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Batch Equilibrium Adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} Ions from Aqueous Solution onto Aluminum Pillared Clay from Karewa (North–Cameroon)

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Abstract

The study of the adsorption of heavy metals and the organic molecules by clays is a contribution to the treatment of water. This work primarily concerns the elimination of the ions Mn^{2+}, Cu^{2+} and PO_4^{3-} of synthetic water, by adsorption on modified clay. Some physicochemical parameters of pillared clay were studied such as the pH (6.83), the water content (22.40%), the swelling number (98.83%), the loss on the ignition (4.35%), the density (1.13) and colloidality (95.75%). Following this view, clay materials of Karewa (North Cameroon), specially made up of smectite, have been pillared with polyoxycations of aluminum. Next, some trials of adsorption of metallic ions Cu^{2+}, Mn^{2+} and PO_4^{3-} in aqueous solution mixture were carried out by varying the time of contact, the pH, the initial concentration of ions, C_o and the temperature, T(°C). The kinetics of the reactions indicate that the adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions is rapid and the equilibrium is reached after 8 minutes. The adsorption capacity, Q_e of the clay modified increases with increasing pH up to pH = 7, and reduces when the pH becomes basic. This phenomenon also increases with the increase in the initial concentration of the metallic ions. It was observed that, temperature has a less influence on the retention capacity. The adsorption isotherms are comparable with the Langmuir and Freundlich models. The adsorbed quantities from the monolayer coverage deducted from Langmuir's model are 21.73 mg/g, 20.62 mg/g and 26.31 mg/g respectively for Cu^{2+}, Mn^{2+} and PO_4^{3-} ions. The nature of the retention phenomenon of both ions is exothermic, spontaneous and physical in the range of temperature 298-313K.

Keywords

Pillared Clay, Adsorption, Heavy Metals, Organic Molecules

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1. Introduction

Water is essential to the life. Indeed in addition to its use as food, water is abundantly implemented in industry either like solvent, or like fluid, hawker of energy or for the cleaning of the machines and the buildings. In the same way water is impossible to circumvent in agriculture. All these activities are at the origin of effluent charged in organic and or inorganic pollutants. Water becomes thus one of the principal polluted mediums and dissemination of the pollutants [1].

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These mineral and organic pollutants are primarily the heavy metals and certain organic molecules equipped with particular chemical properties which confer as well as toxicity to them screw-with - screw of the human being as with regard to the living organisms of the animal and plant species [2]. Adsorption appears the most used nowadays because it is a simple, inexpensive and easily realizable process. Its realization requires a solid adsorbent being able to connect molecules by gravitational attractions, to exchange ions, molecules, to establish chemical and physical bonds and to be easily regenerated [3]. In the ground, the finely divided particles like clays have the characteristic to develop a great specific surface to the contact with water and to have a significant electric surface charge. Nevertheless, the process of adsorption of the phosphate ions, copper and manganese by clay proved one of the most used processes. Thus, various researchers showed that a variety of materials of natural or biological origin had the aptitude to fix significant quantities out of heavy metals starting from solutions [4-6]. Among these natural materials, clays were the subject of various studies for applications varied like adsorption and the catalysis. An alternative solution would consist in using other adsorbent materials like activated alumina [7], some macromolecular resins but especially clays.

These fractions, thanks to their small size (< 2µm) play a privileged role in the retention of water, in the manufacture of water tanks, but also in the retention and biodisponibility of the chemical elements that are essential to the plants. These materials are characterized by their capacity of adsorption, a significant specific surface and their abundance in nature (more than 99% of the composition of the ground). The nature of clay, as well as the decked metallic oxide nature contributes to the increase in the acidity of the solid in a significant way [8]. It is very difficult to find a universal material able to ensure the decontamination that is justified by very different chemical properties of the contaminants; their structures as well as the size of the molecules [9].

Intercalated clays are usually natural smectite clay that is readily pillared because of their low charge density and their swelling ability [10]. Other authors [11, 12] found that the water isotherms of pillared interlayered clay minerals have unusual shapes due to their pore size and hydrophobicity developed in their pore surfaces [13], studying aluminum pillared clay minerals, found that the incorporation of this class of oligocations produces an increase in the acidic sites (principally Lewis sites). Therefore, the aluminum pillared interlayered clay minerals has higher acidic and lower hydrophilic centers compared to the natural clay mineral, which improve their properties for some catalytic and adsorption processes.

In this work, aluminum pillared clay minerals that are synthesized from the natural clay mineral of Karewa from the North Region of Cameroon, were used to remove Cu^{2+}, Mn^{2+} and PO_4^{3-} ions from aqueous solution in order to evaluate if the pillaring of the clay minerals improves the adsorption process.

