การดูดซับไอออนโลหะโดยใช้เรซินแลกเปลี่ยนแคตไอออนที่ผ่านการเผาและดัดแปรผิว

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METAL ION ADSORPTION BY CARBONIZED AND SURFACE-MODIFIED CATION EXCHANGE RESIN

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วัชราภรณ์ คำนา : การดูดซับไอออนโลหะโดยใช้เรซินแลกเปลี่ยนแคตไอออนที่ผ่านการเผาและดัดแปรผิว. (METAL ION ADSORPTION BY CARBONIZED AND SURFACE-MODIFIED CATION EXCHANGE RESIN) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ. ดร. อภิชาติ อิ่มยิ้ม, 66 หน้า.

นำเรซินแลกเปลี่ยนแคตไอออนชนิดซัลโฟเนตโพลิสไตรีน-ไดไวนิลเบนซีนที่ไม่ใช้แล้วมาเผาที่อุณหภูมิต่าง ๆ (300-500 องศาเซลเซียส)จากนั้นพิสูจน์เอกลักษณ์ของเรซินแลกเปลี่ยนแคทไอออนที่ผ่านการเผาด้วยเทคนิคการวิเคราะห์เชิงความร้อน และอินฟาเรดสเปกโทรสโกปี นำเรซินที่ผ่านการเผาที่ 300 องศาเซลเซียส หรือ CCR300 ไปใช้สกัดไอออนคอปเปอร์ แคดเมียม นิกเกิล สังกะสีและตะกั่วในสารละลายน้ำ และทำการดัดแปรผิวเรซินที่เผาที่ 500 องศาเซลเซียสด้วยเซอทิลไตรเมทิลแอมโมเนียมโบรไมด์ (CTAB-CCR500) นำวัสดุที่ได้ไปใช้สกัดโครเมตไอออน ตรวจวัดความเข้มข้นของไอออนโลหะหนักด้วยวิธีเฟลมอะตอมมิกแอบซอร์พชันสเปกโทรเมตรี ในระบบแบทช์ เวลาที่เหมาะสมในการสกัดสำหรับแคตไอออนและโครเมตไอออนอยู่ที่ 30 และ 90 นาที ตามลำดับ ค่าพีเอชที่เหมาะสมสำหรับแคตไอออนและโครเมตไอออนคือ 2 และ 3 ตามลำดับ ค่าความจุการดูดซับสูงสุดของ CCR300 สำหรับไอออนคอปเปอร์ แคดเมียม นิกเกิล สังกะสีและตะกั่วเท่ากับ 34.7, 28.9, 31.9, 39.4 และ 89.6 มิลลิกรัมต่อกรัม ตามลำดับ ในขณะที่ค่าความจุการดูดซับสูงสุดของ CTAB-CCR500 สำหรับโครเมตไอออนมีค่า 4.3 มิลลิกรัมต่อกรัม ไอโซเทอร์มของการดูดซับเป็นแบบแลงเมียร์และจลนศาสตร์การดูดซับเป็นไปตามจลนศาสตร์อันดับสองเทียม ส่วนในระบบคอลัมน์พบว่าเปอร์เซ็นต์การสกัดของไอออนโลหะหนักลดลงเมื่ออัตราการไหลของสารละลายเพิ่มขึ้น เปอร์เซ็นต์การสกัดสูงสุดใกล้เคียง 80% สำหรับแคตไอออนและ 50% สำหรับโครเมตไอออน ได้นำวิธีการที่ได้ไปใช้ในการกำจัดไอออนนิกเกิลในน้ำเสียจากอุตสาหกรรมผลิตนิกเกิลอัลลอยด์ พบว่าในระบบแบทช์สามารถกำจัดไอออนนิกเกิลได้มากกว่าในระบบคอลัมน์ โดยเปอร์เซ็นต์การสกัดในระบบแบทช์ใกล้เคียง 99% ขณะที่ระบบคอลัมน์มีเปอร์เซ็นต์การสกัดเท่ากับ 70%

ภาควิชา เคมี ลายมือชื่อนิสิต วัชราภรณ์ คำนา

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WATCHARAPORN KHAMNA: METAL ION ADSORPTION BY CARBONIZED AND SURFACE-MODIFIED CATION EXCHANGE RESIN. ADVISOR: ASST. PROF. APICHAT IMYIM, Ph.D., 66 pp.

Sulfonated polystyrene-divinylbenzene cation exchange resin waste was carbonized at various temperatures (300-500°C) and the products were characterized by TGA and FT-IR. The cation exchange resin carbonized at 300°C or CCR300 was used to extract cations such as Cu(II), Cd(II), Ni(II), Zn(II) and Pb(II) in aqueous solution. The cation exchange resin carbonized at 500°C was surface-modified by cetyl trimethylammonium bromide, namely CTAB-CCR500 and used to extract chromate ions. The concentrations of heavy metal ions were measured by Flame Atomic Absorption Spectrometry (FAAS). For batch extraction, the optimal contact time for the cations and chromate ions were 30 and 90 min, respectively. The optimum pH for the adsorption of cations and chromate were 2 and 3, respectively. The maximum sorption capacities of CCR300 for Cu(II), Cd(II), Ni(II), Zn(II) and Pb(II) were found to be 34.7, 28.9, 31.9, 39.4 and 89.6 mg g^{-1}, respectively, while the maximum capacity of CTAB-CCR500 for chromate was 4.3 mg g^{-1}. The adsorption isotherm and adsorption kinetics for metal ions followed Langmuir isotherm and pseudo-second order kinetics model, respectively. In case of column extraction, the extraction percentage of heavy metal ions decreased with increasing the solution flow rate. The highest percentage of extraction was nearly 80% for cations and 50% for chromate. The proposed method could be applied to remove Ni(II) present in wastewater from a nickel alloy industry. It was found the removal efficiency by batch method (~99% extraction) was greater than that obtained by column method (~70% extraction).

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LIST OF ABBREVIATIONS

FAAS = Flame atomic absorption spectrometer

ICP-OES = Inductively coupled plasma optical emission spectrometer

FT-IR = Fourier transform infrared spectrometer

TGA = Thermal gravimetric analysis

ATR = Attenuated Total Reflectance

DI = Deionized water

RSD = Relative standard deviation

mM = Millimolar

M = Molar

g = Gram

mg = Milligram

μm = Micrometer

$\mathrm{mg\ L^{-1}}$ = Miligram per liter

$\mathrm{mol\ L^{-1}}$ = Mole per liter

$\mathrm{mmol\ L^{-1}}$ = Millimole per liter

$\mathrm{mg\ g^{-1}}$ = Milligram per gram

$\mathrm{mol\ g^{-1}}$ = Mole per gram

$\mathrm{mg\ g^{-1}}$ = Milligram per gram

$\mathrm{L\ mg^{-1}}$ = Liter per milligram

$\mathrm{L\ mol^{-1}}$ = Liter per mole

$\mathrm{L\ min^{-1}}$ = Liter per minute

$\mathrm{g\ (mg\ min)^{-1}}$ = Gram per milligram minute

$\mathrm{mg\ (g\ min)^{-1}}$ = Milligram per gram minute

$\mathrm{°C\ min^{-1}}$ = Degree Celsius per minute

$\mathrm{mL\ min^{-1}}$ = Milliliter per minute

$\mathrm{m^2\ g^{-1}}$ = square meter per gram

$\mathrm{cm^{-1}}$ = Wave number

°C = Degree Celsius

mL = Milliliter

mmol = Millimole

min = Minute

mA = Centimeter

pzc = Point of zero charge

KJ mol^{-1} = Kilojoules per mole

%w/v = Percentage weight per volume

%v/v = Percentage volume per volume

C = Concentration in the mobile phase

C_F = Feed concentration in the mobile phase

CHAPTER I

INTRODUCTION

1.1 Statement of the problem

Nowadays heavy metals are the most important pollutants in sources and treated water and are becoming a health problem. Many techniques have been proposed for the extraction of metals in various environmental samples, including solvent extraction, co-precipitation, membrane process, sorption and ion exchange [1]. Among these methods, ion exchange and adsorption are highly popular and have been widely practiced in industrial wastewater treatment process. In recent years, various adsorbents have been investigated, e.g. silica gel, zeolites, resin and activated carbon.

In ion exchange, ions of positive charge and negative charge ions from an aqueous solution replace dissimilar ions of the same charge initially in the solid. The ion exchanger contains permanently bound functional groups of opposite charge-type [1].

Activated carbon is one of the materials used to treat wastewater because of its excellent adsorption properties, characterized by a high specific surface area. It is also used to remove metallic ions from solution [2]. Thermal treatment or carbonization are generally employed in the fabrication of activated carbon.

Thus in this research, we attempted to carbonize sulfonated polystyrene divinylbenzene cation exchange resin waste in order to obtain a material which has high surface area and adsorption properties similar to activated carbon. Furthermore, it was economically and environment-friendly reused for removing heavy metal cations. Moreover the modification of carbonized cation exchange resin with quarternary ammonium salt for removing anion in aqueous solution was investigated.

1.2 Objectives and scope of this research

The objective of the research is to study adsorption of metal ion (Zn(II), Pb(II), Ni(II), Cu(II), Cd(II) and chromate ions) using carbonized and surface-modified cation exchange resin.

The scope of this reseach includes:

1) Optimization of carbonization temperature and characterization of carbonized sulfonated polystyrene divinylbenzene cation exchange resin waste by FT-IR spectroscopy and TGA analysis.
2) Study of adsorption of heavy metal cations such as Zn(II), Pb(II), Ni(II), Cu(II), Cd(II) by using carbonized sulfonated polystyrene divinylbenzene cation exchange resin waste in batch and column method.
3) Modification of carbonized sulfonated polystyrene divinylbenzene cation exchange resin waste with quarternary ammonium salt and using modified-carbonized sulfonated polystyrene divinylbenzene cation exchange resin waste for adsorption of chromate anion.
4) Application to real waterwaste sample using the optimum conditions.

In batch method, the effect of pH of metal ions solution, contact time and intial concentration of metal ions solution were investigated. And the flow rate of metal ions solution was studied in column method. The concentration of metal ions solution was measured by flame atomic absorption spectrometer (FAAS).

1.3 The benefits of this research

To obtain a method for improving properties of cation exchange resin waste which was used for the removal of cation and anion in wastewater.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Ion exchange resins

Ion exchange resins have been developed for treatment of solution over the past few years. The reasons why ion exchange resin was used to treat wastewater are the followings:

1. In low concentration, resins can remove ions because they have a very high capacity for adsorption.
2. Resins can be readily regenerated.
3. Resins are stable over a wide range of temperature.
4. The process is suitable for both large and small installations.
5. The process is reversible.

Ion exchange resins are based on the copolymerization of styrene cross-linked with divinylbenzene that carry ion exchangeable functional groups. Ion exchange resins are classified as cation exchangers, which have positively charged mobile ions available for exchange, and anion exchangers, whose exchange ions are negatively charged as shown in Figure 2.1. Both anion and cation resins are produced from the same basic organic polymer. They differ in the ionizable functional group attached to the hydrocarbon network. It is this functional group that determines the chemical behavior of the resin. In an ion exchange process, cations or anions in a liquid solution (usually aqueous) replace dissimilar and displaceable ions of the same charge contained in the exchange resin.

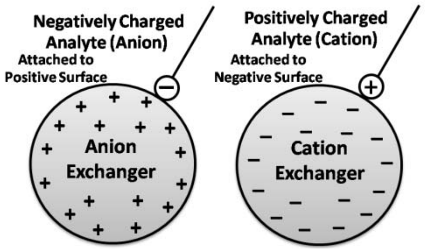


Figure 2.1. Ion exchange particles [3].

2.1.1 Types of ion exchange resins

Ion exchange resins are typically classified into 5 types as shown in Table 2.1.

Table 2.1 Types of ion exchange resins

Type	Functional group	Properties	Example of trade name
Strong acid cation exchange resin	$R\text{-}SO_3H$ (Sulfonic acid)	- In sodium form, they remove hardness (essentially calcium and magnesium) from water and other solutions - In hydrogen form, they remove all cations - Independent of solution pH	Amberlite^{TM} 1000 Na Dowex^{TM} Marathon C Lewatit^{TM} Monoplus S100
Weak acid cation exchange resin	R-COOH (Carboxylic acid)	- In hydrogen form, they remove preferentially divalent ions (e.g. calcium and magnesium) from solutions containing alkalinity - Limited capacity below a pH of 6.0	Amberlite^{TM} IRC86 Dowex^{TM} MAC3 Lewatit^{TM} CNP80
Strong base anion exchange resin	$R\text{-}N(CH_3)_3OH$ (Quaternary ammonium)	- In hydroxyl form, they remove all anions In chloride form, they remove nitrate, sulphate and several other ions - Independent of solution pH	Amberlite^{TM} IRA96 Dowex^{TM} Marathon MWA Lewatit^{TM} Monoplus MP64

Table 2.1 Types of ion exchange resins (continuous)

Type	Functional group	Properties	Example of trade name
Weak base anion exchange resin	$R\text{-}N(CH_3)_2$ (Amines)	- After cation exchange, they remove chloride, sulphate, nitrate, and other anions of strong acids, but they do not remove weak acids (SiO_2 and CO_2) - Limited capacity above a pH of 7.0	Amberlite^{TM} IRA96 Dowex^{TM} Marathon MWA Lewatit^{TM} Monoplus MP64
Selective and chelating resin	Many different types	- They remove metals, boric acid, perchlorate or other ions selectively	Amberlite PWA5 Ambersep GT74 Amberlite IRC747 Amberlite IRC748 Lewatit TP208 Amberlite IRA743 Amberlite PWA10 Dowex M4195 Lewatit TP214
	Functional group	**Target removable ions**	
	Triethylammonium	NO_3^-	
	Thiol	Hg^{2+}, Cd^{2+} etc.	
	Aminophosphonic	Ca^{2+} from brine	
	Iminodiacetic	Ni^{2+}, Cu^{2+} etc.	
	Methyl glucamine	H_3BO_3	
	Bis-picolylamine	Metals at low pH	
	Thiourea	Hg^{2+}, Cd^{2+} etc.	

2.1.2 Applications

The ion exchange resins are used in many applications as follows:

A) Water treatment

- Water Softening

Water from power plant boilers, water pipes and domestic cooking utensils are contained calcium and magnesium ions, called hard waters. Hard waters also cause soap precipitation which forms an undesirable gray curd and a waste of soap. Strong cation exchange resins are usually used to eliminate these ions.

- Dealkalization or Demineralization

Ion exchange resin is used for removal of hardness and alkalinity from a raw water before the water is used in the industrial process.

- Purification

Purification by ion exchange is used to remove contaminating acids, alkalis, salts or mixtures from non-ionized or slightly ionized organic or inorganic substances.

B) Chemical Processing – Catalysis

Ion exchange resins are solid, insoluble acids, bases, or salts, they can replace alkalis, acids and metal ion catalysts in hydrolysis, inversion, esterification, hydration or dehydration, polymerization, hydroxylation and epoxidation reactions. Ion exchange resin is used as catalyst because it is easy to separate from the reaction, repeated reuse and reduce side reaction.

C) Metal Extraction, Separation and Concentration

In aqueous or solvent mixtures containing large amounts of contaminants and small amounts of a desired solute, ion exchange resins can be used to selectively isolate and concentrate the desired solute.

D) Sugar Manufacturing

In the manufacturing of sugar from various sources, ion exchange resins are used to help convert one type of sugar into another type of sugar and to decolorize and purify sugar syrups.

2.2 Adsorbent materials

2.2.1 Activated carbon

2.2.1.1 Production

Activated carbons (activated charcoals) are highly porous and have a very large surface area for adsorption and chemical reaction. They are widely used as adsorbents for separation and purification process for gaseous or aqueous solution system and used as a catalyst and catalyst supports in a variety of industrial and environmental applications. Activated carbon is generated by different carbonization of organic sources. Activated carbon is prepared from carbon black graphite, fiber, coals of several rank, peat, woods, fruit stones and nutshells, as with coconut shells, banana skins, straw, wood cuttings, casings from coffee beans and many other organic waste materials [4].

2.2.1.2 Preparation process

Activated carbon has to be synthesized. The porosities of a carbon, as initially prepared by carbonization, are not sufficiently developed for most applications and some improvement is an essential step. It can be produced by one of the following processes:

- **Physical activation**: material with carbon content is pyrolysed at temperatures of 600-900°C, in inert atmosphere with gas like argon or nitrogen. High porosity carbon can be obtained only at a high degree of charcoal burn off. Then, carbonized material is oxidized by carbon dioxide, oxygen or steam at temperature above 250°C.

- **Chemical activation**: material is impregnated with an activating reagent such as acids like phosphoric acid or bases like potassium hydroxide, sodium hydroxide or salts like zinc chloride, and the impregnated material is heat-treated at temperature in the range of 450-900°C, under an inert atmosphere.

