Research article

Co(II) removal by magnetic alginate beads containing Cyanex 272®

Audrey-Flore Ngomsik [a,b,c,d,e,1], Agnès Bee [a,b,c,*], Jean-Michel Siaugue [a,b,c], Delphine Talbot [a,b,c], Valérie Cabuil [a,b,c], Gérard Cote [d,e]

[a] UPMC Univ Paris 06, UMR7612, Laboratoire Liquides Ioniques et Interfaces Chargées (LI2C), case 51, 4 place Jussieu, F-75005 Paris, France
[b] CNRS, UMR7612, Laboratoire Liquides Ioniques et Interfaces Chargées (LI2C), F-75005 Paris, France
[c] ESPCI, UMR7612, Laboratoire Liquides Ioniques et Interfaces Chargées (LI2C), F-75005 Paris, France
[d] ENSCP, UMR7575, Laboratoire d'Electrochimie et de Chimie Analytique (LECA), 11 rue Pierre et Marie Curie, 75005 Paris, France
[e] CNRS, UMR7575, Laboratoire d'Electrochimie et de Chimie Analytique (LECA), 75005 Paris, France

ABSTRACT

In this study, a series of batch experiments is conducted to investigate the ability of magnetic alginate beads containing Cyanex 272® to remove Co(II) ions from aqueous solutions. Equilibrium sorption experiments show a Co(II) uptake capacity of $0.4 \, \mathrm{mmol \, g^{-1}}$. The data are successfully modelled with a Langmuir equation. A series of kinetics experiments is then carried out and a pseudo-second order equation is used to fit the experimental data. The effect of pH on the sorption of Co(II) ions is also investigated. Desorption experiments by elution of the loaded beads with nitric acid at pH 1 show that the magnetic alginate beads could be reused without significant losses of their initial properties even after 3 adsorption–desorption cycles.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The wide use of heavy metal solutions in many industrial activities (battery manufacturing, painting,...) results in generation of large quantities of effluent that contain high levels of heavy metals. Most of them are toxic and carcinogenic agents and their presence in the aquatic ecosystem poses human health risks due to their non-degradable and persistent nature. Strict regulations concerning their presence in the aquatic environment have thus been introduced in recent years. Consequently, the treatment of industrial effluents is a challenging topic in environmental field and many methods are used for the removal of toxic metals from aqueous solutions such as, for example, chemical precipitation [1], liquid–liquid extraction [2], ion-exchange [3] adsorption [4], filtration [5,6], electrochemical treatment [7], reverse osmosis [8], membrane technologies [9], and evaporation recovery [10]. In this framework, adsorption [11], may be a suitable wastewater technology competitive with the conventional technologies to remove heavy metals. Currently, research is focused on the use of bioadsorbents which are inexpensive, biodegradable and available in large quantities to support potential demand [12].

Alginate, a natural polysaccharide extracted from brown seaweeds, is a very promising bioadsorbent; it was preferred over other materials because of its various advantages such as biodegradability, hydrophilic properties, natural origin, abundance and presence of binding sites due to its carboxylate functions. Alginate consists of linear copolymers composed of β-ᴅ-Mannuronate (M) and α-ʟ-Guluronate (G), linked by β 1,4- and α 1,4-glycosidic bounds. M and G units are organised in homopolymeric M and G blocks and heteropolymeric M–G blocks. The proportions of these blocks and the ratio M/G vary with the source of the alginate polymer. The carboxylate groups of the polymer provide the ability to form biodegradable gels in the presence of multivalent cations and more specifically with calcium ions via ionic interactions [13]. In the environmental field, alginate beads are widely used for the removal of heavy metals from wastewater [14]. On the other hand, alginate beads containing different components to enhance the adsorption capacity of the

---

* Corresponding author at: UPMC Univ Paris 06, UMR7612, Laboratoire Liquides Ioniques et Interfaces Chargées (LI2C), case 51, 4 place Jussieu, F-75005 Paris, France. Tel.: +33 1 44 27 30 98; fax: +33 1 44 27 36 75.
  E-mail addresses: a.ngomsik@qub.ac.uk
(A.-F. Ngomsik), agnes.bee@upmc.fr (A. Bee), jean-michel.siaugue@upmc.fr
(J.-M. Siaugue), valerie.cabuil@upmc.fr
(V. Cabuil), gerard-cote@enscp.fr (G. Cote).
[1] Present address: QUILL Centre, Queen's University Belfast, School of Chemistry and Chemical Engineering, David Keir Building, Stranmillis Road, BT9 5AG Belfast, Northern Ireland, United Kingdom.

Nomenclature

$n(Fe)_P$	Amount of iron of the particles (mol)
q_{eq}	Amount of metallic ions adsorbed at equilibrium (mmol g^{-1})
q_t	Amount of metallic ions adsorbed at any time (mmol g^{-1})
$n(Na^+)_P$	Amount of sodium counterions of the adsorbed citrate on nanoparticles (mol)
N	Avogadro number
DP	Degree of polymerization of alginate
d_0	Diameter of nanoparticles (nm)
C_{eq}	Equilibrium concentration of metallic cations in the aqueous phase (mol L^{-1})
$[M^{2+}]_{added}$	Initial amount of metallic cations dissolved in solution (mol L^{-1})
v_0	Initial sorption rate (mmol g^{-1} h^{-1})
K	Langmuir constant (L mol)
q_{max}	Maximum amount of adsorbed cations (mmol g^{-1})
M	Molar mass of maghemite (mol g^{-1})
M_n	Number average molar weight of alginate (g mol^{-1})
I_P	Polydispersity indice of alginate
k	Rate constant of sorption (g mmol^{-1} h^{-1})
σ	Size distribution width of nanoparticles
s	Specific area of nanoparticles (cm^2 g^{-1})
s_P	Surface of one nanoparticle (cm^2)
t	Time (h)
ϕ	Volume fraction in magnetic material
v_P	Volume of one nanoparticle (cm^3)
ρ	Volumic mass of nanoparticles (g cm^{-3})
q	Unit charge (C)
M_w	Weight average molar weight of alginate (g mol^{-1})
pH$_{50}$	pH where 50% of q_{max} is reached

system are also widely investigated [15].

