



ORIGINAL ARTICLE

Sorption of Pd(II) ion by calcium alginate gel beads at different chloride concentrations and pH. A kinetic and equilibrium study



Salvatore Cataldo, Antonio Gianguzza, Alberto Pettignano *

Dipartimento di Fisica e Chimica, Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy

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Abstract A kinetic and thermodynamic study on the sorption ability of calcium alginate gel beads towards Pd(II) ion was made in aqueous solution at different pH and chloride concentrations. The experimental conditions adopted in the sorption experiments were established on the basis of a speciation study on the Pd²⁺-AA system in which all the side reactions, such as the hydrolysis of Pd(II), the protonation of alginate and the interactions of the ligand and the metal ion with ions of ionic medium were taken into account. In the pH range 2–5 and at chloride concentration in the range $0 \leq C_{Cl^-}/\text{mmol L}^{-1} \leq 10$ the gel beads showed good sorption ability towards Pd(II) ion as confirmed by kinetic and thermodynamic data calculated by a pseudo second order equation and using Langmuir and Freundlich models. The comparison between q_e values related to the kinetics of Pd(II) sorption and Ca(II) release in solution by gel beads indicated that the ion exchange is one of the main sorption mechanisms of the sorbent material. Similarities were found between the trends of sequestering (% PdAA species, $pL_{0.5}$) and the sorption (q_e , q_{\max}) parameters as function of pH and chloride concentration. It confirms a close relation between the behaviour of alginate as sequestering agent for Pd(II) ion in aqueous solution and of calcium alginate gel beads as sorbent material for the removal of the metal ion.

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1. Introduction

The particular physical and chemical properties, especially the catalytic ones, make palladium one of the most important platinum group elements (PGE). This metal is very useful for several purposes in different fields such as industry, agriculture and medicine (Renner and Schmuckler, 1991; Zereini and Alt, 2006). The subsequent recovery of palladium from wastewaters and from no longer used materials is of great importance because of: (i) its toxicity towards

* Corresponding author. Tel.: +39 091 23897959; fax: +39 091 590015.

E-mail address: alberto.pettignano@unipa.it (A. Pettignano).

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plants, animals and humans that imposes very low concentration limits in the environment; (ii) its relatively low availability that makes the recovery of the metal ion very important from the economical point of view (Renner and Schmuckler, 1991; Zereini and Alt, 2006).

Among the different techniques (Hubicki et al., 2008; Liu et al., 2009; Spitzer and Bertazzoli, 2004) commonly used for the removal/recovery of metal ions from wastewaters and other aqueous solutions the biosorption is the most promising (Das, 2010; Mack et al., 2007; Wang and Chen, 2009; Wase and Forster, 1997). The biomaterials used in this technique for the removal of metal ions should be available in large quantities, inexpensive and biodegradables and usually should have high yields in terms of metal ion uptake. Several articles and reviews have been published on the use of different types of biomasses as sorbent material, e.g., algae, bacteria, fungi, pulp and peel of different fruits, etc (Volesky, 2001, 2003). All these biomaterials contain large amounts of polyelectrolytes with high binding capacity towards metal ions that are mainly responsible for the metal uptake ability of these substances (Bailey et al., 1999; Reddad et al., 2002; Volesky, 2003; Wang and Chen, 2009; Wase and Forster, 1997). Among these natural polyelectrolytes the most studied are alginic acid (AA), chitosan and pectin, which are present in large amounts in algae, shell of crustaceans and pulp and peel of several fruits, respectively (Bailey et al., 1999; Kelco, 1987; Mata et al., 2009; Reddad et al., 2002; Thakur et al., 1997).

The use of raw materials as biosorbent for the removal of palladium(II) from water solutions was proposed from several authors (Das, 2010; de Vargas et al., 2004; Mack et al., 2007) but few studies were carried out on the direct use of the natural polyelectrolytes contained therein. In particular, among the cited polyelectrolytes only chitosan and modified chitosan gels were considered for palladium(II) ion removal (Ramesh et al., 2008; Ruiz et al., 2000, 2002; Zhou et al., 2009).

The direct use of these polyelectrolytes can be very useful since their extraction is usually simple and inexpensive (Kelco, 1987; Mata et al., 2009; Thakur et al., 1997) and their sorption capacity towards metal ions may be greater than that of the raw materials from which they are extracted. Moreover, the reuse of the sorbent and the recovery of the metal ion are usually possible and easy to do (Mata et al., 2009, 2010). In this work the use of gel beads of calcium alginate (CaAA) as sorbent material for Pd(II) removal from aqueous solutions is proposed and different techniques were used for its characterization (Section 4.1).

Alginic acid is a copolymer of 1,4 linked β -D-mannuronic and α -L-guluronic acid residues contained in high percentages in brown algae (Kelco, 1987) whose acid-base properties are due to the carboxylic groups of the monomer units (Crea et al., 2009; Lagoa and Rodrigues, 2007).

Alginic acid can easily gel in the presence of divalent cations, especially calcium(II) ion, and calcium alginate salt gel has been widely tested as sorbent material for different metal ions' removal (Cataldo et al., 2013a,b; Gotoh et al., 2004a; Papageorgiou et al., 2006).

According to the chemical behaviour of the metal ion to be removed from aqueous solution and the acid-base properties of the sequestering agent, the right experimental conditions of the solution have to be assessed before the sorption studies. In particular, the formation of uncharged or negatively charged hydrolytic or complex species and low soluble species

of Pd(II) were avoided or reduced. Therefore, a solution speciation study is preliminary needed: (i) to define the pH value useful to avoid metal hydrolysis and to assure an adequate amount of deprotonated binding sites of the sorbent material; (ii) to check for the formation of complex species formed by the metal ion with other ligands potentially present in the solution; (iii) to know the strength of interaction between the metal ion and the sequestering agent. This study is particularly important for Pd(II) ion which undergoes strong hydrolysis at very low pH and is able to form quite stable species with chloride ion which is usually present in natural aqueous systems. Details on the results from the speciation study carried out on the Pd-AA in aqueous solution are reported in Section 4.2.

Adsorption of palladium(II) ion from solution onto calcium alginate gel beads was evaluated by kinetic and thermodynamic investigations carried out in batch mode as function of contact time, chloride concentration and pH, by considering the solution conditions more favourable to the metal sorption, as results from speciation studies. Data from kinetic and thermodynamic measurements were processed by a pseudo second order equation and Langmuir and Freundlich models, respectively (see Sections 4.3 and 4.4).

Several mechanisms of biosorption have been proposed by different authors to justify the sorption ability of CaAA and other biomaterials, towards metal ions such as ion exchange, complexation, chelation, physical adsorption and microprecipitation (Park et al., 2010; Volesky, 2001).

In order to verify the hypothesis according to which the sorption process occurs by an ion exchange mechanism, as we found for other metal ions sorption by calcium alginate gel beads (Cataldo et al., 2013a,b), a parallel study on the kinetics of calcium release from gel beads was also carried out.

Some similarities were found between the parameters of alginate sequestering ability towards Pd(II) ion in aqueous solution (% PdAA species, $pL_{0.5}$), obtained by the results of speciation analysis, and the parameters of sorption process by CaAA gel beads (q_e , q_{max}). A detailed discussion on this point is reported in Section 4.5.

Finally, to put into perspective these results, our data were compared with those of the literature (see Section 4.6).

