



Co adsorption in kaolinite

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ABSTRACT

Adsorption of metal ions in clay minerals has been used as an alternative to water and effluents treatment. Kaolinite is a clay mineral that presents low specific surface area and exchange ion capacity. Nevertheless, structural modifications can be achieved by means of acid or thermal activation. In this paper, it was studied the surface area of kaolinite/bentonite, kaolinite/activated carbon mixtures, thermal activated kaolinite and thermal activated kaolinite/activated carbon mixture. The mixture of kaolinite/activated carbon was tested for pH, contact time, interfering ions and initial concentration effects in the cobalt adsorption. Results showed that the optimized parameters are pH 6 and contact time of 30 min. Chromium acted as a competitive ion, zinc does not appear to have affected adsorption while iron seems to have favored it. Langmuir and Freundlich isotherms indicated that the adsorption of Co in the mixture of kaolinite/activated carbon is a spontaneous process.

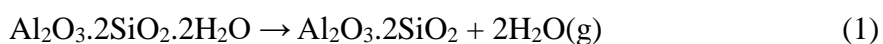
Keywords: Cobalt, adsorption, kaolinite.

1. INTRODUCTION

Several methods have been used to remove metal ions from aqueous solution for water reuse and discharge in water bodies. Among these methods, ion exchange, solvent extraction, flotation, coagulation, electrodeposition, chemical precipitation, membrane separation, and adsorption are the most used [1, 2].

Among the various physicochemical methods commonly employed, the use of clay minerals for metal ion adsorption is well known for being a method considered effective, cheap and of easy handling operation and easy obtainment [3-5]. In addition, it is possible to obtain chemical modifications such as intercalation, pillarization, thermal activation, acid or basic activation [6-8]. Kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) displays low reactivity, low adsorption capacity, and small surface area when compared to classical adsorbents such as bentonite and activated charcoal, and several of these modifications have been tested in order to obtain a good adsorbent from this material [9-13].

The thermal treatment of kaolinite in the temperature range of 530 °C to 630 °C, depending on the structural layer stacking order, results in the loss of water of hydration with the formation of an amorphous product called metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) [14]. The process can be described by equation 1.



Another chemical and thermal change that occurs with kaolinite is the carbon reduction, at high temperatures, in the presence of charcoal. At temperatures between 500 and 1300 °C the overall reaction showed in equation 2 may occur [15].



The treatment presented in equation 2 is generally employed for ceramic applications. However, the adsorptive capacity of the products of this reaction, as far as we know, have not yet been tested. This study proposes to verify the adsorptive capacity of kaolinite; kaolinite calcined at 600 °C and 1000 °C; mixtures of kaolinite with bentonite; mixtures of kaolinite with activated carbon; and mixtures of kaolinite and activated carbon calcined at 600 °C and 1000 °C in the adsorption of cobalt ions in solution.

Cobalt (Co) is an essential element for human and animal health. On the other hand, high concentrations of this element (above 1.0 mg L^{-1}) have detrimental impacts on health, resulting in paralysis, diarrhea, pulmonary irritation and bone defects [16]. Therefore, removal of Co (II) from wastewater is necessary and it has received wide attention in recent years [17].

In addition to stable cobalt there is still concern regarding to ^{60}Co , which is a high energy gamma emitter (1173 and 1332 keV) with half-life of 5.3 years. This radionuclide is generated in relatively high amounts in nuclear plants, being one of the main responsible for the dose radiation received by the workers. Once released into the environment, radionuclides can be transported by water and adsorbed into inorganic particles or deposited in bottom sediments causing adverse situation for living beings [17]. Sediment contamination in the Angra dos Reis region, by ^{60}Co and ^{137}Cs , due to the release of effluents from the cooling circuit of the power plants has been already observed [18, 19]. Thus, it is necessary to search for appropriate and economically viable methods to treat radioactive waste before its disposal [20].

