

Equilibrium studies of sorption of lead(II) ions by different pectin compounds

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Abstract

The adsorption of Pb(II) ions from aqueous solution by different pectin compounds was studied in a batch sorption system. Water-soluble low- and high-esterified pectins and insoluble calcium pectate beads were investigated. The lead-binding capacity of all pectin compounds was highest within the pH range from 7 to 8. The binding capacities and rates of Pb(II) ions by pectin compounds were evaluated. The Langmuir, Freundlich and BET sorption models were applied to describe the isotherms and isotherm constants. Sorption isothermal data could be well interpreted by the Langmuir model. These results obtained through the study suggest that pectin compounds are favorable sorbers. The largest amount of Pb(II) ions were bound by pectin with the low degree of esterification. Therefore, pectin substances may be considered as perspective for sorption and removal of Pb(II) ions from wastewaters.

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1. Introduction

The effluents of industrial wastewaters often contain considerable amounts of toxic and polluting heavy metals. It is well known that heavy metals such as Hg, Pb, Cr, Ni, Cu, Cd and Zn are usually associated with tendency to accumulate in living organisms and are highly toxic when absorbed into body [1]. Releases of Pb(II) ions to the environment have been increasing continuously as a result of industrial activity and technological development, posing a significant threat to the environment and public health because of toxicity, incremental accumulation in the food chain and persistence in the ecosystem [2].

Owing to the wide use of the heavy metals, including lead, the efficient removal of them from wastewaters is an important and widely studied research area where a number of technologies have been developed over the years [3] including filtration, chemical precipitation, adsorption, electrodeposition and membrane systems. All these approaches have their inherent advantages and limitation, but mostly all of them either

expensive or low effective, particularly, in dilute solutions [4]. In recent years studies on polymers binding metal ions have increased significantly, which ion-exchange abilities are used in nuclear chemistry, electrochemistry, hydrometallurgy and environmental protection [5]. Chelation ion-exchange takes advantage of the three-dimensional structure of the molecules to chelate and remove ions [3]. This approach is inherently attractive since only the toxic metals are removed while the harmless ions can be released into the environment. Some of the best chelation ion-exchange materials are biopolymers.

Biopolymers are industrially attractive because they possess a capability of lowering transition metal-ion concentration to parts per billion concentrations, they are widely available and environmentally safe [4]. The group of biopolymers includes cellulose, alginates, carrageenans, lignins, some proteins, chitin and pectins. This study focuses on the pectin compounds and their Pb(II) removing capacity in aqueous solutions.

Pectins are the ionic plant polysaccharides, which main structural features are the linear chains containing more than 100 (1-4)-linked α -D-galacturonic acid residues [6], which metal binding capacity under in vivo and in vitro conditions was proved in the numerous studies [7–10]. At the same time, the studies

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Nomenclature

b	constant of the Langmuir equation
B	BET constant
C_0	initial solute Pb(II) concentration in the aqueous phase (mg L^{-1})
C_e	solute Pb(II) concentration in the aqueous phase at equilibrium (mg L^{-1})
K_F	parameter of the Freundlich equation
n	parameter of the Freundlich equation
q	amount of Pb(II) bound at final equilibrium concentration (mg g^{-1})
q_{max}	maximum sorption at monolayer (mg g^{-1})
R_L	separation factor of the Langmuir isotherm
V	volume of the Pb(II) solution (mL)
W	weight of the dry samples of high-esterified pectin, low-esterified pectin or calcium pectate (g)

on the capacity of different pectins to bind and remove lead ions from wastewaters were not carried out yet.

