

The study of removal efficiency of As, Cr, and Mn ions by a cation exchange resin modified with hydrated ferric oxide nanoparticles

Somchintana Puttamat, Sukrit Tantrawong, and Varong Pavarajarn

Abstract— This research focuses on the removal efficiency of three cations: As, Cr, and Mn that are heavy metal transition elements, which recently are the cause of environment problems. At first, the cation exchange resin Kastel® C300L (R-SO₃-Na) was modified by hydrated ferric oxide (HFO) nanoparticles, and the hybrid material (HFO-300L) was characterized by X-ray diffraction spectroscopy (XRD). The adsorption abilities of HFO-300L resins were found to be more selective to Arsenic, Chromium, and Manganese ions than the parent C300L. Then, column sorption results indicated that the working capacity of HFO-300L was about 10-12 times higher than C300L with respect to the removal of three heavy metals from the simulated water (pH ~3.5). Additionally, HFO-300L was particularly more effective in removing traces of As and Cr ions from simulated standard water than C300L. Moreover, the exhausted HFO-300L beads could be effectively regenerated using HCl-NaCl solution (pH ~3.0) for repeating usages, without any significant capacity losses.

Keywords— hydrated ferric oxide (HFO) nanoparticles, heavy metals, waste water, Arsenic ion, Chromium ion, Manganese ion

1 INTRODUCTION

TRACE heavy metals from aqueous and non-aqueous solution have become increasingly important in environmental pollution. Many efficient technologies, including chemical precipitation, adsorption onto activated carbon, membrane processes, electrolytic methods, and ion-exchange has been developed to improve their removal efficiency from the polluted water [1]. These methods, however, display one or more limitations such as covering high operational costs or appearing to be insufficient to meet strict regulatory requirements as for chemical precipitation. To overcome these limitations, chemists have devoted to develop materials capable of removing low concentration of toxic metal ions from contaminated water. Effective adsorbents with strong affinity and high loading capacity for targeted metal ions were subsequently prepared by functionalizing the surface of various substrates, such as polymers [2], [3], [4] or silicates [5], with metal complex groups. Due to the specific affinity of heavy metal ions and complex groups on the sorbent surfaces, these sorbents exhibited enhanced sorption toward heavy metal ions. However, the thermal and chemical stability of such hybrid sorbents, as well as their regeneration efficiency still need further improvement.

In this study we prepared a novel hybrid adsorbent, i.e., polymer-supported hydrated ferric (III) oxide (HFO), to enhance the removal of heavy metal ions from contaminated water. Kastel® C300L was selected as a host material mainly because of the Donnan membrane effect, resulting from the non-diffusible negatively charged sulfonic acid groups on the exchanger surface [2], would enhance permeation of the targeted metal ions. Arsenic, chromium and manganese, heavy metals listed among the priority pollutants, were selected as the representative toxic metals in this study because of their impact to human health such as serious lesions caused in the central nervous system and even permanent damages particularly in population [6], [7]. This study also investigated the influence of solution pH, sorption kinetics, competitive sorption behaviors, and column experiments to evaluate the performance of the newly developed sorbent for arsenic, chromium and manganese removal.

2 EXPERIMENTAL

2.1 Material

Precipitated hydrated ferric (III) oxide (HFO) nanoparticles were prepared elsewhere [2], and Kastel® C300L (Siam Machinery Thai Co., Ltd.) is a commercially available microporous cation exchange resin with polystyrene matrix and sulfonic acid functional groups. Sizes of exchanger resin beads varied between 450 to 550 nm, as presented on the label. All chemicals used in this research are analytical grade and used without further purification. The preparation of HFO-300L consists of the following three steps of Cumbelet al., [3]:

- Step 1: Loading of ferric ions into the sulfonic acid sites of the cation exchanged by stirring resins in 4% (w/v) FeCl₃ solution at an approximate pH of 2.0 (24 hr);
- Step 2: Desorption of ferric ions and simultaneous precipitation of ferric ions hydroxide within the gel and pore phase of

