PERFORMANCE OF MAGNETIC-MODIFIED SLUDGE ADSORBENT FOR REMOVAL OF CHROMATE IN AQUEOUS SOLUTION

BY

ATTAJAREE SMATA

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
MASTER OF ENGINEERING (ENGINEERING TECHNOLOGY)
SIRINDHORN INTERNATIONAL INSTITUTE OF TECHNOLOGY
THAMMASAT UNIVERSITY
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A Thesis Presented

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ATTAJAREE SMATA

Submitted to
Sirindhorn International Institute of Technology
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In partial fulfillment of the requirements for the degree of
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Abstract

PERFORMANCE OF MAGNETIC-MODIFIED SLUDGE ADSORBENT FOR REMOVAL OF CHROMATE IN AQUEOUS SOLUTION

By

ATTAJAREE SMATA

Bachelor of Science (Environmental Science), Chulalongkorn University, 2015

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Chromium (VI) ion, an ordinary contaminant occurred in effluent from wide range industries, is known as a toxic to both plants, especially as a major cause of cancer, mutations and human diseases such as liver, skin and kidney malfunction. The objective of this study is to utilization sludge from water treatment process as a raw material for chromate adsorbent and investigate chromate adsorption performance of magnetic-modified sludge adsorbent (MSA) including adsorption kinetics and reusability of the adsorbent and study other parameters that may effect on adsorption process such as pH, temperature, time, adsorbent dose, initial chromate concentration, and competing ions. The characterization results of MSA confirmed that MSA has composite of magnetic particles distributed on sludge modified surface. Utilization of sludge with magnetic modification was shown successfully for chromate removal. An optimum molar ratio of MSA synthesis was 4:1 Ca^{2+}/Al^{3+} (MSA41). The maximum adsorption capacities of MSA was 49.50 mg of chromate/g of MSA by the Langmuir adsorption isotherm model with regression coefficients (R^2) of 1. Kinetic experiments showed that the removal reaction was following pseudo-second order reaction with k = 0.24 mg/g•hours. The optimum dose and initial chromate concentration were 1.0 g/L and 50 mg/L, respectively. Adsorption efficiency of MSA was dependent on pH, in which the adsorption increased with decreasing pH values. The adsorption process was found to be increased with the increase of temperature from 4 to 45°C. The presence of different competitive anions, i.e., bicarbonate, sulfate, nitrate, chloride and phosphate ions significantly affected the chromate removal efficiency. The MSA can be reuse more than 8 times before its chromate removal efficiency dropped lower than 20% by using NaOH solution with 0.1M as eluent solution.

Keywords: Sludge utilization, Chromate, Adsorption, Magnetic nanoparticle

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Chapter 1
Introduction

1.1 Introduction

Chromium (VI) (Cr^{6+}) ion is ordinary contaminant occurred in effluent from wide range industries as stainless steel, painting, metal ceramic and tanning leather etc. [1] that has been one of environmental issues. The chromium ion in industrial effluent is mainly occur stable state compound of trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) [2]. The trivalent chromium is one of the living organism's dietary requirement in daily life but hexavalent chromium ion is known as a toxic to both plants and animals as a reason of its toxicity and carcinogenic properties. Chromium accumulated in soil and groundwater are a serious and significant problem worldwide due to chromium is highly toxic known as the reason for cancer, mutations and human diseases such as liver, skin and kidney malfunction [3].

Chromium removal are a range of methods have been developed include reduction [4], chemical precipitation [5], filtration [6], biological treatment [7], ion exchange [8-10] and adsorption [11-13]. The disadvantages of first five conventional separation methods are the high organized cost, the secondary waste production as a sludge contained chromium and high disposal costs with generation of secondary pollution etc. So, adsorption is the one of remediation techniques that widely applied in the removal of hexavalent chromium occurred wastewater by reasons of its easy operation, low treatment cost and high efficiency of removal [14]. There are many kinds of adsorbents derived from industrial wastes, by-product from manufacturing process and agricultural waste have been reported for the removal of hexavalent chromium such as graphene modified by MgAl-layered double hydroxide compound [15], fertilizer industry waste material [16], activated carbon [17], etc. However, the main problem of using absorbent in wastewater treatment is separation after usage because its small and fine powder adsorbents are hard to recycled after usage [18]. Therefore, magnetic adsorbent (MA) have emerged as an alternative wastewater treatment technology. The MA adsorbents is one of material used because they are easy to separate from liquid phase by applied external magnetic field and possible to repeated use of the adsorbents.

This MA can be synthesized by using co-precipitation method due to this method are high yield and better atom economy. Its magnetic properties provide easy separation both in preparation and recovery [19]. An efficient improvement is the combination of adsorbent with magnetic particle, which possessed the features of both magnetic particle (ease of separation) and adsorbent (surface functionalization). The magnetic modified on adsorbents material can used for environmental remediation or absorption (separation and purification) contaminants in wastewater and significant for accomplishment rapid separation and secondary pollution sheering [20]. The composition of the magnetic adsorbent is dependent on the application. Magnetite (Fe_3O_4) with high oxidative stability advantage is currently the only accepted non-toxic magnetic materials. However, many researcher try to replace many kind of material for improve adsorption efficiency for chromate removal. For example, Fe_3O_4-loaded on mesoporous carbon microspheres had a high chromate adsorption efficiency and can reused more than fifth adsorption–desorption cycle [21].

Therefore, this study is aimed to utilization sludge from water treatment process as a raw material for chromate adsorbent, magnetic modified sludge absorbent preparation and investigate adsorption performance for removal of Cr(VI), including adsorption kinetics and regeneration of spent adsorbent, were evaluated by batch adsorption experiments and to study its effectiveness in removal of Cr(VI) under different experimental conditions including pH, time, temperature, adsorbent dose, initial Cr(VI) concentration, and competing ions.

1.2 Objective of the study

1.2.1 To utilization sludge from water treatment process as a raw material for adsorbent preparation

1.2.2 To synthesize magnetic-modified sludge adsorbent (MSA) for effective separation from wastewater stream

1.2.3 To investigate the removal efficiency of Cr(VI) using MSA adsorbents

1.2.4 To characterize physicochemical properties and morphology of MSA adsorbents

Chapter 2
Literature review

2.1 Chromium

Chromium (Cr), is atomic weight of 51.996 g/mol, is a solid phase of gray steel with a high melting point. Chromium occurs naturally in diversity of oxidation states ranging from Cr(-II) to Cr(+VI) [22]. Chromium is one of the most important raw materials that widely uses in the metals and chemical industries such as leather tanning, metals coating, chemical pigments, catalysts production and refractory process etc. The effluence from those industry, for example tanning industry, contains between 2,000 to 5,000 mg/L. There is over recommended permissible limit of 2.0 mg/L [2].

2.1.1 Chromium in the environment

Chromium can enter the natural water resources by weathering of rocks contained chromate element, leaching of soils, among others. However, the main entire is direct discharge from industrial operations. In the aquatic environment, chromium ions can occur chemical and physical reactions such as sorption, desorption, reduction, oxidation, dissolution and precipitation to charge from of chromium ions [23].

The environmental factors and various physicochemical processes can affect to the variance forms of chromium by transformations and changing from one into another under. As a disruption of the chemical balance of chromium species is mostly depends on pH value [24] as shown in figure2.1 (The oxidation states of chromium spices in groundwater are controlled by pH and Eh.). However, chromium exhibits in several oxidation states in environment, but the main occurrence and most stable forms are the trivalent Cr(III) and the hexavalent Cr(VI) species.

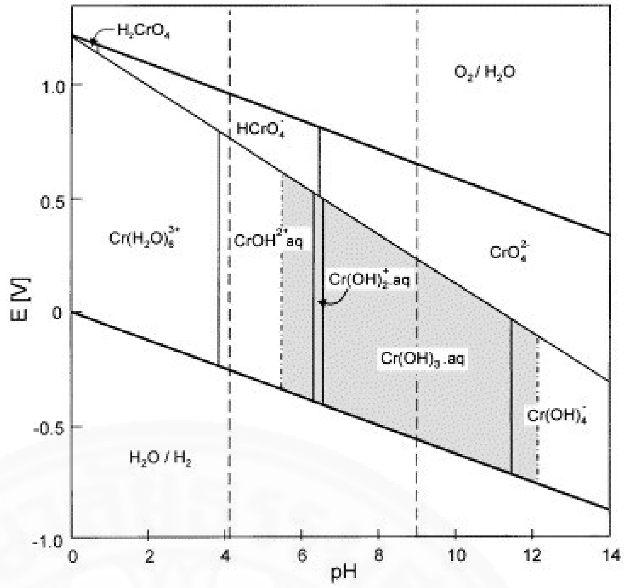

Figure2.1 The pourbaix diagram of variance chromium (Cr) ions species in aqueous solutions [25].

2.1.1.1 Trivalent chromium (Cr(III))

Trivalent chromium is a significant nutrient for the living organisms: it is one part of metabolism carbohydrate, lipid and protein. However, the free Cr(III) ions are biological non-active until they bond with a suitable organic ligand but this properties are not obviously assinged [4]. Cr(III) compounds are quite immobility and poor solubility compared to Cr(VI) compounds that is high mobility, more solubility and bioavailability. This differences properties are offensive to the chemical and biochemical reactivity of both species.

Cr(III) exhibits a strong inclination with a variance solvent such as water, ammonia and other organic compounds containing oxygen, nitrogen to form complexes of hexacoordinate octahedral [25]. The oxides, hydroxides, and sulfates forms of Cr(III) is less toxic due to it is water insoluble, less mobility, and favorable bound with organic matter in soil, sediment and water resources. In addition, Cr(III) can be formed with ferrous ions to hydroxide precipitates at ground water with natural pH values. At high concentrations of manganese oxides or oxygen, Cr(III) can be oxidized to Cr(VI) [26].

In previous, the presence of chromium species is related to pH. Cr(III) normally occur as a hexaaqua complex $Cr(H_2O)_3^{3+}$ and hexaaquachromium could be deprotonated to $Cr(OH)^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3^0$. In nuetral pH range (pH 4-9) in natural water, $Cr(OH)^{2+}$ and $Cr(OH)_3^0$ are the prevalent aqueous forms of Cr(III). At low pH (pH<4), Cr^{3+} hydrolysis and generates $Cr(OH)^{2+}$ and $Cr(OH)_2^+$. When pH increase to alkaline conditions, trivalent chromium can precipitate to $Cr(OH)_3$ which can dissolved and then transformed into $Cr(OH)_4^-$ ion in strong basic condition (pH>12) [26].

2.1.1.2 Hexavalent chromium (Cr(VI))

Hexavalent chromium ions are regarded as toxic forms of chromium due to they have high oxidizing efficiency, high mobility and solubility cause they can pass through the membranes of living organisms [25]. The element chromium in the +6 oxidation state or Cr(VI) is occurred in the chromate ion (CrO_4^{2-}) form and dichromate ion ($Cr_2O_7^{2-}$) form. A variety of characteristics and utilization cause Cr(VI) ions are released to soil in subsurface layer, surface water, and groundwater.

The concentration and pH value has relatively fractions to Cr(VI) ions occurring of solution part. The Cr(VI) in oxyanions form are occur in a natural waters with pH range [27]. At strong acid (below pH 1), Cr(VI) species exhibit H_2CrO_4 form. $HCrO_4^-$ is occurred in solution pH 1-6.5 and/or a Cr(VI) ions concentration lower 10 mmol/L, unless in solution having concentration more than 10 mmol/L Cr(VI) ions occur in form of $Cr_2O_7^{2-}$. As previous, CrO_4^{2-} exhibit at pH solution higher than 6.5 [24].

In addition, Cr(VI) can reduced to Cr(III) follow this three conditions: at acid conditions (low pH), under reducing conditions and when Fe(II) or Mn(II) occur in groundwater.

2.1.2 Toxicity of chromium

The chromium ions (Cr(VI) and Cr(III)) have different properties in parts of physical/chemical characteristics, charge ion, mobility, chemical behavior, bioavailability and toxicity. So, they are differently defined by EPA, which performs an individual characteristic of toxicity of chromium.

Cr(VI) is considered to carcinogen in human and a strong epithelial irritant [3] and it is also toxic to animals, plants and microorganisms. In the other hand, Cr(III) is commonly not harmful and it is necessary metabolism of sugar and lipid and considered a micronutrient in living organism.

In case of particularly crops, low concentrations (0.05-1 mg/L) of chromium is not considered essential to plants but it stimulate plant growth and increase production yield [28]. The bioaccumulation of chromium in plants or crops may evince a potential risk to animal and human health [4].

The United States Environmental Protection Agency (USEPA) and World Health Organization (WHO) consider hexavalent chromium compounds is human carcinogen. Cr(VI) is occurred a carcinogenic in lung, nasal and sinus cancers by the study of toxicological and epidemiologic. The main problem that worldwide concerned about cancer mortality is ingestion/drinking Cr(VI) contaminated drinking water.

Cr(VI) exerts toxic effects on biological systems and ecological system because there was found that many clinical problems are cause from occupational exposure of hexavalent chromium compounds. Inhalation and exposure of materials contained chromium can cause excavation of the nasal septum, asthma, bronchitis, pneumonitis, inflammation of the larynx and liver and may increase potential of bronchogenic carcinoma. Dermal exposure with Cr(VI) compounds may cause skin allergies, dermal corrosion, dermatitis and dermal necrosis.