2. Material and Methods

2.1. Physico–Chemical Characteristics of Clays

The clay used for this work was taken from Karewa's deposit in the Djeboa Sub-Division, North Region of Cameroon. Karewa is a village located at 30 km in the south-east of Garoua, center of the area of Cameroun North. It is located between 9°16' and 9°54' of Northern latitude, 3°52' and 14° of longitude Is Administratively, the village is in the district of Tchéboa, department of Bénoué. The soil, with a surface of 16 km^2, under the traditional authority of the lamidat of the district. The natural clay (rough) used in this work is a montmorillonite, of white color, taken layer of karewa located at the North of Cameroun.

2.2. Preparation of Hydroxyl-Intercalated and Surfactant-Modified Clay

Pillaring solution containing Al_{13} polymeric specie was prepared following an established procedure by slowly adding a 0.2 M solution of sodium hydroxide to a 0.2 M solution of $AlCl_3.6H_2O$ to obtain a final basic ratio (as molar ratio of OH^- / Al^{3+}) of 2/2. The solution obtained is kept for 48 hours, in the absent of the sun to avoid other reactions and so that the solution meets it maturity. The clay was washed using 1 M sodium chloride overnight and was used without conversion into a homo ionic sodium form. The aluminum pillaring solution was aged for 3 hours. After the ageing process 10 g of the clay was added directly into the pillaring solution under vigorous stirring and allowed to aged overnight. The obtained solids were then collected for centrifugation and washed with deionised water until free of chloride ions (as confirmed by the silver nitrate test), and then they were dried at 388 K for 24 hours and finally calcined at 673 K for 3 hours.

2.3. Preparation of the Solutions and Characteristic of the Reagents Used

- Stock solution of phosphates with 1000 $mg.L^{-1}$.

Stock solution was prepared by dissolving 0.288 g of phosphate dihydrogenopotassic (KH_2P0_4) in 1000 ml of distilled water. The solution obtained is preserved in a bottle out of glass. From this stock solution, we prepare, by successive dilutions, a series of derived solutions of well-defined concentrations. These solutions were used for successive dilutions either for establishing the calibration curves or for the preparation of the synthetic solutions used within the framework of the tests.

- Stock solution of Copper.

The aqueous copper stock solution is of concentration mass of 8.5 g/L. It is prepared while making dissolve in one liter of distilled water cuprous chloride 8.61 g ($CuCl_2.2H_2O$; M = 170,48 g/mol) to 99% mass of purity

- Stock solution standard of manganese with 100 mg.L^{-1}.

To dissolve 0.288 g potassium permanganate ($KMnO_4$) in approximately 100 mL of distilled water sulphuric container 3 mL of acid diluted at the 1/20. To add approximately sulphite 0.4 g monosodic, to carry to boiling, to cool and adjust volume to 1000 mL. The solution obtained is preserved in a bottle out of glass. From this stock solution, we prepare, by successive dilutions, a series of derived solutions of well-defined concentrations.

2.4. Adsorption Experiments

The adsorption experiments were carried out using the batch equilibrium technique. For each isotherm, 200 mg of clay was weighed into 50 mL of ions solution (Cu^{2+}, Mn^{2+} and PO_4^{3-}) of given concentration 50 mg/L of solution were added. The pH values of ions solutions were in the range of between 6.4 and 7 without further adjustment in order to simulate the natural water system. The suspensions were mixed on a rotary tumbler for 8 minutes. After phase separation by centrifugation the concentration of heavy metals ions in the supernatant was determined by using a UV absorbance at wavelength of 555 nm, 525 and 720 nm for Cu^{2+}, Mn^{2+} and PO_4^{3-} ions respectively. The adsorbed quantities were then determined by using the mass balance equation:

$$Q_0 = \frac{(C_0 - C_e)V}{m} \tag{1}$$

where, Q_o is adsorbed ion concentration on clay (mg/g), m is the weight of clay used (g), V is volume of ion solution (L), C_0 is metal initial concentration (mg/L), and C_e is metal equilibrium concentration (mg/L).

