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# INVESTIGATION OF SORPTION OF $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ IONS BY A COMPOSITE ADSORBENT OBTAINED FROM BENTONITE-LIKE CLAY AND HYDROXYAPATITE

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## Abstract

The results of the measuring of $pH_{pzc}$ (point zero charge) of the surface of adsorbents by potentiometric titration are presented. It was found that the $pH_{pzc}$ of the bentonite-like clay of the Tam Bo (Lam Dong, Vietnam), the synthesized hydroxyapatite and composite adsorbents based on them is 5.7, 6.9 and 6.8, respectively. A study was made of the dependence of the efficiency of purification of model aqueous solutions on $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions by various adsorbents on the pH values. It was found that the optimal pH values are in the limits of 4 – 6. The highest adsorption capacity of the composite adsorbent towards $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions are 0.73, 0.71 and 0.81 mmol/g respectively, which is over 2.79, 1.92 and 2.43 times higher than the Lam Dong bentonite-like clay.

Keywords: Adsorption, Composite adsorbent, Heavy metal ions, Hydroxyapatite, Montmorillonite, Water purification.

## 1. Introduction

A serious danger to the environment is the pollution of natural and drinking water by heavy metal ions, which have cumulative properties, enter the human body, can accumulate and cause various diseases [1]. Therefore, the problems of developing effective methods for their purification become topical. Heavy metals include mercury, lead, nickel, chromium, cadmium, zinc, copper, etc. The most common ions are $Pb^{2+,}$ $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ [2]. The main sources of pollutant that cause environmental pollution include galvanic bath waste, sewage from machine building, electrical engineering, radio and instrument engineering, electronic, chemical, printing, textile, leather, fur, oil refining, paper, rubber, woodworking industries [3].

There are various methods for removing pollutant from sewage: ion exchange [4], reverse osmosis [5], chemistry [6], electrodialysis [7], solvent extraction [8] and adsorption [9]. However, many of the traditional methods have several drawbacks, such as expensive equipment, continuous replenishment of chemicals, time consuming cleaning and the likelihood of secondary pollution. Charerntanyarak [10] explained that adsorption is the most effective method of fine cleaning contaminated water at the present time. Advantages of adsorption method is the capability of fine cleaning of dirty water containing several pollutants, as well as recuperation of spent adsorbents.

Adsorbents are activated carbons, synthetic organic adsorbents, some production wastes (ash, slag, sawdust), mineral adsorbents-zeolites, clays, flasks, silica gels, aluminum gels and metal hydroxides. At present, the ion exchange method is used for water purification, which allows using a wide range of ion-exchange materials.

The use of clay minerals of structural type 2:1 with changing basal spacing is known to be effective. Molecules of water and organic substances as well as positively or negatively charged ions can be included in the inter-package cavities of the minerals. Ion exchange with the ions from the surroundings can take place in them. Based on studies by Vesentsev et al. [11], the clay minerals concerned can swell because of increase of space between basal layers where ions or molecules absorbed are located.

Hydroxyapatite (HA) $Ca_{10}(PO_4)_6(OH)_2$ has been known as the main inorganic constituent of bones and teeth of mammals and the component of phosphate mineral rocks [12]. Recently, the use of both (HA) and composite adsorbents based on it for the adsorption and immobilization of pollutants is considered a promising technology to remove pollution due to low cost and high adsorption possibility of pollutants ions and dyes from aqueous solutions [13-15].

In recent years, composite materials based on bentonite and hydroxyapatite have been studied as universal sorbents for the removal of toxic metals and dyes from aqueous solutions [16-18]. It is of scientific and practical interest to obtain composite adsorption-active materials based on natural bentonite-like clays combined with synthetic hydroxyapatite.

The aim of this paper is to investigate the adsorption possibility of composite adsorbents based on bentonite-like clay and hydroxyapatite synthesized by chemical precipitation towards pollutants such as $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions.

## 2. Materials and methods

### 2.1. Materials

As adsorbents for the adsorption $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions the following materials were used: the bentonite-like clay of the Tam Bo (Lam Dong, Vietnam), which was assigned the BT6 label, the synthesized hydroxyapatite (HA) and the composite adsorbent (C-HA) obtained by the method described in literature [11].

