Adsorption of Chromium (VI) from Wastewater Using Natural and Modified Akadama Clay

February 2013

Yingxin ZHAO

Adsorption of Chromium (VI) from Wastewater Using Natural and Modified Akadama Clay

A Dissertation Submitted to

the Graduate School of Life and Environmental sciences,

the University of Tsukuba

in Partial Fulfillment of the Requirements

for the Degree of Doctor of Environmental Studies

(Doctoral Program in Sustainable Environmental Studies)

Yingxin ZHAO

Abstract

In aqueous systems, chromium usually exists in both trivalent and hexavalent oxidation states. But Cr (VI) is particularly concerned by public due to its great toxicity. Industrial sources of Cr (VI) are leather tanning, mining of chrome ore, electroplating, production of steel and alloys, etc. Excessive Cr (VI) is carcinogenic and mutagenic to living organisms; it also leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation. Therefore, toxic Cr (VI) must be substantially removed from the wastewater before being discharged into the aquatic system. The Maximum Contaminant Level (MCL) of total chromium in drinking water, suggested by World Health Organization (WHO) is 0.05 mg L^{-1}.

Various technologies such as chemical precipitation, coagulation, ion exchange, membrane technologies, and adsorption are available for Cr (VI) removal. Nowadays, adsorption has become the most versatile and widely used technology for its operation simplicity, availability, and recyclability. However, the most common used adsorbent, activated carbon, is too expensive to be applied in practice, hence there has been increased interest in the use of other adsorbent materials in recent years. Mineral materials are one of the most promising adsorbents.

In this study, a volcanic clay originated in Japan, Akadama clay, with good properties of porosity, permeability, and affinity, was used for Cr (VI) removal from aqueous solution. Batch experiments were carried out to investigate the effect of contact time, initial pH, and adsorbent dose on Cr (VI) adsorption. Results showed that Cr (VI) adsorption on natural Akadama clay reached equilibrium in 180 min. The Cr (VI) removal efficiency of 46.8% without pH adjustment increased to 73.8% at the optimum initial pH of 2 when initial concentration of Cr (VI) was 46.6 mg L^{-1}. The maximum adsorption capacity was 4.29 mg g^{-1} at an initial concentration of 50.0 mg L^{-1} and adsorbent dosage of 5 g L^{-1}. The equilibrium data fitted Freundlich isotherm better than Langmuir isotherm, and they were well explained by pseudo-second-order kinetic model. Adsorption mechanism analysis proved that electrostatic adsorption dominated the removal process. Results from this study demonstrate that natural Akadama clay has the potential to be an efficient adsorbent for Cr (VI) removal compared to other natural mineral adsorbents.

In order to improve the adsorption capacity of Cr (VI) and widen the adsorption conditions, HCl-modified Akadama clay (HMAC) was developed as an adsorbent for the treatment of Cr (VI) contaminated wastewater. The influences of pH, contact time, dose, initial concentrations and coexisting ions were evaluated by batch experiments. Wide pH ranges of 2 - 11 were found to be suitable for Cr (VI) adsorption onto HMAC. The maximum experimental adsorption capacity of 7.47 mg g^{-1} was obtained at an initial concentration of 112.5 mg L^{-1}, dose of 5 g L^{-1} and contact time of 24 h. The kinetic data fitted pseudo-second-order model (R^2 = 1.000) better than pseudo-first-order model (R^2 = 0.893), indicating the Cr (VI) adsorption was mainly a chemical process. The Cr (VI) adsorption process well fitted the Freundlich isotherm

model (R^2 = 0.999) and Dubinin -Radushkevich isotherm model (R^2=0.993) rather than the Langmuir isotherm model (R^2 = 0.874), revealing that heterogeneous adsorption occurred onto HMAC. HMAC had a high selectivity for Cr (VI) ions in presence of coexisting ions. A wide range of application conditions imply that HMAC is a potential adsorbent for effective adsorption of Cr (VI) in practical use.

Inorganic salts were also used to modify the original Akadama clay. Among Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+}, and Mn^{2+}, Fe^{3+} performed the best modification effect on Akadama clay, and the adsorption capacity of Cr (VI) onto Fe-modified Akadama clay (FMAC) was greatly enhanced. A factorial design methodology was applied to evaluate the importance of parameters and to optimize the adsorption process. Results revealed that initial concentration of Cr (VI) is most important for the adsorption capacity, followed by adsorbent dose, and contact time, but solution pH had no effect on the adsorption of Cr (VI). The maximum experimental adsorption capacity of Cr (VI) onto FMAC has been found to be 22.74 mg g^{-1} at a dose of 1 g L^{-1} with initial Cr (VI) concentration of 400.0 mg L^{-1} during pH range of 2 - 8. The experimental data was found to follow pseudo-second order model and Freundlich isotherm model. Thermodynamic studies indicated that the adsorption reaction was spontaneous and endothermic in nature. Therefore, FMAC has the potential to be used as an eco-friendly and economic adsorbent material for the removal of Cr (VI) from wastewater.

The developed adsorbents (natural Akadama clay, HMAC, and FMAC) were used to treat the practical industrial wastewater with a Cr (VI) concentration of 28.24

mg L^{-1} and pH of 9.2. When the adsorbent dosage was 5 g L^{-1} and contact time of 4 h, the removal efficiencies of Cr (VI) were 23.1%, 38.9%, and 94.5%, and adsorption capacities of Cr (VI) were 1.30, 2.20, and 5.34 mg g^{-1} for natural Akadama clay, HMAC, and FMAC, respectively.

In conclusion, the original Akadama clay, HMAC, and FMAC could be effectively used as adsorbents for Cr (VI) removal from wastewater. Among them, FMAC, presenting the best performance based on its low cost, wide pH conditions, and high adsorption efficiency, could be considered in practical application.

Contents

Chapter 1 Introduction

Heavy metals have been excessively released into the environment due to rapid industrialization and have become a great challenge for life on earth [1].Whenever toxic heavy metals are exposed to the natural eco-system, they will accumulate in human body through either direct intake or food chains, thus severely threaten human health [2]. Chromium is one of the most frequently used heavy metal contaminants and has received a lot of attention in recent years.

1.1 Chromium species

Chromium is an odorless and tasteless metallic element, which is found naturally in rocks, plants, soil and volcanic dust, humans and animals. Chromium exists in +2, +3 and +6 oxidation states but Cr^{2+} is unstable and very little is known about its hydrolysis [3]. The most common forms of chromium that occur in natural waters in the environment are trivalent chromium (Cr (III)) and hexavalent chromium (Cr (VI)). Cr (III) is an essential human dietary element and occurs naturally in many vegetables, fruits, meats, grains and yeast. The hydrolysis of Cr (III) is complicated. It produces mononuclear species like $CrOH^{2+}$, $Cr(OH)_2^{+}$, and $Cr(OH)_4^{-}$, neutral species $Cr(OH)_3^{0}$ and polynuclear species $Cr_2(OH)_2$ and $Cr_3(OH)_4^{5+}$ [4]. Cr (VI) occurs naturally in the environment from the erosion of natural chromium deposits but it can also be produced by industrial processes. There are demonstrated instances of chromium being released to the environment by leakage, poor storage, or inadequate industrial waste disposal practices [5]. The hydrolysis of Cr^{6+} produces only neutral and anionic species, predominately CrO_4^{2-}, $HCrO_4^{2-}$, and $Cr_2O_7^{2-}$ [3]. The redox potential Eh–pH diagram (as shown in Fig.1-1) presents equilibrium data and indicates the different oxidation states and chemical forms which exist within specified Eh and pH ranges [3]. Relative distribution of Cr (VI) species in water as a function of pH and Cr (VI) concentration is shown in Fig.1-2 [6]. It can be seen that H_2CrO_4 exists only at pHs less than about 1; $HCrO_4^-$ is the dominated specie at pHs of 1 – 6 and Cr (VI) concentration less than 1 g L^{-1}; CrO_4^{2-} occurs at pHs above about 6; the dichromate ion ($Cr_2O_7^{2-}$) is a dimer of $HCrO_4^-$, which forms when the concentration of chromium exceeds approximately 1 g L^{-1}.

1.2 Industrial uses of chromium

Chromium is widely used in industries such as electroplating, leather tanning, catalysts, pigments and paints, fungicides, ceramics and glass, and photography etc., and it is also used for chrome alloy and chromium metal production, chrome plating, and corrosion control[7]. For instance, in metallurgical industry, the strengthening effect of forming stable metal carbides at the grain boundaries and the strong increase in corrosion resistance made chromium an important alloying material for steel. Take cast iron for example, it contains chromium from 0.5% to 30%, and is of hardness, toughness, corrosion and wear resistance properties [8]. Because of their toxicity, chromium(VI) salts are also used for the preservation of wood. For example, chromated copper arsenate (CCA) is used in timber treatment to protect wood from decay fungi, wood attacking insects, including termites, and marine borers [9].In leather tanning industry, 80-90% of leather is tanned with chromium chemicals; as regards the chromium chemicals, the largest amount is consumed to manufacture pigments for use in paints and inks; chromite is also used in the refractory industry to make bricks, mortar, and ramming and gunning mixes, in which chromium helps enhance their thermal shock and slag resistance, volume stability and strength [8].

1.3 Chromium pollution, hazard, and regulation

Due to the wide use of chromium in industries, chromium contaminated wastewater has become worldwide and more and more serious.

A world-famous case happened in Hinkley (a small desert town in San Bernardino Country, USA). Pacific Gas and Electric Company (PG & E) used hexavalent chromium to prevent pipes from rusting in cooling systems. The effluent of hexavalent chromium contaminated water on the PG&E property, seeped into the ground and contaminated local water supplies. PG & E was ordered to clean up the hexavalent chromium contamination and stop using hexavalent chromium in their operations. They were also ordered to compensate the plaintiffs $333 million, which is the highest compensation award in metal toxicity history [10]. In 2005, the Indian Supreme Court penalized Hema chemicals for their illegal chromium dumping, and a similar case occurred in 2007 in the Asopos River, near Oinofyta, Greece. Clearly this is a continuing problem of ecology and coordination chemistry. In June 2009, the ground water in Midland, Texas (USA) was found to be contaminated with chromium [10].In

2012, 5000 tons of chromic slag was dumped in Qujing city, China, about hundreds of thousands of cubic meter water was contaminated by chromium. And Pearl River, with its source near Qujing, was also under threat.

Cr (III) is a nutritionally essential element in humans and is often added to vitamins as a dietary supplement. Cr (III) has relatively low toxicity and would be a concern in drinking water only at high levels of contamination; Cr (VI) is more toxic and poses potential health risks [5]. Cr(VI) is carcinogenic and mutagenicto living organisms, and it also leads to liver damage, pulmonary congestion and causes skin irritation resulting in ulcer formation [11].

US Environmental Protection Agency (USEPA) has set an enforceable regulation for total chromium, called a maximum contaminant level (MCL), at 0.1 mgL^{-1} or 100 ppb. MCLs are set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies [5].Cr (VI) and Cr (III) are covered under the total chromium in the drinking water standard because these forms of chromium can convert back and forth in water and in the human body, depending on environmental conditions. Measuring just one form may not capture all of the chromium that is present. In order to ensure that the greatest potential risk is addressed, EPA's regulation assumes that a measurement of total chromium is 100 percent Cr (VI), the more toxic form [5]. WHO proposes the limit value of total chromium of 0.05 mg L^{-1} [12].

However, different countries regulated different MCLs of chromium. For example, in developed country of Japan, Ministry of Health, Labour and Welfare

(MHLW) set the MCL of Cr (VI) as 0.05 mg L^{-1} without taking Cr (III) into account. The developing countries such as China implement the same standard with Japan, also have not considered Cr (III). Because Cr (III) possibly converts to Cr (VI) in water system or human body, and then threatens human health, it is necessary to unify the MCL of chromium all over the world, no matter developing countries or developed countries. Therefore, there are significant improvements still to be made in the standard of chromium in drinking water.

1.4 Treatment technologies

1.4.1 Chemical methods

Redox precipitation is the most widely used process in chemical method. This treatment performs chemical reduction of Cr(VI) to the less toxic Cr(III), with a subsequent modification of pH to form slightly soluble $Cr(OH)_3$. The most commonly used reductor agents in this type of process are $FeSO_4$, $Na_2S_2O_5$ and SO_2, in which $Na_2S_2O_5$ has the advantage of generating a lower amount of sludge than $FeSO_4$, and is less toxic than SO_2 [13]. The chemical treatment approach of effluents is easy to implement, and generally does not require sophisticated equipment. However, consumption of high amount of chemicals and large volume of sludge generated make the process costly [14].

Electrochemical processes, highly selective and efficient for Cr (VI) removal, have been very promising for the treatment of Cr (VI) contaminated wastewaters [15]. It could be more clean or competitive considering the operating costs of an electrochemical process at industrial level. Nevertheless, disadvantages such long time (several hours) or low current efficiencies should be remarked [16]. Moreover, the stability, feasibility of the electrodes, cost of salt (conductivity enhancement), post-treatment of high salinity effluent etc. should also be noticed.

1.4.2 Biological methods

Bioremediation is generally mediated by a diverse group of organisms namely bacteria, fungi, and algae [17]. The most frequently studied biosorbents for chromium are bacteria which include Pseudomonas aeruginosa [18],Bacillus sphaericus [19]; fungi such as Ganoderm lucidum [20], Aspergillus niger, Rhizopus oryzae, Saccharomyces cerevisiae and Penicillium chrysogenum [21]; and algae such as Sargassum sp.[22] and Chlorella miniata [23].

Biological methods used for the removal of Cr (VI) are gaining interest among researchers due to several advantages that include:1) possibility of recovery of metal; 2) good performance and low cost of the process; 3) waste from the processes is readily treated and can be easily disposed by incineration; 4) biosorption employs inexhaustible, inexpensive and non-hazardous materials; 5) natural affinity of biological compounds for metallic elements and it does not produce toxic sludge. Further it can be integrated with many systems and does not create serious problem to ecosystem [24].

1.4.3 Physical-chemical method

Physical-chemical methods mainly include membrane separation process, ion exchange, and adsorption, etc.

Mature application of membrane separation processes includes electrodialysis, osmosis, nanofiltration, ultrafiltration, and liquid membrane etc. [25-27]. Among these processes, electrodialysis has been successfully applied in the treatment of Cr (VI) containing wastewater. In electrodialysis process, ions are transported through ion selective barriers from one solution to another using an electric field as the driving force[28]. Chen et al. [29] designed a two-stage electrodialysis system to concentrate and purify chromate from a low pH electroplating wastewater using monovalent selective electrodialysis membranes. They found that with low pH of the raw water (pH 2.2) in the first stage, chromate was presented as $HCrO_4^-$ and monovalent ions ($HCrO_4^-$, $NH_2SO_3^-$, Na^+ and Cl^-) were able to pass through the membrane thus chromate was concentrated up to 191%.

Ion exchange process mainly uses anion exchange resin to remove chromate, and uses cation exchange resin to remove Cr (III) and other heavy metals. The main advantages of ion exchange over chemical precipitation are recovery of metal, selectivity, less sludge volume production and the meeting of strict discharge specifications [30]. Rengaraj et al. [31] performed equilibrium and kinetics experiments to evaluate the adsorption capacity of chromium by three different strongly acid resins. Results obtained by Shi et al. [32] showed that the adsorption pattern on the resins followed Langmuir isotherms and the calculated maximum sorption capacities of D301, D314 and D354 were 152.52, 120.48 and 156.25 mg g^{-1}, respectively.

Adsorption has proved to be an effective and reliable method for the removal of Cr (VI) from wastewater and draws increasingly attention in recent years. Activated carbon is the most widely used absorbent, owing to its highly developed porosity, excellent adsorption capacity and high specific surface area [33]. However, commercially available activated carbons are usually expensive due to their high-cost sources, which restrict their extensive application. Low cost and highly efficient adsorbents could be obtained from raw agricultural wastes or raw material derived activated carbons such as sawdust, sugarcane bagasse, wheat bran, wheat straw, corn stoves, papaya wood, peanut hull pellets, grape stalk wastes etc. [1, 34]. Natural or modified minerals used as adsorbents are also popular for Cr (VI) removal. Many minerals such as zeolite, bentonite, montmorillonite, attapulgite, dolomite, sepiolite etc. have been reported in literatures [35-41]. The adsorption conditions and maximum adsorption capacity using different mineral adsorbents for Cr (VI) removal are given in Table 1-1.

1.5 Objective and contents of this study

As mentioned in section 1.4.3, for the advantages of operation simplicity, cost-effectivity, ready availability, and renewable ability, adsorption is considering to be one of the most promising technologies for Cr (VI) removal. Although various adsorbents are available and have been developed, it is still promising to develop new low-cost adsorbents to effectively remove Cr (VI) from contaminated water.

Akadama clay, a volcanic soil, is mined from a depth of about three meters. The deeper it is mined the harder it becomes. It is then dried and baked to remove any organic matter and diseases. Finally, it is crushed, sieved and graded into different particle sizes and then bagged up. After these treatments, it is available in the market. Akadama clay is usually used by many bonsai growers for its ability to retain water and nutrients while still providing porosity and free drainage. Akadama clay is very porous which means that there should be very good water circulation through the substrate helping prevent any dead spots and providing plant roots with nutrients. Good properties such as porosity, permeability, and affinity, combining with its economical and abundant merits, make Akadama clay possible to be used as an adsorbent.

On account of the mentioned good properties, Akadama clay has been used to adsorb inorganic arsenic from wastewatersuccessfully [46]. Besides, granular adsorbent based on Akadama clay was developed and used for arsenic removal [47]. In present study, it aims to develop new ways to utilize Akadama clay. As the physical and chemical properties of arsenic and chromium are similar, it is possible to remove chromium from wastewater using Akadama clay as an adsorbent.

The contents of this study are divided into three parts to comprehensively evaluate the adsorption performance of Cr (VI) onto original and modified Akadama clay.

In the first part of this study (Chapter 2), original Akadama clay was characterized using X-Ray Diffraction (XRD), scanning electron microscope (SEM), and Brunauer–Emmett–Teller (BET) specific surface analysis devices. Then the effects of contact time, pH, and adsorbent dose on Cr (VI) adsorption onto Akadama clay were investigated. The adsorption isotherms and kinetics were analyzed, and the adsorption mechanism was also discussed.

In the second part of this study (Chapter 3), in order to improve adsorption efficiency and widen adsorption conditions, several inorganic acids (hydrochloric acid, nitric acid, sulfuric acid, and phosphoric acid) were tried to modify the Akadama clay. The optimum acid was determined and its best modification concentration was also obtained. A series of batch experiments were conducted to evaluate the performance of acid-modified Akadama clay. The effects of parameters such as pH, contact time, initial concentration, dosage, and coexisting ions were investigated. Adsorption isotherms and kinetics were also analyzed.

In the third part of this study (Chapter 4), inorganic salts were used to modify Akadama clay. The most effective salt would be confirmed. A factorial design methodology was applied to evaluate the importance of each factor (pH, contact time, adsorbent dosage and initial concentrations) and optimize the adsorption process. The significant parameters on the adsorption of Cr (VI) were investigated. The adsorption performances of the natural Akadama clay, HMAC, and FMAC were compared through remove Cr (VI) from practical tannery wastewater.

The whole structure of this thesis is illustrated in Fig.1-3. The Cr (VI) contaminated wastewater would be effectively treated through the design and method established by this study.

References

[1] W.S. Wan Ngah, M.A.K.M. Hanafiah, Removal of heavy metal ions from

wastewater by chemically modified plant wastes as adsorbents: A review, Bioresource Technology, 99 (2008) 3935-3948.

[2] H.J. Park, S.W. Jeong, J.K. Yang, B.G. Kim, S.M. Lee, Removal of heavy metals using waste eggshell, Journal of Environmental Sciences, 19 (2007) 1436-1441.

[3] D. Mohan, C.U. Pittman, Activated carbons and low cost adsorbents for remediation of tri- and hexavalent chromium from water, Journal of Hazardous Materials, 137 (2006) 762-811.

[4] D. Mohan, K. Singh, V. Singh, Trivalent chromium removal from wastewater using low cost activated carbon derived from agricultural waste material and activated carbon fabric cloth, Journal of Hazardous Materials, 135 (2006) 280-295.

[5] U.S. EPA, Basic Information about Chromium in Drinking Water, United States Environmental Protection Agency, Washington, D.C., 2012.

[6] Dionex, Determination of Cr(VI) in water, wastewater and solid waste extracts, Dionex Corporation, California, 1996.

[7] WHO, Chromium in Drinking-water, Health criteria andother supporting information, World Health Organization, Geneva, Switzerland, 1996.

[8] B. Dhal, H. N. Thatoi, N. N. Das, B.D. Pandey, Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review, Journal of Hazardous Materials, 250-251 (2013) 272-291.

[9] J.A Hingstona, C.D Collinsa, R.J Murphyb, J.N Lester,Leaching of chromated copper arsenate wood preservatives - a review. Environmental Pollution, 111 (2001) 53-66.

[10] B. Saha, C. Orvig, Biosorbents for hexavalent chromium elimination from industrial and municipal effluents, Coordination Chemistry Reviews, 254 (2010) 2959-2972.

[11] M. Cieślak-Golonka, Toxic and mutagenic effects of chromium (VI), Polyhedron, 15 (1996) 3667-3689.

[12] WHO, Guidelines for Drinking-water Quality– 4thed, World Health Organization, Geneva, Switzerland, 2011.

[13] G. Almaguer-Busso, G. Velasco-Martínez, G. Carreño-Aguilera, S. Gutiérrez-Granados, E. Torres-Reyes, A. Alatorre-Ordaz, A comparative study of global hexavalent chromium removal by chemical and electrochemical processes, Electrochemistry Communications, 11 (2009) 1097-1100.

[14] A.K. Golder, A.K. Chanda, A.N. Samanta, S. Ray, Removal of hexavalent chromium by electrochemical reduction–precipitation: Investigation of process performance and reaction stoichiometry, Separation and Purification Technology, 76 (2011) 345-350.

[15] P. Rana, N. Mohan, C. Rajagopal, Electrochemical removal of chromium from wastewater by using carbon aerogel electrodes, Water Research, 38 (2004) 2811-2820.

[16] E.P.L. Roberts, H. Yu, Chromium removal using a porous carbon felt cathode, Journal of Applied Electrochemistry, 32 (2002) 1091–1099.

[17] M. Pandi, V. Shashirekha, M. Swamy, Bioabsorption of chromium from retan chrome liquor by cyanobacteria, Microbiological Research, 164 (2009) 420-428.

[18] A.H. Alvarez, R. Moreno-Sánchez, C. Cervantes, Chromate efflux by means of the

ChrA chromate resistance protein from Pseudomonas aeruginosa, Journal of Bacteriology, 181 (1999) 7398-7400.

[19] A. Pal, AK.Paul, Aerobic chromate reduction by chromium-resistant bacteria isolated from serpentine soil, Microbiological Research, 159 (2004) 347-354.

[20] K. Krishna, L. Philip, Bioremediation of Cr(VI) in contaminated soils, Journal of Hazardous Materials, 121 (2005) 109-117.

[21] D. Park, Y.S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of Ecklonia sp, Chemosphere, 60 (2005) 1356-1364.

[22] L. Yang, J.P. Chen, Biosorption of hexavalent chromium onto raw and chemically modified Sargassum sp, Bioresource Technology, 99 (2008) 297-307.

[23] X. Han, Y.S. Wong, M.H. Wong, N.F.Y. Tam, Biosorption and bioreduction of Cr(VI) by a microalgal isolate, Chlorella miniata, Journal of Hazardous Materials, 146 (2007) 65-72.

[24] S. Mishra, M. Doble, Novel chromium tolerant microorganisms: Isolation, characterization and their biosorption capacity, Ecotoxicology and Environmental Safety, 71 (2008) 874-879.

[25] M. Aleb-Ahmed, R.M. S. Taha, G. Dorange, The influence of physico-chemistry on the retention of chromium ions during nanofiltration, Desalination, 145 (2002) 103-108.

[26] S.D. Avijit Bhowal, Studies on transport mechanism of Cr(VI) extraction from an acidic solution using liquid surfactant membranes, Journal of Membrane Science, 188 (2001) 1-8.

[27] C. Das, P. Patel, S. De, S. DasGupta, Treatment of tanning effluent using nanofiltration followed by reverse osmosis, Separation and Purification Technology, 50 (2006) 291-299.

[28] C. Korzenowski, M.A.S. Rodrigues, L. Bresciani, A.M. Bernardes, J.Z. Ferreira, Purification of spent chromium bath by membrane electrolysis, Journal of Hazardous Materials, 152 (2008) 960-967.

[29] S.S. Chen, C.W. Li, H.D. Hsu, P.C. Lee, Y.M. Chang, C.H. Yang, Concentration and purification of chromate from electroplating wastewater by two-stage electrodialysis processes, Journal of Hazardous Materials, 161 (2009) 1075-1080.

[30] F. Gode, E. Pehlivan, A comparative study of two chelating ion-exchange resins for the removal of chromium(III) from aqueous solution, Journal of Hazardous Materials, 100 (2003) 231-243.

[31] S. Rengaraj, Cheol Kyun Joo, Younghun Kim, J. Yi, Kinetics of removal of chromium from water and electronic process wastewater by ion exchange resins: 1200H, 1500H and IRN97H, Journal of Hazardous Materials, B102 (2003) 257–275.

[32] T. Shi, Z. Wang, Y. Liu, S. Jia, D. Changming, Removal of hexavalent chromium from aqueous solutions by D301, D314 and D354 anion-exchange resins, Journal of Hazardous Materials, 161 (2009) 900-906.

[33] R.L. Tseng, S.K. Tseng, Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob, Journal of Colloid and Interface Science, 287 (2005) 428-437.

[34] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw

and modified lignocellulosic materials: A review, Journal of Hazardous Materials, 180 (2010) 1-19.

[35] S. A. Khan, R. Rehman, M.A. Khan, Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite, Waste Management, 15 (1995) 271-282.

[36] B. Sarkar, Y. Xi, M. Megharaj, G.S.R. Krishnamurti, D. Rajarathnam, R. Naidu, Remediation of hexavalent chromium through adsorption by bentonite based Arquad® 2HT-75 organoclays, Journal of Hazardous Materials, 183 (2010) 87-97.

[37] R. Leyva-Ramos, A. Jacobo-Azuara, P.E. Diaz-Flores, R.M. Guerrero-Coronado, J. Mendoza-Barron, M.S. Berber-Mendoza, Adsorption of chromium(VI) from an aqueous solution on a surfactant-modified zeolite, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 330 (2008) 35–41.

[38] A. Santhana Krishna Kumar, R. Ramachandran, S. Kalidhasan, V. Rajesh, N. Rajesh, Potential application of dodecylamine modified sodium montmorillonite as an effective adsorbent for hexavalent chromium, Chemical Engineering Journal, 211-212 (2012) 396-405.

[39] B. Hu, H. Luo, Adsorption of hexavalent chromium onto montmorillonite modified with hydroxy aluminum and cetyltrimethylammonium bromide, Applied Surface Science, 257 (2010) 769-775.

[40] A.G. Thanos, E. Katsou, S. Malamis, K. Psarras, E.A. Pavlatou, K.J. Haralambous, Evaluation of modified mineral performance for chromate sorption from aqueous solutions, Chemical Engineering Journal, 211-212 (2012) 77-88.

[41] V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Potkonjak, Đ. Janaćković, R.

Petrović, Chromium (VI) removal from aqueous solutions using mercaptosilane functionalized sepiolites, Chemical Engineering Journal, 166 (2011) 198-206.

[42]C.H. Weng, Y.C. Sharma, S.H. Chua, Adsorption of Cr(VI) from aqueous solutions by spent activated clay, Journal of Hazardous Materials, 155 (2008) 65–75.

[43] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Chromium(VI) adsorption from aqueous solution onto Moroccan Al-pillared and cationic surfactant stevensite, Journal of Hazardous Materials, 140 (2007) 104–109.

[44] J.B. Zhou, P.X. Wu, Z. Dang, Polymeric Fe/Zr pillared montmorillonite for the removal of Cr(VI) from aqueous solutions, Chemical Engineering Journal, 162 (2010) 1035–1044.

[45] W. Li, Y. Tang, Y. Zeng, Z. Tong, D. Liang, W. Cui, Adsorption behavior of Cr(VI) ions on tannin-immobilized activated clay, Chemical Engineering Journal, 193–194 (2012) 88–95.

[46] R. Chen, Z. Zhang, C. Feng, Z. Lei, Y. Li, M. Li, K. Shimizu, N. Sugiura, Batch study of arsenate (V) adsorption using Akadama mud: Effect of water mineralization, Applied Surface Science, 256 (2010) 2961-2967.

