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Sodium Alginate-Cellulose-Nano-Clay Composite Adsorbent Applied for Lead Removal from Wastewater

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***Abstract:** A sodium alginate/cellulose/n-clay composite was prepared as potential adsorbent for removal of Pb(II) from wastewater. The results showed that obtained adsorbent used for 4 mg L^{-1} initial concentration of Pb(II) in wastewater after 90 min adsorption time led to 90% removal efficiency and the adsorption capacity of the prepared composite was 0.11 mg $\cdot g^{-1}$. The isotherms and kinetics of adsorption revealed that the equilibrium adsorption and kinetics were well-described by the Langmuir model and pseudo-second-order kinetics, respectively.*

***Keywords**: polysaccharides, n-clay, cellulose, adsorbent, lead pollutant, isotherms, kinetic*

1. Introduction

Water is essential to life, and all living beings cannot survive without it. The rapid rising of the human population and industrial activities have led to an increase pollutants concentration in water [1]. Heavy metals represent a real threat for water quality. A 10 µg L^{-1} of lead ions in water was stipulated as guidelines value by the World Health Organization (WHO) [2]. At this concentration the blood lead levels for a child increased of approx. 0.2 µg L^{-1}. Exceeding the maximum admission allowed concentration of lead (Pb) from water is related to lethal illnesses, such as heart and circulatory diseases, cancer and AIDS [2]. Also, it is expected to increase the lead (Pb) in seawaters because a decreasing pH resulting in enhanced toxicity of lead to marine organisms [3].

Compared to other techniques such as ion exchange [4], a considerable attention has been done to the adsorption method for developing new, effective, and low cost processes to remove cation ions from wastewater [5,6].

Currently, polymeric systems of natural origin tested for the retention of heavy metals in aqueous solutions have received increased attention as material for retaining of pollutants due to their abundance, relatively low cost price, low carbon emissions and low impact on the environment [7-10]. Sodium alginate (SA) is a natural biodegradable polymer that is generally regarded as a safe substance because of its nontoxic properties, simplicity of handling, gel-enhancing properties, and biomedical applications [11,12]. The microspheres of alginate gelatinized by Ca ions have been used for retaining of pollutants [13-16]. Cellulose is a polysaccharides containing β-D-glucopiranosic units joined by β-1,4 glycosides bonds used for removal of a high number of pollutants from due to its special polymeric structure, inherent biodegradability, readily available, renewable source and comparatively low cost [16-18].

Alginate and clay compositions are known as adsorbents for the removal of total organic acid anions, in the form of salt [7], copper (Cu(II)) [19,20]. Spheres based on chitosan, sodium alginate and microcrystalline cellulose in a ratio of 2:8:1 were tested for removal of Pb(II) [21]. The optimal conditions for adsorption were: *p*H 6, adsorbent dosage 4 g, metal concentration 62.5 mg L^{-1} and temperature 50°C. In other paper, it has been shown that the adsorption of Pb(II) is maximum at *p*H

**email: rapa_m2002@yahoo.com; cristina_covaliu@yahoo.com* between 4-5 due to the fact that the number of free carboxyl groups present in the solution increases, which has the effect of intensifying the chemical adsorption [16].

In this work, a composite based on sodium alginate, microcrystalline cellulose and nano-clay has been prepared, characterised and tested as pottential adsorbent for the removal of lead ions from synthetic waters.

2. Materials and methods

Materials

Alginic acid sodium salt (SA) $(C_6H_7O_6Na)_n$ from algae (BioChemica) is characterized by a molecular weight in the range 10,000-600,000 g mol^{-1} and a viscosity of 350-550 mPa·s (1% la 20°C). Microcrystalline cellulose (Acros Organics, Germany) shows the average dimension of particle of 50 μm and a loss at drying 0.5%. n-clay ($H_2Al_2O_6Si$) (Aldrich) is characterized by a density 600 - 1100 kg m^{-3}, the average dimension of particle < 25 μm and a loss at drying < 18.0 %.

Calcium chloride ($CaCl_2{\cdot}2H_2O$) was used as crosslinker. Serial dilutions of 4 mg L^{-1}, 3 mg L^{-1} and 2 mg L^{-1} solutions, respectively, have been performed from 5 mg L^{-1} $Pb(NO_3)_2{\cdot}4H_2O$ stock solution (Merck).

