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Equilibrium Studies of Sorption of Strontium Ions by Different Pectin Compounds

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ABSTRACT

Strontium binding activity of different water soluble pectin compounds varying according to their degree of esterification and insoluble calcium pectate beads in aqueous solution was studied in a batch sorption system. The strontium uptake by all pectin compounds was highest within the pH range from 4.0 to 6.0. The binding capacities and rates of strontium ions by pectin compounds were evaluated. The Langmuir, Freundlich and BET sorption models were applied to describe the isotherms and constants. Sorption isothermal data could be well interpreted by the Langmuir and Freundlich equations. The results obtained through the study suggest that pectin compounds are favorable sorbents. The largest amount of strontium ions is bound by pectin with the degree of esterification lower 20%. Therefore, it can be concluded that low esterified pectins are more effective substances for elimination of strontium ions from nuclear disposals.

Key words: Strontium, equilibrium study, pectin, degree of esterification, nuclear disposals

INTRODUCTION

Nuclear energy is becoming a preferred energy source amidst rising concerns over the impacts of fossil fuel based energy on global warming and climate change. However, the radioactive waste generated by the nuclear power plants contains harmful long-lived fission products such as strontium (Sr^{2+}) (Gaso *et al.*, 2004; Ngwenya and Chirwa, 2011). Generally, strontium exists as four naturally occurring stable (non-radioactive) isotopes and as a number of radioactive isotopes, in particular ^{90}Sr . Long-term environmental soil contamination with ^{90}Sr may be of some concern due to its potential transfer to human through the plant-animal-human food chain causing general population exposure (Stamoulis *et al.*, 1999). Humans can be exposed to low levels of ^{90}Sr by eating food or drinking water containing this isotope (ATSDR, 2004). Once absorbed in bloodstream strontium is distributed throughout the body entering and leaving cells easily. ^{90}Sr is a beta-emitter and a large source of Cherenkov radiation. Its biochemical behavior is similar to calcium. After entering a body, for example by ingestion with contaminated food or water, most of the metal is excreted but part of it remains fixed in bones and bone marrow as well as in blood and soft tissues. Its presence in bones can cause bone cancer, cancer of nearby tissues and leukemia (Mangano and Sherman, 2011). Therefore, the development of simple and effective materials purposed for removal of ^{90}Sr from polluted environment including waters is a topic of current interest (Centi and Joester, 2011).

Among the metal ion removal procedures, ion exchange process is very effective for elimination of various metal ions and can be easily recovered and reused by regeneration operation (Ismail *et al.*, 2003). For strontium, a number of studies have explored materials binding bivalent metal ions, in particular, alginates (Hollriegl *et al.*, 2007), calcium salts (Jagtap *et al.*, 2003; Sonawane *et al.*, 2004) and chitosan (Wang *et al.*, 2009). Generally, biosorption is the most prospective process for removal of heavy metals and other pollutants from wastewaters (Alam, 2004; Zolgharnein *et al.*, 2010). It was figured out that some of the best ion exchange materials are biopolymers which are industrially attractive because of their capability of lowering transition metal-ion contents to parts per billion concentrations, their availability and environmental safety (Ajayan *et al.*, 2011; Khotimchenko *et al.*, 2007).

It was suggested recently that usage of the pectin-rich fruit biomass is effective for removal of the metal ions from water solutions (Hossain *et al.*, 2005; Schiewer and Patil, 2008). Pectin substances belonging to the group of natural biopolymers 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 (Schols and Voragen, 1996). Pectins were found to exert numerous beneficial effects in humans due to their binding activity in gastrointestinal tract (Khotimchenko *et al.*, 2006a; Fontes *et al.*, 2011). Their metal binding capacity was proved in the numerous studies under as *in vivo* as *in vitro* conditions (Dongowski *et al.*, 1997; Kartel *et al.*, 1999; Khotimchenko *et al.*, 2006b). 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 proposed for the metal binding mechanism of pectins (Grant *et al.*, 1973), esterified residues are not active whereas negative charges of the free carboxyl groups in pectin molecules form the covalent bonds with the metal ions. Thus, pectin with the low degree of esterification presumably exerts considerably higher metal binding activity (Ralet *et al.*, 2001). Therefore, the main aim of this work was to investigate the binding of Sr^{2+} ions by the pectin compounds and the influence of the degree of esterification on the sorption capacity of pectins. The results of the work may be used as a basis for development of the new materials purposed for removal of strontium and other similar ions from water disposals. There were studied parameters of the strontium binding processes by four pectin compounds with their degree of esterification varying from 1 to 60% and low esterified calcium pectate in a form of water insoluble tiny beads. The influence of experimental conditions such as pH, agitation period, agitation rate and initial concentrations on the parameters of the binding process were investigated. The Langmuir, Freundlich and BET equations were used to fit the equilibrium isotherm.

