, the amount of TDS of mixed solution was around 4,293 mg/L. Therefore, mean changing the amount of TDS concentration was 90 mg/L. (See appendix F)

The TDS removal efficiency of treatment before and after treating with the selected conditions had been statistical analyzed by using pair t-test analysis at 0.05 level of significance. It was found that selected treatment conditions could not affect to change the TDS concentration ($p\text{-value} = 0.122$, see appendix G).

- **Total Suspended Solids (TSS) removal efficiency:** The TSS of copper-brass pipe industrial wastewater, which has not been treated by selected conditions, was around 64 mg/L. After treated by using selected conditions, the amount of TSS of mixed solution was around 49 mg/L. Therefore, mean amount of TSS removal was around 15 mg/L and mean TSS removal efficiency was 23.86 %. (See appendix F)

The TSS removal efficiency of treatment before and after treating with the selected conditions had been statistical analyzed by using pair t-test analysis at 0.05 level of significance. It was found that selected treatment conditions could affect the TSS removal efficiency ($p\text{-value} = 0.009$, see appendix G).

CHAPTER V

DISCUSSION

5.1 Characterization of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

- Zeolite industrial wastewater characteristics

The zeolite or crystalline aluminosilicate, which composed of silica and alumina, is safe for environment because it degrades to natural substances after being used. To produce zeolite, water is used in the production process and some amount is discharged as wastewater which riching with zeolite. Generally, zeolite was soluble in alkaline solution and the pH of solution is in an alkalinity range (39). Thus it causes the wastewater to be high in pH and TDS value. The analysis is agreed with this reason and found 12.8 pH and 12,082 mg/L TDS. Its COD, BOD and SS were not exceeding those characteristic ranges of wastewater standard requirement. Heavy metals (Cu, Zn, Hg, Ni, Pb, Cr, Fe and Cd) values were low due to the original composition does not consist or contaminate with heavy metals.

Generally, zeolite A is exhibited higher sorption capacities and faster rates. A three-dimensional network of sorption cavities constitutes the pore structure and large enough for molecules can enter the cavity. (7, 40) According to Figure 7, X-ray diffraction analysis confirmed that the studied zeolites were zeolite A and Calcium Aluminum Silicate. At the same time, the XRD pattern for the solids of zeolite industrial wastewater that shows in Figure 8 was determined. It also contained significant amount of Sodium Carbonate Hydrate, Sodium Carbonate, Calcium Magnesium Aluminum Fluoride Silicate and Iron Manganese Aluminum Silicate. It is showed that Zeolite A, after being use, would compose of more complex substances.

As a result, the presence of the OH^- species in solution is a critical factor in some zeolite transformations. The pH of the gel precursor in syntheses determines products and so it is to be expected that alkaline treatment of existing crystalline

zeolites might create structural changes. (7) Since, it is well known that the pH of solution in zeolite industrial wastewater is in an alkalinity range, thus, it causes the structure of zeolite A in wastewater to be changed. The solids of zeolite industrial wastewater were then found as an amorphous particle and did not having fixed form or shape. It has already been shown that the solids of zeolite industrial wastewater were an efficient sorbent for pre-treatment in copper-brass pipe industrial wastewater. Because of the alkaline property to the solids of zeolite industrial wastewater, it can also be evaluated in wastewater treatment to precipitate heavy metallic ions.

Comparing these characteristics of zeolite industrial wastewater with the Industrial Effluent Standard of Thailand (Appendix H), it was found that some parameters such pH and TDS do not meet the standard requirement. If discharged directly, it could harm not only the organisms living in the recipient aquatic environment but also animals and human further up the food chain. Therefore, addition treatment is needed to improve effluent quality before discharging to receiving water body.

- Copper-brass pipe industrial wastewater characteristics

The copper-brass industrial produces plate, sheets and strips by rolling operations, rods and wire by extrusion and drawing operations, and tubes or pipes by piercing or extrusion and drawing. The copper-brass pipe leaving in the pickling bath and bright dip tank are washed with fresh water, which eventually overflows to wastewater. It was contaminated with metallic pollutants together with increased acidity. Thus the influent wastewater would be low in pH value and high concentration of copper and zinc. The results were found in similar direction, which it pH, copper and zinc characteristics were 2, 491.2 mg/L and 184.2 mg/L, respectively. Generally, the organic and inorganic substances were not used in the production process of copper-brass pipe industry. Thus, the wastewater would be low in COD and BOD value. When comparing these characteristics of copper-brass pipe industrial wastewater with the Industrial Effluent Standard of Thailand (Appendix H), it was found that some parameters such copper and zinc do not meet the standard requirement.

Presently, the copper-brass pipe industrial wastewater had been treated by chemical precipitation process. Sodium hydroxide (NaOH) is used as a precipitator. The characteristics of treated wastewater were pH 7.2, copper 6.825 mg/L and zinc 3.85 mg/L, respectively. This pH value of wastewater after treating is meeting with the standard requirement (Appendix H). The amount removed copper and zinc were 484.38 mg/L and 180.35 mg/L, respectively. These results had been calculated to a percentage of copper and zinc removal efficiencies 98.61% and 97.91%, respectively. Nevertheless, copper and zinc were still high and do not meet the standard requirement (Appendix H). If discharged directly, the metal ions in wastewater solution can be translocated into aquatic plants and animals. In addition its may be cause toxicity if the concentration is high. Therefore, additional treatment is needed to improve effluent quality before discharging to water body.

The amount of Sodium hydroxide (NaOH) that used for treatment was 5-7 Kg/m³ of copper-brass pipe industrial wastewater. While the wastewater from production process was around 180 –200 m³/month. Thus, the operation costs of treatment with Sodium hydroxide (NaOH) were 32,400 – 36,000 Baht/month. Therefore, the cheaper alternative materials to replace the costly Sodium hydroxide (NaOH) have intensified in recent years. Attention has been focused on various materials, which are able to adjust pH value and, at the same time, remove some heavy metals from wastewater at low cost. Babel S. and Kurniawan T.A. (4) suggested that their were low cost and local availability natural materials such as chitosan, zeolites, clay or certain waste products from industrial operations, which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water.

Zeolites are naturally occurring structure and phyllosilicate minerals with high cation exchange and ion sorption capacity. (5) Utilization of zeolite in pollution control, including effluent polluted with heavy metals ions, has increased recently. Zeolites represent an appropriate material for removing heavy metals ions from wastewater because of their relatively low price coupled with the fact that their exchangeable ions (Na⁺, Ca⁺ and K⁺) are relatively harmless. (6) Therefore, the zeolite industrial wastewater, which riching with zeolite has pH value in an alkalinity range and might has potential capacity to treat metals from copper-brass pipe industrial wastewater.

This substitution would reduce operational cost and maximize use of industrial waste if application in the suitable condition.

5.2 Heavy metal removal efficiency from copper brass pipe industrial wastewater by using zeolite industrial wastewater.

The mixed solutions of copper-brass pipe industrial wastewater and zeolite industrial wastewater had different heavy metal concentrations and pH values. It is well known that pH, besides various physicochemical factors, is an important variable in the ion exchange and sorption processes by which surface charges may be changed or modified (41). In order to observe the influence of this parameter on the sorption, the solids were contacted with the heavy metals in the mixed solutions, which had different pH values. The outcome pH of the mixed solutions are summarized in Table 8.

For the adjusted pH 7 of zeolite industrial wastewater, the pH of the mixed solutions was varied from neutral to acidity range (pH 6.8-2.5). The pH of the mixed solutions became acid as copper and zinc concentrations in the initial solutions increasing. This was due to the hydrolysis of metals and proton releasing during sorption (42). It can be explained for the lower heavy metals removal efficiencies of solids in zeolite industrial wastewater of the treatment of pH 7. Typically, the copper and zinc concentrations are often removed from metal containing wastewater by precipitation at pH 7 or above (17). The observed pH values for the treatment of pH 12.8 had the pH of the mixed solution in the alkalinity range (pH 12.2 – 12.6). The higher equilibrium pH value may explain that the higher heavy metal removal efficiencies of solids of zeolite industrial wastewater would occur by precipitation mechanism. However, the sorption system is situated to the left of the theoretical solubility curve. When the pH of the solution is sufficiently high, the sorbent appears to be capable of removing more heavy metal from the mixed solution than can be achieved by precipitation alone (43).

In summary, the sorption to the particle surfaces and hydroxide precipitation are probably the principle mechanisms responsible for this heavy metals removal efficiency. Both mechanisms are strongly pH dependent. (43)

- Copper removal efficiency;

The experimental results had been calculated to a percentage of copper removal efficiency for pH 7 and pH 12.8. From results of the treatment of pH 7, the shape of the curves representing copper removal efficiencies versus the initial copper concentrations in the mixture wastewater (Figure 9) was suggested that there were two-stage mechanisms. In the first stage, the copper removal efficiencies were high (82% - 34%) at the neutral pH range (pH 6.8-5.7) of the mixed solution. In the second stage, after increasing the initial copper concentrations from 122.80 to 245.60 mg/L, the copper removal efficiencies were slightly change. The values were not greater than 17%. The effect of pH of the mixed solution can be seen from Table 8 and Figure 9. The copper removal efficiency was high at the neutral range (pH 6.8-5.7) in the first stage of the treatment pH 7. After, the pH of the mixed solutions were sharply decreasing to pH 2.5, therefore they stay constant even at the greater initial copper concentration. Cay et. al (41) had reported similar results from a study on the utilization of tea-industrial waste for removal of copper (II) and cadmium (II) from aqueous solutions. They found that the copper (II) and cadmium (II) removal efficiencies were very low at strong acidic medium (pH 1-3) and after pH 3 up to pH 5.5, the removal was increased sharply.

The relationship between the initial copper concentration in copper-brass pipe industrial wastewater and its removal efficiency was found in term of linear regression. Nevertheless, the relationship of these two parameters for the treatment of pH 7 could be divided into two equations. They were as the following equation (8) for the first stage (from the initial copper concentration 2.46 to 98.24 mg/L) and equation (9) for the second stage (from the initial copper concentration 122.80 to 245.60 mg/L). They were used to explain a sorption of copper in copper-brass pipe industrial wastewater onto solids of zeolite industrial wastewater. In the first stage, the copper removal efficiency was statistical significantly decreased with the increasing of the initial copper concentration ($p\text{-value} < 0.05$). In the second stage, the copper removal efficiency was slightly changed whether increasing the initial copper concentration from 122.80 to 245.60 mg/L). However, it was statistical significantly increased with the increasing of the initial copper concentration ($p\text{-value} < 0.05$). From the result shown in Table 8, the pH of the mixed solutions became acid as copper concentrations

in the initial solutions increasing. Therefore, the copper removal efficiencies were very low. This is due to metal hydroxide precipitation was a bit removed.

For the results of the treatment pH 12.8, the shape of the curves representing copper removal efficiencies versus the initial copper concentration in the mixture wastewater (Figure 10) was suggested that they were rapidly increasing from 65.39 % to 91.80% during increasing the initial copper concentration from 2.46 to 49.12 mg/L. Afterward, the increasing rate was slow down.

The relationship between the initial copper concentration in copper-brass pipe industrial wastewater and copper removal efficiency was also found in term of linear regression. The equation showed a relationship between these two parameters for treatment of pH 12.8 is as the following equation (10). It was used to explain a sorption of copper in copper-brass pipe industrial wastewater onto solids of zeolite industrial wastewater. However, it was statistical significantly increased with the increasing of the initial copper concentration ($p\text{-value} < 0.05$).

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Therefore, equilibrium relationships between sorbent and sorbate are described by sorption isotherm (44).

According to the sorption isotherms from Figure 11 and 12 for the first and second stage, respectively of the treatment of pH 7, the fingerprint was exponential then slightly rising at the initial copper concentration in the mixture wastewater from 2.46 to 98.24 mg/L for the first stage and from 122.80 to 245.60 mg/L for the second stage. At the same time, for the treatment of pH 12.8 as shown in Figure 13, the fingerprint was exponential then slightly rising when the initial copper concentration in the mixture wastewater was increasing from 2.46 to 245.60 mg/L of the end of experiments.

This indicates that initially, there were numerous readily assessable sites for the solids of zeolite industrial wastewater. Consequently, a plateau was reached eventually in the curve and indicated that the sorbent was saturated at this level. The distribution of copper ions between the liquid phase and the solid phase can be

described by several mathematical model equations. In this study two model, the Langmuir and Freundlich isotherms had been selected since they could well explain for the linear form of isotherm such this study.

The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used as a sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous site within the sorbent (44). This isotherm assumes that a single sorbate binds to a single site on the sorbent and that all surface sites on the sorbent have the same affinity for the sorbate (17). The model takes the following form:

$$\frac{C_e}{(x/m)} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (6)$$

Where C_e is equilibrium concentration of copper in the mixture wastewater (mg/L), X/m is the amount of copper in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater (mg/g), b is a direct measure for the intensity of the sorption process (L/mg) and q_{max} is the amount of copper in copper-brass pipe industrial wastewater per unit weight of the solids of zeolite industrial wastewater for monolayer coverage of the surface (mg/g).

For Freundlich isotherm, Freundlich studied the sorption phenomenon extensively and the Freundlich model assumes that the uptake of metal ions occur on a heterogeneous surface by monolayer sorption. The model can be expressed by the following equation;

$$q_e = X/m = K_f C_e^{1/n} \quad (3)$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the sorbent that have different affinities for different sorbates with each site behaving according to the Langmuir isotherm. Where K_f is a constant for the system, related to the bonding energy. K_f can be defined as a sorption or distribution coefficient and represents the quantity of

copper concentration sorbed onto solids of zeolite industrial wastewater for a unit equilibrium concentration (17, 44).

Evaluation of the coefficients K_f and n can be accomplished using the linear form of Eq. (3). The model is described by the following equation;

$$\log (X/m) = \log K_f + 1/n \log (C_e) \quad (4)$$

The Langmuir isotherm parameters q_{max} and b , relating to monolayer sorption capacity and energy of sorption, respectively, are obtained by plotting $C_e/(X/m)$ versus C_e . Also the Freundlich isotherm parameters K_f and n , relating to sorption capacity and intensity, respectively of the sorbent, are obtained by plotting $\log (X/m)$ versus $\log C_e$.

Equations (4) and (6) can then be used to determine values of q_{max} , b , K_f and n by using technique of a linear regression. For the treatment of pH 7, Figure 19 and 20 indicate the Langmuir isotherms for the first and second stage, respectively whereas the Freundlich isotherms for the first and second stage are shown in Figure 21 and 22, respectively.

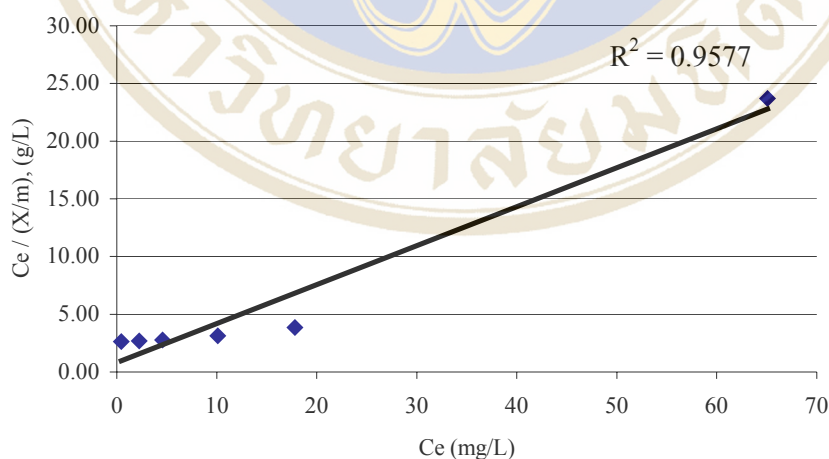


Figure 19 Langmuir sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the first stage of the treatment pH 7.

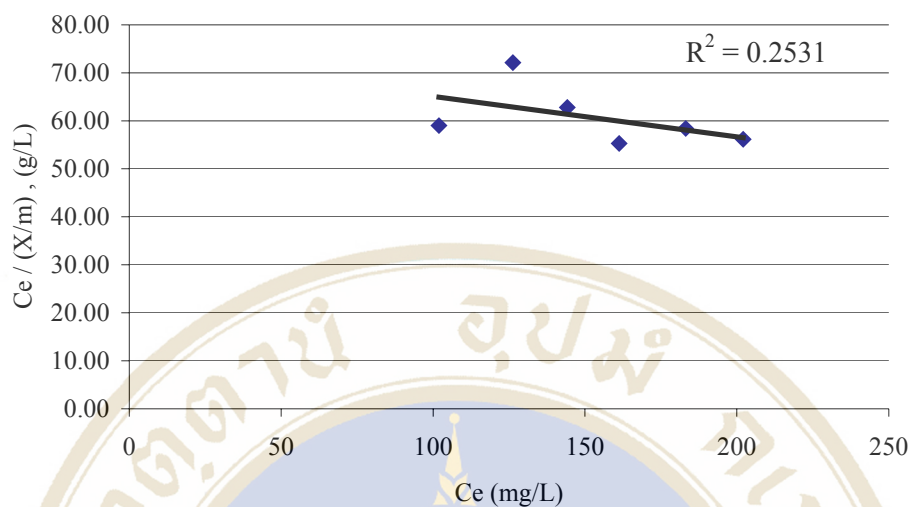


Figure 20 Langmuir sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the second stage of the treatment pH 7.

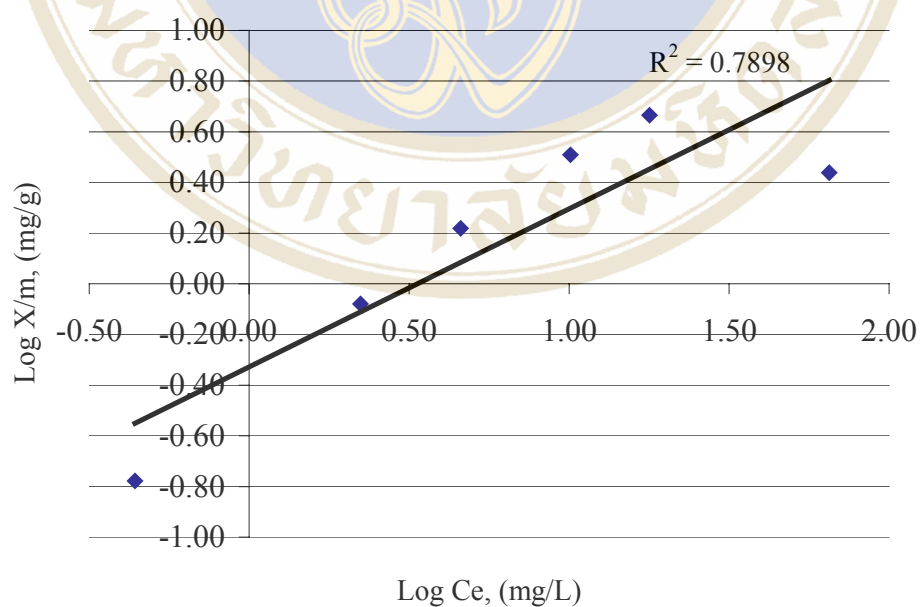


Figure 21 Freundlich sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the first stage of the treatment pH 7.

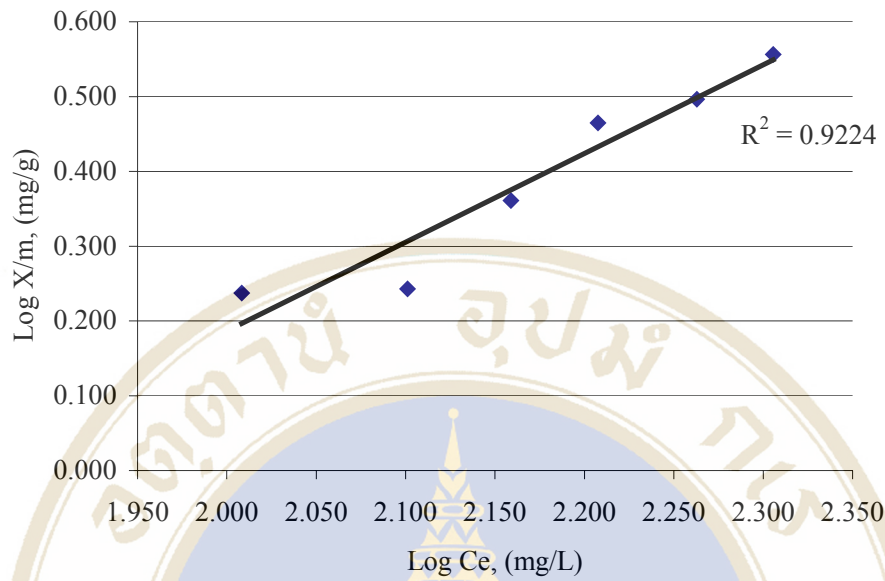


Figure 22 Freundlich sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the second stage of the treatment pH 7.

The isotherm equation had been computed from Figure 19 and 21 as equations (13) and (14), respectively for the first stage of the treatment pH 7.

$$\frac{C_e}{(x/m)} = 0.8202 + 0.3377 C_e \quad (13)$$

$$\log (X/m) = 0.6236 \log C_e - 0.3284 \quad (14)$$

The isotherm equation of the second stage of the treatment pH 7 had been computed from Figure 20 and 22 as equations (15) and (16), respectively.

$$\frac{C_e}{(x/m)} = 73.618 - 0.0849 C_e \quad (15)$$

$$\log (X/m) = 1.1849 \log C_e - 2.1828 \quad (16)$$

For the treatment of pH 12.8, Figure 23 and 24 are indicate the Langmuir and the Freundlich isotherms, respectively.