The main structural characteristic of all pectin substances is their degree of esterification indicating the number of galacturonic acid residues with methanol radical attached. According to the “egg-box” model (Fig. 1) of the metal binding mechanism of pectins [11], esterified residues are not active whereas negative charges of free carboxyl groups in pectin molecules form the covalent bonds with two valence metal ions. Thus, pectin with the low degree of esterification presumably exerts considerably higher sorption activity [12]. In our study, we have carried out batch experiments with three pectin compounds differing by their carboxyl residues of each pyranose cycle (Fig. 2). Low-esterified calcium pectate was in a form of water insoluble tiny beads whereas water-soluble pectins had the degree of esterification 60% and 1%. Water-soluble pectins bind the two valence metal ions forming a strong gel, which is prone to intensive seneresis and, therefore, can be easily filtered after the end of the process. In this study, the equilibrium of sorption of lead ions by pectin compounds were investigated. The influence of experimental conditions such as pH, agitation period, agitation rate and initial concentrations were studied. The Langmuir, Freundlich

and BET equations were used to fit the equilibrium isotherm. This will be useful for further application of system design in the treatment of practical waste effluents.

2. Materials and methods

2.1. Pectin preparation

High-esterified citrus pectin without additives was obtained from Copenhagen Pectin A/S, Lille Skensved, Denmark. The stated degree of esterification of this preparation was 60.0%. The pectin preparation contained no acetyl or amide groups. All other chemicals were of the highest quality available. Distilled water was used throughout.

Preparation of low-esterified pectin was performed using a technique of alkali de-esterification according to ref. [13] with modifications. The sample of high-esterified pectin was used for preparation of samples of low-esterified pectin and calcium pectate. Initially, pectin with the degree of esterification approximately 1.0% was prepared. During this process, 100 g of high-esterified citrus pectin was de-esterified in 1600 mL 50% ethanol containing 20 g NaOH and 20 g KOH (30 min at 20 °C). After acidification, pectin was isolated from ethanol by filtration.

For the preparation of calcium pectate beads 100 g of low-esterified pectin was suspended in 500 mL 70% athenol. Gradually, 100 mL of 70% ethanol solution containing 22.6 g $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ was added. A magnetic stirrer used to stir the solution. After the process was finished, calcium pectate was separated through a glass filter with a pore size 30–40 μm , rinsed with 800 mL 70% ethanol to remove any $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and dried at 60 °C. The beads were then ground by using a laboratory jar mill and sieved to a constant size (<250 μm) before use.

2.2. Pectin analysis

The galacturonan content of the pectin preparation was determined colorimetrically by the *m*-hydroxydiphenyl method [14]. The degree of esterification was characterized using titrimetric analysis with 1 M NaOH solution in 50% ethanol in the presence of Hintone indicator [15]. Intrinsic viscosity of low-esterified pectin was determined in 0.05 M NaCl/0.005 M Na-oxalate at

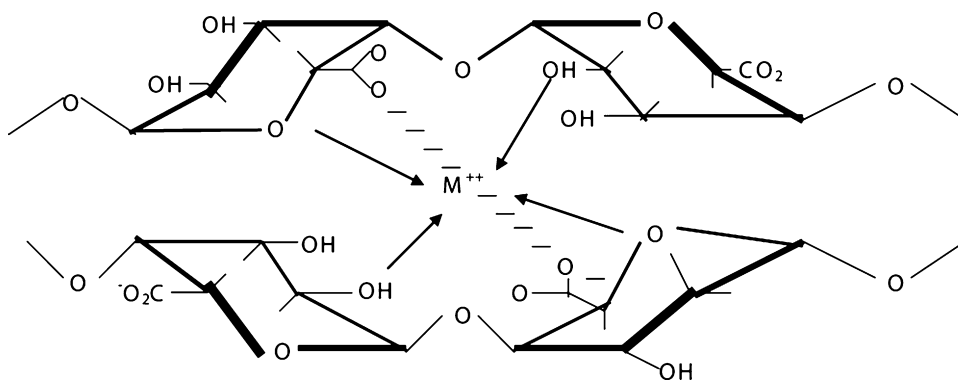


Fig. 1. The “egg-box” model of suggested mechanism for pectin metal binding capacity.