[47] R. Chen, Z. Zhang, Z. Lei, N. Sugiura, Preparation of iron-impregnated tablet ceramic adsorbent for arsenate removal from aqueous solutions, Desalination, 286 (2012) 56-62.

Table 1-1 Comparison of adsorption capacity among different mineral adsorbents

Adsorbent materials	pH	Dose ($g\ L^{-1}$)	Initial Cr (VI) concentration($mg\ L^{-1}$)	Q_m ($mg\ g^{-1}$)	Refer.
Spent activated clay	2	1	0.2-10	1.42	42
Aluminium hydroxypolycation (Al-stevensite)	3.5–6.0	-	0-400	3.92	43
Mercaptosilanefunctionalized sepiolites	3	0.4	5-100	8.00	41
Cetyltrimethylammoniumbromide stevensite (CTA-stevensite)	2.0–6.0	-	0-400	10.17	43
Bentonite based Arquad® 2HT-75 organoclays	5	5	10-200	14.64	36
Polymeric Fe/Zr pillared montmorillonite	3	2	0-80	22.35	44
Dodecylamine modified sodium montmorillonite	2.5	2	-	23.69	38
Tannin-immobilized activated clay (TA-AC)	2.5	-	60-300	24.09	45

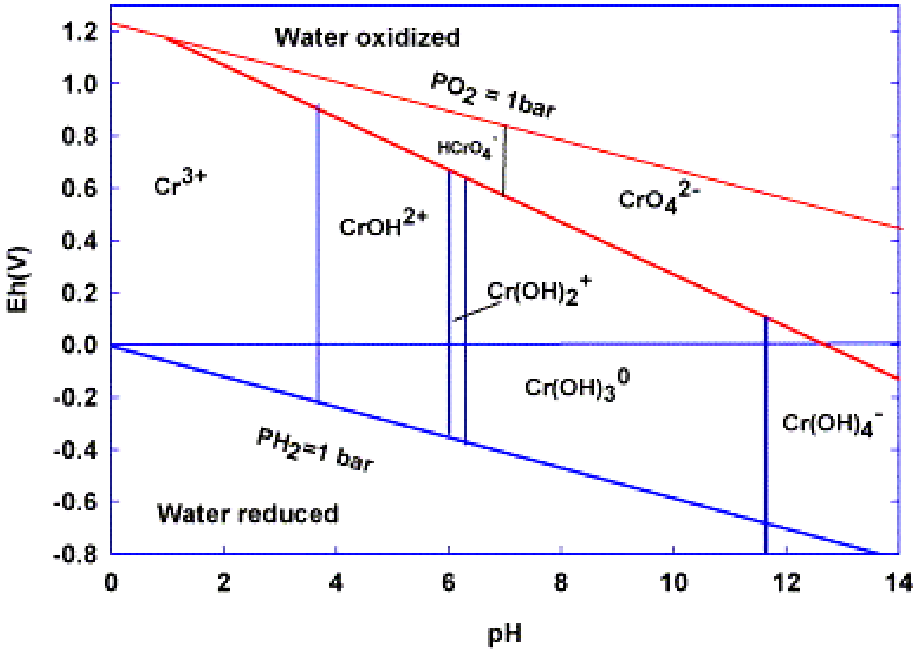


Fig.1-1 Eh–pH diagram for chromium [3]

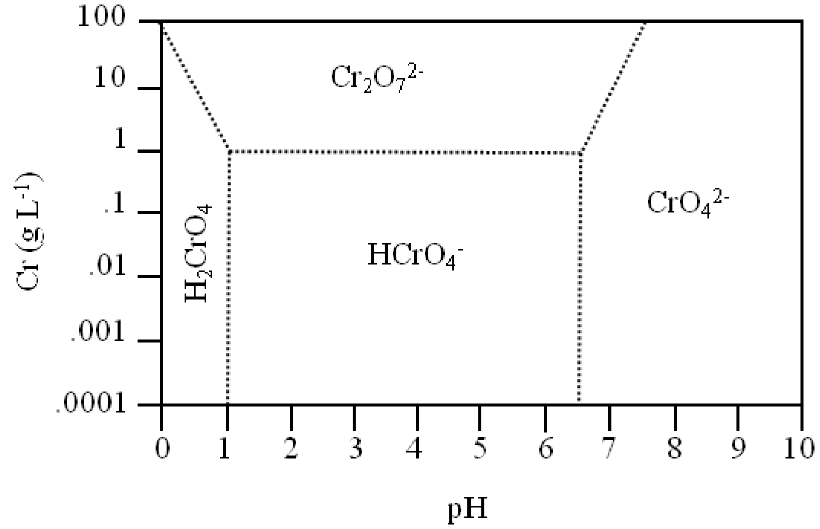


Fig.1-2 Speciation diagram of Cr(VI) as a function of pH and Cr (VI) concentrations[6]

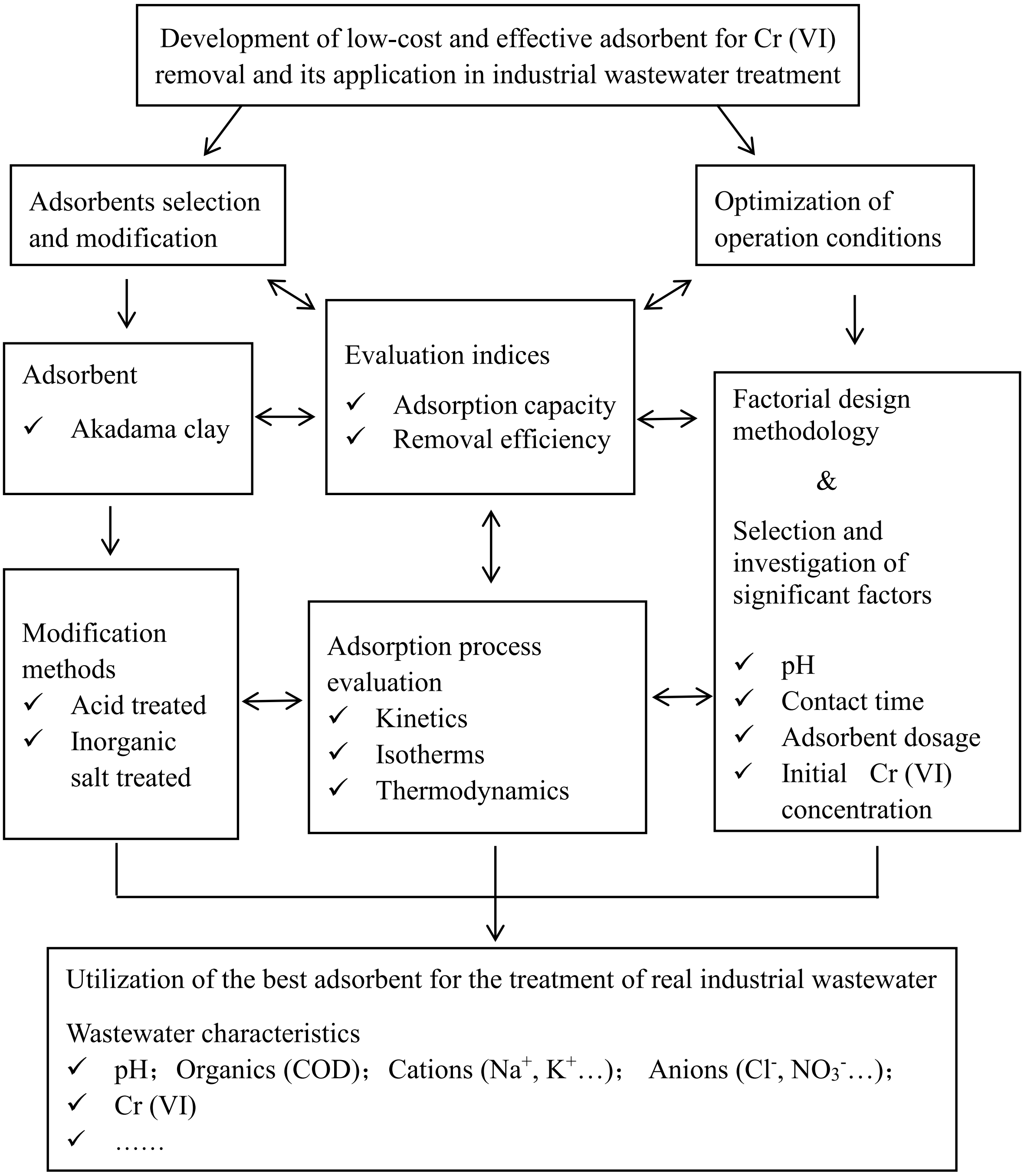


Fig.1-3 Experimental scheme of this thesis

Chapter 2 Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay

2.1 Introduction

Nowadays, with the rapid development of metallurgy, dye and pigment, electroplating, leather tanning, refractory material, catalysts, and wood preservation industries, the discharge of chromium contaminated wastewater into water bodies has become more and more serious [1, 2]. In the aquatic environment, chromium primarily exists in trivalent Cr (III) and hexavalent forms Cr (VI), and the relation between Cr (III) and Cr (VI) depends strongly on pH and the oxidative properties of the location. The public are more concerned about Cr (VI) because its toxicity is 100 times higher than Cr (III), and it can seriously damage people's health due to its carcinogenicity, mutagenicity and teratogenicity in biological systems [3, 4].The limit of Cr (VI) in drinking water proposed by the US EPA is 0.05 mgL^{-1}, while the maximum limit is 0.10 mg L^{-1} in industrial wastewater [5].

Various technologies have been used to remove Cr (VI) from wastewater including chemical reduction, electrocoagulation, membranes (reverse osmosis, nanofiltration, and ultrafiltration), adsorption, and biological processes, etc. [6-11]. It has been reported that traditional physical and chemical methods occasionally suffer from high operative cost and strict reaction conditions, and biological methods have low treatment efficiency [12]. Among the mentioned methods, adsorption draws higher attention for its low cost, simple operation and high efficiency. Different adsorbents such as activated carbon [13, 14], modified chitosan [1, 15, 16], polymer [12, 17], modified lignocellulosic materials [18] have been used to remove Cr (VI) from wastewater. In general, with various polymers and modified adsorbents, large quantities of chemicals and complicated procedures are required, so it is better to use cheaper and natural materials as adsorbents for Cr (VI)treatment [19].Sawdust directly used as an adsorbent in continuous Cr(VI) removal from aqueous solutions was reported by Gupta and Babu [20]. Venugopal and Mohanty [21] used raw Parthenium hysterophorus weed to remove Cr(VI) ions from aqueous solution, and the maximum Cr(VI)adsorption capacity of Parthenium weed was found to be 24.5 mg g^{-1}under optimized conditions. However, research on the use of untreated natural clays is rarely undertaken. Recently, Akar et al. [22] reported Cr (VI) adsorption on natural Turkish montmorillonite clay, and the maximum Cr (VI) adsorption capacity only reached 3.16 mg g^{-1}at an initial concentration of 250 mg L^{-1}, adsorbent dosage of 10 g L^{-1} and pH 1. Therefore, it is worthy of trying to find other low cost natural clays with high removal efficiency as Cr (VI) adsorbents.

Natural Akadama clay, common and cheap in Japan, is a deposit of volcanic ash with a faint yellow color and slightly acidic pH. As a widely used soil medium, it is characterized by high osmotic properties and has strong impounding and water draining properties also. Some researchers used Akadama clay to remove inorganic arsenic as an adsorbent [23]. As far as we know, the removal of Cr (VI) using natural Akadama clay has been not reported by other studies.

The present study aimed to evaluate the performance of natural Akadama clay as an alternative Cr (VI) adsorbent. The effects of contact time, pH, initial Cr (VI) concentration, and adsorbent dosage on Cr (VI) removal efficiency were investigated by batch experiments. The adsorption process was analyzed using various kinetic and isotherm models. The mechanism of Cr (VI) removal on natural Akadama clay was also discussed.

2.2 Materials and methods

2.2.1 Chemicals and materials

All chemical reagents used were of analytical grade without further purification. $K_2Cr_2O_7$(Wako Pure Chemical Industries, Japan) used in this study, was first dried at 105°C in the oven for 24 h. The synthetic solution of Cr (VI) was prepared by dissolving the required amount of dried $K_2Cr_2O_7$ in deionized water. A stock solution with a concentration 1000 mg L^{-1} of Cr (VI) was prepared and subsequently diluted to the designed concentration in the following experiments. 1 M HCl (Wako Pure Chemical Industries, Japan) or 1 M NaOH (Wako Pure Chemical Industries, Japan) was used to adjust the solution pH to the desired value.

Natural Akadama clay used in this study was provided by Makino Store, Kiyosu, Japan. Akadama clay was crushed and sieved until the particle diameter was less than 105 μm. The clay sample was washed with distilled water several times to remove impurities, and then dried at room temperature. The fully dried clay was transferred to a plastic airtight bottle for future adsorption experiments.

2.2.2 Methods

2.2.2.1 Characterization methods

A gravimetric nitrogen Brunauer–Emmett–Teller (BET) specific surface analysis device (Coulter SA3100, US) was used to determine the specific surface area and pore-size distributions of Akadama clay. The morphological features of the natural Akadama clay were acquired by scanning electron microscope (SEM) (JSM-6330F, JEOL, Japan). The mineralogical phase characterization of Akadama clay was carried out by quantitative X-ray diffraction (XRD) (RINT2200, Rigaku, Japan). The concentrations of Cr (VI) were measured according to Diphenyl carbohydrazide spectrophotometric method by ultraviolet spectrophotometer (UV-1800, Japan). The zeta potential value was determined by Zeta Sizer Nano-ZS (England). The inorganic metal elements dissolved out were determined using inductively coupled plasma spectrometry (ICPS-8100, Japan). The pH of the Cr (VI) solution was determined using a pH meter (Mettler-Toledo AG, Switzerland).

2.2.2.2 Batch Cr (VI) adsorption experiments

The experiments were carried out in 15 mL plastic centrifuge tubes. After clay was added to the Cr (VI) solution, the resultant suspensions were shaken constantly (200 rpm) in a shaker so as to ensure sufficient adsorption at ambient temperature (25 ± 2°C). Then the samples were centrifuged at 10000 rpm for 2 min and the supernatant was used for Cr (VI) determination.

The adsorption experiments carried out in present study were summarized in Table 2-1. The mechanism of Cr(VI) adsorption process was studied by analyzing the pH variation, concentrations of Cr(III), Cr(VI) and total Cr in the residual solution when the initial concentration was 50.0 mg L^{-1}, optimum pH 2, and dosage ranges of 5 - 50 g L^{-1}. Each adsorption experiment was carried out at least 3 times, and the result was expressed as an average of the triplicate values.

2.3 Results and discussion

2.3.1 Surface characterization

Natural Akadama clay mainly consists of silica (51.30%),and the major metallic oxide content is aluminum oxide (38.05%),followed by iron (III) oxide (7.67%), magnesia (1.94%), calcium oxide (0.78%) and manganese oxide (0.26%) [23]. The XRD pattern is shown in Fig. 2-1a. The strong peaks of quartz (SiO_2), diaspore (AlOOH), and hematite (Fe_2O_3) further confirm the main chemical compositions of natural Akadama clay. Surface area characterization and pore volume analysis of Akadama clay before and after Cr (VI) adsorption are shown in Table 2-2, and the BJH (Barrett–Joyner–Halenda) adsorption pore size distribution is shown in Fig.2-1b.In this study, the BET specific surface area of natural Akadama clay (< 105μm) was 174.26m^2 g^{-1},and the total pore volume was 0.1920 mLg^{-1}.The BJH adsorption pore size distribution reveals that the observed pore sizes mostly varied between 2 and 50 nm (62.76%). According to the IUPAC classification, Akadama clay is classified as a mesoporous material. The surface morphologies of natural Akadama clay before and after Cr (VI) adsorption are examined by SEM (Fig.2-1c and Fig.2-1d). The unconsolidated and flocky surface texture of natural Akadama clay implies its good porous properties. After Cr (VI) adsorption, loose surface becomes caked and lumpish, indicating that the clay particles might be bonded by chromate ions. The observation could be further demonstrated by the decrease of both the specific areas and total pore volume after Cr (VI) adsorption.

2.3.2 The effect of contact time

Fig.2-2 shows that, in the first 2 min, the initial concentrations of Cr (VI) decreased sharply from 49.7, 19.5, 9.4 mg L^{-1} to 32.5, 8.3, and 3.4 mg L^{-1} with the removal efficiencies of 34.6%, 57.4%, and 63.8%, respectively. Then the decrease rates slowed and finally the equilibrium concentrations were reduced to 26.1, 6.1 and 2.8 mg L^{-1}, and the removal efficiencies increased to 47.5%, 68.7%, and 70.2% during the 240 min period. When the initial concentration was 9.4 mg L^{-1}, and adsorbent dosage was 20 g L^{-1}, the adsorption capacity of 0.30 mg g^{-1} at the 2 min and that of 0.33 mg g^{-1} at 240 min showed no significant increase, indicating that the adsorption of Cr (VI) was quite a rapid process. The Cr (VI) removal rate using Akadama clay was faster than that using many other adsorbents [24]. As the final concentrations became stable in 180, 120, and 30 min for different initial concentrations of 49.7, 19.5, 9.4 mg L^{-1}, the adsorption equilibrium times were set in 180, 120, and 30 min, respectively. The time required to reach equilibrium depending on the initial Cr(VI) concentration was also reported by other studies [25, 26]. In the following experiments, the shaken time of 180 min was chosen to ensure adsorption equilibrium.

2.3.3 The effect of pH

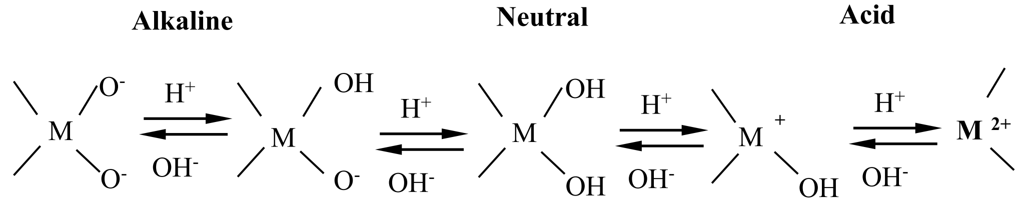
The Cr (VI) adsorption process is greatly affected by the solution pH. Many studies have confirmed that the surface charge of the adsorbents, the degree of ionization, and the different ionic forms of chromium solutions are dependent on the solution pH [1, 27]. Fig.2-3 shows that the maximum adsorption could be obtained at pH 2 with removal efficiency of 73.8% and adsorption capacity of 1.72 mg g^{-1}at conditions of initial Cr (VI)concentration of 46.6 mg L^{-1}, adsorbent dosage of 20 g L^{-1} and contact time of 180 min. Compared with the removal efficiency (46.8%) under the same conditions without pH adjustment the adsorption ability was greatly improved at pH 2. This observation was in agreement with the reports by Alemayehu et al. [4] and Suksabye and Thiravetyan [28].

In order to make clear why there was an adsorption maximum at pH 2, the effect of pH on the clay properties was investigated. In five 15 mL centrifuge tubes, 0.2 g Akadama clay was added to 10 mL deionized water with pH ranges from 1 to 5. The tubes were shaken at 200 rpm for 180 min, and then the solid-liquid separation was carried out by a centrifuge. The dissolved metal ions in the separated liquid were measured by ICP MS (ELAN DRC-e, PerkinElmer). The separated solid was dried at 105 ºC, then 0.05 g solid was suspended in 10 mL deionized water (pH = 5.9) for the zeta potential (ζ) determination. The results were summarized in Table 2-3.

Results showed that with the pH decrease from 5 to 1, the concentrations of dissolved metal ions increased. Small amount of metal ions were dissolved from the clay to solutions in the pH ranges of 2-5. But at pH 1, 336.2 mg L^{-1} Al^{3+} and 13.7 mg

L^{-1} Fe^{3+} were dissolved from the clay. As Al_2O_3 and Fe_2O_3 are the main components of Akadama clay, large dissolution of Al^{3+} and Fe^{3+} indicated that the clay structure was badly damaged at pH 1, possibly resulting in the decrease of adsorption capacity at pH 1.

On the other hand, it was reported that adsorbent surface was positively charged when the pH of the aqueous solution was lower than the pH of zero point charge (pHzpc) [28]. As the pHzpc of Akadama clay was 6.9 [23], it was obvious that the used pHs was lower than pHzpc 6.9 and the surface of the Akadama clay was protonated and favored the uptake of Cr (VI). As the main components of Akadama clay are oxides of Si, Al and Fe, the mechanism for the surface charge property of the metallic oxidic groups can be described through amphoteric dissociation as follows [23, 29]:



where M represents Al, Fe, etc. This statement was demonstrated by the zeta potentials of Akadama clay at different pH ranges from 5 to 1. The zeta potentials ζ increased from +11.5 mV to +42.7 mV when pH decreased from 5 to 2, and then ζ decreased to +18.2 mV with further decreasing pH to 1. The highest ζ at pH 2 indicated that the best stability of soil colloidal dispersions with highly-charged surface was obtained at pH 2.

In aqueous solutions, Cr (VI) exists as several principle species: $Cr_3O_{10}^{2-}$,

$HCr_2O_7^-$, $H_2Cr_2O_7$, $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, etc. depending on the solution pH and Cr (VI) concentration [1, 2]. $Cr_3O_{10}^{2-}$ and $HCr_2O_7^-$ have been tested only in solution at below pH 0 or at Cr (VI) concentration greater than 1M [2]. $H_2Cr_2O_7$ can be detected at pH < 1, and $Cr_2O_7^{2-}$ and $HCrO_4^-$ species mainly exist at solution pH values between 2.0 and 6.0 [12, 18]. Above pH 6.8, only chromate (CrO_4^{2-}) is stable in solution [2]. Since little $Cr_2O_7^{2-}$ exists in low Cr (VI) concentration such as 0.001 M at acid conditions [30], $HCrO_4^-$ is the main species at pH 1 - 5 in the present study. Zimmerman et al. [1] also reported that at concentration of Cr (VI) 0.001M and pH 4.8, the relative abundance observed for the ionic species $HCrO_4^-$ is around 97%. Therefore, Cr (VI) uptake in present study occurred via attracting negative charged $HCrO_4^-$ to the highly protonated surface of clay. Since the highest protonation degree was obtained at pH 2, the optimum adsorption occurred at pH 2. When the initial pH range varied between 3 - 5, the protonation degree of the adsorbent surface gradually decreased, and the increasing OH^- in the solution competing with the coexisting $HCrO_4^-$ ions for the active surface sites also decreased the adsorption ability, hence the adsorption capacity decreased. Among various industrial wastewaters, the effluent pH of most electroplating wastewater is around 2 [31-33], hence Cr (VI) removal onto Akadama clay could be suitable for the treatment of electroplating wastewater.

2.3.4 The effect of dosage

Adsorbent dosage is an important factor influencing the adsorption capacity of an adsorbent under a given initial adsorbate concentration and operating conditions

[34]. Fig.2-4 denotes the removal efficiency and equilibrium capacity of Cr (VI) adsorption onto natural Akadama clay at different dosages (5, 10, 20, 30, and 40 g L^{-1}) at the initial Cr (VI) concentration 50.0 mg L^{-1} and pH 2 in 180 min. When the adsorbent dosages were increased from 5, 10, 20, 30 to 40 g L^{-1}, the removal efficiency increased from 42.9%, 57.4%, 75.0%, 82.8% to 88.1%, while the adsorption capacity decreased from 4.29, 2.87, 1.88, 1.38 to 1.10 mg g^{-1}. It was apparent that the Cr (VI) removal efficiency increased faster when Akadama clay dosage increased from 5 to 20 g L^{-1} than that from 20 to 40 g L^{-1}. This increment could be attributed to the availability of more adsorption sites and larger surface area with the increase in adsorbent dosages [27,34,35]. However, the removal efficiency did not double with the doubled increase in adsorbent dosages. Particularly, the increase of removal efficiency became very small at the dosage of 30 to 40 g L^{-1}. For the adsorption capacity, a declining trend was obviously observed. The decline rate gradually reduced from dosages of 5 to 40 g L^{-1}. This result was due to the fact that for a specific initial concentration, the dosage was higher, the available adsorption sites were larger, so the concentration intensity loaded onto the unit surface area was lower. In addition, other studies proposed that the decrease in Cr (VI) uptake at a higher adsorbent dosage might be attributed to the competition of the Cr (VI) ions for the available adsorption sites [28].

2.3.5 Adsorption isotherms

The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between adsorbate and adsorbent [25]. The most common isotherm models, Langmuir and Freundlich, were applied to analyze the Cr (VI) adsorption process on Akadama clay. When the initial concentrations ranged from 5.0 to 50.0 mg L^{-1} with an adsorbent dosage of 10 g L^{-1}, the effect on the adsorption capacity of Cr (VI) was investigated at the optimum pH of 2 in 180 min, as shown in Fig.2-5.

The linear forms of Langmuir and Freundlich isotherm models can be expressed as Eqs. (2-1) and (2-2), respectively:

$$\frac{c_e}{q_e} = \frac{1}{bq_m} + \frac{c_e}{q_m} \tag{2-1}$$

$$\ln q_e = \ln K_f + \frac{1}{n}\ln c_e \tag{2-2}$$

where q_e is the amount of Cr (VI) adsorbed on Akadama clay at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), c_e is the liquid phase concentration of Cr (VI) at equilibrium (mg L^{-1}) and b is the Langmuir constant related to the adsorption energy (L mg^{-1}), K_f is a constant indicative of the adsorption capacity and 1/n is relative to the adsorption intensity. The plot of $\ln q_e$ versus $\ln c_e$ for the adsorption of Cr (VI) onto Akadama clay was employed to generate the intercept value of K_f and the slope of 1/n.

The linearized Langmuir and Freundlich plots and the calculated adsorption constants are given in Fig. 2-5a and 2-5b, respectively. Based on the regression correlation coefficients obtained, it was obvious that the Freundlich model (R^2=0.995) fitted the adsorption data better than the Langmuir model (R^2=0.900). The result indicates that Cr (VI) adsorption on the surface of Akadama clay from aqueous phase might not occur in a homogeneous monolayer but a heterogeneous complex way. According to the theory of the Freundlich isotherm model, the heterogeneous surface of Akadama clay might have kinds of adsorption sites, and the affinities of these adsorption sites to the Cr (VI) are different. The adsorbed Cr (VI) might not be adsorbed on only one adsorption site, but on two or more adjacent adsorption sites. And the adsorbed Cr (VI) might interact with each other. This observation agrees with the results obtained by Wang et al. [5] and Yavuz et al. [15], but differs from many other studies. For example, when coir pith and root or leaves-derived carbon were used for Cr (VI) adsorption, it was found that the Langmuir isotherm fitted better than Freundlich model [14, 36, 37].

Furthermore, the favorability of reaction is also very important for the adsorption process. For the Freundlich model, the constant of 1/n is the indicator of the adsorption intensity. The n values between 1 and 10 represent favorable adsorption [2]. In this study, the n value was 2.58, which demonstrated a favorable removal condition for Cr (VI)adsorption onto Akadama clay.

2.3.6 Adsorption kinetics

Adsorption kinetic models can reveal the reaction pathway and the rate-controlling mechanism of the adsorption process. Data obtained in this study were applied to the two widely accepted kinetic models, namely pseudo-first-order model and pseudo-second-order model. The adsorption experiments were carried out under conditions of initial Cr (VI) concentration of 53.4 mg L^{-1}, optimum pH 2, and dosage of 40 g L^{-1}.

The integrations of the pseudo-first-order kinetic equation and the pseudo-second-order model are given as Eqs. (2-3) and (2-4) [38], respectively.

$$\log(q_e - q_t) = \log q_e - t\frac{k_1}{2.303} \tag{2-3}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{2-4}$$

where$k_1$is the pseudo first-order rate constant ($\min^{-1}$), k_2 is the pseudo-second-order rate constant (g mg^{-1} min^{-1}), q_t is the amount of Cr (VI)adsorbed at time t (mg g^{-1}), q_e is the adsorption capacity at equilibrium (mg g^{-1}), and t is the contact time (min).