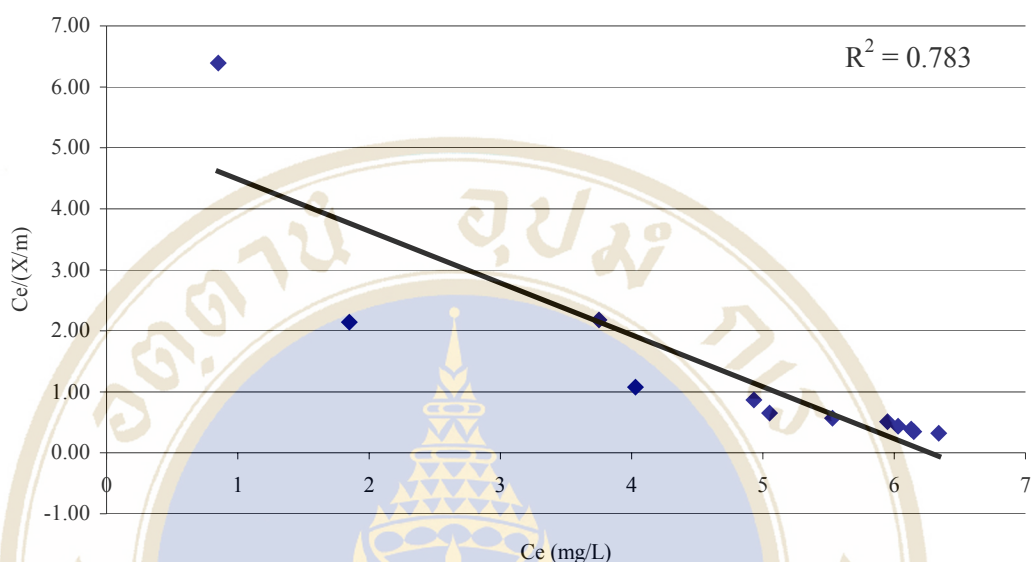


Figure 23 Langmuir sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH 12.8.

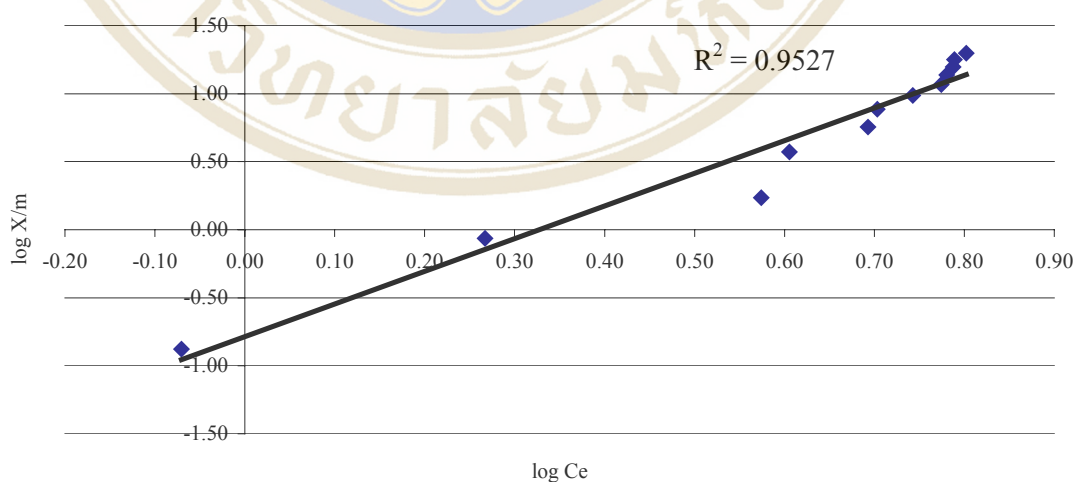


Figure 24 Freundlich sorption isotherms of copper concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH12.8.

For the treatment of pH 12.8, the isotherm equation had been computed from Figure 23 and 24 as equations (17) and (18), respectively.

$$\frac{C_e}{(x/m)} = 5.3368 - 0.8510 C_e \quad (17)$$

$$\log (X/m) = 2.3991 \log C_e - 0.7850 \quad (18)$$

The plots of $C_e/(x/m)$ against C_e are linear (Figure 19 and 20 for the first and second stage, respectively of the treatment pH 7, Figure 23 for the treatment of pH 12.8) and show the relation to Langmuir isotherm. The values of q_{max} and b for the removal of copper concentration in copper-brass pipe industrial wastewater by the solids of zeolite industrial wastewater can be determined from the slopes and intercepts of these lines. Table 19 presents the results of fitting these parameters to Langmuir isotherm and measured sorption capacity (q_{max}).

Besides this, the plots of $\log (X/m)$ against $\log C_e$ could also give the straight line (Figure 21 and 22 for the first and second stage, respectively of the treatment pH 7, Figure 24 for the treatment of pH 12.8) and show a relation to the Freundlich isotherm. The values of K_f and $1/n$ for the removal of copper concentration in copper-brass pipe industrial wastewater by the solids of zeolite industrial wastewater were determined from the slopes and intercepts of these lines and are given in Table 19. The slope $1/n$ is a measure for the sorption intensity. A value for $1/n$ below one indicates a Langmuir isotherm while $1/n$ above one is indicative of cooperative sorption (45).

A statistical parameter often used to judge subjectively how one variable is correlated with another is the coefficient of determination (r^2), which is applied to the results of a linear regression analysis. If a perfect correlation exists between $C_e/(x/m)$ and C_e for the Langmuir model and also between $\log (X/m)$ and $\log C_e$ for the Freundlich model, which if the straight line fit is perfect, then r^2 will equal to 1. If there is no correlation between the two parameters in each isotherm model that is no reasonable fit exists between the data, r^2 will equal to 0. Goodness of fit then is judged by how closely r^2 approaches 1. (17)

Table 19 Isotherm constants of the Langmuir and Freundlich models for the copper concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 7 and pH 12.8.

	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	r^2	K_f (mg/g)	$1/n$	r^2
The treatment of pH 7						
- The first stage	2.9612	0.4117	0.96	2.1301	0.6236	0.79
- The second stage	11.7786	0.0012	0.25	152.3350	1.1849	0.92
The treatment of pH 12.8	1.1751	0.1595	0.78	6.0954	2.3991	0.95

Table 19 presents the Freundlich parameter and indicates the satisfactory good correlation between the model predictions and the experimental data. The values of $1/n$ are 1.1848 and 2.3991 for the second stage of the treatment pH 7 and the treatment of pH 12.8, respectively, which is depicting favorable sorption in the present study. On the other hand, it can be seen that the Freundlich model yields a somewhat better fit than the Langmuir model by comparing the results of correlation (r^2) such 0.92 vs 0.25 and 0.95 vs 0.78 for the second stage of the treatment pH 7 and the treatment of pH 12.8, respectively. For the first stage of the treatment pH 7 was reasonably fitted well with the Langmuir isotherm. The Langmuir model gives a better yield than the Freundlich model as seen from the result of correlation (r^2).

The isotherm shape can be used to predict whether a sorption system is favorable or unfavorable in batch process. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by the following relationship (20, 23, 24):

$$R_L = \frac{1}{1 + b C_o} \quad (7)$$

Where R_L is a dimensionless separation factor, C_o is initial concentration (mg/L) and b is the Langmuir constant. The parameter R_L indicates the shape of the isotherm as following;

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 20 Langmuir parameters and R_L values for the sorption of copper concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 7.

<i>pH</i> <i>conditions</i>	C_o (mg/L)	C_e (mg/L)	X/m (mg/g)	$C_e/(X/m)$ (g/L)	R_L
The treatment of pH 7	2.456	0.44	0.167	2.64	0.4972
	12.28	2.23	0.832	2.68	0.1651
	24.56	4.58	1.654	2.77	0.0900
	49.12	10.10	3.230	3.13	0.0471
	73.68	17.83	4.623	3.86	0.0319
	98.24	65.08	2.745	23.71	0.0241
	122.80	101.93	1.728	59.00	0.8763
	147.36	126.22	1.750	72.13	0.8551
	171.92	144.18	2.296	62.79	0.8349
	196.48	161.25	2.916	55.29	0.8157
	221.04	183.15	3.137	58.39	0.7973
	245.60	202.10	3.601	56.12	0.7798

Table 21 Langmuir parameters and R_L values for the sorption of copper concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 12.8.

pH conditions	C_o (mg/L)	C_e (mg/L)	X/m (mg/g)	$C_e/(X/m)$ (g/L)	R_L
The treatment of pH 12.8	2.456	0.85	0.13	6.39	0.7185
	12.28	1.85	0.86	2.14	0.3380
	24.56	3.75	1.72	2.18	0.2034
	49.12	4.03	3.73	1.08	0.1132
	73.68	4.93	5.69	0.68	0.0784
	98.24	5.05	7.71	0.72	0.0600
	122.80	5.53	9.71	0.45	0.0486
	147.36	5.95	11.71	0.42	0.0408
	171.92	6.03	13.73	0.38	0.0352
	196.48	6.13	15.76	0.40	0.0309
	221.04	6.15	17.79	0.35	0.0276
	245.60	6.34	19.81	0.22	0.0249

From Table 20 and 21, the values of R_L for all treatments were found between zero and one. Therefore, it is showing a favorable shape of this isotherm.

- Zinc removal efficiency;

The experimental results had been calculated to a percentage of zinc removal efficiency for pH 7 and pH 12.8. From results of the treatment of pH 7, the shape of the curves representing zinc removal efficiencies versus the initial zinc concentrations in the mixture wastewater (Figure 14) was suggested that they were rapidly decreasing from 84.80% to 41.10% during increasing the initial zinc concentration from 0.92 to 18.42 mg/L. Afterward, the decreasing rate was slow down. At the same time, the results of the treatment pH 12.8, the shape of the curves representing zinc removal efficiencies versus the initial zinc concentration in the mixture wastewater (Figure 14) was suggested that they were slightly increasing from

83.71% to 95.53% during increasing the initial zinc concentration from 0.92 mg/L until the end of experiment 92.10 mg/L.

The relationship between the initial zinc concentration in copper-brass pipe industrial wastewater and its removal efficiency was found in term of linear regression. The equation showed a relationship between these two parameters for treatment of pH 7 and pH 12.8 are as the following equation (11) and (12), respectively. They were used to explain a sorption of zinc in copper-brass pipe industrial wastewater onto solids of zeolite industrial wastewater. In the treatment of pH 7, the zinc removal efficiency was statistical significantly decreased with the increasing of the initial zinc concentration ($p\text{-value} < 0.05$). From the result shown in Table 8, the pH of the mixed solutions became acid as zinc concentrations in the initial solutions increasing. Therefore, the zinc removal efficiencies were very low. This is due to metal hydroxide precipitation was a bit removed. In the treatment of pH 12.8, the zinc removal efficiency was statistical significantly increased with the increasing of the initial zinc concentration ($p\text{-value} < 0.05$).

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Therefore, equilibrium relationships between sorbent and sorbate are described by sorption isotherm (44)

According to the sorption isotherms from Figure 15 of the treatment pH 7, the fingerprint was exponential then rapidly rising at the initial zinc concentration in the mixture wastewater from 0.92 to 92.10 mg/L. At the same time, for the treatment of pH 12.8 as shown in Figure 16, the fingerprint was exponential then slightly rising when the initial zinc concentration in the mixture wastewater was increasing from 0.92 to 90.21 mg/L of the end of experiments.

This indicates that initially, there were numerous readily assessable sites for the solids of zeolite industrial wastewater. Consequently, a plateau was reached eventually in the curve and indicated that the sorbent was saturated at this level. The distribution of zinc ions between the liquid phase and the solid phase can be described by several mathematical model equations. In this study two models, the Langmuir and

Freundlich isotherms had been selected since they could well explain for the linear form of isotherm such this study.

The Langmuir sorption isotherm has been successfully applied to many pollutants sorption processes and has been the most widely used as a sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous site within the sorbent. (44) This isotherm assumes that a single sorbate binds to a single site on the sorbent and that all surface sites on the sorbent have the same affinity for the sorbate. (17) The model takes the following form:

$$\frac{C_e}{(x/m)} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (6)$$

Where C_e is equilibrium concentration of zinc in the mixture wastewater (mg/L), X/m is the amount of zinc in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater (mg/g), b is a direct measure for the intensity of the sorption process (L/mg) and q_{max} is the amount of zinc in copper-brass pipe industrial wastewater per unit weight of the solids of zeolite industrial wastewater for monolayer coverage of the surface (mg/g).

For Freundlich isotherm, Freundlich studied the sorption phenomenon extensively and the Freundlich model assumes that the uptake of metal ions occur on a heterogeneous surface by monolayer sorption. The model can be expressed by the following equation;

$$q_e = X/m = K_f C_e^{1/n} \quad (3)$$

The Freundlich isotherm can be derived from the Langmuir isotherm by assuming that there exists a distribution of sites on the sorbent that have different affinities for different sorbates with each site behaving according to the Langmuir isotherm. Where K_f is a constant for the system, related to the bonding energy. K_f can be defined as a sorption or distribution coefficient and represents the quantity of zinc

concentration sorbed onto solids of zeolite industrial wastewater for a unit equilibrium concentration. (17, 44)

Evaluation of the coefficients K_f and n can be accomplished using the linear form of Eq. (3). The model is described by the following equation;

$$\log (X/m) = \log K_f + 1/n \log (C_e) \quad (4)$$

The Langmuir isotherm parameters q_{max} and b , relating to monolayer sorption capacity and energy of sorption, respectively, are obtained by plotting $C_e/(X/m)$ versus C_e . Also the Freundlich isotherm parameters K_f and n , relating to sorption capacity and intensity, respectively of the sorbent, are obtained by plotting $\log (X/m)$ versus $\log C_e$.

Equations (4) and (6) can then be used to determine values of q_{max} , b , K_f and n by using technique of a linear regression. For the treatment of pH 7, Figure 25 and 26 indicate the Langmuir isotherms and the Freundlich isotherms, respectively.

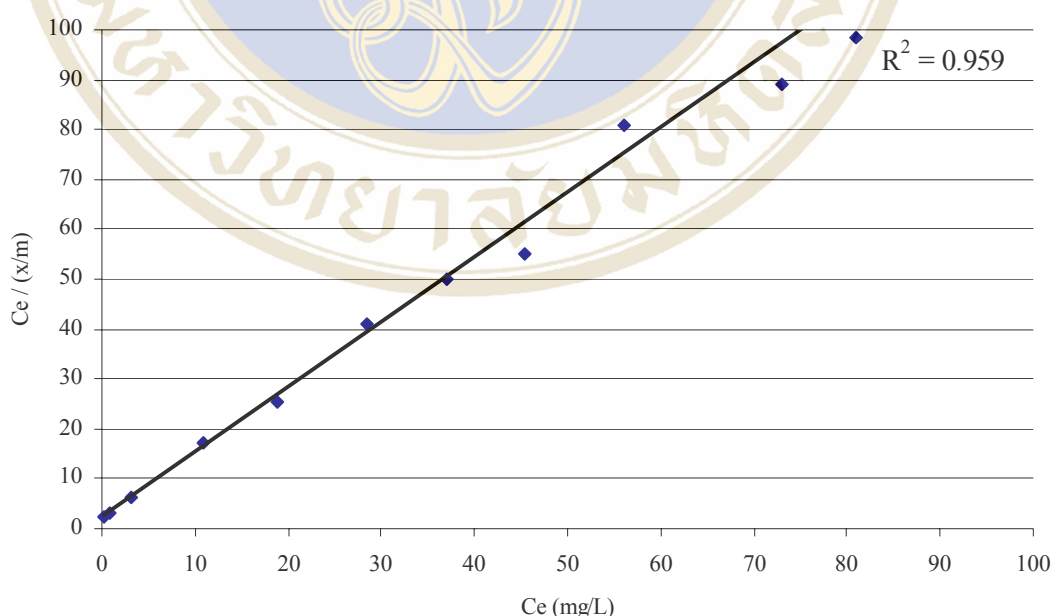


Figure 25 Langmuir sorption isotherms of zinc concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH 7.

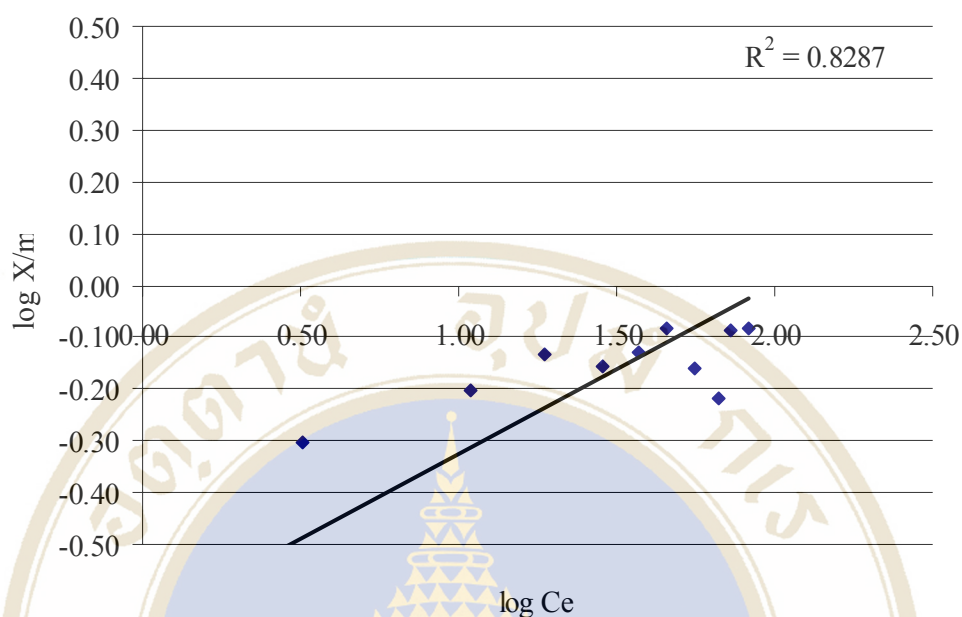


Figure 26 Freundlich sorption isotherms of zinc concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH 7.

The isotherm equation had been computed from Figure 25 and 26 as equations (19) and (20), respectively for the treatment of pH 7.

$$\frac{Ce}{(x/m)} = 2.5548 + 1.2998 Ce \quad (19)$$

$$\log (X/m) = 0.3283 \log Ce - 0.6533 \quad (20)$$

For the treatment of pH 12.8, Figure 27 and 28 are indicate the Langmuir and the Freundlich isotherms, respectively.

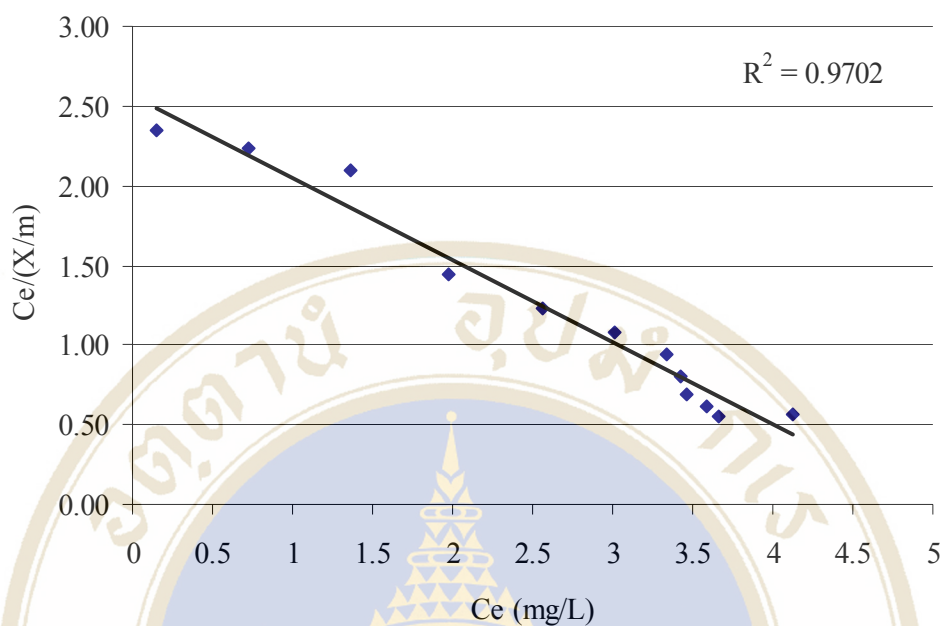


Figure 27 Langmuir sorption isotherms of zinc concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH 12.8.

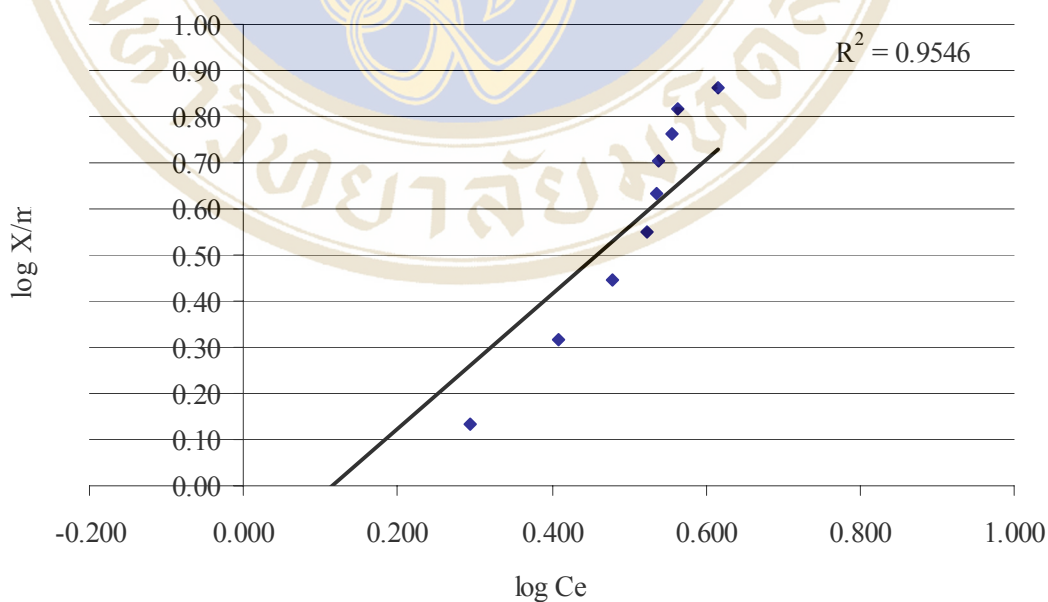


Figure 28 Freundlich sorption isotherms of zinc concentration in copper-brass pipe industrial wastewater loading on the solids of zeolite industrial wastewater for the treatment of pH12.8.

The isotherm equation had been computed from Figure 27 and 28 as equations (21) and (22), respectively for the treatment of pH 12.8.

$$\frac{C_e}{(x/m)} = 2.562 - 0.5144 C_e \quad (21)$$

$$\log (X/m) = 1.4561 \log C_e - 0.1673 \quad (22)$$

The plots of $C_e/(x/m)$ against C_e are linear (Figure 25 and 27 for the treatment of pH 7 and pH 12.8, respectively) and show the relation to Langmuir isotherm. The values of q_{max} and b for the removal of zinc concentration in copper-brass pipe industrial wastewater by the solids of zeolite industrial wastewater can be determined from the slopes and intercepts of these lines. Table 22 presents the results of fitting these parameters to Langmuir isotherm and measured sorption capacity (q_{max}).