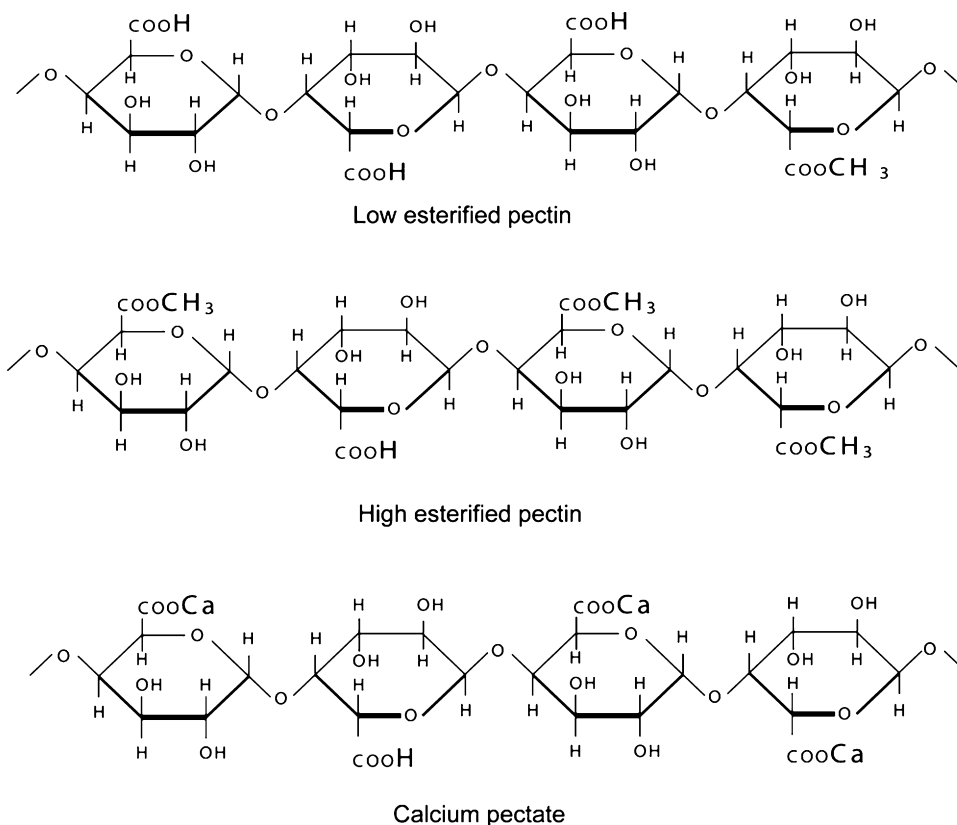


Fig. 2. Proposed structure of the low- and high-esterified pectins and calcium pectate samples used in the study.

25.0 °C and pH 6.0 using an Ubbelohde viscosimeter. The intrinsic viscosity was related empirically to the molecular weight by the Mark-Howink relation [16]. The calcium content in the calcium pectate sample was assayed by atomic-absorption and expressed in mg/g and mg-equivalents/g of sample [17].

2.3. Experimental procedures

Stock solutions (1.0 g L⁻¹) of Pb(II) ions was prepared by using analytical-reagent grade PbCl₂ (BDH). The stock solution was then diluted to give standard solutions of appropriate concentrations with controlled pH at 6.0 achieved by addition of either 0.1 M HCl or 0.1 M NaOH. Batch sorption experiments were conducted in 250 mL beakers and equilibrated using a magnetic stirrer. Then 50 mL aliquots of these standard solutions were placed in 250 mL beakers and added with 50 mL of solution containing 0.2 g of dry pectin preparation or 50 mL of suspension with 0.2 g of dry calcium pectate. Removal of pectin compounds from Pb(II) solution was performed by centrifuging at 3000 rpm for 10–20 min and following filtration through glass filter with a pore size 100–120 μm. Concentration of Pb(II) ions in supernatant was analyzed using an atomic absorption spectrophotometry method. The effect of Pb(II) sorption was studied in pH range 2–10. The pH of the initial solution was adjusted to the required pH value using either 0.1 M HCl or 0.1 M NaOH. Pectins were equilibrated at the particular pH for about 120 min at 400 rpm and at an initial Pb(II) concentration of 0.1 g L⁻¹ using a bath controlled at 30 °C.