MATERIALS AND METHODS

Materials: 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 samples contained no acetyl or amide groups. All other chemicals were of the highest quality available. Distilled water was used throughout.

Preparation of pectin samples with different degree of esterification: Preparation of the pectin samples with the degree of esterification less than 60.0% was executed using the method of alkali de-esterification of high esterified pectin in a water-ethanol solution. Initially the raw high esterified pectin was washed with 50% ethanol solution for purification. In this process 200 g of pectin was suspended in 2 L of the ethanol solution for 30 min, then pectin was separated by

filtration, rinsed on filter with 1.5 L of the 50% ethanol solution and 1 L of the 95% ethanol solution, consecutively and then dried at 70°C. Pectin obtained was pounded and fractioned according to the particle size. In the study was used a fine disperse fraction sifted through a sieve with a mesh size 74 µm. It was made purposefully to minimize the possibility of obtaining the heterogeneous samples regarding degree of esterification due to a different rate of de-esterification process in pectin molecule outside and inside granules caused by different velocity of diffusion of hydrolyzing agent.

Process of alkali de-esterification of pectin included initial neutralization of free carboxyl groups of anhydrogalacturonic acid and then, during increase of pH of the media higher than 8.5, proper pectin de-esterification. Amount of alkali required for neutralization of carboxyl groups was calculated as follows: 1 g of pectin was suspended in 10 mL of 50% ethanol solution and in the presence of Hintone indicator titrated with 1 M NaOH solution in 50% ethanol until the change of the indicator color. According to the titration results the amount of alkali required for pectin neutralization was determined using the following equation:

$$V_1 = m \cdot V_0 \quad (1)$$

where, V_1 is the volume of 1 M NaOH solution necessary for pectin neutralization (mL), m is the weight of a pectin sample (g), V_0 is the volume of 1 M NaOH solution used during titration of 1 g of pectin (mL).

Amount of alkali necessary for achievement of a set degree of esterification of pectin was calculated using the following equation:

$$V_2 = \frac{m \cdot A}{176 \cdot 100} \cdot \frac{DE_{in} - DE_{fn}}{100} \cdot 100 \quad (2)$$

where, V_2 is the volume of 1 M NaOH solution necessary for de-esterification of pectin (mL), m is the weight of a pectin sample (g), A is the anhydrogalacturonic acid content in pectin (%), 176 is the molar weight of anhydrogalacturonic acid, DE_{in} is the initial degree of esterification of a pectin sample (%), DE_{fn} is the final required degree of esterification of a pectin sample (%).

The total volume of alkali necessary for the whole process of pectin de-esterification was found by summarizing of V_1 and V_2 volumes determined earlier.

The proper de-esterification process was carried out as follows. Twenty gram of pectin powder was suspended in 200 mL of 50% ethanol solution intensively stirring and then gradually 1 M NaOH solution in 50% ethanol was added. For the visual control of the process, the indicator phenolphthalein was added into the reactive mixture. The color of phenolphthalein changes at pH 8.2-10.0. The next portion of alkali was added into the reactive volume only after discoloration of indicator. When 95% of calculated amount of alkali was added into reactive volume, the sampling was carried out for determination of the degree of esterification. According to results of this analysis the quantity of alkali was precised. When the preliminary set degree of esterification was achieved the reaction mixture was acidified with 1 M HCl solution in 50% ethanol achieving pH of the media 5.0-6.0 under intensive stirring. Obtained pectin preparation was separated from water-ethanol solution with filtration and consecutively rinsed with 300 mL of 50% ethanol solution and 150 mL of 95% ethanol. Rinsed pectin was dried at 70°C.

Total anhydrogalacturonic acid content, non-methylated (de-esterified) anhydrogalacturonic acid content, degree of esterification and intrinsic viscosity were estimated in the pectin samples obtained.

