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## Uptake of copper ion using protonated dry alginate beads from dilute aqueous solutions

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**Abstract:** This research aimed to identify the copper ion removal mechanism when using protonated dry alginate beads. This mechanism was explained through ion exchange between Cu ions and the protons from the functional groups of the alginate beads. Copper removal increased with stirring velocity, reaching values of  $97.5 \text{ mg g}^{-1}$  ( $97.5 \times 10^{-3} \text{ kg/kg}$  of PDAB) of dry alginate at  $200 \text{ rev min}^{-1}$ , at a solution pH of 6.0 and a run time of 360 min. For the lowest level of copper concentrations, at  $10 \text{ mg dm}^{-3}$  ( $10 \times 10^{-6} \text{ kg dm}^{-3}$ ), full removal was attained. The removal kinetics was represented by a pseudo-first order model. A value of  $0.0131 \text{ min}^{-1}$  was found for the velocity constant. Under equilibrium conditions, the experiment data was fit to the Langmuir adsorption model, and the highest removal values were 270.3, 222.2 ( $222.2 \times 10^{-3} \text{ kg/kg}$  of PDAB) and  $49 \text{ mg g}^{-1}$  ( $49 \times 10^{-3} \text{ kg/kg}$  of PDAB) for pH values of 5.0, 3.5 and 2.5, respectively. These are higher than most sorbents used in the literature for copper removal. Increased temperature leads to higher Cu removal. The activation energy was calculated at  $9.3 \text{ kJ mol}^{-1}$  for the temperature range of 283 to 343K. Observations using SEM and composition measurements of the alginate cross-section taken by EDS showed a uniform distribution of the copper concentration through the structure of the alginate beads, independent of the solution pH, contact time and temperature.

**Keywords:** Removal mechanism, copper ions, alginate beads, pseudo-first order kinetics model, activation energy

### 1. Introduction

A large amount of heavy metals is discharged into the aquatic environment. Acidic drainage from mining is an effluent that contains significant amounts of heavy metals and it is being discharge in greater quantities every year as a result of mineral and mining processing operations (Feng et al., 2000). The main source of heavy metals is the natural oxidation of minerals that contain sulphur (Demopoulos, 1998). The composition of mining drainage is generally copper, zinc, cadmium, lead, etc. Most of these are highly toxic and negatively impact flora and fauna and also human life. For example, copper has adverse effects on the environment and on humans. In humans, copper causes serious problems, such as anaemia, renal damage, and other illnesses (Kandah et al., 2002). New and tighter environmental regulations have been imposed to force treatment of such effluents in order to reduce the concentration levels of heavy metals. Therefore, removal of heavy metal ions from diluted solutions is a subject of growing interest.

The treatment of liquid effluents containing cupric ions has led to studies of different processes such as polymer derivations of poly (Samadi et al., 2017), thermally regenerative electrodeposition battery (Rahimi et al., 2017), electro dialysis process under electroconvection operation (Chang et al., 2017),

sulphur microparticles (Xie et al., 2017), sorption (Sedra et al., 2016) and coprecipitation of copper (Sedra et al., 2016; Khosravi, 2009), extraction with ionic liquid (Huang, 2017), solvent extraction (Kasaie et al., 2017), among others. But on the other hand, processes of ion exchange have been used for the removal of heavy metals such as copper ions. These processes have significant competitive advantages, such as low cost, material reuse, and others. The advantage of using alginate beads is the great removal they have achieved in the works mentioned for metals that are present in very dilute solutions, close to 25 ppm of the metal. For these low concentrations, conventional ion exchange methods can not be used as they become inefficient. Thus, there is increasing interest in studying the use of natural polymeric materials, such as alginate beads, which is a sorbent of controlled size, good physical and chemical properties including high porosity. Alginate beads have already shown their potential for use in the removal of Ni (Aracena et al., 2015), Zn (Ibáñez and Aracena, 2014), Cd (Ibáñez and Umetsu, 2008), Cr (Ibáñez and Umetsu, 2004) and others. Thus, the alginate beads would be a potential sorbent in the removal of copper ions from very dilute solutions

The objective of this research is to study the factors that influence the removal of copper ions, such as stirring, solution pH, run time, load capacity and temperature, through the use of protonated dry alginate beads.

## 2. Materials and methods

Solutions with different copper concentrations were prepared by dissolving the salt  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  in double-distilled water. The chemical analysis was conducted by inductively coupled plasma atomic emission spectrometer (ICP/AES). The chemical composition and morphology of the alginate beads were analysed using a Tescan Vega LDH scanning electron microscope (SEM), a Bruker Quantax system with XFlas 4010 (EDS) detectors and backscattered electron imaging (BEI) with quantification by an EDS Quantax system. For the observation and analysis of the alginate bead samples, they were cut with gold and graphite, respectively.

The protocols from the study by Ibáñez and Umetsu (Ibáñez and Umetsu, 2002) were used to generate the protonated dry alginate beads (PDAB). The alginate beads have alginic acid chains that are treated with Ca and Ba to generate PDAB-Ca and -Ba. They have shown the appropriate physical and chemical properties in aqueous solutions (Ibáñez and Umetsu, 2002), ie, PDABs are chemically and physically stable in highly diluted solutions. The formation of the PDAB leads to a corrugated surface with a bead diameter of around  $1.0 \pm 0.1$  mm, with a high degree of porosity. Protonated dry alginate beads are stable in a high range of pH values of approximately 1 to 6. Outside this range, the Ca and Ba are released from the beads, with a subsequent loss of rigidity and stability (Ibáñez and Aracena, 2014).

