

Removal of Silver Ions on Calcined Verde-Iodo Bentonite Clay: Equilibrium Study

Manuella L. Cantuaria^a, Ambrósio F. de Almeida Neto^a, Eric S. Nascimento^a,
Onélia A.A. dos Santos^b, Melissa G. A. Vieira^{*a}

^aUniversity of Campinas, UNICAMP, School of Chemical Engineering, Av. Albert Einstein, 500, CEP: 13083-852, Campinas-SP, Brazil

^bUniversity of Maringá, UEM, Department of Chemical Engineering, Av. Colombo, 5790, CEP: 87020-900, Maringá-PR, Brazil
melissagav@feq.unicamp.br

The removal of heavy metals from industrial wastewater has been discussed in several research studies due its environmental and economic importance. Among the used methods, 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 many industrial processes. The equilibrium study of silver adsorption onto calcined Verde-Iodo bentonite was conducted in batch. Adsorption experiments were performed to study the adsorption capacity of Verde-Iodo clay. Equilibrium isotherms were obtained in four different temperatures (273 K, 293 K, 313 K and 333 K) and fitted to Langmuir, Freundlich and D-R models towards to evaluate adsorption and thermodynamic parameters. Different eluents were tested to verify their desorption capacity seeking the regeneration of the adsorbent. Then, a second adsorption cycle was performed in order to verify if the adsorbent has maintained its adsorption capacity.

1. Introduction

Silver is one of the most important metals used in industrial activities. The application of this material is extensive in several processes like the production of battery, mirrors and photographic film and also as a disinfectant agent in pharmaceutical and food industries (Çoruh et al., 2010). Besides that, important characteristics like malleability, ductility and thermal and electrical conductivity make this metal a useful and valuable material (Akgül, 2006).

Like other heavy metals, silver is extremely dangerous to human health and aquatic life, especially because of its capacity to remain intact in food chain (Song et al., 2011). This metal, in high concentration, is considered toxic and may cause various negative health effects like algyria (disease that causes skin pigmentation) and liver and kidney degeneration (Fung and Bowen, 1996). Thus, some organizations have established limit concentration for the disposal of wastewater contaminated with silver. The World Health Organization (WHO) and the US Protection Agency have determined the silver concentration in drinking water as 0.1 mgL⁻¹ (Hosoba, 2009).

In the context cited above, it becomes evident the necessity to find methods to remove silver and other heavy metals from contaminated water like membrane filtration, solvent extraction and others (Kentish and Stevens, 2001). Among these methods, adsorption is a good alternative mainly because of its low cost and efficiency (Almeida Neto et al., 2012). Also, the adsorbent's choice is essential to guarantee the effectiveness of the process (Almeida Neto et al., 2013). Beyond common used adsorbents, clays have shown a good adsorption potential in many research studies (Anirudhan et al., 2012).

In this study, the bentonite clay called Verde-Iodo is used for the adsorption of silver ions in a static system. The clay was thermally treated (calcination process) to increase its stability and ion exchange capacity. In adsorption's studies, it is important to analyze the process equilibrium to verify the solute's distribution between the two involved phases (Ruthven, 1984). Also, it was verified the spontaneity of the process by calculating the free Gibb's energy involved. Besides that, different eluents were tested to

measure its desorption's capacity of silver adsorbed in this clay. These results will be used to recovery silver present in industrial effluents, since it is a valuable and noble material.

2. Materials and methods

2.1 Adsorbent's preparation

Bentonitic clay called Verde-Iodo was used as the adsorbent of this study. This material is commercialized by the company Dolomil Ltda. from the state of Paraiba in Brazil. This clay was firstly grinded and sieved in order to assume the average diameter of 0.855 mm. After that, the clay was taken to a muffle (from Quimis, Brazil) over the temperature of 500 °C for the calcination process towards to increase its stability and ion exchange capacity.

2.2 Equilibrium study: adsorption isotherms

The silver's source used in this study was silver nitrate (AgNO_3) from Merck, Germany. This reagent was dissolved in deionised water to prepare silver solutions with different initial concentrations (5 to 600 ppm). These solutions (volume of 50 mL) were put in contact with 0.5 g of Verde-Iodo clay in Erlenmeyer flasks and posteriorly stirred for 24 hours with the use of a shaker SI-600R from Lab Companion, Korea. To determinate the concentration of metal after the equilibrium, solution's samples were centrifuged, diluted and measured by the absorption spectrophotometer AA-7000 from Shimadzu, Japan. This experiment was performed in four different temperatures: 273 K, 293 K, 313 K and 333 K.