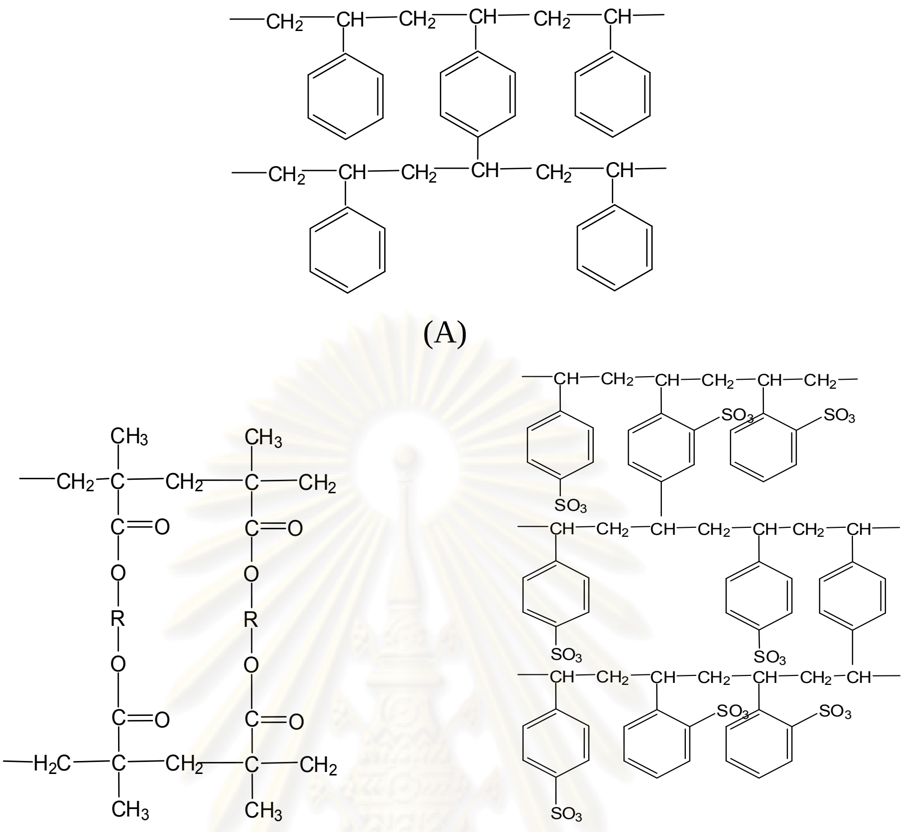
2.2.2 Polymeric adsorbent

2.2.2.1 Chemical structure

The synthetic adsorbents have been developed from ion exchange resins and polymeric adsorbents, generally are porous polymeric solid, polystyrene and styrene divinylbenze copolymer. Polymeric beads are generally prepared by suspension polymerization technique. The features of polymeric adsorbent are:

- Very porous spherical polymer based on highly cross-link
- Hydrophobic adsorbent surface
- Good physical stability
- High surface area and/or porosity

The properties of polymeric adsorbent depend on the surface characteristics. Figures 2.2 (A-C) shows the chemical structure of three widely used polymeric adsorbent classes. The Amberlite XAD-2 and Amberlite XAD-4 (A) is very hydrophobic and it is a cross-linked styrene divinylbenzene. For the Amberlite XAD-7 (B) is a cross-linked polymethacrylate structure that is more hydrophobic [5]. The sulfonated polystyrene divinylbenze (C) is a cross-linked styrene and/or sulfonated styrene and it is more hydrophilic.



(A)

(B) (C)

Figure 2.2. Structures of Amberlite XAD-2 and Amberlite XAD-4 (A), Amberlite XAD-7 (B) and sulfonated polystyrene divinylbenze (C) [5].

2.2.2.2 Physical structure

Mainly, an adsorbent usually has surface area above 5 m^2/g of solid. The physical property of adsorbent is classified into two types such as porous and non porous. The porous particles have size greater than 50 meshes. In contrast, the non porous adsorbents are finely solid (less than 10 μm). The specific surface areas of polymeric and macroreticular materials are between 100 to 600 m^2 g^{-1}, repectively.

2.2.3 Other adsorbents

As activated carbon and polymeric adsorbent have been widely used for removal of metal ions, however, it has a high price and is difficult to generate. Therefore, the waste adsorbents were reused to remove heavy metals from solution because they are nature-friendly and have little or no economic value. The waste adsorbents include for example saw dust [6], waste wood, nut waste, modified cotton [7], waste polystyrene sphere [8], waste newsprint fiber [9], unwanted agricultural solid by-product [10], etc. Mostly, the surface of waste adsorbents was modified by oxidizing or reducing agent for improvement of the extraction efficiency and reported in many researches, the waste adsorbents were carbonized to produce activated carbon which was used in many applications such as adsorption of metal ions and removal of dissolved organic matters in water [11].

2.3 Heavy metal in the environment

2.3.1 Cadmium

Cadmium is a soft, ductile, silver-white, and lustrous metal. Cadmium is almost divalent in all stable compounds, and it can be formed with hydroxides and complex ions with ammonia and cyanide, and also a variety of complex organic amines, sulfur complexes, chlorocomplexes, and chelates. Cadmium forms precipitate with carbonates, arsenates, phosphates, oxalates, and ferrocyanides.

Cadmium is a by-product of Zn industry, which is recovered from the smelting and refining of Zn concentrations. It is mainly used in alloys, in electroplating, in pigment, as stabilizers for polyvinyl plastic, in batteries and for protecting iron and steel against corrosion.

2.3.2 Chromium

Chromium is a slivery, lustrous and malleable. Chromium is found in oxidation states 0, +3 and +6. In sediments and soil, two trivalent forms (the Cr^{3+} cation and the anion CrO_2^-) and two hexavalent anions ($Cr_2O_7^{2-}$ and CrO_4^{2-}) occur.

Chromium is mostly used in the manufacture of stainless steel, for refractory purposes due to it is high melting point and chemical inertness, in the making of mortars and cartable.

2.3.3 Copper

Copper is a reddish, malleable, ductile metal with very good heating and electricity conductivity. Copper has the oxidation states +1 and +2. Cu^{2+} is the most common and it is isomorphous with Zn^{2+}, Fe^{2+} and Mg^{2+} ions.

Copper can be formed a variety of sulfides, sulfates and carbonates. Copper is widely used for wire production and in the electrical industry. Other applications are kitchenware, water delivery system, fertilizers, bactericides and fungicides.

In aquatic system, the free Cu^{2+} ion is considered because copper in aquatic life is more toxic than the complex form.

2.3.4 Nickel

Nickel is a silvery-white, hard, malleable, ductile and ferromagnetic metal. Nickel has oxidation states 0 and +2; the +1 and +3 oxidation states are not stable in aquoes solution, but can exist under certain conditions. Nickel can be formed complexes with organic ligands, but complexes with inorganic ligand are only formed to a small degree in to order $OH^- > SO_4^{2-} > Cl^- > NH_3$.

Nickel is mainly used for electroplating, alloy production, Ni-Cd batteries, electronic components and catalysts for hydrogenation of fats and methanation.

2.3.5 Lead

Lead is a bluish-gray metal, malleable, ductile, a poor electrical conductivity and very resistance to corrosion. Lead has two oxidation states +2 and +4. Mostly, lead is found the +2 oxidation state on inorganic compound. At low pH, lead performs hydrolysis reaction and displays multiple hydrolysis reaction and at pH range 6-10 the formation of $Pb(OH)^+$ is predominant, while as above pH 9 the formation of $Pb(OH)_2$ is precipitation.

Lead is important for any industrial economy and is used for batteries, pigment, rolled and lead is also used as radiation sheeting and as a heat stabilizer in PVC.

2.3.6 Zinc

Zinc is a bluish white soft metal. The oxidation state in nature is +2. The Zn^{2+} ion is colorless. In alkaline solutions, the hydroxide is precipitated. The zincate ion, $Zn(OH)_4^{2-}$ is formed with excess base. Zn forms precipitate with hydroxide and forms water-soluble chlorates, chlorides, sulfates and nitrate while the oxides, carbonates, phosphates and silicates are relatively insoluble in water.

Zinc is mainly used in the automobile industry, for the production of protective coatings for iron and steel, in cosmetics, powders, antiseptics, paint, rubber and linoleum.

2.4 Adsorption

Adsorption is a process that the solid surface (adsorbent) contacts with the liquid or gas (adsorbate) which has interaction between the fields of forces of the surface and the liquid or gas. The adsorption can be split into two types i.e. physisorption and chemisorption.

Physisorption

Physisorption or physical adsorption is a type of adsorption which attracts between adsorbate and adsorbent via Van der Waals force (weak intermolecular), which generates from London dispersion force and the electrostatic force. The enthalpy of adsorption is 10 to 20 kJ mol^{-1} [12]. The physisorption is a reversible reaction which is easy to generate. The multilayer adsorption of adsorbates on the adsorbent surface can occur, when the concentration of adsorbates increases [13].

Chemisorption

Chemisorption is a type of adsorption based on chemical or covalent bond which is stronger than Van der Waals force in physisorption. The enthylpy of adsorption is 40 to 400 kJ mol^{-1}. The adsorption of adsorbate occurs in monolayer and the reaction is irreversible.

2.4.1 Adsorption isotherm

Adsorption in liquid is usually described through isotherms (Figures 2.3 and 2.4), that are functions which connect the amount of adsorbate on the adsorbent at equilibrium of constant temperature. Mathematic models that widely used to describe adsorption processes are namely Langmuir and Freundlich isotherms.

2.4.1.1 Langmuir isotherm

The Langmuir model is a model which predicts the adsorbates in liquid phase adsorbed onto adsorbent surface in a monolayer adsorption at a constant temperature. The general form of the Langmuir isotherm is shown in equation 2.1 and 2.2:

$$q = \frac{q_m b C_e}{1 + bC_e} \qquad (2.1)$$

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (2.2)$$

where C_e = equilibrium concentration of the adsorbate in aqueous solution (mg L^{-1} or mol L^{-1})
q = adsorption capacity of adsorbent (mg g^{-1} or mol g^{-1})
q_m = maximum adsorption capacity of adsorbent (mg g^{-1} or mol g^{-1})
b = Langmuir constant related to the affinity of binding sites (L mg^{-1} or L mol^{-1})

A plot of $\frac{C_e}{q}$ versus C_e yields a straight line with a slope of $\frac{1}{q_m}$ and intercept of $\frac{1}{bq_m}$ (Figure 2.3).

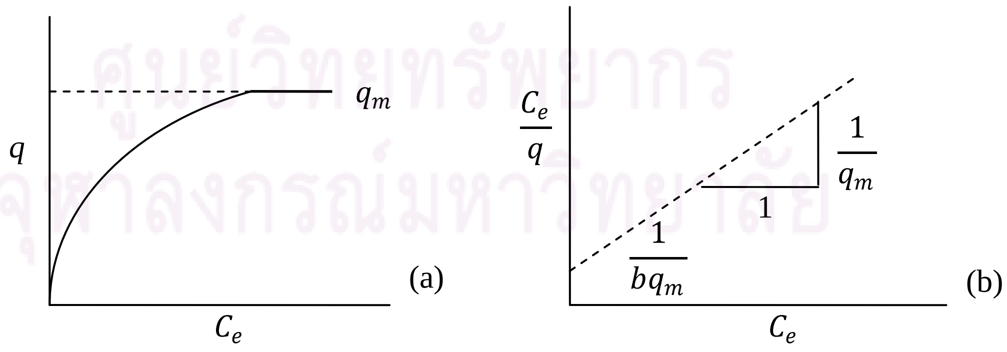


Figure 2.3. The shape (a) and linear plot (b) of Langmuir adsorption isotherm [14].

2.4.1.2 Freundlich isotherm

The Freundlich equation was derived theoretically by assuming the adsorption of solutes on heterogeneous surface active sites of varied affinities and Freundlich isotherm is an empirical model to describe adsorption in aqueous solution. The Freundlich isotherm is expressed by the following equations 2.3 and 2.4:

$$q \quad = \quad K_f \; C_e^{1/n} \tag{2.3}$$

$$\log q \;=\; \log K_f \;+\; \frac{1}{n}\log C_e \tag{2.4}$$

where K_f = Freundlich constant related to adsorption capacity (mg g^{-1} or mol g^{-1})

n = Freundlich constant related to adsorption intensity

A linear plotting of log q versus log C_e gives a slope of $\frac{1}{n}$ and intercept of log K_f (Figure 2.4).

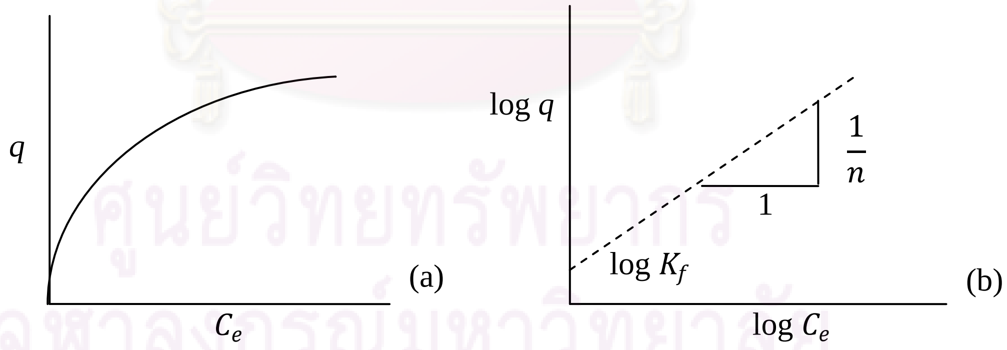


Figure 2.4. The shape (a) and linear plot (b) of Langmuir adsorption isotherm [14].

2.4.2 Adsorption kinetics

The adsorption kinetics describes the adsorbate uptake rate at the solid liquid interface [15].

2.4.2.1 The pseudo-first order kinetics

The pseudo-first order equation can be written as the following equation 2.5 and 2.6 [16]:

$$\frac{dq_{tq}}{dt} = k_2(q_e - q_t) \qquad (2.5)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (2.6)$$

Where q_t = adsorption capacity at time, t (mg g^{-1})

q_e = adsorption capacity at equilibrium (mg g^{-1})

k_1 = rate constant of pseudo-first order adsorption (min^{-1})

The values of $log(q_e - q_t)$ is linearly correlated with t. The k_l and q_e are calculated from the slope and intercept of the plot of $log(q_e - q_t)$ against t (Figure 2.5(a)).

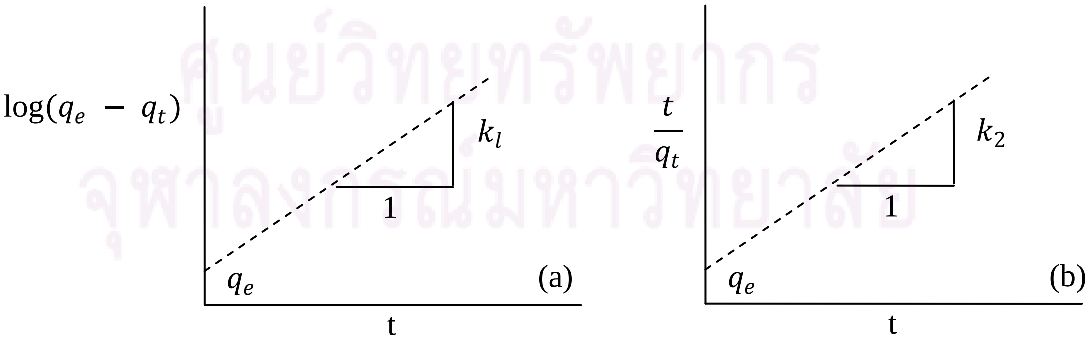


Figure 2.5. The shape of pseudo-first order (a) and of pseudo-second order (b).

2.4.2.2 The pseudo-second order kinetics

The pseudo-second order equation can be presented by the following equations 2.7 to 2.10 [17]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \qquad (2.7)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (2.8)$$

$$h = k_2 {q_e}^2 \qquad (2.9)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \qquad (2.10)$$

Where k_2 = rate constant of pseudo-second order adsorption (g (mg min)$^{-1}$)

q_t = adsorption capacity at time, *t* (mg g^{-1})

q_e = adsorption capacity at equilibrium (mg g^{-1})

h = initial sorption rate constant (mg (g min)$^{-1}$)

The values of $\frac{t}{q_t}$ is linearly correlated with *t*. The k_2 and q_e.are calculated from the slope and intercept of the plot of $\frac{t}{q_t}$ against *t* (Figure 2.5(b)).

The parameters from equations 2.5 to 2.10 can be predicted the order of kinetics, design of sorption system and behavior of sorption process.

