

ANALYSIS OF SILVER'S ADSORPTION ON CALCINED VERDE-LODO CLAY

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ABSTRACT – The removal of heavy metals from wastewater has become an important subject for scientific research. Among the common methods, adsorption has shown good potential to treat contaminated effluents. In this study, the thermally treated clay called “Verde-lodo” was used in the adsorption of silver ions, a metal with wide industrial use and high commercial value. Firstly, the process kinetics was studied in different silver concentrations. The kinetic curves were adjusted by the following models: pseudo-first order, pseudo-second order, intra-particle diffusion, Boyd and mass transfer in the external film models. The adsorbent before and after process was characterized by the techniques: BET and Helium Pycnometry.

1. INTRODUCTION

The recovery of heavy metals has been considered an important topic among scientific research, especially in environmental and economic aspects. This fact is explained by the abrupt changes that these pollutants may cause in the environment. Heavy metals can be easily incorporated by living organisms and be accumulated in the ecosystem (Volesky and Holan, 1995). Several methods are being used to remove these components of wastewater like solvent extraction, membrane filtration and electrolysis (Liu *et al.*, 2009).

In this context, adsorption is also used for this goal, being considered an efficient method with low costs when compared to other treatments (Almeida Neto *et al.*, 2012). Thus, adsorption can be applied both to treat contaminated effluents and also to recover valuable materials, reducing the costs involved in the process. To guarantee the effectiveness of this method, the adsorbent's choice is one of the most relevant step. Among these materials, different groups of clays have shown good adsorption capacity due their several characteristics, as stability, superficial area and capacity of cation exchange (Bailey *et al.*, 1999; Chen *et al.*, 2008; Silva and Ferreira, 2008).

Silver is considered an important metal, used in various industrial processes like the production of mirrors, photographic films and batteries. This material has many characteristics (conductivity, ductility, malleability and others) that make this metal useful, advantageous and valuable (Akgül *et al.*, 2006). Even being considered as a noble metal, silver may cause several negative health effects

(Song *et al.*, 2011). So, treatment methods involving the removal and recovery of this material are an important topic to be studied.

In this study, the adsorption of silver by a bentonitic and thermally treated clay called Verde-lodo will be discussed. For that, the process kinetics is studied towards to analyze the process velocity and the interaction between adsorbent and adsorbate. Also, some characterization techniques (BET and Picnometry) are used to evaluate the changes in the solid caused by the adsorption process.

2. MATERIAL AND METHODS

2.1. Adsorbent's preparation

Bentonitic clay called Verde-lodo was chosen as the adsorbent of this study. This material is naturally found in the state of Paraíba, in Brazil and is commercialized by the company Dolomil Ltda. The clay was firstly crushed and sieved and the diameter used in this system was 0.855 mm. The clay was posteriorly treated in a muffle at 500 °C (calcination process). The reason for this treatment is to increase the material's stability and ion exchange capacity.

2.2. Adsorption kinetics

To evaluate the kinetics of the adsorption of silver by Verde-lodo clay, experiments were performed in a batch system at room temperature (approximately 25 °C). 10 grams of Verde-lodo clay were added to 1 L of silver solution, and the system was constantly shaken towards to keep the homogeneity in the process. Aliquots were collected in different time intervals from 30 seconds to 16 hours. After centrifugation and dilution, the concentration of the supernatant liquid was determined by atomic absorption spectrometry using the spectrophotometer AA-7000 from Shimadzu, Japan. The metal concentration for each time interval is calculated by Equation 1:

$$q(t) = \frac{V}{m}(C_0 - C(t)) \quad (1)$$

Where V is the solution volume, m is the adsorbent mass, C_0 is the initial concentration of silver and C(t) is the metal concentration at time t.

The kinetic curves were adjusted by five different models: pseudo-first order, pseudo-second order, intraparticle diffusion, mass transfer in the external film and Boyd models. Pseudo-first and pseudo-second models were obtained by nonlinear regression showed in Equations 2 and 3.

$$q = q_e(1 - e^{-k_1 t}) \quad (2)$$

$$q = q_e \frac{k_2 q_e t}{(1 + k_2 q_e t)} \quad (3)$$

Where k_1 is the rate constant of pseudo-first order given in min^{-1} and k_2 is the rate constant of pseudo-second order given in $\text{g.mmol}^{-1}.\text{min}^{-1}$.