Comparing the correlation coefficient of the pseudo-first-order model ($R^2 = 0.997$) with that of the pseudo-second-order model ($R^2= 1.000$), though both the correlation coefficients were very high, a slight difference indicated that pseudo-second-order model fitted the data better than the pseudo-first-order model. The comparison between the experimental adsorption capacity and the theoretical values calculated from the two equations are presented in Fig.2-6. Fig.2-6a shows that the theoretical q_e value estimated from the first-order kinetic model was 0.106 mg g^{-1}, indicating a significant difference compared to the experimental values of 1.155 mg g^{-1}. This result implies that the adsorption of Cr (VI) on Akadama clay was not an ideal pseudo-first-order reaction. On the other hand, in the case of pseudo-second-order kinetic, the theoretical q_e values 1.156 mg g^{-1} for the Cr (VI) adsorption on Akadama clay were very close to the experimental q_e values of 1.155 mg g^{-1}, and without doubt the adsorption process followed the pseudo-second-order kinetic model. This indicates that a chemical process dominated the Cr(VI) adsorption on Akadama clay. The result was in accordance with the results demonstrated by many other researchers [22 , 25, 39, 40].

2.3.7 Adsorption mechanism

In this study, the adsorption mechanism of Cr (VI) on natural Akadama clay was achieved by analyzing total Cr, Cr (VI), and final pH in equilibrium solution by batch experiments under the conditions of initial solution pH of 2, initial Cr (VI) concentration of 50.7 mg L^{-1}, and adsorbent dosages of 5 ~ 50 g L^{-1} in 180 min. The pH variations of deionized water under the same conditions (initial pH 2.00, dosage 5 ~ 50 g L^{-1}, and contact time 180 min) were investigated as the blank. The results are illustrated in Fig.2-7.

As shown in Fig.2-7, with increasing the dosages from 5 to 50 g L^{-1}, the pHs of blank increased from 2.00 to 2.25, 2.60, 3.34, 3.62, 3.70 and 3.78, respectively. The rising pH implied that H^+ in the aqueous solution was consumed. The consumed H^+ was utilized for two aspects. The first part was consumed for dissolving the metal ions, exactly as the discussion in Section 3.3. Another part was used to protonate the clay surface, and the inference could be proved by the high zeta potential determined in Table 2-3. Since the amount of dissolving ions was a little, the consumed H^+ was mainly used for surface protonation. Comparing to the final pH value of blank, the equilibrium pH after Cr (VI) adsorption was higher for all adsorbent dosages. The result was ascribed to that Cr (VI) adsorption was a deprotonation process, that is, OH^- was released to the solution during this process.

Fig.2-7 shows that the total Cr concentrations and the Cr (VI) concentrations in the residual solution were all same for all the adsorbent dosages. It revealed that no Cr (III) was detected in the equilibrium solution. Since precipitation form of $Cr(OH)_3$ only exists when pH was higher than 6.8 [41], Cr (III)was not produced in the designed conditions. In consequence, the removal of Cr (VI) on natural Akadama clay was dominated by electrostatic attraction.

2.3.8 Comparison of various mineral adsorbents

A comparison between natural Akadama clay and previously reported mineral adsorbents for Cr (VI) removal is summarized in Table 2-4. As it can be seen, for similar mineral adsorbents, the adsorption capacity (q_m) of the natural Akadama clay was apparently better than most of the other adsorbents. The high Cr (VI) adsorption capacity obtained in this work could be mainly attributed to the large surface area leading to large adsorption sites, and the special clay composition and structure resulting in good adsorption properties for Cr (VI) removal.

2.4 Conclusion

In this study, the Cr (VI) adsorption on natural Akadama clay was evaluated by batch adsorption experiments. Results showed that the Cr (VI) adsorption equilibrium time was 180 min and the optimum adsorption pH was 2. When initial Cr (VI) concentration was 50.0 mg L^{-1}, adsorbent dosage was 5 g $L^{-1}$and contact time was 180 min, the Cr (VI) adsorption capacity on natural Akadama clay was calculated to be 4.29 mg g^{-1}, which was much higher than most other natural mineral adsorbents. Kinetic and isotherm studies revealed that Cr (VI) adsorption data followed the Freundlich isotherm and the pseudo-second-order kinetic model. Cr (VI) adsorption mechanism analysis indicated that electrostatic adsorption dominated the Cr (VI) adsorption on natural Akadama clay, and no Cr (III) reduction occurred in the adsorption process. The use of natural Akadama clay as an adsorbent for Cr (VI) removal is promising and may provide an alternative method for Cr (VI) removal from contaminated wastewater.

References

[1] A.C. Zimmermann, A. Mecabô, T. Fagundes, C.A. Rodrigues, Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe), Journal of Hazardous Materials, 179 (2010) 192-196.

[2] L. Xiao, W. Ma, M. Han, Z. Cheng, The influence of ferric iron in calcined nano-Mg/Al hydrotalcite on adsorption of Cr (VI) from aqueous solution, Journal of Hazardous Materials, 186 (2011) 690-698.

[3] S. Yin, D.E. Ellis, DFT studies of Cr(VI) complex adsorption on hydroxylated hematite surfaces, Surface Science, 603 (2009) 736-746.

[4] E. Alemayehu, S. Thiele-Bruhn, B. Lennartz, Adsorption behaviour of Cr(VI) onto macro and micro-vesicular volcanic rocks from water, Separation and Purification Technology, 78 (2011) 55-61.

[5] X.S. Wang, L.F. Chen, F.Y. Li, K.L. Chen, W.Y. Wan, Y.J. Tang, Removal of Cr (VI) with wheat-residue derived black carbon: Reaction mechanism and adsorption performance, Journal of Hazardous Materials, 175 (2010) 816-822.

[6] L. Alidokht, A.R. Khataee, A. Reyhanitabar, S. Oustan, Reductive removal of Cr(VI) by starch-stabilized FeO nanoparticles in aqueous solution, Desalination, 270 (2011) 105-110.

[7] M.S. Bhatti, A.S. Reddy, A.K. Thukral, Electrocoagulation removal of Cr(VI) from simulated wastewater using response surface methodology, Journal of Hazardous Materials, 172 (2009) 839-846.

[8] T. Ölmez, The optimization of Cr(VI) reduction and removal by electrocoagulation using response surface methodology, Journal of Hazardous Materials, 162 (2009) 1371-1378.

[9] C.E. Barrera-Díaz, V. Lugo-Lugo, B. Bilyeu, A review of chemical, electrochemical and biological methods for aqueous Cr(VI) reduction, Journal of Hazardous Materials, 223-224 (2012), 1-12.

[10] J. Yoon, G. Amy, J. Chung, J. Sohn, Y. Yoon, Removal of toxic ions (chromate, arsenate, and perchlorate) using reverse osmosis, nanofiltration, and ultrafiltration membranes, Chemosphere, 77 (2009) 228-235.

[11] W. Liu, J. Zhang, C. Zhang, L. Ren, Preparation and evaluation of activated carbon-based iron-containing adsorbents for enhanced Cr(VI) removal: Mechanism study, Chemical Engineering Journal, 189–190 (2012) 295-302.

[12] Q. Cheng, C. Li, L. Xu, J. Li, M. Zhai, Adsorption of Cr(VI) ions using the amphiphilic gels based on 2-(dimethylamino)ethyl methacrylate modified with 1-bromoalkanes, Chemical Engineering Journal, 173 (2011) 42-48.

[13] E. Özdemir, D. Duranoğlu, Ü. Beker, A.Ö. Avcı, Process optimization for Cr(VI) adsorption onto activated carbons by experimental design, Chemical Engineering Journal, 172 (2011) 207-218.

[14] A.K. Giri, R. Patel, S. Mandal, Removal of Cr (VI) from aqueous solution by Eichhornia crassipes root biomass-derived activated carbon, Chemical Engineering Journal, 185–186 (2012) 71-81.

[15] A.G. Yavuz, E. Dincturk-Atalay, A. Uygun, F. Gode, E. Aslan, A comparison study of adsorption of Cr(VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composites, Desalination, 279 (2011) 325-331.

[16] A. Baran, E. Bıçak, Ş.H. Baysal, S. Önal, Comparative studies on the adsorption of Cr(VI) ions on to various sorbents, Bioresource Technology, 98 (2007) 661-665.

[17] Q. Wang, Y. Guan, X. Liu, M. Yang, X. Ren, Micron-sized Magnetic Polymer Microspheres for Adsorption and Separation of Cr(VI) from Aqueous Solution, Chinese Journal of Chemical Engineering, 20 (2012) 105-110.

[18] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, Journal of Hazardous Materials, 180 (2010) 1-19.

[19] N. Daneshvar, D. Salari, S. Aber, Chromium adsorption and Cr(VI) reduction to trivalent chromium in aqueous solutions by soya cake, Journal of Hazardous Materials, 94 (2002) 49-61.

[20] S. Gupta, B.V. Babu, Modeling, simulation, and experimental validation for continuous Cr(VI) removal from aqueous solutions using sawdust as an adsorbent, Bioresource Technology, 100 (2009) 5633-5640.

[21] V. Venugopal, K. Mohanty, Biosorptive uptake of Cr(VI) from aqueous solutions by Parthenium hysterophorus weed: Equilibrium, kinetics and thermodynamic studies, Chemical Engineering Journal, 174 (2011) 151-158.

[22] S.T. Akar, Y. Yetimoglu, T. Gedikbey, Removal of chromium (VI) ions from

aqueous solutions by using Turkish montmorillonite clay: effect of activation and modification, Desalination, 244 (2009) 97-108.

[23] R. Chen, Z. Zhang, C. Feng, Z. Lei, Y. Li, M. Li, K. Shimizu, N. Sugiura, Batch study of arsenate (V) adsorption using Akadama mud: Effect of water mineralization, Applied Surface Science, 256 (2010) 2961-2967.

[24] Y. Guo, J. Qi, S. Yang, K. Yu, Z. Wang, H. Xu, Adsorption of Cr(VI) on micro- and mesoporous rice husk-based active carbon, Materials Chemistry and Physics, 78 (2003) 132-137.

[25] L.A. Rodrigues, L.J. Maschio, R.E. da Silva, M.L.C.P. da Silva, Adsorption of Cr(VI) from aqueous solution by hydrous zirconium oxide, Journal of Hazardous Materials, 173 (2010) 630-636.

[26] E. Álvarez-Ayuso, A. García-Sánchez, X. Querol, Adsorption of Cr(VI) from synthetic solutions and electroplating wastewaters on amorphous aluminium oxide, Journal of Hazardous Materials, 142 (2007) 191-198.

[27] N. Zhao, N. Wei, J. Li, Z. Qiao, J. Cui, F. He, Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI), Chemical Engineering Journal, 115 (2005) 133-138.

[28] S. Chen, Q. Yue, B. Gao, X. Xu, Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue, Journal of Colloid and Interface Science, 349 (2010) 256-264.

[29] Y. Wang, Y. Lan, Y. Hu, Adsorption mechanisms of Cr(VI) on the modified bauxite

tailings, Minerals Engineering, 21 (2008) 913-917.

[30]B. Shi,Analysis of existing forms of Cr (VI) in wastewater,Electroplating Pollution Control, 6 (1986), 30.

[31] R. Kumar, N.R. Bishnoi, Garima, K. Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chemical Engineering Journal, 135 (2008) 202–208.

[32] G. Moussavi, B. Barikbin, Biosorption of chromium(VI) from industrial wastewater ontopistachio hull waste biomass, Chemical Engineering Journal, 162 (2010) 893–900.

[33] P. Suksabye, P. Thiravetyan, Cr(VI) adsorption from electroplating plating wastewater by chemically modified coir pith, Journal of Environmental Management, 102 (2012) 1-8.

[34] A. Sarı, M. Tuzen, M. Soylak, Adsorption of Pb(II) and Cr(III) from aqueous solution on Celtek clay, Journal of Hazardous Materials, 144 (2007) 41-46.

[35] R.A.K. Rao, F. Rehman, Adsorption studies on fruits of Gular (Ficus glomerata): Removal of Cr(VI) from synthetic wastewater, Journal of Hazardous Materials, 181 (2010) 405-412.

[36] R. Chand, T. Watari, K. Inoue, T. Torikai, M. Yada, Evaluation of wheat straw and barley straw carbon for Cr(VI) adsorption, Separation and Purification Technology, 65 (2009) 331-336.

[37] P. Suksabye, P. Thiravetyan, Cr(VI) adsorption from electroplating plating

wastewater by chemically modifiedcoir pith, Journal of Environmental Management, 102 (2012) 1-8.

[38] P. Suksabye, A. Nakajima, P. Thiravetyan, Y. Baba, W. Nakbanpote, Mechanism of Cr(VI) adsorption by coir pith studied by ESR and adsorption kinetic, Journal of Hazardous Materials, 161 (2009) 1103-1108.

[39] G. Bayramoğlu, M. Yakup Arica, Adsorption of Cr(VI) onto PEI immobilized acrylate-based magnetic beads: Isotherms, kinetics and thermodynamics study, Chemical Engineering Journal, 139 (2008) 20-28.

[40] M. Kebir, M. Chabani, N. Nasrallah, A. Bensmaili, M. Trari, Coupling adsorption with photocatalysis process for the Cr(VI) removal, Desalination, 270 (2011) 166-173.

[41] N.F. Fahim, B.N. Barsoum, A.E. Eid, M.S. Khalil, Removal of chromium(III) from tannery wastewater usingactivated carbon from sugar industrial waste, Journal of Hazardous Materials, 136 (2006) 303–309.

[42] Y.C.Sharma, C.H. Weng, Removal of chromium(VI) from water and wastewater by using riverbed sand: Kinetic and equilibrium studies, Journal of Hazardous Materials, 142 (2007) 449–454.

[43] S. Ali Khan, R. Rehman, M. Ali Khan, Adsorption of Chromium (III), Chromium (VI) and Silver (I) on bentonite, Waste Management, 15 (1995) 271-282.

[44] Y. C. Sharma, Effect of temperature on interfacial adsorption of Cr(VI) on Wollastonite, Journal of Colloid and Interface Science, 233 (2001) 265–270.

[45] C.H.Weng, Y.C.Sharma, S.H.Chu, Adsorption of Cr(VI) from aqueous solutions

by spent activated clay, Journal of Hazardous Materials, 155 (2008) 65–75.

[46] Y.Li, Q.Y.Yue, B.Y.Gao, Effect of humic acid on the Cr(VI) adsorption onto Kaolin, Applied Clay Science, 48 (2010) 481–484.

Table 2-1 Effect of different adsorption parameters on Cr (VI) adsorption onto Akadama clay

Adsorption parameters			
Contact time (min)	pH	Dosage (g L^{-1})	Initial concentrations of Cr(VI) (mg L^{-1})
(0 - 240)*	original*	20	10.0, 20.0, 50.0
180	(1 - 5)*	20	50.0
180	2	(5 - 40)*	50.0

original* means the original pH of Cr (VI) solution without pH adjustment.

( )* means the effect of this parameter is tested on Cr (VI) adsorption using Akadama clay.

Table 2-2 Surface area characterization and pore volume analysis of Akadama clay before and after Cr (VI) adsorption.

Surface areas	Before adsorption	After adsorption
BET surface area ($m^2 g^{-1}$)	174.26	132.44
Langmuir surface area ($m^2 g^{-1}$)	160.99	109.02
T-plot surface area ($m^2 g^{-1}$)	150.42	144.89
Total pore volume ($cm^3 g^{-1}$)	0.1920	0.1763

Table 2-3 The concentrations of dissolved metal ions and zeta potentials of Akadama clay in pH ranges of 1 – 5.

pH	Concentrations of dissolved metal ions (mg L^{-1})					Zeta potential ζ (mV)
	Al	Fe	Mg	Ca	Mn	
1	336.2	13.7	4.4	18.6	1.5	18.2
2	26.9	ND*	3.2	16.9	0.4	42.7
3	ND	ND	1.7	9.1	0.1	21.5
4	ND	ND	1.5	7.5	ND	11.7
5	ND	ND	1.1	6.4	ND	11.5

ND* means the concentrations of metal ions were not detected due to the concentration below the detection limit of ICPS-8100.

Table 2-4 Adsorption capacities of Cr (VI) on different mineral adsorbents

Mineral adsorbents	Operating conditions				
	pH	Initial concentration(mg L^{-1})	Adsorbent (g L^{-1})	q_m (mg g^{-1})	Refs.
Volcanic rocks	2	0.5-10.0	100	0.046	[4]
Riverbed sanda	2.5	1.05-7.84	20	0.15	[42]
Bentonite	2	0.5-50	50	0.57	[43]
Wollastonite	2.5	5.2	20	0.826	[44]
Spent activated clay	2	0.2-10	1	1.42	[45]
Natural Turkish montmorillonite clay	1	250	10	3.61	[22]
Kaolin	6-8	1-20	0.2	10.4	[46]
Natural Akadama clay	2	5-50	5	4.29	This study

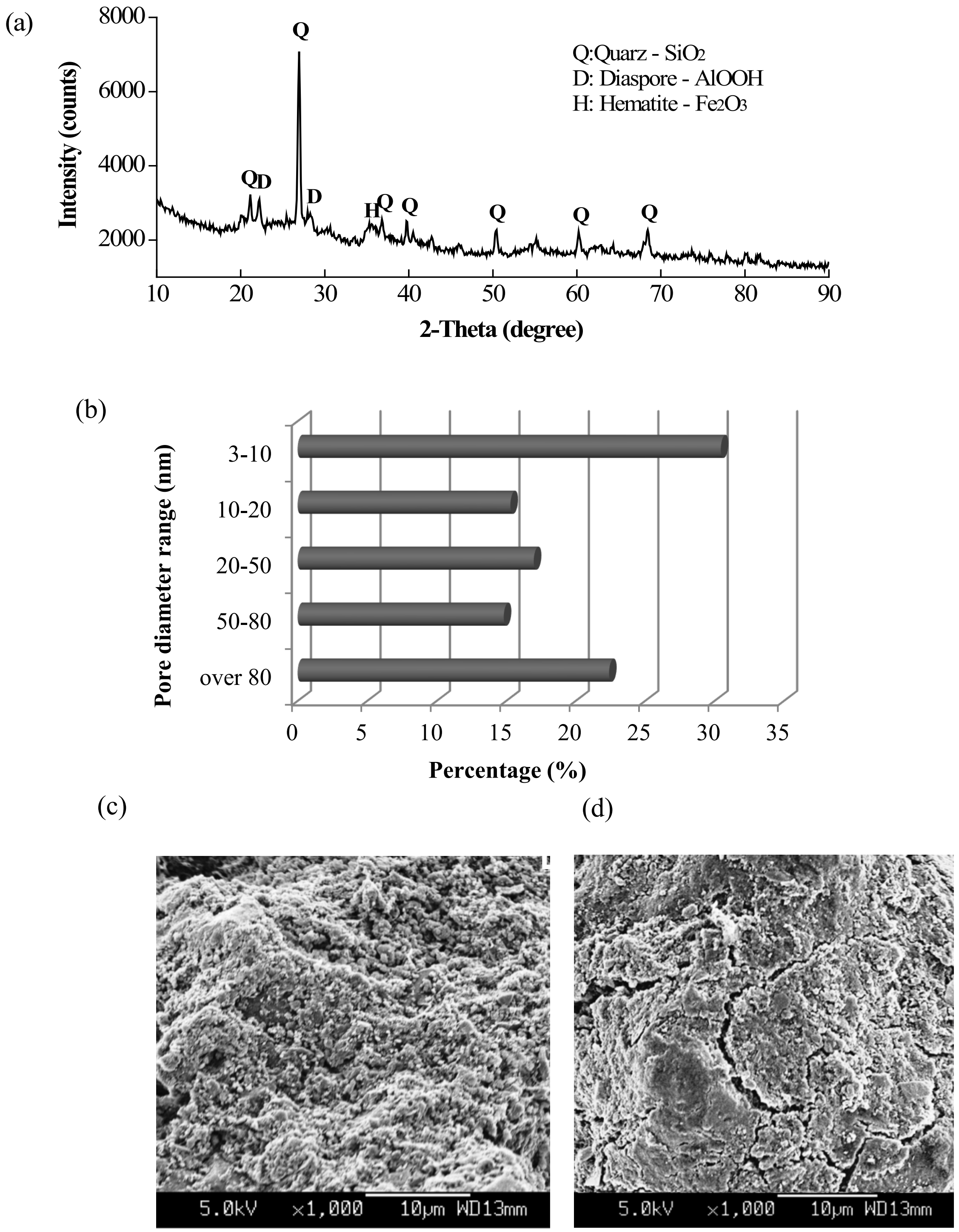


Fig.2-1 XRD patterns of natural Akadama clay (a), adsorption BJH (Barrett–Joyner–Halenda) pore size distribution (b), and SEM images of natural Akadama clay (c) and after Cr (VI) adsorption (d).

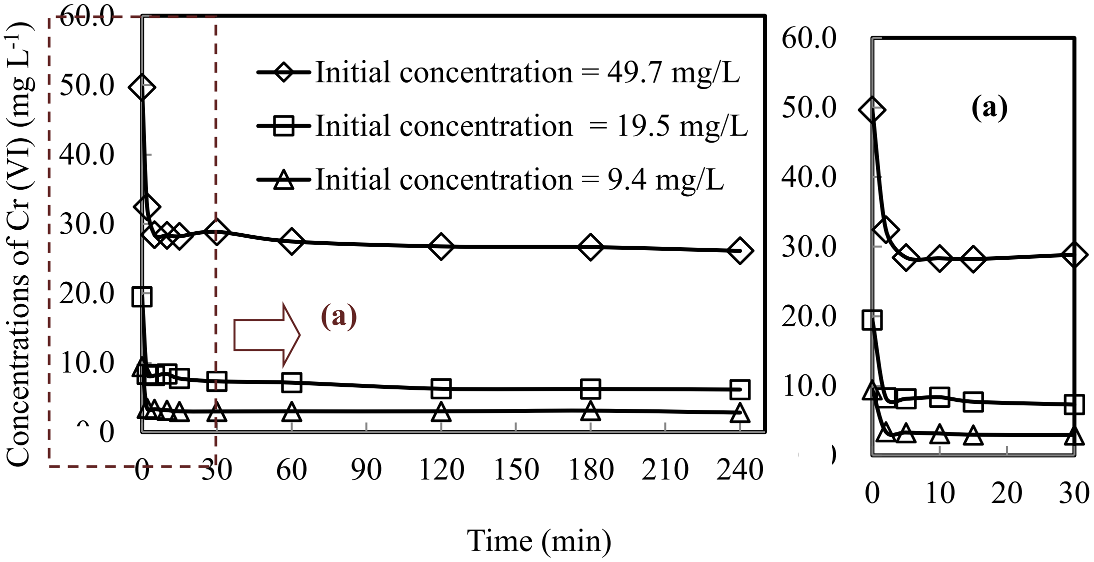


Fig.2-2 Effect of contact time on Cr (VI) adsorption

(Adsorbent dosage = 20 g L^{-1}, initial Cr (VI) concentrations = 49.7, 19.5, 9.4 mg L^{-1})

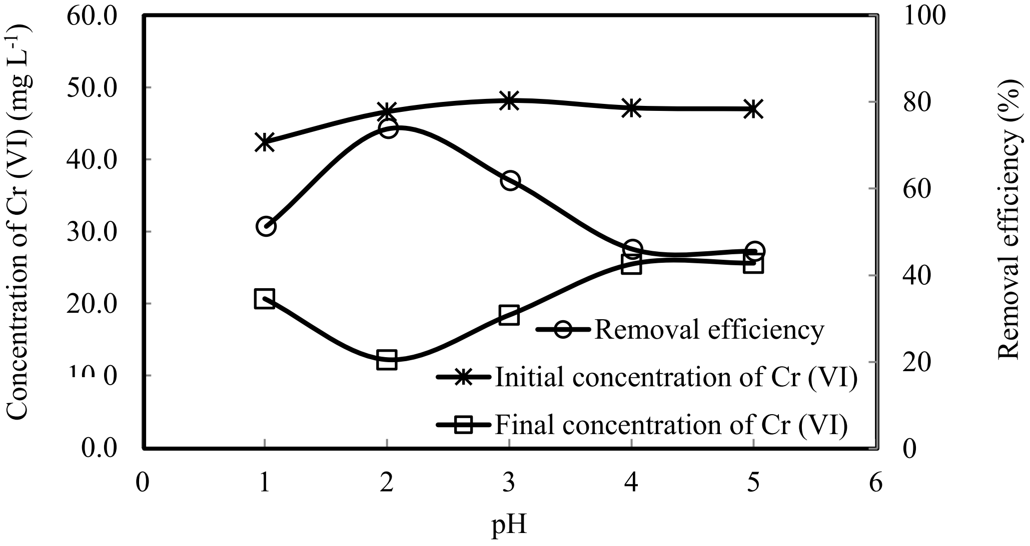


Fig.2-3 Effect of pH on Cr (VI) adsorption

(Adsorbent dosage = 20 g L^{-1}, contact time = 180 min)

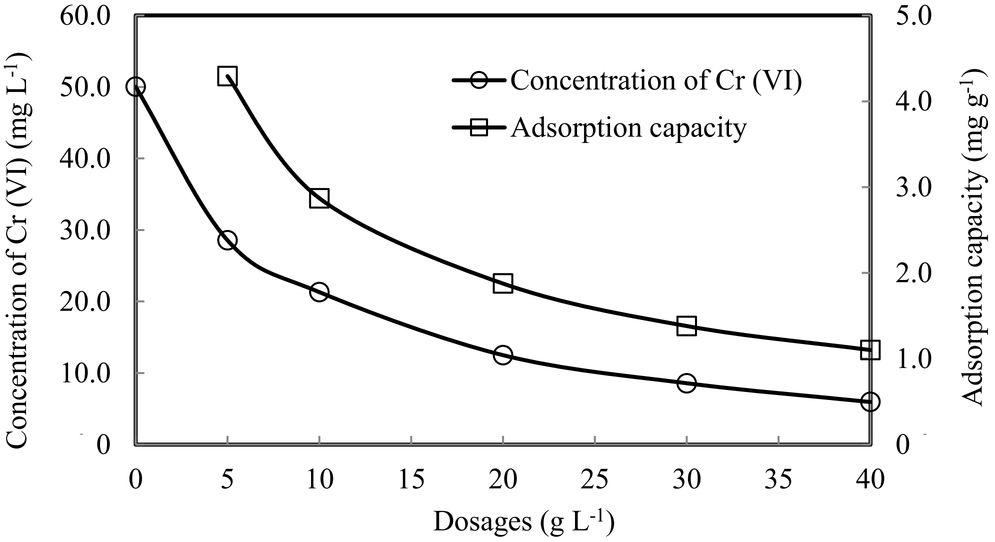
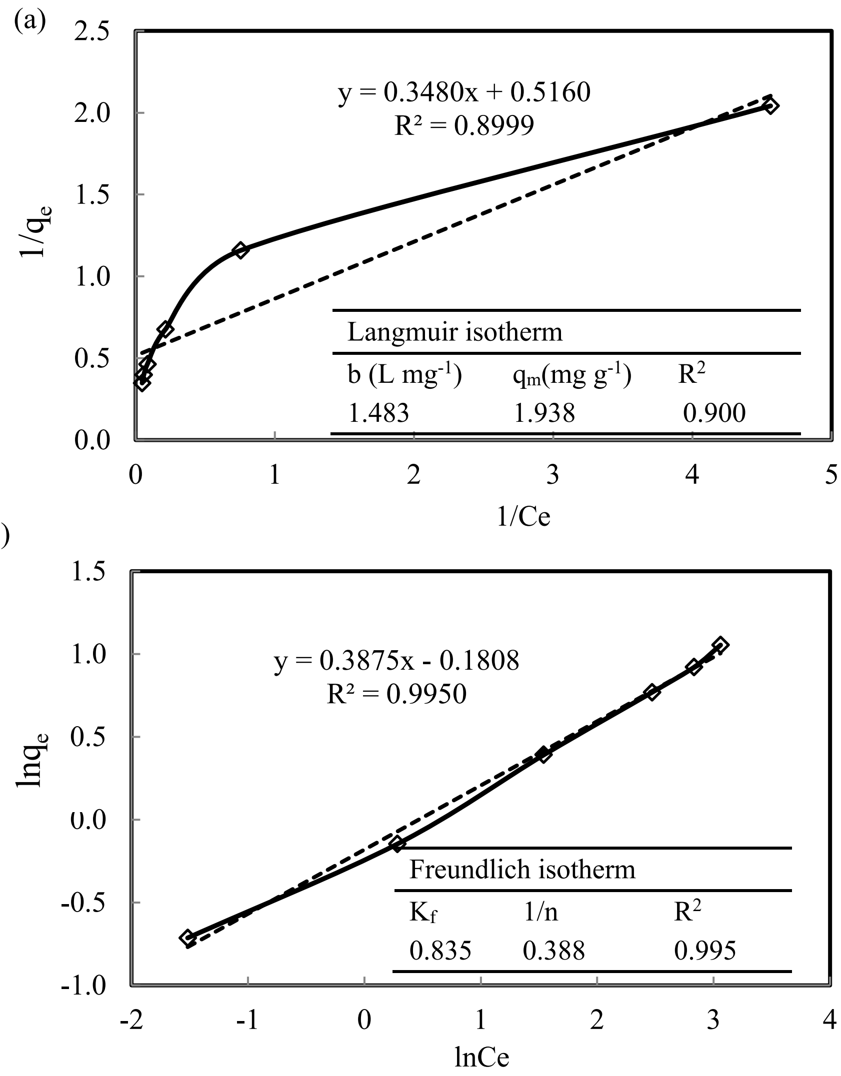


Fig.2-4 Effect of adsorbent dosages on Cr (VI) adsorption

(Initial Cr (VI)concentration = 50.0 mg L^{-1}, contact time = 180 min)



Langmuir isotherm		
b (L mg^{-1})	q_m(mg g^{-1})	R^2
1.483	1.938	0.900

Freundlich isotherm		
K_f	1/n	R^2
0.835	0.388	0.995

Fig.2-5 Plots of isotherms of Cr (VI) adsorption onto natural Akadama clay (Initial Cr (VI) = 5.0, 10.0, 20.0, 30.0, 40.0, 50.0 mg L^{-1}; adsorbent dose = 10 gL^{-1}, pH = 2, contact time = 180 min).