2.5 Literature reviews

2.5.1 Preparation of adsorbent from unwanted materials

In the recent years, many researchers have studied the economical or unwanted materials for removal of heavy metal ions from wastewater. Namasivayam et al. [18] used activated carbon from bicarbonate-treated peanut hulls (BPHC) for removal of mercury ions from aqueous solution. BPHC was an agricultural waste which was treated with sulfuric acid and dried in an air-oven at 145-155°C for 24 hours. An unwanted agricultural solid by-product, coirpith carbon was prepared by mixing coirpith : sulfuric acid : ammonium persulphate in ratio of 1 : 1.8 : 0.1 and kept in an air oven at 80°C for 12 hours and afterward used for adsorption of mercury [10]. Sugi wood powder was carbonized at 200, 600 and 1000°C in a nitrogen atmosphere for 1 hour [19]. Wood powder carbonized at 1000°C achieved the best removal of heavy metals. Aoyama et al. [9] removed inorganic mercury by newsprint fiber waste which was carbonized at temperatures ranging from 600 to 900°C for 3 hours in a nitrogen atmosphere. Then, the carbonized material was soaked in dilute HNO_3 overnight and dried at 1050°C in an oven.

2.5.2 Surface modification of adsorbent for improving adsorbent capacity

Many researchers have demonstrated the surface modification of some materials for water-contaminant removal. Some examples of chromate ion adsorption by surface-modified sorbents are summarized hereafter. Wartelle et al. [20] investigated the use of dimethyloldihydroxyethylene urea (DMDHEU) and the quarternary choline chloride modified on lignocellulosic-based agricultural by-product such as soybean hulls, sugarcane bagasse and corn stover for removal of hexavalent chromium. The clay materials such as kaolinite, montmorillonite and pillared montmorillonite modified with hexadecyl trimethylammonium (HDTMA) bromide could adsorb chromate ions [21]. Montmorillonite showed a high adsorption capacity for chromate because it possessed a lot of anion-exchangeable sites. Hong et al. [22] investigated the removal of arsenate, chromate and ferricyanide by using cationic surfactant (cetylpyridinium chloride) modified powdered activated carbon.

2.6.3 Reuse of exhausted ion exchange resins

There are a very few literature data in this aspect. In our knowledge, Wang et al. [8] examined the adsorption of dibenzothiophene by polystyrene-based activated carbon sphere waste produced by carbonizing at 900°C for 3 hours in a nitrogen atmosphere and steam activating for 0.5-0.75 hour. After that, the activated carbon was treated by HNO_3, H_2O_2, H_2 and $(NH_4)_2S_2O_8$ before used.

In conclusion, many reports have published on the development of low-cost activated carbon adsorbents which were cheaper than the commercial activated carbon and readily available materials such as unwanted agricultural products (e.g. peanut hulls, coirpith) and unwanted materials (e.g. waste newsprint fiber, wood powder). Some researches have demonstrated the surface-modification of adsorbent for improvement of their sorption capacity towards an expected solute in water. These sorbent products were used to remove metal ions in aqueous solution. In order to save cost and be friendly to the environment, this work intended to demonstrate the improvement of adsorption ability of sulfonated polystyrene-divinylbenzene waste by carbonization and surface modification and the use in removal of heavy metal ions in wastewater.

CHAPTER III

EXPERIMENTAL

3.1 Instruments

In this thesis, the analytical instruments used for all measurements are listed in Table 3.1.

Table 3.1 List of analytical instruments/apparatus

Analytical Instruments/apparatus	**Manufactor : Model**
1. Fourier transform infrared spectrometer (FT-IR)	Thermo Nicolet 6700
2. Flame atomic absorption spectrometer (FAAS)	Perkin-Elmer : AAnalyst 100
3. Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES)	Thermo Scientific, iCAP 6000 series
4. Thermo gravimetric analyzer (TGA)	Perkin-Elmer : Pyrisl
5. pH meter	Hanna instrument : pH 211 Mettler Toledo : Inlab® Basics pH
6. Transferpipette : 0.5-10, 10-100, 100-100 μL and 0.5–5.00 mL	Brand
7. Stirrer	Gem : MS 101
8. Oven	Memert : UM500
9. Vacuum pump	Buchi : V-700
10. Manifold	Supelco

3.2 Chemicals

All chemicals were of analytical grade and listed in Table 3.2.

Table 3.2 List of chemicals

Chemicals	Suppliers
Cadmium(II) nitrate standard solution	Merck
Copper(II) nitrate standard solution	Merck
Nikel(II) nitrate standard solution	Merck
Lead(II) nitrate standard solution	Merck
Zinc(II) nitrate standard solution	Merck
Potassium chromate	Fisher Scientific
Nitric acid, 65%	Merck
Sodium hydroxide	Merck
Picric acid	Sigma-aldrich
1,2-dicholromethane	Fluka
Cetyl trimethylammonium bromide	Merck
Hydrochloric acid, 37%	Merck

3.3 Experimental procedures

3.3.1 Preparation of chemicals and reagents

De-ionized (DI) water was used for preparation of all reagents.

Metal solutions

Metal working solutions were prepared by using metal standard solutions to desired concentrations in DI water.

Potassium chromate

Potassium chromate solution (1000 mg L^{-1}) was prepared by dissolving 0.0836 g of K_2CrO_4 in 50 mL of DI water.

Nitric acid solution/Acid carrier

Nitric acid solutions (1 and 5 %v/v) were prepared by dilution of the concentrated nitric acid solution with DI water and used for pH adjustment and used in cadmium, copper, chromate, nickel, lead and zinc analysis by FAAS.

Sodium hydroxide solution

Sodium hydroxide solution (1 and 5 %w/v) were prepared by dissolving the appropriate amount of NaOH in DI water and used for pH adjustment.

Cetyl trimethylammonium bromide solution (CTAB)

CTAB solutions were prepared by dissolving the appropriate amount of cetyl trimethylammonium bromide in DI water.

Picric acid solution

Picric acid solution (0.1% w/v) was prepared by dissolving 0.02 g of picric acid in 0.002 M 250 mL of NaOH and used for determination of concentration of CTAB.

Potassium nitrate solution

Potassium nitrate solution (0.03 M) was prepared by dissolving 0.1516 g of KNO_3 in 50 mL of DI water and used for pH of point of zero charge determination.

3.3.2 Carbonization of cation exchange resin waste

Cation exchange resin waste was carbonized at 300-500°C for 3 hours in an electric furnance. Then, the carbonized materials were washed with DI water and dried at 100°C overnight. The carbonized cation exchange resins (CCR) which was carbonized at 300, 400 and 500°C were named CCR300, CCR400 and CCR500, respectively. Finally, the CCR300, CCR400 and CCR500 were characterized by FT-IR and TGA.

3.3.3 Preparation of modified carbonized cation exchange resin waste

0.4 grams of the CCR500 was immersed in 50 mL of 0.03-0.5 mM cetyl trimethylammonium bromide (CTAB) solution and stirred thoroughly for 1-6 hours. Then the CCR500 was separated by 0.45μm membrane filtration and dried at 70-80°C overnight in an oven. 1 mL of filtrate solution was mixed with 0.30 mL of 0.1% picric acid in 0.02 M NaOH and 0.50 mL of 1,2-dichloroethane and then the mixtures were stirred until equilibrium [23]. The organic phase was pipetted into a cuvatte. Then, the organic phase was analysed by a UV-vis spectrophotometer at 375 nm for determination of the concentration of CTAB. Thereafter, the modified-carbonized cation exchange resin waste (CTAB-CCR500) was characterized by FT-IR.

3.3.4 Measurement of point of zero charge

Mass titrations (MT) method was used to measure the point of zero charge [24], different weights of CCR300, CCR500 and CTAB-CCR500 within the concentration range of 0.5, 1, 5 and 10%w/v were put into contact with a 0.03 M KNO_3 solution. The aqueous suspensions were stirred for 24 hours until equilibrium pH was reached. The pH of point of zero charge (pH_{PZC}) is the pH at which a plateau is achieved when plotting equilibrium pH versus weight percent per volume of CTAB-CCR in KNO_3 solution.

3.4 Characterization

The characterization is required to confirm the successful preparation of CCR300, CCR400, CCR500 and CTAB-CCR500. The techniques used to characterize the materials were FT-IR and TGA. FT-IR was used to confirm the presence of functional groups on CCR300, CCR400, CCR500 and CTAB-CCR500. The amount of carbon on CCR500 was determined by TGA.

a) Fourier transform infrared spectroscopy (FT-IR)

Infrared spectra were recorded from 400 to 4000 cm^{-1} in transmittance mode using Attenuated Total Reflectance (ATR) technique.

b) Thermal gravimetric analysis (TGA)

Thermogravimetric measurements were performed using a heating rate of 50°C min^{-1} under nitrogen atmosphere. The amount of carbon (mmol) per sorbent amount (g) was calculated from the thermogram obtained.

3.5 Adsorption study using batch method

Batch method was used to study the adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions in aqueous solution by CCR300 while the CTAB-CCR500 was used to study the selective adsorption of chromate. 20 mg of adsorbent were added to 5 mL of metal ions solutions. The adsorbent was separated by 0.45 μm membrane filter. The concentration of metal ions after extraction was determined by FAAS. The instrumental conditions are listed in Table 3.3.

Table 3.3 FAAS condition for determination of metal ions solution

Operating conditions	Cd	Cr	Cu	Ni	Pb	Zn
Wavelength (nm)	228.8	357.9	324.8	232.0	283.3	213.9
Slit width (nm)	0.70	0.70	0.70	0.20	0.70	0.70
Lamp type	HCL*	HCL*	HCL*	HCL*	HCL*	HCL*
Lamp current (mA)	4	25	15	25	10	15
C_2H_2 flow rate (mL/min)	2	4	2	2	2	2
Air flow rate (mL/min)	4	3	4	4	4	4

*Hollow Cathode Lamp

The parameters in batch method such as effect of pH of metal ions solution, contact time and initial concentration (adsorption isotherm) were studied. All adsorption experiment were performed in triplicate (n=3).

3.5.1 Effect of pH of metal ions solutions

The effect of pH on adsorption was studied in the pH range from 2 to 10. The initial concentration of metal ions solution is 5 mg L^{-1} for Cu(II), Ni(II), Zn(II), Cd(II) and chromate and 25 mg L^{-1} for Pb(II). The extraction experiment started with 20 mg of adsorbent and 5 mL of metal ions solution in a test tube after that it was stirred for 60 min. The pH of metal ions solution was adjusted to a desired value with NaOH (1 and 5%w/v), HNO_3 (1 and 5 %v/v) and HCl (1 and 5 %v/v) solutions.

3.5.2 Effect of contact time

The effect of contact time was investigated by varying the contact time in the range from 5-90 min for Cd(II),Cu(II), Ni(II), Pb(II)and Zn(II) and 15-120 min for chromate at room temperature. The initial concentrations were 5 mg L^{-1} for Cu(II), Ni(II) Zn(II) and chromate, 2 mg L^{-1} for Cd(II) and 25 mg L^{-1} for Pb(II) .

3.5.3 Effect of initial concentration (Adsorption isotherm)

The initial concentrations of metal ions solution were varied between 5- 400 mg L^{-1} for Cu(II) and Ni(II), 5-300 mg L^{-1} for Cd(II), 15-1000 mg L^{-1} for Pb(II), 5-500 mg L^{-1} for Zn(II) and 5-50 mg L^{-1} for chromate under the optimal pH and contact time as obtained from the section 3.5.1 and 3.5.2. The temperature was controlled at 25°C.

3.6 Adsorption study using column extraction

The flow rate of Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) and chromate ions in aqueous solution was investigated using column method. A disposable syringe was packed with 0.1 g of CCR300 for Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) adsorption study. Then 5 mL of 0.0001 M of Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) solutions were passed through the syringe by means of a manifold connected to a vacuum pump.

The flow rate of metal ions solution was studied in the range of 0.5-5 mL/min. The amount of residual metal ions in the solution was determined by FAAS. All adsorption experiments were performed in triplicate (n=3). The study of chromate adsorption onto CTAB-CCR500 column was done using the same experimental set up.

3.7 Application of real wastewater sample

In this work, the real water sample was wastewater from a nikel alloy industry. Before the application for extraction experiment, the wastewater sample was filtered and analyzed for the concentration of metal by ICP-OES.

For column extraction, the sample solution of 10.0 mL was extracted by using 0.10 g of CCR300 which was packed into a disposable syringe and the flow rate of sample solution was around 0.8-1.0 mL/min. Finally, the amount of residual metal ions in the solution was determined by ICP-OES.

For batch extraction, 0.10 g of CCR300 was added to 10.0 mL of sample solution in a test tube and it was stirred for 45 min. The concentration of metal ions after extraction was determined by FAAS.

CHAPTER IV

RESULT AND DISCUSSION

The results and discussion in this chapter are divided into 5 parts; i.e. preliminary investigation of carbonization effect on adsorption property and the characterization results (section 4.1), modification of the carbonized resin (section 4.2), adsorption study by batch method (section 4.3) and by column method (section 4.4) and lastly application to real wastewater sample (section 4.5).

4.1 Carbonization of cation exchange resin waste

Sulfonated polystyrene divinylbenzene cation exchange resin waste was carbonized at 300-500°C for 3 hours and the materials carbonized at 300°C, 400°C and 500°C namely CCR300, CCR400 and CCR500, respectively, were obtained. These materials were subjected to evaluate the adsorption efficiency towards Ni(II), Zn(II) and Pb(II) ions in aqueous solution, and the results are presented in Table 4.1.

Table 4.1 Comparison of the extraction percentage of exhausted resin and CCR300 on adsorption of metal ions

Metal ion	Exhausted resin		CCR300	
	Extraction (%)	**RSD (%)**	**Extraction (%)**	**RSD (%)**
Ni(II)	87.76	1.41	98.91	0.00
Zn(II)	87.50	1.20	100.0	0.00
Pb(II)	67.47	4.62	100.0	0.00

Table 4.1 shows the comparison of the used-exhausted resin and CCR300 on the adsorption of Ni(II), Zn(II) and Pb(II). It was found that CCR300 could extract metal ions more than the untreated resin presumable due to the fact that the thermal

treatment could allow CCR300 to have a suitable adsorption property for metal ions such as higher surface area and having more appropriate active and ion-exchangeable surface (sulfonyl group, the evidence will be shown and discussed in section 4.1.1.1) which was favorable for metal ions. The detail of characterization and adsorption property study of all materials will be discussed later on.

4.1.1 Characterization

4.1.1.1 Fourier transforms infrared spectroscopy

The IR spectra of CCR500, CCR400 and CCR300 are presented in Figure 4.1(A), 4.1(B) and 4.1(C), respectively. The absorption of aromatic functional group was found at 1650 cm^{-1}. The peaks appeared at 1190 and 1040 cm^{-1} were assigned to $–SO_3H$ [25]. In Figure 4.1(A), the peak of sulfonyl group disappeared because the sulfonyl moiety degraded and the structure of CCR500 changed with increasing carbonization temperature. The new peak appeared at 1447 cm^{-1} may assign to aliphatic $-CH_2-$ due to the broken polymeric main chain. From Figure 4.2, it was found that the carbonization temperature affected the extraction efficiency. The material obtained from the carbonization temperature at 300°C provided the highest extraction efficiency for Ni(II), Pb(II), Zn(II), Cu(II) and Cd(II) because the resin contained more sulfonyl groups acting for ion exchange comparing with other carbonized materials.

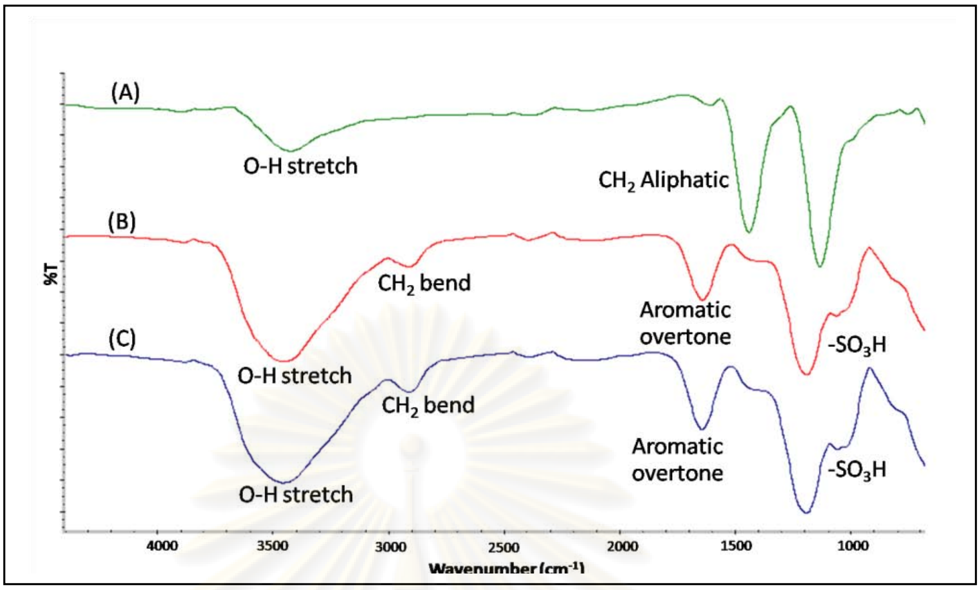


Figure 4.1 FT-IR spectra of (A) CCR500 (B) CCR400 and (C) CCR300.