*Hydroxyapatite synthesis:* HA was synthesized by adding a 10% (mass) solution of ortho-phosphoric acid to $Ca(OH)_2$ solution with the rate 1.5 - 2.2 mL/min per liter of the saturated solution of calcium hydroxide. The reaction mixture was stirred for 20 - 30 minutes with the stirring shaft HS 100D (1000 rpm), then the mixture was allowed to settle for 24 hours. The product obtained was separated from the mother liquor by filtration, rinsed with distilled water and then dried at $105 \pm 5^0$C for 5h. The samples were powdered in a porcelain mortar.

*The preparation of the composite sorbent (C-HA):* A 5 g sample of bentonite-like clay was added to a 5 L vessel containing 1880 mL of the saturated solution of $Ca(OH)_2$. The suspension was stirred with the stirring shaft mentioned above for 2 h. The required volume of a 10% solution of ortho-phosphoric acid was added with the rate 1 mL/min at intensive stirring (1000 rpm) to provide the mole relation Ca:P equal to 1.67. Then the solution was stirred for 2 h. The precipitate formed was allowed to settle for 24 h at room temperature and then separated, filtered, dried and powdered asdescribed above.

### 2.2. Methods

The pH value of the solutions was maintained by the addition of NaOH 0.1M and HCl 0.1M solutions and monitored with the pH meter "Multitest IPL-101".

Trofimov et al. [19] reported that the $pH_{pzc}$ was measured by the potentiometric titration method according in literature. The adsorption capacity is calculated by the formula (1) [20].

$$q_e = \frac{(C_i - C_e)V}{m}, \quad (1)$$

The adsorption efficiency *(H %)* $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions from model aqueous solutions is calculated using formula (2).

$$H = \frac{C_i - C_e}{C_i} \; 100\,\%, \quad (2)$$

where $q_e$ - adsorption capacity, *mmol/g*; $C_i$, $C_e$ - initial and equilibrium concentration of $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions, *mmol/L*; *V* is the volume of a solution containing of $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2}$ ions, *L*; m - the mass of the adsorbent, *g*.

The equations of the experimental Langmuir adsorption isotherm in the linearized form and Freundlich are determined in accordance with formulas (3) and (4) [14]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b.q_m}, \quad (3)$$

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e, \quad (4)$$

where $q_m$ is the maximum adsorption capacity, *mmol/g*; *b* - constant of Langmuir adsorption equilibrium, *L/mmol*; $k_f$, *n* are the constants of the Freundlich equation.

The adsorption capacity studied samples towards $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions was determined by constructing adsorption isotherms using the variable concentration method under static conditions at room temperature (25 ± 2°C) using model solutions of cadmium (II) nitrate, zinc (II) nitrate and copper (II) sulfate in distilled water with concentration of ions in a range from 0.3 to 3.0 mmol/L. To study the adsorption of $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions by adsorbent samples into volumetric flasks of 0.1 L containing 0.1 ± 0.001 g samples, 0.05 L model solutions were added. At the end of the process, the suspensions were filtered. The residual concentration ions in the solutions was determined using UV-visible spectrophotometer SPECORD 210Plus (Germany).

## 3. Results and Discussion

### 3.1. Determination $pH_{pzc}$

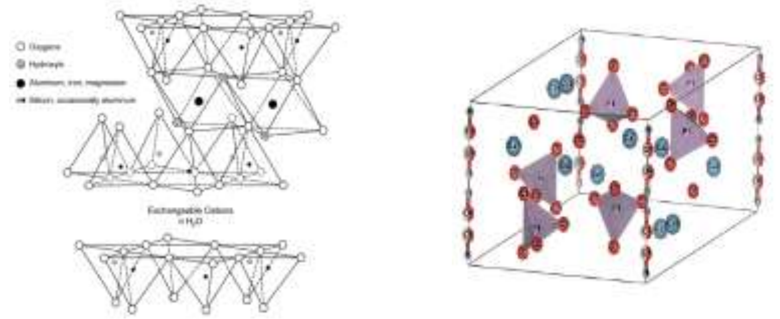
It is well known in literature [21], that montmorillonite carried two kinds of electric charge: the first is an variable charge that depends on the pH of the medium, due to the appearance of adsorption-desorption reactions of protons on the hydroxyl groups of the surface layer, Fig. 1(a), the second is the structural negative charge arising due to the isomorphous replacement of $Si^{4+}$ by $Al^{3+}$ in the structure of montmorillonite. There are also hydroxyl groups on the surface of the edges of montmorillonite crystals. They arise due to breakage and hydrolysis of Al-O and Si-O bonds. On the other hand, it is well known that $pH_{pzc}$ value is an important parameter to play a decisive role in many chemical phenomena, such as adsorption, particle interaction in colloidal suspensions, coagulation, dissolution of hydroxide-based minerals, electrochemical phenomena. At lower pH values than $pH_{pzc}$ (pH values above zero charge the surface), the surface of samples has a positive charge. At pH higher than the $pH_{pzc}$ value, the surface is negatively charged.

