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ADSORPTION OF ZINC IONS IN WATER ON NATURAL AND TREATED CLAY

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Abstract. Adsorption of zinc ions in water on natural and treated clay has been studied. Natural clay before and after activation was characterized using TGA/DTA techniques and chemical analysis.The effects of various parameters, such as an initial concentration, temperature, pH, contact time and adsorbent concentration, has been examined. It was shown that treated clay is a good adsorbent compared to natural clay for removing Zn^{2+} ions and can be used instead of expensive adsorbents. The thermodynamic parameters have been calculated which have shown that the adsorption of Zn^{2+} on natural and activated clay is endothermic.

Keywords: activated clay, adsorption isotherm, thermodynamic parameters, montmorillonites, endo-thermic, exothermic.

1. Introduction

The elimination of pollutants and heavy metals from water and wastewater is important in terms of protecting public health and the environment [1].

Industrial activities are based on a number of pollutants such as fertilizers and battery manufacture, and dyeing in textile industries introduces heavy metals into the environment *via* their residual effluents [2]. Adsorption and ion exchange are the usual methods for the removal of organic and inorganic heavy metals from aqueous solutions [3].

Copper and zinc ions are identified with clinical problems [4]. They are found in soils, surface and underground waters by industrial discharges [5]. Copper and zinc ions as the pollutants, can be fixed by clay adsorption [6]. Studies devoted to the zinc fixation on clay minerals, bentonites namely, are not significant in number [7, 8]. To enhance the retention ability of clay minerals, they are chemically modified [9].The most important modification reactions in the adsorption are acid activation and cation exchange [10, 11]. Adsorption is one of the most efficient methods in the field of extracting heavy metals from aqueous solutions because of its simplicity and high efficiency [12, 14]. Some studies have been carried out to test the effectiveness of various types of clay of heavy metals adsorption from aqueous solutions [8, 13, 15-17].

The primary objective of this study is to evaluate the equilibrium adsorption of zinc ions on natural and treated clay, consisting mainly of secretite and montmorillonite.

2. Experimental

2.1. Materials

The clay used in this study was an Algerian clay treated and purified by the following method. The clay was washed with distilled and deionized water several times, and completely dispersed in water. After 7 h at least, the dispersion was centrifuged for 1 h at 2400 rpm. The size of the clay particles obtained was 2 µm. Then it was heated to 343 K in the presence of a solution composed of the sodium salts of 1M bicarbonate, 0.2M chloride and 2M citrate[18, 19]to eliminate the organic and inorganic compounds, present in inter-layer spaces. The carbonates were removed by adding 0.4M HCl and the chloride was removed after several washings.

The organic matter was eliminated completely by treatment with H_2O_2 (30 % v/v) at 343 K. The purified clay was dried at 383 K, and then saturated with calcium (Ca^{+2}). To ensure complete transformation into the calcium form, all samples were washed several times with $Ca(OH)_2$ solution (1M).

2.2. Metal Solutions

The aqueous solution was prepared using analytical $ZnCl_2$ in 1000 ml of ultrapure water. The concentration of metals in aqueous solutions submitted

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to zinc adsorption tests was determined by the Perkin-Elmer atomic absorption spectrophotometer.

1.0 g of adsorbent and 100 ml of metal solution were used at the initial concentration of 3.0 mg/l and pH 4.5. The value of pH was adjusted using 0.1M HCl and 0.1M NaOH. The flasks were stored at room temperature (296 K) under constant stirring of 200 rpm. The adsorption capacity of zinc ion by natural and treated clay calculated from Eq.(1) is the difference between the final and initial concentrations:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where q_e is the amount of metal ions adsorbed on the clay,l·mol/g;C_0 and C_e are the initial and equilibrium concentrations in 1M solution, respectively, mg/l; V is the volume of medium, l; m is the weight of the clay sample, g.

2.3. Adsorption Isotherm Models

To describe the relationship between the amount of adsorbed Zn ions and their equilibrium concentration two models (Freundlich and Langmuir) were used in this study.

Freundlich isotherm [20] is expressed as follows:

$$q_e = K_F \sqrt[n]{C_e} \quad (2)$$

where C_e is an equilibrium concentration of the adsorbate, mg/l; q_e is the amount adsorbed under equilibrium, mg/g; K_F and n are the Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent, respectively.

The linear form of the Freundlich isotherm model is given by the following relation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

Values of K_F and 1/$n$can be calculated from the linear slope between lnq_e and lnC_e [21].

The adsorption isotherm of Langmuir is based on the assumption of single-layer adsorption on the surface [21].

2.4. Kinetic Studies

The study of zinc ion kinetics was carried out using different concentrations (20, 50, 100 and 150 mg/l). Under experimental conditions pH was 8 and 10; the weight of clay and zinc was 0.2 and 1 g, respectively.