2. MATERIALS AND METHODS

Commercial samples of kaolinite (k), bentonite ($\text{Al}_2\text{H}_2\text{Na}_2\text{O}_{13}\text{Si}_4$) (b), and activated carbon (ac) were obtained, dried in a ventilated oven at $100 \text{ }^\circ\text{C}$ till constant weight, crushed and sieved to $63 \text{ }\mu\text{m}$. After that, mixtures of kaolinite and bentonite and, kaolinite and activated carbon were prepared in the proportions showed in Table 1. Pure kaolinite and mixtures of kaolinite and activated carbon were calcined at $600 \text{ }^\circ\text{C}$ and $1000 \text{ }^\circ\text{C}$ for 4 hours. The specific surface area (S, in $\text{m}^2 \text{ g}^{-1}$) was determined to all adsorbents (raw materials and mixtures) with and without calcination, following the method proposed by Sears [21]. The ash content of all adsorbents was also determined at $450 \text{ }^\circ\text{C}$ and $1000 \text{ }^\circ\text{C}$. For the adsorption experiments, the adsorbent that presented the highest specific surface areas was chosen and the following parameters were determined: effect of the pH, effect of the contact time, effect of the initial concentration and effect of interfering ions (Cr, Fe and Zn).

2.1. Stock solution preparation

The stock solutions of cobalt (Co), chromium (Cr), iron (Fe) and zinc (Zn) ions used in all the experiments were prepared by diluting standard solutions (SPEX Certiprep) to the desired concentration. The pH of the solutions, whenever necessary, was adjusted using small quantities of concentrated hydrochloric acid (HCl) or ammonium hydroxide (NH₄OH). All chemicals used in this work has analytical reagent grade and they were used without any further purification.

Table 1: Composition of the mixtures kaolinite x bentonite and kaolinite x activated carbon used for specific surface area determination.

kaolinite x bentonite	% of bentonite	kaolinite x activated carbon	% of activated carbon
kb1	10	kac1	10
kb2	20	kac2	20
kb3	30	kac3	30
kb4	40	kac4	40
kb5	50	kac5	50

2.2. Adsorption experimental procedure

In all adsorption experiments 0.5 g of the adsorbent was added to 20 mL of solution, stirred (60 rpm), transferred to falcon tubes, centrifuged at 3,500 rpm for 20 min and the solutions were separated from the remaining solid. The solid was dried in ventilated oven and a 0.1 g aliquot was taken to be analyzed by neutron activation analysis (NAA).

The pH effect on the Co adsorption was performed in the range of 2 to 10 for a 0.1 mg L⁻¹ cobalt solution during 30 and 60 min. The effect of contact time was tested in the range of 10 to 120 min for a 0.1 mg L⁻¹ Co solution in pH 6. The effect of initial concentration was verified varying the concentration of Co solution from 0.025 to 0.4 mg L⁻¹, pH 6 with a contact time of 30 min. To verify the effect of interfering ions, solutions of 0.1 mg L⁻¹ of Co were prepared with varying concentrations of Cr (0.04 to 0.4 mg L⁻¹), Fe (1,000 to 8,000 mg L⁻¹) and Zn (0.1 to 0.5 mg L⁻¹). The adsorption capacity (q_t) was calculated according to equation 3.

$$q_t = (C_0 - C_t) V/m \quad (3)$$

where C_0 is the initial concentration of the solution (mg L^{-1}), C_t is the concentration in a given time (mg L^{-1}), V is the volume (L) and m is mass of the adsorbent (g).

2.3. Neutron activation analysis

NAA was used to determine the concentrations of the ions of interest in all raw material adsorbents and mixtures before and after the adsorption experiments. For these measurements, 0.1 g of each material was weighted, sealed in polyethylene bags and irradiated in the IEA-R1 nuclear reactor in IPEN/CNEN/SP with a neutron flux of $10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. After irradiation and a cooling time of approximately 10 days, samples were counted in a gamma spectrometer EG&G Ortec with relative efficiency of 20% and resolution of 2.3 keV for the 1,332 keV transition photopeak of ^{60}Co .

3. RESULTS AND DISCUSSION

Table 2 shows the concentrations of the ions of interest in pure kaolinite, bentonite and activated carbon and in their mixtures and the percentage of ash after calcination at 450 °C and 1,000 °C. It can be observed that Co presents higher concentration in the activated carbon sample, Cr is higher in kaolinite and high values of Fe and Zn are observed in bentonite. For the mixture, it is possible to see that the final concentration is proportional to the amount of bentonite and activated carbon added. The yield in ash after calcination showed that the activated carbon was almost entirely lost in both 450 °C and 1,000 °C and that kaolinite presented lower ash content than bentonite after calcination also in both temperatures. This calcination can be an alternative to treat this material before its storage.

