

Treatment of Cd²⁺ ions using aluminum doped hydroxyapatite (AlHAp) powder

Nguyen Thi Thom^{1*}, Dinh Thi Mai Thanh^{2,3}, Pham Thi Nam¹, Nguyen Thu Phuong¹, Cao Thi Hong¹,
Nguyen Thi Xuyen¹, Nguyen Van Trang¹, Claudine Buess-Herman⁴

¹*Institute for Tropical Technology, Vietnam Academy of Science and Technology*

²*University of Science and Technology of Hanoi, Vietnam Academy of Science and Technology*

³*Graduate University of Science and Technology, Vietnam Academy of Science and Technology*

⁴*Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles, Belgium*

Received 16 January 2017; Accepted for publication 28 August 2017

Abstract

Pollution of heavy metals in water is an important problem and is attracting the attention of scientists. It affects the health of humans and destroys the environment, therefore removal of heavy metal ions is necessary. This work is about treatment of Cd²⁺ ions in the water using aluminum doped hydroxyapatite (AlHAp) powder. The effect of some factors such as contact time, initial Cd²⁺ concentration, pH solution and mass of AlHAp on adsorption capacity and efficiency was investigated. The experimental adsorption data showed that the Cd²⁺ removal process follows the pseudo-second-order law. The results about the effect of initial Cd²⁺ concentration were evaluated using Langmuir and Freundlich adsorption isotherms. Maximum monolayer adsorption capacity was 103 mg/g.

Keywords. Aluminum doped hydroxyapatite (AlHAp), Cd²⁺ ions, adsorption, adsorbent.

1. INTRODUCTION

The pollution of heavy metal in water affects the health of humans and destroys the environment. Therefore, treatment heavy metal ions is getting the attention of scientists. The heavy metals such as cadmium (Cd), mercury (Hg), lead (Pb) and arsenic (As) are known as highly toxic elements. All of which appear in the World Health Organization's list of 10 chemicals of major public concern. Besides, there are some toxic heavy metals such as manganese (Mn), chromium (Cr), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), selenium (Se), and silver (Ag). According to WHO standards, the allowable content of heavy metal ions in drinking water is very low, for example, Cd: 0.003 mg/L, Pb: 0.05 mg/L; Hg: 0.5 mg/L; As: 50 mg/L. If concentrations of heavy metals exceed the permitted level they will affect the health of the human.

Among toxic heavy metals, cadmium (Cd) is one of the most dangerous for human health. Cd can cause serious damage to the kidneys and bones. Cd can also cause bone demineralization, either through direct bone damage or indirectly as a result of a renal dysfunction, impair lung function and increase

the risk of lung cancer. Itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy are all harmful effects of cadmium [1]. Therefore, Cd should be prevented before it reaches to the natural environment.

Heavy metal ions can be removed by adsorption [2], chemical precipitation [3], ion exchange [4], and electrochemical treatment [5]. Among them, adsorption is a common method which is used widely due to its high efficiency, simplicity, and availability of different adsorbents.

There are some materials which are used to treat heavy metal ions such as activated carbon, zeolites, clays, polymers, and hydroxyapatite [6-11]. In which, hydroxyapatite is one of the new adsorbent promising to treat fluorine and heavy metals by adsorption, ion exchange, precipitation or complexing with high efficiency.

Hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) is the main component of bone, teeth and hard tissues of the human body and other mammals [12]. It is osteoconductive, biocompatible and has excellent bioactive properties. Therefore, it is applied widely in many fields such as calcium supplemental drugs or biomedical materials. Besides, HAp was used to

treat heavy metal ions in the water [1, 13, 14]. These results show that HAp can remove heavy metal ions with high efficiency. Some trace elements are found in the natural bone such as aluminum (Al), zinc (Zn), and magnesium (Mg). Doping ions of these trace elements on HAp leading to the materials which have higher specific surface area and adsorption ability for toxic ions in the water [15-22].

In this work, aluminum doped hydroxyapatite (AlHAp) was used to treat Cd²⁺ ions in the water. The effect of contact time, initial Cd²⁺, pH solution, adsorbent mass on adsorption capacity and efficiency was also investigated.

