Removal of cadmium from aqueous solutions by palygorskite

E. Álvarez-Ayuso [a,*], A. García-Sánchez [b]

[a] *Institute of Earth Sciences "Jaume Almera" (CSIC), C/Lluís Solé i Sabarís, s/n, 08028 Barcelona, Spain*
[b] *Department of Environmental Geochemistry, IRNASA, CSIC, Apto. 257, Salamanca, Spain*

Abstract

The sorption characteristics of palygorskite with respect to cadmium were studied with the aim of assessing its use in water purification systems. Using a batch method the influence of time (0.5–48 h), initial Cd concentration (5–150 mg/l or 0.044–1.34 mmol/l), ionic strength ([Ca(II)]: 0–0.1 mol/l), pH (3–7) and mineral dose (1–20 g/l) on Cd removal was evaluated. The sorption of Cd on palygorskite appeared as a fast process, with equilibrium being attained within the first half an hour of interaction. This process could be described by the Langmuir model and gave a maximum Cd sorption of 4.54 mg/g. This sorption capacity value was greatly affected by both pH and ionic strength. Thus, Cd sorption decreased as initial pH lessened, especially at proton concentrations similar to those of Cd, at which competition for variable charge sites (silanol groups on palygorskite surface) appeared to be important. High competing electrolyte concentrations also decreased significantly (close to 60%) the amount of sorbed Cd, suggesting a great contribution of replacement of exchange cations in this metal removal by palygorskite. The increase of mineral dose provoked a Cd removal raise; removal values in the range 85–45% were attained for Cd initial concentrations of 10–150 mg/l (0.089–1.34 mmol/l) when a palygorskite dose of 20 g/l was employed. Column studies were also performed in order to estimate the potential of palygorskite to be used in continuous flow purification systems, showing the effectiveness of this mineral to purify down to the legal limit of waste moderate volumes of Cd-containing solutions with a similar concentration (50 mg/l or 0.445 mmol/l) to those mostly found in the upper range of concentrations usually present in industrial wastewaters.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Palygorskite; Cadmium; Sorption; Water purification

1. Introduction

Cadmium is a non-essential element and one of the most hazardous trace elements, being considered a "priority metal" from the standpoint of potential hazard to human health [1]. Cd can cause chronic health problems, such as bone disease, lung edema, renal dysfunction, liver damage, anemia and hypertension [2–4]. Its presence in aquatic systems poses, therefore, serious risks to humans, and also to living organisms in water and to other consumers of it. Aquatic ecosystem pollution by Cd usually arises from several industrial processes, such as electroplating, battery and accumulator manufacturing, production of ceramics and pigments, plastic manufacturing, metallurgical alloying, smelting and acid mine drainage.

Methods proposed for Cd removal from wastewaters are those employed for most heavy metals, these include precipitation, ion exchange resins, vacuum evaporation, solvent extraction and membrane technologies [5,6]. Among them, precipitation is the treatment most widely applied due to its simple equipment, capability to treat large volumes of water containing high metal concentrations and low cost. Nevertheless, precipitation is often incapable of meeting the legislation requirements for wastewaters to be discharged to surface waters and sewage (0.1 mg/l [7]). Furthermore, this treatment produces large amounts of sludge hard to handle. The other existing methods, although usually effective, are not free of drawbacks, high capital cost with recurring expenses and capability to treat only small volumes, are the most common. Economical, practical and efficient alternative techniques are, therefore, required to purify Cd-containing wastewaters. New practices have been focused on the study of processes based on sorption approaches. Sorption appears as a simple and low-cost method, with a great potential of becoming an actual alternative to conventional ones, overcom-

---

ing the problems of insufficient efficiency and difficult waste handling derived from the precipitation method. Different materials have been subject of study in this regard, most of them can be classified in two groups, bio-materials, such as agricultural by-products [8–12], algae [13–16], fungi [17] and chitin based sorbents [18,19], and minerals, such as iron hydroxides and oxyhydroxides [20–22], aluminium hydroxides and oxides [23,24], clays [25–30], zeolites [31–33], calcite [34,35] and wollastonite [36,37]. In general, bio-materials display higher Cd sorption capacity values, which could make their use in purification systems preferable face to minerals; nevertheless, most bio-materials present the important shortcoming of being affected by the place or season of harvesting and by the growing conditions [38], what could limit greatly their application. Among minerals, clays and zeolites, due to their chemical and structural characteristics, are those most suitable for Cd sorption processes. Numerous clays have been subject of study in this regard, including mainly lamellar clays, such as kaolinite, montmorillonite and vermiculite, while the study of fibrous clays has been restricted to sepiolite. Thus, although the feasibility of palygorskite for the stabilisation of soils contaminated with Cd has been reported [39], so far the study of the sorption properties of this natural mineral for its application in the purification of Cd-containing waters has not been considered yet.

