

Adsorption recovery of Ag(I) and Au(III) from an electronics industry wastewater on a clay mineral composite

Y. Rakhila¹, A. Elmchaouri¹, A. Mestari¹, S.A. Korili², M. Abouri¹, A. Gil²

1) Université Hassan II de Casablanca, Faculté des Sciences et Techniques, Laboratoire de Chimie Physique et de Chimie Bioorganique, BP 146, 20650 Mohammedia, Morocco

2) INAMAT - Department of Sciences, Los Acebos Building, Public University of Navarra, Campus of Arrosadia, E-31006 Pamplona, Spain

Corresponding author: Antonio Gil.

E-mail: andoni@unavarra.es

Abstract

The aim of this work is to investigate the ability of an adsorbent of a clay mineral composite to remove and recover gold and silver ions from wastewater. The composite was prepared by mixing phosphogypsum (PG), obtained from an industrial waste, and a natural clay mineral. The materials were characterized before and after use in adsorption by several techniques. Batch adsorption experiments were carried out, and the effects of the contact time and the pH and temperature of solution on the removal processes were investigated. The optimum pH for the adsorption was found to be 4. The adsorption of these metal ions reached equilibrium after 2 h of contact. The pseudo-first- and the pseudo-second-order kinetic models, as well as the Freundlich and the Langmuir isotherm equations, were considered to describe the adsorption results. The maximum adsorbed amount of 85 mg/g Ag(I) and 108 mg/g Au (III) was found. The recovery of the adsorbed gold and silver ions from the adsorbent was also analyzed. Strong acids appeared to be the best desorption agents to recover gold and silver ions. The use

of aqua regia gave regeneration rates close to 95.9% and 94.3% for Ag(I) and Au(III), respectively. Finally, the removal of gold and silver ions from an industrial wastewater was tested in batch experiments, and percentage recoveries of 76.5% and 79.9% for Ag(I) and Au(III), respectively, were obtained. To carry out the industrial application of the proposed methodology, an economic viability study is required.

Keywords: adsorption, clay composite, industrial wastewater, gold, silver, waste.

1. Introduction

Gold production cost and its market price have increased rapidly in recent years due to the increase in gold consumption. Gold is commonly used in the jewelry and electronics industry [1]. Some gold compounds are biologically active and are used in pharmaceutical applications [2]. Silver is another highly consumed metal used in various applications; it is used in the pharmaceutical industry, in photographic films, as catalysts and as antimicrobial materials [3]. Industrial waste contains large amounts of noble metals relative to their other minerals and, therefore, such waste can be considered as a secondary origin of noble metals [4].

Several methods, such as precipitation [4], ion exchange [4–7], solvent extraction, and adsorption [2,8] have been used for separation, preconcentration, and removal of gold and silver ions from aqueous solutions. Among these methods, the adsorption on a porous solid material has been considered as a promising and simple technology to recover metal ions with high efficiency [9–11]. Several types of low-cost natural sorbents, which are identified in Table 1, have high capacities for Ag(I) and Au(III) adsorption.

Phosphogypsum (PG) is a waste yielded from phosphate beneficiation plants. It is formed during the production of phosphoric acid by chemical attack of natural phosphates using sulfuric acid [12]. Approximately 4.5 tons of PG are produced in the production of one ton of phosphoric acid using a wet process [13]. The global average annual production of PG exceeds 100 million tons [14–17]. Phosphogypsum consists of more than 90 wt.% of calcium sulfate hydrate (gypsum) and approximately 6 wt.% of impurities, including heavy metals, fluoride, and radionuclides [18].

In the present study, a composite from a phosphate-containing industrial waste and a clay mineral was used as adsorbent of Ag(I) and Au(III). The study is mainly focused on

providing a methodology to recover Ag(I) and Au(III) from industrial wastewater by adsorption processes.

Table 1. Comparison of various low-cost adsorbents on adsorption of Ag(I) and Au(III).

Adsorbents	Adsorbate	Concentration (mg/dm ³)	S _{BET} (m ² /g)	T _{adsorption} (°C)	q _e (mg/g)	Ref
Biochar	Ag (I)	500	710	22	43.9	[30]
Bentonite	Ag (I)	5–600	–	20	55.6	[31]
Immobilized crab shell beads	Ag (I)	100	11	45	2.9	[32]
Immobilized coffee ground beads	Ag (I)	50	10	45	36.3	[33]
Vermiculite	Ag (I)	10–400	15	50	69.2	[21]
Zeolitic material	Ag (I)	20	4	20–40	1.1	[34]
Raw date pits	Au(III)	10	285	25	78	[35]
Durio zibethinus husk	Au (III)	200	–	30–50	89.0	[2]
Chitosan- coated Fe ₃ O ₄ nanoparticles	Au (III)	200–3000	–	25	59.5	[8]
Activated carbon	Au (III)	20–150	1387	25	30.2	[25]

2. Experimental section

2.1. Raw materials and preparation of the composite adsorbent

The industrial byproduct used in this study was generated by a phosphate industry and was recovered near Khouribga region (Morocco). The clay mineral used was collected from Ben-Ahmed district (Morocco). The adsorbent was prepared by mixing the PG and the clay mineral in a proportion of 30 wt.% with 0.75 dm³ of ultrapure water and stirring vigorously at

room temperature for 30 min. Phosphoric acid was slowly added drop wise, and the pH of the slurry was adjusted to 11 by adding an aqueous hydroxide solution. The obtained product was then removed from the solution by filtration, and the resulting powder was dried at 80°C and calcined for 2 h at 250°C.