Besides this, the plots of $\log (X/m)$ against $\log C_e$ could also give the straight line (Figure 26 and 28 for the treatment of pH 7 and pH 12.8, respectively) and show a relation to the Freundlich isotherm. The values of K_f and $1/n$ for the removal of copper concentration in copper-brass pipe industrial wastewater by the solids of zeolite industrial wastewater were determined from the slopes and intercepts of these lines and are given in Table 22. The slope $1/n$ is a measure for the sorption intensity. A value for $1/n$ below one indicates a Langmuir isotherm while $1/n$ above one is indicative of cooperative sorption. (45)

A statistical parameter often used to judge subjectively how one variable is correlated with another is the coefficient of determination (r^2), which is applied to the results of a linear regression analysis. If a perfect correlation exists between $C_e/(x/m)$ and C_e for the Langmuir model and also between $\log (X/m)$ and $\log C_e$ for the Freundlich model, which if the straight line fit is perfect, then r^2 will equal to 1. If there is no correlation between the two parameters in each isotherm model, that is no reasonable fit exists between the data, r^2 will equal to 0. Goodness of fit then is judged by how closely r^2 approaches 1. (17)

Table 22 Isotherm constants of the Langmuir and Freundlich models for the zinc concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 7 and pH 12.8.

	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	r^2	K_f (mg/g)	$1/n$	R^2
The treatment of pH 7	0.7693	0.5081	0.96	4.5009	0.3283	0.83
The treatment of pH 12.8	1.9440	0.2008	0.97	1.4699	1.4561	0.95

Table 22 presents the Freundlich parameter and indicates the satisfactory good correlation between the model predictions and the experimental data. The values of $1/n$ are 1.4561 for the treatment pH 12.8 which depicting favorable sorption in the present study. For the treatment pH 7 was reasonably fitted well with the Langmuir isotherm. The Langmuir model gives a better yield than the Freundlich model as seen from the result of correlation (r^2).

The isotherm shape can be used to predict whether a sorption system is favorable or unfavorable in batch process. The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L , which is defined by the following relationship (20, 23, 24):

$$R_L = \frac{1}{1 + b C_o} \quad (7)$$

Where R_L is a dimensionless separation factor, C_o is initial concentration (mg/L) and b is the Langmuir constant. The parameter R_L indicates the shape of the isotherm as following;

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 23 Langmuir parameters and R_L values for the sorption of zinc concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 7.

<i>pH</i> <i>conditions</i>	C_o (mg/L)	C_e (mg/L)	X/m (mg/g)	$C_e/(X/m)$ (g/L)	R_L
The treatment of pH 7	0.921	0.14	0.065	2.17	0.681
	4.605	0.91	0.306	2.98	0.299
	9.21	3.20	0.498	6.43	0.176
	18.42	10.85	0.627	17.31	0.097
	27.63	18.73	0.737	25.42	0.066
	36.84	28.43	0.696	40.84	0.051
	46.05	37.08	0.743	49.94	0.041
	55.26	45.32	0.823	55.08	0.034
	64.47	56.08	0.695	80.74	0.030
	73.68	66.38	0.604	109.85	0.026
	82.89	72.98	0.820	88.96	0.023
	92.10	80.97	0.921	98.30	0.021

Table 24 Langmuir parameters and R_L values for the sorption of zinc concentration in copper-brass pipe industrial wastewater loading onto the solids of zeolite industrial wastewater for the treatment of pH 12.8.

pH conditions	C_o (mg/L)	C_e (mg/L)	X/m (mg/g)	$C_e/(X/m)$ (g/L)	R_L
The treatment of pH 12.8	0.921	0.15	0.064	2.35	0.844
	4.605	0.72	0.322	2.24	0.520
	9.21	1.36	0.650	2.09	0.351
	18.42	1.97	1.362	1.45	0.213
	27.63	2.56	2.075	1.23	0.153
	36.84	3.01	2.800	1.07	0.119
	46.05	3.34	3.536	0.94	0.098
	55.26	3.43	4.291	0.80	0.083
	64.47	3.46	5.050	0.69	0.072
	73.68	3.59	5.802	0.62	0.063
	82.89	3.66	6.559	0.56	0.057
	92.10	4.12	7.283	0.57	0.051

From Table 23 and 24, the values of R_L for all treatments were found between zero and one. Therefore, it is showing a favorable shape of this isotherm.

The parameter q_{max} and b from Langmuir equation and K_f and $1/n$ from Freundlich equation of this research had been compared to other studies. For example, a study of Nathalie C et.al. (46), who used grafted silica as a sorbent for removing Cu (II), found that the Langmuir model could fits well with the experimental data. The maximum sorption capacity (q_{max}) was calculated and found to be 16.57 mg/g at pH condition 5.5-6. In this study, the sorption capacity of solids of zeolite industrial wastewater (q_{max}) was around 2.96 mg/g for the first stage of the treatment pH 7 (the pH of the mixed solution was 6.8-5.7). Cay S et.al. (41) used tea industrial waste as a sorbent for removing Cu (II) from aqueous solutions. They found that the experimental data fitted with the Freundlich isotherm model excellently ($r^2 = 0.992$).

The maximum sorption capacity (q_{max}) was calculated and found to be 8.64 mg/g. The sorption of solids of zeolite industrial wastewater was found that experimental data fitted with the Freundlich isotherm model excellently $r^2=0.92$ for the second stage of the treatment of pH 7 and $r^2=0.95$ for the treatment of pH 12.8. The maximum sorption capacity (q_{max}) was calculated and found to be 11.78 and 1.18 mg/g for the second stage of the treatment of pH 7 and the treatment of pH 12.8, respectively. Am J et.al (47) used hardwood bark as a sorbent for removing copper and zinc. They found that the sorption of these metals on hardwood bark conformed to the linear form of the Langmuir sorption equation. At pH 5 and 6, the Langmuir constant (q_{max}) for each metals were found to be 20.59 and 22.81 mg/g Cu and 12.10 and 12.23 mg/g Zn, respectively. Wong K. et. al (48), who used tartaric acid modified rice husk (TARH) for the removal of copper from aqueous solutions, found that the sorption to the Langmuir isotherm with maximum sorption capacity of 29 mg/g. Lisa N. et.al (49), who used biosolids as a sorbent for removing zinc from aqueous solutions, found that the Langmuir sorption isotherms at pH 4 indicate the sorption capacity (q_{max}) of the dry biosolids to be 36.87 mg/g. Ouki et.al (50), who used the natural zeolite chabazite for zinc sorption and determined the maximum sorption capacity to be 5.23 mg/g at pH 5. Solari et.al (51), investigated the use of non-living digested sewage sludge as a sorbent. The maximum zinc sorption capacity (q_{max}) of 25.63 mg/g at pH 7 was reported, which compares favorably with the value of zinc sorption capacity 0.7693 and 1.9440 mg/g for the treatment pH 7 and pH 12.8, respectively were obtained in this study.

From this comparison, the sorption capacities (q_{max}) of this research were less than other studies. It might cause from influence of various variations of content in both real wastewater (copper-brass pipe industrial wastewater and zeolite industrial wastewater) and other chemical interferences. However, the solids of zeolite industrial wastewater were an efficient sorbent for pre-treatment in copper-brass pipe industrial wastewater because of the alkaline property to the solids of zeolite industrial wastewater. It can also be evaluated in wastewater treatment to precipitate heavy metallic ions.

5.3 Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies.

The efficiencies of copper and zinc removal from copper-brass pipe industrial wastewater were measured at five pH conditions and five contact times. They were studied at various pH values of 3, 5, 7 and 9 of the adjusted pH of zeolite industrial wastewater and pH 12.8 from the real zeolite industrial wastewater. The pH and contact time profiles are given in Figure 17 and 18 for copper and zinc removal efficiency, respectively. It can be seen from these plots that the highest removal efficiency of copper and zinc took place at pH 12.8 of the real zeolite industrial wastewater and the maximum copper and zinc removal efficiencies for the adjusted wastewater pH was found at pH 7.

The pH of the real zeolite industrial wastewater could give the highest heavy metals removal efficiencies might come from a reason that, at higher pH value of copper would precipitates as $\text{Cu}(\text{OH})_2$ the mixed solution greater than 7, metals could precipitate well. For example, at the pH 12.8, zinc ions undergoes complexes as $[\text{Zn}(\text{OH})_4]^{2-}$. (52) The increase in heavy metals removal efficiencies at a higher pH may be attributed from the hydrolysis of copper and zinc. (53) A similar behavior has been reported by Reyad S. et.al (52) for the removal of copper and zinc by treated oil shale ash. They found the increasing both metals in removal efficiencies at high pH value. Therefore, the treatment of pH 7 from the adjusted wastewater and pH 12.8 from the real zeolite industrial wastewater, which gave high heavy metals removal efficiencies, were selected for further experiments. They had been compared to other studies. For example, a study of Nuhoglu Y. et.al (54), who used the cone biomass of *Thuja orientalis* for the removal of copper from aqueous solution, found that copper removal efficiency was increased with pH and the maximum copper removal occurred at pH 7.7. It might come from a reason that, as pH increased the biosorbent surface became more and more negatively charged and therefore the biosorbent of positively charged Cu^{2+} and $\text{Cu}(\text{OH})^+$ species were more favorable. Moreover, at higher pH values (basic solution), precipitation of copper hydroxide were occurred and precipitated on surface of the cone biomass. Seyed A. et.al (55), who used pecan shell activated carbon for the removal of copper from aqueous solution, found that copper removal efficiency was increased with increase in pH. Loading is less pH dependent

around pH 3. It is well known that with the increase of pH, due to the decrease in the competition between the protons and metal ions for surface sites, metal ion removal by the activated carbon increases. It should further be noted that experiments must be carried out in a range of pH in which metal ion removal can be associated only with adsorption, and not to a combination of adsorption and metal hydroxide precipitation were occurred.

The effect of contact time on the reaction of copper and zinc removal can be seen Figure 17 and 18, respectively. The removal efficiencies of copper and zinc were increased with the time up to 30 minutes and thereafter decreased. The copper removal efficiency was 17.35% and 98.47% at 30 minutes for the treatment of pH 7 and pH 12.8, respectively. At the same time, the zinc removal efficiency was 9.94% and 94.21% at 30 minutes for the treatment of pH 7 and pH 12.8, respectively. According to the results, the equilibrium reached at 30 minutes and was taken as the optimum contact time for the further experiments.

The selected condition of this research, the pH condition of pH 7 and pH 12.8, and the 30 minutes of contact time, had been compared to other studies. For example, a study of Cay S. et.al (41), who used tea industrial waste for the removal of copper from aqueous solution, found that sorbed amount was increased from 30 to 60 minutes. The maximum removal efficiency was observed at 60 minutes. Am J. et.al (47), who used mulch for the removal of copper and zinc from urban runoff, found that the contact time to sorption equilibrium can be considered relatively fast since approximately 90%. It was clearly indicates that the equilibrium was attained within 30 minutes. Nurgul B. et.al (56), who used wheat shell for the removal of copper from aqueous solution, found that sorption efficiency was increased with increasing contact time. The equilibrium time was obtained at a contact time of 120 minutes. Nuhoglu Y. et.al (54), who used the cone biomass of *Thuja orientalis* for the removal of copper from aqueous solution, found that the sorption occurred in two steps; an initial first step that lasted for 20 minutes, the slower second phase which continued until the end of the experimental period. The equilibrium was reached within 60 minutes. Further increase in contact time did not show an increasing in sorption. Abou Mesalam (57), who used silico antimonite for removing copper and zinc found that the copper and zinc removal efficiencies were increased with increasing of contact time. The

maximum removal efficiency was observed at 120 minutes for copper and at 150 minutes for zinc. Vinod K. et.al (53), who used bagasse fly ash (a sugar industrial waste) for the removal of copper and zinc from wastewater found that the heavy metals removal efficiencies were around 90-95%. It was clearly indicates that the equilibrium for copper and zinc were attained in 60 and 70 minutes of contact times, respectively. In this study, the maximum removal efficiency was observed at 30 minutes for both copper and zinc.

As a result, in order to establish the practical utility of the copper and zinc removal, these two metals could be treated at the same reaction time conditions.

Therefore, to enhance the removal efficiency from the view of economy, it is wise to consider the investment for smaller reactor that retains only 30 minutes of contact time.

5.4 Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiencies.

The effect of ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for copper and zinc removal efficiencies was investigated at ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol) of the treatment of pH 7 from the adjusted pH of zeolite industrial wastewater and the treatment of pH 12.8 from the real zeolite industrial wastewater at contact times of 30 minutes.

Considering to the results of copper and zinc removal efficiencies, pH of the mixed solution and the amount of heavy metals sludge in each ratio, which are given in Table 15, the highest removal efficiency of copper and zinc was took place at pH 12.8 of the real zeolite industrial wastewater. It might come from a reason that, at higher pH value of the mixed solution, greater than 7, metals could precipitate well. (52) The sorption is greatest at only a pH value that is just slightly more acidic than the pH at which there is bulk precipitation of the metal hydroxide. As pH is further raised, once the bulk solubility limit is reached, the sorption is greatly reduced because the metal ions are removed from solution by the precipitation. (21)

By this result, all the treatments of real zeolite industrial wastewater had higher amount of heavy metals sludge than those treatments of pH adjusted.

According to the results of the treatment of real zeolite industrial wastewater shown in Table 16 and 17, which presents the amount of copper and zinc removal, it can be observed that most of copper and zinc were removed more when increasing concentrations of copper-brass pipe industrial wastewater from ratio 1:1 to 3:1 (vol:vol). The increased in heavy metals removal efficiencies at ratio 1:1 to 3:1 (vol:vol) may be attributed the difference in pH values of the mixed solution (pH 7-12.4), most of copper and zinc were achieved the optimum pH interval for precipitation as copper and zinc hydroxide compounds. (32) A similar behavior has been reported by Nuhoglu Y. et.al (54) for the removal of copper from aqueous solutions by the cone biomass of *Thuja orientalis*. They found the removal of copper by the cone biomass was increased with increasing pH from pH 2.1 to 7.7. The greatest increasing was observed at pH 7.7. As pH increased the sorbent surface became more and more negatively charged and therefore the sorption of positively charged (Cu^{2+} and $\text{Cu}(\text{OH})^+$) were more favorable. At pH 7.7, the copper ions get precipitated due to hydroxide anions were forming.

On the contrary, the amount of copper and zinc removal were decreased when giving more concentrations of zeolite industrial wastewater from ratio 1:1 to 1:3 (vol:vol). The effect of zeolite industrial wastewater on the pH of the mixed solution was investigated in Table 15, which the pH values of the mixed solution were generally a bit increased from 12.4-12.7 with the increasing in concentration of zeolite industrial wastewater from ratio 1:1 to 1:3 (vol:vol). Erol M et. al (58) had reported similar results from a study on the utilization of fly ash for removal of copper from aqueous solutions. They found that the pH values were increased with the increasing in concentration of the fly ash samples. The pH value of the copper solution was measured as 4.7, but fly ash addition to this solution causes an increase in it pH value. It was observed that the final pH value of the mixture was exceeds 6, a sharp decrease in the copper concentration occurs and at the pH level of 8-9, the copper removal approaches 100%. Chien J.L. et.al (59), who used fly ash for the removal of copper from aqueous solution, found that the pH increases as the fly ash is added into the solution. Because of the alkaline nature of fly ash, when the above occurs, the copper

ions are expected to precipitate out of the solution under higher pH conditions. Generally, zeolite was soluble in alkaline solution and the pH of solution is in an alkalinity range. (39) Thus, it causes the wastewater to be high in pH value. Attention has been focused on the pH of the solution at this minimum metal ion concentration is the optimum pH level for precipitation. Hydroxide precipitation is based on the low solubility of the heavy metal hydroxides. (58) The solubility of metal hydroxides is sensitive to pH because of its amphoteric property. In the presence of sufficiently strong base at high pH, the metal hydroxides may dissolve, thus eliminating the hydroxide precipitate. (21, 27, 58) An increasing application of zeolite industrial wastewater in these cases could not enhance more heavy metals removal efficiencies.

The pH of mixed solution has a significant impact on copper and zinc removal since it can influence both the characters of the precipitation ions and the character of zeolite industrial wastewater itself. In addition, the functional groups of zeolite surface may dissociating at higher pH values and leaving anionic surface site that may make a significant contribution to the metal removal. (60) In this research, the solids of zeolite industrial wastewater were also contained significant amount of Sodium Carbonate Hydrate, Sodium Carbonate, Calcium Magnesium Aluminum Fluoride Silicate and Iron Manganese Aluminum Silicate. They were the major cations released in the mixed solution. This may contribute some problem in copper and zinc removal efficiencies since they were not the pure products but rather contain a variety of impurities such as calcium carbonate, unaltered glass, clays, etc., which are occluded during the formation of the zeolite. (60)

Comparing the pH of mixed solution with the Industrial Effluent Standard of Thailand (Appendix H), it was found that the pH adjusted of zeolite industrial wastewater at ratio 1:3 and the treatment of real zeolite industrial wastewater at ratio 3:1 do meet the standard requirement (pH 5.5-9). However, the treatment of real zeolite industrial wastewater at ratio 3:1 had higher percentage of heavy metals removal efficiencies than the treatment of the pH adjusted of zeolite industrial wastewater at ratio 1:3 (vol:vol).

As evident from the treatment of real zeolite industrial wastewater at ratio 3:1 (vol:vol), the pH of the mixed solution was most of copper and zinc ions were precipitated due to the forming of copper and zinc hydroxide. For this reason, the

treatment of real zeolite industrial wastewater at ratio 3:1 (vol:vol) gave high heavy metals removal efficiencies and pH range in the standard requirement. Therefore, the treatment of real zeolite industrial wastewater at ratio 3:1 (vol:vol) was selected for further experiments. It indicates that the use of this alternative cheaper sorbent, zeolite industrial wastewater is economically attractive. It is a waste product and available for adjusting pH value of wastewater. This option could successfully remove copper and zinc from wastewater up to 98% and 92%, respectively.

5.5 Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition.

The selected conditions for other pollutants (COD, TS, TDS and TSS) removal efficiencies were investigated at pH 12.8 from the real zeolite industrial wastewater, 30 minutes of contact times and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater 3:1 (vol:vol).

Table 18 listed the amount of other pollutants removal and their efficiencies. It can be observed that the removal efficiencies by using the selected conditions were resulted in increasing the COD and TSS removal efficiencies. It might come from a reason that, at the pH value of the mixed solution (pH 7), the treatment of the selected condition could precipitate well. Therefore, the COD and TSS removal efficiencies after treating with the selected conditions were rendered the remaining wastewater COD below 120 mg/L and wastewater TSS below 50 mg/L, which are in the current discharge standard of Industrial wastewater in Thailand (Appendix H).

On opposite, the reduction in terms of TS and TDS were less affected. This was due to the characteristic of zeolite industrial wastewater itself (Appendix B). Generally, zeolite was soluble in alkaline solution (39), which it causes the wastewater to be high in TS and TDS values. When comparing these characteristics of the mixture with the Industrial Effluent Standard of Thailand (Appendix H), it was found that the concentration of other pollutants (TS and TDS) were not met the standard requirement. Therefore, the additional treatment is needed to improve effluent quality before discharging to receiving water body. A number of different unit operations and

processes have been investigated in various advanced wastewater treatment applications. Although many of them are technically feasible, other factors, such as cost, operational requirements, and aesthetic considerations, are not favorable in some cases. Nevertheless, it is important that operators should be familiar with the more important operations and processes so that in any given situation they can consider all treatment possibilities. These important operations and processes for removal of TS and TDS are chemical precipitation, ion exchange, ultrafiltration, reverse osmosis, and electrodialysis. (11)

Despite the fact that operations and process was a good pathway for removal of certain pollutants but in this study, the further treatment was needed for study of the changing concentrations of TS and TDS. This suggests that given sufficient time of contact for TS and TDS precipitate. Also, addition of a sufficient was excess of precipitating agent to drive the precipitation reaction to completion.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

6.1 Conclusion

6.1.1 Characterization of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

6.1.1.1 Zeolite industrial wastewater characteristics were ranged between 12-13 for pH, 30-32 °C for temperature, 54-82 mg/L for BOD₅, 182-207 mg/L for COD, 12,437-12,705 mg/L for TS, 97-122 mg/L for TSS and 11,745-12,418 mg/L for TDS. In addition, the concentrations of total copper, zinc, mercury, nickel, lead, chromium, iron and cadmium were 0.070, 0.121, 0.001, ND, 0.228, 0.052, 0.850 and ND, respectively.

6.1.1.2 The XRD patterns were contained significant amount of Sodium Carbonate Hydrate, Sodium Carbonate, Calcium Magnesium Aluminum Fluoride Silicate and Iron Manganese Aluminum Silicate. The zeolite industrial wastewater had low concentration of heavy metals and high pH and TDS value. Therefore, the alkaline property of the solids of zeolite industrial wastewater were an efficient sorbent for pre-treatment in copper-brass pipe industrial wastewater. It can also be evaluated in wastewater treatment to precipitate heavy metallic ions.

6.1.1.3 Copper-brass pipe industrial wastewater characteristics were ranged between 1-2 for pH, 31-34 °C for temperature, 6-15 mg/L for BOD₅, 11-28 mg/L for COD, 4,528-4,563 mg/L for TS, 8-12 mg/L for TSS and 4,428-4,495 mg/L for TDS. In addition, the concentrations of total copper, zinc, mercury, nickel, lead, chromium, iron and cadmium were 491.2, 184.2, 0.001, 0.040, 0.514, 0.030, 6.175 and ND, respectively. The copper-brass pipe industrial wastewater had low pH and high concentration of heavy metals such as copper and zinc. Thus, some parameters such as pH, copper and zinc should be improved effluent quality before discharging to receiving water body.

6.1.1.4 The zeolite industrial wastewater, which riching with zeolite had pH value in an alkalinity range and might had potential capacity to treat metals from copper-brass pipe industrial wastewater. This substitution could reduce operational cost and maximize use of industrial waste in the selected condition.

6.1.2 Heavy metal removal efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

6.1.2.1 Experimental conditions for determining the relationship between heavy metals (copper and zinc) concentration and its (copper and zinc) removal efficiencies were selected from Appendix D, which gave the maximum efficiency of heavy metals removal. Experimental conditions were pH of 7 from the adjusted pH of zeolite industrial wastewater and pH 12.8 from the real wastewater of zeolite industrial at 30 minutes of contact time.