2. EXPERIMENTAL

2.1. Materials

Hydroxyapatite doped aluminum was synthesized by chemical precipitation using Ca(NO₃)₂·4H₂O, Al(NO₃)₃·9H₂O and (NH₄)₂HPO₄. The obtained powder is a single phase of HAp, cylinder shape with the specific surface area of 205 m²/g [23]. HCl and NaOH were used to adjust the pH solution in the treatment process. The materials were pure in France.

2.2. Adsorption experiments

The Cd²⁺ removal experiments were conducted in 250 ml flasks containing 50ml of Cd(NO₃)₂ solution with the change of some factors: the contact time, initial Cd²⁺ concentration, pH solution and the mass of AlHAp.

Influence of the contact time was investigated at the condition as following: 0.1 g of AlHAp powder was dispersed into 50 ml of 281 mg/L Cd(NO₃)₂ solution, the mixtures were agitated with rate 750 rpm by magnetic stirrer (VMS-C7 advanced) for different times (5; 10; 15; 20; 30; 45; 60; 90 and 120 minutes) at 20 °C. The experimental data were analyzed using three kinetic models: Lagergren's pseudo-first order law; McKay and Ho's pseudo-second-order law and the intra-particle diffusion model. The equation of three models is (1), (2) and (3), respectively:

$$\text{Log } q_e - q_t = \text{Log } q_e - \frac{k_1}{2.303} t \quad (1)$$

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

$$q_t = k_p t^{1/2} + C \quad (3)$$

Where, q_t (mg/g) is adsorption capacity at time t ; q_e (mg/g) is adsorption capacity at the equilibrium and k_1 (min⁻¹) is the pseudo-first order adsorption rate constant; k_2 (g/min.mg) is the pseudo-second-order rate constant for adsorption; k_p is the intra-particle

diffusion rate constant (mg/g.min^{1/2}g); C is the intercept that provides the ideal boundary layer thickness.

The adsorption capacity Q (mg/g) and efficiency H (%) were calculated according to the following equations (4) and (5):

$$Q = (C_0 - C_e)V/m \quad (4)$$

$$H = (C_0 - C_e).100/C_0 \quad (5)$$

Where, C_0 (mg/L) is the initial Cd²⁺ concentration in the solution, C_e (mg/L) is the Cd²⁺ concentration in the solution after treatment at the equilibrium, V (L) is the solution volume, m (g) is the mass of AlHAp.

In order to describe the Cd²⁺ adsorption isotherm by AlHAp powder, the experiment data about the influence of initial concentration from 56 to 281 mg/L of Cd²⁺ were analyzed using Langmuir and Freundlich adsorption isotherms. The linear form of the Langmuir and Freundlich isotherm equations can be expressed by (6) and (7) as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (6)$$

$$\text{Log } q_e = \text{Log } k_F + \frac{1}{n} \text{Log } C_e \quad (7)$$

Where Q_m (mg/g) is the monolayer adsorption capacity; b (L/g) is the Langmuir constant that is related to the free energy of adsorption; C_e (mg/L) and q_e (mg/g) are the equilibrium concentrations of adsorbate in solution and on the surface of HAp; k_F and n are Freundlich parameters and are determined via plotting $\text{Log } q_e$ versus $\text{Log } C_e$.

Initial pH values of solution were adjusted in the range from 2 to 8 by using 65 % HNO₃ or 5 % NaOH solution with pH meter (827 pH lab). The effect of adsorbent mass on the adsorption capacity and efficiency was done in the range of 0.05 g to 0.15 g of AlHAp with stirring rate 750 rpm, pH 6 for 60 minutes at 20 °C. The concentration of Cd²⁺, Ca²⁺ in the solutions after treatment was determined using atomic absorption spectrometer (AAS – PERKIN ELMER 3110).

