



## A Kinetic and Equilibrium Study of Heavy Metals Removal by Clay as Low Cost Adsorbent from Aqueous Solutions: Case of an Akjoujt clay from Mauritania

Cheikh Ahmed Babe<sup>1,2</sup> | Ousseynou M'bodj<sup>1</sup> | Abdoulaye Demba N'diaye<sup>3✉</sup> | Mohammed Ben Ali<sup>2</sup> | Asmae El-Yahyaoui<sup>2</sup> | Fouzia Allali<sup>2</sup> | Mohamed Kankou<sup>3</sup> | El Mostapha Lotfi<sup>2</sup>

1. Laboratory of Materials Sciences, Faculty of Sciences and Technology of Nouakchott, Mauritania, Nouakchott-Mauritania.
2. Laboratory of Spectroscopy, Molecular Modeling, Materials, Nanomaterials, Water and Environment, Materials for Environment Team, ENSAM, Mohammed V University in Rabat, Morocco.
3. Unité de Recherche Eau, Pollution et Environnement, Département de Chimie, Faculté des Sciences et Technique, Université de Nouakchott, Nouakchott, Mauritanie.

Article Info	ABSTRACT
<b>Article type:</b> Research Article	The present research investigated the adsorption of Gold (Au(I)), Copper (Cu(II)) and Zinc (Zn(II)) ions from aqueous solution using a natural clay from Akjoujt region in Mauritania as an low cost adsorbent. The natural Akjoujt clay were characterized by several physical and chemical methods such as X-Ray fluorescence (XRF), X-ray diffraction (XRD), Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), BET surface Area, cation exchange capacity (CEC) and Thermal Gravimetric Analysis (TGA). The removal efficacy of the Akjoujt clay adsorbent for Au (I), Cu(II) and Zn(II) ion was studied in batch mode as a function of contact time and temperature. Adsorption kinetics data were modelled using pseudo-first-order (PFO) and pseudo-second-order (PSO) kinetics. The behaviour and the nature of Au (I), Cu (II) and Zn (II) adsorption were analysed by employing the Langmuir, and Freundlich isotherm models. The adsorption kinetics followed the PSO kinetics whereas the adsorption data fitted well with the Langmuir isotherm model. The adsorption capacities (qm) from the Langmuir isotherm for Au(I), Cu(II) and Zn(II) are found as 2.90, 7.93 and 6.45 mg/g respectively. The effectiveness of Akjoujt clay in the adsorption of the three metals from aqueous system was Cu(II) > Zn(II) > Au(I). The thermodynamic calculations suggested the spontaneous nature ( $\Delta G^\circ < 0$ ) of the adsorption process, along with the endothermic characteristics ( $\Delta H^\circ > 0$ ) in all cases. These findings highlight the promising potential of natural clay Akjoujt for efficiently adsorbing Au(I), Cu(II) and Zn(II) from aqueous solutions.
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## INTRODUCTION

Pollutants are worldwide environmental problems because of their harmful impact on living beings. The industrialization, urbanization and high pollution activities growth in most parts of the world. That generates a huge source of wastewater which contributes to the deterioration of the environment, impacts human health (Aly et al., 2021) and disrupts ecological integrity in general (Hall, 2020). The presence of the pollutants, even in small amounts, is very threatening,

\*Corresponding Author Email: [abdouldemba@yahoo.fr](mailto:abdouldemba@yahoo.fr)

making humans, aquatic organisms, wildlife and plants vulnerable to various diseases and even death (Miyah et al., 2021). There are many sources that generate various types of pollutants of water: metallurgical industry and engineering, mining operation, chemicals, sewage sludge, agro-food industry, textile and clothing industry, pesticides, pigment, nuclear power operations, and other natural sources as well (El Babacha et al., 2021). These different sources produce organic and inorganic pollutants.

The heavy metals are inorganic pollutants and a serious environmental problem. They are recognized as bioaccumulative elements and non-degradable (Ait Ichoura et al., 2020; Sarayanam et al., 2021), and mostly contaminate soil, water, plants, animals and man (Okereafor et al., 2020; Bogardi et al., 2020). The most toxic are chromium (Cr), manganese (Mn), copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) (Sarayanam et al., 2021). Many heavy metals are known to cause diseases such as gastrointestinal distress, vomiting, nausea, abdominal pain, poisoning, anemia, dysfunction of the kidneys, high blood pressure chronic bronchitis and they can be carcinogens or co-carcinogens cause lung insufficiency (Men et al., 2020). Given the impact of these metals on human health and other living organisms, it is urgently necessary to find a way of eliminating them from water, or finding a solution that reduces their impact for the protection of human health and the environment.

Several techniques have been used to remove the heavy metals from water. These unit operations include: chemical precipitation and ion exchange (Peng & Guo, 2020), chemical versus electrocoagulation (Khan et al., 2023), solvent extraction (Wang et al., 2020), complexation (Du et al., 2020), electrochemical (Choumane & Peulon, 2022), bioelectrochemical (Sukrampal Kumar & Patil, 2020), biological (Arora, 2020), filtration (Calabrò et al., 2020), membrane processes (Tian et al., 2020) and adsorption (Hamood et al., 2023).