All the chemical reagents used in this work are summarized in Table 2.

Table 2. List of chemical reagents with their purities.

Reagent	Purity
AgNO ₃	99.8% (Merck)
HAuCl ₄	≥ 99.9% (Merck)
HNO ₃	70% (Sigma Aldrich)
NaOH	98% (Sigma Aldrich)
HCl	37% (Sigma Aldrich)
H ₂ O ₂	30% (Sigma Aldrich)
The standards of the elements (Na, K, P, Mg, S, Ca, Si, Al, Fe, Cu, Mn, and Zn) used in the analysis by ICP-AES.	1000 ppm (Sigma Aldrich)

2.2. Characterization techniques

The mineralogical phases were identified by X-ray diffraction (XRD) using a Phillips Xpert-pro diffractometer Bruker D8 Advance, operating at 50 kV and 20 mA in the range 2θ of 5 to 85°. The chemical composition was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). A Thermo Scientific iCAP 6300 Series Echelle-type spectrometer with 52.91 grooves/mm ruled grating, 383 mm effective focal length, and 9.5° UV fused silica cross dispersion prism was used; its detector is a high-performance CID86 chip, and its RF source is of 27.12 MHz solid state, 750–1500 watts output power (Duo

restricted to 1350 watts). The samples to be analyzed were first subjected to the action of aqua regia (mixture of HCl and HNO₃) using microwaves according to a defined program, and all the elements were analyzed by standards of 1000 mg/L obtained from Sigma Aldrich Company. The extract was then filtered and adjusted to volume with nitric acid. The uncertainty of the ICP-AES measurement of the Ag(I) and Au(III) concentration was 0.01, whereas it was 5 for the major elements (Na, K, P, Mg, S, Ca, Si, and Al) and 0.1 for Fe, Cu, Mn, and Zn (Table 2).

2.3. Adsorption experiments

Solutions of Ag(I) and Au(III) were prepared by dissolving AgNO₃ and HAuCl₄ from Merck in ultrapure water considering a concentration of 1000 mg/dm³. The synthetic solutions were then prepared by diluting the gold and silver stock standard solutions. In all cases, the concentrations of gold and silver had been determined by ICP-AES after centrifugation and filtration.

The initial pH of the aqueous solution is the most important parameter in the adsorption process because it affects the state of ionization of the surface of the adsorbent. To study the effect of pH, the tests were carried out by agitating 50 cm³ of aqueous solutions of Ag(I) (400 mg/dm³) and Au(III) (450 mg/dm³) with 0.2 g of the sample for 3 h at 25°C. The pH values of the solutions were adjusted between 1 and 10 by adding a few drops of concentrated solutions of HNO₃ or NaOH (0.1 mol/dm³).

Another important factor in the adsorption process is the appropriate reaction time necessary to reach equilibrium. The evolution of adsorption process as a function of time was studied using a mixture of 0.2 g of the adsorbent and 50 cm³ of a solution of Ag(I) (400 mg/dm³) and Au(III) (450 mg/dm³) left to stand for 3 h with a levy on each 30 min after centrifugation and filtration.

The effect of the initial Ag(I) and Au(III) concentrations on the adsorption capacity was determined using a mixture of 50 cm³ aqueous solutions of concentration ranging from 10 to 600 mg/dm³ and 0.2 g of prepared clay composite, with a contact time of 3 h at room temperature.

To determine the effect of the temperature on the adsorption of Ag(I) and Au(III), 0.2 g of product was added to 50 cm³ of solution Ag(I) (400 mg/dm³) and Au(III) (450 mg/dm³) and stirred using a magnetic stirrer at 20°C, 30°C, and 50°C.

In all the cases, the amounts of gold and silver adsorbed were calculated from the initial and final concentrations according to the following equation:

$$q_t = \frac{V \cdot (C_0 - C_t)}{m}$$

where C_0 and C_t are the initial and liquid-phase concentration at any time t (mg/dm³), respectively; V (cm³) is the volume of the solution; and m (mg) is the adsorbent mass.

The desorption of gold and silver and the regenerative capacity of the adsorbent were also evaluated. The composite samples with gold and silver retained were dried at 90 °C and brought into contact with nitric acid (2 mol/dm³), hydrochloric acid (2 mol/dm³), aqua regia (75% HCl, 25% HNO₃), sulfuric acid (2 mol/dm³), and hydrogen peroxide, H₂O₂. Each slurry was constantly stirred for 24 h. After equilibrium, the solutions were separated by centrifugation, and the gold and silver concentration was determined by ICP-AES. The resulting composite was characterized after regeneration.

The removal of gold and silver from a real industrial wastewater was tested in batch experiments. The wastewater samples were from an electronics industry located in Casablanca (Morocco). The samples were collected in 1 dm³ polyethylene bottles which had been previously cleaned with 1:1 aqueous acid solution (HNO₃) overnight and then rinsed

with deionized water. The wastewater was passed through a 0.45 μm membrane filter. The wastewater was characterized before and after filtration by ICP-AES and stored immediately in a refrigerator at about 4 $^{\circ}\text{C}$. In a typical experiment, 0.5 g of clay mineral composite was added in 50 cm^3 of wastewater of pH 4 and 50 $^{\circ}\text{C}$; after 3 h, the system was centrifuged, and the supernatant was stored for metal analysis. The aspects of the wastewater before and after filtration and after adsorption are presented in Figure 1.

