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Synthesis of Surfactant-Supported Algerian Clay for the Adsorption of Ni (II) in Water Media

Zahra Fedlaoui[1]*, Mahmoud Charef[1], Abdelkader Ouakouak[2,3], Mohamed Benabdallah Taouti[1]

[1] *Laboratory of Physical-Chemistry of Materials LPCM, University of Laghouat, ALGERIA*
[2] *Hydraulic and Civil Engineering Department, University of El Oued, ALGERIA*
[3] *Research Laboratory in Subterranean and Surface Hydraulics, University of Biskra, ALGERIA*

*Corresponding Author: minatasnim08@gmail.com
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Clay, surfactant, adsorption, nickel, wastewater

Abstract

The purpose of this research is to prepare HDTMA-modified Algerian clay (HDTMA-Ac) and examine its ability to adsorb ions of nickel in water media. Characterization techniques such as X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis (TGA), and the point of zero charges (pH_{pzc}) were used to analyse the sample properties. The adsorption capacity of HDTMA-Ac towards Ni (II) ions was investigated under several operating conditions, such as pH and initial concentration of Ni (II). Results showed that the raw clay was successfully modified by intercalation of the surfactant ions in the interlayer space of clay. The maximum removal efficiency of Ni(II) on HDTMA-Ac was found to be 95.71, 84.47, 72.82 and 79.29 % (at pH≈7), respectively, for initial concentrations of 10, 100, 200, and 300 mg/L. The pseudo-second-order model well described the adsorption kinetics of Ni(II). The Langmuir isotherm provided the best fit to the experimental data with a maximum monolayer adsorption capacity of 59.6 mg/g. The findings of this work suggest the potential of the produced HDTMA-Ac material that can be used to remove toxic metals from wastewater.

1. Introduction

Environmental pollution has resulted from rapid industrial growth and a massive increase in the global population[1-3]. Heavy metals are a type of pollution that has a negative impact on the environment. Because of their extreme toxicity and proclivity for bioaccumulation in the food chain, even at relatively low concentrations, heavy metals are a major source of concern in the environment [4], [5]. The US Environmental Protection Agency (USEPA) compiled a list of organic and inorganic pollutants found in wastewater that pose a serious health risk in 1978. Arsenic, antimony, chromium, copper, beryllium, cadmium, lead, silver, mercury, zinc, selenium, thallium, and nickel are among the thirteen metals mentioned in this list [6]. Metal plating, mining, electroplating, metal finishing, paper manufacturing, paint, and leather tanning are just a few of the industries that discharge heavy metal-contaminated wastewater into the environment. For this reason, wastewater contaminated with heavy metals must be treated before being discharged[7-9]. Nickel is a highly toxic metal that can be found in waste. Nickel salts are widely used in metal plating, with concentrations ranging from 3.40 to 900 mgL^{-1} in industrial

wastewater [10]. Nickel's long-term toxicity to humans and the environment is well documented, and high nickel concentrations are linked to lung and bone cancers [11].

Chemical sedimentation, solvent extraction, membrane filtration, dialysis/electrolysis, reverse osmosis, ion exchange, flotation, and adsorption are just a few of the methods that have been used to remove heavy metals from wastewater [5], [12], [13]. Of these, the adsorption method is the most commonly used, and several studies have identified several low-cost adsorbents [3]. The application of clay minerals as adsorbents has attracted much attention in recent years owing to their natural abundance, high specific surface area, layered structure, and large ion exchange capability [14]. In soils, sediments, and deposits, they are mainly phyllosilicate minerals with particle sizes of less than 2 μm. Their structure is similar, consisting of layered units with one or two tetrahedral silica sheets attached to an octahedral aluminium sheet, which is primarily bonded together in 2:1 (T-O-T) and 1:1 (T-O) proportions [15]. According to Bergaya *et al.* [16], the octahedral aluminium sheet is formed of $Al_2(OH)_6$ units, whereas the tetrahedral silica sheet is composed of $Si_2O_6(OH)_4$ units. Based on the structure, the clay minerals can be classified as 1:1 type layer (kaolinite), 1:1 type tube (halloysite), 2:1 type layer (montmorillonite, bentonite, smectite, etc.) and 2:1 type layer-chain type (attapulgite, sepiolite), etc. [17].

