

EFFECT OF CO-IONS ON CADMIUM SORPTION KINETICS FROM AQUEOUS SOLUTIONS BY DRIED ACTIVATED SLUDGE

H. BENAÏSSA* and M-A. ELOUCHDI

* Laboratory of Sorbent Materials and Water Treatment, Department of Chemistry-Faculty of Sciences, University of Tlemcen, P.O. Box. 119, 13 000 Tlemcen - Algeria –
Tél./Fax: 00 (213) 43 21 16 47; E-mail.: ho_benaïssa @ yahoo.fr

ABSTRACT

The effect of ions presence such as: Na^+ , K^+ , Ca^{2+} , Cl^- , SO_4^{2-} and CO_3^{2-} , at various initial concentrations, on the kinetics of cadmium sorption by dried activated sludge was studied at 25°C and free initial pH solution in batch conditions. The presence of these ions in solution was found to inhibit slightly the uptake of cadmium by dried activated sludge at different degrees: sodium, potassium, calcium and chloride ions have no significant effect. For SO_4^{2-} and CO_3^{2-} ions, the effects ranged from an inhibition of cadmium by CO_3^{2-} to a weak inhibition by SO_4^{2-} . No ion was found to enhance cadmium uptake level. The results also showed that the kinetics of sorption were described by a pseudo-second order rate model.

Keywords: sorption; cadmium; dried activated sludge; kinetics; ions effect

INTRODUCTION

Industrial wastewater effluents bearing heavy metals, pose a serious problem for the environment. Cadmium has been well recognized for its negative effect on the environment where it accumulates readily in living systems (Hutton & Symon [1], Nriagu [2]). Because dried activated sludge from many waste water treatment plants is broadly available and relatively inexpensive, an investigation of its use as a sorbent material seems most appropriate. Various studies have shown that dried activated sludge has the aptitude to remove important quantities of metallic cations from simple solutions (Gourdon et al. [3,4], Tien & Huang [5,6], Kasan [7], Imai & Gloyna [8], Shi et al. [9]). However, most of the studies presented on this subject have been based on the sorption of single metal solutions in the absence of others ions. In wastewater streams, the metal of interest is usually found in a matrix containing several metal ions (Fourest [10], Tobin et al. [11], Chong & Volesky [12], De Carvalho et al. [13], Blanco et al. [14]). These various components can interact with heavy metals and to modify thus their behaviour towards the sorbent material used.

The present study describes the results of the experimental investigation and modelling of the influence of the different ions presence such as: sodium, potassium, calcium, sulphate, chloride and carbonate, at various initial concentrations, on cadmium sorption kinetics by dried activated sludge, in batch conditions. The choice of these ions has been made because of their permanent presence in industrial waste waters.

MATERIALS AND METHODS

Dried activated sludge (a mixed microbial community) from a conventional biological wastewater treatment plant in Maghnia, Algeria, in the form of large flakes having a 0.2-5.0 mm particle size, was used throughout this work without any preliminary purification.

Solutions of determined concentration in cations and anions have been prepared respectively from nitrate salts of cadmium (Windor Laboratories Limited), sodium (Rhône-Poulenc), magnesium (Merck), and calcium (Merck); and salts of chloride (Nentech), sulphate (Merck) and carbonate of sodium (Azochim) by dissolving the exact quantities of these salts in the distilled water. All chemicals were commercial products used without purification.

The initial cadmium concentration was 100 mg/L for all experiments. Different concentrations in co-ions chosen: cations and anions, have been tested for their effects on cadmium sorption by activated sludge. For metal removal kinetics studies, 0.6 g of dried activated sludge was contacted with 300 mL of metal solutions in a beaker agitated vigorously by a magnetic stirrer using a water bath maintained at a constant temperature of 25°C. In all cases, the working pH was that of the solution and was not adjusted. The residual cadmium concentration in the aqueous solution at appropriate time intervals was obtained by using a Cd²⁺- ion selective electrode technique. The electrode used for measurement of cadmium was Orion Model 9448 and was used in conjunction with Orion Model reference electrode and an Orion Model 710A meter, which provided readings accurate to ± 0.1 mV. For the measurement of pH, an Orion Model 9107 combination electrode, with the aforementioned meter, was used. pH readings were monitored to + 0.01 unit. For certain experiments, this cadmium concentration was also done using a Perkin Elmer Model 2280 atomic absorption spectrophotometer. No differences in the results obtained by these two methods of analysis were observed. The metal uptake q (mg metal ion /g dried sorbent) was determined as follows:

$$q = (C_0 - C_t) \cdot V/m$$

where C_0 and C_t are the initial and final metal ion concentration (mg/L), respectively, V is the volume of solution (mL), and m is activated sludge weight (g) in dry form.