Over the past few decades, the adsorption process with activated carbon has remained one of the most efficient and compelling proposals for the removal of metals-contaminated wastewater (N'dah et al., 2022). This is considered an economical alternative since it does not necessitate any extra pre-treatment steps if inexpensive adsorbents are used. In this aspect, a lot of recent research has focused on finding an economical and accessible bio adsorbent alternative to replace activated carbon, as it is expensive and difficult to regenerate.

Recently, many materials have been investigated to determine their adsorption capacity (Darvish et al., 2020 ; Dim et al., 2020 ; Zafar et al., 2020 ; Bakhtiari et al., 2021). Therefore, the major drawback of this kind of adsorbents is their high-cost, complicated processes for the activation using acids and corrosives and are time-consuming.

The adsorption of fluoride from aqueous solutions using available and natural Mauritanian clay has been studied (N'diaye et al., 2020a). Langmuir isotherm represent well the experimental adsorption data. The maximum adsorption capacity for fluoride on natural Mauritanian clay adsorbent was found to be 0.22 mg/g. The comparison clearly showed that the adsorbent developed is effective for the removal of fluoride from an aqueous solution compared to some adsorbents previously reported by the literature.

The adsorption of Copper from aqueous solutions using available and natural Mauritanian clay has been studied (N'diaye et al., 2020b). The equilibrium is perfectly adapted to the Langmuir model with the maximum adsorption capacities for Copper on Mauritanian clay adsorbent at pH 6.8 and pH 9 were found to be 0.081 and 0.31 mg/g, respectively on a single layer. The comparison clearly showed that the adsorbent developed is effective for the removal of Copper from an aqueous solution compared to some adsorbents previously reported by the literature.

Encouraging results obtained by the adsorption of pollutants using mauritanian clays as low-cost adsorbents (N'diaye et al., 2021a ; N'diaye et al., 2021b ; Soko et al., 2023) have incited us to search new route to study the elimination of heavy metals from aqueous solutions. The use of locally available clay has considerable economic and environmental advantages.

Their low cost, as well as their adsorption properties, present an advantage compared to other commercially available adsorbents.

Thus, in this research, we are interested in studying the adsorption capacities of natural Akjoujt clay. The investigation will concern the adsorption of Au (I), Cu (II) and Zn (II), by natural Akjoujt clay. In the study of heavy metal retention by natural Akjoujt clay, the adsorption kinetics, isotherm, and thermodynamic properties were explored, as they contribute to explain the adsorption process.

## MATERIALS AND METHODS

### *Adsorbates*

The metal ions studies are Au(I) Cu(II) and Zn(II). Stock solutions of Au(II) Cu(II) and Zn(II) were prepared by dissolving in distilled water the appropriate amounts of analytical reagent grade  $\text{NaAu}(\text{CN})_2$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ . The concentrations of Au (I), Cu (II) and Zn (II) in the solutions were determined using an a Flame Atomic Absorption Spectroscopy Agilent Technologies 200 Series AA spectrometer. Analysis Center Innovation City, Sidi Ben Abdellahi University, Fez, Morocco.

### *Preparation and characterization of Akjoujt clay adsorbent*

The sample comes from the Akjoujt region in central-western Mauritania, provided by the National agency for mining heritage. The clay is dried at  $110^\circ\text{C}$ , crushed, pulverized and sieved at  $63 \mu\text{m}$ , and labelled Akjoujt before use. The chemical composition of Akjoujt clay was analysed using a PAN Analytical. Oxford-MDX1000 X-ray fluorescence (XRF) Spectrometer, X-ray Diffractograms (XRD) on Akjoujt powder were performed using a Bruker D8 Advance analytical XRD, with Cu-K $\alpha$  radiation. Infrared spectra are recorded between  $400$  and  $4000 \text{ cm}^{-1}$  using a Perkin Elmer 1000 FTIR Spectrometer. Scanning Electron Microscopy (SEM) was used to observe the Akjoujt clay texture. The Thermal Gravimetric Analysis (TGA), were run in a TGA/DSC3 Mettler Toledo, apparatus. The BET surface was measured by 3P Instrument model Micro 200 B. After drying in the oven at  $150^\circ\text{C}$  for 24 hours, the sample was degassed under vacuum at  $150^\circ\text{C}$ . The method is used to determine external surface area, pore volume and pore size. Analysis Center Innovation City, Sidi Ben Abdellahi University, Fez, Morocco.

### *Batch adsorption studies*

Metals ions (Au(I) Cu(II) and Zn(II)) batch adsorption using natural Akjoujt clay adsorbent was conducted in batch experiments. The effect of process conditions, mass effect ( $2\text{--}20 \text{ g/L}$ ), contact time ( $2\text{--}320 \text{ min}$ ), and effect of temperature ( $30\text{--}40^\circ\text{C}$ ) at pH ( $5.2\text{--}6.78$ ), which was put on an orbital shaker (orbital shaker Stuart) which was firstly regulated at  $180 \text{ rpm}$ .

