A COMPOSITE SORBENT BASED ON BENTONITE-LIKE CLAY AND HYDROXYAPATITE

Alexander I. Vesentsev
Belgorod State University.308015, Belgorod, Pobeda Street, 85, Russia
Lidiya F. Peristaya
Belgorod State University.308015, Belgorod, Pobeda Street, 85, Russia
Nadezda A. Glukhareva
Belgorod State University.308015, Belgorod, Pobeda Street, 85, Russia
Dang Minh Thuy
Belgorod State University.308015, Belgorod, Pobeda Street, 85, Russia

Abstract. The results of development of a composite sorbent based on bentonite-like clay and synthetic hydroxyapatite and investigation of its properties are discussed. Morphological, structural characteristics and phase composition of the experimental sorbents are studied by X-ray diffraction analysis, scanning electron microscopy, and infrared spectroscopy. The composite sorbent has been found to have more sorption capacity toward Pb2+ ions (1250.3 mg/g) as compared to the initial sorption active materials and conventional sorbents (activated carbon, bentonite, zeolites, etc.) as well as some composite sorbents based on hydroxyapatite. The developed composite sorbent provides 100% purification of water from Pb2+ ions at their initial concentration in an aqueous solution equal to 200 mg/g and sorbate : sorbent mass relation equal to 1:10.

Keywords: hydroxyapatite, montmorillonite, adsorption, composite sorbent.

1 Introduction

Waste water treatment has become a current problem all over the world since the latter half of the twentieth century. Some of the main pollutants of native water are heavy metal ions in waste waters from electroplating, mining plants, ironworks, non-ferrous smelters, machinery plants. Nowadays adsorption seems to be one of the most efficient techniques of fine purification of water (Charerntanyarak ,1999). The advantages of the sorption technique are the ability of fine purification of waste water from several pollutants and reactivation of waste adsorbents.

Activated carbons, synthetic organic products, some waste products such as ash, slags, wood scrap, mineral materials such as zeolites, clays, gaize, as well as silica, aluminogels, metal hydroxides have been explored as sorbents. Today ion exchange is also widely used for water treatment and a wide variety of ion-exchange materials has been developed. 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. The clay minerals concerned can swell because of increase of space between basal layers where ions or molecules absorbed are located (Vezentsev et al. ,2008).

Hydroxyapatite (HAP) $Ca_{10}(PO_4)_6(OH)_2$ has been known as the main inorganic constituent of bones and teeth of mammals and the component of phosphate mineral rocks (Gupta et al. ,2012). HAP can be used for the removal of toxic heavy metal ions, dyes, fluoride ions from aqueous solutions (Wang et al. ,2011). However, to separate suspended highly dispersed solid particles of HAP from the aqueous solutions after adsorption is quite difficult (Choi and Jeong ,2008; Dong et al. ,2010). Positive results of the application of composite materials based on HAP for water purification are known (Dong et al. ,2010). For instance, the composite materials such as hydroxyapatite hydrogel – polyacrylamide (Hyun et al. ,2008), hydroxyapatite – polyurethane (Jang et al. ,2008), hydroxyapatite – chitozan (Hou et al. ,2012, Fiorino, Víctor Martin, and Amparo Holguín. 2018) and hydroxyapatite – magnetite (Dong et al. ,2010) were used to remove toxic metals and dyes from aqueous solutions.

The development of composite sorbents based on bentonite-like clays combined with hydroxyapatite is of scientific interest. The aim of the work was the obtaining of the composite sorbents based on bentonite-like clays and hydroxyapatite prepared by the chemical precipitation and the investigation of sorption activity of the sorbents toward heavy metal ions as illustrated by Pb^{2+} as one of the most widespread pollutant.