2.1.3 Chromium(VI) removal

The attendance of chromium is a problem in wastewater streams due to it can affect to human health and other organisms in environment. So, amount of chromium in wastewater and wastewater that is discharged into water resources is seriously controlled and minimized [29].

Chromium removal are a range of many different treatment methods have been developed. Each technologies require information of remediation design, site-specific conditions and creativity in optimization strategies that explained in more detail. The processes include chemical precipitation adsorption/desorption, and biologically remediation that consist of biodegradation and indirectly as microorganisms changing the form of contaminants.

2.1.3.1 Chemical precipitation

The chemical treatment can be accomplished include two steps by the addition of ferrous sulfate ($FeSO_4$) and lime ($Ca(OH)_2$) or sodium hydroxide (NaOH) for the formation of a separable solid substrate [30]. The first step is additional of $FeSO_4$. Ferrous ion reduces Cr(VI) to Cr(III) by simultaneous oxidation of ferrous ion to ferric. And then the second step is addition lime for precipitation by using hydroxide ion (-OH) follow chemical reaction below.

The limitation of this process is process have to added other chemicals, which leads to sludge generation in final process, and the disposal of sludge is cost intensive. Another limitation, pH and the presence of other salted ions affect to efficiency of precipitation and this process is ineffective in removed of low chromium concentration.

$$Cr^{3+} + OH^- \rightarrow Cr(OH)_3$$

(Chromium is precipitated as hydroxide compound)

The previous study [31] reported maximum removal efficiencies of the precipitating agents of sodium hydroxide (94.97%) with initial chromium concentrations of 5010 mg/L at optimum pH values were not significantly different. However, there was a significant difference in sludge volume of NaOH (590 mL), $Ca(OH)_2$ (412 mL) and MgO (85 mL).

2.1.3.2 Adsorption

The seriousness chromium pollution are developed to remediation of Cr contaminated in soils and waters. Chromium ion compound usually behave as a negative charged ion such as $Cr_2O_7^{2-}$ ion when it’s adsorbed onto adsorbent surfaces. As pH decrease in acid conditions, there are increase the attraction between

$Cr_2O_7^{2-}$ and the surface due to surfaces are protonated. Therefore, sorption is enhanced as pH decrease.

Adsorption plays an important role in water and wastewater treatment process and applied environmental technology. Due to the advantages of adsorption technique are high efficiency removal, easy to operation and possible to adsorbent recovery or reuse.

Today, new types of adsorbents are consistently developed. For example Li, Z. *et al.* [32] reported a montmorillonite modified with liquids contain calcium ions can used for chromate removal in aqueous solution, with an adsorption efficiency of 22.04 mg/g. A preparation under acidic conditions of lignin-based resin by sodium lignosulfonate condensation polymerized with glucose can adsorbed chromate with the maximum adsorption capacity 57.681 mg/g [9].

In addition, the waste utilization had also researched for Cr(VI) removal. Hango *et al.* reports concrete sludge used as a raw material in calcium extraction, and then calcium was precipitated with aluminum nitrate for the preparation of Ca-Al layered double hydroxide. The chromate concentrations was decrease of up to 0.4 mg/L from the initial chromate concentration of 180 mg/L [33]. Moreover, the production of microporous activated carbon derived form bael fruit shell with $ZnCl_2$ activation can be also used for removal of chromate. Prepared activated carbon was very practical removal. The maximum removal (82.3%) with adsorption efficiency of 43.54 mg/g [11].

Nowadays, magnetic nanoparticle adsorbents are more attending because they are easy separation from liquid phase by applying external magnetic field and they can possibility repeated use. The magnetic nanoparticle is constituted by two parts as magnetic core and functionalized outer magnetic core. The composition of the magnetic adsorbent is dependent on the application. The high oxidative stability magnetite (Fe_3O_4) is currently the only accepted as a non-toxic magnetic materials. This compound with high yield production can be synthesized by co-precipitation method [19]. Threrfore, many researcher try to replace many kind of material for improve adsorption efficiency for chromate removal. For example, Fe_3O_4-loaded on mesoporous carbon microspheres had a high chromate adsorption efficiency of 156.3 mg/g. They can reused more than fifth adsorption–desorption cycle with adsorption capacity of 123.9 mg/g at fifth cycle [21]. Guocheng *et al.* [34] modified Fe(II) onto natural zeolite that the particle size aggregated of 1.4–2.4 mm. The results showed the natural zeolite modified with Fe(II) increase chromate adsorption efficiency to 6 mmol/kg. Moreover, The results of Xu *et al.* [12] showed that zero-valent iron loaded on graphite for producing a composite material has Cr(VI) removal of 98.80% which this composite material was higher than that for both graphite and zerovalent iron material.

2.1.3.3 Other chromium removal technics

Such biological treatment, bacterial surfaces can non-metabolically reduced Cr(VI) by enzymatic reactions in bacterial metabolism [35]. Fein *et al.* (2001) reported the main pathway for reduction unlike other studies focused on the first mechanism that chromium ions are reduced metabolically in the presence of large amounts of electron donors but Fein *et al.* (2001) reported third mechanism can be intra-cellular precipitation of chromium reduction. However, Hu *et al.* (2018) [36] reported low concentration of chromate (concentration lower than 0.5 mg/L) increase methane production efficiency of anaerobic granular sludge because anaerobic granular sludge had structure that can resistance against toxic Cr(VI). *Trichoccus accelerated* which bacteria used in low Cr(VI) concentration process can degrade organic substances and then generate acetates. It cause enhance methane production by acetotrophic methanogens.

However, limitation of this method is this process is ineffective in removed of high chromium concentration.

2.2 Adsorption

Adsorption is the accumulation of molecular species onto the solid surface or liquid phase. The adsorption process happens because residual forces or unbalanced at the surface of liquid or solid phase which have inclination to attract the molecular species to contact with the surface.

Adsorption process consist of two parts. First is an adsorbent which is the solid surface or liquid phase substance of adsorption takes place on. And second is an adsorbate which is the substance or molecular species adsorbed on the surface of solid surface or liquid phase adsorbent.

There are completely different between adsorption and absorption. Due to absorption is uniform distribution of the molecular species substance throughout the bulk. Unlikely, adsorption have to occur on the surface of the substance that adsorption phenomenon happens [37]. Therefore, when both adsorption and absorption processes happen together, this two processes are called sorption.

2.2.1 Type of adsorption

These forces attracted between adsorbate and adsorbent can be van der waal forces which are weak forces not a result from any chemical electronic bond or chemical bond which are strong forces between functional groups of adsorbate and adsorbent surface. This basis forces types of attraction adsorption can be separated into two types include physical adsorption and chemical adsorption.

2.2.1.1 Physical adsorption

Physical adsorption is the attraction of der waal's interaction forces between the adsorbent surface and the adsorbate. There arise on adsorbent surfaces provided. Physical adsorption is reversible reaction with temperature and pressure affect to adsorption efficiency. While pressure increasing causes volume of gas decreases, there results to gas is adsorbed better. So, decreasing of pressure, gas can be removed from the adsorbent surface. At low temperature, physical adsorption is promoted but high temperature cause the rate of adsorption decreases (shown in figure2.2). Under appropriate conditions, forming multiple layers of adsorbed molecules are result from physical adsorption. So, desorption is stimulated by high temperature or heating due to it makes adsorbate more available to active and leave from adsorption site. An evidence of physical adsorption characteristic is the adsorbate molecules are removed at the same adsorption occurred temperature [38].

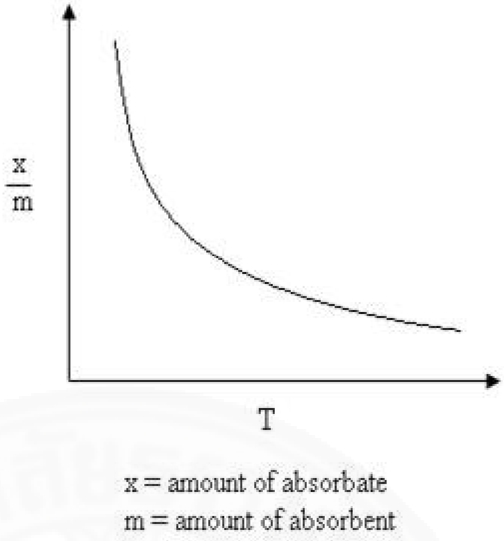

Figure2.2 The relative between physical adsorption and temperature

2.2.1.2 Chemical adsorption

Chemical adsorption is attraction result of chemical reaction forces which involved valence forces of chemical compounds formation and also result from the electrons sharing between adsorbate and surface of adsorbent. Chemical adsorption is irreversible [39]. The adsorbate contact directly contact with the adsorbent surface. So, it is considered to be a single-layer process. The removal of chemically adsorbed molecules require some energy for breaking adsorption bonds due to a adsorbed molecule make a strongly bonds with the adsorbent surface and cannot destroy bond without the bond energy. The required bong energy of chemisorption is high compared with physically bound molecule required.

As shown in figure2.3, chemical adsorption is promoted by increasing temperature and/or high pressure [40]. This is an exothermic process but the process at low temperature still slowly occurs. The cleaning chemically adsorbed molecules from a surface or desorption process is required more energy by heating at high temperatures over the boiling point of the adsorbate.

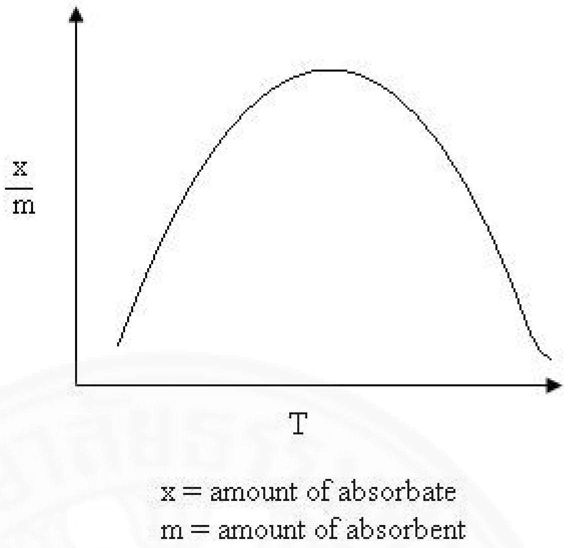

Figure2.3 The relative between chemical adsorption and temperature

2.2.2 Adsorption kinetic

The sorption plays an important role in wastewater treatment for removal of many pollutants in aqueous solution. The adsorbent used sorption processes have developed to have higher adsorption efficiency that make a high quality effluent after treatment, more recyclable ability, low cost of sorbents preparation and avoid secondary waste occurred after adsorption process.

The study of adsorption kinetics is important for explaining about the mechanism of adsorption and reaction pathways [41]. Moreover, the kinetics describe the adsorption rate at the adsorbent-adsorbate interface with adsorption contact time controlled due to it can be predicted the rate of pollutants removal from aqueous solutions for designing suitable adsorption treatment process.

The development of sorption kinetics for describing the sorption system required a knowledge of the rate law which includes three primary requirements follow below:

- Information of adsorbate reaction details such as the stereochemistry of chemically adsorbate and energetics
- distances and angles of interatomic in adsorption reaction
- The mechanism of individual molecular steps

The kinetic is only investigated by experimentation, it cannot determined by only chemical reaction equation. Nowadays, there are two favorite kinetic modals include pseudo first order and pseudo second order.

2.2.2.1 Pseudo first order

Lagergren (in 1898s) describe the kinetics adsorption in term of a first-order rate equation based on the adsorption capacity. The oxalic acid and malonic acid was explained kinetic liquid-solid phase adsorption onto charcoal substance. In that time this modal believed to be the earliest model. There was presented as equation below [42]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

Where

q_e is the adsorption efficiency at equilibrium (mg/g)

q_t is the adsorption efficiency at time (mg/g)

t is adsorption times (min)

k_1 is the rate constant of pseudo-first order reaction (min^{-1})

In the conditions of $t = t$ and $q_e = q_t$, the equation was integrated become follow equation below;

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

Lagergren’s equation was called pseudo-first order and this equation was widely used for explanation of the adsorption kinetic in the removal of pollutants from wastewater.

2.2.2.2 Pseudo second order

In 1999, Ho described another the adsorption kinetics modal from pseudo first order due to he found the chemical bonding effect among metal ions and adsorbent surface functional groups so as ketone group, acid group and phenolic group etc. The functional groups on adsorbent surface behave as cationic charge and they have ion exchange capacity. The main assumptions of this study may be due to the rate limiting step and chemical adsorption which related to the electrons exchange forces between divalent metal ions and peat surface. The pseudo second order was presented as equation below [41]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2$$

Where

q_e is the adsorption capacities at equilibrium (mg/g)

q_t is the adsorption capacities at time (mg/g)

t is adsorption times (min)

k_2 is the rate constant of pseudo-second order reation (g/mg•min)

In the conditions of t = t and $q_t = q_t$, the equation was transform become to equation below:

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

Then rate law of pseudo second order reaction was integrated rate law for a pseudo second order reaction and was shown in term of linear equation follow:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

2.2.3 Adsorption isotherm

Adsorption efficiency used in the study is amounts of pollutant absorbed per units of absorbent mass. Adsorption is the amount of pollutant functioned pressure or concentration adsorbed on the adsorbent surface with constants temperature which studied through the relative graphs of adsorption isotherm [14]. So, figure2.4 shows relative between amounts of pollutant absorbed per units of absorbent mass and pressure. An adsorption at low pressure is independent of pressure. At saturation pressure (P_s), adsorption exhibits stable graph which is there are limitation adsorbed on the adsorbent surface and pressure increasing is not affected to adsorption process [43].