The intra-particle diffusion model considers the mass transfer inside the adsorbent particle as the limiting step of the process. This model is presented in Equation 4.

$$q = k_i(t)^{-0.5} + c \quad (4)$$

Where k_i is the intra-particle diffusion rate constant and c represents the boundary layer thickness. This, the values of these parameters are found by the q versus $t^{0.5}$ graph.

The mass transfer in external film model considers the mass transfer between the solution and a film formed in the solid adsorbent surface as the prevalent step of the process kinetics. To establish the equations of this model, Puranik (1999) considers a batch system with concentration C_0 , volume V and mass m . Thus, Equation 5 describes the variation of the amount of metal adsorbed:

$$\frac{dq}{dt} = \frac{V}{m} K_{TM} [C(t) - C_I(t)] \quad (5)$$

Where K_{TM} is the mass transfer coefficient, C is the concentration of metal in solution and C_I is the metal concentration in the film.

The model given by Boyd et al. (1947) was also studied to verify the prevalent step of the adsorption process. To use this method, the constant Bt is calculated by Equation 6, where F is the fraction of metal adsorbed in instant t . With the graph Bt versus t , the curve linearity indicates the limiting step of the process. If the straight line passes through the origin, the intra-particle diffusion is the predominant step of the process. If not, the external transportation controls the system.

$$Bt = -0,4977 - \ln(1 - F) \quad (6)$$

2.3. Adsorbent's characterization

To verify the modifications caused in the solid adsorbent by the adsorption process, several techniques are commonly used to reach this goal. Among them, in the study presents the techniques of BET method and Helium Pycnometry.

BET analysis: The BET (Branauer-Emmett-Teller) method, established by Branauer *et al.* (1938) is the most used technique to calculate tge surface area of solid materials. This method is based on Equation 7, where W is the weight of gas adsorbed at relative pressure P/P_0 , W_m is the weight of adsorbate considering a monolayer adsorption and C is the BET constant.

$$\frac{1}{W(P_0/P)-1} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0}\right) \quad (7)$$

For this technique, it was used the equipment NOVA 1200e from Quantachrome (USA). Clay samples were thermally treated in vacuum conditions for 2 hours. This analysis may also provide a complete isotherm of nitrogen adsorption and desorption, with pressure variation of $P/P_0=0.1$ to $P/P_0=0.99$. Using values of adsorbed volume of nitrogen (V_{ads}), it is possible to calculate the volume of micropores and mesopores by Equation 8 and 9 (Gomez *et al.*, 2006):

$$V_{mi} = V_{ads\left(\frac{P}{P_0}=0.10\right)} \quad (8)$$

$$V_{mes} = V_{ads\left(\frac{P}{P_0}=0.95\right)} - V_{ads\left(\frac{P}{P_0}=0.10\right)} \quad (9)$$

Helium Picnometry: The Helium Picnometry seeks to measure the total volume of a solid, considering all the material's pores. This analysis is based on a pressure variation of a gas. The equipment used is Accupyc 1330 from Micromeritics (USA) over a temperature of 31 °C and equilibrium rate of 0.005 psig/min.

2. RESULTS AND DISCUSSION

2.1. Adsorption kinetics

The kinetic study was performed for three different initial concentration of silver: 50, 100 and 200 ppm. The kinetic curves for these concentrations are shown in Figure 1.

