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Ultrasound-assisted Adsorption of Copper from Aqueous Solution by using Natural Mauritanian Clay as Low-cost Adsorbent: A Preliminary Study

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Abstract

The aim of the present study concerns the feasibility of using natural Mauritanian clay for the removal of Copper from an aqueous solution. The proposed adsorbent was characterized by pH, moisture, bulk density, loss mass ignition, X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infra-Red Spectroscopy (FTIR), and Scanning Electron Microscopy (SEM). The effects of adsorbent mass and contact time were analyzed. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models and the results showed that the PSO model best described the adsorption kinetics. The adsorption equilibrium of Copper was described by Langmuir and Freundlich equations. 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^{-1}, respectively on a single layer. This study convinced that the Mauritanian clay is a promising adsorbent and could be an alternative, attractive, economic, and environmentally friendly adsorbent for Copper removal from aqueous solution via ultrasound-assisted adsorption.

Keywords: Ultrasound-assisted adsorption, Mauritanian clay, Kinetics, Isotherms, Adsorbent

1 Introduction

The industrial effluents which contain different derivatives of heavy metals are continuously discharging to the ecosystem and producing a significant toxic impact on the aquatic environment. Among the heavy metals, Copper is the major available type of heavy metal in the aquatic environment. The toxicological studies showed that the Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids, and DNA [1]. The excess copper compound in the body may also affect aging, schizophrenia, mental illness, Wilson's, and Alzheimer's diseases [2]. Copper has damaged the marine ecosystem and damaged the gills, liver, kidneys, the nervous system, and changing the sexual life of fishes [3]. The World Health Organization recommended a maximum acceptable concentration of Copper in drinking water less than 1.5 mg L^{-1} [4]. It is therefore important to remove excess Copper in industrial effluents before charging it into surface water and groundwater, for the protection of human health and the environment [5].

Many specialized processes have been developed for the removal of copper and other metals from water. These unit operations include: chemical precipitation and ion exchange [6], chemical versus electrocoagulation [7], solvent extraction [8], complexation [9], electrochemical [10], bioelectrochemical [11], biological [12], filtration [13], membrane processes [14] and adsorption [15]. However, one of the innovative technologies used in combination with adsorption is sonication. Ultrasonics is found efficient for removing a variety of pollutants in wastewater with less cost and environmentally safe byproducts [16]. The cavitation mechanism generates convection in the media via microstreaming, microturbulence, acoustic waves, and microjets. Further, it increases the mass transfer rate by reducing diffusion resistance [17]. These effects have been found to enhance adsorption processes. Few recent reports indicated a synergic effect of the ultrasound and adsorption process using a range of pollutants and adsorbents [18-20]. The use of ultrasound assists in the adsorption process and was found effective to control the concentration of pollutants. Furthermore, the process was found to be an economically viable alternative to conventional techniques in terms of reduced chemical utilization and associated environmental impacts. Recently, many materials have been investigated to determine their adsorption capacity for Copper such as fly ash [21], wheat shell [22], spent activated clay [23], lentil shell [24], wheat shell [24], rice shell [24], inactive biomass [25], kaolinite [26] and treated rice husk [27]. Therefore, the

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major drawback of this kind of adsorbents is their high-cost, complicated processes for the activation using acids and corrosives and are time-consuming.

However, the development of cost-effective adsorbent materials with greater efficiency for the removal of aquatic pollutants is highly needed. Therefore, in this study, we aimed to investigate an effective, easy and rapid approach to valorize the clay into environmentally friendly adsorbents. Then, the adsorption efficiency of Copper on natural and available Mauritanian clay was evaluated using the ultrasound-assisted adsorption batch operation. The characteristic investigations of Mauritanian clay adsorbent were examined by pH, moisture, bulk density, loss mass ignition, X-Ray Fluorescence (XRF), X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR), and Scanning Electron Microscopy (SEM). The effects of contact time and adsorbent mass on the adsorption efficiency of Copper were studied. The kinetics of Copper adsorption on Mauritanian clay was analyzed by Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. Experimental equilibrium data were fitted to the Langmuir and Freundlich isotherm equations to determine the best-fit isotherm equation.

2 Material and methods

2.1 Copper preparation and analysis

The standard solution containing 1,000 mg L^{-1} of Copper was used as given by the Chinese Cooperation in Mauritania. Copper solutions were prepared by diluting the standard solution of Copper to the desired concentrations in distilled water. The concentrations of Copper in the solutions before and after adsorption were determined using an Atomic Absorption Spectroscopy PGG 990.