Preliminary experiments had shown that cadmium adsorption losses to the container walls were negligible.

RESULTS AND DISCUSSION

1- Effect of cations

To study the effect of the presence of some cations frequently met in metallic solutions on the kinetics of cadmium sorption by dried activated sludge, we have chosen as ions: sodium, potassium and calcium whose the concentrations 0.2; 1.0 and 2.0 g/L have been chosen from the literature (Fourest [10], Diard [15], Matheickal et al. [16]). To facilitate the comparison of results, all data in this present study have been obtained with nitrate salts. Figures 1 to 3 present respectively kinetics curves of cadmium sorption by dried activated sludge in the presence of competitor ions: Na⁺, K⁺, and Ca²⁺. Whatever the nature and the tested ion concentration, the kinetics of cadmium removal by dried activated sludge presents a same

shape characterized by a strong increase of the capacity of cadmium removal during the first minutes of contact solution - sludge, follow-up of a slow increase until to reach a state of equilibrium.

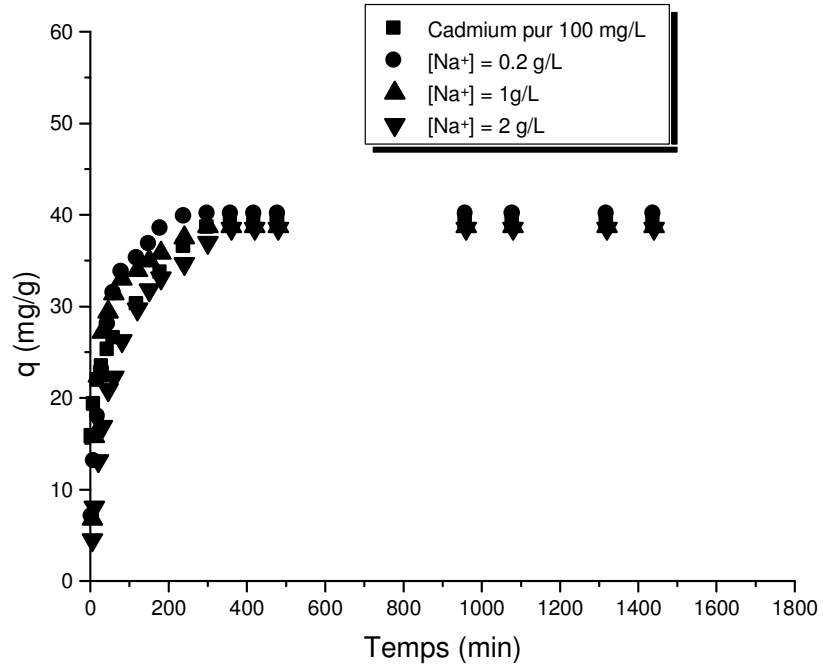


Figure 1: Effect of Na^+ ion on the kinetics of cadmium sorption by dried activated sludge