Results for the specific surface area S for the raw materials and the kaolinite x bentonite (kb1-5), and kaolinite x activated carbon (kac1-5) mixtures are shown in Figure 1a. Figure 1b shows the S obtained for the kaolinite (kt1) and its mixtures with activated carbon (kcat1-5) calcined at 600 °C. The results for the kaolinite (kt2) and its mixtures with activated carbon (kact1-5) calcined at 1,000 °C are shown in Figure 1c. Surface area for the raw materials was 14.9, 67.8 and $346 \text{ m}^2 \text{ g}^{-1}$ for kaolinite, bentonite and activated carbon, respectively. Surface area obtained for the first two are

in good agreement with values found in literature [22, 23] but the activated carbon here employed showed a lower S value [24], although, as expected higher than the other adsorbents.

Table 2: Concentrations of Co, Cr, Fe and Zn in the raw materials (kaolinite, bentonite and activate carbon) and in their mixtures, and the ash yield after calcination.

	Co	Cr	Fe	Zn	Ash %	
	$\mu\text{g g}^{-1}$	$\mu\text{g g}^{-1}$	%	$\mu\text{g g}^{-1}$	450 °C	1000 °C
K	0.44 ± 0.04	23.0 ± 0.8	0.34 ± 0.01	158 ± 17	87.3	86.1
B	1.2 ± 0.05	7.4 ± 0.5	2.58 ± 0.03	323 ± 24	96.2	91.9
AC	8.73 ± 0.13	12.4 ± 0.4	0.37 ± 0.01	66 ± 15	5.4	5.1
kb1	0.82 ± 0.04	21.9 ± 0.8	0.61 ± 0.01	44 ± 3	88.8	85.8
kb2	0.61 ± 0.05	19.1 ± 0.8	0.96 ± 0.01	18 ± 2	88.6	86.2
kb3	1.01 ± 0.07	19.5 ± 0.8	1.17 ± 0.01	48 ± 3	90.4	87.8
kb4	1.08 ± 0.08	18.3 ± 0.8	1.44 ± 0.01	27 ± 3	91.1	87.5
kb5	0.82 ± 0.05	15.2 ± 0.7	1.71 ± 0.02	50 ± 3	93.1	88.4
kac1	1.27 ± 0.05	22.3 ± 0.8	0.36 ± 0.01	31 ± 2	79.9	78.1
kac2	2.44 ± 0.06	21.0 ± 0.8	0.360 ± 0.006	33 ± 2	71.8	70.8
kac3	3.25 ± 0.07	19.5 ± 0.8	0.335 ± 0.004	30 ± 2	62.8	62.2
kac4	4.42 ± 0.08	19.9 ± 0.8	0.352 ± 0.004	22 ± 2	54.5	53.7
kac5	5.17 ± 0.09	17.9 ± 0.7	0.352 ± 0.004	ND	46.3	45.5

Considering the mixtures (Fig. 1a), S values increase with the content of bentonite and activated carbon added. The mixture kaolinite x activated carbon (Fig. 1b) calcined at 600 °C showed a small variation independent of the carbon content and the values were very close to the one obtained for pure kaolinite calcined at the same temperature ($66 \text{ m}^2 \text{ g}^{-1}$). Calcination at 1000 °C, on the other hand, caused a remarkable decrease in S values for both k and kac mixtures.

It is clear that the higher the proportion of activated carbon in the mixture, the higher is the S obtained. On the other hand, economically this is not an advantage due to the cost of activated carbon. The calcination of kaolinite at 600 °C increased its surface area from 13 to $66 \text{ m}^2 \text{ g}^{-1}$, but this process involved the cost of energy consume. Also, the S obtained by the addition of activated carbon was not significantly different from that obtained by the calcination of pure kaolinite.

Based in these results the non-calcined mixture of kaolinite x activated carbon at 10%, with a surface area of $50.2 \text{ m}^2 \text{ g}^{-1}$, was considered to present the best cost benefit for the purpose of this study since it uses a small amount of activated carbon without energy consume.

3.1. pH Effect

On adsorption processes, the pH is one of the most important parameters since it can either modify the adsorbent surface or change the speciation of the adsorbate [25]. In Figure 2, the effect of initial pH on the adsorption capacity is showed for the times of 30 min (Fig 2a) and 60 min (Fig. 2b) of contact time. No significant difference was observed between the different times and in both cases, maximum adsorption capacity is achieved from pH 4.