- Somchintana Puttamat is currently pursuing graduated degree program in Chemical engineering, Faculty of Engineering in Chulalongkorn University, Thailand, PH-6625644483.
E-mail: psmochin@tu.ac.th
- Sukrit Tantrawong is a Physicalchemistry lecture and hold the Associate Profesor at Chemistry, Faculty of Science and tecnology in Thammasat University, Thailand, PH-6625644483.
E-mail: sukrittan@hotmail.com
- Varong Pavarajarn is a Associate Profesor in Chemical engineering and the research adviser at Chemical engineering, Faculty of Engineering in Chulalongkorn University, Thailand, PH-6622186890.
E-mail: pavarajarnv@chula.ac.th

the exchanger through a passage of a solution containing NaCl and NaOH, each at 5% (w/v) concentration;

Step 3: Rinsing and washing with a 1:1 (v/v) ethanol-water solution followed by a mild thermal treatment (60 °C, 1 hr).

2.2 Column sorption

Column experiments were carried out with a polyethylene column (Ø 14 mm and 350 mm length) equipped with a water bath to maintain constant temperature. Twenty grams of either C300L or HFO-300L particles were packed into two separate columns. Simulated waste water containing different concentrations of heavy metals along with other commonly occurring electrolytes were prepared as a feed solution; their chemical compositions are described in the related Figures. A peristaltic pump (BT100M/MC6, Baoding Shenchen Precision Pump Co., Ltd.) was used to ensure a constant flow rate. The hydrodynamic conditions, i.e., superficial liquid velocity (SLV) and empty bed contact time (EBCT), are also mentioned in the Figures. Concentrations of all the heavy metal ions were analyzed using an inductively coupled plasma-optimal emission spectrometer (ICP-OES) (Optima 8000, Perkin Elmer).

2.3 Characterization

The C300L particles loaded with HFO were observed with a scanning electron microscope (SEM) (JSM-5410LV, Jeol), fourier transfer infrared spectrometer (FTIR) (Perkin Elmer, SpectrumX) and the ion-exchange mechanism was determined by X-ray diffraction patterns (X'Pert Pro MPD, PANalytical Model).

3 RESULTS AND DISCUSION

3.1 Characterization of HFOs

The HFO-300L prepared in this study was characterized by XRD, SEM, FT-IR analyses. The FT-IR spectra of HFO showed two major adsorption peaks (Fig. 2). The peak at 3453 cm⁻¹ is for the stretching vibration of lattice water and hydroxyl group, while that located at 1643 cm⁻¹ is for -OH bending vibration of adsorbed water molecules. The spectra also showed significant band of metal at 682 and 583 cm⁻¹ for Fe³⁺ adsorption. The hybrid sorbent HFO-resin retained the spherical geometry and developed a deep brown color after being loaded with ferric oxide. The content of HFO loaded within the cation exchange resin was about 12.3% in Fe mass (Table I).

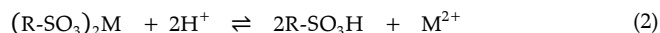
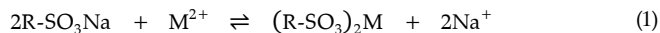
TABLE 1

SOME PROPERTIES OF THE CATION EXCHANGER (KASTEL® C300L) AND HFO-300L

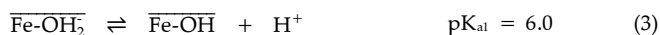
	Sorbents	
	Kastel® C300L	HFO-300L
Matrix structure	Polystyrene	Polystyrene
Functional groups	R-SO ₃ Na	R-SO ₃ Na; HFO
BET surface area (m ² ·mg ⁻¹)	22.7	29.4
Average pore diameter (nm)	30.8	21.7
Apparent density (g·m·cm ⁻³)	0.46	0.62
HFO content (%Fe mass)	0	12.3

3.2 Effect of solution pH

HFO-300L is composed of the host resin C300L and the impregnated HFO nanoparticles. Both can effectively sorb heavy metal cations. For C300L, the sorption of heavy metal ions can be represented by the following reactions [2]:



For heavy metal ions uptaken on HFO, it is mainly the result of the formation of monodentate complexes and bidentate complexes between heavy metal cations and the negatively charged species of HFO nanoparticles, which are considered to be a weak diprotic acid with the following two dissociation constants [3]:



It is generally known that uptaking of heavy metal ions onto a cation-exchanger resin, as C300L, is a nonspecific ion-exchange process, and high acidity is unfavorable for C300L sorption [8], as inferred from Eqs. (1) and (2). The preliminary studies indicated that the minimum concentration of the sorbent dosage was 0.001 g·L⁻¹. Eqs. (3) and (4) also imply that high acidity is similarly unfavorable for metal ion sorption into the loading HFO. It can be noted that uptake ratios of heavy metal ions onto HFO-300L are noticeably in the range of pH 3.0-5.0 even though pK_{a1} of the protonation of Fe-OH is 6.0. This may be associated with the different H⁺ activities inside and outside the polymeric phase of nanopores [3], which enable HFO-300L beads to be more active than the bulky HFO particles in the removal of heavy metal ions from an acidic solution. As mentioned earlier, heavy metal ion sorption on HFO particles decreases dramatically at pH lower than 7.2 and is usually ineffective at below 4.5 [1], [3], [4].

3.3 Effect of contact time

The sorptions of As(II), Cr(II), and Mn(II) on HFO-300L were studied as a function of contact time at pH 6.0 and 30 °C. It was found that the initial fast step completed within 30 min, followed by a slower second stage, 90 min, and sorption equilibrium between HFO-300L and heavy metal ions was achieved within 120 min [5]. The pseudo-first-order kinetic model was employed to describe such sorption process as:

$$\log \left(1 - \frac{q_t}{q_e} \right) = - \frac{k_1}{2.303} t \quad (5)$$

where q_t is the amount sorbed at time t, q_e is the amount of heavy metal ion sorbed at equilibrium and k₁ is the rate constant of the kinetic model. The values of k₁ for Mn(II), As(II), and Cr(II) sorption are 0.092, 0.073, and 0.049 min⁻¹, respectively. All the correlation coefficients (R²) were larger than 0.95, indicating that all three metal sorptions onto HFO-300L could be well represented by the pseudo-first-order model.

3.4 Sorption mechanism

HFO-300L comprises the host exchanger C300L and HFO nanoparticles highly dispersed onto the inner surface of C300L. Thus, specific sorption mechanism of heavy metal ions onto HFO-300L can be describe as follow: first, the non-diffusible sulfonate functional