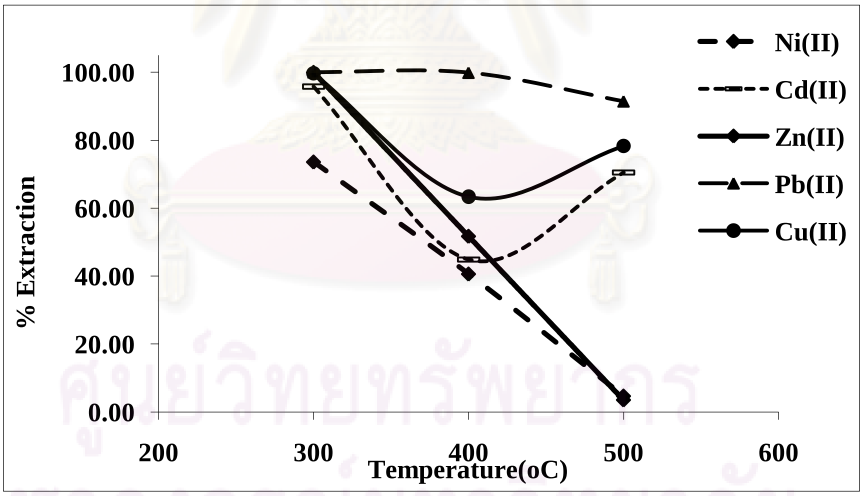


Figure 4.2 Effect of carbonization temperature on extraction efficiency of metal ions. [initial metal concentration = 5 mM: corresponding to 29 mg L^{-1} for Ni(II), 32 mg L^{-1} for Zn(II), 56 mg L^{-1} for Cd(II), 31 mg L^{-1} for Cu(II), 103 mg L^{-1} for Pb(II), (n=3)].

4.1.1.2 Thermo gravimetric analysis

The thermogravimetric analysis (TGA) of resin waste (A), CCR300 (B), CCR400 (C) and CCR500 (D) were investigated by a thermogravimeter operating with the temperature range of 50-800°C with a heating rate of 50°C/min and the results are shown in Figure 4.3. All four curves show a small initial weight loss (5-10%) over the temperature range of 50-100°C due to the loss of moisture [26]. The loss weight of resin waste and CCR300 (~20%) occurred at the temperature between 450 and 510°C [27, 28] and it could be attributed to the decomposition of the polymer backbone. This observation suggested that CCR300 was still polymeric material after carbonization. Finally, the weight loss of resin waste, CCR300 and CCR400 showed around 510-800°C was assigned to the decomposition of the residual solid after carbonization. The thermogram of CCR500 shows only 20% weight loss at 800°C which reveals that during carbonization at 500°C, the polymeric resin had already degraded. The residual solid (~80% by weight) remained in the crucible was assigned to be fixed carbon. However, fixed carbon commonly defined in proximate analysis method is a carbonaceous residual solid after being carbonized at 950°C for 6 hours. In our interpretation, we assume that CCR500 contains 80% of fixed carbon and the amount of carbon of CCR500 is approximately 67 mmol g^{-1}.

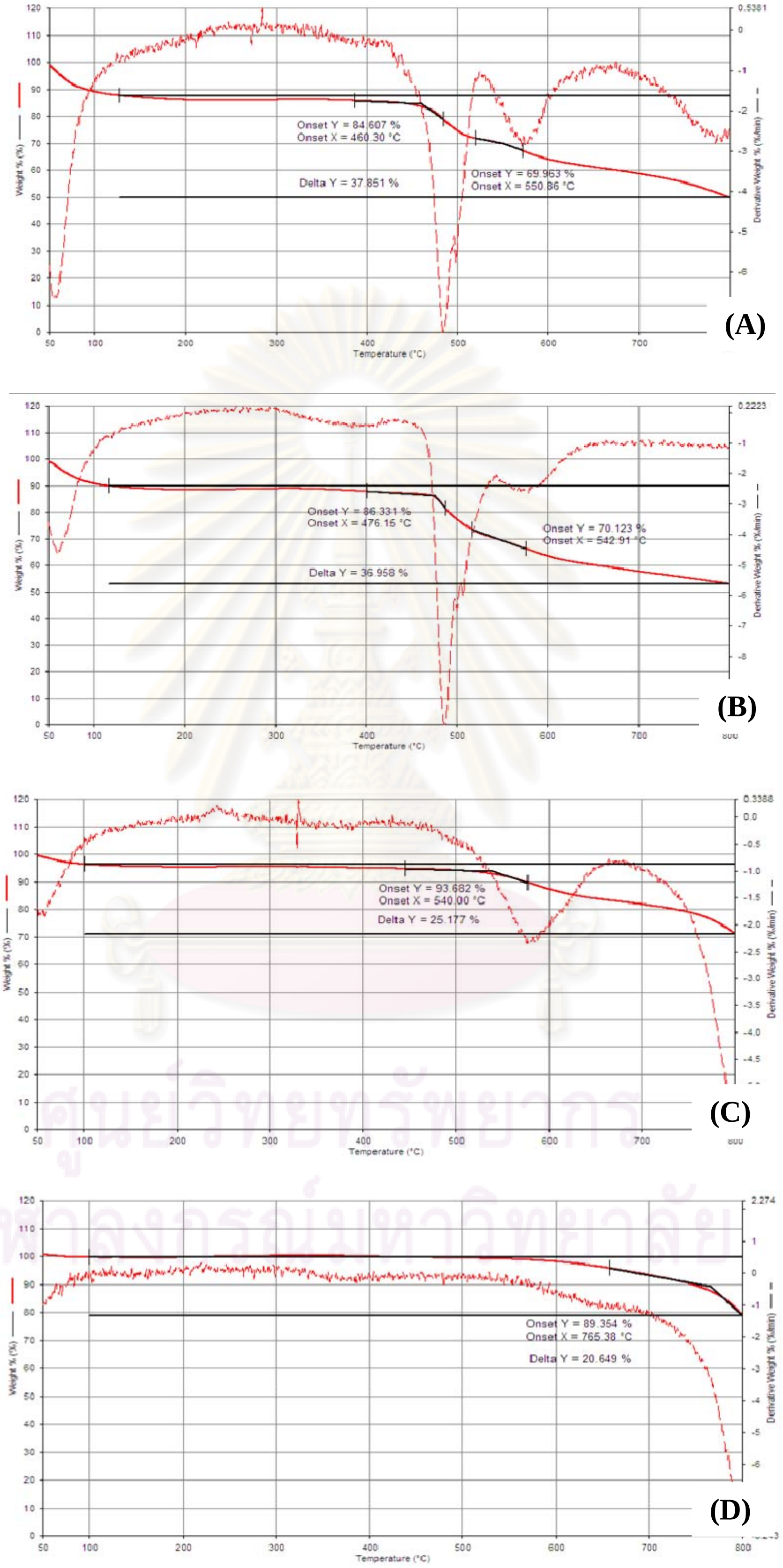


Figure 4.3 Thermograms of resin waste (A), CCR300 (B), CCR400 (C) and CCR500 (D) (heating rate of 50°C min^{-1} under nitrogen atmosphere).

4.2 Modification of carbonized cation exchange resin waste

Cetyl trimethylammonium bromide $(C_{16}H_{33})N(CH_3)_3Br$, CTAB is a surfactant which has a long chain hydrocarbon and quaternary amine moiety. It is widely used in extraction of DNA [29], modification of adsorbent [20], synthesis of gold nanoparticle [30] and application as surfactant [21], etc. In the work, CTAB was used as modifying agent for CCR500. The reason why CCR500 were chosen and used to be modified is that CCR500 contains the highest amount of fixed carbon which is suitable for CTAB adsorption due to the van der Waals force between the long chain hydrocarbon and adsorbent surface. Therefore, CCR500 was chosen for surface modification using CTAB for the removal of chromate ions in aqueous solution. The results of characterization and adsorption study will be discussed here.

4.2.1 Characterization of modified-carbonized cation exchange resin waste by FT-IR

The FT-IR spectra of CTAB, CCR500 and CTAB-CCR500 are shown in Figure 4.4. The absorption bands of CTAB can be grouped into two categories: which associated with methylene tails and alkylammonium head group. The peak around 3020 cm^{-1} was assigned to the symmetric stretching mode of the trimethylammonium headgroup $(CH_3)_3$-N of CTAB and the most intense absorption bands at around 2920 and 2850 cm^{-1} may be assigned to CH_2 asymmetric and symmetric stretching mode of methylene group, respectively. The bands around 2951 and 2866 cm^{-1} are due to the asymmetric and symmetric stretching mode of terminal CH_3-R group. The absorption of methylene scissoring mode and methylene rocking mode were found at 1467-1490 and 722 cm^{-1}, respectively [31]. For FT-IR spectra of CTAB-CCR500, the new appeared peaks at 2920 and 2850 cm^{-1} were assigned to the asymmetric and symmetric stretching mode of CH_2 and the absorption band at around 3020 cm^{-1} may be assigned to CH_3-N of CTAB. So it indicates that CTAB was successfully modified on the CCR500 surface.

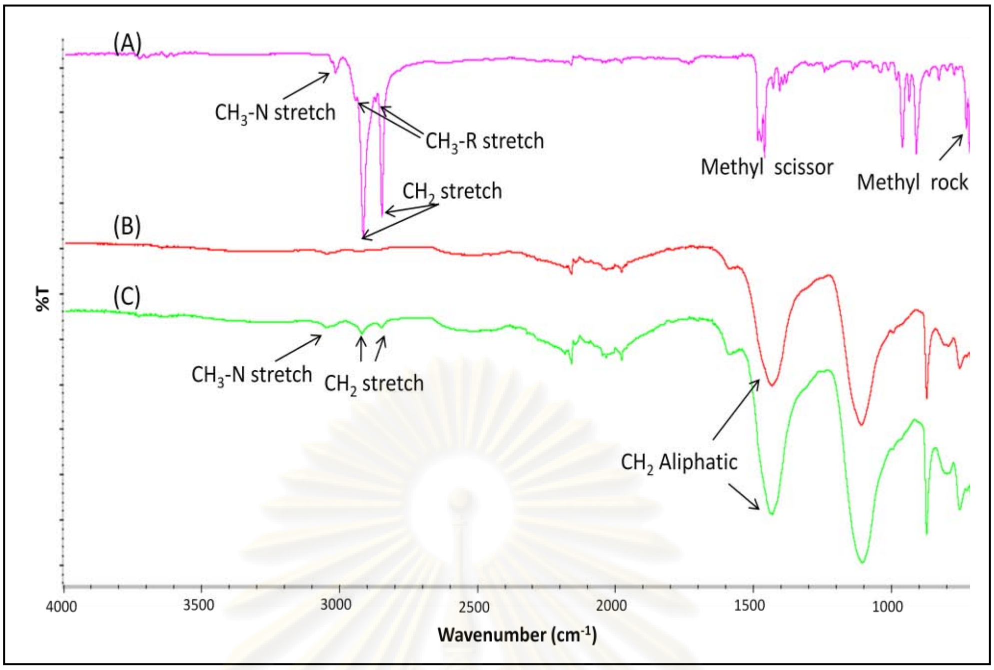


Figure 4.4 FT-IR spectra of (A) CTAB, (B) CCR500 and (C) CTAB-CCR500.

4.2.2 Effect of concentrations of CTAB

The modification efficiency of adsorbent depends on the concentration of CTAB. The critical micelle concentration (CMC) of CTAB is 0.9 mM [32]. When the concentration of CTAB is above the CMC, the micelle is formed. On the other hand, the concentration of CTAB is below the CMC, the CTAB molecules form monomer which has positive charge. Thus, the CTAB concentrations below the CMC (0.003 to 0.5 mM) were experimentally considered because, for better adsorption efficiency of monomeric CTAB, the formation of micelles is unwanted. CTAB could modify onto CCR500, due to the fact that hydrocarbon tails of CTAB molecules could interact with the carbonaceous CCR500 surface. And positively charged $[R\text{-}N(CH_3)_3]^+$ moiety would be an exchange site on the modified CCR500 towards negatively charged chromate ions.

The effect of initial concentrations of CTAB was studied in order to observe the adsorption of CTAB on CCR500 by varying the concentrations of CTAB in the range of 0.03 to 0.5 mM (50 mL) using 0.4 g of CCR and 6 hours of shaking time. The residual concentration of CTAB in filtrate was determined by UV-vis technique.
]

The amount of CTAB adsorbed onto the solid was estimated by mass balance calculation and the results are illustrated in Figure 4.5.

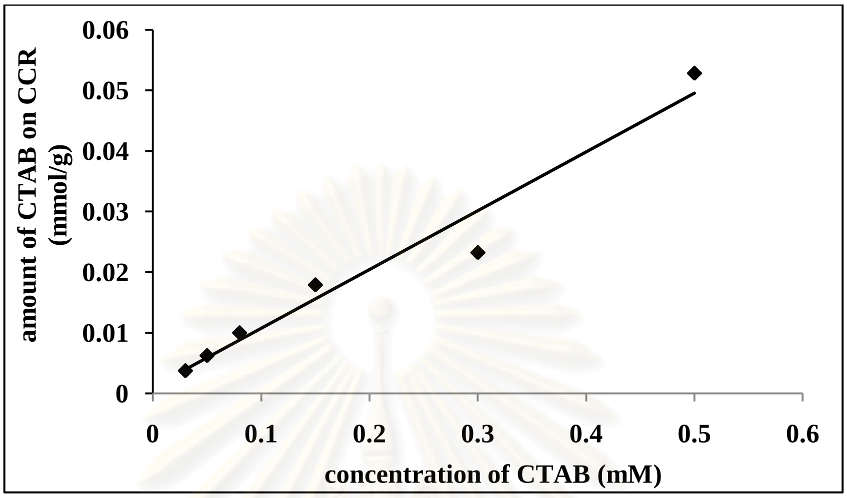


Figure 4.5 Effect of concentrations of CTAB on adsorbed amount of CTAB on CCR500 (CCR500 = 0.4 g, volume = 50 mL, contact time = 6 hrs).

In Figure 4.5, the result showed that the adsorption of CTAB onto the surface of CCR500 increased when increasing the concentration of CTAB. Therefore, 0.5 mM CTAB was chosen for modification of CCR500 because using 0.5 mM CTAB resulted in the highest adsorbed amount of CTAB onto the adsorbent.

Table 4.2 Effect of concentration of CTAB on adsorbed amount of CTAB onto CCR500 and extraction efficiency for chromate ions

Initial concentration of CTAB (mM)	Amount of CTAB on CCR500 (mmol/g)	Extraction of chromate ion (%)	RSD (%)
0.00	-	3.36	2.63
0.03	0.0038	26.48	1.26
0.05	0.0063	25.64	1.93
0.08	0.0100	26.80	0.73
0.15	0.0179	28.58	3.83
0.30	0.0232	41.19	1.93
0.50	0.0528	40.77	0.73

The effect of concentration of CTAB in CCR500 modification step on the removal of chromate ion was investigated. The results are shown in Table 4.2. Comparing the extraction efficiency of unmodified CCR500 and the modified ones, the percentage extractions of the later were significantly higher than that of the former. This result suggests that the CTAB modification could facilitate the extraction of chromate which was in agreement with our previous hypothesis. It is seen that the adsorption efficiency of chromate ion on CTAB-CCR500 increased from 26.48 to 41.19% when CTAB concentration increased from 0.03 to 0.3 mM, suggesting that sufficient adsorption sites were available at high concentration of CTAB. If the surface of CTAB-CCR500 has more exchange site, chromate would be more adsorbed. Although from Table 4.2 at 0.3 and 0.5 mM CTAB, the values of percentage extraction of chromate were not significantly different, 0.5 mM CTAB was chosen for further adsorption study due to its higher adsorbed amount of CTAB. This adsorption experiment was a batch method which was a static adsorption mode; the percentage extraction depends on the equilibrium between free chromate ions in solution and chromate ions adsorbed on the sorbent.

4.2.3 Effect of contact time for modification of CCR500

Figure 4.6 shows the effect of contact time in the modification of CCR500 with CTAB when using contact times of 1 to 6 hours, 0.1 g of CCR500 and 0.5 mM of CTAB (50 mL). The results indicated that the adsorption of CTAB onto the surface of CCR increased with increasing the contact time and reaching the equilibrium after 4 hours. Therefore, the contact time of 6 hours was chosen for the modification of CCR in order to assure the adsorption equilibrium.

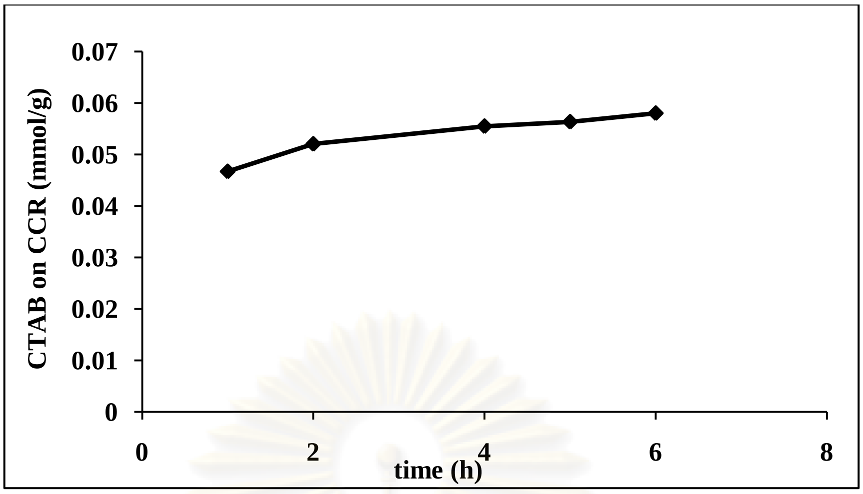


Figure 4.6 Effect of contact time in modification of CCR500 by CTAB (initial concentration = 0.5 mM, 50 mL CCR500 = 0.1 g).