. To assess the adsorption properties of the Akjoujt clay, the adsorption isotherms were conducted by changing the initial metal ions concentrations from  $5$  to  $80 \text{ mg/L}$ . The concentration of metals in solution was measured by using a flame atomic absorption spectroscopy Agilent Technologies 200 Series AA Spectrometer.

Equations (1), (2), and (3) express the adsorption uptake at equilibrium time ( $q_t$ ), equilibrium quantity ( $q_e$ ) in  $\text{mg/g}$ , and the percentage of removal (R %) respectively.

$$q_t = \frac{(C_i - C_t)V}{m} \quad (1)$$

$$q_e = \frac{(C_i - C_e)V}{m} \quad (2)$$

$$R (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

Where  $C_0$ ,  $C_t$  and  $C_e$  (mg/L) represent the concentrations of Au (I), Cu (II) and Zn (II) at the initial time, at the time  $t$ , and the equilibrium time, respectively.  $V$  is the solution volume (L) and  $m$  is the mass of Akjoujt clay adsorbent used (g).

## RESULTS AND DISCUSSION

### *Characterization of natural Akjoujt clay adsorbent*

The characterisation results for Akjoujt clay show in Fig. 1, a reflection at 14.2 Å corresponding to a (001) of a TOT 2:1 clay. The reflections at 10.6 Å, and 7.14 Å. corresponding respectively to illite and kaolinite. The diffractogram shows reflections at 3.33 Å and 4.26 Å related to the presence of an important quantity of quartz.

XRF was utilized to perform an elemental chemical analysis on the Akjoujt clay material used in this experiment; the findings are shown in Table 1. Chemical analysis, by XRF has shown that the sample is mainly constituted of silica and aluminum oxides. Higher content of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  together with total mass loss on ignition indicate higher content of clay minerals in the samples. The overall composition of the other oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{P}_2\text{O}_5$ ,  $\text{MnO}$ ,  $\text{ZrO}_2$ ,

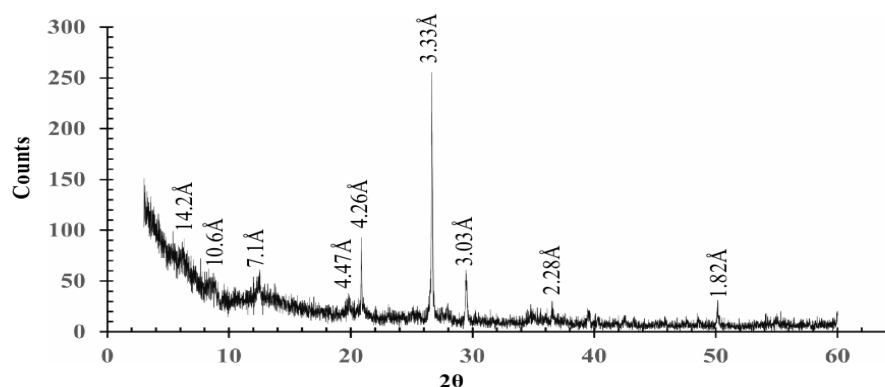


Fig. 1. X-ray diffractogram of Akjoujt powder clay

Table 1. Chemical composition of the Akjoujt clay

Components	Value (%)
$\text{SiO}_2$	72.75
$\text{Al}_2\text{O}_3$	10.30
$\text{Fe}_2\text{O}_3$	4.153
$\text{CaO}$	3.195
$\text{MgO}$	2.541
$\text{K}_2\text{O}$	1.184
$\text{Na}_2\text{O}$	0.7796
$\text{P}_2\text{O}_5$	0.0981
$\text{MnO}$	0.06695
$\text{TiO}_2$	0.5564
$\text{ZrO}_2$	0.07214

TiO<sub>3</sub>, MgO and K<sub>2</sub>O) reaches a percentage of 12.65 %, which shows that our clay is not pure.

FTIR spectra (Fig. 2) a dioctahedral character with Al-Al-OH vibrations bands at 3621 and 910 cm<sup>-1</sup>. The vibrations at 3691 and 700 cm<sup>-1</sup> are related to a kaolinitic clay. It shows a hydration bands at 3435 and 1638 cm<sup>-1</sup> (H-O-H). Quartz manifests as vibrations at 792 and 780cm<sup>-1</sup>. The presence of carbonation is confirmed by the small band at 1441cm<sup>-1</sup>.

The SEM were applied to detect the morphological structure of the natural Akjoujt clay sample, the obtained results are illustrated in Fig. 3, where the SEM image of the natural Akjoujt clay indicates the presence of a smooth surface within the material, characterized by a fine particle, and almost of a regular shape. The TGA thermogram (Fig. 4) shows mass loss (4.70%) between 69 and 151°C corresponding to loss of hygroscopic water. A second mass loss (3.18%) between 455 and 554°C, corresponding to the Akjoujt clay dihydroxylation.

The cation exchange capacity (CEC) is 11.81. The BET results shows that single point BET Surface Area (p/p<sub>0</sub> =0.2) and BET surface area are respectively 4.42 and 6.09 m<sup>2</sup>/g. The pore volume (adsorption/desorption (p/p<sub>0</sub> =0.99)) is equal to 0.013 cm<sup>3</sup>/g, and the average pore size is 8.86 nm.