The effect of agitation period also studied to determine the optimum condition for sorption of Pb(II) ions. For batch kinetic studies, 0.08 g calcium pectate or 8 mL of solution containing the same amount of dry pectin were equilibrated at optimum condition as mentioned earlier. The sorption system was placed in 250 mL beakers and stirred by a magnetic stirrer. At preset time intervals, the aqueous samples (5 cm³) were taken and the concentration of Pb(II) was analyzed.

Sorption equilibrium studies were conducted at optimum condition using a contact time of 120 min at pH 6 using a bath controlled at 30 °C. Isotherm studies were conducted with a constant pectin preparation amount (0.1 g) and varying initial concentration of Pb(II) in the range of 0.1–1.0 g L⁻¹. Each experiment was at least duplicated under identical conditions.

The metal accumulation (q) was determined as follow:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 is the initial Pb(II) concentration (mg L⁻¹), C_e the final or equilibrium Pb(II) concentration (mg L⁻¹), V the volume of the Pb(II) solution (mL) and W is the weight of the dry samples of high-esterified pectin, low-esterified pectin or calcium pectate (g).

The amount of the metal bound by the pectin compounds was expressed in milligram per gram of the dry sorbent.

3. Results and discussion

3.1. Pectin substrate

Chemical analysis of the pectin samples showed the following results. The content of pure galacturonan in the high-esterified pectin sample used in the experiments was 78.0%, degree of esterification was approximately 60.2%. The intrinsic viscosity of high-esterified pectin used was 352 mL/g of galacturonan. Molecular weight calculated using Mark-Howink equation was around 225 kDa.

The galacturonan concentration of the low-esterified pectin was 77.1%. The assay showed degree of esterification to be approximately 1.2%. The intrinsic viscosity of this pectin sample was 201 mL/g of galacturonan. Calculated molecular weight of low-esterified pectin was approximately 20 kDa. The free and esterified carboxyl groups in the both pectin macromolecules were distributed in a random pattern. Both pectins are water soluble at pH values higher than 2.0.

Degree of esterification of the calcium pectate beads prepared from the low-esterified pectin was also approximately 1.2%. Molecular weight was 20 kDa. Eighty six percent of carboxyl groups were presented in calcified form meaning calcium contents in the sample 38 mg/g of the pectate. Calcium pectate beads were not soluble in water.

3.2. Effect of pH

In our study, knowledge of pH is important because the pH of solution strongly affects the sorption capacity of the pectin compounds regarding lead ions. Fig. 3 shows the effects of pH on the lead binding by low- and high-esterified pectin and calcium pectate. The maximum lead uptake by the high-esterified pectin was found at pH 8, whereas it is for calcium pectate was found at pH 7. Maximum sorption activity of low-esterified pectin was registered at the pH range from 4 to 8 with a slight decrease toward the pH rise. At pH values higher than 8 there was registered a dramatic decrease of the uptake capacity of all compounds studied, because this obviously results in polysaccharides becoming unstable [18] and Pb(II) forming an insoluble hydroxide. Below

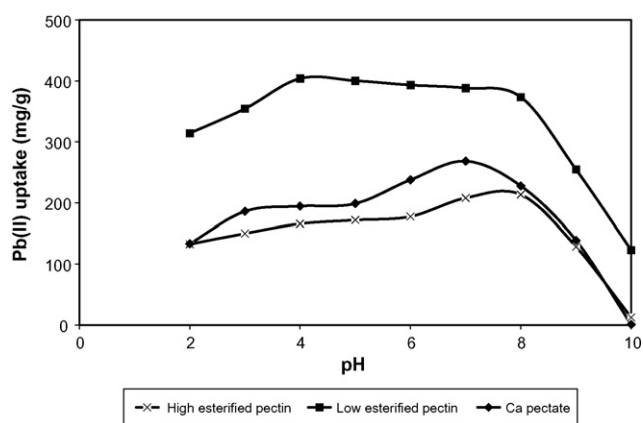


Fig. 3. Effects of pH on the Pb(II) uptake by low- and high-esterified pectins and calcium pectate.