The lattice of hydroxyapatite has a hexagonal structure. The hydroxyl groups are located along the hexagonal axis, and the phosphate groups are distributed as isosceles triangles around the hexagonal axis, Fig. 1(b). The surface of HA in the medium (below PZC) has a positive charge, mainly due to the dissociation of the main groups of the type: $Ca – OH^+ \leftrightarrow Ca^{2+} + OH^-$ with the release of $OH^-$ groups into the outer layer of the double electric layer. In an alkaline medium, this process is suppressed and dissociates mainly the acid groups according to the reaction $H_2PO_{4-} \leftrightarrow HPO_4^{2-} + H^+$. At the same time, the proton is split off and the surface is charged negatively [22].

The $pH_{pzc}$ is the point of intersection of the titration curves plotted on the graph. In Fig. 2 shows that the points of zero charge of bentonite-like clay, hydroxyapatite and composite sorbent (C-HA) are 5.7, 6.9 and 6.8.

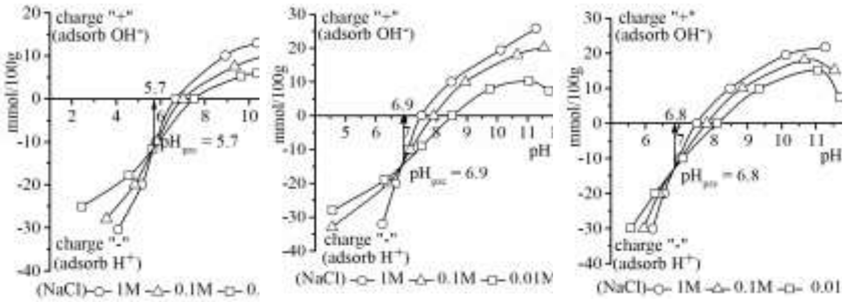
### 3.2. The influence of the pH

It is known that the pH value of the medium is an important parameter in the study of the adsorption process [20]. To assess the effect of the pH of the medium on the extraction efficiency $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions from model aqueous solutions, a study was carried out in the pH limit from 2 to 8 (Fig. 3).



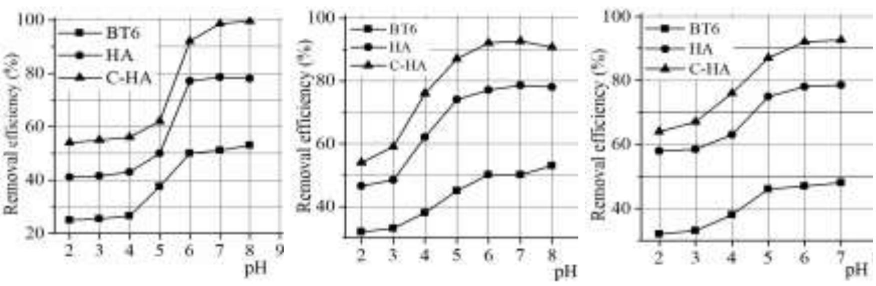
**(a) (b)**

**Fig. 1. Model of the structure of the crystal lattice:**
**a) montmorillonite [23]; b) hydroxyapatite [24]**




**(a) (b) (c)**

**Fig. 2. Determination of the $pH_{pzc}$ by potentiometric titration:**
**a) – BT6; b) – HA; c) – C-HA**




**(a) (b) (c)**

**Fig. 3. Dependence of purification efficiency of model solutions: a) – $Cd^{2+}$; b) – $Zn^{2+}$; c) – $Cu^{2+}$ sorbents of BT6, HA and C-HA from the pH value**

The obtained results showed that the efficiency of ion adsorption increases significantly in the limit of the pH 4 – 6: BT6 $Cd^{2+}$ (26 – 50)%; $Zn^{2+}$ (38 – 50)%; $Cu^{2+}$ (38 – 47)%, on HA $Cd^{2+}$ (43 – 77)%; $Zn^{2+}$ (62 – 77)%; $Cu^{2+}$ (63 – 78)% and on C-HA $Cd^{2+}$ (56 – 92)%; $Zn^{2+}$ (76 – 92)%; $Cu^{2+}$ (75 – 93)%. At a lower pH value than the pH value of the indicated range, the adsorption efficiency of the investigated adsorbents towards $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions decreases. This can be explained not only at low values pH < $pH_{pzc}$, on the surface of sorbents is a positive charge [19], but also adsorption competition occurs between $H^+$ ions and heavy metals [25].

