Introduction

The possible use of low cost and environmental friendly materials to remove toxic metal ions from aqueous solutions has been widely investigated with the aim to set-up new sorption and biosorption technologies [1–7], alternative to the conventional electrochemical, flotation and precipitation treatments [8–14]. The most investigated sorbent materials are derived from natural biomass, especially fungi [15–18], algae [19–23], humic substances from soil [24] and byproducts from industrial processes, such as wood and food industries, agriculture, fishery and textile manufacturing [25–32]. Also some inorganic materials (zeolites, clays, etc.) are used for the same purpose [7,8,33,34]. These sorbent materials all exhibit characteristics of being low cost, causing low environmental impact, presenting high degradability, great availability and high sorption capacity towards metal ions [35–37]. The sorption ability of these materials is strictly related to their chemical composition containing high percentages of macromolecules with a great number of binding groups such as –O, –N, and –S donors [4,37] able to form stable species with the metal ions to be removed [38–40]. Several investigations have been carried out using a variety of materials for wastewaters and contaminated sites treatment. Reviews and textbooks cited in Refs. [1–8,36,37] give a general picture of potential sorbent materials used. In particular, algae and fruits have been widely tested as sorbents for metal removal, including copper and cadmium [19–23,30,41–47] from polluted aqueous solutions. Most of these studies refer to metal sorption capacity of raw materials and only few of them report results on the sorption by alginate and/or pectin in gel phase [41,45,48–53]. Alginic acid is a polysaccharide constituted by monomer units of mannuronic and guluronic acids [54,55]. It is the main component of brown algae where it is present up to 40% dry weight [56]. Pectin, mostly constituted by polygalacturonic acid with different extent of acetylation [57], is the main component of peel and pulp of several fruits. Both these materials are able to form hydrogels in the
presence of small amounts of divalent cations, especially calcium ion [58,59]. The removal capacity of both these biopolymers can be attributed to the presence of several ligand carboxylic groups per molecule. Therefore, it can be assumed that they are the main responsible for the sorption process of metal ion by algae and fruits. For the above reasons we carried out the present study with the aim to test the removal capacity of cadmium(II) and copper(II) from aqueous solutions using directly alginate and pectin in gel phase. To that end, the biopolymers under investigation, mixed in various concentration ratios to form a new hybrid alginate/pectin sorbent material, were used as calcium gel beads which are more easily to handle and give more accurate results than the raw biomaterials. The sorption capacity of mixed materials was compared to that of calcium alginate beads, used as a reference material. Several studies report that ion exchange is the predominant mechanism in metal sorption by algal biomass [40,54,55,60] and a pseudo-second order kinetic model is generally used to describe the sorption process when the chemical sorption is the rate – controlling step [32,61]. In order to confirm the hypothesis, i.e., if the sorption process occurs via ion exchange between calcium ion of sorbent materials and copper(II) or cadmium(II) ions present in the solution, the amount of calcium released by gel beads during the kinetic experiments was determined. The effect of contact time, initial metal concentration and different alginate/pectate concentration ratios on the kinetics of metal adsorption was investigated by batch experiments. A pseudo second order model was used to quantify the sorption capacity of gel materials under investigation. Both Langmuir and Freundlich isotherm models were used to fit the equilibrium data. A comparison with some results reported by different authors using the same models and similar experimental conditions is also given.

To obtain the best metal removal efficiency, the most suitable conditions of pH, ionic strength and medium of solutions containing the metal ion to be removed, were assessed on the basis of the results of previous speciation studies [62–64]. In these studies the acid–base properties of alginic [62,63] and pectin [64] and the ability of these polymers to bind copper(II) and cadmium(II) ions in aqueous solution were defined over a wide pH range.

Materials and methods

Chemicals

Cadmium(II), copper(II) and calcium(II) nitrate salts solutions were prepared by diluting standard (1000 mg L⁻¹ in HNO₃ 0.5 mol L⁻¹) Merck solutions. Commercial pectin, as potassium salt extracted by citrus peel, was supplied by Aldrich (lot. 077K1583). Commercial alginic acid (AA, molecular weight in the range 70–100 kDa), as sodium salt extracted from Macrocystis pyrifera, with an average content of mannuronic and guluronic acids of 61% and 39%, respectively, was supplied by Sigma (lot. 60K1443). Nitric acid and sodium hydroxide solutions used to adjust the pH of the metal ion standard solutions were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. Calcium chloridehydrate (Fluka) was used to prepare calcium alginate and mixed calcium alginate/pectate gel beads. All the solutions were prepared using freshly prepared CO₂-free ultra pure water (ρ ≥ 18 MΩ cm) and grade A glassware.

