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USE OF SLUDGE FROM WASTEWATER TREATMENT PLANTS AS ADSORBENTS FOR REMOVAL OF HEAVY METAL IONS FROM WATER

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กากตะกอนจากโรงบำบัดน้ำเสียชุมชนและโรงบำบัดน้ำเสียอุตสาหกรรมถูกใช้เป็นตัวดูดซับไอออนโลหะหนักในน้ำ กากตะกอนจากทั้งสองแหล่งได้มาจากระบบบำบัดน้ำเสียชนิดตะกอนเร่งด้วยวิธีทางชีวภาพ การศึกษาการดูดซับกระทำในระบบแบทช์ (Batch) และประสิทธิภาพในการดูดซับของกากตะกอนทั้งสองแหล่งในการกำจัดไอออนโลหะแคดเมียม นิกเกิล และตะกั่ว จะถูกเปรียบเทียบกันภายใต้ตัวแปรในสภาวะต่างๆ และวิเคราะห์หาปริมาณไอออนโลหะหนักที่เหลือจะถูกวิเคราะห์โดยเทคนิค Flame atomic absorption spectroscopy ผลจากการศึกษาลักษณะพื้นที่ผิว และองค์ประกอบทางเคมีแสดงให้เห็นว่ากากตะกอนจากทั้งสองแหล่งมีพื้นที่ผิวต่ำ และประกอบไปด้วยสารคาร์บอน จากการศึกษาการดูดซับพบว่าระยะเวลาที่เหมาะสมในการดูดซับไอออนของโลหะแคดเมียม นิกเกิล และตะกั่ว คือ 1 ชั่วโมง และค่าพีเอชที่เหมาะสมในการดูดซับโลหะหนักแคดเมียมและนิกเกิล คือ พีเอช 7 และค่าพีเอชที่เหมาะสมในการดูดซับโลหะตะกั่ว คือ พีเอช 5 ตามลำดับ การดูดซับไอออนของโลหะหนักบนกากตะกอนนั้นเป็นไปตามความสัมพันธ์ของแลงเมียร์ และอัตราการดูดซับนั้นเป็นไปตามความสัมพันธ์แบบ Pseudo-second-order เป็นที่สังเกตได้ว่าการเพิ่มปริมาณตัวดูดซับส่งผลให้ประสิทธิภาพและอัตราเร็วในการดูดซับสูงขึ้น โดยความจุในการดูดซับสูงสุดของไอออนโลหะแคดเมียม นิกเกิล และตะกั่ว คือ 0.140, 0.053 และ 0.171 มิลลิโมลต่อกรัมเมื่อใช้กากตะกอนจากโรงบำบัดน้ำเสียชุมชนและ0.147, 0.064 และ 0.150 มิลลิโมลต่อกรัมเมื่อใช้กากตะกอนจากโรงบำบัดน้ำเสียอุตสาหกรรมตามลำดับ ตัวดูดซับเหล่านี้ถูกนำไปประยุกต์ใช้สำหรับกำจัดไอออนของโลหะหนักในน้ำเสียจริง ซึ่งความเข้มข้นของไอออนโลหะแคดเมียม นิกเกิล และตะกั่วมีค่าเท่ากับ 8.3, 5.1 และ 27.4 มิลลิกรัมต่อลิตรตามลำดับ โดยไอออนของโลหะหนักทั้งหมดถูกกำจัดเมื่อใช้กากตะกอนปริมาณ 2 มิลลิกรัมต่อลิตร จากการศึกษา Sequential extraction แสดงให้เห็นว่าการกระจายตัวของโลหะบนกากตะกอนที่ใช้เป็นตัวดูดซับนั้นจะอยู่ในทุกส่วนของกากตะกอนที่มีคุณสมบัติแตกต่างกัน และจะอยู่ในส่วน residual fraction ของกากตะกอนมากที่สุด ผลจากการศึกษาการชะหลุดด้วยวิธีการชะมาตรฐานแสดงให้เห็นว่าความเข้มข้นของโลหะหนักทั้ง 3 ชนิดที่ถูกชะหลุดมีค่าเกินค่ามาตรฐานที่กำหนดไว้ ดังนั้นกากตะกอนที่ใช้เป็นตัวดูดซับโลหะหนักแล้วจึงจัดเป็นของเสียอันตราย จากผลการวิจัยทั้งหมดพบว่ากากตะกอนที่ได้จากโรงบำบัดน้ำเสียชุมชนและโรงบำบัดน้ำเสียอุตสาหกรรม มีประสิทธิภาพที่ดีในการใช้เป็นตัวดูดซับไอออนของโลหะแคดเมียม นิกเกิล และตะกั่วในน้ำ อย่างไรก็ตามตัวดูดซับที่ใช้แล้วเหล่านี้จำเป็นต้องกำจัดอย่างถูกวิธี

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SARUD THUMNIYOM: USE OF SLUDGE FROM WASTEWATER TREATMENT PLANTS AS ADSORBENTS FOR REMOVAL OF HEAVY METAL IONS FROM WATER. THESIS ADVISOR: ASST.PROF. FUANGFA UNOB, Ph.D., THESIS CO-ADVISOR; CHAROENKWAN KRAIYA, Ph.D., 94 pp.

The sludge from municipal and industrial wastewater treatment plants were used as adsorbents for removal of heavy metal ions from water. Both of sewage sludge were obtained from activated sludge biological treatment processes. The adsorption studies were performed using batch method and the adsorption efficiency of both sludge for Cd(II), Ni(II) and Pb(II) ions were compared under influence of certain parameters. The residual metal concentrations were determined by FAAS. The results from surface characterization and elemental analysis indicated that both sludge had low surface area and consisted of carbonaceous substances. The results from adsorption studies showed that suitable contact time for removal of Cd(II), Ni(II) and Pb(II) ions were 1 hour and the suitable pH values were 7 for Cd(II) and Ni(II), and 5 for Pb(II), respectively. The adsorption of the metal ions on both sewage sludge fit well Langmuir model and the adsorption kinetics followed the pseudo-second-order kinetics. It was observed that an increase in adsorbent resulted in an increase in removal efficiencies and a faster adsorption rate. The maximum adsorption capacities of Cd(II), Ni(II) and Pb(II) ions were 0.140, 0.053 and 0.171 mmol g^{-1} by municipal sludge, and 0.147, 0.064 and 0.150 mmol g^{-1} by industrial sludge, respectively. The adsorbents were applied to remove the metal ions in real wastewater containing 8.3 mg L^{-1} of Cd(II), 5.1 mg L^{-1} of Ni(II) and 27.4 mg L^{-1} of Pb(II) ions and the total removal of the metal ions was obtained when using 2 g L^{-1} of sludge. The results from sequential extraction indicated that metal distributed in different fractions of the sewage sludge, and mostly in the residual fraction. The results from the standard leaching test showed that the concentrations of metal in the leachate were greater than the total threshold limit concentration (TTLC) for all metals. Therefore, the used sludge was classified as hazardous waste. All of the results showed that the adsorbents derived from municipal and industrial sludge have a good potential to be used as adsorbents for removal of Cd(II), Ni(II) and Pb(II) ions in water. However, the used adsorbents had to dispose correctly.

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Academic Year: ………..2007…………… Co-advisor's Signature: ………………

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LIST OF ABBREVIATIONS

°C	Degrees Celsius
EA	Elemental analysis
EPA	Environmental protection agency
FAAS	Flame atomic absorption spectrometry
g	Gram
HCL	Hollow Cathode Lamp
hr	Hour
L	Liter
M	Molar concentration
mg	Milligram
min	Minute
mL	Milliliter
nm	Nanometer
rpm	Round per minute
SEM	Scanning electron microscope
TCLP	The toxicity characteristic leaching procedure

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Rapidity of industrial and agricultural growth causes the increase of pollution in water. One of the most crucial problems is contamination of heavy metals. Although heavy metals can be removed by physical and chemical processes such as chemical precipitation, flotation, ion exchange and reverse osmosis, but each treatment has its inherent limitation [1-2]. For example, in the chemical precipitation, pH must be adjusted to be alkaline enough for metal precipitation. Moreover, conventional method costs high funding [3]. Consequently, some new techniques have been developed for a long time to remove heavy metals from water such as adsorption [4-5].

Adsorption has become one of the interesting alternative treatments for the disposal of heavy metals at present [6]. Basically, adsorption is a mass transfer process of substance from liquid phase to a surface of solid phase via physical and/or chemical interaction [7]. One of the most commonly used adsorbents for wastewater treatment is activated carbon which has large surface area and high adsorption capacity but it has high cost [8-9]. Therefore, some researches are developed to study other adsorbents that have good efficiency and low cost, such as cocoa shell [10], sawdust [11], banana peel [12], almond husk [13], rice husk [14] and sewage sludge [15-16].

Recently, sewage sludge generated from the wastewater treatment processes has increased very rapidly in amount, due to the increase in quantity of wastewater resulted from the development of population and industries. The terminal sewage sludge treatment process is landfill or application in agriculture. These kinds of methods are not worthwhile, and may increase the risk of contamination in soil and ground water with some toxic substances left in sewage sludge [17]. Therefore, recycle of sewage sludge for the use as adsorbent in wastewater treatment is being investigated [18]. Recently, some researches have demonstrated a good efficiency of sewage sludge in removal of heavy metals proficiently compared to its cost and activated carbon. However, the used sewage sludge or the used adsorbent must be treated correctly so that the heavy metals will not escape to the environment [19].

The main objective of this research is to investigate the use of sludge from municipal and industrial wastewater treatment plants as adsorbents. These sludge contain organic compounds and have high carbon content suitable for the use as adsorbent. For these reasons, municipal and industrial sludge are studied. The adsorption efficiency of both sludge were compared for the removal of Cd(II), Ni(II) and Pb(II) from aqueous solutions. Furthermore, the metal leaching from used adsorbents was investigated.

1.2 Objectives and scope of the research

The objectives of this research are to study the utilization of sludge from municipal and industrial wastewater treatment plants as adsorbents for removal of Cd(II), Ni(II) and Pb(II) from water. The adsorption efficiency and leachability of metals from used adsorbents of both adsorbents are compared.

Several parameters such as contact times, adsorbent dosage and kinetics, pH, adsorption isotherms, competitive adsorption and comparison of adsorption capacities of sewage sludge collected from another place and the commercial adsorbents were studied. Furthermore, utilization of sludge to remove heavy metal ions from real wastewater and leaching tests were performed. Finally, the proposed low-cost adsorbents derived form sewage sludge from municipal and industrial wastewater treatment plants were validated to remove Cd(II), Ni(II) and Pb(II) from water.

1.3 Benefits of this research

To obtain low-cost adsorbents derived from sewage sludge from municipal and industrial wastewater treatment plants that have good efficiency and suitable for removal heavy metal ions from wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Heavy metals

A heavy metal is any element that has specific gravity greater than 4.0. It is in the group of elements between the fourth to the seventh period of periodic table. It has the properties of metallic substance such as solid (except mercury), ductile, polish, etc. Furthermore, it has several oxidation states [20]. Some of heavy metals are essential and some are toxic. Toxic metals can be accumulated in biological process of animal and can enter the food chain. Therefore, the toxic elements must be removed from water before releasing to the environment.

2.1.1 Cadmium

Cadmium [21] is a highly toxic, lustrous, silver-white, ductile, and very malleable metal. Its surface has a bluish tinge and the metal is soft enough to be cut with a knife, but it tarnishes in air. It is soluble in acids but not in alkalis. Its properties are similar to zinc because cadmium and zinc are in the same group on the periodic table. The most common oxidation state is +2, but +1 can also be found. Three-fourth of cadmium is used in Ni-Cd batteries; most of the remaining one-fourth is used for pigments, coatings and plating, and as stabilizers for plastics. Cadmium is recognized for its toxicity to human health. Long-term occupational exposure can cause adverse health effects on the lungs and kidneys. Under normal conditions, adverse human health effects have not been encountered from general population exposure to cadmium. Cadmium can replace zinc in many biological system of human

[22]. Moreover, it has effect in the bone and stomach. This was observed in a syndrome which is known as “Itai itai” in Japan. In the environment, cadmium can be transported over great distances when it is adsorbed by sludge. This cadmium-rich sludge can pollute surface waters as well as soils [23].

2.1.2 Nickel

Nickel [24] is a silver- white metal which is hard, ductile and high polish. The most common oxidation state is +2, and the oxidation state of +1, +3 and +4 are observed in Ni complexes. Nickel is also found in meteoric iron and on the ocean surface. Moreover, it can be found in the soil from volcanoes. It is naturally magnetic material which is stable in air and inert to oxidation. It is used to make coins, jewelry, magnets and super alloys because it can be combined with other metals such as chromium, copper and zinc to form alloys [25]. However, most nickel is used in stainless steel. Nickel was found to be the cause of allergic reaction and adverse effects in human because of its use in jewelry. People can be sensitive to nickel due to the direct contact with the jewelry or other products containing nickel for a long time. Furthermore, it may cause lung and nasal sinus cancer when people inhale high levels of nickel compound.

2.1.3 Lead

Lead [26] is an extremely toxic metal which is luster, very soft, ductile, and highly malleable and has poor electrical conductivity. The most common oxidation state is +2. Lead has the highest atomic number of all stable elements on periodic table which is the end product of a new radioactive decay. It is used in lead acid batteries, building construction, bullets and shots, pewter, color pigment, etc. Lead is a poisonous metal that can be accumulated in bone and soft tissues, and causes blood and brain disorder including nervous connection damage.

2.2 Treatment of heavy metals in wastewater

There are many different types of wastewater pretreatment system that are used for wastewater contaminated with heavy metals. They have been developed by governmental organizations, universities and the private sectors depending on many factors such as [27]:

- The volume and nature of wastewater.
- The desired degree of pretreatment system automation.
- The difficulty of system installation within an existing facility.
- The cost and space for process.
- The quality of water after treatment process.

Wastewater treatment technologies for decontamination of metals can be classified into six types as followed:

2.2.1 Chemical precipitation /Coprecipitation

Chemical precipitation [28] is the process that ions in solutions form insoluble compounds via a chemical reaction or when the solution is supersaturate by a compound. One of the eminent precipitation reactions is hydroxide precipitation of heavy metals.

Coprecipitation [29] is the process that inorganic contaminants form insoluble complexes with coagulant. Both the pH of solution and the valence of inorganic contaminant are important. The obtained solid can be separated by particulate separation process, such as gravimetric clarification or filtration [27].

Both reactions are useful in many industrial and scientific applications such as wastewater treatment plant, chemical analysis, etc.

2.2.2 Oxidation

Oxidation [29] is the chemical reaction involving the loss of electrons from an atom or compound. Oxidizing agents such as peroxides, permanganate, hydrogen peroxide, chlorine, hypochlorite, and ozone are used to add oxygen to a compound via oxidation reactions [27]. This process is commonly utilized to change the toxic compounds to other compounds that are less toxic or non-toxic. It is usually used for wastewater treatment plants of electroplating.

2.2.3 Biological process

Biological treatment is the process that uses aerobic or anaerobic microbial organisms to reduce organic wastes or some toxic compounds in wastewater [29]. Many inorganic contaminants, such as heavy metal ions, can be adsorbed onto biosolids produced during the treatment process [27]. This process requires specific conditions suitable for bacteria (e.g. temperature, pH) by pretreatment of wastewater with various physical or chemical processes.

2.2.4 Ion exchange

Ion exchange is the reversible interchange of ions between an electrolyte solution and ion exchanger. It is developed for large-scale application to remove dissolved ionic compounds.

Ion exchangers are either cation exchangers that exchange ions of positive charge or anion exchangers that exchange ions of negative charge. However, there are amphoteric exchangers that are able to exchange both cation and anion simultaneously [30].

Ion exchange process requires specific pH range for good operation and it is susceptible to degradation by oxidizers and fouled by organic compounds and suspended solid. Typical ion exchangers are ion exchange resins that are based on cross-linked polymer matrix such as polystylene cross-linked with vinylbenzene. Furthermore, zeolite, clay and soil humus can able be used as ion exchangers [29].

Ion exchange is a reversible process. It can be regenerated or loaded with desired ions by washing with an excess of these ions. It is widely used for water softening, water decontamination, etc.

2.2.5 Reverse osmosis

Reverse osmosis (RO) is a membrane separation process that uses a pressure in excess of osmosis pressure to force solvent through a semi–permeable membrane [29]. The membranes have a dense barrier layer in the polymer matrix where most separation occurs and are able to remove many different kinds of dissolved solid such as heavy metals in water [31]. However, it can readily be fouled by oil, grease and suspended solids [27]. Furthermore, the operation is usually expensive. Therefore, it is considered in certain applications such as purification of fresh water for medical and industrial purpose, desalination, brackish water conversion, etc.

2.2.6 Adsorption

Adsorption is a technique which is developed for water treatment based on solid phase extraction. It is used for removing low concentration of organic contaminants and inorganic compounds such as heavy metals from wastewater [27]. Because adsorption is efficient, easy to maintain and used in any treatment plants, it has become an interesting alternative treatment to remove heavy metal at present. The most common adsorbent used in water treatment is activated carbon which has high adsorption capacity and large surface area but the activated carbon may be costly [8-9]. Therefore, low-cost adsorbents having good adsorption capacity have drawn a lot of attention.

This research aims to investigate the use of some low-cost adsorbents to remove heavy metal ions by adsorption process.

2.3 Adsorption Process

Adsorption is a process which occurs when a substance from gas or liquid phase is accumulated at a surface of adsorbent via mass transfer process. It is different from absorption that a substance diffuses into a liquid or solid [32].

