SILVER ADSORPTION ON BENTONITE CALCINED CLAY USING A FIXED BED COLUMN SYSTEM

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ABSTRACT: The removal and recovery of silver ions from industrial wastewater has been the focus of several studies due its environmental and economic importance. Adsorption on bentonite clays has demonstrated a high removal potential for several metal´s ions. In this study, the component studied is silver, since it is a valuable material commonly used in several industrial processes. This article presents a dynamic study of silver's adsorption using a fixed bed column and a calcined bentonite clay called "Verde-lodo" as adsorbent. A fluid dynamic study was performed to verify the better conditions for silver removal. The parameters evaluated were the capacity of metal removal (q_u and q_t), the Mass Transfer Zone (MTZ) and the percentage of total removal. Adsorption/desorption cycles were carried out using nitric acid as eluent to evaluate the useful life time of the column and to verify if the adsorbent has maintained its adsorption capacity. The breakthrough curves were fitted to the Bohart-Adams model (*quasichemical*) and the parameters k and q_0 obtained were analyzed.

KEYWORDS: adsorption, silver, dynamic system, breakthrough curve.

1. INTRODUCTION

Wastewater contaminated with heavy metals has been subject of much research due the several problems that it may cause to environment and human health. The pollution caused by these components increases continuously due the raise of industrial activity (Fu and Wang, 2011). Various methods have been studied to remove and/or recovery these metals like membrane filtration, solvent extraction and others (Kentish and Stevens, 2001). Among these methods, adsorption is being considered a method with many benefits, especially its efficiency and low cost (Almeida Neto *et al*., 2012).

In this method, the choice of the adsorbent is extremely important and the use of low cost adsorbents is the focus of many studies (Sari and Tuzen, 2013). Clays have shown a good potential in metal ions adsorptions because of its important characteristics as high superficial area and physical and chemical stability. (Chen *et al*., 2008; Baley *et al*., 1999). Thus, several types of clay have been investigated as diatomite, illite, sepiolites and bentonites (Anirudhan *et al*., 2012).

Among the heavy metals considered as industrial pollutants, silver is considered an important one. The main reason of that is its wide use in industrial activities like the production of battery, mirrors and photographic film and also as a disinfectant agent in pharmaceutical and food industries (Çoruh *et al*., 2010). This metal, in elevated concentrations, may cause several negative health effects like algiria (disease that causes skin pigmentation) and liver and kidney degeneration. (Song *et al*., 2011; Fung and Bowen, 1996). Also, the silver may be accumulated in human organs like brain and muscles (Venugopal and Luckey, 1978).

Several studies have presented results related to silver´s adsorption using a static system (Sari and Tuzen, 2013; Khan *et al*., 1995). In this study, the adsorption of silver by a bentonite clay called "Verde-lodo", from the state of Paraíba in Brazil, was investigated in a dynamic system. This clay showed good affinity with silver in previous study (Kakiuthi *et al*., 2013). Thus, the experiments were conducted in a fixed bed column to verify the potential of removal and recovery of silver. Thus, three adsorption/desorption cycles were carried out, with the use of nitric acid as eluent.

2. MATERIALS AND METHODS

2.1. Reagents and equipments

Silver solution (concentration of 100 mg/L) was prepared with the dissolution of silver nitrate ($AgNO_3$), from Merck, Germany, in deionized water. Nitric acid solution (concentration of 0,1M) was made by the dilution of nitric acid solution from Chemco, Brazil.

The determination of silver concentrations was done by atomic absorption spectrophotometric using the spectrophotometer AA-7000 from Shimadzu, Japan. To guarantee the efficiency of the measure, the samples were diluted with the use of automatic pipettor from Gilson, USA.

2.2. Adsorbent's preparation

The adsorbent used for this study is bentonite clay called "Verde-lodo" from the state of Paraíba, in Brazil and commercialized by the company Dolomil Ltda.