2.1. Materials and Methods.

The following initial raw materials were used to prepare the composite sorbents: calcium hydroxide (analytical-reagent grade, GOST 9262-77), ortho-phosphoric acid (high grade, GOST 6552-80), and montmorillonite clay from Tam Bo deposite (province Lam Dong, Vietnam). The chemical composition of the clay was as follows (mass.%): SiO_2 (56.62), Al_2O_3 (20.90), Fe_2O_3 (6.71), MgO (2.26), CaO (0.62), TiO_2 (0.75), K_2O (1.38), MnO (0.040), Na_2O (0.067), others (0.035), mass loss ignition (10.58). The mineral composition was (mass.%) montmorillonite (47%), kaolinite (12%), illite (10%), dolomite (4%), quartz (21%), goethite (3%), chlorite (3%) (Vezentsev et al., 2015).

2.2. Hydroxyapatite synthesis

Hydroxyapatite was synthesized using the modified procedure (Borisovich et al. 2008, Nirmala, J. 2017)=) according to the following equation

$$10Ca(OH)_2 + 6H_3PO_4 = Ca_{10}(PO_4)_6(OH)_2\downarrow + 18H_2O.$$

To prepare nanosized colloidal hydroxyapatite we used a saturated calcium hydroxide aqueous solution elutriated from precipitated portlandite-like aggregates of calcium hydroxide after 24h settling. The concentration of the saturated calcium hydroxide solution was 0.02 mol/L.

HAP 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) till the pH of the mixture achieved 10.5±0.5, 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 in a baker at 105±5^{0}C for 5h. The samples were powdered in a porcelain mortar.

2.3. The preparation of the composite sorbent

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 pH10.5±0.5 was adjusted by adding a 2% ammonia solution. pH was measured with the pH meter Multitest IPL-101 (Russian Federation). The precipitate formed was allowed to settle for 24 h at room temperature and then separated, filtered, dried and powdered as described above. The particle size in the prepared composite sorbent was in the range 1– 10 μm.

The chemical and phase composition as well as structural-morphological characteristics of the products obtained were determined at BelSU Common Use Centre for Diagnostics of Nanomaterials' Structure and Properties. X-ray diffraction (XRD) patterns were recorded on a general purpose type diffractometer Rigaku Ultima IV (Japan) with D/teX Ultra detector. The electron-microscopic measurements were performed on a scanning electron/ion microscope Quanta 200 3D (USA) with an energy dispersive x-ray detector EDAX. IR-specters were made on a IR Fourier spectrometer IRPrestige-21 (Shimadzu). The measurement range was 4000-400 sm^{-1}, the reference material was KBr.

The sorption ability of bentonite-like clay, HAP and the composite sorbent bentonite–hydroxyapatite (CBH) was determined at static conditions using model solutions of lead (II) nitrate. Pb^{2+} concentrations in the solutions were measured using spectrophotometry on SPECORD 50 PLUS (Germany).

The sorption capacity q_e was calculated as

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where q_e (mg/g) is the sorption capacity at equilibrium, C_0 and C_e are the initial and final concentrations of Pb^{2+} ions (mg/L), m is the mass of a sorbent (g), V is volume of a model solution Pb^{2+} (L).

The maximal sorption capacity q_m (mg/g), and the constant of the sorption equilibrium b (L/mg) were calculated according the linearized Langmuir isotherm
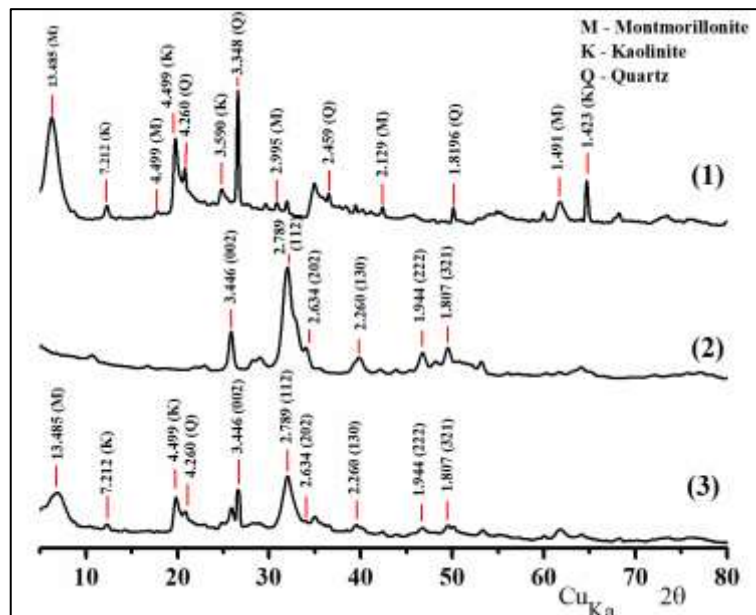
$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{2}$$

.