groups bound to host C300L, which are nonspecific for heavy metal

pre-enrichment of metal cations within HFO-300L phase prior to

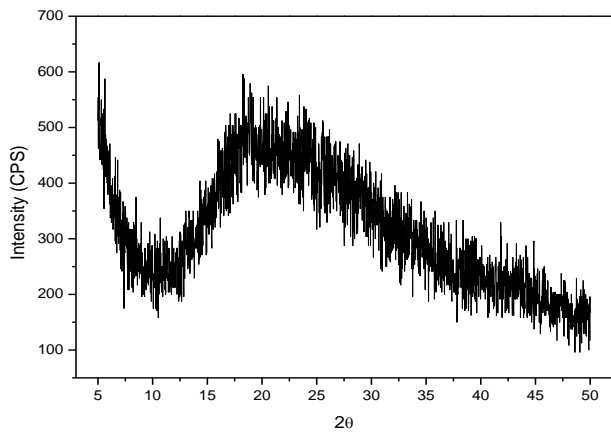


Fig.1. XRD chromatogram for HFO-resin

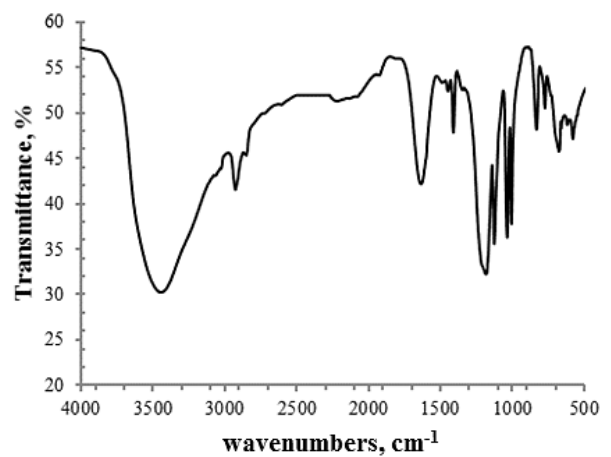


Fig. 2. FTIR chromatogram for HFO-resin

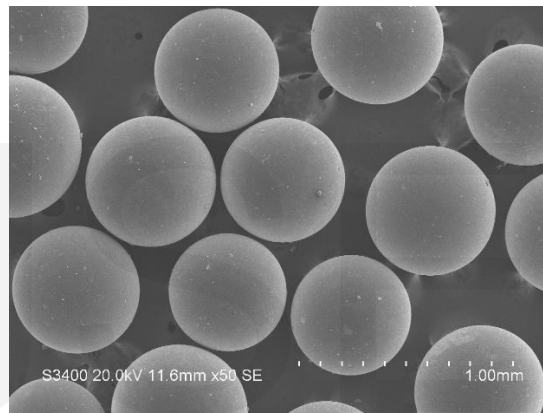


Fig. 3. SEM micrographs of HFO-resin

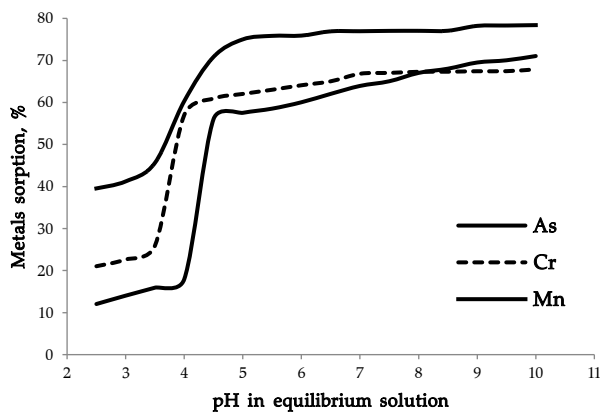


Fig. 4 Effect of pH in equilibrium solution on HFO-300L sorption of three heavy metal ions at 303 K. Initial concentration of each heavy metal ion was 10 mg/L and the sorbent dosage was 5.0 g.

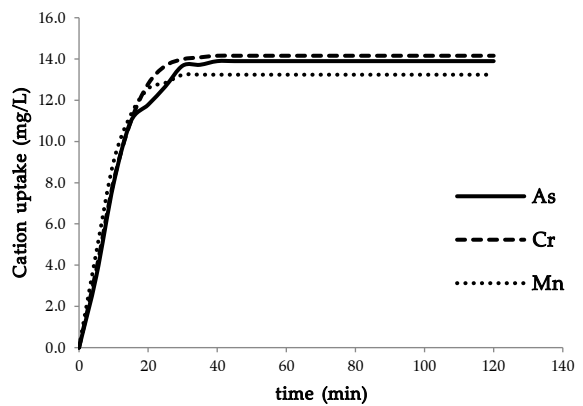


Fig. 5 Uptakes of three heavy metal ions onto HFO-300L at 6.0 with 303 K. 5.0 g sorbent added into 1000 mL solution containing 100 mg/L of each heavy metal

sorption onto HFO nanoparticles impregnated in the polymeric

framework of C300L, which is favorable for enhanced metal reten-

tion by HFO particles. The phenomenon is called Donnan membrane effect and is clearly explained elsewhere [3], [4], [5], [6], [7], [8]. It was further confirmed by the fact that the hybrid sorbent HFO-300L exhibits more efficient removal of heavy metal ions than a simple binary mixture of HFO and C300L. Second, the highly dispersive HFO nanoparticles are expected to exhibit a specific sorption toward heavy metal ions through electrostatic (i.e., ion exchange) and Lewis acid-base (i.e., metal-ligand) interactions.