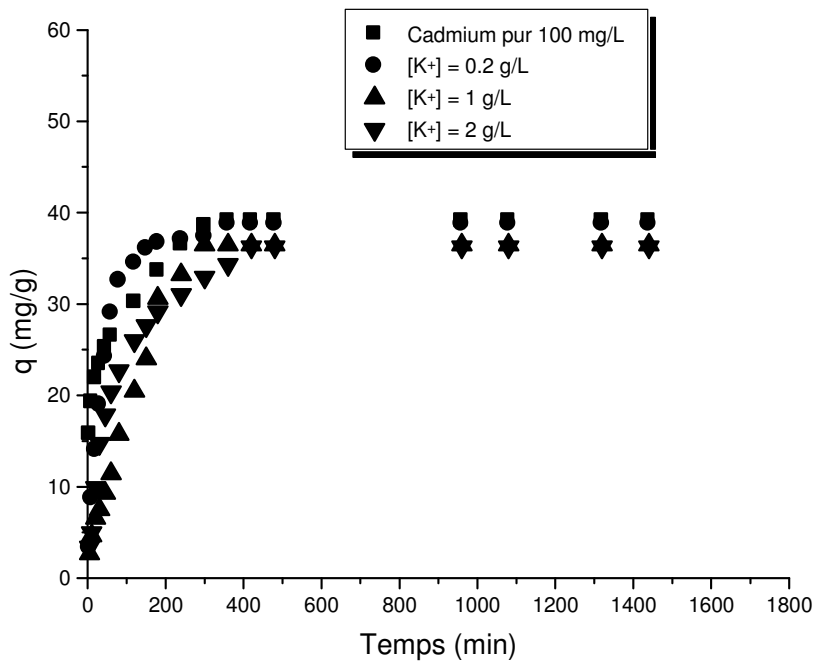


Figure 2: Effect of K^+ ion on the kinetics of cadmium sorption by dried activated sludge

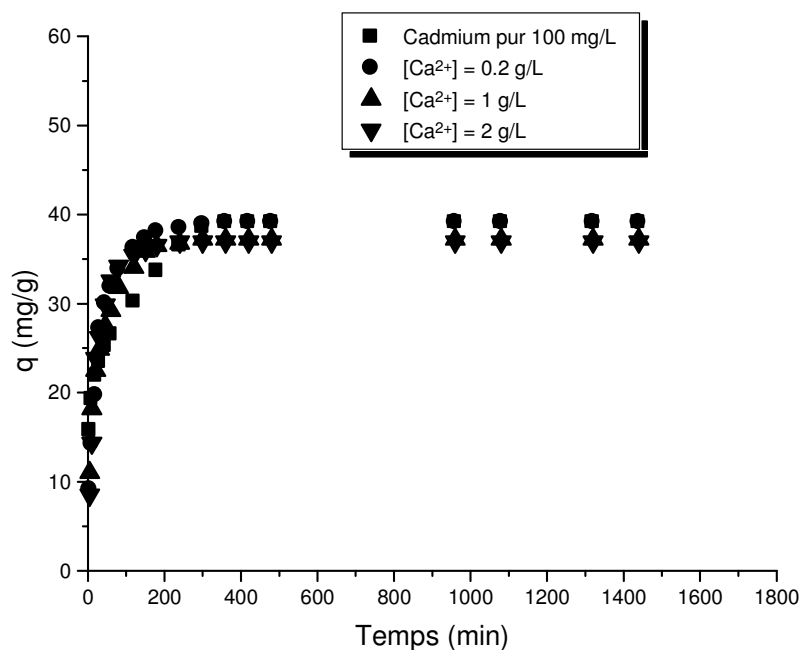


Figure 3: Effect of Ca^{2+} ion on the kinetics of cadmium sorption by dried activated sludge

The presence of co-cations has an influence on the time of equilibrium reached by cadmium alone in the absence of these ions. For sodium as a typical example, as its concentration increased, a slight augmentation in the equilibrium time was observed: 5 h for cadmium alone and approximately 4-6 hours in presence of sodium at different concentrations. Although that sodium concentrations used were largely superior to that of cadmium, the curves of kinetics of cadmium sorption, in the absence or in presence of sodium at different initial sodium concentrations (see Figure 1), are practically superposed indicating that sodium does not disturb significantly the sorption of cadmium by activated sludge. In the presence of potassium and calcium (see Figures 2 and 3), the curves of kinetics of cadmium sorption are slightly staggered to that corresponding to the cadmium sorption in their absence indicating well a phenomenon of competition between Cd^{2+} and K^+ / Ca^{2+} ions for the sites of binding on activated sludge. Potassium compared to calcium, is more inhibitor that its concentration is raised. These observations are in agreement with those observed by Muzzarelli et al. [17] who have indicated that large quantities of divalent cations of the group IIA were not prejudicial to heavy metal removal in solution by another sorbent material: chitin. Elsewhere, Tobin et al. [11] have shown that monovalent alkaline metals did not bind on *Rhizopus arrhizus* biomass thus they confirm therefore our results particularly obtained with sodium ion.