Preparation and characterization of sorbent materials

Calcium alginate and mixed calcium alginate/pectate gel beads were prepared using the dropping technique. A peristaltic pump (Gilson, Minipin 3) was used to dispense the suspension in a stirred reservoir containing 200 mL of a CaCl₂ 0.1 M solution used for gel formation. At the end of the dispensing tube a micropipette tip (yellow type 5–200 μL) cut out to get a final diameter of 1 mm was attached and positioned approximately 1 cm above the surface of the fixing solution. The beads formed were allowed to cure, under continuous stirring, in the same CaCl₂ solution for 24 h; they were rinsed three times with distilled water to ensure the removal of unbound calcium(II) ion. The following gel beads were prepared: 2% calcium alginate (Ca-A), 2% calcium alginate 1% calcium pectate (Ca-AP₁), 2% calcium alginate 1.5% calcium pectate (Ca-AP₂) and 2% calcium alginate 2% calcium pectate (Ca-AP₃).

To define the physico-chemical and mechanical properties of gel beads, different analysis were carried out. The density of gel beads was measured by a helium pycnometer (Accupyc 1330) at T = 20 °C. A digital caliper (mitutoyo, model 500-181-U) was used to measure the diameter of beads and the mean value was calculated on 50 beads together with the relative standard deviation. The water content was evaluated by Thermo Gravimetric Analysis using a Q5000 IR apparatus (TA Instruments). Experiments were carried out in a temperature range 25–300 °C, under the nitrogen flow of 25 cm³ min⁻¹ for the samples and 10 cm³ min⁻¹ for the balance. The weight of each sample was 10 mg and the heating rate was set at 10 °C min⁻¹. The mechanical resistance of gel beads was measured by using a Texture Analyser (model TA-XTS2i, Stable Micro Systems, England). This parameter represents the mean force necessary to generate the 10% compression on a bead placed under a cylinder probe P10 (Batch 2370, Stable Micro Systems, England). The measurements of mechanical resistance were repeated 40 times for each type of gel beads and the mean value was calculated together with the standard deviation. The morphology of sorbent materials was investigated by an electronic microscope ESEM FEI QUANTA 200F coupled with an EDX (Energy Dispersive X-ray spectroscopy) system. Before the analysis the gel beads were dried at T = 105 °C and their surface was coated with gold in the presence of argon by an Edwards Sputter Coater S150A in order to prevent charging under electronic beam. The electron beam was opportunely set in order to avoid the damage of the samples. SEM micrographs were registered within the micrometer range.

Experimental procedures for kinetic and equilibrium investigations

Batch kinetic experiments were carried out by placing twenty gel beads in Erlenmeyer flasks containing each one 15 mL of Cu(NO₃)₂ or Cd(NO₃)₂ salt solutions (C₅⁰ = 200 mg L⁻¹) at room temperature and at pH ~ 5.5. The solutions were shaken for different time in the range 1–300 min by using an orbital Stuart Scientific-Rotator Drive STR4 (Instruments s.r.l., Bernareggi, MI) apparatus and then filtered with filters WHATMAN (grade 520 a1/2). No precipitation occurs during the filtration. The equilibrium study was also carried out by means of batch experiments, placing a variable number of spheres (from 5 to 100) in 25 mL of solution containing Cu(NO₃)₂ or Cd(NO₃)₂ at the same concentration and at the same experimental conditions as for kinetic experiments. The solutions were shaken for 24 h by using the same orbital rotator apparatus and then filtered. The residual concentration of metal ions (Cu²⁺, Cd²⁺ and Ca²⁺) in the filtrates from both kinetic and equilibrium experiments were determined by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) using a Perkin Elmer Model Optima 2100 spectrophotometer equipped with autosampler (model AS-80).

The hydrogen ion concentration of the solutions was checked by a potentiometer (Metrohm, Model 654) equipped with a combined ISE-H⁻ glass electrode (Ross type 8102). Metal
adsorption and/or calcium release at different contact times \( t (q_t, \mu\text{mol bead}^{-1}) \) were calculated considering:

\[
q_t = \frac{V(C_0 - C_t)}{n_{\text{beads}}}
\]

where \( V, C_0 \) and \( C_t \) are the volume and the metal concentration in solution expressed as \( \mu\text{mol L}^{-1} \) at \( t = 0 \) and \( t = t \), respectively. All sorption experiments were carried out in duplicate and the averaged results are presented.