To improve the absorption efficiency of heavy metal ions, the pH value above $pH_{pzc}$ is desirable. However, at pH > 7, the precipitation of metal hydroxides was occurred. Absorption was decreased, which is explained by the formation of insoluble species of metal hydroxide [20].

### 3.3. Adsorption kinetics

One of the most important factors to evaluate the effectiveness of the use of sorbents is the investigative kinetics of the adsorption process. For this purpose, the dependence of the adsorption capacity of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions onto the adsorbent based on change of contact times the was studied. The kinetic curves are shown in Fig. 4.

In Figs. 4(a), (c), and (e) is represented that the kinetic curves for decreasing the concentration of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions onto the adsorbents. Adsorption of ions onto the bentonite-like clay BT6, HA and C-HA composite under static conditions with high speed are occurred the first from 1 to 5 minutes, Figs. 4(b), (d), and (f). In that, the highest adsorption rate is observed with a composite adsorbent.

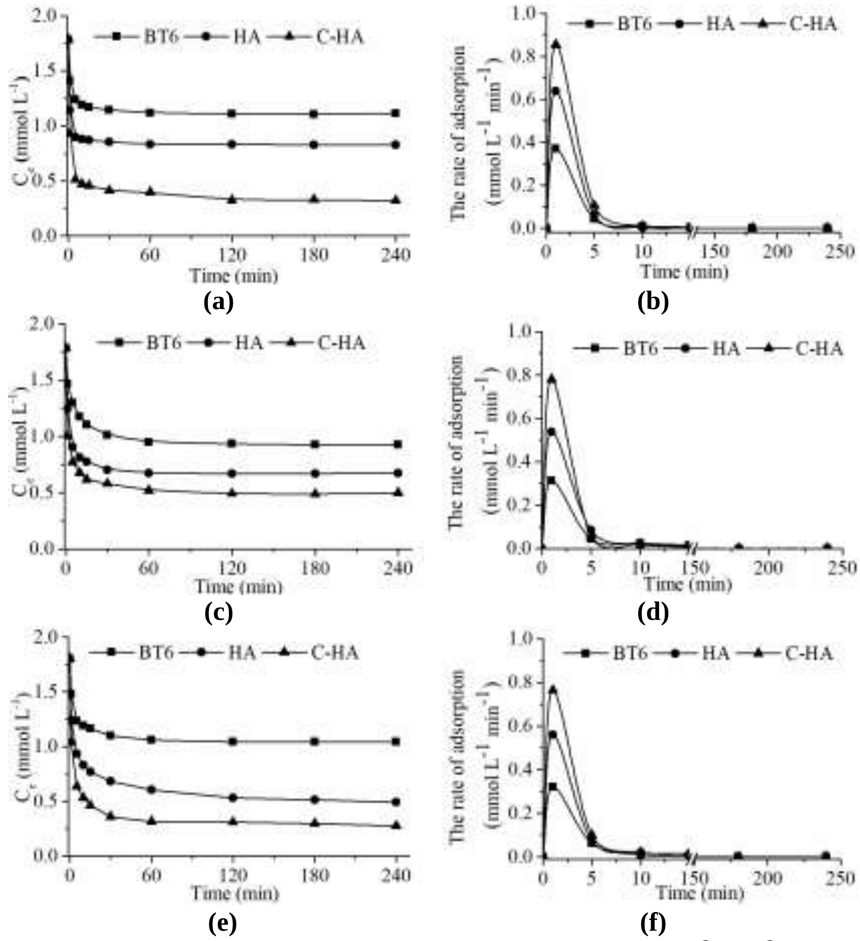
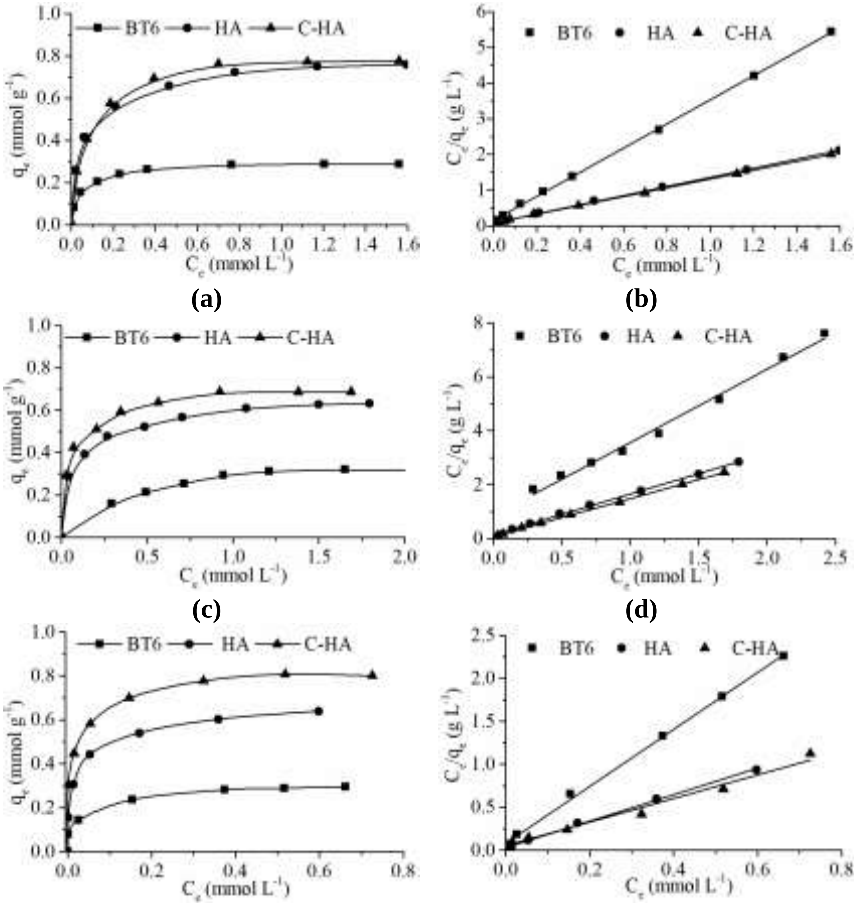