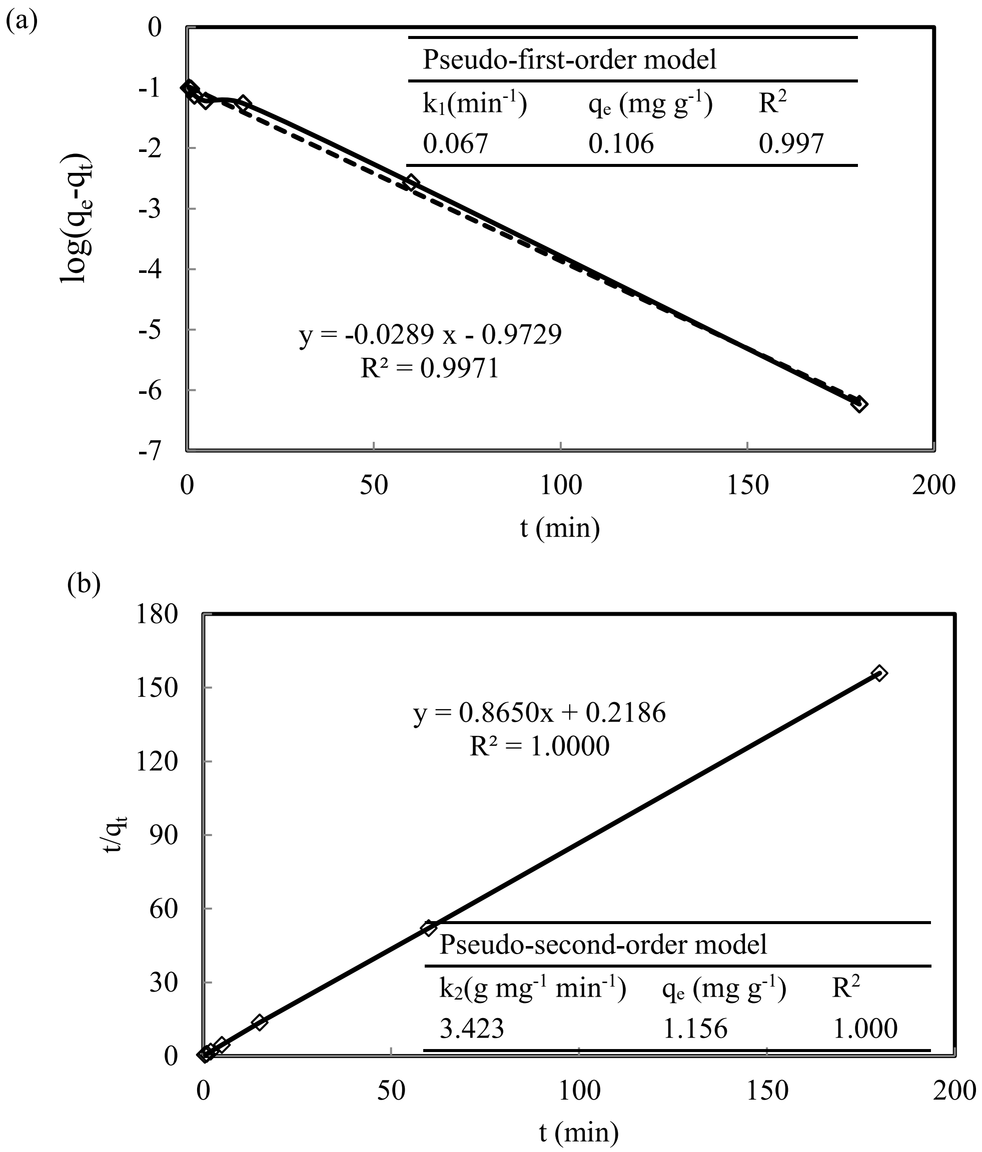


Fig.2-6 Plots of kinetics of Cr (VI) adsorption onto natural Akadama clay

(Initial Cr (VI) = 53.4 mg L^{-1}; adsorbent dose= 40 g L^{-1}, pH = 2).

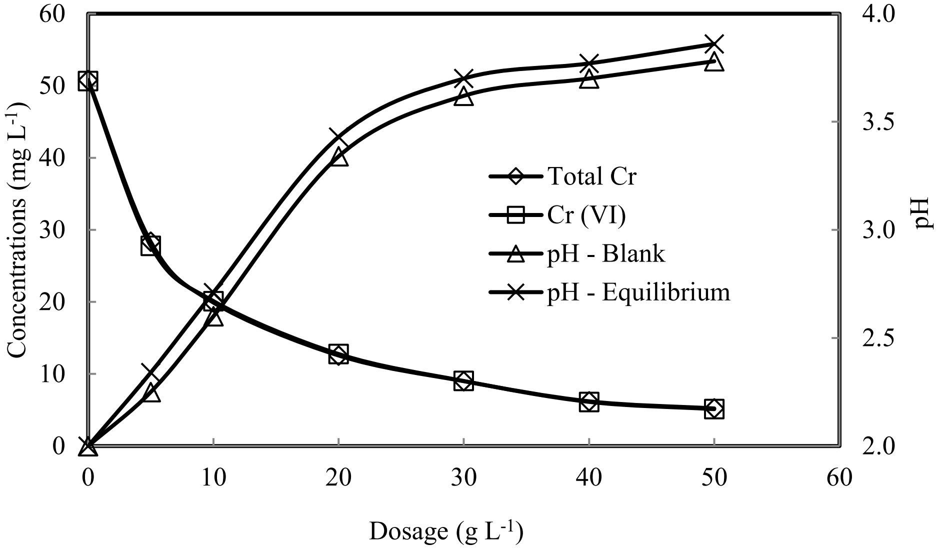


Fig.2-7 Variations of blank pH, equilibrium pH, the residual Cr (VI) concentration and the total Cr concentration under different adsorbent dosage conditions

(Initial concentration = 50.7 mgL^{-1}; initial solution pH = 2, contact time = 180 min).

Chapter 3 Acid modified Akadama clay used as an adsorbent for removal of chromium (VI) from wastewater

3.1 Introduction

Chromium is one of the important strategic materials for its qualitative hard, wear-resistant, high temperature and corrosion resistant properties; it has been widely used in refractory materials, metallurgical, and chemical industries. However, excessive chromium discharged from wastewater, especially hexavalent chromium Cr (VI) severely threatens environmental quality and human health [1, 2]. Cr (VI) compounds are highly toxic for their marked carcinogenic, teratogenic and mutagenic effects on living organisms [1]. The Maximum Contaminant Level (MCL) of total Cr in drinking water proposed by the US EPA is 0.1 mgL^{-1} [3], and maximum level required by WHO is 0.05 $mg\ L^{-1}$ [4].The same value is also proposed by China [5].

Adsorption is generally recognized as an alternative and promising method for eliminating chromium contaminants from water and wastewaters [6, 7]. Compared to other physical and chemical methods such as ion exchange[8], chemical precipitation [9], electrodialysis [10] and membrane filtration [11], adsorption has some obvious advantages of low cost, easy operation, and high efficiency. Therefore, natural minerals such as bentonite, kaolin, montmorillonite, wollastonite used for Cr (VI) removal have been reported in previous studies [12-15]. Natural bioadsorbents for Cr (VI) treatment, such as hysterophorus weed, fruits of Ficus, pistachio hull, sawdust, and seaweed etc. [6, 16-19] can also be reviewed in literature. However, natural materials usually have low adsorption efficiency and limits to their practical application. For example, the maximum adsorption capacity of natural montmorillonite is only 3.61 mg g^{-1}at optimum conditions [15]. In order to improve Cr (VI) adsorption efficiency, some modified methods have been developed. These methods mainly contain activated carbonization, organic polymer modification, acid and metal salt modification [20-24]. The adsorption capacity of Cr (VI) increased 2.8 times using montmorillonite modified with hexadecyltrimethyl ammonium bromide (HDTMA) [15]. Wen et al. also reported that the adsorption capacity of Cr(VI) on chitosan-coated fly ash composite was higher than that on fly ash [22].

Akadama clay, common and inexpensive in Japan, is a volcanic ash deposit with a faint yellow color and slightly acidic pH. It is usually used as soil for bonsai trees and other container-grown plants. It is highly prized for its ability to retain water and nutrients while still providing porosity and free drainage. In our previous study, it was proved that natural Akadama clay had good adsorption affinity for Cr (VI), but the adsorption capacity was relatively low, and its optimal pH was limited at 2 [25]. The real Cr (VI) containing wastewater is very complicated. For example, the pH ranges of tannery wastewater vary from 4.0 to 9.0 [26, 27], and diverse coexisting ions and organics also exist [27]. Therefore, it is necessary for improvement of the Cr (VI) adsorption performance at a wide application condition.

Acid activation is a typical modification method, which can increase the effective groups of adsorbent surface and improve adsorption capacity [24]. Some researchers used HNO_3 to oxidize active carbon, and revealed that the modified active carbon exhibited excellent Cr (VI) adsorption performance [24, 28]. Akar et al. [29] used H_2SO_4 to activate

Turkish montmorillonite clay and the adsorption capacity of Cr (VI) increased 24.5%.

In this study, various acids (HCl, HNO_3, H_2SO_4, and H_3PO_4) were used to modify natural Akadama clay so as to improve the adsorption performance of Cr (VI). The major objective of this study was to: 1) select the optimum acid from common inorganic acids for modification; 2) characterize the changes in Akadama clay after modification; 3) investigate the effect of pH, contact time, initial concentration, and adsorbent dosage on Cr (VI) adsorption capacity; 4) analyze the adsorption process using various kinetics and isotherms; 5) evaluate the practical applicability of these processes in the presence of coexisting ions.

3.2Materials and methods

3.2.1 Reagents

All chemical reagents used were of analytical grade without further purification. Potassium dichromate ($K_2Cr_2O_7$, Wako Pure Chemical Industries, Japan) used in this study, was first dried at 105°C in an oven for 24 h. The dried $K_2Cr_2O_7$ was used for the preparation of the stock solution (500 mg L^{-1}). The working solutions of Cr (VI) were prepared by proper dilution of the stock solution with deionized water.1M HCl, HNO_3, H_2SO_4, and H_3PO_4 (Wako Pure Chemical Industries, Japan) were prepared and diluted to the desired strength for the modification of Akadama clay. 1 M NaOH (Wako Pure Chemical Industries, Japan) was also prepared to adjust the solution pH to the required value.

3.2.2 Preparation of the acid-modified Akadama clay

Akadama clay, provided by Makino Store, Kiyosu, Japan, was crushed and sieved until the particle diameter was less than 105 μm, then washed with distilled water several times so as to remove impurities, finally dried in an oven at 105 °C for 24 h. 2 g dried Akadama clay was then immersed in 20 mL HCl, HNO_3, H_2SO_4, and H_3PO_4 solutions (0.01 mol L^{-1}, volume of acid solution/mass of clay (v/m) = 10/1) in four centrifuge tubes, respectively. The centrifuge tubes were set in a shaker (200 rpm) at room temperature for 24 h. After full immersion, the mixtures were separated using filter paper and then dried in an oven at 105 °C. A preliminary trial was carried out to test the adsorption performance of the Akadama clay modified by the four common inorganic acids. The experimental conditions were set at initial concentration of Cr (VI) 100.0 mg L^{-1}, acid-modified Akadama clay 40 g L^{-1}, contact time 24 h, shaking speed 200 rpm, and no pH adjustment at room temperature. The results showed that the Cr (VI) removal efficiencies of Akadama clay modified by HCl, HNO_3, H_2SO_4, and H_3PO_4 were 83.3%, 73.2%, 57.0%, 49.4%, respectively. And the removal efficiency of Cr (VI) onto unmodified Akadama clay was 60.0%. It revealed that the removal efficiency of Cr (VI) increased 23.3% with HCl modified Akadama clay (HMAC). Therefore, HMAC was selected as the acid-modified adsorbent to perform the following experiments.

3.2.3 Adsorption procedure

3.2.3.1 Optimization of modification conditions

The concentrations of HCl solution (0.001, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mol L^{-1}) and the ratios of HCl solution (mL) to clay (g) (v/m = 10/1, 10/2, 10/3, 10/4, 10/5, 10/6, 10/7, 10/8, 10/9) were used to the modification.

3.2.3.2 Evaluation of the adsorption performance

The effects of pH (1 - 11), contact time (0 -48 h), adsorbent doses (5 - 80 g L^{-1}), initial concentrations of Cr (VI) (10 -200 mg L^{-1}), and coexisting ions (Na^+, K^+, Ca^{2+}, and Mg^{2+}; Cl^-, NO_3^-, SO_4^{2-}, CH_3COO^-;) on Cr (VI) adsorption onto HMAC were evaluated. Adsorption kinetics and isotherms were analyzed. Desorption study was also conducted. All experiments were carried out at a shaking speed of 200 rpm and at room temperature. Each adsorption experiment was carried out at least 3 times, and the result was expressed as an average of the triplicate values.

3.2.4 Analytical methods

The specific surface area and BJH (Barrett–Joyner–Halenda) pore-size distributions of HMAC were analyzed using a gravimetric nitrogen Brunauer–Emmett–Teller (BET) specific surface analysis device (Coulter SA3100, US). The morphological features of the HMAC were acquired by scanning electron microscope (SEM) (JSM-6330F, JEOL, Japan). The mineralogical phase characterization of HMAC was carried out by quantitative X-ray diffraction (XRD) (X'Pert PRO, PANalytical). The chemical elements of Akadama clay and HMAC are determined using an EDX detector equipped on a JSM 7000F field emission scanning electron microscope. Membrane filters (Minisart RC 15, Germany) with 0.45 μm pore diameter were used to filtrate the solution after adsorption, and the concentrations of Cr (VI) were measured by ultraviolet spectrophotometer (UV-1800, Japan) according to diphenyl carbohydrazide spectrophotometric method. The pH of the Cr (VI) solution was determined using a pH meter (Mettler - Toledo AG, Switzerland). The zeta potential was measured by ZETA SIZER Nano series (England).

3.3Results and discussion

3.3.1 Optimum modification conditions

The effect of HCl concentrations on the modification of Akadama clay was investigated at the range of 0.001 - 0.6 mol $L^{-1}$with initial Cr (VI) concentration of 100.2 mg L^{-1}, contact time of 24 h, dosage of 40 g L^{-1}, ratio of HCl solution to clay of 10:1 (v/m), and without pH adjustment (Fig.3-1). When HCl concentrations were 0, 0.001, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4,0.5 and 0.6 mol L^{-1}, the concentrations of Cr (VI) in equilibrium solution were 41.1, 40.0, 16.7, 13.1, 12.5, 11.9, 12.6, 13.1, 13.9, and 15.9 mg L^{-1}, respectively. The best HCl concentration was obtained at 0.2 mol L^{-1}, which might be attributed to the fact that low HCl concentration could not fully activate the surface of the clay, and higher HCl concentration would dissolve the structure of the clay, so both decreased the Cr (VI) removal. The accordant results were demonstrated in our previous study [25]. At the optimum HCl concentration (0.2 mol L^{-1}), the maximum removal efficiency of 88.1% was obtained in this study.

Fig.3-2 shows the effect of ratios of HCl solution to clay (v/m = 10/1 - 10/9) on the Cr (VI) adsorption at the optimum HCl concentration of 0.2 mol L^{-1}. Although the Cr (VI) concentration in equilibrium solution was slightly fluctuated, the difference between the minimum and maximum removal efficiencies in the range of 10/1 to 10/9 was only 2.4%, indicating that HCl solution-clay ratios had no obvious effect on the performance of modified Akadama clay for Cr (VI) adsorption. In the present study, the best ratio of 10:5 was selected.

3.3.2 Characterization

Unmodified Akadama clay and HMAC were immersed in deionized water (pH = 6.0) and then zeta potentials ζ of their surfaces were determined. Data showed that ζ of unmodified Akadama clay was +21.6 mV, while ζ of HMAC increased to + 54.1 mV. The XRD patterns of unmodified Akadama clay and HMAC are shown in Fig.3-3a. It can be seen that, comparing with the pattern of unmodified Akadama clay, neither new peaks appear nor old peaks disappear for HMAC. That is, the main crystal structure of HMAC are not changed after modification, they might still be quartz (SiO_2), diaspore (AlOOH), and hematite (Fe_2O_3).The result could be demonstrated by EDX analysis (Fig.3-3b), which shows that main chemical elements such as Si, Al, Fe, and O are not changed for Akadama clay and HMAC; the detection of Cr (VI) in HMAC after adsorption indicates that Cr (VI) atoms had successfully adhered onto the adsorbent of HMAC.

Surface area characterization and pore volume analysis of HMAC and Cr (VI) loaded HMAC are shown in Table 3-1, and the BJH (Barrett–Joyner–Halenda) adsorption pore size distributions are shown in Fig.3-3c. The BET specific surface area of HMAC was 143.57 $m^2 g^{-1}$, and the total pore volume was 0.177 mLg^{-1}. After Cr (VI) adsorption, the BET specific surface area decreased to 131.04 $m^2 g^{-1}$, and the total pore volume reduced to 0.160 mLg^{-1}. The BJH adsorption pore volume distribution of HMAC shows that the observed pore sizes generally varied between 2 and 50 nm (63.40%). According to the IUPAC classification (pore widths < 2 nm : micropores; 2 - 50 nm : mesopores; > 50 nm :macropores), HMAC is classified as a mesoporous material. For Cr (VI) loaded HMAC, the BJH adsorption pore diameter over 50 nm apparently decreased, and ranges of 2 - 50 nm increased. These changes indicate that the pore volume was occupied after Cr

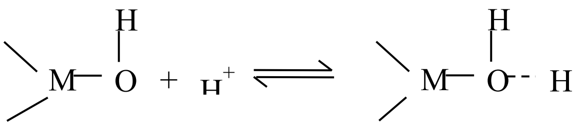
(VI) adsorption, and might be attributed to the fact that Cr (VI) ions were bonded to not only the surface but also the inside of the clay particles [25]. This statement can be further proved by the SEM images shown in Fig.3-3d and Fig.3-3e. The unconsolidated and flocky surface texture before Cr (VI) adsorption becomes caked and smooth after Cr (VI) adsorption, revealing the surface structure was changed through Cr (VI) adsorption.

3.3.3 Effect of pH

Fig.3-4 shows the removal of Cr (VI) versus the pH at Cr (VI) concentrations about 100.0 mg L^{-1}, adsorbent dosage of 40 g L^{-1} and a contact time of 48 h at room temperature for unmodified Akadama clay and HMAC. Fig.3-4 indicates that removal efficiency was greatly affected by pH for unmodified Akadama clay. The maximum removal efficiency of 83.0% was peaked at pH 2, and the removal efficiency of Cr (VI) greatly decreased from 63.3% to 46.3% at pH 3 - 11. For HMAC, the optimum pH condition was widened to 2-11 with a higher removal efficiency of 92.8%. At pH range of 2- 11, Cr (VI) removal efficiency by HMAC was significantly higher than that by unmodified Akadama clay.

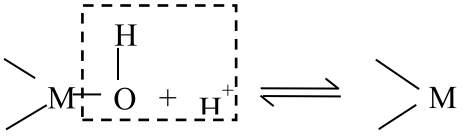
It is well known that Cr (VI) adsorption is a pH dependent process for most adsorbents, whether minerals or bioadsorbents [16, 30]. In our previous study, it has been demonstrated that the mechanism of Cr (VI) adsorption onto Akadama clay is mainly electrostatic adsorption in acidic conditions [25]. The adsorption process was that the surface of the clay was well positively charged in acidic conditions, and then the negative forms of chromium ions were adsorbed to the positively charged surface, which can be seen in the following equations:

Positively charged process:



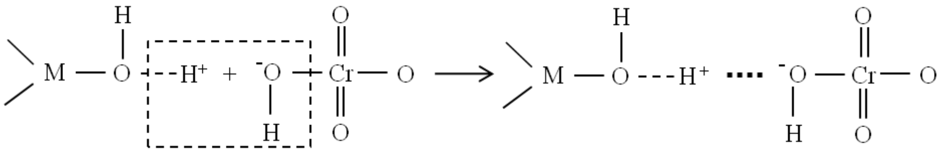
(3-1)

or



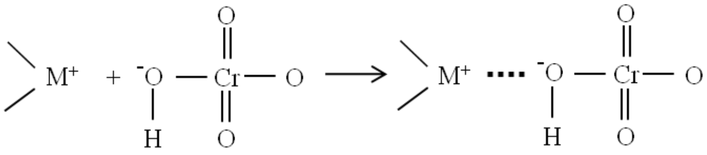
(3-2)

Cr (VI) adsorption process:



(3-3)

or



(3-4)

Where M represents Si, Al, Fe, etc.

In the present study, at pH range of 1 to 11, $Cr_2O_7^{2-}$, $HCrO_4^-$ and $CrO_4^{2-}$are the principle species in aqueous solutions [31, 32]. For natural Akadama clay, it was proved that the positive charge on clay surface was highest at pH 2 (ζ=+ 42.7 mV), and the zeta potentials decreased at pH 1 (ζ= +18.2 mV) and pH $\geq$ 3 (ζ< +21.5 mV). Zeta potential value can be related to the stability of colloidal dispersions, indicating the degree of repulsion between adjacent, similarly charged particles (the clay particles) in the dispersion. Higher zeta potential (positive or negative) values can reflect higher-charged surfaces. Therefore, low zeta potentials at pH 1 and pH $\geq$ 3 indicated weaker electrostatic force for negative chromium ions, hence the removal efficiencies of Cr (VI) decreased at pH 1 and 3 – 11 [25]. However, for HMAC, acid activation could generate large amount of available positively charged sites through protonation of ≡Si−OH groups or acceptance of protons by metallic oxidic groups such as Al, Fe [29]. The statement could be proved through the zeta potential value of HMAC (ζ= + 54.1 mV) in solution (pH = 6.0) being much larger than that of unmodified Akadama clay (ζ= + 21.6 mV). Under alkaline conditions, the highly protonated surfaces were able to neutralize part of OH^- ions and weaken the competition of $OH^-$for negative Cr (VI) ions, which might be the reason why the adsorption efficiency of Cr (VI) onto HMAC is much better than unmodified Akadama clay at pH 7- 11. On the other hand, during the modification process, acid might remove the impurities existing in the pore structures of the clay, and dredged passage ways for Cr (VI) ions, hence also improve the adsorption efficiency of Cr (VI).

Since the effluent pHs from various industrial wastewaters are different (e.g. electroplating wastewater: pH ≈ 2, and tannery wastewater: pH 4.3 –9.0) [6, 26, 27, 33, 34], it is laborious to adjust the effluent pH to fit the optimum pH of adsorbents. Therefore, the application for most adsorbents is limited due to their restricted pH conditions [16, 29]. In contrast, HMAC in the present study can overcome this disadvantage and cope with more extensive pH conditions. The original pH of Cr (VI) solution (100 mg L^{-1}) used in the present study was about 4.7. Therefore, the following studies were carried out without pH adjustment.

3.3.4 Effect of contact time

Effect of contact time on Cr (VI) adsorption by HMAC was investigated at a constant initial concentration of 100.0 mg L^{-1}, adsorbent dose of 40 g L^{-1} and without pH adjustment

(Fig.3-5). The removal of Cr (VI) sharply increased in the first 5 min, and the removal efficiency reached 82.8% with adsorption capacity of 2.07 mg g^{-1}, indicated that the adsorption of Cr (VI) on HMAC was a rapid process. Thereafter, the removal rate became slow, and the removal efficiencies at the contact time of 1 h, 6 h, 12 h, 24 h, and 48 h were 86.4%, 91.0%, 92.5%, 92.6% and 92.6%, with adsorption capacities of 2.16, 2.21, 2.30, 2.32, and 2.32 mg g^{-1}, respectively. The increase of removal efficiency was not significant with increasing contact time. Since there are no obvious difference between the removal efficiencies at 24 h and 48 h, contact time of 24 h is considered to be sufficient for complete adsorption in this study.

3.3.5 Effect of initial concentration

As shown in Fig.3-6, the effect of the initial concentration on the Cr (VI) adsorption was investigated at the range of 10 to 200 mg L^{-1} at adsorbent dose 40 g L^{-1} and contact time 24 h. In accordance with other reports [6, 35], the removal efficiency of Cr (VI) decreased with increase in initial concentrations, while the adsorption capacity increased when the initial concentration increased. In this study, the removal efficiency was more than 97.3% in the initial concentration ranged from 10.0 to 50.0 mg L^{-1}, and it decreased to 77.4% at an initial concentration of 200 mg L^{-1}. The adsorption capacity increased from 0.31 to 3.78 mg g^{-1} when the initial concentration increased from 10 to 200 mg L^{-1}.The decrease in removal efficiency was attributed to the fact that the increased initial concentration aggravated the burden of the constant adsorbent. It indicated that the adsorbent could not bear all Cr (VI) loadings, and also its bearing capacity was limited[36]. The increase in adsorption capacity was ascribed to the fact that, on the constant adsorption site, an increasing initial concentration brought a stronger driving force generated from the higher concentration gradient and then possibly contributed to higher adsorption capacity [25].

3.3.6 Effect of adsorbent dosage

Fig.3-7 shows the effect of HMAC doses on the removal of Cr (VI) at different dosages ranged from 5 to 80 g L^{-1}, contact time of 24 h, and initial concentration of 112.5 mg L^{-1}. When the HMAC doses increased from 5 to 40 g L^{-1}, the removal efficiency of Cr (VI) increased from 32.6% to 90.1%, while the Cr (VI) adsorption capacity decreased from 7.47 to 2.55 mg g^{-1}. Further increasing the dosage up to 80 g L^{-1}, the removal efficiency reached 94.9%, while the Cr (VI) adsorption capacity decreased to 1.34 mg g^{-1}. The results revealed that, when adsorbent dosage ranged from 40 to 80 g L^{-1}, removal efficiency only increased 4.8%, but the Cr (VI) adsorbent capacity decreased 47.5%. This observation indicated that high adsorbent dosage is an important factor influencing the adsorption capacity, but only slightly affecting the removal efficiency. The result was consistent with results reported by Sari et al. [37] and Rawajfih et al. [35]. This could be due to the following reasons. Firstly, the available adsorption sites or surface area were increased or enlarged by increasing the adsorbent dose, so more Cr (VI) could be adsorbed; and because of the more available adsorbent sites, the Cr (VI) concentration gradient loaded onto the unit surface area became lower, hence adsorption capacity decreased. Secondly, the partial aggregation of high HMAC dosage resulted in ineffective utilization of the surface area, which also lengthened the diffusion path for Cr (VI), thus affects the adsorption efficiency [37, 38]. Thirdly, the repulsive interaction between adsorbed Cr (VI) ions and Cr

(VI) ions in the solution also might lead to the reduction of adsorption capacity.

3.3.7 Adsorption kinetics

In order to evaluate the reaction pathway and the rate-controlling mechanism of the adsorption process, the adsorption kinetics were studied by the pseudo-first-order kinetic model, the pseudo-second-order model, and the intra-particle diffusion model. The linear forms of them are given as Eqs. (2-3), (2-4), and (3-5) [39], respectively.

$$q_t = k_p t^{0.5} + C \tag{3-5}$$

where q_t is the amount of Cr (VI) adsorbed at time t (mg g^{-1}), t is the contact time (min), and k_p is the diffusion coefficient of the intra-particle diffusion model (mg $min^{-0.5}$ g^{-1}), and C is the intercept.