2.2 Preparation and Characterization of clay

The raw clay was taken from Hassi El Ebyed in Moughataa of M'Bout, Wilaya of Gorgol, in Mauritania. The sample was grounded, sieved of the sample powder (< 100 μm), drying in the oven for 24 hours at 60 °C, and used as without any pretreatment (Figure 1).

Figure 1: Aspect of used natural Mauritanian clay

The pH, moisture, bulk density, and loss mass ignition are determined by described methods [28]. The proposed adsorbent was characterized using several techniques such as XRF, XRD, FTIR, and SEM.

2.3. Batch experiments

The various doses consisting of 0.5 to 3 g/50 mL of the Mauritanian clay are mixed with the copper at 1 mg L^{-1} at pH 6.8. To investigate the effect of contact time on Copper removal by adsorption, 1.5 g of Mauritanian clay was added to 50 mL of Copper at 1 mg L^{-1} at pH 6.8. Adsorption isotherms were obtained by varying the initial Copper concentration from 2.5 to 100 mg L^{-1} at pH 2, 6.8, and pH 9. In all sets of experiments were sonicated in an ultrasonic bath HS3120 Benchtop Cleaners. At the end of each experiment, the sonicated solution mixture was microfiltered and the residual concentration of Copper was determined by Atomic Absorption Spectroscopy PGG 990. The adsorption uptake at equilibrium time, q_e, and the percentage of the removal R (%) was expressed by equations (1) and (2), respectively:

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

$$\text{R}(\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (2)$$

where q_e is the amount of Copper adsorbed by Mauritanian clay (mg g^{-1}), C_i is the initial Copper concentration (mg L^{-1}), C_e is the Copper concentration at equilibrium (mg L^{-1}), V is the solution volume (L) and m is the mass of Mauritanian clay used (g). All batch experiments were conducted in triplicate and the mean values are reported. The Sum of the Squares of the Errors (SSE) and correlation coefficient (R^2) analysis is used to fit experimental data with kinetic and isotherm using the Excel Solver determined by following equations (3) and (4), respectively:

$$\text{SSE} = \left(q_{\text{exp}} - q_{\text{mod}}\right)^2 \quad (3)$$

$$\text{R}^2 = 100\left(1 - \frac{\left\|q_{\text{exp}} - q_{\text{mod}}\right\|^2}{\left\|q_{\text{exp}} - q_{\text{avr}}\right\|^2}\right) \quad (4)$$

where q_{exp} (mg g^{-1}) is equilibrium capacity from the experimental data, q_{avr} (mg g^{-1}) is equilibrium average capacity from the experimental data, and q_{mod} (mg.g^{-1}) is equilibrium from the model. So that $R^2 \leq 100$ – the closer the value is to 100, the more perfect is the fit.

3 Results and discussion

3.1 Characterization of clay adsorbent

The physicochemical results showed pH of 7.95, a low moisture content of 1.49 %, bulk density of 0.83 g $mL^{-1,}$ and loss on ignition of 30.11 %. From XRF analysis the oxide content was stated as: SiO_2: 42.1 %, Al_2O_3: 18.6 %, Fe_2O_3: 5.96 %, TiO_2: 1.30 %, SO_3: 0.22 %, K_2O: 0.18 %, MgO: 0.15 %, P_2O_5: 0.12 %, CaO: 0.081 %, Na_2O: 0.051 % and MnO: 0.013 %. These results showed that the predominant constituents are Silica and Aluminium oxide and other elements in minor quantities such as iron, titanium, sulfate, potassium, magnesium, phosphor, calcium, sodium, and manganese oxides considered as impurities.

Figure 2 shows the FTIR spectrum of the Mauritanian clay. The result of the FTIR study of Mauritanian clay adsorbent showed absorption peaks located 3671, 3613, 3504, 1537, 946, 819, 744, 721, 626, 487and 437 cm^{-1}. Most of the bands such as 3671 cm^{-1}, 3613 cm^{-1}, 3504 cm^{-1}, 947 cm^{-1}, 819 cm^{-1}, 744 cm^{-1}, and 487 cm^{-1} show the presence of kaolinite. The Si–O stretching vibrations were observed at 744 cm^{-1}, 721 cm^{-1}, 487 cm^{-1}, and 437 cm^{-1} showing the presence of quartz [29].