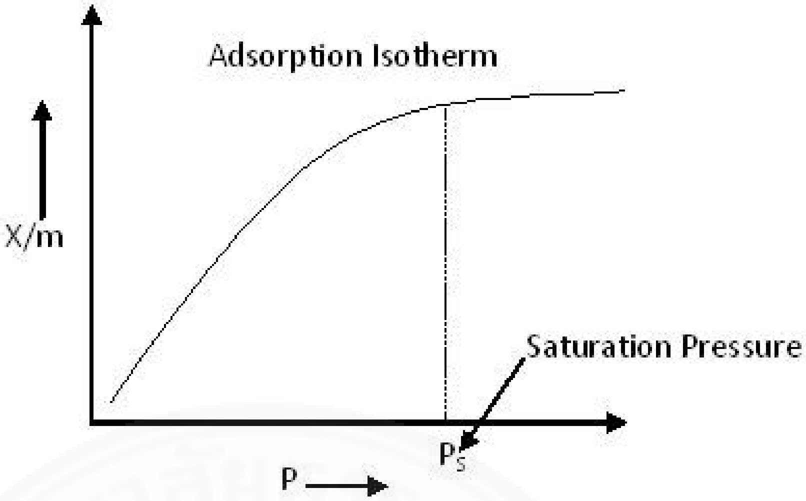

Figure2.4 Adsorption isotherm

2.2.3.1 Langmiur isotherm

The Langmuir adsorption isotherm model assume the behavior at isothermal conditions of adsorbate as ideal gas. The adsorption of gas pollutant molecules on solid surfaces is original description of Langmuir isotherm. And then the Langmuir isotherm was developed for using with the adsorption of pollutant in aqueous solution adsorbed onto solid surfaces.

This isotherm are used in explanations for gas adsorption on homogeneous surfaces but many adsorbents of industrial utility, such as silica gels, activated carbons etc., adsorb pollutant on heterogeneous surfaces. Several research explained single type of gas adsorption on homogeneous adsorbent with this isotherm. It is very interesting to modify the isotherm modal for forecast of mixed gas adsorption by using parameters of single gas adsorption systems. Langmiur isotherm is based on four assumptions below [44]:

- The adsorbent surface is uniform which sites of adsorption are equivalent.
- At the maximum adsorption, the adsorbent form a monolayer which adsorbate is only adsorbed on surface of the adsorbent
- Pollutant adsorbed on adsorbent do not react with each other.
- All adsorption occurs with same mechanism.

The Langmuir isotherm can be fitted with adsorption efficiency by using equation below:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where

C_e is the equilibrium concentration of pollutants adsorbate (mg/L)

q_e is the amount of adsorbate adsorbed per mass units of adsorbent (mg/g) at equilibrium

q_m is the maximum adsorption capacity of adsorbate per mass units of adsorbent (mg/g)

b is the Langmuir adsorption constant (L/mg)

2.2.3.2 Freundlich isotherm

Freundlich isotherm descripted reversible adsorption and non-ideal adsorption. This isotherm model would applied to random adsorption which is multilayer adsorption and related to heterogeneous surface. This isotherm is developed from the charcoal adsorption since there is non-constant ratio between the adsorbate and mass of adsorbent at variance adsorbate solution concentrations [45]. It can be due to adsorbate removed form solution is sum of adsorption site which better adsorbed by stronger binding sites at early process and decreased when occur the completion of adsorption process [46].

The Fruendlich isotherm can be fitted with adsorption efficiency by using equation below:

$$\ln q_e = \ln k_f + {}^{1}\!/_{n} \ln C_e$$

Where

C_e is the equilibrium concentration of pollutants adsorbate (mg/L)

q_e is the amount of adsorbate adsorbed per mass units of adsorbent (mg/g) at equilibrium

n is a adsorption favorability constant

k_f is the freundlich adsorption constant (L/mg)

Limitation of Freundlich adsorption isotherm is boundary adsorption at saturated pressure is difference form normal pressure and Freundlich adsorption isotherm usually failed at pressure higher saturated point.

Chapter 3
Methodology

3.1 Synthesis of magnetic particles (MP)

MP were prepared by using the co-precipitation technique. 0.2M Fe^{3+} form $FeCl_3 \cdot 6H_2O$ was mixed with 0.1M Fe^{2+} from $FeCl_2 \cdot 7H_2O$ in 50mL deionized water under nitrogen atmosphere. Nitrogen gas was flowed through solution to keep a nitrogen atmosphere during reaction and the reaction was vigorous stirred at 200 rpm. 0.5M 30mL ammonia solution was added dropwise (5 mL/min). After 3 hours stirring, the particles was magnetically separated by ND magnet and was washed by deionized (DI) water until pH leached solution was neutral. Then, MP was dried in oven at 80°C for 24 hours and was stored in desiccator for MSA preparation.

3.2 Preparation of magnetic-modified sludge adsorbent (MSA)

Sludge (5g) was prepared by sonication with 80 mL deionized water for 20 min at room temperature. 20 mL nitric acid solution was added into DI water contained sludge. Sample was stirred for 2 hours at 100ºC. The sample was separated into a sludge solution part and solid part by centrifuge 12,000 rpm for 10 min. Then, MP (2g) were dispersed in 10mL deionized water by sonication for 20 min and then was mixed with solution from sludge and $Al(NO_3)_3 \cdot 9H_2O$ to promote co-precipitation on magnetic surface by using 3.5g NaOH. The final pH of mixture was 12. Molar ratios of Ca^{2+} (form sludge; sludge is 90% $CaCO_3$)/Al^{3+} were prepared at 3/1, 4/1 and 5/1. The mixture was stirred (200rpm) and heated to 65ºC for 18 hours. Finally, sludge absorbent coated magnetic particles were magnetically separated. The adsorbent was washed with DI water until pH of leached solution was neutral. Then, MP was dried in oven at 80°C for 24 hours and was stored in desiccator.

3.3 Physicochemical characterization of MSA

3.3.1. The composition crystalline structures of adsorbents by X-ray diffraction (D8 advance, Bruker, Germany) using CuKα radiation. The samples were scanned for angular variation of 10-80° (2θ) with 0.02° step and a scan rate of 0.5 sec per step.

3.3.2. The morphological characteristics of the material was obtained using Filed Emission Scanning Electron Microscopy (FESEM) (FESEM SU5000, Hitachi, Japan) at a 5.0 kV accelerating voltage, 70,000 magnification and Transmission electron microscopy (TEM) (JEM-2100Plus, JEOL, US) at 200 kV, 30,000 magnification.

3.3.3. Functional group of adsorbent surface was analyzed using FTIR spectroscopy (Nicolet 6700, Thermo Scientific, US) with Attenuated total reflection (ATR) sampling. Spectra were analyzed in transmittance mode (4000 - 400 cm^{-1}) using 4 cm^{-1} resolution of 8 scans.

3.3.4. Elemental compositions were determined by Energy-dispersive X-ray spectroscopy (EDX) TEM/EDS analyses (JEM-2100Plus, JEOL, US). X-ray EDS analyses were carried out using EDS system at a 200 kV accelerating voltage. The samples were prepared onto copper grid coated carbon films. Sample images were then reported at 60,000 magnification. Elemental mapping analysis by using EDX was carried out randomly selected areas of distribution sample on the adsorbent surface.

3.3.5. The magnetic properties of the adsorbent was measured with a vibrating sample magnetometer (VSM) (VSM series 7404, Lake shore, US). The magnetic hysteresis loops were examined the applied sweeping from -1,000 to 1,000 Oe at room temperature.

3.3.6. Leaching of iron, calcium, aluminum ions in solution through from MSA Cr(VI) adsorption were determined by Inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICP-AES 9820, Shimadzu, Japan) for secondary waste analysis.

3.3.7. The adsorbent surface charge was investigated by Zeta potential (zetasizer nano zs, Malvern, UK). The sample was dispersed in DI water and/or chromate solution.

3.4 Adsorption experiments and chromate detection

The chromate solutions was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) into DI water. The adsorption capacity of adsorbent was determined from the chromate concentrations 50mg/L with 1.0 g/L of adsorbents for 0.25, 0.5, 1, 2, 3, 4, 6, 8 and 24 hours. Every sampling time, MSA was put on magnet for MSA settle down in 2 minute. 2mL of supernatant liquid was taken a sample of each sampling. The residual concentration of chromate in the supernatant liquid was determined standard procedure at 540 nm (λ_{max}) using an UV–visible spectrophotometer (Lambda650, Perkin Elmer, US).

Cr(VI) concentration in chromate solution was determined follow USEPA description Method 7196A (colorimetric method). 0.5 mL of chromate ions residual concentration from adsorption experiment was added into 1.0% sulfuric acid (H_2SO_4) solution (5.5 mL) and then added 0.1 mL diphenylcarbazide (DPC) solution (5 mg/L 1,5-diphenylcarbazide in acetone) for forming a 1,5-diphenylcarbazide-Cr(VI) complex. All of this process have to react in dark environment. After that DPC-Cr complex solution was measured absorbance at 540 nm (λ_{max}) using an UV–visible spectrophotometer (Lambda650, Perkin Elmer, US).

The chromate removal efficiency of each sample was calculated by equation(3.1) and equation(3.2) respectively :

$$\%\mathrm{removal} = \frac{C_0 - C_e}{C_e} \times 100 \qquad \text{Equation(3.1)}$$

$$q_e = \frac{(C_0 - C_e)V}{M} \qquad \text{Equation(3.2)}$$

Where ; q_e is the amount of chromate adsorbed at equilibrium (mg/g)
C_o is the initial concentrations (mg/L) of chromate in solution
C_e is the equilibrium concentrations (mg/L) of chromate in solution
V is the volume of solution (L)
M is the mass of adsorbent (g)

3.5 Effect of dosage, pH, temperature and interference ions on chromate adsorption

3.5.1 Effect of dosage on chromate adsorption

The effect of dosage MSA was investigated in the range of 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 and 2.0 g/L with initial chromate concentration 50 mg/L. Each batch contained 30mL chromate solution and was not adjusted pH, and then those adsorption time for 3 hours at room temperature.

After adsorption, MSA was magnetic separated from the solution. The residual concentration of chromate in the supernatant liquid was determined standard procedure at 540 nm (λ_{max}) using an UV–visible spectrophotometer.

3.5.2 Effect of pH on chromate adsorption

The effect of pH was investigated in the range of pH 3–12 at initial chromate concentration 50 mg/L. The pH values were adjusted by addition of 0.1 M NaOH and 0.1M HCl solution. Each batch contained 1.0 g/L of adsorbent, 30mL chromate solution and was adjusted pH parallel with keeping the similar chromate concentration of all batch samples, and then those adsorption time for 3 hours at room temperature.

After adsorption, MSA was magnetic separated from the solution. The residual concentration of chromate in the supernatant liquid was investigated using colorimetric method with UV–visible spectrophotometer at 540 nm (λ_{max}).

3.5.3 Effect of temperature on chromate adsorption

A chromate concentration of 50 mg/L was prepared to study the effect of temperature on adsorption efficiency. The temperature was varied in the range of 25ºC, 30ºC and 45ºC. Each batch contained 1.0 g/L of adsorbent, 200mL Cr(VI) solution and was not adjusted pH, and then those adsorption sampling time for 0.25, 0.5, 1, 2, 3, 4, 6, 8 and 24 hours at room temperature.

Every sampling time, MSA was put on magnet for MSA settle down in 2 minute. 2mL of supernatant liquid was taken a sample of each sampling. The residual concentration of chromate in the supernatant liquid was investigated using colorimetric method with UV–visible spectrophotometer at 540 nm (λ_{max}).

3.5.4 Effect of interference ions on chromate adsorption

Effect of interference ions of chloride (Cl^-), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and nitrate (NO_3^-) in difference concentrations were determined. A batch of sample with chromate concentration of 50 mg/L and various NaCl, Na_3PO_4, Na_2CO_3, Na_2SO_4 and $NaNO_3$ concentration in the range of 10 -100 ppm was conducted to estimate the effect of interference anion on adsorption efficiency. Each batch contained 1.0 g/L of adsorbent, 50mg/L 50mL chromate solution that was added the chemical in table3.1 and was not adjusted pH, and then those adsorption time for 3 hours at room temperature.

Table3.1 amount of chemicals that added into chromate solution as interference ions for study of effect of interference anion on chromate adsorption

Interference concentrations (mg/L)	Amount of chemical added (mg)				
	NaCl	Na_3PO_4	Na_2CO_3	Na_2SO_4	$NaNO_3$
10	0.82	0.63	0.88	0.74	0.69
25	2.06	1.58	2.21	1.85	1.71
50	4.12	3.16	4.42	3.70	3.43
75	6.17	4.74	6.62	5.55	5.14
100	8.23	6.31	8.83	7.39	6.85

3.6 Adsorption isotherm and adsorption kinetic

The chromate solutions was prepared by dissolving $K_2Cr_2O_7$ into DI water in variance concentration of 25, 50, 75, 100, 150, 200 and 300 mg of chromate/L. The adsorption efficiency of adsorbent was determined by using 200mL chromate solution and 1.0 g/L of MSA for 0.25, 0.5, 1, 2, 3, 4, 6, 8 and 24 hours. Every sampling time, MSA was put on magnet for MSA settle down in 2 minute. 2mL of supernatant liquid was taken a sample of each sampling. The residual concentration of chromate in the supernatant liquid was determined by standard procedure at 540 nm (λ_{max}) using an UV–visible spectrophotometer (Lambda650, Perkin Elmer, US).