Palygorskite is a hydrated magnesium silicate mineral with a fibrous morphology, and with a structure consisting of parallel ribbons of 2:1 layers. In contrast to its close relative sepiolite, palygorskite contains cations other than Mg^{2+} in the octahedral sheets in significant amounts, such as Al^{3+} and Fe^{3+}. The presence of trivalent cations in octahedral positions creates an excess of positive charge which is compensated by vacancies, conferring dioctahedral characteristics to the mineral. Palygorskite is characterised by a high viscosity, a high surface area, a moderate layer charge and a large number of silanol groups on its surface as a result of its inverted structure and its fibrous morphology. Based on these properties, the industrial applications of this mineral are numerous (drilling muds, agricultural carriers, industrial floor absorbents, cat box absorbents, catalyst supports, gelling agents in paints, adhesives and cosmetics, reinforcing filler in rubbers and plastics and so on) [40–42], although those related to environment protection are much more scarce.

The main objectives of the present work are to study the sorbent behaviour of palygorskite with respect to Cd, and to explore the possibility of using this mineral in continuous flow systems for the purification of Cd-containing waters.

2. Materials and methods

2.1. Chemicals

Cd-containing solutions were prepared from a standard of 1000 ± 2 mg/l (Panreac) and their initial pH was adjusted using 0.01, 0.1 and 1 M HNO_3 and NaOH solutions.

2.2. Sorbent mineral

A natural palygorskite from the Tenebrón mineral deposit, Salamanca province (Spain) was employed in this study. The

Table 1
Mineralogical composition, textural properties and cation exchange capacity of palygorskite sample

Property	Value
Mineralogical composition (%)	Palygorskite (70), quartz (30)
Specific surface area (m^2/g)	112
Specific total pore volume (cm^3/g)	0.18
Cation exchange capacity (cmol (+)/kg)	13.9
Exchange cations (cmol (+)/kg)	Mg^{2+} (9.3), Ca^{2+} (3.4), Na^+ (0.9), K^+ (0.3)

properties of palygorskite sample are given in Table 1. The mineralogical composition was determined by X-ray diffraction (XRD); the semiquantitative analyses were based on diffractometer traces of unoriented powder samples using the methods employed by Schultz [43] and by Islam and Lotse [44]. The textural analyses were carried out from the nitrogen adsorption isotherms at $-196\,^{\circ}$C obtained from a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyser). The cation exchange capacity (CEC) was determined by the ammonium acetate method [45].

2.3. Batch sorption studies

All batch sorption studies were carried out in centrifuge tubes of 30 ml by subjecting a given amount of palygorskite to a period of shaking with 25 ml of Cd solution on a vertical rotary shaker (50 turns/min) in a chamber set at 22 °C. After the interaction period the sorbent was separated using a centrifugation step (4000 rpm) over 10 min. Cd concentrations in the supernatant and those of Mg were determined with a VARIAN SPECTRA AA-2002 Atomic Absorption Spectrophotometer equipped with either a cadmium or a magnesium hollow cathode lamp. The instrumental parameters employed in Cd determinations using an air-acetylene flame were: wavelength (λ) 228.8 nm, lamp intensity 4 mA, and slit width 0.5 nm, and the corresponding analytical characteristics at the working conditions were: linearity range up to 3 mg/l, and quantification limit (sensibility) 0.01 mg/l. The instrumental parameters employed in Mg determinations using a nitrous oxide-acetylene flame were: wavelength (λ) 202.6 nm, lamp intensity 4 mA, and slit width 1.0 nm, and the corresponding analytical characteristics at the working conditions were: linearity range up to 20 mg/l, and quantification limit (sensibility) 0.09 mg/l. Deionised water was used as blank. All assays were carried out in triplicate and only mean values are presented. The following batch sorption studies, using the procedure and the general conditions just aforementioned and the specific conditions described below, were performed.

Kinetic studies. Palygorskite dose 10 g/l (palygorskite amount 0.25 g, and Cd solution volume 25 ml); mineral particle size <0.1 mm; initial metal concentrations: 10, 50, 100 and 150 mg/l (0.089, 0.445, 0.890 and 1.34 mmol/l); pH 6; shaking time: 0.5, 1, 2, 4, 8, 24 and 48 h.

Sorption isotherms. Palygorskite dose 10 g/l (palygorskite amount 0.25 g, and Cd solution volume 25 ml); mineral par-

ticle size <0.1 mm; initial metal concentrations: 5, 10, 25, 50, 75, 100 and 150 mg/l (0.044, 0.089, 0.222, 0.445, 0.667, 0.890 and 1.34 mmo/l); pH 6; shaking time 24 h. The effect of ionic strength in Cd removal by palygorskite was studied simultaneously using $Ca(NO_3)_2 \cdot 4H_2O$ as background electrolyte, varying its concentration from 0 to 0.10 mol/l.

Effect of pH. Palygorskite dose 10 g/l (palygorskite amount 0.25 g, and Cd solution volume 25 ml); mineral particle size <0.1 mm; initial metal concentrations: 50 and 150 mg/l (0.445 and 1.34 mmol/l); pH: 3, 4, 5, 6 and 7; shaking time 24 h.