The clay was crushed by a grinder and posteriorly sieved towards to assume the average diameter of 0,855 mm. After that, the clay was thermally treated (calcination process) to increase its ion exchange capacity and stability, important for its use in a column system. This process was carried out in a muffle (from Quimis, Brazil) over the temperature of 500 °C.

2.3. Column system assembly

The experiments were performed in a glass column with internal diameter of 1.5 cm filled with Verde-lodo clay towards to reach a bed height of 15 cm. The silver solution passed through Verde-lodo clay bed in up flow with the use of a peristaltic pump (from Masterflex, USA). To collect the effluent samples, an automatic fraction collector FC203 (from Gilson, USA) was used. The time intervals to collect the samples were previously determined. All experiments were performed at room temperature and the adsorbent was firstly washed with 100 mL of deionized water. The system used for all the essays in this study is shown in Figure 1.

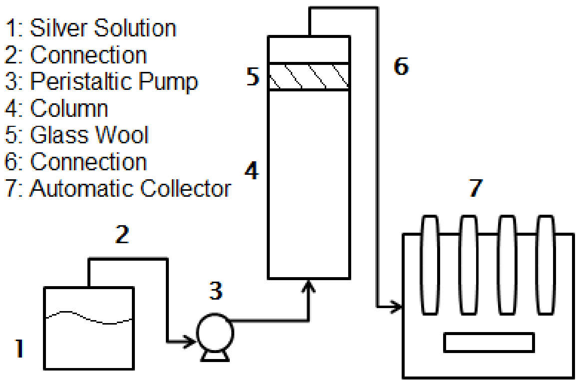

Figure 1. Experimental system used in this study.

The first experiment was conducted in three different flow rates of 3, 4 and 5 mL/min. Those flows were tested in order to verify which one of them could present a better silver removal in a dynamic assessment. The parameters evaluated were the capacity of metal removal (q_u and q_t), the Mass Transfer Zone (MTZ) and the percentage of total removal.

Using the better flow rate determined by the first experiment, another adsorption cycle was performed to reach again the saturation of the bed. After that, a desorption cycle was performed with the same flow and using nitric acid (HNO_3) as eluent, chosen due its use in other studies (Mattuschka and Straube, 1993; Vernon and Zin, 1981). Besides that, other eluents were tested in a static system to verify their desorption capacity: sodium chloride (NaCl), calcium clhloride ($CaCl_2$), hydrochloric acid (HCl), thiourea ($SC(NH_2)_2$), sodium phosphate (NaH_3PO_4) and sulfuric acid (H_2SO_4). Among those eluents, nitric acid has presented the best desorption capacity for silver. Other two adsorption/desorption cycle were carried out to verify if the adsorbent has maintained its adsorption capacity.

2.3. Column system analysis

In order to verify the removal of silver during the experiments performed, some important parameters were calculated. The capacity of silver removal was verified by the amount of total removal until the saturation point (q_t) and the amount of useful removal until de breakthrough point (q_u). Those parameters were calculated by Equations 1 and 2, obtained by the mass balance in the column.

$$q_t = \frac{C_0 . Q}{m} \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \qquad (01)$$

$$q_u = \frac{C_0 . Q}{m} \int_0^{t_r} \left(1 - \frac{C}{C_0}\right) dt \qquad (02)$$

Where C_0 is the initial concentration of silver (mmol/L), Q is the flow used in the system (L/min), m is the mass of the adsorbent put in the column (g), C is the concentration of silver at time t and t_r is the time until the rupture point (min). The integrate part was calculated by the area below the curve 1-C/C_0 versus time until the bed exhaustion (q_t) and until the breakthrough point (q_u). The area was calculated with the software Origin 6.0.

The Mass Transfer Zone (MTZ) was calculated by the Equation 3 (Geankoplis, 1993):

$$MTZ = \left(1 - \frac{q_u}{q_t}\right) . H_L \qquad (03)$$

Where H_L is the bed height. It can be observed that the maximum value of MTZ is the value of the bed height, when the amount of useful removal of silver is zero. So, the ideality is reached when MTZ is zero, which means that lower the value of MTZ, better is the removal process efficiency.