In order to verify and analyze the relationship between the amount of adsorbed silver in the solid and the concentration of silver equilibrium solution, three different models were used for the adjustment of the curves: Langmuir, Freundlich and Dubinin-Radushkevich.

The model of Langmuir (1918) assumes the uniformity of the monolayer adsorption and a finite number of adsorption sites (Ruthven, 1984). The Langmuir isotherm is described by Eq (1).

$$q^* = \frac{q_m bC}{1 + bC} \quad (1)$$

Where C is the concentration of silver in the liquid phase at equilibrium (mmol.L^{-1}), q^* is the concentration of the metal in the adsorbent (mmol.g^{-1}) and b (L.g^{-1}) and q_m (mmol.g^{-1}) are Langmuir constants related to the adsorption and desorption rate and the maximum adsorbed amount on the monolayer, respectively.

The Langmuir model can also be used to calculate a constant called R_L , known as the equilibrium parameter. This constant is calculated by Eq (2).

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

Where C_0 is the highest concentration of solute. If R_L is higher than 1, the equilibrium is not favorable and the opposite indicates that the equilibrium is favourable.

The Freundlich (1926) model considers an infinite number of adsorption sites, assuming that the adsorbent will never be saturated. This model is shown by Eq (3).

$$q^* = KC^n \quad (3)$$

Where K is a constant related to the adsorptive concentration of the adsorbent and n is an empirical constant.

Another model studied is the Dubinin-Radushkevich model, which does not consider the homogeneity of the process (Kilisioglu and Bilgin, 2003). This model has been recently used in several researches (Akar et al., 2009) and is given by Eq (4).

$$\ln(q^*) = \ln(X_m) - k\varepsilon^2 \quad (4)$$

Where X_m indicates the adsorption capacity (mmol.g^{-1}), k is a constant associated with the sorption energy ($\text{mol}^2.\text{J}^{-2}$) and ε is Polanyi potential, which is calculated by Eq (5).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C}\right) \quad (5)$$

In Eq (5), R is the gas constant ($\text{J.mol}^{-1}.\text{K}^{-1}$) and T is temperature in K.

2.3 Thermodynamic analyzes

The thermodynamic parameter ΔG (Gibbs free energy) was calculated by the method given by Xiaofu et al. (2009), shown in Eq(6).

$$\Delta G/(RT) = (A_0) \ln(1 - x/y) + (W_0\beta) \ln(1 - x/\beta) \quad (6)$$

Where A_0 is the initial concentration of silver (mg.L^{-1}), x is the ratio of the equilibrium concentration of silver onto solid surface (mg.L^{-1}), $y = A_0/W_0$ is the relation between A_0 and the adsorbent's concentration W_0 (g.L^{-1}) and β is the maximum adsorption capacity (mg/g).

2.4 Desorption study

The desorption of silver adsorbed by Verde-Iodo clay is an important issue to be evaluated since silver is a valuable metal that should be recovered to guarantee the sustainability of the process. In order to verify the best eluent to be used in future experiments, seven possible eluents were tested to evaluate their desorption potential: sodium chloride (NaCl), calcium chloride (CaCl_2), hydrochloric acid (HCl), thiourea ($\text{SC}(\text{NH}_2)_2$), sodium phosphate (NaH_2PO_4) and sulphuric acid (H_2SO_4) and nitric acid (HNO_3).

These solutions (with concentration of 0.1 M) were put in contact in different Erlenmeyer flasks with saturated clay adsorbed by silver. The samples were constantly shaken for 24 h to reach the equilibrium. The concentration of silver after desorption process was determined by absorption spectrophotometry. Thus, the eluent which has obtained the highest concentration of metal in solution was considered the best eluent.