During the course of cadmium removal by activated sludge, whatever the nature and the tested ion concentration, we have also noticed that their presence beside cadmium does not affect the evolution of the pH initial of solution (see Figure 4 as a typical example). We have always an increase in the initial value of pH analogous to that observed in the case of the sorption of cadmium alone without reaching the value of its precipitation. This can be interpreted by a competition between cadmium ions and H_3O^+ for binding sites.

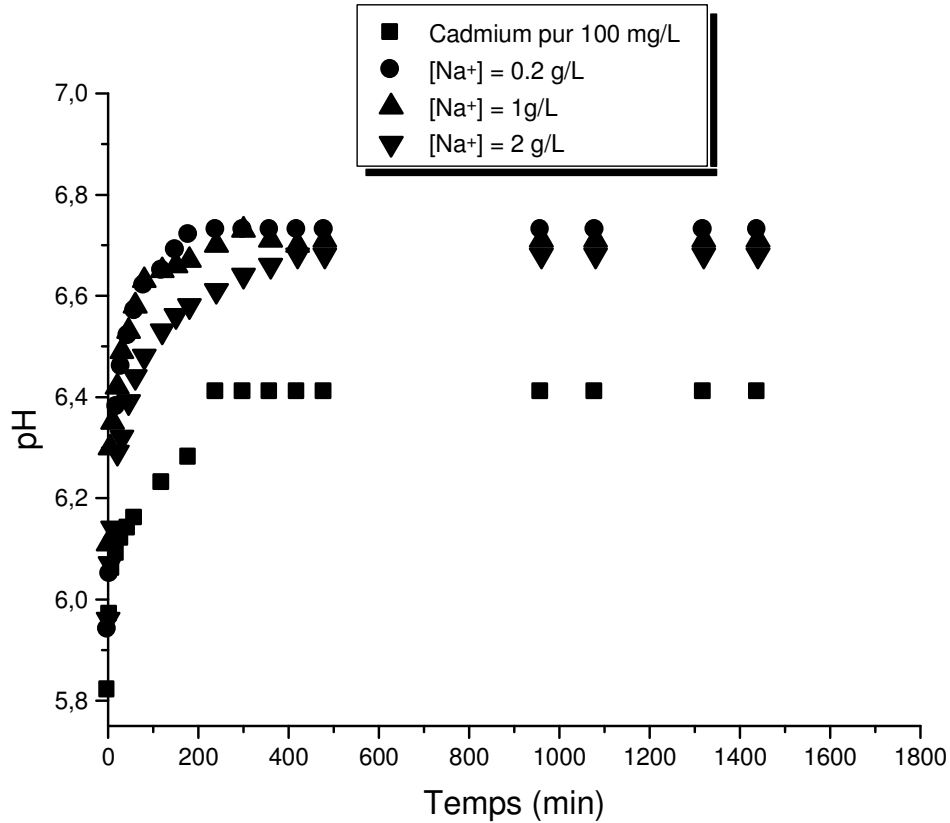


Figure 4: pH profile of cadmium sorption by activated sludge in presence of sodium cation

The kinetics of cadmium sorption by activated sludge were modelled using a pseudo- second order rate equation developed by Ho & McKay [18]. The kinetic rate equation is:

$$t / q_t = 1 / 2K'q_e^2 + t / q_e \quad (1)$$

where K' ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant of sorption, q_e and q_t are the amounts of metal ion sorbed ($\text{mg} \cdot \text{g}^{-1}$) at equilibrium and at time t , respectively. As shown in Figure 5 as a typical example, the pseudo second-order reaction rate model adequately described the kinetics of cadmium sorption with high correlation coefficient. The K' values from the slopes and intercepts are summarized in the Table 1.