The kinetic plots are depicted in Fig.3-8 and the corresponding parameters were summarized in Table 3-2. As it can be seen, for the pseudo-first-order model, the correlation coefficient value was found to be low ($R^2 = 0.893$). Moreover, the experimental values (q_e = 2.32 mg g^{-1}) were apparently different from the theoretical values obtained from Eq (1) (q_e = 0.29 mg g^{-1}). It could be concluded that the adsorption of Cr (VI) onto HMAC did not follow a pseudo-first-order model.

For the pseudo-second-order model, the high correlation coefficient ($R^2 = 1.000$) and no difference in the experimental values (q_e = 2.32 mg g^{-1}) and the theoretical value calculated from Eq (2-4) (q_e = 2.32 mg g^{-1}) indicated that the adsorption of Cr (VI) onto HMAC was well explained by the pseudo-second-order kinetic model, implying the adsorption is controlled by a chemical process. The result is in agreement with available literatures on the adsorption of Cr (VI) onto various materials [21, 23].

For the intra-particle diffusion model, due to the good porous property of the adsorbent, surface diffusion (film diffusion) in addition to pore diffusion (intra-particle diffusion) may contribute to the overall Cr (VI) adsorption [16]. In Fig.3-8c, step I relates to surface diffusion and step II relates to the pore diffusion within the adsorbent. The correlation coefficient of step I (R^2 = 0.961) and step II (R^2 = 0.953) were both high, indicating that boundary layer diffusion and intra-particle diffusion occurred in the adsorption process. In addition, the q_t versus $t^{0.5}$ plots for both step I and step II did not pass through the origin and a positive intercept was observed, indicating that other adsorption processes were also involved in Cr (VI) adsorption onto HMAC [6].

3.3.8 Adsorption isotherms

To get more information on the Cr (VI) adsorption onto HMAC, three important adsorption isotherm models were used to evaluate the experimental data, which are Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherm models.

The Langmuir model assumes that the maximum uptake occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbates [37]. The linear form of the Langmuir isotherm is represented in Eqs.(2-1). The dimensionless constant separation parameter $R_L = 1/(1 + bC_i)$ expresses the essential characteristics of the Langmuir isotherm[7], where C_i is the initial concentration of Cr(VI) (mg L^{-1}). R_L determines the feasibility of the adsorption process. The value of R_L indicates the isotherm model is either unfavorable ($R_L > 1$) or linear ($R_L = 1$) or favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [21].

The Freundlich isotherm is an empirical expression for modeling the adsorption on heterogeneous surface. The isotherm can be expressed as Eqs. (2-2). It is worth to mention that 1/n is relative to the adsorption intensity. The exponent ‘n’ gives an indication of the favorability of the adsorption. It is generally stated that ‘n’ values ranging from 2 - 10 represent favorable, 1 - 2, moderately difficult, and less than 1, poor adsorption characteristics [7].

The equilibrium data were also applied to the D-R isotherm model and validated the nature of Cr (VI) adsorption onto HMAC is physical or chemical process. The linear form of the D-R isotherm can be expressed as [37]:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (3\text{-}6)$$

where q_e is the amount of Cr (VI) adsorbed on per unit weight of HMAC (mol L^{-1}), q_m is the maximum adsorption capacity (mol g^{-1}), β is the activity coefficient related to mean adsorption energy (mol^2 J^{-2}), and ε is the Polanyi potential ($\varepsilon = RT\ln(1+1/C_e)$). R is the gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), C_e is the equilibrium concentration of Cr (VI) (mol L^{-1}).

The mean free energy E (kJ mol^{-1}) = $1/\sqrt{2\beta}$ gives information about adsorption mechanism, physical or chemical. E values between 8 and 16 kJ mol^{-1} indicate chemical adsorption, while E less than 8 kJ mean physical adsorption [37].

The isotherm experiments were carried out at conditions of initial concentrations from 10 to 200 mg L^{-1}, adsorbent dose of 40 g L^{-1}, and contact time of 24 h. The isotherm parameters were listed in Table 3-3. It can be seen that the correlation coefficients of Langmuir isotherm model ($R^2 = 0.874$) was lower than those of Freundlich isotherm ($R^2 = 0.999$) and D - R isotherm model ($R^2 = 0.993$), indicating that Cr (VI) adsorption onto HMAC did not occur on homogeneous surface by monolayer sorption. However, $R_L$varied from 0.066 to 0.004 during the initial concentrations of 10 - 200 mg L^{-1}, which indicates the favorable conditions for Cr (VI) adsorption on HMAC. Other studies also reported that the Freundlich model described a much better fit than the Langmuir model in relation to Cr (VI) adsorption [40]. In addition, the constant 'n' in the Freundlich model is 2.97, which further verifies the favorability of HMAC as a suitable adsorbent for Cr (VI) removal. Based on the results of D-R model, the mean free energy E of 13.13 kJ mol^{-1} indicated that chemical adsorption dominated the Cr (VI) adsorption onto HMAC [37]. This conclusion was consistent with the results deduced from the pseudo-second-order kinetic model.

3.3.9 Effect of coexisting ions

Real industrial wastewater contains different kinds of anion and cation ions, as well as organic materials, which might hinder the uptake of Cr (VI) ions by adsorbent. Therefore, the effect of the independent presence of each coexisting ion (sodium-based anions: Cl^-, NO_3^-, SO_4^{2-}; sodium-based organics: CH_3COO^-; chlorine-based cations: Na^+, K^+, Ca^{2+}, Mg^{2+}) on the removal efficiency and adsorption capacity of Cr (VI) onto HMAC were studied and the results are shown in Fig.3-9. As the concentrations of coexisting ions such as Na^+, SO_4^{2-}, Cl^- etc. in real wastewater are several thousand mg L^{-1} [34, 41], the concentrations of coexisting ions in the present study were prepared at 0.1 mol L^{-1}.

Results showed that, compared with the blank removal efficiency of 87.9%, all the removal efficiencies of Cr (VI) in the presence of coexisting anions, organics, and cations decreased. For the coexisting cations of Na^+, K^+, Ca^{2+}, and Mg^{2+}, the removal efficiencies were 68.6%, 69.4%, 67.6%, 64.7%, respectively, showing little difference of the effect on Cr (VI) adsorption. For the organics, the removal efficiency of 63.8% indicated that even in the presence of high concentration organics, HMAC still had high adsorption ability on the Cr (VI) ions. For the coexisting anions, the removal efficiencies of Cr (VI) in presence of SO_4^{2-}, Cl^-, and NO_3^-decreased to 24.8%, 68.6%, and 74.5%, respectively, presenting an influence order of SO_4^{2-}> Cl^-> NO_3^-. Since the adsorption mechanism of Cr (VI) on HMAC was the negative charged Cr (VI) ions bonding to the positive charged surface of the clay, the existing anions doubtlessly competed with Cr (VI) ions on the available adsorption sites, also they exhibited a negative effect on the diffusion of Cr (VI) ions to the clay surface by restricting their mobility, resulting in decreased removal efficiencies of Cr (VI) [20]. On the other hand, according to surface chemistry theory, when solid adsorbent comes into contact with an adsorbate species in solution, they are bound to be surrounded by an electrical double layer owing to electrostatic interaction [42]. Increasing coexisting ionic strength could result in a decrease in the thickness of the electrical double layer, which might lead to a decrease in adsorption uptake of Cr (VI) ions [43].

It was obvious that SO_4^{2-}had a great negative effect on the Cr (VI) adsorption onto HMAC, as the same result was obtained by other study [23]. The result was ascribed to two reasons. The most likely reason was that negative bivalent of SO_4^{2-} would produce stronger electrostatic attraction onto the positive charged surface and result in greater competition with the negative Cr (VI) ions on the adsorption site. Another reason might be attributed to the fact that the positive charged metal ions on HMAC surface would generate complexes in the presence of abundant anion ionsand decrease the protonation degree of the clay [23]. On the whole, the removal efficiency of Cr (VI) onto HMAC was still higher than 63.8% at conditions of most anions and cations coexistence, indicating that HMAC had a high selectivity for Cr (VI) in real industrial wastewater. A comparison of adsorption capacity among different mineral adsorbents is presented in Table 3-4 [43-46].

3.3.10 Desorption studies

Attempts were made to desorb Cr (VI) by batch process. 30 mg L^{-1}Cr (VI) solution (10 mL) was treated with 0.4 g adsorbent for 1 h, and the Cr (VI) was completely adsorbed onto HMAC. After separation of the HMAC and solution, the Cr (VI)-loaded adsorbent was treated with 0.01, 0.015, 0.02, 0.025, and 0.03 M NaOH solution (10 mL) for1 h, respectively. Every experiment was repeated three times to ensure the reproducibility. Results shows that the desorption efficiencies of Cr (VI)were 3.2%, 68.3%, 77.0%, and 85.5% with NaOH concentration of 0.01, 0.015, 0.02, 0.025 M, respectively. The desorption efficiency with NaOH concentration of 0.03 M was almost same with 0.025 M. Therefore, the optimum NaOH concentration for Cr (VI) desorption was selected at 0.025 M.

3.4 Conclusion

HCl-modified Akadama clay (HMAC) was used to adsorb Cr(VI) from wastewater. No change in the main chemical composition of Akadama clay was observed by XRD patterns for HMAC. About 90.0% of Cr (VI) was removed at pH ranges of 2 to 11. The maximum experimental adsorption capacity of 7.31 mg g^{-1} was obtained at an initial concentration of 112.5 mg L^{-1}, dose of 5 g L^{-1} and contact time of 24 h. SO_4^{2-} presented an obvious negative effect on the Cr (VI) adsorption onto HMAC, and the influence of anion ions followed the order of SO_4^{2-}> Cl^{-}> NO_3^{-}. The experimental data fitted the pseudo-second-order kinetic model and D-R isotherm model, denoting that the nature of Cr (VI) adsorption onto HMAC is chemical. The high R^2 values for the two steps of the intra-particle diffusion model indicated that both boundary layer diffusion and intra-particle diffusion occurred in the adsorption process. Wide pH conditions and high selectivity in Cr (VI) adsorption obtained in this study indicate that HMAC could be promising for Cr (VI) removal from wastewater in practical.

References

[1] W. Liu, J. Zhang, C. Zhang, L. Ren, Preparation and evaluation of activated carbon-based iron-containing adsorbents for enhanced Cr(VI) removal: Mechanism study, Chemical Engineering Journal, 189-190 (2012) 295-302.

[2] X.S. Wang, L.F. Chen, F.Y. Li, K.L. Chen, W.Y. Wan, Y.J. Tang, Removal of Cr (VI) with wheat-residue derived black carbon: Reaction mechanism and adsorption performance, Journal of Hazardous Materials, 175 (2010) 816-822.

[3] U.S. EPA, Basic Information about Chromium in Drinking Water, United States Environmental Protection Agency, Washington, D.C., 2012.

[4] WHO, Guidelines for Drinking-water Quality– 4thed, World Health Organization, Geneva, Switzerland, 2011

[5] GB5749-2006, Standards for Drinking Water Quality, P.R.C. National Standard, China, 2006.

[6] G. Moussavi, B. Barikbin, Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass, Chemical Engineering Journal, 162 (2010) 893-900.

[7] M. Jain, V.K. Garg, K. Kadirvelu, Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass, Journal of Environmental Management, 91 (2010) 949-957.

[8] S.A. Cavaco, S. Fernandes, M.M. Quina, L.M. Ferreira, Removal of chromium from electroplating industry effluents by ion exchange resins, Journal of Hazardous Materials, 144 (2007) 634-638.

[9] M. Gheju, I. Balcu, Removal of chromium from Cr(VI) polluted wastewaters by reduction with scrap iron and subsequent precipitation of resulted cations, Journal of Hazardous Materials, 196 (2011) 131-138.

[10] G. Almaguer-Busso, G. Velasco-Martínez, G. Carreño-Aguilera, S. Gutiérrez-Granados, E. Torres-Reyes, A. Alatorre-Ordaz, A comparative study of global hexavalent chromium removal by chemical and electrochemical processes, Electrochemistry Communications, 11 (2009) 1097-1100.

[11] A. Jayalakshmi, S. Rajesh, S. Senthilkumar, D. Mohan, Epoxy functionalized poly(ether-sulfone) incorporated cellulose acetate ultrafiltration membrane for the removal of chromium ions, Separation and Purification Technology, 90 (2012) 120-132.

[12] Y. Li, Q.Y. Yue, B.Y. Gao, Effect of humic acid on the Cr(VI) adsorption onto Kaolin, Applied Clay Science, 48 (2010) 481-484.

[13] Y.C. Sharma, Effect of Temperature on Interfacial Adsorption of Cr(VI) on Wollastonite, Journal of Colloid and Interface Science, 233 (2001) 265-270.

[14] S.A. Khan, R. Rehman , M.A. Khan, Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite, Waste Management, 15 (1995) 271-282.

[15] S.T. Akar, Y. Yetimoglu, T. Gedikbey, Removal of chromium (VI) ions from aqueous solutions by using Turkish montmorillonite clay: effect of activation and modification Desalination, 244 (2009) 97-108.

[16] V. Venugopal, K. Mohanty, Biosorptive uptake of Cr(VI) from aqueous solutions by Parthenium hysterophorus weed: Equilibrium, kinetics and thermodynamic studies, Chemical Engineering Journal, 174 (2011) 151-158.

[17] R.A.K. Rao, F. Rehman, Adsorption studies on fruits of Gular (Ficus glomerata):

Removal of Cr(VI) from synthetic wastewater, Journal of Hazardous Materials, 181 (2010) 405-412.

[18] S. Gupta, B.V. Babu, Modeling, simulation, and experimental validation for continuous Cr(VI) removal from aqueous solutions using sawdust as an adsorbent, Bioresource Technology, 100 (2009) 5633-5640.

[19] S.S. Baral, N. Das, G. Roy Chaudhury, S.N. Das, A preliminary study on the adsorptive removal of Cr(VI) using seaweed, Hydrilla verticillata, Journal of Hazardous Materials, 171 (2009) 358-369.

[20] J. Zhou, P. Wu, Z. Dang, N. Zhu, P. Li, J. Wu, X. Wang, Polymeric Fe/Zr pillared montmorillonite for the removal of Cr(VI) from aqueous solutions, Chemical Engineering Journal, 162 (2010) 1035-1044.

[21] A.K. Giri, R. Patel, S. Mandal, Removal of Cr (VI) from aqueous solution by Eichhornia crassipes root biomass-derived activated carbon, Chemical Engineering Journal, 185-186 (2012) 71-81.

[22] Y. Wen, Z. Tang, Y. Chen, Y. Gu, Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent, Chemical Engineering Journal, 175 (2011) 110-116.

[23] D.W. Cho, C.M. Chon, Y. Kim, B.H. Jeon, F.W. Schwartz, E.S. Lee, H. Song, Adsorption of nitrate and Cr(VI) by cationic polymer-modified granular activated carbon, Chemical Engineering Journal, 175 (2011) 298-305.

[24] G. Huang, J.X. Shi, T.A.G. Langrish, Removal of Cr(VI) from aqueous solution using activated carbon modified with nitric acid, Chemical Engineering Journal, 152 (2009) 434-439.

[25] Y. Zhao, S. Yang, D. Ding, J. Chen, Y. Yang, Z. Lei, C. Feng, Z. Zhang, Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay, Journal of Colloid and Interface Science, 395 (2013) 198-204.

[26] Sirajuddin, L. Kakakhel, G. Lutfullah, M.I. Bhanger, A. Shah, A. Niaz, Electrolytic recovery of chromium salts from tannery wastewater, Journal of Hazardous Materials, 148 (2007) 560-565.

[27] G.M. Ayoub, A. Hamzeh, L. Semerjian, Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption, Desalination, 273 (2011) 359-365.

[28] A.H. El-Sheikh, Effect of oxidation of activated carbon on its enrichment efficiency of metal ions: comparison with oxidized and non-oxidizedmulti-walled carbon nanotubes, Talanta, 75 (2008) 127-134.

[29] S.T. Akar, Y. Yetimoglu, T. Gedikbey, Removal of chromium (VI) ions from aqueous solutions by using Turkish montmorillonite clay: effect of activation and modification, Desalination, 244 (2009) 97-108.

[30] E. Alemayehu, S. Thiele-Bruhn, B. Lennartz, Adsorption behaviour of Cr(VI) onto macro and micro-vesicular volcanic rocks from water, Separation and Purification Technology, 78 (2011) 55-61.

[31] L. Xiao, W. Ma, M. Han, Z. Cheng, The influence of ferric iron in calcined nano-Mg/Al hydrotalcite on adsorption of Cr (VI) from aqueous solution, Journal of Hazardous Materials, 186 (2011) 690-698.

[32] P. Miretzky, A.F. Cirelli, Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, Journal of Hazardous Materials, 180

(2010) 1-19.

[33] R. Kumar, N.R. Bishnoi, Garima, K. Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chemical Engineering Journal, 135 (2008) 202-208.

[34] V. Vinodhini, N. Das, Packed bed column studies on Cr (VI) removal from tannery wastewater by neem sawdust, Desalination, 264 (2010) 9-14.

[35] Z. Rawajfih, N. Nsour, Thermodynamic analysis of sorption isotherms of chromium(VI) anionic species on reed biomass, The Journal of Chemical Thermodynamics, 40 (2008) 846-851.

[36] Y. Zhao, Y. Yang, S. Yang, Q. Wang, C. Feng, Z. Zhang, Adsorption of high ammonium nitrogen from wastewater using a novel ceramic adsorbent and the evaluation of the ammonium-adsorbed-ceramic as fertilizer, Journal of Colloid and Interface Science, 393 (2013) 264-270.

[37] A. Sari, M. Tuzen, Biosorption of total chromium from aqueous solution by red algae (Ceramium virgatum): equilibrium, kinetic and thermodynamic studies, Journal of Hazardous Materials, 160 (2008) 349-355.

[38] A. Shukla, Y.H. Zhang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, Journal of Hazardous Materials, B95 (2002) 137–152.

[39] P. Suksabye, A. Nakajima, P. Thiravetyan, Y. Baba, W. Nakbanpote, Mechanism of Cr(VI) adsorption by coir pith studied by ESR and adsorption kinetic, Journal of Hazardous Materials, 161 (2009) 1103-1108.

[40] A.G. Yavuz, E. Dincturk-Atalay, A. Uygun, F. Gode, E. Aslan, A comparison study of

adsorption of Cr(VI) from aqueous solutions onto alkyl-substituted polyaniline/chitosan composites, Desalination, 279 (2011) 325-331.

[41] K. Sumathi, Use of low-cost biological wastes and vermiculite for removal of chromium from tannery effluent, Bioresource Technology, 96 (2005) 309-316.

[42] A.C. Zimmermann, A. Mecabô, T. Fagundes, C.A. Rodrigues, Adsorption of Cr(VI) using Fe-crosslinked chitosan complex (Ch-Fe), Journal of Hazardous Materials, 179 (2010) 192-196.

[43] C.H. Weng, Y.C. Sharma, S.H. Chu, Adsorption of Cr(VI) from aqueous solutions by spent activated clay, Journal of Hazardous Materials, 155 (2008) 65-75.

[44] A. Benhammou, A. Yaacoubi, L. Nibou, B. Tanouti, Chromium(VI) adsorption from aqueous solution onto Moroccan Al-pillared and cationic surfactant stevensite, Journal of Hazardous Materials, 140 (2007) 104–109.

[45] V. Marjanović, S. Lazarević, I. Janković-Častvan, B. Potkonjak, Đ. Janaćković, R. Petrović, Chromium (VI) removal from aqueous solutions using mercaptosilane functionalized sepiolites, Chemical Engineering Journal, 166 (2011) 198-206.

[46] B. Sarkar, Y. Xi, M. Megharaj, G.S.R. Krishnamurti, D. Rajarathnam, R. Naidu, Remediation of hexavalent chromium through adsorption by bentonite based Arquad® 2HT-75 organoclays, Journal of Hazardous Materials, 183 (2010) 87-97.

Table 3-1 Surface area characterization and pore volume analysis of HMAC before and after Cr (VI) adsorption.

Surface areas	Before adsorption	After adsorption
BET surface area ($m^2\ g^{-1}$)	143.57	131.04
Langmuir surface area ($m^2\ g^{-1}$)	132.87	118.70
T-plot surface area ($m^2\ g^{-1}$)	132.53	122.13
Total pore volume ($cm^3\ g^{-1}$)	0.177	0.160

Table 3-2 Kinetic parameters calculated from pseudo-first-order model, pseudo-second-order model and intra-particle diffusion model for Cr (VI) adsorption onto HMAC

Pseudo-first-order model			Pseudo-second-order model			Intra-particle diffusion model			
k_1(min^{-1})	q_e (mg g^{-1})	R^2	k_2(g min^{-1} mg^{-1})	q_e (mg g^{-1})	R^2	K_{p1}	R_1^2	K_{p2}	R_2^2
0.005	0.29	0.893	0.096	2.32	1.000	0.013	0.961	0.002	0.953

Table 3-3Langmuir, Freudlich, and D - R isotherm constants for Cr(VI) adsorption onto HMAC.

Langmuir isotherm			Freundlich isotherm			D - R isotherm		
b (L mg^{-1})	q_m (mg g^{-1})	R^2	K_f	n	R^2	q_m (mg g^{-1})	R^2	E (kJ mol^{-1})
1.42	2.17	0.8736	1.09	2.97	0.9985	8.66	0.9928	13.13

Table 3-4 Comparison of adsorption capacity among different mineral adsorbents

Adsorbent material	pH	Dose (gL^{-1})	Concentration range (mg L^{-1})	Q_m (mg g^{-1})	Refer.
Spent activated clay	2	1	0.2-10	1.42	[43]
Aluminium hydroxypolycation (Al-stevensite)	3.5–6.0	5	0-400	3.92	[44]
Akadama clay	2	5	50	4.29	This study
Acid-activatedmontmorillonite clay	1	10	250	4.51	[29]
HCl-modified Akadama caly	3 - 9	5	112.5	7.47	This study
Mercaptosilanefunctionalized sepiolites	3	0.4	5-100	8.00	[45]
Bentonite based Arquad® 2HT-75 organoclays	5	5	10-200	14.64	[46]

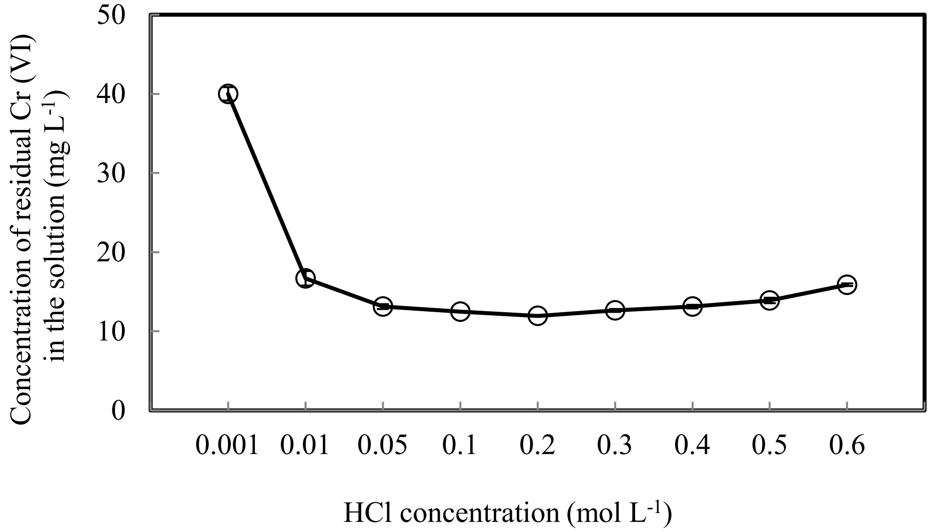


Fig.3-1 Effect of HCl concentrations on the modification of Akadama clay (Initial concentration of Cr (VI) = 100.2 mg L^{-1}, contact time = 24 h, dosage = 40 g L^{-1})

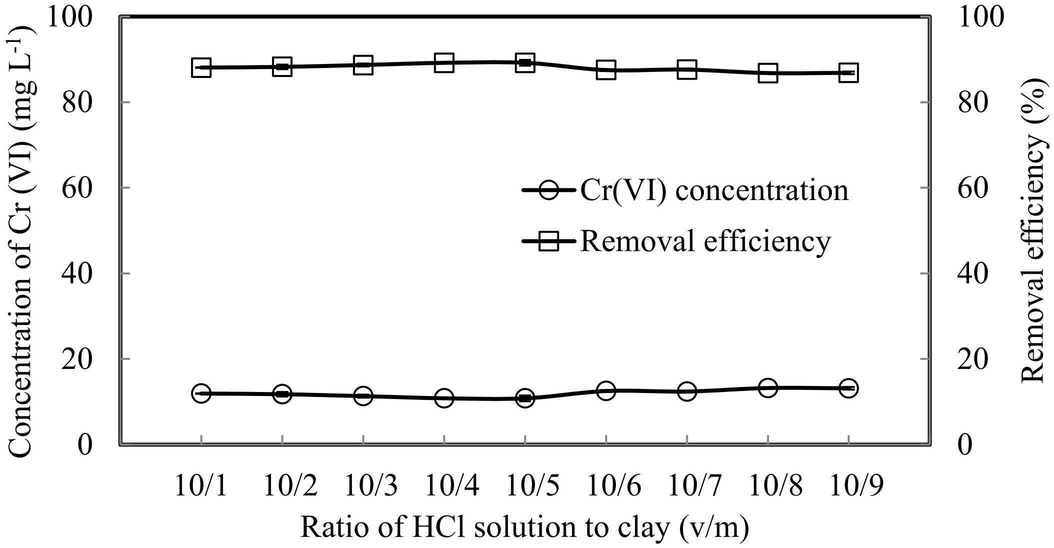
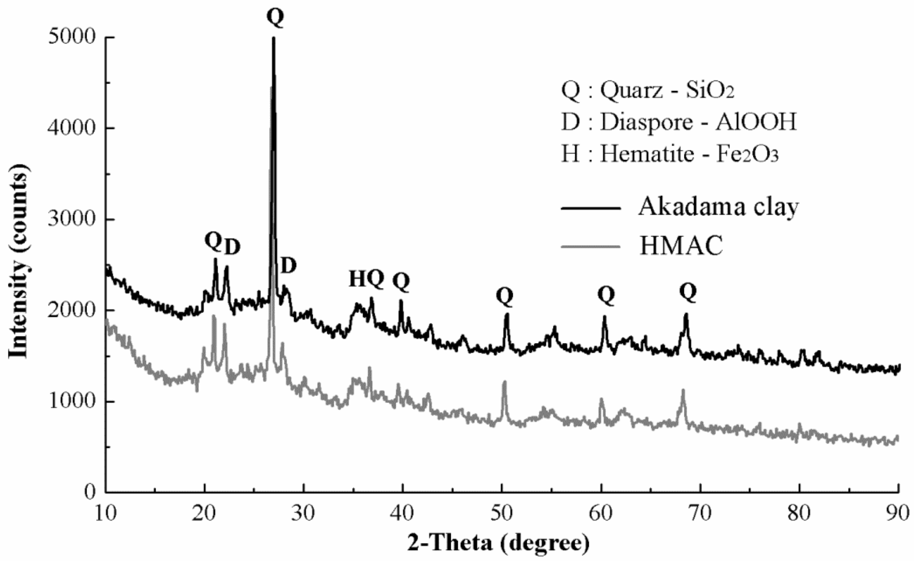
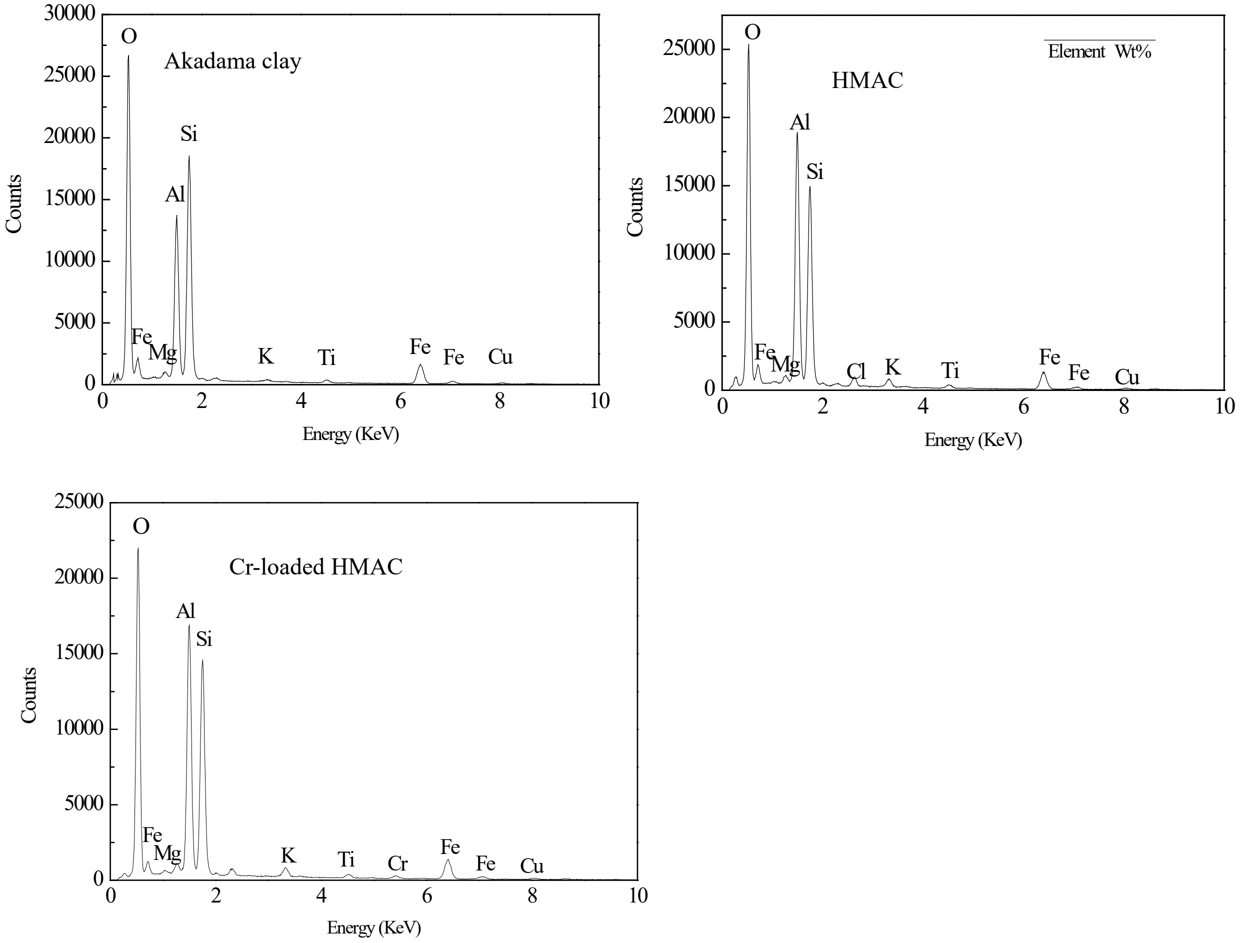