**Fig. 4. Kinetic curves for reducing the concentration of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions and the dependence of the rate of adsorption onto BT6, HA and C-HA: a, b) – $Cd^{2+}$; c, d) – $Zn^{2+}$; e, f) – $Cu^{2+}$**

To explain the experimental data, the Langmuir isotherm equations in the linear form (3) and Freundlich (4) are applied.

In Fig. 5 showed the isotherms of adsorption of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions onto the adsorbents. The shapes of all adsorption isotherms have a characterization corresponding to the adsorption isotherms of Langmuir. The adsorption capacity of studied adsorbents towards $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ ions increases in the following order: BT6 < HA < C-HA.




**(a) (b)**

**(c) (d)**

**(e) (f)**

**Fig. 1. Isotherms of adsorption of ions: a, b) – $Cd^{2+}$; c, d) – $Zn^{2+}$; e, f) – $Cu^{2+}$ in the coordinates of Ce – qe and in the coordinates of Ce – Ce/qe**

The isotherm parameters determined by the graphical method of the Langmuir (1) and Freundlich (2) equations are presented in Table 1.

From the data in Table 1, it is established that the Langmuir isotherm is most fit for describing the adsorption of the ions onto the bentonite-like clay BT6, HA, and composite sorbent C-HA.

It has been established that the $q_m$ of the composite adsorbent towards $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions is 0.81; 0.71 and 0.73 mmol/g, respectively, which is over higher than of bentonite-like clay at 2.79; 1.92 and 2.43 times.

**Table 1. Parameters of the adsorption isotherm of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions calculated from the Langmuir and Freundlich models.**