An innovative technology that gains attention is the use of magnetic materials for magnetic separation of pollutants from effluents. In environmental applications, magnetic separation can be a promising method for a novel purification technique because it produces no contaminants such as flocculants and has the capability to treat a large amount of wastewater within a short time. Moreover, this approach is particularly appropriate when the problem of separation is complex, *i.e.* when polluted water contains solid residues which exclude their treatment in column with regards with the risks of filling. In this framework, our purpose is to develop magnetic alginate beads to remove heavy metal from effluents at reasonable cost. In environmental applications, the use of magnetic alginate beads remains rare [16,17]. Nevertheless the incorporation of magnetic particles in a polymer matrix might provide several advantages such as the facility to remove beads from the effluent to reuse them after their regeneration. In our previous papers, we have synthesized magnetic alginate beads for the removal of nickel ions or organic pollutants [18,19].

We propose in the present work to investigate the uptake of Co(II) ions from aqueous solutions by magnetic alginate beads using batch experiments. The beads are obtained by encapsulation within a Ca-alginate matrix of magnetic nanoparticles and Cyanex 272® (bis (2,4,4-trimethylpentyl) phosphinic acid), a common extractant [20] known in liquid/liquid extraction for its good affinity with cobalt(II). Results are compared with those of our previous work concerning Ni(II) extraction by the same kind of beads. The effects of contact time, initial concentration of metal cations and pH on the cations removal are investigated. A study about the regeneration of the beads in acidic medium is also reported.

2. Experimental

2.1. Materials

Sodium alginate is purchased from Fluka and used without further purification. Calcium(II) and cobalt(II) solutions are prepared by dissolution of CaCl$_2$, 2H$_2$O and Co(NO$_3$)$_2$, 6H$_2$O (R. P. Norma-pur, Prolabo) in deionized water, respectively. The extractant agent, Cyanex 272®, composed of bis (2,4,4-trimethylpentyl) phosphinic acid (pKa = 3.38) [21] is supplied by Cytec (Canada) and used without purification. Its molar weight is equal to 290 g mol^{-1}.

2.2. Preparation of magnetic alginate beads

2.2.1. Preparation of alginate solution

The weight average molar weight (M_w) and the number average molar weight (M_n) of alginate are respectively equal to 1.65×10^5 and 9.65×10^4 g mol^{-1}, leading to a polydispersity indice (I_P) equal to 1.7. The ratio M/G, obtained from NMR measurements, is equal to 0.90. The alginate stock solution is prepared by dissolving sodium-alginate in a known volume of distilled water; sodium azide (1.54×10^{-4} mol L^{-1}) is added to prevent the solution from the development of bacteria. The sodium content of the alginate polymer, obtained by atomic absorption spectrophotometry using a PerkinElmer Analyst 100 apparatus, is equal to (4.4 ± 0.5) mmol g^{-1} leading to a repeating unit molar mass equal to (227 ± 26) g mol^{-1}. This value agrees with the theoretical value (195 g mol^{-1}); the deduced degree of polymerization (DP) is equal to 762. The high polydispersity of the sodium content is due to the heterogeneity of the alginate powder used as can be expected with this natural product.

2.2.2. Preparation of magnetic nanoparticles

The magnetic material used is a ferrofluid composed of maghemite (γ-Fe$_2$O$_3$) nanoparticles coated by citrate ions and dispersed in an aqueous solution. It is synthesized by using the improved Massart process [22] described in our previous work [18] and has the same characteristics as the one used in this work. The iron concentration of the ferrofluid is equal to 1.81 mol L^{-1} which corresponds to a volume fraction in magnetic material (ϕ) equal to 2.85%, *i.e.* about 2×10^{17} nanoparticles per cm^3. The ferrofluid is a polydispersed system of rocklike nanoparticles which can be approximated as spheres. Magnetization measurements allow determining the mean diameter $d_0 = 6.8$ nm and the distribution width $\sigma = 0.4$ of the nanoparticles.

2.2.3. Preparation of magnetic alginate beads

The preparation of magnetic alginate beads has been described elsewhere [18]. 60 mL of an aqueous mixture containing 5.46 mL of ferrofluid ([Fe] = 1.81 mol L^{-1}), 0.5 g of sodium-alginate and 0.4 g of Cyanex 272® are introduced dropwise using a syringe (diameter = 1 mm) into 100 mL of 0.5 mol L^{-1} CaCl$_2$. The beads are formed upon contact with calcium ions and left 16 h at room temperature in the CaCl$_2$ bath without agitation. After their removal from the calcium bath, the beads are washed with deionized water to remove the excess of calcium ions and dried in an oven at 60 °C for 2 days. Weight measurements before and after drying show that wet beads contain 90% w/w water. Beads are spherical and red-brown due to the presence of maghemite nanoparticles. An example of a size distribution curve fitted with a Gaussian distribution is given in Fig. 1. The mean diameter of the dried beads and the polydispersity factor are 0.89 mm and 0.02, respectively. The results obtained for different synthesis show a good reproducibility. Table 1 reports the principal characteristics of the beads such as their weight, mean diameter and calcium, sodium, iron and Cyanex 272® contents. The amounts of calcium, sodium and iron are determined by
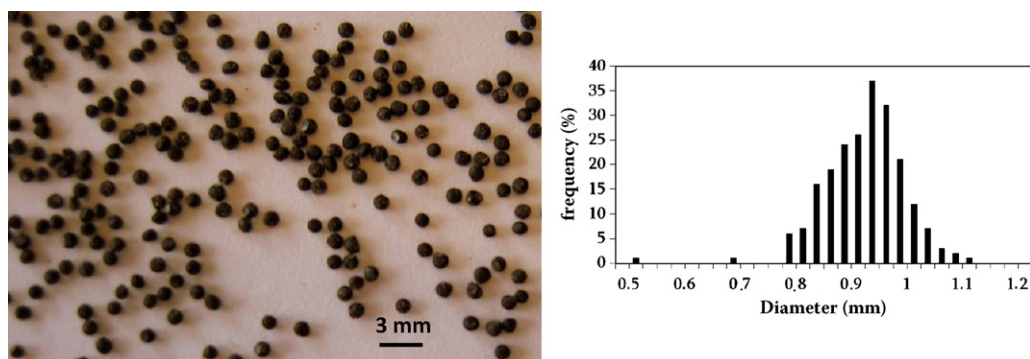
Fig. 1. Optical microscopy picture and size distribution of dried magnetic beads.