Fig.3-2 Effect of ratios of HCl solution to clay on the modification of Akadama clay (Initial concentration of Cr (VI) = 100.6 mg L^{-1}, contact time = 24 h, dosage = 40 g L^{-1})

(a)


Q
5000
4000
3000
2000
1000
0
Intensity (counts)
Q : Quarz - SiO2
D : Diaspore - AlOOH
H : Hematite - Fe2O3
Akadama clay
HMAC
Q D
D
HQ
Q
Q
Q
Q
10
20
30
40
50
60
70
80
90
2-Theta (degree)

(b)


30000
25000
20000
15000
10000
5000
0
Counts
O
Akadama clay
Si
Al
Fe
Mg
K
Ti
Fe
Fe
Cu
0
2
4
6
8
10
Energy (KeV)
25000
20000
15000
10000
5000
0
Counts
O
Element Wt%
HMAC
Al
Si
Fe
Mg
Cl
K
Ti
Fe
Fe
Cu
0
2
4
6
8
10
Energy (KeV)
25000
20000
15000
10000
5000
0
Counts
O
Cr-loaded HMAC
Al
Si
Fe
Mg
K
Ti
Cr
Fe
Fe
Cu
0
2
4
6
8
10
Energy (KeV)

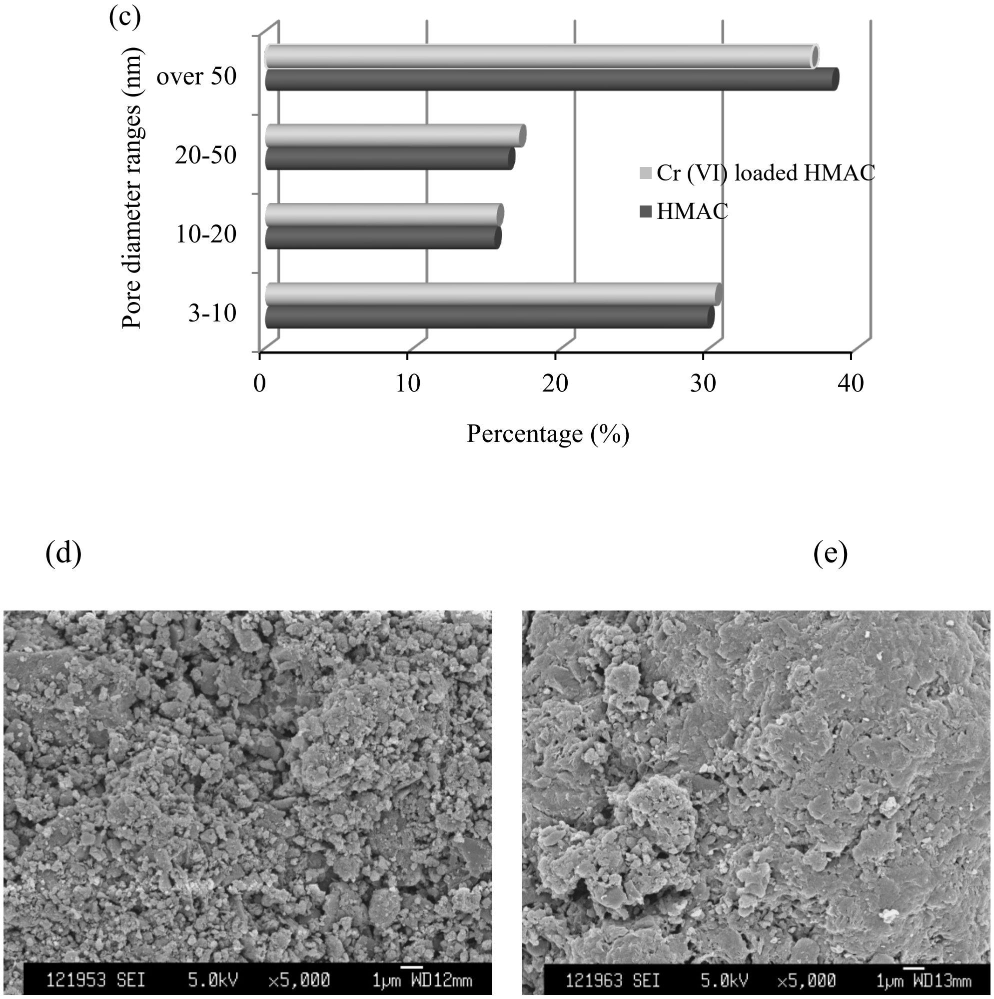


Fig.3-3 XRD patterns of Akadama clay and HMAC (a), EDX results of Akadama clay, HMAC, and Cr-loaded HMAC (b), adsorption BJH (Barrett–Joyner–Halenda) pore size distribution of HMAC and Cr (VI) loaded HMAC (c), and SEM images of HMAC (d) and after Cr (VI) adsorption (e).

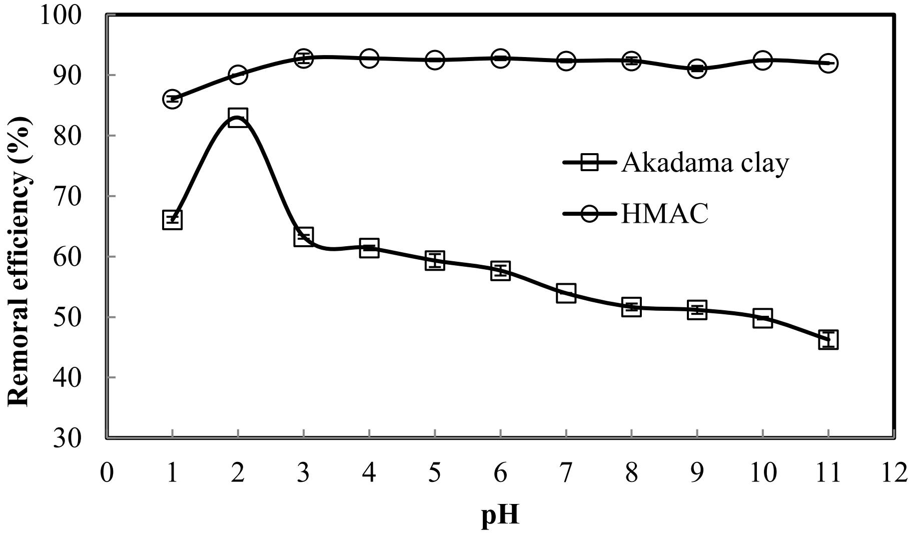


Fig.3-4 Effect of pH on Cr (VI) adsorption onto HMAC and Akadama clay (Initial Cr (VI) concentration = 100.0 mg L^{-1}, adsorbent dose = 40 g L^{-1}, contact time = 48 h)

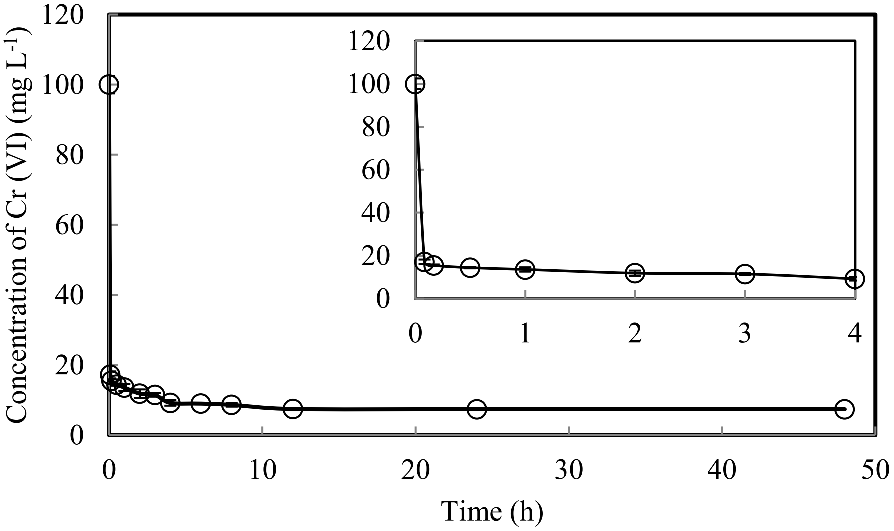


Fig.3-5 Effect of contact time on Cr (VI) removal (Adsorbent dose = 40 g L^{-1}, initial concentration of Cr (VI) = 100. 0 mg L^{-1})

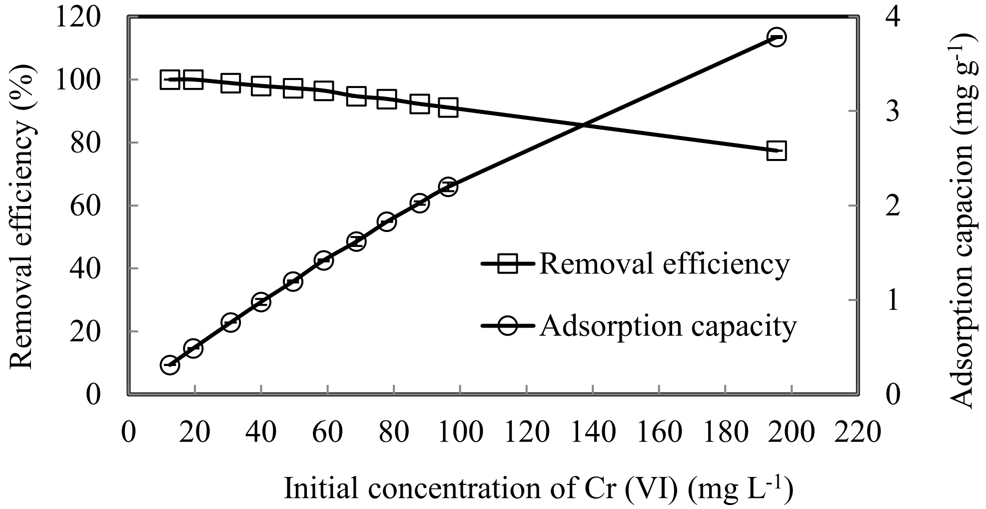


Fig.3-6 Effect of initial concentration on Cr (VI) removal (Adsorbent dose = 40 g L^{-1}, contact time = 24 h)

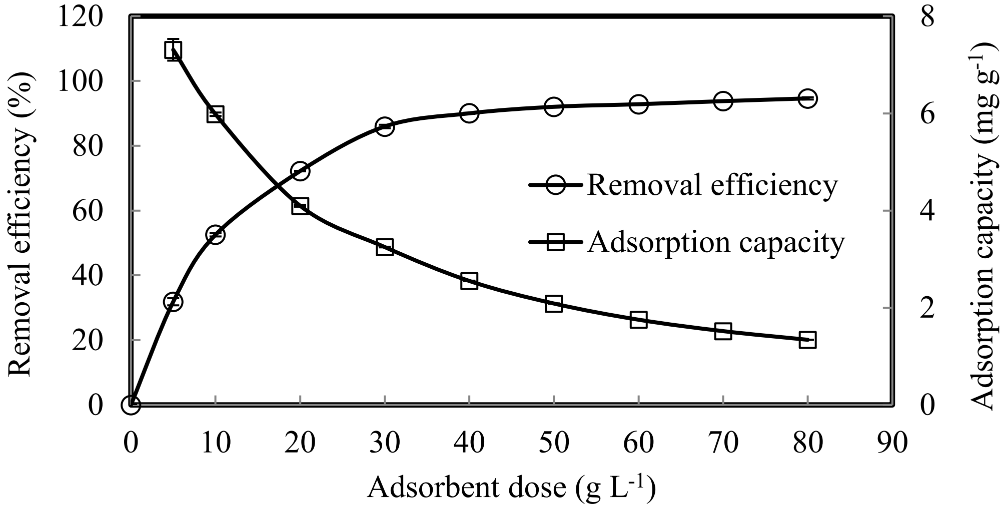


Fig. 3-7 Effect of HMAC dose on Cr (VI) removal (Initial concentration of Cr (VI) = 112.5 mg L^{-1}, contact time = 24 h)

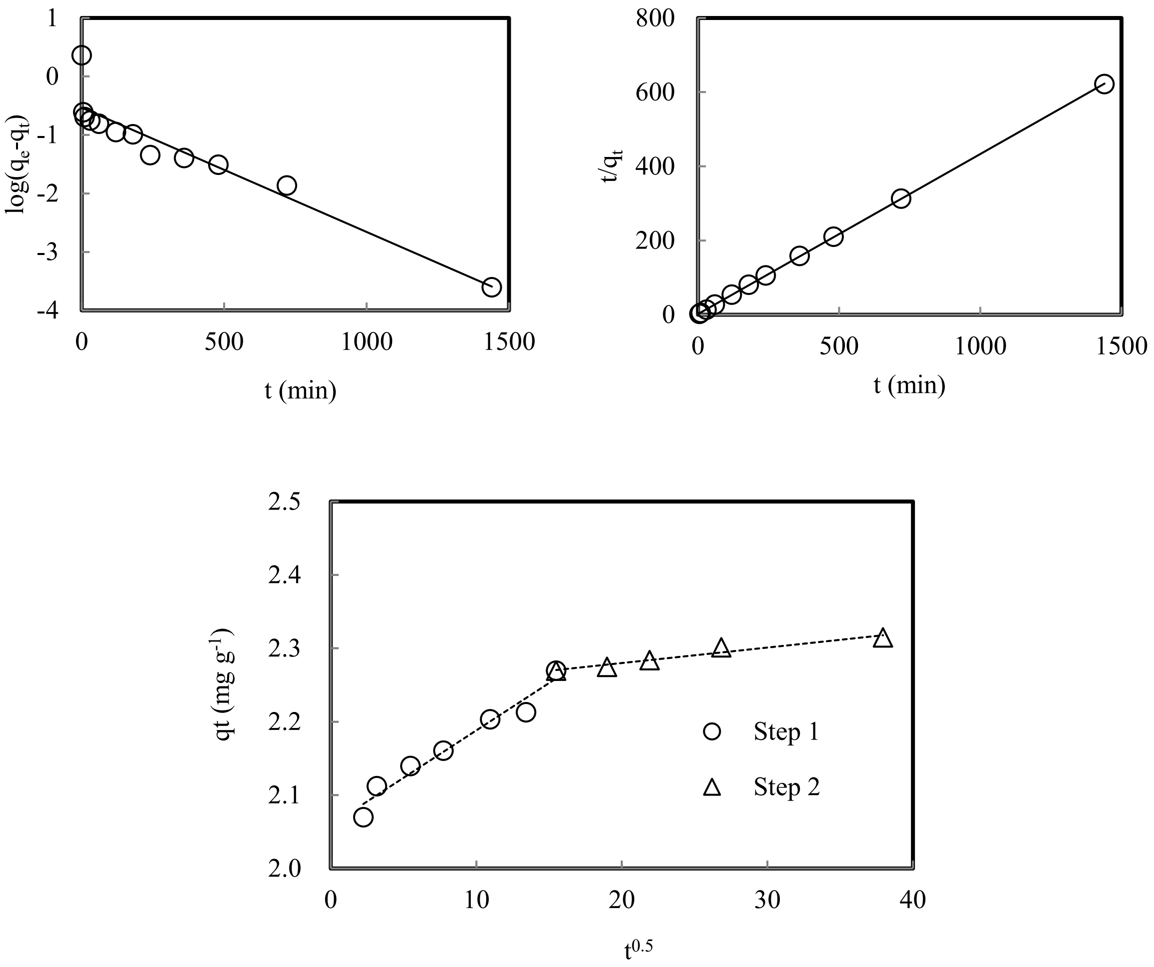


Fig.3-8 Plots of kinetics (a. pseudo-first-order model; b. pseudo-second-order model; c. intra-particle diffusion model) of Cr (VI) adsorption on HMAC. (Initial concentration of Cr (VI)=100.0 mg L^{-1}; adsorbent dose= 40 g L^{-1}, contact time = 0 -24 h)

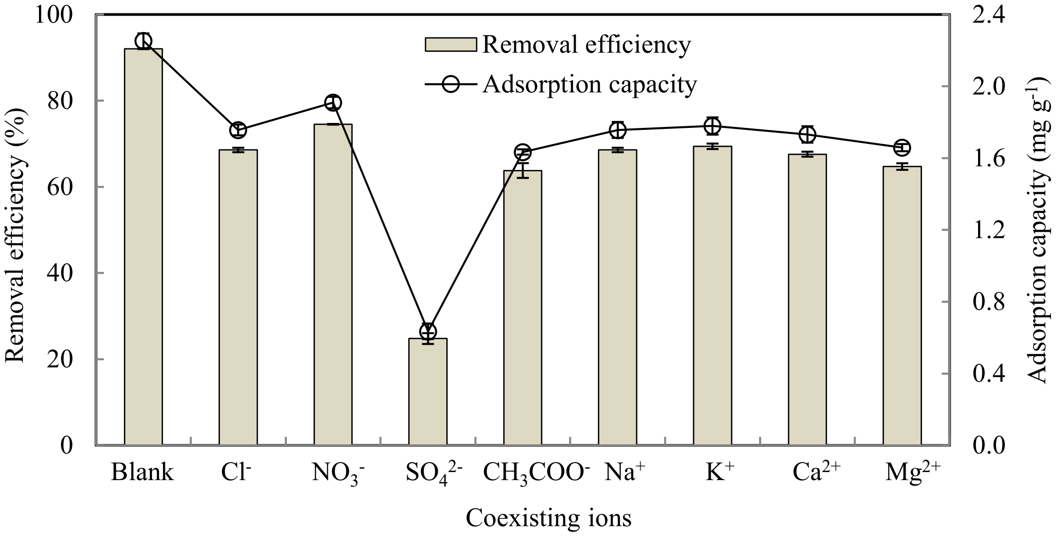


Fig.3-9 Effect of coexisting ions on the Cr (VI) adsorption onto HMAC (Initial concentration of Cr (VI) = 102.5 mg L^{-1}, adsorbent dose = 40 g L^{-1}, contact time = 24 h, concentrations of each coexisting ion = 0.1 mol L^{-1})

Chapter 4 Application of factorial design for experimental optimization and evaluation of Cr (VI) adsorption using Fe-modified Akadama clay

4.1 Introduction

Generally, chromium element exists in nature mainly in two most common forms: Cr (III) and Cr (VI). Chromium (III) has relatively low toxicity and would be a concern in drinking water only at very high levels of contamination. Cr (VI) occurs naturally in the environment from the erosion of natural chromium deposits, but it can also be produced by industrial processes such as leather tanning, electroplating, pigment and metallurgy etc. [1]. Recently, more and more attention is paid to Cr (VI) removal due to its high toxicity, persistency and carcinogenicity in living organisms, which cause various diseases and severe risk [2]. Since Cr (VI) and Cr (III) can convert back and forth in water and in the human body, depending on environmental conditions, the two forms are usually covered under the total chromium drinking water standard. The World Health Organization recommended that the maximum permissible concentration value in drinking water for total Cr should be 0.05 mgL^{-1} (Guidelines for drinking-water quality - 4thed., WHO, 2011), while the maximum contaminant level of total Cr in drinking water is regulated to below 0.10 mgL^{-1} by USEPA (National Primary Drinking Water Regulations, USEPA, 2009).

The conventional techniques used for Cr(VI) removal from industrial effluents include chemical precipitation, electrochemical treatment, ion exchange and membrane process, and liquid extraction etc. [3, 4]; however, due to some undesirable characteristics such as high cost, low efficiency and selectivity, complex procedure, high-energy requirements, and secondary pollution, their large scale application is restricted[5]. By contrast, adsorption overcomes most of the mentioned disadvantages and receives more concern recently. As a mineral adsorbent, Akadama clay has been confirmed to be efficient for Cr (VI) removal from wastewater [5]. In our previous study, it was proved that the adsorption mechanism for Cr (VI) onto Akadama clay was mainly electrostatic attraction. In acid conditions, the clay surface was positively charged, and the negative forms of chromium ions were then adsorbed to the positively charged surface. However, the maximum adsorption capacity of Cr (VI) onto Akadama clay was only 4.29 mg g^{-1}, and its optimal application condition was restricted at pH 2.

Inorganic salt activation is a typical method for adsorbent modification. After modification, the adsorption capacity of adsorbents will be greatly improved through activating or increasing available adsorption site, changing the surface charge of adsorbents, or affecting the dispersing properties of adsorbent in solution. Zhao et al. [6] used $Fe(NO_3)_3$ to modify activated carbon and found that the adsorption capacity of Cr (VI) increased from 10.90 mg g^{-1} to 15.23 mg g^{-1} after modification. The similar experiments were carried out by Han et al. [7], in which $AlCl_3$ and $FeCl_3$ were used to modify red mud, and the removal efficiency of Cr (VI) increased by 21.6% for $FeCl_3$ modification, but it decreased by 6.38% for $AlCl_3$ modification. Until now, inorganic salt modified Akadama clay used for Cr (VI) adsorption has not been reported by other studies.

The experimental design methodology in adsorption process can be applied to estimate the significance of parameters, reduce process variability, and confirm the output response of nominal and target requirements, hence save time and cost, and also reduce the number of experiments [8].

In present study, inorganic salt modified Akadama clay was prepared and the adsorption performance of Cr (VI) was investigated. Factorial experimental design (FD) was applied in order to determine the main influencing factors (pH, contact time, adsorbent dose, and initial concentration) on Cr (VI) adsorption by modified Akadama clay.

4.2 Materials and methods

4.2.1 Materials

Akadama clay used in this study was provided by Makino Store, Kiyosu, Japan. It was ground and sieved with particles diameter less than 105μm, then was dried in an oven (EYELA WFO-700, Japan) at 105°C and used for further modification. The inorganic salts, $AlCl_3$, $FeCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$ (Wako Pure Chemical Industries Ltd, Japan), with the same metal composition of Akadama clay, were of analytical grade and used for Akadama clay modification. Potassium dichromate ($K_2Cr_2O_7$, Wako Pure Chemical Industries, Japan) was used for preparation of Cr (VI) solution. Pure water generated from a Millipore Elix 3 water purification system

(Millipore, USA) equipped with a Progard 2 pre-treatment pack was used throughout this study. 1M HCl or NaOH (Wako Pure Chemical Industries, Japan) were prepared and diluted to the desired strength for pH adjustment.

4.2.2 Preparation of salt-modified Akadama clay

10 mL $AlCl_3$, $FeCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$ (1 mol L^{-1}) were used to soak 5 g dried Akadama clay in five centrifuge tubes, respectively. The centrifuge tubes were shaken at speed of 200 rpm and room temperature for 24 h. After full impregnation, the mixtures were separated through filter paper and the resultant modified clay was dried in an oven at 105°C. Then the five samples were ground and sieved again, finally preserved in an airtight bottle and used in the following study.

4.2.3 Determination of optimum modification conditions

Batch experiments were carried out to evaluate the modification efficiency of the five salt-modified Akadama clays. The optimum modifying agent would be chosen from $AlCl_3$, $FeCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$. The adsorption conditions were: initial Cr (VI) concentration of 100 mg L^{-1}, dose of 10 g L^{-1}, contact time of 24 h, and shaking speed of 200 rpm. After that, the optimum concentration of modifying agent solution (0.1, 0.25, 0.5, 0.75, and 1 mol L^{-1}) was investigated.

4.2.4 Experimental design

Factorial design (FD) was conducted to investigate which factor has important effects on a response as well as how the effect of one factor varies with the level of the other factors on Cr (VI) adsorption. The principle steps of the statistically designed experiments are determination of response variables, factors and factor levels, choice of the experimental design, and the statistical analysis of the data [8]. A full 2-level factorial (2^k), led to a total number of 16 experiments employed for the evaluation of main and interaction effects of factors on Cr (VI) adsorption. The independent process variables used in this study were: pH value (X_1), contact time (X_2), adsorbent dosage (X_3) and initial concentration (X_4). Cr (VI) adsorption capacity (Y_1) was considered as a dependent factor (responses). The values of process variables and their variation limits were selected based on the preliminary adsorption experiments.

4.2.5 Batch experimental procedure

From FD experiments, the significant factors on Cr (VI) would be further evaluated by batch experiments. Adsorbents were put into 15 mL capped centrifuge tubes. The tubes were shaken at 200 rpm for a certain contact time at room temperature. After adsorption, the samples were filtrated using a RC-membrane (Minisart RC 15) with a pore size of 0.45 μm, and then Cr (VI) concentration in filtrate was determined. Experimental parameters were arranged as follows: (1) contact times ranged from 0 to 60 min with 10 g L^{-1} adsorbent immersed in (100 mg L^{-1}) Cr (VI) solution; (2) different initial concentrations of Cr (VI) solution were from 50 to 500 mg L^{-1} with an adsorbent dosage of 10 g L^{-1} at equilibrium time; (3) adsorbent dosages were increased from 1 to 40 g L^{-1} with 400 mg $L^{-1}$of initial Cr (VI) solution at equilibrium time; (4) effect of temperatures (298K, 308K, and 318K) were investigated under conditions of initial Cr (VI) concentration of 100 mg L^{-1}, dosage of 5 g L^{-1}, and contact time of 24 h without shaking. Finally, the adsorption process was analyzed by various adsorption kinetics and isotherms.

4.2.6 Analytical methods

The specific surface area and BJH (Barrett–Joyner–Halenda) pore size distribution of the modified adsorbent were determined using Brunauer–Emmett–Teller (BET) specific surface analysis device (Coulter SA3100, US). Adsorption and desorption techniques are employed to determine pore area and specific pore volume in BJH analysis. This technique characterizes pore size distribution independent of external area due to particle size of the sample. The morphological features of the adsorbents before and after adsorption were acquired using a scanning electron microscope (SEM) (JSM-6330F, JEOL, Japan). The mineralogical phase characterization of the adsorbent was carried out by quantitative X-ray diffraction (XRD) (X'Pert PRO, PANalytical). Zeta potential was tested by Zeta Sizer (Nano-ZS, England). The concentrations of Cr (VI) were measured by ultraviolet spectrophotometer (UV–1800, Japan) according to diphenylcarbohydrazide spectrophotometric method. The pH of the Cr (VI) solution was determined using a pH meter (Mettler–Toledo AG, Switzerland).