The instability of clay charge is caused by isomorphic substitution, chemical bond breaking at the edge, and the replacement of hydrogen (H^+) with hydroxyls (OH^-), which causes ion adsorption to stabilise the structure. The cation exchange capacity (CEC), which is measured in mEq per 100 g of clay, is used to determine the number of ions exchanged in clay. CEC allows for chemical modification of clay [2],[18], which can occur via a reaction of cations in an aqueous solution without changing the crystalline structure of the clay plasticity [19], [20]. Clay is modified in a variety of ways to increase its adsorption capacity, including processing with inorganic and organic compounds, acids, and bases, as well as heat treatment [2], [21]. Many studies have investigated their increasing adsorption capacity for organic contaminants. They reported that the adsorption of various organic compounds by clay minerals has been greatly improved by replacing the natural inorganic interlayer cations with certain organic cations such as quaternary ammonium cations (QACs), which may be represented as $[(CH_3)_3NR]^+$, or $[(CH_3)_2NR_2]^+$ where R is a relatively short hydrocarbon substituent group [22]. The aluminosilicate sheets of common clay minerals possess a net negative electrical charge compensated for by inorganic exchange cations (e.g. Na^+ and Ca^{2+}), which are strongly hydrated in the presence of water. Surface properties of natural clays can be modified by simply ion exchange with organic cations. By introducing cationic surfactant molecules into the interlamellar space through ion exchange, the properties of clay minerals are enhanced to those of organoclays [18]. The intercalation of a cationic surfactant between the clay layers changes the surface properties from highly hydrophilic to increasingly hydrophobic. In addition, modification of the swelling clay with a cationic surfactant results in an increase in the basal spacing of the layer and exposure of new sorption sites of clays [14], [23].

The present research aims at investigating new Algerian illitic-kaolinitic clay (R-Ac) as raw material and its modification by the Hexadecyltrimethylammonium $CH_3(CH_2)_{15}N(CH_3)_3Br$ ($HDTMA^+$) surfactant to get in new adsorbent (HDTMA-Ac). The raw clay (R-Ac) and modified clay (HDTMA-Ac) samples were characterized by diffraction of X-rays (XRD), Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and the pH of point of zero charge (pH_{PZC}). In batch mode, several parameters were investigated to understand better the adsorption process of Ni (II), including stirring duration, pH, and initial Ni (II) concentration. The modelling of experimental data was also investigated here.

2. Materials and Methods

2.1 Chemical

Solutions of Ni (II) were prepared by diluting 1 g/L of Ni $(NO_3)2{\cdot}6H_2O$ stock solution from Sigma Aldrich with deionised water to the desired range of concentrations from 10 to 300 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value using diluted and concentrated HCl and NaOH solutions of analytical grade purchased from Sigma Aldrich, respectively. Because only small adjustments in the final equilibrium pH were noticed, the pH was assumed to be constant during the uptake. The bromide salt of Hexadecyltrimethylammonium $CH_3(CH_2)_{15}N(CH_3)_3Br$ ($HDTMA^+$), a cationic surfactant by Sigma Aldrich with molecular weight 364.45 g/mol, is used to make organo-clay.

2.2 Preparation of Homo-ionic Clay

The raw clay samples (R-Ac) used in this work were obtained from 30 kilometres west of Laghouat (Algeria) , we chose these samples from this region because it is found in abundance, has not been studied yet and to know its characterization and properties and its ability to trait pollutants from wastewater. The conductometric titration method was used to estimate the cation exchange capacity (CEC) of the used clay, which was 40 meq/100 g. A natural Algerian clay (Ac) consisting mainly of inter-stratified illite-kaolinite (I-k) with minor phyllosilicate, dolomite, quartz, and calcite impurities identified by X-ray diffraction was used in this work. For the experiments, 120 g of the raw clay (R-Ac) was ground and sieved at a particle size of less than 80 μm, then washed three times

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with deionised water. Then, it was mixed with 1 M of NaCl for 24 hours [24], and the procedure was repeated three times. The mixture was dialysed in deionised water until the chloride was free to obtain homo-ionic clay. Finally, the inferior of a 2 µm-sized fraction was recovered using sedimentation in deionised water, drying at 65°C, and grinding [25]. The obtained purified clay was noted as Na-Algerian clay (Na-Ac).

2.3 Preparation of Organo-clay

HDTMA-modified Algerian clay (HDTMA-Ac) was prepared according to the batch procedure described by Maghni *et al.* [26]. The molar ratio of HDTMA to the CEC of Na-Ac was set to 1.0.

10 g of Na-Ac were mixed with 500 mL of HDTMA surfactant solution with an initial concentration of 1.0 CEC (0.1M of HDTMA was a mixture with 1000mL of HCl (1M) at 80°C); after 3 hours of stirring, we added Na-Ac in this solution. At a natural pH of 5–6, the flasks were stirred for 24 hours on a mechanical shaker at 2700 rpm. The HDTMA-modified Algerian clay prepared by Na-Ac, denoted as HDTMA-Ac, was separated from the suspension by sedimentation, then it was washed with deionised water several times and dried at 80°C [27],[25],[28].