The phase component of adsorbent before and after treatment Cd²⁺ ions was analyzed by X-Ray diffraction (XRD) (Siemens D5000 Diffract meter, CuK_α radiation ($\lambda = 1.54056 \text{ \AA}$) with step angle of 0.030°, the scanning rate about 0.04285°s⁻¹, and 2θ degree in the range of 20-70°.

3. RESULTS AND DISCUSSION

3.1. Influence of contact time

The variation of the cadmium adsorption capacity and efficiency according to the contact time is presented in figure 1. The contact time increases

from 5 to 30 minutes, the adsorption capacity increases rapidly from 79 mg/g to 127 mg/g. After that, the adsorption capacity, as well as the efficiency, increases slowly when the contact time increases from 30 to 60 minutes (from 127 mg/g and 90 % to 134 mg/g and 95 %, respectively). The contact time continues to increase up to 120 minutes, the efficiency does not change. Therefore, the contact time of 60 minutes is the equilibrium of removal Cd²⁺ process, which was chosen for further experiments. The efficiency is about 95 % corresponding to the adsorption capacity at the equilibrium about 134 mg/g.

The experimental data were analyzed using three kinetic models: Lagergren's pseudo-first order law; McKay and Ho's pseudo-second-order law and the intra-particle diffusion model (figure 2).

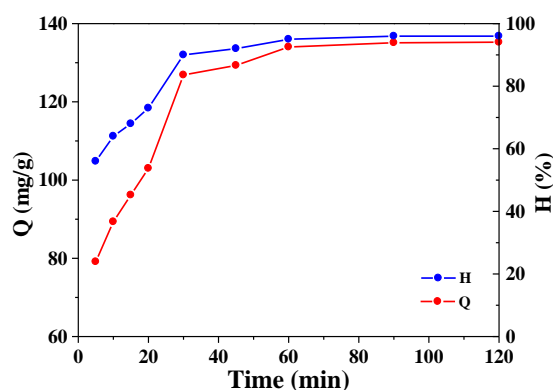


Figure 1: The variation of the Cd²⁺ adsorption capacity and efficiency of 0.1g AIHAp according to the contact time

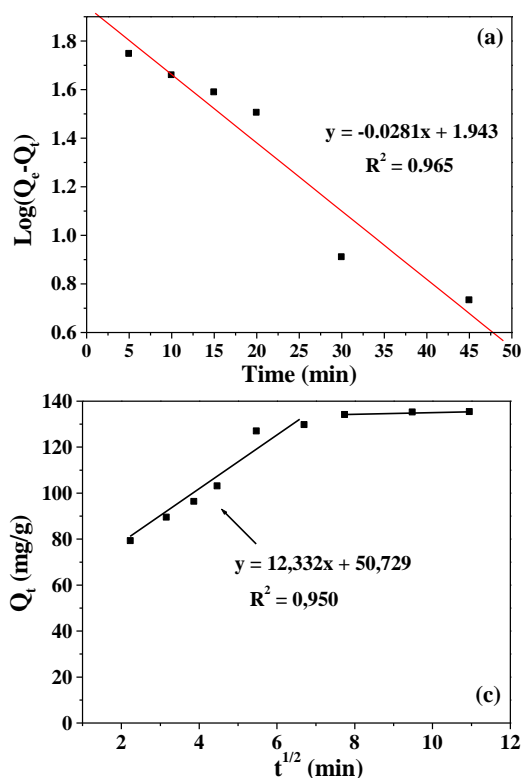


Figure 2: Adsorption data modeled using three kinetic models: (a) Lagergren's pseudo-first order law; (b) McKay and Ho's pseudo-second-order law, and (c) the intra-particle diffusion model

A linear relationship with high correlation coefficient ($R^2 = 0.9999$) between t/q_t and t is obtained which indicates the applicability of the pseudo second-order model to describe the Cd²⁺ adsorption process. The parameters of this model were calculated as seen in table 1.