3. Results and Discussion

3.1. Kinetics Studies

In order to determine the kinetics of Cu^{2+}, Mn^{2+} and PO_4^{3-} by modified clay, 200 mg of pillared clay was mixed with 50 mg/L of three ions solution in centrifuge tubes. The dispersions were shaken for amount5 min at 30 min on a shaker. Figure 1 shows the results of the kinetics studies of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions uptake by pillared clay of Karewa at 50 mg/L in ions initial concentration. As shown in Figure 1, the amount of heavy metal ion absorption increases with increased time, especially in the range between 5 minutes to 8 minutes. Before reaching 8 minutes, two distinct adsorption stages with different slopes were detected. The first stage (5 < t < 8 min) was characterized by a steep slope due to the rapid adsorption rate during the initial stage. This stage could be attributed to the instantaneous monolayer adsorption of heavy metals at the surfaces of the investigated samples [2]. The second stage (8 < t < 20 min) is assigned to a gentle slope as a result of the decreasing adsorption rate. The reduction in ions uptake in the second stage could be attributed to the rearrangement of metallic ions absorbed on the surface and a more thorough utilization of the adsorption sites in the studied samples [14, 15].

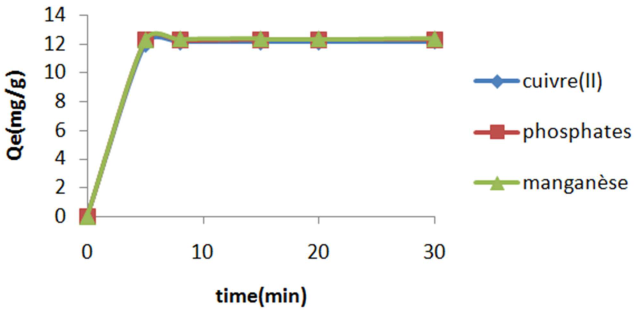

Figure 1. Kinetics study for Cu^{2+}, PO_4^{3-} and Mn^{2+} ions uptake by pillared clay from Karewa.

3.2. Kinetics Models

Several kinetic models are used to examine the controlling mechanism of the adsorption processes and also to test the experimental data obtained. The experimental data was fitted with pseudo-first-order differential equation as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2,303} \tag{2}$$

where, q_e and q_t are the amounts of heavy metal ions absorbed (mg/g) at equilibrium and time, t (min), respectively. K_1 is the rate constant of first – order adsorption (min^{-1}). The first- order- rate K_1 can be obtained from the slope of the plot of log(q_e−q_t) vs. time.

A pseudo – second - order equation can be expressed in the form of:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where, k_2 is the rate constant of the second – order adsorption (min^{-1}). A good agreement of the experimental data with the second – order kinetic model was obtained (Figure 2). The correlation coefficients, R_2 are greater than 0.98, which suggests a strong relationship between the parameters and also explains that the process follows pseudo – second – order kinetics. The adsorption process involves transportation of the solute molecules from the aqueous solution to the surfaces of pillared clay followed by intra – particle diffusion/transport process [16].

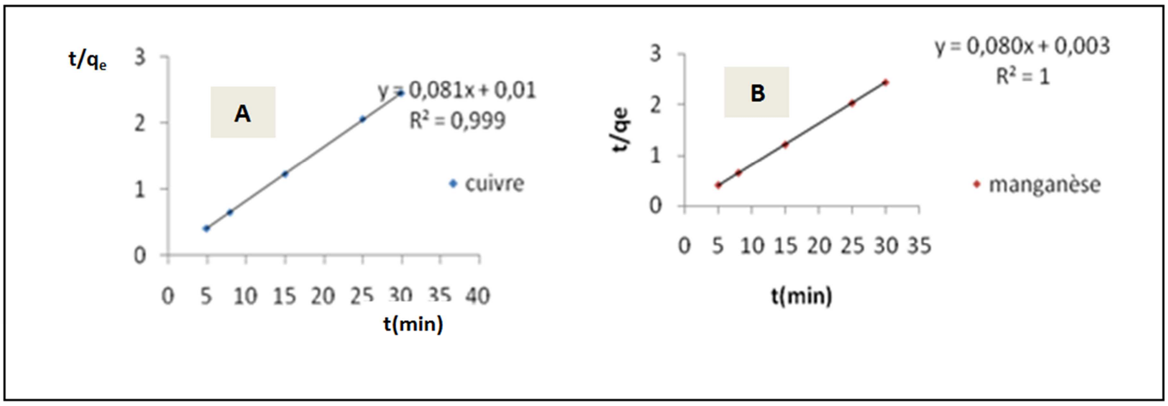

Figure 2. Plots for second – order model for heavy metal ions uptake by pillared clay mineral from Karewa: (A) Cu^{2+}, (B) Mn^{2+}.

