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Removal of lead (Pb^{2+}) from synthetic wastewater using calcium pectate

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The present work deals with the use of calcium pectate as a biosorbent for Pb(II) ions removal from aqueous solutions. Surface morphology of the adsorbent was analysed by scanning electron microscopy (SEM). The surface chemical nature of the biosorbent was studied by Fourier transform infrared spectroscopy (FTIR). The FTIR results revealed that amide, ether, alcohol and carbonyl functional groups are responsible for Pb(II) biosorption onto calcium pectate. Batch experiments were carried out to investigate the effects of pH, time, and initial metal ion concentration on the adsorption of Pb(II) ions by the biosorbent in synthetic wastewater. The optimum contact time and pH for the removal of Pb(II) ions were 480 min and pH 5.0, respectively. It was found that the maximum loading capacity of the biosorbent was 4.45 $mg \cdot g^{-1}$ for Pb(II) ions. Results indicated that the mechanism of Pb(II) ions adsorption onto calcium pectate is ion exchange between Ca(II) and Pb(II) ions in the solution. The equilibrium data were analysed according to the linear forms of the Langmuir and Freundlich isotherms. Freundlich model gives a better fit than the Langmuir model. The results suggest that calcium pectate can be used as an effective, low cost, and eco-friendly green adsorbent for the removal of Pb(II) ions from aqueous solutions.

Keywords: Calcium pectate; Adsorption; Lead; Langmuir isotherm; Freundlich isotherm.

INTRODUCTION

Heavy metal pollution has become one of the most serious environmental problems today [1]. Lead and other heavy metals are often detected in industrial wastewaters originating from metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing and photographic industries, etc. Heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders; therefore they must be removed before discharge [2]. Many wastewater treatment techniques are used worldwide for pollutant removal from aqueous solutions such as reverse osmosis, coagulation, membrane filtration, ion exchange and adsorption. Among all techniques, adsorption is considered as the most suitable process, because of its simplicity and cost effectiveness [3]. Currently a high number of experimental studies are carried out where modified or synthetic adsorbents are used for removal of heavy metals from water, but there is still not enough data about biosorbent usage for this purpose. Biosorption can be used as a cost-effective and efficient technique for the removal of toxic heavy metals from wastewater. Waste materials from industries such as food processing and agriculture may act as biosorbents [4]. Different biosorbents are tested for heavy metals removal form water, e.g. fruit wastes [4-6], fruit peels [7-13], watermelon rinds [14], passion fruit skins [15], garlic peels [16], chemically treated lemon residues [17], modified orange peels [18,19], chemically modified muskmelon peels [20].

The objective of this work was to determine the possibility of using calcium pectate as an effective adsorbent for the removal of Pb(II) ions from wastewater.

MATERIALS AND METHODS

Stock solutions of Pb (1000±2 ppm, Buck Scientific, USA) and Ca (1000±2 ppm, Carl Roth, Germany) were used for FAAS or GFAAS calibration. Standard solutions with the required Pb(II) concentrations (0.5, 1.0, 2.5, 5.0 mg L^{-1}) were prepared by appropriate dilution with deionized water. The pH of every solution was maintained at a desired value by adding 0.01 M NaOH or 0.01 M HNO_3.

Adsorbent acquisition and preparation

The modified pectin type LM-101 AS, supplied by CP Kelco, Denmark was used in the experiments. This type of pectin was selected because of its low degree of esterification (36%), which displays a higher calcium sensitivity than pectins of higher degree of esterification. This enables the formation of calcium pectate gels [21]. In order to obtain a biosorbent with higher adsorption capacity the method suggested by Jakóbik-Kolon *et al.* [22] was

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selected. Obtained hydrogels were filtered through glass fiber filter with 0.45 µm pore size and washed with deionized water to remove excess of calcium. Then the beads were dried at 30˚C for 72 h to obtain xerogels which were used for the adsorption and desorption of Pb(II).

Functional groups

A sample of the biosorbent was mixed with KBr and the functional groups were determined using a Perkin Elmer FTIR spectroscope.

Surface morphology

SEM examination of the biosorbent was done at 5 kV of accelerating voltage to study the surface texture and morphology of the biosorbent.