3. Results and Discussion

3.1 Adsorption isotherms

The equilibrium isotherms were obtained for 273 K, 293 K, 313 K and 333 K in order to compare the temperature influence in the equilibrium. The curves were adjusted by three different models: Langmuir, Freundlich and Dubinin-Radushkevich (D-R). Results including the isotherms and the adjustments are shown in Figure 1. The modeling parameters obtained with the isotherm's adjustments are exhibited in Table 1.

Regarding Figure 1, it is possible to notice that the isotherms presented the same behavior for all the temperatures. This behavior is characterized by the curve's shape, indicating that the equilibrium is favorable. From Figure 1, it can be also observed that the adsorbed amount of silver is higher for the temperature of 20 °C. On the other hand, the lowest adsorbed amount of metal was detected when temperature was 0 °C. Besides that, it is observed that a higher process temperature (excepting the temperature of 0 °C) leads to less adsorbed amount of metal, which indicates that the process is exothermic for this temperature range. However, for the temperature range of 0 °C to 20 °C, the process is considered endothermic.

From Table 1, it is possible to observe the effectiveness of the curves adjustments. The values of determination coefficients (R^2) show that the 0 °C isotherm's experimental data presented more limitation for the adjustments. Also, in a general way, the Langmuir model produced better fitting results to describe the isotherms of silver adsorption, presenting better results for 0 °C, 40 °C and 60 °C. For 20 °C isotherm, Freundlich model showed a better result. This fact indicates that the assumptions made by Langmuir and Freundlich models well describe the characteristics of interaction between the adsorbent and silver.

The Langmuir model parameters are according to experimental data verified, since the values obtained for q_m (maximum adsorbed amount) follow the same order as the experimental adsorbed amount of silver observed in Figure 1. Besides that, with the values of equilibrium parameter (R_L) showed in Table 1, it may be concluded that the equilibrium is favourable for all the temperature, due the fact that R_L is less than 1 for all the isotherms.

The results obtained for the Freundlich model showed that the values obtained for constant K (related to the adsorptive concentration of the adsorbent) are similar, which was expected since the adsorbent was the same for all experiments. For the parameters obtained for D-R model, it can be notice that they have similar behaviours as the adsorbed amount of silver verified by experimental data: temperature of 20 °C presented the highest values of the constants k and X_m , followed by 40 °C, 60 °C and 0 °C. These facts indicate that the process is more effective for the temperature of 20 °C.