2. Materials and methods

2.1. Chemicals

Alginic acid (by Sigma, lot 051M1864V, molecular weight in the range 70–100 kDa), extracted from *Macrocystis pyrifera*, with an average content of mannuronic (m) and guluronic (g) acids of 61% and 39%, respectively, was used as sodium salt. Palladium(II) ion solutions were prepared starting from palladium(II) nitrate dihydrate salt (by Sigma–Aldrich, purum). NaNO_3 , NaClO_4 and NaCl solutions were prepared by weighing the pure salts (Fluka) after drying at 110 °C for 2 h. Nitric and hydrochloric acids and sodium hydroxide solutions used to adjust the pH of the metal ion solutions and in the ISE- H^+ potentiometric titrations were prepared by diluting concentrated Fluka ampoules and standardized against sodium carbonate and potassium hydrogen phthalate, respectively. Calcium chloride dihydrate (by Fluka) was used to prepare calcium alginate (Ca-AA) gel beads. Standard

solutions of calcium(II) ion were prepared by diluting concentrated Sigma Aldrich ampoules. Standard solutions of palladium(II) ion were prepared from a 1000 $\mu\text{g mL}^{-1}$ standard solution in 10% HCl (SCP Science). All the solutions were prepared using fresh CO_2 -free ultra pure water ($\rho \geq 18 \text{ M}\Omega \text{ cm}$).

2.2. Preparation and characterization of calcium alginate gel beads

Gel beads were prepared by following the classical procedure used in Reference Cataldo et al. (2013b). The beads were stored in ultrapure water at 4 °C before use.

The physical and mechanical properties of Ca-AA gel beads were investigated by different techniques. The diameter of beads was measured with a digital calliper (MITUTOYO, model 500–181-U) on fifty beads. A helium pycnometer (AccuPyc 1330) was used to measure the density of gel beads at $T = 20 \text{ }^\circ\text{C}$. The experiment was repeated three times on different gel beads. The water content of gel beads was determined as follows: fifty beads of gel were dried in an oven for three days at 40 °C and the dry weight was measured after a constant weight was reached. The weight of the wet beads was determined by weighting the same number of gel beads after they were placed on a cellulose filter for 30 s. The procedure was repeated three times. The mechanical resistance of gel beads, measured by a Texture Analyser (model TA-XTS2i, Stable Micro Systems, England), represents the mean force (expressed in Newton's) necessary to generate the 10% compression on a bead placed under a cylinder probe P10 (Batch 2370, Stable Micro Systems, England). The experiments were repeated on 40 beads and the average value was calculated together with the standard deviation.

The morphology of gel beads before and after sorption of Pd(II) ion (at $C_{\text{Pd}^{2+}} = 30 \text{ mg L}^{-1}$, $\text{pH} = 2$, in NaNO_3 medium, at $I = 0.01 \text{ mol L}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$) was investigated by an electron microscope ESEM FEI QUANTA 200F. Before the analysis the gel beads were oven-dried at $T = 105 \text{ }^\circ\text{C}$ for 24 h 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.

2.3. Experimental equipment and procedures for speciation study

Speciation study of the Pd(II)-AA system in $\text{NaCl}/\text{NaClO}_4$ mixed media, at $I = 0.1 \text{ mol L}^{-1}$ and $T = 25 \text{ }^\circ\text{C}$ was carried out by using the potentiometric technique. An apparatus consisting of a model 713 Metrohm potentiometer, equipped with a combination glass electrode (Ross type 8102, from Orion), and a Model 765 Metrohm motorized burette was employed. Estimated accuracy was 0.2 mV and 0.003 mL for electromotive force (e.m.f.) and titrant volume readings, respectively. The apparatus was connected to a PC, and automatic titrations were performed using a suitable computer program to control titrant delivery and data acquisition and to check for e.m.f. stability. All titrations were carried out in thermostated cells under magnetic stirring, bubbling purified presaturated N_2 through the solution in order to exclude O_2 and CO_2 . In each titration 25 mL of solution containing palladium(II)

nitrate 0.4–0.5 mmol L^{-1} , sodium alginate 1–2 mmol L^{-1} and the right amount of the two salts (NaCl and NaClO_4) of the ionic medium were titrated with NaOH in the pH range 2–5. The titrand solutions were acidified with known amounts of HClO_4 or HCl in order to start the titrations from $\text{pH} \approx 2$. For each experiment, independent titrations of strong acidic solution with standard base were carried out under the same medium and ionic strength conditions as the system to be investigated, with the aim of determining E^0 (standard potential). In this way, the pH scale used was the total scale, $\text{pH} = -\log[\text{H}^+]$, where $[\text{H}^+]$ is the free proton concentration (not activity).

2.4. Experimental equipment and procedures for kinetics and adsorption isotherm

Batch kinetic experiments at $25 \pm 1 \text{ }^\circ\text{C}$ were carried out by putting 25 beads in Erlenmeyer flasks containing each 25 mL of solution of palladium(II) 30 mg L^{-1} as $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$. Kinetic experiments were performed in $\text{NaClO}_4/\text{NaCl}$ mixed media at $I = 0.01 \text{ mol L}^{-1}$ by varying the concentration of chloride in the range $0 \leq C_{\text{Cl}^-} (\text{mmol L}^{-1}) \leq 10$ in the pH range 2–5. The solutions were shaken at 180 rpm using an orbital mixer (model M201-OR, MPM Instruments). Samples were withdrawn at different times in the range 1–360 min and 10 mL of each solution was pipetted and stored in plastic tubes. For each set of kinetic experiments, sixteen samples of 10 ml were collected for the ICP-OES measurements. The variation of H^+ concentration was checked by a potentiometer (Model 654 Metrohm) equipped with a combined ISE- H^+ glass electrode (Ross type 8102). For sorption isotherm experiments a different number of Ca-AA gel beads (ranging between 5 and 150) was added to 25 mL of $\text{Pd}(\text{NO}_3)_2$ solution at 30 mg L^{-1} . The range of pH as well as the chloride concentration and the temperature of the solutions were similar to those of kinetic experiments. The solutions were shaken at 180 rpm for six hours and then filtered and stored in plastic tubes. The concentration of Ca(II) and Pd(II) ions in the filtrates obtained from both kinetic and isotherm experiments was determined by ICP-OES (Perkin Elmer Model Optima 2100, equipped with an auto sampler model AS-90).

3. Calculation

3.1. Calculations in speciation study

The following computer programs (De Stefano et al., 1997) were used for the elaboration of potentiometric data: (i) ESAB2M for the refinement of all of the parameters from the acid–base titration (E^0 , the ion product constant of water K_w , the liquid junction potential coefficient j_a , and the analytical concentration of reagents), (ii) BSTAC and STACO for the calculation of complex formation constants, (iii) ES4ECI to draw the speciation diagrams. Formation constants of Pd^{2+} -AA complex species are given according to the following equilibrium:



where p , q and r are the stoichiometric coefficients.