Other parameter calculated in this study was the percentage of total removal (%RT). This parameter is calculated by the comparison of the amount of silver adsorbed from the total of metal in the effluent until the saturation point. The amount of silver adsorbed is verified by the area below the curve 1-C/C_0 versus time.

To evaluate the desorption process, the eluted amount of silver was calculated by Equation 4 (Voleski *et al*., 2003):

$$q_{el} = \frac{Q}{m} \int C_{el} . dt \qquad (04)$$

Where C_{el} is silver concentration after the elution process at time t. The integrate part is calculated by the area below the elution curve (C_{el} versus time). The percentage of elution (%E) was also calculated considering the amount of total removal (q_t) as 100% of the metal that could be eluted from the adsorbent.

The Bohart-Adams model, also known as *quasiquemical*, was used to fit the breakthrough curves of this study. The removal ratio of silver is described by Equation 5 (Ruthven, 1984):

$$\frac{C}{C_0} = \frac{e^{\tau}}{e^{\tau} + e^{\xi} - 1} \qquad (05)$$

The parameters τ and ξ are calculated by Equations 6 and 7:

$$\tau = kC_0\left(t - \frac{z}{v}\right) \qquad (06)$$

$$\xi = \frac{kq_0 z}{v}\left(\frac{1-\varepsilon_L}{\varepsilon_L}\right) \qquad (07)$$

Where z is the bed height, v is the fluid flow velocity and ε_L is the bed´s porosity. The parameter k represents the removal ratio *quasichemical* constant and q_0 represents silver concentration in the adsorbent before the elution process.

The adjust of the curves was made with the software Mathcad 2011 Professional.

3. RESULTS AND DISCUSSION

3.1. Study of different flow rates

Dynamic experiments were carried out for different flow rates: 3, 4 and 5 mL/min. The breakthrough curves are shown in Figure 2.

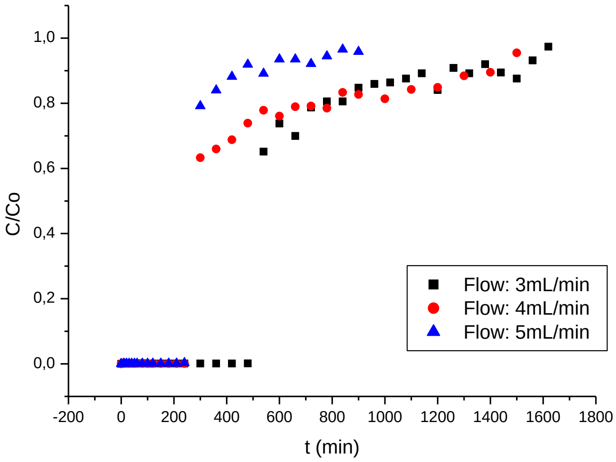

Figure 2. Breakthrough curves obtained for three flow rates analyzed: 3, 4 and 5 mL/min.

Regarding Figure 2, it is possible to notice that all the curves presented the same behavior. They had an abrupt step-change in the rupture point's region. It indicates that the curves present a behavior close to the ideality. Also, they presented a resistance to bed saturation. The parameters obtained for the experimental curves are shown in Table 1.

Table 1. Parameters obtained for the experimental breakthrough curves.

Parameters	Flow rate (mL/min)		
	3	4	5
q_t (mmol/g)	0.234	0.230	0.191
q_u (mmol/g)	0.164	0.063	0.139
MTZ (cm)	4.500	10.887	4.085
%RT	32.62	34.00	36.61

With the parameters exposed in Table 1, the flow rate choice for the next experiments was made based on the percentage of total removal (%RT) and the Mass Transfer Zone. The adsorption process is more efficient when the percentage of total removal is higher and the MTZ is lower. Comparing the values, it is observed that the flow rate 5 mL/min conferred better results. So, that was the flow rate selected for the next essays.