atomic absorption spectrophotometry using a PerkinElmer Analyst 100 apparatus. The Cyanex 272® content of the beads is checked by measuring the amount of phosphorus by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The amounts of the different species are expressed in mmol per weight of dried beads. The iron content of the beads ($3.8 \, \text{mmol g}^{-1}$) is close to the amount of magnetic nanoparticles initially added to the alginate solution ($3.9 \, \text{mmol g}^{-1}$). It agrees with the absence of nanoparticles release. Iron content corresponds to a volume fraction of nanoparticles in the beads equal to about 9.4%, *i.e.* a number of nanoparticles per bead close to 2.3×10^{14}. The sodium content of the beads is low compared to calcium content due to the ion exchange between sodium and calcium ions at the time of the gelation process. The beads contain two kinds of calcium ions: free calcium ions and calcium ions bound to the active sites of the beads resulting from the presence of the phosphinic functions of Cyanex 272® and the carboxylate functions of both citrate adsorbed on the magnetic nanoparticles and alginate.

2.3. Adsorption experiments

The efficiency of the Co(II) ions removal from aqueous solutions using magnetic alginate beads is studied in a batch mode by mixing 10 mL of aqueous solutions of Co(NO$_3$)$_2$ at different concentrations with $(7.2 \pm 0.3) \times 10^{-2}$ g of dried beads (*i.e.* 107 ± 5 beads). The pH value is adjusted to pH = 5.2 ± 0.2 with either nitric acid or tetramethylammonium hydroxide (TMAOH) solution. The solutions are not buffered to mimic potential industrial practice. The influence of pH solution on the uptake of Co(II) ions by beads is also investigated by mixing 10 mL of Co(NO$_3$)$_2$ solution ([Co]$_{added}$ = 1.5×10^{-2} mol L^{-1}, *i.e.* 2.1 mmol g^{-1}) with $(7.2 \pm 0.3) \times 10^{-2}$ g of dried beads. The pH solution is adjusted with either nitric acid or tetramethylammonium hydroxide (TMAOH) solution. The experiments are carried out with initial pH values lower than 8 since insoluble Co(II) hydroxide starts precipitating from solution at higher pH values making sorption studies difficult.

All the samples are shaken for 48 h at room temperature for complete equilibration and equilibrium pH values are measured.

Table 1
Beads characteristics. The amounts of calcium, sodium, iron and Cyanex 272® are expressed in mmol g^{-1} of dried beads.

Weight of dried beads (g)	2.55 ± 0.04
Diameter (mm)	0.89 ± 0.02
[Fe]	3.8 ± 0.2
[Na]	0.27 ± 0.01
[Ca]	2.7 ± 0.3
Cyanex 272®	0.46 ± 0.01

The beads are then easily removed from the solution by magnetic separation using a magnet (≈ 1 T) as shown in Fig. 2.

Kinetic experiments are performed by preparing different flasks containing $(7.2 \pm 0.3) \times 10^{-2}$ g of dried beads and 10 mL of a Co(NO$_3$)$_2$ solution ([Co]$_{added}$ = 1.5×10^{-2} mol L^{-1}, *i.e.* 2.1 mmol g^{-1}). pH values of the samples are adjusted to 7.5 with a TMAOH solution and the flasks are vigorously stirred. At different contact times, the pH is measured and beads are removed from the solution by magnetic separation for analysis.

The removal of Co(II) ions from a solution containing Co(II) and Ni(II) ions is also investigated in order to study the competition between the two cations for adsorption by alginate beads. Samples containing Ni(II) and Co(II) at the same concentration ([Co(II)]$_{added}$ + [Ni(II)]$_{added}$ = 1.5×10^{-2} mol L^{-1}, *i.e.* 2.1 mmol g^{-1}) are prepared at different pH.

For all the samples, the amounts of calcium, cobalt, nickel and iron in the beads and/or in the solution are determined by atomic absorption spectrophotometry. The validity of the analysis is verified by comparing the initial amount of cations to the sum of the amounts of cations present in the solution and in the beads; good recoveries are observed.

2.4. Regeneration of the beads

In order to study the reusability of the beads, consecutive adsorption–desorption cycles are realized as follows: samples containing $(7.2 \pm 0.3) \times 10^{-2}$ g of dried beads in 10 mL of a Ni(NO$_3$)$_2$ or Co(NO$_3$)$_2$ solution ([Co]$_{added}$ or [Ni]$_{added}$ = 1.5×10^{-2} mol L^{-1}, *i.e.* 2.1 mmol g^{-1}) are prepared, pH solution is adjusted to 5.2 ± 0.2. After 48 h stirring, beads are removed from the solution by the use of a magnet and washed with distilled water. The loaded beads are

Fig. 2. Photograph of magnetic alginate beads attracted by a magnet.

then placed 48 h in a nitric acid solution at pH 1. The regenerated beads are introduced again in a solution containing nickel or cobalt ions at pH 5.2 ± 0.2. This adsorption–desorption cycle is repeated 3 times. The amounts of remaining nickel, cobalt and iron in the beads are determined by atomic absorption spectrophotometry.