6.1.2.2 The pH of mixed solutions was varied from neutral to acidity range (pH 6.8-2.5) and pH in alkalinity range (pH 12.2-12.6) for the adjusted pH 7 of zeolite industrial wastewater and the real zeolite industrial wastewater, respectively.

6.1.2.3 Copper removal efficiencies;

- The trend of copper removal efficiency of treatment pH 7 could generally be divided into two stages as showed in Figure 9. In the first stage, the copper removal efficiencies were decreased when giving more initial copper concentration from 2.46 to 98.24 mg/L. In the second stage, after varying the initial copper concentration from 122.80 to 245.60 mg/L, the copper removal efficiencies were slightly change whether increased the initial copper concentration. Therefore, the maximum and minimum copper removal efficiencies for these two stages were 82.08% and 14.35%, respectively.

- The trend of copper removal efficiency of treatment pH 12.8 was increased when giving more the initial copper concentration. The maximum and minimum copper removal efficiencies were 97.42% and 65.39%, respectively.

- The relationship between the initial copper concentration in copper-brass pipe industrial wastewater and copper removal efficiency was linear regression, which had the equation of the relationship as follow;

$$\begin{array}{lcl} \text{Copper removal efficiency for the} & = & 90.008 - 0.407 \text{ the initial copper} \\ \text{first stage of treatment pH 7} & & \text{concentration} \end{array} \quad (8)$$

$$\begin{array}{lcl} \text{Copper removal efficiency for the} & = & 13.765 + 0.016 \text{ the initial copper} \\ \text{second stage of treatment pH 7} & & \text{concentration} \end{array} \quad (9)$$

$$\begin{array}{lcl} \text{Copper removal efficiency for the} & = & 81.835 + 0.082 \text{ the initial copper} \\ \text{treatment pH 12.8} & & \text{concentration} \end{array} \quad (10)$$

6.1.2.4 Zinc removal efficiencies;

- The trend of zinc removal efficiency of treatment pH 7 was decreased when giving more the initial zinc concentration from 0.92 to 73.68 mg/L. Afterward, they were slightly changed whether increased the initial zinc concentration from 82.89 to 92.10 mg/L. Therefore, the maximum and minimum zinc removal efficiencies were 84.80 % and 9.91 %, respectively.

- The trend of zinc removal efficiency of treatment pH 12.8 was slightly increased when giving more the initial zinc concentrations. The maximum and minimum zinc removal efficiencies were 95.58 % and 83.71 %, respectively.

- The relationship between the initial zinc concentration in copper-brass pipe industrial wastewater and zinc removal efficiency was linear regression, which had the equation of the relationship as follow;

$$\begin{array}{lcl} \text{Zinc removal efficiency for the} & = & 67.469 - 0.779 \text{ the initial zinc} \\ \text{treatment pH 7} & & \text{concentration} \end{array} \quad (11)$$

$$\begin{array}{lcl} \text{Zinc removal efficiency for the} & = & 85.444 + 0.132 \text{ the initial zinc} \\ \text{treatment pH 12.8} & & \text{concentration} \end{array} \quad (12)$$

6.1.2.5 Sorption isotherms for heavy metals concentration in copper-brass pipe industrial wastewater by using zeolite industrial wastewater for the treatment pH 7 and pH 12.8.

- Copper sorption isotherm of copper-brass pipe industrial wastewater was illustrated graphically by the phase partitioning relationships show in figure 11 and 12 for the first stage and the second stage of treatment pH 7, respectively and figure 13 for the treatment pH 12.8. The term C_e and X/m in all figure represented the equilibrium concentration of copper in copper-brass pipe industrial wastewater after sorption (mg/L) and the amount of sorbed copper from copper-brass pipe industrial wastewater (X) per the solids of zeolite industrial wastewater (m , mg/L). It indicated the linear relationship characteristic of favorable sorption. In addition, the experimental data in the first stage of the treatment pH 7 fitted to Langmuir isotherm, which had the equation as follow;

$$\frac{C_e}{(x/m)} = 0.8202 + 0.3377 C_e \quad (13)$$

On the other hand, for the second stage of the treatment pH 7 and the treatment of pH 12.8 were reasonably fitted well with the Freundlich isotherm, which had the equation for the second stage of the treatment pH 7 and the treatment of pH 12.8, respectively as follow;

$$\log (X/m) = 1.1849 \log C_e - 2.1828 \quad (16)$$

$$\log (X/m) = 2.3991 \log C_e - 0.7850 \quad (18)$$

- Zinc sorption isotherm of copper-brass pipe industrial wastewater was illustrated graphically by the phase partitioning relationships show in figure 15 and 16 for the treatment of pH 7 and the treatment of pH 12.8, respectively. The term C_e and X/m in all figure represented the equilibrium concentration of zinc in copper-brass pipe industrial wastewater after sorption (mg/L) and the amount of sorbed zinc from copper-brass pipe industrial wastewater (X) per the solids of zeolite industrial wastewater (m , mg/L). It indicated the linear relationship characteristic of favorable sorption. In addition, the experimental data in the treatment of pH 7 fitted to Langmuir isotherm, which had the equation as follow;

$$\frac{C_e}{(x/m)} = 2.5548 + 1.2998 C_e \quad (19)$$

On the other hand, for the treatment of pH 12.8 was reasonably fitted well with the Freundlich isotherm, which had the equation as follow;

$$\log (X/m) = 1.4561 \log C_e - 0.1673 \quad (22)$$

6.1.3 Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies.

6.1.3.1 The pH values of the mixed solution were in an acidity range for the adjusted pH of zeolite industrial wastewater. There were pH 2, 2.3, 2.5 and 2.8 for the pH of the adjusted zeolite industrial wastewater 3, 5, 7 and 9, respectively. On opposite, the real zeolite industrial wastewater had the pH of mixed solution in an alkalinity range (pH 12.4).

6.1.3.2 There are significantly different of heavy metals removal efficiencies in copper-brass pipe industrial wastewater by using zeolite industrial wastewater at different pH conditions of zeolite industrial wastewater and contact times. The maximum heavy metals removal efficiencies at pH 3, 5, 7, 9 and 12.8 were found at 30 minutes of contact time. The highest removal efficiency around 98.47% and 94.21% for copper and zinc, respectively were found at pH 12.8 of the real zeolite industrial wastewater. For the pH adjusted wastewater, the maximum removal efficiency around 17.35% and 9.94% for copper and zinc, respectively were found at pH 7. According to the results, the equilibrium reached at 30 minutes and was selected the optimum contact time for the further experiment. Therefore, pH 7 was selected from the adjusted wastewater pH for further experiment. At the same time, pH 12.8 from the real zeolite industrial wastewater also selected since it gave the highest heavy metals removal efficiencies.

6.1.3.3 In order to establish the practical utility of the copper and zinc removal, these two metals could be treated at the same reaction conditions.

6.1.4 Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiencies.

6.1.4.1 The ratios were varied as 3:1, 2:1, 1:1, 1:2 and 1:3 (vol:vol), respectively and all experiments had different the pH value of mixed solution. The pH values of the mixed solution were in an acidity range (pH 2.0-5.7). On opposite, the mixing of real zeolite industrial wastewater had pH in an alkalinity range (pH 7.0-12.7).

6.1.4.2 The amount of copper and zinc were removed more when increasing concentrations of copper-brass pipe industrial wastewater from ratio 1:1 to 3:1 (vol:vol) and decreased when giving more concentration of zeolite industrial wastewater from 1:1 to 1:3 (vol:vol).

6.1.4.3 The highest percentage of heavy metals removal efficiencies were 98.47% and 94.21% for copper and zinc, respectively at ratio 1:1 (vol:vol) of the treatment of real zeolite industrial wastewater. Moreover, all the treatments of real zeolite industrial wastewater had higher amount of heavy metals sludge than those treatments of pH adjusted.

6.1.4.4 The pH of mixed solution of the real zeolite industrial wastewater at ratio 3:1 and that of the pH adjusted of zeolite industrial wastewater at ratio 1:3 (vol:vol) had pH range in the Industrial Effluent Standard of Thailand requirement (pH 5.5-9) (appendix H).

6.1.4.5 The highest efficiency of heavy metals removal at the ratio 1:1 of real zeolite industrial wastewater was not much higher than those of the ratio 3:1 of real zeolite industrial wastewater. Moreover, mixture of treatment of the real zeolite industrial wastewater at ratio 3:1 had a pH range in the standard requirement. Therefore, the ratio 3:1 of copper-brass pipe industrial wastewater to zeolite industrial wastewater was selected. It was used for further experiment as an experimental condition for a study of other pollutants (COD, TS, TDS and TSS) treating efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater.

6.1.5 Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition.

6.1.5.1 The selected conditions from all experiments for using observation of their influence to other pollutants treating efficiency were pH 12.8 (the real pH of zeolite industrial wastewater), 30 minutes of contact time and ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater 3:1 (vol:vol).

6.1.5.2 Other pollutants removal efficiencies of copper-brass pipe industrial wastewater by using the selected conditions, including COD, TS, TDS and TSS were 38.71%, 2.36%, 2.05% and 23.86%, respectively (appendix F).

6.1.5.3 The COD and TSS removal efficiencies by using the selected conditions were resulted in increasing. Therefore, the COD and TSS removal efficiencies after treating with the selected conditions were rendered the remaining wastewater COD below 120 mg/L and wastewater TSS below 50 mg/L, which are in the current discharge the Industrial Effluent Standard of Thailand (appendix H).

6.1.5.4 The reduction in terms of TS and TDS by using the selected conditions were less affected. Moreover, the remaining concentrations of TS and TDS after treating with the selected conditions were not met the Industrial Effluent Standard of Thailand (appendix H). Therefore, the additional treatment is needed to improve effluent quality before discharging to receiving water body.

6.2 Recommendation

6.2.1 Recommendation for application

6.2.1.1 Zeolite industrial wastewater could pre-treat copper and zinc well, the application of zeolite industrial wastewater for pre-treatment of the wastewater containing other heavy metals to precipitate as heavy metallic ions should be investigate.

6.2.1.2 In case of zeolite industrial wastewater, it gave high pH value and could also applied to adjust pH value from acidity wastewater industrial.

6.2.2 Recommendation for further study

6.2.2.1 Since the amount of copper and zinc concentration after treated by using the selected conditions were still high and did not meet the standard requirement, therefore, the in-depth study of improving copper and zinc removal efficiencies by using zeolite industrial wastewater should be continued investigate.

6.2.2.2 The reduction in terms of Total Solids (TS) and Total Dissolved Solids (TDS) were poor, the additional treatment study should be done to enhance its study of the changing concentrations.

6.2.2.3 A study of heavy metals sludge waste management such as handling and disposal should be conducted for finding the suitable practices measures.

6.2.2.4 These study results provide information on the zeolite industrial wastewater application, heavy metals removal efficiencies and other pollutants (COD, TS, TDS and TSS) removal efficiencies. Further experiment should be study the economic possibility of using zeolite industrial wastewater and Sodium Hydroxide (NaOH) to enhance the wastewater treatment plant. This is a technical possibility of using zeolite industrial wastewater should also be reviewed together with cost benefit analysis.

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Appendix A

Pretest and Results of Pretest

1. Objective of the study

- 1.1 To study zeolite industrial wastewater characteristics.
- 1.2 To study copper-brass pipe industrial wastewater characteristics.
- 1.3 To study the possibility of using zeolite industrial wastewater as an adsorbent for removal copper from synthetic wastewater.

2. Scope of the study

2.1 This experiment was conducted under the adsorption system at laboratory study scale in the laboratory room condition at Department of Environmental Health Science, Faculty of Public Health, Mahidol University.

2.2 Zeolite industrial wastewater was collected from zeolite industrial at outlet point of collection tank from process production. The random samples were 5 times at only period of time by grab sample. The samples were fixed with conc. nitric acid for preservation and kept in the refrigerator (4°C).

2.3 Copper-brass pipe industrial wastewater was collected from copper-brass pipe production industrial at outlet point of collection tank from process production. The random samples were 5 times at only period of time by grab sample. The samples were fixed with conc. nitric acid for preservation and kept in the refrigerator (4°C).

2.4 Synthetic wastewater used in pretest experiment, it was prepared from a standard solution of copper concentration 1,000 ppm and diluted with deionized water.

2.5 The adsorption condition was performed at pH 4, contact time 30 minutes and ratio of synthetic wastewater to zeolite industrial wastewater 100 mL : 250 mL, respectively.

3. Procedure of the experiment

3.1 Determination characteristics of zeolite industrial wastewater and copper-brass pipe industrial wastewater.

- The sample were analyzed for pH, Temperature, BOD, COD, TS, TDS, TSS and heavy metals (Cu and Zn) as a method described in Table A-1

3.2 Determination of the possibility of using zeolite industrial wastewater as an adsorbent for removal copper from synthetic wastewater.

- *Preparation of synthetic wastewater and experiment.*

Copper solution was prepare from a standard solution of copper concentration 1,000 ppm and diluted with deionized water. It was then made up to a concentration of copper solution 5, 10, 15, 20 and 25 mg. Cu per 100 mL, respectively the Erlenmeyer flask size 500 mL and added with 250 mL of zeolite industrial wastewater. All samples were shaken at 120 rpm by reciprocal shaker for 30 minute at room temperature and before shaken, they were adjusted to pH 4 with nitric acid. After shaking, all units were filtered by filter through GF/C paper with 47 mm Ø and digested by nitric acid for determined heavy metals remaining in solution by Atomic Absorption Spectrophotometer (AAS).

- *Efficiency of copper removal from synthetic wastewater by using zeolite industrial wastewater as an adsorbent.*

$$\text{Copper removal efficiency (\%)} = \frac{[C_i - C_f] \times 100}{C_i}$$

Where

C_i - The initial copper concentration (mg/L)

C_f - The final copper concentration (mg/L)

Table A-1 Parameters and analytical methods.

Parameter	Method of analytical
pH	Electrometric method
Temperature	Thermometer
BOD ₅	Azid modification of the Winkler method
COD	Closed reflux method
TS	Evaporation, then oven dried at 103 – 105 °C
TDS	Filtrate through GF/C, then filtrated water oven dried at 103 – 105 °C
TSS	Filtrate through GF/C, then oven dried at 103 – 105 °C
Heavy metals (Copper and Zinc)	Digesting with Conc. HNO ₃ , filtering through filter paper No.42 and analyzing by Atomic Absorption Spectrophotometer method (AAS)

Source: Franson MAH, et al. and American Public Health Association (36, 37)

4. Results of the experiment

4.1 The characteristics of zeolite industrial wastewater and copper-brass pipe industrial wastewater are shown in Table A-2 and Table A-3.

4.2 The efficiency of copper removal from synthetic wastewater.

- Zeolite industrial wastewater was used to adsorb various concentrations of copper solutions 4.080, 8.163, 12.246, 16.326 and 20.408 mg/L, respectively (5, 10, 15, 20 and 25 mg. Cu 100 mL) for 30 minutes at room temperature. The results are showed in Table A-4 and Figure A-1. It was indicated that the higher copper concentration gave the higher color removal efficiency. The average copper removal efficiency was 73.27 %.

Table A-2 Characteristics of zeolite industrial wastewater.

Parameters	Characteristic
pH	11.61
Temperature ($^{\circ}\text{C}$)	32
BOD (mg/L)	54
COD (mg/L)	219
TS (mg/L)	2,850
TDS (mg/L)	2,669
TSS (mg/L)	102
Copper (mg/L)	0.36
Zinc (mg/L)	< 0.02

Table A-3 Characteristics of copper-brass pipe industrial wastewater.

Parameters	Characteristic
pH	1.03
Temperature ($^{\circ}\text{C}$)	35
BOD (mg/L)	15
COD (mg/L)	46
TS (mg/L)	11,691
TDS (mg/L)	11,490
TSS (mg/L)	80
Copper (mg/L)	1,120
Zinc (mg/L)	494

Table A-4 The percentage of copper removal efficiency from synthetic wastewater by using zeolite industrial wastewater as a sorbent.

The initial copper concentration (mg/L)	The final copper concentration (mg/L)	(%) Copper removal efficiency
4.080	1.121	72.52
8.163	2.188	73.20
12.246	3.281	73.21
16.326	4.291	73.72
20.408	5.366	73.71

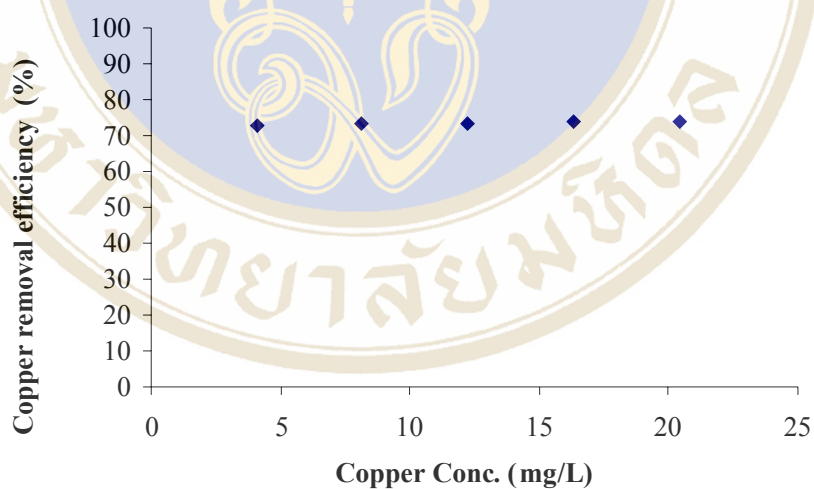


Figure A-1 Removal of copper concentration at various concentrations by using zeolite industrial wastewater.

Appendix B

Experimental results of part 1:

Characterization of zeolite industrial wastewater and Copper-brass pipe industrial wastewater

Table B-1 Characteristics of zeolite industrial wastewater.

Parameters	Wastewater Characteristic
pH	12-13
Temperature (°C)	30-32
BOD ₅ (mg/L)	54-82
COD (mg/L)	182-207
TS (mg/L)	12,437 – 12,705
SS (mg/L)	97-122
TDS (mg/L)	11,745-12,418
Heavy metals	
- Cu (mg/L)	0.070
- Zn (mg/L)	0.121
- Hg (mg/L)	0.001
- Ni (mg/L)	ND
- Pb (mg/L)	0.228
- Cr (mg/L)	0.052
- Fe (mg/L)	0.850
- Cd (mg/L)	ND

Table B-2 Characteristics of copper-brass pipe industrial wastewater.

Parameters	Wastewater Characteristic
pH	1-2
Temperature ($^{\circ}\text{C}$)	31-34
BOD ₅ (mg/L)	6-15
COD (mg/L)	11-28
TS (mg/L)	4,528-4,563
SS (mg/L)	8-12
TDS (mg/L)	4,428-4,495
Heavy metals	
- Cu (mg/L)	491.200
- Zn (mg/L)	184.200
- Hg (mg/L)	0.001
- Ni (mg/L)	0.040
- Pb (mg/L)	0.514
- Cr (mg/L)	0.030
- Fe (mg/L)	6.175
- Cd (mg/L)	ND