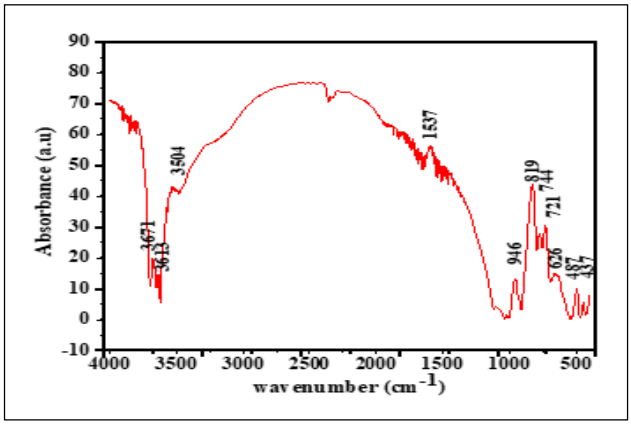

Figure 2: FTIR Spectrum of the studied clay

The XRD for the Mauritanian clay adsorbent is shown in Figure 1S (in supplementary material). The results reflect that the studied clay fraction consists mainly of kaolinite and Quartz. SEM slide of the studied clay revealed the presence of the silica (Figure 2S in supplementary material) as confirmed by XRF and FTIR. The surface features of Mauritanian clay are regular with homogeneous morphology.

3.2 Effect of adsorbent dosage

The effect of the amount of Mauritanian clay on the efficiency of adsorption was also studied. Variation of doses in the range 0.5–3 g at a fixed Copper concentration (1 mg L^{-1}) for Copper removal by Mauritanian clay is shown in figure 3.

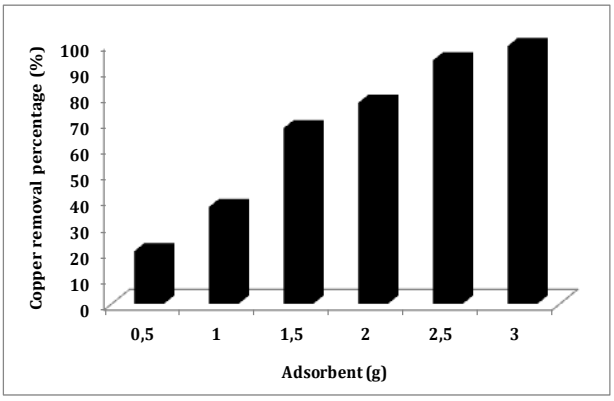

Figure 3: Effect of the studied clay dosage on Copper removal percentage

The results suggest that the increase in the dose of clay adsorbent increases adsorption, probably due to an increase in the retention surface area, pores, active sites, and the number of unsaturated sites [30]. The optimal Mauritanian clay adsorbent dose obtained is 1.5 g.

3.3 Effect of contact time

The contact time between the Copper and Mauritanian clay adsorbent has a strong effect on the adsorption process. Figure 4 shows adsorption for contact time on the surface of Mauritanian clay adsorbent. The Copper removal efficiency increased from 59.6 % to 67.8 % when contact time increased from 10 to 40 min. The percentage removal efficiency of clay increases with increasing the contact time and reached equilibrium within 40 min. The same results were reported by other investigators [31; 32] who found that the equilibrium time clays were short.

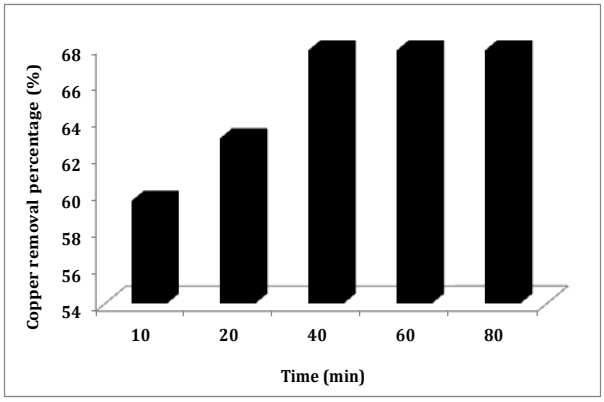

Figure 4: Effect of contact time on copper adsorption on the studied clay

3.4. Kinetic Study

To estimate the adsorption mechanism can be considered as a physical or chemical mechanism, PFO and PSO models were applied to investigate the adsorption data [33]. The nonlinear kinetics PFO and PSO models may be expressed by (5) and (6), respectively:

$$q_t = q_e(1-\exp^{-k_1 t}) \quad (5)$$

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

where q_t is the amount of Copper adsorbed per unit mass of Mauritanian clay (mg g^{-1}) at time t, k_1 (L min^{-1}) is the PFO rate constant, k_2 (mg $g^{-1}min^{-1}$) is the PSO rate constant for adsorption, q_e (mg g^{-1}) the amount of Copper adsorbed at equilibrium and t is the contact time (min). Figure 5 shows the experimental data and the predicted theoretical kinetics for the adsorption of Copper onto Mauritanian clay for 1 mg L^{-1}. The values of model parameters q_e, k_1, k_2, SSE, and R^2 are presented in Table 1.