2.4 Characterization

Batch equilibrium experiments were utilised to determine the point of zero charge (pH_{pzc}) of the samples that were prepared, which was measured using the technique published in the literature by[28],[29]. HCl or NaOH were used to modify the pH values (pH_i) of 50 ml of aqueous solutions to a range of 2–12. After that, a mass of 0.05 g of HDTMA-Ac was added to each sample. The dispersions were agitated at room temperature for 48 hours before being filtered by filter paper, and the final pH of the solutions (pH_f) was measured. The cationic exchange capacity (CEC) of the R-Ac was determined using a conductometric method. The process for determining CEC is described in detail elsewhere [30]. The adsorbents were analysed using an FT/IR-4200; JASCO with a resolution of 4 cm^{-1} was carried out on KBr pellets in the range of 4000–400 cm^{-1}. The KBr pellets were prepared by combining clay with KBr at a 1 wt.% concentration. A diffractometer of type PHILIPS X'PERT in shape 0/2θ was used to record the spectrum of diffraction of X-rays (DRX) of powder, which was accomplished systematically. Using the K_n α line with a wavelength of 1.5406 Å, the diffractometer is fitted with a copper anticathode. The acquisition settings are a 2θ angle varying from 5 to 50° per step of 0.016 with a 0.5-second accumulation per step. The thermogravimetric analysis (TGA) was performed using a Mettler-Toledo GMBH mod TGA/DSC1 with an FRS5 sensor and a microbalance with a precision of 0.1 g. The samples were heated in a nitrogen atmosphere between 30 and 1000°C at 10°C/min. The atomic absorption spectroscopy (AAS) model of the Perkin–Elmer atomic absorption spectrophotometer assisted by a microcomputer (Model Jena) was used to measure the concentration of Ni (II) in samples.

2.5 Adsorption Studies

Batch equilibrium adsorption tests were carried out. The influence of pH (1–7) and initial concentration of Ni (II) C_0 (10, 100, 200, and 300 ppm) was examined. A few drops of dilute NaOH or HCl (0.1M) were used to adjust the initial pH. The isotherms were examined from 10 to 260 ppm of initial concentrations of Ni (II) at room temperature (T = 24 ± 1°C) and the optimal pH of the dispersion.

0.025 g of HDTMA-Ac was added to 25 mL of Ni (II) solution and agitated at 150 rpm. The clay was extracted and centrifuged after each period of contact for kinetic investigations, and at equilibrium time for isotherm studies, the clay was removed and centrifuged [22]. The residual Ni (II) concentrations were analysed using the atomic absorption spectrophotometer model Perkin–Elmer. The quantity of Ni (II) adsorbed was obtained from the initial and final concentrations of Ni (II) in the liquid phase. The following equations (1) and (2) were used to evaluate Ni (II) adsorption by HDTMA-Ac adsorbent [26]:

$$q_t = (C_0 - C_t).\frac{V}{m} \quad (1)$$

$$q_e = (C_0 - C_e).\frac{V}{m} \quad (2)$$

C_0 is the initial concentration (mg/L), and Ct and Ce are the liquid-phase concentrations of Ni (II) at equilibrium and any time t (mg/L), respectively. V is the volume of solution (mL) and is the mass of adsorbent used (g).

Adsorption experiments for the effect of pH were conducted using a solution with 20 ppm of Ni (II) concentration with an HDTMA-Ac dosage of 1g/L and stirring for 1 hour, with pH adjusted from 1 to 7. In this study, the contact time was varied from 2 to 90 min, the optimum pH of solutions was also studied, the initial nickel concentration varies from 10 to 300 ppm, and the amount of HDTMA-Ac adsorbent is 1g/L.

3. Results and Discussion

3.1 Characterization of the Clays

Fig. 1 shows the FTIR spectra of the samples Na-Ac and HDTMA-Ac. The main characteristic bands of these clays are as follows: The bands at 3612 cm-1 and 3442 cm-1 are very wide bands that correspond to the vibration of the OH group of the octahedral layers of aluminum atoms in hydroxyl form (Al-O-H) [31], [32]. The bands of 2929 cm-1 and 2844 cm-1 are characteristic of carbonate compounds. At 1631 cm-1, it is attributed to the deformation vibrations of the O-H band of the constitutional water [33], [34]. The wide band at 1030 cm-1 corresponds to the vibrations of the valence of the Si-O band, which is characteristic of aluminosilicates [35]. At 776 cm-1 is the characteristic of the C-O of calcite (CaCO3) [36]. Then, at 689 cm-1 corresponding to quartz (crystalline silica: SiO2), and 466 cm-1 is the deformation vibration band of Si-O and Si-O-AL bands in the cages of SiO4 tetrahedra and Al (OH)6 octahedra [37]. These results clearly show that our materials are essentially formed of clay compounds (aluminosilicates) and non-clay compounds (quartz and calcite). The FTIR spectra of the modified clays reveal the presence of the characteristic absorption bands of the HDTMA molecules. The strong bands at 2929 and 2844 cm-1 were detected in organoclays. They were attributed to CH2 asymmetric and symmetric stretching vibrations, respectively, for the HDTMA alkylammonium [38].