| Ions | Adsorbent | Model parameters | | | | | |
|---|---|---|---|---|---|---|---|
| | | Langmuir | | | Freundlich | | |
| | | $q_m$, mmol/g | b L/mmol | $R^2$ | $k_f$ | n | $R^2$ |
| $Cd^{2+}$ | BT6 | 0.29 | 22.63 | 0.99 | 0.59 | 4.00 | 0.89 |
| | HA | 0.78 | 16.03 | 0.99 | 0.80 | 3.70 | 0.86 |
| | C-HA | 0.81 | 15.33 | 0.99 | 0.90 | 3.71 | 0.92 |
| $Zn^{2+}$ | BT6 | 0.37 | 3.25 | 0.99 | 0.60 | 4.00 | 0.91 |
| | HA | 0.66 | 10.45 | 0.99 | 0.74 | 4.00 | 0.87 |
| | C-HA | 0.71 | 17.47 | 0.98 | 0.84 | 4.76 | 0.93 |
| $Cu^{2+}$ | BT6 | 0.30 | 41.59 | 0.99 | 0.63 | 4.55 | 0.98 |
| | HA | 0.65 | 42.90 | 0.99 | 0.90 | 4.17 | 0.97 |
| | C-HA | 0.73 | 25.39 | 0.99 | 0.97 | 2.89 | 0.86 |

The $q_m$ of the composite adsorbent and hydroxyapatite towards $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions increases in the following order: $Cd^{2+} > Zn^{2+} \approx Cu^{2+}$. Increasing in the $q_m$ towards these ions can be explained that when adsorption of heavy metal ions with hydroxyapatite and a composite adsorbent, the replacement of calcium ions by heavy metal ions in the hydroxyapatite structure is one of the four adsorption mechanisms (ion-exchange, surface complexation, dissolution of surface hydroxyapatite and the formation of a new phase of metal phosphate, replacement of calcium ions by metal ions in the structure of hydroxyapatite) [26]. The degree of replacement of calcium ions by other cations depends on the ionic radius of the metal cation. Xu et al. [27] concluded that cations whose ionic radius were smaller than calcium (0.99Å) can be incorporated in the apatite structure to a much lesser extent than those cations of larger ionic radius. These results are consistent with our experimental results. Cations $Zn^{2+}$ (0.74Å) and $Cu^{2+}$ (0.74Å) can be more difficult to co-precipitate with calcium to form apatite structure than $Cd^{2+}$ cation (0.97Å). Therefore, the $q_m$ of both hydroxyapatite and composite adsorbent towards $Cd^{2+}$ cations is higher than to the $Zn^{2+}$ and $Cu^{2+}$ cations (Table 1).

**Table 2. Maximum adsorption capacity of various adsorbents towards $Cu^{2+}$, $Zn^{2+}$ and $Cd^{2+}$ ions.**

| Adsorbent | Maximum adsorption capacity, mmol/g | | | References |
|---|---|---|---|---|
| | $Cd^{2+}$ | $Zn^{2+}$ | $Cu^{2+}$ | |
| **Natural bentonite** | 0.45 | 0.322 | 0.20 | [28, 29] |
| **Kaolinite** | 0.078 | 0.45 | 0.02 | [9, 30] |
| **Hydroxyapatite** | 0.592 | 0.568 | 0.58 | [27, 31] |
| **Bentonite-like clay (BT6)** | 0.29 | 0.37 | 0.30 | In this work |
| **Hydroxyapatite (HA)** | 0.78 | 0.66 | 0.65 | In this work |
| **Composite sorbent (C-HA)** | 0.81 | 0.71 | 0.73 | In this work |

The results for determining the maximum adsorption capacity of studied adsorbents towards $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions are presented in Table 2. From these data, it can be showed that the $q_m$ of the composite adsorbent (C-HA) is over higher than the adsorption capacity of traditional sorbents, for example: the comparation with natural clay (1.80, 2.21 and 3.65 times, respectively), kaolinite (10.4, 1.58 and 36.50 times, respectively), zeolite (16.26, 11.25 and 5.18 times respectively), active carbon (5.08, 4.20 and 7.30 times, respectively) and hydroxyapatite adsorption capacity (1.37, 1.25 and 1.26 times, respectively). The maximum adsorption capacity of the composite adsorbent (C-HA) towards $Cd^{2+}$ ions is also higher than that of the composite bentonite - magnetite (1.45 times), composite polyvinyl alcohol - hydroxyapatite (1.72 times) and composite polyacrylonitrile-organobentonite (1.74 times).