Adsorbent obtaining

For the purpose of composite obtaining, 2 g alginic acid sodium salt has been dissolved in 100 mL distilled water by means of a magnetic stirrer at temperature of 90°C, for 4 h and 200 rot/min. 3 wt.% n-clay solution was prepared in distilled water. The alginic acid sodium salt solution/cellulose/n-clay composition at a weight ratio between components 1:25:2.5 was obtained by stirring for 1 h at room temperature and 200 rpm. With the help of a Syringe pump (Tong Li Tech device) with the following specifications: volume of syringe 50 mL, flow rate 180 mL/h, size of needle 18G, the obtained solutions have been poured into a 1.5M $CaCl_2{\cdot}2H_2O$ solution. The microspheres prepared have been maintained for 24 h in contact with the $CaCl_2$ solution and after that they were washed with distilled water and dried at 60°C for 8 h.

Investigation methods

The morphology and structure of composite adsorbent were examined using a scanning electron microscope (SEM, QUANTA 450 FEG) at a 1.2 nm resolution.

Zeta potential values of sodium alginate/cellulose/n-clay adsorbent were measured by the mean electrophoretic mobility (Zetasizer Nano, Malvern Instruments, UK) based on the dynamic light scattering technique. The solution surface charge was evaluated for pH values ranging from 2 to 12.

The adsorption capacity of adsorbent was carried out by contacting 1000 mg of adsorbent with 40 mL of Pb(II) solution at concentrations ranging from 2-4 mg L^{-1}, with stirring (200 rpm) at room temperature, for a maximum time of 90 minutes. The *p*H of the prepared solutions was in the range of 5-5.5 (measured with a Consort C831 Multiparameter analyzer). After reaching equilibrium, the solutions were filtered (Whatman filter paper No. 1) and the Pb(II) concentration in the filtrate was detected at 217 nm wavelength by an atomic absorption spectrometer (GBC 932 AB PLUS, from GBC Scientific Equipment PTY Ltd., Australia) with acetylene flame.

The removal of Pb (%) and adsorption capacity (q_e) were calculated according to Eq.(1) and Eq.(2):

$$Pb(II)\,(\%) = \frac{(C_0 - C_e)}{C_0} \cdot 100 \qquad (1)$$

$$q_e(mg \cdot g^{-1}) = \frac{(C_0 - C_e)\,x\,V}{m} \qquad (2)$$

where: C_0(mg L^{-1}) and C_e(mg L^{-1}) are the initial and equilibrium concentration of the Pb solution; m (g) is the weight of the adsorbent used; and V (L) is the volume of the metal ion solution.

In order to understand the adsorption mechanism of the pollutant, the pseudo-first-order kinetic model [22] and pseudo-second-order kinetic model [23] are used, represented by the following equations:

$$\text{Log}(q_e - q_t) = \log(qe) - k_1t/2{,}303 \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2\, q_e^2} + \frac{t}{q_e} \qquad (4)$$

where: q_e and q_t are the amount of Pb(II) ion removal per unit mass of adsorbent (mg g^{-1}) at equilibrium measured in time t (min), k_1 is the pseudo-first-order kinetic rate constant (L min^{-1}), and k_2 (g ($mg^{-1}min^{-1}$) is the pseudo-second-order kinetic constant.

Langmuir and Freundlich adsorption isotherms are used to describe the adsorption isotherms [24] based on the Eq. (5) and Eq. (6):

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L C_e} \qquad (5)$$

$$q_e = K_F\, C_e^{\frac{1}{n}} \qquad (6)$$

where:

Ce (mg L-1) is the equilibrium concentration of the Pb solution; q_e is the amount of Pb(II) ion removal per unit mass of adsorbent (mg g^{-1}) at equilibrium; q_{max} is the maximum adsoption capacity (mg g^{-1}); K_L is Langmuir isotherm constant (L mg^{-1}); K_F is Freundlich isotherm constant; n is the intensity of adsorption process.

Fourier transform infrared spectroscopy characterization (FTIR) with attenuated total reflectance (ATR) (Interspec 200-X Spectrophotometer, Interspectrum, Estonia) were applied to characterize the prepared adsorbent, in transmittance mode. The spectra of the prepared adsorbent before and after adsorption of Pb(II) were carried out in the 4000-700 cm^{-1} wavenumber range.