Adsorption procedure under dynamic conditions

Pb(II) solutions of desired concentrations (0.5, 1.0, 2.5, 5.0 mg L^{-1}) were prepared from the stock solution of Pb (1000±2 ppm) by appropriate dilutions at different pH values (2.0, 3.0, 4.0 and 5.0). Higher pH values were avoided to prevent lead precipitation as hydroxide. Above preci-pitation pH (5.0) Pb(II) ions are removed by both adsorption and precipitation. For determination of the effect of contact time on the adsorption of Pb(II) from the solution, the experiments were conducted by varying the agitation time from 0.5 h to 8 h until equilibrium was reached at the most efficient pH of the solution containing the highest concentration of lead. In order to describe whether the adsorption is physical or chemical the calcium release was measured on an atomic absorption spectrometer. All adsorption experiments were carried out using 1.0 g L^{-1} of calcium pectate xerogel beads. They were added to 50 mL of Pb(II) solutions in bottles with screwed tops which were closed hermetically. The biosorbent was shaken at room temperature (20±1^{o}C) for selected time intervals at a speed of 20 rpm (RS12, Labos Shake-Gerhardt, Germany) and vacuum filtered through 0.45 µm glass fiber filter. The amount of Pb(II) ions adsorbed at a time t, q_t (mg g^{-1}), was calculated using the following formula:

$$q_t = \frac{(Co - Ct)V}{(W)} \tag{1}$$

where C_t (mg L^{-1}) is the liquid phase concentration of Pb(II) ions at any time, C_0 (mg L^{-1}) is the initial concentration of Pb(II) ions in the solution. V is the volume of the solution (L) and W is the mass of dry biosorbent (g).

Effect of metal concentration

The concentration of Pb(II) was determined by assessing the static Pb(II) adsorption from the aqueous solution.

Freundlich isotherm

Freundlich isotherm is widely applied in heterogeneous systems [18]. Freundlich isotherm is expressed as:

$$\log qe = \log K_F + \frac{\log C_e}{n} \tag{2}$$

where qe is the amount of adsorbate in the biosorbent at equilibrium (mg g^{-1}); K_F - Freundlich isotherm constant (mg g^{-1}); C_e - equilibrium concentration of Pb(II) (mg L^{-1}); *n* - adsorption intensity.

Langmuir isotherm

Langmuir isotherm is expressed as:

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{bQ_oC_e} \tag{3}$$

where qe is the amount of adsorbate in the biosorbent at equilibrium (mg g^{-1}); Q_o - maximum monolayer coverage capacity (mg g^{-1}); b - Langmuir isotherm constant (L mg^{-1}); C_e - equilibrium concentration of Pb(II) (mg L^{-1}).

Analytical methods

Lead and calcium ion concentrations were determined using atomic absorption spectrometry (AAS; model Buck Scientific 210 VGP, USA) operated with an air-acetylene flame or graphite furnace, a slit of 0.7 mm at 283.2 and 400.7 nm wavelength, respectively.

Desorption procedure

After adsorption experiments the biosorbents were dried at 30±1˚C for 72 h and then mixed with 20 mL of 0.1 N HNO_3 solution. Samples were shaken on a RS-12 Rotoshake rotary shaker (Gerhard, Germany) for 0.5 h; 1 h; 4 h; 24 h at a speed of 20 rpm. After that the samples were filtered through glass fiber filter with 0.45 µm pore size. All experiments were conducted in triplicate and the mean of the three is presented. Blank samples (without Pb(II) ions) were used for validation studies. Concentrations of the Pb(II) ions in the blank solutions were below the detection limit.

RESULTS AND DISCUSSION

Imaging the surface of pectin gel beads using SEM microscope

The SEM image of calcium pectate xerogel was recorded (Fig 1). Though the beads seem to be oval in shape, the closer look reveals that their shape is uneven. The lighter colour shows salients and darker colour shows recesses. It is noticeable that the surface is irregular. One side of the bead is rougher than the other one. Steep slopes are also present. The biggest contrast between colours is at a zoom ×5000 which indicates that even at very low levels there is significant roughness. However, the pores of the biosorbent are not seen here.