For the preparation of calcium pectate beads 100 g of pectin with degree of esterification about 1% was suspended in 500 mL 70% ethanol. 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.

Pectin analysis: The galacturonan content of the pectin preparation was determined colorimetrically by the m-hydroxydiphenyl method (Blumenkratz and Asboe-Hansen, 1973). The degree of esterification was characterized using titrimetric analysis with 1 M NaOH solution in 50% ethanol in the presence of Hintone indicator (Afanasyev *et al.*, 1984). Intrinsic viscosity of low esterified pectin was determined in 0.05 M NaCl/0.005 M Na-oxalate at 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 equation (Kravtchenko and Pilnik, 1990) presented as $\eta = KM^\alpha$ that is generally used for definition of the pectin molecular weight using values for the constants α (0.79) and K ($216 \cdot 10^{-8}$) that are suitable for pectins (Grassi *et al.*, 1996). The calcium content in the calcium pectate sample was assayed by atomic-absorption and expressed in mg g^{-1} of a sample (Kostecka, 2000).

Experimental procedures: 0.1 M stock solutions (8.762 g L^{-1}) of Sr^{2+} ions was prepared using analytical-reagent grade SrCl_2 . 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 20 mL beakers and equilibrated using a magnetic stirrer. Then 1.0 mL aliquots of these standard solutions were placed in 20 mL beakers with 10 mL of solution containing 0.05 g of dry pectin preparation or 10 mL of suspension with 0.05 g of dry calcium pectate added. Then the total volume of the solution prepared was made up to 20 mL by addition of distilled water. Removal of pectin compounds from Sr^{2+} solution was performed by use in centrifugal force unit 3000 g for 10-20 min and following filtration through a glass filter with a pore size 100-120 μm . Concentration of Sr^{2+} ions in the supernatant obtained was analyzed using an atomic absorption spectrophotometry method. The effect of Sr^{2+} sorption was studied in a pH range 2.0-8.0. 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 initial Sr^{2+} concentration of 0.6 g L^{-1} using a bath controlled at 24°C. Each experiment was triplicated under identical conditions. A negative control experiment with no pectin added was simultaneously carried out to ensure that the strontium removal was caused by the polysaccharide binding activity and not by the beaker or filter influence. The parameters obtained were subjected to a one-way analysis of variance using a software package SPSS (Statistical Package for Social Sciences) for Windows, version 11.0 with a confidence level of 95% ($p < 0.05$).

The effect of agitation period was also studied to determine the optimum condition for sorption of Sr^{2+} ions. For batch kinetic studies 0.05 g calcium pectate or 10 mL of solution containing the same amount of dry pectin were equilibrated at optimum condition as mentioned earlier. The

sorption system was placed in 20 mL beakers and stirred by a magnetic stirrer. At preset time intervals, the aqueous samples (5 cm³) were taken and the concentration of Sr²⁺ was assessed.

Sorption equilibrium studies were conducted at optimum condition using a contact time of 120 min at pH 2.0-8.0. According to the preliminary results pH value 6.0 was considered as most acceptable because all polysaccharides at this point possess highest binding activity and pH control requires minimum amounts of HCl and NaOH. Bath controlled temperature was 24°C. Isotherm studies were conducted with a constant pectin preparation amount (0.05 g) and varying initial concentration of Sr²⁺ in the range of 0.05-0.6 g L⁻¹. Each experiment was at least duplicated under identical conditions.

The metal accumulation (q) was determined as follows:

$$q_e = \frac{(C_0 - C_e) \cdot V}{W} \quad (3)$$

where, C₀ is the initial Sr²⁺ concentration (mg L⁻¹), C_e is the final or equilibrium Sr²⁺ concentration (mg L⁻¹), V is the volume of the Sr²⁺ solution (mL) and W is the weight of the dry samples of pectin or calcium pectate (g).

The amount of the metal ions bound by the pectin compounds was expressed in mg per g of the dry sorbent.