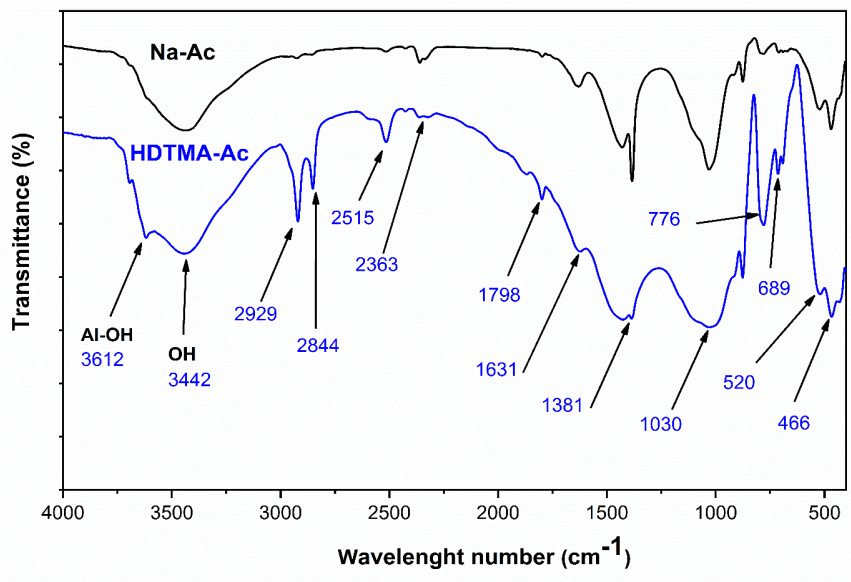

Fig. 1 *FTIR spectra of the Na-Ac and HDTMA-Ac samples*

XRD measurements illustrated in Fig. 2 on Na-Ac and HDTMA-Ac showed specific reflections corresponding to the illite and kaolinite phases. There are peaks of impurities in minerals like quartz, calcite, and dolomite. The intercalation of HDTMA between the clay lamellae can be seen through the increased separation of the d001 basal planes from 9.95 to 14.84 Å for HDTMA-Ac. The increase in basal spacing is due to the intercalation of HDTMA molecules onto the interlayer space of (I-k), which expanded its interlayer spacing. Also, the amounts of HDTMA have a significant effect on the arrangement of the intercalary surfactant, and this is consistent with the results of several research reported by other researchers [39], [40].

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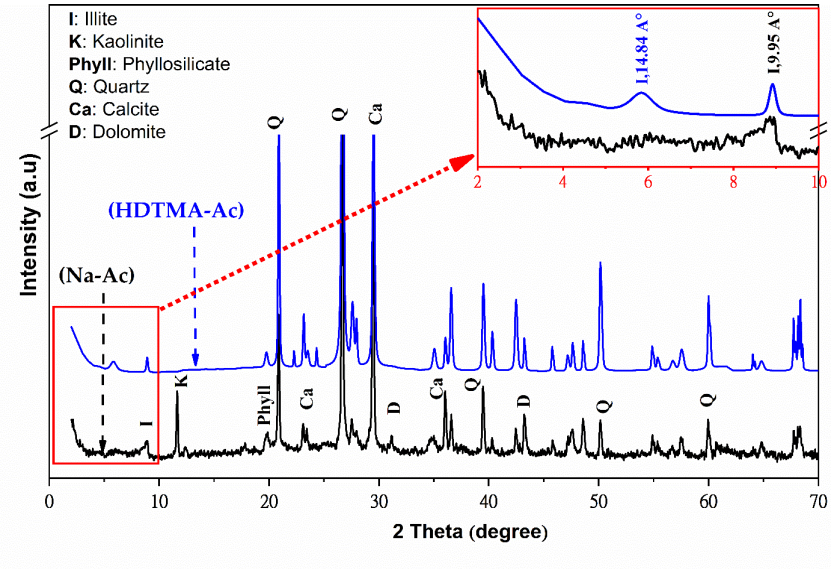

Fig. 2 *XRD patterns of the Na-Ac and HDTMA-Ac samples*

The structure of the Na-Ac and HDTMA-Ac was investigated using thermogravimetric analysis TGA. Fig. 3 depicts the various stages of the material's disintegration: approximately 28, 200, 400, 625, and 775°C. There are three significant mass loss steps. The first phase of mass loss is at a temperature below 200°C, which is caused by the loss of water molecules present in the adsorbent. The second phase of mass loss occurs at temperatures between 350-500°C. This is due to the decomposition of the surfactant and the third stage at higher temperatures (600 -775°C) due to the dehydroxylation process, which is the release of –OH on the illitic-kaolinitic mineral structure framework. Between 800 and 1090°C, however, no mass loss is recorded, indicating thermal resilience at high temperatures. When comparing Na-Ac mass loss with HDTMA-Ac mass loss, we find that the latter is the greatest due to the presence of surfactant HDTMA in HDTMA-Ac material [41], [42] also found similar conditions to those obtained in this study.