2.3.1 Adsorption mechanisms

Adsorption involves a mass transfer process of molecules or substances from liquid solution to pores of porous adsorbent. Some steps in adsorption process are rapid and some are slow. The slow step is important because it will be a rate determining step of the process. Adsorption process consists of [33]:

- **Bulk transport**, a process which substances are transported from bulk solution to the surface of liquid layer covering the surface of adsorbent. This step occurs very quickly.
- **Film transport or surface transport**, substances are transported from liquid layer to the surface of adsorbent. This is called external diffusion or film diffusion.
- **Intraparticle transport**, a process that substances at the surface of adsorbent diffuse into the pores of adsorbent. This is called internal diffusion.

The quantity of substance adsorbed on surface depends on several conditions and surface features such as temperature, pressure, surface energy distribution and the surface area of adsorbent. However, adsorption process is generally classified as process exhibiting physisorption and chemisorption.

2.3.2 Physical adsorption or physisorption

Physisorption is the result of weak electrical attractive force that is called Van der Waall's interaction between the adsorbate and surface of solid. It can result in adsorbed molecule forming multiple layers. A quantity of layers depends on concentration of adsorbate. Physisorption is a nonspecific process which adsorbates can be adsorbed on all sites of adsorbent surface when temperature and pressure conditions are suitable. It is also easily reversed.

2.3.3 Chemical adsorption or chemisorption

Chemisorption is a result of the sharing of electrons between the adsorbate and the adsorption sites on surface of solid via chemical bond which is stronger than interaction in physisorption. In chemisorption, analytes can contact directly with the surface and form a single-layer on surface. Chemisorption is a specific process occurring only between certain sites of adsorbents and adsorptive species so it is difficult to reverse.

2.4 Adsorption equilibrium

In adsorption process, analytes can be adsorbed on surface of adsorbent and then desorbed in the solution. The processes of adsorption and desorption continue until equilibrium is reached and the concentration of analytes on surface of adsorbent does not change. It is called adsorption equilibrium. Adsorption equilibrium is usually described through a plot of the capacity of adsorbent versus the remaining of analytes concentration in solution at equilibrium at constant temperature that is called the “adsorption isotherm”. The commonly used models are Freundlich and Langmuir relations [34-35].

2.4.1 Freundlich isotherm

Freundlich isotherm is the first exponential model derived by Freundlich and Küster (1854). It is usually used to describe the adsorption on heterogeneous surface. Freundlich relation is shown in equation 2-1

$$q_e = KC_e^{1/n} \qquad 2\text{-}1$$

where, q_e is adsorbed quantity of analytes per mass of adsorbent, (mg/g)

C_e is the concentration of analytes in solution at equilibrium, (mg/L)

K is the Freundlich adsorption coefficient

$1/n$ is coefficient

A plot of q_e versus C_e results in a curve of the form shown in Figure 2.1

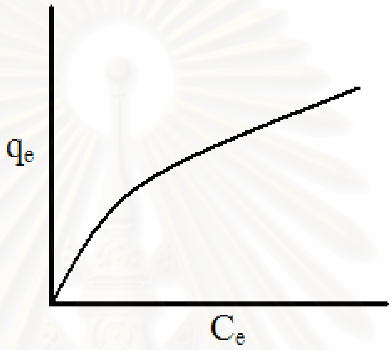


Figure 2.1 Form of Freundlich adsorption isotherm.

From equation 2-1 the exponential function can be changed using logarithm to equation 2-2:

$$\log q_e = \log K + 1/n \log C_e \qquad 2\text{-}2$$

By the linear plot of log q_e versus log C_e, the value of n and K can be determined by the slope and the intercept of the linear plot, respectively.

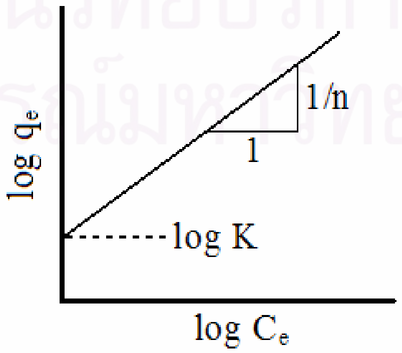


Figure 2.2 Conventional linear form of Freundlich adsorption isotherm.

2.4.2 Langmuir Isotherm

Langmuir isotherm relation (equation 2-3) was proposed by Langmuir (1916). It is based on some reasonable assumptions, as following [33]:

1. Adsorbed molecules do not interact with each other.
2. The surface of adsorbent is uniform.
3. All adsorption occurs through the same mechanism.
4. At the maximum adsorption, only a monolayer is formed.

$$q_e = \frac{(q_m b C_e)}{(1 + bC_e)} \qquad 2\text{-}3$$

where, q_e is adsorbed quantity of analytes per mass of adsorbent, (mg/g)

q_m is adsorbed quantity of ananlytes per mass of adsorbent that can be adsorbed only monolayer, (mg/g)

C_e is the concentration of analytes in solution at equilibrium, (mg/L)

b is the equilibrium constant or Langmuir constant (L/mg)

Data are plotted as shown in Figure 2.3

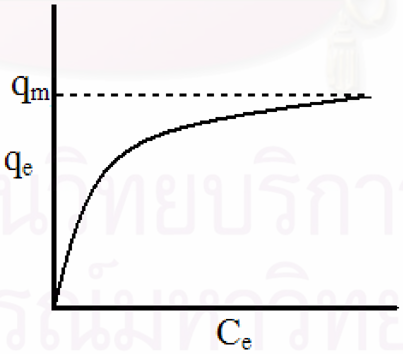


Figure 2.3 Form of Langmuir adsorption isotherm.

Taking reciprocals and rearranging, the equation 2-4 is obtained.

$$\frac{1}{q_e} = \left(\frac{1}{b q_m C_e}\right) + \left(\frac{1}{q_m}\right) \qquad 2\text{-}4$$

By the linear plot of $1/q_e$ versus $1/C_e$, the value of b and q_m can be calculated by using the slope and intercept of the linear plot, respectively.

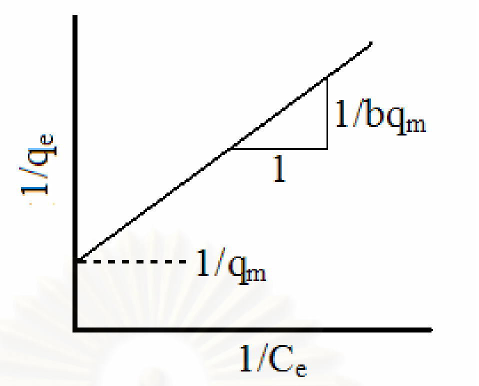


Figure 2.4 Conventional linear form of Langmuir adsorption isotherm.

2.4.3 BET Adsorption Isotherm

The Brunauer- Emmett –Teller (BET) relation (equation 2-5) is a model developed from Langmuir equation to describe a multilayer adsorption which adsorption of each layer follows in Langmuir equation.

$$q_e = \frac{q_m b C_e}{(C_s - C_e)[1 + (b-1)(C_e - C_s)]} \qquad \text{2-5}$$

where, q_e is adsorbed quantity of analytes per mass of adsorbent, (mg/g)

q_m is adsorbed quantity of ananlytes per mass of adsorbent that can be adsorbed only monolayer, (mg/g)

C_e is the concentration of analytes in solution at equilibrium, (mg/L)

C_s is saturation concentration in the liquid, (mg/L)

b is adsorption coefficient

Its assumptions are:

1. Adsorbed molecules stay on any layers.
2. Enthalpy of adsorption is the same for any layer.
3. Energy of adsorption is the same for layers other than the first layer.
4. A new layer can start before another is finished.

From equation 2-5, it can be rearranged to give:

$$\frac{C_e}{q_e(C_s - C_e)} = \left(\frac{1}{bq_m}\right) + \left(\frac{b-1}{bq_m}\right)\left(\frac{C_e}{C_s}\right) \qquad 2\text{-}6$$

By the linear plot of $C_e/q_e(C_s\text{-}C_e)$ versus (C_e/C_s), the value of b and q_m can be calculated by using the slope and intercept of the linear plot.

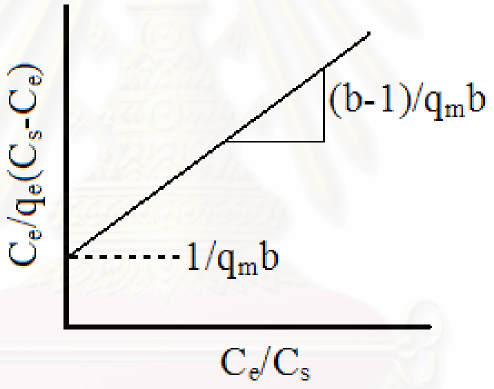


Figure 2.5 Conventional linear form of BET adsorption isotherm.

2.5 Adsorbents

The nature and properties of the adsorbents are important in adsorption process. Adsorbents are usually used in the form of spherical pellets, rods, moldings or monoliths. The important properties of adsorbent are high sorption capacity, wide working pH range, fast and quantitative sorption and elution, accessibility and reusability. Furthermore, high surface area and hydrophilicity of adsorbent are required to achieve fast kinetics of adsorption process. Adsorbents can be derived from organic and inorganic based materials. In industries, adsorbents can be divided into three classes [33]:

- **Oxygen–containing compounds:** hydrophilic and polar adsorbents such as silica gel and zeolites.
- **Carbon-based compounds:** hydrophobic and non – polar adsorbents, such as activated carbon.
- **Polymer-based compounds:** polar or non-polar functional groups in a porous polymer matrix.

2.5.1 Silica gel

Silica gel is inorganic based sorbent that is a chemically inert, nontoxic and stable amorphous from of SiO_2. It is prepared by the reaction between sodium silicate and sulphuric acid. The advantages of silica gel are not swell, thermal and chemical stability under various conditions, but it has a narrow pH stability range [36].

2.5.2 Zeolite

Zeolite is inorganic based sorbent that seems to be one of the most promising sorbents for water purification. It is natural material and it can also be obtained by synthesis of aluminum silicates that form a regular crystal lattice and release water at high temperature. The advantages of zeolite are not swell, high surface area, wide working pH range, thermal and chemical stability, and good for reusability [37-39].

2.5.3 Activated carbon

Activated carbon is organic based sorbent which is non-polar. It can be obtained from carbonaceous materials including coal. Because of the different raw materials used, there are four types of activated carbon based on size and shape: powder, granular, fibrous and cloth. The manufacturing process of activated carbon includes carbonization and activation. The carbonization is a heating process to separate any by-products at 400-600°C under an oxygen-deficient atmosphere. The activation is a process that exposes the carbonized products to an oxidizing agent such as carbon dioxide at high temperature. Activated carbon is highly porous material that has large surface area (300-1000 m^2/g) and it is well-recognized for its strong sorption of both organic compounds and metal ions. It is usually used as adsorbent for sorption of organic substances and non-polar adsorptive compounds in wastewater treatment [40-42].

Although these adsorbents are widely used in wastewater treatment but they have inherent limitation such as high cost [43]. Therefore, some researches proposed some materials as new adsorbents that have high sorption capacity and are easy to derive and low cost to replace high-cost adsorbents [41]. Sewage sludge from wastewater treatment processes were also proposed as low-cost adsorbents. The composition and properties of sludge may depend on the nature of wastewater and also the treatment processes used.

2.6 Wastewater treatment

Wastewater treatment [44] is the process of removing contaminants from wastewater, in particular the toxic contaminants that have impact on human health and organisms in environmental system. Many contaminants are the variety of organic and inorganic compounds, including other compounds that are not toxic but can pose an indirect threat to environmental system, for example high loading of nutrients can cause the effect known as “eutrophication”.

- **Municipal wastewater treatment**

  Municipal wastewater comes from local resident areas, tourist villages and general communities such as schools, temples, hospitals, etc. The treatment process generally used is activated sludge biological process because wastewater from human activities mostly contains organic compounds. The treated water specifications have to be in full compliance with the limits specified by the environmental protection law of each country. In Thailand, it is defined by Ministry of Natural Resources and Environment.

- **Industrial Wastewater Treatment**

  The processes used to treat industrial wastewater have to be considered case by case, depending on the nature of the wastewater and the specific pollutants. Industrial wastewater that contains biodegradable pollutants is usually treated with activated sludge biological process. Whenever the sewage is not biodegradable, its treatment is carried out by adopting either a chemical-physical or a membrane separation process. Such treatment may include specific pre-treatments in order to achieve an effluent quality level that is suitable for discharging and for reusing in industrial activities.

Typically, there are three types of wastewater treatment systems as followings [45]:

- **Physical process:** this process is used to separate components associated with particulate matter in wastewater without altering the chemical structure of material. Most of large solid or particles that suspend in wastewater can be removed or settled by gravity in this process. Examples of physical processes are filtration, grinding and flotation.
- **Biological process:** living microbial organisms are used to metabolize organic substances in wastewater. There are two types of microbial. Aerobic microbial organisms require oxygen for their living metabolisms while anaerobic microbial organism can live in an oxygen-limited environment. Both are the most important microbial to be used in biological wastewater treatment.
- **Chemical process:** this process is used to change the chemical structure of some substances in wastewater. Examples of chemical processes are precipitation of heavy metals, adsorption and using of ultraviolet light, chlorine and ozone. Because chemical process costs higher operating price than other processes, it is usually used only in tertiary treatment to obtain high purity of water or used for removing refractory and toxic compounds that are not suitable for biological processes.

The fundamental systems that are used in wastewater treatment process can be divided in four steps as follow [46-49]:

2.6.1 Preliminary treatment

Preliminary treatment is used for removing the large solid which can damage the equipment. Typically, the equipment is set up in the order as following, grinder, bar screens and grit channels, respectively. The preliminary treatment is usually a physical process.

2.6.2 Primary treatment

This is the step for removing suspended materials and small size solids which could be settled in settling tank or clarifier. The material such as fat, oils and greases, rock, sand, gravels including human waste floating material are removed. The equipment set up consists of screening, grit chamber, and sedimentation tank. The machinery is often used in this step, so the name of this step is “mechanical treatment”

2.6.3 Secondary treatment

This step is typically the use of biological treatment processes, that microorganism as bacteria, fungi, algae and protozoa consume biodegradable soluble organic contaminants and bind nonsettleable contaminant into floc. In the majority of municipal and industrial wastewater treatment plants, aerobic biological processes which utilize aerobic microbial organisms that require both oxygen and substrate to live are used. The options for biological treatment include activated sludge, trickling filters, oxidation ditch, aeration lagoons and stabilization ponds.

Activated sludge is the most common option used to deal with the treatment of municipal and industrial wastewater [50]. Air or pure oxygen is bubbled to wastewater containing organic contaminants which aerobic organisms use for living and develop biological floc. As a result, the amount of organic materials is reduced. The biological floc containing the bacteria cells is called “activated sludge” that can be reused by sending back to aeration tank for another treatment.

2.6.4 Tertiary treatment or advance treatment

Tertiary treatment provides a final step to increase the quality of water before releasing to environment. This step includes the process to remove nutrients such as nitrogen and phosphorous which are the cause of eutrophication and to remove chemical contaminants left from the secondary treatment such as phenols and detergent.

From these processes, the materials obtained from primary and secondary treatment settling tanks are called “sewage sludge”. Because it may contain some substances that are toxic or can cause disease, it must be treated and disposed properly. The sludge treatment is explained in the next topic.

2.7 Sludge treatment and disposal [48-49]

The purpose of sludge treatment is to reduce the volume of sludge, the amount of organic matter and the number of disease-causing microorganisms found in the sewage sludge. As a consequence, the cost for trucking sludge is reduced and handlings of sludge are generally easier. This process includes thickening, stabilization, conditioning and dewatering.

- **Thickening:** to enhance the sludge concentration and separate it from wastewater by sedimentation.
- **Stabilization:** to digest organic matter with aerobic and anaerobic micro organism.
- **Conditioning:** to modify the physical and chemical properties of solid to be suitable for utilizing or disposing.
- **Dewatering:** to reduce the volume and weight of sludge for easier transportation.

After that, the sewage sludge which underwent sludge treatment must be disposed properly. Typically, there are three methods of sludge disposal as following [47]:

2.7.1 Landfill

It is the most common methods of sludge disposal and used in many places around the world. This method requires the extensive space for non-toxic sludge. Furthermore, to be environmentally viable, a landfill must be utilized with specific area for sludge containing some toxic substances [51].

2.7.2 Incineration

It is an easier method used in progress. High thermal temperature is applied to burn any organic and inorganic compounds contained in sludge. This method has a high cost and causes air pollution. Therefore, the incinerator has to be designed correctly for not causing much air pollution.

The disposal of sewage sludge with typical methods is not worthwhile utilized, expensive, and may cause contamination of environment with toxic substances. Therefore, many researches demonstrated the re-use of sewage sludge e.g. as adsorbents. In this research, the sludge from municipal and industrial wastewater treatment plants were used as adsorbents to remove toxic metal ions from water.

However, the use of any adsorbents to adsorb some toxic substances such as heavy metals can be the cause of contamination in soil and ground water with these substances when apply the used adsorbents to landfill. Therefore, the used adsorbent derived from sewage sludge must be treated properly and tested to evaluate the potential of leaching of hazardous substances. There are the limits specified by the environment protection law of each country. These test methods are called “Leaching tests”. When the leaching of toxic substances is higher than the legal limits, the solid will be specified as hazardous waste and has to be treated and disposed properly.

2.8 Leaching tests [52-53]

Leaching tests are widely used to evaluate the total amount of contaminants that can be released from waste materials. The release is studied to assess short – and long – term stability of waste materials. These include ignitability, corrosivity, reactivity and especially toxicity. The release of contaminants from waste materials can be affected by physical parameters such as particle size, temperature and porosity and chemical parameters such as pH, sorption properties, etc.