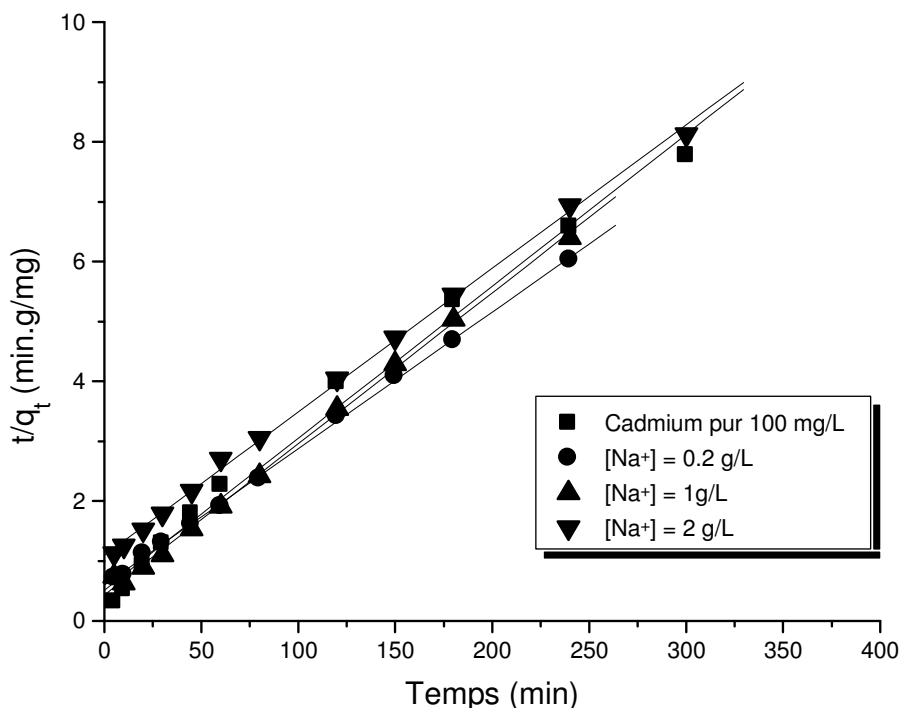


Figure 5: Linearization of cadmium sorption kinetics by activated sludge in presence of sodium cation using a pseudo-second order rate model

Table 1: Pseudo second-order rate constants for cadmium sorption kinetics by activated sludge in presence of cations

Concentrations	$K' \text{ (min}^{-1} \cdot \text{g / mg)} \cdot 10^{+4}$	R^2
Pure Cadmium 100 mg/L	6.25	0.990
[Na ⁺] = 0.2 g/L	4.37	0.998
[Na ⁺] = 1.0 g/L	7.33	0.998
[Na ⁺] = 2.0 g/L	2.62	0.998
[K ⁺] = 0.2 g/L	2.96	0.990
[K ⁺] = 1.0 g/L	0.65	0.790
[K ⁺] = 2.0 g/L	2.16	0.996
[Ca ²⁺] = 0.2 g/L	6.68	0.998
[Ca ²⁺] = 1.0 g/L	7.99	0.998
[Ca ²⁺] = 2.0 g/L	8.07	0.988

B - Effect of anions

In the presence of calcium, the cadmium sorption by activated sludge is strongly reduced: curves of kinetics of cadmium sorption (see figure 3) are clearly less staggered to that corresponding to the sorption of cadmium in absence of calcium. The competitor effect of potassium towards the sorption of cadmium is more important than those of sodium and calcium.

The nature of the counter - ions, destined to stabilize heavy metals in the cationic form, can also influence their sorption by sorbent materials. Some anions can have an affinity towards the metal that they form an insoluble or soluble complex, displaced with difficulty in the presence of the sorbent material (Fourest [10]). For these reasons, we have respectively studied the effect of the presence of three classic anions: chloride, sulphate and carbonate on the kinetics of cadmium sorption by activated sludge in the same operative conditions. Studied anions were in the form of sodium salts since sodium did not disturb the sorption of cadmium by chitin already confirmed previously. The chosen concentrations were respectively: 0.2; 1.0 and 2.0 g/L for chloride and sulphate ions; and 0.05; 0.1 and 0.2 g/L for carbonate ion, chosen from bibliographical data (Fourest [10]). Figures 6 to 8 present, respectively, the kinetics curves of cadmium sorption by activated sludge in the presence of these anions at different initial concentrations. Here also, whatever the nature and the tested anion concentration, the kinetics curves obtained have the same shape characterized by a strong increase of the amount of cadmium sorbed by activated sludge during the first minutes of contact solution - sludge, follow-up of a slow increase until to reach a state of equilibrium. The presence of anions has a certain influence on the time of equilibrium reached by cadmium alone in the absence of these anions. According to the Figure 6, the kinetics curves of cadmium sorption by activated sludge, in the absence or in the presence of chloride ion, are approximately superposed for all concentrations chosen. Concerning the presence of sulphate and carbonate ions, their influence on the sorption kinetics of cadmium by activated sludge is more marked than that observed in the presence of chloride ions (see Figures 7 and 8). Thus, curves of kinetics obtained are slightly staggered to that corresponding to the cadmium sorption in the absence of anions. For carbonate anion, the kinetic curve of cadmium sorption is strongly reduced compared to that observed in presence of sulphate anions. These results show that cadmium sorption can be inhibited only by anions forming sufficiently stable complexes. Table 2 gives constants of complex stability between cadmium and various anions (Sillen & Martell [19]; Smith & Mortell [20]).