3.2. Models for kinetic and thermodynamic studies of palladium(II) sorption and calcium(II) release

The kinetic study of Pd(II) sorption and of Ca(II) release by calcium alginate gel beads was carried out by processing the experimental data by the pseudo second order Eq. (2) (Ho and Ofomajia, 2006):

$$\frac{dq_t}{dt} = K(q_e - q_t)^2 \quad (2)$$

where q_e and q_t are the amount of Pd(II) adsorbed or Ca(II) released by gel beads (mmol/g dry beads) at equilibrium and at time t , respectively; K is the rate constant of sorption or release ($\text{mmol}^{-1} \text{min}^{-1}$). The integrated form of Eq. (2) for the boundary conditions ($t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$) is:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (2a)$$

that can be rearranged to obtain:

$$q_t = \frac{t}{\frac{1}{kq_e} + \frac{t}{q_e}} \quad (2b)$$

The thermodynamic approach to the sorption of metal ions by gel beads was made by applying Langmuir and Freundlich isotherm models according to Eqs. (3) and (4), respectively (Gotoh et al., 2004b).

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

$$q_e = K_F C_e^{1/n} \quad (4)$$

where q_e and C_e are the amount of palladium(II) ion adsorbed by the beads (mg g^{-1} of dry beads) and the concentration of the metal ion in solution (mg L^{-1}) at the equilibrium, respectively. q_{\max} is the maximum sorption capacity of gel beads (mg g^{-1} of dry beads), K_L is the Langmuir constant which gives information on the affinity between the sorbent and the sorbate (Pd(II) ion in this case) at the conditions adopted in the experiments. In the Eq. (4), K_F is the Freundlich constant and accounts for the adsorption capacity; n is an empirical parameter, which gives information on the intensity of the sorption of gel beads towards the metal ion. Langmuir model describes the metal sorption on the sorbent material as a monolayer sorption, whilst Freundlich model takes into account the heterogeneous adsorption of the metal ion on the binding sites of the sorbent material. In this particular case the heterogeneity of the sorption can be attributable only to the different charged species of palladium(II) in solution which

change by varying the experimental conditions, especially, the pH and the chloride concentration, as will be shown below (see Section 4.2).

Kinetic and isotherm equations were fitted to experimental data by using the Linear and Non Linear data Analysis home-made computer program (LIANA) (De Stefano et al., 1997).

4. Results and discussion

4.1. Characterization of Ca-AA gel beads

The results of characterization of gel beads are reported in Table 1. They are very close to those reported in Reference Cataldo et al. (2013b) for gel beads of the same biomaterial and this confirms the reproducibility of the method used to produce the gel beads. Among the experimental data reported in the Table, it is worth mentioning the mechanical resistance of the sorbent material. In fact, the hardness of the sorbent material is very important when it is employed in the removal/recovery of metal ions from water solutions. Although the gel beads have a 97.4% of water, they have a good mechanical resistance (0.19 N to generate the 10% compression of the bead).

In Fig. 1 are reported the micrographs obtained from SEM analysis at 100 and 500 magnifications for Ca-AA gel beads after contact for six hours with solutions, at pH = 2, in NaNO_3 medium, $I = 0.01 \text{ mol L}^{-1}$ with (Fig. 1b and d) and without Pd(II) ion 30 mg L^{-1} (Fig. 1a and c). Differences in morphology can be noted after Pd(II) sorption. The surface of gel beads, initially smooth, becomes wrinkled with an increase in creases and pores. The same surface change was noted after Cd(II) and Cu(II) sorption on calcium alginate and calcium alginate/pectate gel beads as reported in a previous paper (Cataldo et al., 2013a) and, as in that case, it can be attributed to the shrinkage of the beads at high concentrations of metal ions different from Ca(II).

4.2. Speciation study of the palladium(II) – alginate system

To assess the more appropriate solution conditions to be adopted in order to obtain the best efficiency in the palladium(II) sorption by calcium alginate gel beads, a preliminary speciation study was carried out on the Pd-AA system in aqueous solution, at $I = 0.1 \text{ mol L}^{-1}$, in mixed $\text{NaClO}_4/\text{NaCl}$ ionic medium and at different chloride concentrations. As an example, in Fig. S1 is reported the ISE- H^+ potentiometric curve of a solution containing $\text{Pd}^{2+} 0.38 \text{ mmol L}^{-1}$, AA 0.57 mmol L^{-1} , in $\text{NaCl}/\text{NaClO}_4$ medium, at $I = 0.1 \text{ mol L}^{-1}$ and $C_{\text{Cl}^-} = 0.01 \text{ mol L}^{-1}$. Previous investigations on the chemical behaviour of Pd(II) ion in aqueous solution (Gianguzza et al., 2010) show that: (i) Pd(II) undergoes strong hydrolysis starting from very acidic solution condition ($\text{pH} \approx 2$) and low soluble hydroxide formation occurs over $\text{pH} \approx 4.5$ in the absence of ligands; (ii) the presence of chloride ions in solution leads to the formation of quite stable PdCl_x^{2-x} ($x = 1-4$) and mixed $\text{Pd}(\text{OH})\text{Cl}_3^-$ species, (iii) the formation of these complex species allows to keep palladium(II) in solution in a slightly large pH range, up to ~ 5 , (iv) some solution components, such as nitrate or perchlorate, do not interact with Pd(II) ion. Moreover, quantitative data on the protonation of alginate are reported in ref (Crea et al., 2009).

Table 1 Characteristics and physical properties of Ca-AA gel beads.

Properties	
Average bead diameter (mm)	3.44 ± 0.04
Average bead density (g/mL) ^a	1.023 ± 0.001
Dry weight of one bead (mg)	0.70 ± 0.02
Water content (%)	97.4 ± 0.6
Mechanical resistance (N/bead)	0.19 ± 0.03

^a Density of wet gel beads at $T = 20^\circ\text{C}$.