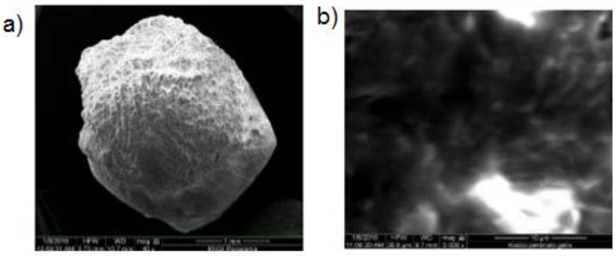

Fig. 1. SEM images of calcium pectate gel beads surface: a) ×40; b) ×5000.

Compared to the images recorded by Mata *et al.* [21], it is noticeable that the surface roughness is similar. Furthermore, authors' micrographs of the hydrogel revealed that, when hydrated, the gel bead pores open up and the structure becomes sponge-like. Thus, the pores open up and are visible in hydrogel state. The bead size was almost the same (about 3 mm) - two times bigger than that recorded by Mata *et al.* [21].

Functional groups of calcium pectate gel beads

The FTIR spectrum of calcium pectate xerogel was recorded and is shown in Fig. 2.

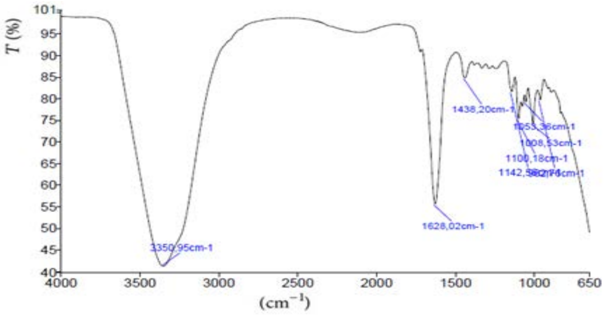

Fig. 2. FTIR spectrum of calcium pectate xerogel at 4000.0-650.0 cm^{-1}.

In the FTIR spectrum of calcium pectate xerogel, the peaks at 3350.95 cm^{-1} and 1628.02 cm^{-1} may be due to the presence of amide (N-H) groups. This bond is very important because highly amidated pectin does not need a lot of calcium to form gels. The other groups are: ethers (C-O), alcohols (C-O), carbonyls (C=O).

Effect of initial pH on the adsorption of Pb(II) ions

The effect of pH of the initial solution on the adsorption of Pb(II) ions onto calcium pectate beads was studied by varying pH from 2.0 to 5.0 at 20±1 °C (Fig. 3).

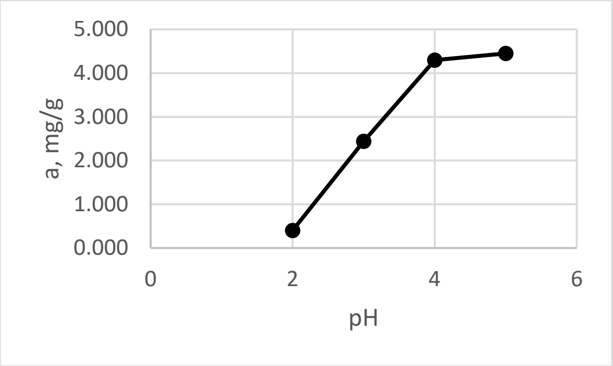

Fig. 3. Effect of pH on the adsorption of Pb(II) onto biosorbent. Pb(II) concentration = 5.0 mg L^{-1}, adsorbent:solution ratio = 1:1000 w:v, T = 20±1 °C, 480 min contact time.

The results indicate that the uptake capacity for Pb(II) ions increased from 0.41 mg g^{-1} to 4.3 mg g^{-1} in the pH range from 2.0 to 4.0. With further increase in pH of the solution from 4.0 to 5.0, the Pb(II) uptake capacity increased from 4.3 mg g^{-1} to 4.45 mg g^{-1}. The contact time was selected according to Mata *et al.* [22] and Gata-Jakobik *et al.* [23], where equilibrium contact time of 8 h was indicated. As optimal for Pb(II) removal the pH range from 4.0 to 5.0 was considered.

Effect of initial Pb(II) concentration on the adsorption of Pb(II) ions

The effect of initial Pb(II) concentration on the adsorption of Pb(II) ions onto calcium pectate was evaluated by means of adsorption isotherms. For this study, Langmuir and Freundlich isotherm equations were used to predict adsorption capacities of Pb(II) on calcium pectate. Figs. 4 and 5 show the Freundlich and Langmuir adsorption isotherms of Pb(II) by calcium pectate beads at an initial pH of 5.0.