Tableau 2: Stability constants of complexes between cadmium and various anions

Anion	log k
Cl ⁻	1.98
SO ₄ ²⁻	2.4
CO ₃ ²⁻	4.02

During experiments of sorption, we have also observed an evolution in the initial pH value of solutions, similar to that observed previously for cations, for only chloride and sulphate anions. Concerning the presence of carbonate anion, we have observed a slight diminution in initial pH value of the solution for the initial concentration in carbonate 0.2 g/L provoking the training of a precipitate (see Figure 9).

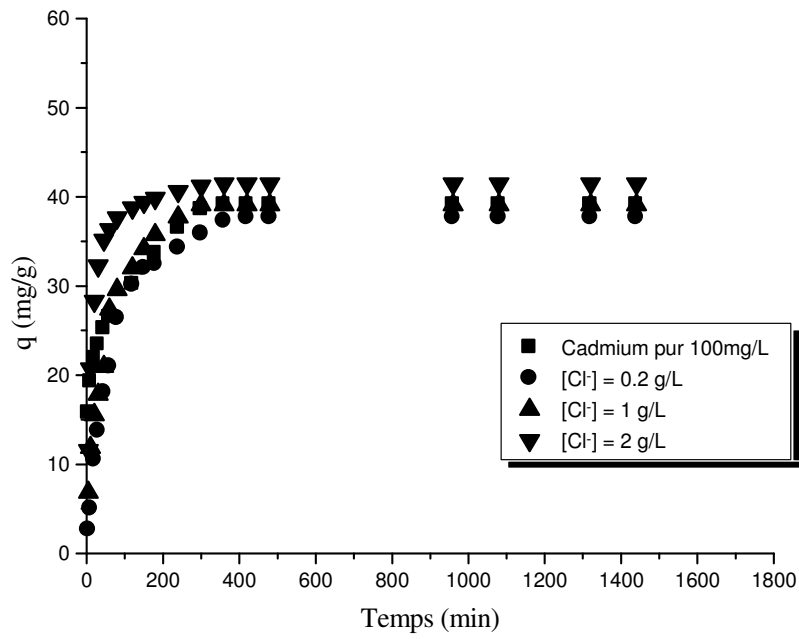


Figure 6: Effect of Cl^- ion on the kinetics of cadmium sorption by activated sludge