3. Results and Discussion

3.1. Chemical Composition

The chemical composition of the clay used for the experiments is shown in Table 1. It was determined by XRD analysis. On the basis of XRD results the structural formulas (Eqs. (4) and (5)) were derived, which are in agreement with the composition ofillite, as the predominant phase in the clay sample. Illite in clay was calculated by the XRD analysis showing the impurities of quartz. The sodium cation dominates in the illite interlayer; the sum of the (Na^+,Ca^{2+}, K^+) ions exchangeable calculated by structure formula is equal to 0.057, this charge indicates the presence of smectite.

$$[Si_{3.53}\,Al_{0.46}]\,O_{10}\,(Mg_{0.13}\,Al_{0.76}\,Fe^{III}{}_{0.25})\,(OH)_2\,K_{0.34}\,Ca_{0.2}\,Na_{0.06} \quad (4)$$

$$[Si_{3.08}\,Al_{0.92}]\,O_{10}\,(Mg_{0.17}\,Al_{0.61}\,Fe^{III}{}_{0.27})\,(OH)_2\,K_{0.086}\,Ca_{0.04}\,Na_{0.061} \quad (5)$$

3.2. Thermal Analyses

Fig. 1 shows the results of TGA analysis and Table 2 gives information corresponding to the clay fraction. The mass loss observed in the range of ambient temperatures and 473 K is related to the elimination of the adsorbed and intercalated water molecules. The mass loss due to evaporation and dehydroxylation is between 673–1073 K [23, 24].

Table 1

Chemical composition of natural and treated clay

Oxides	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	CaO	H_2O
Natural Clay	58.17	24.48	6.82	2.2	0.6	1.28	0.72	5.73
Treated Clay	59.23	19.15	6.82	2.19	0.88	3.13	3.81	4.79

Table 2

Thermogravimetric mass loss of clay

Temperature, K	Mass loss, %
RT–473	8.69
473–773	2.04
773–1073	1.5
RT–1073	12.23

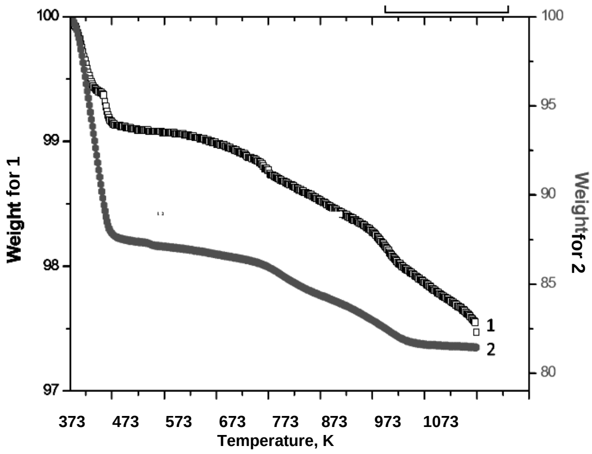

Fig. 1. TGA curve of treated (1) and natural (2) clay

3.3. Effect of pH

The study of pH effect on the zinc adsorption by clay is realized by metal solutions of 100 ml in volume and 100 mg/l in concentration at pH ranging from 2 to 12. In this work the clay dose was kept constant (0.2 g) and the stirring time was determined at 3 h at 300 rpm. The results are shown in Fig. 2.

The highest efficiency of Zn^{2+}removal by adsorption on natural clay was obtained at pH > 8. At lower pH values the adsorption efficiency decreases. The effect of the pH changes depends on the adsorbent type and its behavior in the solution, as well as on the type of adsorbed ions [25]. In this work, the removal of Zn ion by the clay is optimized at pH values of 8–9 or the cations present in the clay structure are exchanged for Zn ion present in the aqueous solution. At high values of pH the hydroxyl complexes of zinc, such as $ZnOH^+$ and $Zn(OH)_2$ are formed. They can participate in adsorption and precipitate on the clay structure. Optimum pH values equal to 8.5 were used further to determine the effect of other factors such as clay dose, metal concentration, and agitation time.

3.4. Effect of Clay Concentration

In this study to determine the optimum concentration of clay, solutions with metal initial concentration of 100 mg/l were used at optimum pH values. During 5 h contact time, the amount of clay added to the solutions varied between 0.1 and 1 g. The results are shown in Fig. 3.

During the removal of zinc, it was found that the adsorption efficiency increases as the amount of clay increases. The increase in efficiency is explained by the increase of the surface area where the adsorption takes place. The optimum clay concentration was found to be 0.6 g/100 ml.