4.3 Adsorption study by batch method

In batch method, the CCR300 was used as adsorbent in adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) ions and the CTAB-CCR500 was used in adsorption of chromate in aqueous solution. The effect of initial pH of metal ions solution and contact time were investigated to obtain optimized conditions for metal ions extraction and adsorption isotherm study was also performed.

The metal ions extraction efficiency was presented in term of percentage extraction and sorption amount, which were calculated according to equation 4.1 and 4.2, respectively.

$$\text{Extraction (\%)} = \frac{\mathrm{C_i - C_e}}{\mathrm{C_i}} \times 100 \qquad (4.1)$$

$$\text{Sorption amount } (q) = \frac{(C_i - C_e)\, V_s}{1000\, m} \qquad (4.2)$$

Where C_i = initial concentration of metal ions in aqueous solution (mg L^{-1})
C_e = equilibrium concentration of metal ions in aqueous solution (mg L^{-1})

q = sorption amount (mg g^{-1})

V_s = volume of metal ions solution (mL)

m = weight of adsorbent (g)

4.3.1 Effect of pH of metal ions solution

The pH of metal ions solutions is an important parameter which affected the efficiency of metal ions extraction. Experiments were performed by using 5 mg L^{-1} of Cu(II), Ni(II), Zn(II), Cd(II) and chromate and 25 mg L^{-1} of Pb(II). The pH of metal solutions were adjusted ranging from 2 to 10 using 1% and 5%v/v HCl, 1% and 5%v/v HNO_3 and 1% and 5%w/v NaOH. A suspension of 20 mg of adsorbent and 5 mL of metal ions solution in a test tube was stirred for 60 min at room temperature. The aqueous solution was brought off and the amount of residual metal ion in the solution was determined by FAAS.

In this work, CCR was used to adsorb cations including Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) because CCR300 are strong cation exchange resin with sulfonic acid groups and it could effectively be used at all pH ranges. However, in strong basic solution, the metal ions can precipitate in hydroxide form; therefore, the extraction of metal ions was not successfully obtained.

The initial pH values of Cd(II),Cu(II), Ni(II) and Zn(II) ions solution used in this study were in the range of pH 2.0-10.0 and pH 2.0-6.0 for Pb(II) ions.

Figure 4.7 shows the effect of pH of metal ions solution on adsorption of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II). It was found that Cd(II), Cu(II), Ni(II) and Zn(II) could be extracted with good percentage extraction in the whole pH range of 2.0-10.0. For Pb(II), it could be extracted at the pH range of 2.0-6.0. The extraction was not performed in higher pH due to the precipitation of $Pb(OH)_2$ in basic solution.

In order to adsorb any anion, the modified surface must either possess positively charged exchange sites, or there should be replacement of weakly held counter ions of the surfactant by more strongly held adsorbate counter ions. Some cationic surfactants provide such a modified surface for anions. In case of chromate ions it could be removed by CTAB modified CCR500.

The effect of the solution pH can be attributed to the electrostatic interactions between the surface of CTAB-CCR500 and chromate. The pH at which the charge of the solid surface is zero is referred to the point of zero charge (pH_{PZC}). The surface charge of the sorbent is positive below pH_{PZC} while it is negative above pH_{PZC} [33]. The point of zero charge of CTAB-CCR500 was determined by Mass Titration (MT) and the value was 8.80 as shown in Figure 4.8. The CTAB-CCR500 was positively charged at pH < 8.80 due to the dissociation of Br^- resulting in obtaining predominant CCR500-CTA^+ and the chromate anion in solution was attracted to the CCR500-CTA^+ surface. On the other hand, CTAB-CCR500 at pH > 8.80 was negatively charged since high OH^- in the solution could be adsorbed to the surface. Thus the extraction percentage of chromate was low.

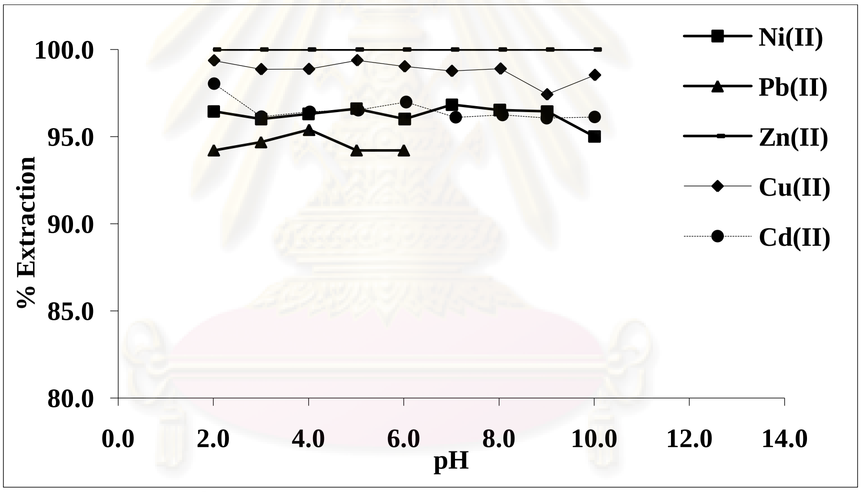


Figure 4.7 Effect of pH on adsorption of Ni(II), Pb(II), Zn(II), Cu(II) and Cd(II) by CCR300 [initial metal concentration = 5 mg L^{-1} for Ni(II), Zn(II), Cu(II), 2 mg L^{-1} for Cd(II) and 25 mg L^{-1} for Pb(II), contact time = 60 min, volume = 5 mL, (n=3)].

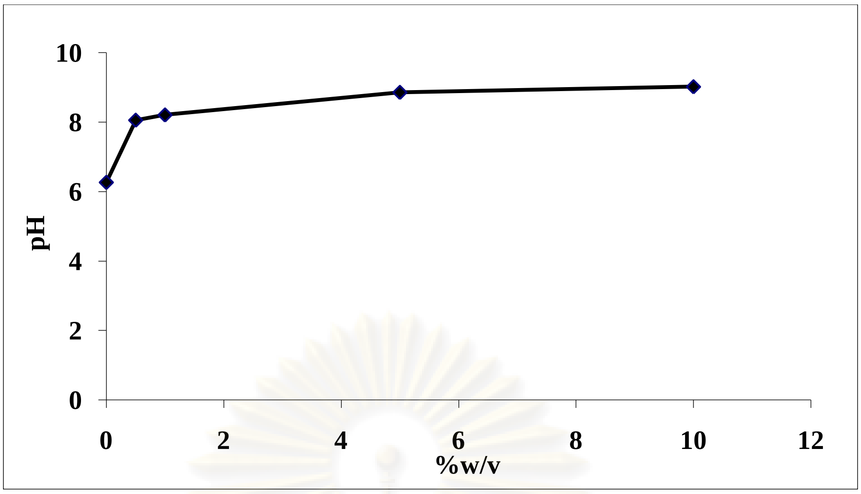


Figure 4.8 The point of zero charge of CTAB-CCR500 determined by Mass titration.

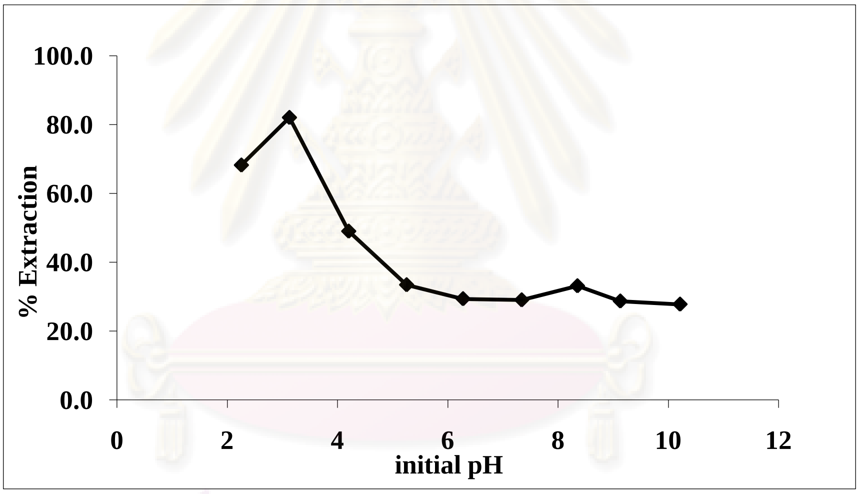


Figure 4.9 Effect of pH on adsorption of chromate by CTAB-CCR500 [initial chromate concentration = 5 mg L^{-1}, contact time = 60 min, volume = 5 mL, (n=3)].

The effect of pH on the adsorption of chromate is shown in Figure 4.9. In this process, the anion is not a simple monovalent anion but rather a series of chromate anions depending upon the pH and concentration of the solution. The chromate maybe represented in various forms such as H_2CrO_4, $HCrO_4^-$, CrO_4^{2-}, $HCr_2O_7^-$ and $Cr_2O_7^{2-}$ in the solution phase as a function of pH and concentration. At pH 1, chromium ions exist in the form of $HCrO_4^-$, while in the pH range of 2-6, different forms of chromium ions such as $HCrO_4^-$, CrO_4^{2-} and $Cr_2O_7^{2-}$ coexit, being $HCrO_4^-$

predominant. As the pH increases, this form shifts to CrO_4^{2-} and $Cr_2O_7^{2-}$[34]. From the result, at the pH 3 the maximum adsorption of Cr(VI) species on the CTAB-CCR500 occurred because the present species are $HCrO_4^-$ ions. The $HCrO_4^-$ anion could displace the surfactant counter ion; Br^-, from the surface of CTAB-CCR500 forming $[CCR500\text{-}CTA]^+[HCrO_4]^-$. The equivalents of $[CCR500\text{-}CTA]^+$ and $[HCrO_4]^-$ should be equal resulting in zero net charge on the surface (charge balance).

4.3.2 Effect of contact time

The contact time of metal ions is one of important parameters in the study of adsorption kinetics of metal ions. The effect of contact time of metal ions was studied using metal solution at pH 2 which is an optimum pH. A suspension of 20 mg of CCR300 and CTAB-CCR500 and 5 mL of metal ions solution in a test tube was stirred for different times between 5-120 min at room temperature. The aqueous solution was taken off and the amount of residual metal ions in the solution was determined by FAAS.

The results of each metal extraction as a function of time are shown in Figure 4.10. The contact time of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) reached the plateau value after 30 min because the strong acid cation exchanger has fast kinetics in the uptake of transition metals [35]. While the contact equilibrium time of chromate was found to be 90 min as long sorption kinetics because chromate ions are large molecules, the time to extract chromate ions from aqueous solution would be longer than that of metal ions which are smaller than the formers.

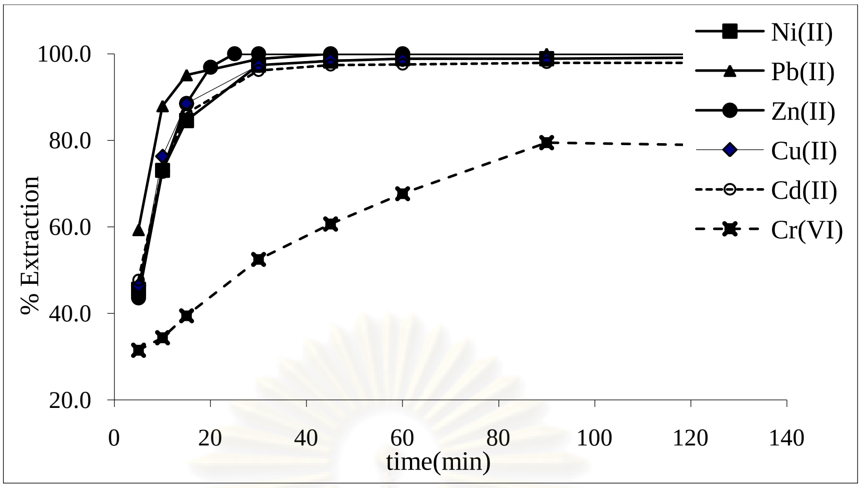


Figure 4.10 Effect of contact time on adsorption of Cd(II), chromate, Cu(II), Ni(II),Pb(II) and Zn(II) [initial metal concentration = 5 mg L^{-1} for Ni(II), Zn(II), Cu(II), 2 mg L^{-1} for Cd(II), 25 mg L^{-1} for Pb(II) and 5 mg L^{-1} for chromate, (n=3)].

4.3.3 Adsorption kinetics

The kinetics of metal ions adsorption on CCR300 and CTAB-CCR500 were investigated using the pseudo-first order equation proposed by Lagergren [16] and the pseudo-second order kinetic model proposed by McKay [17]. The linear forms of the pseudo-first order and pseudo-second order equation are given by the following Equations (4.3) and (4.4), respectively. The derived equation of linearized pseudo-second order equation is expressed by Equation (4.6), in which *h* value is defined by equation (4.5).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t \qquad (4.3)$$

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \qquad (4.4)$$

$$h = k_2 {q_e}^2 \qquad (4.5)$$

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t \qquad (4.6)$$

Where q_t = adsorption capacity at time t (mg g^{-1})
q_e = adsorption capacity at equilibrium (mg g^{-1})
k_1 = rate constant of pseudo first order adsorption (l min^{-1})
k_2 = rate constant of pseudo second order adsorption (g mg^{-1} min^{-1})
h = initial sorption rate constant (mg g^{-1} min^{-1})

The pseudo-first order and pseudo-second order models for the adsorption of metal ions are shown in Figure 4.11 and 4.12, respectively. The comparison between experimental data and the model predicted values was expressed by correlation coefficients (R^2, values close or equal to 1).

As a result, the calculated correlation coefficients are close to 1 for pseudo-second order kinetics model than pseudo-first order kinetics model. These results indicated that the studied adsorption process agreed with the pseudo-second order kinetics model. From the literature, the pseudo-second order kinetics model includes different sorptions such as surface complexation, ion exchange, etc. [36]. The assumption of the model is based on the rate-limiting step may be chemical sorption involving valence force through sharing or exchange of electrons between adsorbent and adsorbate [37].

The pseudo-first order and pseudo-second order kinetics models parameters used to evaluate the experimental data are summarized in Table 4.3 and 4.4, respectively. The k_1 and k_2 values for the metal ions were in the range of 0.0025–0.0166 (min^{-1}) and 0.03-0.6 (g mg^{-1} min^{-1}), respectively. The h values for the metal ions were in the order of 0.1-0.7 (mg g^{-1} min^{-1}). The k_2 and h indicate that the adsorption process is fast. The values of calculated adsorption capacity at equilibrium; $q_{e(\mathrm{cal})}$, are very close to those of experimental adsorption capacity at equilibrium; $q_{e(\mathrm{exp})}$, showing that the pseudo-second order kinetics model is valid.