Figure 1: Surface area obtained for a) raw material and mixtures, b) mixtures of k and ac calcined at $600 \text{ }^\circ\text{C}$ and c) mixtures of k and ac calcined at $1000 \text{ }^\circ\text{C}$

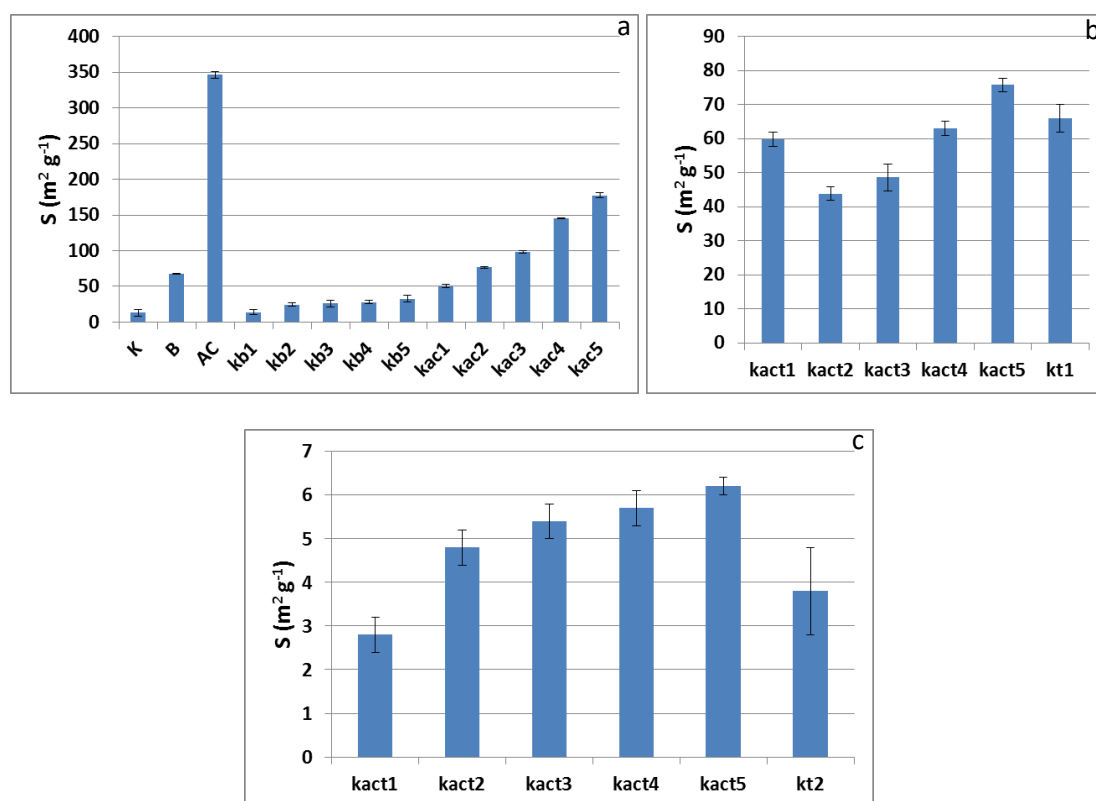
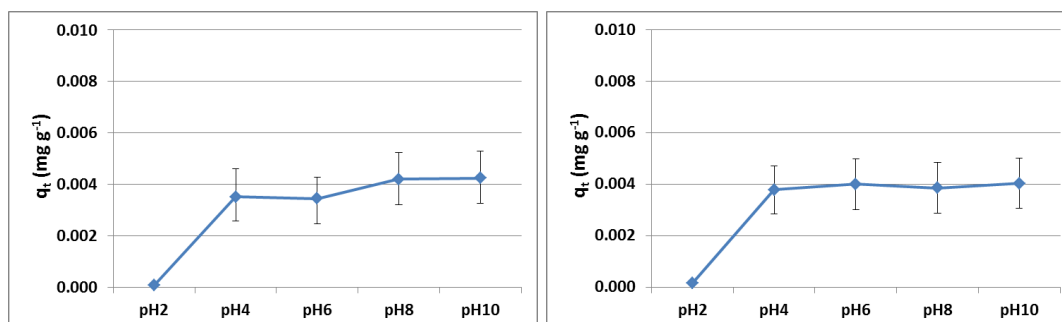