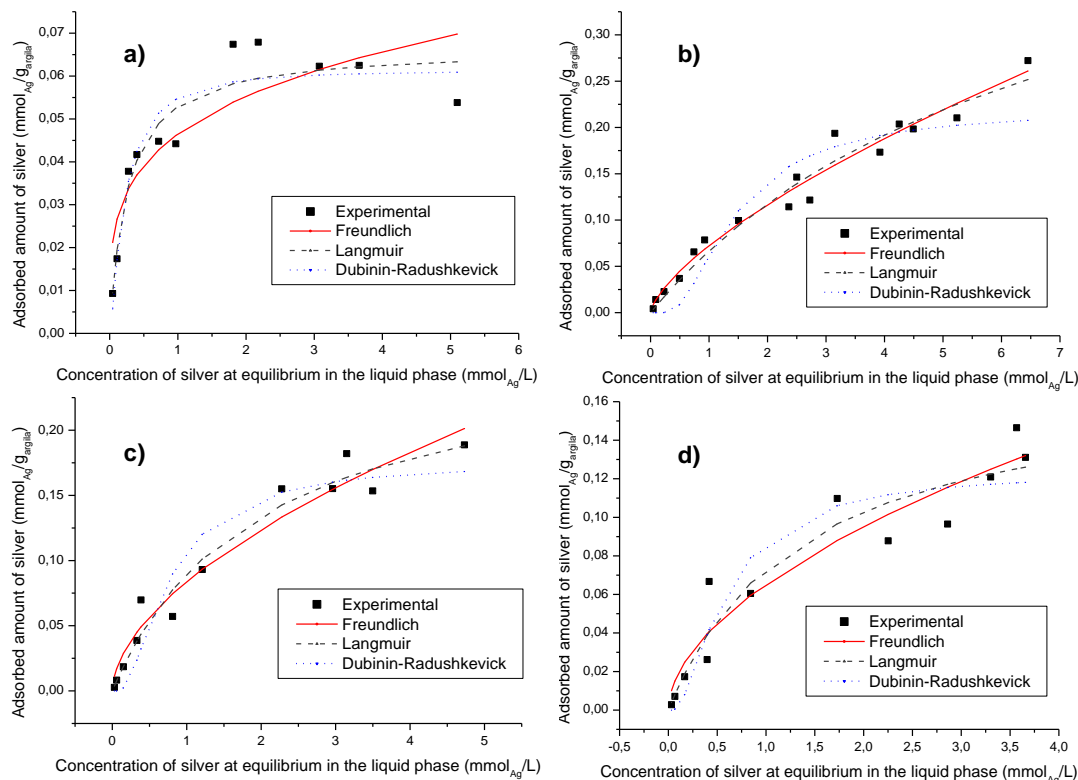


Figure 1: Equilibrium isotherms and Freundlich, Langmuir and D-R adjustments obtained for silver ions adsorption on calcined Verde-Iodo clay for different temperatures: a) 273 K (0 °C); b) 293 K (20 °C); c) 313 K (40 °C); d) 333 K (60 °C)

Table 1: Parameters obtained for the adjustment of the isotherms using Langmuir, Freundlich and D-R models

Model	Parameter	Temperature			
		0 °C	20 °C	40 °C	60 °C
Langmuir	q_m (mmol.g ⁻¹)	0.066	0.515	0.266	0.173
	b (L.mmol ⁻¹)	3.861	0.148	0.507	0.729
	R_L	0.044	0.424	0.230	0.216
	R^2	0.907	0.964	0.964	0.916
Freundlich	K (L.mmol ⁻¹)	0.046	0.072	0.084	0.065
	n (mol ² .kJ ²)	4.008	1.453	1.778	1.846
	R^2	0.777	0.971	0.955	0.916
Dubinin-Radushkevich	X_m (mmol.g ⁻¹)	0.061	0.219	0.175	0.123
	k	0.045	0.447	0.152	0.094
	R^2	0.900	0.872	0.912	0.884

3.2 Thermodynamics study

To verify the process thermodynamics, the method stated by Xiaoufu (2009) was used. Table 2 summarizes the results obtained for this method, for each temperature and initial silver concentration A_0 . The value of β was given by the maximum adsorbed amount of silver verified in Figure 1 for each temperature multiplied by silver's molar mass. For temperature 273 K, $\beta = 7.3$ mg/g; at 293 K, $\beta = 29.4$ mg/g; for 313 K, $\beta = 20.4$ mg/g and for 333 K, $\beta = 15.8$ mg/g. The table presents the value of ΔG (Gibbs free energy) for each condition. It is verified that all of these values are negative, revealing the spontaneity of the silver adsorption process using Verde-Iodo clay as the adsorbent. This fact is in accordance with thermodynamics principles and was also verified by other studies (Khan et al., 1995).

Table 2: Equilibrium adsorption density x (mg/g), and calculated values of ΔG (free Gibb's energy) for silver ion adsorption on Verde-Iodo clay at different values of initial silver concentration A_0 (mg/L) and temperature (K)