3. Results and discussion

3.1. Adsorption studies

3.1.1. Adsorption isotherms

The sorption isotherms are used to characterize the interaction of Co(II) ions with the adsorbent. It expresses the relation between the amount of adsorbed Co(II) ions per unit mass of dried beads (q_{eq}) and the Co(II) concentration in solution (C_{eq} in mol L^{-1}) at equilibrium. The isotherm obtained at pH = 5.2 ± 0.2 in a wide range of initial Co(II) concentrations (2–160 mmol L^{-1}, i.e. 0.3–23 mmol g^{-1}) is shown in Fig. 3. The equilibrium amount of adsorbed Co(II) first increases by increasing the Co(II) concentration of the solution. It then reaches a constant value equal to 0.38 mmol g^{-1}. Few studies on the adsorption of Co(II) by alginate beads or by other biosorbents are reported in the literature [12,23–25]. It is difficult to directly compare the sorption capacity values expressed in mmol g^{-1} of beads, because the beads do not always have the same composition. The results obtained, for example, by Ozdemir et al. with alginate beads [25] showed that the maximum amount of cobalt sorbed is 0.7 mmol g^{-1} of alginate. If we express our result in the same unit we obtain 1.9 mmol g^{-1} of alginate. So, it seems that our magnetic alginate beads present better extraction ability upon cobalt(II) due to the presence of magnetic nanoparticles and Cyanex 272® encapsulated in alginate beads allowing an increase of the number of available sites. It has to be noticed that generally a lower uptake by biosorbents of Co(II) than others cations like lead, copper or cadmium is reported [13,25–27].

Among the available models for sorption data analysis, the Langmuir adsorption model is employed to describe the sorption process. This model assumes a monolayer adsorption process on a homogeneous surface. Although the Langmuir model cannot provide any mechanistic understanding of the sorption phenomena, it may be conveniently used to estimate the maximum uptake of cations from experimental data. The mathematical equation is:

$$q_{eq} = \frac{q_{max}KC_{eq}}{1 + KC_{eq}}$$

where C_{eq} (mol L^{-1}) and q_{eq} (mmol g^{-1}) are the equilibrium concentrations of Co(II) in the solution and adsorbed by the beads, respectively; q_{max} (mmol g^{-1}) is the maximum amount of adsorbed Co(II) and K (L mol^{-1}) the Langmuir constant related to the affinity of the adsorbate for the adsorbent. The q_{max} value is found

to be equal to 0.41 mmol g^{-1} with a Langmuir constant equal to 53 L mol^{-1}. As it is shown in Fig. 3, the experimental data are well fitted by the Langmuir plots. The sorption process is thus well described by the Langmuir model. In one hand it can mean that even if different chemical groups are available in our system, it acts as a homogeneous surface. On the other hand, it is consistent with a monolayer or less of Co(II) ions on the binding sites of the beads.

For all the samples, the calcium content of the beads is also determined. As it is shown in Fig. 3, calcium ions are released from the beads while Co(II) is gradually sorbed by them. The calcium concentration in the beads initially equal to 0.53 mmol g^{-1} decreases to reach 0.12 mmol g^{-1} when the maximal amount of Co(II) ions is adsorbed (0.38 mmol g^{-1}). So the amount of released calcium ions is equal to 0.41 mmol g^{-1}. The uptake of Co(II) is thus governed by a competition mechanism between Co(II) ions and Ca(II) ions for binding sites as it has been shown previously with Ni(II). In both cases, one calcium ion is roughly replaced by one cobalt or nickel ion.

3.1.2. Effect of pH on adsorption

pH is an important factor affecting the removal of cations from aqueous solutions. The dependence of metal biosorption on pH is related to both the metal chemistry in solution and the ionization state of the functional groups of the biosorbent which affects the availability of binding sites. So, the dependence of Co(II) uptake on equilibrium pH is studied (Fig. 4). It can be seen that higher pH leads to higher metal uptake. A weak adsorption occurs in acid medium. Acid conditions are not favourable because most of the functional groups of the components of the beads (alginate, citrate and Cyanex 272®) are protonated leaving few available ionized groups. Competition between protons and metal species could thus explain the weak adsorption in acid medium. An increase of pH leads to an ionization of the functional sites inducing an increase of adsorption. Several researchers investigated the effect of pH on adsorption of metals by using different kinds of biosorbents [13,28]. For example, Bayramoglu et al. [29] studied the adsorption of Hg(II), Pb(II) and Cd(II) on immobilized microalgae in Ca-alginate beads using simple Ca-alginate beads as a control system. In all cases, they observed a maximum metal ions adsorption between pH 5 and 6. They also explained the weak adsorption in acidic medium by the protonation of active sites which adversely affects the sorption capacity of their biosorbents. The value of pH$_{50}$ corresponding to 50% of Co(II) extraction is equal to 4.9. It is close to the value obtained by Tsakiridis and Agatzini-Leonardou [30] or Sarangi et al. [31] in liquid/liquid extraction of Co^{2+} with Cyanex 272® (pH$_{50}$ = 4.5). Consequently, it can reasonably be assumed that adsorption in this range of pH is mainly due to the presence of Cyanex 272® which
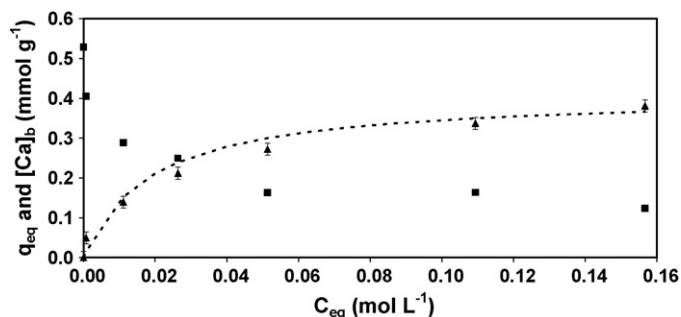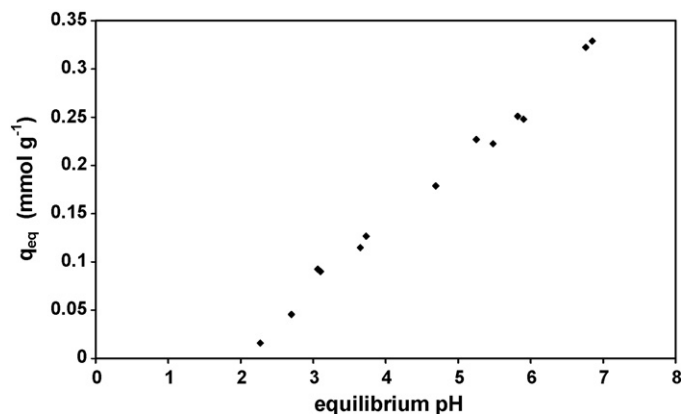