The minimum selected Pb(II) concentration is 0.5 mg/L which is the limit concentration value in wastewaters to be discharged to a wastewater collection system, according to the respective legislation [23].

Results presented in Fig. 4 show that the removal rate of Pb(II) ions can be described with the Freundlich isotherm.

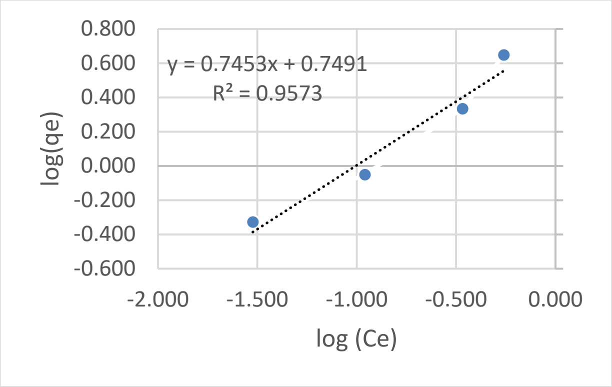

Fig. 4. Freundlich plots for Pb (II) adsorption at pH 5.0 onto the biosorbent. Adsorbent:solution ratio = 1:1000 w:v, T = 20±1 °C, 480 min contact, Freundlich isotherm parameters: n=1.342, K_F=5.612.

The Freundlich constant, K_F, unlike the Langmuir constant, Q_o, does not predict a saturation of the solid surface by the monolayer coverage of the adsorbate but it gives a relative measure of the adsorption capacity and estimates the bond strength. Favorable adsorption was registered because n was in the range of $1 < n < 10$.

Results presented in Fig. 5 show that the removal rate of Pb(II) ions can be described with the Langmuir isotherm.

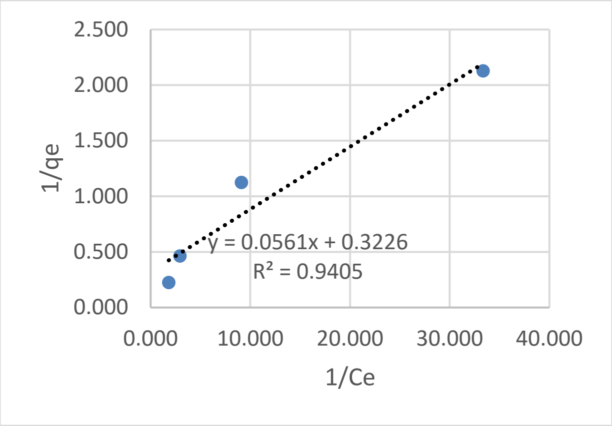

Fig. 5. Langmuir plots for Pb(II) adsorption at pH 5.0 onto the biosorbent. Adsorbent:solution ratio = 1:1000 w:v, T = 20±1 °C, 480 min contact, Langmuir isotherm parameters: Qo=3.1, b=5.75.

According to Hamdi *et al.* [24], the separation factor (R_L) can be used to determine whether or not the adsorption process will be favorable. The values of R_L were between 0.258 and 0.034 at an initial concentration of Pb(II) ions of 0.5-5.0 mg L^{-1}. These values are between zero and one indicating that the adsorption was favorable. The Langmuir model is an indication of the surface homogeneity of the adsorbent. The values of R^2 were found to be near 1.0, showing favorable adsorption. The values of the correlation coefficients of the Langmuir and Freundlich isotherms indicate that these models fit very well all adsorption equilibrium data throughout the studied experimental range. Therefore, it is assumed that adsorption involves a direct contact of metal ions onto the surface of biosorbent resulting in monolayer coverage. Freundlich model gives a better fit than the Langmuir model.

Effect of contact time on the adsorption of Pb(II) ions and the release of Ca(II) ions

Fig. 6 illustrates Pb(II) adsorption from synthetic wastewater as a function of contact time.