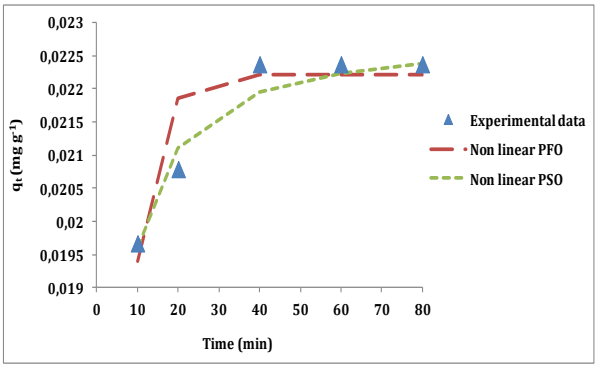

Figure 5: PFO and PSO kinetics model of Copper adsorption by the studied clay

Table 1: Non-linear kinetic models parameters

Model	Parameters	Values
PFO	q_{exp}	0.022
	q_e	0.022
	K_1	0.20
	SSE	1.34
	R^2 (%)	81.37
PSO	q_e	0.023
	K_2	26.4
	SSE	0.35
	R^2 (%)	97.6

These results demonstrate that the PSO model displays a more satisfactory correlation in comparison with the PFO model for the adsorption of Copper, suggesting that the adsorption process was predominantly controlled by chemical reactions between the Copper and the adsorption sites of the Mauritanian clay adsorbent [34].

3.5. Adsorption isotherm

To evaluate the efficacy of the adsorption process, two adsorption models, namely, Langmuir and Freundlich's models were employed. A monolayer adsorption is defined by the Langmuir model upon the homogeneous surface of the adsorbent [35] and represented as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (7)$$

where q_e is the amount of Copper adsorbed per unit mass of clay adsorbent (mg g^{-1}), k_L is the Langmuir constant related to the adsorption capacity (L g^{-1}), C_e is the concentration of Copper in the solution at equilibrium (mg L^{-1}), q_m is the maximum uptake per unit mass of clay adsorbent (mg g^{-1}). The factor of separation of Langmuir, R_L, which is an essential factor characteristic of this isotherm is calculated by equation (8):

$$R_L = \frac{1}{(1 + k_L C_0)} \quad (8)$$

where C_0 is the higher initial concentration of Copper and K_L is the Langmuir constant. The R_L value implies the adsorption to be unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0). A multilayer adsorption is described by the Freundlich model upon the heterogeneous surface of adsorbent material [35] and illustrated as in equation (9):

$$q_e = K_F C_e^{1/n} \quad (9)$$

where K_F (mg g^{-1}) (L mg^{-1}) ^{n} and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The isotherms constants related to Langmuir and Freundlich's models determined from the plots shown in Figures 6 and 7 are listed in Table 2.