RESULTS AND DISCUSSION

Pectin substrate: There were obtained four samples of pectins by means of alkali de-esterification method and insoluble calcium pectate beads. The samples were ranged according to more or less gradual reduction of their degree of esterification from 60.2 to 1.2%. Physicochemical parameters of the pectin samples obtained are shown in Table 1. It was found that the pectin samples which were subjected to de-esterification procedure, are characterized by similar contents of anhydrogalacturonic acid making up from 66.6 to 73.7% of a sample mass. The differences of the anhydrogalacturonic acid content may be explained by partial degradation of uronic acids and removal of side chains during the process of alkali esterification. Also neutral sugars are washed out due to the rinsing with ethanol. Simultaneously with the decrease of the degree of esterification from 60.2 to 1.2% a relative rise of the non-methylated anhydrogalacturonic acid content was registered from 31.6 to 72.8%, i.e., 2.3 times more. Generally intrinsic viscosity of pectin samples corresponds to the degree of esterification. But at the very beginning of the de-esterification process

Table 1: Physicochemical parameters of pectin preparations used in the study

Parameter	Pectin sample				Ca pectate
	DE = 60%	DE = 40%	DE = 20%	DE = 1%	
Degree of esterification (%)	60.2	40.1	18.8	1.2	1.2
Total anhydrogalacturonic acid content (%)	79.4	70.4	66.6	73.7	73.8
Non-methylated anhydrogalacturonic acid content (%)	31.6	42.2	54.1	72.8	72.6
Intrinsic viscosity, mL g ⁻¹ anhydrogalacturonic acid	915	533	433	408	-
Ca ²⁺ content (mg g ⁻¹)	-	-	-	-	38
Water solubility	Yes	Yes	Yes	Yes	No

DE: Degree of esterification

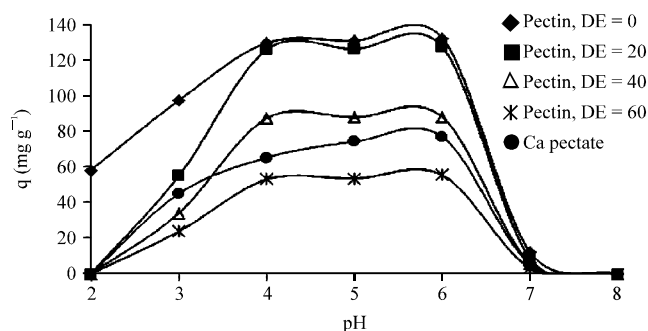


Fig. 1: Effects of pH on the Sr²⁺ uptake by pectin with different degree of esterification and calcium pectate, DE: Degree of esterification

a dramatic reduction of intrinsic viscosity was noted. In correspondence with Mark-Houwink equation relating intrinsic viscosity and molecular weight of pectin, the difference found in the study conforms to 2.8 fold reduction of an average molecular weight. Because molecular weight of initial high esterified pectin was substantially high (more than 200 kDa), the sample with the degree of esterification 1.2% and intrinsic viscosity 408 mL g⁻¹ may be considered as a high molecular pectin.

Physicochemical parameters of the calcium pectate beads prepared from the low esterified pectin were similar to those of that sample, except they were not soluble in water.

Effect of pH: In the study with natural polysaccharides, solution pH is an important parameter because the system is strongly pH dependent due to the properties of both pectin compounds (charge and potential) and the solution composition, i.e. metal ion speciation which changes with pH (Schiewer and Patil, 2008; Lofgren *et al.*, 2002). The number of active binding sites presented with free carboxyl group residues of the pectin molecule may change with varying pH. Figure 1 depicts the effect of pH values on the Sr²⁺ uptake by soluble pectins and calcium pectate. The binding capacities were found to be relatively low at lower pH values and increased with the rise of pH. The optimum pH range of 4.0-6.0 is obtained for all compounds studied. This can be explained by the pKa value of pectins varying from 3.5 to 4.1 for different pectin samples (Schols and Voragen, 1996). At the pH values higher than 4.0 the majority of carboxyl groups are in dissociated condition, therefore, metal binding processes are easily initiated. Low pH would favor protonation of the carboxyl sites of the pectin molecule resulting in a reversal of their charge leading to a reduced metal binding activity of pectin. In the media with pH values lower than 2.0 all pectin substances except de-esterified sample are usually precipitated and this sedimentation results in dramatic decrease of the binding activity of polysaccharides (Lofgren *et al.*, 2002). At pH values higher than 7.0 strontium binding capacity of all compounds studied was close to zero due to the alkaline shift which obviously results in polysaccharides becoming unstable (Lofgren *et al.*, 2002). Moreover, binding process at these pH values must be disrupted due to the formation of hydro-complexes of Sr²⁺ ions. According to the literature (Patnaik, 2002), the chemical species of Sr²⁺ existing in the solution at pH 6.0 and higher are mostly Sr(OH)₂. Since such species possess a large size and are unable to dissociate, they barely interact with active sites of carboxyl groups in the pectin molecule. Moreover, the Sr(OH)₂ molecules are prone to precipitation in the case of high concentration, hence, their interaction with polymer molecules is barely possible. Therefore, it was considered unreasonable to measure Sr²⁺ binding capacity of pectin at pH values higher than 8.0.