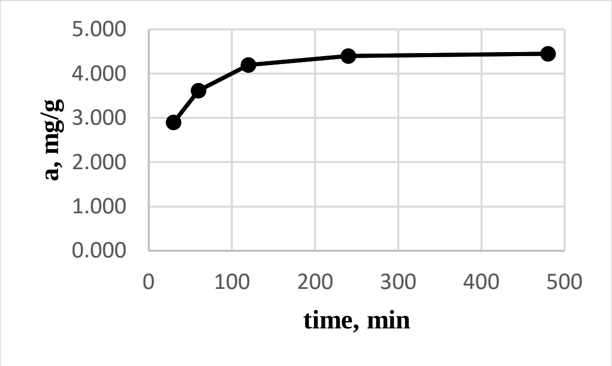

Fig. 6. Effect of contact time on Pb(II) adsorption at pH 5.0. Pb(II) concentration = 5 mg L^{-1}, adsorbent: solution ratio = 1:1000 w:v, T = 20±1 °C.

It is seen that the adsorption between 0.5 h and 8 h increased by 1.55 mg g^{-1} Pb(II). After 120 min the adsorption rate slowed down (Fig. 6). Fig. 7 illustrates the effect of contact time on Ca(II) release from the biosorbent into solution at pH 5.0 at a Pb(II) concentration of 5 mg L^{-1}.

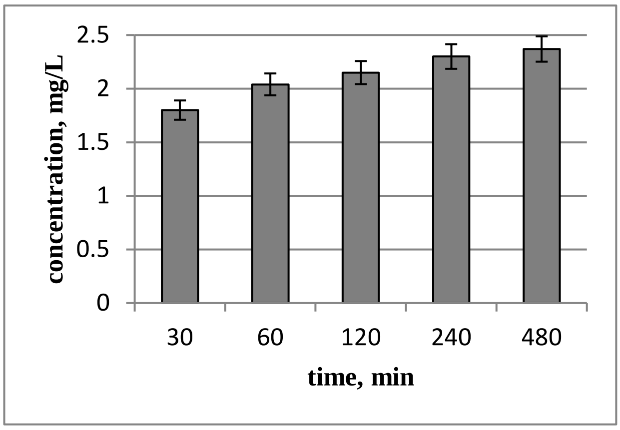

Fig. 7. Effect of contact time on calcium release from the biosorbent into solution at pH 5.0. Pb(II) concentration = 5 mg L^{-1}, adsorbent:solution ratio = 1:1000 w:v, T = 20±1 °C.

The contact time used in this experiment was 0.5 h; 1 h; 2 h; 4 h and 8 h. After the adsorption process was completed, calcium concentration was also determined. Mata *et al.* [25] have found a correlation between calcium release and metals uptake in calcium alginate and calcium pectate gel beads. Experimental results obtained in the present work were similar to those of Mata *et al*. [25] (Fig. 7). This correlation indicated that the process is ion exchange-based adsorption. Webb [26] has shown that both physical and chemical adsorption may simultaneously occur on the surface. A layer of molecules may be physically adsorbed on top of an underlying chemisorbed layer. This suggests that after all calcium was replaced, physical adsorption might took place. This can indicate two theories. Firstly, it can be assumed that there is more than one mechanism in this adsorption. Ion exchange mechanism is responsible for the release of calcium into the solution, and physical adsorption can also take place, as the organic material tends to attract heavy metals. Secondly, as FTIR results show, this particular pectin is not sensitive to gelation in the presence of calcium ions. This means that lower calcium amounts are adsorbed in the biosorbent preparation stage. Therefore, both theories do not contradict to each other and both can explain the obtained results.

Effect of contact time on the desorption of Pb(II) ions

Desorption helps the recovery of Pb(II) from the waste and the regeneration of the adsorbent in order to assess its potential as an adsorbent for commercial application. The desorption studies were carried out with the biosorbent after 8 h of adsorption. The results are presented in Fig. 8.