**Computer programs**

Linear and non linear regression data analysis as well as the determination of kinetic and equilibrium parameters were carried out using Origin Professional 8.6 software.

**Results and discussion**

**Characterization of sorbent materials**

The results obtained for the characterization of sorbent materials investigated are reported in Table 1.

From the results shown in Table 1 the following considerations can be made. The density values of the mixed polymers gel beads (Ca-AP\(_1\), Ca-AP\(_{1.5}\), and Ca-AP\(_2\)) are similar (differences are within the experimental errors). The lowest density value was observed for calcium alginate gel beads (Ca-A).

The mechanical resistance of gel beads containing pectin (0.21–0.22 N/ bead) is a little higher than that of Ca-A gel beads (0.19 N/ bead). This can be evidently attributed to the higher concentration of biopolymers which contributes to make more compact the structure of the gel due to the higher number of cross-linking among the molecules of alginate, pectate and Ca\(^{2+}\) ions.

Micrographs from Scanning Electron Microscopy (SEM) analysis show wrinkled surfaces of gel beads with creases and pores, especially in the presence of Cd\(^{2+}\) and Cu\(^{2+}\) ions. This morphology may be attributed to the shrinkage of the beads at higher metal concentrations [59]. As an example, SEM surface micrographs of Ca-A and Ca-AP\(_2\) biopolymers before and after contacting with 200 mg L\(^{-1}\) copper(II) and cadmium(II) solutions for 48 h are depicted in Figs. 1 and 2, respectively.

All the sorbent materials investigated show analogous behavior. As pointed out before, SEM analysis was coupled with EDX measurements which allow to obtain semi-quantitative results on the metal content in the different dried gel beads.

EDX results, reported in Table 2, clearly show that calcium percentage in gel beads lowers when the calcium–biopolymer system is in contact with the solutions containing cadmium(II) or copper(II) ions. In particular, the loss of calcium ion from mixed Ca-AP\(_2\) gel beads is comparable with the amount of copper(II) or cadmium(II) ions adsorbed by the sorbent material.

This evidence supports the hypothesis according to which ion exchange is the main mechanism governing the metal ions removal from aqueous solution by pectin–alginate biopolymers in gel phase.

**Preliminary speciation analysis**

The sorption process mechanism is based on the possibility that metal ions present in solution interact with carboxylic binding groups of polymer biomaterials to form stable species. In order to facilitate this interaction and to obtain the best metal sorption performance, the most suitable experimental conditions of solutions were fixed on the basis of a speciation analysis previously carried out on the Cu–Cd/alginate/pectate systems in aqueous solution [62–64]. The results of speciation analysis showed that a pH value of about 5.5 is the most appropriate one to avoid or minimize the hydrolysis of metal ions under investigation as well as the protonation of biopolymers. Moreover, at this pH, fairly stable metal complex species are formed with alginate and pectate, as confirmed by the following formation constants values: \( \log K_{\text{Cu-AP}} = 3.626 \) and \( \log K_{\text{Cd-AP}} = 3.072 \) [63]; \( \log K_{\text{Cu-pect}} = 5.278 \) and \( \log K_{\text{Cd-pect}} = 3.636 \) [64] in NaNO\(_3\), at \( I = 0.1 \text{ mol L}^{-1} \) and \( T = 25^\circ \text{C} \). As expected, copper(II) complex species formed with both alginate and pectate are more stable than the corresponding species of cadmium(II).

**Kinetic study of cadmium(II) and copper(II) sorption and calcium(II) release by gel beads**

Kinetcs of Cd(II) and Cu(II) sorption onto the beads and Ca(II) released from alginate/pectate gel beads can be appropriately described by a pseudo second order rate law according to the following equation [61]:

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

where \( q_t \) and \( q_e \) are the values of the amount of metal ion (Cd\(^{2+}\) or Cu\(^{2+}\)) adsorbed (\( \mu\text{mol bead}^{-1} \)) at equilibrium and at different contact times \( t \), respectively; \( k_2 \) is the pseudo–second order rate coefficient (\( \mu\text{mol}^{-1} \text{ min}^{-1} \) bead). The integrated form of Eq. (2) for the boundary conditions \( t = 0 \) to \( t = t \) and \( q_t = 0 \) to \( q_t = q_e \) is:

\[
\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t
\]

that can be rearranged to obtain:

\[
q_t = \frac{t}{1/k_2 q_e^2 + t/q_e}
\]