Figure 2: pH effect on the adsorption capacity at a) 30 min and b) 60 min

a

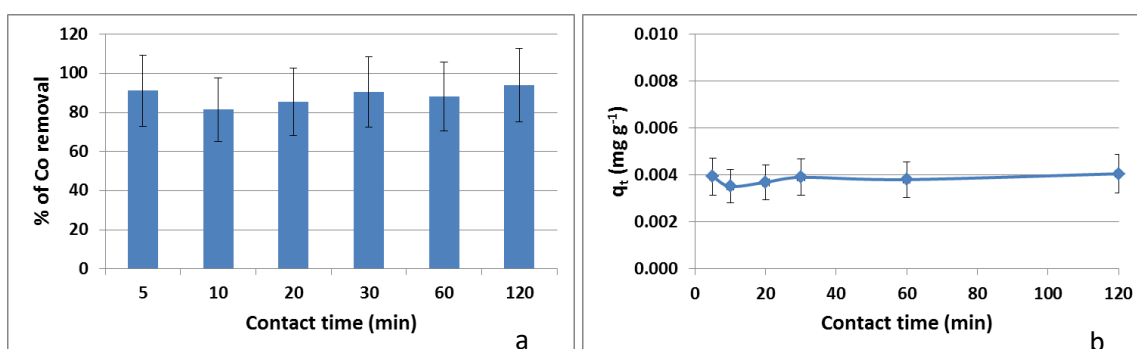
b



3.2. Effect of the contact time

In Figure 3 is showed the removal efficiency (Fig. 3a) and adsorption capacity (Fig. 3b) as function of the contact time. The removal efficiency was higher than 80% after the first 5 min and it remained almost constant with time. The adsorption capacity reflects the efficiency of removal and is almost constant in all times. At the initial time, the adsorption capacity must be due to the availability of adsorption sites and after the equilibrium has been reached these sites becomes saturated and less available to the adsorption of ions from the solution [26] indicating that equilibrium has been reached.

Figure 3: a) percent of Co removal as a function of the contact time and b) effect of the time contact in the adsorption capacity