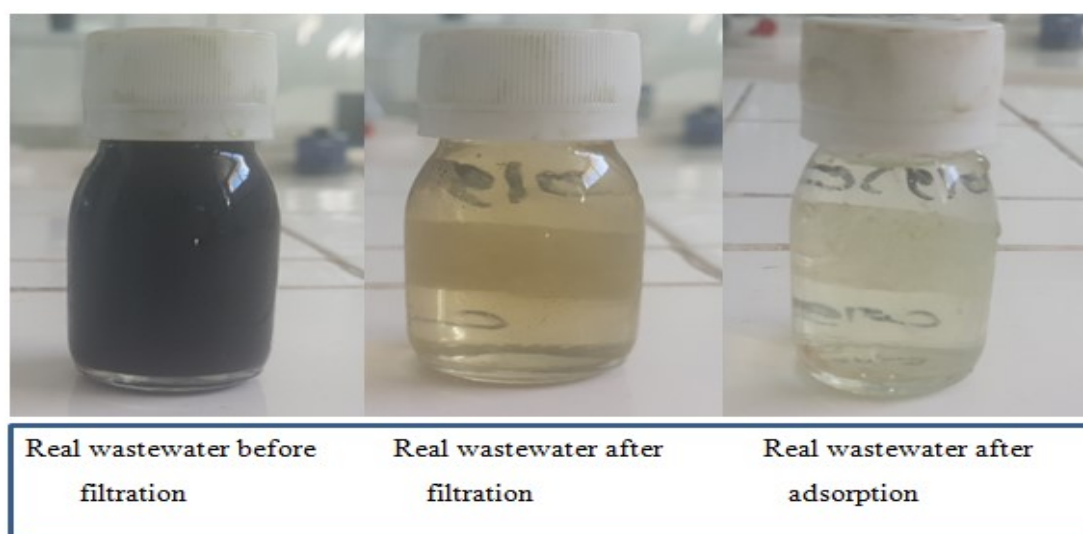


Fig. 1. Aspects of the wastewater before (a) and after filtration (b) and after adsorption (c).

3. Results and discussion

3.1. Characterization of the sample before and after adsorption of Ag(I) and Au(III)

3.1.1. Chemical analysis

The chemical compositions of the clay mineral, the PG, and the clay mineral composite before and after adsorption and after regeneration are summarized in Table 3. The PG was composed mainly of calcium sulfate (78 wt.%) mixed with calcium phosphate in various forms. Silica and other impurities such as iron, magnesium and aluminum oxides, organic matter, and traces of metals were also detected. The quantity of silica was very low (0.23 wt.%), which would lower the heating temperature during the manufacture of ceramics. The

clay mineral, a silico-aluminate, also contained non-negligible proportions of Fe_2O_3 , CaO , and MgO which indicated the presence of calcite. The chemical composition of the prepared mixture is also presented in Table 3.

Table 3. Chemical composition of the clay mineral, PG, and prepared composite before, after adsorption and after regeneration (wt.%).

	CuO	ZnO	CaO	K₂O	MgO	Na₂O	P₂O₅	SO₃	Al₂O₃	Fe₂O₃	SiO₂	Ag(mg/kg)	Au(mg/kg)
Clay mineral	0.01	0.02	2.10	0.18	1.57	0.80	0.12	0.75	11.44	4.29	59.32	0	0
PG	0.001	0.001	33.11	0.08	0.008	0.13	1.64	45.13	0.06	0.06	0.23	0	0
Clay mineral + PG	0.001	0.001	14.97	0.16	0.86	0.57	0.64	6.88	8.47	3.19	54.27	0	0
Clay mineral + PG after adsorption	0.001	0.001	12.15	0.10	0.80	0.50	0.68	6.90	8.00	3.20	54.89	62.41	102.51
Clay mineral + PG after regeneration	0.001	0.001	13.01	0.14	0.80	0.52	0.60	6.81	8.10	3.14	54.127	9.21	13.21

3.1.2. XRD analysis

X-ray diffraction patterns of the clay mineral, the PG, and the prepared sample are shown in Figures 2 and 3. The mineral composition of PG was dominated by gypsum and quartz. The XRD pattern of the material after adsorption showed a peak relative to Au(III) at $2\theta = 44^\circ$ [19] and others related to Ag(I) at $2\theta = 52^\circ$ and at 68° [20].