Effect of sorbent dose. Palygorskite dose: 1, 2.5, 5, 10, 15 and 20 g/l (palygorskite amount: 0.025, 0.0625, 0.125, 0.25, 0.375 and 0.50 g, and Cd solution volume 25 ml); particle size <0.1 mm; initial metal concentrations: 10, 50, 100 and 150 mg/l (0.089, 0.445, 0.890 and 1.34 mmol/l); pH 6; shaking time 24 h.

2.4. Continuous flow studies

Continuous flow studies were carried out using percolating tubes filled with 40 g of palygorskite (mineral particle size: 0.1–0.5 mm). The Cd-containing solution (initial Cd concentration: 50 mg/l or 0.445 mmol/l; pH 6) was passed through the column (height 12.3 cm, diameter 2.9 cm, bed-volume (bed-volume (BV) is the volume occupied in the column by the palygorskite amount, 81 ml)) with a flow rate of 75 ml/h using a peristaltic pump. Effluent samples were collected periodically with a fraction collector (Foxy Jr., ISCO), and analysed by AAS for Cd concentrations.

3. Results and discussion

3.1. Batch sorption studies

3.1.1. Kinetic studies

The kinetic curves obtained for the sorption of Cd by palygorskite are shown in Fig. 1. Sorption on palygorskite is a fast process with equilibrium attained within the first half an hour of interaction, regardless of the initial cadmium concentration used. The short time required to reach the equilibrium suggests that most Cd sorption could take place on the mineral exter-

Fig. 1. Kinetic curves of Cd sorption on palygorskite at different initial Cd concentrations (C_i). (Error bars indicate standard error of the mean.)
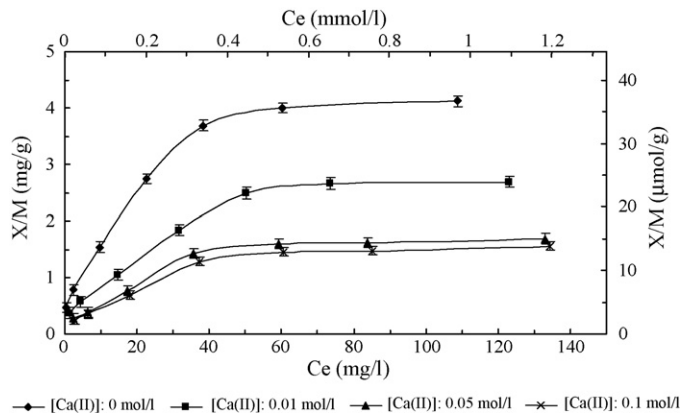

Fig. 2. Equilibrium isotherms of Cd sorption on palygorskite at different ionic strength conditions. (Error bars indicate standard error of the mean.)

nal surface since diffusion processes generally limit greatly the sorption rate. The porous structure of palygorskite with channels of relatively small dimensions (3.7 Å × 6.4 Å) could hinder or even avoid such processes [46]. It is also important to note that after reaching the equilibrium period, much longer times of interaction did not provoke release of Cd sorbed amounts, spite of the proven instability of this mineral under very dilute acid conditions, or even under neutral conditions [47,48].

3.1.2. Sorption isotherms

The sorption isotherms are shown in Fig. 2. The determination of sorption isotherms is considered the most suitable form of characterising the sorption phenomena in a simply approach. The nature of slope of the initial portion of isotherms gives information about the affinity between sorbent and solute, the "plateau" of isotherms gives information about the sorption capacity of the sorbent material subject of study. Furthermore, the determination of isotherms is required for the application of the Langmuir equation which is considered one of the most useful equations for the empirical description of sorption data. According to the classification of Giles et al. [49], all isotherms are divided into four main groups (S, L, H and C) in accordance with their initial slope. The isotherm initial slope depends on the rate of change of site availability with increase in solute sorbed. According to this classification, all the isotherms of Cd sorption on palygorskite are L-type, reflecting that as more sites on palygorskite are filled it becomes increasingly difficult for Cd to find a vacant site available. The L curve is considered to be indicative of a high affinity between sorbent and solute.

The sorption data were fitted to the Langmuir equation

$$\frac{X}{M} = \frac{KbC_e}{1 + KC_e} \tag{1}$$

where X/M is the amount of solute sorbed per unit weight of the sorbent, C_e the equilibrium concentration of solute remaining in the solution, K the equilibrium constant (affinity term) and b represents the maximum amount that can be sorbed. The rearranged expression of Eq. (1) used to obtain its most suitable
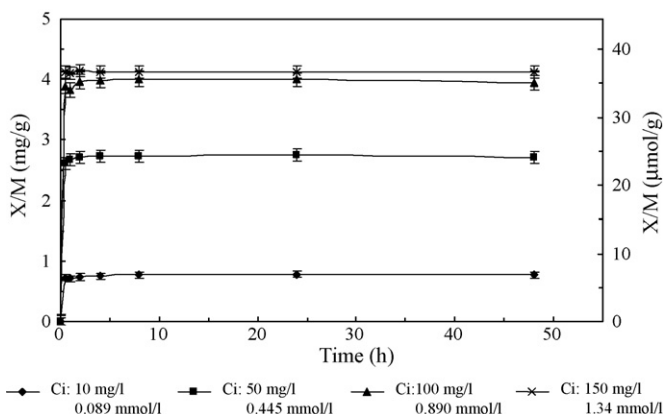
Table 2
Characteristic parameters and determination coefficient of equilibrium data of Cd sorption on palygorskite according to the Langmuir equation