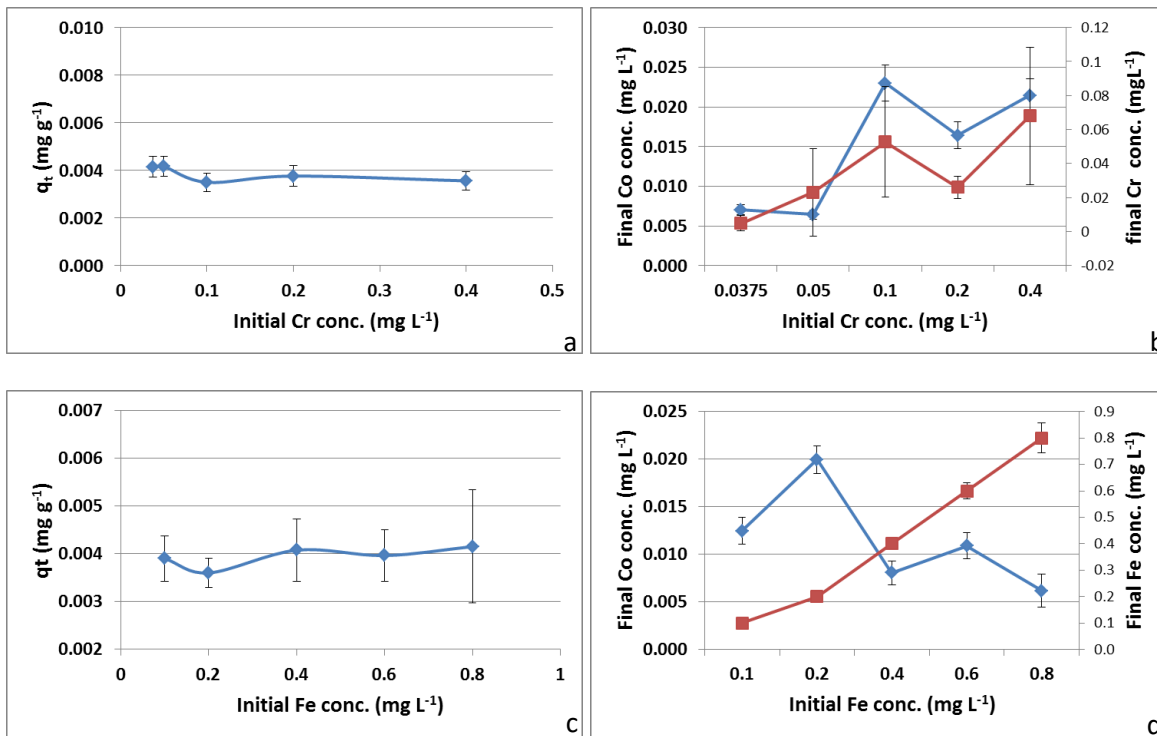
3.3. Effect of interfering ion

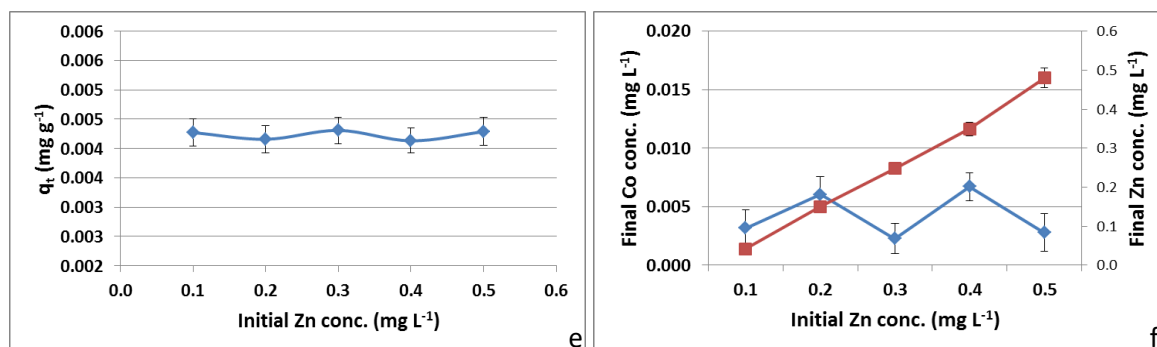
Ionic competition can interfere in adsorption processes depending on the affinity of the interfering ion with the adsorbent [27]. The effect of the Cr, Fe and Zn presence in the cobalt solution is

showed in Figure 4 (a to f) for the adsorption capacity and the final Co concentration. No significant trend is observed in q_t of Co due to the presence of Cr in solution (Fig. 4a) and the adsorption behavior of these ions follow the same pattern with the increase of Cr concentration (Fig. 4b).

The Co adsorption capacity seems to be slightly affected by the Fe presence in solution with q_t rising with the iron concentration (Fig 4c). Comparing the final concentrations (Fig. 4d) it is noted that the higher the Fe concentration, the lower is that for Co indicating that the iron presence may favor the cobalt adsorption.

Figure 4: Effect of the interfering ions Cr (a), Fe (c) and Zn (e) in the adsorption capacity and relation of Co final concentration with Cr (b), Fe (d) and Zn (f) final concentration





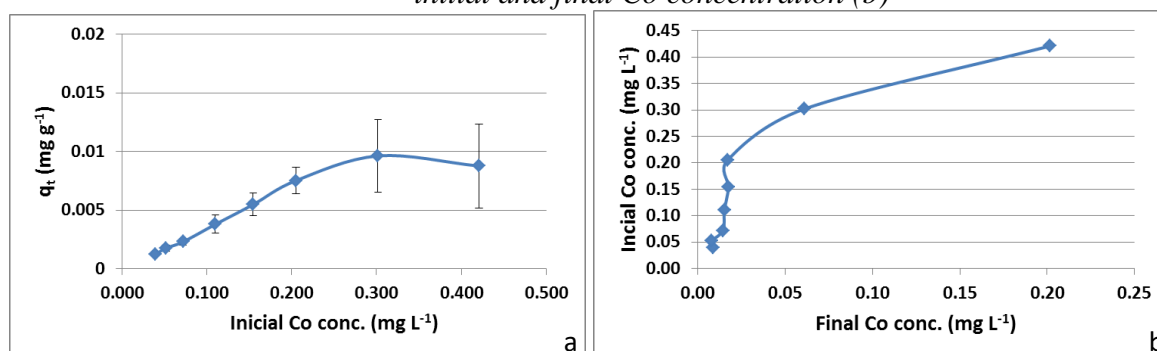
The tests for the interfering ions were performed at pH 6, in which Fe exists mainly as the colloidal Fe-hydroxide that acts as a trap for other ions in solution and it can be adsorbed in the particles of the adsorbent.