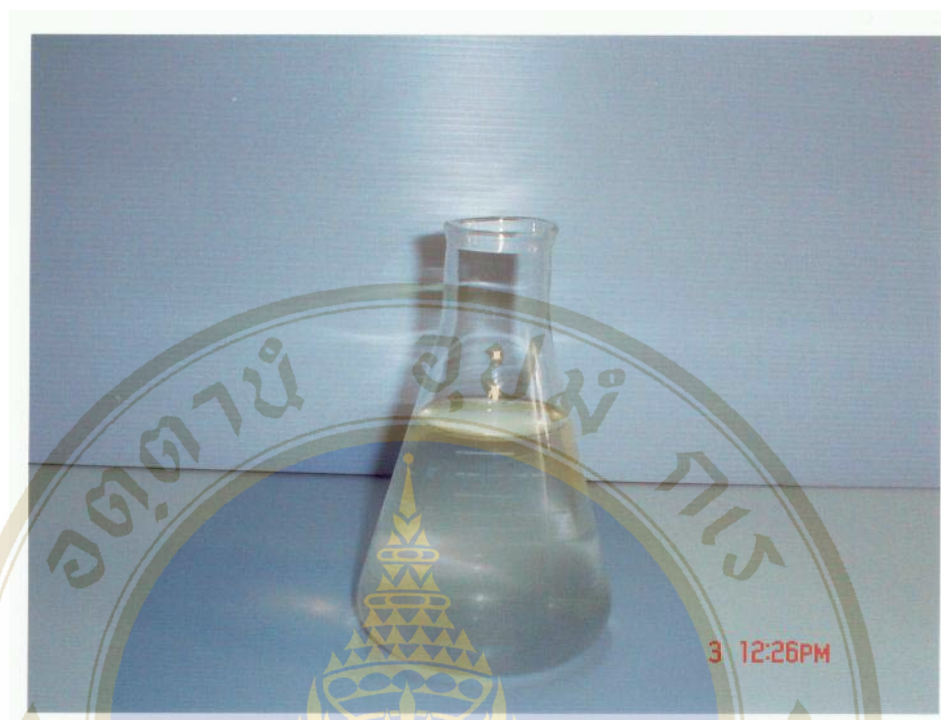


Figure B-1 Zeolite industrial wastewater



Figure B-2 Copper-brass pipe industrial wastewater

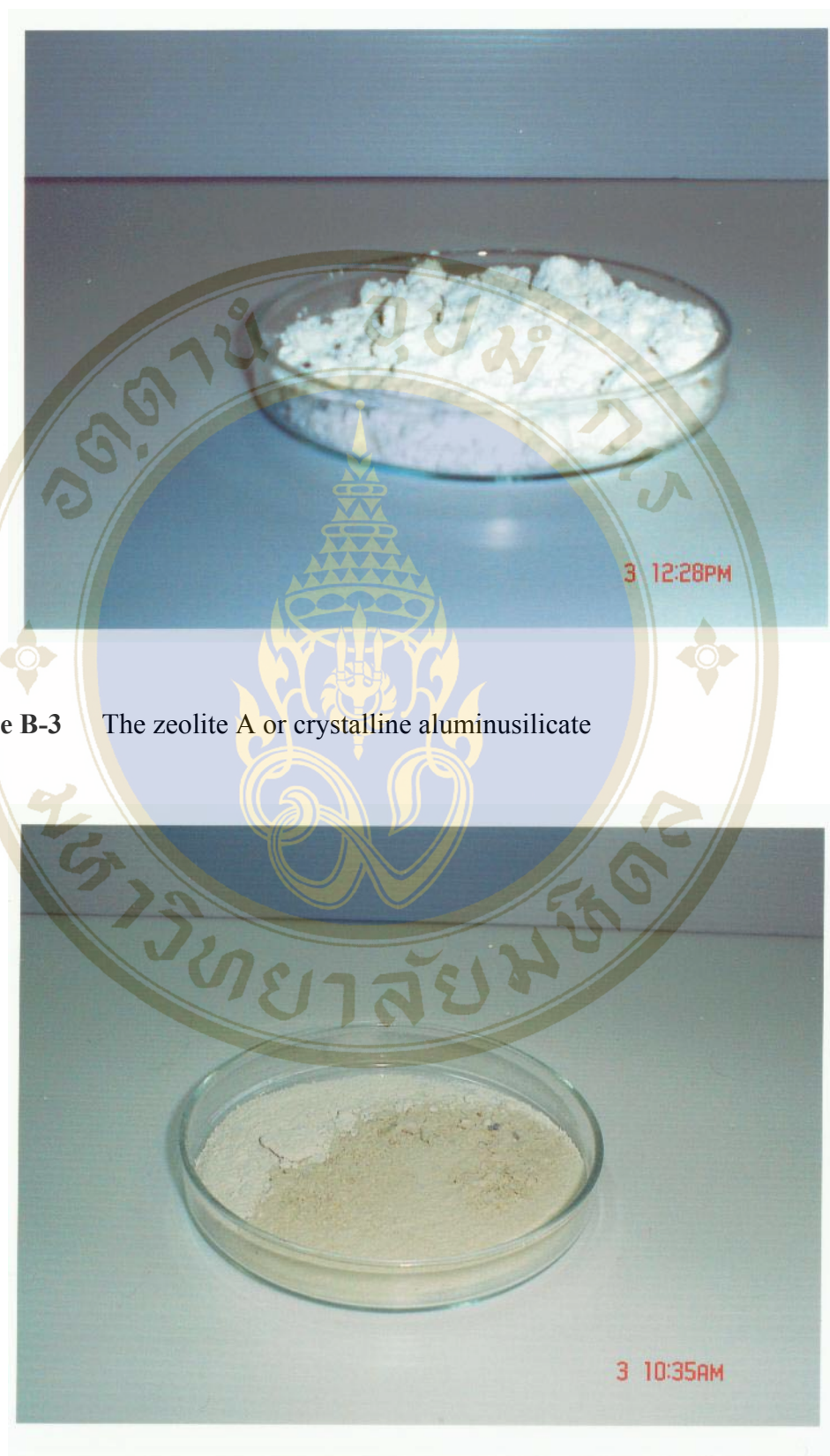


Figure B-3 The zeolite A or crystalline aluminosilicate

Figure B-4 The solids of zeolite industrial wastewater

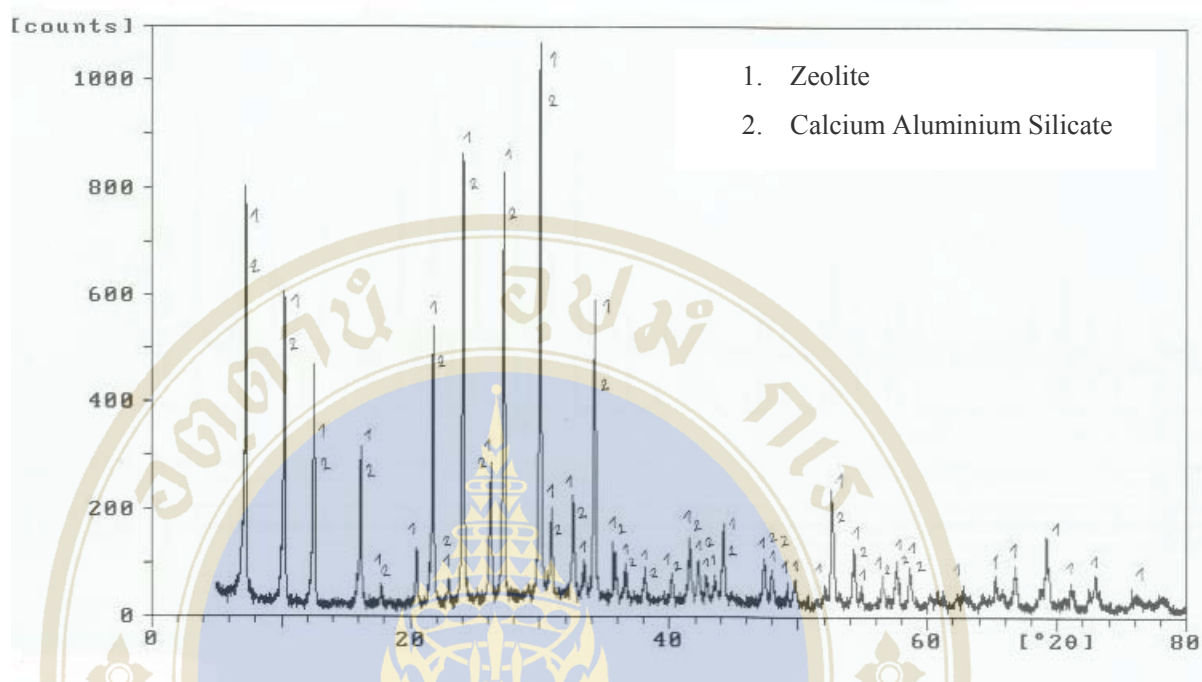


Figure B-5 X-ray diffraction analysis of Zeolite A

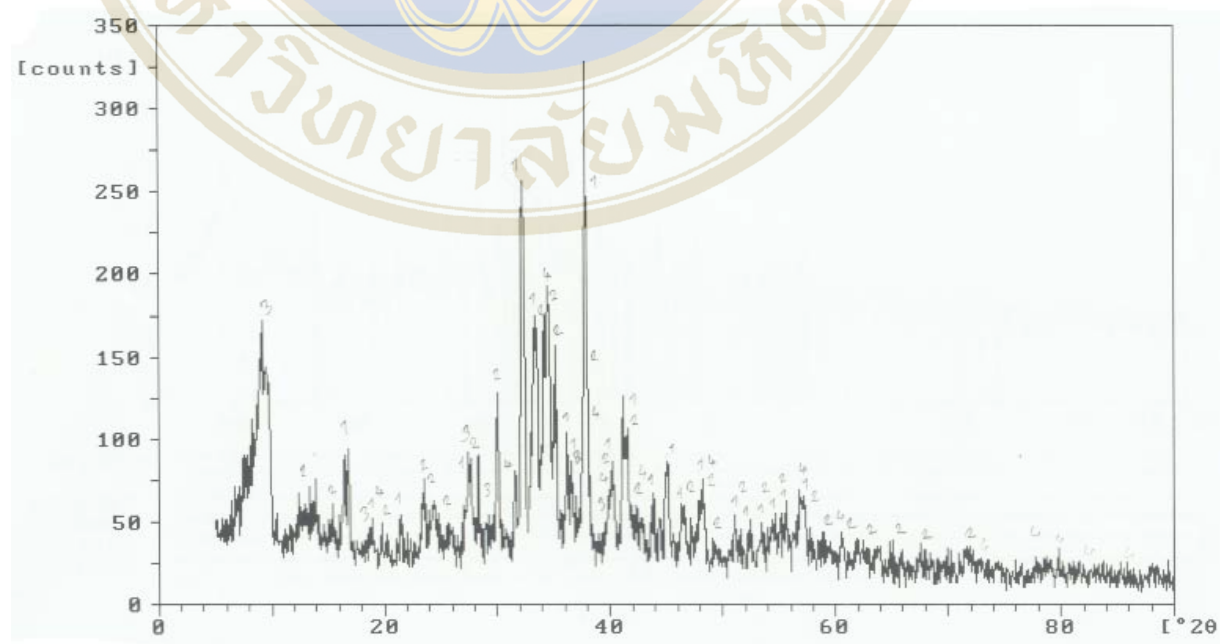


Figure B-6 X-ray diffraction analysis of the solids of zeolite industrial wastewater

Appendix C

Experimental results of part 2:

Heavy metal removal efficiency from copper-brass pipe industrial wastewater by using zeolite industrial wastewater

Table C-1 The copper and zinc concentrations at various dilutions of copper-brass pipe industrial wastewater.

Copper-brass pipe industrial wastewater (mL)	Copper concentration (mg/L)	Zinc concentration (mg/L)
1	4.91	1.84
5	24.56	9.21
10	49.12	18.42
20	98.24	36.84
30	147.36	55.26
40	196.48	73.68
50	245.60	92.10
60	294.72	110.52
70	343.84	128.94
80	392.96	147.36
90	442.08	165.78
100	491.20	184.20

Table C-2 The percentage of copper removal efficiencies from copper-brass pipe industrial wastewater (CIW) at various initial concentrations of copper by using zeolite industrial wastewater (ZIW) for the treatment of pH 7 and pH12.8 conditions.

The treatment of pH	Copper conc. in CIW	Initial copper conc. in the mixture			Final copper conc. in the mixture			% Copper removal		
		1	2	3	1	2	3	1	2	3
pH 7	4.912	2.456	2.456	2.456	0.52	0.43	0.38	78.83	82.49	84.53
	24.56	12.28	12.28	12.28	2.24	2.08	2.36	81.76	83.06	80.78
	49.12	24.56	24.56	24.56	4.55	4.73	4.47	81.47	80.74	81.80
	98.24	49.12	49.12	49.12	9.72	10.76	9.83	80.21	78.09	79.99
	147.36	73.68	73.68	73.68	17.58	18.23	17.68	76.14	75.26	76.00
	196.48	98.24	98.24	98.24	64.74	67.03	63.47	34.10	31.77	35.39
	245.60	122.80	122.80	122.80	100.33	103.04	102.42	18.30	16.09	16.60
	294.72	147.36	147.36	147.36	130.02	124.86	123.77	11.77	15.27	16.01
	343.84	171.92	171.92	171.92	141.37	145.36	145.82	17.77	15.45	15.18
	392.96	196.48	196.48	196.48	159.27	162.4	162.08	18.94	17.35	17.51
	442.08	221.04	221.04	221.04	181.67	184.42	183.36	17.81	16.57	17.05
pH 12.8	491.20	245.60	245.60	245.60	203.01	202.15	201.14	17.34	17.69	18.10
	4.912	2.456	2.456	2.456	1.02	0.92	0.61	58.47	62.54	75.16
	24.56	12.28	12.28	12.28	1.64	2.11	1.79	86.64	82.82	85.42
	49.12	24.56	24.56	24.56	3.42	3.74	4.08	86.07	84.77	83.39
	98.24	49.12	49.12	49.12	3.88	4.06	4.15	92.10	91.73	91.55
	147.36	73.68	73.68	73.68	4.90	4.92	4.96	93.35	93.32	93.27
	196.48	98.24	98.24	98.24	5.01	5.07	5.06	94.90	94.84	94.85
	245.60	122.80	122.80	122.80	5.51	5.50	5.57	95.51	95.52	95.46
	294.72	147.36	147.36	147.36	5.96	5.94	5.94	95.96	95.97	95.97
	343.84	171.92	171.92	171.92	6.06	6.02	6.01	96.48	96.50	96.50
	392.96	196.48	196.48	196.48	6.37	6.21	5.80	96.76	96.84	97.05
	442.08	221.04	221.04	221.04	6.27	6.12	6.07	97.16	97.23	97.25
	491.20	245.60	245.60	245.60	6.72	6.22	6.07	97.26	97.47	97.53

Table C-3 MEAN, SD and RANGE of the % copper removal efficiencies from copper-brass pipe industrial wastewater (CIW) at various initial concentrations of copper by using zeolite industrial wastewater (ZIW) for the treatment of pH 7 and pH12.8 conditions.

The treatment of pH	Copper conc. in CIW	% Copper removal			MEAN	SD	RANGE
		1	2	3			
pH 7	4.912	78.83	82.49	84.53	82.08	2.89	78.83-84.53
	24.56	81.76	83.06	80.78	81.84	1.14	80.78-83.06
	49.12	81.47	80.74	81.80	81.35	0.54	80.74-81.80
	98.24	80.21	78.09	79.99	79.44	1.16	78.09-80.21
	147.36	76.14	75.26	76.00	75.80	0.48	75.26-76.14
	196.48	34.10	31.77	35.39	33.75	1.84	31.77-35.39
	245.60	18.30	16.09	16.60	17.00	1.16	16.09-18.30
	294.72	11.77	15.27	16.01	14.35	2.27	11.77-16.01
	343.84	17.77	15.45	15.18	16.14	1.42	15.18-17.77
	392.96	18.94	17.35	17.51	17.93	0.88	17.35-18.94
	442.08	17.81	16.57	17.05	17.14	0.63	16.57-17.81
pH 12.8	491.20	17.34	17.69	18.10	17.71	0.38	17.34-18.10
	4.912	58.47	62.54	75.16	65.39	8.70	58.47-75.16
	24.56	86.64	82.82	85.42	84.93	1.95	82.82-86.64
	49.12	86.07	84.77	83.39	84.73	1.34	83.39-86.07
	98.24	92.10	91.73	91.55	91.80	0.28	91.55-92.10
	147.36	93.35	93.32	93.27	93.31	0.04	93.27-93.35
	196.48	94.90	94.84	94.85	94.86	0.03	94.84-94.90
	245.60	95.51	95.52	95.46	95.50	0.03	95.46-95.52
	294.72	95.96	95.97	95.97	95.96	0.01	95.96-95.97
	343.84	96.48	96.50	96.50	96.49	0.02	96.48-96.50
	392.96	96.76	96.84	97.05	96.88	0.15	96.76-97.05
	442.08	97.16	97.23	97.25	97.22	0.05	97.16-97.25
	491.20	97.26	97.47	97.53	97.42	0.14	97.26-97.53

Table C-4 The percentage of zinc removal efficiencies from copper-brass pipe industrial wastewater (CIW) at various initial concentrations of copper by using zeolite industrial wastewater (ZIW) for the treatment of pH 7 and pH12.8 conditions.

The treatment of pH	Zinc conc. in CIW	Initial zinc conc. in the mixture			Final zinc conc. in the mixture			% Zinc removal		
		1	2	3	1	2	3	1	2	3
pH 7	1.842	0.921	0.921	0.921	0.21	0.12	0.09	77.20	86.97	90.23
	9.21	4.605	4.605	4.605	0.76	1.05	0.92	83.50	77.20	80.02
	18.42	9.21	9.21	9.21	3.07	3.35	3.18	66.67	63.63	65.47
	36.84	18.42	18.42	18.42	11.00	10.62	10.93	40.28	42.35	40.66
	55.26	27.63	27.63	27.63	19.04	18.40	18.76	31.09	33.41	32.10
	73.68	36.84	36.84	36.84	27.86	29.16	28.27	24.38	20.85	23.26
	92.10	46.05	46.05	46.05	37.25	36.59	37.39	19.11	20.54	18.81
	110.52	55.26	55.26	55.26	45.69	44.95	45.32	17.32	18.66	17.99
	128.94	64.47	64.47	64.47	55.84	56.03	56.38	13.39	13.09	12.55
	147.36	73.68	73.68	73.68	65.87	66.78	66.48	10.60	9.36	9.77
	165.78	82.89	82.89	82.89	72.82	73.44	72.67	12.15	11.40	12.33
pH 12.8	184.20	92.10	92.10	92.10	81.27	80.60	81.04	11.76	12.49	12.01
	1.842	0.921	0.921	0.921	0.14	0.13	0.17	84.80	85.88	81.54
	9.21	4.605	4.605	4.605	0.84	0.61	0.71	81.76	86.75	84.58
	18.42	9.21	9.21	9.21	1.38	1.26	1.43	85.02	86.32	84.47
	36.84	18.42	18.42	18.42	2.04	1.93	1.95	88.93	89.52	89.41
	55.26	27.63	27.63	27.63	2.55	2.38	2.74	90.77	91.39	90.08
	73.68	36.84	36.84	36.84	2.98	2.96	3.10	91.91	91.97	91.59
	92.10	46.05	46.05	46.05	3.30	3.28	3.43	92.83	92.88	92.55
	110.52	55.26	55.26	55.26	3.47	3.54	3.28	93.72	93.59	94.06
	128.94	64.47	64.47	64.47	3.51	3.39	3.47	94.56	94.74	94.62
	147.36	73.68	73.68	73.68	3.63	3.60	3.54	95.07	95.11	95.20
	165.78	82.89	82.89	82.89	3.84	3.53	3.62	95.37	95.74	95.63
	184.20	92.10	92.10	92.10	4.10	4.16	4.09	95.55	95.48	95.56

Table C-5 MEAN, SD and RANGE of the % zinc removal efficiencies from copper-brass pipe industrial wastewater (CIW) at various initial concentrations of copper by using zeolite industrial wastewater (ZIW) for the treatment of pH 7 and pH12.8 conditions.

The treatment of pH	Zinc conc. in CIW	% Zinc removal			MEAN	SD	RANGE
		1	2	3			
pH 7	1.842	77.20	86.97	90.23	84.80	6.78	77.20-90.23
	9.21	83.50	77.20	80.02	80.24	3.15	77.20-83.50
	18.42	66.67	63.63	65.47	65.26	1.53	63.63-66.67
	36.84	40.28	42.35	40.66	41.10	1.10	40.28-42.35
	55.26	31.09	33.41	32.10	32.21	1.16	31.09-33.41
	73.68	24.38	20.85	23.26	22.83	1.80	20.85-24.38
	92.10	19.11	20.54	18.81	19.48	0.93	18.81-20.54
	110.52	17.32	18.66	17.99	17.99	0.67	17.32-18.66
	128.94	13.39	13.09	12.55	13.01	0.42	12.55-13.39
	147.36	10.60	9.36	9.77	9.91	0.63	9.36-10.60
	165.78	12.15	11.40	12.33	11.96	0.49	11.40-12.33
pH 12.8	184.20	11.76	12.49	12.01	12.08	0.37	11.76-12.49
	1.842	84.80	85.88	81.54	83.71	2.26	81.54-85.88
	9.21	81.76	86.75	84.58	84.36	2.50	81.76-86.75
	18.42	85.02	86.32	84.47	85.23	0.95	84.47-86.32
	36.84	88.93	89.52	89.41	89.31	0.32	88.93-89.52
	55.26	90.77	91.39	90.08	90.73	0.65	90.08-91.39
	73.68	91.91	91.97	91.59	91.83	0.21	91.59-91.97
	92.10	92.83	92.88	92.55	92.75	0.18	92.55-92.88
	110.52	93.72	93.59	94.06	93.79	0.24	93.59-94.06
	128.94	94.56	94.74	94.62	94.63	0.09	94.56-94.74
	147.36	95.07	95.11	95.20	95.13	0.06	95.07-95.20
	165.78	95.37	95.74	95.63	95.58	0.19	95.37-95.74
	184.20	95.55	95.48	95.56	95.53	0.04	95.48-95.55

Appendix D

Experimental results of part 3:

Effect of pH conditions of zeolite industrial wastewater and contact times to heavy metals removal efficiencies

Table D-1 The amount of copper concentration removal from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Initial Cu conc. (mg/L)			Final Cu conc. (mg/L)			Amount of copper removal (mg/L)		
		1	2	3	1	2	3	1	2	3
pH 3	0 min.	245.60	245.60	245.60	242.20	242.58	242.03	3.40	3.02	3.57
	15 min.	245.60	245.60	245.60	240.00	240.00	240.40	5.60	5.60	5.20
	30 min.	245.60	245.60	245.60	222.03	221.00	221.40	23.57	24.60	24.20
	60 min.	245.60	245.60	245.60	241.20	241.40	241.40	4.40	4.20	4.20
	120 min.	245.60	245.60	245.60	242.00	242.03	241.00	3.60	3.57	4.60
pH 5	0 min.	245.60	245.60	245.60	243.08	243.25	242.50	2.52	2.35	3.10
	15 min.	245.60	245.60	245.60	240.70	241.85	240.80	4.90	3.75	4.80
	30 min.	245.60	245.60	245.60	225.95	223.53	224.98	19.65	22.07	20.62
	60 min.	245.60	245.60	245.60	230.52	230.35	229.10	15.08	15.25	16.50
	120 min.	245.60	245.60	245.60	240.57	240.75	240.69	5.03	4.85	4.91
pH 7	0 min.	245.60	245.60	245.60	243.25	243.75	243.50	2.35	1.85	2.10
	15 min.	245.60	245.60	245.60	209.78	212.10	214.35	35.82	33.50	31.25
	30 min.	245.60	245.60	245.60	207.18	201.48	200.28	38.42	44.12	45.32
	60 min.	245.60	245.60	245.60	209.85	209.35	215.85	35.75	36.25	29.75
	120 min.	245.60	245.60	245.60	229.35	229.48	234.60	16.25	16.12	11.00
pH 9	0 min.	245.60	245.60	245.60	243.75	243.25	243.18	1.85	2.35	2.42
	15 min.	245.60	245.60	245.60	225.78	223.10	221.68	19.82	22.50	23.92
	30 min.	245.60	245.60	245.60	215.38	215.60	216.33	30.22	30.00	29.27
	60 min.	245.60	245.60	245.60	229.10	221.35	221.60	16.50	24.25	24.00
	120 min.	245.60	245.60	245.60	235.35	236.35	237.77	10.25	9.25	7.83
pH 12.8	0 min.	245.60	245.60	245.60	3.88	4.88	4.19	241.72	240.72	241.41
	15 min.	245.60	245.60	245.60	3.69	4.75	3.88	241.91	240.85	241.72
	30 min.	245.60	245.60	245.60	3.42	4.23	3.63	242.18	241.37	241.97
	60 min.	245.60	245.60	245.60	3.74	4.73	3.97	241.86	240.87	241.63
	120 min.	245.60	245.60	245.60	3.77	4.80	4.13	241.83	240.80	241.47