The adsorption capacity (q_e) of each concentration was calculated by equation(2) and plotted to fit with standard model.

3.7 Reusability of MSA for chromate removal

Regeneration performance of MSA was tested for repeatedly use in practice applications. The MSA was used for chromate removal for several adsorption-desorption cycles until adsorption capacity of MSA is lower than 20% of first cycle adsorption capacity.

Each cycle, the adsorption efficiency of MSA was determined from the chromate concentrations 50mg/L with 1.0 g/L of adsorbents and was not adjusted pH, and then those adsorption time for 3 hours at room temperature. The MSA through chromate adsorption experiment (MSA-Af) was separated by using magnet and dried in oven at 80°C for 24 hours.

MSA-Af was added into eluent solution include deionized water, NaOH solution, $NaNO_3$ solution and Na_2CO_3 in a range of concentrations 0.1-1.0 mg/L and was immersed for 6 hours to desorb the loaded Cr(VI) ions. Then, solid/liquid phase was magnetic separated. The liquid part was taken a sample to determined using colorimetric method with UV–visible spectrophotometer at 540 nm (λ_{max}) for Cr(VI) released of MSA-Af calculation. The solid part was dried at 80ºC for 24 hours, and then adsorbent through desorption experiment was used as MSA for chromate adsorption in next cycle.

Chapter 4

Results and Discussion

4.1 Characterization of MSA adsorbent

4.1.1 Preparation and Physicochemical characterization

Sludge adsorbent without magnetic particles (SA) that show in figure4.1(a). The color of SA is quite white (pale yellow). The particles is fine and light. After dried, particle is pack and hard. There was crushed hardly by using mortar, there are crushed by ball mill. Particles from preparation of magnetic particle that shows in figure4.1(b) is fine and black color. There can used magnetic for separation. The black color indicated the particles is magnetite particle which iron oxide of both Fe(II) and Fe(III) or ferromagnetic is black color. When modified with sludge, the color of particle turn to brown color that mean to the magnetic properties may be decreased but MSA can separated from the solution as showed in figure4.6. In addition, figure4.1(c)-(e), MSA31, MSA41 and MSA51 were quite similar. Thus, the variance the ratio of Ca/Al was at 3/1, 4/1 and 5/1 were not effect to an appearance of MSA.


(a) (b) (c)

(d) (e)

Figure4.1 Photographs of SA(a), MP(b), MSA31(c), MSA 41(d) and MSA51(e)

4.1.2 Crystalline structures

The crystalline structures of samples were identified using X-ray diffraction (XRD). The SA sample (figure4.2(a)) match to the standard of katoite ($Ca_3Al_2(SiO_4)(OH)_8$) diffraction pattern which is a layered calcium aluminum hydroxide compound. Figure4.2(b) exhibits the XRD patterns of the MP. This sample pattern has six major peaks located at 32.46º, 35.75º, 43.39º, 54.06º, 57.50º and 63.17º that can be well match to XRD pattern of magnetite phase (Fe_3O_4). The MSA pattern, shown in figure4.2(c), shows composite between MP at peak position of 32.46º, 35.75º, 43.39º, 57.50º and 63.17º and SA at 29.38º, 39.44º and 47.96º locations. There is confirmed that MP distribute on SA surface.

The crystalline structure of MSA was not charge peak composition when it's through chromate adsorption. There shows chemical reaction was not occur on adsorbent surface but intensity of MSA after chromate sorption (MSA-Af) and MSA after desorption (MSA-De) were slightly decreased in peak position indicated SA surface at 2theta = 29.38º. There may due to some of Ca^{2+} and Al^{3+} ions leached into solution after adsorption and cause some of crystal structure were lose.

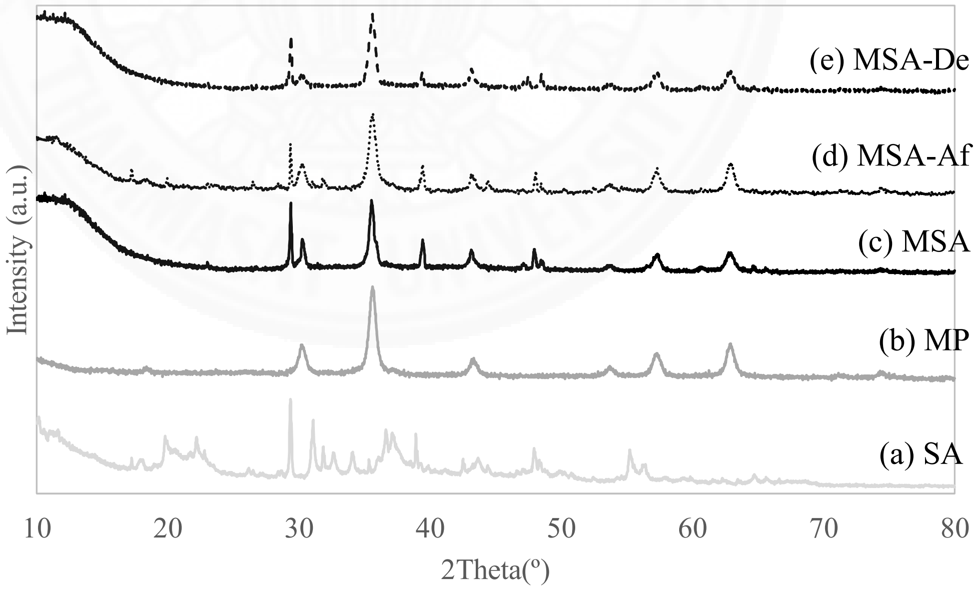

Figure4.2 XRD spectrums of SA(a), MP(b), MSA(c), MSA-Af(d) and MSA-De(e)

4.1.3 Particle size and morphology

The morphological structures are investigated by FESEM and TEM, as shown in figure4.3 and figure4.4, respectively. The SEM image of SA (figure4.3(a)) exhibits a structure with formation of smooth surface crystals corresponding to the layered hydroxide compound. Magnetic particle (MP) (figure4.3(b)) shows a rough surface that agglomerated from small-sized particles. Diameter of each MP small particle is about 15 nm. After synthesis MP with sludge absorbent, surface of MSA samples (figure4.3(c)) has composite between SA larger substrate and the small particle of MP random disperse on SA surface. TEM image of MSA (figure4.4(c)) are also confirm the composite of SA larger plan structure and MP small particle distributed on surface. Moreover, this is mainly explained that can confirm XRD results.

When observed with SEM and TEM, morphological structures of MSA after chromate adsorption; MSA-Af (figure4.3(d) and figure4.4(d)) are quite similar to that of original MSA sample, which shows SA structure has small MP on the surface. This indicates that chromate adsorbed on MSA does not change the morphology of the adsorbent.

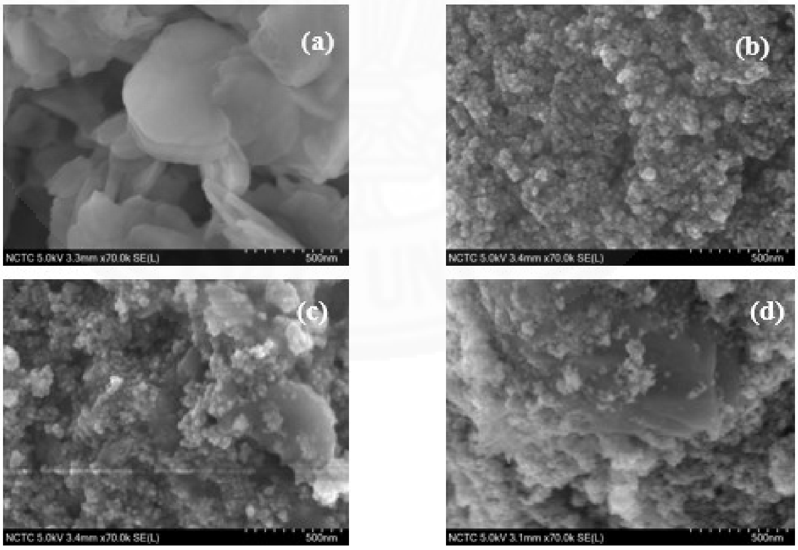

Figure4.3 SEM image (70,000 magnification) of SA (a), MP (b), MSA (c) and MSA-Af (d)

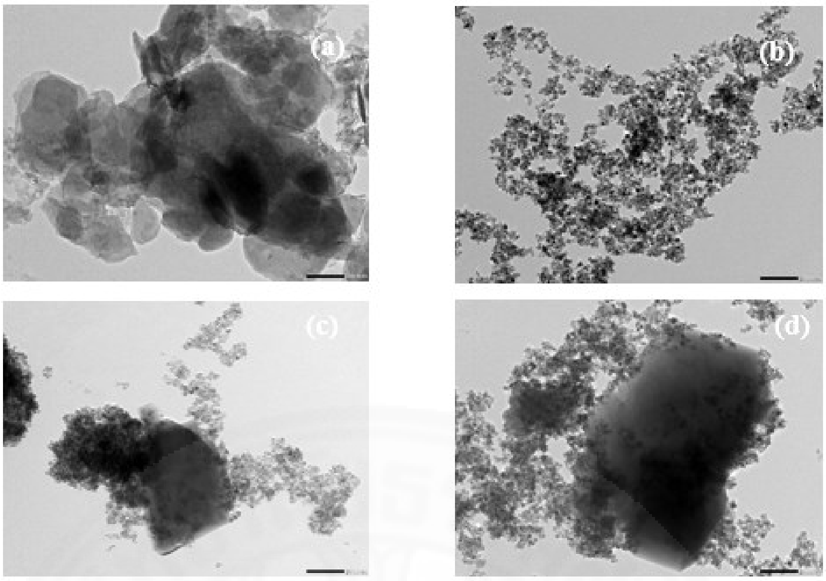

Figure4.4 TEM image (60,000 magnification) of SA (a), MP (b), MSA (c) and MSA-Af (d)

4.1.4 Elemental compositions

Figure4.5 shows elemental composition on MSA surface after chromate adsorption (MSA-Af) by using TEM-EDX detector. EDX elemental mapping obviously shows the oxygen, calcium, aluminum and iron distributed in MSA sample. The main element of larger substrate is calcium that is confirmed structure from sludge adsorbent ($CaCO_3$ based). There has MP follow composition of iron (Fe K) distribute on surface and mainly occur same position of small particle distributed on sample surface.

Moreover, elemental mapping is also confirmed the chromium loading (in CrK) on adsorbent surface. Chromium spread on the surface of absorbent and mainly occur in same position of Ca that indicate chromium can adsorbed on both MP and MSA surface but SA surface is better active site than MP surface.

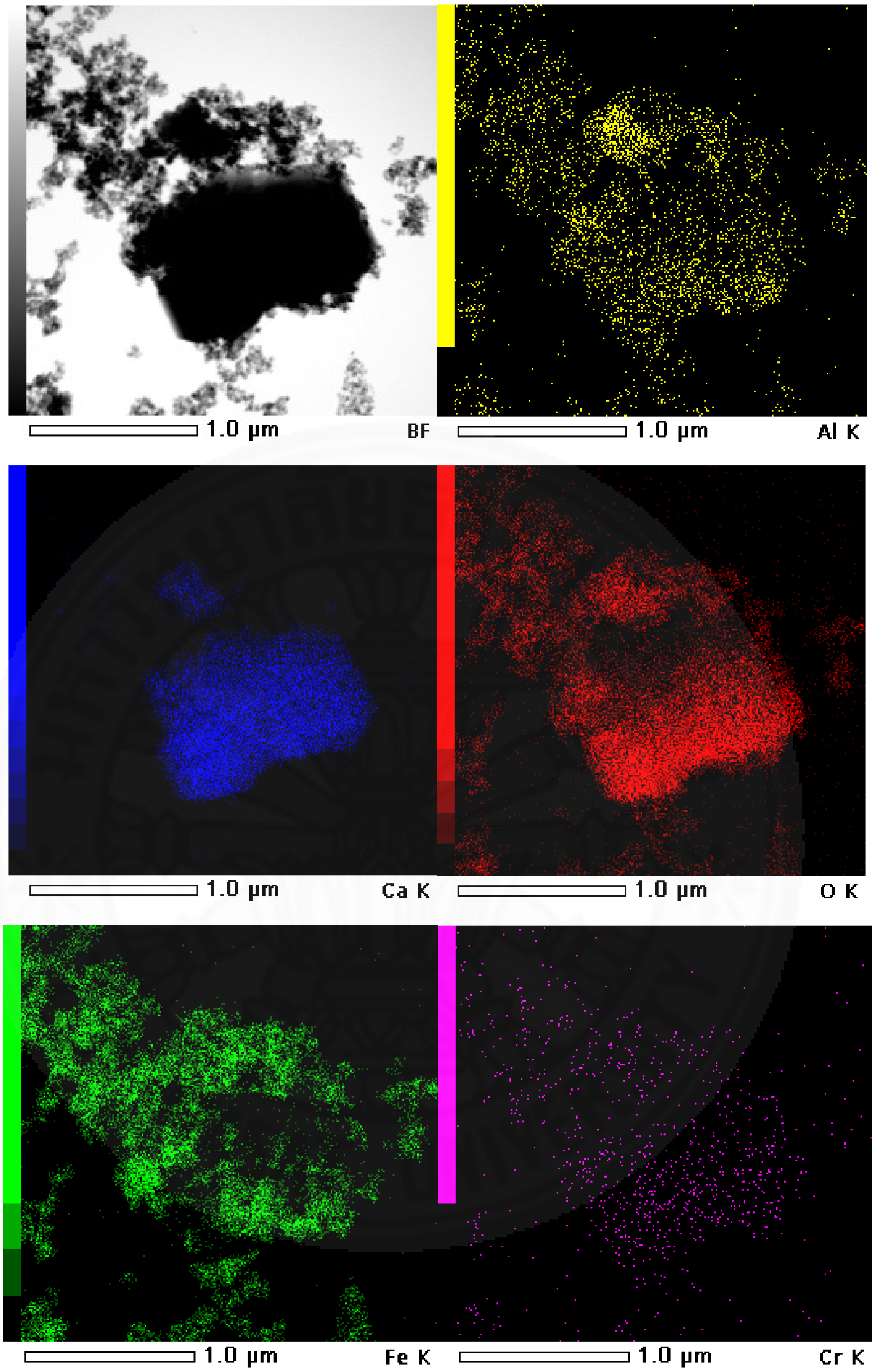

Figure4.5 Elemental composition of MSA-Af form TEM-EDX detector (200 kV, 60k magnification)

4.1.5 Functional group surface

The functional groups were identified using FTIR spectroscopy. The bands between 3400 – 3600 cm^{-1} refer to the stretching vibrations of hydroxyl groups (-OH) in the interlayer adsorbent surface and H_2O molecules adsorbed in the sample. A water O-H bending band is also observed at 1620 cm^{-1}.