The concentration of Ca²⁺ in the solution after treatment and the concentration of Cd²⁺ removal are presented in Figure 3. The data show that with all contact times, the concentration of Cd²⁺ removal is always higher than Ca²⁺ leached concentration. The mechanism of Cd²⁺ removal process in the water can

be predicted: the dissolution of a part of AIHAp powder; the adsorption Cd²⁺ on the surface of AIHAp and the exchange ions between Cd²⁺ adsorption with Ca²⁺ and/or Al³⁺ of AIHAp.

Table 1: The parameters of Cd²⁺ removal process calculated from McKay and Ho's pseudo-second-order law model

K ₂ (g/mg.min)	Q _e (mg/g)	R ²
0.0039	131.6	0.999

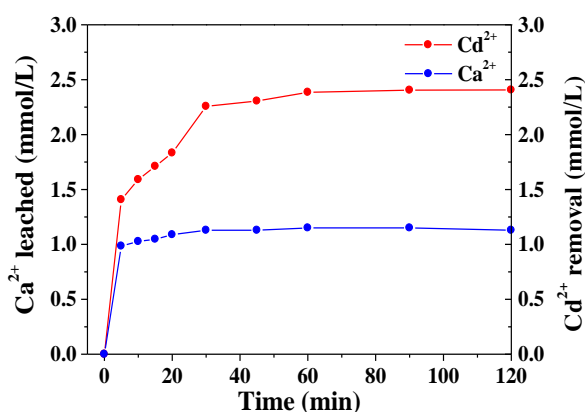


Figure 3: Concentration of Ca^{2+} leached from AlHAp into the water and concentration of Cd^{2+} removal following the contact time

3.2. Influence of initial Cd^{2+} concentration

Figure 4 presents adsorption capacity and efficiency of 0.1 g AlHAp dispersed in 50 ml Cd^{2+} with the different initial concentration of Cd^{2+} at 20 °C with stirring rate of 750 rpm during 60 min. The results indicate that the adsorption capacity increases corresponding to the increase of initial Cd^{2+} concentration. The initial Cd^{2+} concentration increases from 56 to 281 mg/L, the efficiency decreases slightly which is in the range of 96 to 99 %. However, the adsorption capacity increases strongly from 28 mg/g to 135 mg/g, respectively.

The increase can be explained as follows: the higher initial concentrations are able to overcome mass transfer related resistances existing between the aqueous and solid absorber phase by effectively creating a driving force [14].

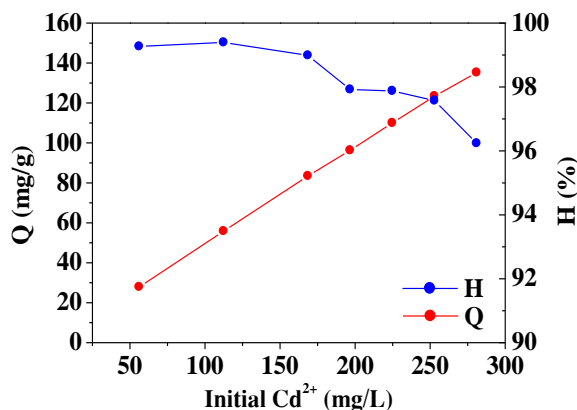


Figure 4: The variation of the Cd^{2+} adsorption capacity and efficiency of 0.1g AlHAp according to the initial Cd^{2+} concentration

The Langmuir and Freundlich adsorption isotherms are used to describe Cd^{2+} removal process by AlHAp powder, see figure 5. The Langmuir adsorption isotherm plot displays good linear fit ($R^2 = 0.994$). From the slope of the fit the calculated maximum monolayer adsorption capacity is about 103 mg/g.