Ionic strength	b (mg/g)	b (μmol/g)	K (l/mg)	R^2
[Ca(II)] = 0 mol/l	4.54	40.4	0.093	0.9831 ($p < 0.001$)
[Ca(II)] = 0.01 mol/l	3.15	28.0	0.054	0.9779 ($p < 0.001$)
[Ca(II)] = 0.05 mol/l	1.98	17.6	0.050	0.9853 ($p < 0.001$)
[Ca(II)] = 0.1 mol/l	1.85	16.5	0.045	0.9869 ($p < 0.001$)

linear form is:

$$\frac{C_e}{X/M} = \frac{1}{Kb} + \frac{C_e}{b} \qquad (2)$$

The Langmuir model parameters and the statistical fits of equilibrium data to this equation are given in Table 2. This model effectively describes sorption of Cd on palygorskite with R^2-values > 0.97. The K parameter values reflect a decrease in the affinity of Cd for the palygorskite surface with the ionic strength increase, as was derived from the decreasing slope of the first part of the isotherms as the ionic strength was raised. The b parameter reflects a moderate sorption capacity (4.54 mg/g), but decreasing with the ionic strength increase, this decease ranges from 30 to 60% for Ca concentrations increasing from 0.01 to 0.1 mol/l.

Table 3 shows the concentration of Mg present in solution after the interaction processes. In absence of calcium cations Mg release increased progressively with Cd sorbed amounts, whereas at high Ca concentrations (0.05 and 0.1 mol/l) the Mg concentrations in solution remained more or less constant. This behaviour is consistent with the avoidance of Cd removal by cation exchange at high competing electrolyte concentrations. In all the conditions, the released amounts of Mg were higher than the Cd sorbed amounts, indicating the slight dissolution of palygorskite at the conditions subject of study; this dissolution appeared to be promoted by the ionic strength increase. It is worth mentioning that Ca can compete with Cd for exchange positions in a very effective way due to their similar hydrated radius, rh, (rh$_{Cd}$: 4.26 Å, rh$_{Ca}$: 4.12 Å; [50]) and to the lesser energy required by Ca to break its coordination sphere of H_2O molecules (hydration energy, ΔGh, values: ΔGh$_{Cd}$, −1755 kJ/mol; ΔGh$_{Ca}$, −1505 kJ/mol; [51]), making easier its accessibility to sorption sites. Evaluation of the effect of ionic strength in sorption represents a macroscopic method of inferring sorption mechanisms. Thus, taking into account the important decrease produced in Cd removal in high competing electrolyte concentration, and the progressive increase of Mg release with Cd sorbed amounts, it can be assumed that a great amount of Cd was sorbed by replacement of exchange cations. From the light of the derived sorption values, it could be concluded that about 50–60% of Cd removal by palygorskite must take place by such a mechanism. Other different mechanisms of sorption can be responsible for the further sorbed amounts of Cd. These include precipitation, replacement of the Mg located at the edges of the octahedral sheets of palygorskite, and sorption by reaction with silanol groups (really numerous on the surface of this mineral).

The participation of precipitation processes in the removal of Cd by palygorskite at the conditions subject of study can be neglected since the pH increase produced after the interaction periods (Table 3), either by proton sorption and/or by mineral dissolution, did not reach the pH values required for cadmium hydroxide precipitation. Concerning the replacement of the Mg located at the edges of the octahedral sheets of palygorskite, this sorption mechanism was proven by Corma et al. [52] for a copper-exchanged sepiolite; afterwards, Brigatti et al. [53] also suggested this replacement when studying the sorption of zinc and lead on sepiolite. Mg has a hydrated radius very similar to that of Cd (rh$_{Mg}$: 4.28 Å; [50]), what makes feasible its substitution at the edges of the octahedral sheets of palygorskite. Nevertheless, this mechanism could be greatly restricted due to the slight dissolution experienced by this mineral at the medium conditions employed in this study. Therefore, the further sorbed amounts of Cd on palygorskite should be related to its reaction with the silanol groups present on the surface of this mineral.