The removal experiments were carried out by making contact between  $0.40 \text{ dm}^3$  of copper solution (with a concentration of  $23 \text{ mg dm}^{-3}$  ( $23 \times 10^{-6} \text{ kg dm}^{-3}$ ) for most experiments) and  $80 \text{ mg}$  ( $80 \times 10^{-6} \text{ kg}$ ) of PDAB for 360 minutes at  $290.0 \pm 0.1 \text{ K}$ . The pH of the solution was maintained constant through the addition of NaOH depending on the conditions of each experiment. In each experiment  $0.001 \text{ dm}^3$  of sample was extracted at different time intervals and sent for chemical analysis by ICP/AES. The samples were diluted to  $0.010 \text{ dm}^3$  with double-distilled water and then filtered through cellulose membrane filters. The remnant copper, barium and calcium concentrations in the filtrates were analysed by ICP/AES. The beads were collected at the end of the experiments. They were then washed with double-distilled water, dried in air and stored for observation by SEM-EDS and BEI. The reproducibility of the experiments was evaluated by performing the experiments in duplicate and in triplicate, showing variations of below 2.0%. Average values were calculated (Aracena et al., 2015).

## 3. Result and discussion

### 3.1. Effect of agitation speed

The effect of agitation speed applied to the solution on the removal of copper ions was analysed for an initial Cu concentration of  $23 \text{ mg dm}^{-3}$  ( $23 \times 10^{-6} \text{ kg dm}^{-3}$ ), pH = 6.0 and run time of 360 minutes. The results are shown in Fig. 1. It can be seen that as the solution stirring velocity increases, the uptake of copper increase. For a velocity of  $50 \text{ rev min}^{-1}$ , a copper of  $55 \text{ mg g}^{-1}$  ( $55 \times 10^{-3} \text{ kg/kg}$  of PDAB) is attained, while increasing the revolutions to  $100 \text{ rev min}^{-1}$ , gives a maximum copper of  $106 \text{ mg g}^{-1}$  ( $106 \times 10^{-3} \text{ kg/kg}$

of PDAB). It can also be seen that if the solution is not stirred, a minimum uptake value of up to  $2.5 \text{ mg g}^{-1}$  ( $2.5 \times 10^{-3} \text{ kg/kg}$  of PDAB) is reached. The removal process has been found to be independent of mass transfer above a fig. of approximately  $100 \text{ rev min}^{-1}$ . Therefore, a stirring velocity of  $200 \text{ rev min}^{-1}$  was chosen for future experiments (Aracena et al., 2015).

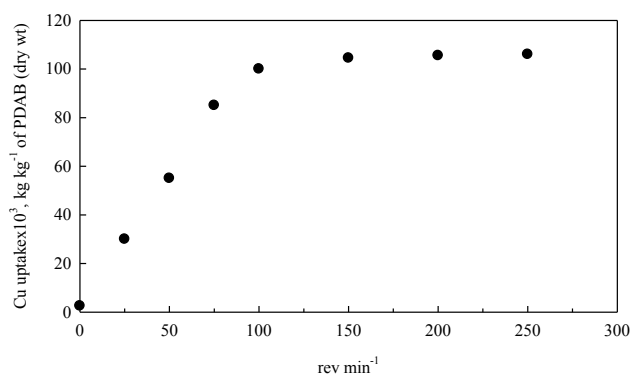


Fig. 1. Uptake of copper as a function of stirring velocity ( $\text{rev min}^{-1}$ )

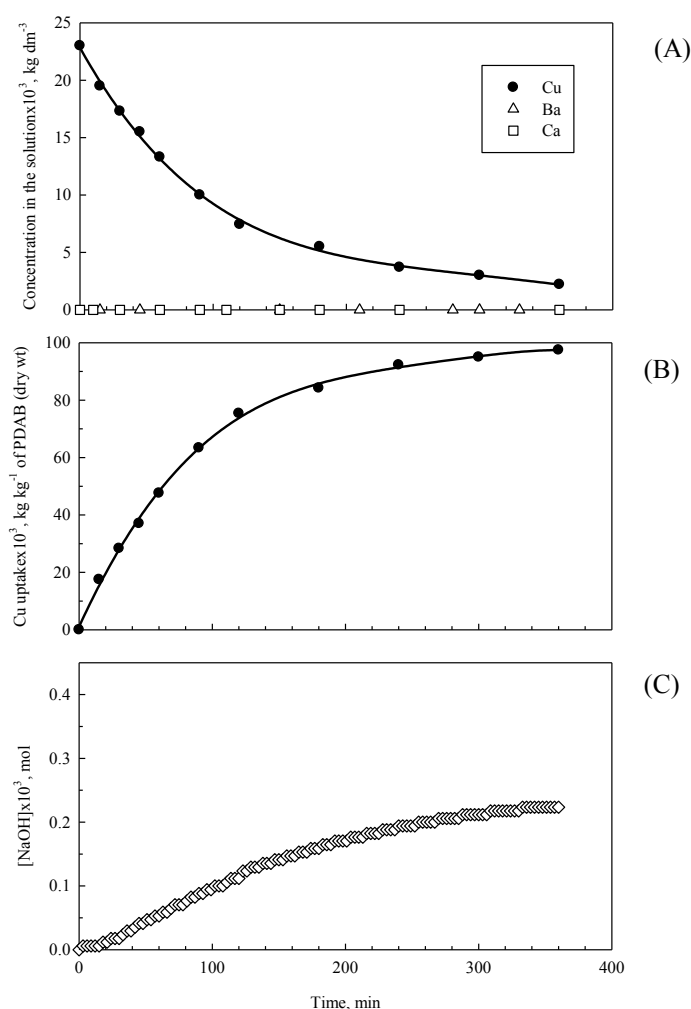


Fig. 2. Experiment data as a function of solution pH. (A) Cu and Ba concentration in the solution, (B) Cu removal using Ba-PDAB and Ca-PDAB, (C) NaOH consumption

### 3.2. Effect of solution pH

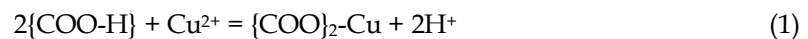
Fig. 2 gives a summary of the experiment data as a function of pH for a contact time of 360 minutes. Fig. 2-A shows almost no variation in the copper concentration for a pH value of 2.0, while above this value

the reduction of copper ions in the solution begins, reaching around  $2.2 \text{ mg dm}^{-3}$  ( $2.2 \times 10^{-6} \text{ kg dm}^{-3}$ ) at a pH of 5.0. No evidence was found of a significant variation in the residual copper concentration above this pH value. The graph also shows that no barium was released from the PDAB for all solution pH values, demonstrating the chemical stability of the alginate beads (Aracena et al., 2015).