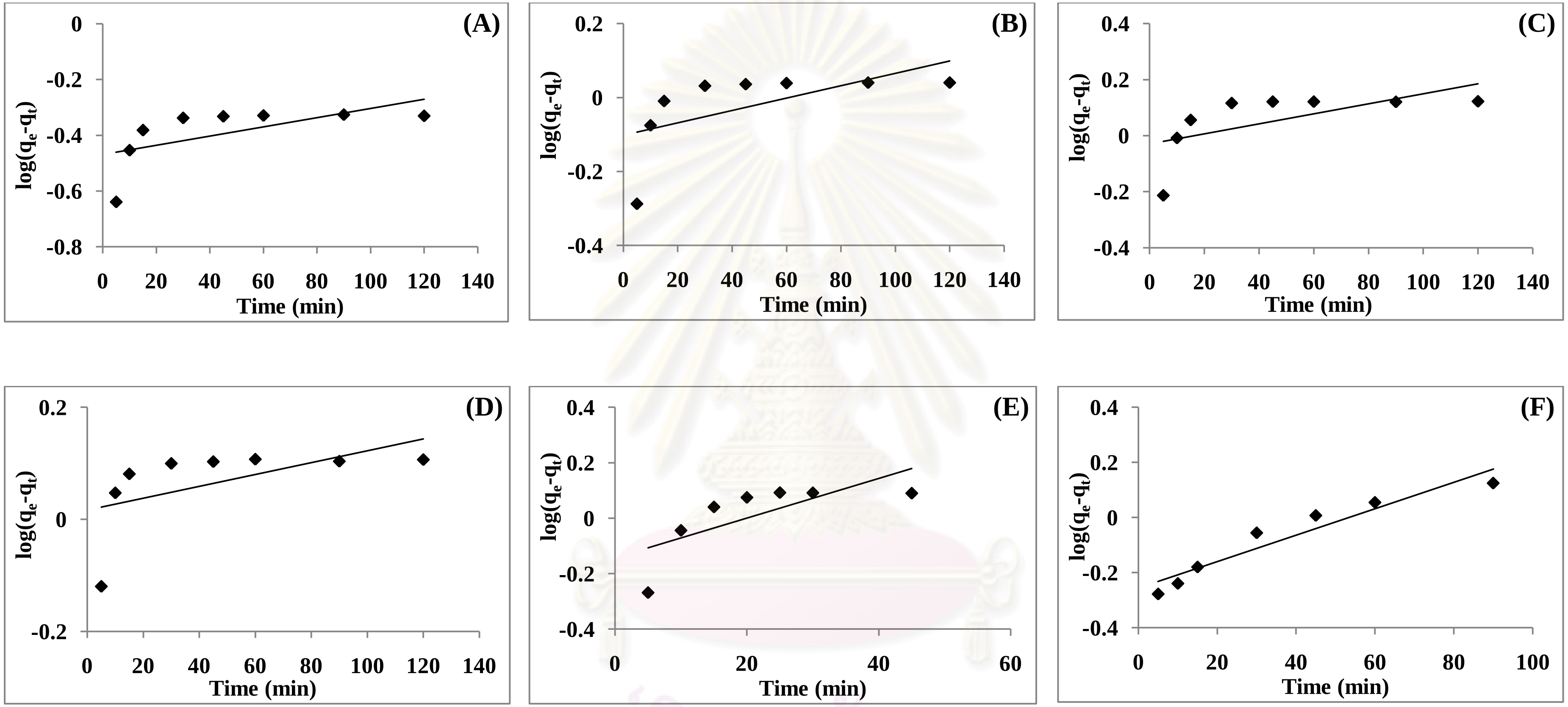


Figure 4.11 Pseudo-first order kinetics plots of adsorption of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions [initial metal concentration = 5 mg L^{-1} for Ni(II), Zn(II), Cu(II), 2 mg L^{-1} for Cd(II), 25 mg L^{-1} for Pb(II) and 5 mg L^{-1} for chromate, (n=3)].

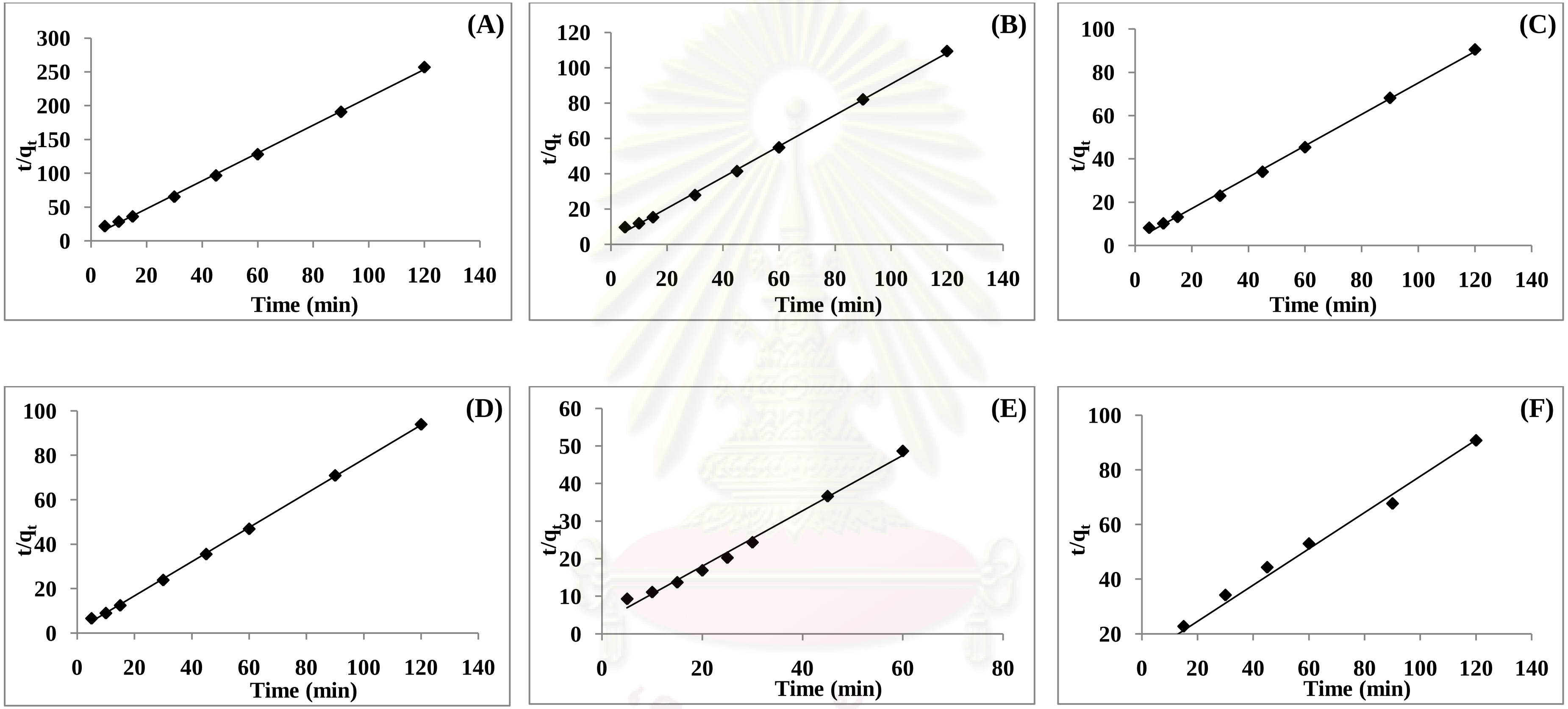


Figure 4.12 Pseudo-second order kinetics plots of adsorption of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions [initial metal concentration = 5 mg L^{-1} for Ni(II), Zn(II), Cu(II), 2 mg L^{-1} for Cd(II), 25 mg L^{-1} for Pb(II) and 5 mg L^{-1} for chromate, (n=3)].

Table 4.3 Pseudo-first order kinetics constant for adsorption of metal ions

Metal ions	**Equations**	**R^2**	k_1 **(min^{-1})**	$q_{e\,(exp)}$ **(mg/g)**	$q_{e\,(cal)}$ **(mg/g)**
Pb(II)	y = 0.0011x + 0.0164	0.3120	0.0025	1.3	1.0
Cu(II)	y = 0.0017x – 0.1016	0.3611	0.0039	1.1	0.8
Cd(II)	y = 0.0016x – 0.4687	0.3829	0.0037	0.5	0.3
Ni(II)	y = 0.0018x – 0.0290	0.3844	0.0041	1.3	0.9
Zn(II)	y = 0.0072x – 0.1430	0.5293	0.0166	1.2	0.7
Chromate	y = 0.0048x – 0.2559	0.9184	0.0111	1.2	0.6

Table 4.4 Pseudo-second order kinetics constant for adsorption of metal ions

Metal ions	**Equations**	**R^2**	k_2 **(g mg^{-1} min^{-1})**	$q_{e\,(exp)}$ **(mg/g)**	$q_{e\,(cal)}$ **(mg/g)**	h **(mg g^{-1} min^{-1})**
Pb(II)	y = 0.7687x + 1.3516	0.9995	0.4372	1.3	1.3	0.7
Cu(II)	y = 0.8794x + 2.8420	0.9988	0.2721	1.1	1.1	0.3
Cd(II)	y = 2.0597x + 6.4715	0.9988	0.6556	0.5	0.5	0.1
Ni(II)	y = 0.7257x + 2.5453	0.9986	0.2069	1.3	1.4	0.4
Zn(II)	y = 0.7365x + 3.2605	0.9908	0.1663	1.2	1.4	0.3
Chromate	y = 0.6635x + 11.317	0.9882	0.0389	1.2	1.5	0.1

4.3.4 Effect of initial concentration and adsorption isotherm study

The effect of initial metal concentration was evaluated using the following procedure; a suspension of 20 mg of CCR300 and CTAB-CCR500 in 5.00 mL of metal ions solution of which the concentration were varied between 5- 400 mg L^{-1} of Cu(II) and Ni(II), 5-300 mg L^{-1} of Cd(II), 15-1000 mg L^{-1} of Pb(II), 5-500 mg L^{-1} of Zn(II) and 5-50 mg L^{-1} for chromate at pH 2-3 and the contact time was 45 min. The temperature was controlled at 25 ± 0.5°C.

Adsorption isotherm

Figure 4.13 shows the maximum sorption capacity of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions with the initial concentration of 30 mg L^{-1} for chromate, 200 mg L^{-1} for Cd(II), 250 mg L^{-1} for Cu(II) and Ni(II), 300 mg L^{-1} for Zn(II), and 500 mg L^{-1} for Pb(II). The estimated maximum sorption capacities of CCR300 for Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) adsorption were found to be 28.9, 34.7, 31.9, 89.6 and 39.4 mg g^{-1}, respectively, while the maximum capacity of CTAB-CCR500 for chromate was 4.3 mg g^{-1}.

Adsorption isotherm is a very convenient way of presenting the variation of sorption with respect to the concentration of adsorbate in the bulk solution at constant temperature. Sorption data are described by Langmuir and Freundlich adsorption isotherms. The Langmuir adsorption isotherm was used to describe sorption phenomena and applied to adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules [38]. The Langmuir isotherm is represented by the following equation (4.7).

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (4.7)$$

where C_e = equilibrium concentration of adsorbate in aqueous solution (mg L^{-1} or mol L^{-1})

q = adsorption capacity of adsorbent (mg g^{-1} or mol g^{-1})

q_m = maximum adsorption capacity of adsorbent (mg g^{-1} or mol g^{-1})

b = Langmuir constant related to the affinity of binding sites
($\mathrm{L\ mg^{-1}}$ or $\mathrm{L\ mol^{-1}}$)

The Freundlich adsorption isotherm is an empirical model used to describe adsorption in aqueous systems and used for the heterogeneous surface. The isotherm is presented by the following equation (4.4).

$$\log q = \log K_f + \frac{1}{n}\log C_e \qquad (4.8)$$

where K_f = Freundlich constant related to adsorption capacity
($\mathrm{mg\ g^{-1}}$ or $\mathrm{mol\ g^{-1}}$)
n = Freundlich constant related to adsorption intensity

The experimental data of initial metal concentration were taken for linear plotting using Langmuir and Freundlich models (Figures 4.14 and 4.15). The Langmuir and Freundlich parameters were also calculated and listed in Table 4.5 and 4.6, respectively.

As seen in Table 4.5, the correlation coefficients (R^2) are considerably high for Cd(II), chromate, Cu(II), Ni(II), Pb(II) and Zn(II) ions ($R^2 > 0.99$). Therefore the Langmuir isotherm model is valid for these ions. It could be assumed that the adsorption was monolayer and adsorption sites were uniformly distributed. As Langmuir constant (b) was in the range of 0.55×10^4 – 3.87×10^4 ($\mathrm{L\ mol^{-1}}$) corresponds to strong binding affinity, it could conclude that the adsorbent had strong binding affinity to metal ions. Moreover, Langmuir adsorption isotherm allows to estimate the maximum adsorption capacity of CCR300 as follow: Cd(II) > Ni(II) > Cu(II) > Zn(II) > Pb(II). The experimental and calculated maximum adsorption capacity values are in the same magnitude, comfirming that the adsorption behavior obeyed Langmuir isotherm model. The CCR300 in the present study showed higher adsorption capacities for metal ions compared with the adsorption capacities of sawdust adsorbent [6].

In the case of the Freundlich isotherm, in Table 4.6 shows the $R^2 < 0.99$ that indicated that the Freundlich isotherm model was not valid for these ions.

Table 4.5 Parameters of Langmuir isotherm for sorption of metal ions

Metal ions	**Equation**	**R^2**	$q_{m,\mathrm{cal}}$ **(mg/g)**	$q_{m,\mathrm{exp}}$ **(mg/g)**	$b \times 10^4$ **(L/mol)**
Pb(II)	y = 0.0112x + 0.0619	0.9990	89.3	89.6	3.75
Cu(II)	y = 0.0285x + 0.0468	0.9992	35.1	34.7	3.87
Cd(II)	y = 0.0338x + 0.1470	0.9984	29.6	28.9	2.59
Ni(II)	y = 0.0302x + 0.0997	0.9992	33.1	31.9	1.78
Zn(II)	y = 0.0249x + 0.0942	0.9989	40.2	39.4	1.73
Chromate	y = 0.1906x + 1.7932	0.9901	5.3	4.3	0.55

Table 4.6 Parameters of Freundlich isotherm for sorption of metal ions

Metal ions	**Equation**	**R^2**	K_f **(mg/g)**	n
Pb(II)	y = 3.7759x – 5.0580	0.9667	89.6	0.265
Cu(II)	y = 4.2703x – 4.6098	0.9654	34.7	0.234
Cd(II)	y = 3.4199x – 3.0838	0.9690	28.9	0.292
Ni(II)	y = 3.0842x – 2.8418	0.9251	31.9	0.324
Zn(II)	y = 3.0151x – 2.8873	0.8400	39.4	0.332
Chromate	y = 2.1311x + 0.1961	0.9672	4.2	0.469

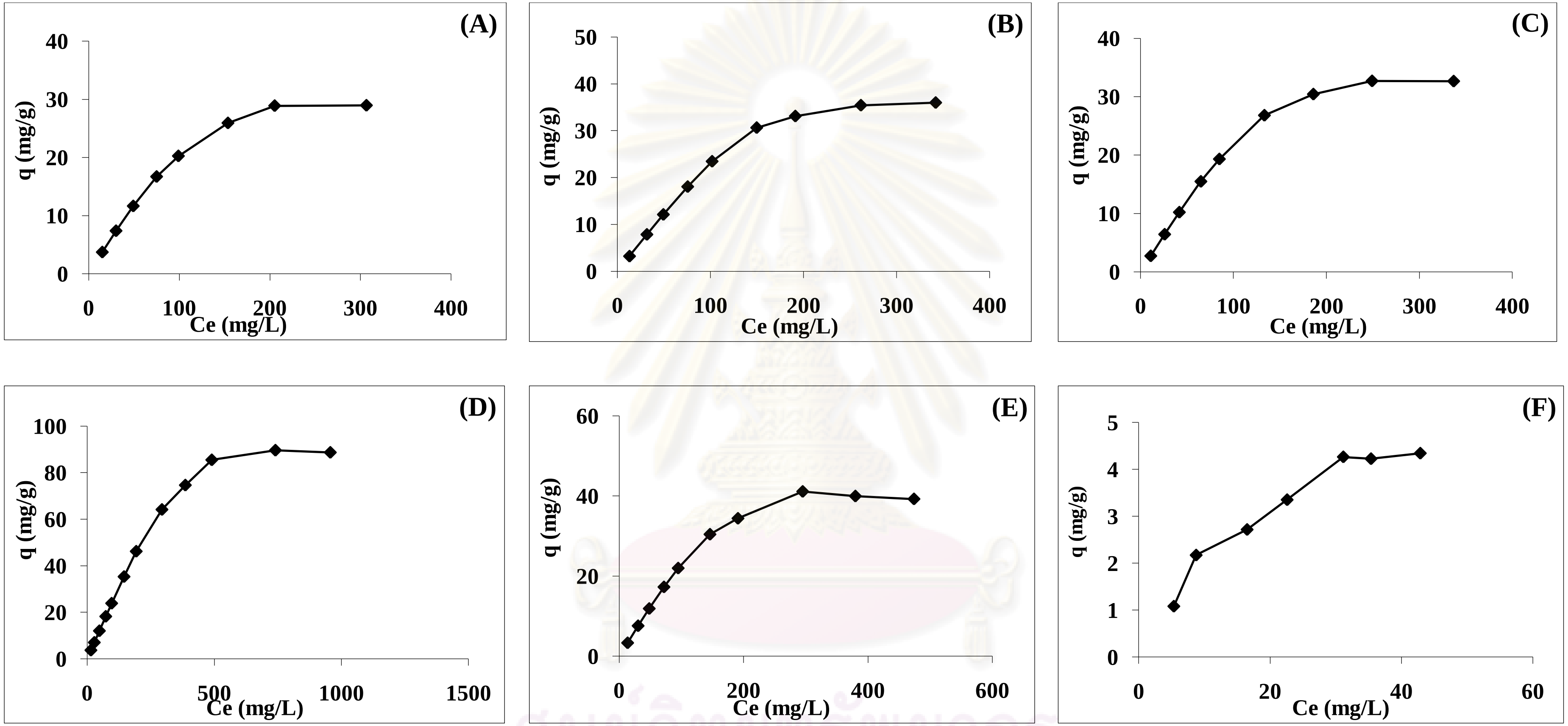


Figure 4.13 Adsorption isotherm of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions at 25.0 ± 0.5°C [initial concentration 5- 400 mg L^{-1} for Cu(II) and Ni(II), 5-300 mg L^{-1} for Cd(II), 15-1000 mg L^{-1} for Pb(II), 5-500 mg L^{-1} for Zn(II) and 5-50 mg L^{-1} for chromate volume = 5 mL, contact time 45 min and 90 min for chromate, (n = 3)].