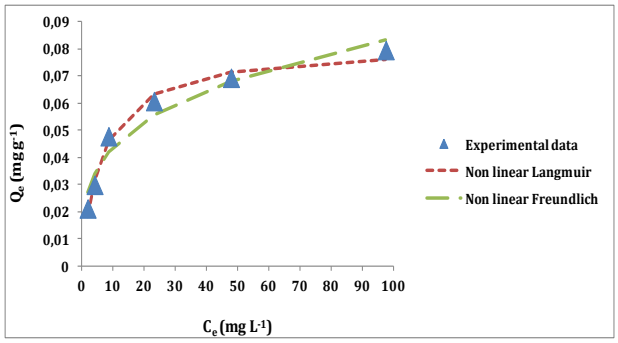

Figure 6: non-linear Langmuir and Freundlich for the studied clay at pH 6.8

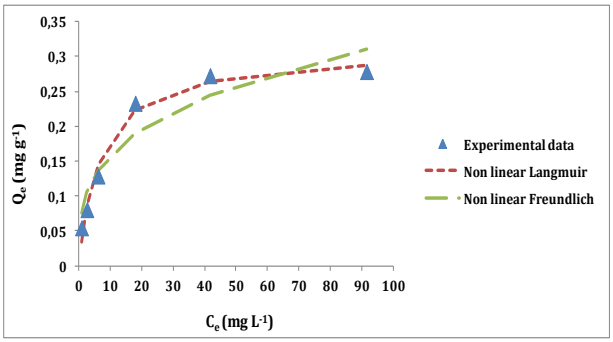

Figure 7: non-linear Langmuir and Freundlich for the studied clay at pH 9

Table 2: Non linear isotherm model parameters

Model	Parameters	pH=6.8	pH=9
Langmuir	q_m	0.081	0.310
	K_L	0.15	0.14
	R_L	0.063	0.067
	SSE	3.8 10^{-5}	0.0009
	R^2 (%)	98.5	98.1
Freundlich	n	3.52	3.28
	K_F	0.023	0.078
	SSE	1.3 10^{-4}	0.005
	R^2 (%)	94.9	90.2

The results compiled in Table 2 indicate that the Langmuir model fitted very well to the experimental data, showing high R^2 values and low SSE values compared to Freundlich isotherm. Langmuir model describes the homogenous distribution of active site with monolayer adsorption of Copper onto Mauritanian clay. The maximum adsorption capacities, q_m, for Copper on

Mauritanian clay adsorbent at pH 6.8 and pH 9 were found to be 0.081 and 0.31 mg g^{-1}, respectively. The high adsorption of Copper obtained at pH 9, could be attributed to the electrostatic attraction between Copper ions and negatively charged surface sites (reaction) (I):

$$\text{Clay Surface-OH} + H_2O \longrightarrow \text{Surface } -O^- + H_3O^+ \quad \text{(I)}$$

However, at pH 2 (in a very acidic medium), the q_m is almost zero. This could be attributed to the electrostatic repulsion between Copper ions and positively charged surface sites (reaction) (II):

$$\text{Clay Surface-OH} + H_3O^+ \longrightarrow \text{Clay Surface-}OH_2^+ + H_2O \quad \text{(II)}$$

The values of R_L and K_L are in between 0 and 1 indicates the favorability of the adsorption of Copper onto Mauritanian clay adsorbent. The magnitude of the exponent n indicates the favorability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics. The studied natural Mauritanian clay is a good adsorbent for Copper (n > 2) (table 2). A comparison of q_m for Copper using different adsorbents which are previously reported was performed and presented in Table 3. 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. Although there are many reported adsorbents with higher adsorption capacity towards Copper, 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.

Table 3: Comparison of maximum adsorption capacities of various types of adsorbents for Copper removal

Adsorbent	q_m (mg g^{-1})	References
N(2-Carboxybenzyl) grafted chitosan	0.027	[36]
Untreated fruit peel	0.137	[37]
Sugar beet pulp	0.15	[38]
Palm shell activated carbon	0.228	[39]
Treated fruit peel	0.486	[37]
Modified Gmelina arborea leaves	3.971	[40]
Natural Mauritanian clay	0.081 at pH 6.8	present study
Natural Mauritanian clay	0.31 at pH 9	present study

4 Conclusions

To conclude, the ultrasound-assisted adsorption of Copper from an aqueous solution using natural Mauritanian clay has been studied in a batch system. The results obtained indicate that the Langmuir model fitted well with the experimental data and was used to estimate the model parameters. Adsorption kinetics followed the PSO model. The Mauritanian clay showed a good Copper adsorption capacity compared to other adsorbents. It can be, therefore, concluded that this Mauritanian clay, without any treatment, could be a promising adsorbent for Copper removal from the water via ultrasound-assisted adsorption.

Ethical issue

Authors are aware of and comply with, best practices in publication ethics specifically concerning authorship (avoidance of guest authorship), dual submission, manipulation of figures, competing interests, and compliance with policies on research ethics. Authors adhere to publication requirements that submitted work is original and has not been published elsewhere in any language.

Competing interests

The authors declare that no conflict of interest would prejudice the impartiality of this scientific work.

Authors' contribution

Abdoulaye Demba N'diaye: Investigation, Writing – original draft, Methodology. Mohamed Abdallahi Bollahi: Resources-Review & Editing. Mohamed Sid'Ahmed Kankou: Methodology, Resources- Review & Editing.

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