T(K)	A_0															
273	5	13	32	45	80	107	198	238	335	398	553	~	~	~	~	~
x	0.1	0.1	0.2	0.2	0.2	0.2	0.4	0.4	0.3	0.3	0.3	~	~	~	~	~
y	0.5	1.3	3.2	4.5	8.0	10.7	19.9	23.9	33.5	39.8	55.3	~	~	~	~	~
x/y	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	~	~	~	~	~
x/β	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1	0.0	~	~	~	~	~
ΔG	-2.3	-4.4	-9.5	-10.4	-11.2	-11.0	-16.8	-16.9	-15.5	-15.5	-13.3	~	~	~	~	~
293	5	10	26	55	84	104	168	261	278	300	350	433	470	495	576	711
x	0.0	0.1	0.1	0.2	0.4	0.4	0.5	0.6	0.8	0.7	1.1	0.9	1.1	1.1	1.1	1.5
y	0.5	1.0	2.6	5.5	8.4	10.4	16.8	26.1	27.8	30.0	35.0	43.3	47.0	49.5	57.6	71.1
x/y	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
x/β	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
ΔG	-1.1	-3.8	-6.1	-9.8	-17.5	-20.9	-26.5	-30.4	-39.0	-32.3	-51.8	-46.2	-54.4	-52.9	-56.1	-72.9
313	3	7	17	38	45	91	135	253	328	350	386	521	~	~	~	~
x	0.0	0.1	0.1	0.2	0.4	0.3	0.5	0.8	0.8	1.0	0.8	1.0	~	~	~	~
y	0.3	0.7	1.7	3.8	4.5	9.1	13.5	25.4	32.8	35.0	38.6	52.1	~	~	~	~
x/y	0.1	0.1	0.1	0.01	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	~	~	~	~
x/β	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	~	~	~	~
ΔG	-0.8	-2.4	-5.3	-11.1	-20.1	-16.2	-26.6	-44.3	-44.3	-52.1	-43.8	-53.9	~	~	~	~
333	4	8	19	44	49	94	193	248	314	363	393	402	~	~	~	~
x	0.0	0.0	0.1	0.1	0.4	0.3	0.6	0.5	0.5	0.7	0.8	0.7	~	~	~	~
y	0.3	0.8	1.9	4.4	4.9	9.4	19.3	24.8	31.4	36.3	39.3	40.2	~	~	~	~
x/y	0.0	0.1	0.1	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	~	~	~	~
x/β	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	~	~	~	~
ΔG	-0.8	-2.0	-4.9	-7.4	-19.2	-17.2	-31.4	-25.0	-27.4	-34.5	-41.9	-37.4	~	~	~	~

3.3 Desorption study

The selection of a substance to be used as an eluent is important to guarantee the recovery of the adsorbed material. With this aim, the study of the best eluent was performed. Figure 2 shows silver concentration after desorption process. Thus, the higher the silver concentration in solution, the better is the desorption capacity of the eluent.

Regarding Figure 2, it is observed that sulphuric acid (H_2SO_4) came up with the highest value of silver concentration in solution. However, nitric acid (HNO_3) presented a result very similar. Considering that sulphuric acid is more harmful to the environment, nitric acid was chosen as the eluent to be used in future studies. To verify if the clay kept its adsorption capacity after desorption process, another adsorption cycle was performed with the desorbed clay. It was observed that the desorbed clay presented a removal percentage of 30 % approximately. This result shows that, although the desorption process decreases the silver removal percentage, the adsorption capacity was maintained, which indicates that nitric acid may be used for future experiments.

4. Conclusion

This study presented an equilibrium study of the adsorption of silver in "Verde-Iodo" calcined clay, which is an important study to comprehend and analyze the entire process. The isotherms obtained for different temperatures presented the same behaviour, indicating a favourable equilibrium. From the adjustments of the curves, the models Langmuir, Freundlich and Dubinin-Radushkevich showed satisfactory results and, in a general way, Langmuir model produced better fitting parameters. Also, it was verified that the process is exothermic for the temperature range of 20 °C to 60 °C. From the thermodynamics' analysis, it was also observed the spontaneity of the process for all the temperatures and initial concentrations of silver. Finally, the results of elution tests of silver showed that nitric acid could be used as eluent for future experiments due its desorption capacity.

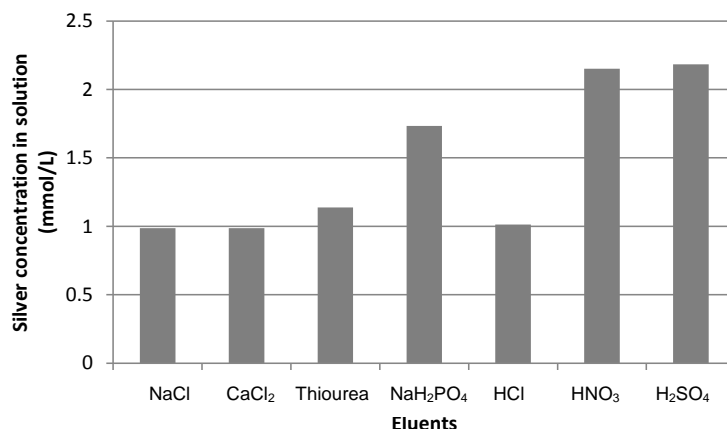


Figure 2: Concentration of silver after desorption process using different eluents

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