## 4. Conclusions

Potentiometric titration was used to establish that the $pH_{pzc}$ value of the bentonite-like clay of the Tam Bo (Lam Dong, Vietnam), synthesized hydroxyapatite and composite sorbent are 5.7, 6.9 and 6.8, respectively. A study was carried out the dependence of the efficiency of purification of model aqueous solutions $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions onto sorbents from the pH value. It was found that the optimum pH values are in the range 4 – 6. It was established that the adsorption of $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions from the model aqueous solution by the studied sorbents is consistent with the Langmuir adsorption model. The maximum adsorption capacity of the composite adsorbent towards $Cd^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ions is 0.81, 0.71 and 0.73 mmol/g, respectively, which is over 2.79, 1.92 and 2.43 times higher than the Lam Dong bentonite-like clay. The maximum adsorption capacity of the composite adsorbent towards $Cd^{2+}$ ions is higher than the $Zn^{2+}$ and $Cu^{2+}$ ions, which is explained by the difference in their radius.

### Nomenclatures

| | |
|---|---|
| $C_e$ | Equilibrium concentration of heavy metals ions, mmol/L |
| $C_i$ | Initial concentration of heavy metals ions, mmol/L |
| $m$ | Mass of the adsorbent, g |
| $q_e$ | Adsorption capacity, mmol/g |
| $q_m$ | Maximum adsorption capacity, mmol/g |
| $V$ | Volume of a solution containing of heavy metals ions, L |

***Greek Symbols***

| | |
|---|---|
| $b$ | Constant of Langmuir adsorption equilibrium, L/mmol |
| $k_f$, $n$ | Constants of the Freundlich equation |

**Abbreviations**

| | |
|---|---|
| BT6 | The bentonite-like clay of the Tam Bo (Lam Dong, Vietnam) |
| C-HA | Composite adsorbents based on bentonite-like clay and hydroxyapatite |
| HA | Hydroxyapatite |
| PZC | The point of zero charge |

## References

1. Goldovskaya, L.F. (2005). *Chemistry of ambient environment* (in Russian). Moscow: MIR.

2. Kostin, A.V.; Mostalygina, L.V.; and Bukhtoyarov, O.I. (2012). Study of the mechanism of sorption of copper and lead ions on bentonite clay. *Sorption and Chromatographic Processes* (in Russian), 12(6), 949-957.
3. Gupta, V.; Rastogi, A.; Saini, V.K.; and Jain, N. (2006). Biosorption of copper (II) from aqueous solutions by Spirogyra species. *Journal of Colloid and Interface Science*, 296(1), 59-63.
4. Dai, X.; Breuer, P.L.; and Jeffrey, M.I. (2010). Comparison of activated carbon and ion-exchange resins in recovering copper from cyanide leach solutions. *Hydrometallurgy*, 101(1-2), 48-57.
5. Csefalvay, E.; Pauer, V.; and Mizsey, P. (2009). Recovery of copper from process waters by nanofiltration and reverse osmosis. *Desalination*, 240(1-3), 132-142.
6. Feng, D.; Aldrich, C.; and Tan, H. (2000). Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Minerals Engineering*, 13(6), 623-642.
7. Ribeiro, A.B.; Mateus, E.P.; Ottosen, L.M.; and Bech-Nielsen, G. (2000). Electrodialytic removal of Cu, Cr, and As from chromated copper arsenate-treated timber waste. *Environmental Science and Technology*, 34(5), 784-788.
8. Zhu, Z.; Zhang, W.; Pranolo, Y.; and Cheng, C.Y. (2012). Separation and recovery of copper, nickel, cobalt and zinc in chloride solutions by synergistic solvent extraction. *Hydrometallurgy*, 127-128, 1-7.
9. Jiang, M.-q.; Jin, X.-y.; Lu, X.-Q.; and Chen, Z.-l. (2010). Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. *Desalination*, 252(1-3), 33-39.
10. Charerntanyarak, L. (1999). Heavy metals removal by chemical coagulation and precipitation. *Water Science and Technology*, 39(10-11), 135-138.
11. Vesentsev, A.I.; Peristaya, L.F.; Glukhareva, N.A.; and Thuy, D.M. (2018). A composite sorbent based on bentonite-like clay and hydroxyapatite. *Journal of Fundamental and Applied Sciences*, 10(4S), 1099-1111.
12. Gupta, N.; Kushwaha, A.K.; and Chattopadhyaya, M.C. (2012). Adsorptive removal of $Pb^{2+}$, $Co^{2+}$ and $Ni^{2+}$ by hydroxyapatite/chitosan composite from aqueous solution. *Journal of the Taiwan Institute of Chemical Engineers*, 43(1), 125-131.
13. Corami, A.; Mignardi, S.; and Ferrini, V. (2007). Copper and zinc decontamination from single- and binary-metal solutions using hydroxyapatite. *Journal of Hazardous Materials*, 146(1-2), 164-170.
14. Hou, H.; Zhou, R.; Wu, P.; and Wu, L. (2012). Removal of Congo red dye from aqueous solution with hydroxyapatite/chitosan composite. *Chemical Engineering Journal*, 211, 336-342.
15. Wang, Y.; Chen, N.; Wei, W.; Cui, J.; and Wei, Z. (2011). Enhanced adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by low-molecular-weight organic acids. *Desalination*, 276(1-3), 161-168.
16. Ersan, M.; Guler, U.A.; Acıkel, U., and Sarioglu, M. (2015). Synthesis of hydroxyapatite/clay and hydroxyapatite/pumice composites for tetracycline removal from aqueous solutions. *Process Safety and Environmental Protection*, 96, 22-32.