There are many different leaching tests used worldwide which have been developed to evaluate the release of toxic substances from waste materials under the variety of conditions such as:

- **The toxicity characteristic leaching procedure (TCLP):** this procedure evaluates the mobility of organic and inorganic contaminants in liquid, solid, and multiphase wastes adopted by the US EPA under the Hazardous and Solid Waste Amendment of 1984.
- **The German Leach Test Procedure (Din 38414 54):** this procedure is developed to assess leaching of toxic substances from sludge and sediments obtained from water and wastewater treatment. The method is considered applicable to solid, pastes, and sludge.
- **The French Leach Test (AFNOR 1988):** this procedure is restricted to solid residues. The method is similar to German procedure but the pH is not controlled in the French procedure.

In Thailand, there are laws and regulation which define that the leachate extraction procedure and analysis method for leachable substances should follow The Notification of Ministry of Industry B.E. 2548 (2005) [54]. When the extract of wastes contains any heavy metals or toxic substances at the concentration equal to or greater than the total threshold limit concentration (TTLC), shown in Table 2.1, the wastes are considered as hazardous wastes that have to be redetoxified in order to meet properties as specified.

Table 2.1 Total threshold Limit Concentration of toxicity specified in Notification of Ministry of Industry B.E. 2548 (2005).

Heavy metals or toxic substances	*Total threshold Limit Concentration (TTLC)*
Antimony and/or antimony compounds	500 mg/kg
Arsenic and/or arsenic compounds	500 mg/kg
Asbestos	1.0(as percent)
Barium and/or barium compounds (excluding barite and barium sulfate)	10,000 mg/kg
Beryllium and/or beryllium compounds	75 mg/kg
Cadmium and/or cadmium compounds	100 mg/kg
Chromium (VI) compounds	500 mg/kg
Chromium and/or chromium (III) compounds	2,500 mg/kg
Cobalt and/or cobalt compounds	8,000 mg/kg
Copper and/or copper compounds	2,500 mg/kg
Fluoride salts	18,000 mg/kg
Lead and/or lead compounds	1,000 mg/kg
Mercury and/or mercury compounds	20 mg/kg
Molybdenum and/or molybdenum compounds (excluding molybdenum disulfide)	3,500 mg/kg
Nickel and/or nickel compounds	2,000 mg/kg
Selenium and/or selenium compounds	100 mg/kg
Silver and/or silver compounds	500 mg/kg
Thallium and/or thallium compounds	700 mg/kg
Vanadium and/or vanadium compounds	2,400 mg/kg
Zinc and/or zinc compounds	5,000 mg/kg
Aldrin	1.4 mg/kg
Chlordane	2.5 mg/kg
DDT, DDE, DDD	1.0 mg/kg
2,4-Dichlorophenoxyacetic acid	100 mg/kg
Dieldrin	8.0 mg/kg
Dioxin (2,3,7,8-TCDD)	0.01 mg/kg
Endrin	0.2 mg/kg
Heptachlor	4.7 mg/kg
Kepone	21 mg/kg
Lead compounds, organic	13 mg/kg
Lindane	4.0 mg/kg
Methoxychlor	100 mg/kg
Mirex	21 mg/kg
Pentachlorophenol	17 mg/kg
Polychlorinated biphenyls (PCBs)	50 mg/kg

Table 2.1 (continue)

Heavy metals or toxic substances	*Total threshold Limit Concentration (TTLC)*
Polychlorinated biphenyls (PCBs)	50 mg/kg
Toxaphene	5 mg/kg
Trichloroethylene	2,040 mg/kg
Silvex; 2,4,5-Trichlorophenoxypropionic acid	10 mg/kg

2.9 Literature review

Although heavy metals in wastewater can be removed by typical physical and chemical process such as chemical precipitation, ion exchange, reverse osmosis, etc. [1-2], those processes have their limitation and are high cost [3]. In recent years, adsorption process becomes an interesting alternative technique that removal of heavy metals is achieved via mass transfer process [7]. Because activated carbon has large surface area, high sorption capacity and surface activity [8-9], many researchers were interested in using the activated carbon to adsorb some metal ions such as Cd(II) [8], Cu(II) [55], Ni(II) [56], Zn(II) [57], etc. in solutions. However, the utilization of activated carbon may be costly.

In the present, many studies have been focused on searching of low-cost adsorbents that have good potential to remove heavy metals. Kurniwan et al. (2006) [43] gave an overview of the low-cost adsorbents ability. The sorption capacity of these adsorbents (e.g. banana peel, red mud, kaolinite and sewage sludge) were evaluated and compared under many conditions such as pH, adsorbent dose, and initial metal concentration. It is found that sewage sludge from wastewater treatments had a good efficiency for removal of heavy metals, especially when compared with its cost. Therefore, there are many researches concerning the utilization of sewage sludge as adsorbent.

Calace et al. (2003) [58] studied the metal ions removal from water by sorption on paper mill sludge. This research found that the acid-base conditions are the most effective for the metal ions adsorption, and this adsorbent could be packed in column but it could not be reused.

Zhai et al.(2004) [59] prepared the adsorbent derived from sewage sludge through chemical pyrolysis and used it for removal of Cd(II) and Ni(II) ions from aqueous solution. The effect of some parameters such as the agitation time, metal ion concentration, adsorbent dosage and pH were studied. The results showed that the pyrolysis sludge could remove both metal ions. The pH of metal solutions was the most important factor that affected the adsorption efficiency of Cd(II) and Ni(II) ions and the ion exchange seemed to be an important process for adsorption of metal ions by this adsorbent.

Gasco et al. (2005) [60] studied the removal of Na^+, K^+, Ca^{2+} and Mg^{2+} ions from saline water by using adsorbent obtained by pyrolysis of sewage sludge. It was found that the pyrolysis sludge could remove some metals in saline water and could be applied for various solutions.

Wang et al. (2006) [61] investigated the removal of Cd(II) and Pb(II) ions from aqueous solutions by using activated sludge. The result from FT-IR analysis showed that amide played an extremely important role in binding Cd(II) and Pb(II) ions. Moreover, the group of –OH and C-O-C also involved in metal ions binding to some extent.

Hammaini et al. (2007) [62] demonstrated the biosorption of heavy metals by activated sludge. The results indicated that the pH value was an important variable in the sorption process. When the pH levels increased, activated sludge with negative charge would be exposed with the subsequent increase in number of attraction sites for positively charged metal ions. Furthermore, biomass could not be reused in subsequent loading and unloading cycles.

Bouzid et al. (2007) [63] studied the removal of copper from aqueous solution by sewage sludge. The results showed that the adsorption efficiency increased with increasing pH value and temperature. The mechanisms of copper removal by this material included adsorption and precipitation.

All the previous researches show that sewage sludge is an interesting alternative, inexpensive and effective material for the removal of heavy metals ions from wastewater. However, the used adsorbents derived from sewage sludge must be treated correctly to prevent the release of some contaminants to environment. Many researches showed that some contaminants in sewage sludge could be released to environment.

Fytianos et al. (1998) [53] studied the leaching of heavy metals from municipal sewage sludge. The parameters which affected the leaching such as liquid to solid (L/S) ratio, contact time, pH, type of leaching agents, and particle size, were studied. It was found that the amount of metal released increased when L/S ratio and contact time increased, and pH values and particle size decreased. Furthermore, EDTA showed the greatest mobilization ability, followed by NaOH, acid solutions and water.

Obrador et al. (2001) [64] studied the influence of thermal treatment on extraction and leaching behavior of trace metal in a contaminated sewage sludge at 180ºC, 300ºC and 400ºC. The results showed that the heating helped to reduce the possible release of metals to the environment. The heating at 300ºC and 400ºC could be a good treatment for sludge to be disposed in a solid-waste disposal site, because of a significant decrease in weight, volume and leachability.

All the previous researches indicate that heavy metals contaminated in sewage sludge can be released under certain conditions. Therefore, the used adsorbents derived from sewage sludge must be passed the leaching tests to specify the degree of hazard. Moreover, up on our knowledge, there are not any researches that use and compare the utilization of sewage sludge from municipal and industrial wastewater treatments plants, and compare its leachability after used as adsorbent.

The main objective of this research is to utilize sludge from municipal and industrial wastewater treatment plants as adsorbents for removal of Cd(II), Ni(II) and Pb(II) ions from water. The adsorption efficiency for the metal ions and the leachability of metals from used adsorbents are compared.

CHAPTER III

EXPERIMENTAL SECTIONS

3.1 Apparatus

The apparatuses used in this study are listed in Table 3.1.

Table 3.1 Apparatus list.

	Apparatus	*Model(company)*	*Purpose*
1	Flame atomic absorption spectrometer (FAAS)	AAnalyst 100 (Perkin-Elmer)	determination of metal concentration (operating parameters are shown in table 3.2)
2	Scanning electron microscope (SEM)	JSM 6400 (JEOL)	surface analysis of materials
3	CHNS/O analyzer	PE2400 Series II (Perkin-Elmer)	elemental analysis of material
4	Surface area analyzer	Autosorb-1 (Quantachrome)	surface analysis of materials
5	Mechanical shaker	SA-31 (Yamato shaker)	agitation of solutions in adsorption experiments
6	Orbital mixer incubator	OM-11 (Ratek)	agitation of solutions in adsorption experiments with temperature control
7	Centrifuge	CENTAUR 2 (Sanyo)	separation of adsorbents from extracted metal solution
8	pH meter	7104 (ORION)	pH measurement
9	Digital balance	AT200 (Mettler)	weighing materials

Table 3.2 Operating parameters for FAAS.

Operating conditions	***Cd***	***Ni***	***Pb***
Wavelength (nm)	228.8	232.0	283.3
Slit width (nm)	0.70	0.20	0.70
Lamp type	HCL[a]	HCL[a]	HCL[a]
Lamp current (mA)	4	8	10
C_2H_2 flow-rate (L min^{-1})	3.0	3.0	3.0
Air flow-rate (L min^{-1})	10.0	10.0	10.0

[a] Hollow Cathode Lamp (HCL)

3.2 Chemicals

All chemicals were of standard analytical grade and listed in table 3.3.

Table 3.3 Chemical list.

Chemicals	***Supplier***	***Grade***
Cadmium standard solution (1000 mg L^{-1})	BDH	analytical
Activated charcoal	MERCK	analytical
Hydrochloric acid 37%	MERCK	analytical
Ion exchange resin	MAZUMA	food grade
Lead standard solution (1000 mg L^{-1})	Fisher	analytical
Nickel standard solution (1000 mg L^{-1})	Fisher	analytical
Nitric acid 65%	MERCK	analytical
Sodium acetate	CARLO ERBA	analytical
Sodium hydroxide	MERCK	analytical

3.3 Procedures

3.3.1 Preparation of Adsorbents

The adsorbents were derived from sewage sludge from municipal and industrial wastewater treatment plants. The municipal sludge was obtained from Chatuchak water environment control plant (Bangkok, Thailand). The industrial sludge was provided from the central wastewater treatment plants of Lad Krabang industrial estate by Global utilities services company (GUSCO) (Bangkok, Thailand). All adsorbents were prepared by drying in the sun (30-40 °C). After that they were grinded and sieved to 212 µm. All adsorbents were kept in desiccators

3.3.2 Characterization of adsorbents

The adsorbents were analyzed for surface characteristics, surface area, total pore volume, average pore diameter, and C, H, N compositions by using the techniques listed in table 3.4.

Table 3.4 The techniques for characterization of adsorbents.

Characteristics	***Techniques***
Characteristics of surface	Scanning Electron Microscope (SEM)
Surface area, total pore volume and average pore diameter	Surface area analyzer (BET)
C,H,N content	CHNS/O Analyzer

3.3.3 Adsorption studies

The studies of adsorption were carried out by utilization of two adsorbents i.e. municipal sludge and industrial sludge. All experiments were performed in triplicate using batch method.

3.3.3.1 Effect of contact time

The effect of contact time on removal of Cd(II), Ni(II) and Pb(II) ions were studied by varying contact time of 5, 15, 30 min. and 1, 3, 6 and 24 hr. Solutions containing 20 mg L^{-1} of cadmium, nickel and lead ions were prepared in 0.05 M acetate buffer and adjusted pH value to 5, 5 and 4 for Cd(II), Ni(II) and Pb(II) ions, respectively with HNO_3 or NaOH.

Each series of 50 mL polyethylene bottles containing 0.05 g of municipal sludge were added with 25 mL of each metal solution. The mixture was shaken in mechanical shaker at room temperature. A series of experiments were performed for each metal ions using different contact time. At the end of mixing, the adsorbents were separated from solution by centrifugation at 3000 rpm for 5 min and pH of solutions was measured. Finally, the residual metal concentrations were determined by FAAS. All experiments were repeated using industrial sludge.

3.3.3.2 Effect of adsorbent dosage and adsorption kinetics

The effect of adsorbent dosage was studied by varying the adsorbent dose in the range of 0.01 to 0.10 g of sewage sludge. The metal ions solution (20 mg L^{-1}) was prepared in 0.05 M acetate buffer at pH 5, 5 and 4 for Cd(II), Ni(II) and Pb(II) ions, respectively. Each series of 50 mL bottles containing 0.01, 0.05 and 0.10 g of sludge were added with 25 mL of each metal solution. All mixtures were shaken at room temperature for 1 hr and the solid was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solution was measured and metal concentrations were determined by FAAS.

The adsorption kinetics was studied by varying the contact time of 5, 15, 30 min. and 1, 3, 6 and 24 hr. with the adsorbent dose in the range of 0.01 to 0.10 g of sewage sludge. The metal ions solution (20 mg L^{-1}) was prepared in 0.05 M acetate buffer at pH 5, 5 and 4 for Cd(II), Ni(II) and Pb(II) ions, respectively. Each series of 50 mL bottles containing 0.01, 0.05 and 0.10 g of sludge were added with 25 mL of each metal solution. All mixtures were shaken at room temperature. A series of experiments were performed for each metal ions using different contact time. At the end of mixing, the adsorbents were separated from solution by centrifugation at 3000 rpm

3.3.3.3 Effect of pH

The effect of pH was investigated by varying the pH values of metal ions solutions. Initially, pH was adjusted to values below the pH of metal precipitation to assure complete dissolution of each metal. The initial pH adjustment was carried out using 0.05 M acetate buffer to the desired values in the range pH 2 to 8 for Cd(II) and Ni(II) and pH 2 to 6 for Pb(II) ions, respectively with HNO_3 or NaOH.

Solutions containing 20 mg L^{-1} of metal ions were prepared in 0.05 M acetate buffer at different pH. The adsorption experiments were performed using 0.05 g of sludge for 25 mL of each metal ions solution. All mixtures were shaken at room temperature for 1 hr and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and metal concentrations were determined by FAAS.

3.3.3.4 Adsorption isotherms

The adsorption isotherms were studied at 30 °C by varying the initial metal concentrations from 5 to 150 mg L^{-1}. The results were fitted with Langmuir and Frundlich adsorption models to describe the adsorption equilibrium occurred at the solid-liquid interface and estimate the maximum sorption capacity for metal ions of the sewage sludge.

All metal ions solutions were prepared in 0.05 M acetate buffer at pH 5, 5 and 4 for Cd(II), Ni(II) and Pb(II) ions, respectively. The solutions of metal ions were kept in a shaker at 30 °C for 2 hr to assure the constant temperature. Each series of 50 mL polyethylene bottles containing 0.05 g of sludge were added with 25 mL of each metal solution The mixture was shaken for 1 hr at 30 °C and the solid was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and residual metal concentrations were determined by FAAS.

3.3.3.5 Competitive adsorption

Cadmium, nickel and lead ions were mixed in the same concentration for the competitive adsorption experiments. The mixed solutions of three metal ions with concentration of 0.30 mmol L^{-1} for each metal ion were prepared in acetate buffer at pH 5. A series of bottles containing 0.05 g of sludge was added with 25 mL of mixed solution. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and residual metal concentrations were determined by FAAS.

3.3.3.6 Comparison of adsorption capacities of sewage sludge from different sources

The adsorption capacity of sewage sludge from different sources were evaluated and compared. Municipal sludge obtained from Chatuchak water environment control plant was compared to Dindaeng water environment control plant. The samples of industrial sludge, provided by the central wastewater treatment plants of Lad Krabang industrial estate, were collected at the same place but different cycle of water treatment.

Metal solutions containing 20 mg L^{-1} of each metal ions were prepared in acetate buffer at pH 7, 7 and 5 for Cd(II), Ni(II) and Pb(II) ions, respectively. A series of 50 mL bottles containing 0.05 g of adsorbent were added with 25 mL of each metal solution. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and residual metal concentrations were determined by FAAS.

3.3.3.7 Comparison of adsorption capacities of sewage sludge and commercial adsorbents

To evaluate their potential to be used as effective adsorbent for removal of heavy metal ions among other adsorbents, the adsorption capacities of sewage sludge were compared with commercial adsorbents i.e. activated charcoal and ion exchange resin.

Metal solutions containing 20 mg L^{-1} of each metal ions were prepared in acetate buffer at pH 7, 7 and 5 for Cd(II), Ni(II) and Pb(II) ions, respectively in case of both sludge and activated charcoal, and pH 4 for all metal ions in case of ion exchange resin. A series of 50 mL bottles containing 0.05 g of adsorbent were added with 25 mL of each metal solution. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and residual metal concentrations were determined by FAAS.

3.3.3.8 Utilization of sewage sludge to remove heavy metal ions from real wastewater

Municipal and industrial sludge were used to remove Cd(II), Ni(II) and Pb(II) ions in the mixed solution obtained by mixing real wastewater of each metal ions. The wastewater was collected from a laboratory in department of chemistry, faculty of science, Chulalongkorn University.

The pH of the mixed wastewater was adjusted to pH 5. Three series of 50 mL bottles containing 0.01, 0.05 and 0.10 g of sludge were added with 25 mL of wastewater. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. After that, pH of solutions was measured and residual metal concentrations were determined by FAAS.