Fig. 3. Sorption isotherm of Co(II) onto beads (▲) and evolution of Ca(II) in the beads (■). The dashed line represents the fit of the isotherm by a Langmuir equation. Equilibrium pH = 5.2 ± 0.2; equilibrium time = 48 h; $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g.

Fig. 4. Effect of equilibrium pH on Co(II) (▲) sorption by beads. [Co]$_{added}$ = 2.1 mmol g^{-1}; equilibrium time = 48 h; $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g.
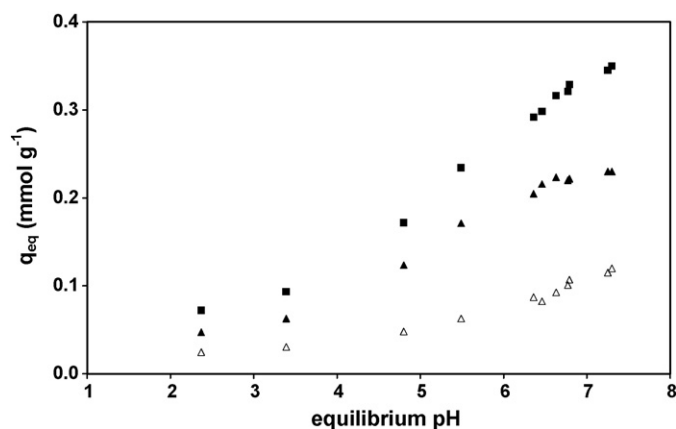
Fig. 5. Effect of equilibrium pH on Co(II) (▲) and Ni(II) (△) sorption by beads in a bimetallic solution; (■) total amount of cations adsorbed. $[Ni]_{added} = [Co]_{added} = 2.1$ mmol g^{-1}, $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g, equilibrium time = 48 h.

Fig. 6. Kinetics of the uptake of Co(II). Adsorbed Co (q_t: ▲); Co in solution ($[Co]_s$: △); remaining Ca in the beads ($[Ca]_b$: ■). The dashed line represents the fit with a pseudo-second order rate equation. $[Co]_{added} = 2.1$ mmol g^{-1}; $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g; pH$_{initial}$ = 7.5.

confers its properties to the beads. For pH about 7, the quantity of adsorbed Co(II) is equal to about 0.33 mmol g^{-1}. The amount of calcium ions remaining in the beads at the same pH is equal to 0.42 mmol g^{-1}. By assuming that the free calcium is released in the solution, the total amount of adsorbed cations is equal to 0.8 mmol g^{-1} which is close to the estimate quantity of available sites in the beads. It has to be noticed that the amount of remaining Ca(II) ions into the beads roughly corresponds to the number of Ca(II) ions bound to alginate. These Ca(II) ions contribute to the formation of the alginate gel and seem to be more difficult to displace by ionic exchange with Co(II) ions.

The influence of equilibrium pH on the removal of Co(II) and Ni(II) ions by beads from a solution containing the two cations simultaneously at the same concentration is also investigated (Fig. 5). The adsorption isotherms present the same features as previously. On the other hand, in spite of Ni(II) and Co(II) are introduced at the same concentration, the affinity of the beads is more important for Co(II) than for Ni(II). At pH = 7.3, the adsorbed cations correspond to 35% of Ni(II) and 65% of Co(II). Anyway the maximum amount of cations adsorbed is close to the one obtained for monometallic Co(II) solution. Moreover, at the same pH, the amount of Ca(II) beads is equal to 0.46 mmol g^{-1}. So the total amount of adsorbed cations (0.8 mmol g^{-1}) is always close to the number of active sites.

It has to be noticed that in all the range of pH used, no release of the magnetic nanoparticles is observed. Thus the magnetic properties of the beads are preserved.