4.3 Results and discussion

4.3.1 Determination of optimum modification conditions

Fig.4-1 shows the modification effect of five salts (1 mol L^{-1}) on Akadama clay for Cr (VI) adsorption under conditions of initial concentrations of 100 mg L^{-1}, dosage of 10 g L^{-1}, contact time of 24 h without pH adjustment. Results revealed that, comparing with original Akadama clay, the removal efficiencies of Cr (VI) onto five salts modified Akadama clay were all improved. Mg^{2+}, Mn^{2+}, and Ca^{2+} modified Akadama clay showed similar removal efficiency on Cr (VI) adsorption, followed by Al^{3+} modified Akadama clay with removal efficiency of 71.8%, and Fe^{3+} modified Akadama clay presented the highest adsorption efficiency of 91.3%. Similar results were obtained by Liu et al. [9], who chose $FeCl_3$ as the impregnating agent and devised an iron-tailored activated carbon. They found that Fe-modified activated carbon significantly improved the Cr (VI) adsorption capacity by nearly three times as compared to the original activated carbon. In present study, Fe^{3+} was selected as the optimum ion for Akadama clay modification.

Fig.4-2 shows the effect of Fe concentrations (0.1 - 1 mol L^{-1}) on the modification efficiency of Akadama clay for Cr (VI) adsorption at initial concentration of 100 mg L^{-1}, dosage of 10 g L^{-1}, contact time of 24 h without pH adjustment. As seen in Fig.4-2, removal efficiency of Cr (VI) onto Fe-modified Akadama clay (FMAC) increased from 61.5% to 91.4% with increasing Fe concentrations from 0.1 mol L^{-1} to 0.5 mol L^{-1}, and then kept stable from 0.5 mol L^{-1} to 1 mol L^{-1}. In this study, Fe concentration for

Akadama clay modification was chosen as 0.5 mol L^{-1}.

4.3.2 Characterization

The XRD patterns of original Akadama clay and Fe-modified Akadama clay (FMAC), and Cr-loaded FMAC are shown in Fig.4-3a. It can be seen that intensity of peaks slightly changed for original Akadama clay and Fe-modified Akadama clay (FMAC), and Cr-loaded FMAC. However, neither new peaks appear nor old peaks disappear, revealing that the main crystal structure of FMAC was unaltered from the unmodified Akadama clay. Though effective Cr (VI) adsorption onto FMAC was obtained, chromium containing substance cannot be detected from the XRD peaks, which might be due to the low percentage of Cr (VI) loaded in the total mass of the adsorbent.

Energy dispersive X-ray spectroscopy (EDX) analysis of natural and FMAC were given in Table 4-1. It showed that the weight percentage of Fe was 4.20% for natural Akadama clay, while it increased to 11.74% for FMAC, revealing that Fe was successfully inlaid to Akadama clay. Besides, because $FeCl_3$ was used for modification, the element of Cl was detected and its weight percentage was 4.37%. The total weight percentage of O and Si decreased from 76.61 to 63.92% after modification, indicating the amount of total metal elements increased. In order to confirm that Cr (VI) was adsorbed onto FMAC, elemental mapping results of Cr before and after adsorption were investigated and illustrated in Fig.4-3b and Fig.4-3c. It was obvious that Cr was not detected on the FMAC surface before adsorption, but

Cr element distribution was quite apparent on the FMAC surface after adsorption, demonstrating the successful adsorption of Cr onto FMAC.

4.3.3 Statistical design of experiments

The factors involved in the adsorption experiments were evaluated by full factorial design (2^k) using Design-Expert® 8.0.5 program software including ANOVA in order to obtain the interactions between the process variables. The levels (－) and (+) in the adsorption of Cr (VI) onto FMAC for pH (X_1), contact time (X_2), adsorbent dosage (X_3), and initial concentration (X_4) are given in Table 4-2. Adsorption capacity of Cr (VI) onto FMAC was chosen as the response. The experimental design and result are presented in Table 4-3. The number of experiments required for fully understanding all the effects is given by $a^k= 2^4 = 16$, where a is the number of levels and k is the number of factors. The analysis of variance for the full 24 factorial design is presented in Table 4-4.

The Model F-value of 537.90 implies the model is significant.Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case X_2, X_3, X_4, X_2X_3 are significant model terms.Values greater than 0.1000 indicate the model terms are not significant.

The experimental response associated to a 2^4 factorial design is represented by a linear polynomial model with interaction:

$$Y=b_0+b_1X_1+b_2X_2+b_3X_3+b_4X_4+b_{12}X_1X_2+b_{13}X_1X_3+b_{14}X_1X_4+b_{23}X_2X_3+b_{24}X_2X_4+b_{34}X_3X_4 \quad (4\text{-}1)$$

where$Y$ represents the experimental response, X_i is the coded variable (−1 or +1), b_i represents the estimation of the effect of the factor i for the response Y, whereas b_{ij} represents the estimation of interaction effect between the factor i and j for the response. The coefficients of the polynomial model calculated by means of Design-Expert® 8.0.5 program software were as follows:

$$Y=8.18-0.038X_1+0.37X_2-2.33X_3+2.53X_4-0.023X_1X_2+0.026X_1X_3-0.067X_1X_4-0.21X_2X_3+0.042X_2X_4-0.042X_3X_4 \quad (4\text{-}2)$$

From Eq. (4-2), it can be indicated that the average adsorption capacity of the 16 assays was 8.18. The most important influencing factor is the initial concentration (b_4=+2.53), which has positive effect on the adsorption capacity. The second most important factor is adsorbent dosage with a negative effect (b_3=-2.33). However, the effects of pH (b_1=-0.038) and contact time (b_2=+0.37) seem relatively weak and pH has negative effect on adsorption capacity of Cr (VI). Among the interaction terms, X_2X_3(contact time and adsorbent dosage) has the most important effect with the coefficient of −0.21. Besides, X_1X_2, X_1X_3, X_1X_4, X_2X_4, X_3X_4have less important effect to the uptake amount with a coefficient between -0.1 and +0.1. In order to evaluate and compare the importance of the factors and interaction much more clearly, graphical Pareto analysis is applied and more significant information is depicted in Fig.4-4. This analysis calculates the percentage effect of each factor on the response, according to the following relation:

$$P_i=\left(\frac{b_i^2}{\sum b_i^2}\right)\times 100 \quad (i\neq 0) \qquad (4\text{-}3)$$

whereb_i represents the estimation of the principal effect of the factor i. The contributions of the principal effects (X_1, X_2, X_3, X_4) on the Cr (VI) adsorption capacity onto FMAC are 0.01%, 1.12%, 45.15%, and 53.17%, respectively. The contribution of the interation effects ($X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4$)on the Cr (VI) adsorption capacity are the following: 0, 0, 0.04%, 0.37%, 0.02%, and 0.02%, respectively. The results indicated that all the effects except $X_2, X_3, X_4,$ and X_2X_3 are negligible because their effects are less than 0.1% in total. The results are consistent with that revealed in Table 4-4. Moreover, the percentage effects of $X_2, X_3,$ and X_4 (1.12%, 45.15%, and 53.17%,) are much more thanX_2X_3 (0.37%), therefore, only contact time, adsorbent dosage and initial concentration are worth being investigated in the following experiments. Since pH had no effect on Cr (VI) adsorption onto FMAC during pH range of 2 to 8, and the pH values of Cr (VI) solution are between 4.5 and 5.5 for the initial concentration of Cr (VI) between 50 mg L^{-1} to 500 mg L^{-1}, hence pH was not adjusted in the following study.

4.3.4 Effect of contact time and adsorption kinetics

Fig.4-5 shows the Cr (VI) and total Cr uptake by FMAC with contact time from 0 to 60min. The initial concentration of Cr (VI) was 103.4 mg L^{-1}, and the adsorbent dosage was 10 g L^{-1}.

The results revealed that the removal of Cr (VI)and total Cr are almost same during the contact time of 0 to 60 min, indicating that no Cr (III) was generated or no redox reaction occurred in the process. As demonstrated in our previous study, the adsorption mechanism was unchanged and it mainly dominated by electrostatic attraction [5]. As seen in Fig.4-5, Cr (VI) adsorption by FMAC was a very rapid process within the first 10 min, and the Cr (VI) uptake gradually increased to the maximum value of 9.30 mg g^{-1}in the 30 min, and then kept stable in the following 30 min.

Adsorption kinetics modeling is very important for a better understanding of both the reaction pathway and the rate-controlling mechanism of exchange reactions[10]. Several models have been utilized to model adsorption kinetics. The most well-known are Lagergrens pseudo-first-order and Ho’s pseudo-second-order. To evaluate the adsorption process of Cr (VI)onto FMAC, the above two models were employed to analyze the obtained Cr (VI) adsorption experimental data. The nonlinear models are as follows [11]:

Lagergren pseudo first-order kinetic model:

$$q_t = q_e(1 - e^{-k_1 t}) \qquad (4\text{-}4)$$

Ho’s pseudo second-order kinetic model:

$$q_t = q_e^2 k_2 t/(1 + q_e k_2 t) \qquad (4\text{-}5)$$

where q_t and q_e (mg g^{-1}) represent the adsorption capacity of Cr (VI)onto FMAC at time t and equilibrium, t (min) is the contact time, k_1 is the pseudo-first-order rate constant (min^{-1}), and k_2 is the pseudo-second-order rate constant (g min^{-1} mg^{-1}).

The fitted curves for the pseudo-first-order, and the pseudo-second-order model are presented in Fig. 4-6, and the parameters calculated from the model are given in

Table 4-5. It was obvious that the correlation coefficient of pseudo-second-order model (R^2 = 0.999) was slightly higher than that of pseudo-first-order model (R^2 = 0.988), but the differences were not far. Though the calculated adsorption capacities at equilibrium time were also similar for pseudo-first-order model (q_e = 9.07 mg g^{-1}) and pseudo-second-order model (q_e=9.26 mg g^{-1}), but the value calculated from pseudo-second-order model was closer to the experimental value (q_e = 9.30 mg g^{-1}). The results suggested that pseudo-second-order model fitted the experimental data better than the pseudo-first-order model.

In order to further demonstrate the result, chi-square test analysis was applied to estimate the degree of difference (χ^2) between the experimental data and the calculated value from the model, which is defined as [9, 12]:

$$\chi^2 = \sum \frac{(q_{exp.} - q_{cal.})^2}{q_{cal.}} \qquad (4\text{-}6)$$

where q_{exp} and q_{cal} (mgg^{-1}) are the experimental and calculated uptake amounts of Cr (VI) by FMAC. A smaller χ^2 value means little deviation between the values calculated from the model and the experimental data.

As shown in Table 4-5, χ^2 of 0.08 for pseudo-first-order model and χ^2 of 0.01 for pseudo-second-order model indicated that, better agreement was presented between q_{cal} and q_{exp} for pseudo-second-order model. On the basis of the higher R^2 together with the smaller χ^2, pseudo-second-order model was considered as the ideal model to describe the adsorption of Cr (VI) onto FMAC. The similar result, which is related to the kinetics of Cr(VI) adsorption onto various adsorbents, was reported in previous studies [2, 13, 14].

4.3.5 Effect of initial concentration and adsorption isotherms

In order to analyze the effect of the initial concentrations of Cr (VI) onto FMAC, the following tests were carried out with initial Cr (VI) concentrations ranging from 50 to 500 mg L^{-1} at contact time of 60min and adsorbent dosage of 10 g L^{-1}, as seen in Fig.4-7.

The results show that the initial Cr (VI) concentration had a significant impact on the adsorption of Cr (VI) onto FMAC. With increasing initial concentration of Cr (VI), the adsorption capacity of Cr (VI) increased from 5.02 mg g^{-1} at initial concentration of 50 mg L^{-1}, reaching the maximum value of 17.21 mg g^{-1} when the initial Cr (VI) concentration was 500 mg L^{-1}. However, the removal efficiency of Cr (VI) decreased from 100% to 34.2% when initial concentration varied from 50 mg L^{-1} to 500 mg L^{-1}. The increase of adsorption capacity may be attributed to the fact that for the same unit mass adsorption site, a higher initial concentration of Cr (VI) resulted in a stronger driving force generated from the higher concentration gradient thus conduced higher adsorption capacity. However, the increase could not continue to grow indefinitely, as seen in Fig.4-7, the growth rate of adsorption capacity of 85.1% during initial concentration from 50 mg L^{-1} to 100 mg L^{-1} gradually reduced to 3.1% during initial concentration from 400 to 500 mg L^{-1}. It indicated that at dosage of 10 g L^{-1}, maximum adsorption capacity could be achieved by further increasing initial concentration of Cr (VI).

The adsorption process was analyzed according to the well recognized isotherm models: Langmuir and Freundlich isotherms. The nonlinearized forms of these models are:

Langmuir isotherm:

$q_e= q_m bC_e/(1+bC_e)$ (4-7)

Freundlich isotherm:

$q_e= k_f C_e^n$ (4-8)

where q_e (mg g^{-1}) is the adsorption capacity of Cr (VI) adsorbed at equilibrium, C_e (mg L^{-1}) is the concentration of Cr (VI) at equilibrium, b (L mg^{-1}) is a constant related to the free energy, q_m (mg g^{-1}) is the maximum adsorption capacity at the isotherm temperature. k_f and n are equilibrium constants of Freundlich isotherm which indicate adsorption capacity and adsorption intensity.

The Langmuir and Freundlich fitting curves and parameters for the adsorption of Cr (VI) onto FMAC are listed in Fig. 4-8 and Table 4-6. It can be seen that the regression correlation coefficient of the Langmuir model ($R^2 = 0.867$) was much lower than that of the Freundlich model ($R^2 = 0.995$), suggesting that Cr (VI) removal by FMAC from the aqueous solution did not follow Langmuir isotherm model. The result revealed that Cr (VI) adsorption onto FMAC did not occur on a homogeneous surface by monolayer sorption, but more like a heterogeneous surface desorption. Similar studies also reported that the Freundlich model yielded a much better fit than the Langmuir model in relation to Cr (VI) adsorption [15, 16]. Furthermore, the values of the empirical parameter *n* lying between $0.1< n < 1$ indicated favorable adsorption for

Cr (VI) [17]. The value of n 0.175 in the present study was smaller than 1, and it represented favorable removal conditions.

4.3.6 Effect of adsorbent dosage

The results about the effect of adsorbent dosage on Cr (VI) removal with an initial concentration of 400 mg L^{-1} are shown in Fig. 4-9 and revealed that the adsorption capacity of Cr (VI) onto FMAC decreased with an increase in adsorbent dosage. It reduced from 22.74 to 9.38 mg g^{-1}whenadsorbent dosages increased from 1 g L^{-1} to 40 g L^{-1}; however, the removal efficiency increased from 5.69% to 91.86%. This tendency was consistent with that observed by other studies [18, 19]. It was obvious that the available exchange sites were enlarged with the increase of the adsorbent dosage, then resulting in increased adsorption amount of Cr (VI), thus improved the removal efficiency. The decrease of adsorption capacity may be due to the fact that the intensity of the concentration gradient for unit mass adsorbent dosage diminished when the interface area expanded with the increase in adsorbent dosage.

4.3.7 Thermodynamic studies

The temperatures used in this study were 298, 308, and 318 K at 100 mg L^{-1} Cr (VI) solution concentration and adsorbent dosage of 5 g L^{-1}. The decrease in the values of the sorption capacities from 11.36 to 13.01 mgg^{-1} indicated that temperature favors the adsorption of Cr (VI).

Thermodynamic parameters such as enthalpy, $\triangle H^{o}$ and entropy, $\triangle S^{o}$ for Cr (VI) adsorption onto FMAC are calculated by using the following equation [20]:

$$\ln K_d = \frac{\triangle S^o}{R} - \frac{\triangle H^o}{RT} \tag{4-9}$$

where T is the temperature (K), R the ideal gas constant = 8.314(Jmol^{-1} K^{-1}), and K_d the distribution coefficient (mL g^{-1}), which is calculated as follows [21]:

$$K_d = \frac{C_0 - C_t}{C_t} \times \frac{V}{M} \tag{4-10}$$

where C_0 and C_t (mg L^{-1}) are the initial concentration of Cr (VI)and concentration at time *t*, V (mL) is the volume of Cr (VI) solution and M (g) is the mass of adsorbent used.

Free energy values (△G) are calculated on the basis of the following equation:

$$\triangle G^o = \triangle H^o - T\triangle S^o \tag{4-11}$$

The plot of ln K_d versus 1/T (Eq. (4-9)) is as shown in Fig.4-10, and $\triangle H^o$ and $\triangle S^o$ values can be obtained from the slope and the intercept respectively. Values of thermodynamic parameters are summarized in Table4-7. The positive value of $\triangle H^o$ confirms the endothermic nature of Cr (VI) adsorption onto FMAC. Also an endothermic process indicates increased solution temperature would result in increased uptake of Cr (VI) from aqueous solution, which is consistent with our experimental result. Negative values of $\triangle G^o$ indicate the feasibility and spontaneous nature of adsorption process. The value of $\triangle G^o$ becomes more negative with increasing temperature. This also reveals that an increase in temperature favors the Cr (VI) removal process. The positive value of $\triangle S^o$ further confirms the nature of Cr (VI) adsorption onto FMAC: endothermic and spontaneous.

4.3.8 Adsorption studies using industrial wastewater

To evaluate the adsorption performance of natural Akadama clay, HMAC, and FMAC, tannery industry wastewater was collected from Khargia wastewater treatment plant located at Ulan Bator, Mongolia. About 30 tannery industries discharged wastewater to this plant. The wastewater used in this study was the mixed effluent from the 30 industries. The physico-chemical characteristics of industrial wastewater are given in Table 4-8. The Cr (VI) concentration in the industrial wastewater was 28.24 mg L^{-1}, and pH of this wastewater was 9.2. Adsorbent dosage was maintained at 5 g L^{-1} for 4 h (shaking speed 200 rpm), and the results were summarized in Table 4-9. Percent removals were found to be 23.1%, 38.9% and 94.5% respectively for natural Akadama clay, HMAC and FMAC, and the corresponding adsorption capacity were 1.30, 2.20, and 5.34 mg g^{-1}, respectively. The results revealed that even in the presence of other ions and impurities like suspended solids, COD, Ca^{2+}, K^{+}, Cl^{-}, and SO_4^{2-}asillustrated in the Table 4-8, all natural Akadama clay, HMAC, and FMAC exhibited adsorption ability on Cr (VI). Among them, FMAC showed the best adsorption performance on Cr (VI) removal. Therefore, FMAC could be considered as a favorable adsorbent for Cr (VI) removal in practice.

4.4 Conclusion

This study investigated the performance of Cr (VI)adsorption onto modified

Akadama clay. Fe^{3+} performed best modification effect on original Akadama clay, and the adsorption capacity of Cr (VI) onto Fe-modified Akadama clay was greatly enhanced. A factorial design of experiments showed that factors such as initial concentration, adsorbent dose, and contact time were important, but pH of the solution had no effect on the removal of Cr (VI). The maximum Cr(VI) adsorption capacity onto FMAC was found to be 22.74 mgg^{-1} at a dose of 1.0 gL^{-1} with initial Cr(VI) concentration of 400 mg L^{-1}.The kinetics of adsorption of Cr (VI) was found to follow pseudo-second order reaction. Isotherm studies revealed that Freundlich isotherm model best fitted the experimental data. Thermodynamic studies indicated that the adsorption reaction was spontaneous and endothermic in nature. Moreover, FMAC presented the best adsorption performance for the treatment of industrial wastewater comparing to the HMAC and natural Akadama clay. Therefore, FMAC has the potential to be used as an eco-friendly and economic adsorbent material for the removal of Cr (VI) from wastewater.

References

[1] D. Vasanth, G. Pugazhenthi, R. Uppaluri, Biomass assisted microfiltration of chromium(VI) using Baker's yeast by ceramic membrane prepared from low cost raw materials, Desalination, 285 (2012) 239-244.

[2] H. Deveci, Y. Kar, Adsorption of hexavalent chromium from aqueous solutions by bio-chars obtained during biomass pyrolysis, Journal of Industrial and Engineering Chemistry, 19 (2013) 190-196.

[3] L. Ramrakhiani, R. Majumder, S. Khowala, Removal of hexavalent chromium by heat inactivated fungal biomass of Termitomyces clypeatus: Surface characterization and mechanism of biosorption, Chemical Engineering Journal, 171 (2011) 1060-1068.

[4] S. Mona, A. Kaushik, C.P. Kaushik, Biosorption of chromium(VI) by spent cyanobacterial biomass from a hydrogen fermentor using Box-Behnken model, International Biodeterioration & Biodegradation, 65 (2011) 656-663.

[5] Y. Zhao, S. Yang, D. Ding, J. Chen, Y. Yang, Z. Lei, C. Feng, Z. Zhang, Effective adsorption of Cr (VI) from aqueous solution using natural Akadama clay, Journal of Colloid and Interface Science, 395 (2013) 198-204.

[6] N. Zhao, N. Wei, J. Li, Z. Qiao, J. Cui, F. He, Surface properties of chemically modified activated carbons for adsorption rate of Cr (VI), Chemical Engineering Journal, 115 (2005) 133-138.

[7] Y. Han, J. Wang, M. Tang, Adsorption of Hexavalent Chromium in Wastewater on Modified Red Mud, Environmental Protection of Chemical Industry, 25 (2005)

132-136.

[8] D. Kavak, Removal of boron from aqueous solutions by batch adsorption on calcined alunite using experimental design, Journal of Hazardous Materials, 163 (2009) 308-314.

[9] W. Liu, J. Zhang, C. Zhang, Y. Wang, Y. Li, Adsorptive removal of Cr (VI) by Fe-modified activated carbon prepared from Trapa natans husk, Chemical Engineering Journal, 162 (2010) 677-684.

[10] Y. Zhao, Y. Yang, S. Yang, Q. Wang, C. Feng, Z. Zhang, Adsorption of high ammonium nitrogen from wastewater using a novel ceramic adsorbent and the evaluation of the ammonium-adsorbed-ceramic as fertilizer, Journal of Colloid and Interface Science, 393 (2013) 264-270.

[11] Y. Khambhaty, K. Mody, S. Basha, B. Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine Aspergillus niger, Chemical Engineering Journal, 145 (2009) 489-495.

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

[13] N. Ertugay, Y.K. Bayhan, Biosorption of Cr (VI) from aqueous solutions by biomass of Agaricus bisporus, Journal of Hazardous Materials, 154 (2008) 432-439.

[14] S. Chen, Q. Yue, B. Gao, X. Xu, Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue, Journal of Colloid and

Interface Science, 349 (2010) 256-264.

[15] A.B. Albadarin, C. Mangwandi, A.a.H. Al-Muhtaseb, G.M. Walker, S.J. Allen, M.N.M. Ahmad, Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent, Chemical Engineering Journal, 179 (2012) 193-202.

[16] D.P. Mungasavalli, T. Viraraghavan, Y.C. Jin, Biosorption of chromium from aqueous solutions by pretreated Aspergillus niger: Batch and column studies, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 301 (2007) 214-223.

[17] L. Xiao, W. Ma, M. Han, Z. Cheng, The influence of ferric iron in calcined nano-Mg/Al hydrotalcite on adsorption of Cr (VI) from aqueous solution, Journal of Hazardous Materials, 186 (2011) 690-698.

[18] Z. Rawajfih, N. Nsour, Thermodynamic analysis of sorption isotherms of chromium(VI) anionic species on reed biomass, The Journal of Chemical Thermodynamics, 40 (2008) 846-851.

[19] R. Kumar, N.R. Bishnoi, Garima, K. Bishnoi, Biosorption of chromium(VI) from aqueous solution and electroplating wastewater using fungal biomass, Chemical Engineering Journal, 135 (2008) 202-208.

[20] A. Iddou, M.S. Ouali, Waste-activated sludge (WAS) as Cr(III) sorbent biosolid from wastewater effluent, Colloids and Surfaces B: Biointerfaces, 66 (2008) 240-245.

[21] D. Ding, Y. Zhao, S. Yang, W. Shi, Z. Zhang, Z. Lei, Y. Yang, Adsorption of cesium from aqueous solution using agricultural residue - walnut shell: Equilibrium, kinetic and thermodynamic modeling studies, Water Research, 47 (2013) 2563-2571.

Table 4-1 EDX analysis of Akadama clay and FMAC

Element	Akadama clay (Wt%)	FMAC(Wt%)
O	56.08	49.61
Mg	1.04	0.51
Al	15.22	17.48
Si	20.13	14.31
Cl	------	4.37
K	2.57	0.37
Cr	------	------
Fe	4.20	11.74
Cu	0.76	1.61

Table 4-2 Data for optimization operation: experimental range and levels of independent process variables.

Factor (X_i)	Experimental field		$x_{1,0}$	$\triangle x_i$
	Min. value (−1)	Max. value (+1)		
X_1: pH	2	8	5	3
X_2: Contact time (min)	1	59	30	29
X_3: Adsorbent dosage (g L^{-1})	5	15	10	5
X_4: Initial concentration (mg L^{-1})	50	150	100	50

Table 4-3 Experimental factorial matrix in the 2^4 design and the experimental results.