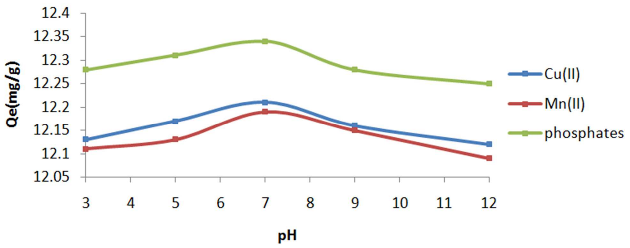

Figure 3. Effect of solution pH on adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} on to pillared clay from Karewa.

3.3. Effect of Solution pH on Cu^{2+}, Mn^{2+} and PO_4^{3-} Ions Adsorption

The adsorption of these three ions is a phenomenon that is highly influenced by solution pH; this is due to the implication of mechanisms that are pH dependent, through reactions such as ions exchange, complexation reactions, or by the retention of electrostatic forces [17]. The adsorption of the three ions (Cu^{2+}, Mn^{2+} and PO_4^{3-}) on pillared clay at different pH is showed in the Figure 3. This figure shows that, the adsorbed quantity increases in the acid medium ($pH < 7$) and decreases in the basic one ($pH > 7$). This change is reproduced by the three ions. In this way, we remark that, at $pH = 3$, the adsorption is low; it is of 12.13, 12.09 and 12.28 for the Cu^{2+}, Mn^{2+} and PO_4^{3-} ions respectively. Therefore, when the solution is acidic, Cu^{2+}, Mn^{2+} and PO_4^{3-} ions are in competition with H^+ ions present in great concentration in the solution. These ions (H^+) are then more adsorbed than the three ions, considering their easy mobility in solution [17]. When the value of pH is between 5 and 7, the competitive effect of the H^+ diminishes; this explains the high adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions [18]. For high values of pH ($pH > 7$) the adsorbed quantities diminish. This decrease is caused on one hand by the precipitation of metallic ions by the hydroxides (HO^-) ions and on the other hand, by adsorption. However, the greatest adsorption effectiveness of Cu^{2+} (12.21 mg/g), Mn^{2+} (12.19 mg/g) and PO_4^{3-} (12.34) is obtained at neutral pH ($pH = 7$).

3.4. Effect of Solution Concentration on These Three Ions Adsorption

In order to examine the changes of pillared clay and non-pillared clay, concerning the Cu^{2+}, Mn^{2+} and PO_4^{3-} when the latter change the initial concentration without any condition, six concentrations in Cu^{2+}, Mn^{2+} and PO_4^{3-} ions have been chosen.

Figures 4 and 5 below represent the percentage of Cu^{2+}, Mn^{2+} and PO_4^{3-} ion elimination from the initial ion concentration. These figures show that the rate of elimination at equilibrium on the modified clay for both ions increases as the initial heavy metal ion concentration increases. This may be justified by the fact that the more the solution is concentrated, the more the heavy metal ions will go through the surface active sites the pillared clay and consequently, the retention becomes more important. This same phenomenon has been observed by Ucun et et al., Park et al. and Zheng et Al.[19-21]. Contrary to the results of [22] who found a percentage of elimination 23.5% for Mn^{2+} ion on the pillared clay of Boboyo what leads us to say that the modified clay of Karewa adsorbs better the ions Mn^{2+} that that of Boboyo. The results obtained in Fig.4 shows that the rates of elimination at equilibrium of the Cu^{2+} ion are of 99.22%, and of 94.94%, respectively for pillared clay and not pillared. This explains the hypothesis that pillaring of clay permits an amelioration of the percentage of elimination of metallic ions from aqueous solution. Whereas, increasing of adsorption ends when the clay its maximum eliminating rate (98.55 for Cu^{2+} and 99.89% for PO_4^{3-} on pillared clay).