3.2. Kinetic studies

The adsorption rate of Co(II) ions uptake by beads is studied by following the decrease of the Co(II) concentration within the solution and the increase of Co(II) concentration within the beads with time (Fig. 6). A two-stage kinetics behaviour is observed. A rather fast uptake of Co(II) ions, related to a small decrease of the pH value from 7.5 to 6.5, occurs within the first hour probably due to an adsorption on the surface of the beads. It has to be noticed that this pH decrease is not observed for the beads which are immersed in water without Co(II) during the same time. So it can be attributed to the adsorption process and indicates a competition for binding sites between Co(II) ions and remaining protons on the alginate matrix. After 1 h, about 55% of the maximum sorption capacity is reached. A slower increase of the amount of adsorbed Co(II) ions is then observed while the pH value of the solution remains constant. This slower step is controlled by mass transfer
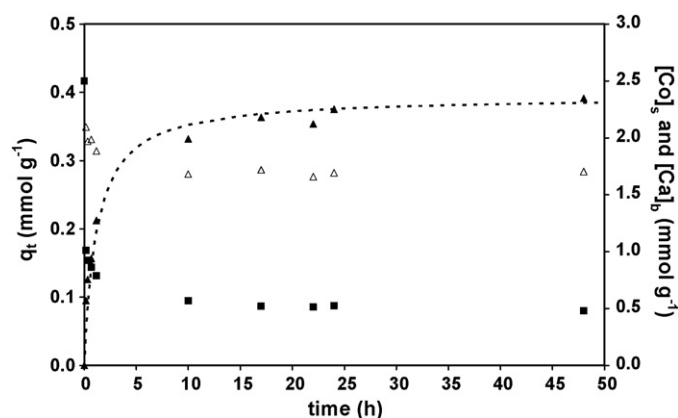
through the alginate network. After 17 h, the amount of adsorbed Co^{2+} (q_{eq}) is equal to (0.39 ± 0.03) mmol g^{-1} (93% of the maximum sorption capacity). These results could be compared with those obtained with Ni^{2+} ions removal by the same beads in our previous study [18]. A two-stage kinetics behaviour was also observed. But the amount of adsorbed Ni^{2+} ions in the first hour was smaller (30%) than for Co(II) ions. Equilibrium was reached at 20 h. Nevertheless the adsorbed amounts at equilibrium are the same for the two cations. Ozdemir et al. studying the recovery of Co(II) and Cd(II) by different kinds of beads: alginate, alginate-EPS (exocellular polysaccharide), alginate-cell or alginate-EPS-cell [25] also observed a two-stage kinetic behaviour, their equilibrium times are smaller than our value (about 1 h). Nevertheless, it is difficult to compare studies published in the literatures, which are often carried out under different experimental conditions. In our case, we use dried beads while Ozdemir et al. used wet beads which favour the sorption kinetics [25].

As previously with Ni(II), the kinetic data of sorption of Co(II) ions are modelled using a pseudo-second order rate equation which is often successfully used to describe the kinetics of the extraction of pollutants by an adsorbent [32]. The kinetic rate equation is:

$$\frac{dq_t}{dt} = k(q_{eq} - q_t)$$

where k (g mmol^{-1} h^{-1}) is the rate constant of sorption, q_{eq} (mmol g^{-1}) the amount of Co(II) ions adsorbed at equilibrium and q_t (mmol g^{-1}) the amount of Co(II) ions adsorbed at any time t (h). Integrating this equation for the boundary conditions $t = 0$ ($q_t = 0$) to t_{eq} ($q_t = q_{eq}$) and then linearizing it leads to:

$$\frac{t}{q_t} = \frac{1}{kq_{eq}^2} + \frac{1}{q_{eq}}t$$

By plotting t/q_t versus t, a straight line is obtained (the correlation coefficient is equal to 0.9982) allowing the determination of q_{eq} (0.39 mmol g^{-1}) and k (2.2 g mmol^{-1} h^{-1}). The value of equilibrium sorption capacity shows a good agreement with the experimental equilibrium Co(II) uptake and a good fit of the experimental curve is observed (Fig. 6).

The time evolution of the Ca content of the beads ($[Ca]_b$) is also studied (Fig. 6). In the first minutes the amount of calcium ions in the beads drastically decreases. The calcium loss (1.5 mmol g^{-1}) is attributed to the release of unbound calcium entrapped in the alginate network. The remaining Ca(II) in the beads (about 1.1 mmol g^{-1}) is close to the number of binding sites of the beads (≈ 1 mmol g^{-1}) estimated previously [18] from the amount of
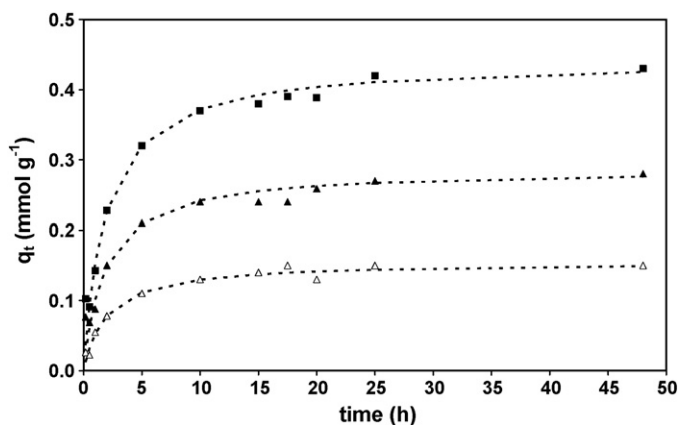
Fig. 7. Kinetics of the uptake of Co(II) and Ni(II) from a bimetallic solution: adsorbed Co (▲); adsorbed Ni (△) and total amount of adsorbed cations (■). The dashed lines represent the fits with a pseudo-second order rate equation. $[Co]_{added} = [Ni]_{added} = 2.1 \text{ mmol g}^{-1}$; $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g; $pH_{initial} = 7.5$.

Table 2
Regeneration of beads by consecutive adorption (A)/desorption (D) cycles. Adsorption is realized at pH 5.4. Desorption occurs by elution with nitric acid at pH 1. $[Co]_{added}$ or $[Ni]_{added} = 2.1 \text{ mmol g}^{-1}$, $m_{beads} = (7.2 \pm 0.3) \times 10^{-2}$ g, $[Co]_{adsorbed}$ or $[Ni]_{adsorbed}$ and $[Co]_{released}$ or $[Ni]_{released}$ in mmol g^{-1}.