The band at 539 cm-1 of magnetic particle (MP) spectra as shown in figure4.6(light grey line) can be assigned to Fe-O stretching of Fe_3O_4 particle.

FTIR spectra of SA, MSA, MSA-AF and MSA-De are shown in figure4.6(grey), figure4.6(black), figure4.6(black dashed line) and figure4.6(black dotted line), respectively. The stretching vibrations of Me–O and Me–OH (Me can be either Ca or Al) in the layered hydroxide compound in SA, MSA, MSA-Af and MSA-De appear around 420 and 520-530 cm^{-1} [47]. The bands located at 1360-1400 cm^{-1} were assigned to the stretching bands of interlayer carbonate anions (C-O) and the band at 1560 cm^{-1} can be defined to the symmetric stretching of interlayer carbonate (C-O) [48].

The stretching vibration of chromate bonds (Cr-O) are associated with the 870 cm^{-1} band [49] which is clearly observed in MSA-Af sample and slightly occurred in the MSA-De sample. This confirms that chromate ion was adsorbed on MSA surface and desorption experiment can remove the chromate ion from the MSA surface. However, this is not a complete removal.

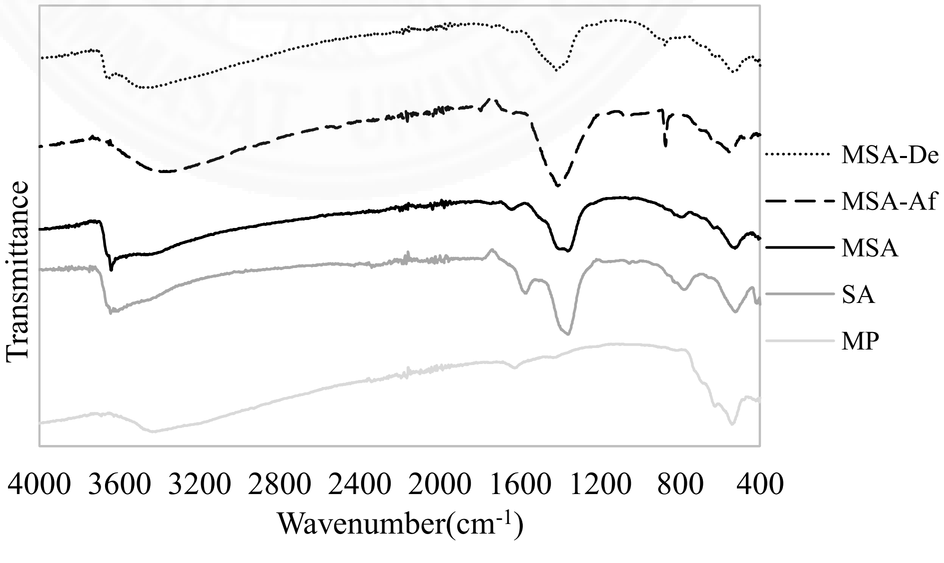

Figure4.6 FTIR spectra of SA (grey line), MP (light grey line), MSA (black line), MSA-Af (black dashed line) and MSA-De (black dotted line)

4.1.6 Magnetic properties

The magnetic property of SA, MP, MSA, MSA-Af and MSA-De were investigated, as shown in Figure4.7. The saturation magnetizations (M_s) of MP and MSA are 66.79, 39.82 emu/g which those magnetic properties value are lower than magnetization value of superparamagnetic particles (M_s = 90 emu/g) [50] However, MP and MSA were enough for separation by using Nd magnet. The reducing of MSA M_s value compared with MP can be due to the SA surrounding the Fe_3O_4 cores (MP) that the SA has low magnetic moment value (M_s value of SA is very low and cannot used magnetic separation). The applying magnet as shown in figure4.8 was simulated MSA separation method. When the dispersion of MSA is close to magnet, the brown composite of MSA was moved and attracted to the magnet, and then solution become seen clear within 2 min and after 2 min the dispersion was not obviously changed shown in Figure4.8.

After the chromate adsorption and desorption, the M_s values of MSA, MSA-Af and MSA-De show a slight change. Graph of MSA, MSA-Af and MSA-De are close and almost overlapping. This indicates that the adsorption and desorption experiments did not effect to the magnetic properties.

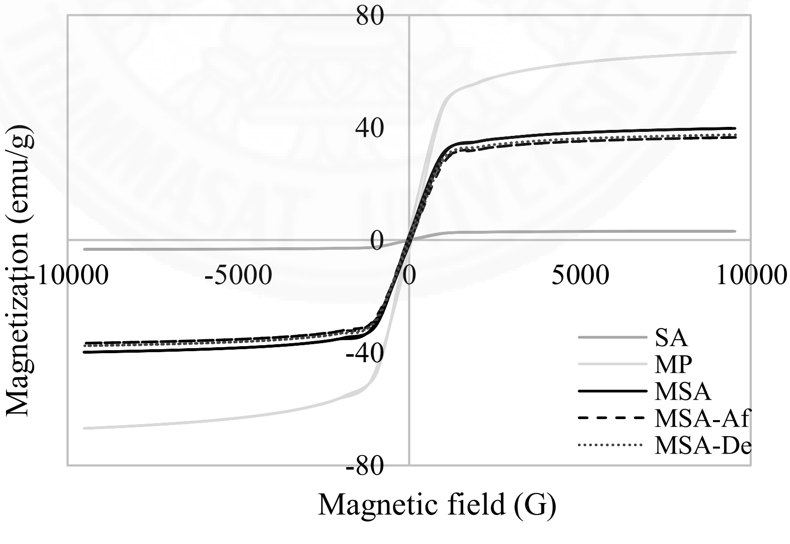

Figure4.7 Magnetization curve of SA (grey), MP (light grey), MSA (dashed line), MSA-Af (black) and MSA-De (dotted line)

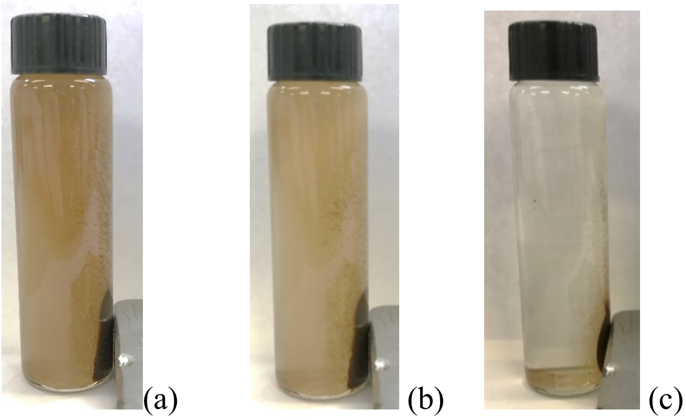

Figure4.8 Photographs of MSA separation at difference time (a) 5s, (b)30s and (c) 2min

4.1.7 Leaching of ions

The leaching of iron, calcium and aluminum were studied in chromate solution after adsorption (contact time 24 hours, room temperature, not adjusted pH, initial chromate concentration 50 mg/L, MSA Dosage 1.0 g/L). Leaching calcium and aluminum ions concentration were 2.58 mg/L and lower 1.0 ppb, respectively, as shown in Table4.1. The concentration of these ion is lower than concentration in domestic water and/or wastewater. This solution did not considered hard water and the concentration of calcium leached is lower than a permissible limit (calcium ion concentrations <120 mg/L) [51]. So, MSA would be safe to utilized for treating industrial wastewater containing Cr(VI) ion and less occur secondary wastewater.

Table4.1 Chemical component of solution from chromate adsorption experiment form MSA adsorbent (room temperature, not adjusted pH, initial chromate concentration 50 mg/L, MSA dosage 1.0 g/L, contact time 24 hours) and control (room temperature, not adjusted pH, initial chromate concentration 50 mg/L, sludge unmodified dosage 1.0 g/L, contact time 24 hours)

Leaching ions	Ion concentrations (mg/L)	
	Control	MSA
Fe ion	Not detected	Not detected
Ca ion	Not detected	2.58
Al ion	Not detected	<1.0 ppb

4.2 Adsorption efficiency

4.2.1 Adsorption capacity of SA, MP, MSA31, MSA 41 and MSA51

For evaluation of chromate removal, concentrations of chromate were measured using UV-spectrophotometer. The initial chromate concentration was 50 mg/L and the dose of SA, MP, MSA31, MSA41 and MSA51 were 1.0 g/L. The chromate solutions were vigorously stirred at room temperature. After sorption, the MP, MSA31, MSA41 and MSA51 were magnetically separated from the solution (as shown in figure4.8) and the SA was separated by syringe filtration.

The initial pH of chromate solution was 5.7 and after chromate adsorption of SA, MP, MSA31, MSA 41 and MSA51, pH were about 8.2, 6.1, 8.7, 8.3 and 8.7, respectively (table4.2). The pH increasing may be due to ions were leached form adsorbent and there have ion exchange cause hydroxyl group (-OH) on adsorbent released into adsorbate solution.

The chromate capacity at 24 h after adsorption of SA, MP, MSA31, MSA 41 and MSA51 are 35.14, 32.12, 36.69, 41.42 and 39.10 mg/g of each adsorbent, respectively. This results shows magnetic modification is increase chromate sorption capacity and MSA at the molar ratio of 4:1 Ca^{2+}/Al^{3+} (MSA41) showed to be the best removal efficient which indicated MSA41 has great potential to be used in the chromate treatment and evaluate the effect of several factors such as pH, dosage, temperature and competitive anion.

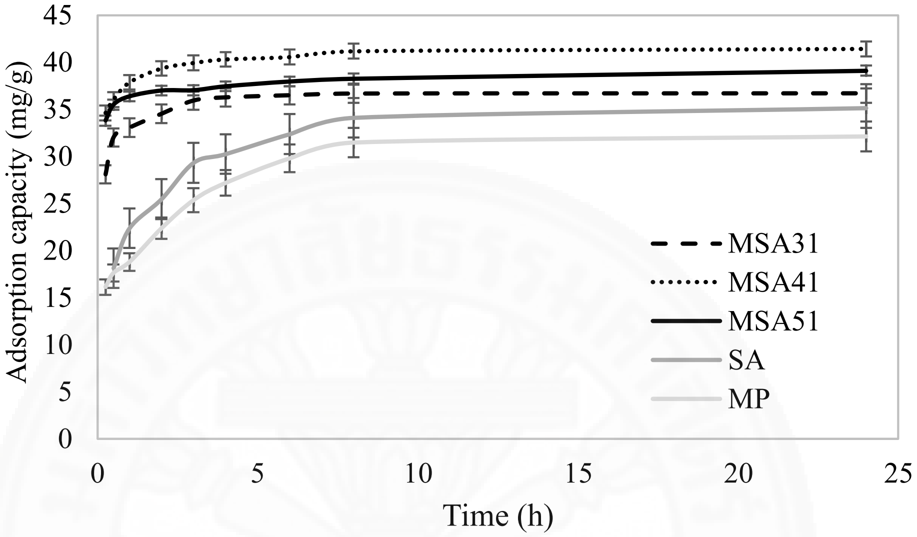

Figure4.9 Adsorption capacity of SA, MP, MSA31, MSA 41 and MSA51 (room temperature, not adjusted pH, initial chromate concentration 50 mg/L, Dosage 1.0 g/L)

Table4.2 pH of solution through adsorption experiment of SA, MP, MSA31, MSA41 and MSA51 (room temperature, not adjusted pH, initial chromate concentration 50 mg/L, Dosage 1.0 g/L)

Sample	Initial pH Cr(VI) solution	Final pH Cr(VI) solution
SA	5.7-6.1	8.2-8.5
MP		5.9-6.1
MSA31		8.7-9.3
MSA41		8.3-9.0
MSA51		8.7-9.4

4.2.2 Comparison with other work

The maximum adsorption efficiency of MSA41 obtained from the Langmuir model for chromate removal compared with other adsorbents are summarized in table4.3. This indicates that MSA has higher adsorption efficiency than many other adsorbents.