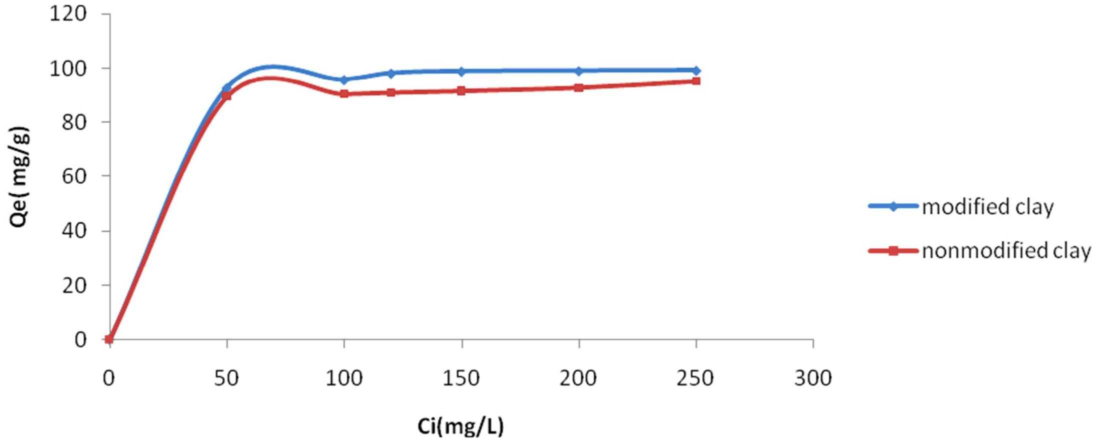

Figure 4. Effect of initial concentration on adsorption of Cu^{2+} on to pillared clay and natural clay from Karewa.

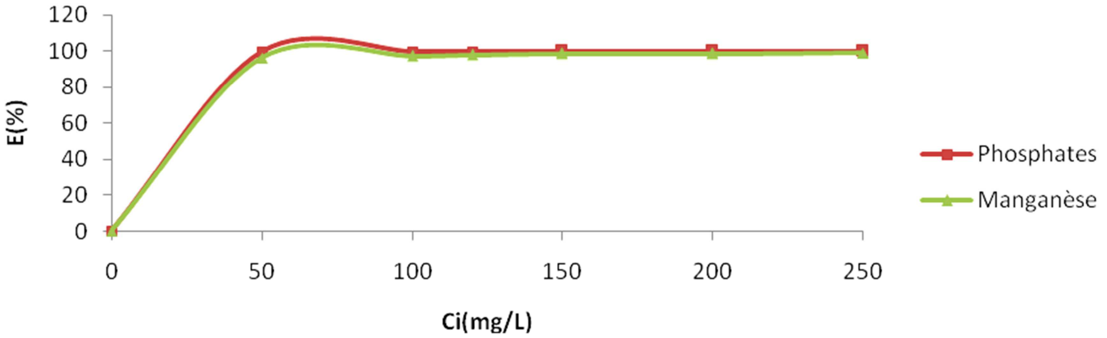

Figure 5. Effect of initial concentration on adsorption of Mn^{2+} and PO_4^{3-} on to pillared clay mineral from Karewa.

3.5. Influence of Temperature

The evolution of the fixation of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions has been studied for an initial tenor which is static for each of the two ions (50 mg/L) and at different temperatures (between 20°C and 50°C). The measurement of the residual tenor in heavy metal ions for each case study has been realized after 8 min of contact with modified clay.

Figure 6 shows the adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions with the pillared clay. The result in Figure 6 allows to understand that the temperature does not seem to have any significant influence on the adsorption of these three ions studied. The absorbed quantities are situated between 12.43 mg/g for Cu^{2+}, 12.46 mg/g for Mn^{2+} and 12.42 for PO_4^{3-} ions. These values decrease very little with increasing temperature, indicating the exothermic character of adsorption process. A decreasing of the absorbed quantities with the temperature implies physisorption [23].

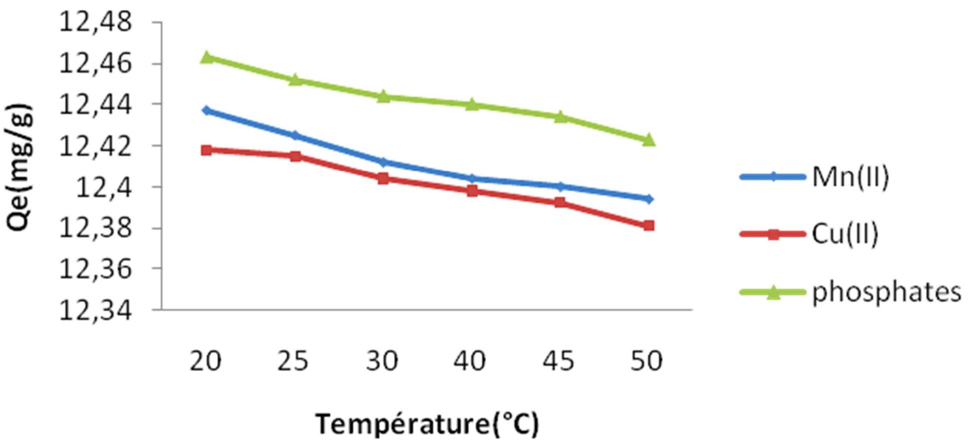

Figure 6. Effect of temperature on adsorption of Cu^{2+}, Mn^{2+} and PO_4^{3-} on to the pillared clay mineral of Karewa.