By fitting the experimental data to Eq. (2b), the second order rate constant \( k_2 \) and \( q_e \) were determined. The values of both parameters for Cu(II) and Cd(II) sorption onto Ca-A, Ca-AP\(_1\), Ca-AP\(_{1.5}\) and Ca-AP\(_2\) systems and the corresponding calcium release are reported in Tables 3 and 4. The plots of \( q_t \) as function of \( t \) for cadmium(II) and copper(II) sorption and calcium(II) release are

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Physico-chemical and mechanical properties of gel beads.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Properties</strong></td>
<td><strong>Gel beads</strong></td>
</tr>
<tr>
<td>Bead diameter (mm)</td>
<td>3.45 ± 0.05(^a)</td>
</tr>
<tr>
<td>Bead density (g/mL)(^b)</td>
<td>1.023 ± 0.003</td>
</tr>
<tr>
<td>Dry weight of one bead (mg)</td>
<td>0.7 ± 0.1</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>97.3</td>
</tr>
<tr>
<td>Mechanical resistance (N/ bead)</td>
<td>0.19 ± 0.02</td>
</tr>
</tbody>
</table>

\(^a\) = Std. dev.  
\(^b\) Density of wet gel beads at \( T = 20^\circ \text{C} \).
shown in Figs. 3 and 4 for all the systems investigated, including calcium alginate (Ca-A) polymer gel used here as a reference sorbent material. As expected, the removal ability of the simple calcium alginate gel beads is less than that of the mixed alginate/pectate gel beads, especially when the pectin concentration in mixed gel beads increases according to the following sorption ability trend: Ca-AP$_1 < $ Ca-AP$_{1.5} < $ Ca-AP$_2$. The quite high values of correlation coefficients $R^2$ show that the pseudo-second order model fits satisfactorily to the experimental data for all the systems examined.

The higher amount of Cu$^{2+}$ adsorbed as compared with Cd$^{2+}$ (see the $q_e$ values in Tables 3 and 4) is in accordance with the stability trend of complex species formed by alginate and pectate with the two metal ions in aqueous solution (see Section "Preliminary speciation analysis").

Since alginate and pectate are used as calcium salts in gel phase, it is presumable that the removal process of metal ions from solution occurs via ion exchange between calcium of gel beads and metal ions present in solution. With the aim to check this hypothesis, the kinetics of the release of Ca$^{2+}$ ion in solution by the different gel beads was also investigated, in the presence and in absence of Cu$^{2+}$ and Cd$^{2+}$ ions, under the same experimental conditions. The results of this investigation are shown in Figs. 3b and 4b (presence of Cu(II) and Cd(II) ions) and Fig. 5 (absence of Cu(II) and Cd(II) ions). The kinetic parameters are reported in Tables 3 and 4.

The amount of Ca$^{2+}$ ion released by the alginate and hybrid alginate/pectate gel beads in distilled water is very low as confirmed by the values of $q_e$ calculated: $q_e$ release of Ca$_{A}$ = 0.001 m mol bead$^{-1}$ and $q_e$ release of Ca$_{AP}$ = 0.002 m mol bead$^{-1}$ for Ca-A, Ca-AP$_1$, Ca-AP$_{1.5}$ and Ca-AP$_2$ gel beads, respectively.

The results obtained confirm the above hypothesis. Indeed, the amount of Cu$^{2+}$ released by gel beads increases in the presence of metal ions (Cu$^{2+}$ or Cd$^{2+}$) in solution; for example, the kinetic parameter $q_e$ for the calcium release by Ca-AP$_1$ gel beads is: $q_e$ release of Ca$_{AP}$ = 0.80 and 0.008 m mol bead$^{-1}$ in presence and in absence of Cu$^{2+}$, respectively.

In general, the amount of copper(II) or cadmium(II) adsorbed is slightly higher than the calcium(II) released by gel beads. This apparently anomalous behavior may be attributed to other factors, such as, for example, the presence of other calcium-free binding groups present in the alginate and pectate structure [65].