3. Results and discussions

Scanning Electron Microscopy (SEM)

The SEM images of sodium alginate/cellulose/n-clay microspheres and the image obtained after prearation of adsorbent are shown in Figure 1(a-d).

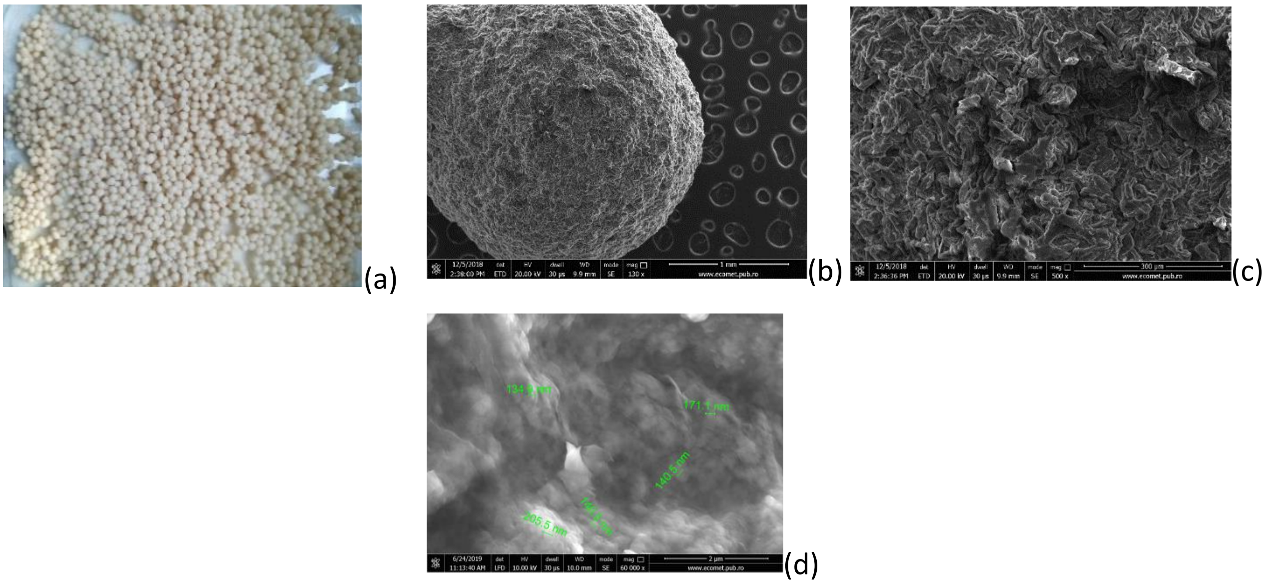


Figure 1. The image obtained after preparation of alginate/cellulose/n-clay microspheres (a) and the SEM images of sodium alginate/cellulose/n-clay microspheres (b-d).

The morphological characterisation of the obtained adsorbent revealed rough microspheres with a thickness ~3 mm (Figure 1b) and irregular surfaces with the particles having an average dimension in the range 134-205 nm (Figure 1d). The carboxyl (-COO-) and hydroxyl (-OH) groups present in sodium alginate and hydroxyl (-OH) groups of cellulose and clay facilitate the adsorption of metallic ion through the alginate/cellulose/n-clay composite.

EDX patterns of alginate/cellulose/clay composite are shown in Figure 2.