3.6. Adsorption Isotherm Studies

Adsorption isotherms indicate distribution of adsorbate between solution and adsorbent at the equilibrium state of the adsorption process [24]. The type of adsorption isotherm model is very important in order to understand the adsorption behavior for solid-liquid adsorption system [25]. In the present study, Langmuir and Freundlich models were tested to study the adsorption behavior of heavy metal ions (Cu^{2+}, Mn^{2+} and PO_4^{3-}).

Langmuir isotherm.

The Langmuir isotherm is based on the assumptions that adsorption takes place at specific homogeneous sites within the adsorbent, there is no significant interaction among adsorbed species, and the adsorbent is saturated after the formation of one layer of adsorbate on the surface of adsorbent (Hoda et al., 2006). The Langmuir isotherm equation can be written as follows:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{k_1 q_{\max}} \cdot \frac{1}{C_e} \qquad (4)$$

where, C_e is the equilibrium concentration of the remaining solute in the solution (mg/L), qe is the amount of the solute adsorbed per mass unit of adsorbent at equilibrium (mg/g), q_{max} is the amount of adsorbate per mass unit of adsorbent at complete monolayer coverage (mg/g), and k_1 (L/mg) is a Langmuir constant. The qmax and k1 values were calculated from the slopes ($1/q_{max}$) and intercepts ($1/ k_1q_{max}$) of linear plots of C_e/q_e versus C_e (Figure 7). The deducted parameters of adsorption of Langmuir isotherm are summarized in Table 1. The plots were found to be linear with good correlation coefficients ranging from 0.991 to 0.995. This indicates the applicability of Langmuir model in the present study.