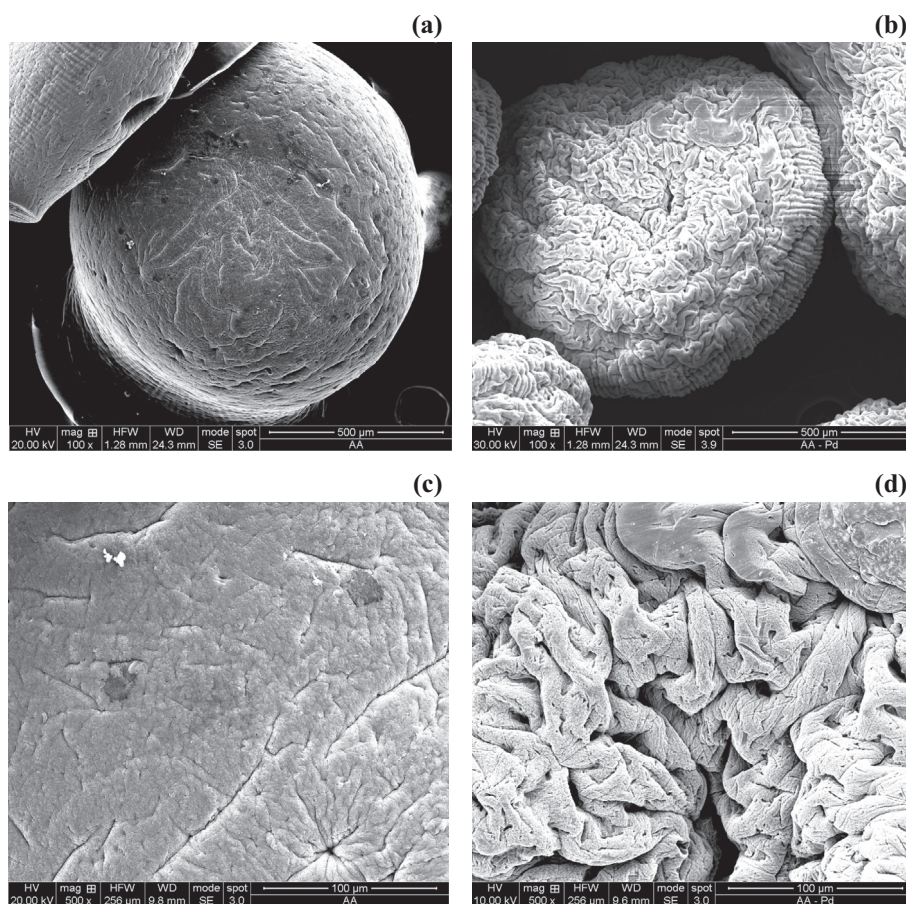


Figure 1 SEM micrographs obtained at 100 and 500 magnifications of (a, c) Ca-AA after contact with a solution at pH = 2, in NaNO₃ medium at $I = 0.010 \text{ mol L}^{-1}$ and (b, d) Ca-AA after contact with a solution containing $C_{\text{Pd}^{2+}} = 30 \text{ mg L}^{-1}$ at pH = 2, in NaNO₃ medium at $I = 0.010 \text{ mol L}^{-1}$.

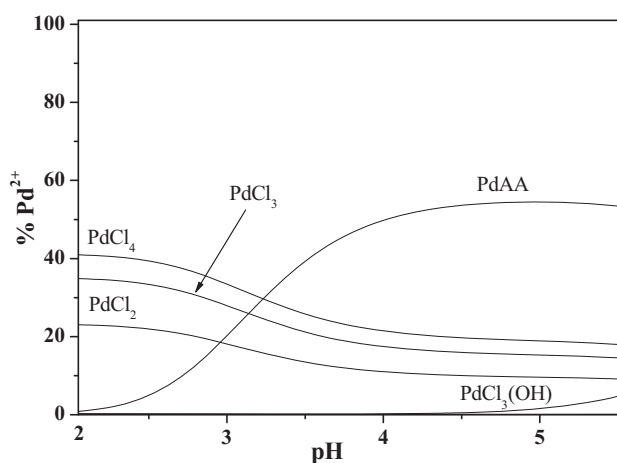


Figure 2 Distribution of species vs pH in the system Pd²⁺-AA, in NaCl/NaClO₄ ionic medium, at $I = 0.1 \text{ mol L}^{-1}$ and at $T = 25 \text{ }^\circ\text{C}$. Experimental conditions: $C_{\text{NaClO}_4} = 0.09 \text{ mol L}^{-1}$, $C_{\text{NaCl}} = 0.01$, $C_{\text{Pd}} = 0.28 \text{ mmol L}^{-1}$, $C_{\text{AA}} = 0.60 \text{ mmol L}^{-1}$.

On the basis of these information, the chemical speciation study, carried out by potentiometric measurements, gave evidence for the formation of a stable Pd-AA species, with

formation constant $\log K_{110} = 9.124 \pm 0.008$, which achieves the maximum percentage formation at pH ≈ 5 in the presence of chloride ion 0.01 mol L^{-1} (see speciation diagram reported in Fig. 2). As shown by results reported in Table 2, the formation percentage of Pd-AA species decreases with the decreasing of pH at the same chloride concentration, while it increases with the decreasing of chloride concentration for the same pH value. This different trend is clearly attributable to the gradual protonation of carboxylic groups of alginate with the lowering of pH, to the predominance of hydrolytic species over pH = 2 which lowers the concentration of Pd(II) ion available to interact with alginate ligand and confirms the role of chloride in keeping Pd(II) ion in solution. Although the protonation of carboxylic groups of alginate increases with the decreasing of pH, at pH = 2 a sufficient amount of COOH groups is present in deprotonated form available to react (Cataldo et al., 2013b). On the basis of these results, the Pd(II) sorption process has been set up considering a solution from where Pd(II) must be removed, containing different chloride concentrations ($0 \leq C_{\text{Cl}^-} / \text{mmol L}^{-1} \leq 10$) in a pH range 2–5.

4.3. Kinetic results

Particular attention has been paid to the conditions where the maximum formation percentage of Pd-AA species was

Table 2 Percentages of Pd(AA) species at different chloride concentrations and pH, in NaClO₄/NaCl medium, at $I = 0.1 \text{ mol L}^{-1}$ and at $T = 25 \text{ }^\circ\text{C}$.

pH	% of Pd(AA) species ^a				
C_{Cl^-} ^b	10	7.5	5	2.5	0
2	0.83	2.13	6.90	29.46	98.75
3	20.22	36.17	60.28	87.11	–
4	49.79	67.73	85.03	–	–
5	54.48	–	–	–	–

^a Speciation diagrams were drawn with the following reagent concentrations: $C_{\text{AA}} = 0.60 \text{ mmol L}^{-1}$; $C_{\text{Pd}^{2+}} = 0.28 \text{ mmol L}^{-1}$;
^b mmol L^{-1} .

achieved, i.e., at pH = 2 in the absence of chloride (PdAA % = 98.75) and at pH 3, 4 and 5 at the lower C_{Cl^-} achievable without precipitation of low soluble hydrolytic species of palladium(II) (see the percentages of PdAA reported in Table 2). To verify the hypothesis according to which the ion exchange

between the Pd(II) in solution and the Ca(II) present in the calcium alginate sorbent gel is the main sorption mechanism, the kinetic measurements were carried out to check both Pd(II) sorption and Ca(II) release at different contact times.

In Table 3 are reported the results of kinetic experiments at different pH values and for different chloride concentrations for both palladium(II) ion sorption and calcium(II) ion release. In general, the R^2 values obtained show that the pseudo-second order Eq. (2) fits well the experimental data. No significant trends were found in the rate of Pd(II) sorption and of Ca(II) release by gel beads as function of C_{Cl^-} and pH. The kinetic constant (K) values range between $0.21 \leq K/\text{g mmol}^{-1} \text{ min}^{-1} \leq 0.93$ and $0.21 \leq K/\text{g mmol}^{-1} \text{ min}^{-1} \leq 0.79$ for palladium(II) sorption and calcium(II) release, respectively.

As can be seen, the amount of Pd(II) adsorbed by CaAA at pH = 2 increases with the decreasing of the chloride concentration in solution ($q_e = 0.431$ and $0.072 \text{ mmol g}^{-1}$ for C_{Cl^-} equal to 0 and 10 mmol L^{-1} , respectively). This trend is clearly shown in Fig. 3a where the experimental kinetic data for Pd(II) sorption are reported together with the curve fits obtained by

Table 3 Pseudo-second order kinetic parameters for Pd(II) sorption onto AA gel beads and Ca(II) release in solution at different pH and chloride concentration values and at $T = 25 \text{ }^\circ\text{C}$.