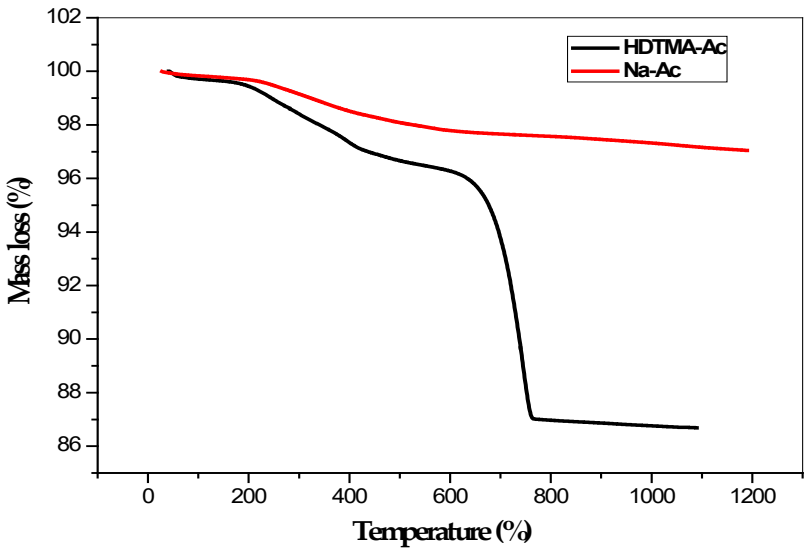

Fig. 3 *TGA of the Na-Ac and HDTMA-Ac samples*

The results of the pH_{PZC} measurements of Na-Ac and HDTMA-Ac are shown in Fig. 4. Because it affects the characteristics of both the adsorbent and the adsorbate, the pH of the solution does have a major effect on adsorption. The adsorbent's surface charge is determined by the pH of the solution and its pH_{PZC}; the surface is negatively charged at pH>pH_{PZC} and positively charged at pH<pH_{PZC}. The adsorbate is mostly in protonated (anion species) form at pH>pKa and molecular form at pH<pKa. The pH_{PZC} of the Na-Ac and HDTMA-Ac clay samples is

9.68 and 8.69, respectively. When the pH of the solution is less than 9.68, Na-Ac clay has a positive surface charge and attracts anions extremely well.

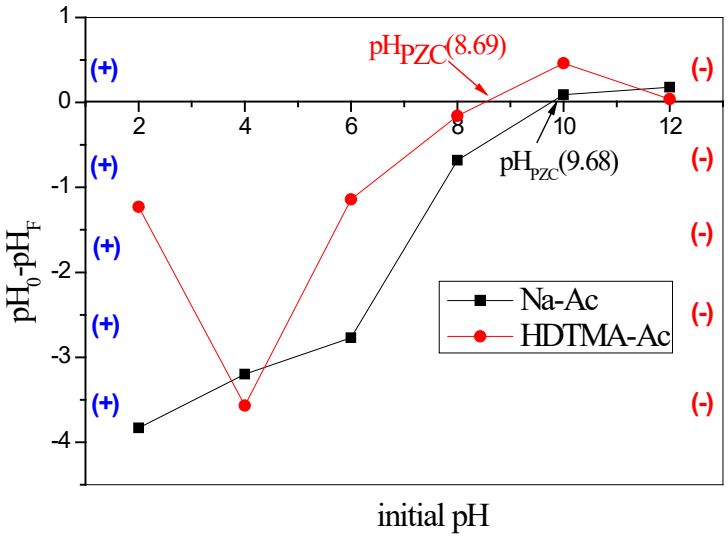

Fig. 4 *pH_{PZC} of Na-Ac and HDTMA-Ac samples*

3.2 Adsorption Studies

3.2.1 Effect of Initial pH on Ni (II) Adsorption

The pH of the solution impacted the adsorbent surface charge, degree of ionisation of the functional groups, and metal ion speciation, all of which influenced the removal of metal ions from aqueous solution by adsorption [43]. According to most studies, the optimum pH varies with different metal ions [44]. At a lower pH, H^+ ions compete with metal cations for exchange sites in the system, causing the latter to be partly released [45]. Under extremely acidic conditions, the heavy metal cations are totally released. The above fact related to the effect of pH on adsorption was also supported by several earlier workers [46]. Experiments were carried out across a pH range of 1 to 7 to discover the optimal pH for efficient Ni (II) ion adsorption. Fig. 5 shows the fluctuation of metal ion uptake at equilibrium with the starting pH for a Ni (II) concentration of 20 mgL^{-1} (at 25°C). At pH 1, the adsorption percentage equals 60.34 %, and the percentage absorbed is the smallest, increasing as the pH increases and then decreasing to pH 5. The most adsorption occurs at pH 7, where equal to 96.63 %. The lowest adsorption at pH 1 might be because hydrogen ions are preferentially adsorbed above Ni (II) ions due to the high concentration and mobility of H^+ ions. This result is comparable to those obtained by other authors [47].