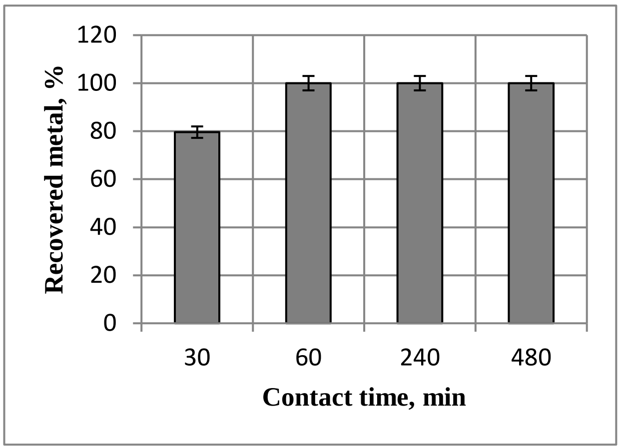

Fig. 8. Influence of contact time on the desorption of Pb(II) from 0.1 g of biosorbent in 20 mL of 0.1 N HNO_3 solution.

The results (Fig. 8) revealed that full desorption of lead was achieved in 60 min. Mata *et al.* [21] obtained the same result for lead. However, Agata-Jakobik *et al.* [22] did not reach 100 % of desorption. According to Mata *et al.* [25] a part of lead was retained in the biosorbent after each desorption cycle. Comparing to the desorption results of Isaac and Sivakumar [27] with apple peels, lead desorption was the same (almost 97 %) and equilibrium time was also 60 min. The equilibrium time for heavy metals removal using pectin is quite long (8 h) compared to other biosorbents (from 10 to 60 min depending on the particular natural biosorbent). However, the efficiency of Pb(II) removal is higher compared to natural biosorbents.

Studies have shown (Figs. 4–7) that the adsorption efficiency of lead onto calcium pectate beads depends not only on contact time and concentration, but also on pH of the solution. The remarkable results obtained in this study prompt us to use calcium pectate beads as an adsorbent for the treatment of wastewater polluted with lead.

CONCLUSIONS

1. FTIR analysis revealed the presence of different functional groups in the biosorbent - amide N-H, ether (C-O), alcohol (C-O) and carbonyl (C=O) functional groups which participate in the adsorption process.
2. Pb(II) uptake increases with an increase in contact time. The efficiency of Pb (II) adsorption increased from 58.0 to 89.0 % with an increase in contact time from 30 to 480 min. The adsorption equilibrium was achieved in 480 min.
3. A correlation was found between calcium release and metals uptake in calcium alginate and calcium pectate gel beads. This correlation indicated that the process is ion exchange-based adsorption.
4. Desorption from the biosorbent was influenced by the contact time. The desorption of Pb(II) at equilibrium (100 %) was reached in 60 min.
5. This study showed that the Freundlich and Langmuir equations can be used to describe the adsorption phenomena of Pb(II) onto calcium pectate gel beads.

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ОТСТРАНЯВАНЕ НА ОЛОВО (Pb^{2+}) ОТ СИНТЕТИЧНИ ОТПАДНИ ВОДИ С ИЗПОЛЗВАНЕ НА КАЛЦИЕВ ПЕКТАТ

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(Резюме)

Настоящата работа се отнася до използването на калциев пектат като биосорбент за отстраняване на Pb (II) йони от водни разтвори. Повърхностната морфология на адсорбента е анализирана чрез сканираща електронна микроскопия (SEM). Повърхностната химична природа на биосорбента е изследвана чрез инфрачервена спектроскопия с Фурие трансформация (FTIR). Резултатите от FTIR показват, че амидни, етерни, алкохолни и карбонилни функционални групи са отговорни за Pb (II) биосорбцията върху калциев пектат. Проведени са количествени експерименти за да се изследват ефектите на pH, времето и началната концентрация на металните йони върху адсорбцията на Pb (II) йони от биосорбент в синтетичните отпадни води. Оптималното време за контакт и pH за отстраняване на Pb (II) йони са съответно 480 минути и pH 5.0. Установено е, че максималният капацитет на биосорбента е 4.45 mg g^{-1} за Pb (II) йони. Резултатите показват, че механизмът на адсорбцията на Pb (II) йони върху калциев пектат е йонен обмен между Ca (II) и Pb (II) йони в разтвора. Данните за равновесието са анализирани в съответствие с линейната форма на изотермите на Langmuir и Freundlich. Моделът Freundlich е по-подходящ от модела Langmuir. Резултатите показват, че калциевият пектат може да бъде използван като ефективен, евтин и екологичен адсорбент за отстраняване на Pb (II) йони от водни разтвори.