Fig. 2-B shows a continuous increase in the copper ion removal beginning at a pH of 2.0 until a value of 5.0 and reaching a removal value of  $102.0 \text{ mg g}^{-1}$  ( $102.0 \times 10^{-3} \text{ kg/kg}$  of PDAB) of alginate (dry weight). The removal value remains constant at high pH values. This behaviour is in agreement with the NaOH consumption shown in Fig. 2-C, which shows an increase in consumption for pH values above 3.0. The data of mols of NaOH for pH values below 3.0 were not included as an imprecise reading was given due to the low number of protons released to the solution at these low pH values.

The observed pH effect on Cu removal is supported by the fact that the functional group of alginic acid chains forming the PDAB is carboxylic, which is considered a weak acid. Therefore, at low pH a drop is seen in the removal capacity of the alginate, as shown in Figs 2-A and 2-B. The situation changes at higher pH values, for which the dissociation of the functional group promotes copper removal. According to Fig. 2, maximum dissociation of the carboxylic functional group takes place at a pH of 5.0. This coincides with the results of previous studies (Aracena et al., 2015; Ibáñez and Aracena, 2014; Ibáñez and Umetsu, 2008; Ibáñez and Umetsu, 2004; Ibáñez and Umetsu, 2002), as the apparent dissociation constant of alginic acid reported by Fourest and Volesky (Fourest and Volesky, 1996) is  $10^{-4}$ . This change at higher pH values is due to the fact that the alginate beads have a rigid structure and a high density of carboxylic groups compared to free alginic acid (Ibáñez and Aracena, 2014).

According to the results shown in Figs 2, copper removal occurs with proton release, which was quantified by the NaOH consumption. No Ba was detected in the residual solution after the removal experiments. An ion exchange mechanism during the Cu removal with the alginate can therefore be posited. This ion exchange may be represented by reaction (1):



In this reaction it is considered that the copper species that is present is  $\text{Cu}^{2+}$ . This presence is corroborated in the predominance diagram of the Cu-H<sub>2</sub>O system at 278, 290 and 353K (Fig. 3). It was constructed considering the copper concentration of  $23.0 \times 10^{-3} \text{ kg dm}^{-3}$ . Thermodynamic data used to construct this diagram in equilibrium were primarily obtained from the database of the HSC Chemistry program (Roine, 1999). The copper component presents in this diagram were  $\text{Cu}^{2+}$ ,  $\text{Cu}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_2^{-2}$ ,  $\text{Cu}_2\text{O}$  and Cu. This diagram shows that the area of predominance of  $\text{Cu}^{2+}$ , a major ion in the ion exchange, is above the values of potential of 0.24 volts, and acid pH's values. As temperature increases, the copper cation predominance area becomes small. Thus, for a temperature of 278 to 353K, the balance lines between  $\text{Cu}^{2+}$  and  $\text{Cu}(\text{OH})_2$  are at pH values of 5.2 and 4.1, respectively. Instead, the Eh ranges (balance line between  $\text{Cu}^{2+}$  and Cu) maintain small differences despite the increase of temperature.

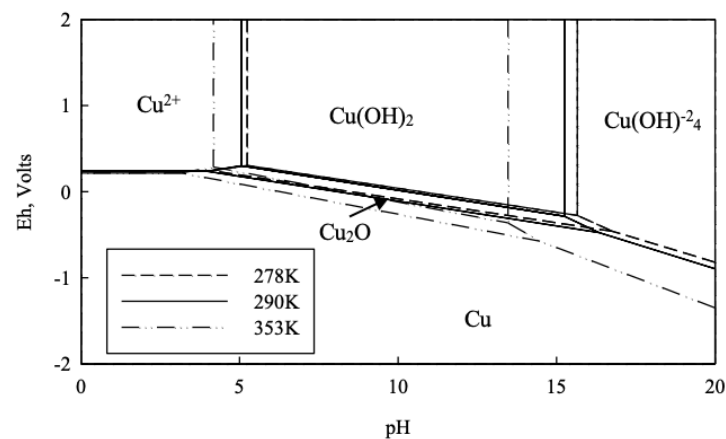


Fig. 3. Eh-pH diagram of the Cu-H<sub>2</sub>O system at a concentration of  $\text{Cu}=23.0 \times 10^{-3} \text{ kg dm}^{-3}$ . The equilibria obtained at 278 K are shown as dashed lines, equilibria at 290 K in fine lines and at 353 K in short dash dot lines

In the pH range studied, where the predominant copper ion ( $\text{Cu}^{2+}$ ), it can be concluded that it is possible that this mechanism of ion exchange which would be feasibly viable from a temperature between 278 to 353K for a range of acid pH. Therefore, this ion exchange can be represented by the reaction (1).

If reaction (1) represents the copper ion removal from the solution, then a molar ratio between released protons and Cu ions taken from the solution must have a value of 2. Fig. 4 shows the values of this ratio as a function of pH for the 360-minute period. It can clearly be seen that the molar ratio  $d[\text{H}^+]/d[\text{Cu}^{2+}]$  has a value of 2. This result suggests that reaction (1) represents the Cu removal, i.e. copper removal takes place through an ion exchange mechanism.