Table4.3 the maximum adsorption capacity of common adsorbents used in chromate removal process

Material	Maximum Cr(VI) removal efficiency (mg/g)	Reference
MSA	49.50	This study
Ca-montmorillonite	24.04	[52]
Chabazite modified with hexadecyltrimethylammonium bromide	8.83	[53]
Ca-Al layered double hydroxide using concrete sludge as raw material	13.0	[54]
Sewage sludge compost biomass	1.88	[55]
Biochar derived from municipal sludge	7.0	[56]
Imidazole-modified silica	47.79	[57]
Malachite nanoparticles	14.2	[58]
Drinking water sludge	41.3	[59]
Coal fly ash	41.7	[59]
Modified fly ash with NaOH	47.5	[59]
Alum sludge	24.35	[60]
Activated carbon derived waste sawdust	13.85	[61]
Biochar derived from wastewater hyacinth supported with ZnO nanoparticle	43.48	[62]
Biochar derived from herb-residue modified with magnetic	22.75	[63]
Carbon nanocomposite fabrics	3.74	[64]
Humic Acid Coated on Magnetite	4.7	[65]
Iron based nanoparticles	20.50	[66]

Magnetic nanoparticle-multiwalled carbon nanotubes composites	42.02	[67]
Magnetic magnetite (Fe_3O_4) nanoparticles	34.87	[68]

4.3 Adsorption kinetic

Adsorption kinetic of chromate onto MSA41 was investigated in range of adsorption time 0.25 - 24 hours with initial chromate concentrations 50 mg/L and 1 g/L of MSA41. The adsorption kinetics were calculated by pseudo first order and pseudo second order followed equation (4.1) and equation (4.2), respectively. And then there were plotted graph as shown in figure4.10.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad \text{Equation (4.1)}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \text{Equation (4.2)}$$

Where q_e is the amount of Cr(VI) adsorbed of unit on MSA (mg/g) at equilibrium. q_t is the amount of Cr(VI) adsorbed of unit on MSA (mg/g) at time.

k_1 is the rate constant for pseudo-first order adsorption (hours^{-1}).

k_2 is the rate constant for pseudo-second order adsorption (g/mg•hours).

t is time of adsorption (hours)

The rate constant, the amount of chromate adsorbed form equation calculation and linear regression coefficients (R^2) for chromate by MSA are summarized in table4.4. The value of regression coefficients (R^2) is criteria for best fitting of adsorption kinetic model selection. The pseudo second order modal is better fitted than of the pseudo first order (R^2 higher and closes to linear equation) which suggested that pseudo second order modal was more reasonable for kinetic describing. The calculated adsorption efficiency value (q_e^{cal}) from pseudo second order modal was close to value of experimental data adsorption efficiency (q_e^{exp}). This results indicated that the adsorption kinetic of MSA is chemisorption by sharing or exchange of electrons between the MSA and chromate ions rather than physical adsorption [69].

Moreover, the overall adsorption amount was thought to be dependent on zeta-potential value of adsorbent as shown in table4.5. The zeta potential of MSA has more positive charge that correlate to adsorption efficiency of MSA is better than SA and MP. After chromate adsorption, positive charge of MSA-Af was decreased due to chromate adsorbed on surface has negative charge when it was adsorbed on MSA surface cause to charge decreased.

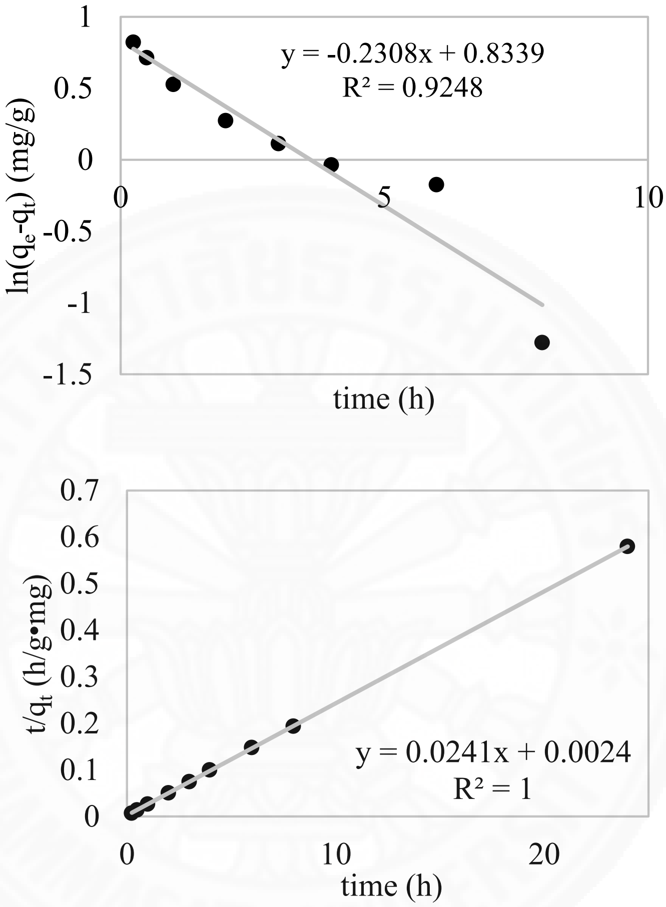

Figure4.10 pseudo first order (a) and pseudo second order (b) kinetic for chromate removal of MSA41

Table4.4 pseudo first order and pseudo second order kinetic parameters of MSA41 for chromate removal

q_e^{exp} (mg/g)	**pseudo first order**			**pseudo second order**		
	k_1 (hour^{-1})	q_e^{cal} (mg/g)	R^2	k_2 (mg/g•hour)	q_e^{cal} (mg/g)	R^2
41.42	0.23	2.30	0.92	0.24	41.49	1

Table4.5 Zeta potential of SA, MP, MSA, MSA-Af disperse in deionized water at room temperature

Sample	Zeta potential (mV)
SA	26.33
MP	12.37
MSA	29.77
MSA-Af	13.03

4.4 Adsorption isotherm

Adsorption isotherm of chromate onto MSA41 was investigated in range of chromate concentrations 25 – 300 mg/L and adsorption time 24 hours with 1 g/L of MSA41. The adsorption isotherm were calculate by using Langmuir and Freundlich adsorption isotherm modal followed equation (4.3) and equation (4.4), respectively. And then there were plotted graph as shown in figure4.11.

$$\frac{C_e}{q_e} = \frac{1}{k_a q_m} + \frac{C_e}{q_m} \qquad \text{Equation (4.3)}$$

$$\ln q_e = \ln k_f + {}^{1}\!/_{n} \ln C_e \qquad \text{Equation (4.4)}$$

Where

C_e is the equilibrium concentration of chromate in solution (mg/L)

q_e is the amount of chromate adsorbed of unit on MSA (mg/g) at equilibrium

q_m is the maximum adsorption capacity of chromate on MSA (mg/g)

b is the Langmuir adsorption constant (L/mg)

n is a adsorption favorability constant

k_f is the Freundlich adsorption constant (L/mg)

The Langmuir and Freundlich adsorption constant, maximum adsorption capacity and regression coefficients (R^2) for chromate by MSA are summarized in table4.5. The value of regression coefficients (R^2) is criteria for best fitting of adsorption isotherm model selection. The R^2 values of the Langmuir adsorption isotherm model were higher than value of R^2 of Freundlich adsorption isotherm model. This result indicated that chromate take place on a homogeneous surface, which the process of chromate adsorption is monolayer adsorption, without interaction between chromate molecules [66]. The calculated maximum adsorption capacities value (q_m^{cal}) derived from Langmuir isotherm model was 49.50 mg/g. Moreover, a dimensionless constant separation factor of Langmuir isotherm can calculated by using equation(4.5). R_L value is between 0 to 1 indicated this adsorption is favorable.

$$R_L = \frac{1}{1+bC_0} \qquad \text{Equation (4.5)}$$

Where

R_L is dimensionless constant separation factor

C_e is the equilibrium concentration of chromate in solution (mg/L)

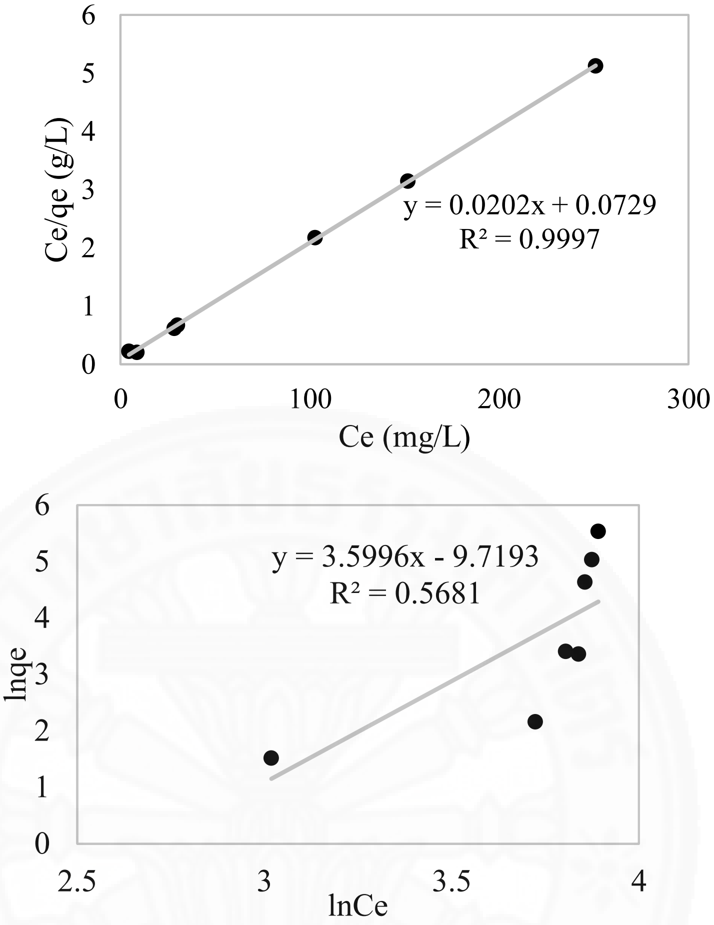

Figure4.11 Langmuir and Freundlich adsorption isotherm for chromate removal of MSA41

Table4.6 Langmuir and Freundlich adsorption isotherm parameters of MSA41 for chromate removal

q_e^{exp} (mg/g)	**Langmuir model**			**Freundlich model**		
	b (L/mg)	q_m^{cal} (mg/g)	R^2	k_f (mg/g)	n	R^2
41.42	0.27	49.50	0.99	0.06	0.28	0.57

4.5 Effect of pH, contact time, dosage, temperature, initial concentration, competitive anions on chromate removal efficiency

4.5.1 Effect of initial pH on chromate removal efficiency

For evaluation effect of pH on chromate removal, the performance of MSA41 was investigated in range of 3-12. Concentrations of chromate were measured using UV-spectrophotometer. The initial concentration of chromate was 50 mg/L and dose of MSA41 was 1.0 g/L at room temperature. The pH values was adjusted by addition of 0.1 M NaOH solution and 0.1M HCl solution.

The pH are an important in chromate adsorption. It's not only effect the degree of Cr(VI) speciation, but also on surface charge of the adsorbent. Figure4.12 shows adsorption efficiency was depended on pH. Adsorption efficiency was increase when pH decrease. The difference chromate adsorption efficiency at pH3 to pH12 is about 10 mg/g of MSA41.

At low pH, the removal efficiency increasing may be due to the conversion of Cr(VI) species. At pH 7 (neutral pH), Cr(VI) species generally occurred as chromate ions (CrO_4^{2-}) but at acid condition (pH 2) Cr(VI) species present as hydrogen chromate ($HCrO_4^{-}$). Hydrogen chromate is lower negative charge than other two Cr(VI) species (chromate and dichromate form) cause to it favorably adsorbed than other two at same concentration. When pH increase, $HCrO_4^{-}$ was converted to dichromate form ($Cr_2O_7^{2-}$) and CrO_4^{2-}.

Moreover, the surface of adsorbent with lower pH was surrounded by abundant proton (H^{+}) was easily to be protonated and there increase positive characteristic of the adsorbent surface by H^{+} ion, which can adsorb $HCrO_4^{-}$ by electrostatic attraction. On the other hand, the protonation degree reduced form pH increasing and the increasing of OH^{-} ions concentration, that making low anion adsorbed sites available, results in the degeneration of removal efficiency. This result reveals that MSA41 exhibits a high adsorption efficiency at lower pH.

The zeta potential results can confirm a changing of surface charge when pH was changed as shown in figure4.13. The zeta potential of MSA at various pH were investigated by dispersing MSA in chromate solution at pH 3-12 (figure4.13 grey triangle) compare with dispersing in DI water (figure4.13 black circle). The surface of MSA saturated with chromate become more negative charge than MSA in DI water due to chromate ion increase negative charge on adsorbent. The surface charge are more positive change at lower pH. This result was corresponding to results of adsorption capacity at difference pH (figure4.12).