Table 3
Equilibrium values from the sorption of Cd on palygorskite at the different initial Cd concentrations (C_i) and ionic strength conditions: pH, released Mg and sorbed Cd

C_i		[Ca(II)] = 0 mol/l			[Ca(II)] = 0.01 mol/l			[Ca(II)] = 0.05 mol/l			[Ca(II)] = 0.1 mol/l		
mg/l	mmol/l	pH	Mg	Cd	pH	Mg	Cd	pH	Mg	Cd	pH	Mg	Cd
5	0.044	7.5	0.27	0.04	7.1	0.56	0.03	6.9	0.70	0.02	6.7	0.74	0.02
10	0.089	7.0	0.30	0.07	7.0	0.60	0.05	6.8	0.70	0.03	6.6	0.75	0.03
25	0.222	6.8	0.37	0.14	6.8	0.61	0.09	6.7	0.69	0.07	6.5	0.75	0.06
50	0.445	6.8	0.48	0.24	6.8	0.62	0.16	6.7	0.70	0.13	6.5	0.75	0.11
75	0.667	6.8	0.55	0.33	6.8	0.66	0.22	6.7	0.69	0.14	6.5	0.74	0.13
100	0.890	6.8	0.57	0.36	6.5	0.69	0.24	6.5	0.69	0.15	6.4	0.74	0.13
150	1.34	6.8	0.64	0.37	6.5	0.70	0.24	6.5	0.70	0.15	6.4	0.75	0.13

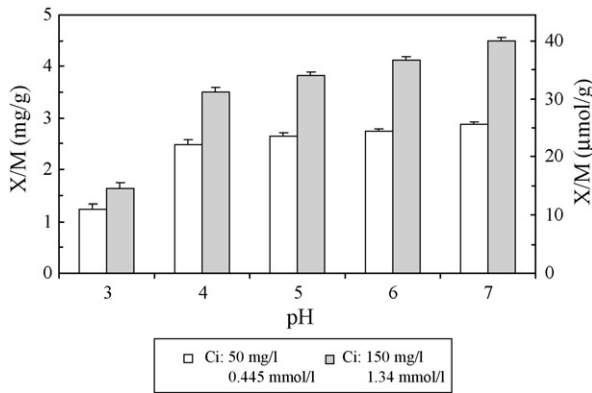Released Mg and sorbed Cd (mmol/l). S.D. for pH values is <0.2 and for Mg and Cd concentration values <5%.

Fig. 3. Effect of pH in the sorption of Cd on palygorskite at different initial Cd concentrations (C_i). (Error bars indicate standard error of the mean.)

Fig. 4. Effect of palygorskite dose in Cd removal at different initial Cd concentrations (C_i). (Error bars indicate standard error of the mean.)

3.1.3. Effect of pH

The effect of pH in the sorption of Cd by palygorskite is illustrated in Fig. 3. When pH decreased Cd sorption by palygorskite decreased slightly in a steady way for moderately acid solutions (pH 6–4), to underwent a much sharper decrease for lower initial pH values (pH 3) at which proton concentrations attained values similar to those of Cd; in such conditions protons can compete more effectively with Cd for sorption sites. The tendency of protons to react with permanent charge sites (cation exchange positions) is very limited, and only monovalent cations can be substantially subjected to hydrolytic exchange at low electrolyte concentrations [1]. Therefore, taking into account that divalent cations are the major exchange cations present in palygorskite, competition of protons with Cd for variable charge sites seems to be the main cause for the sorption decreases produced with the proton concentration increase. Palygorskite is characterised for having a large number of silanol groups on its surface, this kind of sites seems, therefore, to play an important role in the sorption of Cd by palygorskite, especially at neutral or slightly acid conditions. The sorption reaction taking place can be summarised as follows:

$$>Si–OH + Cd^{2+} \rightarrow \ >Si–OCd^+ + H^+ \tag{3}$$
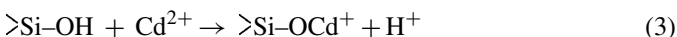
Therefore, as was suggested before, reaction of Cd with silanol groups appears as the other dominant mechanism responsible for the sorption of Cd on palygorskite.

3.1.4. Effect of sorbent dose

The influence of palygorskite dose in the removal of Cd is shown in Fig. 4. An increase in the percentage uptake of Cd is produced with increased palygorskite dose. For low Cd concentrations (10 mg/l or 0.089 mmol/l) this increase is produced in a sharp way for the first palygorskite dose increments, becoming much less marked for the highest mineral doses, what suggests that the palygorskite dose at which the percentage removal of Cd is maximum is close to 20 g/l. For intermediate (50 mg/l or 0.445 mmol/l), and especially for high Cd concentrations (100 and 150 mg/l or 0.890 and 1.34 mmol/l), the percentage uptake of Cd showed a constant increase with the palygorskite dose increase; thus, in such cases higher Cd removals could
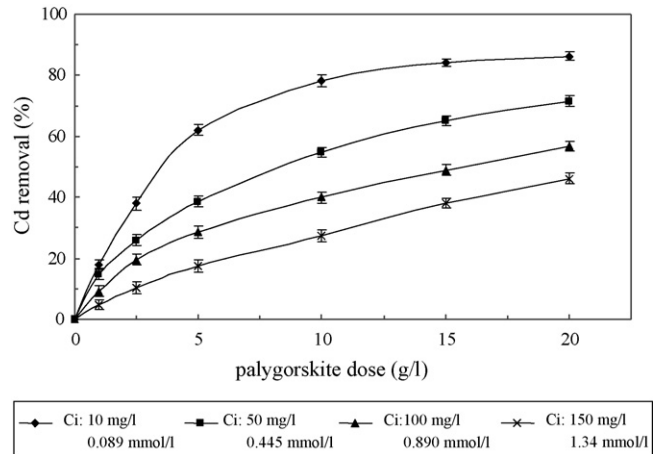
be attained using higher palygorskite doses. The Cd removals attained using a palygorskite dose of 20 g/l were about 85, 70, 55 and 45% for solutions with Cd concentrations of 10, 50, 100 and 150 mg/l (0.089, 0.445, 0.890 and 1.34 mmol/l), respectively. In such conditions the residual Cd concentrations in solution after sorption (1, 14, 43 and 81 mg/l, respectively) were still above the legal limit for effluent discharge (0.1 mg/l). Therefore, consecutive sorption cycles would be necessary to fulfil the required limit, the number of sorption cycles to perform being dependent on the initial Cd concentration.