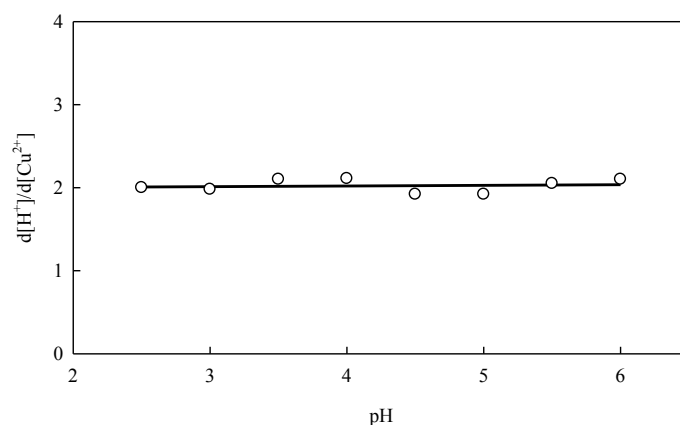


Fig. 4. Variation in molar ratio  $d[\text{H}^+]/d[\text{Cu}^{2+}]$  as a function of working pH. A value of 2 was taken

The copper composition was analysed in the alginate beads using BEI with EDS. It can be seen in the BEI images that the cross section of the alginate shows a uniformity in the cross section, even working at very acidic pH levels (2.0). This would show the physical resistance of the alginate.

The copper profile through the alginate particles was measured along the dotted line in Fig. 5. The measurement values are given in Table 1 as a Cu percentage at each point of analysis

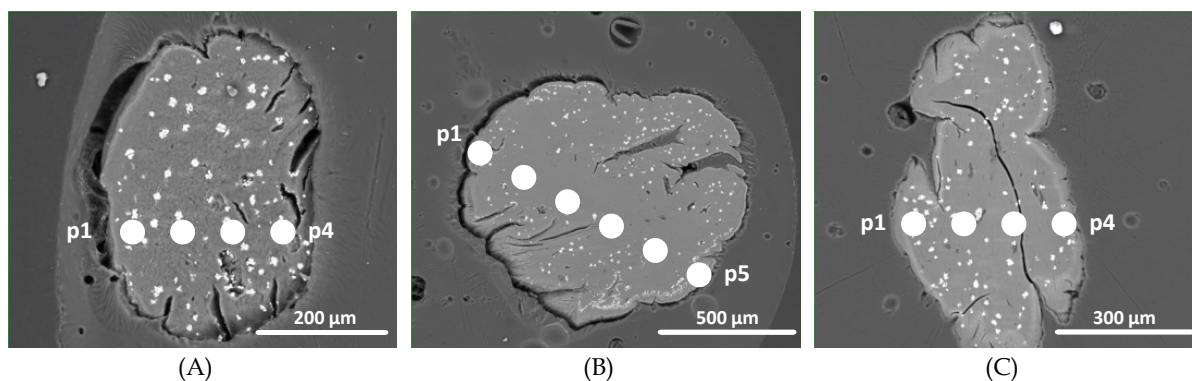


Fig. 5. BEI micrographs of alginates in a sample treated at: (A) pH=2.0; (B) pH=3.5; (C) pH=6.0. The copper concentration was measured along the dotted line.

Table 1. Profile of copper concentration through the alginate seen by EDS for pH values of 2.0, 3.5 and 6.0

Point	Copper concentration, %		
	pH=2.0	pH=3.5	pH=6.0
1	2.78	21.91	26.86
2	2.68	15.04	23.89
3	2.23	17.46	21.85
4	1.11	17.87	23.18

The EDS results indicate that copper concentration through the alginate beads is high on the external surface, especially at low pH (2.0). This behaviour is consistent with the low removal Fig.s. The concentration profile tends to disappear at high pH values, for instance at pH 6.0 the cross-section profile is almost flat.

### 3.3. Effect of experiment run time

Fig. 6 shows the experiment data as a function of time for an initial Cu concentration of  $23 \text{ mg dm}^{-3}$  ( $23 \times 10^{-6} \text{ kg dm}^{-3}$ ), pH of 6.0 and 80 mg of PDAB. Fig. 6-A shows the residual copper concentration and Ba and Ca ion concentrations. Fig. 6-B shows the copper ion removal per gram of PDAB and Fig. 6-C represents the molar consumption of NaOH.