	A1	D1	A2	D2	A3	D3
Ni(II)						
$[Ni]_{adsorbed}$	0.14	0	0.11	0	0.12	–
$[Ni]_{desorbed}$	–	0.14	–	0.11	–	–
$[Fe]_{released}$	–	9.6%	–	18.6%	–	–
Co(II)						
$[Co]_{adsorbed}$	0.17	–	0.11	–	0.12	0.001
$[Co]_{desorbed}$	–	0.16	–	0.11	–	0.12
$[Fe]_{released}$	–	5.5%	–	8.9%	–	11.8%

encapsulated Cyanex 272® by considering a complex 1:2 with calcium ions [33] and from the amount of carboxylate groups coming from both magnetic nanoparticles and alginate. After the first few minutes, a slower decrease of the Ca(II) concentration into the beads occurs. At equilibrium, the amount of expulsed calcium cations ($\sim$0.5 mmol g^{-1}) is close to the maximum adsorbed amount of Co(II). It suggests an ionic exchange process, about one calcium ion being replaced by one cobalt ion. It agrees with the results of Reddad et al. [23,24,34] and Gerente et al. [23] which studied the adsorption of heavy metals by *beet sugars*. Indeed, by following the evolution of the quantity of ions Ca^{2+} during the adsorption of the ions Cu^{2+}, they also observed an ionic exchange of type 1:1 between the two cations. Moreover, when the release of free calcium is achieved, the total amount of calcium and cobalt ions present in the beads remains constant. It is equal to about 0.9 mmol g^{-1} which is close to the available sites roughly estimated previously (1 mmol g^{-1}).

Most of the effluent solutions represent a case of multimetal situation rather than monometal situation. This is why it is essential to study the effect of the presence of co-cations on the sorption capacity of the beads. The kinetics of the removal of Co(II) and Ni(II) ions by magnetic alginate beads from a solution containing simultaneously the two cations at the same concentration is thus investigated (Fig. 7). 55% of the maximum amount of adsorbed cations is reached after 2 h. A competitive adsorption occurs between the two cations which share the available sites. Nevertheless Co(II) ions are preferentially adsorbed by the beads. It could be due to the presence of Cyanex 272® entrapped in the beads which presents a better affinity for Co(II) ions. At equilibrium the total amount of adsorbed cations is the same than for monometallic solutions. As for monometallic experiments, the curves are well fitted with a pseudo-second order equation.

3.3. Regeneration of beads

To use magnetic alginate beads at an industrial scale, it is necessary to make them attractive with regard to the usual methods of cleanup. So, regeneration of loaded alginate beads and metal recovery in a concentrated form are key factors for improving process economics. A successful desorption process must restore the sorbent close to its initial properties for effective reuse. In this objective adsorption–desorption cycles are realized. The adsorption step of Ni(II) or Co(II) ions is realized at pH 5.4, adsorbed ions being then desorbed by elution with nitric acid (pH = 1). The results are reported in Table 2. All the cations are removed at pH 1 and the adsorption capacity of the beads is maintained. The evolution of the quantity of iron shows that after the adsorption–desorption

cycles, it still stays 81% (minimum value) of iron in the beads, the loss in iron being due to the dissolution of the magnetic nanoparticles in acid medium. So, alginate beads remain magnetic enough to be extracted from the solution with a magnet. These experiments show that the magnetic alginate beads could be reused without significant loss of their initial properties.

4. Conclusion

In this study a new biosorbent consisting in magnetic alginate beads containing Cyanex 272® is developed. In a previous work we studied the nickel sorption capacity of these magnetic beads. In this work, complementary experiments are carried out with nickel ions, and the removal of cobalt ions from aqueous solution is studied. The adsorption process is well described with a Langmuir model. A pseudo-second order equation is used to describe the adsorption kinetics. 50% of the maximum sorption capacity is achieved within 1 h. Because there is a wide variation of the pH of the effluents, we study the effects of pH on adsorption of Co(II) ions onto alginate beads from single and binary metal solutions containing Co(II) and Ni(II). The adsorption of Co(II) and Ni(II) ions is pH dependent. An increase in pH increases the availability of the negatively charged free sites for electrostatic attraction of cations, thereby resulting in an increase of the cation binding capacity. In a binary system (Ni(II)–Co(II)), beads exhibit preference for Co(II) sorption over Ni(II). This affinity for Co(II) could be attributed to the presence of Cyanex 272® in the beads. The alginate beads could be also regenerated using nitric acid. Moreover, they could be reused in successive biosorption–desorption cycles without losing their adsorption capacities and magnetic properties. The experiments conducted in this work provide encouraging results for the application of these magnetic beads to the recovery of Ni(II) and Co(II) ions from aqueous solutions in large-scale operations. Magnetic alginate beads are promising heavy metal adsorbents because they combine a good adsorption capacity, selectivity and magnetic properties.

References

[1] K. Azetsu-Scott, P. Yeats, G. Wohlgeschaffen, J. Dalziel, S. Niven, K. Lee, Precipitation of heavy metals in produced water, influence on contaminant transport and toxicity, Mar. Environ. Res. 63 (2007) 146–167.

[2] B. Dousova, D. Kolousek, F. Kovanda, V. Machovic, M. Novotna, Removal of As(V) species from extremely contaminated mining water, in: EUROCLAY 2003, Appl. Clay Sci. 28 (2005) 31–42.

[3] A. Oehmen, R. Viegas, S. Velizarov, M.A.M. Reis, J.G. Crespo, Removal of heavy metals from drinking water supplies through the ion exchange membrane bioreactor, in: Euromembrane 2006, Desalination 199 (2006) 405–407.

[4] D. Borah, K. Senapati, Adsorption of Cd(II) from aqueous solution onto pyrite, Fuel 85 (2006) 1929–1934.

[5] C. Blocher, J. Dorda, V. Mavrov, H. Chmiel, N.K. Lazaridis, K.A. Matis, Hybrid flotation-membrane filtration process for the removal of heavy metal ions from wastewater, Water Res. 37 (2003) 4018–4026.

[6] K. Trivunac, S. Stevanovic, Effects of operating parameters on efficiency of cadmium and zinc removal by the complexation-filtration process, in: The Second

Membrane Science and Technology Conference of Visegrad Countries (PERMEA 2005), Desalination 198 (2006) 282–287.

[7] K. Juttner, U. Galla, H. Schmieder, Electrochemical approaches to environmental problems in the process industry, Electrochim. Acta 45 (2000) 2575–2594.

[8] S.M.C. Ritchie, D. Bhattacharyya, Membrane-based hybrid processes for high water recovery and selective inorganic pollutant separation, J. Hazard. Mater. 92 (2002) 21–32.