4. Continuous flow studies

Continuous flow systems appear, at first, more suitable to perform purification processes. On the one hand, this method allows a continuous displacement of reaction in the sorption direction, which could drive to higher Cd removals. On the other, the column systems allow to perform the whole purification process by means of a single stage, whereas the batch method involves several steps (shaking, settling and/or filtration) performed repeatedly, requiring, therefore, more time and place to perform the purification process in an effective way.

A small particle size (0.1–0.5 mm), allowing the easy percolation of Cd solution, was chosen to perform the column sorption studies. In not shaking systems this factor could influence in a great extent the removal of Cd, removal decreasing as the mineral particle size increases. The relatively short residence times attained in these systems make especially important this aspect. The results obtained after percolating the Cd solution through the palygorskite column are illustrated in Fig. 5. The reflected curve shows the Cd concentration remaining in the effluent after the Cd solution treatment in function of the percolated solution volume. The Cd concentration in the effluent displayed very low values (<0.1 mg/l, discharge limit established by law) along a moderate percolated volume (33 BV, BV = 81 ml). Subsequently, the Cd concentration values in the effluent increased quickly in a continuous way to reach the saturation level when the percolated volume was 51 BV, from which the Cd concentration in
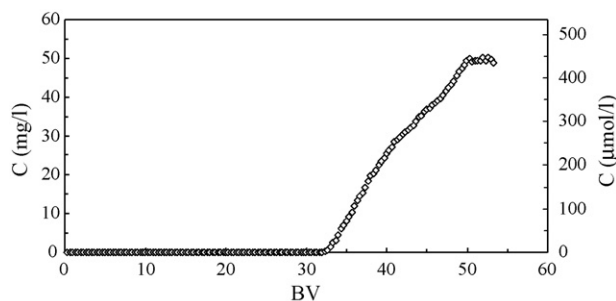
Fig. 5. Elution curve of a water solution containing 50 mg/l (0.445 mmol/l) of Cd filtered through a palygorskite bed; C: concentration in the effluent.

the effluent attained similar values to that present in the influent (50 mg/l or 0.445 mmol/l). At this point the Cd sorption capacity showed by palygorskite was 4.15 mg/g, and that displayed at the percolated volume below which Cd solution was purify below the limit of discharge (33 BV) was 3.34 mg/g, both values are higher than that obtained for the same concentration at equilibrium conditions using the batch method (2.74 mg/g). This proves that using the continuous flow system the Cd sorbed amounts are increased, this happens as a consequence of the constant displacement of reaction in the sorption direction that takes place in such systems. Therefore, the continuous flow system above described was able to purify below the limit of discharge a moderate volume (33 BV) of Cd solution with a similar concentration (50 mg/l or 0.445 mmol/l) to those mostly found in the upper range of concentrations usually present in industrial wastewaters, using about 80% of the maximum sorption capacity displayed by the palygorskite column. Higher volumes of purification could be attained in similar conditions for solutions with lower initial Cd concentrations, while similar or higher volumes of purification for solutions with higher initial Cd concentrations would require the use of longer palygorskite beds.

5. Conclusions

Palygorskite exhibited sorption properties towards Cd, the sorption process appearing to be relatively fast with equilibrium being attained within the first half an hour of interaction. The maximum removal capacity was 4.54 mg/g as determined by the Langmuir model. This sorption capacity value was greatly affected by both pH and ionic strength. Thus, Cd sorption decreased as initial pH lessened, especially at proton concentrations similar to those of cadmium, at which competition for variable charge sites (silanol groups on palygorskite surface) appeared to be important. High competing electrolyte concentrations also decreased significantly (close to 60%) the amount of sorbed Cd, suggesting a great contribution of replacement of exchange cations in the removal of Cd by palygorskite. Continuous flow systems were proven to be effective to purify (down to the legal limit of waste: 0.1 mg/l) moderate volumes of Cd-containing solutions with a similar concentration (50 mg/l or 0.445 mmol/l) to those mostly found in the upper range of concentrations usually present in industrial wastewaters.

References

[1] M.B. McBride, Environmental Chemistry of Soils, Oxford University Press, New York, 1994.