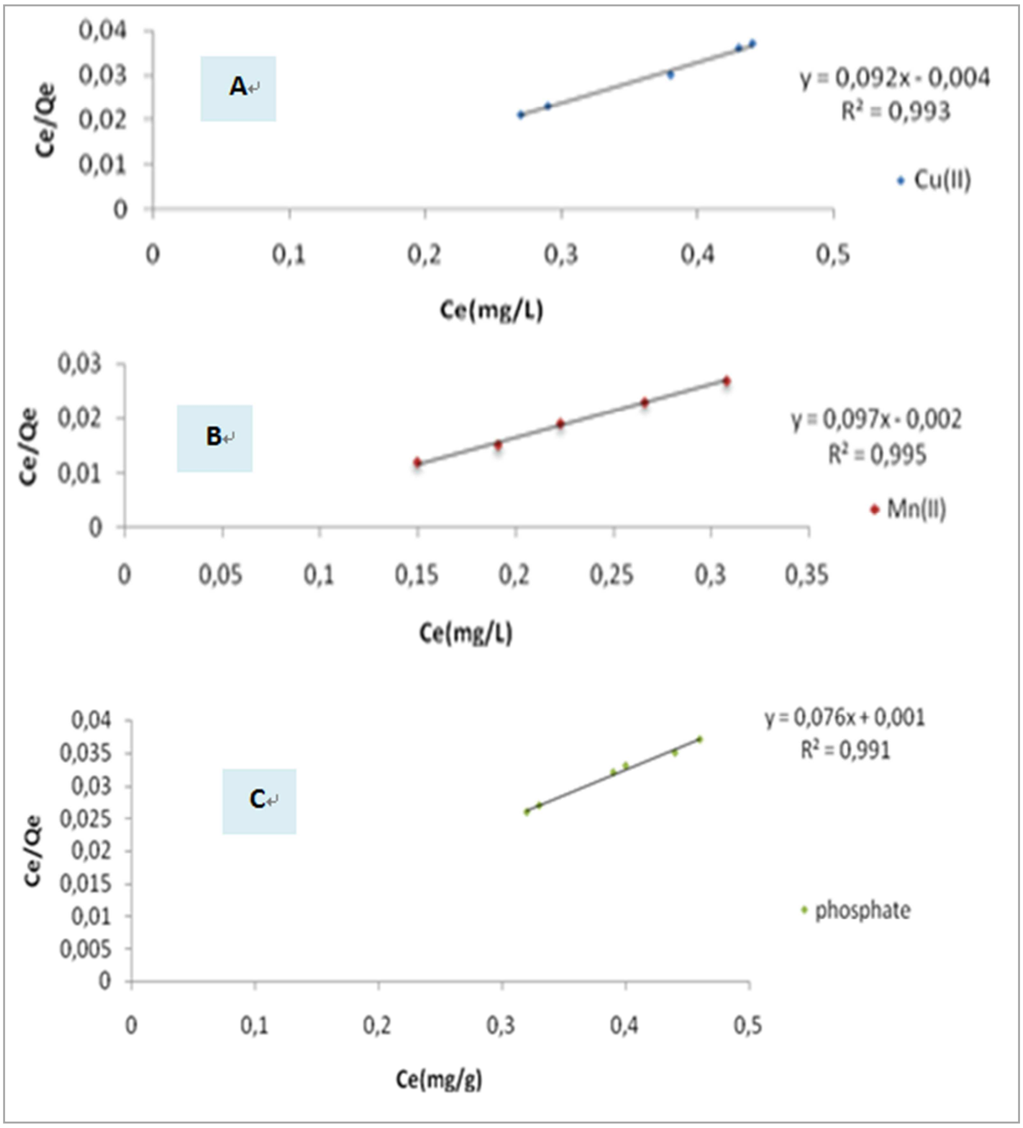

Figure 7. Langmuir plots for (A) Cu^{2+}, (B) Mn^{2+} and (C) PO_4^{3-} ions uptake by pillared clay mineral from Karewa.

Table 1. Parameters of the Langmuir and Freundlich models fitted to the experimental adsorption data.

Adsorbent	Langmuir Model			Freundlich Model		
	q_{max} (mg/g)	K_L (L/mg)	R²	n	K_F	R²
Cu^{2+}	21.73	11.50	0993	0,22	0.97	0.992
Mn^{2+}	20.62	24.24	0.995	0,20	0.94	0.944
PO4^{3-}	26.31	38.01	0.991	0,21	0.99	0.926

Freundlich isotherm.

Freundlich isotherm model can be used to describe the non–ideal adsorption of a heterogeneous system and reversible adsorption. The isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \tag{5}$$

This expression can be linearized to give the following equation:

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \tag{6}$$

Where, K_F (mg/g) and n are Freundlich adsorption isotherm constants. The values of K_F and 1/n are determined from the intercept and slope of the linear regressions. The value of $1/n_f$ higher than 1 for Cu^{2+}, PO$_4^{3-}$ and Mn^{2+} ions suggests that the link of adsorption are fragile [9]. A plot of *ln(q$_e$) vs. ln(C$_e$)* for the studied samples is shown in Figure 8. The deducted parameters of adsorption of Freundlich isotherm are summarized in Table 1. The plots were found to be linear with good correlation coefficients ranging from 0.926 to 0.992. This indicates the applicability of Freundlich model in the present study. The values of n for the studied samples are more than unity and therefore, adsorption is favorable.