The breakthrough curves shown in Figure 2 were fitted by Bohart-Adams model. Figure 3 shows the *quasichemical* adjustment for the experiment with the flow rate of 5 mL/min. The other flow rates presented a similar fitting curve. Table 2 exhibits the parameters k and q_0 obtained for the three flows analyzed.

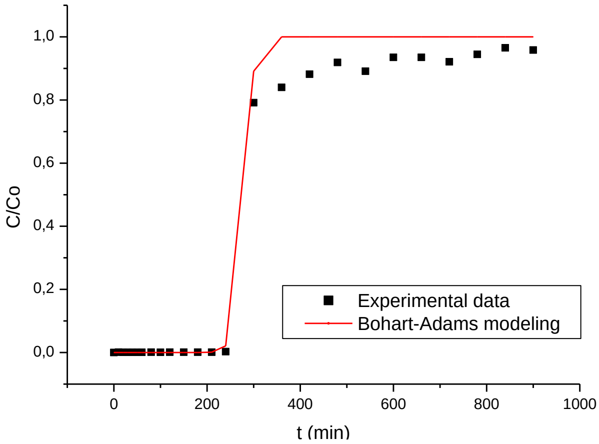

Figure 3. Bohart-Adams adjustments for the breakthrough curve of silver removal using a flow of 5mL/min.

Table 2. Bohart-Adams Parameters obtained for the three flows analyzed.

Parameters	Flow rate (mL/min)		
	3	4	5
k (L/mmol.min)	0,0018	0,020	0,036
q_0 (mmol/g)	285	240	290

The parameters presented in Table 2 show that the *quasichemical* constant k increases with the increment of the flow rate used in the essay. This fact reveals that an upper flow rate increases the removal rate of silver. The parameter q_0 indicates the concentration of silver in the adsorbent, indicating that this concentration was higher for 5 mL/min flow.

The solvent recovery efficiency (SRE) describes the relation between the volume of water used to prepare the eluents (V_E) with the volume of purified water until the breakthrough point (V_b). These values are presented in Table 3 for the three flow rate values.

Table 3. Solvent recovery efficiency (SRE) of the adsorption process.

Parameters	Flow rate (mL/min)		
	3	4	5
V_E (mL)	4960	6000	4500
V_b (mL)	1440	960	1200
SRE (%)	29.0	16.0	26.7

According to Table 3, it can be notice that the flow rate of 4 mL/min presented the lower SRE, which is not a favorable result. Although the result is a bit better for 3 mL/min, the flow 5 mL/min was still selected for the next essays.

3.2. Adsorption and desorption cycles

The previous essays showed that 5 mL/min was considered the best flow to perform the dynamic adsorption of silver using Verde-lodo clay. Thus, three adsorption-desorption cycles were carried out to verify the breakthrough curves after the regeneration of the adsorbent. Figure 4 presents the adsorption curves obtained for the three different cycles and Table 4 exhibits the parameters calculated for the experimental data.

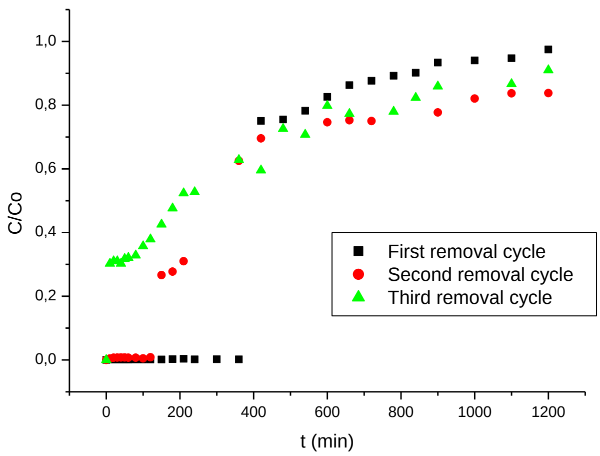

Figure 4. Breakthrough curves obtained for three adsorption cycles after the regeneration of the adsorbent.