3. Results and Discussion

3.1. Phase composition of the experimental sorbents

Phase composition and purity of the products prepared were confirmed by XRD. X-ray powder diffraction patterns are shown in Fig. 1.

Fig. 1 X-ray powder diffraction patterns of bentonite-like clay (1), HAP (2), CBH (3)

The curve 1 demonstrates the presence of the some minerals, namely montmorillonite with the main reflection 13.485, 4.499, 2.995, 2.129, 1.491 Å, kaolinite with 7.212, 4.499, 3.590, 1.423 Å, quartz 4.260, 3.348, 2.459, 1.189 Å.

The curve 2 obtained for the synthesized HAP is absolutely identical with that for typical hydroxyapatite (PDF card № 01-074-3709), other phases are not detected.

Peaks corresponding to X-rays reflection from families of Miller planes of the crystalline lattice with values of interplane distance of 3.446 (002), 2.789 (112), 2.634 (202), 2.260 (130), 1.944 (222), 1.807 (321) Å are observed on XRD pattern for the composite sorbent (curve 3). These reflections confirm the formation of the crystalline structure of HAP (Jie and Yubao 2004; Wang et al. 2011) in the composite sorbent as well.

3.2. Morphological characteristics of the experimental sorbents

Particle morphology of bentonite-like clay, HAP, and CBH is shown in Fig. 2. The particles of bentonite-like clay are detected either as aggregates with size in the range 5–10 μm or as separate, predominately platelike particles with size to 3 μm (Fig. 2.1). HAP is a white powder consisting of agglomerated particles from 1 to 10 μm (Fig. 2.2). Fig. 2.3 shows that the surface of bentonite-like clay particles (5–10 μm) is covered by the crystals of hydroxyapatite (1–5 μm).
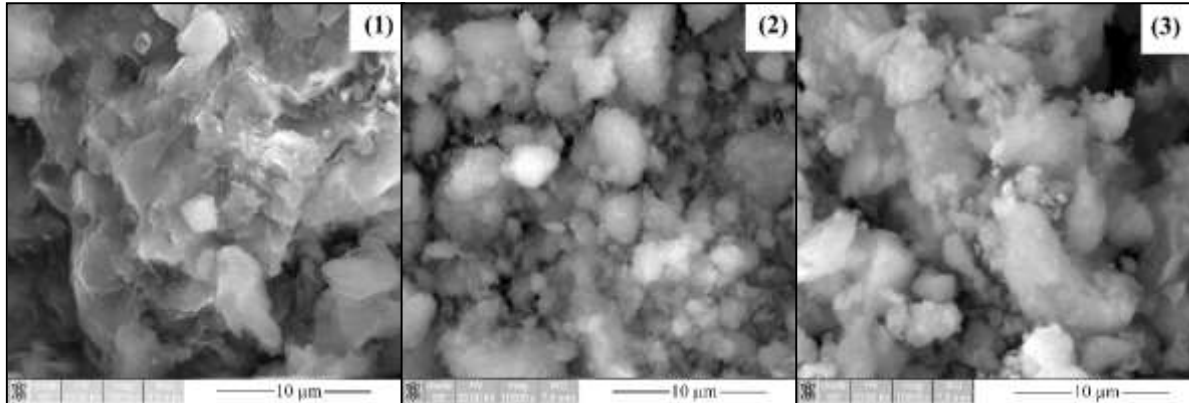

Fig. 2 SEM images of bentonite-like clay (1), HAP (2), CBH (3)