17. Yakub, I. and Soboyejo, W. (2013). Adsorption of fluoride from water using sintered clay-hydroxyapatite composites. *Journal of Environmental Engineering*, 139(7), 995-1003.
18. Lenka, P.; Jana, K.; Hundakova, M.; Jana, S.; and Martynkova, G.S. (2016). Sorption of $Cd^{2+}$ on clay mineral/hydroxyapatite nanocomposites. *Journal of Nanoscience and Nanotechnology,* 16(8), 7788-7791.
19. Trofimov, S.Y.; Gorshkova, E.I.; and Salpagarova, I.A. (2008). *Ion exchange and adsorption in soils (in Russian)*. Moscow: KDU.
20. Mortada, W.I.; Kenawy, I.M.M.; Abdelghany, A.M.; Ismail, A.M.; Donia, A.F.; and Nabieh, K.A. (2015). Determination of $Cu^{2+}$, $Zn^{2+}$ and $Pb^{2+}$ in biological and food samples by FAAS after preconcentration with hydroxyapatite nanorods originated from eggshell. *Materials Science and Engineering C*, 52, 288-296.
21. Sokolova, T.A.; and Trofimov, S.Y. (2009). *Sorption properties of soils. Adsorption and ion exchange*. Moscow: Tula.
22. Tarasevich, Y.I.; Shkutkova, E.V.; and Janusz, W. (2012). Sorption of ions of heavy metals from aqueous solutions on hydroxyapatite. *Journal of Water Chemistry and Technology*, 34(3), 125-132.
23. Murray, H.H. (2007). *Applied clay mineralogy: Occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clays.* Amsterdam: Elsevier.
24. Kasamatsu, S.; and Sugino, O. (2018). First-principles investigation of polarization and ion conduction mechanisms in hydroxyapatite. *Physical Chemistry Chemical Physics*, 20(13), 8744-8752.
25. Mobasherpour, I.; Salahi, E.; and Pazouki, M. (2011). Removal of divalent cadmium cations by means of synthetic nano crystallite hydroxyapatite. *Desalination*, 266(1-3), 142-148.
26. Corami, A.; Mignardi, S.; and Ferrini, V. (2008). Cadmium removal from single-and multi-metal ($Cd^{2+}$ $Pb^{2+}$, $Zn^{2+}$ and $Cu^{2+}$) solutions by sorption on hydroxyapatite. *Journal of Colloid and Interface Science*, 317(2), 402-408.
27. Xu, Y.; Schwartz, F.W.; and Traina, S.J. (1994). Sorption of $Zn^{2+}$ and $Cd^{2+}$ on hydroxyapatite surfaces. *Environmental Science and Technology*, 28(8), 1472-1480.
28. Orolinovaa, Z.; Mockovciakova, A.; and Skvarla, J. (2010). Sorption of cadmium (II) from aqueous solution by magnetic clay composite. *Desalination and Water Treatment*, 24(1-3), 284-292.
29. Kubilay, Ş.; Gurkan, R.; Savran, A.; and Şahan, T. (2007). Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite. *Adsorption*, 13(1), 41-51.
30. Arias, F.; and Sen, T.K. (2009). Removal of zinc metal ion ($Zn^{2+}$) from its aqueous solution by kaolin clay mineral: A kinetic and equilibrium study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 348(1-3), 100-108.
31. Wang, Y.-J.; Chen, J.-H.; Cui, Y.-X.; Wang, S.-Q., and Zhou, D.-M. (2009). Effects of low-molecular-weight organic acids on Cu (II) adsorption onto hydroxyapatite nanoparticles. *Journal of Hazardous Materials,* 162(2-3), 1135-1140.