Table 4. Parameters obtained for the removal cycles analyzed.

Parameters	Desorption cycle		
	1st	2nd	3rd
q_t (mmol/g)	0.178	0.102	0.104
q_u (mmol/g)	0.131	0.026	0
MTZ (cm)	3.961	11.151	15
%RT	40.69	38.72	31.01

Figure 4 shows that the first removal cycle presented the same behavior (close to the ideality), with an abrupt step-change in the rupture point's region, what was expected. However, the following removal cycles moved away from the original behavior, presenting a more extensive region between the rupture point and the exhausting point. It indicates that the regeneration process changes the characteristics of the fixed bed adsorption. Besides that, during the experiments, it was observed that, in the last removal cycle, the flow rate fell down to approximately half of its original value. This occurrence indicates that the dynamic adsorption of silver by Verde-lodo clay should be carried out in two removal/regeneration cycles, at maximum.

Comparing the results shown in Table 4 for the first and the second cycle, it is observed that the removal efficiency decreases, what was expected. This fact may be observed by the decrease of the amount of total removal (q_t), the amount of useful removal (q_u) and the percentage of removal (%RT). Also, it is noticed that the MTZ increases significantly, showing that the process is moving away from the ideality.

As mentioned above, the third cycle presented a change in the flow rate due to the exhaustion of the column. However, even in the third cycle, the bed kept its adsorption capacity after the regeneration process using HNO_3 as the eluent. Nevertheless, the amount of useful removal until de breakthrough point (q_u) was zero, which means that the silver amount was not completely adsorbed even during the beginning of the experiment (Figure 4). Because of this, the value of MTZ found was 15 cm, which is the maximum value, indicating that this cycle presented the behavior further from the ideality.

The curves of the three adsorption cycles were fitted by Bohart-Adams model. Table 5 exhibits the parameter obtained for the first and second cycle. Due the behavior of the third cycle, this breakthrough curve could not be adjusted by *quasichemical* model.

Table 5. Bohart-Adams parameters obtained for the first and second adsorption cycles.

Parameters	Removal cycle		
	1st	2nd	3rd
k (L/mmol.min)	0,03	0,018	-
q_0 (mmol/g)	262	110	-

Comparing the Bohart-Adams parameters for the first and second adsorption cycle, it is possible to notice that the constant k decreases with the cycle's sequence. It shows that the regeneration of the column modifies the removal ratio of silver. Also, the parameter q_0 decreases, implying that the amount of silver adsorbed in Verde-lodo clay is significant lower in the second cycle.

The solvent recovery efficiency (SRE) was also calculated for the two first adsorption cycles (Table 6). Because of the behavior of the third cycle, this parameter was not verified in this case.

Table 6. Solvent recovery efficiency (SRE) for the removal cycles.

Parameters	Removal cycle		
	1st	2nd	3rd
V_E (mL)	6000	6000	-
Vb (mL)	1800	600	-
SRE (%)	30.0	10.0	-

Regarding Table 6, it may be verified that the solvent recovery efficiency is reduced after the regeneration of the column from 30% of recovery to 10% of recovery. It shows that this process decreases the column efficiency, what was expected.

The silver desorption was verified after the three removal cycles and HNO_3 was used as eluent. The desorption curves for the first and second cycle, that maintained the flow rate during the entire essay, are shown in Figures 5 and 6.