Table D-2 Mean, SD and Range of the amount of copper concentration removal from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Amount of copper removal (mg/L)			MEAN	SD	RANGE
		1	2	3			
pH 3	0 min.	3.40	3.02	3.57	3.33	0.28	3.02-3.57
	15 min.	5.60	5.60	5.20	5.47	0.23	5.20-5.60
	30 min.	23.57	24.60	24.20	24.12	0.52	23.57-24.60
	60 min.	4.40	4.20	4.20	4.27	0.12	4.20-4.40
	120 min.	3.60	3.57	4.60	3.92	0.59	3.57-4.60
pH 5	0 min.	2.52	2.35	3.10	2.66	0.39	2.35-3.10
	15 min.	4.90	3.75	4.80	4.48	0.64	3.75-4.90
	30 min.	19.65	22.07	20.62	20.78	1.22	19.65-22.07
	60 min.	15.08	15.25	16.50	15.61	0.78	15.08-16.50
	120 min.	5.03	4.85	4.91	4.93	0.09	4.85-5.03
pH 7	0 min.	2.35	1.85	2.10	2.10	0.25	1.85-2.35
	15 min.	35.82	33.50	31.25	33.52	2.29	31.25-35.82
	30 min.	38.42	44.12	45.32	42.62	3.69	38.42-45.32
	60 min.	35.75	36.25	29.75	33.92	3.62	29.75-36.25
	120 min.	16.25	16.12	11.00	14.46	2.99	11.00-16.25
pH 9	0 min.	1.85	2.35	2.42	2.21	0.31	1.85-2.42
	15 min.	19.82	22.50	23.92	22.08	2.08	19.82-23.92
	30 min.	30.22	30.00	29.27	29.83	0.50	29.27-30.22
	60 min.	16.50	24.25	24.00	21.58	4.40	16.50-24.25
	120 min.	10.25	9.25	7.83	9.11	1.22	7.83-10.25
pH 12.8	0 min.	241.72	240.72	241.41	241.28	0.51	240.72-241.72
	15 min.	241.91	240.85	241.72	241.49	0.57	240.85-241.91
	30 min.	242.18	241.37	241.97	241.84	0.42	241.37-242.18
	60 min.	241.86	240.87	241.63	241.45	0.52	240.87-241.86
	120 min.	241.83	240.80	241.47	241.37	0.52	240.80-241.83

Table D-3 The percentage of copper removal efficiencies from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Initial Cu conc. (mg/L)			Final Cu conc. (mg/L)			% Copper removal		
		1	2	3	1	2	3	1	2	3
pH 3	0 min.	245.60	245.60	245.60	242.20	242.58	242.03	1.38	1.23	1.45
	15 min.	245.60	245.60	245.60	240.00	240.00	240.40	2.28	2.28	2.12
	30 min.	245.60	245.60	245.60	222.03	221.00	221.40	9.60	10.02	9.85
	60 min.	245.60	245.60	245.60	241.20	241.40	241.40	1.79	1.71	1.71
	120 min.	245.60	245.60	245.60	242.00	242.03	241.00	1.47	1.45	1.87
pH 5	0 min.	245.60	245.60	245.60	243.08	243.25	242.50	1.03	0.96	1.26
	15 min.	245.60	245.60	245.60	240.70	241.85	240.80	2.00	1.53	1.95
	30 min.	245.60	245.60	245.60	225.95	223.53	224.98	8.00	8.99	8.40
	60 min.	245.60	245.60	245.60	230.52	230.35	229.10	6.14	6.21	6.72
	120 min.	245.60	245.60	245.60	240.57	240.75	240.69	2.05	1.97	2.00
pH 7	0 min.	245.60	245.60	245.60	243.25	243.75	243.50	0.96	0.75	0.86
	15 min.	245.60	245.60	245.60	209.78	212.10	214.35	14.58	13.64	12.72
	30 min.	245.60	245.60	245.60	207.18	201.48	200.28	15.64	17.96	18.45
	60 min.	245.60	245.60	245.60	209.85	209.35	215.85	14.56	14.76	12.11
	120 min.	245.60	245.60	245.60	229.35	229.48	234.60	6.62	6.56	4.48
pH 9	0 min.	245.60	245.60	245.60	243.75	243.25	243.18	0.75	0.96	0.99
	15 min.	245.60	245.60	245.60	225.78	223.10	221.68	8.07	9.16	9.74
	30 min.	245.60	245.60	245.60	215.38	215.60	216.33	12.30	12.21	11.92
	60 min.	245.60	245.60	245.60	229.10	221.35	221.60	6.72	9.87	9.77
	120 min.	245.60	245.60	245.60	235.35	236.35	237.77	4.17	3.77	3.19
pH 12.8	0 min.	245.60	245.60	245.60	3.88	4.88	4.19	98.42	98.01	98.29
	15 min.	245.60	245.60	245.60	3.69	4.75	3.88	98.50	98.07	98.42
	30 min.	245.60	245.60	245.60	3.42	4.23	3.63	98.61	98.28	98.52
	60 min.	245.60	245.60	245.60	3.74	4.73	3.97	98.48	98.07	98.38
	120 min.	245.60	245.60	245.60	3.77	4.80	4.13	98.46	98.05	98.32

Table D-4 Mean, SD and Range of the percentage of copper removal efficiencies from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	% Copper removal			MEAN	SD	RANGE
		1	2	3			
pH 3	0 min.	1.38	1.23	1.45	1.36	0.11	1.23-1.45
	15 min.	2.28	2.28	2.12	2.23	0.09	2.12-2.28
	30 min.	9.60	10.02	9.85	9.82	0.21	9.60-10.02
	60 min.	1.79	1.71	1.71	1.74	0.05	1.71-1.79
	120 min.	1.47	1.45	1.87	1.60	0.24	1.45-1.87
pH 5	0 min.	1.03	0.96	1.26	1.08	0.16	0.96-1.26
	15 min.	2.00	1.53	1.95	1.83	0.26	1.53-2.00
	30 min.	8.00	8.99	8.40	8.46	0.50	8.00-8.99
	60 min.	6.14	6.21	6.72	6.36	0.32	6.14-6.72
	120 min.	2.05	1.97	2.00	2.01	0.04	1.97-2.05
pH 7	0 min.	0.96	0.75	0.86	0.86	0.10	0.75-0.96
	15 min.	14.58	13.64	12.72	13.65	0.93	12.72-14.58
	30 min.	15.64	17.96	18.45	17.35	1.50	15.64-18.45
	60 min.	14.56	14.76	12.11	13.81	1.47	12.11-14.76
	120 min.	6.62	6.56	4.48	5.89	1.22	4.48-6.62
pH 9	0 min.	0.75	0.96	0.99	0.90	0.13	0.75-0.99
	15 min.	8.07	9.16	9.74	8.99	0.85	8.07-9.74
	30 min.	12.30	12.21	11.92	12.15	0.20	11.92-12.30
	60 min.	6.72	9.87	9.77	8.79	1.79	6.72-9.87
	120 min.	4.17	3.77	3.19	3.71	0.50	3.19-4.17
pH 12.8	0 min.	98.42	98.01	98.29	98.24	0.21	98.01-98.42
	15 min.	98.50	98.07	98.42	98.33	0.23	98.07-98.50
	30 min.	98.61	98.28	98.52	98.47	0.17	98.28-98.61
	60 min.	98.48	98.07	98.38	98.31	0.21	98.07-98.48
	120 min.	98.46	98.05	98.32	98.28	0.21	98.05-98.46

Table D-5 The amount of zinc concentration removal from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Initial Zn conc.			Final Zn conc.			Amount of zinc removal		
		(mg/L)			(mg/L)			(mg/L)		
		1	2	3	1	2	3	1	2	3
pH 3	0 min.	92.10	92.10	92.10	91.83	91.93	91.92	0.27	0.17	0.18
	15 min.	92.10	92.10	92.10	91.02	91.22	91.16	1.08	0.88	0.94
	30 min.	92.10	92.10	92.10	86.47	85.62	86.66	5.63	6.48	5.44
	60 min.	92.10	92.10	92.10	88.25	88.10	88.23	3.85	4.00	3.87
	120 min.	92.10	92.10	92.10	90.75	91.07	91.01	1.35	1.03	1.09
pH 5	0 min.	92.10	92.10	92.10	91.62	91.83	91.58	0.48	0.27	0.52
	15 min.	92.10	92.10	92.10	90.48	90.33	90.50	1.62	1.77	1.60
	30 min.	92.10	92.10	92.10	89.25	88.73	88.72	2.85	3.37	3.38
	60 min.	92.10	92.10	92.10	89.73	89.25	90.02	2.37	2.85	2.08
	120 min.	92.10	92.10	92.10	89.33	89.45	89.42	2.77	2.65	2.68
pH 7	0 min.	92.10	92.10	92.10	91.73	91.80	91.75	0.37	0.30	0.35
	15 min.	92.10	92.10	92.10	89.73	88.72	89.22	2.37	3.38	2.88
	30 min.	92.10	92.10	92.10	83.05	82.37	83.42	9.05	9.73	8.68
	60 min.	92.10	92.10	92.10	88.93	89.37	87.70	3.17	2.73	4.40
	120 min.	92.10	92.10	92.10	91.90	91.70	91.42	0.20	0.40	0.68
pH 9	0 min.	92.10	92.10	92.10	91.62	91.50	91.25	0.48	0.60	0.85
	15 min.	92.10	92.10	92.10	88.97	88.10	89.10	3.13	4.00	3.00
	30 min.	92.10	92.10	92.10	87.02	85.97	87.53	5.08	6.13	4.57
	60 min.	92.10	92.10	92.10	90.15	89.57	89.70	1.95	2.53	2.40
	120 min.	92.10	92.10	92.10	90.90	90.30	90.53	1.20	1.80	1.57
pH 12.8	0 min.	92.10	92.10	92.10	6.30	6.18	6.25	85.80	85.92	85.85
	15 min.	92.10	92.10	92.10	6.05	5.96	6.10	86.05	86.12	86.00
	30 min.	92.10	92.10	92.10	5.33	5.50	5.18	86.77	86.60	86.92
	60 min.	92.10	92.10	92.10	6.13	6.03	6.08	85.97	86.07	86.02
	120 min.	92.10	92.10	92.10	6.18	6.10	6.15	85.92	86.00	85.95

Table D-6 Mean, SD and Range of the amount of zinc concentration removal from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Amount of zinc removal (mg/L)			MEAN	SD	RANGE
		1	2	3			
pH 3	0 min.	0.27	0.17	0.18	0.21	0.06	0.17-0.27
	15 min.	1.08	0.88	0.94	0.97	0.10	0.88-1.08
	30 min.	5.63	6.48	5.44	5.85	0.55	5.44-6.48
	60 min.	3.85	4.00	3.87	3.91	0.08	3.85-4.00
	120 min.	1.35	1.03	1.09	1.16	0.17	1.03-1.35
pH 5	0 min.	0.48	0.27	0.52	0.42	0.13	0.27-0.52
	15 min.	1.62	1.77	1.60	1.66	0.09	1.60-1.77
	30 min.	2.85	3.37	3.38	3.20	0.30	2.85-3.38
	60 min.	2.37	2.85	2.08	2.43	0.39	2.08-2.85
	120 min.	2.77	2.65	2.68	2.70	0.06	2.65-2.77
pH 7	0 min.	0.37	0.30	0.35	0.34	0.04	0.30-0.37
	15 min.	2.37	3.38	2.88	2.88	0.51	2.37-3.38
	30 min.	9.05	9.73	8.68	9.15	0.53	8.68-9.73
	60 min.	3.17	2.73	4.40	3.43	0.87	2.73-4.40
	120 min.	0.20	0.40	0.68	0.43	0.24	0.20-0.68
pH 9	0 min.	0.48	0.60	0.85	0.64	0.19	0.48-0.85
	15 min.	3.13	4.00	3.00	3.38	0.54	3.00-4.00
	30 min.	5.08	6.13	4.57	5.26	0.80	4.57-6.13
	60 min.	1.95	2.53	2.40	2.29	0.30	1.95-2.53
	120 min.	1.20	1.80	1.57	1.52	0.30	1.20-1.80
pH 12.8	0 min.	85.80	85.92	85.85	85.86	0.06	85.80-85.92
	15 min.	86.05	86.12	86.00	86.06	0.06	86.00-86.12
	30 min.	86.77	86.60	86.92	86.76	0.16	86.60-86.92
	60 min.	85.97	86.07	86.02	86.02	0.05	85.97-86.07
	120 min.	85.92	86.00	85.95	85.96	0.04	85.92-86.00

Table D-7 The percentage of zinc removal efficiencies from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	Initial Zn conc. (mg/L)			Final Zn conc. (mg/L)			% Zinc removal		
		1	2	3	1	2	3	1	2	3
pH 3	0 min.	92.10	92.10	92.10	91.83	91.93	91.92	0.29	0.18	0.20
	15 min.	92.10	92.10	92.10	91.02	91.22	91.16	1.17	0.96	1.02
	30 min.	92.10	92.10	92.10	86.47	85.62	86.66	6.11	7.04	5.91
	60 min.	92.10	92.10	92.10	88.25	88.10	88.23	4.18	4.34	4.20
	120 min.	92.10	92.10	92.10	90.75	91.07	91.01	1.47	1.12	1.18
pH 5	0 min.	92.10	92.10	92.10	91.62	91.83	91.58	0.52	0.29	0.56
	15 min.	92.10	92.10	92.10	90.48	90.33	90.50	1.76	1.92	1.74
	30 min.	92.10	92.10	92.10	89.25	88.73	88.72	3.09	3.66	3.67
	60 min.	92.10	92.10	92.10	89.73	89.25	90.02	2.57	3.09	2.26
	120 min.	92.10	92.10	92.10	89.33	89.45	89.42	3.01	2.88	2.91
pH 7	0 min.	92.10	92.10	92.10	91.73	91.80	91.75	0.40	0.33	0.38
	15 min.	92.10	92.10	92.10	89.73	88.72	89.22	2.57	3.67	3.13
	30 min.	92.10	92.10	92.10	83.05	82.37	83.42	9.83	10.56	9.42
	60 min.	92.10	92.10	92.10	88.93	89.37	87.70	3.44	2.96	4.78
	120 min.	92.10	92.10	92.10	91.90	91.70	91.42	0.22	0.43	0.74
pH 9	0 min.	92.10	92.10	92.10	91.62	91.50	91.25	0.52	0.65	0.92
	15 min.	92.10	92.10	92.10	88.97	88.10	89.10	3.40	4.34	3.26
	30 min.	92.10	92.10	92.10	87.02	85.97	87.53	5.52	6.66	4.96
	60 min.	92.10	92.10	92.10	90.15	89.57	89.70	2.12	2.75	2.61
	120 min.	92.10	92.10	92.10	90.90	90.30	90.53	1.30	1.95	1.70
pH 12.8	0 min.	92.10	92.10	92.10	6.30	6.18	6.25	93.16	93.29	93.21
	15 min.	92.10	92.10	92.10	6.05	5.96	6.10	93.43	93.51	93.38
	30 min.	92.10	92.10	92.10	5.33	5.50	5.18	94.21	94.03	94.38
	60 min.	92.10	92.10	92.10	6.13	6.03	6.08	93.34	93.45	93.40
	120 min.	92.10	92.10	92.10	6.18	6.10	6.15	93.29	93.38	93.32

Table D-8 Mean, SD and Range of the percentage of zinc removal efficiencies from copper-brass pipe industrial wastewater (CIW) by using zeolite industrial wastewater (ZIW) at pH conditions and contact times.

pH condition	Contact times	% Zinc removal			MEAN	SD	RANGE
		1	2	3			
pH 3	0 min.	0.29	0.18	0.20	0.22	0.06	0.18-0.29
	15 min.	1.17	0.96	1.02	1.05	0.11	0.96-1.17
	30 min.	6.11	7.04	5.91	6.35	0.60	5.91-7.04
	60 min.	4.18	4.34	4.20	4.24	0.09	4.18-4.34
	120 min.	1.47	1.12	1.18	1.26	0.18	1.12-1.47
pH 5	0 min.	0.52	0.29	0.56	0.46	0.15	0.29-0.56
	15 min.	1.76	1.92	1.74	1.81	0.10	1.74-1.92
	30 min.	3.09	3.66	3.67	3.47	0.33	3.09-3.66
	60 min.	2.57	3.09	2.26	2.64	0.42	2.26-3.09
	120 min.	3.01	2.88	2.91	2.93	0.07	2.88-3.01
pH 7	0 min.	0.40	0.33	0.38	0.37	0.04	0.33-0.40
	15 min.	2.57	3.67	3.13	3.12	0.55	2.57-3.67
	30 min.	9.83	10.56	9.42	9.94	0.58	9.42-10.56
	60 min.	3.44	2.96	4.78	3.73	0.94	2.96-4.78
	120 min.	0.22	0.43	0.74	0.46	0.26	0.22-0.74
pH 9	0 min.	0.52	0.65	0.92	0.70	0.20	0.52-0.92
	15 min.	3.40	4.34	3.26	3.67	0.59	3.26-4.34
	30 min.	5.52	6.66	4.96	5.71	0.86	4.96-6.66
	60 min.	2.12	2.75	2.61	2.49	0.33	2.12-2.75
	120 min.	1.30	1.95	1.70	1.65	0.33	1.30-1.95
pH 12.8	0 min.	93.16	93.29	93.21	93.22	0.07	93.16-93.29
	15 min.	93.43	93.51	93.38	93.44	0.07	93.38-93.51
	30 min.	94.21	94.03	94.38	94.21	0.17	94.03-94.38
	60 min.	93.34	93.45	93.40	93.40	0.05	93.34-93.45
	120 min.	93.29	93.38	93.32	93.33	0.04	93.29-93.38

Appendix E

Experimental results of part 4:

Determination of a suitable ratio of copper-brass pipe industrial wastewater to zeolite industrial wastewater for heavy metals removal efficiency

Table E-1 The amount of heavy metals sludge at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	Heavy metals sludge (mg/L)			MEAN	SD	RANGE
		1	2	3			
pH 7	3:1	148	160	140	149.33	10.07	140-160
	2:1	128	148	120	132	14.42	120-148
	1:1	104	112	96	104	8.00	96-112
	1:2	162	173	247	194	46.23	162-247
	1:3	205	189	189	194.33	9.24	189-205
pH 12.8	3:1	1,276	1,352	1,340	1,322.67	40.86	1,276-1,352
	2:1	1,448	1,452	1,460	1,453.33	6.11	1,448-1,460
	1:1	1,136	1,140	1,116	1,130.67	12.86	1,116-1,140
	1:2	888	892	836	872	31.24	836-892
	1:3	716	684	704	701.33	16.17	684-716

Table E-2 The amount of copper removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	The initial Cu conc.			The final Cu conc.			Amount of Cu removal		
		(mg/L)			(mg/L)			(mg/L)		
		1	2	3	1	2	3	1	2	3
pH 7	3:1	368.40	368.40	368.40	327.65	320.90	322.15	40.75	47.50	46.25
	2:1	327.47	327.47	327.47	304.97	293.22	303.47	22.50	34.25	24.00
	1:1	245.60	245.60	245.60	207.18	201.48	200.28	38.42	44.12	45.32
	1:2	163.73	163.73	163.73	-	144.70	144.67	8.81	19.03	19.06
	1:3	122.80	122.80	122.80	103.15	-	103.63	19.65	26.49	19.17
pH 12.8	3:1	368.40	368.40	368.40	6.28	6.65	6.18	362.12	361.75	362.22
	2:1	327.47	327.47	327.47	17.33	15.98	16.53	310.14	311.49	310.94
	1:1	245.60	245.60	245.60	3.42	4.23	3.63	242.18	241.37	241.97
	1:2	163.73	163.73	163.73	9.95	8.83	8.73	153.78	154.90	155.00
	1:3	122.80	122.80	122.80	14.70	14.85	15.40	108.10	107.95	107.40

Table E-3 Mean, SD and Range of the amount of copper removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	Amount of Cu removal			MEAN	SD	RANGE
		(mg/L)					
		1	2	3			
pH 7	3:1	40.75	47.50	46.25	44.83	3.59	40.75-47.50
	2:1	22.50	34.25	24.00	26.92	6.39	22.50-34.25
	1:1	38.42	44.12	45.32	42.62	3.69	38.42-45.32
	1:2	-	19.03	19.06	19.04	0.02	19.03-19.06
	1:3	19.65	-	19.17	19.41	0.34	19.17-19.65
pH 12.8	3:1	362.12	361.75	362.22	362.03	0.25	361.75-362.22
	2:1	310.14	311.49	310.94	310.86	0.68	310.14-311.49
	1:1	242.18	241.37	241.97	241.84	0.42	241.37-242.18
	1:2	153.78	154.90	155.00	154.56	0.68	153.78-155.00
	1:3	108.10	107.95	107.40	107.82	0.37	107.40-108.10

Table E-4 The percentage of copper removal efficiencies at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	The initial Cu conc.			The final Cu conc.			% Copper removal		
		(mg/L)			(mg/L)					
		1	2	3	1	2	3	1	2	3
pH 7	3:1	368.40	368.40	368.40	327.65	320.90	322.15	11.06	12.89	12.55
	2:1	327.47	327.47	327.47	304.97	293.22	303.47	6.87	10.46	7.33
	1:1	245.60	245.60	245.60	207.18	201.48	200.28	15.64	17.96	18.45
	1:2	163.73	163.73	163.73	-	144.70	144.67	-	11.62	11.64
	1:3	122.80	122.80	122.80	103.15	-	103.63	16.00	-	15.61
pH 12.8	3:1	368.40	368.40	368.40	6.28	6.65	6.18	98.30	98.19	98.32
	2:1	327.47	327.47	327.47	17.33	15.98	16.53	94.71	95.12	94.95
	1:1	245.60	245.60	245.60	3.42	4.23	3.63	98.61	98.28	98.52
	1:2	163.73	163.73	163.73	9.95	8.83	8.73	93.92	94.61	94.67
	1:3	122.80	122.80	122.80	14.70	14.85	15.40	88.03	87.91	87.46

Table E-5 Mean, SD and Range of the percentage of copper removal efficiencies at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	% Copper removal			MEAN	SD	RANGE
		1	2	3			
pH 7	3:1	11.06	12.89	12.55	12.17	0.97	11.06-12.89
	2:1	6.87	10.46	7.33	8.22	1.95	6.87-10.46
	1:1	15.64	17.96	18.45	17.35	1.50	15.64-18.45
	1:2	-	11.62	11.64	11.63	0.01	11.62-11.64
	1:3	16.00	-	15.61	15.81	0.28	15.61-16.00
pH 12.8	3:1	98.30	98.19	98.32	98.27	0.07	98.19-98.32
	2:1	94.71	95.12	94.95	94.93	0.21	94.71-95.12
	1:1	98.61	98.28	98.52	98.47	0.17	98.28-98.61
	1:2	93.92	94.61	94.67	94.40	0.41	93.92-94.67
	1:3	88.03	87.91	87.46	87.80	0.30	87.46-88.03