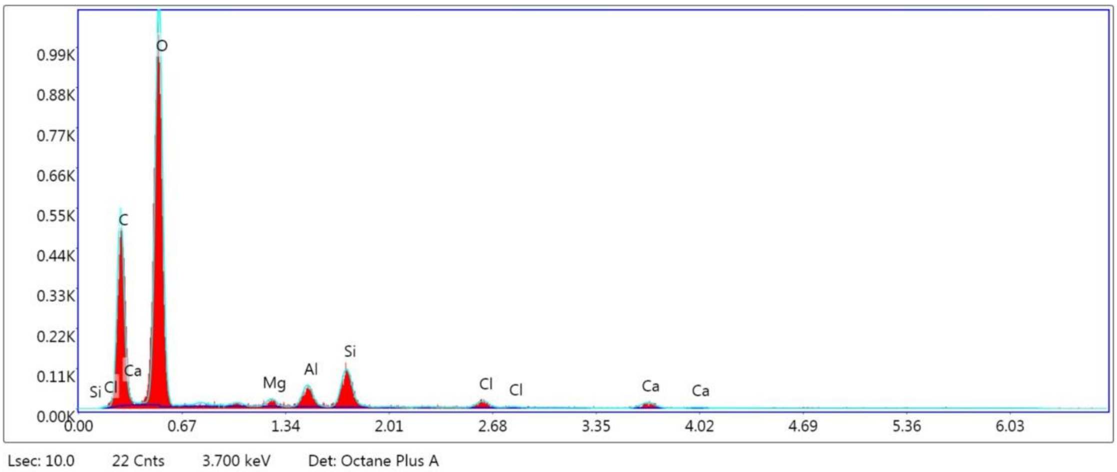


Figure 2. Energy dispersive X-ray patterns of alginate/cellulose/n-clay composite.

The energy dispersive X-ray (EDX) patterns of alginate/cellulose/n-clay composite exhibit following elemental composition: carbon 33.48 wt%, oxygen 52.73 wt.%, magnezium 0.88 wt.%, aluminium 2.66 wt.%, silicium 5.08 wt.%, and calcium 3.36 wt.%, confirming the presence of all components.

Zeta potential measurement

Zeta potential (Figure 3) shows that the investigated adsorbent has a negatively charged surface and the particle dispersions are stable in a pH range of 4 - 12. The proposed adsorption mechanisms for the retention of positively charged metal ions (Pb(II)) are electrostatic attraction and chelating process requiring that the adsorbent has the negatively charged surface.

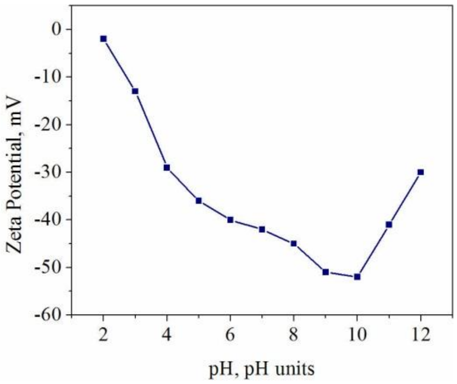
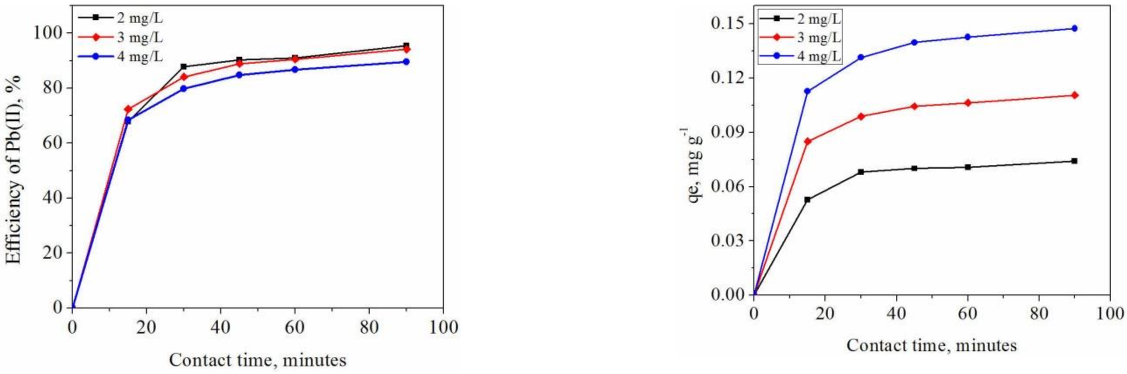


Figure 3. Zeta potential of sodium alginate/cellulose/n-clay adsorbent in the *p*H values ranging from 2 to 12.

Adsorption investigation

Efficiency of Pb(II) retention on microspheres, at different pollutant concentrations and the amount of metal adsorbed on one gram of microspheres, at different pollutant concentrations are shown in Figure 4.