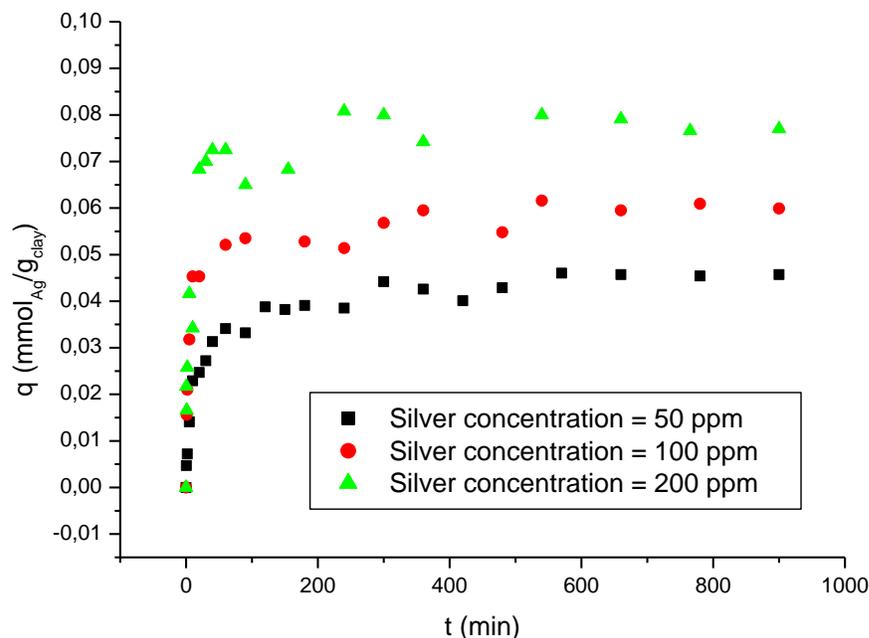


Figure 1 – Kinetic curves for the adsorption of silver onto Verde-lodo calcined clay for different initial concentrations of metal: 50, 100 and 200 ppm.

From Figure 1, it can be noticed that the three curves presented similar behaviors. Also, it was observed that higher silver concentration presented a higher amount of adsorbed silver in equilibrium (q_e). The kinetic adjusts by pseudo-first order, pseudo-second order, intra-particle diffusion, mass transfer in external film and Boyd model for silver concentration of 50 ppm (as example) are shown in Figure 2.