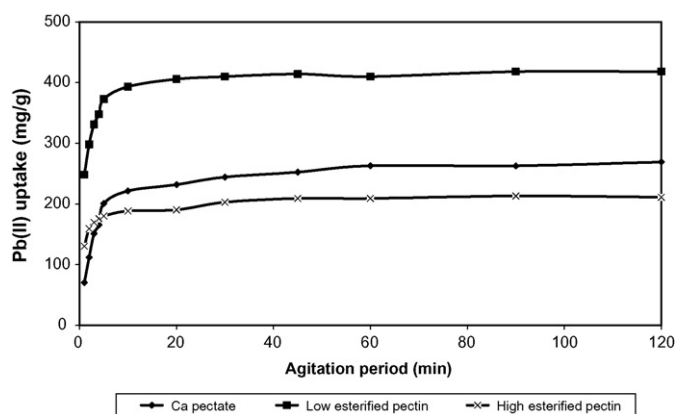


Fig. 4. Effect of the agitation period on the Pb(II) uptake by low- and high-esterified pectins and calcium pectate.

pH 8.0, sorption gradually increases with the rise of pH of the solution. This could be explained by the phenomenon that the lower is pH the more protons are available in a free form to protonate carboxyl groups, reducing the number of binding sites in the pectin molecule.

3.3. Effect of agitation period

Fig. 4 shows the effects of agitation period on the metal uptake of pectins. Period required for equilibrium concentration between pectins and Pb(II) ions to be achieved can be found on the base of different Pb(II) uptake values obtained after various periods of incubation of the batch sorption system. Amount of Pb(II) bound by low- and high-esterified pectins increases within the beginning of agitation period and attains equilibrium at about 60 min. Pb(II) uptake by calcium pectate increases slower and attains equilibrium in 120 min. The main differences in the sorption rates between these compounds were observed within the first minutes of the agitation period. So, during the first minute of the period soluble pectins bound 60% of their highest uptake under given conditions whereas insoluble calcium pectate bound only 26%. In 10 min, the differences of the Pb(II) uptake between soluble and insoluble pectin substances became insignificant. Longer period required for calcium pectate to bind Pb(II) ions is dependent on the rate of metal diffusion into pectate beads.

3.4. Effect of agitation rate

The influence of agitation rate on the binding of lead by pectin compounds was studied using following stirring speeds: 100, 200, 300, 400 and 500 rpm. There was found that agitation rate has no influence on the values of lead uptake by low- and high-esterified pectins and calcium pectate.

3.5. Equilibrium studies

Removal of lead by low- and high-esterified pectin and calcium pectate as a function of initial metal concentration was studied at pH 7. Since the data for the curve are obtained at the same temperature, the curve is an isotherm. In a sorption

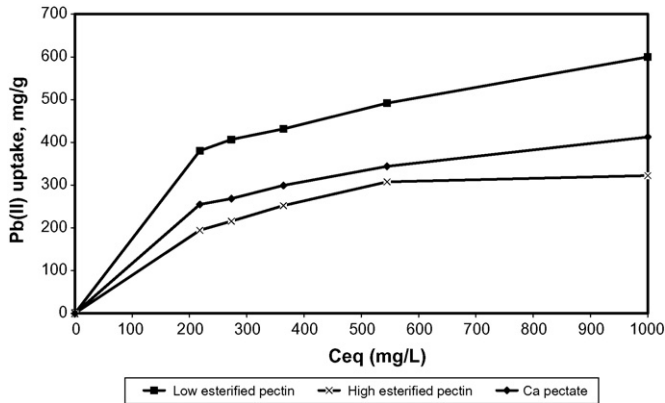


Fig. 5. Equilibrium sorption of Pb(II) from aqueous solution using low- and high-esterified pectins and calcium pectate.

system, the processes result in the removal of metal ions from the solution and their concentration onto the sorbent sites, until the remaining ions in the solution are in dynamic equilibrium with the ions bound to the sorbent sites. Therefore, there is a defined distribution of the metal ions in the sorption system, which can be expressed by one or more isotherms [19]. Fig. 5 shows the sorption curve indicating the amount of lead ions bound to the pectin molecules increasing with rise of the initial metal concentration in solution. For description of the interaction between sorbent and sorbate sorption isotherm plotting is usually used. The isotherms are characterized by the initial region, which is represented as being concave to the concentration axis. The isotherm reaches a plateau, which can typically be described by the Langmuir isotherm (4). The results of the Pb(II) dependence study were subjected to analysis by means of both Langmuir and Freundlich adsorption isotherms.