C_{Cl^-} ^a	K ($\text{g mmol}^{-1} \text{ min}^{-1}$)	q_e (mmol g^{-1})	R^2
<i>Sorption of Pd(II)</i>			
pH = 2			
0.0	0.24 ± 0.01	0.431 ± 0.004	0.9960
2.5	0.21 ± 0.02	0.226 ± 0.004	0.9894
5.0	0.66 ± 0.09	0.179 ± 0.005	0.9622
7.5	0.42 ± 0.10	0.103 ± 0.005	0.9308
10.0	0.42 ± 0.08	0.072 ± 0.003	0.9708
pH = 3			
2.5	0.44 ± 0.02	0.280 ± 0.001	0.9976
5.0	0.37 ± 0.03	0.290 ± 0.004	0.9915
7.5	0.21 ± 0.01	0.241 ± 0.001	0.9990
10.0	0.42 ± 0.03	0.241 ± 0.005	0.9900
pH = 4			
5.0	0.93 ± 0.12	0.143 ± 0.006	0.9673
10.0	0.48 ± 0.02	0.157 ± 0.004	0.9977
pH = 5			
10.0	0.38 ± 0.04	0.170 ± 0.003	0.9902
<i>Release of Ca(II)</i>			
pH = 2			
0.0	0.26 ± 0.02 (0.22 ± 0.02) ^b	2.34 ± 0.03 (2.26 ± 0.02) ^b	0.9857 (0.9937) ^b
2.5	0.24 ± 0.01	2.55 ± 0.02	0.9914
5.0	0.40 ± 0.05	2.36 ± 0.04	0.9290
7.5	0.23 ± 0.01	2.34 ± 0.02	0.9907
10.0	0.30 ± 0.01	2.43 ± 0.02	0.9931
pH = 3			
2.5	0.32 ± 0.02 (0.79 ± 0.04)	0.862 ± 0.008 (0.422 ± 0.003)	0.9896 (0.9914)
5.0	0.22 ± 0.01	0.870 ± 0.009	0.9904
7.5	0.21 ± 0.01	0.867 ± 0.008	0.9929
10.0	0.204 ± 0.009	0.878 ± 0.007	0.9953
pH = 4			
5.0	0.48 ± 0.04 (0.69 ± 0.06)	0.425 ± 0.005 (0.356 ± 0.005)	0.9878 (0.9811)
10.0	0.20 ± 0.01	0.376 ± 0.005	0.9945
pH = 5			
10.0	0.79 ± 0.08 (0.31 ± 0.03)	0.381 ± 0.006 (0.289 ± 0.005)	0.9886

^a mmol L^{-1} .

^b In parentheses are reported the parameters of pseudo-second order kinetic equation and R^2 values for the release of Ca(II) ion in the absence of Pd(II) ions in solution.

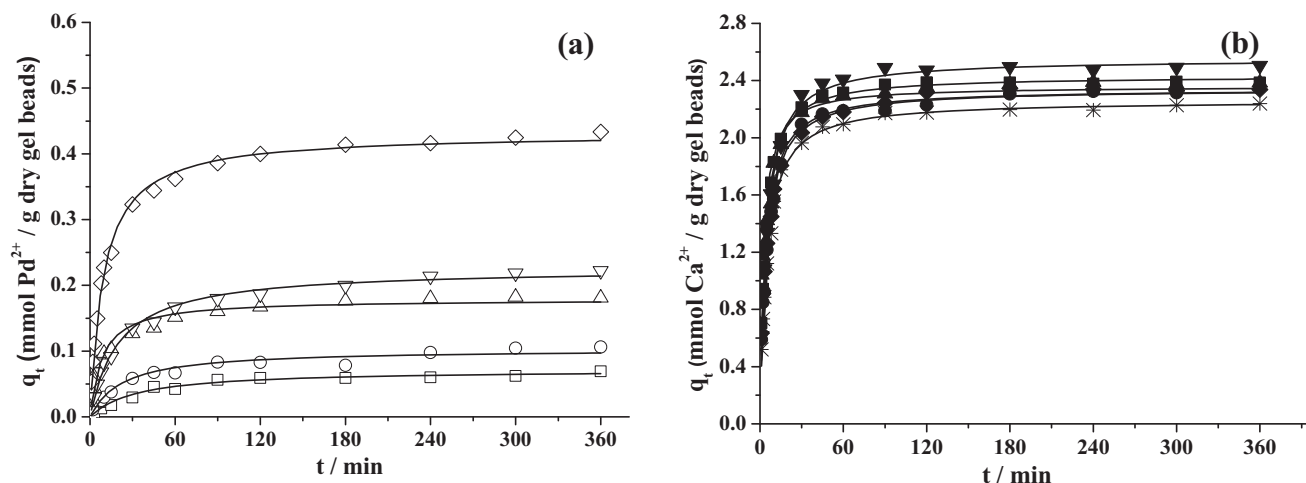


Figure 3 Dependence of q_t (mmol Pd(II) adsorbed/g dry gel beads) (a) or (mmol Ca(II) released/g dry gel beads) (b) on contact time of calcium alginate gel beads with aqueous solutions at different chloride concentrations, at $I = 0.01 \text{ mol L}^{-1}$ ($\text{NaClO}_4/\text{NaCl}$ mixed medium), $T = 25^\circ\text{C}$ and $\text{pH} = 2$. Symbols used for the adsorption of Pd(II) ion at different chloride concentrations (mmol L^{-1}): (0, \diamond); (2.5, $\$$); (5.0, \triangle); (7.5, \circ); (10.0, \square). The corresponding solid symbols refer to the release of Ca(II) ions by gel beads. The symbol * refers to the release of Ca(II) of gel beads in solutions that do not contain Pd(II) ion, at the same pH and ionic strength of the corresponding experiments. The lines represent the fits of kinetic equation.

Eq. (2). The chloride content in solution seems to have very low or no influence in the palladium sorption at $\text{pH} = 3$ and 4 in comparison with the effect shown at $\text{pH} = 2$, probably owing to the contemporary formation of hydroxo species (Gianguzza et al., 2010).

Therefore, by the first inspection of speciation results it could be affirmed that the best conditions for removal of Pd(II) ion from aqueous solutions are at $\text{pH} = 2$ in the absence of chloride, as shown in Fig. 3a. This hypothesis is also confirmed by the high q_e values obtained from kinetic experiments carried out under the above cited conditions, as reported in Table 3. Nevertheless, these conditions are far from those usually found in the natural waters and wastewaters and can be used only for particular acidic industrial effluents or for the recovery process of palladium(II) ion. Therefore, the adsorption capacity of Pd(II) ion by CaAA has to be checked also under solution conditions more close to natural aquatic systems. Unfortunately, owing to the formation of low soluble hydrolytic species of Pd(II) at higher pH values, the maximum pH value achievable before the precipitation is about 5 in the presence of chloride ions which allow to keep palladium in solution by PdCl_x^{2-x} and $\text{Pd}(\text{OH})\text{Cl}_3^-$ soluble species formation.

Table 3 reports also the results obtained by kinetic measurements carried out at $\text{pH} = 3, 4$ and 5 in the presence of variable chloride concentration. As can be seen, it was possible to carry out measurements at $\text{pH} = 4$ and 5 only for chloride concentration of 5 and 10 mmol L^{-1} . In general the q_e values obtained for palladium adsorption in the presence of chloride are lesser than the q_e value obtained at $\text{pH} = 2$ in the absence of chloride, as also shown in Fig. S2 of Supplementary data file. From the q_e values obtained in chloride solution at different pH values, the $\text{pH} = 3$ seems to be the best pH value to be adopted for Pd(II) sorption in the presence of chloride. Nevertheless, an acceptable adsorption of palladium can be also noted at $\text{pH} = 5$ in 10 mmol L^{-1} chloride concentration (the achievable conditions more close to natural

aqueous systems), as shown by q_e value: $0.170 \text{ mmol g}^{-1} \approx 18 \text{ mg g}^{-1}$ dried gel beads. This result let us to affirm that a fairly good adsorption of Pd(II) ion by CaAA gel beads can be still obtained by setting-up a $\text{pH} = 5$ in the solution containing an adequate chloride concentration.