### *Kinetic study*

Contact time is an important issue in adsorption, which is mainly an equilibrium process,

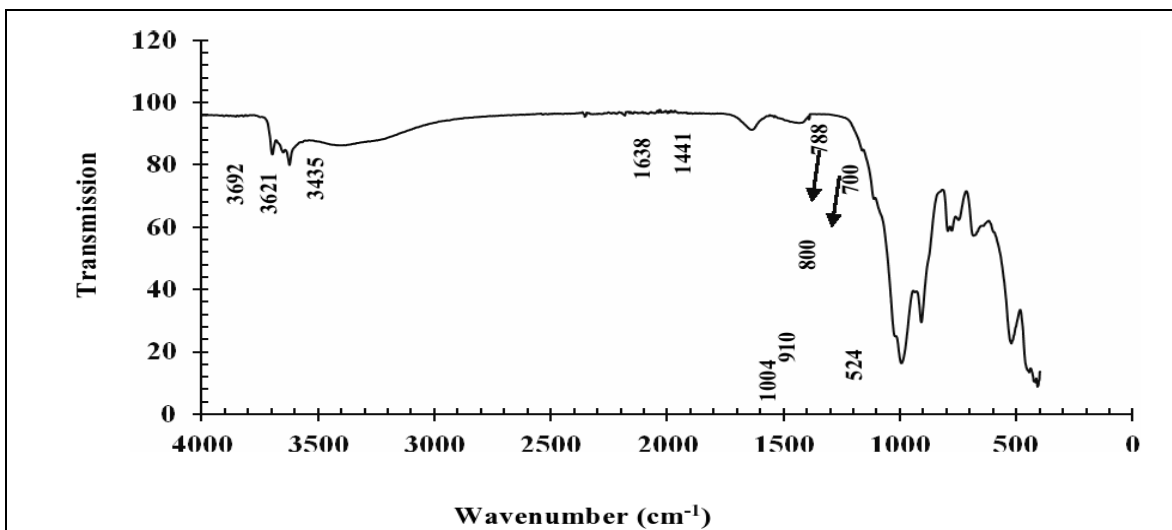


Fig. 2. Infrared spectra of the Akjoujt clay

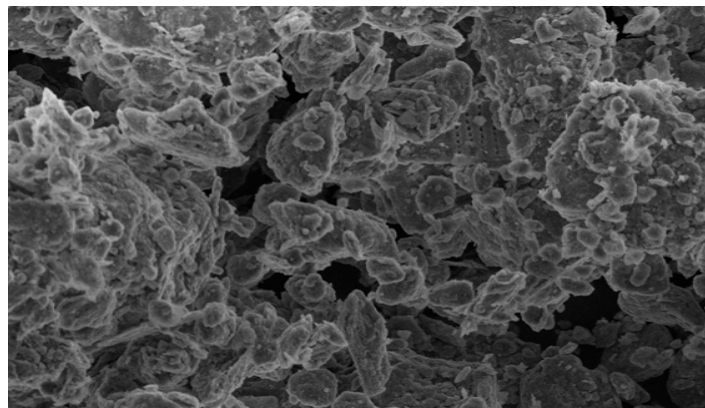


Fig. 3. SEM image of dried Akjoujt clay

and determining the equilibrium time is of real importance. The Figs. 5-7 shows the variations of the effect of the contact time on the removal efficiency (%) (a) of Au (I), Cu (II) and Zn (II), respectively.

The removal of Au (I), Cu (II) and Zn (II) by adsorption on clay was found to be rapid at the initial period of contact time and then to slow down with increasing in contact time. The equilibrium time of Au (I), Cu (II) and Zn (II) are respectively 240, 120 and 180 min. The initial faster adsorption rates may also be due to the presence of a large number of active sites