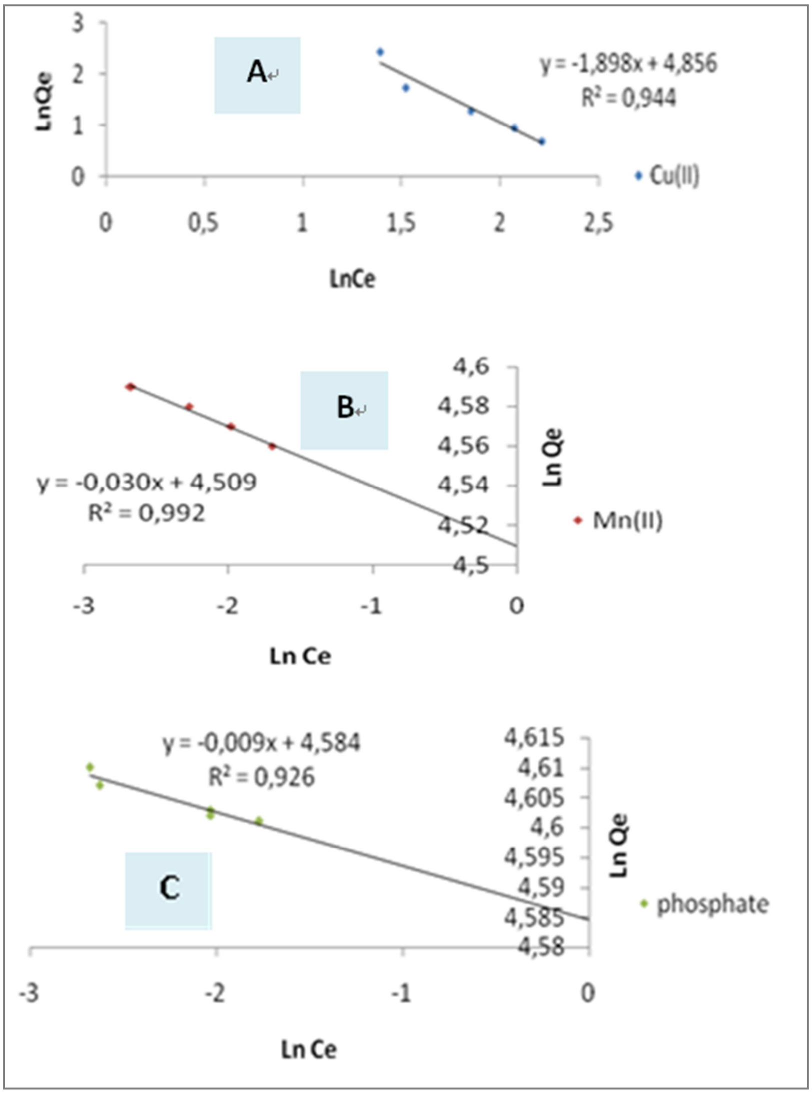

Figure 8. Freundlich plots for: (A) Cu^{2+}, (B) Mn^{2+} and (C) PO$_4^{3-}$ ions uptake by pillared clay mineral from Karewa.

3.7. Thermodynamic Studies

Thermodynamic parameters have been determined for the qualification of adsorption phenomenon of t Cu^{2+}, Mn^{2+} and PO_4^{3-} ions on pillared clay of Karewa.

The studies were carried out at temperatures of 293, 308 and 318 K. The relative absorbed quantities at each temperature have been used for calculation of particular thermodynamic parameters such as Gibbs free standard energy ΔG°(kJ.mol^{-1}), standard enthalpy ΔH° (kJ.mol^{-1}) and standard entropy ΔS° (kJ.mol^{-1}). Gibbs free standard energy is calculated by using the following equation:

$$\Delta G^\circ = -RT \ln Kc \tag{7}$$

$$lnK_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{8}$$

Where kc is the adsorption constant of each ion, R is the perfect gas constant and T is the working temperature in kelvin. The values of ΔH° and ΔS° have been deduced from graph of lnk$_c$ vs. 1/T which is linear with a slope of $-\frac{\Delta H}{R}$ and $\frac{\Delta S^\circ}{R}$ and represents it's y-coordinned at the origin.

The deducted estimates of ΔG°, ΔH° and ΔS° of the experimental data are found in Table 2.

As illustrated from the results in Table 2, the negatives values of standard energy of Gibbs (ΔG°) of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions indicate that the adsorption is thermodynamic possible and spontaneous. The positives values of standard entropy (ΔS°) show the crescent aspect to interface this solid/liquid during the adsorption of copper, of manganese and of the phosphate ions on decked clay. The negative value of ΔH° indicates the positive nature of the present adsorption phenomenon. Also, the negative value of ΔH° proves the exothermic and physical nature of this retained phenomenon of ions [26]. These results are in agreement with the above studied model.

Table 2. Thermodynamic parameters relative of adsorption of Cu^{2+}, PO_4^{3-} and Mn^{2+} on modified clay mineral from Karewa at different temperatures.

Ions	Free Enthalpy, ΔG° (kJ/mol)					Enthalpy, ΔH°	Entropy, ΔS°	R^2
	20°C	25°C	30°C	40°C	45°C	(kJ/mol)	kJ/mol/K	
Cu^{2+}	-12.72	-12.71	-12.17	-12.91	-12.85	0.0053	14.2	0.966
Mn^{2+}	-14.15	-13.75	-13.63	-14.01	-14.02	0.0085	8.87	0.930
PO_4^{3-}	-12.23	-12.36	-12.17	-12.74	-12.68	-0.012	16.24	0.904

4. Conclusions

The study of the adsorption of Copper, Manganese and the phosphate ions by decked clay is a contribution to the water treatment. This present study aimed at, the application of modified clays of Karewa in the adsorption of some micropolluants (heavy metals and organic molecules) present in water. The study in particular of the influence of some parameters (pH, concentrations, thermodynamic parameters, isotherms) on the retention of these adsorbates held our attention. Various trials of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions adsorption on pillared clay of Karewa have shown that the fixation reaction on modified clay was quite fast. The eliminated accounts of Cu^{2+}, Mn^{2+} and PO_4^{3-} ions seem to improve with increasing by initial concentration of solution. The adsorbed quantities decrease with the increase in the mass of adsorbent and the increase in the temperature but they increase with the increase in the concentration of the ions in solution. The adsorbed quantity increases in acid medium (pH < 7) and decreases in basic medium (pH > 7).

The nature of the retainment phenomenon of three metallic ions is exothermic, spontaneous and physical. The pillared clay is more practical and efficient than natural clay for the retainment of metallic ions.

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