3.3.4 Sequential extraction

Sequential extraction procedure described by Tessier et al. [65] was employed in this study by using 1.00 g of used adsorbents. Municipal and industrial sludge were used to remove Cd(II), Ni(II) and Pb(II) ions in the solutions containing mixed metal ions. The mixed solutions of three metal ions having concentration of 0.20 mmol L^{-1} for each metal ion were prepared in acetate buffer at pH 5. A series of bottles containing 0.25 g of sludge was added with 125 mL of mixed solution. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. The pH values of solutions were measured and residual metal concentrations were determined by FAAS. After that, 1.00 g of used adsorbent was used in the extraction of different fractions as following:

Fraction 1 - Exchangeable: The samples were extracted with 8 mL of magnesium chloride solution (1 M $MgCl_2$, pH 7.0) at room temperature for 1 hour with continuous agitation.

Fraction 2 - Bound to carbonates: The solid residue from extraction of fraction 1 was further extracted with 8 mL of 1 M sodium acetate adjusted to pH 5.0 with acetic acid (HOAc) at room temperature for 3 hours with continuous agitation.

Fraction 3 - Bound to iron, manganese oxides: The solid residue from the extraction of fraction 2 was extracted with 20 mL of 0.04 M $NH_2OH \bullet HCl$ in 25% (v/v) HOAc. This experiment was performed at 95 ± 5 °C with occasional agitation for 5 hours.

Fraction 4 - Bound to organic matter: The solid residue from fraction 3 was extracted with 3 mL of 0.02 M HNO_3 and 5 mL of 30% H_2O_2 (adjusted to pH 2 with HNO_3), and the mixture was heated to 85 ± 5 °C for 2 hours with occasional agitation. After separation by centrifugation, 3 mL aliquot of H_2O_2 (adjusted to pH 2 with HNO_3) was then added to the solid and the sample was heated again to 85 ± 5 °C for 3 hours with intermittent agitation.

Fraction 5 – Residual: The residue from the extraction of fraction 4 was digested with 10 mL of concentrated HF and 16 mL of DI water, and the mixture was heated to 85 ± 5 °C for 2 hours with occasional agitation.

After the prescribed time interval for each extraction (fractions 1-4), samples and the supernatant were filtered through Whatman filter papers No.42 (110mm). The remaining solid sample was washed twice with DI water before continuing with the next extraction step. After that, the metal concentrations in solution of each fraction were determined by FAAS.

3.3.5 Leaching tests

In Thailand, the Ministry of Industry defined the leachate extraction procedure and analysis method for solid waste or unusable material samples following Method 3050 in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 2nd edition, U.S. Environmental Protection Agency, 1982. The method used in this study was adapted from the procedure given by the Ministry of Industry (Thailand). Municipal and industrial sludge were used to remove Cd(II), Ni(II) and Pb(II) ions in the solutions containing mixed metal ions. The mixed solutions of three metal ions having concentration of 0.20 mmol L^{-1} for each metal ion were prepared in acetate buffer at pH 5. A series of bottles containing 0.25 g of sludge was added with 125 mL of mixed solution. The mixture was shaken for 1 hr at room temperature and the adsorbent was separated by centrifugation at 3000 rpm for 5 min. The pH values of solutions were measured and residual metal concentrations were determined by FAAS. After that, 1.00 g of used adsorbent was used in the procedure given by the Ministry of Industry (Thailand), as following.

1. The vessel containing 1.00 g of used adsorbent was added with 10 mL of 1:1 HNO_3. Mix the slurry and cover with a watch glass. Heat the sample to 95 °C ± 5 °C and reflux for 10 to 15 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the cover, and reflux for 30 minutes. If brown fumes are generated, indicating oxidation of the sample by HNO_3, repeat this step (addition of 5 mL of conc. HNO_3) over and over until no brown fumes are given off by the sample indicating the complete reaction with HNO_3. Evaporate the solution to approximately 5 mL without boiling or heat at 95 °C ± 5 °C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

2. After the step 1 has been completed and the sample has cooled, add 2 mL of water and 3 mL of 30% H_2O_2. Cover the vessel with a watch glass and return the covered vessel to the heat source for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cools the vessel.

3. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

4. Cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL or heat at 95 °C ± 5 °C without boiling for two hours. Maintain a covering of solution over the bottom of the vessel at all times.

5. Add 10 mL conc. HCl to the sample digest from step 4 and cover with a watch glass. Place the sample on/in the heating source and reflux at 95 °C ± 5 °C for 15 minutes.

6. Filter the digestate through Whatman No. 41 filter paper (or equivalent) and collect filtrate in a 100 mL volumetric flask. Make to volume and determine metal

concentrations by FAAS. When the results of analysis of total threshold limit concentration (TTLC) shows a value exceeding such standard as set forth in Table 2.1, the waste has to be treated as hazardous waste.

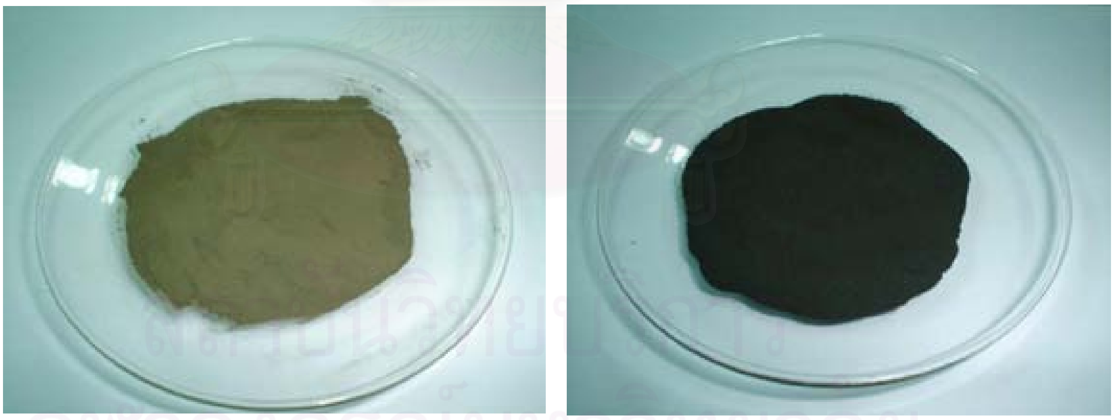
If any substance was determined less than the TTLC value in Table 2.1, the Waste Extraction Test (WET) shall be used to determine the soluble threshold limit concentration (STLC) in next step. If any substance was determined less than STLC value, it shall be non-hazardous waste.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of adsorbents

Adsorbents derived from sewage sludge from municipal and industrial wastewater treatment plants were employed in this research. The municipal sludge obtained from Chatuchak Water Environment Control Plant and industrial sludge provided by the central wastewater treatment plants of Lad Krabang industrial estate by Global utilities services company (GUSCO) were dried under the sun, grinded and sieved through a 0.48 µm sieve shown in Figure 4.1. The sludge from municipal wastewater treatment plants were brown powder and those from industrial wastewater treatment plant were blackish brown powder.



(a) Municipal sludge (b) Industrial sludge

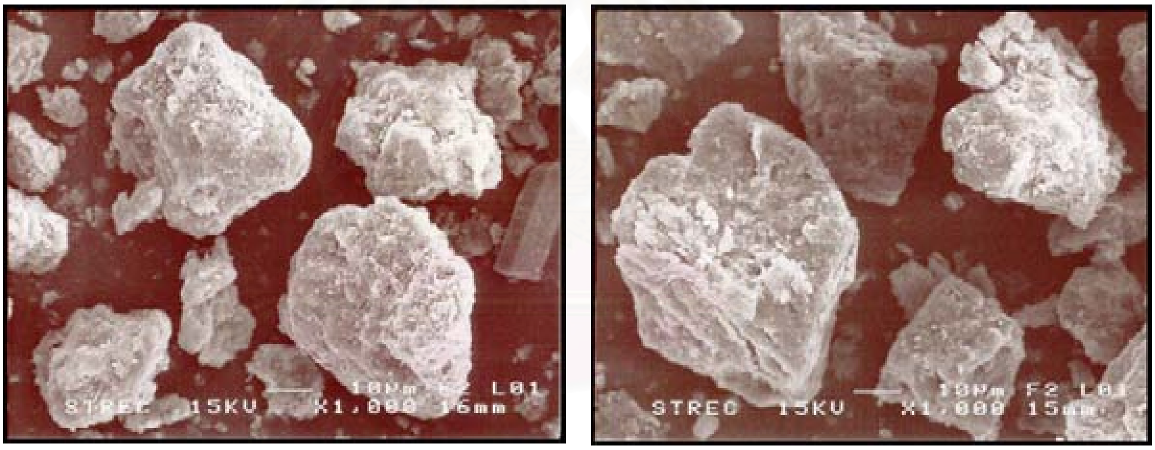
Figure 4.1 The municipal sludge (a) and industrial sludge (b).

The characteristics of the surface, surface area, total pore volume, average pore diameter of sewage sludge were evaluated by SEM, nitrogen adsorption (BET), and the chemical composition was obtained by CHNS/O analyzer. The results are presented in the following.

4.1.1 Scanning Electron Microscope (SEM)

Scanning electron microscope (SEM) is used to exhibit the surface morphology and fundamental physical properties of the sewage sludge.

The SEM micrographs (Figure 4.2) show the similarity between municipal and industrial sludge surfaces. The surfaces appear in amorphous form.



(a) Municipal sludge (b) Industrial sludge

Figure 4.2 The SEM micrographs of municipal sludge (a) and industrial sludge (b).

4.1.2 Surface Analysis

The N_2 adsorption by the sludge and the BET isotherm were performed to give the average surface area, pore volume and pore diameter of municipal and industrial sludge. The surface analysis by nitrogen adsorption using BET method is shown in Table 4.1.

Table 4.1 The results of surface analysis.

Sample	***Surface area*** ***($m^2\ g^{-1}$)***	***Total pore volume*** ***($cm^3\ g^{-1}$)***	***Average pore diameter*** ***(A°)***
Municipal sludge	5.22	0.0302	231.0
Industrial sludge	1.19	0.0066	221.3

The surface analysis results showed that, pore size of municipal and industrial sludge are slightly different, and the surface area and total pore volume of municipal sludge are a little greater than industrial sludge. Regarding the surface area, the sludge possesses smaller surface area compared to commercial adsorbents (e.g. activated carbon: 300-1000 m^2/g).

4.1.3 Elemental Analysis (EA)

The EA results from CHNS/O analyzer are shown in Table 4.2.

Table 4.2 The C, H and N content of two adsorbents.

Sample	***%C***	***%H***	***%N***
Municipal sludge	17.6	4.4	2.5
Industrial sludge	32.8	5.8	2.6

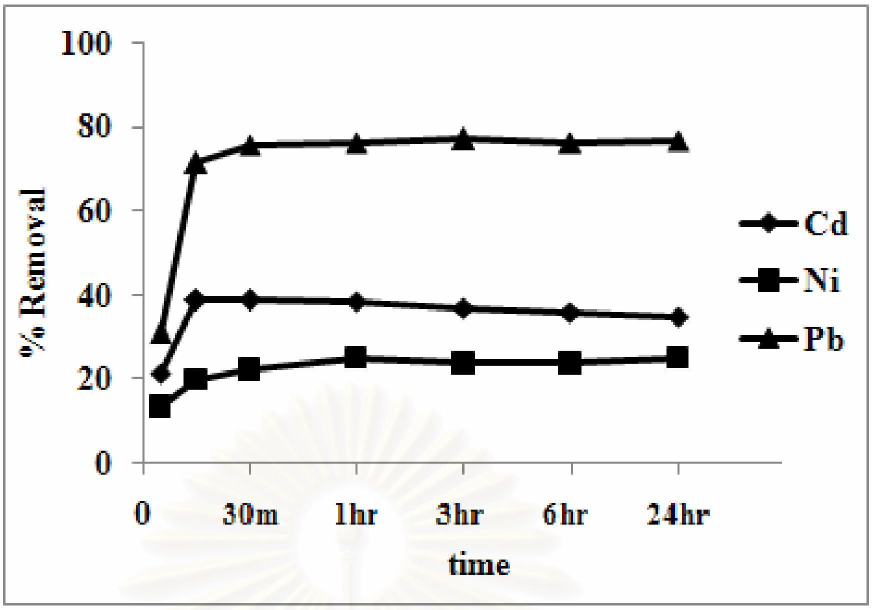
The EA results show that industrial sludge consisted of carbon in a higher content than municipal sludge. This result may lead to an assumption that industrial sludge could have a good efficiency to remove heavy metals ions.

The higher percentages of carbon in the industrial sludge may be due to the higher loading of organic substances in the industrial wastewater compared to municipal wastewater. These organic matters may be left over along with the excess bacteria cells in the sludge from the activated sludge treatment process. The industrial sludge was provided from the central wastewater treatment plants of Lad Krabang industrial estate where there is abundance of factories for food productions. Therefore, high carbon content in industrial sludge is probably a result from high carbonaceous substances (e.g. organic matter and/or inorganic carbon) loading in wastewater discharged from industry.

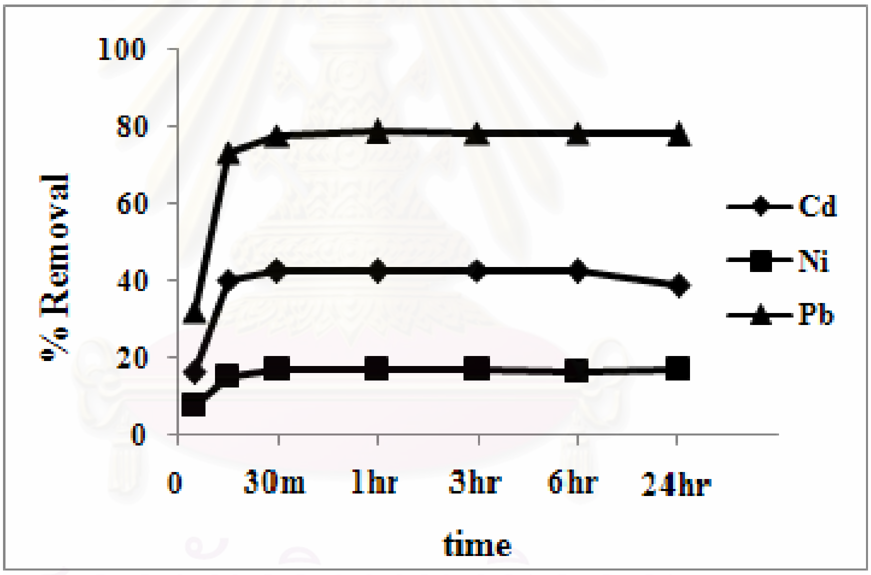
4.2 Adsorption studies

4.2.1 Effect of contact time

Effect of contact time on the removal of Cd(II), Ni(II) and Pb(II) ions are demonstrated in Figure 4.3 The results show that the removal efficiency increased with an increase of contact time before equilibrium was reached. The removal of all metals increased rapidly within 30 minutes and thereafter increased very slowly. Similar trends were observed for both adsorbents. Adsorption equilibrium was attained within 60 minutes for all metal ions. Starting with solutions containing 20 mg L^{-1} of each metal ion, the percentages of metal removal by municipal and industrial sludge were 38.38 and 42.44 for Cd (II), 25.07 and 17.35 for Ni(II) and 76.12 and 78.61 for Pb(II). The results show that municipal sludge exhibited adsorption efficiencies that were close to those of industrial sludge for metal ions studied.



(a) Municipal sludge



(b) Industrial sludge

Figure 4.3 Effect of contact time on the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) and industrial sludge (b). (0.05 g of sludge : 25 mL of metal solutions (20 mg L^{-1}) at pH 5, 5 and 4 for Cd(II), Ni(II) and Pb(II) ions, respectively)

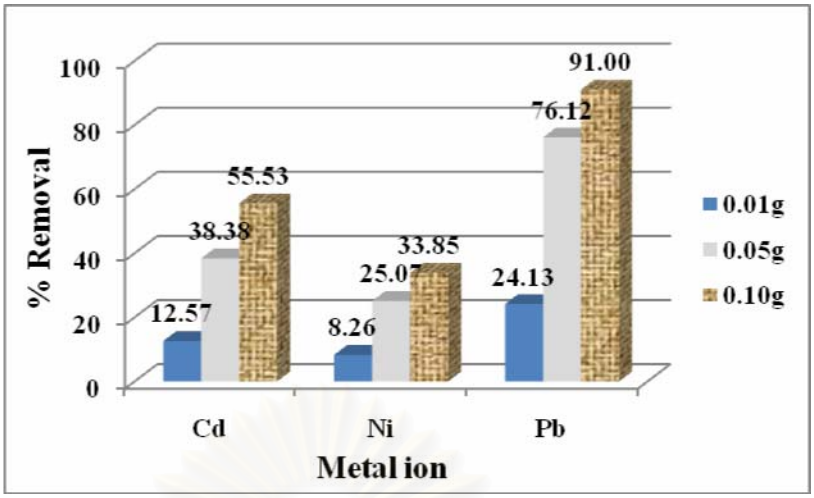
The equilibrium time is one of the important parameters for an economical wastewater treatment application. According to these results, the equilibrium could be reached within 60 minutes when this experimental set up was used. This contact time was taken for next experiments to assure the adsorption equilibrium of the studied process.