Experiment number	Experimental design				Adsorbent capacity(mg g^{-1})
	X_1	X_2	X_3	X_4	
1	-1	1	-1	1	13.91
2	-1	-1	1	-1	3.30
3	-1	1	1	-1	3.37
4	1	1	1	1	8.54
5	1	-1	-1	1	12.49
6	1	1	1	-1	3.41
7	-1	-1	-1	-1	7.33
8	-1	1	-1	-1	8.46
9	-1	-1	-1	1	12.59
10	1	-1	1	-1	3.33
11	1	1	-1	1	13.34
12	1	-1	1	1	8.04
13	-1	1	1	1	8.68
14	1	-1	-1	-1	7.31
15	1	1	-1	-1	8.64
16	-1	-1	1	1	8.07

Table 4-4Analysis of variance table

Source	Sum of Squares	d_f	Mean Square	F Value	p-value Prob > F
Model	192.71	10	19.27	537.90	< 0.0001
X_1	0.02	1	0.02	0.65	0.4570
X_2	2.17	1	2.17	60.52	0.0006
X_3	87.10	1	87.10	2431.05	< 0.0001
X_4	102.57	1	102.57	2862.88	< 0.0001
X_1X_2	0.01	1	0.01	0.24	0.6457
X_1X_3	0.01	1	0.01	0.29	0.6114
X_1X_4	0.07	1	0.07	2.00	0.2167
X_2X_3	0.71	1	0.71	19.81	0.0067
X_2X_4	0.03	1	0.03	0.78	0.4167
X_3X_4	0.03	1	0.03	0.78	0.4167
Residual	0.18	5	0.04		
Cor Total	192.89	15			

Table 4-5 Kinetic parameters calculated from pseudo-first-order model and pseudo-second-order model for Cr (VI) adsorption onto FMAC

Pseudo-first-order model				Pseudo-second-order model			
k_1(min^{-1})	q_e (mg g^{-1})	R^2	χ^2	k_2(g min^{-1} mg^{-1})	q_e (mg g^{-1})	R^2	χ^2
3.288	9.07	0.988	0.08	0.878	9.26	0.999	0.01

Table 4-6 Isotherm parameters calculated from Langmuir model and Freundlich model for Cr (VI) adsorption onto FMAC

Langmuir isotherm			Freundlich isotherm		
b (L mg^{-1})	q_m (mg g^{-1})	R^2	K_f	n	R^2
0.118	16.57	0.867	6.313	0.176	0.995

Table 4-7 Thermodynamic parameters of Cr (VI) adsorption onto FMAC

△H° (J mol^{-1})	△S° (J mol^{-1} K^{-1})	△G° (J mol^{-1})		
		298 K	308 K	318 K
13583.11	91.87	-13794.15	-14712.85	-15631.55

Table 4-8 Physico-chemical analysis of tannery industrial wastewater

No.	Parameter	Characteristics
1	Suspended solids (mg/L)	650
2	COD (mg O_2/L)	2976
3	BOD (After 5 days) (mg/L)	1035
4	Nitrate (mg/L)	2.03
5	Ammomium (mg/L)	94.97
6	Chloride (mg/L)	5.81
7	Dissolved solids (mg/L)	4982
8	Sulfate (mg/L)	306.64
9	Sulfide (mg/L)	13.99
10	Calcium (mg/L)	39790
11	Potassium (mg/L)	1753
12	Sodium (mg/L)	224424
13	pH	9.20
14	Total Alkalinity (m mol/L)	7.15
15	Chromium (VI) (mg/L)	28.24

Table 4-9 Comparison of Cr (VI) adsorption performancesof natural Akadama clay, HMAC, and FMAC using real industrial wastewater

Adsorbents	pH	Dosage (g L^{-1})	Initial Cr (VI) concentration (mg L^{-1})	Contact time (h)	Removal efficiency (%)	Adsorption capacity (mg g^{-1})
Natural Akadama clay	9.2	5	28.24	4	23.05%	1.30
HMAC					38.87%	2.20
FMAC					94.50%	5.34

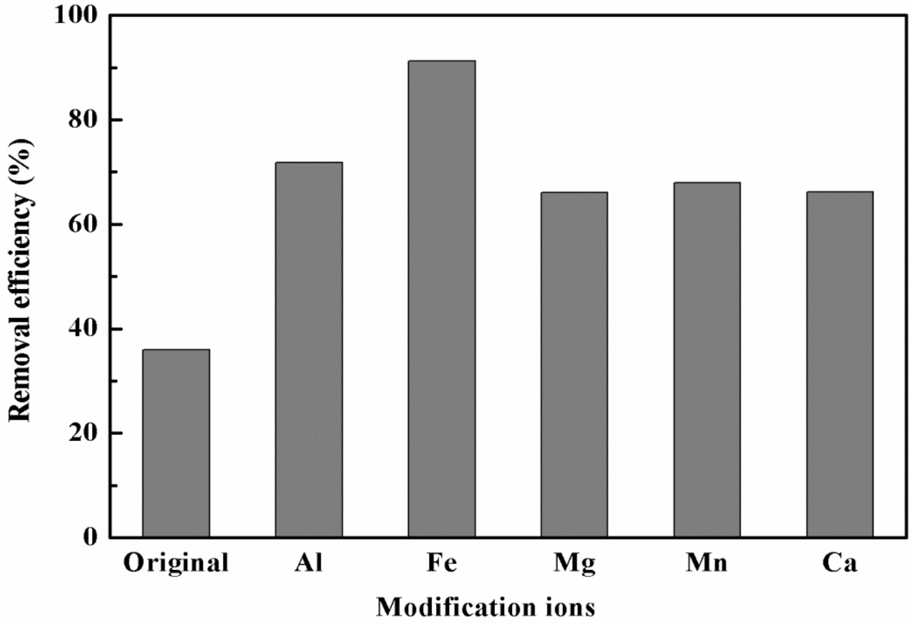


Fig.4-1 Effect of different modification ions on the Cr (VI) adsorption onto modified Akadama clay (Initial concentration of Cr (VI) = 100.0 mg L^{-1}, dosage = 10 g L^{-1}, contact time = 24 h)

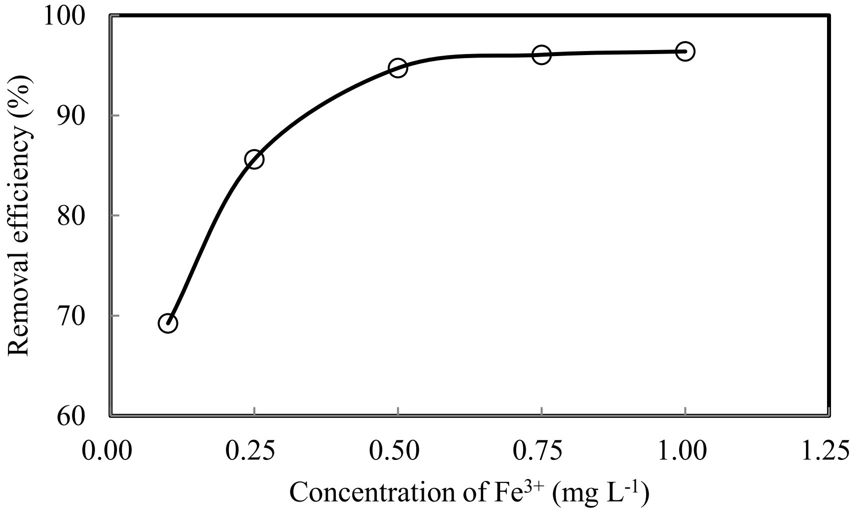


Fig.4-2 Effect of Fe concentrations on the removal of Cr (VI) (Initial concentration of Cr (VI) = 100 mg L^{-1}, dosage = 10 g L^{-1}, contact time = 24 h)

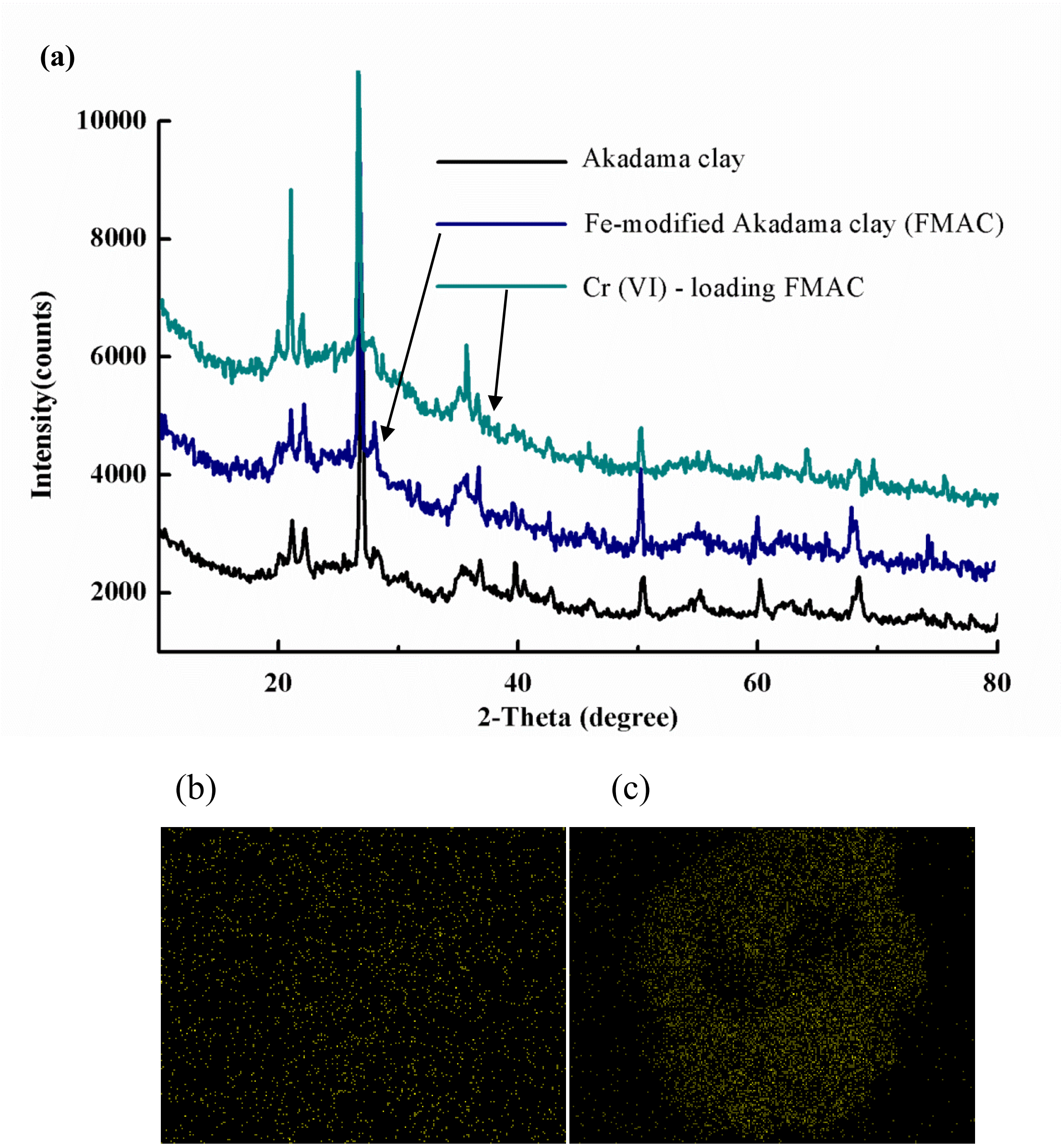


Fig.4-3 XRD patterns of original Akadama clay, Fe-modified Akadama clay (FMAC), and Cr (VI) loaded FMAC (a); Cr mapping of FMAC surface before adsorption (b); and Cr mapping of FMAC surface after adsorption (c).

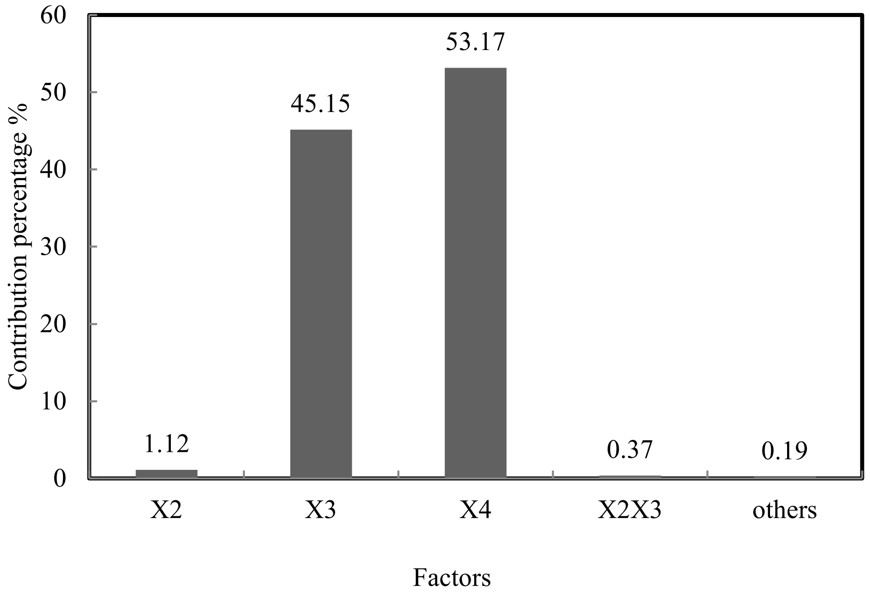


Fig.4-4 Graphical Pareto analysis of the effect of different factors (X_2: contact time, X_3: adsorbent dose, X_4: initial concentration, X_2X_3: interaction effect of X_2 and X_3; Others: total contribution of all other factors)

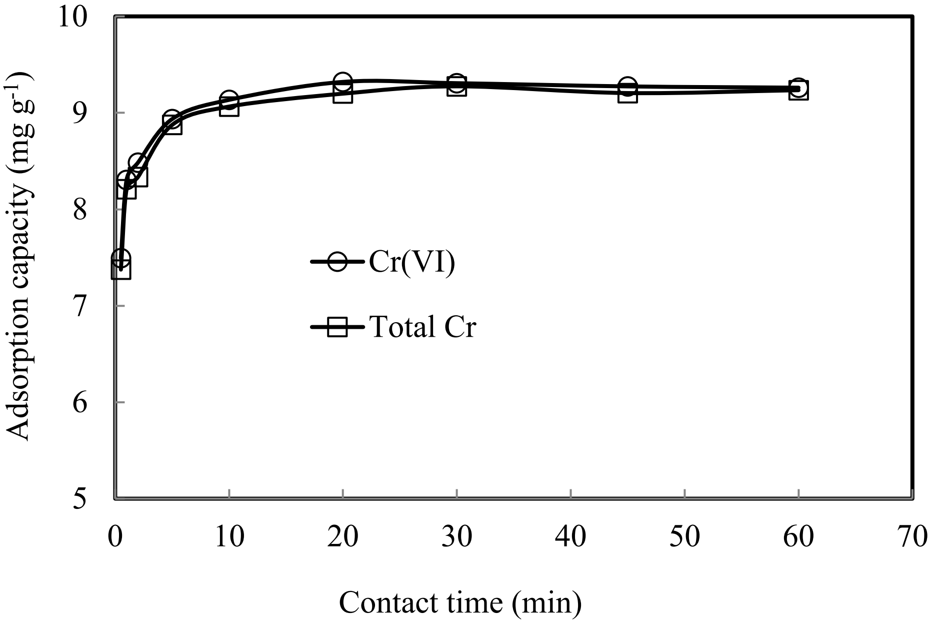


Fig.4-5 Effect of contact time on Cr (VI) adsorption onto FMAC (Initial concentration = 103.4 mg L^{-1}, dosage = 10 g L^{-1})

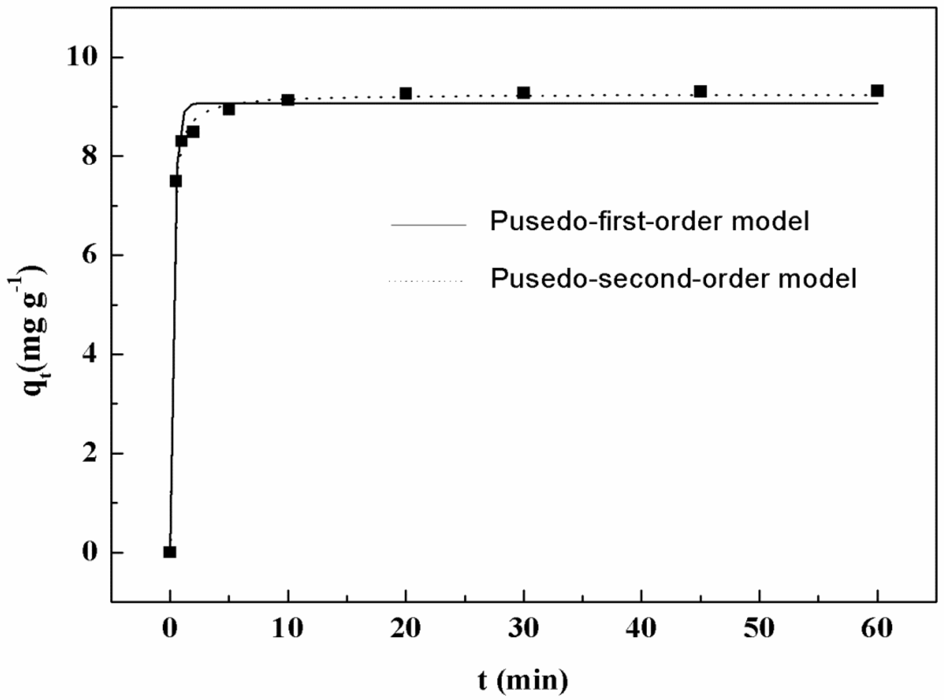


Fig.4-6 Kinetic plots of Cr (VI) adsorption onto FMAC (Initial concentration of Cr (VI) = 103.4 mg L^{-1}, dosage = 10 g L^{-1})

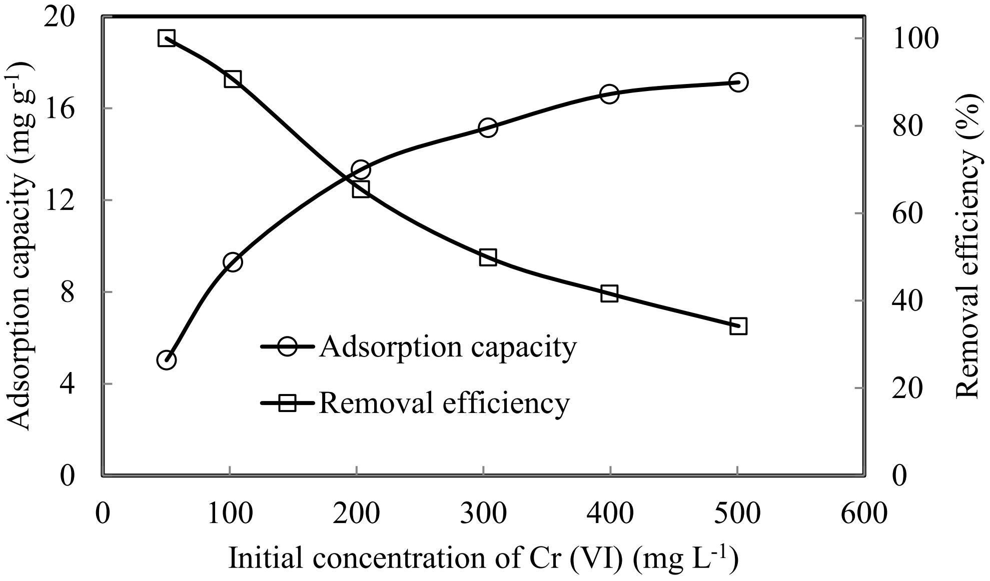


Fig.4-7 Effect of initial concentration on Cr (VI) removal by FMAC (Adsorbent dosage: 10 g L^{-1}, contact time: 60 min)

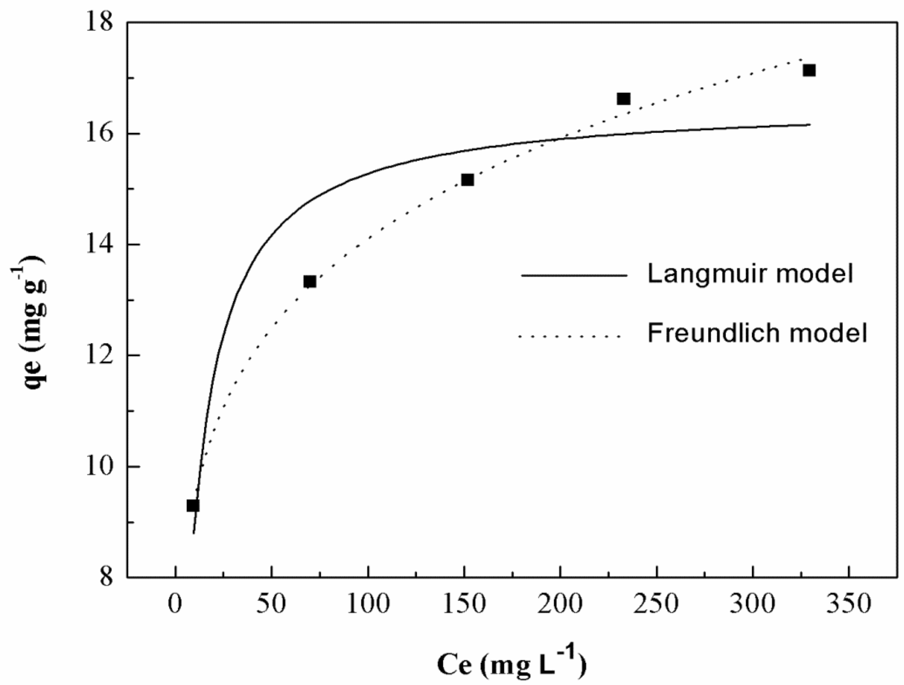


Fig.4-8 Isotherm plots for Cr (VI) adsorption onto FMAC (Initial concentration of Cr (VI) = 50 - 500 mg L^{-1}, dosage = 10 g L^{-1}, contact time = 60 min)

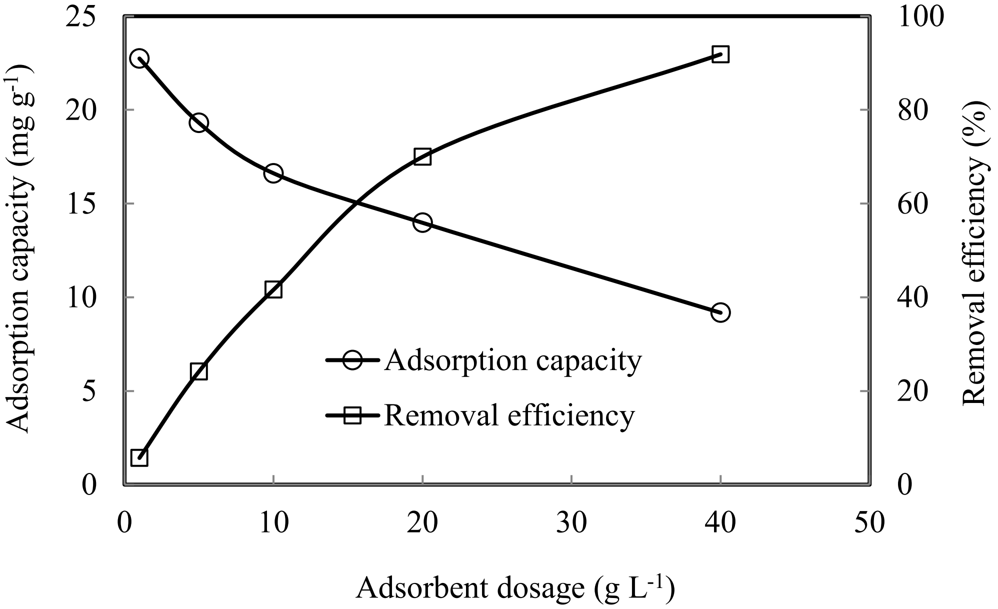


Fig.4-9 Effect of adsorbent dosage on Cr (VI) adsorption (Initial concentration: 400 mg L^{-1}, contact time: 60 min)

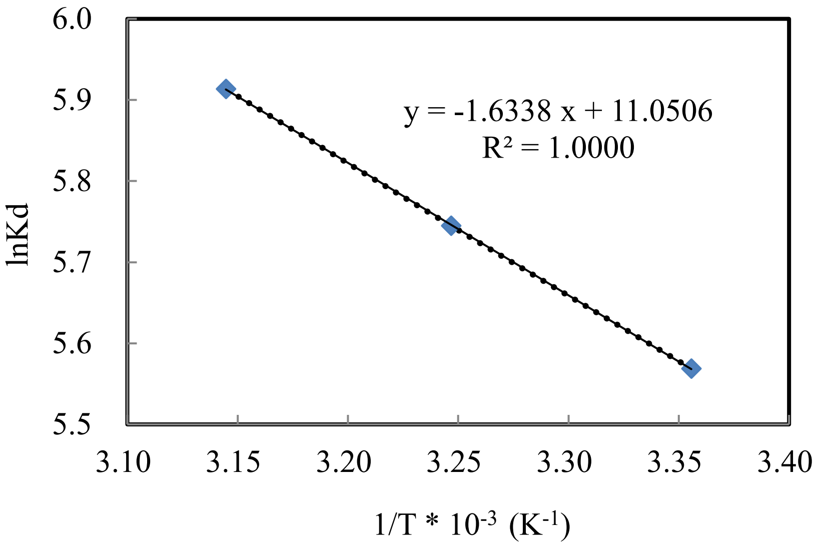


Fig.4-10 Plot to determine thermodynamic parameters of Cr (VI) adsorption onto FMAC (Initial concentration of Cr (VI) = 100.0 mg L^{-1}, dosage = 5 g L^{-1}, contact time = 60 min)

Chapter 5 Conclusions and future work

In the present study, original Akadma clay was used to remove Cr (VI) from aqueous solution. In order to improve adsorption efficiency of Cr (VI), inorganic acids and inorganic salts were utilized to modify original Akadama clay. HCl showed the best modification efficiency among common inorganic acids (HCl, HNO_3, H_2SO_4, and H_3PO_4); Fe^{3+} presented the best modification efficiency among inorganic salts ($AlCl_3$, $FeCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$).

5.1 Original Akadama clay

Akadama clay, consisting of various metallic oxide minerals, was used for Cr (VI) removal from aqueous solution. The conclusions were summarized as follows.

1) Original Akadama clay is a low-cost and effective adsorbent for Cr (VI) removal from water solution.
2) The adsorption of Cr (VI) onto Akadama clay could get equilibrium in 180 min. The optimum pH for Cr (VI) adsorption was found to be 2.
3) Kinetic and isotherm studies showed that Cr (VI) adsorption data followed the Freundlich isotherm and the pseudo-second-order kinetic model, revealing a heterogeneous and complex adsorption of Cr (VI) onto Akadama clay.
4) Cr (VI) adsorption mechanism analysis indicated that electrostatic adsorption was dominated Cr (VI) adsorption onto Akadama clay, and no Cr (III) reduction occurred in the adsorption process.
5) The maximum experimental adsorption capacity of Cr (VI) was 4.29 mg g^{-1} with initial Cr (VI) concentration of 50.0 mg L^{-1} and adsorbent dosage of 5 g L^{-1} at pH 2, which

was much higher than most other natural mineral adsorbents.

5.2 HCl-modified Akadama clay

HCl-modified Akadama clay effectively enhanced adsorption capacity of Cr (VI) from water solution and widened its application conditions.

1) The XRD patterns showed that the main chemical composition of Akadama clay did not change after modification.

2) Removal efficiency of Cr (VI) maintained stable in pH ranges of 2 to 11. Both initial concentration of Cr (VI) and adsorbent dosage effected adsorption capacity. Adsorption capacity increased with the increase in initial concentration, but decreased with the increase in adsorbent dosage.

3) Even at high concentrations of most coexisting ions (0.1 mol L^{-1}), the removal efficiency of Cr (VI) was still higher than 63.8%. SO_4^{2-} presented an obvious negative effect on the Cr (VI) adsorption, and the anion ions had an influence in order of $SO_4^{2-} > Cl^- > NO_3^-$.

4) The experimental data fitted the pseudo-second-order kinetic model and D-R isotherm model validated that the nature of Cr (VI) adsorption onto HMAC is chemical. The high R^2 values in two steps of the intra-particle diffusion model indicated that both boundary layer diffusion and intra-particle diffusion occurred in the adsorption process.

The overall results of this study indicate that HMAC could be favorably utilized for Cr (VI) removal from wastewater under practical conditions.

5.3 Fe-modified Akadama clay

This study investigated the performance of Cr (VI)adsorption onto Fe-modified Akadama clay.

1) Comparing to original Akadama clay, removal efficiency of Cr (VI) by Fe-modified

Akadama clay increased 53%.

2) A factorial design experiments showed that factors such as initial concentration, adsorbent dose, and contact time were important, but pH of the solution had no effect on the removal of Cr (VI). The interaction effect between these factors could also be negligible.

3) The maximum adsorption capacity of Cr (VI)onto FMAC has been found to be 22.74 mg g^{-1} at a dose of 1.0 g $L^{-1}$and initial Cr (VI) concentration of 400 mgL^{-1} during pH range of 2 - 8.

4) Thermodynamic studies indicated that the adsorption reaction was spontaneous and endothermic in nature.

Therefore, FMAC has the potential to be used as an eco-friendly and economic adsorbent material for the removal of Cr (VI) from wastewater.

5.4Adsorption performance comparison of natural Akadama clay, HMAC, and FMAC in practice

The adsorption performances of Natural Akadama clay, HMAC, and FMAC were evaluated using tannery wastewater. FMAC presented the highest adsorption efficiency, followed by HMAC, and natural Akadama clay. Based on the wide pH condition, high adsorption capacity, high Cr (VI) selectivity, and low cost, FMAC would be a potential alternate for the removal of Cr (VI) from wastewater.

5.5 Future work

In our previous study, batch experiments were conducted to evaluate the performance of Akadama clay, HMAC, and FMAC. Batch experiment is limited in the treatment of continuous effluents, therefore, column study will be carried out to investigate the adsorption ability of developed adsorbents.

Organic modification is considered to be effective for the modification of mineral adsorbent. Organic modification or other modification methods will be developed to further improve adsorption capacity of Cr (VI) onto Akadama clay in the future.

The practical application and the lab-scale experiments are quite different because of the complexity of real wastewater. Real industrial wastewater will be used for the evaluation of developed adsorbents.

Biosorbents from the agriculture wastes are promising for their high adsorption capacity of Cr (VI). New and effective biosorbents will be found and used in the application of Cr (VI) treatment.

Acknowledgements

First and foremost, I would like to express my sincere appreciation to my advisor, Professor Zhenya Zhang, for providing me the opportunity to undertake my research. His enthusiasm, amicability, and generosity make me feel warm in Japan, and his erudition and encouragement always guide me forward. I also would like to express my sincere appreciation to my co-supervisor, associate professor Yingnan Yang, for her profound expertise, dedication, and patience during my doctor study. She always teaches me the right way to get along with people, the right way to treat things, and help me correctly view myself.

I would also like to express my great appreciation to my thesis committee members, Professor Zhenya Zhang, Yingnan Yang, Zhongfang Lei, and Motoo Utsumi for their patient reading and listening, numerous suggestions and comments. All their instructors provided great help for the improvement of my dissertation and future study.

Special gratitude is expressed to all the professors in the EDL program who gave me comprehensive knowledge during the past two years. I have benefited so much from their courses and constant encouragement. Heartfelt thanks are given to Devena, who spent lots of time for English revision of my manuscripts.

I would also like to thank Professor Chuanping Feng for the recommendation and the support for my abroad study. He taught me the truth in life, and I will remember it all my life.

Then I would like to thank ShengjiongYang and Dahu Ding, who often discuss with me and I learned a lot of experiment design and data analysis methods from them. I would

also like to thank Wansheng Shi, Chunguang Liu, Dawei Li, and Qinghong Wang for their help in my study. I also wish to thank my friends of Xin Wang, Xiaowei Tian, Yaning Wang, Jie Chen, Cang Yu, Leilei He, He Huang, and many others for being with me for my beautiful life in Tsukuba.

Finally, I would like to thank my dearest parents. This dissertation would not have been completed without their love and support.