Table E-6 The amount of zinc removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	The initial Zn conc.			The final Zn conc.			Amount of Zn removal		
		(mg/L)			(mg/L)			(mg/L)		
		1	2	3	1	2	3	1	2	3
pH 7	3:1	138.15	138.15	138.15	125.55	126.92	126.03	12.60	11.23	12.12
	2:1	122.80	122.80	122.80	114.10	114.15	114.50	8.70	8.65	8.30
	1:1	92.10	92.10	92.10	83.05	82.37	83.42	9.05	9.73	8.68
	1:2	61.40	61.40	61.40	-	57.79	57.95	-	3.61	3.45
	1:3	46.05	46.05	46.05	41.57	-	41.71	4.48	-	4.34
pH 12.8	3:1	138.15	138.15	138.15	11.23	10.48	11.18	126.92	127.67	126.97
	2:1	122.80	122.80	122.80	8.35	8.45	8.58	114.45	114.35	114.22
	1:1	92.10	92.10	92.10	5.33	5.50	5.18	86.77	86.60	86.92
	1:2	61.40	61.40	61.40	10.63	10.85	10.10	50.77	50.55	51.30
	1:3	46.05	46.05	46.05	15.13	15.98	15.23	30.92	30.07	30.82

Table E-7 Mean, SD and Range of the amount of zinc removal at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	Amount of Zn removal			MEAN	SD	RANGE
		(mg/L)					
		1	2	3			
pH 7	3:1	12.60	11.23	12.12	11.98	0.70	11.23-12.60
	2:1	8.70	8.65	8.30	8.55	0.22	8.30-8.70
	1:1	9.05	9.73	8.68	9.15	0.53	8.68-9.73
	1:2	-	3.61	3.45	3.53	0.11	3.45-3.61
	1:3	4.48	-	4.34	4.41	0.10	4.34-4.48
pH 12.8	3:1	126.92	127.67	126.97	127.19	0.42	126.92-127.67
	2:1	114.45	114.35	114.22	114.34	0.12	114.22-114.45
	1:1	86.77	86.60	86.92	86.76	0.16	86.60-86.92
	1:2	50.77	50.55	51.30	50.87	0.39	50.55-51.30
	1:3	30.92	30.07	30.82	30.60	0.46	30.07-30.82

Table E-8 The percentage of zinc removal efficiencies at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	The initial Zn conc.			The final Zn conc.			% Zinc removal		
		(mg/L)			(mg/L)					
		1	2	3	1	2	3	1	2	3
pH 7	3:1	138.15	138.15	138.15	125.55	126.92	126.03	9.12	8.13	8.77
	2:1	122.80	122.80	122.80	114.10	114.15	114.50	7.08	7.04	6.76
	1:1	92.10	92.10	92.10	83.05	82.37	83.42	9.83	10.56	9.42
	1:2	61.40	61.40	61.40	-	57.79	57.95	-	5.88	5.62
	1:3	46.05	46.05	46.05	41.57	-	41.71	9.73	-	9.42
pH 12.8	3:1	138.15	138.15	138.15	11.23	10.48	11.18	91.87	92.41	91.91
	2:1	122.80	122.80	122.80	8.35	8.45	8.58	93.20	93.12	93.01
	1:1	92.10	92.10	92.10	5.33	5.50	5.18	94.21	94.03	94.38
	1:2	61.40	61.40	61.40	10.63	10.85	10.10	82.69	82.33	83.55
	1:3	46.05	46.05	46.05	15.13	15.98	15.23	67.14	65.30	66.93

Table E-9 Mean, SD and Range of the percentage of zinc removal efficiencies at various ratios of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol) for the treatment of pH 7 and pH 12.8.

pH conditions	Ratio	% Zinc removal			MEAN	SD	RANGE
		1	2	3			
pH 7	3:1	9.12	8.13	8.77	8.67	0.50	8.13-9.12
	2:1	7.08	7.04	6.76	6.96	0.18	6.76-7.08
	1:1	9.83	10.56	9.42	9.94	0.58	9.42-10.56
	1:2	-	5.88	5.62	5.75	0.18	5.62-5.88
	1:3	9.73	-	9.42	9.58	0.21	9.42-9.73
pH 12.8	3:1	91.87	92.41	91.91	92.06	0.30	91.87-92.41
	2:1	93.20	93.12	93.01	93.11	0.09	93.01-93.20
	1:1	94.21	94.03	94.38	94.21	0.17	94.03-94.38
	1:2	82.69	82.33	83.55	82.86	0.63	82.33-83.55
	1:3	67.14	65.30	66.93	66.46	1.01	65.30-67.14

Appendix F

Experimental results of part 5:

Other pollutants (COD, TS, TDS and TSS) treating efficiency of copper-brass pipe industrial wastewater by using zeolite industrial wastewater at selected reaction condition

Table F-1 The amount of other pollutants removal in the mixture at selected conditions.

Other pollutants	Amount of other pollutants in the mixture (mg/L)								
	Before treatment			After treatment			Amount of other pollutants removal		
	1	2	3	1	2	3	1	2	3
COD	47.35	47.82	49.66	28.33	29.33	31.14	19.02	18.49	18.52
TS	4,490	4,545	4,728	4,388	4,431	4,619	102	114	109
TDS	4,302	4,420	4,428	4,217	4,325	4,338	85	95	90
TSS	60	68	64	47	50	49	13	18	15

Table F-2 Mean, SD and Range of the amount of other pollutants removal in the mixture at selected conditions.

Other pollutants	Amount of other pollutants removal			MEAN	SD	RANGE
	1	2	3			
COD	19.02	18.49	18.52	18.68	0.30	18.49-19.02
TS	102	114	109	108.33	6.03	102-114
TDS	85	95	90	90.00	5.00	85-90
TSS	13	18	15	15.33	2.52	13-18

Table F-3 The percentage of other pollutants removal efficiencies at selected conditions.

Other pollutants	Amount of other pollutants in the mixture (mg/L)						% other pollutants removal		
	Before treatment			After treatment					
	1	2	3	1	2	3	1	2	3
COD	47.35	47.82	49.66	28.33	29.33	31.14	40.17	38.67	37.29
TS	4,490	4,545	4,728	4,388	4,431	4,619	2.27	2.51	2.31
TDS	4,302	4,420	4,428	4,217	4,325	4,338	1.98	2.15	2.03
TSS	60	68	64	47	50	49	21.67	26.47	23.44

Table F-4 Mean, SD and Range of the percentage of other pollutants removal efficiencies at selected conditions.

Other pollutants	% other pollutants removal			MEAN	SD	RANGE
	1	2	3			
COD	40.17	38.67	37.29	38.71	1.44	37.29-40.17
TS	2.27	2.51	2.31	2.36	0.13	2.27-2.51
TDS	1.98	2.15	2.03	2.05	0.09	1.98-2.15
TSS	21.67	26.47	23.44	23.86	2.43	21.67-26.47

Appendix G

Statistical analysis

**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater and the initial copper concentration
for the first stage of treatment pH 7
(Linear regression test at 0.05 level of significant)**

Descriptive statistics

CONC	Mean	N	Std. Deviation
2.456	81.95000	3	2.888114
12.280	81.86667	3	1.143737
24.560	81.33667	3	.542433
49.120	79.43000	3	1.165676
73.680	75.80000	3	.472864
98.240	33.75333	3	1.834730
Total	72.35611	18	17.946718

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.794(a)	.631	.608	11.239581

a Predictors: (Constant), CONC

ANOVA(b)

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	3454.189	1	3454.189	27.343	.000(a)
	Residual	2021.251	16	126.328		
	Total	5475.440	17			

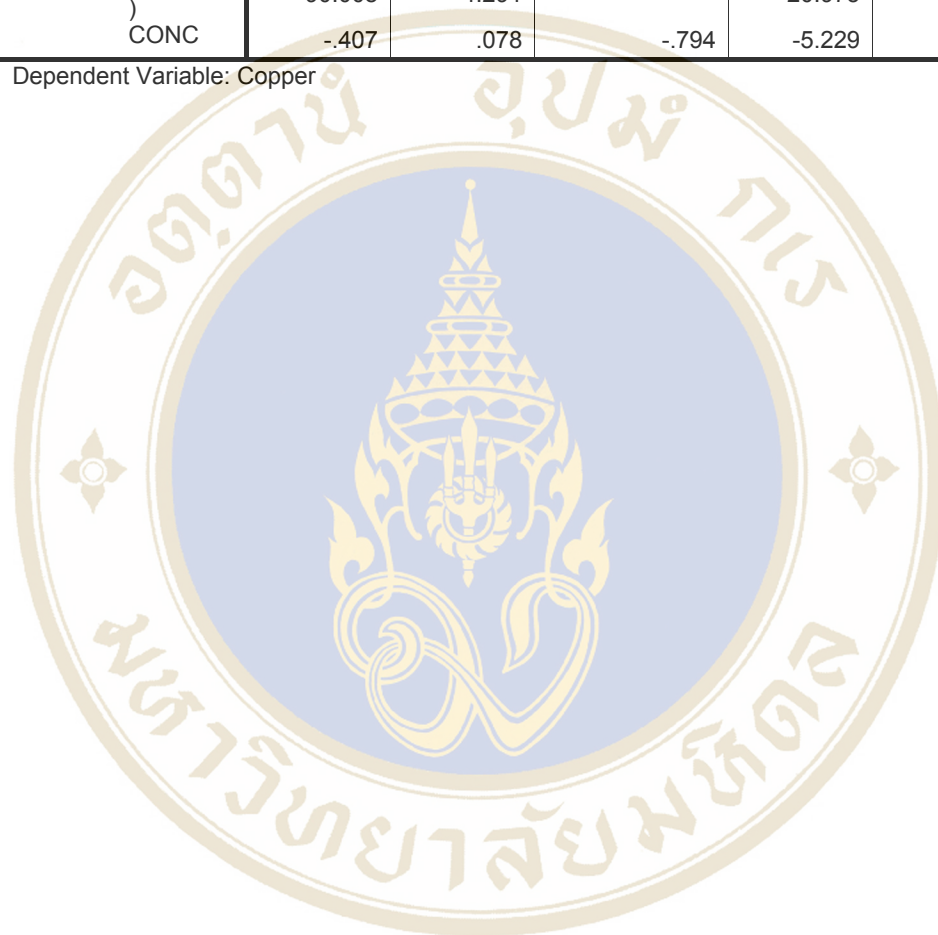
a Predictors: (Constant), CONC

b Dependent Variable: Copper

Coefficients(a)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	90.008	4.291		20.975	.000
	CONC	-.407	.078	-.794	-5.229	.000

a. Dependent Variable: Copper



**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater and the initial copper concentration**

for the second stage of treatment pH 7

(Linear regression test at 0.05 level of significant)

Descriptive statistics

CONC	Mean	N	Std. Deviation
122.800	16.99667	3	1.157166
147.360	14.35000	3	2.264774
171.920	16.13333	3	1.423809
196.480	17.93333	3	.875462
221.040	17.14333	3	.625247
245.600	17.71000	3	.380395
Total	16.71111	18	1.637807

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.421(a)	.178	.126	1.530977

a Predictors: (Constant), CONC

ANOVA(b)

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	8.099	1	8.099	3.455	.082(a)
	Residual	37.502	16	2.344		
	Total	45.601	17			

a Predictors: (Constant), CONC

b Dependent Variable: Copper

Coefficients(a)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	13.765	1.625		8.470	.000
	CONC	.016	.009	.421	1.859	.082

a Dependent Variable: Copper

**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater and the initial copper concentration
for the treatment of pH 12.8**

(Linear regression test at 0.05 level of significant)

Descriptive statistics

CONC	Mean	N	Std. Deviation
2.456	65.39000	3	8.702350
12.280	84.96000	3	1.951102
24.560	84.74333	3	1.340199
49.120	91.79333	3	.280416
73.680	93.31333	3	.040415
98.240	94.86333	3	.032146
122.800	95.49667	3	.032146
147.360	95.96667	3	.005774
171.920	96.49333	3	.011547
196.480	96.88333	3	.149778
221.040	97.21333	3	.047258
245.600	97.42000	3	.141774
Total	91.21139	36	9.238168

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.725(a)	.525	.511	6.459893

a Predictors: (Constant), CONC

ANOVA(b)

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	1568.204	1	1568.204	37.580	.000(a)
	Residual	1418.827	34	41.730		
	Total	2987.031	35			

a Predictors: (Constant), CONC

b Dependent Variable: Copper

Coefficients(a)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	81.835	1.870		43.752	.000
	CONC	.082	.013	.725	6.130	.000

a Dependent Variable: Copper

**The comparison of the zinc removal efficiencies from copper-brass pipe
industrial wastewater and the initial zinc concentration
for the treatment of pH 7**

(Linear regression test at 0.05 level of significant)

Descriptive statistics

CONC	Mean	N	Std. Deviation
.921	84.80000	3	6.780627
4.605	80.24000	3	3.155757
9.210	65.25667	3	1.531187
18.420	41.09667	3	1.101923
27.630	32.20000	3	1.163228
36.840	22.83000	3	1.803857
46.050	19.48667	3	.924464
55.260	17.99000	3	.670000
64.470	13.01000	3	.425676
73.680	9.91000	3	.631744
82.890	11.96000	3	.493254
92.100	12.08667	3	.370990
Total	34.23889	36	26.787271

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.886(a)	.784	.778	12.622346

a Predictors: (Constant), CONC

ANOVA(b)

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	19697.523	1	19697.523	123.632	.000(a)
	Residual	5417.003	34	159.324		
	Total	25114.526	35			

a Predictors: (Constant), CONC

b Dependent Variable: Zinc

Coefficients(a)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	67.469	3.655		18.461	.000
	CONC	-.779	.070	-.886	-11.119	.000

a Dependent Variable: Zinc

**The comparison of the zinc removal efficiencies from copper-brass pipe
industrial wastewater and the initial zinc concentration
for the treatment of pH 12.8**

(Linear regression test at 0.05 level of significant)

Descriptive statistics

CONC	Mean	N	Std. Deviation
.921	84.07333	3	2.259410
4.605	84.36333	3	2.502046
9.210	85.27000	3	.950000
18.420	89.28667	3	.313741
27.630	90.74667	3	.655312
36.840	91.82333	3	.204287
46.050	92.75333	3	.177858
55.260	93.79000	3	.242693
64.470	94.64000	3	.091652
73.680	95.12667	3	.066583
82.890	95.58000	3	.190000
92.100	95.53000	3	.043589
Total	91.08194	36	4.339924

Model Summary

Model	R	R Square	Adjusted R Square	Std. Error of the Estimate
1	.927(a)	.860	.856	1.646517

a Predictors: (Constant), CONC

ANOVA(b)

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	567.048	1	567.048	209.164	.000(a)
	Residual	92.175	34	2.711		
	Total	659.223	35			

a Predictors: (Constant), CONC

b Dependent Variable: Zinc

Coefficients(a)

Model		Unstandardized Coefficients		Standardized Coefficients	t	Sig.
		B	Std. Error	Beta		
1	(Constant)	85.444	.477		179.223	.000
	CONC	.132	.009	.927	14.463	.000

a Dependent Variable: Zinc

**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater at pH conditions (pH 3, 5, 7, 9 and 12.8)
for 5 contact times (0, 15, 30, 60 and 120 minutes)
(Two-way ANOVA test at 0.05 level of significant)**

Dependent Variable: copper removal efficiencies

pH	Time	Mean	Std. Deviation	N
3.0	0	242.2700	.28160	3
	15	240.1333	.23094	3
	30	221.4767	.51926	3
	60	241.3333	.11547	3
	120	241.6767	.58620	3
	Total	237.3780	8.26791	15
5.0	0	242.9433	.39323	3
	15	241.1167	.63705	3
	30	224.8200	1.21791	3
	60	229.9900	.77544	3
	120	240.6700	.09165	3
	Total	235.9080	7.45038	15
7.0	0	243.5000	.25000	3
	15	212.0767	2.28509	3
	30	202.9800	3.68646	3
	60	211.6833	3.61709	3
	120	231.1433	2.99427	3
	Total	220.2767	15.52613	15
9.0	0	243.3933	.31086	3
	15	223.5200	2.08202	3
	30	215.7700	.49729	3
	60	224.0167	4.40407	3
	120	236.4900	1.21606	3
	Total	228.6380	10.44932	15
12.8	0	4.3167	.51189	3
	15	4.1067	.56518	3
	30	3.7600	.42036	3
	60	4.1467	.51811	3
	120	4.2333	.52272	3
	Total	4.1127	.47396	15
Total	0	195.2847	98.83682	15
	15	184.1907	93.88258	15
	30	173.7613	88.33358	15
	60	182.2340	92.72512	15
	120	190.8427	96.66411	15
	Total	185.2627	91.87947	75

Tests of Between-Subjects Effects

Dependent Variable: copper

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	624553.583(a)	24	26023.066	9138.724	.000
Intercept	2574169.175	1	2574169.175	903991.198	.000
pH	618055.200	4	154513.800	54261.824	.000
Time	4112.693	4	1028.173	361.072	.000
pH * Time	2385.690	16	149.106	52.363	.000
Error	142.378	50	2.848		
Total	3198865.135	75			
Corrected Total	624695.961	74			

a. R Squared = 1.000 (Adjusted R Squared = 1.000)

1. pH

Dependent Variable: copper

pH	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
3.0	237.378	.436	236.503	238.253
5.0	235.908	.436	235.033	236.783
7.0	220.277	.436	219.402	221.152
9.0	228.638	.436	227.763	229.513
12.8	4.113	.436	3.238	4.988

2. Time

Dependent Variable: copper

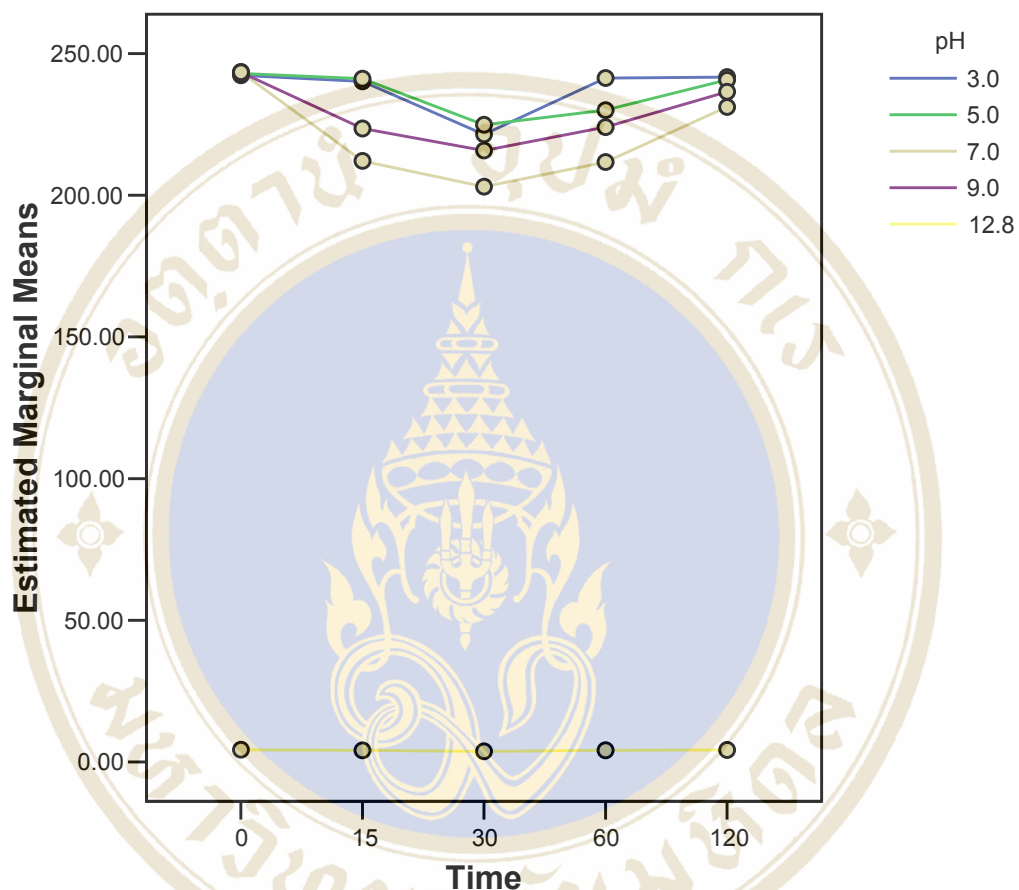
Time	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
0	195.285	.436	194.410	196.160
15	184.191	.436	183.316	185.066
30	173.761	.436	172.886	174.636
60	182.234	.436	181.359	183.109
120	190.843	.436	189.968	191.718

3. Time * pH

Dependent Variable: copper

Time	pH	Mean	Std. Error	95% Confidence Interval	
				Lower Bound	Upper Bound
0	3.0	242.270	.974	240.313	244.227
	5.0	242.943	.974	240.986	244.900
	7.0	243.500	.974	241.543	245.457
	9.0	243.393	.974	241.436	245.350
	12.8	4.317	.974	2.360	6.274
15	3.0	240.133	.974	238.176	242.090
	5.0	241.117	.974	239.160	243.074
	7.0	212.077	.974	210.120	214.034
	9.0	223.520	.974	221.563	225.477
	12.8	4.107	.974	2.150	6.064
30	3.0	221.477	.974	219.520	223.434
	5.0	224.820	.974	222.863	226.777
	7.0	202.980	.974	201.023	204.937
	9.0	215.770	.974	213.813	217.727
	12.8	3.760	.974	1.803	5.717
60	3.0	241.333	.974	239.376	243.290
	5.0	229.990	.974	228.033	231.947
	7.0	211.683	.974	209.726	213.640
	9.0	224.017	.974	222.060	225.974
	12.8	4.147	.974	2.190	6.104
120	3.0	241.677	.974	239.720	243.634
	5.0	240.670	.974	238.713	242.627
	7.0	231.143	.974	229.186	233.100
	9.0	236.490	.974	234.533	238.447
	12.8	4.233	.974	2.276	6.190

Estimated Marginal Means of copper



**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater at pH conditions (pH 3, 5, 7, 9 and 12.8)**

for 30 minutes of contact time

(Oneway ANOVA test at 0.05 level of significant)

Descriptive statistics

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
3.0	3	221.4767	.51926	.29980	220.1867	222.7666	221.00	222.03
5.0	3	224.8200	1.21791	.70316	221.7945	227.8455	223.53	225.95
7.0	3	202.9800	3.68646	2.12838	193.8223	212.1377	200.28	207.18
9.0	3	215.7700	.49729	.28711	214.5347	217.0053	215.38	216.33
12.8	3	3.7600	.42036	.24269	2.7158	4.8042	3.42	4.23
Total	15	173.7613	88.33358	22.80763	124.8438	222.6788	3.42	225.95

ANOVA

copper

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	109207.957	4	27301.989	8657.990	.000
Within Groups	31.534	10	3.153		
Total	109239.491	14			

Multiple Comparisons

Dependent Variable: copper

LSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
3.0	5.0	-3.34333*	1.44992	.044	-6.5739	-.1127
	7.0	18.49667*	1.44992	.000	15.2661	21.7273
	9.0	5.70667*	1.44992	.003	2.4761	8.9373
	12.8	217.71667*	1.44992	.000	214.4861	220.9473
5.0	3.0	3.34333*	1.44992	.044	.1127	6.5739
	7.0	21.84000*	1.44992	.000	18.6094	25.0706
	9.0	9.05000*	1.44992	.000	5.8194	12.2806
	12.8	221.06000*	1.44992	.000	217.8294	224.2906
7.0	3.0	-18.49667*	1.44992	.000	-21.7273	-15.2661
	5.0	-21.84000*	1.44992	.000	-25.0706	-18.6094
	9.0	-12.79000*	1.44992	.000	-16.0206	-9.5594
	12.8	199.22000*	1.44992	.000	195.9894	202.4506
9.0	3.0	-5.70667*	1.44992	.003	-8.9373	-2.4761
	5.0	-9.05000*	1.44992	.000	-12.2806	-5.8194
	7.0	12.79000*	1.44992	.000	9.5594	16.0206
	12.8	212.01000*	1.44992	.000	208.7794	215.2406
12.8	3.0	-217.71667*	1.44992	.000	-220.9473	-214.4861
	5.0	-221.06000*	1.44992	.000	-224.2906	-217.8294
	7.0	-199.22000*	1.44992	.000	-202.4506	-195.9894
	9.0	-212.01000*	1.44992	.000	-215.2406	-208.7794

* . The mean difference is significant at the .05 level.