4.2.2 Effect of adsorbent dosage and adsorption kinetics

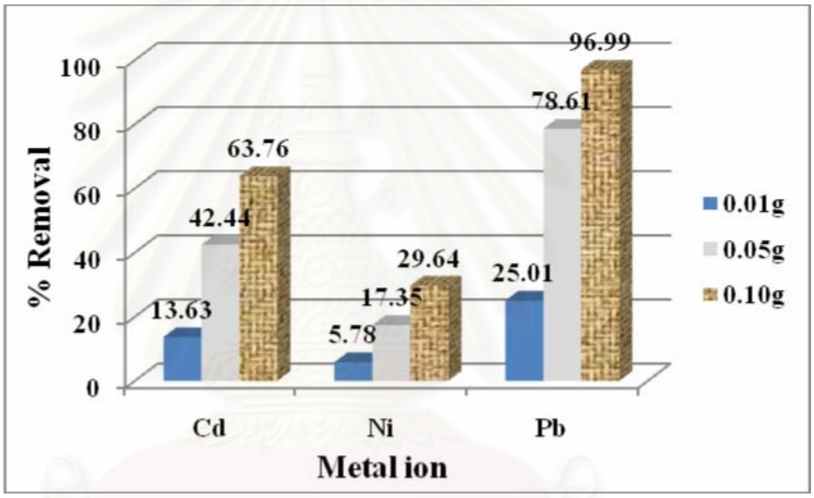
4.2.2.1 Effect of adsorbent dosage

Effects of adsorbent dosage for removal of Cd (II), Ni (II) and Pb (II) ions were investigated by varying the amount of adsorbent as 0.01, 0.05 and 0.10 g. The results are shown in Figure 4.4. The removal efficiency of all metal ions improved with increasing dose. This can be explained by the fact that the adsorbent of higher doses provide more surface area and greater number of active sites for metal ions adsorption.

However, the amount of adsorbed ions per mass of the adsorbent decreased with increasing adsorbent dosage. It is basically due to adsorption sites that remain unoccupied during the adsorption process when using high dosage.



(a) Municipal sludge



(b) Industrial sludge

Figure 4.4 Effect of adsorbent dosage on the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) and industrial sludge (b) (25 mL of metal solutions (20 mg L^{-1}) at pH 5, 5 and 4 for Cd(II), Ni(II) and Pb(II), respectively, using contact time of 60 min.)

4.2.2.2 Adsorption kinetics

Kinetics of sorption, which is expressed in terms of the rate of solute removal, is one of the important characteristics used in defining the efficiency of sorption process. In order to investigate the mechanism [66-67], characteristic constants of adsorption rate were usually determined using kinetics models. A pseudo-first order model derived by Lagergren [68] based on solid capacity, is widely used for the sorption of analytes from aqueous solution, and the pseudo-first order equation is expressed as following.

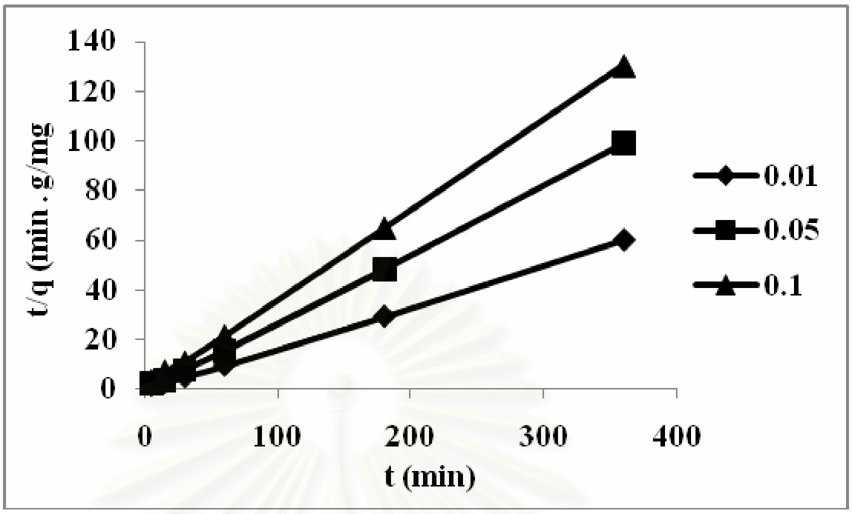
$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad 4\text{-}1$$

where q_e and q_t are the amount of adsorbed analytes at equilibrium and at any time t (mg g^{-1}), and k_l is the equilibrium rate constant of pseudo-first order sorption (min^{-1}). The value of the rate constant (k_l) and calculated equilibrium adsorption capacity ($q_{e,cal}$) can be calculated from the slope and intercept of the linear plot of log (q_e - q_t) versus t , respectively (the plot are not shown). After that, the $q_{e,cal}$ values are compared to the q_e values from the experiment ($q_{e,exp}$) to evaluate whether the kinetics model fits well with the experimental data.

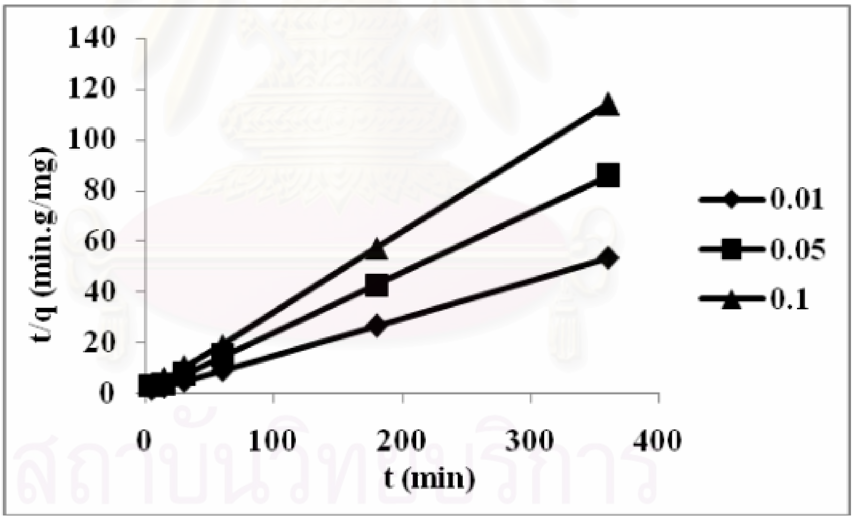
In addition, the pseudo-second order model based on solid phase adsorption and intraparticle diffusion is also one of the widely used kinetics models [69], and the pseudo-second order equation is expressed as following.

$$\frac{t}{q_t} = \left(\frac{1}{k_2.q_e^2}\right) + \frac{t}{q_e} \qquad 4\text{-}2$$

k_2 is the equilibrium rate constant of pseudo-second order adsorption (g mg^{-1} min^{-1}). If the second-order kinetics is applicable, then the plot of t/q_t versus t should give a linear relationship. The k_2 and $q_{e,cal}$ can be calculated from the intercept and slope of the linear plot, respectively. The plots of pseudo-second order kinetics for adsorption of each metal ion on sewage sludge were shown in Figure 4.5.

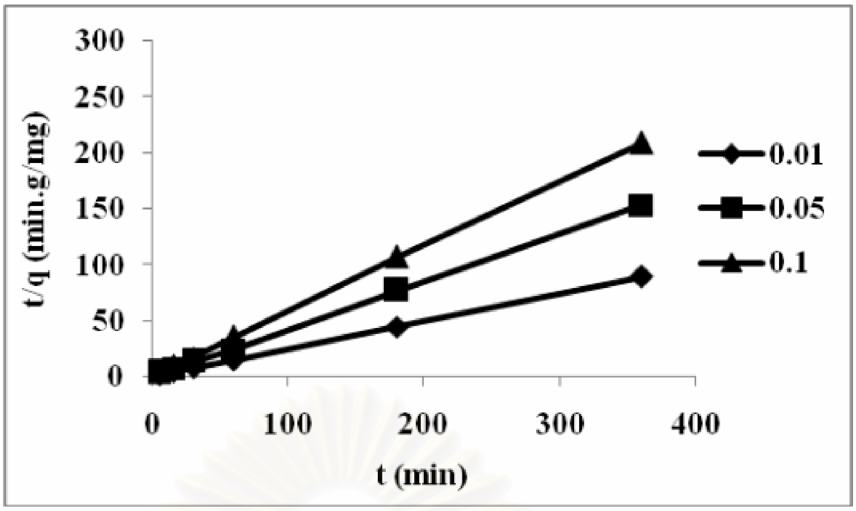


(a) Municipal sludge

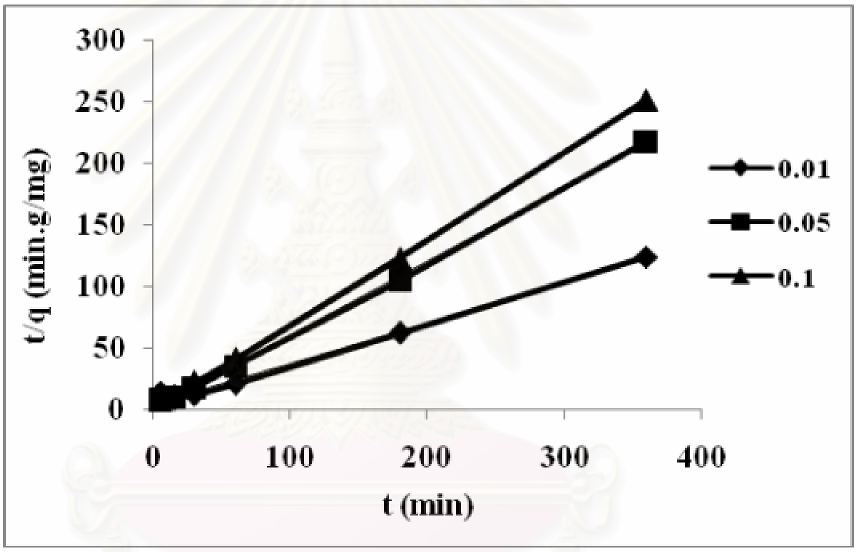


(b) Industrial sludge

Figure 4.5 Pseudo-second order kinetics plots for adsorption of Cd(II) ions by municipal sludge (a) and industrial sludge (b) studied at various adsorbent dose; 0.01, 0.05 and 0.10 g.

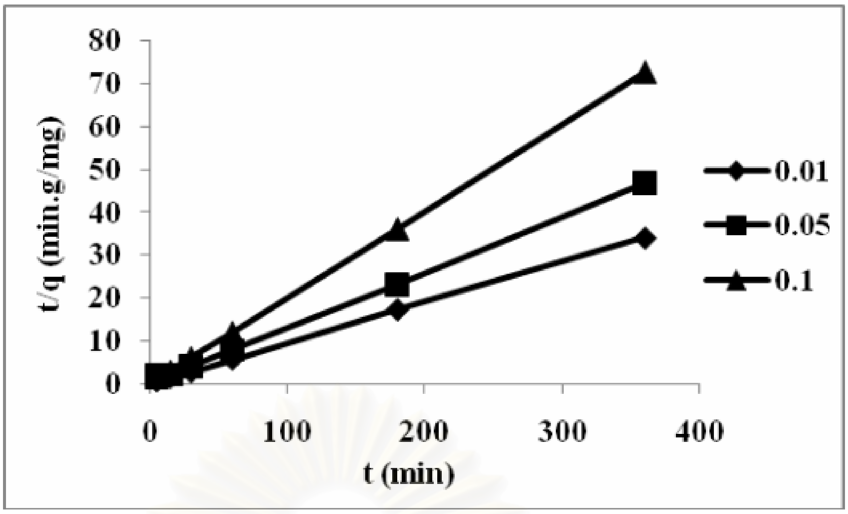


(a) Municipal sludge

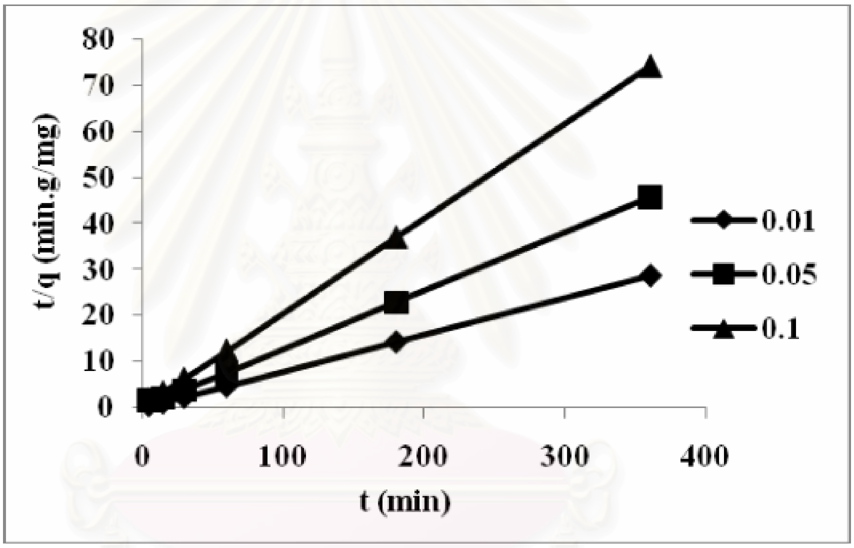


(b) Industrial sludge

Figure 4.6 Pseudo-second order kinetics plots for adsorption of Ni(II) ions by municipal sludge (a) and industrial sludge (b) studied at various adsorbent dose; 0.01, 0.05 and 0.10 g.



(a) Municipal sludge



(b) Industrial sludge

Figure 4.7 Pseudo-second order kinetics plots for adsorption of Pb(II) ions by municipal sludge (a) and industrial sludge (b) studied at various adsorbent dose; 0.01, 0.05 and 0.10 g.

The pseudo-first and pseudo-second order kinetics model were used in this study. Unfortunately, the number of data points were not many enough to fit the curve when attempted to plot pseudo-first order relation (log (q_e - q_t) versus t). Therefore, this model was left aside. On the other hand, when fitted the experimental data with pseudo-second order model, the results showed that the adsorption data of all metal ions could fit well by the model as demonstrated by the r^2 values that were higher than 0.99.

A similar phenomenon was observed for both municipal and industrial sludge. Moreover, the $q_{e,cal}$ obtained from linear plot of the pseudo-second order, q_e from the experiment ($q_{e,exp}$) and the rate constants (k_2) for each system, are shown in Table 4.3.

The results from kinetics study indicate that the adsorptions on sewage sludge follow the assumptions of the pseudo-second order model that are [68]:

- A monolayer of metal ions adsorbed on the surface.
- The energy of the sorption for each ion is the same and independent of surface coverage.
- The sorption occurs only on localised sites and involves no interactions between sorbed ions.
- The rate of sorption is almost negligible in comparison with the initial rate of sorption.

Table 4.3 Parameters calculated by pseudo-second-order kinetics of adsorption of Cd(II), Ni(II) and Pb(II) ions by sewage sludge

Sample	*Metal*	*Adsorbent dose (g)*	$q_{e.exp}$ *(mg g^{-1})*	$q_{e,cal}$ *(mg g^{-1})*	k_2 *(g mg^{-1} min^{-1})*	r^2
Municipal sludge	Cd	0.01[a]	6.35	-	-	-
		0.05[a]	3.90	-	-	-
		0.10	2.80	2.79	0.147	0.9997
	Ni	0.01	4.03	4.07	0.098	0.9999
		0.05	2.49	2.36	0.271	0.9997
		0.10	1.72	1.72	0.317	0.9999
	Pb	0.01	10.89	10.54	0.088	0.9999
		0.05	7.68	7.78	0.049	0.9994
		0.10	4.97	4.98	0.179	0.9999
Industrial sludge	Cd	0.01	6.76	6.83	0.053	0.9999
		0.05	4.21	4.25	0.096	0.9995
		0.10	3.16	3.19	0.132	0.9999
	Ni	0.01	2.90	3.04	0.025	0.9934
		0.05	1.72	1.67	1.361	0.9992
		0.10	1.47	1.44	0.827	0.9995
	Pb	0.01	12.53	12.58	0.084	0.9999
		0.05	7.89	7.94	0.054	0.9997
		0.10	4.87	4.89	0.163	0.9999

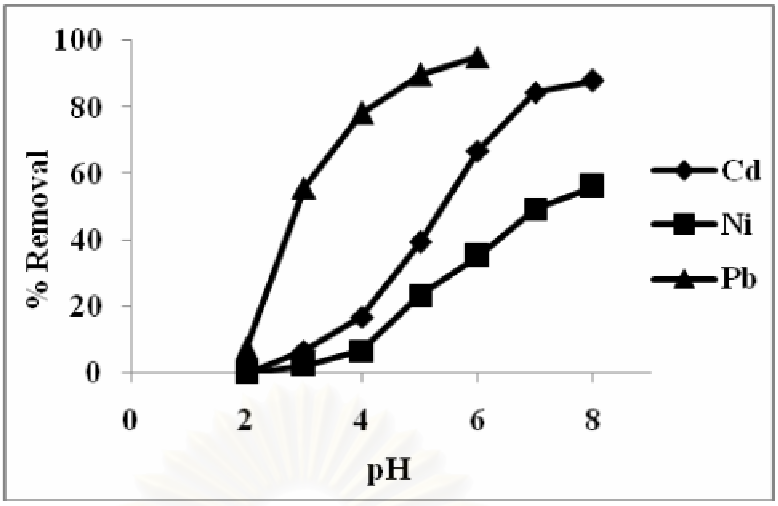
[a] could not obtain the results from curve fitting.

The results showed that the q_e values calculated by the linear equation of pseudo-second order model ($q_{e,cal}$) were close to those obtained from the experiments ($q_{e.exp}$). This confirms that the pseudo-second order model fit well the experimental data.