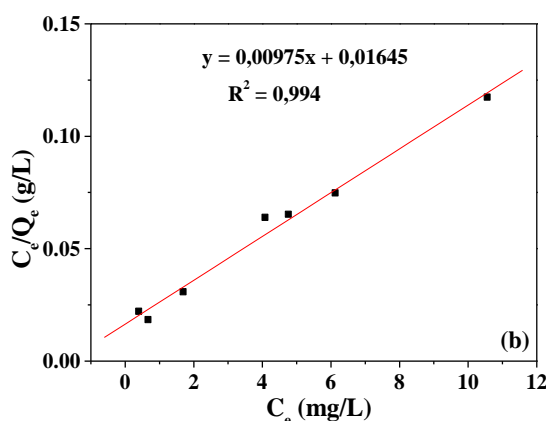
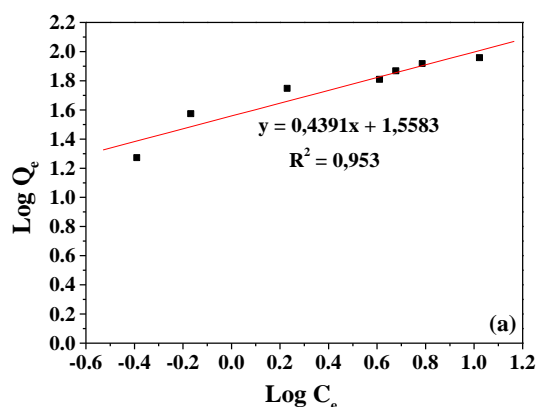


Figure 5: (a) Freundlich and (b) Langmuir adsorption isotherms for Cd^{2+} adsorption by AlHAp powder

3.3. Influence of pH solution

In the water, cadmium exists in different forms such as Cd^{2+} , $\text{Cd}(\text{OH})^+$, $\text{Cd}(\text{OH})_2^0$, and $\text{Cd}(\text{OH})_{2(s)}$. [24] which is affected by cadmium concentration and pH solution. Cd^{2+} ions are ionic species only in the solution with $\text{pH} < 6$ [25]. At $\text{pH} > 8$, Cadmium forms dominant species as $\text{Cd}(\text{OH})_2$ precipitation

and in $\text{pH} < 8$ forms Cd^{2+} and $\text{Cd}(\text{OH})^+$ [26, 27]. So, the pH range is chosen to treat Cd^{2+} from 2 to 8. Figure 6 presents the effect of the initial pH solution on the adsorption capacity and efficiency to treat Cd^{2+} by AlHAp powder. It shows that at low pH solution ($\text{pH} \sim 2$), the efficiency of Cd^{2+} removing is low. It can be explained on the basis of proton-competitive sorption reactions. At lower pH

solution, H^+ ions compete with Cd^{2+} ions for the surface binding sites of HAp leading to the reduction of Cd^{2+} adsorption. When the pH solution increases, the competing effect of H^+ ions decreases the efficiency of Cd^{2+} removal process increases. In the pH range of 6 to 8, the efficiency changes not much (95-97 %). So, pH value of 6 (pH_0) was the optimum pH value for the Cd^{2+} removal process.

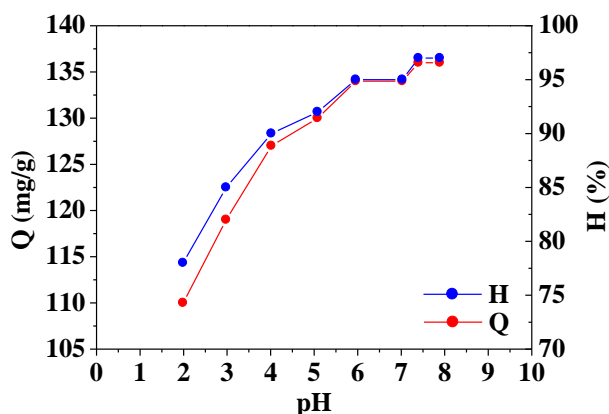


Figure 6: The variation of Q, H according to the initial pH

3.4. Effect of adsorbent mass

The effect of the amount of AlHAp adsorbent ranging from 0.05 to 0.15 g on the adsorption capacity and efficiency is presented in figure 7. The result shows that the efficiency increases rapidly with the increasing of AlHAp mass from 0.05 g to 0.1 g. However, the mass of AlHAp continues to increase from 0.1 g to 0.15 g, the efficiency does not change from 97 % to 99 %, but the adsorption capacity decreases strongly from 135 mg/g to 92 mg/g. Therefore, the optimum mass of AlHAp is 0.1 g.