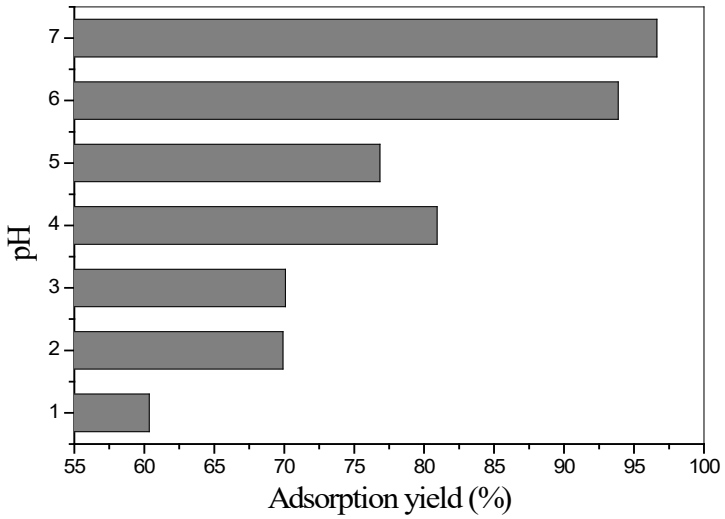

Fig. 5 *Effect of pH for Ni (II) on HDTMA-Ac*

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3.2.2 Effect of Contact Time and Initial Ni (II) Concentration

Contact is one of the elements that influence Because a given mass of adsorbent can only adsorber a certain amount of the solute, the initial concentration of adsorbate is also because, given a particular mass of adsorbent, it can only adsorber a certain amount of the solute. The elimination of Ni (II) ions by HDTMA-Ac increased from 9.57 to 265.49 mg/g by raising the metal ion concentration from 10 to 300 mg/L with the percentage of elimination equal 79.29 % to 95.71 %, respectively, at a temperature of 25°C ± 1°C and pH 7.

As seen in Fig. 6, at the beginning of the process, the adsorption capacity was rapid and progressively slowed in the later phases until it attained saturation point. This is evident from the fact that a large number of surface sites are accessible for adsorption in the initial stages because of resistance between the solute molecules of the solid and liquid phases. The remaining surface sites are hard to occupy after a period of time. The time that it takes to achieve equilibrium in the case of metal ion adsorption is 10 minutes. As shown in Fig. 6, the equilibrium time was unaffected by the change in the initial concentration of the metal ion solution. Various initial Ni (II) concentrations of 10, 100, 200, and 300 mg/L have been used in a series of contact tests. The surface mass transfer causes a rapid uptake of metal ions at low concentrations. The adsorption time variation graphs are simple, flat, and continuous, showing the formation of a monolayer on the clay surface. This result is comparable to those obtained by other authors [28],[48-50]

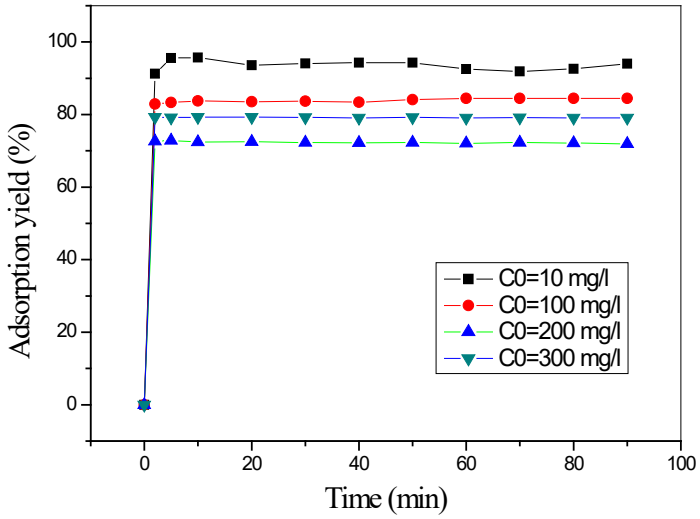

Fig. 6 *Effect of initial concentration on the kinetic of Ni (II) sorption onto HDTMA-Ac*

3.2.3 Kinetic Study

The kinetics of adsorption are essential for controlling the efficiency of the process of adsorption of a solute by a solid in an aqueous solution. Several aspects linked to the state of the material, which usually has a relatively heterogeneous reactive surface, and the physical-chemical circumstances under which adsorption occurs have a massive effect on the adsorption rate. Several studies have employed various kinetic models, such as pseudo-first-order [51], [52] and pseudo-second-order [53]**.** The kinetic data is correlated using pseudo-first and pseudo-second-order models, as seen in (Fig. 7) and (Fig. 8). The adsorption of solid/liquid systems was studied using the pseudo-first-order kinetics adsorption model, which may be stated in linear form using Equation (3)[54], [55]:

$$Ln(q_e - q_t) = Lnq_e - t.K_1 \quad (3)$$

q_1 is the adsorption rate constant (min^{-1}), and q_e, qt are the adsorption loadings of Ni (II) (mg/g) at equilibrium and at time t (min), respectively. Plotting ln (qe-qt) vs t (Fig. 7) should include a linear line. If the pseudo-first-order kinetic is appropriate, K_1 is calculated from the slope. The second-order kinetic model is stated in linear form using Equation (4) [56] and is written the following way:

$$\frac{1}{q_t} = \frac{1}{q_e^{\,2}.K_2} + \frac{1}{q_e}.t \quad (4)$$

k_2 is the second-order rate constant (g/mg min), and by plotting t/q vs t is a linear relationship. Values of k_2 and qe were determined from the intercept and slope of the plots of t/q vs t.