3.5 Fixed-bed column sorption and regeneration

The feed solutions (pH 4.0) containing known amount of heavy metal ions along with other ubiquitous cations was used in these experiments. In detail, before a 1% breakthrough of target metal ions, the treatment volume for C300L is about 120 bed volumes (BV) for all cations investigated, whereas that for HFO-300L is greatly increased to about 880, 650, and 440 BV for As(II), Cr(II) and Mn(II), respectively. It should be noted the breakthrough curves showed C/C_0 that was greater than one for Cr(II) and Mn(II) sorption, which was attributed to the chromatographic elution effect [2], [3], [10], [11], [12].

At the completion of the column flow-through experiment, regeneration of the HFO-300L column performed at 303 K by using HCl-NaCl solution (pH~3) as a regeneration agent. The regeneration profiles showed that the sorbed Cr(II), Mn(II), and As(II) could be effectively eluted by a limited volume of acidic NaCl solution. It should be note that HFO loss for one sorption-regeneration cycle is less than 1%. The superposition of the breakthrough curves for all the toxic metals in the 7th and 11th cycles confirmed that HFO-300L can be employed for repeated use without noticeable capacity loss.

4 CONCLUSION

In this work, a hybrid sorbent was prepared by immobilizing nanoparticle hydrated ferric (III) oxide (HFO) into a strongly acidic cation exchanger Kastel® C300L. Adsorption of As(II), Cr(II) and Mn(II) into HFO-300L was a pH-dependent process due to the ion-exchange mechanism. Sorption selectivity of HFO-300L are As, Cr, and Mn ions respectively. Column sorption results indicated the working capacity of HFO-300L was about 10-12 times more than C300L with respect to removal of three heavy metals from simulated wastewater (pH~3.5). In addition, HFO-300L is particularly effective in removing trace As and Cr ions from simulated standard waters, with treatment volume orders of magnitude higher than C300L. More attractively, the exhausted HFO-300L beads can be effectively regenerated by HCl-NaCl solution (pH~3.0) for repeated use without any significant capacity loss.

ACKNOWLEDGMENT

Authors are thankful to Scientific and Technological Research Equipment Centre, Chulalongkorn University for equipping the analyses and Department of Chemistry, Faculty of Science and Technology, Thammasat University for core research work where this research worked out.