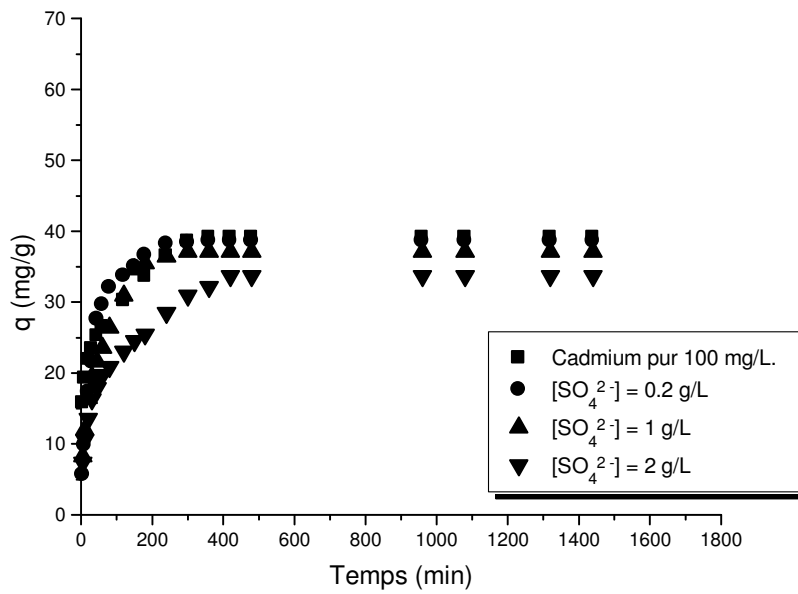


Figure 7: Effect of CO_3^{2-} ion on the kinetics of cadmium sorption by activated sludge

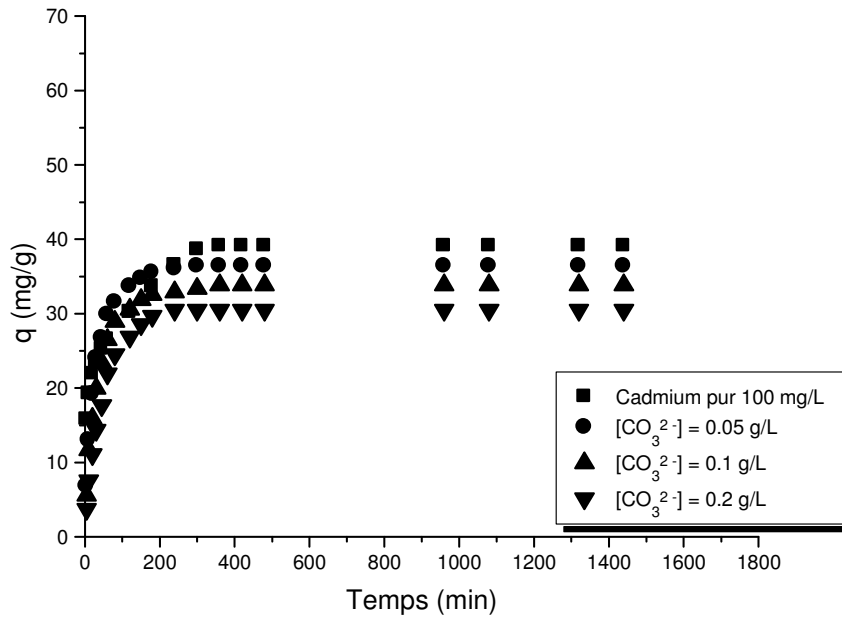


Figure 8: Effect of CO_3^{2-} ion on the kinetics of cadmium sorption by activated sludge

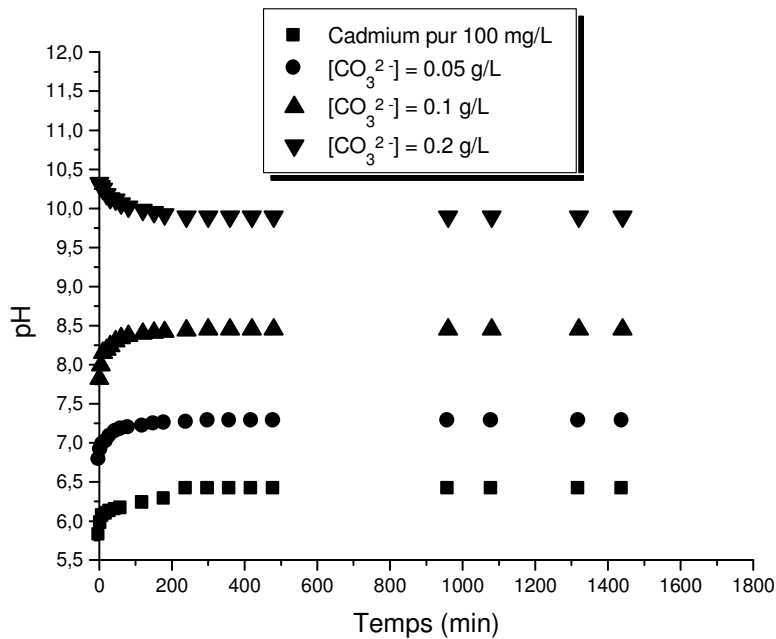


Figure 9: pH profile of cadmium sorption by activated sludge in presence of carbonate anions

The inhibitive force of the anion towards the cation in sorption is proportional to the constant of stability of the couple of ions considered. We notice according to the table above, that for chloride and sulphate anions, the constant of stability is weak compared to that of carbonate anion which is very important: this justifies the substantial inhibition of cadmium sorption in the presence of carbonate ion.