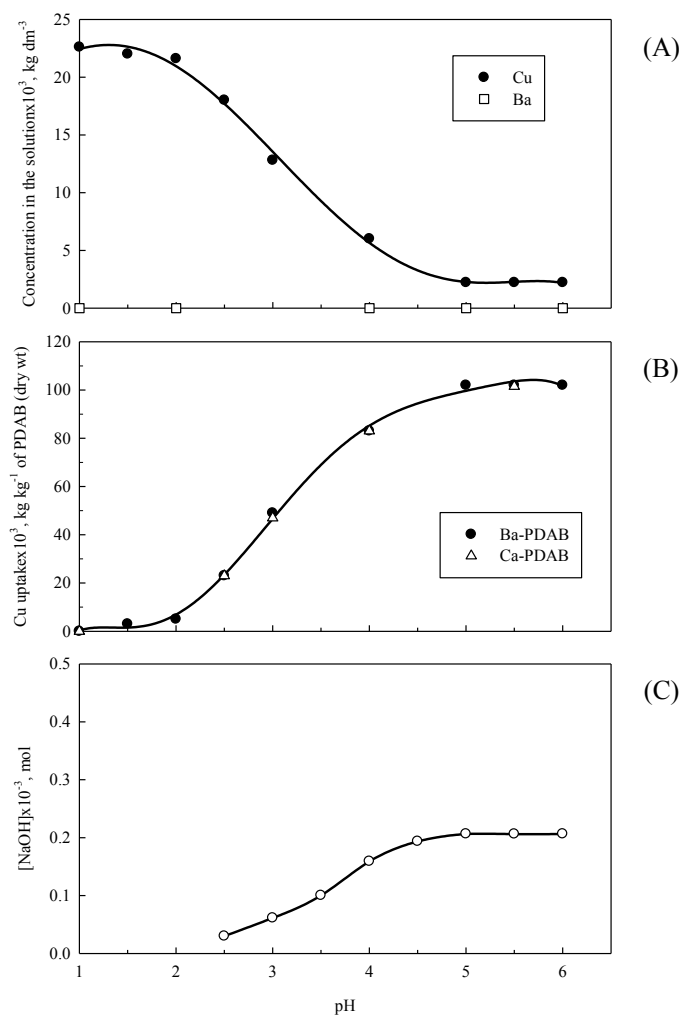


Fig. 6. Removal data for: (A) residual Cu, Ca and Ba concentration in the solution, (B) copper removal (C) NaOH consumption

Fig. 6-A shows a sharp decrease in Cu concentration over the experiment run time which is not associated with a release of Ba and Ca ions. This finding suggests that intertwined cations of the alginic acid chains of the PDAB are not part of the removal process (Ibáñez and Aracena, 2014). Fig. 6-B shows the copper ion removal, reaching a value of  $97.5 \text{ mg g}^{-1}$  of PDAB ( $97.5 \times 10^{-3} \text{ kg/kg}$  of PDAB) (dry weight) after 360 minutes of contact time. This Fig. also shows two steps for copper ion removal: the first lasts until around 120 minutes when copper removal reaches approximately 80%, and the second stage is markedly slower, reaching almost equilibrium at 360 minutes. NaOH consumption by removed Cu shown in Fig. 6-C presents similar behaviour to what is seen in Fig. 6-A and 6-B, rapid consumption in the first 120 minutes followed by slow consumption until a constant value is reached at 360 minutes. Given that NaOH is used to neutralise the protons, the removal process may arise due to an ion

exchange mechanism, exchanging protons from the functional groups of the PDAB and copper ions in the solution (Aracena et al., 2015; Ibáñez and Aracena, 2014), as shown in Fig. 4.

The solids were analysed using the technique of BEI and EDS. The results by BEI show that the alginate spheres maintain their uniformity in their transversal structure, even tripling their experimental time (from 120 to 360 minutes). With these results they demonstrate their rigidity and form again as time passes. The EDS results were compared with the original alginate sample and the pH was set at 6.0. The results are shown in Fig. 7, in which dotted lines can be seen through the three alginate bead samples. Table 2 gives the copper percentages at each point of analysis. These results prove that with increased reaction time between the alginate and the copper solution, the amount of Cu throughout the alginate increases also. In addition, with increased contact time (from 120 to 360 minutes), an increase of copper in the PDAB is also seen. Therefore, the behaviour of the amount of copper in the alginate is in line with the behaviour seen in Fig. 6.

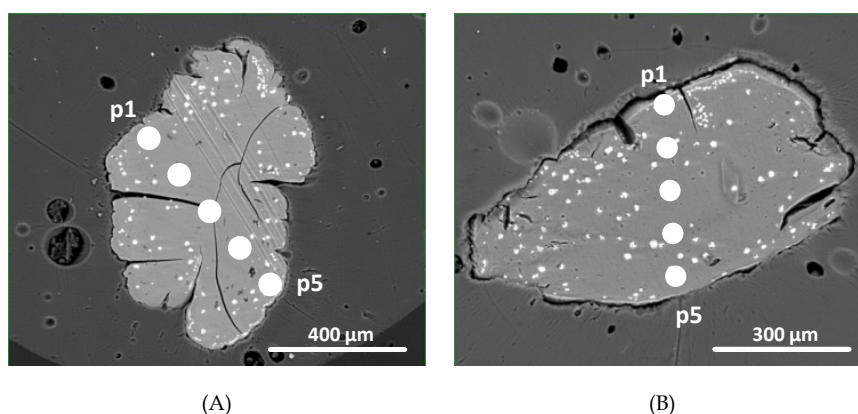


Fig. 7. BEI micrographs of alginates in a sample treated at: (A) sample at 120 minutes; (B) sample at 360 minutes. The copper concentration was measured along the dotted line

Table 2. Profile of copper concentration through the alginate seen by EDS for different experiment run times

Point	Copper concentration, %	
	120 min	360 min
1	14.78	27.03
2	19.22	24.61
3	19.78	21.94
4	19.51	23.46

### 3.4. Load capacity and models

Fig. 8 shows the copper ion removal results as a function of concentration in equilibrium at pH values of 2.5, 3.5 and 5.0. Work at pH equal to 6.0 was not considered because it was previously shown that removal values on identical to those obtained at pH = 5.0 (see Fig. 2). This Fig. (Fig. 8) shows full saturation of the PDAB with Cu when the concentration in equilibrium reaches a value of approximately  $0.40 \text{ kg dm}^{-3}$  for all pH values. The maximum load value was 252, 202 and 45  $\text{mg g}^{-1}$  ( $\times 10^{-3} \text{ kg/kg}$  of PDAB) of dry alginate for pH values of 5.0, 3.5 and 2.5, respectively. It should also be noted that when the initial Cu concentration was  $10 \times 10^{-6} \text{ kg dm}^{-3}$ , no copper was found in the final solution at a pH value of 5.0, and therefore, full copper removal from the solution was achieved.

The experiment data shown in Fig. 8 were fit to the Langmuir, Freundlich and Temkin adsorption isotherm models, and Table 3 shows the parameters of these models. The table also shows that the experiment data fits the Langmuir model ( $R^2 \geq 0.985$ ) for the pH values. The maximum removal value given by the model was 270.3, 222.2 and 49  $\text{mg g}^{-1}$  ( $\times 10^{-3} \text{ kg/kg}$  of PDAB) for pH values of 5.0, 3.5 and 2.5, respectively. These values are close to those obtained experimentally, shown in Fig. 8.