[2] G.F. Nordberg, Health hazards of environmental cadmium pollution, Ambio 3 (1974) 51–65.

[3] R. Nath, R. Prasad, V.K. Palinal, R.K. Chopra, Molecular basis of cadmium toxicity, Prog. Food Nutr. Sci. 8 (1984) 109–163.

[4] J.A. Staessen, H.A. Roels, D. Emelianov, T. Kuznetsova, L. Thijs, J. Van-gronsveld, R. Fagard, Environmental exposure to cadmium, forearm bone density, and risk of fractures: prospective population study, Lancet 353 (1999) 1140–1144.

[5] W.J. McLay, F.P. Reinhard, Waste minimization and recovery technologies, Met. Finish. 98 (2000) 817–850.

[6] S.E. Kentish, G.W. Stevens, Innovations in separations technology for the recycling and re-use of liquid waste streams, Chem. Eng. J. 84 (2001) 149–159.

[7] Real Decreto, 849/1986, de 11 de abril, por el que se aprueba el reglamento del Dominio Público Hidráulico, que desarrolla los Títulos Preliminar, I, IV, V, VI, y VII de la Ley 29/1985, de 2 de agosto, de Aguas. BOE núm. 103, de 30/4/1986.

[8] A. Saeed, M. Iqbal, Bioremoval of cadmium from aqueous solution by black gram husk (*Cicer arientinum*), Water Res. 37 (2003) 3472–3480.

[9] R. Leyva-Ramos, L.A. Bernal-Jacome, I. Acosta-Rodriguez, Adsorption of cadmium(II) from aqueous solution on natural and oxidized corncob, Sep. Purif. Technol. 45 (2005) 41–49.

[10] U. Kumar, M. Bandyopadhyay, Fixed bed column study for Cd(II) removal from wastewater using treated rice husk, J. Hazard. Mater. B129 (2006) 253–259.

[11] U. Kumar, M. Bandyopadhyay, Sorption of cadmium from aqueous solution using pretreated rice husk, Bioresour. Technol. 97 (2006) 104–109.

[12] G.H. Pino, L.M.S. de Mesquita, M.L. Torem, G.A.S. Pinto, Biosorption of cadmium by green coconut shell powder, Miner. Eng. 19 (2006) 380–387.

[13] J.T. Matheickal, Q. Yu, G.M. Woodburn, Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*, Water Res. 33 (1999) 335–342.

[14] P. Kaewsarn, Q. Yu, Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina* sp., Environ. Pollut. 112 (2001) 209–213.

[15] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green, and red seaweeds, Chem. Eng. J. 97 (2004) 249–255.

[16] P. Lodeiro, B. Cordero, J.L. Barriada, R. Herrero, M.E. Satre de Vicente, Biosorption of cadmium by biomasa of brown marine macroalgae, Bioresour. Technol. 96 (2005) 1796–1803.

[17] P. Yin, Q. Yu, B. Jin, Z. Ling, Biosorption removal of cadmium from aqueous solution by using pretreated fungal biomass cultured from starch wastewater, Water Res. 33 (1999) 1960–1963.

[18] M.S.D. Erosa, T.I.S. Medina, R.N. Mendoza, M.A. Rodriguez, E. Guibal, Cadmium sorption on chitosan sorbents: kinetic and equilibrium studies, Hydrometallurgy 61 (2001) 157–167.

[19] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[20] S. Pivovarov, Adsorption of cadmium onto hematite: temperature dependence, J. Colloid Interface Sci. 234 (2001) 1–8.

[21] G. Mustafa, B. Singh, R.S. Kookana, Cadmium adsorption and desorption behaviour on goethite at low equilibrium concentrations: effects of pH and index cations, Chemosphere 57 (2004) 1325–1333.

[22] E.A. Deliyanni, K.A. Matis, Sorption of Cd ions onto akaganeite-type nanocrystals, Sep. Purif. Technol. 45 (2005) 96–102.

[23] R. Weerasooriya, H.K.D.K. Wijesekara, A. Bandara, Surface complexation modeling of cadmium adsorption on gibbsite, Colloids Surf. A Physicochem. Eng. Aspects 207 (2002) 13–24.

[24] R.R. Bell, G.C. Saunders, Cadmium adsorption on hydrous aluminium (III) oxide: effect of adsorbed polyelectrolyte, Appl. Geochem. 20 (2005) 529–536.

[25] M.J. Angove, B.B. Johnson, J.D. Wells, Adsorption of cadmium(II) on kaolinite, Colloids Surf. A Physicochem. Eng. Aspects 126 (1997) 137–147.

[26] M.F. Brigatti, G.C. Franchini, L. Medici, L. Poppi, A. Stewart, Behaviour of sepiolite in Co^{2+} Cu^{2+} and Cd^{2+} removal from a simulated pollutant solution, Annal. Chim. 88 (1998) 461–470.

[27] M.F. Brigatti, C. Lugli, L. Poppi, Kinetics of heavy-metal removal and recovery in sepiolite, Appl. Clay Sci. 16 (2000) 45–57.