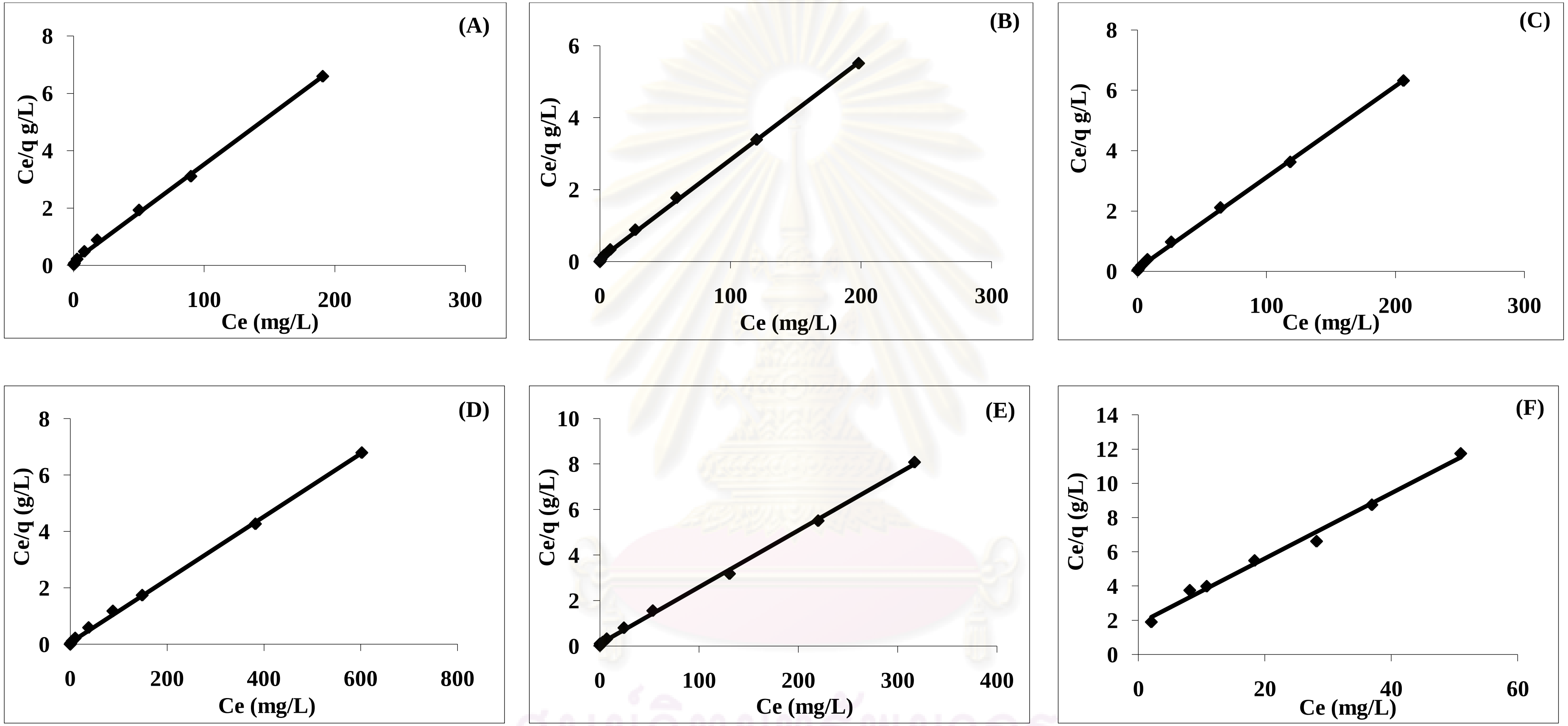


Figure 4.14 Langmuir isotherm plots of adsorption of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ion at 25.0 ± 0.5°C (initial concentration 5- 400 mg L^{-1} for Cu(II) and Ni(II), 5-300 mg L^{-1} for Cd(II), 15-1000 mg L^{-1} for Pb(II), 5-500 mg L^{-1} for Zn(II) and 5-50 mg L^{-1} for chromate volume = 5 mL, contact time 45 min and 90 min for chromate, n = 3).

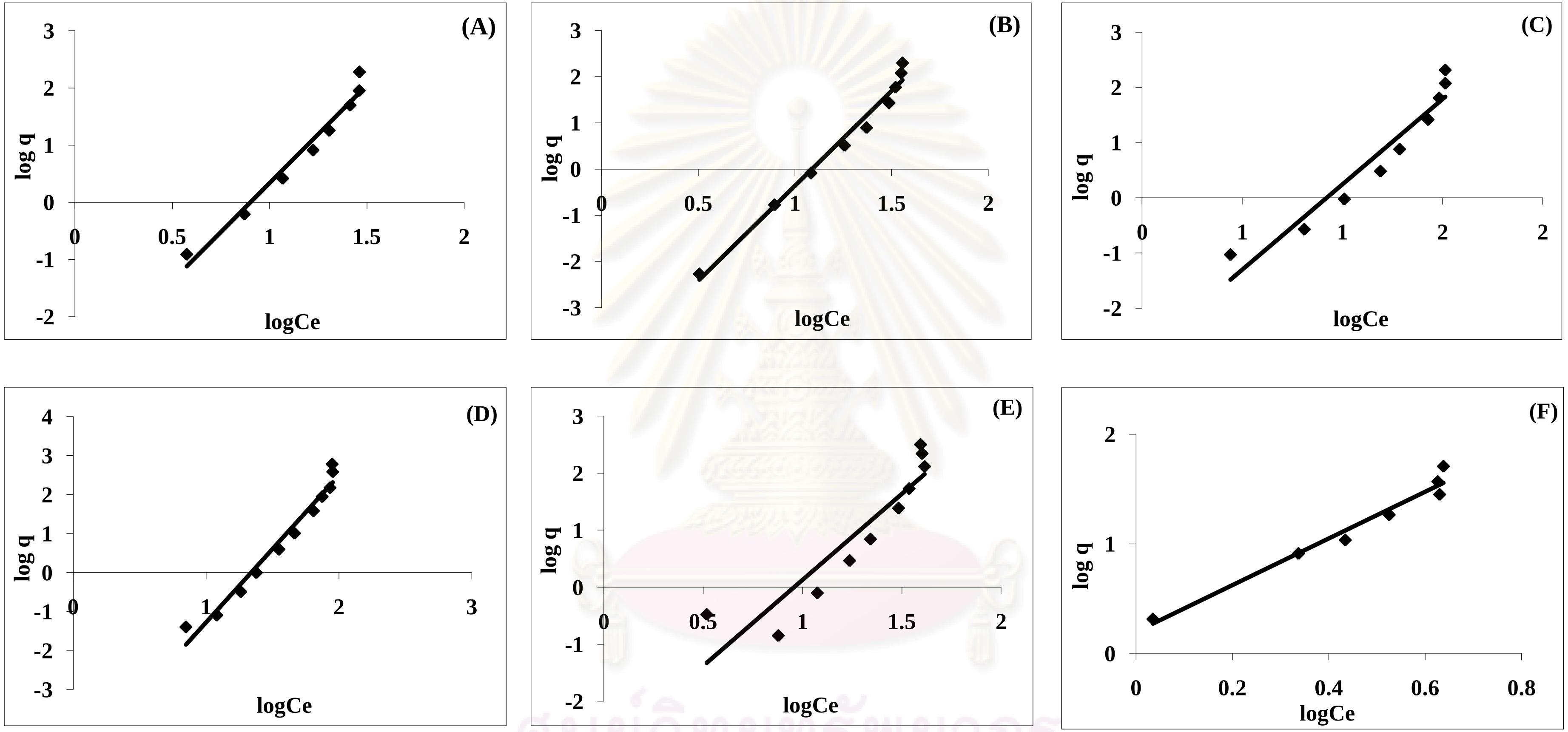


Figure 4.15 Freundlich isotherm plots of adsorption of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions at 25.0 ± 5 (initial concentration 5- 400 mg L^{-1} for Cu(II) and Ni(II), 5-300 mg L^{-1} for Cd(II), 15-1000 mg L^{-1} for Pb(II), 5-500 mg L^{-1} for Zn(II) and 5-50 mg L^{-1} for chromate volume = 5 mL, contact time 45 min and 90 min for chromate, n = 3).

4.4 Adsorption study using column extraction

In column method, the flow rate of Cd(II), Cu(II), Ni(II), Pb(II), Zn(II) and chromate ions was investigated. The results are shown in Figure 4.16.

The solution flow rate was examined at the flow rates of 1-8 mL/min. As results, the percentage extraction of Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) on CCR300 at the flow rates of 0.5-2.0 mL min^{-1} are 51-74, 54-61, 56-70, 66-78 and 54-67, respectively. At higher flow rates, the percentage extraction was lower. At the flow rates of 2.0-6.0 mL min^{-1}, the percentage extraction of Cd(II) was almost constant between 38 up to 45. For Ni(II), the percentage extraction was constant at 35 at the flow rates of 4.0-6.0 mL min^{-1}. At the flow rates of 6.0-9.0 mL min^{-1}, the percentage extraction of Zn(II) was constant at 30. The percentage extractions of Pb(II) and Cu(II) decreased gradually as the increase of the flow rate. For CTAB-CCR500, at the flow rate less than 1 mL min^{-1}, the percentage extraction was 16-48 and the percentage extraction was constant at the flow rates of 1.5-3.7 ml min^{-1}.

Thus, the maximum sorption of metal ions was obtained at the flow rates less than 2 mL min^{-1}. However, a decrease in the percentage of extraction was observed at the flow rates greater than 2.0 mL min^{-1} due to the insufficient contact time of the feed solution with the sorbent. The percentage extraction depends on contact time between the solute and the adsorbent. At the flow rate less than 2 mL min^{-1}, the solution was passed through the column slowly, the metal solution and the adsorbent could be contacted for long time, so the percentage extraction increased.

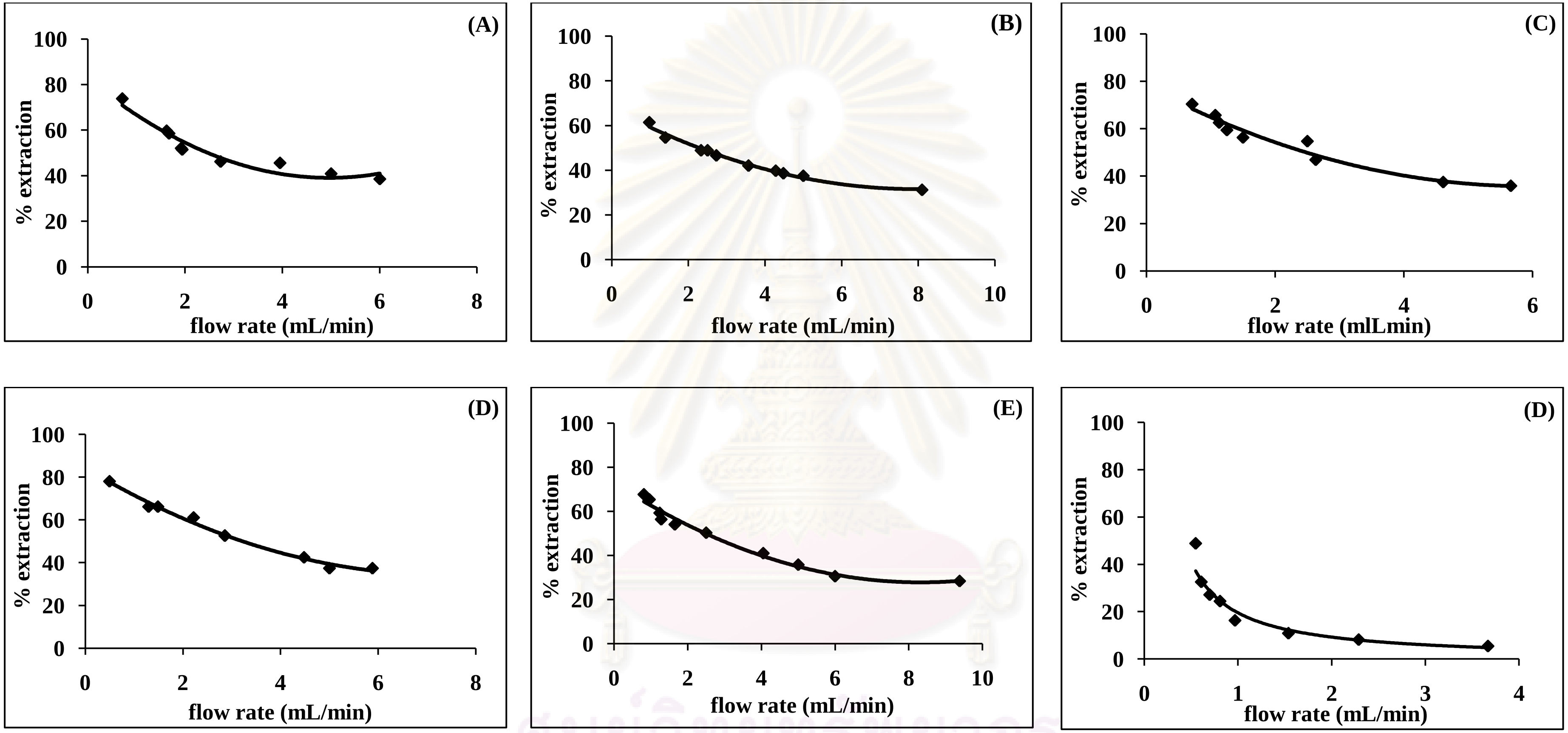


Figure 4.16 Column extraction of (A) Cd(II), (B) Cu(II), (C) Ni(II), (D) Pb(II), (E) Zn(II) and (F) chromate ions [CCR300 and CTAB-CCR500 = 100 mg, initial concentration = 0.0001 M: corresponding to 5.8 mg L^{-1} for Ni(II), 6.5 mg L^{-1} for Zn(II), 11.2 mg L^{-1} for Cd(II), 6.3 mg L^{-1} for Cu(II), 20.7 mg L^{-1} for Pb(II) and 11.6 mg L^{-1} for chromate].

4.5 Application to real wastewater sample

The CCR300 was applied to remove Ni(II) in real wastewater sample from a Ni alloy industry under the optimum conditions in column and batch method. The batch experiments were performed in triplicate (n=3).

Column method

The wastewater was firstly filtered and the pH of sample solution was measured. The concentration of Ni(II) ions in the wastewater was determined before being used in the extraction experiments. It was found that the pH of the wastewater was 7.5 and the concentration of Ni(II) ions was 10.82 mg L^{-1}. The extraction experiments were performed by using 0.1 g of CCR300, 10.0 mL of sample solution, the flow rate of 2.0 mL min^{-1} and the adsorbent was consecutively used for 12 times.

Figures 4.17 shows in the first time that the adsorbent could extract Ni(II) ions of 70% extraction. Then the percentage extraction decreased slowly. From 3 to 10 times of use corresponding to the treated volume of 30-100 mL, the percentage extraction was constant and then it was decreased gradually upon the times due to the reduction of exchange or adsorbing active sites on the adsorbent surface.

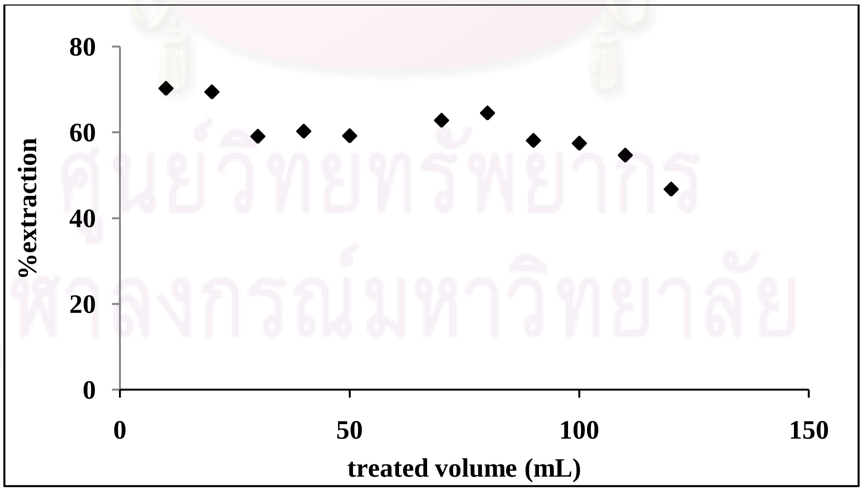


Figure 4.17 Usability of CCR300 column for removal of Ni(II) ions (CCR300 = 0.1 g, sample solution = 10 mL of each fraction, flow rate = 2.0 mL min^{-1}).