The presence of Zn in the Co solution seemed not to present any effect since no variation was observed both in adsorption capacity and final cobalt concentration.

3.4. Effect of initial concentration

The influence of the initial Co concentration in solution over the adsorption process is showed in Figure 5 for the range of 0.025 to 0.4 mg L⁻¹. It can be seen that q_t rises with the initial cobalt concentration (Fig. 5a) up to 0.3 mg L⁻¹ and that the remaining Co in solutions is lower than 20% (0.05 mg L⁻¹) up to this same concentration (Fig. 5b).

Figure 5: Effect of the Co initial concentration in the adsorption capacity (a) and relation between initial and final Co concentration (b)



3.4. Adsorption isotherm

The interaction between adsorbent and adsorbate and the possible mechanism of interaction involved in the process are commonly described by adsorption isotherms. The most used ones are the Langmuir and Freundlich isotherms [28, 29]. Langmuir isotherm describes adsorption processes occurring in a monolayer surface, in which adsorption occur in specific sites in the adsorbent, while in the Freundlich isotherm heterogeneous multilayers are involved. The linear equations of those models are expressed in equation 4 and 5.

$$\frac{C_0}{q_t} = \frac{C_0}{Q_0} + \frac{1}{K_L Q_0} \quad (\text{linear Langmuir model}) \quad 4$$

$$\log q_t = \log K_f + \frac{1}{n C_0} \quad (\text{linear Freundlich model}) \quad 5$$

where q_t is the adsorption capacity of the adsorbent at equilibrium (mg g^{-1}), C_0 is the equilibrium ion concentration (mg L^{-1}), Q_0 is the monolayer adsorption capacity (mg g^{-1}), K_L is Langmuir constant related to the free energy of adsorption, K_f is a Freundlich constant that indicates the relative adsorption capacity of the adsorbent (mg g^{-1}) and n is an empirical parameter that indicates the adsorption intensity.

The Langmuir isotherm plot C_0/q_t versus C_0 gives $1/Q_0$ in the slope and $1/K_L Q_0$ in the intercept. The plot of $\log q_t$ versus $\log C_0$ gives $1/n$ in the slope and $\log K_f$ in the intercept. The obtained results for the cobalt adsorption in the conditions of this experiment are showed in Table 2.

Table 2: Obtained parameters for Langmuir and Freundlich isotherm models.

Langmuir				Freundlich		
Q_0	K_L	R_L	R^2	K_f	n	R^2
mg g^{-1}	L mg^{-1}			mg g^{-1}		
0.0105	32.2	0.093 - 0.440	0.906	30.2	1.81	0.598

Both determination coefficients were significant at $p = 0.05$. The higher R^2 value for the Langmuir model indicates that it can better describe the Co adsorption in the conditions of this experiment. The coefficients Q_0 and K_f indicate empirically the adsorption capacity of the used adsorbent

and the R_L and n indicated the type of isotherm. Adsorption is favorable if R_L lies between 0 and 1 in the Langmuir model and if $n > 1$ in the Freundlich model. The results indicate that Co adsorption is favorable in the kaolinite/activated carbon mixture.

4. CONCLUSION

The adsorptive capacity of kaolinite; kaolinite calcined at 600 °C and 1000 °C; mixtures of kaolinite with bentonite; mixtures of kaolinite with activated carbon; and mixtures of kaolinite and activated carbon calcined at 600 °C and 1000 °C was evaluated by means of the specific surface area determination. The mixture of kaolinite and 10% of activated carbon presented almost the same S value than thermal activated kaolinite at 600 °C, named metakaolinite, with the advantage that no thermal treatment had to be done therefore saving energy consume. The maximized parameters for Co adsorption in this mixture are pH 6 and time of contact of 30 min. The effect of the presence of Cr, Fe and Zn in the solution indicated that Cr is a competitive ion, Zn has no effect and Fe may favor the Co removal from solution. Calculated Langmuir and Freundlich isotherms parameters indicated that the adsorption process of Co in the mixture of kaolinite/activated carbon is spontaneous and the best fitted model is that considering a homogeneous monolayer surface.

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