When these data were fitted to the pseudo-second order rate equation cited above, straight lines were only obtained (see Figure 10 as typical example) indicating that the process follows a pseudo second-order kinetics. The rate constants calculated from their slopes and intercepts are shown in Table 3.

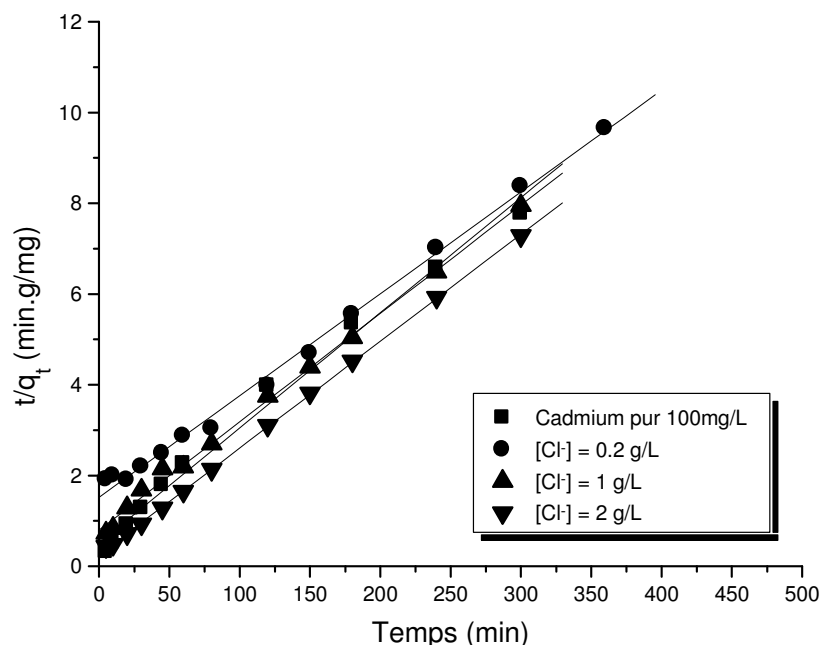


Figure 10: Linearization of cadmium sorption kinetics by activated sludge in presence of chlorate anion using a pseudo-second order rate equation

Table 3: Pseudo second-order rate constants for cadmium sorption kinetics by activated sludge in presence of anions

Concentrations	K' ($\text{min}^{-1} \cdot \text{g} / \text{mg}$). 10^{+4}	R^2
Pure cadmium (100 mg/L)	6.25	0.990
[Cl ⁻] = 0.2 g/L	1.60	0.994
[Cl ⁻] = 1.0 g/L	3.54	0.996
[Cl ⁻] = 2.0 g/L	10.92	0.998
[SO ₄ ²⁻] = 0.2 g/L	4.03	0.998
[SO ₄ ²⁻] = 1.0 g/L	3.75	0.988
[SO ₄ ²⁻] = 2.0 g/L	4.79	0.982
[CO ₃ ²⁻] = 0.05 g/L	6.06	0.998
[CO ₃ ²⁻] = 0.10 g/L	5.85	0.998
[CO ₃ ²⁻] = 0.20 g/L	3.00	0.996

CONCLUSION

Results obtained from this study show that the presence of some ions can inhibit or exert between them a competitive action in the presence of a sorbent material. This means that they bind to sites of identical sorption, and the competition plays in favour of the element that possesses the best affinity for these groups. It appears that cations: sodium, potassium and calcium, are not sorbed in quantity relatively important at the same time that cadmium. Concerning the effect of the presence of anions on the kinetics of cadmium sorption by activated sludge, except for the weak influence of chloride ion monovalent that lets to think that the interactions of monovalent charges participate in negligible manner in the process of cadmium sorption, sulphate and particularly carbonate anions slightly inhibit this sorption.

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