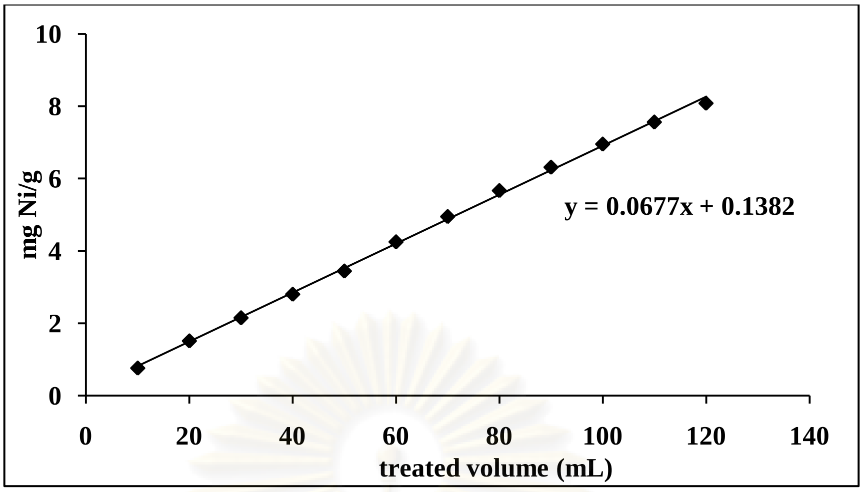


Figure 4.18 Cumulative amount of Ni(II) ions on CCR300.

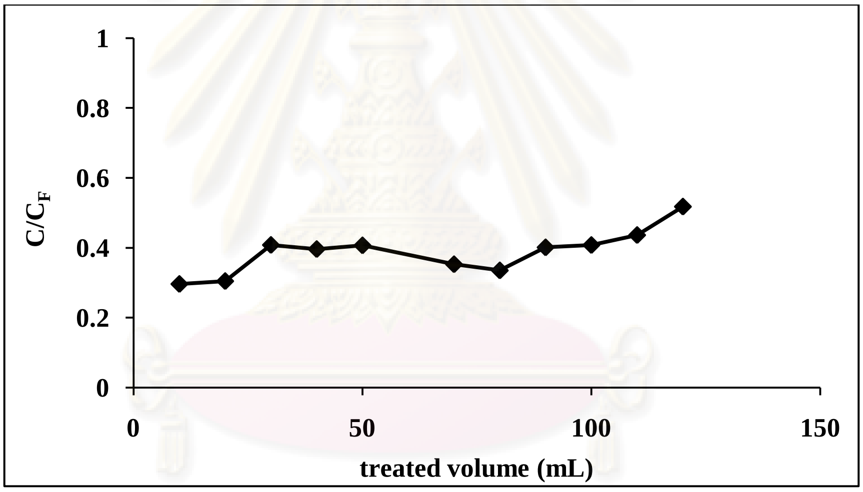


Figure 4.19 Breakthrough curve of removal of Ni(II) ions in wastewater.

Figure 4.18 shows the cumulative amount of Ni(II) ions on CCR300 which was plotted the amount of Ni(II) on CCR300 (mg g^{-1}) versus the treated volume of sample solution (mL). It was found that the amount of Ni(II) ions adsorbed onto CCR300 increased continuously when increasing the treated volume. The cumulative adsorbed amount of Ni(II) after 120 mL of treated sample volume reached about 8 mg g^{-1} which was much lower than the maximum adsorption capacity calculated from Langmuir isotherm (~33 mg g^{-1}). This observation suggests that CCR300 could adsorb more Ni(II).

In principle the breakthrough curves is plotted between normalized concentration (C/C_F) against time or treated volume, where normalized concentration (C/C_F) is defined as the measured concentration in the mobile phase (C) divided by the feed concentration in the mobile phase (C_F). The breakthrough curves (Figure 4.19) shows that the amount of metal present in the solution was removed by sorbent inside a continuous packed bed column system [39]. As seen in Figure 4.19, the breakthrough curve was plotted between Ni(II) concentration in the solution (C/C_F) and treated volume (mL). It was found that the amount of Ni(II) present in the solution was removed with the CCR300 inside a column system. Generally, the breakthrough curve is S shape but in this experiment the graph is still contant and gradually increased until 100 mL of treated volume, showing that the S shape may start. This point is defined as the breakthrough volume (V_B) [40]. The S shape and the appearance of the breakthrough point describe a typical behavior of adsorbate inside column system and breakthrough curve is use for the adsorption column design which is studied with the help of sorption isotherm [39]. However, a second point on a starting plateau of the breakthrough curve defined as the maximum treated sample volume (V_M) was not achieved due to the very high sorption capacity of CCR300. The experiment was not continued until the V_M caused by the limitation of the wastewater volume collected from the industry.

Batch method

The extraction experiments were performed by using 0.1 g of CCR300, 10.0 mL of sample solution with the contact time of 45 min. The result showed that the percentage of extraction was 99.35%, 0.40% RSD, so CCR300 0.1 g could be nearly removed all Ni(II) ions in the wastewater.

In conclusion, the application for real wastewater from Ni alloy industry was investigated. The result showed that CCR300 could be used as adsorbent to remove Ni(II) ions in real wastewater.

Comparison of batch and column extraction

The comparison of column and batch extraction indicated that in the first time, the percentage of extraction of Ni(II) ions was about 70%. On the other hand, from batch extraction, the percentage of extraction was around 99%. Thus, the batch extraction was more efficient than the column extraction because Ni(II) ions had more contact time with CCR300 surface. The suggestion for improvement of extraction efficiency for Ni(II) ions from wastewater by using column are as follows: (i) the flow rate of the feed solution should be reduced, (ii) the recirculation of the feed solution should be done and (iii) more CCR300 amount should be used.

CHAPTER V

CONCLUSION

The carbonized sulfonated polystyrene cation exchange resin waste was successfully prepared by carbonization at 300-500°C for 3 hours and the materials were characterized by Fourier transform infrared spectrometry (FT-IR) and thermal gravimetric analysis (TGA). The cation exchange resin carbonized at 300°C (CCR300) could adsorb cations in aqueous solution such as Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II). Chromate ions were adsorbed by cation exchange resin carbonized at 500°C (CCR500) and modified by 0.5 mM cetyl trimethylammonium bromide (CTAB).

In batch extraction, the adsorbent was put into contact with metal ions solution. Various parameters affecting the adsorption efficiency were studied. The optimal initial pH of metal ions solution was in the range of pH 2-10 for Cd(II), Cu(II), Ni(II), Zn(II) and chromate and pH 2-6 for Pb(II). The equilibrium contact times were 30 and 90 minutes for cations and chromate ion, respectively. The initial metal ions solution was varied between 5- 500 mg L^{-1}. The adsorption behaviors of all metal ions fitted well the pseudo-second order kinetics and Langmuir adsorption isotherm. The high value of Langmuir constants (*b*) showed that adsorbent had strong binding affinity to metal ions and the adsorption was monolayer.

In column extraction, the solution flow rates were studied. The smaller the flow rates, the higher the extraction percentage.

The optimal operating conditions in both batch and column methods for adsorption of metal ions are summarized in Table 5.1.

Table 5.1 Optimal operating conditions for adsorption of metal ions

	Cd(II)	**Cu(II)**	**Ni(II)**	**Pb(II)**	**Zn(II)**	**Chromate**
Batch extraction						
Solution pH	2-10	2-10	2-10	2-6	2-10	3
Contact time	45	45	45	45	45	90
Maximum adsorption capacity (mg g^{-1})	28.9	34.7	31.9	89.6	39.4	4.3
Column extraction						
Flow rate (mL min^{-1})	< 2	< 2	< 2	< 2	< 2	< 2

Furthermore, the CCR300 was applied for the removal of Ni(II) ion from real wastewater sample under the optimal adsorption conditions using batch and column method. The results showed a good adsorption and the extraction percentage of nearly 99% was achieved in batch method.

In conclusion, exhausted cation exchange resin could be successfully reused as an adsorbent after being thermally treated and chemically modified for removal of various cations and chromate ion present in aqueous solution.

Suggestionsfor the future woks:

- The present method should be applied to the adsorption of all metal ions in real sample as wastewater from other industry.
- CCR500 should be modified with other surfactants such as dioctyl dimethyl ammonium chloride $[(C_8H_{17})_2(CH_3)_2NCl]$ for comparison of effect of hydrocarbon chain on the attraction onto the surface of CCR500. Longer hydrocarbon chain may improve the loaded amount of surfactant resulting in higher adsorption efficiency towards anions.
- CCR500 should be activated by activating reagent such as phosphoric acid or potassium hydroxide or sodium hydroxide or zinc chloride for improvement of CCR500 like commercial activated carbon.

- The column extraction of other metal ions should be studied.

REFERENCES

[1] Pehlivan, E., and Altun, T. "The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+} and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin" *J. Hazard. Mater*. 2006, *B134*, 149-156.

[2] Pulido, L.L.; Hata, T.; Imamura, Y.; Ishihara, S., and Kajimoto, T. "Removal of mercury and other metals by carbonized wood powder from aqueous solution of their salts" *J. Wood Sci*. 1998, *44*, 237-243.

[3] HPLC separation modes. [online] avaiable from: http://www.waters.com/waters [2011, March 3]

[4] March, H., and Reinoso, R. "Activated carbon" *Elsevier*, 2006.

[5] Kunin, R. "The use of macroreticular polymeric adsorbents for the treatment of waste effluents" *Pure Appl. Chem*. 1976, *46*, 205-211.

[6] Yang, J.S.; Oark, T.Y.; Baek, K., and Choi, J. "Removal of metal ions from aqueous solutions using sawdust modified with citric acid or tartaric acid" *Separ. Sci. Technol.* 2010, *45*, 1963-1974.

[7] Yu, B.; Zhang, Y.; Shukla, A.; Shukla, S.S., and Dorris, K.L. "The removal of heavy metal from aqueous solutions by sawdust adsorption – removal of copper" *J. Hazard. Mater*. 2000, *B80*, 33-42.

[8] Wang, Q.; Liang, X.; Qiao W.; Liu C.; Liu, X.; Zhang, R., and Ling, L. "Modification of polystyrene-based activated carbon spheres to improve adsorption of dibenzothiophene" *Appl . Surf. Sci*. 2009, *255*, 3499-3506.

[9] Aoyama, M., et al. "Removal of inorganic mercury from aqueous solutions by carbonized waste newsprint fiber" *Environ. Technol.* 2000, *21*, 1013-1018.

[10] Namasivayam, C., and Kadirvelu, K. “Uptake of mercury(II) from wastewater by activated carbon from an unwanted agricultural solid by-product: coirpith” *Carbon*. 1999**,** *37*, 79-84.

[11] Ali, P.A.; Reza, M.M., and Hossein, S.M. “Removal of dissolved organic carbon by multi-walled carbon nanotubes, powdered activated carbon and granular activated carbon” *Res. J. Chem. Environ.* 2010, *14*, 59-66**.**

[12] Bansal, R.C., and Goyal, M. “Activated carbon adsorption” *Taylor & Francis*, 2005.

[13] Adsorption process. [online] avaiable from: http://pradthana.wordpress.com/ [2011, February 13]

[14] Goldberg, S.; Criscenti, L.J.; Davis, J.A., and Cantrell, K.J. “Adsorption-desorption process in surface reaction modeling” *Vadose Zone J*. 2007, *6*, 407-435.

[15] Demirbas, E.; Kobya, M.; Senturk E., and Ozkan, T. “Adsorption kinetic for the removal of chromium (VI) from aqueous solution on the activated carbons prepared from agricultural wastes” *Water SA*. 2004, *30*, 533-539.

[16] Lagergren, S. “About the theory of so-called adsorption of soluble substances” *Handlinger*, 1898, 147, 24.

[17] Ho, Y. S., and Mckay, G. “A two stage batch sorption optimized design for dye removal to minimize contact time” *Trans. IChem. E*. 1998, *76*, 313.

[18] Namasivayam, C., and Periasamy, K. “Bicarbonate-treated peanut hull carbon for mercury(II) removal from aqueous solution. *Water Res*. 1993**,** *27*, 1663-1668.

[19] Pulido, L.L.; Hata, T.; Imamura, Y.; Ishihara, S., and Kajimoto, T. “Removal of mercury and other metals by carbonized wood powder from aqueous solution of their salts” *J. Wood Sci*. 1998, *44*, 237-243

[20] Wartelle, H.L., and Wartelle, E.W. “Chromate ion adsorption by agricultural by-product modified with dimethylodihydroxyethylene urea and choline chloride” *Water Res*. 2005, *39*, 2869-2876.

[21] Krishna, B.S.; Murty, D.S.R., and Parkash, J.B.S. “Surfactant-modified clay as adsorbent for chromate” *Appl. Clay Sci*. 2001, *20*, 65-71.

[22] Hong, J.H.; Kim, H.; Baek, K., and Yang, J.W. “Removal of arsenate, chromate and ferricyanide by cationic surfactant modified powered activated carbon” *Desalination*. 2008, *223*, 221-228.

[23] Rosen, M.J., and Goldsmith, H.A. “Systematic Analysis of Surface-Active Agent”, *Wiley-Interscience*. 1972.

[24] Fiol, N., and Villaescusa, I. “Determination of sorbent point zero charge: usefulness in sorption studies” *Environ. Chem. Lett*. 2009, *7*, 79-84.

[25] Piboonsatsanasakul, P.; Wootthikanokkhan, J., and Thnawan, S. “Preparation and characterization of direct methanol fuel cell membrane from sulfonated polystyrene/poly(vinylidene fluoride) blend compatibilized with poly(styrene)-*b*-poly(methyl methacrylate) block copolymer” *J. Appl. Polym. Sci.*, 2008, *107*, 1325-1336.

[26] Sloan, J.M.; Suleiman, D.; Napadensky, E., and Crawford, M.D. “Thermo Stability of Highly Sulfonated poly(styrene-isobutylene-styrene) Block Copolymers: Effects of Sulfonation and Counter-Ion Substitution” *U.S. Army Research Laboratory* ,2008.

[27] Smitha, B.; Sridhar, S., and Khan, A.A. “Synthesis and characterization of proton conducting polymer membranes for fuel cells” *J. Membrane Sci.*, 2003, *225*, 63-76.

[28] Hwang, H.Y.; Koh, H.C.; Rhim, J.W., and Nam, S.Y. “Preparation of sulfonated SEBS block copolymer membranes and their permeation properties” *Desalination*, 2008, *233*, 173-182.

[29] Zhenga, H.Z.; Panga, D.W.; Lua, Z.X.; Zhanga, Z.L., and Xieb, Z.X. “Combing DNA on CTAB-coated surfaces” *Biophys. Chem.* 2004, *112*, 27–33.

[30] Sakai, T.; Enomoto, H.; Torigoe, K.; Sakai, H., and Abe, M. “Surfactant- and reducer-free synthesis of gold nanoparticles in aqueous solutions” *Colloid Surfaces A*. 2009, *347*, 18–26.

[31] Silvio R., and Jurge, R. “Adsorption of sodium dodecyl benzene sulfonate from aqueous solution using a modified natural zeolite with CTAB” *Miner. Eng.* 2010, *23*, 771-779.

[32] Iqbal, J.; Kim, H.J.; Yang, J.S.; Baek, K., and Yang, J.W. “Removel of arsenic from groungwater by micellar-enhanced ultrafiltration (MEUF)” *Chemosphere.* 2007, *66*, 970.

[33] Zeng, Y.; Woo, H.; Lee, G., and Park, J. “Removal of chromate from water using surfactant modified Pohang clinoptilolite and Haruna chabazite” *Desalination*. 2010, *257*, 102-109.

[34] Gurgel**,** L.V.A.; de Melo**,** J.C.P.; de Lena**,** J.C., and Gil**,** L.F. “Adsorption of chromium (VI) ion from aqueous solution by succinylated mercerized cellulose functionalized with quaternary ammonium groups “*Bioresource Technol.* 2009, *100*, 3214-3220.

[35] Pehlivan, E., and Altum, T. “The study of various parameters affecting the ion exchange of Cu^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, and Pb^{2+} from aqueous solution on Dowex 50W synthetic resin” *J. Hazard. Mater.* 2006, *B134*, 149-156.

[36] Lazarević, S. et al. "Iron-Modified Sepiolite for Ni^{2+} sorption from aqueous solution: an equilibrium, kinetic and thermodynamic study" *J. Chem. Eng.* 2010, *55*, 5681-5689.

[37] Namasivayam, C., and Sureshkumar, M.V. "Removal of chromium(VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent" *Bioresource Technol.* 2008, *99*, 2218-2225.

[38] Atkins, P.W. "Physical chemistry", 5th Edition, *H.W. Freeman and Co.*, New York, 1994, 992.

[39] Ramirez, C.M.; da Silva, P.M.; Selma G.; Ferreira L., and Oscar V.E. "Mathematical models applied to the Cr(III) and Cr(VI) breakthrough curves" *J. Hazard. Mater*. 2007, *146*, 86–90.

[40] Imyim, A., and Prapalimrungsi, E. "Humic acids removal from water by aminopropyl functionalized rice husk ash" *J. Hazard. Mater*. 2010, 184, 775-781.

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