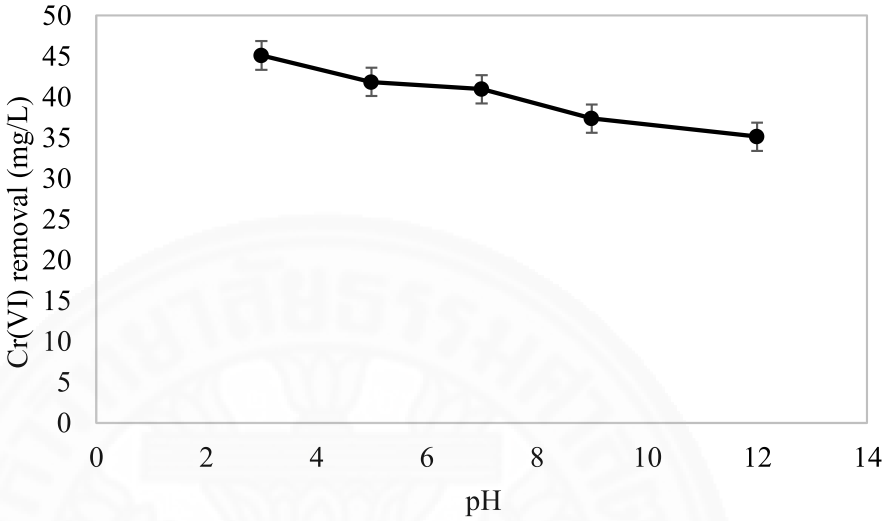

Figure4.12 Adsorption capacity of MSA41 at difference pH (contact time 3 hours, room temperature, initial chromate concentration 50 mg/L, MSA Dosage 1.0 g/L)

Table4.7 pH of solution in adsorption experiment at difference pH of MSA41 (contact time 3 hours, room temperature, initial chromate concentration 50 mg/L, Dosage 1.0 g/L)

Sample	Initial pH Cr(VI) solution	Final pH Cr(VI) solution
MSA41	3.3-3.5	3.6-4.5
	5.0-5.2	8.4-9.1
	7.2-7.7	8.7-9.3
	9.3-9.4	10.8-12.2
	12.0-12.2	13.1-13.5

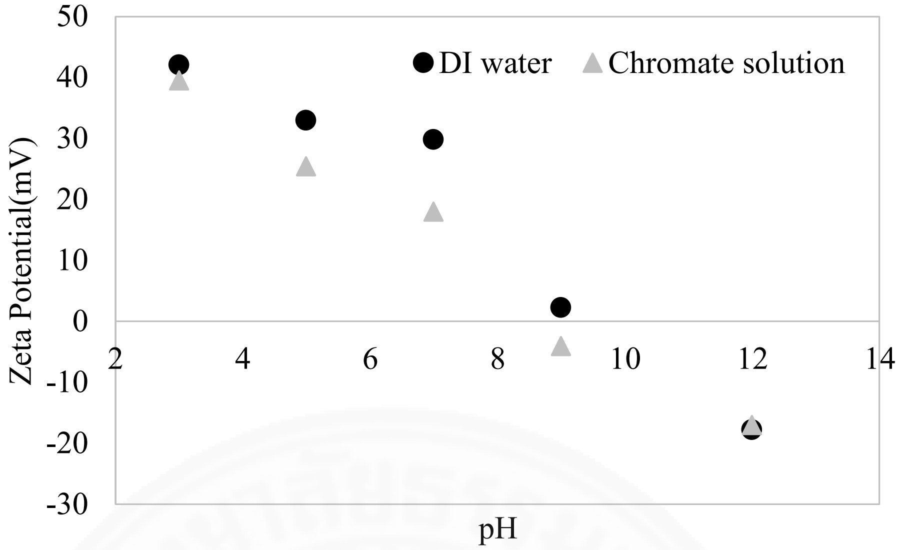

Figure4.13 Zeta potential of MSA disperse in deionized water (black circle) and 50mg/L chromate solution (grey triangle) at difference pH

4.5.2 Effect of temperature on chromate removal efficiency

For evaluation effect of temperature on chromate removal efficiency, the performance of MSA41 was investigated at room temperature (about 25ºC), 4ºC, 35ºC and 45ºC. The initial chromate concentration was fixed at 50 mg/L and dose of MSA41 was fixed at 1 g/L.

The results show that the adsorption efficiency of MSA41 increased when the temperature increased from 4 to 45 °C, which may be because the increase of the temperature leads to higher internal diffusion rate of chromate. The maximum adsorption of MSA at 45ºC is 47.88 mg/g of adsorbent (about 96% removal). This results can be obviously seen as figure4.14. The practical applications was preferred at room temperature (25ºC). In addition, the highest adsorption capacities for chromate was 41.42 mg/g of adsorbent, obtained from MSA41 at room temperature.

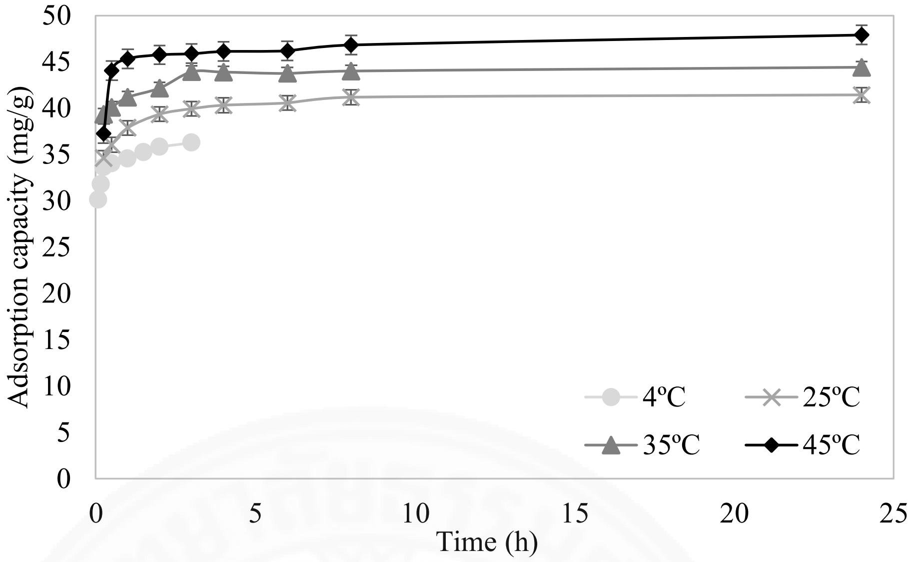

Figure4.14 Adsorption capacity of MSA41 at difference temperature (not adjusted pH, initial chromate concentration 50 mg/L, MSA Dosage 1.0 g/L)

In addition, thermodynamics of removal process were examined at different temperatures, i.e. 4°C, 25°C, 35°C and 45°C. The standard free energy (ΔG^{o}) value was calculated from equation (4.6) and equation (4.7).

$$\Delta G^0 = -\mathrm{RT}\ln K \qquad \text{Equation (4.6)}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad \text{Equation (4.7)}$$

Where

ΔG^o is the gibbs free energy (KJ/mol)

R is gas constant (8.314 J/mol•K)

T is the temperature (K)

K is the equilibrium constant

ΔH^o is the standard enthalpy (KJ/mol)

ΔS^o is the standard entropy (J/mol•K)

Table 4.8 shows thermodynamic parameters for the adsorption. The negative standard free energy (ΔG^o) indicate a spontaneous reaction and the positive value of standard entropy (ΔS°) explicate increasing of interface randomness at and more favorable adsorb at high temperature. Moreover, the positive value of standard chromate adsorption enthalpy (ΔH°) represent this reaction is endothermic process, which also means adsorption increases with temperature increasing.

Table 4.8 Thermodynamic parameters for the adsorption of chromate by MSA

Temperature	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol•K)
4°C (277 K)	-2.25	4.23	16.06
25°C (298 K)	-3.90		
35°C (308 K)	-5.30		
45°C (318 K)	-8.24		

4.5.3 Effect of MSA dosage on chromate removal efficiency

The critical application of pollutant removal in wastewater treatment process is the optimize dosage of adsorbents used because high dose cause to high adsorbent cost and then cause to those cannot be widely apply.

For evaluation effect of dosage on chromate removal, the performance of MSA41 was investigated in range of 0.25-2.0 g/L at room temperature. Concentrations of chromate were measured using UV-spectrophotometer. The initial concentration of chromate was 50 mg/L. So, the effect of the MSA41 dose on the removal efficiency was shown in figure4.15.

The efficiency increased promptly with dosage increase from 0.25 to 1.0 g/L, and then quite remained stable. Increasing of adsorbent dosage cause the available adsorption sites surface area increased and give higher removal efficiency. At adsorption equilibrium, the removal efficiency is stable which the adsorbent was achieved mostly chromate in the solution. Therefore, adsorption efficiency was more than 80% Cr(VI) ion removal with 1.0 g/L MSA used which suggested that was high enough for using in the further adsorption assays and enough to wide chromate removal application from large scale of wastewaters.

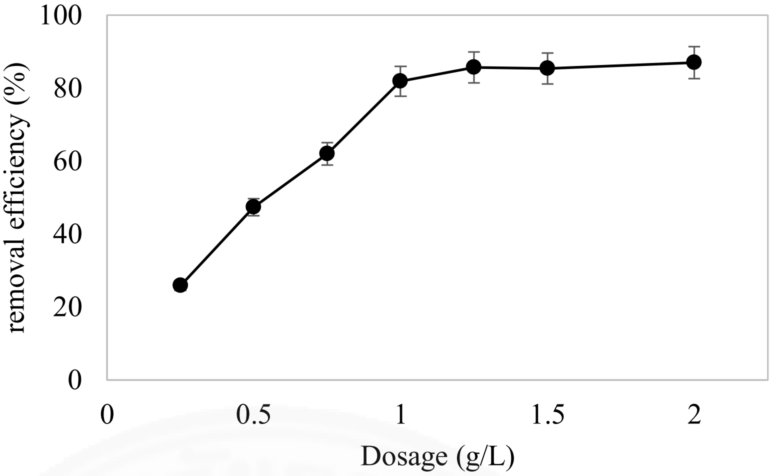

Figure4.15 Adsorption capacity of MSA41 at difference dosage of absorbent (contact time 3 hours, room temperature, not adjusted pH, initial chromate concentration 50 mg/L)

4.5.4 Effect of initial chromate concentrations on chromate removal efficiency

For evaluation effect of initial chromate concentrations on chromate removal, the initial concentration of chromate was investigated in range of 25-300 mg/L with MSA41 dose was 1 mg/L at room temperature. Concentrations of chromate were measured using UV-spectrophotometer.

The effect of the initial concentration of MSA41 on the removal efficiency was shown in Figure4.16. The maximum adsorption efficiency with initial concentration 300 mg/L was 48.99 mg/g of MSA. The removal efficiency increased rapidly, and then remained stable in the range of 50-300 mg/L which difference adsorption efficiency is lower than 20%. So, the initial concentration of 50 mg/L can be represent was used for the further adsorption assays.

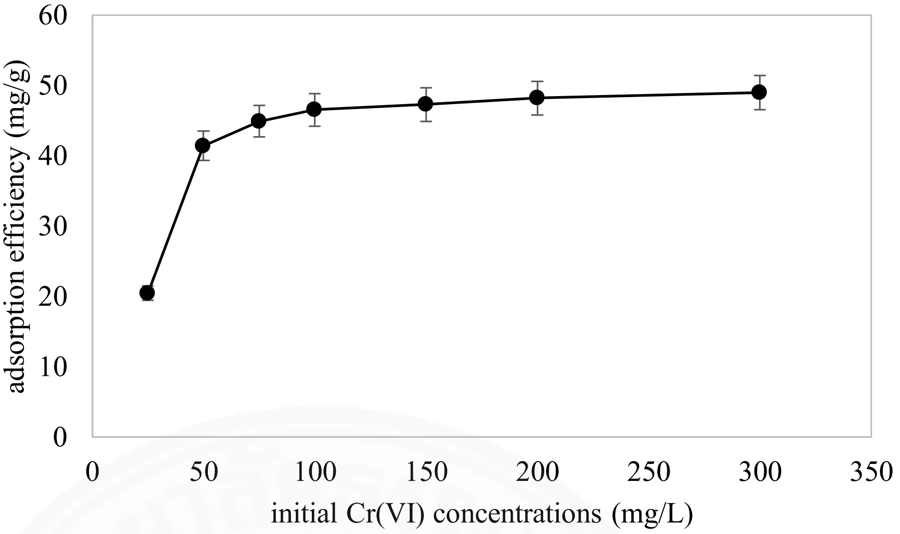

Figure4.16 Adsorption capacity of MSA41 at difference initial chromate concentrations (contact time 24 hours, room temperature, not adjusted pH, MSA Dosage 1.0 g/L)

4.5.5 Effect of competitive anions on Cr(VI) removal

In industrial wastewater and/or natural water were contained variety of ions such as phosphate, sulfate and bicarbonate etc which can be effect to Cr(VI) ions removal. So, sorbent is necessary to have a high selectivity hazardous ion removal.

For evaluation effect of competitive anion on chromate removal, the performance of MSA41 was investigated with difference concentration of chloride (Cl^-), phosphate (PO_4^{3-}), carbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and nitrate (NO_3^-). Concentrations of chromate were measured using UV-spectrophotometer. The initial concentration of chromate was adjusted to 50 mg/L. The chromate solutions were vigorously stirred at room temperature.