The Langmuir equation is most often used to describe equilibrium sorption isotherm, which is valid for monolayer sorption with a finite number of identical sites and is given by (Fig. 6):

$$q = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

where q_{\max} is the maximum sorption at monolayer (mg g^{-1}), C_e a final equilibrium concentration of Pb(II), q the amount of

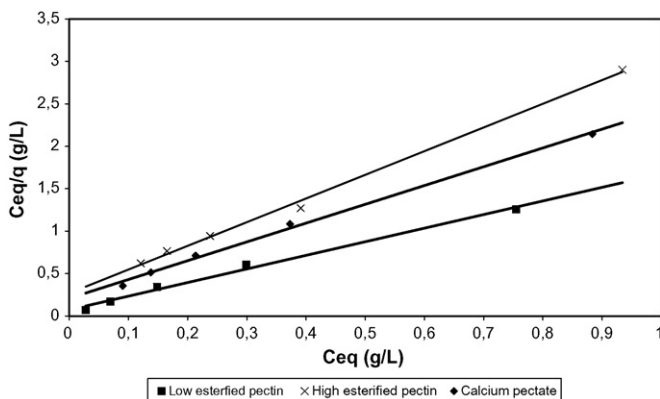


Fig. 6. Langmuir plot for the sorption of Pb(II) by low- and high-esterified pectins and calcium pectate.

Pb(II) bound per unit weight of the pectin compound at final equilibrium concentration (mg g^{-1}) and b is the Langmuir constant related to the affinity of binding sites (mL mg^{-1}) and is considered as a measure of the energy of sorption.

The following linearized plot of the Langmuir equation was used in this study:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_{\max}} \right) + \left(\frac{1}{q_{\max}} \right) b \quad (3)$$

which gives q_{\max} and b .

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F and n are Freundlich constants indicating sorption capacity (mg g^{-1}) and intensity, respectively. K_F and n can be determined from linear plot of $\log q_e$ against $\log C_e$.

The BET equation is given by:

$$\frac{C_e}{(C_0 - C_e)q_e} = \left(\frac{1}{Bq_{\max}} \right) + \left(\frac{B-1}{Bq_{\max}} \right) \left(\frac{C_e}{C_0} \right) \quad (5)$$

where q_{\max} is the maximum adsorption at monolayer (mg g^{-1}), C_e the equilibrium concentration of Pb(II) (mg L^{-1}), C_0 the saturation concentration of the solute (mg L^{-1}), q_e the amount of Pb(II) adsorbed per unit weight of the pectin compounds at equilibrium concentration (mg g^{-1}) and B is the BET constant expressive of the energy of interaction with surface.

Calculated results of the Langmuir, Freundlich and BET isotherms are given in Table 1. They show that sorption of Pb(II) by pectin compounds were better correlated ($R > 0.99$) with the Langmuir equation as compared to Freundlich and BET equation under the concentration range studied. It can be explained by the presence of finite number of homogenous binding sites on the pectin molecules, which is the basic condition of the Langmuir sorption model. According to calculated Langmuir parameters, highest binding capacity is characteristic of low-esterified pectin. The sorption coefficient b , that is related to the apparent energy of sorption for low-esterified pectin was also greater than of high-esterified pectin and calcium pectate.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L that is used to predict if an adsorption system is “favourable” or “unfavourable”. The separation factor, R_L is defined by:

$$R_L = \frac{1}{(1 + bC_0)} \quad (6)$$

where C_0 is the initial Pb(II) concentration (mg mL^{-1}) and b is the Langmuir adsorption equilibrium constant (mL mg^{-1}). The results of the R_L factor calculation (Table 2) showed that based on the effect of separation factor on isotherm shape, the R_L values of all three pectin compounds studied were in the range of $0 < R_L < 1$, which indicates that the sorption of Pb(II) by these substances are favourable. Thus, low- and high-esterified pectins as well as calcium pectate are favourable materials for binding