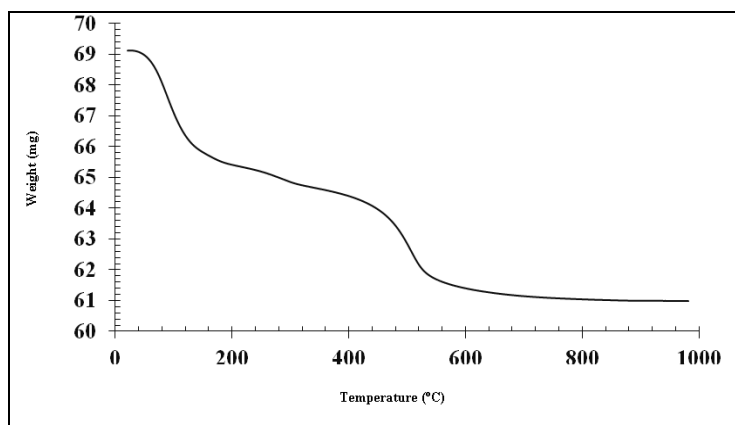


Fig. 4. Thermogram of Akjoujt clay

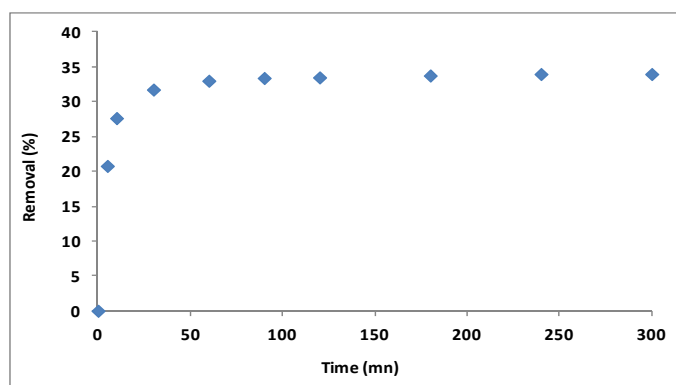


Fig. 5. Effect the contact time on the yield of Au (I)

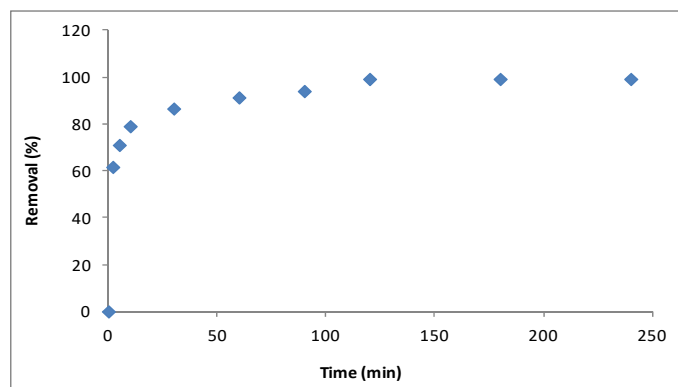


Fig. 6. Effect the contact time on the yield of Cu (II)

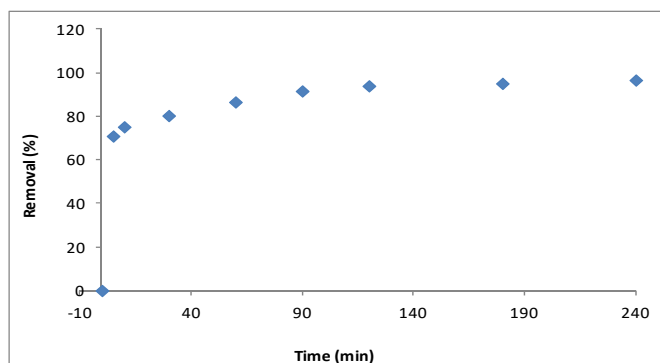


Fig. 7. Effect the contact time on the yield of Zn (II)

for adsorption and the slower adsorption rates at the end could be attributed to the saturation of the binding sites.

The kinetic study is very important in the adsorption study, which gives an idea of adsorbate uptake rate and efficiency of adsorption. The mechanism of adsorption depends upon the physical and chemical characteristics of the adsorbent as well as the mass transfer process. Several kinetic adsorption models were used to examine the mechanism and adsorption rate in the adsorption study. In this work the rate of adsorption in the solid phase (adsorbate) was obtained using the pseudo-first-order (PFO) which is usually applicable in the first minutes of the adsorption process. This model can be a monitoring step to the mechanism of adsorption. The non linear and linear forms of this model were represented by equation (4) and (5), respectively:

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad (4)$$

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (5)$$

The pseudo-second order (PSO) kinetic model predicted that the hypothesis of the rate-limiting step can be chemisorption, implying either an exchange or a valence force, through electron sharing between the adsorbate and the adsorbent. The non-linear and linear kinetics PSO model may be expressed by equation (6) and (7), respectively :

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (6)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where  $q_t$  is the amount of metal adsorbed per unit mass of clay adsorbent (mg/g) at time  $t$ ,  $k_1$  is the PFO rate constant (L/min),  $k_2$  ( $\text{gmg}^{-1}\text{min}^{-1}$ ) is the PSO rate constant for adsorption,  $q_e$  (mg/g),  $t$  is the contact time (min).

Figs. 8-10 shows the experimental equilibrium data and the predicted theoretical kinetics for the adsorption of Au (I), Cu (II) and Zn (II) by Akjoujt clay adsorbent. The parameters obtained from fitting of the PFO, and PSO models are listed in Table 2.

As seen in Table 2, the correlation coefficients ( $R^2$ ) obtained from PSO model were found to be higher than those of the PFO model. From the above results, it is evident that for all heavy metal ions studied in this study, the adsorption process followed the PSO model based on the assumption that the rate-limiting step may be chemical sorption. Similar results are reported by

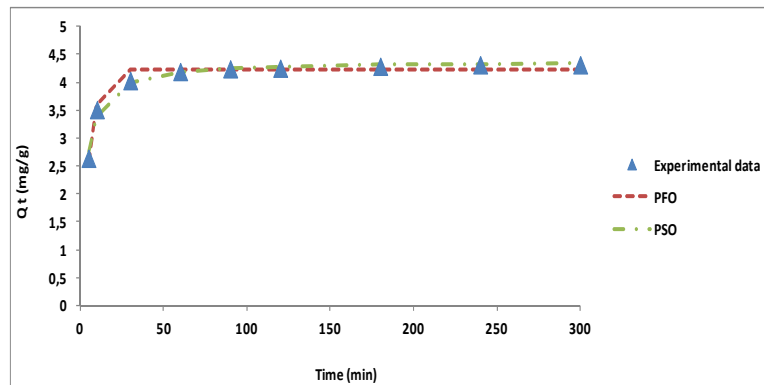


Fig. 8. PFO and PSO non linear for the adsorption of Au (I) by Akjoujt clay adsorbent