In this work, we used pseudo-first-order and pseudo-second-order kinetic models for the adsorption of Ni (II) ions onto HDTMA-Ac. The parameters obtained for all kinetic models are shown in Table 1. As shown in this table, the correlation coefficients R^2 and parameters were calculated for the two models. The correlation coefficient R^2 is lower than 0.999 for the pseudo-first-order kinetic model and was much lower than for the pseudo-second-order rate equation; for all initial concentrations, the second-order model agreed well with the data for R^2 is higher than 0.999 and q_e (cal), has values that are close to q_e (exp). The linear regression analysis for this model yielded high results. The results reported in Table 1 show that the correlation coefficient value for the pseudo-second-order kinetic model was about 0.999, indicating the applicability of the model to describe the adsorption process, which is similar to the result reported by previous studies [49], [48], [57], [28].

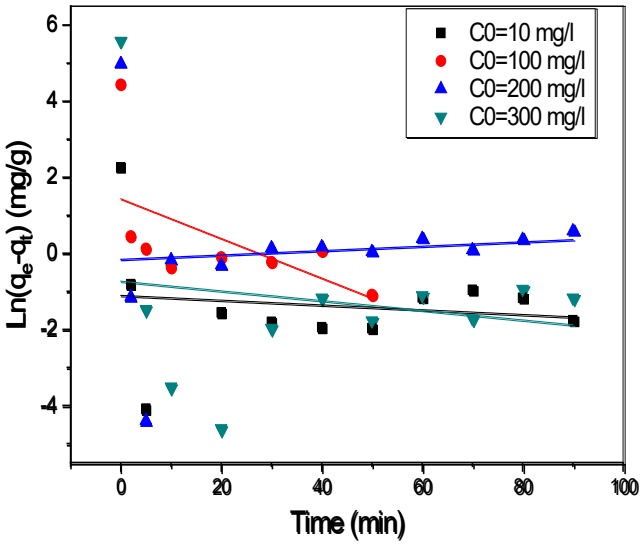

Fig. 7 *Plot of the pseudo-first-order kinetic model*

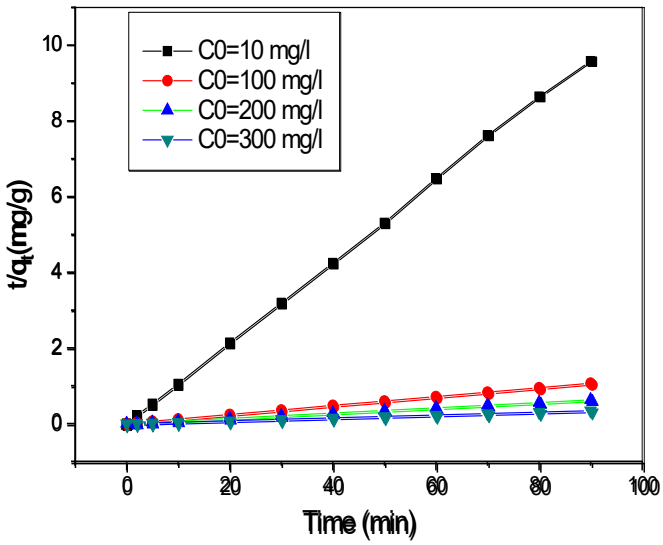

Fig. 8 *Plot of the pseudo-second order kinetic model*

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Table 1 *Pseudo-second order and Pseudo-first order kinetic model parameters*

		Pseudo-first order kinetic model			Pseudo-second order kinetic model		
C_0 (mg/l)	q_e exp (mg/g)	q_e cal (mg/g)	K_1 mn^{-1}	R^2	q_e cal (mg/g)	K_2 (g/mg mn)	R^2
10	9.57	0.33	-0.0142	-0.0908	9.29	-0,0158	0,9997
100	84.47	4.19	-1.20×10^{-1}	0.2215	84.53	1.74×10^{-3}	0.9999
200	145.65	0.85	-0.0132	-0.0912	144.09	-4.77×10^{-5}	0.9999
300	265.52	0.48	-0.0292	-0.0838	265.25	-3.67×10^{-5}	1

3.2.4 Adsorption Isotherm

Ni (II) adsorption isotherms were used to fit the Freundlich Equation (5) and Langmuir Equation (6) models for various initial concentrations of metal (10, 20, 40, 60, 80, and 100 to 260 mg/L). The Freundlich and Langmuir equations have a linear form as follows [58], [59]:

$$Lnq_e = LnK_F + LnC_e \tag{5}$$

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{q_{\max}.K_L} \tag{6}$$

qe and C_e represent the amount of Ni (II) ions adsorbed on the adsorbent (mg/g) at equilibrium and the equilibrium Ni (II) ion concentration in solution (mg/L), respectively. At the same time, K_F (L/g) and n are the Freundlich adsorption constants. q_{max} is the adsorbent's maximum adsorption amount (mg/g), K_L is the Langmuir adsorption constant (L/mg), and the rest of the symbols are the same as in Equation (5). The choice between Langmuir and Freundlich isotherms depends mainly on the nature of equilibrium data [60], where adsorption isotherms are an essential form of data for the practical design of adsorption systems and for understanding the interaction between the adsorbent and the adsorbate, the adsorption processes at Langmuir and Freundlich isotherm parameters are listed in Table 2. Langmuir isotherm assumes monolayer adsorption (Fig. 10), and the R^2 values for Ni (II) ions were very close to 1, which revealed the extremely good applicability of the Langmuir model to these adsorption [61]. The Freundlich model has generally been considered an empirical equation based on adsorption on a heterogeneous surface and has also been used widely to fit experimental data [62]. Compared with the Langmuir isotherm, all the R^2 values of the Freundlich model were also greater than 0.97. the solid-liquid interface was typically represented by the adsorption isotherm mode [63]. As indicated in Table 2 and Fig. 9, the coefficients of determination (R^2) of both models were approximately 0.9, indicating that both models adequately described the experimental data of metal adsorption experiments. Similar results were obtained by Youness *et al.* [31].

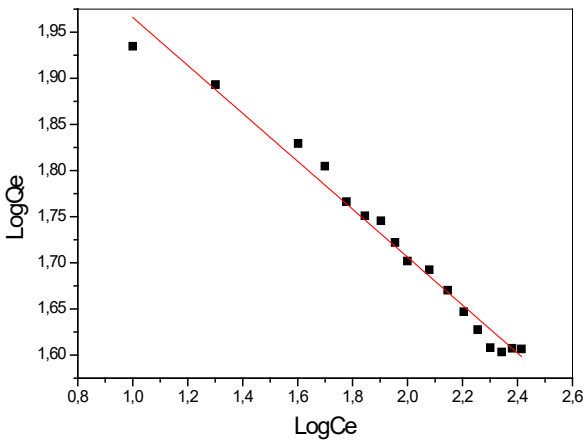

Fig. 9 *Plot of Freundlich model*

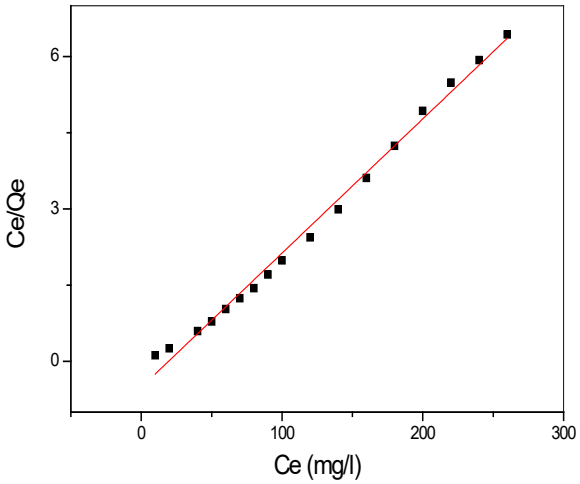

Fig. 10 *Plot of Langmuir model*

Table 2 *Langmuir and Freundlich model parameters for the Ni (II) adsorption equilibrium*

	Langmuir				Freundlich		
	q_{exp} (mg/g)	q_{max} (mg/g)	k_L (L/g)	R^2	1/n	K_f (L/g)	R^2
HDTMA-Ac	40.10	37.83	-0.0135	0.9930	-0.2598	168.162	0.9811

4. Conclusion

Organoclay was prepared with HDTMA equivalent to 1.0 CEC of Na-Ac form HDTMA-Ac and was used to remove ionic metal (Ni (II)) from the aqueous media. Typical characterization results demonstrated that HDTMA brought some changes to the structure and surface properties of Na-Ac. The HDTMA intercalated into Na-Ac to form HDTMA-Ac, which was more conducive to increasing the adsorption capacity of Ni (II). The adsorption of Ni (II) was also affected by pH and concentration. At pH 7, the highest adsorption amounts of Ni (II) were 9.57, 84.47, 145.65, and 265.52 mg/L. Within 10 minutes, Ni (II) adsorption on HDTMA-Ac was equilibrated. The pseudo-second-order kinetic model and the Langmuir isotherm model accurately describe the adsorption data of Ni (II) onto HDTMA-Ac. This research might lead to the development of adsorbents based on organoclay for the removal of heavy metals in polluted water.

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Conflict of Interest

Authors declare that there is no conflict of interest regarding the publication of the paper.

Author Contribution

The authors confirm contribution to the paper as follows: ***study conception and design****: Zahra Fedlaoui, Mahmoud Charef;* ***data collection****: Mohamed Benabdallah Taouti;* ***analysis and interpretation of results****: Zahra Fedlaoui, Mohamed Benabdallah Taouti, Abdelkader Ouakouak;* ***draft manuscript preparation****: Zahra Fedlaoui, Abdelkader Ouakouak. All authors reviewed the results and approved the final version of the manuscript.*

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