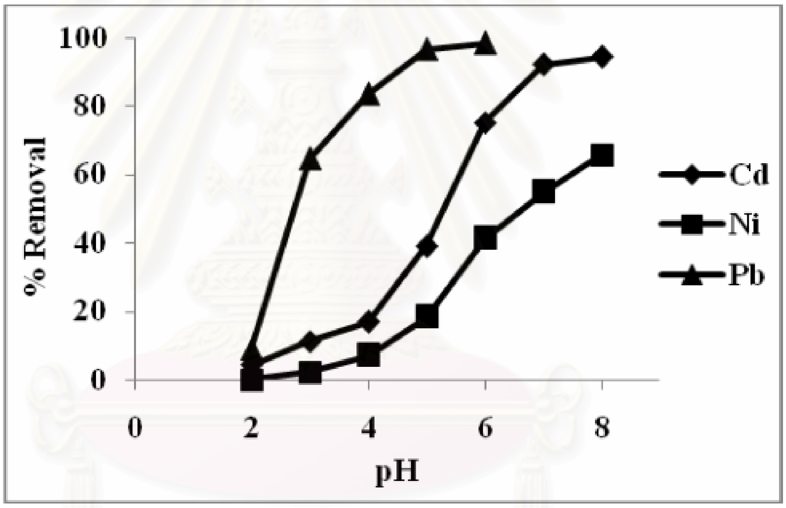
Regarding the k_2 values, it was found that the adsorption rate were similar for each metal ion when used different adsorbent dose. It seems that an increasing of adsorbent dose in the studied range did not affect the adsorption kinetics.

4.2.3 Effect of pH

The effect of pH on the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal and industrial sludge are shown in Figure 4.8. Similar trends were observed for all metal ions. The removal of all metal ions increased obviously with an increase of pH of solution from 2 to 8 for Cd (II) and Ni (II), and 2 to 6 for Pb(II). These pH values are lower than the critical pH of hydroxide precipitation (pH 8.5, 8.1 and 6.1 for Cd(II), Ni(II) and Pb(II), respectively). The results indicate that the suitable pH values for adsorption of Cd(II), Ni(II) and Pb(II) were 7, 7 and 5, respectively for both sludge. The maximum adsorption capacity of municipal and industrial sludge were 8.63 and 8.74 mg g^{-1} at pH 8 for Cd(II); 5.52 and 5.94 mg g^{-1} at pH 8 for Ni(II) and; 9.36 and 9.21 mg g^{-1} at pH 6 for Pb(II).



(a) Municipal sludge



(b) Industrial sludge

Figure 4.8 Effect of pH on the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) and industrial sludge (b).

It is well known that adsorption of heavy metal ions depends strongly on pH of the aqueous solution and the nature of adsorbent surface (e.g. functional groups). At low pH values, the H^+ concentration increases and may compete with metal cations to adsorb on negatively charged active sites on sludge surface [70]. The further access of metal ions to the surface would be restricted as a result of repulsive force. At high pH values, the overall negative charge of sludge would be exposed, resulting in an increase in attraction sites for positively charged metal ions [71]. The similar effect of pH was also observed in the adsorption of metal ions on sewage sludge and other adsorbents having similar compositions [72-73].

4.2.4 Adsorption Isotherm

The adsorption isotherm is important for the design of the adsorption system [74]. It can describe how adsorbates interact with adsorbent. Several isotherm equations are available but only two important isotherm equations are widely used. Langmuir adsorption isotherm assumes monolayer sorption at high concentrations onto the homogeneous surface with a specific number of sites. The equation is shown as following,

$$q_e = \frac{\left(q_m b C_e\right)}{\left(1 + bC_e\right)}$$

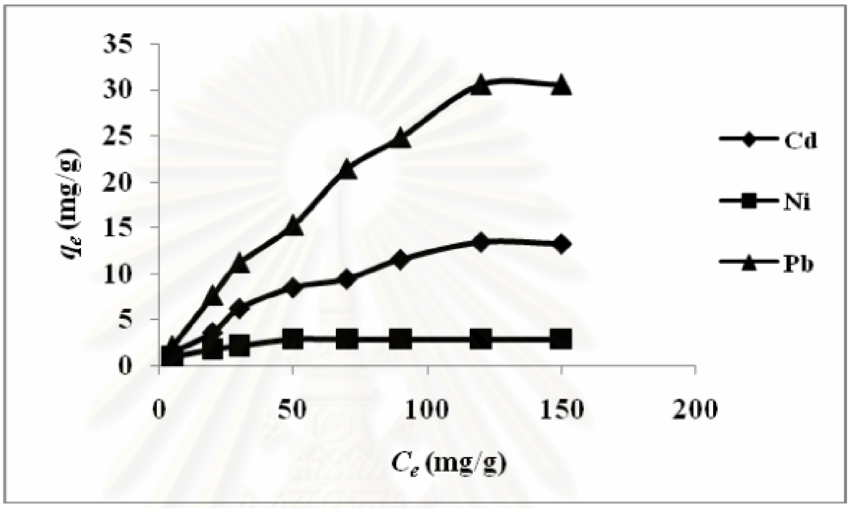
2-3

where q_e is adsorbed quantity per the mass of adsorbent (mg g^{-1}), q_m is maximum adsorbed quantity per mass of adsorbent (mg g^{-1}), C_e is the concentration at equilibrium (mg L^{-1}), and b is the equilibrium constant or Langmuir constant related to the affinity of binding sites (L mg^{-1}). In addition, Freundlich adsorption isotherm assumes that the uptake of metal ions occurs on a heterogeneous surface resulting in multilayer adsorption. The model is presented as the following equation,

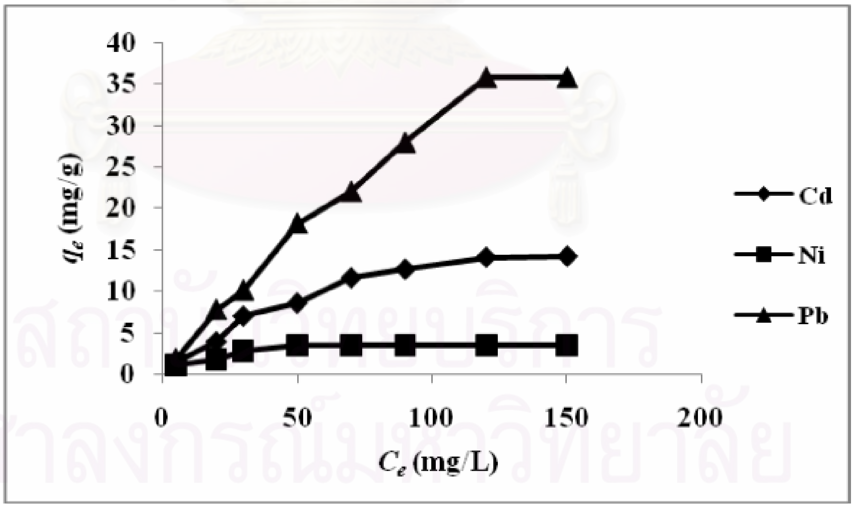
$$q_e = \mathrm{K} C_e^{1/n} \qquad 2\text{-}1$$

where K is the Freundlich adsorption coefficient, and $1/n$ is coefficient.

The adsorption isotherm experiments were carried out at initial pH of 5 for Cd(II) and Ni(II) ions, and 4 for Pb(II) ions by varying the initial concentration of these metal ions in the range of 5-150 mg L^{-1} at 30°C. The plots of initial concentration of metal ions solution and sorption capacity on sewage sludge were presented in Figure 4.9.



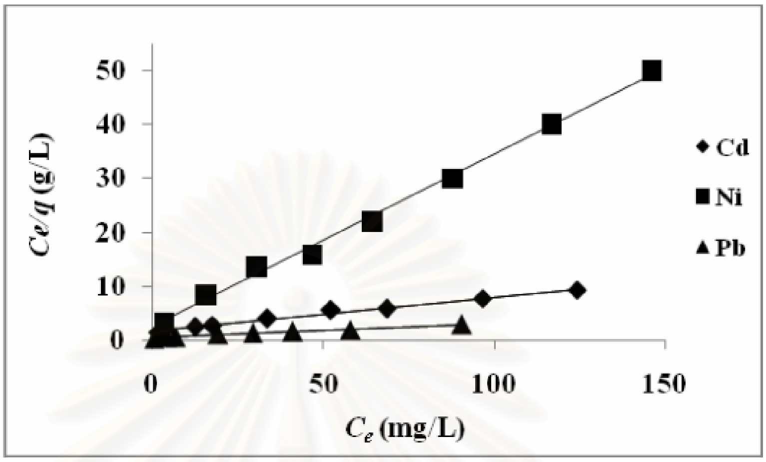
(a) Municipal sludge



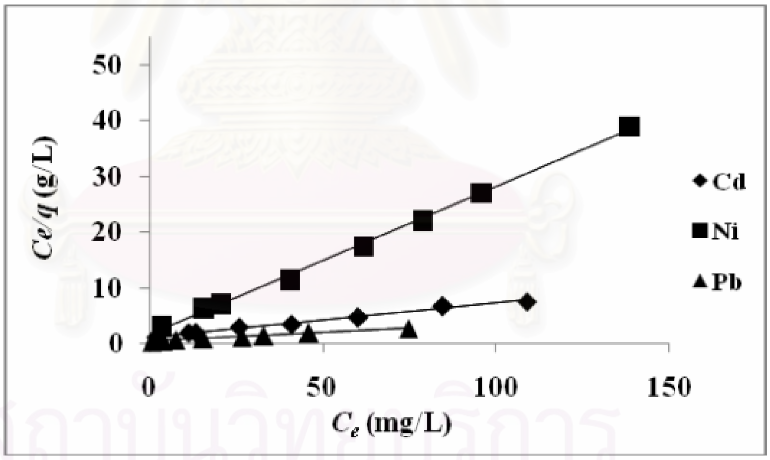
(b) Industrial sludge

Figure 4.9 The relation between concentration at equilibrium of metal ions and sorption capacity for the adsorption on municipal sludge (a) and industrial sludge (b).

The linear plots of Langmuir equation (C_e/q_e versus C_e) and Freundlich equation (log q versus log C_e), are shown Figure 4.10 and 4.11, respectively.

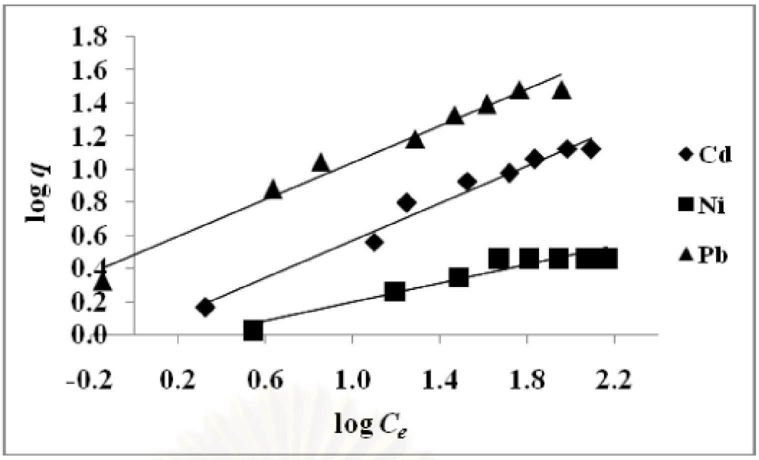


(a)Municipal sludge

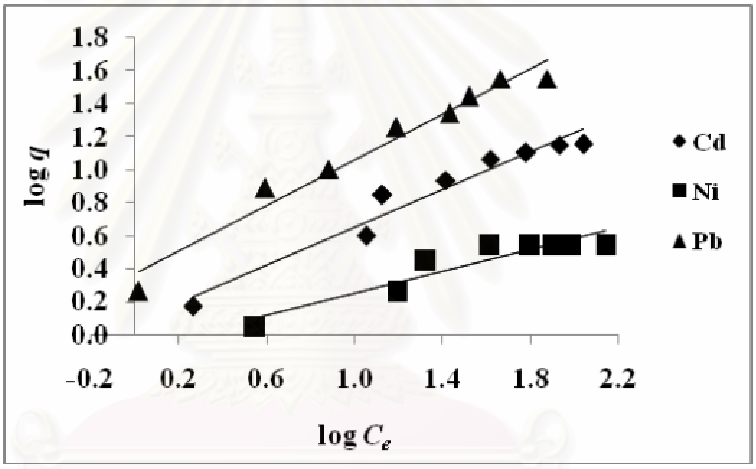


(b) Industrial sludge

Figure 4.10 Langmuir plot for the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) and industrial sludge (b).



(a)Municipal sludge



(b) Industrial sludge

Figure 4.11 Freundlich plot for the adsorption of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) and industrial sludge (b).

By fitting the experimental data, the Langmuir and Freundlich constants could be determined as listed in Table 4.4.

Table 4.4 Langmuir and Freundlich constants for adsorption of metal ions on municipal and industrial sludge

Sorbent	***Metal ions***	***Langmuir contants***					***Freundlich constants***		
		q_m (mg g^{-1})	***q_m (mmol g^{-1})***	***b (L mg^{-1})***	***r^2***	***R_L***	***K***	***n***	***r^2***
Municipal sludge	Cd	15.75	0.140	0.038	0.9908	0.149-0.840	1.02	1.77	0.9738
	Ni	3.12	0.053	0.131	0.9960	0.048-0.604	0.83	3.56	0.9149
	Pb	35.34	0.171	0.062	0.9900	0.097-0.763	3.08	1.81	0.9767
Industrial sludge	Cd	16.50	0.147	0.050	0.9924	0.118-0.800	1.19	1.75	0.9491
	Ni	3.76	0.064	0.161	0.9976	0.040-0.554	0.85	3.04	0.8676
	Pb	31.06	0.150	0.073	0.9911	0.084-0.733	2.35	1.44	0.9660

As shown in Table 4.4, the experimental data were better fit by Langmuir model than Freundlich model for all metal ions. All of the r^2 values from Langmuir fitting were higher than 0.99. The results lead to an assumption that the uptake of metal ions occurs as monolayer sorption without interaction between sorbed molecules. This result was confirmed by the results from kinetics study that fit to pseudo-second order model (Topic 4.2.2.2.) that was derived based on the same assumption.

The isotherm shape predicts whether an adsorption system is favorable or unfavorable. The essential features of the Langmuir isotherm can be expressed in term of a dimensionless constant separation factor or equilibrium parameter (R_L), defined as [75],

$$R_L = \frac{1}{1 + bC_0}$$

where b is the Langmuir constant and C_0 is the initial concentration of metal ion. The R_L value indicates the shape of the isotherm as follows:

Table 4.5 The R_L values associated to the types of adsorption

Value of R_L	***Types of adsorption***
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

The values of R_L were calculated from the data (Table 4.4) and compared to the values given in Table 4.5. The results indicate that the adsorption of Cd(II), Ni(II) and Pb(II) ions on both sewage sludge is favorable.

The maximum adsorption capacities were 15.75, 3.12 and 35.34 mg g^{-1} for adsorption of Cd(II), Ni(II), and Pb(II) ions onto municipal sludge, and 16.50, 3.76 and 31.06 mg g^{-1} for adsorption of Cd(II), Ni(II), and Pb(II) ions onto industrial sludge, respectively. The results show that the adsorption efficiencies of both sewage sludge were close to each other. This evidence is probably explained by the same composition and also surface properties of both sludge.

The b values can be used for predicting whether an adsorption process is favorable or unfavorable [76]. In this work, the results indicate the stronger binding affinity of Ni(II) onto both municial and industrial sewage sludge, compared to Pb(II) and Cd(II) ions. The binding affinity of metal ions onto the sludge followed the order Ni > Pb > Cd.

The maximum sorption capacities (q_m) indicated the following sorption order: Pb > Cd > Ni that was not relational with the order of b values. The contradiction between the b value order and q_m order were also observed by Hammaini et al. [62] who studied the sorption of Cu(II), Cd(II), Zn(II), Ni(II) and Pb(II) on activated sludge.

Furthermore, the sorption capacities of many low-cost materials were interesting for the comparison with sewage sludge, some of which were given in Table 4.6

Table 4.6 Adsorption capacities of some adsorbent for Cd(II), Ni(II) and Pb(II)

Type of adsorbent	*Adsorption capacity (mg g^{-1}) of metal ions*	*Reference*
Sewage sludge		
Municipal sludge	15.75 of Cd(II), 3.12 of Ni(II), 35.34 of Pb(II)	*From this research*
Industrial sludge	16.50 of Cd(II), 3.76 of Ni(II), 31.06 of Pb(II)	
Another adsorbents		
Anaerobic sludge	5.82 of Cd(II)	[77]
Bagasse	0.001 of Ni(II)	[78]
Cassava waste	18.05 of Cd(II)	[79]
Chitosan	16.36 of Pb(II)	[80]
Clay (Thai kaolin)	1.41 of Pb(II)	[81]
Cocoa shell	4.94 of Cd(II), 2.63 of Ni(II)	[82]
Fly ash	1.70 of Ni(II)	[83]
Fly ash type	0.99 of Ni(II)	[84]
Kaolinite	3.04 of Cd(II)	[77]
Mucor rouxii	16.62 of Pb(II)	[85]
Na-Montmorillonite	5.20 of Cd(II), 3.63 of Ni(II)	[86]
Peanut hull pellets	6.00 of Cd(II)	[87]
Pennicillium digitatum	5.5 of Pb(II)	[88]
Rice husk	2.0 of Cd(II)	[89]
Waste baker's yeast	17.49 of Pb(II)	[90]

These results show that the sewage sludge had fairly good efficiencies for removal of Cd(II), Ni(II) and Pb(II) ions in solutions, compared to many types of low-cost adsorbents. Moreover, the efficiencies of some of commercial adsorbents such as activated charcoal, silica gel and ion exchange resin were also compared in Topic 4.2.7.

4.2.5 Competitive adsorption

The competitive test was carried out to investigate adsorption efficiencies of the adsorbents in the presence of three metal ions in solution. The efficiencies of adsorbents on adsorption of each metal ion in mixed solution were compared to the efficiencies observed for solutions containing single metal ions. The results are shown in Table 4.7. The initial concentration of each metal ion in the mixed solutions was 0.30 mmol L^{-1} (pH 5). It can be seen that under the competitive condition between three metal ions, their adsorption capacities of each metal significantly decreased for both municipal and industrial sludge.