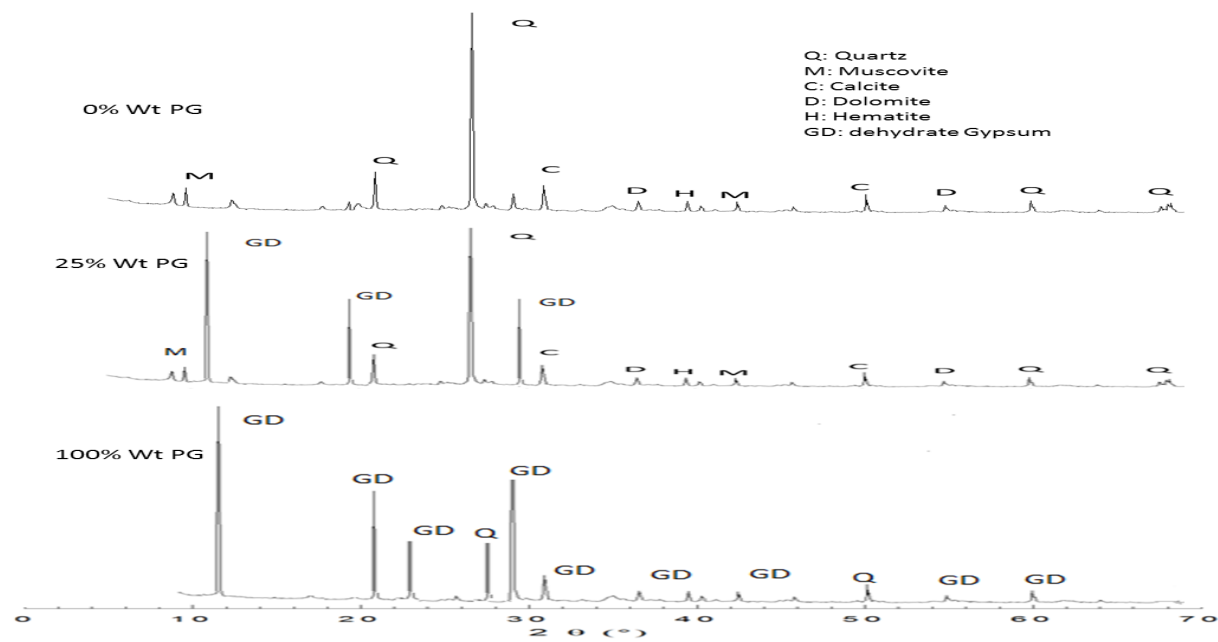


Fig. 2. XRD patterns of the materials.

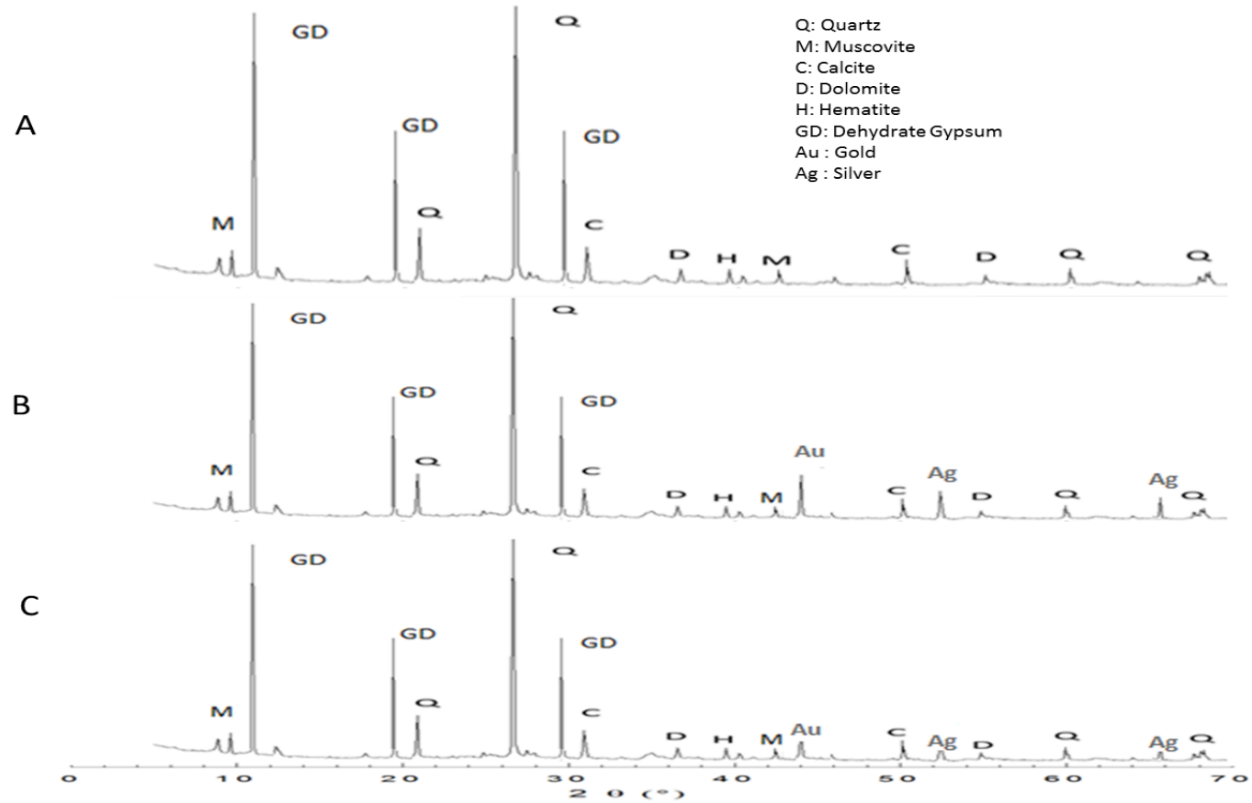


Fig. 3. XRD patterns of the sample: (A) before adsorption, (B) after adsorption, and (C) after regeneration.

3.2. Adsorption capacity of the materials

The observed effect of pH on the adsorption of Ag(I) and Au(III) by the composite is presented in Figure 4. The adsorption capacity increased with pH up to a maximum of 107 mg/g for Au(III) and 81 mg/g Ag(I) at pH = 4; then, it gradually decreased with further increase in pH. The decrease of adsorption as pH increased may be due to the increasing amount of the OH. This is because OH may result in electrostatic repulsion between the metals oxyanions and hydroxylic functional groups (generated by accumulation of OH) on the composite surface. This result is similar to those of other studies that confirmed that the optimum pH for adsorption of arsenic on several adsorbents was around 5 [2,3].