3.3. The structural characteristics of the experimental sorbents

IR spectra of the experimental sorbents are shown in Fig. 3. The curve 1 for bentonite-like clay from Tam Bo demonstrates specific bands in the range of stretching and deformation vibrations of structural groups for the main mineral montmorillonite. A sharp and intensive band with good resolution at 3619; 3697 and 913 cm^{-1} in the range of deformation stretch vibrations of the X-OH groups (where X is Al, Si) is associated with octahedral cations (Zhirong et al. 2011). The peaks of maximal absorption at 3419 and 1643 cm^{-1} are attributed to the stretching and deformation vibrations of water molecules (Tarasevich and Ovcharenko 1975; Tyagi et al. 2006). Peaks in the range 1000–1100 cm^{-1}, namely the bands at 1032 cm^{-1} correspond to the stretching of bridging linkages Si–O–Si in the crystalline lattice. The bands at 462 и 693 cm^{-1} are assigned to the deformation vibration of the Si–O–Si angle (Zhirong et al. 2011).

Fig. 3 IR-spectres of bentonite-like clay (1), HAP (2), CBH (3)
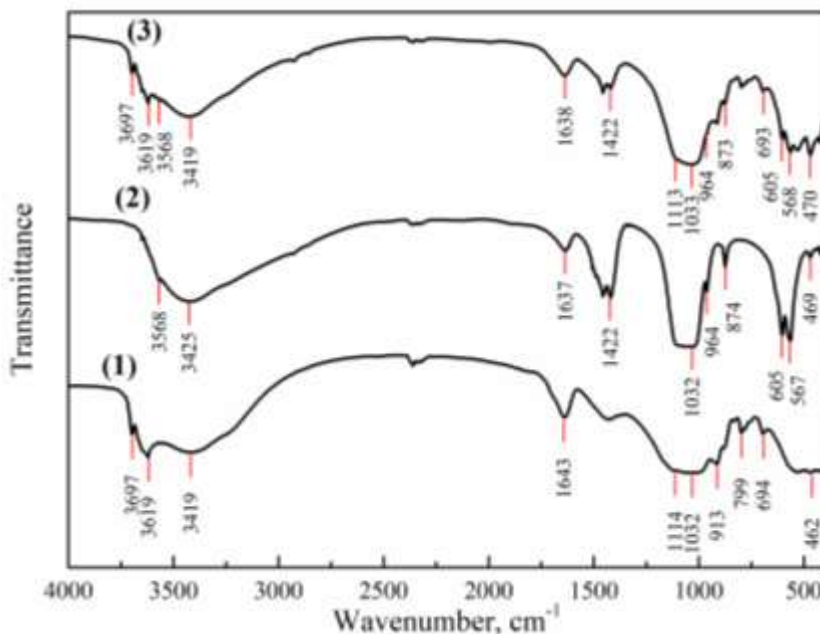
The typical of stoichiometric HAP bands can be seen on Fig. 3 (curve 2). They are the $(OH)^-$ band at 3570 cm$^-$^{1}, the bands of $(PO)_4^{3-}$ stretch vibrations at 1092 (a weak shoulder), 1033, and 963 cm^{-1}, the bands of $(PO)_4^{3-}$ deformation vibrations at 604, 566, and 470 cm^{-1}. The bands that are characteristic for vibrations of $(OH)^-$ groups and carbonate groups at 1420 и 875 cm^{-1} (Shahmohammadi et al. 2010; Thamaraiselvi et al. 2006) are also detected on the spectrum. These groups partially replace $(PO)_4^{3-}$ when been introduced into HAP structure during the synthesis due to absorption of CO_2 from air. However, the amounts of these impurities are negligible, so that carbonates cannot be revealed by X-ray diffraction. An effective surface of HAP nano-powder encourages sorption of a substantial amount of water. Stretching vibrations of absorbed water and crystallization water give rise to absorption in the range 3500–2900cm^{-1}, the band at 1671 cm^{-1} corresponds to deformation vibrations of H–O–H (Zakharov and Sentsov 2011). The bands that are specific to both of bentonite-like clay and stoichiometric HAP are present in the spectrum of the composite sorbent (curve 3).