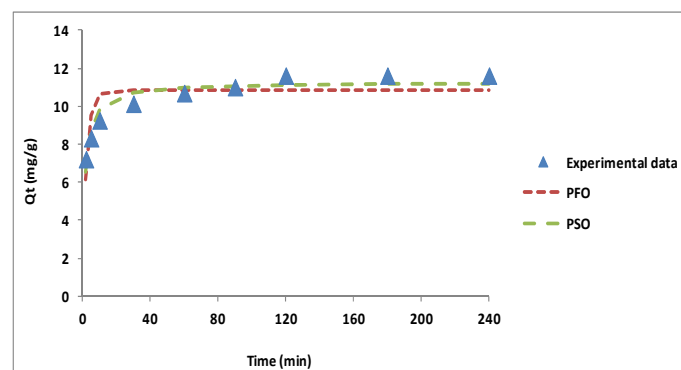


Fig. 9. PFO and PSO non linear for the adsorption of Cu (II) by Akjoujt clay adsorbent

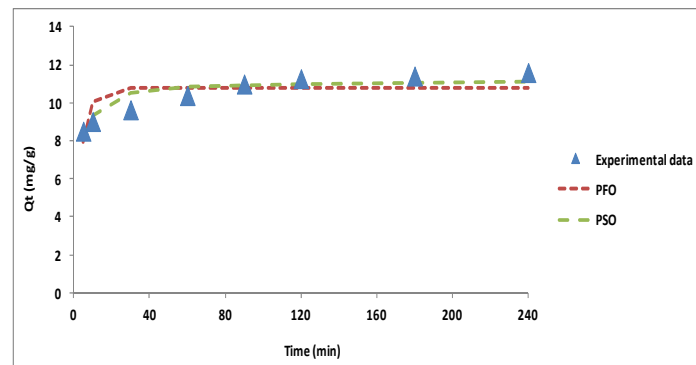


Fig. 10. PFO and PSO non linear for the adsorption of Zn (II) by Akjoujt clay adsorbent

other authors (Malima et al., 2021 ; Ghasemi et al., 2023).

On the other hand, the adsorbate transport from the solution to the surface of the Akjoujt clay adsorbent occurs in several steps. This phenomenon may be controlled by one or more steps such as film or external diffusion, pore diffusion, surface diffusion and adsorption on the pore surface, or a combination of more than one step through the adsorption process. The probability of intra-particle diffusion resistance affecting adsorption process have been explored by various researchers by using the intra-particle diffusion model (Andelescu et al., 2018).

#### *Adsorption isotherm*

Freundlich and Langmuir two parameter models are applied for the analysis of the

**Table 2.** PFO and PSO models constants for the adsorption of Au(I), Cu(II) and Zn(II) by Akjoujt clay adsorbent

Model	Parameters	Au (I)	Cu (II)	Zn (II)
PFO	$q_{exp}$	4.32	11.61	11.59
	$q_e$	4.23	10.81	10.79
	$K_1$	0.187	6.42	0.267
	$R^2$	0.975	0.658	0.764
PSO	$q_e$	4.38	11.24	11.17
	$K_2$	0.077	0.062	0.0459
	$R^2$	0.998	0.868	0.821

experimental data obtained for adsorption. A monolayer adsorption is defined by the Langmuir model upon the homogeneous surface of the adsorbent. The non linear and linear forms of Langmuir isotherm model can be symbolized as :

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (8)$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_e} + \frac{1}{K_L q_m} \quad (9)$$

Where  $q_e$ : amount of adsorbate adsorbed per unit mass of Akjoujt clay as a low-cost adsorbent (mg/g),  $K_L$ : Langmuir constant related (L/g),  $C_e$ : concentration of adsorbate in the solution at equilibrium (mg/L),  $q_m$ : maximum uptake per unit mass of Akjoujt clay as low cost adsorbent (mg/g). To characterize the Langmuir isotherm model, the separation factor  $R_L$  was utilized, which was calculated via equation (10):

$$R_L = \frac{1}{1 + K_L C_0} \quad (10)$$

The adsorption process is deemed unfavourable when  $R_L > 1$ , favourable when  $0 < R_L < 1$ , linear when  $R_L = 1$ , and irreversible when  $R_L = 0$ .