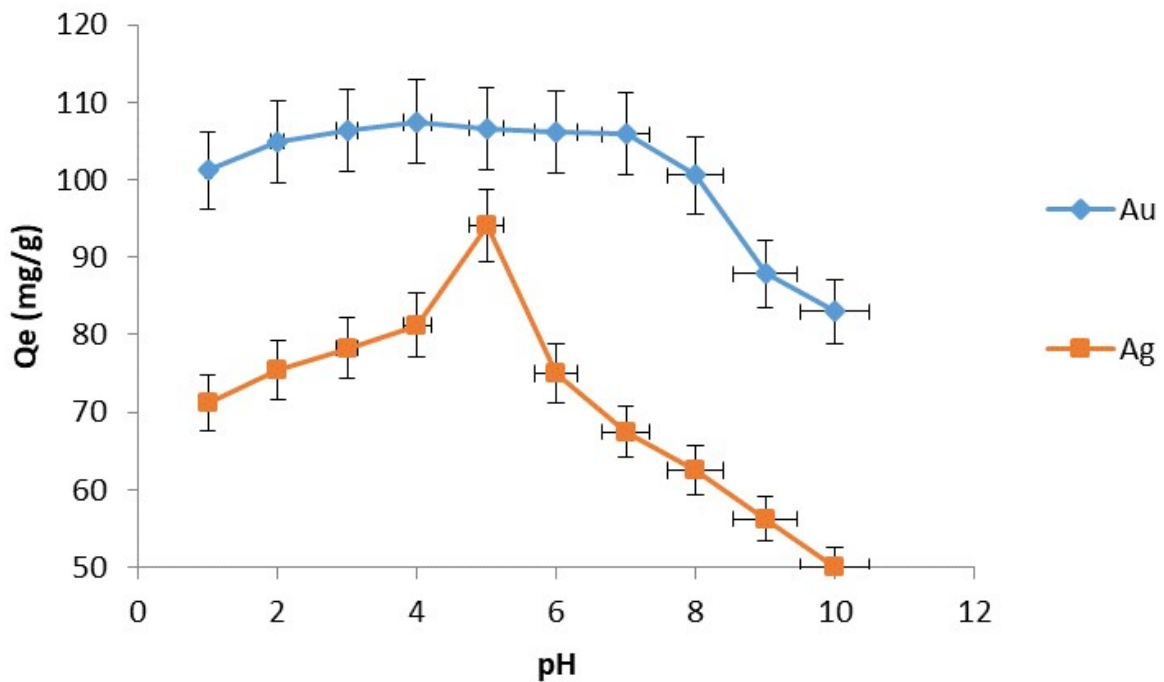


Fig. 4. Effect of pH on Ag (450 mg/dm³) and Au (450 mg/dm³) adsorption.

Studying the adsorption kinetics is necessary to determine the equilibrium time between the solute and the adsorbent. The result of the kinetic experiments (Figure 5) showed that the

equilibrium time for Ag(I) and Au(III) adsorption was reached after 2 h. These results showed that the sorption rate of Ag(I) and Au(III) on this adsorbent was relatively rapid compared with those of others studies in the literature [21,22].

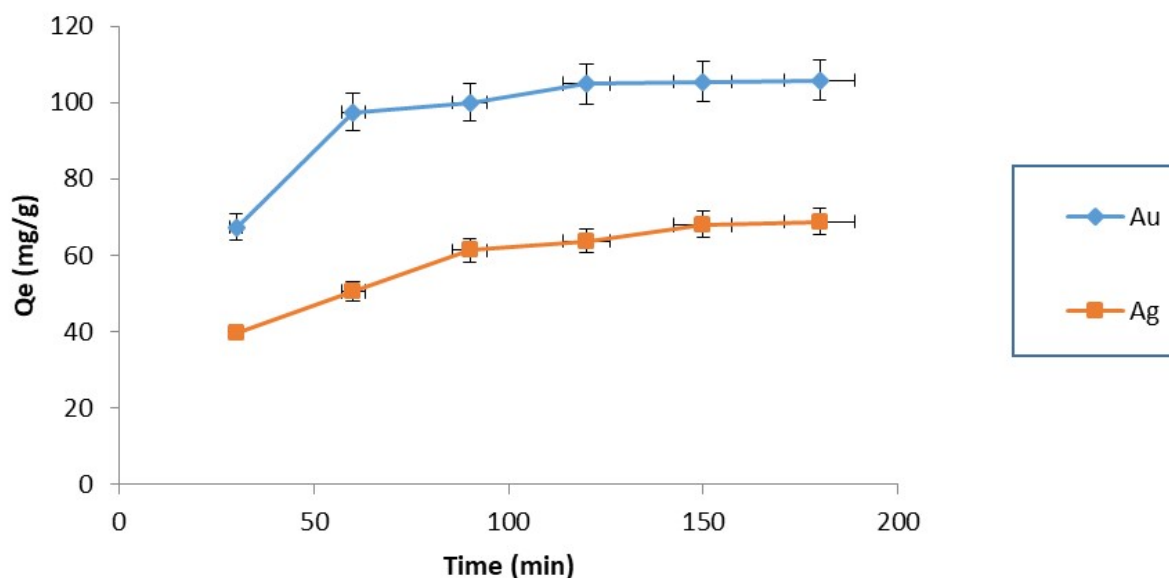


Fig. 5. Kinetic adsorption of Ag (450 mg/dm³) and Au (450 mg/dm³) at T = 25 °C and pH = 4.