REFERENCES

- [1] A. Dabrowski, Z. Hubicki, P. Podkoscielny, E. Robens, "Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method," *Chemosphere*, Vol. 56, pp. 91-106, 2004.
- [2] B. Pan, J. Wu, B. Pan, L. Lv, W. Zhang, L. Xiao, X. Wang, X. Tao, S. Zheng, "Development of polymer-based nanosized hydrated ferric oxides (HFOs) for enhanced phosphate removal from waste effluents," *Water Research*, Vol. 43, pp.4421-4429, July 2009.
- [3] L. Cumbal, A.K. Sengupta, "Arsenic removal using polymer-supported hydrated iron(III) oxide nanoparticles: Role of Donnan membrane effect," *Environmental Science and Technology*, Vol. 39, pp. 6508-6515, 2005.
- [4] L. Cumbal, J. Greenleaf, D. Leun, A.K. SenGupta, "Polymer supported inorganic nanoparticles: characterization and environmental applications," *Reactive and Functional Polymers*, Vol. 54, pp. 167-180, 2003.
- [5] A.O. Dada, A.P. Olalekan, A.M. Olatunya, O. DADA, "Langmuir, Freundlich, Temkin and Dubinin-Raduskevich Isotherms Studies of Equilibrium Sorption of Zn^{2+} Unto Phosphoric Acid Modified Rich Husk," *IOSR J. of Applied Chemistry*, Vol. 3, pp. 38-45, Nov.-Dec. 2012.
- [6] A. Demirbas, E. Pehlivan, F. Gode, T. Altun, G. Arslan, "Adsorption of Cu(II), Zn(II), Ni(II), Pb(II), and Cd(II) from aqueous solution on Amberlite IR-120 synthetic resin," *Journal of Colloid and Interface Science*, Vol. 282, pp. 20-25, 2005.
- [7] N. Tewari, P. Vasudevan, B.K. Guha, "Study on biosorption of Cr(VI) by *Mucor hiemalis*," *Biochemical Engineering Journal*, Vol. 23, pp. 186-192, January 2005.
- [8] D.W. Oscarson, P.M. Huang, C. Defosse, A. Herbillon, "Oxidative power of Mn(IV) and Fe(III) oxides with respect to As(III) in terrestrial and aquatic environments," *Nature*, Vol. 291, p. 50-56, 1981.
- [9] B. Pan, B. Pan, X. Chen, W. Zhang, X. Zhang, Q. Zhang, Q. Zhang, J. Chen, "Preparation and preliminary assessment of polymer-supported zirconium phosphate for selective lead removal from contaminated water," *Water Research*, Vol. 40, pp.2938-2946, July 2006.
- [10] Q.R. Zhang, W. Du, B.C. Pan, B.J. Pan, W.M. Zhang, Q.J. Zhang, Z.W. Xu, Q.X. Zhang, "A comparative study on Pb^{2+} , Zn^{2+} and Cd^{2+} sorption onto zirconium phosphate supported by a cation exchanger," *J. of Hazardous Material*, Vol. 152, pp. 469-475, July 2007.
- [11] Q. Su, B. Pan, S. Wan, W. Zhang, L. Lv, "Use of hydrous manganese dioxide as a potential sorbent for selective removal of lead, cadmium and zinc ion from water," *J. of Colloid and Interface Science*, Vol. 349, pp. 607-612, May 2010.
- [12] S. Wan, X. Zhao, L. Lv, Q. Su, H. Gu, B. Pan, W. Zhang, Z. Lin, J. Luan, "Selective Adsorption of Cd(III) and Zn(III) Ions by Nano-Hydrous Manganese Dioxide (HMO)-Encapsulated Cation Exchanger," *Ind. Eng. Chem. Res.*, Vol. 495, pp. 757-7579, 2010.
- [13] A. Yuchi, T. Sato, Y. Morimoto, H. Mizuno, H. Wada, "Adsorption mechanism of trivalent metal ions on chelating resins containing iminodiacetic acid groups with reference to selectivity," *Analytical Chemistry*, Vol. 69, pp. 2941-2944, 1997.
- [14] M. Edwards, "Chemistry of arsenic removal during coagulation and Fe-Mn oxidation," *J AWWA*, Vol.76, pp. 64-78, 1994.
- [15] N.N. Nassar, "Rapid removal and recovery of Pb(II) from wastewater by magnetic nanoadsorbents, in *Journal of Hazardous Material*," Vol. 184, pp. 538-546, August 2010.
- [16] P. Puttamraju and A.K. SenGupta, "Evidence of tunable On-Off Sorption Behaviors of Metal Oxide Nanoparticles: Role of Ion Exchanger Support," *Ind. Eng. Chem. Res.*, Vol. 45, pp. 7737-7742, 2006.
- [17] S. Mandal, T. Padhi, R.K. Patel, "Studies on the removal of arsenic (III) from water by a novel hybrid material, in *J. of Hazardous Material*," Vol. 192, pp. 899-908, June 2011.

- [18] US EPA, 2004. 2004 Edition of the Drinking Water Standards and Health Advisories (EPA 822-R-04-00).
- [19] W. Driefhaus, R. Seith, M. Jekel, "Oxidation of arsenic (III) with manganese oxides in water treatment," Water Research, Vol. 29, pp. 297-305, 1995.
- [20] World Health Organization Guideline for drinking-water quality (first addendum to 3rd edition): Recommendations WHO, Geneva, 2006

IJSER