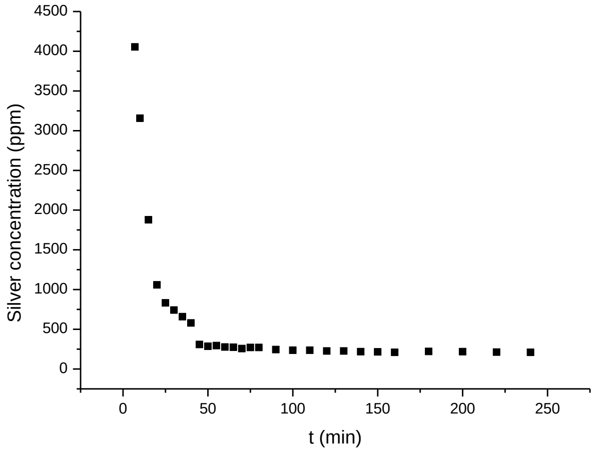

Figure 5. First desorption cycle for the adsorbent's degeneration

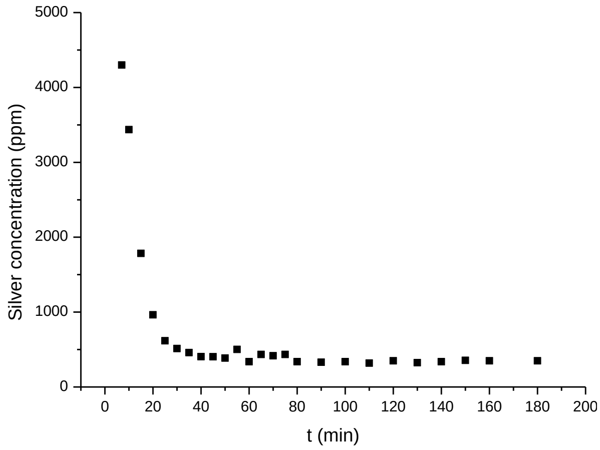

Figure 6. Second desorption cycle for the adsorbent's degeneration

Figures 5 and 6 demonstrated the typical behavior of a desorption curve. During the initial time intervals, high values of silver concentration were verified, indicating an elevated desorption in the beginning of the process. After a while, the silver concentration keeps constant showing the limit of the desorption. Both curves present exponential decay behavior.

Comparing Figures 5 and 6, it is possible to notice that the final concentration of silver in the first cycle is lower than the final concentration for the second cycle. Another way to compare the desorption cycles is the analysis of the eluted amount of silver (q_{el}) and the percentage of elution (%E). These parameters are shown in Table 7.

Table 7. Parameters obtained for the desorption cycles.

Parameters	Removal cycle		
	1st	2nd	3rd
q_{el} (mmol/g)	0.084	0.067	0.071
%E	47.28	65.63	68.50

The results presented in Table 7 reveal that the eluted amount of silver is higher for the first desorption cycle. This fact indicates that the desorption capacity decreases in the sequencing essays. However, the percentage of elution increased according to the cycle number. This fact may be explained by the significant lower amount of total removal (q_t) during the second and third adsorption cycles. As the percentage of elution is calculated by the comparison between the amount of silver in the column and the eluted amount, this value increased for the last two cycles.

5. CONCLUSION

This study presented several experiments to analyze the dynamic adsorption of silver using a bed column system and calcined bentonite clay called Verde-lodo. Results have shown that the breakthrough curves revealed a behavior close to the ideality for the first removal cycles for all the flow rates studied. Comparing the parameters obtained for the different flow rates, the flow 5 mL/min came up with better results for the Mass Transfer Zone and the percentage of removal.

The following removal cycles were carried out with the selected flow rate. For each removal cycle, the adsorbent was regenerate with acid nitric as the adsorbent. It was verified that the following removal cycles moved away from the original behavior, showing that the desorption process modifies the characteristics of the fixed bed adsorption. The experimental desorption curves presented an exponential decay behavior and similar behavior for all cycles. Also, the flow rate reduction during the third cycle revealed that dynamic adsorption of silver by Verde-lodo clay should be performed in two adsorption/desorption cycles, at maximum.

The Bohart-Adams model presented good results to fit the breakthrough curves of this study, with the exception of the third adsorption cycle's curve. Besides that, the Solvent Recovery Efficiency was also studied, being another important parameter to be analyzed to verify the efficiency of the process.

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7. ACKNOWLEDGEMENT

The authors thank CNPq and FAPESP (Proc. 2013/00732-1) for the financial support.