3.4. The investigation of the ability of the experimental sorbents to absorb Pb^{2+}ions

To determine the maximal sorption capacity of the developed sorbents the experiments were carried out at the following conditions: mass of a sorbent sample was 0.1 ± 10^{-3}g, the initial concentration of Pb^{2+} in model aqueous solutions varied from 40 mg/L to 2600 mg/L, temperature was 20 – 22°C, pH = 5 – 5.5, sorption time was up to 3 h.

Kinetic curves of Pb^{2+} ions sorption by the experimental sorbents from model aqueous solutions are shown in Fig. 4. The concentration of Pb^{2+} ions is lowered by a factor of 1.3 after 5 min of sorption by bentonite-like clay, and sorption equilibrium is virtually achieved in an hour at the final concentration 58.65 mg/L. The initial rate of Pb^{2+} sorption by HAP is higher than that by clay, the concentration of Pb^{2+} ions halves after 5 min, but sorption equilibrium is attained much slower. Additional experiments have shown that the equilibrium state is achieved after 24 h and the equilibrium concentration is 11 mg/L. The highest rate of sorption is observed for the composite sorbent CBH which absorbs Pb^{2+} completely in one hour.
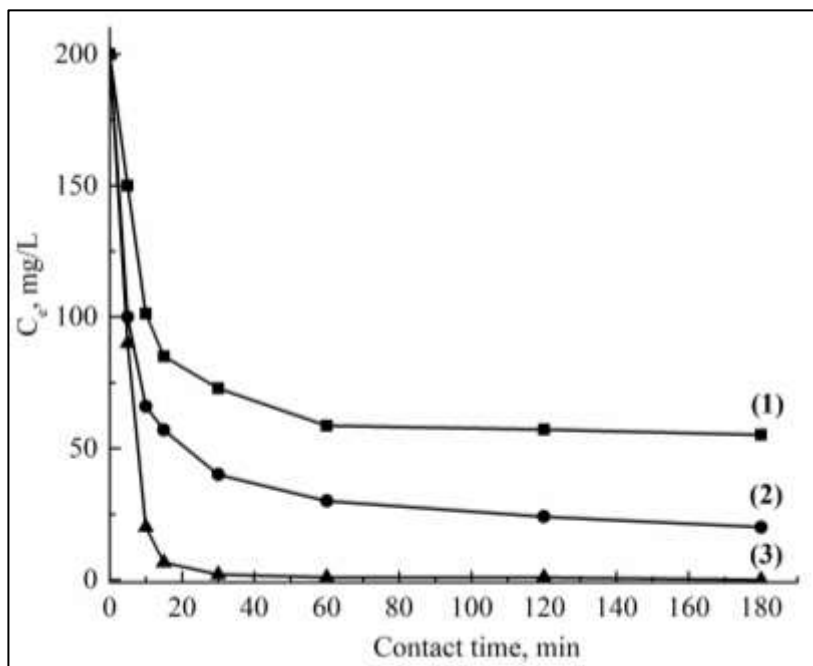

Fig. 4 Kinetic curves of Pb^{2+} ions sorption from model aqueous solutions of the initial concentration 200mg/L: bentonite-like clay (1), HAP (2), CBH (3).

Data on lead removal efficiency from model aqueous solutions are summarized in Table 1. They exhibit that water purification efficiency is 71.7 % after 3 hour exposure of bentonite-like clay and 90 % for hydroxyapatite whereas the composite sorbent demonstrates the maximal efficiency equal to 100 % at the same conditions.