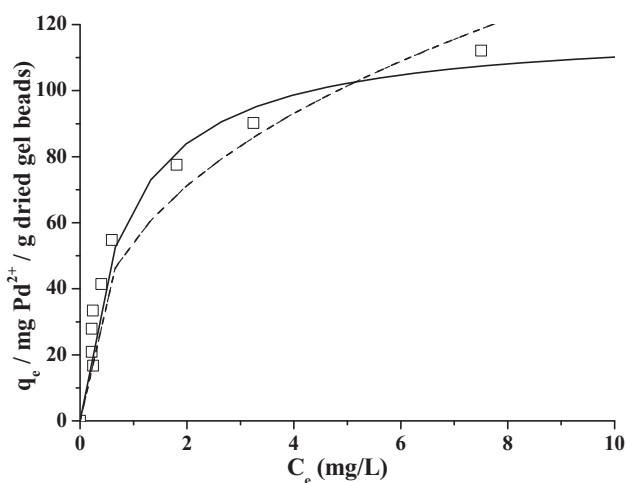
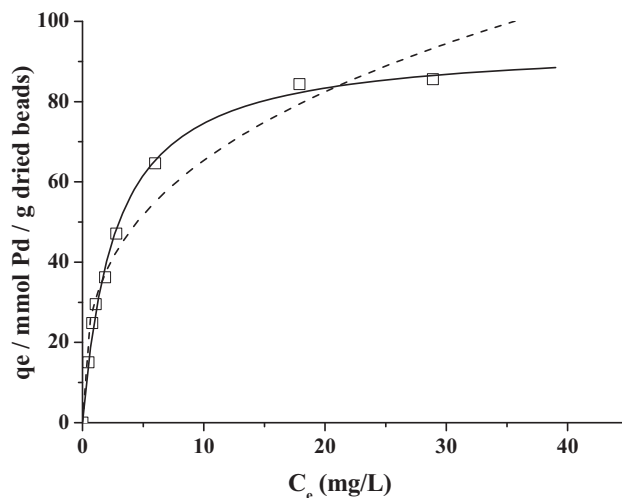
The results obtained from kinetic measurements on calcium release by CaAA (see Table 3) can give us some information about the adsorption mechanism. Since we are obliged to operate in an acidic pH range, a consistent part of calcium present in the gel beads is exchanged with protons of solution. This is especially evident for calcium release at $\text{pH} = 2$, where the amount of calcium release in the presence and in absence of palladium(II) ions in solution is nearly the same, confirming that the $\text{Ca}^{2+}-\text{H}^+$ exchange is the predominant mechanism. At $\text{pH} = 3, 4$ and 5 a more consistent Pd–Ca exchange occurs, as shown by the q_e values for calcium release if compared with the corresponding values obtained in the absence of Pd(II) ion in solution. This trend confirms an ion exchange mechanism between Pd(II) in solution and Ca(II) present in the calcium alginate gel occurs for pH values over 2. Although the great part of Ca(II) released by gel beads at $\text{pH} = 2$ is caused by the exchange with the proton of solution, in our opinion also at this pH the ion exchange can be considered the main mechanism of Pd(II) ion sorption, similar to that experimentally confirmed at higher pH.

4.4. Adsorption isotherms

In order to know the maximum sorption capacity of gel beads towards Pd(II) ion, the sorption isotherm study was made at the same experimental conditions adopted in speciation and kinetic investigations. The data were processed by Langmuir and Freundlich isotherms Eqs. (3) and (4) and the results obtained are reported in Table 4. Both the models closely fit the experimental data ($R^2 \geq 0.94$) although Langmuir model gave slightly better results. The use of Langmuir isotherm

Table 4 Parameters of Langmuir and Freundlich isotherms for the adsorption of palladium(II) ion by calcium alginate gel beads in the pH range 2–4, at $I = 0.01 \text{ mol L}^{-1}$, at different chloride concentrations and $T = 25 \text{ }^\circ\text{C}$.

pH	C_{Cl^-} ^a	Langmuir parameters			Freundlich parameters		
		q_{max} ^b	K_L ^c	R^2	K_F	n	R^2
2	0.0	119 ± 6	1.2 ± 0.2	0.9759	54 ± 3	2.6 ± 0.3	0.9492
2	2.5	32 ± 1	0.9 ± 0.2	0.9748	16.1 ± 0.6	4.3 ± 0.3	0.9858
2	5.0	22.0 ± 0.8	0.56 ± 0.08	0.9864	11.1 ± 0.08	4.7 ± 0.08	0.9638
2	7.5	17.1 ± 0.8	0.26 ± 0.03	0.9942	5.5 ± 0.5	2.9 ± 0.3	0.9898
2	10.0	16 ± 1	0.09 ± 0.01	0.9942	3.0 ± 0.4	2.4 ± 0.3	0.9929
3	2.5	127 ± 6	0.29 ± 0.03	0.9853	34 ± 4	2.3 ± 0.3	0.9435
3	5.0	97 ± 3	0.27 ± 0.02	0.9945	26 ± 0.7	2.4 ± 2	0.9614
3	7.5	94 ± 2	0.37 ± 0.02	0.9960	30 ± 3	3.0 ± 0.3	0.9599
3	10.0	74 ± 3	0.20 ± 0.03	0.9857	18.7 ± 0.9	2.5 ± 0.1	0.9923
4	10.0	93 ± 9	0.09 ± 0.02	0.9698	13 ± 2	1.9 ± 2	0.9475

^a mmol L⁻¹.^b mg g⁻¹.^c L mg⁻¹.**Figure 4** Sorption isotherms of Langmuir (continuous lines) and Freundlich (dashed lines) for the adsorption of palladium(II) ion (30 ppm) by calcium alginate gel beads in aqueous solution at pH = 2, at $I = 0.01 \text{ mol L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$ and $C_{\text{Cl}^-} = 0 \text{ mol L}^{-1}$.**Figure 5** Sorption isotherms of Langmuir (continuous lines) and Freundlich (dashed lines) for the adsorption of palladium(II) ion (30 ppm) by calcium alginate gel beads in aqueous solution at pH = 3, at $I = 0.01 \text{ mol L}^{-1}$, $T = 25 \text{ }^\circ\text{C}$ and $C_{\text{Cl}^-} = 0.0075 \text{ mol L}^{-1}$.

allows to calculate the important parameter q_{max} that gives quantitatively information on the sorption ability of the sorbent material. As an example, the curve fits of the two equations using the experimental data at pH = 2 and at $C_{\text{Cl}^-} = 0 \text{ mol L}^{-1}$ and at pH = 3 and at $C_{\text{Cl}^-} = 0.0075 \text{ mol L}^{-1}$ are reported in Figs. 4 and 5. As can be seen from the data of Table 4, the sorbent material shows higher and comparable, within the experimental errors, sorption ability at pH = 2 and $C_{\text{Cl}^-} = 0 \text{ mmol L}^{-1}$ and at pH = 3 and $C_{\text{Cl}^-} = 2.5 \text{ mmol L}^{-1}$, with q_{max} values of 119 and 127 mg g⁻¹, respectively. In these experimental conditions a right compromise is achieved between the amount of deprotonated COOH groups of alginate and the amount of palladium(II) present as positively charged species in solution. Owing to the high formation percentages of Pd–Cl species and to the low percentage of deprotonated form of alginate, at pH = 2 and in the presence of chloride in solution, there is a significant decrease of q_{max} that at $C_{\text{Cl}^-} = 10.0 \text{ mmol L}^{-1}$ is equal to 16 mg g⁻¹.