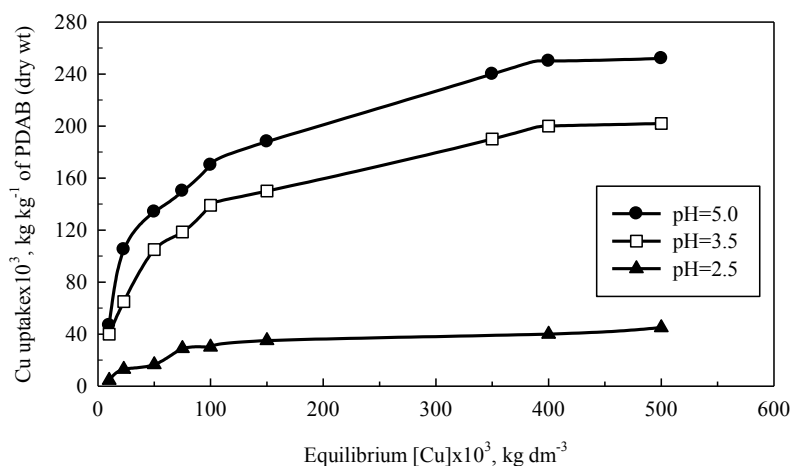


Fig. 8. Copper removal as a function of concentration at Cu equilibrium

Table 3. Parameters of the Langmuir, Freundlich and Temkin adsorption models and correlation coefficients ( $R^2$ )

Langmuir			Freundlich		Temkin			
$q_{\max}$	B	$R^2$	k	n	$R^2$	a	b	$R^2$
49.0	0.019	0.985	4.5	0.3887	0.965	1.28	6.89	0.878
222.2	0.030	0.992	33.9	0.3092	0.987	1.29	32.41	0.971
270.3	0.042	0.991	222.3	0.2842	0.884	60.37	29.31	0.931

$q_{\max}$ : Langmuir maximum uptake

b: Langmuir isotherm, parameter

k, n: Freundlich isotherm constants

a, b: Temkin isotherm constants

### 3.5. Copper removal kinetics

The copper removal kinetics was obtained by fitting the experiment data using pseudo-first order and pseudo-second order kinetics models (Ibáñez and Aracena, 2014). The initial copper concentrations used were  $23 \times 10^{-6}$ ,  $30 \times 10^{-6}$  and  $40 \times 10^{-6}$  kg dm<sup>-3</sup> with  $80 \times 10^{-6}$  kg of PDAB, a pH value of 6.0 and a contact time of up to 360 minutes.

The Lagergren (So, 2004) pseudo-first order kinetics expression is described generally by equation (2):

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

where  $q_t$  is the removal at time  $t$ ,  $q_e$  is the removal at equilibrium in mg g<sup>-1</sup>,  $t$  is time in minutes and  $k_1$  is the kinetics constant in min<sup>-1</sup>. Integrating and applying boundary conditions,  $t=0$  at  $q_t=0$  and  $q_t=q_e$  at time  $t$ , equation (2) become the following expression:

$$\log(q_e - q_t) = \log(q_e) - \left( \frac{k_1}{2.303} \right) t \quad (3)$$

The kinetics constant  $k_1$  was obtained from the gradient of the line produced by graphing  $\log(q_e - q_t)$  versus  $t$ , as shown in Fig. 9-A for the three different initial copper concentrations.

The pseudo-second order kinetics model was also analysed by fitting the experiment data using expression (4) (Ho and McKay, 2000):

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (4)$$

where,  $k_2$  is the pseudo-second order reaction constant in g mg<sup>-1</sup> min<sup>-1</sup>. Thus, integrating equation (4) for the boundary conditions  $q_t=0$  at  $t=0$  and  $q_t$  at time  $t$ , gives expression (5):



$$\frac{t}{q_t} = \left(\frac{1}{h}\right) + \left(\frac{1}{q_e}\right)t \quad (5)$$

where  $h = k^2 \cdot q_e^2$  is the initial sorption rate. Thus, expression (5) can be used to generate Fig. 9-B, which represents  $t/q_t$  as a function of  $t$ .

Fig. 9-A shows a good correlation between the experiment data at pH=6.0 and the pseudo-first order kinetics model. For the pseudo-second order model, the experiment data moves away from the linear fit. Table 4 gives a summary of the relevant information from the two models applied to Cu removal. It can be seen that the pseudo-first order model fits the experiment data very well, obtaining an  $R^2$  value of 0.99 for the three initial copper concentration values

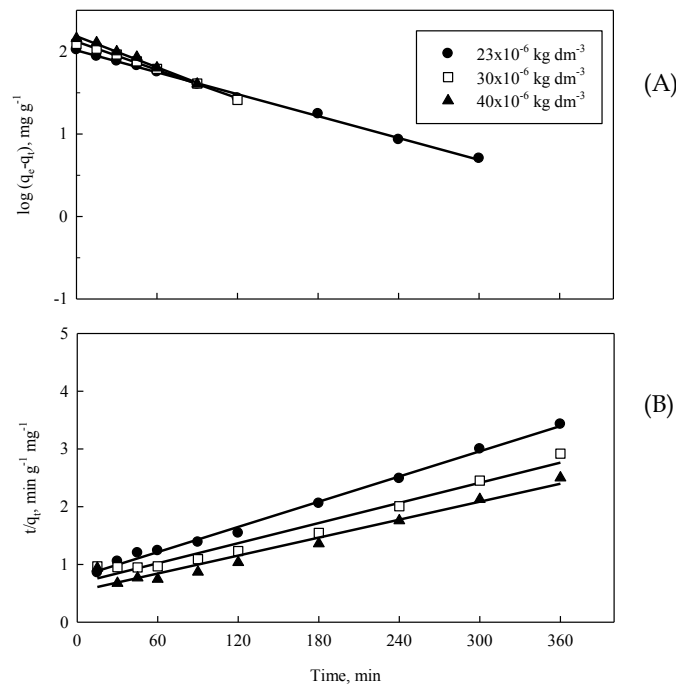


Fig. 9. Linear representation of pseudo-first order (A) pseudo-second order (B) kinetics model for copper removal at 290 K. Initial Cu concentrations= $23 \times 10^{-6}$ ,  $30 \times 10^{-6}$  and  $40 \times 10^{-6}$   $\text{kg dm}^{-3}$