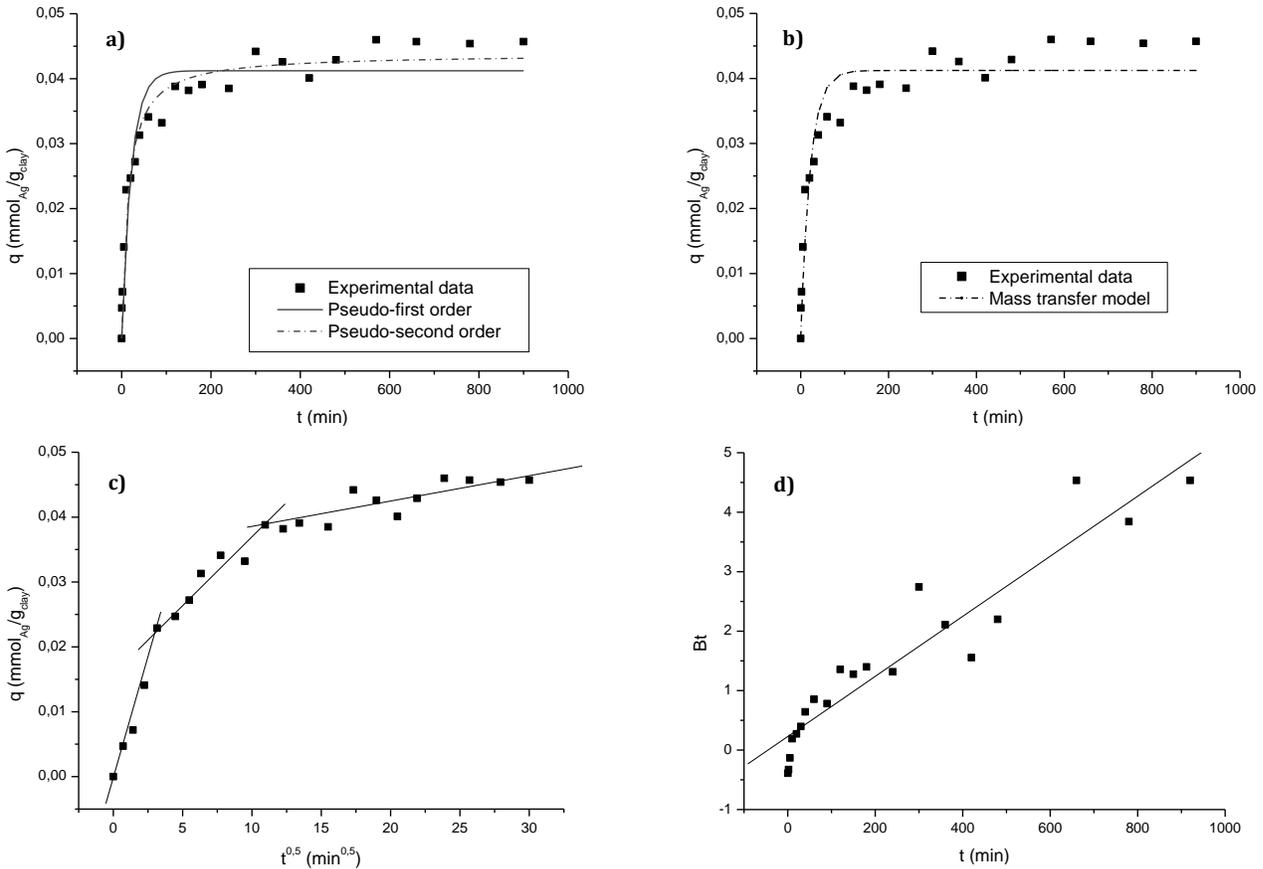


Figure 2 – Kinetic adjusts for the adsorption of silver (concentration of 50 ppm) onto Verde-lodo calcined clay: a) pseudo-first and pseudo-second order; b) mass transfer in external film; c) intraparticle diffusion; d) Boyd model

From Figure 2c, it is possible to observe the three different stages that control the process kinetics. Firstly, the external surface diffusion occurs. After that, the second step is related to the gradual diffusion intra-particle and the third step corresponds to the beginning of the equilibrium. In Figure 2d, it is noticed that the line did not pass through the origin, indicating that the process kinetics is controlled by external transport. The modeling parameters obtained for the three concentrations and the determination coefficient (R^2) for each model are exhibited in Table 1.

Regarding the values of the determination coefficient (R^2) in Table 1, it is verified a good adjustment of the curves in most cases. In a general way, the mass transfer in external film presented the best adjustment for all the concentration showing that the external transport is the predominant step of the process kinetics. This occurrence also confirms the results obtained for Boyd Model due the fact that the line did not cross the origin for any concentration, indicating that external diffusion controls the adsorption process. Despite that, it was noticed that intra-particle diffusion model also presented good adjustments, which shows that internal diffusion also interferes in the velocity although it is not the controlling factor of that.

Table 1 – Parameters obtained for kinetic curves' adjustment.

Model	Parameter	Concentration		
		50 ppm	100 ppm	200 ppm
	q_e (mmol.g ⁻¹)	0.046	0.062	0.077
Pseudo-first order	q_e (mmol.g ⁻¹)	0.041	0.056	0.074
	k_1 (min ⁻¹)	0.046	0.184	0.118
	R^2	0.920	0.944	0.907
Pseudo-second order	q_e (mmol.g ⁻¹)	0.044	0.057	0.077
	k_2 (g.mmol ⁻¹ .min ⁻¹)	1.620	4.906	2.727
	R^2	0.969	0.974	0.934
Mass transfer in external film	K_{TM} (min ⁻¹)	0.026	0.089	0.047
	R^2	0.966	0.973	0.964
Intra-particle diffusion (Weber and Morris)	k_i (mmol.g ⁻¹ .min ^{-0,5})	0.002	0.001	0.001
	c (mmol.g ⁻¹)	0.019	0.040	0.063
	R^2	0.921	0.952	0.825
Boyd Model	D_i (cm ² .min ⁻¹)	$9.351.10^{-7}$	$1.093.10^{-6}$	$1.020.10^{-6}$
	R^2	0.894	0.710	0.671

For pseudo-first and pseudo-second order fitting results, it is verified that the values of q_e (amount of silver adsorbed in equilibrium) are higher for greater values of silver initial concentration. Comparing this parameter for both models, it is noticed their similarity. However, comparing these parameters with experimental q_e for each concentration, it is observed the distance between them. The same result was found by Phothitontimongkol *et al.* (2013) for the adsorption of silver in hectorite clay.