Due to the higher percentage of dissociated COOH groups of alginate, at pH ≥ 3 the effect of chloride on the sorption capacity of gel beads is less noticeable and causes a more little decrease of the q_{max} (e.g., the q_{max} goes from 127 to 74 mg g⁻¹ at pH = 3 and $C_{\text{Cl}^-} = 2.5$ and 10.0 mmol L⁻¹, respectively). Even if the formation of chloride and hydroxo species affects the sorption capacity of gel beads, independently of the chloride concentration and of the pH of the solution, at the experimental conditions adopted in this work the q_{max} values are high enough. This is a confirmation that the calcium alginate gel beads can be considered a good biosorbent material for the removal of Pd(II) from aqueous solution even if its affinity towards the metal ion changes with the changing of experimental conditions (e.g., at pH = 2 the K_L goes from 1.2 to 0.09 L mg⁻¹ for $C_{\text{Cl}^-} = 0$ and 10.0 mmol L⁻¹, respectively). The affinity of gel beads towards Pd(II) ions in the pH range considered at $C_{\text{Cl}^-} = 0.01 \text{ mol L}^{-1}$ (the only chloride

concentration used for three different pH values) is almost the same ($K_L = 0.09, 0.20$ and 0.09 L mg^{-1} for $\text{pH} = 2, 3$ and 4 , respectively).

4.5. Comparison between the Pd(II) sequestration by alginate in aqueous solution and Pd(II) removal by sorption onto alginate in gel phase

The preliminary speciation study on the Pd-AA system was carried out to assess the best experimental conditions to be used and also to define the strength of the interaction between Pd(II) ion and alginate sequestering agent in aqueous solution ($\log K_{\text{PdAA}} = 9.124 \pm 0.008$). By assuming that this interaction is quantitatively similar to that of Pd(II) with alginate as sorbent gel material, some correlations can be found between the results obtained for palladium sequestration in aqueous solution and palladium removal by sorption, in the same experimental conditions. To this end, the q_e and q_{max} values will be compared with $\text{pL}_{0.5}$ values which give quantitative information on the sequestering capacity of a ligand towards a metal ion in solution. In particular, $\text{pL}_{0.5}$ represents the concentration of ligand necessary to sequestrate the 50% of a metal ion present in solution, and can be expressed by the following Boltzmann equation:

$$x = \frac{1}{1 + 10^{(\text{pL} - \text{pL}_{0.5})}} \quad (5)$$

where pL is the $-\log(\text{total ligand concentration in mol L}^{-1})$ and x is the fraction of metal ion complexed by the ligand (AA in our case) that is given by the equation:

$$x = \frac{[M]_{\text{tot}} - [M]_{\text{free}} - \sum [M]_{\text{other}}}{[M]_{\text{tot}}} \quad (6)$$

with $[M]_{\text{tot}}$ = analytical concentration of the metal, $[M]_{\text{free}}$ = free metal concentration and $[M]_{\text{other}}$ = sum of the species formed by the metal with other ligands present in the solution, such as the anion of the ionic medium or the hydroxide ion.

When the metal ion in solution is present as trace, $\text{pL}_{0.5}$ is independent of the analytical concentration of the metal ion and varies with the experimental conditions (pH, ionic strength, supporting electrolyte, temperature, etc.).

More details about the calculation and the meaning of the $\text{pL}_{0.5}$ are reported in References [Gianguzza et al. \(2012, 2010\)](#). In [Table 5](#) are reported the $\text{pL}_{0.5}$ values of AA towards Pd(II) ion at different pH and different chloride concentrations (the same pH values and chloride concentrations adopted in sorption experiments). As an example, in [Fig. 6](#) are reported

Table 5 $\text{pL}_{0.5}$ values calculated by eq. 6 for the sequestration of Pd(II) ion by AA at different chloride concentrations and pH, in $\text{NaClO}_4/\text{NaCl}$ medium, at $I = 0.1 \text{ mol L}^{-1}$ and at $T = 25 \text{ }^\circ\text{C}$.

pH	$\text{pL}_{0.5}$				
$C_{\text{Cl}^-}^{\text{a}}$	0.0100	0.0075	0.0050	0.0025	0
2	0.93	1.32	1.83	2.61	6.28
3	2.57	2.96	3.47	4.25	
4	3.27	3.66	4.17		
5	3.37	3.76	–		

^a mol L^{-1} .

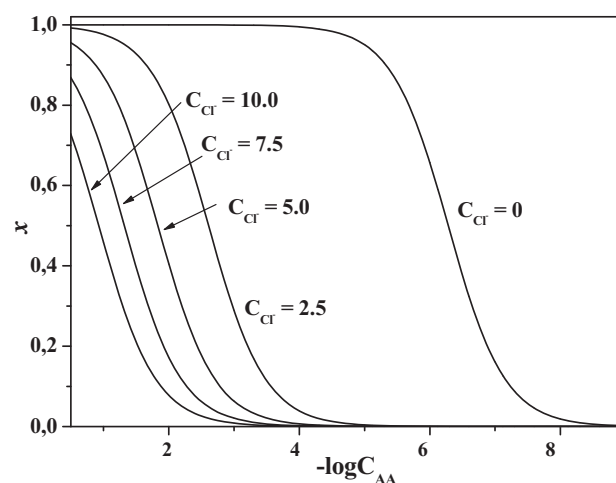


Figure 6 Fraction (x) of Pd(II) ion complexed by AA vs. $-\log C_{\text{AA}}$, in mixed $\text{NaClO}_4/\text{NaCl}$ medium, at $I = 0.1 \text{ mol L}^{-1}$ and at $T = 25 \text{ }^\circ\text{C}$. Experimental conditions: $C_{\text{Pd}^{2+}} = 10^{-10} \text{ mol L}^{-1}$ (trace), $\text{pH} = 2$, $0 \leq C_{\text{NaCl}} (\text{mmol L}^{-1}) \leq 10$.

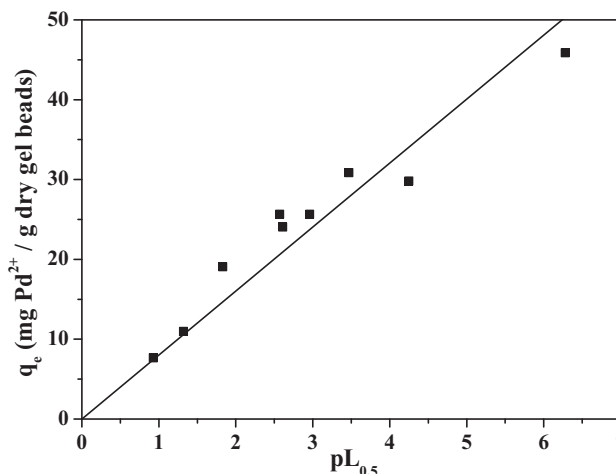


Figure 7 Linear correlation between $\text{pL}_{0.5}$ and q_e calculated at different pH and chloride concentrations, at $T = 25 \text{ }^\circ\text{C}$.

the sequestering curves obtained at different concentrations of chloride ion in solution, at $\text{pH} = 2$ and at $T = 25 \text{ }^\circ\text{C}$. As can be seen, at the same pH the sequestering ability of alginate towards Pd(II) ion increases with the decreasing of chloride concentration.