Table 4. Kinetics parameters for pseudo-first and second order models applied to the PDAB

Cu concentration $\text{kg dm}^{-3}$	Pseudo-first order kinetic model			
	$k_1, \text{min}^{-1}$	$R^2$	$q_e, \text{mg g}^{-1}$	
$23 \times 10^{-6}$	0.0101	0.997	102.80	
$30 \times 10^{-6}$	0.0131	0.995	131.76	
$40 \times 10^{-6}$	0.0145	0.990	153.11	
	Pseudo-second order kinetic model			
	$k_2, \text{g mg}^{-1} \text{min}^{-1}$	$R^2$	$h, \text{mg g}^{-1} \text{min}^{-1}$	
	$23 \times 10^{-6}$	$6.85 \times 10^{-5}$	0.995	1.29
	$30 \times 10^{-6}$	$5.01 \times 10^{-5}$	0.968	1.49
$40 \times 10^{-6}$	$5.09 \times 10^{-5}$	0.954	1.88	

### 3.6. Effect of temperature

The effect of temperature on the copper ion removal velocity was also studied. Fig. 10 summarises the results in a range of temperatures from 283 to 343K for an initial copper concentration of  $23 \times 10^{-6}$   $\text{kg dm}^{-3}$  and a pH of 6.0. It can be seen that as the temperature increased, Cu removal also rises. At a temperature of 283K, copper removal reached a value of  $43 \text{ mg g}^{-1}$  ( $43 \times 10^{-3}$   $\text{kg/kg}$  of PDAB) at a time

of 90 minutes, while increasing the temperature to 323K led to a removal value of 81 mg g<sup>-1</sup> (81×10<sup>-3</sup> kg/kg of PDAB) for the same time, i.e. Cu removal was doubled by increasing the temperature by 40 K.

To evaluate copper removal, EDS analysis and scanning electron microscope (SEM) was carried out on the alginate beads. The solid samples were obtained for temperature conditions of 290 and 343K. The results are shown in Table 5, as Cu concentration through the alginate particles. The measurements taken are presented in Fig. 11.

It can be seen that the copper concentration through the alginate beads remains constant for both temperatures. It can also be seen that increasing the temperatures raises the copper concentration in the alginate, thus corroborating the data shown in Table 5.

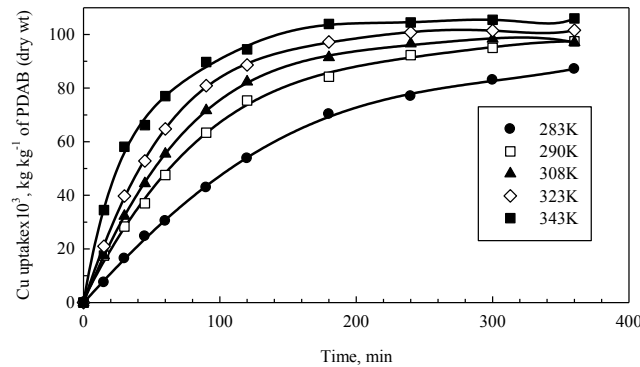


Fig. 10. Effect of temperature on copper ion removal for an initial concentration of  $23 \times 10^{-6}$  kg dm<sup>-3</sup> and a pH of 6.0

Table 5. Profile of copper concentration through the alginate seen by EDS for different temperatures

Point	Copper concentration, %	
	290K	343K
1	1.76	12.26
2	2.12	15.64
3	2.81	15.62
4	1.46	15.18

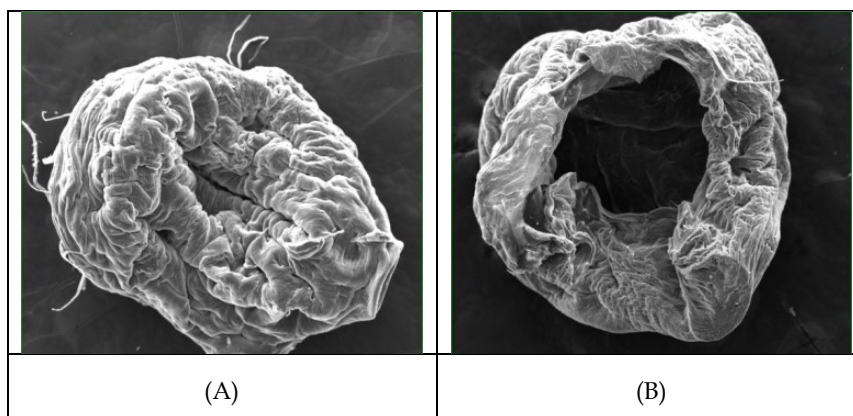


Fig. 11. Scanning electron microscope (SEM) of alginates in a sample treated at: (A) 290 K, (B) 343 K

Given that the Lagergren pseudo-first order kinetics model fit the experiment data very well, this model was used to fit the experiment data in Fig. 10. Fig. 12 shows a graph of  $\log(q_e - q_t)$  as a function of time for the experiment data in Fig. 10 in the temperature range of 283 to 343K. In this Fig. it can be seen that the linear fit of the kinetics data is good, with the regression coefficients,  $R^2$ , from 0.98 to 0.99 for the entire temperature range, indicating the applicability of equation (3). The values of the kinetics constants for the studied temperature range were obtained from the gradients of the straight lines and are shown in Table 6.