Multilayer adsorption is described by the Freundlich model upon the heterogeneous surface of adsorbent material. The non linear and linear forms of Freundlich isotherm model can be symbolized as :

$$q_e = K_F C_e^{1/n} \quad (11)$$

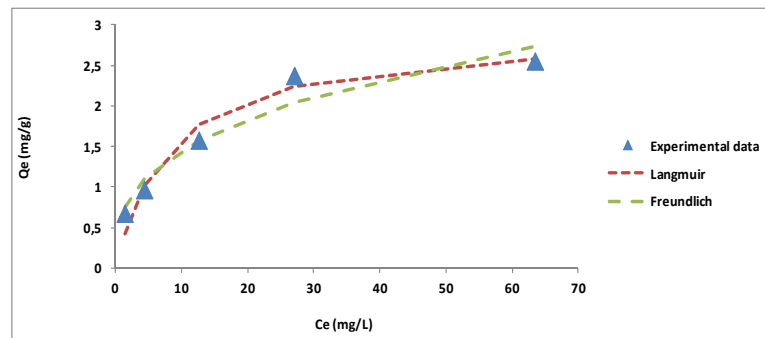
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (12)$$

Where  $K_F$ : Freundlich constant related to adsorption capacity (mg/g) (L/mg)<sup>n</sup> and 1/n: Freundlich constant related to adsorption intensity.

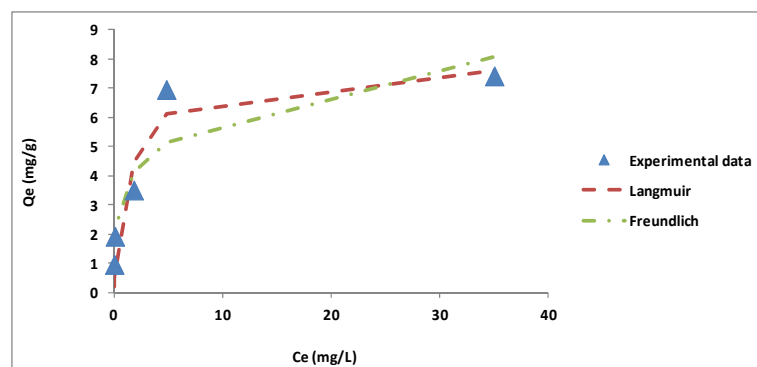
Figs. 11-13 shows the experimental equilibrium data and the predicted theoretical isotherms for the adsorption of Au (I), Cu (II) and Zn (II) by Akjoujt clay adsorbent. The parameters obtained from fitting of the Langmuir and Freundlich models are listed in Table 3.

Langmuir model is a better model to explain the adsorption isotherm based on  $R^2$  values. The Langmuir monolayer capacities adsorptions are 2.90, 7.93 and 6.45 mg/g for Au (I), Cu (II) and Zn (II) respectively. Additionally, the 1/n values fall within the range of 0-1, indicating favourable adsorption of Au (I), Cu (II) and Zn (II) by the Akjoujt clay adsorbent.

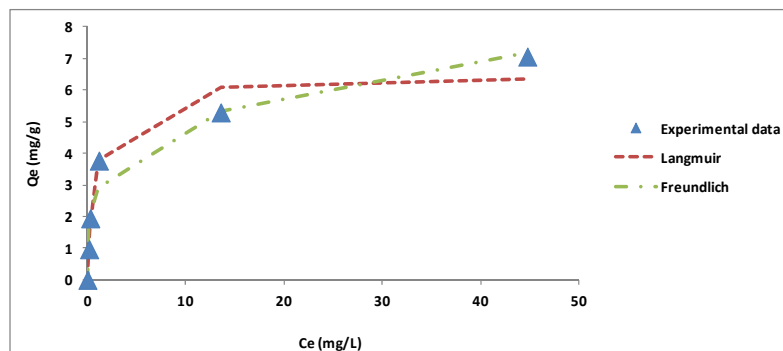
On the other hand, the separation parameters for the three metals are less than unity indicating that Akjoujt clay is an appropriate adsorbent for the three metal ions. The smaller  $R_L$  value indicates a highly favorable adsorption. The effectiveness of Akjoujt clay in the sorption of the



**Fig. 11.** Comparison between the experimental and predicted isotherms for the adsorption of Au (I) by Akjoujt clay adsorbent



**Fig. 12.** Comparison between the experimental and predicted isotherms for the adsorption of Cu (II) by Akjoujt clay adsorbent



**Fig. 13.** Comparison between the experimental and predicted isotherms for the adsorption of Zn (II) by Akjoujt clay adsorbent

three metals from aqueous system was  $\text{Cu(II)} > \text{Zn(II)} > \text{Au(I)}$ .

Table 4 displays the adsorption capabilities of different adsorbents documented in the literature for Au(I), Cu(II) and Zn(II) removal, facilitating comparison. These findings indicate that, compared with certain previously studied adsorbents, the natural Akjoujt clay adsorbent is notably more efficient at eliminating Au(I), Cu(II) and Zn(II) from aqueous solutions. Notably, the production of our natural Akjoujt clay adsorbent consumed less energy and involved no chemical modification, underscoring its environmentally friendly characteristics as an adsorbent, which poses no threat to human health.