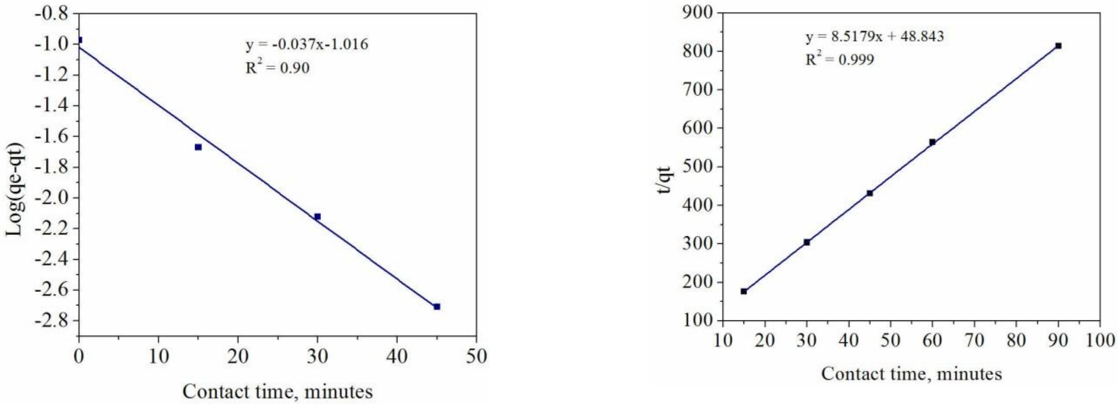


(a) (b)

Figure 4. Efficiency of Pb(II) retention on microspheres, for different pollutant concentrations (a) and the amount of lead adsorbed on one gram of microspheres, for different pollutant concentrations (b)

For 1g of adsorbent, the functional groups of sodium alginate, cellulose and n-clay lead to the increase of the number of active adsorption centers of the adsorbent, which has the effect of improving the adsorption of pollutant from water. After 15 min of investigation, for a concentration of 4 mg L^{-1} Pb (II) in water, an efficiency of over 60% of the investigated microspheres is recorded. After 90 minutes, the efficiency of Pb (II) removal from water increase to approx. 90% (Figure 4a). The increase of the pollutant concentration leads to a saturation of the active sites of adsorption, so that a decrease of about 10% of the efficiency of this composite material in contact with the pollutant at the concentration of 4 mg L^{-1} is observed compared with that of the pollutant of concentration 2 mg L^{-1}. Also from Figure 4b) is observed that the increase of the pollutant concentration is directly proportional with the amount of metal adsorbed on one gram of microspheres (q_e). In the case of other microspheres prepared from sodium alginate or other polysacharides [25] to retain methylene blue, the maximum adsorption capacity was 0.6 mg g^{-1}, after a contact time of 60 minutes.

In order to investigate the kinetic of the adsorption process of alginate/cellulose/n-clay microspheres, two models were used: the pseudo-first order kinetic model and the pseudo-second-order kinetic model (Figure 5(a, b)).



(a) (b)

Figure 5. Adsorption kinetic data for sodium alginate/cellulose/n-clay composite. Psedo-first-order kinetic model (a) and the pseudo-second-order kinetic model (b)

The obtained results are presented in Table 1.

Table 1. Kinetic parameters of sodium alginate/cellulose/n-clay adsorbent

at a 3 mg L^{-1} pollutant concentration

Pollutant concentration (Pb)	**Pseudo-first-order kinetic model**				**Pseudo-second-order kinetic model**		
	k_1 (L min^{-1})	$q_{e,\ calc.}$^{a} (mg g^{-1})	$q_{e,\ exp.}$^{b} (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	$q_{e,\ calc.}$ (mg g^{-1})	R^2
3 mg L^{-1}	0.0923	0.1123	0.1064	0.9000	1.488	0.1173	0.9990

[a] q_e, calc. is the calculated equilibrium adsorption capacity
[b] q_e, exp. is the experimental equilibrium adsorption capacity.

The experimental data obtained for the pseudo-second-order kinetic model indicates significantly higher correlation coefficients (R^2) compared to the pseudo-first-order kinetic model (Table 1). This allows us to conclude that the pseudo-second-order kinetic model best describes the behavior of the sodium alginate/cellulose/n-clay adsorption system. The equilibrium adsorption capacity calculated by the pseudo-second-order kinetic equation (0.1173 mg g^{-1}) was closer to the experimental value (0.1064 mg g^{-1}).