Table 1 The efficiency of lead ions removal from model aqueous solutions by the experimental sorbents

Purification efficiency mass %	Time, min					
	10	15	30	60	120	180
Bentonite-like clay	45	59.4	67.5	63.6	70.7	71.4	77.7
Hydroxyapatite (HAP)	60	67	71.5	80	85	88	90

| Composite (CBH) | | 9 | 9 | 9 | 1 | 1 | 1 |
| | 5 | 0 | 6.8 | 9 | 00 | 00 | 00 |

All the sorption isotherms for the experimental sorbents shown in Fig. 5a resemble Langmuir adsorption isotherms. Experimental data taken as C_e/q_e versus C_e fit straight lines with the correlation index more than 0.99 (Fig. 5b). The maximal sorption capacities (q_m) and the constants of sorption equilibrium (b) for the investigated samples calculated from these linearized isotherms are given in Table 2. The sorption capacity of the experimental sorbents toward Pb^{2+} ions increases in the same consequence like as the initial rate of sorption that is bentonite-like clay – HAP – CBH.
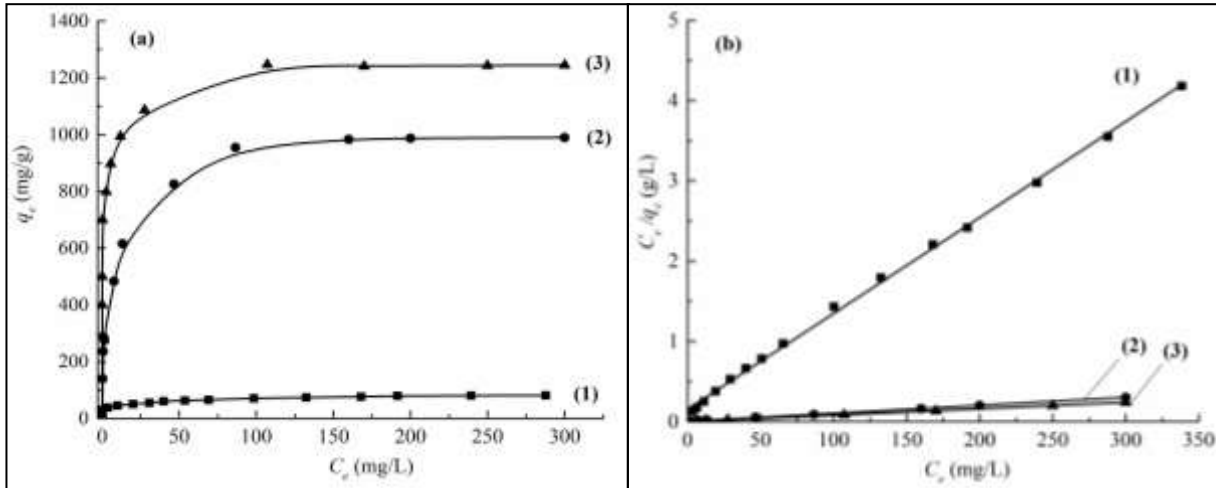

Fig. 5 Sorption isotherms (a) and linearized sorption isotherms (b) of Pb^{2+} ions from aqueous solutions by bentonite-like clay (1), HAP (2), CBH (3).

Table 2 The sorption characteristics of the experimental sorbents

Sorbent	q_m (mg/g)	b (L/mg)
Bentonite-like clay	82.6	0.093
Hydroxyapatite (HAP)	1005.1	0.385
Composite (CBH)	1250.3	0.727

Values of the maximal sorption capacity of some sorption active materials including some hydroxyapatite based composites are compared in Table 3.The maximal sorption capacity of our composite sorbent (CBH) is much more than those for conventional sorbents such as activated carbon (40.06 fold), kaolinite (68.5 fold), natural bentonite (65.14 fold), natural and synthetic zeolite (18.94 and 9.4 fold respectively). It is also higher than that for hydroxyapatite and Ca-deficient carbonated hydroxyapatite (1.25 and 2.96 fold respectively) as well as for hydroxyapatite– magnetite composite (2.1 fold), being approximately close to the maximal sorption capacity for chitozan/Fe-hydroxyapatite composite.