To investigate the adsorption process of Ag(I) and Au(III) on the adsorbents, pseudo-first and pseudo-second-order models [23,24] were used and applied to test the experimental data. The values of the constants of pseudo-first- and pseudo-second-order models and the regression coefficients R^2 are summarized in Table 4. The analysis of these results show a good correlation of the experimental points ($R^2 = 0.996$), indicating that the kinetics of Au(III) adsorption on the sample was second-order, with constant of adsorption $k_{ads} = 0.0005 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$. A comparison of the pseudo-first- and second-order kinetic models indicates that the adsorption of Ag ions onto the sample reasonably followed the pseudo-second-order, with $R^2 = 0.997$ and constant of adsorption $k_{ads} = 0.0003 \text{ g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$. This same result was found in several other studies, which confirms that the adsorption of gold and silver on an

inorganic material follows the second-order model, except that our adsorption quickly reached equilibrium (2h) compared to other studies whose adsorptions were very slow [20,22,25,26]. These results show that the sorption process followed the pseudo-second-order model, indicating that the rate-limiting step is chemisorption, which involves valence forces through the sharing or exchange of electrons between the sorbent and the sorbate [27].

Table 4. Kinetic parameters for the adsorption of Ag(I) and Au(III) at T = 25 °C and pH = 4.

First-order kinetic model			Second-order kinetic model			Experimental	Element
$q_{e,cal}/(\text{mg/g})$	$k_{ads}/(1/\text{min})$	R^2	$q_{e,cal}/(\text{mg/g})$	$k_{ads}/(\text{g/mg}\cdot\text{min})$	R^2	$q_{exp}/(\text{mg/g})$	
7.87	0.0167	0.97	117.6	0.0005	0,996	108.3	Au(III)
6.80	0.0126	0.83	82.0	0.0003	0,998	85	Ag(I)

The adsorption isotherm is the most common representation of adsorbate concentration and quantity of material adsorbed. The result of the impact of the initial gold and silver concentration on the adsorption is presented in Figure 6. The results showed that concentrations of $450 \text{ mg}\cdot\text{dm}^{-3}$ and $400 \text{ mg}\cdot\text{dm}^{-3}$ of Au(III) and Ag(I), respectively, could be adsorbed on the clay composite. The adsorption of Au(III) and Ag(I) was observed to increase linearly with the increase of Au(III) and Ag(I) initial concentrations up to 400 ppm for Au(III) and 300 ppm for Ag(I), after which the material tended to saturate. The Freundlich and Langmuir isotherm equations were used to model the experimental data [28,29]. The values of the Langmuir and Freundlich constants are presented in Table 5. By adjusting the experimental points on these models and based on the values of the coefficient R^2 , the Langmuir model appears to express the type of adsorption better than the Freundlich.

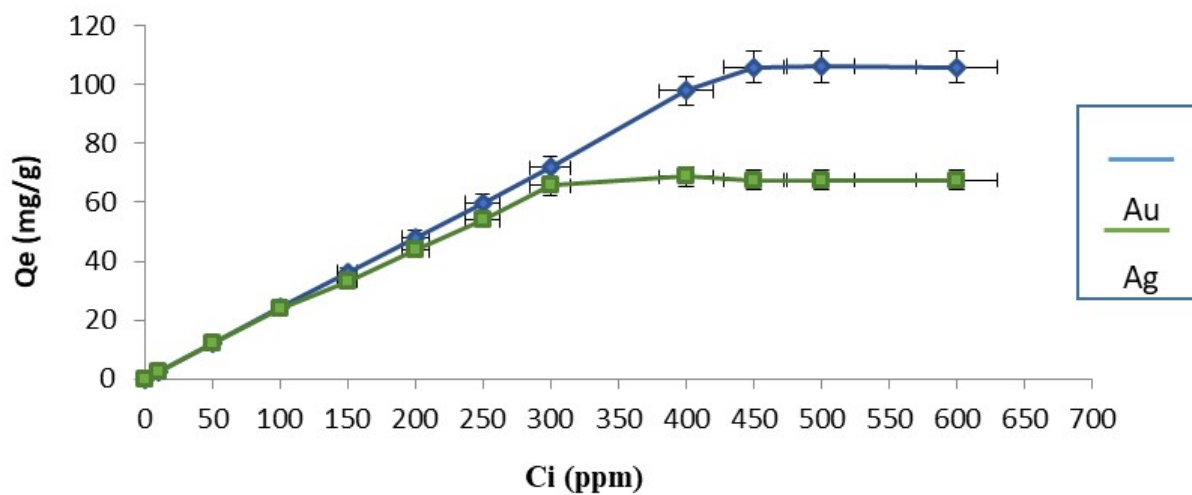


Fig. 6. Effect of the initial concentration of Ag(I) and Au(III) adsorption.
 Equilibrium time = 2 h, T = 25 °C, pH = 4.

Table 5. Freundlich and Langmuir parameters for the adsorption of Ag(I) and Au(III). Equilibrium time = 2 h, T = 25 °C, pH = 4.