The effect of difference concentrations of variance anion on chromate adsorptions are given on Figure4.17. the effect of competitive anion such as chloride (Cl^-), phosphate (PO_4^{3-}), bicarbonate (CO_3^{2-}), sulfate (SO_4^{2-}) and nitrate (NO_3^-). Chloride and phosphate ions less affect the chromate removal. However, the presence of bicarbonate, sulfate and nitrate ions is quite strong affect to adsorption which may be due to anion can be replaced in intercalating layer instead chromate ion and charge of bicarbonate and sulfate are divalent ion similar to chromate. So, bicarbonate and sulfate can compete to adsorbed on MSA surface more chromate. This results show

MSA was non-specific anion adsorbent, it can be develop to use as other anion adsorbent in future.

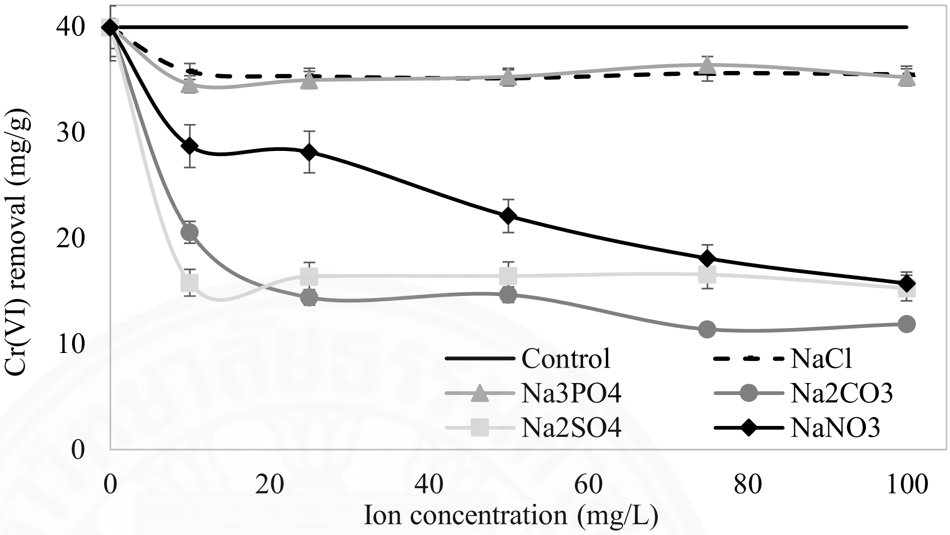

Figure4.17 Adsorption capacity of MSA41 at difference competitive anion (contact time 3 hours, room temperature, not adjusted pH, initial chromate concentration 50 mg/L, MSA Dosage 1.0 g/L)

4.6 Reusability and regeneration of MSA adsorbent

4.6.1 Desorption efficiency

Every cycle, the adsorption capacity of MSA was determined from the chromate concentrations 50 mg/L with 1.0 g/L of adsorbents and was not adjusted pH, and then those adsorption time for 3 hours at room temperature. After chromate adsorption, MSA-Af was treated with different elution solutions include Na_2CO_3, NaOH, $NaNO_3$ solution and DI water and immersed at room temperature for 6 hours to desorb the loaded Cr(VI) ions. The concentration of Cr(VI) ions released was determined using an UV–visible spectrophotometer. The MSA was used for chromate removal for several adsorption-desorption cycles until adsorption capacity of MSA is lower than 20% of first cycle adsorption capacity.

Figure14.18 shows Cr(VI) ion desorbed concentration of difference eluent solution. The 0.1 M Na_2CO_3 and 0.1 M NaOH represents high desorption yield and have potential to used as eluent solution for MSA regeneration. Maximum desorption yield of 0.1 M Na_2CO_3 and 0.1 M NaOH are 33.50 and 27.38 mg/g, respectively.

And result of the difference concentrations of Na_2CO_3 and NaOH (as shown in table4.9), the variance concentrations of Na_2CO_3 and NaOH are slightly increase desorption capacity when it was increased concentrations. Increasing of NaOH concentration form 0.1 to 1.0 mg/L was about 20% desorption yield increase and increasing of Na_2CO_3 concentration form 0.1 to 1.0 mg/L was also desorption yield increase about 10% of desorption capacity of 0.1M Na_2CO_3.

Amount of Cr(VI) ions released from MSA-Af by using Na_2CO_3 solution as eluent solution is higher than using NaOH solution in first cycle(shown in figure4.19). In later cycles, amount of Cr(VI) ions released into Na_2CO_3 solution was decreased and no released into Na_2CO_3 solution in forth cycle. Although, Cr(VI) ions released into NaOH solution was decrease in later cycle but it was still released in forth cycle toward. This result show NaOH solution can be eluent solution better than another.

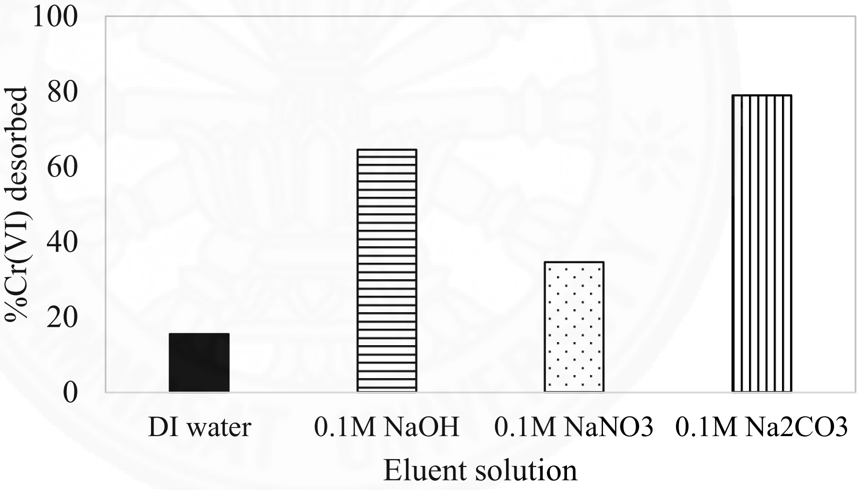

Figure4.18 % Cr(VI) desorption concentration of difference eluent solution (desorption contact time 6 hours, room temperature, not adjusted pH, MSA Dosage 1.0 g/L)

Table4.9 %Cr(VI) desorbed into difference NaOH and Na_2CO_3 concentration (contact time 6 hours, room temperature, not adjusted pH, MSA Dosage 1.0 g/L)

Eluent solution	Eluent solution concentration (M)	%Cr(VI) desorbed
NaOH	0.1	64.10
	0.5	72.90
	1	81.18
Na_2CO_3	0.1	78.42
	0.5	81.05
	1	87.56

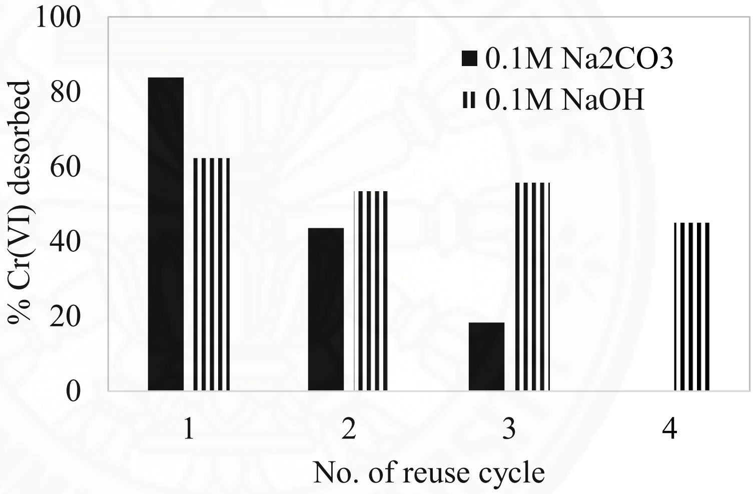

Figure4.19 %Cr(VI) concentrations desorbed of MSA-De by using 0.1M Na_2CO_3 (black) and NaOH (stripe) as a eluent solution (desorption time 6 hours, room temperature, not adjusted pH, MSA Dosage 1.0 g/L, Adsorbate chromate concentration 50 mg/L)

4.6.2 Reusability of MSA41 adsorbent

Each regeneration cycle, The MSA was used for chromate removal for several adsorption-desorption cycles until adsorption capacity of MSA is lower than 20% of first cycle adsorption capacity. Figure4.20 shows the reusability in chromate removal efficiency of MSA41. The adsorption efficiency trend to decrease with increasing of reuse cycle. MSA can be reused about 8 times. The adsorption efficiency at eighth reused cycles was 7.65 mg/g that is about 17% of adsorption efficiency first cycle.

There was revealed that NaOH can recover MSA without destroying active site surface. Moreover, this result indicated MSA has feasibility in reuse which can decline amount of waste dispose to environment and can employed MSA in chromate treatment.

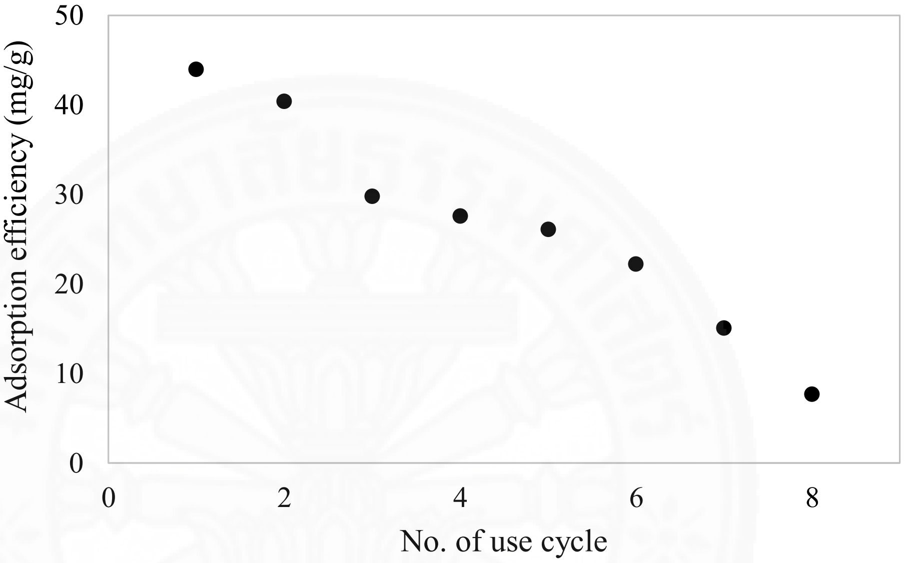

Figure4.20 chromate removal efficiency of reused MSA by using 0.1M NaOH as a eluent solution (desorption time 6 hours, room temperature, not adjusted pH, MSA Dosage 1.0 g/L, Adsorbate chromate concentration 50 mg/L)

Chapter 5
Conclusions and Recommendations

5.1 Conclusions

The characterization results of MSA from XRD, SEM, TEM and EDX confirmed that MSA consist of composite between modified sludge that is larger substrate and small magnetic particles, in which the magnetic particles occurred and distributed on the sludge modified surface.

The sludge with magnetic modification was successfully utilized in chromate removal process. It is observed that the composite between the modified sludge and the magnetic particles can increase the removal efficiency, higher than pure sludge modified and/or pure magnetic particle. An optimum molar ratio of MSA synthesis was 4:1 Ca^{2+}/Al^{3+} (MSA41). The maximum adsorption capacities of MSA was 49.50 mg of chromate/g of MSA. The equilibrium time was reached within 3 hours of contact time. The optimum dosage and initial chromate concentration were 1.0 g/L and 50 mg/L, respectively. Adsorption efficiency of MSA was dependent on pH which adsorption was increase with pH decreasing. At pH12, the chromate adsorption efficiency was decrease to lower than 10 mg/g. The adsorption efficiency was found to increase with the temperature increasing from 4 to 45°C. The study on effect of the presence of different competitive anions exhibited that chromate removal efficiency decrease with bicarbonate, sulfate and nitrate ions, but slightly decrease with chloride and phosphate ions.

MSA exhibited the pseudo second order model as reasonable kinetic explanation, indicated chemisorption by sharing or exchange of electrons between the MSA and chromate ions rather than physical adsorption. Moreover, MSA fit with the Langmuir adsorption isotherm model that indicated chromate take place on a homogeneous surface of MSA by monolayer adsorption, without interaction between chromate molecules.

In MSA regeneration process, Na_2CO_3 solution can desorbed Cr(VI) ions higher than NaOH solution in first cycle. However, in later cycles, amount of Cr(VI) ions released into Na_2CO_3 solution was decreased and no released in the forth cycle.

Although, Cr(VI) ions released into NaOH solution was decrease in later cycles, but these are still released after the forth cycles. So, NaOH solution with 0.1M was used as eluent solution. The MSA can be reuse more than 8 times before its chromate removal efficiency dropped to lower than 20%.

5.2 Recommendations

It is observed that MSA is quite non-selective for anion adsorption, as results of effect of competitive anion. Therefore, insights into anions adsorption efficiency and mechanisms should be further examined for potential applications. In addition, this laboratory scale study should be developed into bigger scales, and to pilot scale or industrial scale. The application of the materials in real situation in wastewater treatment should be studied because in reality there have many factor that can effect to Cr(VI) ion adsorption.

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