The best sequestering capacity of AA towards Pd(II) ion is obtained for $\text{pH} = 2$ and $C_{\text{Cl}^-} = 0$, confirming the results obtained in sorption process at the same experimental conditions. Accordance with sorption results can be also noted in the presence of different chloride concentrations: the effect of chloride on the sequestration of Pd(II) by AA decreases with the increasing of pH. For example, at $C_{\text{Cl}^-} = 0.01 \text{ mol L}^{-1}$ the $\text{pL}_{0.5}$ is equal to 0.93, 2.57, 3.27 and 3.37 at $\text{pH} = 2, 3, 4$ and 5 , respectively.

Moreover, the q_e , q_{max} and $\text{pL}_{0.5}$ parameters showed similar trends as function of some variables, such as the pH and the chloride concentration in solution. As an example, in [Fig. 7](#) is reported the linear correlation between the $\text{pL}_{0.5}$ and the

Table 6 Comparison of sorption ability of different biomaterials towards palladium(II) ion at $T = 20\text{--}25\text{ }^{\circ}\text{C}$.

Biosorbent	pH	$C_{\text{Cl}^-}/\text{mol L}^{-1}$	q_{max}	References
Alginate gel beads	2	0	119 ^a	This work
	2	0.01	16	
	3	0.01	74	
GCC ^b	2	0.011	162.6	Ruiz et al. (2000)
	2	0.1	138.4	
	2	1	52.2	
GLGC ^c	2	~ 0.01	120.39	Ramesh et al. (2008)
TGC ^d	2	~ 0.01	112.4	Zhou et al. (2009)

^a mg g^{-1} .^b Glutaraldehyde crosslinked chitosan.^c Glycine derivative of crosslinked chitosan.^d Thiourea derivative of crosslinked chitosan.

kinetic parameter q_e , both calculated at different pH and chloride concentrations. In Fig. S3 of Supplementary data file is also reported the comparison of the trend of $pL_{0.5}$ and of q_{max} as function of chloride concentration of solution at pH = 2. The good linear correlation ($R = 0.97$) between q_e and $pL_{0.5}$ (Fig. 7) and the similar trend of $pL_{0.5}$ and q_{max} parameters at different chloride concentrations (Fig. S3) indicate that the affinity of alginate towards Pd(II) ion as ligand in solution and as sorbent material is strictly related to each other.

Therefore, although the gelation could alter the number of available binding sites of alginate (Kalis et al., 2009), it can be affirmed that alginate shows a good and similar sequestration capacity in solution and as sorbent gel material, confirming the assumption made before, and pointing out, once again, the importance of speciation studies for the aquatic ecosystem characterization.

4.6. Literature data comparison

To our knowledge this is the first study on the sorption ability of calcium alginate gel beads towards palladium(II) ion. Some papers are reported in the literature on the binding ability of raw materials (Das, 2010; de Vargas et al., 2004; Mack et al., 2007) and synthetic resins (Hubicki and Leszczynska, 2005; Hubicki et al., 2006, 2008) towards Pd(II) ion. Among the natural polyelectrolytes, only derivative and non derivative crosslinked chitosan gels were used as sorbent material for this metal ion (Ramesh et al., 2008; Ruiz et al., 2000; Zhou et al., 2009). Some q_{max} literature values are reported in Table 6 together with those we found for alginate gel beads. As can be seen, at the same pH the effect of chloride concentration on the sorption ability of chitosan and of alginate gels is different and this is attributable to the different functional groups of the two polyelectrolytes. The protonated amino groups of chitosan bind preferentially the negatively charged chloride species of palladium [PdCl_3^- and PdCl_4^{2-} , $\text{PdCl}_3(\text{OH})^{2-}$], in the acidic pH range, whilst the carboxylate groups of alginate, partially deprotonated in the pH range investigated, bind the positively charged species of the metal ions [Pd^{2+} , PdCl^+ , $\text{Pd}(\text{OH})^+$]. No data were found on the sorption ability of chitosan in the absence of chloride but it is presumable that in the pH range 2–4 alginate gel is a better sorbent material in comparison with chitosan gel in the absence of chloride in solution. The q_{max} values reported in Table 6, show that cal-

cium alginate can be considered a valid alternative sorbent material to chitosan gel, especially in solution with low concentrations or without chloride. Moreover, the gel beads used in this work do not contain additional chemical agents, as in chitosan gel material used by the other authors, that cause an increase in cost of their production and also in the following disposal.

5. Conclusions

On the basis of the results obtained the following conclusions can be made:

1. the speciation study carried out on the Pd^{2+} -AA system gave evidence for the formation of a stable Pd(AA) species with $\log K_{\text{PdAA}} = 9.124$ in mixed $\text{NaClO}_4/\text{NaCl}$ medium, at $I = 0.1\text{ mol L}^{-1}$ and $T = 25\text{ }^{\circ}\text{C}$;
2. the sequestering ability of alginate towards Pd(II) ion has been evaluated by calculating the $pL_{0.5}$ parameter, a semi-empirical parameter that represents the total ligand concentration necessary to sequestrate the 50% of trace metal ion present in solution. The sequestering ability of alginate changes by varying the pH and chloride concentration in solution with a maximum $pL_{0.5}$ value of 6.28 found at pH = 2 and at $C_{\text{Cl}^-} = 0$;
3. a kinetic and thermodynamic study on the sorption capacity of Ca-AA gel beads towards Pd(II) ion was carried out in the pH range 2–5 and at different chloride concentrations. The experimental data were fitted with a pseudo second order kinetic equation and with Langmuir and Freundlich isotherms, respectively;
4. the experimental conditions to be adopted in the sorption study were chosen on the basis of the results of the speciation study on the Pd^{2+} -AA system, assuming that the sequestering capability of the ligand in solution and the sorption capacity of its calcium salt gel beads towards Pd(II) ion are strictly correlated;
5. the good linear correlation and the similarities between the trends of binding/sequestering ($pL_{0.5}$, % of PdAA) and sorption (q_e , q_{max}) parameters as function of pH and chloride concentration confirm our

hypothesis about the analogous behaviour of alginate as ligand in aqueous solution and as sorbent gel material towards Pd(II) ion;

- kinetic and thermodynamic studies on the sorption capacity of calcium alginate gel beads showed that in the pH and C_{Cl^-} ranges investigated CaAA is a good sorbent towards Pd(II) ion. The highest q_{max} values were found at pH = 2 and $C_{Cl^-} = 0 \text{ mmol L}^{-1}$ and at pH = 3 and $C_{Cl^-} = 2.5 \text{ mmol L}^{-1}$. A fairly good palladium uptake was also found at pH = 5 and $C_{Cl^-} = 0.01 \text{ mol L}^{-1}$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2014.10.031>.

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