The low variation of pH (within ±0.2 log units), monitored by potentiometry during the kinetic experiments, lets us to affirm that: (i) no hydrolysis of metal ions in solution occurs, and (ii) the release of Ca$^{2+}$ from gel beads partially depends on the ion exchange with H$^+$ and, therefore, it must be mostly attributed to the ion exchange with metal ions present in solution.
Isotherms for Cd\textsuperscript{2+} and Cu\textsuperscript{2+} sorption by gel beads

Equilibrium data were analyzed using Langmuir and Freundlich isotherm models. According to the Langmuir model, the sorption is assumed as a chemical process occurring on homogeneous binding sites of the sorbent material and is generally expressed by the following non-linear equation:

\[ q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \]  \hspace{1cm} (3)

where \( q_e \) (\( \mu \text{mol bead}^{-1} \)) is the metal concentration adsorbed by gel beads at equilibrium; \( q_{\text{max}} \) (\( \mu \text{mol bead}^{-1} \)) represents the monolayer sorption capacity of the sorbent; \( K_L \) (L mg\textsuperscript{-1} bead) is the Langmuir constant that provides information on the sorption process free energy; \( C_e \) (mg L\textsuperscript{-1}) is the metal ion concentration in solution.

The Freundlich isotherm model is an empirical relationship based on the assumption that the sorption process takes place on the surface of sorbent by heterogeneous sites with different heat of sorption. The Freundlich isotherm model is expressed by the following exponential equation:

\[ q_e = K_F C_e^{1/n} \]  \hspace{1cm} (4)

where \( K_F \) (\( \mu \text{mol L mg}^{-1} \text{ bead}^{-1} \)) is the Freundlich constant related to the sorption capacity and \( 1/n \) is an empirical parameter correlated to the sorption intensity depending on the heterogeneity of sorbent material. The Langmuir and Freundlich isotherm plots for the sorption of Cu\textsuperscript{2+} and Cd\textsuperscript{2+} by Ca-A, Ca-AP\textsubscript{1}, Ca-AP\textsubscript{1.5} and Ca-AP\textsubscript{2} are reported in Figs. 6 and 7. The values of parameters for Langmuir and Freundlich models are given in Table 5. From the plot of Fig. 6 and also considering the correlation coefficient values \( R^2 \), the Langmuir model seems to fit the equilibrium data slightly better than the Freundlich model.

In Fig. 8 the \( q_{\text{max}} \) values obtained for copper(II) and cadmium(II) sorption by using Langmuir model (Eq. (3)) are plotted vs. the percentage of pectin in gel beads. As can be seen, the sorption capacity of gel beads shows a linear increase when increasing the pectin percentage. According to the experimental conditions used...
in this work, this relationship can be expressed by the equation:

\[
q_{\text{max}} = q_{\text{max(Ca-A)}} + \gamma P_x
\]  

(5)

where \( q_{\text{max(Ca-A)}} \) is the maximum sorption capacity exhibited by calcium alginate beads towards Cu\textsuperscript{2+} or Cd\textsuperscript{2+} ions; \( \gamma \) is an empirical parameter (equal to 0.549 \( \mu \text{mol bead}^{-1} \) and 0.795 \( \mu \text{mol bead}^{-1} \)) and \( P_x \) is the percentage of pectin in gel beads.

**Table 3**

Pseudo-second order kinetic parameters for Cu\textsuperscript{2+} sorption into and Ca\textsuperscript{2+} release from alginate and alginate/pectin gel beads at pH = 5.5 and at room temperature.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Parameters for Cu\textsuperscript{2+} sorption</th>
<th>Parameters for Ca\textsuperscript{2+} release</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_a^a ) ( k_2^b ) ( R^2 )</td>
<td>( q_a^a ) ( k_2^b ) ( R^2 )</td>
</tr>
<tr>
<td>Ca-A</td>
<td>0.73 \pm 0.02 0.66 \pm 0.15 0.8666</td>
<td>0.64 \pm 0.01 0.54 \pm 0.08 0.9469</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{1}</td>
<td>0.84 \pm 0.02 0.48 \pm 0.08 0.9243</td>
<td>0.80 \pm 0.02 0.26 \pm 0.04 0.9539</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{1.5}</td>
<td>0.96 \pm 0.02 0.35 \pm 0.04 0.9669</td>
<td>0.84 \pm 0.02 0.27 \pm 0.04 0.9613</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{2}</td>
<td>1.03 \pm 0.03 0.55 \pm 0.11 0.8660</td>
<td>0.90 \pm 0.02 0.28 \pm 0.04 0.9595</td>
</tr>
</tbody>
</table>

\( ^a \mu \text{mol bead}^{-1} \).