Table 1
Langmuir, Freundlich and BET isotherm constants and correlation coefficients of Pb(II) binding capacity of different pectin compounds

Sample	Langmuir			Freundlich			BET		
	B (mL mg ⁻¹)	q_{\max} (mg g ⁻¹)	R^2	K_F (mg g ⁻¹)	n	R^2	Q (mg g ⁻¹)	B	R^2
Low-esterified pectin	21.41	624.84	0.9923	647.38	5.92	0.8719	162.50	2.5865	0.8818
High-esterified pectin	10.34	358.72	0.9970	351.76	3.88	0.8907	26.32	5.2055	0.7224
Ca pectate	10.49	452.20	0.9966	423.04	4.57	0.9936	14.49	1.6240	0.9042

Table 2
 R_L values based on the Langmuir equation

Pb(II) initial concentration (mg mL ⁻¹)	R_L value		
	Low-esterified pectin	High-esterified pectin	Calcium pectate
0.2	0.1893	0.3259	0.3228
0.4	0.1045	0.1947	0.1924
0.6	0.0722	0.1388	0.1371
0.8	0.0551	0.1078	0.1065
1.0	0.0446	0.0882	0.0870

of the Pb(II) ions. The mechanism of sorption is to be elucidated by binding of the metal ions with non-esterified carboxyl groups located on the pectin molecules and acting as the binding sites. The results obtained show that intensity of binding processes and sorption capacity does not depend on solubility of the compound studied but closely relates to the number of the free carboxyl groups in its structure [11]. This implies formation of the junction zones between free carboxyl groups of pectin and Pb(II) according to the “egg-box” model, which is closely related to the degree of esterification of pectin, and was confirmed by the batch studies performed. It was found earlier that affinity of pectin to the Pb(II) is much higher than to Ca(II) [7], therefore, the ion-exchange process obviously has a place when calcium pectate binds Pb(II) ions.

Values of the calculated parameters suggest that low-esterified pectin possesses higher affinity and sorption capacity regarding the Pb(II) ions in comparison to low-esterified pectin and calcium pectate. The mechanism responsible for binding of the Pb(II) ions is provided by formation of the ionic bonds between metal and non-esterified carboxyl groups and the hydrogen bonds between metal and oxygen atoms.

4. Conclusions

Physical properties of the pectin substances such as molecular weight, galacturonic acid content, degree of esterification, intrinsic viscosity, calcium content was determined before the experiments. Equilibrium studies of the preparations and lead(II) solution were performed at 30 °C. The following results were obtained.

(1) Sorption process is rapid within the first 20 min of contact with all polysaccharide samples studied. In experiment with insoluble calcium pectate intensity of sorption was a little slower. The rate of sorption implies chemisorption. Maximum metal uptake was achieved in the first 30 min. It seems

that sorption of Pb(II) is not influenced by such external factor as agitation rate.

- (2) The most effective pH for the removal of Pb(II) was a range from 7 to 8. Low-esterified pectin effectively bound Pb(II) within pH range from 4 to 8.
- (3) The study shows that pectin substances bind heavy metals, in particular Pb(II). The metal uptake is dependent on the chemical structure of pectin and increases according to the reduction of the degree of esterification. Thus, the highest sorption activity was registered in low-esterified pectin. Equilibrium studies showed that the Langmuir model of sorption processes is well fitted implying the homogeneous character of the binding sites and their finite number. Although, low- and high-esterified pectins possess water-soluble properties sorption of the Pb(II) ions on their structure was the same as it was with calcium pectate beads. It can be concluded that pectin compounds are effective substances for the collection of metal ions in greater concentrations and the next steps of the studies should be performed to estimate lead-binding capacity of these compounds in low concentrations.

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