3.5. Characterization of adsorbent before and after treatment

From the above results, the optimum condition to treat Cd^{2+} ions in the water is chosen as follows: 0.1g AlHAp powder is used to treat 50 ml of 281 mg/L Cd^{2+} , $\text{pH}_0 = 6$ for 60 minutes of the contact time at 20 °C. At above treatment condition, AlHAp powder can remove Cd^{2+} with high efficiency about 97 % and the adsorption capacity reaches 135 mg/g. The phase composition of the adsorbent before and after treatment process was analyzed using X-Ray diffraction (figure 8). Before treatment, the adsorbent is a single phase of HAp, see figure 8(1). After treatment, the phase of HAp is nearly complete replaced by the CdHAp crystal phase. The results confirm that there are the exchange ions between

Cd^{2+} adsorption on the surface of AlHAp and Ca^{2+} and/or Al^{3+} of AlHAp to form CdHAp.

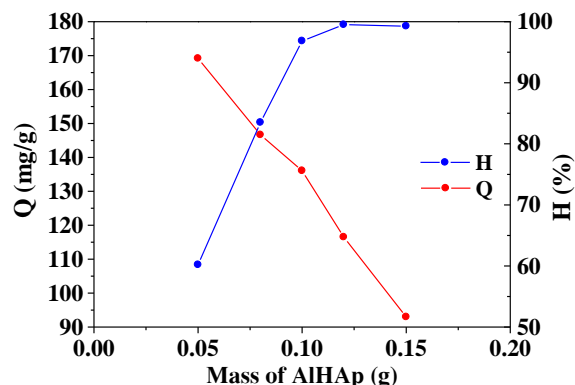


Figure 7: The variation of the Cd^{2+} adsorption capacity and efficiency according to the mass of AlHAp

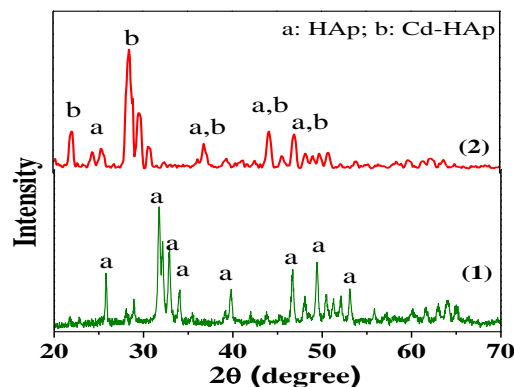
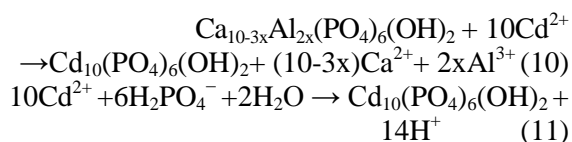
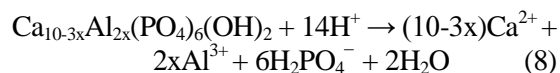


Figure 8: XRD patterns of AlHAp (1) before and (2) after treatment Cd^{2+}

3.6. Cd^{2+} uptake mechanism

The Cd^{2+} uptake mechanism can be suggested as follows: The dissolution of AlHAp in aqueous solution containing Cd^{2+} ions follows the equation (8). The adsorption of Cd^{2+} on the surface of AlHAp (Eq.9) and the exchange ions reaction between Cd^{2+} adsorbed and Ca^{2+} and/or Al^{3+} of AlHAp takes place to form CdHAp (Eq.10).



4. CONCLUSION

The current work provided Cd²⁺ ions removal process using aluminum doped hydroxyapatite. The results show that 0.1 g AlHAp powder can remove 97 % Cd²⁺ from 50 ml of 281 mg/L Cd(NO₃)₂ solution with the adsorption capacity of 135 mg/g. The adsorption experiment data displays a good fit by the pseudo-second-order law model with the high interrelation coefficient (R² = 0.999). The Cd²⁺ removal process is best described by the Langmuir adsorption isotherm (R² = 0.994). The maximum monolayer adsorption capacity calculated from the fit of the Langmuir adsorption isotherm is about 103 mg/g. The mechanisms of Cd²⁺ ions removal process are as follows: the dissolution/precipitation of AlHAp, the adsorption of Cd²⁺ on the surface of AlHAp, and the exchange ions reaction between Cd²⁺ adsorbed and Ca²⁺ and/or Al³⁺ of AlHAp to form CdHAp.