[28] E. Álvarez-Ayuso, A. García-Sánchez, Removal of heavy metals from waste waters by natural and Na-exchanged bentonites, Clays Clay Miner 51 (2003) 475–480.

[29] E. Álvarez-Ayuso, A. García-Sánchez, Removal of heavy metals from waste waters by vermiculites, Environ. Technol. 24 (2003) 615–625.

[30] A. Bentouami, M.S. Oulai, Cadmium removal from aqueous solutions by hydroxy-8 quinoleine intercalated bentonite, J. Colloid Interface Sci. 293 (2006) 270–277.

[31] E. Álvarez-Ayuso, A. García-Sánchez, X. Querol, Purification of metal electroplating waste waters using zeolites, Water Res. 37 (2003) 4855–4862.

[32] V.O. Vasylechko, G.V. Gryschchouk, Y.B. Kuz'ma, L.O. Lebedynets, O.Y. Oliyarnyk, Adsorption of cadmium on Transcarpathian clinoptilolite, Adsorpt. Sci. Technol. 18 (2000) 621–630.

[33] L.O. Vasylechko, G.V. Gryschchouk, Y.B. Kuz'ma, V.P. Zakordonskiy, L.O. Vasylechko, L.O. Lebedynets, M.B. Kalytovs'ka, Adsorption of cadmium on acid-modified - Transcarpathian clinoptilolite, Microporous Mesoporous Mater. 60 (2003) 183–196.

[34] C.Y. Xu, F.W. Schwartz, S.J. Traina, Treatment of acid-mine water with calcite and quartz sand, Environ. Eng. Sci. 14 (1997) 141–152.

[35] A. García-Sánchez, E. Álvarez-Ayuso, Sorption of Zn, Cd and Cr on calcite. Application to purification of industrial wastewaters, Miner. Eng. 15 (2002) 539–547.

[36] G.S. Gupta, Y.C. Sharma, Environmental management of textile and metallic industrial effluents, J. Colloid Interface Sci. 168 (1994) 118–124.

[37] Y.C. Sharma, Economic treatment of cadmium(II)-rich hazardous waste by indigenous material, J. Colloid Interface Sci. 173 (1995) 66–70.

[38] E. Fourest, B. Volesky, Contribution of sulfonate groups and alginate to heavy metal biosorption by the dry biomass of *Sargassum*, Environ. Sci. Technol. 30 (1996) 277–282.

[39] E. Álvarez-Ayuso, A. García-Sánchez, Palygorskite as a feasible amendment to stabilize heavy metal polluted soils, Environ. Pollut. 125 (2003) 337–344.

[40] E. Galan, Properties and applications of palygorskite-sepiolite clays, Clay Miner. 31 (1996) 443–453.

[41] H.H. Murray, Traditional and new applications for kaolin, smectite, and palygorskite: a general overview, Appl. Clay Sci. 17 (1999) 207–221.

[42] H.H. Murray, Applied clay mineralogy today and tomorrow, Clay Miner. 34 (2000) 39–49.

[43] L.G. Schultz, Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale, US Geol. Surv. Prof. Paper, 391-C, 1965.

[44] A.K.M.E. Islam, E.G. Lotse, Quantitative mineralogical analysis of some Bangladesh soils with X-ray, ion exchange and selective dissolution techniques, Clay Miner. 21 (1986) 31–42.

[45] K.H. Tan, Soil Sampling, Preparation and Analysis, Marcel Dekker Inc., New York, 1996.

[46] A. Corma, A. Mifsud, E. Sanz, Influence of the chemical compositon and textural characteristics of palygorskite on the acid leaching of octahedral cations, Clay Miner. 22 (1987) 225–232.

[47] A. Singer, Dissolution of two Australian palygorskites in dilute acid, Clays Clay Miner. 25 (1977) 126–130.

[48] A. Neaman, A. Singer, Kinetics of palygorskite hydrolysis in dilute salt solutions, Clay Miner. 35 (2000) 433–441.

[49] C.H. Giles, T.H. McEwans, S.N. Nakhwa, D. Smith, Studies in adsorption: Part IX. A System of classification of solution adsorption isotherms and its use on diagnosis of adsorption mechanisms and in measurement of specific areas of soils, J. Chem. Soc. 786 (1960) 3973–3993.

[50] E.R. Nightingale Jr., Phenomenological theory of ion solvation. Effective radii of hydrated ions, J. Phys. Chem. 63 (1959) 1381–1387.

[51] Y. Marcus, Thermodynamics of solvation of ions. Part 5. Gibbs free energy of hydration at 298.15 K, J. Chem. Soc. Faraday Trans. 87 (1991) 2995–2999.

[52] A. Corma, J. Perez-Pariente, J. Soria, Physico-chemical characterization of Cu^{2+}-exchanged sepiolite, Clay Miner. 20 (1985) 467–475.

[53] M.F. Brigatti, L. Medici, L. Poppi, Sepiolite and industrial wastewater purification: removal of Zn^{2+} and Pb^{2+} from aqueous solutions, Appl. Clay Sci. 11 (1996) 43–54.