[9] D. Zamboulis, S.I. Pataroudi, A.I. Zouboulis, K.A. Matis, The application of sorptive flotation for the removal of metal ions, Desalination 162 (2004) 159–168.

[10] M.D. Neville, C.P. Jones, A.D. Turner, The EIX process for radioactive waste treatment, in: Progress in Nuclear Energy Global Environmental and Nuclear Energy Systems-2, vol. 32, 1998, pp. 397–401.

[11] J. Qu, Research progress of novel adsorption processes in water purification: a review, J. Environ. Sci. 20 (2008) 1–13.

[12] P. Arundhati, G. Suchhanda, A.K. Paul, Biosorption of cobalt by fungi from serpentine soil of Andaman, Bioresource Technol. 97 (2006) 1253–1258.

[13] J.P. Ibanez, Y. Umetsu, Potential of protonated alginate beads for heavy metals uptake, Hydrometallurgy 64 (2002) 89–99.

[14] A.K. Pandey, S.D. Pandey, V. Misra, S. Devib, Role of humic acid entrapped calcium alginate beads in removal of heavy metals, J. Hazard. Mater. 98 (2003) 177–181.

[15] I. Moreno-Garrido, O. Campana, L.M. Lubian, J. Blasco, Calcium alginate immobilized marine microalgae, experiments on growth and short-term heavy metal accumulation, in: Marine Pollution Bulletin 4th International Conference on Marine Pollution and Ecotoxicology, vol. 51, 2005, pp. 823–829.

[16] S.F. Lim, J.P. Chen, Synthesis of an innovative calcium-alginate magnetic sorbent for removal of multiple contaminants, Appl. Surf. Sci. 253 (2007) 5772–5775.

[17] L. Huidong, L. Zhao, L. Ting, X. Xiao, P. Zhihui, D. Le, A novel technology for biosorption and recovery hexavalent chromium in wastewater by biofunctional magnetic beads, Bioresource Technol. 99 (2008) 6271–6279.

[18] A.-F. Ngomsik, A. Bee, J.-M. Siaugue, V. Cabuil, G. Cote, Nickel adsorption by magnetic alginate microcapsules containing an extractant, Water Res. 40 (2006) 1848–1856.

[19] V. Rocher, J.-M. Siaugue, V. Cabuil, A. Bée, Removal of organic dyes by magnetic alginate beads, Water Res. 42 (2008) 1290–1298.

[20] J.E. Silva, A.P. Paiva, D.A. Soares, C.F. Labrincha, Solvent extraction applied to the recovery of heavy metals from galvanic sludge, J. Hazard. Mater. B 120 (2005) 113–118.

[21] R.K. Biswas, M.A. Habib, H.P. Singha, Colorimetric estimation and some physicochemical properties of purified Cyanex 272, Hydrometallurgy 76 (2005) 97–104.

[22] R. Massart, Preparation of aqueous magnetic liquids in alkalin and acidic media, IEEE Trans. Magn. 17 (1981) 1247.

[23] C. Gerente, P. Couespel du Mesnil, Y. Andres, J.-F. Thibault, P. Le Cloirec, Removal of metal ions from aqueous solution on low cost natural polysaccharides, sorption mechanism approach, React. Funct. Polym. 46 (2000) 135–144.

[24] Z. Reddad, C. Gérente, P. Andrés, P. Le Cloirec, Adsorption of several metal ions onto a low cost biosorbent, kinetic and equilibrium studies, Environ. Sci. Technol. 36 (2002) 2067–2073.

[25] G. Ozdemir, N. Ceyhan, E. Manav, Utilization of an exopolysaccharide produced by Chryseomonas luteola TEM05 in alginate beads for adsorption of cadmium and cobalt ions, Bioresource Technol. 96 (2005) 1677–1682.

[26] N. Lazaro, A. Lopez Sevilla, S. Morales, A.M. Marques, Heavy metal biosorption by gellan gum gel beads, Water Res. 37 (2003) 2118–2126.

[27] R.P. Dhakal, K.N. Ghimire, K. Inoue, M. Yano, K. Makino, Acidic polysaccharide gels for selective adsorption of lead (II) ion, Sep. Purif. Technol. 42 (2005) 219–225.

[28] H. Mohapatra, R. Gupta, Concurrent sorption of Zn(II), Cu(II) and Co(II) by Oscillatoria angustissima as a function of pH in binary and ternary metal solutions, Bioresource Technol. 96 (2005) 1387–1398.

[29] G. Bayramoglu, I. Tuzun, G. Celik, M. Yilmaz, M.Y. Arica, Biosorption of mercury(II), cadmium(II) and lead(II) ions from aqueous system by microalgae Chlamydomonas reinhardtii immobilized in alginate beads, Int. J. Miner. Process. 81 (2006) 35–43.

[30] P.E. Tsakiridis, S. Agatzini-Leonardou, Process for the recovery of cobalt and nickel in the presence of magnesium from sulphate solutions by Cyanex 272 and Cyanex 302, Miner. Eng. 17 (2004) 913–923.

[31] K. Sarangi, B.R. Reddy, R.P. Das, Extraction studies of cobalt II and nickel II from chloride solutions using Na-Cyanex 272, separation of Co II/Ni II by the sodium salts of D_2EHPA, PC88A and Cyanex 272 and their mixtures, Hydrometallurgy 52 (1999) 253–265.

[32] Y.S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, Chem. Eng. J. 70 (1998) 115–124.

[33] S.K. Sahu, A. Agrawal, B.D. Pandey, V. Kumar, Recovery of copper, nickel and cobalt from the leach liquor of a sulphide concentrate by solvent extraction, Miner. Eng. 17 (2004) 949–951.

[34] Z. Reddad, C. Gérente, P. Andrés, P. Le Cloirec, Comparison of the fixation of several metal ions onto a low cost biopolymer, Water Sci. Technol. 2 (2002) 217–224.