2.2. Adsorbent's characterization

The techniques of BET and Helium Picnometry were used to determinate the surface area and the density of Verde-lodo calcined clay before and after adsorption of silver ions. The results are shown in Table 2. It is verified that the surface area is larger for natural Verde-lodo, indicating the filling of adsorption sites by silver in Verde-lodo clay after adsorption process. Consequently, the contaminated clay presents a lower volume, showing that the adsorption reduces the clay's density, which is observed in Table 2.

Table 2 – Parameters obtained for BET and Picnometry analysis.

Property	Natural Verde-lodo clay	Contaminated Verde-lodo clay
Surface area (m ² .g ⁻¹)	81.060	79.008
Real density (g.cm ⁻³)	2.629	2.506

The BET technique may also obtain the complete isotherm for nitrogen adsorption and desorption. By these isotherms, it was verified the values of micropore volume (V_{mi}) and mesopore volume (V_{mes}) of Verde-lodo clay: $V_{mi} = 4.1$ cc/g and $V_{mes} = 5.0$ cc/g for natural clay and $V_{mi} = 3.9$ cc/g and $V_{mes} = 4.6$ cc/g for contaminated clay. This fact indicates again the presence of silver ions in the solid's adsorption sites. Figure 3 shows the isotherms for natural verde-lodo clay and contaminated clay. It is observed a similar behavior for both curves, including the presence of hysteresis loop, related to capillary condensation taking place in mesopores. This type of isotherm is normally found for mesoporous industrial adsorbents (IUPAC, 1982).

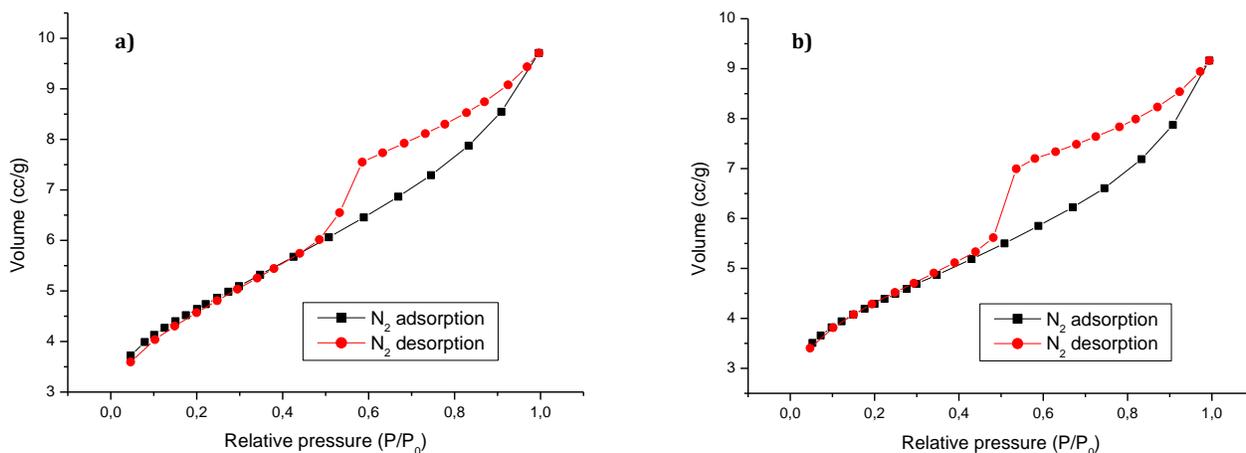


Figure 3 –Nitrogen adsorption and desorption isotherms (at 77 K) obtained for: a) Natural Verde-lodo clay; b) Contaminated Verde-lodo clay.

4. CONCLUSION

In the kinetics study for silver's adsorption onto calcined Verde-lodo clay, it was verified a good adjustment of the curves by the proposed models. Comparing the obtained results, the mass transfer in external film presented the best adjustment for all the concentration which reveals that the external transport is the predominant step of the process kinetics. For the adsorbent's characterization, results indicate the filling of adsorption sites by silver, reducing the surface area, density and pore volumes of the clay after adsorption process.

5. ACKNOWLEDGEMENT

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