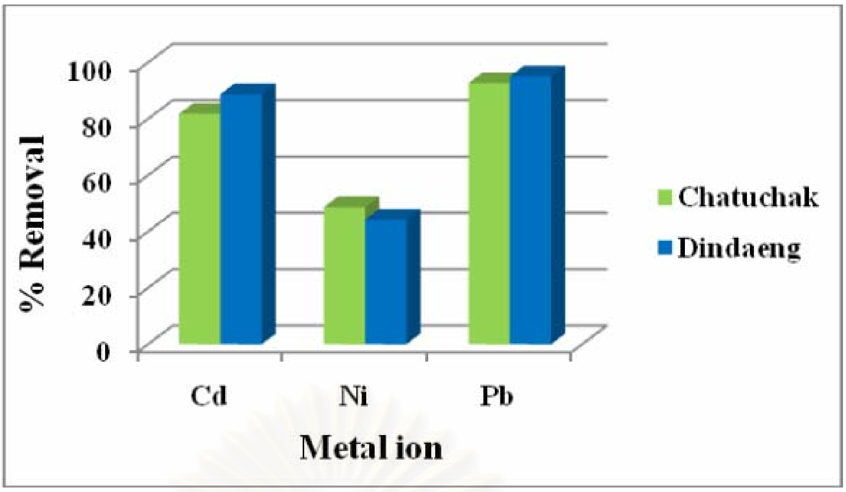
Table 4.7 Adsorption capacities (mmol g^{-1}) for the individual and competitive adsorption of Cd(II), Ni(II) and Pb(II) by sewage sludge

Sorbent	***Adsorption capacity (mmol g^{-1})***					
	Individual adsorption			***Competitive adsorption***		
	Cd	***Ni***	***Pb***	***Cd***	***Ni***	***Pb***
Municipal sludge	0.046	0.032	0.117	0.039	0.012	0.104
Industrial sludge	0.048	0.034	0.127	0.045	0.024	0.124

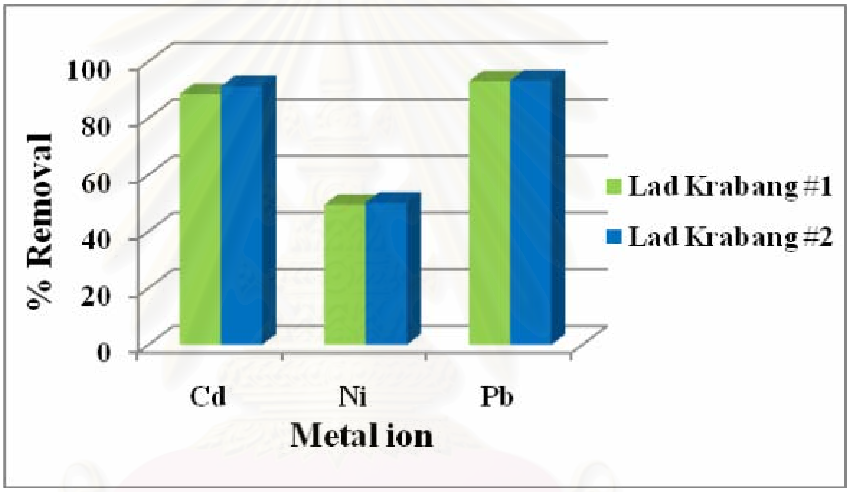
Although, under the competition, the reduction in sorption efficiencies was observed for all metal ions but these effects was different for each metal ions. The sorption capacity of Cd(II) decreased by nearly 15% and 6% due to competitive adsorption on municipal and industrial sludge, respectively. For Ni(II), a decrease by 63% and 29%, and for Pb(II), a decrease by 11% and 2% were observed on municipal and industrial sludge, respectively. Therefore, the competition affected of metal sorption in the order Ni > Cd > Pb respectively. Furthermore, when all three metals were present together, the adsorption of Pb(II) was greater than Cd(II) and Ni(II). It can be concluded that under the competitive condition, the sorption efficiency of heavy metals by both sewage sludge is favorable in the order Pb > Cd > Ni, respectively. This result is in agreement with the order of maximum adsorption capacities (q_m) determined previously by the Langmuir isotherm (Topic 4.2.3).

4.2.6 Comparison of adsorption capacities of sewage sludge from different sources

Sewage sludge from other sources were collected and evaluated for adsorption capacities. Municipal sludge obtained from Chatuchak Water Environment Control Plant was compared with Dindaeng Water Environment Control Plant. Industrial sludge, provided by the central wastewater treatment plants of Lad Krabang Industrial Estate was compared with sludge collected from the same plant but another cycle of wastewater treatment. The results are shown in Figure 4.12.



(a)Municipal sludge



(b) Industrial sludge

Figure 4.12 Comparison of adsorption capacities of Cd(II), Ni(II) and Pb(II) ions by municipal sludge (a) industrial sludge (b), with initial concentration of 20 mg L^{-1} for all metal ions.

According to these results, the removal efficiencies of the two municipal sludge were vicinal. The adsorption capacities of municipal sludge obtained from Chatuchak and Dindaeng were 7.90 and 8.57 mg g^{-1} for Cd(II), 4.68 and 4.62 mg g^{-1} for Ni(II) and, 8.75 and 8.97 mg g^{-1} for Pb(II), respectively.

Similar trends were observed for industrial sludge collected from two lot of water treatment cycle. The adsorption capacities of industrial sludge obtained from Lad Krabang lot one and lot two were 8.55 and 8.81 mg g^{-1} for Cd(II), 4.75 and 4.83 mg g^{-1} for Ni(II) and, 8.78 and 8.80 mg g^{-1} for Pb(II), respectively.

The results lead to an assumption that sewage sludge from different sources or another cycle of wastewater treatment may have similar metal removal efficiency, if they were generated from similar wastewater treatment process. Moreover, it may be assumed that these sludge would have similarity in compositions and properties.

4.2.7 Comparison of adsorption capacities among sewage sludge and commercial adsorbents

The two commercial adsorbents i.e. activated charcoal and ion exchange resin that are usually used for water purification were employed to compare the efficiency with municipal and industrial sludge. The efficiency in metal ions adsorption of these adsorbents were investigated and compared using suitable experimental condition. The pH of metal ions solutions was pH 7 for Cd(II) and Ni(II) and pH 5 for Pb(II). These pH value were suitable pH values for adsorption of Cd(II), Ni(II) and Pb(II) by both sludge as shown previously, and for activated charcoal (as reported in appendix C). On the other hand, the suitable pH value for adsorption of all metals was pH 4 for ion exchange resin (as reported in appendix C), was used in this study. Therefore, the adsorption efficiency would be decreased slightly from its maximum value when the resin was used at pH 7 as in the adsorption experiments in this study. The results were presented in Figure 4.13.

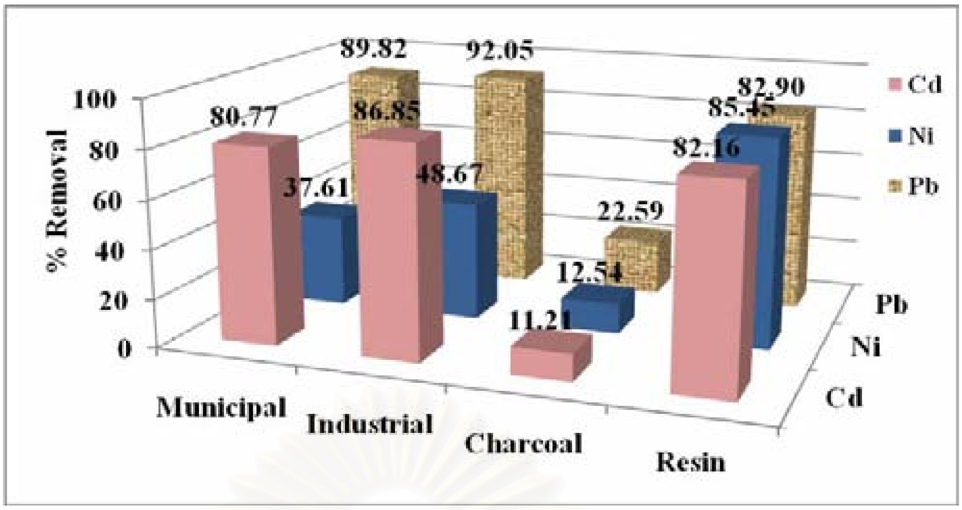


Figure 4.13 Comparison of adsorption capacities of Cd(II), Ni(II) and Pb(II) ions by 0.05 g of sewage sludge and commercial adsorbents with initial concentrations are 20 mg L^{-1} for all metal ions.

According to these results, the removal efficiency of sewage sludge was clearly higher than activated charcoal. This can be explained that absorbents derived from sewage sludge may contain the organic matter such as lignin, tannin and cellulose with functional group such as hydroxyl, carbonyl, carboxylic and amino groups [91] that are suitable for heavy metal ions adsorption [92]. However, the removal efficiencies of sewage sludge were close to those of ion exchange resin and less than that of resin significantly in case of Ni(II) ion. This can be due to the greater number of negative charge on surface of ion exchange resin.

Therefore, the adsorbents derived from sewage sludge are an inexpensive and promptly available material that can be used as interesting alternative adsorbents to replace these commercial adsorbents in wastewater treatment process.

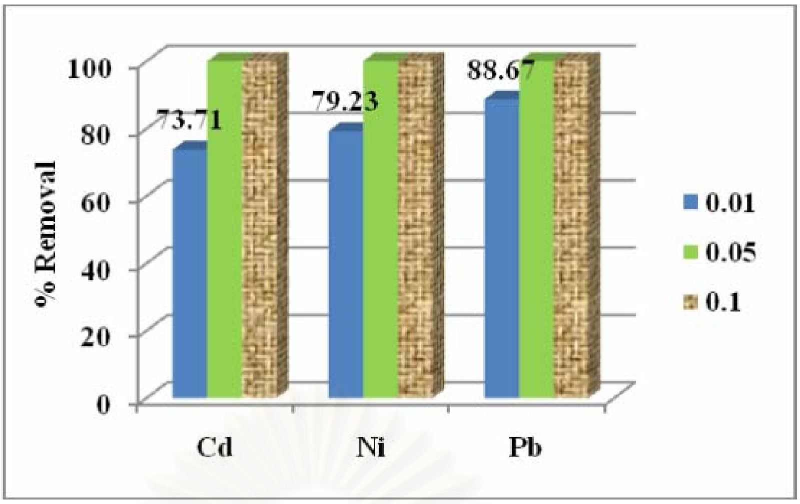
4.2.8 Utilization of sewage sludge to remove heavy metal ions from real wastewater

The real wastewater obtained from a laboratory was a mixed waste that contained 8.3 mg L^{-1} of Cd(II), 5.1 mg L^{-1} of Ni(II) and 27.4 mg L^{-1} of Pb(II) at pH 4.28. The results were summarized in Table 4.8.

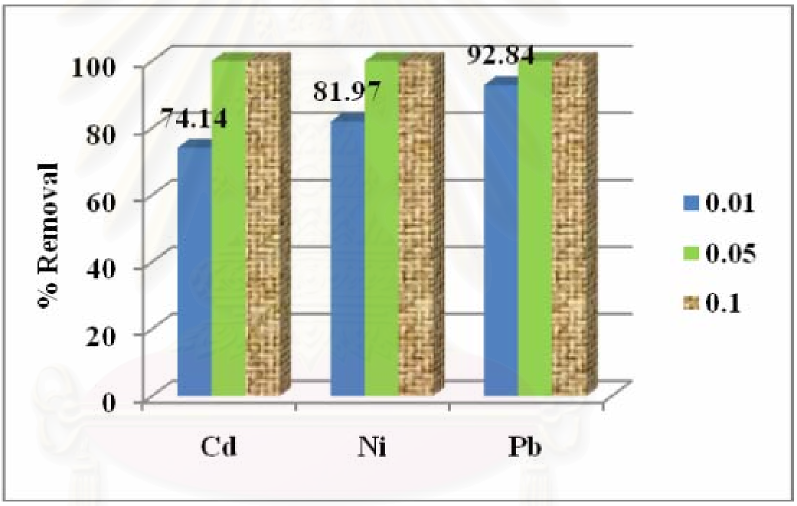
Table 4.8 The percentage of metal removal of Cd(II), Ni(II) and Pb(II) by 0.01g of sewage sludge at pH adjusted to 5

Metal ion	***Initial concentration (mg L^{-1})***	***% Removal***	
		municipal sludge	***industrial sludge***
Cd	8.3	73.71	74.14
Ni	5.1	79.23	81.97
Pb	27.4	88.67	92.84

In Thailand, the Notification of the Ministry of Science, Technology and Environment B.E 2539 (1996) defined that the metal concentration in industrial effluent must not exceed 0.03, 1.00 and 0.20 mg L^{-1} for Cd, Ni and Pb, respectively. Nevertheless, the results of this experiment showed that 0.01g of sewage sludge could not remove all metal ions in 25 mL of wastewater to less than the standard values of the notification. Therefore, higher doses were employed. The heavy metal removal efficiency increased with increasing adsorbent dosage. When the sewage sludge dosage was 0.05 g and higher, the removal efficiencies of all metal ions were increased up to 100%. The results are shown in Figure 4.14.



(a) Munipal sludge



(b) Industrial sludge

Figure 4.14 Percentage removals of three metal ions in real wastewater using 0.01, 0.05 and 0.10 g of municipal sludge (a) and industrial sludge (b).

These results reveal that sewage sludge could be successfully used as low-cost adsorbents to remove Cd(II), Ni(II) and Pb(II) ions from wastewater and suitable for the application in the wastewater treatment plants.

4.3 Sequential extraction

Sequential extraction procedures were applied to fractionate heavy metals in sewage sludge used as adsorbent according to the Tessier et al. (1979) method [65]. These procedures were useful to assess indirectly the mobility of heavy metals regarding the order of decreasing solubility of metals in different solid fraction: water soluble and exchangeable (EXC) > carbonate bound (CAR) > Fe and Mn oxide bound (Fe-Mn) > organic bound and/or sulfides (ORG) > residual (RES).

The total amounts of metals bound to these fractions in used adsorbents in this study were shown in Table 4.9. In addition, the amounts of metals bound to different fractions of used sewage sludge being expressed as percentages with respect to the total amount were shown in Fig 4.14.

Table 4.9 Total mean amount of Cd(II), Ni(II) and Pb(II) extracted by step 1-5 from used adsorbent derived from municipal and industrial sludge

Metal ion	***Metals content (mg g^{-1})***	
	Municipal sludge	***Industrial sludge***
Cd	4.21	5.77
Ni	2.14	2.62
Pb	22.33	25.0

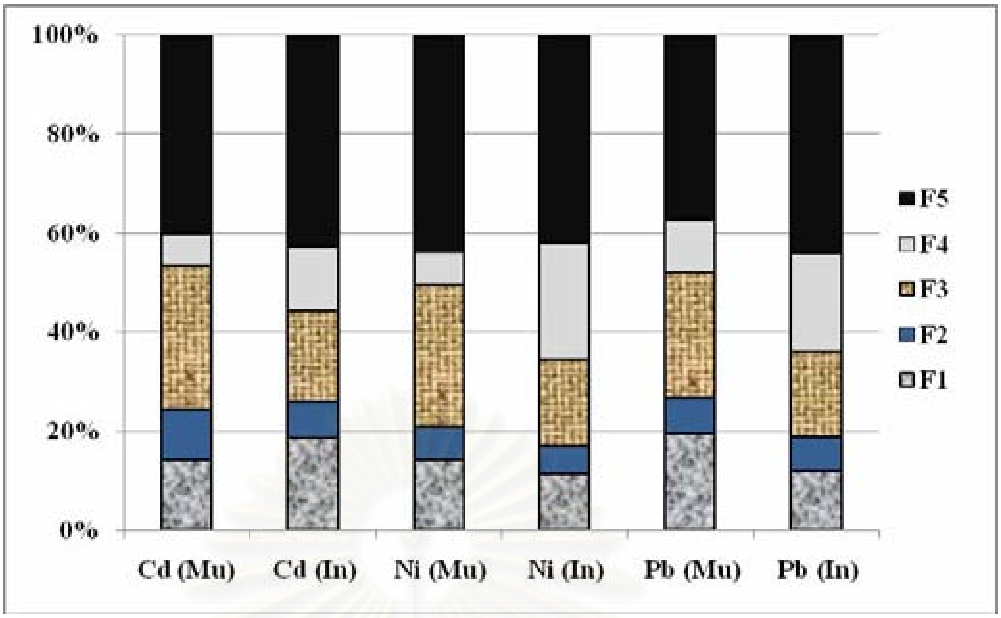


Figure 4.15 Percentage of exchangeable (F1), carbonate bound (F2), Fe-Mn oxide bound (F3), organic matter (F4), and residual fractions (F5) of Cd, Ni and Pb in used municipal sludge (Mu) and industrial sludge (In).

In the municipal sludge, percentage distribution of Cd followed the order: RES > Fe-Mn > EXC > CAR > ORG; Ni followed the order RES > Fe-Mn > EXC > CAR ≈ ORG; and Pb followed the order: RES > Fe-Mn > EXC > ORG > CAR. In the industrial sludge, percentage distribution of Cd followed the order: RES > Fe- Mn ≈ EXC > ORG > CAR; Ni and Pb followed the order: RES > ORG > Fe-Mn > EXC > CAR. It can be seen that for each sludge, the metal ions distributed in the different fractions of solid in the same manner. However, when the sludge were different, the results of metal fractionation were different. This is probably due to the difference in mineral and organic composition of these sludge.