Element		Au(III)																	
Models		Langmuir									Freundlich								
Parameters	$q_{m,cal} /(\text{mg/g})$			$k_L/(\text{dm}^3/\text{g})$			R^2			n			$k_F /(\text{mg}^{1-1/n} \cdot \text{dm}^{3/n} \cdot \text{g}^{-1})$			R^2			
Values	30.21	1.72	109.89	0.005	0.021	0.184	0.78	0.996	0.997	1.08	4.31	2.36	0.160	2.40	20.18	0.997	0.990	0.93	
Ref.	[21]	[2]	This work	[21]	[2]	This work	[21]	[2]	This work	[21]	[2]	This work	[21]	[2]	This work	[21]	[2]	This work	

Element		Ag(I)																	
Models		Langmuir									Freundlich								
Parameters	$q_{m,cal} /(\text{mg/g})$			$k_L/(\text{dm}^3/\text{g})$			R^2			n			$k_F /(\text{mg}^{1-1/n} \cdot \text{L}^{1/n} \cdot \text{g}^{-1})$			R^2			
Values	46.2	8.46	69.93	6.9	374	374	0.995	0.9998	0.994	1.64	1.54	2.70	1.67	9.08	11.38	0.97	0.98	0.95	
Ref.	[18]	[6]	This work	[18]	[6]	This work	[18]	[6]	This work	[18]	[6]	This work	[18]	[6]	This work	[18]	[6]	This work	

The result of the effect of the temperature on Ag(I) and Au(III) removal by the prepared sample is presented in Figure 7. The adsorbed amount of final ions of gold and silver on the material slightly decreased as the temperature increased from 20°C to 50°C. With increase in temperature, the bonds between the active sites of the clay composite and the Ag(I) and Au (III) become less stable. The calculated thermodynamic parameters are included in Table 6. The ΔG values indicates that the Au (III) and Ag(I) fixation on the used materials was a non-spontaneous process. The ΔH values indicate that the Ag(I) and Au (III) adsorption is an exothermic process, which confirms that the adsorption is more favored at low temperatures.

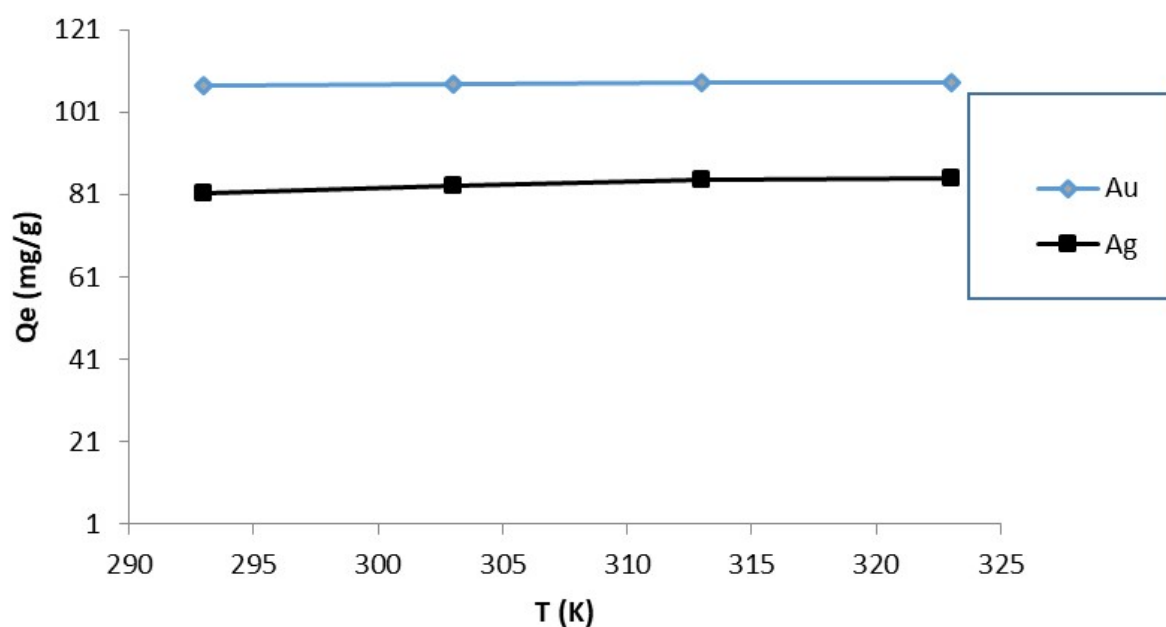


Fig. 7. Effect of the temperature on the amount of Ag(I) and Au(III) adsorbed.

Table 6. Thermodynamic parameters for the adsorption of Ag(I) and Au(III). Equilibrium time = 2 h, T = 25 °C, pH = 4.

Parameters	T/K	ΔS /(J/K·mol)	ΔH /(J/mol)	R ²	ΔG /(J/mol)
Au(III)	293.15	-34.2	-5915	0.96	4117.66
	303.15				4460.06
	313.15				4802.46
	323.15				5144.86
	293.15				7572.52
Ag(I)	303.15	-42.2	-4783	0.95	7994.22
	313.15				8415.22
	323.15				8837.62

To highlight the mechanism of the adsorption of metal ions on the composite, the concentrations of Ca²⁺, K⁺, Mg²⁺, and Na⁺ ions released from the solid in the solution during the adsorption process were studied. The variation of these concentrations as a function of the concentration of the retained metal is summarized in Figure 8. The results indicate that the release of Ca²⁺ ions from the solid increased as the concentration of retained metal ions Ag(I) and Au (III) increased. The amount of metal fixed by the composite is more important than that of Ca²⁺ ions released in the solution. This suggests that the metal ions Ag(I) and Au (III) are not totally exchanged with the Ca²⁺ ions of the composite but are also adsorbed and/or complexed on the surface as previously described. Based on the results of this work, the fixation of the metal ions on the prepared material took place by a combination of several possible mechanisms: ion exchange between the M²⁺ ions contained in the contaminated solution and the Ca²⁺ ions present in the solid; complexation of metal ions on the surface of the solid via the deprotonation of this surface, as described during the study of the pH variation; and adsorption of metal ions by the composite.