REFERENCES

1. I. Mobasherpour, E. Salahi, M. Pazouki. *Removal of divalent cadmium cations by means of synthetic nanocrystallite hydroxyapatite*, *Desalination*, **266**, 142-148 (2011).
2. P. R. Puranik, K. M. Paknikar. *Biosorption of lead and zinc from solutions using *Streptomyces cinnamomeum* waste biomass*, *J. Biotechnol.*, **55**, 113-124 (1997).
3. S. Azabou, T. Mechichi, S. Sayadi. *Zinc precipitation by heavy-metal tolerant sulfate-reducing bacteria enriched on phosphogypsum as a sulfate source*, *Miner. Eng.*, **20**, 173-178 (2007).
4. Z. Hubicki, A. Jakowicz, A. Łodyga. *Application of the ion-exchange method to remove metallic ions from waters and sewages*, *Stud. Surf. Sci. Catal.*, **120**, 497-531 (1999).
5. P. Guillaume, N. Leclerc, F. Lapique, C. Boulanger. *Electroleaching and electrodeposition of zinc in a single-cell process for the treatment of solid waste*, *J. Hazard. Mater.*, **152**, 85-92 (2008).
6. Yu Yang Long, Yi Jian Feng, Si Shi Cai, Li Fang Hu, Dong Sheng Shen. *Reduction of heavy metals in residues from the dismantling of waste electrical and electronic equipment before incineration*, *Journal of Hazardous Materials*, **272**, 59-65 (2014).
7. Masahiro Oguchi, Hirofumi Sakanakura, Atsushi Terazono, Hidetaka Takigami. *Fate of metals contained in waste electrical and electronic equipment in a municipal waste treatment process*, *Waste Management*, **32**, 96-103 (2012).
8. Swagat S. Rath, Pradeep Nayak, P. S. Mukherjee, G. Roy Chaudhury, B. K. Mishra. *Treatment of electronic waste to recover metal values using thermal plasma coupled with acid leaching. A response surface modeling approach*, *Waste Management*, **32**, 575-583 (2012).
9. Sadia Ilyas, Jae-chun Lee, Byung-su Kim. *Bioremoval of heavy metals from recycling industry electronic waste by a consortium of moderate thermophiles: process development and optimization*, *Journal of Cleaner Production*, **70**, 194-202 (2014).
10. Mona Karnib, Ahmad Kabbani, Hanafy Holail, Zakia Olama. *Metals Removal Using Activated Carbon, Silica and Silica Activated Carbon Composite*, *ScienceDirect, Energy Procedia*, **50**, 113-120 (2014).
11. Phuong Vu Thi, Nam Pham Thi, Phuong Nguyen Thu, Hai Do Thi, Thanh Dinh Thi Mai. *Defluoridation behavior of nano Zn-hydroxyapatite synthesized by chemical precipitation method*, *Vietnam Journal of Chemistry*, **50(6B)**, 239-244 (2012).
12. Lai Thi Ngoan, Nguyen Thu Phuong, Khuat Quang Son, Pham thi Nam, Dinh Thi Mai Thanh. *Synthesis and determine about characterization of nano hydroxyapatite doped aluminum by precipitation*, *Vietnam Journal of Chemistry*, **52(6)**, 677-683 (2014).
13. I. Mobasherpour, E. Salahi, M. Pazouki. *Comparative of the removal of Pb²⁺, Cd²⁺ and Ni²⁺ by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study*, *Arabian Journal of Chemistry*, **5**, 439-446 (2012).
14. Gérrard Eddy Jai Poinern, Sridevi Brundavanam, Suraj Kumar Tripathy, Mrutyunjay Suar, Derek Fawcett. *Kinetic and Adsorption Behaviour of Aqueous Cadmium Using a 30 nm Hydroxyapatite Based Powder Synthesized Via a Combined Ultrasound and Microwave Based Technique*, *Physical Chemistry*, **6(1)**, 11-22 (2016).
15. Yulun Nie, Chun Hu, Chuipeng Kong. *Enhanced fluoride adsorption using Al(III) modified calcium hydroxyapatite*, *Journal of Hazardous Materials*, **233-234**, 194-199 (2012).
16. Thomas J. Webster, Elizabeth A. Massa-Schlueter, Jennifer L. Smith, Elliot B. Slamovich. *Osteoblast response to hydroxyapatite doped with divalent and trivalent cations*, *Biomaterials*, **25**, 2111-2121 (2004).
17. Samar J. Kalita, Himesh A. Bhatt. *Nanocrystalline hydroxyapatite doped with magnesium and zinc: Synthesis and characterization*, *Materials Science and Engineering C*, **27**, 837-848 (2007).
18. E. Boanini, M. Gazzano, A. Bigi. *Ionic substitution in calcium phosphates synthesized at low temperature*, *Acta Biomaterialia*, **6**, 1882-1894 (2010).
19. Celaletdin Ergun. *Effect of Ti ion substitution on the structure of hydroxyapatite*, *Journal of the European Ceramic Society*, **28**, 2137-2149 (2008).