Effect of agitation period: Figure 2 shows the effects of agitation period on the strontium uptake by pectins. Period required for achievement of the equilibrium concentration between pectins and Sr^{2+} ions was found on the base of different uptake values obtained after various periods of interaction between polysaccharide compounds and metal ions being in the batch sorption system. Amount of Sr^{2+} bound by all water soluble compounds increases within the beginning of agitation period and attains equilibrium in about 45 min. Sr^{2+} uptake by calcium pectate increases significantly slower and attains equilibrium in 80 min. The main differences in the sorption rate between soluble compounds and insoluble calcium pectate were observed within the first minutes of the agitation period. So, during the first minute of the period soluble pectins have bound 47-55% of their highest strontium uptake under given conditions whereas insoluble calcium pectate beads have bound only 14.1%. In 10 min the difference of the Sr^{2+} uptake between soluble and insoluble pectin substances was found to be insignificant. Taking to consideration that all pectin were hydrated before taken into the batch, longer period required for calcium pectate to bind Sr^{2+} ions depends only on the rate of metal diffusion into pectate beads.

Effect of agitation rate: The influence of agitation rate on the binding of Sr^{2+} by pectin compounds was studied using the following stirring speeds: 0, 100, 200, 300, 400 and 500 rpm. There was found that agitation rate has no influence on the values of Sr^{2+} uptake by water soluble pectins and insoluble calcium pectate beads. Even if the batch sorption system was not stirred at all there was found no differences in the Sr^{2+} uptake values registered.

Equilibrium studies: Removal of Sr^{2+} ions by pectins with different degree of esterification and calcium pectate as a function of equilibrium metal concentration was studied at pH 6.0. The sorption processes in the batch result in the metal ions being removed from the solution and concentrated on the sorbent sites, until the remaining ions in the solution are in the dynamic equilibrium with the ions bound to the active binding sites (Eba *et al.*, 2012). Therefore, there is a defined distribution of the metal ions in the sorption system which can be expressed by one or more isotherms (Zhang *et al.*, 2008). Figure 3 shows the sorption curve indicating the amount of

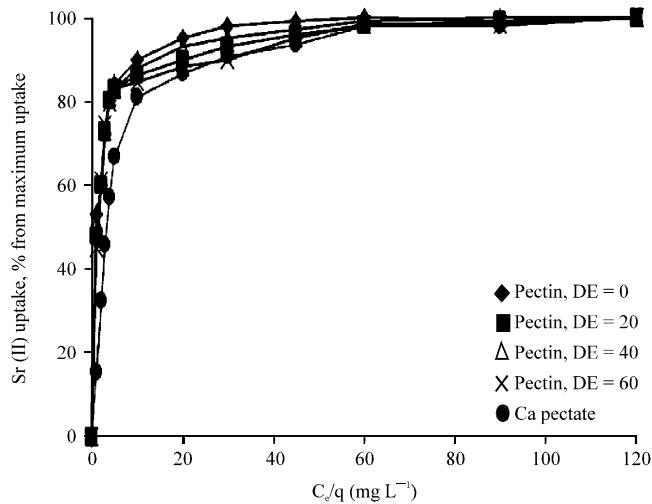


Fig. 2: Effect of the agitation period on the Sr^{2+} uptake pectin with different degree of esterification and calcium pectate, DE: Degree of esterification