Table 3 The comparison of the maximal sorption capacity toward Pb^{2+} ions

Sorbent	The maximal sorption capacity, mg/g	Ref.
Activated carbon	31.2	(Machida et al. 2005)
Kaolinite	18.25	(Adebowale et al. 2006)
Natural bentonite	19.19	(Kul and Koyuncu 2010)
Natural zeolite	66	(Kragović et al. 2012)
Modified zeolite	133	(Kragović et al. 2012)
Hydroxyapatite	1000	(Mobasherpour et al. 2012)
Hydroxyapatite – magnetite composite	598.8	(Dong et al. 2010)
Chitozan/Fe- hydroxyapatite composite	1385	(Saber-Samandari et al. 2014)

	Ca-deficient carbonated hydroxyapatite (mole relation Ca/(P+C) – is 1.67)	422	(Dat et al. 2015)
0	Bentonite-like clay	82.6	The author's data
1	Hydroxyapatite (HAP)	1005.1	The author's data
2	Composite (CBH)	1250.3	The author's data

2 Conclusion

The composite sorbent based on bentonite-like clay and synthetic hydroxyapatite has been developed. It is found by X-ray diffraction analysis, scanning electron microscopy, and infrared spectroscopy that hydroxyapatite prepared according the modified technique is of high purity. Hydroxyapatite crystals are found to be located on the surface of minerals composing bentonite-like clay in the developed composite sorbent. The investigated sorbents can be arranged in increasing order according to their sorption rate and efficiency as follows bentonite-like clay < hydroxyapatite< composite sorbent.

Pb^{2+} ions sorption from model aqueous solutions by the developed sorbents is found to be described by Langmuir sorption equation in the range of initial concentrations $40 - 2600$ mg/L. The composite sorbent has the higher sorption capacity toward Pb^{2+} ions as compared to hydroxyapatite and bentonite-like clay from Lam Dong and provides the maximal purification efficiency (100%) at the initial concentration of Pb^{2+} equal to 200 mg/L and mass relation Pb^{2+} : sorbent equal to 1:10.

References

1. Adebowale, K. O., Unuabonah, I. E., Olu-Owolabi, B. I., 2006. The effect of some operating variables on the adsorption of lead and cadmium ions on kaolinite clay. Journal of Hazardous Materials, 134: 130-139.
2. Borisovich, I. M., Nikolaevna, V. N., Romanovich, K. Y., 2008. RU. Patent No. 2342319. Official publication of the patent of the Russian Federation.
3. Charerntanyarak, L., 1999. Heavy metals removal by chemical coagulation and precipitation. Water Science and Technology, 39: 135-138.
4. Choi, S., Jeong, Y., 2008. The removal of heavy metals in aqueous solution by hydroxyapatite/cellulose composite. Fibers and Polymers, 9: 267-270.
5. Dat, D. V., Troubitsyn, M. A., Thuan, L. V., Cao, N. P., Gudkova E.A., 2015. Investigation of sorption of lead ion from simulated body fluid solution by nanocrystalline Ca-deficient carbonated hydroxyapatite Sorption and chromatographic processes, 15:269-279.
6. Dong, L., Zhu, Z., Qiu, Y., Zhao, J., 2010. Removal of lead from aqueous solution by hydroxyapatite/magnetite composite adsorbent. Chemical Engineering Journal, 165:827-834.
7. Fiorino, Víctor Martin, and Amparo Holguín. "El otro en Laín Entralgo: encuentro interhumano, diálogo y convivencia." Opción 34.86 (2018): 518-546.
8. Gupta, N., Kushwaha, A. K., 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: 125-131.
9. Hou, H., Zhou, R., Wu, P., Wu, L., 2012. Removal of Congo red dye from aqueous solution with hydroxyapatite/chitosan composite. Chemical Engineering Journal, 211:336-342.
10. Hyun, J. S., Gyu, J. Y., Gil, M. B., Seok, L. W., Cheol, L. S., 2008. Preparation and lead ion removal property of hydroxyapatite/polyacrylamide composite hydrogels. Journal of Hazardous Materials, 159:294-299.
11. Jang, S. H., Min, B. G., Jeong, Y. G., Lyoo, W. S., Lee, S. C., 2008. Removal of lead ions in aqueous solution by hydroxyapatite/polyurethane composite foams. Journal of Hazardous Materials, 152: 1285-1292.
12. Jie, W., Yubao, L., 2004. Tissue engineering scaffold material of nano-apatite crystals and polyamide composite. European Polymer Journal, 40:509-515.
13. Kragović, M., Daković, A., Sekulić, Ž., Trgo, M., Ugrina, M., Perić, J., Gatta, G. D., 2012. Removal of lead from aqueous solutions by using the natural and Fe (III)-modified zeolite. Applied Surface Science, 258:3667-3673.
14. Kul, A. R., Koyuncu, H., 2010. Adsorption of Pb (II) ions from aqueous solution by native and activated bentonite: kinetic, equilibrium and thermodynamic study. Journal of Hazardous Materials, 179: 332-339.
15. Machida, M., Yamazaki, R., Aikawa, M., Tatsumoto, H., 2005. Role of minerals in carbonaceous adsorbents for removal of Pb (II) ions from aqueous solution. Separation and purification technology, 46: 88-94.
16. Mobasherpour, I., Salahi, E., Pazouki, M., 2012. Comparative of the removal of Pb^{2+}, Cd^{2+} and Ni^{2+} by nano crystallite hydroxyapatite from aqueous solutions: Adsorption isotherm study. Arabian Journal of Chemistry, 5: 439-446.
17. Nirmala, J. (2017). Structure of liquid and comparison of adhesive force with cohesion force. International Journal of Engineering, Science and Mathematics, 6(2), 19-27.