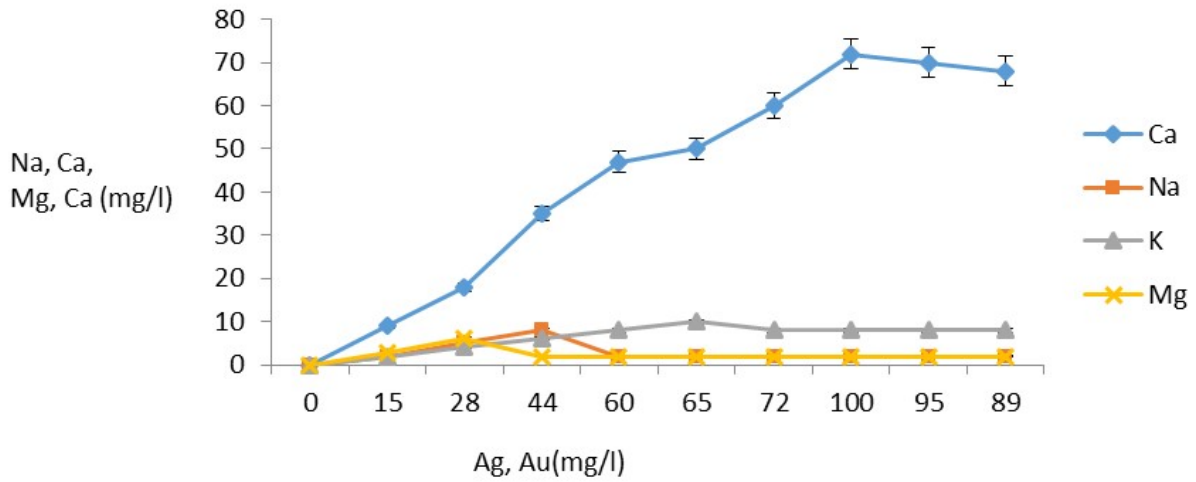


Fig. 8. Variation of the concentration of Ca^{2+} , K^+ , Mg^{2+} , and Na^+ ions released as a function of the concentration of the retained metals.

3.3. Regeneration capacity of the materials

The regeneration of the adsorbed metals is an important consideration for the low-cost treatment and recovery of these metals in a concentrated form. In this work, the regenerations of the adsorbed gold and silver were tested using various acids, and the results are presented in Table 7. The results showed that aqua regia was more compatible to retrieve the adsorbed gold and silver since it gave a performance of 94.26% for Au(III) and 95.33% for Ag (I). Oxygenated water had a negligible effect on the adsorbent containing the gold and silver.

Table 7. Effect of several reagents on the regeneration of the adsorbent.

Element	Acid	Reference/(mg/dm ³)	Final concentration/(mg/dm ³)	Yield (%)
Au(III)	HCl	0	314.25	91.35
	HNO ₃	0	305	88.66
	H ₂ SO ₄	0	281.45	81.81
	Aqua regia	0	324.25	94.26
	H ₂ O ₂	0	35.27	10.25
Ag(I)	HCl	0	241.35	87.76
	HNO ₃	0	239.91	87.24
	H ₂ SO ₄	0	172.48	62.72
	Aqua regia	0	262.15	95.33
	H ₂ O ₂	0	15.73	5.72

3.4. Application to the treatment of industrial wastewater

The physicochemical composition of the wastewater is given in Table 8. After filtration, the concentration of the macroelements was very low, while the silver and gold concentration remained high. The silver and gold concentrations in the wastewater after adsorption were very low, and the percentage recoveries of silver and gold on the prepared composite were 76.47% and 79.85%, respectively.

Table 8. Chemical composition of the wastewater before and after filtration and after adsorption.

(mg/dm ³)	Before filtration	After filtration	After adsorption
Na	621.23	21.10	15.74
K	421.30	10.24	8.57
Ca	1250.84	21.57	17.59
P	1.29	0.84	0.84
Mg	210.34	14.59	12.23
Cu	1.78	0.12	0.10
Mn	0.98	0.14	0.12
Fe	4.52	0.51	0.27
Zn	1.29	0.71	0.25
Cd (μg/dm ³)	0.8	0.7	0.7
Pb (μg/dm ³)	7	6	5
Ni (μg/dm ³)	10	10	8
Cr (μg/dm ³)	12	11	5
Ba (μg/dm ³)	165	98	71
Co (μg/dm ³)	10	8	4
As (μg/dm ³)	17	10	8
Ag	154	102	24
Au	172	134	27

4. Conclusion

The adsorption kinetics of silver and gold ions on a mineral clay composite at the optimum pH of 4 were evaluated by several models: pseudo-first- and pseudo-second-order. The silver-composite and gold-composite systems attained equilibrium in 2 h. The results of thermodynamic analysis revealed that adsorption of silver and gold was exothermic and spontaneous. According to the results of isotherm adjustment, Langmuir model presented the best fitting results. The maximum adsorption capacities verified for the composite was 108.25

mg/g for Au (III) and 85 mg/g for Ag (I), indicating the clay composite is an effective adsorbent for silver and gold removal. The removal of gold and silver from the industrial wastewater was also tested in batch experiments. The percentage recoveries of silver and gold from the wastewater on the prepared composite were 76.47% and 79.85%, respectively. An economic feasibility study is necessary to implement this metal recovery methodology at the industrial level.

Acknowledgements

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