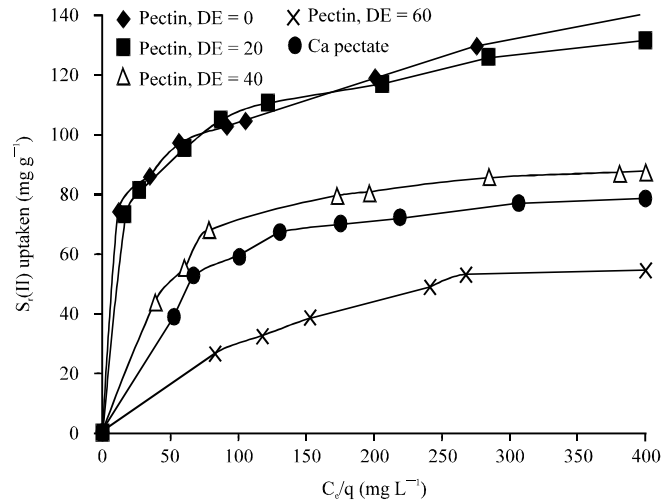


Fig. 3: Equilibrium sorption of Sr^{2+} from aqueous solution pectin with different degree of esterification and calcium pectate, DE: Degree of esterification

Sr^{2+} ions bound to the pectin molecules increasing with rise of the equilibrium metal concentration in solution. For description of the interaction between sorbent and the metal ions being bound the 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, Freundlich or BET isotherms (Nabizadeh *et al.*, 2006) which were used for analysis of the results obtained through this part of experiment.

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:

$$q = q_{\max} \frac{bC_e}{1+bC_e} \quad (4)$$

where, q_{\max} is the maximum sorption at monolayer (mg g^{-1}), C_e is a final equilibrium concentration of Sr^{2+} , q is the amount of Sr^{2+} bound per unit weight of the pectin compound at final equilibrium concentration (mg g^{-1}), 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:

$$C_e/q_e = (C_e/q_{\max}) + 1/(q_{\max}b) \quad (5)$$

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

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:

$$\frac{C_e}{(C_0 - C_e)q_e} = \left(\frac{1}{Bq_{max}}\right) + \left(\frac{B-1}{Bq_{max}}\right)\left(\frac{C_0}{C_e}\right) \tag{7}$$

where, q_{max} is the maximum uptake at monolayer ($mg\ g^{-1}$), C_e is the equilibrium concentration of Sr^{2+} ($mg\ L^{-1}$), C_0 is the saturation concentration of the solute ($mg\ L^{-1}$), q_e is the amount of Sr^{2+} bound 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 the Table 2. They show that sorption processes between Sr^{2+} and pectin compounds were better correlated ($R^2 > 0.96$) with the Langmuir equation as compared to Freundlich and BET equations under the given range of concentration. It can be explained by the presence of finite number of homogenous binding sites on the pectin molecules presented with free active carboxyl groups which is the basic condition of the Langmuir sorption model (Volesky, 2003). According to calculated Langmuir parameters obtained from the plot C/q vs C (Fig. 4), the highest binding capacity is characteristic of pectins with the low degree of esterification (1, 20%) and calcium pectate beads. Despite equal value of the q_{max} of these compounds the sorption coefficient b that is related to the apparent energy of sorption was significantly different. Coefficient b for low esterified pectin was much greater than that of pectin with higher degree of esterification and calcium pectate.

The essential features of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L that is used to predict if a sorption system is “favorable” or “unfavorable”. The separation factor, R_L is defined by:

$$R_L = 1/(1+bC_0) \tag{8}$$

where, C_0 is the initial Sr^{2+} concentration ($mg\ mL^{-1}$) and b is the Langmuir adsorption equilibrium constant ($mL\ mg^{-1}$).

The results of the R_L factor calculation showed that based on the effect of separation factor on isotherm shape, the R_L values of all pectin compounds studied were in the range of $0 < R_L < 1$ which indicates that the binding of Sr^{2+} by these substances is favorable. Thus, de-esterified pectin is a favorable material for binding of the Sr^{2+} ions. R_L values for other pectin compounds were also between 0 and 1 but they were significantly different from those of de-esterified pectin suggesting the lower capacity of these substances to bind Sr^{2+} . The obvious mechanism of sorption is related to the formation of covalent and hydrogen bonds between the metal ions and non-esterified carboxyl groups and hydrogen atoms located on the pectin molecules and acting as the binding sites (Grant *et al.*, 1973). Results obtained show that intensity of binding processes and sorption capacity

Table 2: Langmuir, Freundlich and BET isotherm constants and correlation coefficients of Sr^{2+} binding capacity of pectin compounds