**The comparison of the zinc removal efficiencies from copper-brass pipe
industrial wastewater at pH conditions (pH 3, 5, 7, 9 and 12.8)
for 5 contact times (0, 15, 30, 60 and 120 minutes)
(Two-way ANOVA test at 0.05 level of significant)**

Dependent Variable: zinc removal efficiencies

pH	Time	Mean	Std. Deviation	N
3.0	0	91.5600	.54745	3
	15	90.2600	1.05418	3
	30	85.7100	1.10014	3
	60	88.3200	.52943	3
	120	90.5033	.31565	3
	Total	89.2707	2.23554	15
5.0	0	87.9267	2.88836	3
	15	86.2633	2.88805	3
	30	84.7267	2.60924	3
	60	85.4933	3.01001	3
	120	85.2267	2.93873	3
	Total	85.9273	2.68686	15
7.0	0	86.1033	.49963	3
	15	83.6767	.97141	3
	30	77.9500	1.56205	3
	60	82.6700	1.26048	3
	120	85.8000	.76974	3
	Total	83.2400	3.17788	15
9.0	0	87.0200	2.58192	3
	15	83.6433	2.34086	3
	30	82.0933	1.58576	3
	60	84.7267	2.71379	3
	120	85.4967	2.66474	3
	Total	84.5960	2.67097	15
12.8	0	6.2433	.06028	3
	15	6.0433	.06028	3
	30	5.4600	.11533	3
	60	6.0867	.05132	3
	120	6.1433	.04041	3
	Total	5.9953	.29174	15
Total	0	71.7707	34.00044	15
	15	69.9773	33.21745	15
	30	67.1880	32.09694	15
	60	69.4593	32.89177	15
	120	70.6340	33.47273	15
	Total	69.8059	32.27004	75

Tests of Between-Subjects Effects

Dependent Variable: Zinc

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	76902.004(a)	24	3204.250	1012.024	.000
Intercept	365464.427	1	365464.427	115427.510	.000
pH	76646.824	4	19161.706	6051.993	.000
Time	173.234	4	43.309	13.678	.000
pH * Time	81.946	16	5.122	1.618	.099
Error	158.309	50	3.166		
Total	442524.740	75			
Corrected Total	77060.313	74			

a. R Squared = .998 (Adjusted R Squared = .997)

1. pH

Dependent Variable: Zinc

pH	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
3.0	89.271	.459	88.348	90.193
5.0	85.927	.459	85.005	86.850
7.0	83.240	.459	82.317	84.163
9.0	84.596	.459	83.673	85.519
12.8	5.995	.459	5.073	6.918

2. Time

Dependent Variable: Zinc

Time	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
0	71.771	.459	70.848	72.693
15	69.977	.459	69.055	70.900
30	67.188	.459	66.265	68.111
60	69.459	.459	68.537	70.382
120	70.634	.459	69.711	71.557

3. Time * pH

Dependent Variable: Zinc

Time	pH	Mean	Std. Error	95% Confidence Interval	
				Lower Bound	Upper Bound
0	3.0	91.560	1.027	89.497	93.623
	5.0	87.927	1.027	85.863	89.990
	7.0	86.103	1.027	84.040	88.167
	9.0	87.020	1.027	84.957	89.083
	12.8	6.243	1.027	4.180	8.307
15	3.0	90.260	1.027	88.197	92.323
	5.0	86.263	1.027	84.200	88.327
	7.0	83.677	1.027	81.613	85.740
	9.0	83.643	1.027	81.580	85.707
	12.8	6.043	1.027	3.980	8.107
30	3.0	85.710	1.027	83.647	87.773
	5.0	84.727	1.027	82.663	86.790
	7.0	77.950	1.027	75.887	80.013
	9.0	82.093	1.027	80.030	84.157
	12.8	5.460	1.027	3.397	7.523
60	3.0	88.320	1.027	86.257	90.383
	5.0	85.493	1.027	83.430	87.557
	7.0	82.670	1.027	80.607	84.733
	9.0	84.727	1.027	82.663	86.790
	12.8	6.087	1.027	4.023	8.150
120	3.0	90.503	1.027	88.440	92.567
	5.0	85.227	1.027	83.163	87.290
	7.0	85.800	1.027	83.737	87.863
	9.0	85.497	1.027	83.433	87.560
	12.8	6.143	1.027	4.080	8.207

Multiple Comparisons

Dependent Variable: Zinc

LSD

(I) pH	(J) pH	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
3.0	5.0	3.3433*	.64974	.000	2.0383	4.6484
	7.0	6.0307*	.64974	.000	4.7256	7.3357
	9.0	4.6747*	.64974	.000	3.3696	5.9797
	12.8	83.2753*	.64974	.000	81.9703	84.5804
5.0	3.0	-3.3433*	.64974	.000	-4.6484	-2.0383
	7.0	2.6873*	.64974	.000	1.3823	3.9924
	9.0	1.3313*	.64974	.046	.0263	2.6364
	12.8	79.9320*	.64974	.000	78.6270	81.2370
7.0	3.0	-6.0307*	.64974	.000	-7.3357	-4.7256
	5.0	-2.6873*	.64974	.000	-3.9924	-1.3823
	9.0	-1.3560*	.64974	.042	-2.6610	-.0510
	12.8	77.2447*	.64974	.000	75.9396	78.5497
9.0	3.0	-4.6747*	.64974	.000	-5.9797	-3.3696
	5.0	-1.3313*	.64974	.046	-2.6364	-.0263
	7.0	1.3560*	.64974	.042	.0510	2.6610
	12.8	78.6007*	.64974	.000	77.2956	79.9057
12.8	3.0	-83.2753*	.64974	.000	-84.5804	-81.9703
	5.0	-79.9320*	.64974	.000	-81.2370	-78.6270
	7.0	-77.2447*	.64974	.000	-78.5497	-75.9396
	9.0	-78.6007*	.64974	.000	-79.9057	-77.2956

Based on observed means.

*. The mean difference is significant at the .05 level.

Multiple Comparisons

Dependent Variable: Zinc

LSD

(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
0	15	1.7933*	.64974	.008	.4883	3.0984
	30	4.5827*	.64974	.000	3.2776	5.8877
	60	2.3113*	.64974	.001	1.0063	3.6164
	120	1.1367	.64974	.086	-.1684	2.4417
15	0	-1.7933*	.64974	.008	-3.0984	-.4883
	30	2.7893*	.64974	.000	1.4843	4.0944
	60	.5180	.64974	.429	-.7870	1.8230
	120	-.6567	.64974	.317	-1.9617	.6484
30	0	-4.5827*	.64974	.000	-5.8877	-3.2776
	15	-2.7893*	.64974	.000	-4.0944	-1.4843
	60	-2.2713*	.64974	.001	-3.5764	-.9663
	120	-3.4460*	.64974	.000	-4.7510	-2.1410
60	0	-2.3113*	.64974	.001	-3.6164	-1.0063
	15	-.5180	.64974	.429	-1.8230	.7870
	30	2.2713*	.64974	.001	.9663	3.5764
	120	-1.1747	.64974	.077	-2.4797	.1304
120	0	-1.1367	.64974	.086	-2.4417	.1684
	15	.6567	.64974	.317	-.6484	1.9617
	30	3.4460*	.64974	.000	2.1410	4.7510
	60	1.1747	.64974	.077	-.1304	2.4797

Based on observed means.

*. The mean difference is significant at the .05 level.

**The comparison of the copper removal efficiencies from copper-brass pipe
industrial wastewater at various ratio (3:1, 2:1, 1:1, 1:2 and 1:3)
for the treatment pH 7 and 12.8 at 30 minutes of contact time
(Two-way ANOVA test at 0.05 level of significant)**

Dependent Variable: Copper removal efficiencies

pH	Ratio	Mean	Std. Deviation	N
7.0	1	323.5667	3.59108	3
	2	300.5533	6.39499	3
	3	202.9800	3.68646	3
	4	144.6850	.02121	2
	5	103.3900	.33941	2
	Total	229.0346	86.66409	13
12.8	1	6.3700	.24759	3
	2	16.6133	.67885	3
	3	3.7600	.42036	3
	4	9.1700	.67735	3
	5	14.9833	.36856	3
	Total	10.1793	5.11457	15
Total	1	164.9683	173.75068	6
	2	158.5833	155.57352	6
	3	103.3700	109.14252	6
	4	63.3760	74.22617	5
	5	50.3460	48.42332	5
	Total	111.7907	125.32432	28

Tests of Between-Subjects Effects

Dependent Variable: Copper

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	423929.539(a)	9	47103.282	6167.777	.000
Intercept	345828.381	1	345828.381	45283.304	.000
pH	286130.756	1	286130.756	37466.404	.000
Ratio	49039.334	4	12259.833	1605.322	.000
pH * Ratio	49951.854	4	12487.964	1635.193	.000
Error	137.466	18	7.637		
Total	773987.591	28			
Corrected Total	424067.005	27			

a R Squared = 1.000 (Adjusted R Squared = 1.000)

1. pH

Dependent Variable: Copper

pH	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
7.0	215.035	.782	213.393	216.677
12.8	10.179	.714	8.680	11.678

2. Ratio

Dependent Variable: Copper

Ratio	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
1	164.968	1.128	162.598	167.339
2	158.583	1.128	156.213	160.954
3	103.370	1.128	101.000	105.740
4	76.928	1.261	74.277	79.578
5	59.187	1.261	56.537	61.837

3. Ratio * pH

Dependent Variable: Copper

Ratio	pH	Mean	Std. Error	95% Confidence Interval	
				Lower Bound	Upper Bound
1	7.0	323.567	1.596	320.215	326.919
	12.8	6.370	1.596	3.018	9.722
2	7.0	300.553	1.596	297.201	303.905
	12.8	16.613	1.596	13.261	19.965
3	7.0	202.980	1.596	199.628	206.332
	12.8	3.760	1.596	.408	7.112
4	7.0	144.685	1.954	140.580	148.790
	12.8	9.170	1.596	5.818	12.522
5	7.0	103.390	1.954	99.285	107.495
	12.8	14.983	1.596	11.631	18.335

**The comparison of the zinc removal efficiencies from copper-brass pipe
industrial wastewater at various ratio (3:1, 2:1, 1:1, 1:2 and 1:3)
for the treatment pH 7 and 12.8 at 30 minutes of contact time
(Two-way ANOVA test at 0.05 level of significant)**

Dependent Variable: Zinc removal efficiencies

pH	Ratio	Mean	Std. Deviation	N
7.0	1	126.1667	.69515	3
	2	114.2500	.21794	3
	3	82.9467	.53257	3
	4	57.8700	.11314	2
	5	41.6400	.09899	2
	Total	89.9315	32.37947	13
12.8	1	10.9633	.41932	3
	2	8.4600	.11533	3
	3	5.3367	.16010	3
	4	10.5267	.38553	3
	5	15.4467	.46458	3
	Total	10.1467	3.44140	15
Total	1	68.5650	63.10155	6
	2	61.3550	57.94378	6
	3	44.1417	42.51020	6
	4	29.4640	25.93251	5
	5	25.9240	14.35053	5
	Total	47.1896	45.97866	28

Tests of Between-Subjects Effects

Dependent Variable: Zinc

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	57076.195(a)	9	6341.799	40626.518	.000
Intercept	61173.620	1	61173.620	391887.382	.000
pH	37769.504	1	37769.504	241957.101	.000
Ratio	6412.832	4	1603.208	10270.390	.000
pH * Ratio	7582.691	4	1895.673	12143.964	.000
Error	2.810	18	.156		
Total	119431.152	28			
Corrected Total	57079.005	27			

a R Squared = 1.000 (Adjusted R Squared = 1.000)

1. pH

Dependent Variable: Zinc

pH	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
7.0	84.575	.112	84.340	84.809
12.8	10.147	.102	9.932	10.361

2. Ratio

Dependent Variable: Zinc

Ratio	Mean	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
1	68.565	.161	68.226	68.904
2	61.355	.161	61.016	61.694
3	44.142	.161	43.803	44.481
4	34.198	.180	33.819	34.577
5	28.543	.180	28.164	28.922

3. Ratio * pH

Dependent Variable: Zinc

Ratio	pH	Mean	Std. Error	95% Confidence Interval	
				Lower Bound	Upper Bound
1	7.0	126.167	.228	125.687	126.646
	12.8	10.963	.228	10.484	11.443
2	7.0	114.250	.228	113.771	114.729
	12.8	8.460	.228	7.981	8.939
3	7.0	82.947	.228	82.467	83.426
	12.8	5.337	.228	4.857	5.816
4	7.0	57.870	.279	57.283	58.457
	12.8	10.527	.228	10.047	11.006
5	7.0	41.640	.279	41.053	42.227
	12.8	15.447	.228	14.967	15.926

The comparison of other pollutants removal efficiencies from copper-brass pipe industrial wastewater at pH 12.8, 30 minutes of contact time and ratio 3:1 of copper-brass pipe industrial wastewater to zeolite industrial wastewater (vol:vol)

(Paired Sample t-test at 0.05 level of significant)

Paired Samples Statistics				
	Mean	N	Std. Deviation	Std. Error Mean
COD				
Before	48.2767	3	1.22083	0.70485
After	29.6000	3	1.42432	0.82233
TS				
Before	4587.67	3	124.605	71.941
After	4479.33	3	40.216	23.219
TDS				
Before	4383.33	3	70.550	40.732
After	4293.33	3	35.346	20.407
TSS				
Before	64.0000	3	4.0000	2.30940
After	48.6667	3	1.52753	0.88192

Paired Samples Test

	Paired Differences					t	df	Sig. (2-tailed)
	Mean	Std. Deviation	Std. Error Mean	95% Confidence Interval of the Difference				
				Lower	Upper			
COD Before After	18.67667	0.29771	0.17188	17.93711	19.41623	108.658	2	.000
TS Before After	108.333	91.358	52.746	-118.613	335.280	2.054	2	.176
TDS Before After	90.0000	60.100	34.699	-59.296	239.296	2.594	2	.122
TSS Before After	15.33333	2.51661	1.45297	9.08172	21.58494	10.553	2	.009

Appendix H

Industrial Effluent Standards

Parameters	Standard Values
1. pH value	5.5-9.0
2. Total Dissolved Solids (TDS)	- not more than 3,000 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 5,000 mg/l - not more than 5,000 mg/l exceed TDS of receiving water having salinity of more than 2,000 mg/l or TDS of sea if discharge to sea
3. Suspended solids (SS)	- not more than 50 mg/l depending on receiving water or type of industry or wastewater treatment system under consideration of PCC but not exceed 150 mg/l
4. Temperature	- not more than 40°C
5. Color and Odor	- not objectionable
6. Sulphide as H ₂ S	- not more than 1.0 mg/l
7. Cyanide as HCN	- not more than 0.2 mg/l
8. Fat, Oil & Grease (FOG)	- not more than 5.0 mg/l depending of receiving water or type of industry under consideration of PCC but not exceed 15.0 mg/l
9. Formaldehyde	- not more than 1.0 mg/l
10. Phenols	- not more than 1.0 mg/l
11. Free Chlorine	- not more than 1.0 mg/l

Industrial Effluent Standards (continued)

Parameters	Standard Values
12.Pesticides	- not detectable
13.Biochemical Oxygen Demand (BOD)	- not more than 20 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 60 mg/l
14.Total Kjeldahl Nitrogen (TKN)	- not more than 100 mg/l depending on receiving water or type of industry under consideration of PCC but not exceed 200 mg/l
15.Chemical Oxygen Demand (COD)	- not more than 120 mg/l depending on receiving water of type of industry under consideration of PCC but not exceed 400 mg/l
16.Heavy metals	
Zinc (Zn)	- not more than 5.0 mg/l
Chromium (Hexavalent)	- not more than 0.25 mg/l
Chromium (Trivalent)	- not more than 0.75 mg/l
Copper (Cu)	- not more than 2.0 mg/l
Cadmium (Cd)	- not more than 0.03 mg/l
Barium (Ba)	- not more than 1.0 mg/l
Lead (Pb)	- not more than 0.2 mg/l
Nickel (Ni)	- not more than 1.0 mg/l
Manganese (Mn)	- not more than 5.0 mg/l
Arsenic (As)	- not more than 0.25 mg/l
Selenium (Se)	- not more than 0.02 mg/l
Mercury (Hg)	- not more than 0.005 mg/l

Remarks:

- 1) PCC Pollution Control Committee
- 2) The standards were summerized from the Notification of the Ministry of Science, Technology and Environment, No. 3, B.E. 2539 (1996) and it

specifies that pollution sources that the above standards are to be applied are factories group II and III issues under the Factory Act B.E.2535 (1992) and every kind of industrial estates.

3) Notification of the Pollution Control Committee, No. 3, B.E. 2539 (1996) dated August 20, B.E. 2539 (1996) has issued types of factories (category of factories issued under the Factory Act B.E.2535 (1992) that are allowed to discharge effluent having different standards from the Ministerial Notification No. 3 above as follows:

1. BOD up to 60 mg/l

- animal furnishing factories (category 4 (1))
- starch factories (category 9 (2))
- food from starch factories (category 10)
- textile factories (category 15)
- tanning factories (category 22)
- pulp and paper factories (category 29)
- chemical factories (category 42)
- pharmaceutical factories(category 46)
- frozen food factories (category 92)

2. COD up to 400 mg/l

- food furnishing factories (category 13 (2))
- animal food factories (category 15 (1))
- textile factories (category 22)
- pulp and paper factories (category 38)

3. TKN

- 100 mg/l - effective after 1 year from the date published in the Royal Government Gazette of the Ministerial Notification No. 4
- 200 mg/l - effective after 2 year from the date published in the Royal Government Gazette of the Ministerial Notification No. 4 for the following factories:

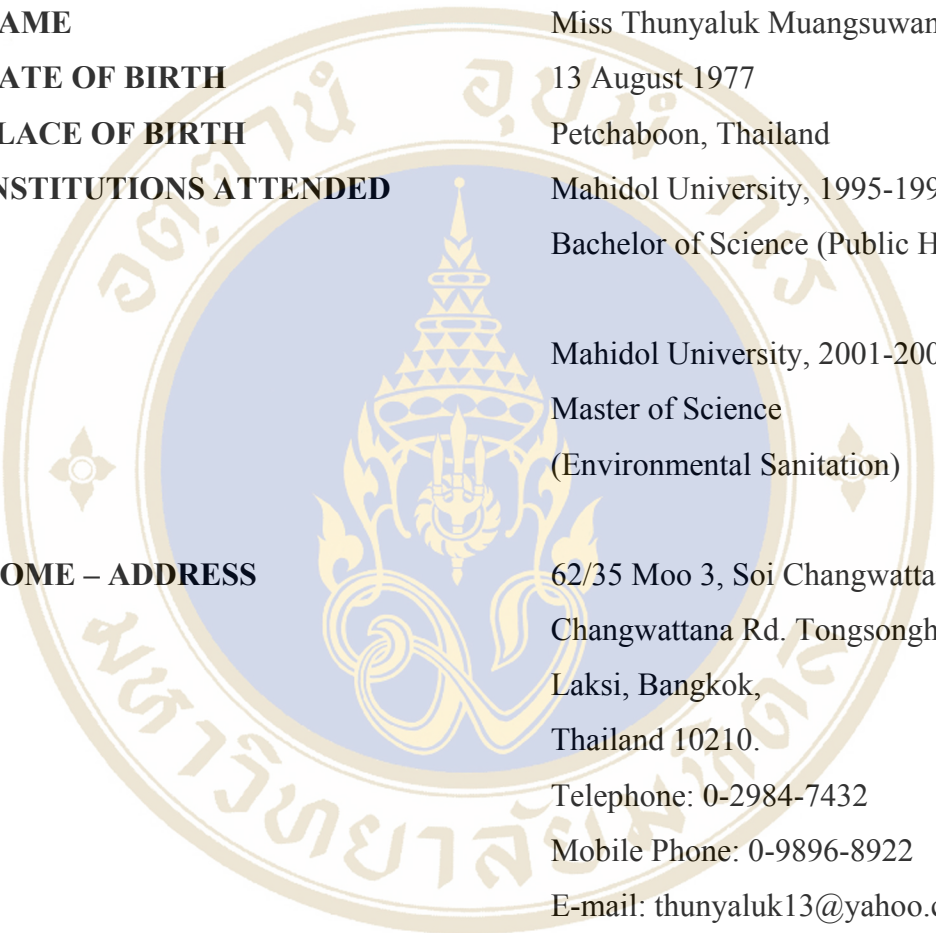
1. food furnishing factories (category 13 (2))
2. animal food factories (category 15 (1))

Sources:

1. Notification the Ministry of Science, Technology and Environment, No. 3, B.E.2539 (1996) issued under the Enhancement and Conservation of the National Environmental Quality Act B.E.2535 (1992), published in the Royal Government Gazette, Vol. 113 Part 13 D, dated February 13, B.E.2539 (1996)



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