#### *Comparison of adsorption capacity of Akjoujt clay with other available adsorbents*

Adsorption capacity of Akjoujt clay was correlates with other available adsorbents are

**Table 3.** Freundlich and Langmuir coefficients for adsorption of Au(I), Cu(II) and Zn(II) on natural Akjoujt clay

Metal ion	Freundlich			Langmuir			
	$K_F$	$1/n$	$R^2$	$q_m$	$R_L$	$k_L$	$R^2$
Au(I)	0.66	0.34	0.941	2.90	0.098	0.12	0.976
Cu(II)	3.61	0.23	0.864	7.93	0.019	0.71	0.911
Zn(II)	2.78	0.25	0.959	6.45	0.021	0.59	0.965

**Table 4.** Comparing the maximum adsorption capacities of different adsorbent types for removing Au(I), Cu(II) and Zn(II)

Adsorbents	SBET (m <sup>2</sup> /g)	Metal ions	$q_m$ (mg/g)	References
shell activated carbon	441	Cu(II)	48.64	Demirbas et al., 2009
Kaolinite	12.76	Zn(II)	4.95	Shahmohammadi et al., 2011
Kaolinite	12.76	Cu(II)	4.42	Shahmohammadi et al., 2011
Sepiolite	194	Zn(II)	0.265	Padilla-ortega et al., 2013
Vermiculite	15.2	Zn(II)	0.513	Padilla-ortega et al., 2013
date palm trunk	2.104	Cu(II)	25.25	Amin et al., 2016
Albizia lebbeck pods	34.07	Zn(II)	8.26	Mustapha et al., 2019
Albizia lebbeck pods	34.07	Cu(II)	8.68	Mustapha et al., 2019
Natural clay	...	Cu(II)	6.25	Es-Sahabanya et al., 2021
Natural Akjoujt clay	6.09	Au(I)	2.90	This work
Natural Akjoujt clay	6.09	Cu(II)	7.93	This work
Natural Akjoujt clay	6.09	Zn(II)	6.45	This work

indicated in Table 4. The comparison clearly showed that the adsorbent developed is much more effective for the removal of heavy metals from aqueous solution compared to some adsorbents previously reported. Although, there are many reported adsorbent with higher adsorption capacity towards heavy metals, they need complicated processes for the activation using acids and corrosives and are time consuming. It is important to note that the preparation of our clay adsorbent required less energy and has not undergone any chemical modification. Indeed, compared to other adsorbent such as shell activated carbon.

#### Thermodynamic parameters

The thermodynamic parameters are very important and contribute significantly to evaluate the adsorption process. These parameters  $\Delta H^\circ$  (kJ/mol),  $\Delta S^\circ$  (J/Kmol) and  $\Delta G^\circ$  (kJ/mol) are obtained using the equations (13), (14) and (15):

$$\Delta G^\circ = -RT \ln K_T \quad (13)$$

$$\ln(K_d) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (14)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

$K_d$ , represents the distribution coefficient of the adsorbate. T is the solution temperature (°K), and R (8.314J/mol/K) is the universal gas constant. The plot of  $\ln k_d$  vs  $1/T$  should be linear and will be used to define the thermodynamic parameters ( $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ ).

The thermodynamic parameters are listed in Table 5, where  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  values were obtained by plotting  $\ln K$  against  $1/T$  for the Langmuir data. The enthalpy results obtained show that the metallic ions are retained by an endothermic process. Indeed,  $\Delta H^\circ$  is equal 13.9, 22.52 and 21.46 kJ/mol for Au (I), Cu (II) and Zn (II) respectively. All entropy values are positive,

**Table 5.** Thermodynamic data's for adsorption of Au(I), Cu(II) and Zn(II) on Akjoujt clay

Metal ion	$\Delta H^\circ$	$\Delta S^\circ$	$\Delta G^\circ$ (kJ/mol)		
	kJ/mol	(J/(kmol))	303 K	308 K	313 K
Au(I)	13.90	105.11	17.43	18.22	19.12
Cu(II)	22.52	182.04	6.11	7.59	9.04
Zn(II)	21.46	168.81	4.21	6.02	7.98

indicating an increase in the disorder of the system. Similar findings were observed by (Wang & Zhang, 2021 ; Teġin et al., 2023).

## CONCLUSION

This research evaluated the potential of natural clay from Akjoujt in Mauritania as a low-cost adsorbent for the removal of Au (I), Cu (II) and Zn (II) from aqueous solutions. The results demonstrate that the adsorption process is well described by the pseudo-second-order kinetic model. The Langmuir monolayer adsorption capacities are 2.90, 7.93 and 6.45 mg/g for Au (I), Cu (II) and Zn (II) respectively. The thermodynamic calculations suggested the spontaneous nature of the adsorption process, along with the endothermic characteristics in all cases. As a result of this study, it may be concluded that Akjoujt clay may be used for removal of Au (I), Cu (II) and Zn (II) pollution from water since it is of low-cost, environmentally friendly, abundant and a locally available adsorbent. For to improve the retention capacity of Au (I), Cu (II) and Zn (II) from water and wastewater, the setting up of activation processes of the clay is necessary. For future studies, the usability of Akjoujt clay for Au (I), Cu (II) and Zn (II) removal from real water and wastewater will be tested and as comparison, a fixed bed column will be employed to investigate the effect of reactor design.

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## CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

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