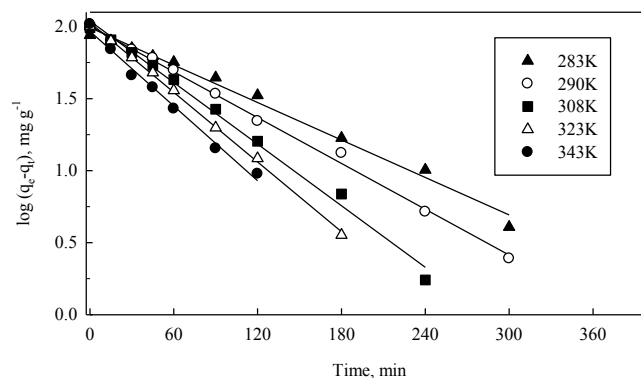


Fig. 12. Cu removal kinetics from PDAB for conditions shown in Fig. 10

Table 6. Kinetics constants for copper removal from PDAB

T (K)	1000 T <sup>-1</sup> (1 K <sup>-1</sup> )	k <sub>1</sub>	-ln k <sub>1</sub>
(283)	3.5336	9.90×10 <sup>-3</sup>	4.615
(290)	3.4483	12.21×10 <sup>-3</sup>	4.405
(308)	3.2468	16.35×10 <sup>-3</sup>	4.113
(323)	3.0960	18.65×10 <sup>-3</sup>	3.982
(343)	2.9155	19.81×10 <sup>-3</sup>	3.922

The values calculated for kinetics constant,  $k_1$ , were used to draw an Arrhenius plot shown in Fig. 13. A good linear fit can be seen in this Fig. ( $R^2=0.92$ ) for the dependence of temperature on the linear kinetics constants. The activation energy was calculated at 9.3 kJ mol<sup>-1</sup> for the temperature range of 283 to 343K.

Table 7. Uptake of copper by some biosorbents since 2000

Sorbent material	Uptake, mg g <sup>-1</sup>	pH	Reference
Tomato waste	46.0	8.0	Yargiç et al., 2015
Saccharomyces cerevisiae biomasses	28.8	6.0	Di Caprio et al., 2014
Dried activated sludge	62.5	5.0	Benaïssa and Elouchdi, 2011
Lyngbya putealis	7.8	6.0	Kiran and Thanasekaran, 2011
Caustic baker's yeast	5.7	5.0	Zhang et al., 2010
Ethanol baker's yeast	3.3	5.0	Zhang et al., 2010
Pristine baker's yeast	2.4	5.0	Zhang et al., 2010
Pycnoporus sanguineus	2.8	5.0	Yahaya et al., 2009
Sour orange residue	21.7	5.0	Khormaei et al., 2007
Chlorella vulgaris	58.8	5.0	Abu et al., 2006
Acidosasa edulis shoot shell	2.51	5.0	Hu et al., 2005
Padina sp.	72.4	5.0	Sheng et al., 2004
Sargassum sp.	62.9	5.0	Sheng et al., 2004
Ulva sp.	47.7	5.0	Sheng et al., 2004
Gracillaria sp.	37.5	5.0	Sheng et al., 2004
Peat	14.3	5.0	Ho and McKay, 2003
Grafted silica	16.6	5.5-6.0	Chiron et al., 2003
Protonated dry alginate beads	222.2-270.3	3.5-5.0	This work

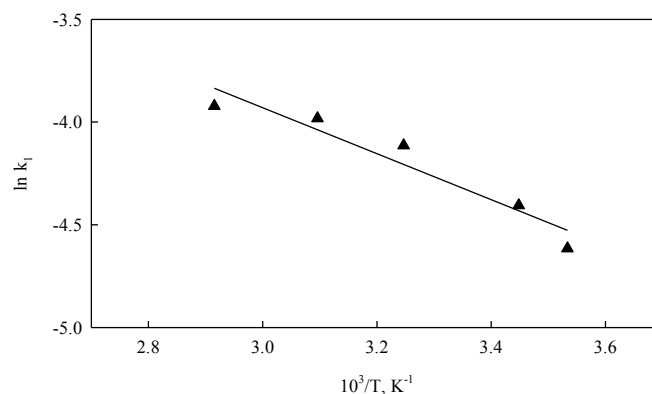


Fig. 13. Arrhenius plot for copper ion removal from PDAB

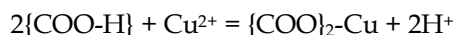
### 3.7. Comparison with other absorbents

A comparison was made of copper removal using different biosorbent materials found in the literature. Table 7 shows a summary of the research carried out since 2000. The Cu removal by PDAB is also included. It can clearly be seen that the copper removal is significantly higher in the latter case in comparison to the other biosorbents.

In the future, alginate beads could be subjected to a process of elution for the subsequent reuse of the beads. A copper-rich solution would be obtained and could be used in the process of electro-generation and subsequent production of copper metal, also allowing the same alginate beads to be reused for further copper ion removal.

## 4. Conclusions

The results obtained in this research have shown that using PDAB can efficiently remove copper ions from highly diluted solutions, reaching higher removal values than those reported so far with other biosorbents. It was also demonstrated through analysis by ICP / AES, SEM-EDS and BEI that the mechanism of copper removal is developed by means of ion exchange.



The samples observed by SEM showed that the PDAB contained a large amount of pores and fine channels that would help the Cu to be exchanged internally and externally in the sphere. This quality makes the biosorbent material contain a high permeability and high capacity. The copper ion intraparticle diffusion mechanism was validated by the pseudo first order model

Temperature played an important role, as an increase of 33K led to double the copper removal. The activation energy was calculated at 9.3 kJ mol<sup>-1</sup> for the temperature range of 283 to 343K.

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