\( ^b \mu \text{mol bead}^{-1} \text{ min}^{-1} \text{ bead}. \)

**Table 4**

Pseudo-second order kinetic parameters for Cd\textsuperscript{2+} sorption into and Ca\textsuperscript{2+} release from alginate and alginate/pectin gel beads at pH = 5.5 and at room temperature.

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Parameters for Cd\textsuperscript{2+} sorption</th>
<th>Parameters for Ca\textsuperscript{2+} release</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( q_a^a ) ( k_2^b ) ( R^2 )</td>
<td>( q_a^a ) ( k_2^b ) ( R^2 )</td>
</tr>
<tr>
<td>Ca-A</td>
<td>0.63 \pm 0.01 0.74 \pm 0.09 0.9502</td>
<td>0.43 \pm 0.01 1.05 \pm 0.16 0.9365</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{1}</td>
<td>0.75 \pm 0.02 0.46 \pm 0.08 0.9229</td>
<td>0.76 \pm 0.03 0.21 \pm 0.04 0.9403</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{1.5}</td>
<td>0.82 \pm 0.02 0.38 \pm 0.07 0.9216</td>
<td>0.77 \pm 0.02 0.22 \pm 0.04 0.9450</td>
</tr>
<tr>
<td>Ca-AP\textsubscript{2}</td>
<td>0.89 \pm 0.02 0.36 \pm 0.05 0.9494</td>
<td>0.79 \pm 0.03 0.23 \pm 0.04 0.9357</td>
</tr>
</tbody>
</table>

\( ^a \mu \text{mol bead}^{-1} \).

\( ^b \mu \text{mol bead}^{-1} \text{ min}^{-1} \text{ bead}. \)

**Literature analysis and data comparisons**

Relatively few studies have been carried out on cadmium and copper sorption by alginate and pectate gel only [48–53,59,66–72], i.e. in absence of other molecules or substances encapsulated inside or mixed. Results reported show much discrepancies owing to the different experimental conditions used, such as pH, initial metal concentration, size and dry weight of gel.
beads and the amount of sorbent biomaterial. The large heterogeneity of data reported in the literature is confirmed by the values of \( q_{\text{max}} \) (expressed as mmol g\(^{-1}\)) found by the different authors for copper and cadmium adsorption onto calcium alginate gel beads, ranging between 1.20 and 2.04 for copper [49, 50, 52, 68, 69] and between 0.21 and 2.09 for cadmium [50, 52, 66–68, 70, 71]. Moreover, no studies are reported in the literature on the sorption by mixed alginate/pectate gel beads of Cd\(^{2+}\) and Cu\(^{2+}\) ions, respectively. Deze et al. [68] found, at the same pH and for the same metal ions, \( q_{\text{max}} = 1.53 \) and 1.78 mmol g\(^{-1}\). Chen et al. [49] found for cadmium ion a

\[ q_{\text{max}} = 2.04 \text{ mmol g}^{-1} \] at pH = 4. These results are the more close to those obtained in this work, i.e., \( q_{\text{max}} = 2.44 \) and 2.71 mmol g\(^{-1}\) for cadmium and copper sorption by calcium alginate gel beads, respectively, at pH = 5.5. In particular, a fairly good accordance can be noted between the \( q_{\text{max}} \) values found for cadmium ion. As pointed out before, the differences can be attributed to the different experimental conditions used, with particular reference to pH values.