The fitting parameters are listed in Table 2.

Table 2. The isothermal adsorption parameters of sodium alginate/cellulose/n-clay adsorbent at 2 mg L^{-1}, 3 mg L^{-1} and 4 mg L^{-1} pollutant concentration, respectively

Langmuir Parameters				**Freundlich Parameters**		
q_{max} (mg g^{-1})	k_L (L mg^{-1})	R_L	R^2	k_F	1/n	R^2
0.300	1.813	0.22	0.9814	11.358	0.62	0.9592

As observed from Table 2, the correlation coefficient of the Langmuir model ($R^2 > 0.98$) was higher than that of the Freundlich model ($R^2 > 0.95$), which indicated that the experimental data fitted well with the Langmuir model.

The values of separation factor (R_L) indicates the tendency of the adsorption process, which can be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), irreversible ($R_L = 0$), and unfavorable (RL < 0) [26]. In the present study, the value of the separation factor (R_L) is 0.22 indicating that the adsorption of sodium alginate/cellulose/n-clay microspheres was favorable. Also, the maxim adsorption capacity (q_{max}) of this adsorbent (0.3 mg g^{-1}) is close to the experimental value. These data suggest that the adsorption takes place in a single monomolecular layer of the adsorbent. Chemosorption is the main mechanism of interaction between cationic pollutants and monolayer adsorption of adsorbents.

FTIR analysis

The attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra for sodium alginate/cellulose/n-clay composite before and after adsorption of Pb(II) are presented in Figure 6.

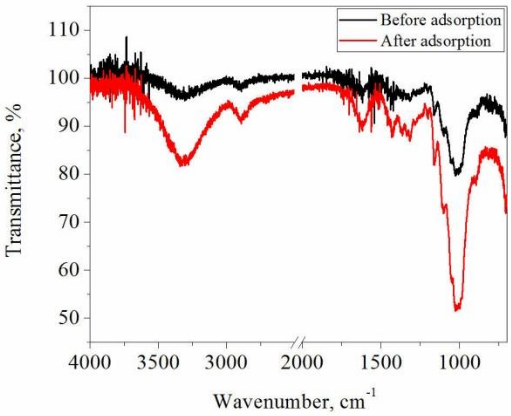


Figure 6. FTIR spectroscopy spectra of sodium alginate/cellulose/n-clay composite before and after adsorption of Pb(II)

The alginate/cellulose/n-clay adsorbent showed a maximum absorption at 3314 cm^{-1}, due to the stretching bond of the OH groups (due to alginate, cellulose and n-clay). The absorptions that appear at 1616 cm^{-1} and 1427 cm^{-1} are due to the symmetrical and asymmetrical stretching vibrations of the free carboxyl groups [27]. These peaks are shifted to smaller wavenumbers (1609 cm^{-1} and 1425 cm^{-1} respectively) after adsorption of the Pb ions. This indicates the formation of electrostatic interactions between the carboxyl groups of calcium alginate with the positive charge in clay. Peaks observed at 1016 cm^{-1} (in the case of the adsorbent) and respectively 1049 cm^{-1} (in the case of the absorbent that retained Pb) are attributed to the stretching vibration of the Si-O-Si bond. After the Pb(II) retention on the surface of the adsorbent is observed a wide absorption peak located at 3325 cm^{-1}. This confirms the formation of the bonds between Pb(II) and OH of the specific groups of the polysaccharides and the clay, as well as the presence of the stretching vibration of the water-specific O-H bond [28].

4. Conclusions

In this study, the sodium alginate/cellulose/n-clay microspheres with thickness ~3 mm and porous surfaces have been prepared.

The investigated microspheres showed ~90% efficiency to retain Pb(II) after 90 minutes in contact with the pollutant solutions at concentrations of 2-4 mg L^{-1}.

Testing the adsorption capacity of the composite revealed that the adsorption of Pb(II) corresponds to the pseudo-kinetic model of order II. The adsorption isotherms revealed that the adsorption takes place in a single monomolecular layer of the adsorbent.

The ATR/FTIR analysis used to highlight the Pb(II) retention by the prepared adsorbent revealed the shifting of the characteristic adsorption bands towards smaller wavelengths and the increase of the OH band adsorption intensity.

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