18. Saber-Samandari, S., Saber-Samandari, S., Nezafati, N., Yahya, K., 2014. Efficient removal of lead (II) ions and methylene blue from aqueous solution using chitosan/Fe-hydroxyapatite nanocomposite beads. Journal of environmental management, 146:481-490.

19. Shahmohammadi, M., Jahandideh, R., Behnamghader, A., Rangie, M., 2010. Sol-gel synthesis of FHA/CDHA nanoparticles with a nonstochiometric ratio. International Journal of Nano Dimension, 1:41-45

20. Tarasevich, U. I., Ovcharenko, F. D., 1975. Adsorption on clay minerals. Kiev: Naukova Dumka. (In Russian).

21. Thamaraiselvi, T. V., Prabakaran, K., Rajeswari, S., 2006. Synthesis of hydroxyapatite that mimic bone minerology. Trends Biomater Artif Organs, 19: 81-83

22. Tyagi, B., Chudasama, C. D., Jasra, R. V., 2006. Determination of structural modification in acid activated montmorillonite clay by FT-IR spectroscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 64: 273-278.

23. Vezentsev, A. I., Goldovskaja L.F., Volovicheva N.A., Korol'kova S.V., 2008. Investigation of sorption efficiency of Cu(II) ions of Pb(II) by native forms of montmorillonite clays of the Belgorod region. Sorption and chromatographic processes, 8: 807-811.

24. Vezentsev, A. I., Nguen, H. C., Sokolovskiy, P. V., Bukhanov, V. D., Milyutin, V. V., Konkova, T. V., Alekhina, M. B., 2015. Composite sorbent on the basis of mineral and vegetable raw materials Sorption and chromatographic processes, 15: 127-133.

25. Wang, Y., Chen, N., Wei, W., Cui, J., Wei, Z., 2011. Enhanced adsorption of fluoride from aqueous solution onto nanosized hydroxyapatite by low-molecular-weight organic acids. Desalination, 276:161-168.

26. Zakharov, N. A., Sentsov, M. Y., 2011. The interaction of calcium hydroxyapatite and methylcellulose whencoprecipitazione. Sorption and chromatographic processes, 11: 177-184.

27. Zhirong, L., Uddin, M. A., Zhanxue, S., 2011. FT-IR and XRD analysis of natural Na-bentonite and Cu (II)-loaded Na-bentonite. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 79: 1013-1016.