20. Burcin Basar, Aysen Tezcaner, Dilek Keskin, Zafer Evis. *Improvements in microstructural, mechanical, and biocompatibility properties of nano-sized hydroxyapatites doped with yttrium and fluoride*, *Ceramics International*, **36**, 1633-1643 (2010).
21. Alieh Aminia, Mehran Solati-Hashjin, Ali Samadikuchaksaraei, Farhad Bakhshi, Fazel Gorjipour, Arghavan Farzadi, Fattolah Moztarzadeh, Martin Schmucker. *Synthesis of silicon-substituted hydroxyapatite by a hydrothermal method with two different phosphorous sources*, *Ceramics International*, **37**, 1219-1229 (2011).
22. Ilaria Cacciotti, Alessandra Bianco, Mariangela Lombardi, Laura Montanaro. *Mg-substituted hydroxyapatite nanopowders: Synthesis, thermal stability and sintering behaviour*, *Journal of the European Ceramic Society*, **29**, 2969-2978 (2009).
23. Nguyen Thu Phuong, Pham Thi Nam, Do Thi Hai, Nguyen Thi Thom, Nguyen Thi Thu Trang, Thai Hoang, Dinh Thi Mai Thanh. *Comparison of fluoride adsorption ability of magnesium, zinc, aluminum-doped hydroxyapatite synthesized by precipitation method*, *Analytica Vietnam Conference*, 283-291 (2015).
24. V. L. Snoeyink, D. Jenkins, *Water Chemistry*, John Wiley and Sons, *Water Chemistry*, New York (1980).
25. V. C. Srivastava, I. D. Mall, I. M. Mishra. *Equilibrium modeling of single and binary adsorption of Cadmium and nickel onto bagasse fly ash*, *Chem. Eng. J.*, **117**, 79-91 (2006).
26. Ramos R. L., Mendez J. R. R., Barron J. M., Rubio L. F. and Coronado R. M. G. *Adsorption of Cd(II) from aqueous solutions onto activated carbon*, *Water Science Technology*, **35**, 205-211 (1997).
27. B. M. Babic, S. K. Milonjic, M. J. Polovina, S. Cupic, B. V. Kaludjerovic. *Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth*, *Carbon*, **40**, 1109-1115 (2002).

Corresponding author: **Nguyen Thi Thom**

Institute for Tropical Technology
 Vietnam Academy of Science and Technology
 No. 18, Hoang Quoc Viet Road, Cau Giay Dist., Hanoi
 E-mail: nguyenthomsp@gmail.com; Telephone: 0973197326.