Sample	Langmuir	Freundlich	BET		R^2	q_{max} ($mg\ g^{-1}$)	B	R^2	
	b ($mL\ mg^{-1}$)	q_{max} ($mg\ g^{-1}$)	R^2	K_F ($mg\ g^{-1}$)					n
Pectin, DE = 1%	0.051	135.1	0.99	5.274	5.40	0.960	70.9	1.08	0.017
Pectin, DE = 20%	0.052	131.6	0.998	5.261	5.52	0.966	63.7	1.20	0.131
Pectin, DE = 40%	0.021	98.4	0.994	3.439	3.52	0.900	76.9	1.44	0.410
Pectin, DE = 60%	0.005	80.6	0.942	1.453	1.83	0.979	32.2	1.30	0.088
Ca pectate	0.017	92.6	0.993	2.855	2.85	0.873	192.38	0.03	0.002

DE: Degree of esterification

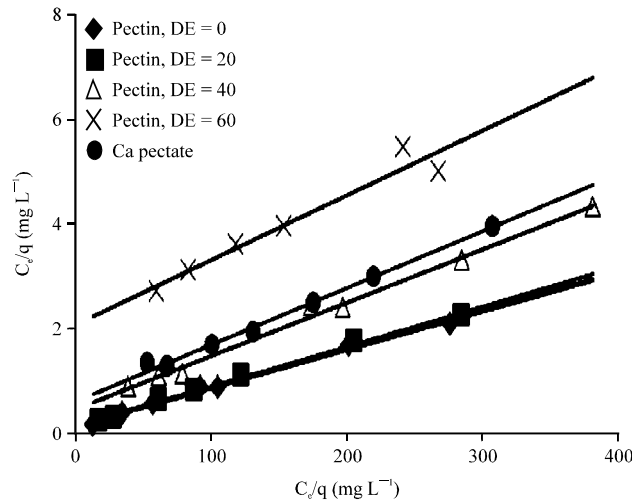


Fig. 4: Langmuir plot for the sorption of Sr^{2+} by pectin with different degree of esterification and calcium pectate, DE: Degree of esterification

does not depend on solubility or other physicochemical parameters of the compound studied but closely relates to the number of the free carboxyl groups in its structure (Volesky, 2003). The q_{max} parameter of the Langmuir model indicating the number of active binding sites of molecules shows that the lower is the degree of esterification of the pectin molecule the more active sites on the carboxyl groups are taking part in the process of Sr^{2+} binding. Changes of the b coefficient reflecting affinity of the pectin to metal ions were also strongly corresponding to the degree of esterification with highest values of affinity possessed by pectin with the degree of esterification about 1% and little lower values typical of pectin with 20% of esterified residues. The similar tendency was found after calculation of the Freundlich equation parameters; despite some of them were considered insignificant. This suggests the formation of the junction zones between free carboxyl groups of pectin and Sr^{2+} occurs according to the "egg-box" model (Grant *et al.*, 1973) which is closely related to the degree of esterification of pectin and was confirmed by the batch studies performed. Combining these data with the value of the rate of sorption found in experiments the main mechanism is obviously chemisorption. Calcium pectate, despite its very low degree of esterification, showed significantly lower strontium binding capacity in comparison with structurally close de-esterified pectin. Results obtained through evaluation of experimental data by means of Langmuir equation showed that low esterified calcium pectate contain the lower quantity of active binding sites and lower affinity compared to the low esterified pectin. Obviously the presence of the calcium ions disrupts formation of the junction zones with Sr^{2+} ions. According to the binding properties of the pectins (Kartel *et al.*, 1999), it may be supposed that affinity of pectin to the Ca^{2+} ions is relatively high and cause poor ion-exchange activity of calcium pectate regarding Sr^{2+} ions and slow release of calcium ions into the media. The values of the calculated parameters suggest that low esterified pectin possesses higher affinity and sorption capacity regarding the Sr^{2+} ions in comparison to higher esterified pectins and calcium pectate.

The results obtained through this study suggest that pectin substances, in particular, the ones with the low degree of esterification possess relatively high strontium binding activity. Such property may be useful for creation of cheap and effective materials purposed for removal Sr^{2+} ions from various contaminated water sources and reservoirs. These materials can be easily elaborated

using a pectin-rich biomass usually disposing after fruit processing. The main advantages of these materials are their availability and low cost because generally they are a disposal of the food industry. Chemical modifications may markedly increase metal binding activity of natural pectin containing materials purposed for Sr²⁺ removal from water disposals and contribute to higher degree of water purity.

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