### Table 5

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Langmuir model</th>
<th>Freundlich model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cadmium(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-A</td>
<td>( q_{\text{max}} = 1.71 \pm 0.05 )</td>
<td>( K_F = 0.23 \pm 0.02 )</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.9958</td>
<td>0.96286</td>
</tr>
<tr>
<td>Ca-AP(_1)</td>
<td>( q_{\text{max}} = 2.27 \pm 0.09 )</td>
<td>( K_F = 0.35 \pm 0.03 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.049 ± 0.006</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.98819</td>
<td>0.98174</td>
</tr>
<tr>
<td>Ca-AP(_{1.5})</td>
<td>( q_{\text{max}} = 2.58 \pm 0.09 )</td>
<td>( K_F = 0.46 \pm 0.05 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.068 ± 0.001</td>
<td>2.9 ± 0.2</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.98820</td>
<td>0.99020</td>
</tr>
<tr>
<td>Ca-AP(_2)</td>
<td>( q_{\text{max}} = 2.79 \pm 0.04 )</td>
<td>( K_F = 0.55 \pm 0.08 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.083 ± 0.004</td>
<td>3.0 ± 0.3</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99796</td>
<td>0.98992</td>
</tr>
<tr>
<td><strong>Copper(II)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca-A</td>
<td>( q_{\text{max}} = 1.9 \pm 0.1 )</td>
<td>( K_F = 0.05 \pm 0.01 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.009 ± 0.001</td>
<td>1.6 ± 0.1</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.999335</td>
<td>0.97809</td>
</tr>
<tr>
<td>Ca-AP(_1)</td>
<td>( q_{\text{max}} = 2.39 \pm 0.09 )</td>
<td>( K_F = 0.10 \pm 0.01 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.012 ± 0.001</td>
<td>1.82 ± 0.08</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.996989</td>
<td>0.99326</td>
</tr>
<tr>
<td>Ca-AP(_{1.5})</td>
<td>( q_{\text{max}} = 3.06 \pm 0.19 )</td>
<td>( K_F = 0.11 \pm 0.02 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.012 ± 0.001</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.992277</td>
<td>0.98281</td>
</tr>
<tr>
<td>Ca-AP(_2)</td>
<td>( q_{\text{max}} = 3.4 \pm 0.1 )</td>
<td>( K_F = 0.14 \pm 0.02 )</td>
</tr>
<tr>
<td>( K_L )</td>
<td>0.014 ± 0.001</td>
<td>1.76 ± 0.09</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.99750</td>
<td>0.99068</td>
</tr>
</tbody>
</table>

\( ^{a} \mu \text{mol bead}^{-1} \)

\( ^{b} \text{mg}^{-1} \)

\( ^{c} \) Std. dev.
Conclusions

New mixed alginate/pectate sorbent materials were used in gel phase for cadmium(II) and copper(II) removal from aqueous solutions. Physical and mechanical properties of these materials were characterized by different techniques, such as thermogravimetric analysis and SEM–EDX.

The sorption process of Cd(II) and Cu(II) ions from solution by mixed alginate/pectin gel beads at different concentrations ratios was evaluated on the basis of kinetic and equilibrium studies.

The results obtained from kinetic investigations show that: (i) the removal of cadmium(II) and copper(II) ions from the solution occurs prevalently by ion exchange with calcium(II) ion present in the gel beads and useful correlations were found between the amount of Cu²⁺ and/or Cd²⁺ absorbed and the Ca²⁺ released; (ii) the sorption ability of mixed alginate/pectin gel beads is higher in comparison with the calcium alginate polymer gel; (iii) the sorption process follows a pseudo second-order kinetic model and the sorption capacity increases with the increasing of pectin percentage in the mixed alginate/pectate gel system, according to the trend Ca-AP₂ > Ca-AP₁ > Cd-AP₁; (iv) the Langmuir isotherm model fits equilibrium data better than the Freundlich model.

The results of preliminary speciation analysis [62–64] allowed us to assess the pH value of about 5.5 as the most appropriate one (i) to avoid or minimize the hydrolysis of metal ions under investigation as well as the protonation of biopolymers, (ii) to favor the formation of stable metal–biopolymer complex species. The higher stability of copper species in comparison with cadmium species, as shown by aqueous speciation analysis, is confirmed also by the sorption trend (Cu > Cd) obtained using the biopolymers in gel phase.

A literature data analysis was made on the cadmium and copper sorption by calcium alginate and a comparison of results obtained in this work was also given. No results are reported in the literature on the metal sorption by the mixed alginate/pectin gel system investigated in this work.

The results obtained from this study show that the hybrid alginate/pectate system in gel phase, never before tested, can be considered a good material to be used as low cost and environmental friendly sorbent for cadmium(II) and copper(II) removal from aqueous solution.

Acknowledgments

The authors S.C., A.G., G.L., A.P., and D.P. carried out this work thanks to a grant from the project “Development of innovative technologies for the treatment of fluid wastes from shipping activities and for marine environment protection” (PON02_00153_2849085 “Ricerca e competitività 2007–2013, asse 1”).

References