The results indicated that the largest amount of metals in both sludge were found in residual fraction (>37% of the total), and high percentages were also found in Fe-Mn oxide fraction (17-29% of the total). The percentage up to 20% of metal were found in water and soluble exchangeable fraction of both sludge. These results indicate that the metals would bind to sludge via both ion exchange mechanism and physisorption.

Furthermore, it could be observed that the percentages of metals bound in organic matter fraction of industrial sludge was higher than in the same fraction of municipal sludge. This result lead to an assumption that industrial sludge consisted of carbon from organic matter in a higher content than municipal sludge. This confirms the EA results reported previously in Topic 4.1.3.

4.4 Leaching test

The standard leachate extraction procedure specified in the Notification of Ministry B.E. 2548 (2005) of Thailand was applied for each sample of used adsorbents. Each metal ion in mixed solution was adsorbed on municipal and industrial sludge at suitable condition. The initial concentration of each metal ion in the mixed solutions was 0.30 mmol L^{-1} (pH 5), and the metal ions content in the used adsorbents are listed in Table 4.10. In addition, the metal ions content in the leachate was summarized in Table 4.11. The experiments were performed in triplicate.

Table 4.10 The amount of metal ions in the used adsorbents

Metal ion	***Metals content (mg g^{-1})***	
	Municipal sludge	***Industrial sludge***
Cd	4.98	5.92
Ni	2.12	2.95
Pb	22.02	26.19

Table 4.11 The amount of metals found in the leachate

Metal ion	***Total threshold Limit Concentration (mg kg^{-1})^a***	***Concentration of metal ion (mg kg^{-1})***	
		Used municipal sludge	***Used industrial sludge***
Cd	100	4,490	5,893
		4,490	5,426
		4,490	5,426
Ni	2,000	2,048	2,524
		2,048	2,524
		2,048	3,000
Pb	1,000	21,000	25,000
		21,000	25,000
		21,000	25,000

[a] Total threshold Limit Concentration of toxicity specified in Notification of Ministry of Industry B.E. 2548 (2005). 26190

The results show that the extract of both sludge after used as adsorbents contained Cd(II), Ni(II) and Pb(II) ions at the concentration greater than the total threshold limit concentration (TTLC) specified in Notification of Ministry of Industry B.E. 2548 (2005), as shown in Table 2.1. Therefore, the adsorbents derived from municipal and industrial sludge after the use in removal of heavy metal ions with the maximum capacity were hazardous wastes that have to be redetoxified in order to meet properties as specified.

CHAPTER V

CONCLUSION

The studies of adsorption were carried out by utilization of two adsorbents i.e. municipal sludge and industrial sludge. All results are demonstrated and concluded in the following topics.

5.1 Characterization of adsorbents

The results from scanning electron microscope show the similarity between municipal and industrial sludge surfaces that were in amorphous form. Moreover, the pore diameters of municipal and industrial sludge were in the vicinity, and the surface area and total pore volume of municipal sludge were a little greater than those of industrial sludge. The elemental analysis results show that the industrial sludge consisted of carbon in a higher content than municipal sludge and that may be due to the higher loading of organic substances in wastewater discharged from food industry.

5.2 Adsorption studies

The results of adsorption studies of Cd(II), Ni(II) and Pb(II) ions show that the removal efficiency increased with an increase of contact time before equilibrium was attained. The equilibrium time could be reached within 60 minutes for both municipal and industrial sludge.

The removal efficiency of all metal ions improved with increasing dose between 0.01 to 0.10 g. The adsorption kinetics followed the pseudo-second order kinetics for both sludge and it showed that the rate of adsorption increased with increasing of adsorbent dosage at constant temperature.

The removal of all metal ions increased obviously with an increasing of pH of solution and the suitable pH values for metal ions extraction were pH 7 for Cd (II) and Ni (II), and pH 5 for Pb(II), respectively. Moreover, it was found that both sludge could not adsorb all metal ions in solution having pH values less than 2.

From the adsorption isotherm studies, the results showed that the adsorption of Cd(II), Ni(II) and Pb(II) ions on the sewage sludge fit the Langmuir model better than Freundlich model. The results let to assume that the uptake of metal ions occurs as monolayer sorption without interaction between sorbed molecules. From the maximum sorption capacities (q_m), it was found that both sewage sludge could adsorb metals in the order Pb > Cd > Ni, respectively. The adsorption capacities of the sludge are fairly good compared to other low cost adsorbents.

The competitive test showed that when all three metal ions were present together, the sorption efficiency of heavy metals by both sewage sludge was in order Pb > Cd > Ni which is similar to the trend found by Langmuir isotherm.

When compared the adsorption capacities of sewage sludge obtained from different sources, it was found that the removal efficiencies of two municipal sludge from different souces were resemblance. Similar trends were observed for industrial sludge collected from two lots of water treatment cycle. It may be assumed that sewage sludge from different sources or another cycle of wastewater treatment could have simililarity in metal removal efficiency, if they are generated from the same wastewater treatment process and have similarity in compositions and properties.

From the results of comparison of adsorption capacities among sewage sludge and commercial adsorbents, the removal efficiency of sewage sludge was clearly higher than that of activated charcoal and close to those of ion exchange resin. The results from utilization of sewage sludge to remove heavy metal ions from real wastewater show that the municipal and industrial sewage sludge could be used to remove metal ions from wastewater containing mixed metal ions. The removal efficiencies increased when increased the adsorbent dose and the adsorption efficiency was in the order Pb>Cd>Ni, respectively.

The adsorption studies indicate that the municipal sludge and industrial sewage sludge had similar adsorption properties and very close adsorption efficiency for metal ions in water.

5.3 Sequential extraction

The results of sequential extraction indicated that the distribution of metals on sewage sludge after used as adsorbent was most in residual fraction with percentages ranging 39-51% for all metals.

5.4 Leaching test

The results of leaching test of used adsorbents derived from sewage sludge indicate that the total amount of metal ions in the leachate were greater than the total threshold limit concentration (TTLC) in Notification of Ministry of Industry B.E. 2548 (2005). Therefore, the adsorbents derived from municipal and industrial sludge after used in removal of heavy metal ions with the maximum capacity were hazardous wastes that have to be redetoxified in order to meet properties as specified.

All of the results indicate that the adsorbents derived from municipal and industrial sludge have a good potential to be used as adsorbents for removal of Cd(II), Ni(II) and Pb(II) ions in water. However, the used adsorbents had to dispose correctly because it were hazardous wastes that could release some heavy metals to the environment.

SUGGESTION FOR FUTURE WORK

This research aims to investigate the use of sludge from municipal and industrial wastewater treatment plants as low-cost adsorbents for removal of Cd(II), Ni(II) and Pb(II) from water, thus other metal ions were not investigated yet. It is also interesting to study the adsorption of other toxic metal ions by these adsorbents. Moreover, the adsorbents used in this research were obtained from activated sludge biological treatment processes, the next research should further focus on the use of sludge from other wastewater treatment process such as anaerobic biological treatment processes.

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APPENDICES

APPENDIX A

Effect of adsorbent dosage and adsorption kinetics

Table A-1 Adsorption capacities (mg g^{-1}) for kinetics plots of Cd(II), Ni(II) and Pb(II) ions by municipal sludge

Metal		*Cd*	*Ni*	*Pb*
weight (g)	*time*	*Sorption Capacity [a] (mg g^{-1})*	*Sorption Capacity [a] (mg g^{-1})*	*Sorption Capacity [a] (mg g^{-1})*
0.01	5 min	4.21 ± 0.39	2.57 ± 0.63	7.49 ± 0.56
	15 min	6.18 ± 0.26	3.30 ± 0.00	10.05 ± 0.00
	30 min	6.35 ± 0.15	3.66 ± 0.63	10.69 ± 0.56
	1h	6.35 ± 0.15	4.03 ± 0.63	10.37 ± 0.28
	3h	6.18 ± 0.26	4.03 ± 0.63	10.37 ± 0.28
	6h	6.00 ± 0.15	4.03 ± 0.63	10.53 ± 0.00
	24h	5.92 ± 0.26	4.03 ± 0.63	10.69 ± 0.28
0.05	5 min	2.16 ± 0.14	1.32 ± 0.00	2.81 ± 0.15
	15 min	3.90 ± 0.00	1.98 ± 0.00	7.17 ± 0.20
	30 min	3.90 ± 0.05	2.19 ± 0.00	7.62 ± 0.15
	1h	3.87 ± 0.03	2.49 ± 0.13	7.68 ± 0.00
	3h	3.72 ± 0.08	2.34 ± 0.13	7.78 ± 0.10
	6h	3.63 ± 0.08	2.34 ± 0.13	7.68 ± 0.10
	24h	3.51 ± 0.06	2.49 ± 0.13	7.75 ± 0.11
0.1	5 min	1.45 ± 0.01	1.17 ± 0.13	2.99 ± 0.03
	15 min	2.07 ± 0.01	1.54 ± 0.00	4.89 ± 0.03
	30 min	2.75 ± 0.09	1.72 ± 0.06	4.84 ± 0.03
	1h	2.80 ± 0.00	1.68 ± 0.06	4.94 ± 0.03
	3h	2.77 ± 0.00	1.68 ± 0.06	4.97 ± 0.03
	6h	2.76 ± 0.03	1.72 ± 0.06	4.95 ± 0.00
	24h	2.69 ± 0.03	1.68 ± 0.06	4.97 ± 0.03

[a] average of adsorption capacity ± SD (N=3)

Table A-2 Adsorption capacities (mg g^{-1}) for kinetics plots of Cd(II), Ni(II) and Pb(II) ions by industrial sludge

Metal		***Cd***	***Ni***	***Pb***
weight (g)	***time***	***Sorption Capacity*** [a] ***(mg g^{-1})***	***Sorption Capacity*** [a] ***(mg g^{-1})***	***Sorption Capacity*** [a] ***(mg g^{-1})***
0.01	5 min	3.26 ± 0.65	0.39 ± 0.62	7.79 ± 0.22
	15 min	5.77 ± 0.19	1.82 ± 0.62	12.28 ± 0.00
	30 min	6.32 ± 0.19	2.54 ± 0.62	12.53 ± 0.22
	1h	6.76 ± 0.68	2.90 ± 0.62	12.53 ± 0.22
	3h	6.76 ± 0.38	2.90 ± 0.62	12.53 ± 0.22
	6h	6.76 ± 0.19	2.90 ± 0.62	12.53 ± 0.22
	24h	6.32 ± 0.19	2.90 ± 0.62	12.28 ± 0.38
0.05	5 min	1.61 ± 0.04	0.79 ± 0.12	3.25 ± 0.09
	15 min	3.99 ± 0.00	1.51 ± 0.00	7.35 ± 0.04
	30 min	4.21 ± 0.04	1.72 ± 0.00	7.81 ± 0.04
	1h	4.21 ± 0.08	1.72 ± 0.00	7.89 ± 0.04
	3h	4.23 ± 0.04	1.72 ± 0.21	7.87 ± 0.04
	6h	4.21 ± 0.04	1.65 ± 0.12	7.87 ± 0.04
	24h	3.84 ± 0.04	1.72 ± 0.00	7.84 ± 0.00
0.1	5 min	1.56 ± 0.04	0.68 ± 0.16	2.88 ± 0.08
	15 min	2.81 ± 0.07	1.47 ± 0.06	4.61 ± 0.00
	30 min	3.02 ± 0.02	1.40 ± 0.00	4.79 ± 0.02
	1h	3.16 ± 0.04	1.47 ± 0.06	4.87 ± 0.02
	3h	3.15 ± 0.02	1.47 ± 0.06	4.87 ± 0.02
	6h	3.16 ± 0.04	1.43 ± 0.06	4.86 ± 0.02
	24h	3.03 ± 0.02	1.47 ± 0.06	4.84 ± 0.00

[a] average of adsorption capacity ± SD (N=3)

APPENDIX B

Adsorption isotherms

Table B-1 Adsorption capacities (mg g^{-1}) for adsorption isotherm of Cd(II), Ni(II) and Pb(II) ions by municipal and industrial sludge

Metal	*Initial concentration* C_i *(mg L*$^{-1}$*)*	*Municipal sludge*		*Industrial sludge*	
		Equilibrium concentration C_e *(mg L*$^{-1}$*)*	*Adsorption capacity* q_e *(mg g*$^{-1}$*)*	*Equilibrium concentration* C_e *(mg L*$^{-1}$*)*	*Adsorption capacity* q_e *(mg g*$^{-1}$*)*
Cd	5	2.1	1.48 ± 0.00	1.8	1.48 ± 0.02
	20	12.5	3.65 ± 0.23	11.2	3.98 ± 0.00
	30	17.8	6.26 ± 0.00	13.4	7.08 ± 0.00
	50	33.8	8.53 ± 0.00	25.9	8.65 ± 0.00
	70	52.3	9.46 ± 0.33	41.1	11.67 ± 0.23
	90	68.6	11.56 ± 0.66	60.3	12.70 ± 0.45
	120	96.6	13.45 ± 0.33	84.9	14.15 ± 0.39
	150	124.3	13.26 ± 0.33	109.0	14.27 ± 0.23
Ni	5	3.5	1.07 ± 0.17	3.5	1.13 ± 0.12
	20	15.6	1.84 ± 0.17	15.5	1.85 ± 0.12
	30	30.6	2.24 ± 0.18	20.7	2.85 ± 0.23
	50	46.8	2.93 ± 0.00	40.6	3.54 ± 0.23
	70	64.3	2.92 ± 0.00	61.8	3.54 ± 0.23
	90	87.7	2.92 ± 0.00	78.9	3.55 ± 0.23
	120	117.0	2.92 ± 0.00	95.9	3.54 ± 0.23
	150	146.2	2.92 ± 0.00	138.4	3.54 ± 0.23
Pb	5	0.7	2.14 ± 0.00	0.8	1.86 ± 0.00
	20	4.3	7.68 ± 0.24	3.9	7.82 ± 0.05
	30	7.1	11.23 ± 0.00	7.6	10.17 ± 0.00
	50	19.4	15.31 ± 0.00	15.5	18.23 ± 0.49
	70	29.6	21.42 ± 0.00	26.8	22.07 ± 0.49
	90	41.2	24.82 ± 0.59	33.1	27.97 ± 0.00
	120	58.2	30.62 ± 0.00	46.0	35.88 ± 0.49
	150	90.8	30.61 ± 0.00	74.9	35.87 ± 0.98

APPENDIX C

Adsorption efficiency of commercial adsorbents

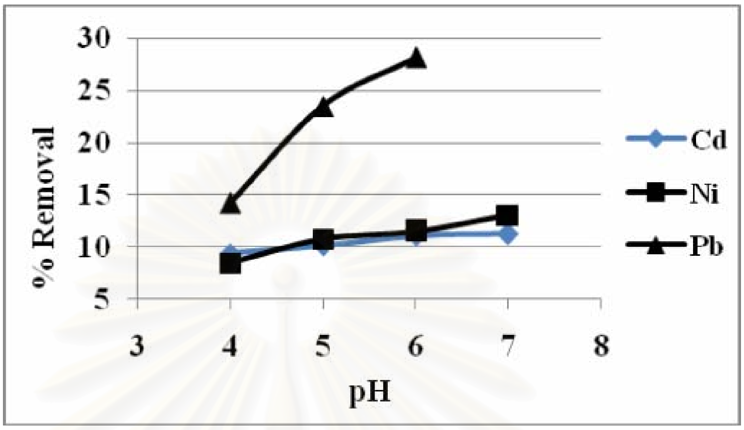

Figure C-1 Effect of pH on the adsorption of Cd(II), Ni(II) and Pb(II) ions by activated charcoal (commercial) with initial concentration of 20 mg L^{-1} for all metal ions.

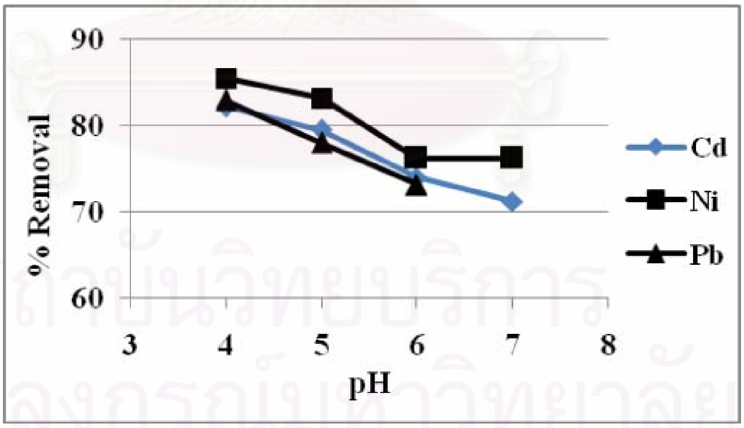

Figure C-2 Effect of pH on the adsorption of Cd(II), Ni(II) and Pb(II) ions by ion exchange resin (commercial) with initial concentration of 20 mg L^{-1} for all metal ions.

APPENDIX D

Sequential extraction

Table D-1 Average values of metal in different fractions of used adsorbents derived from municipal and industrial sludge (% of total content): water soluble and exchangeable (F1), carbonate bound (F2), Fe and Mn oxide bound (F3), organic bound and/or sulfides (F4), and residual (F5)

Metals	***adsorbents***	***Fractions (%)***				
		F1	***F2***	***F3***	***F4***	***F5***
Cd	Municipal	14.07	10.37	28.89	6.67	40.00
	Industrial	18.38	7.57	18.38	12.97	42.71
Ni	Municipal	14.07	6.66	28.87	6.66	43.68
	Industrial	11.52	5.45	17.58	23.64	41.82
Pb	Municipal	19.41	7.46	25.38	10.45	37.32
	Industrial	12.00	6.67	17.33	20.00	44.00

VITA

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