3.5. Effect of Zn^{2+} Concentration

Optimal concentrations were determined after experiments carried out at concentrations of Zn^{+2}ranging within 20–150 mg/l. The adsorption efficiency increases at a certain level of saturation and remains stable with further increase in the concentration. The optimal concentration of $Zn^{2+}$was found to be 100 mg/l. The results obtained from this study are shown in Fig. 4.

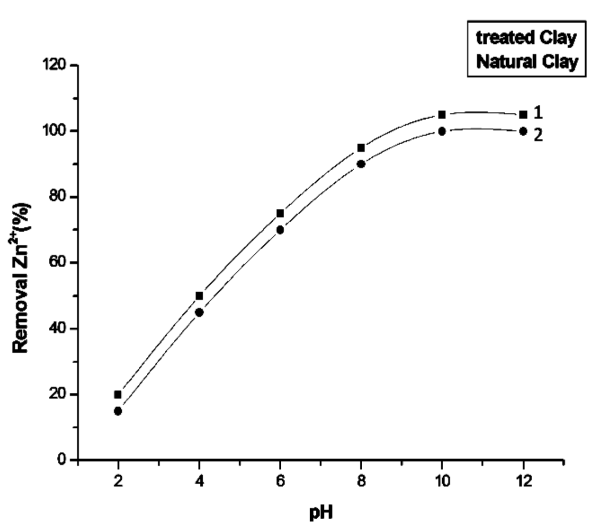

Fig. 2. Effect of pH on the Zn^{2+}removal by treated (1) and natural (2) clay. Initial concentration of zinc ions 100 mg/l, clay concentration 0.6 g/100 ml, contact time 5 h

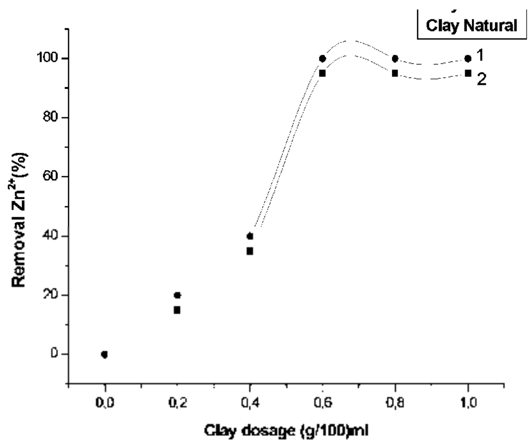

Fig. 3. Effect of clay concentration on the removal of $Zn^{2+}$by treated (1) and natural (2) clay. Initial concentration of zinc ions 100 mg/l, pH 8–9, contact time 5 h

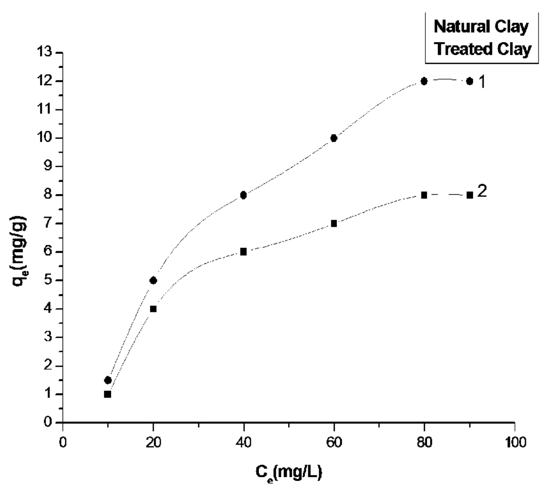

Fig. 4. Effect of Zn^{+2} concentration on the on the adsorption efficiency of treated (1) and natural (2) clay. Clay concentration 0.6 g/100ml; pH 8–9; contact time 5 h

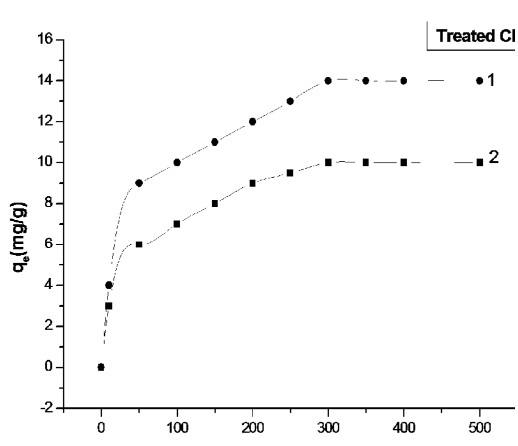

Fig. 5. Kinetic studies for Zn^{2+} adsorption on treated (1) and natural (2) clay. Clay concentration 0.6 g/100ml; solution volume 100 ml; initial concentration zinc ion 100 mg/l; contact time 5 h; pH 7; temperature 293 K

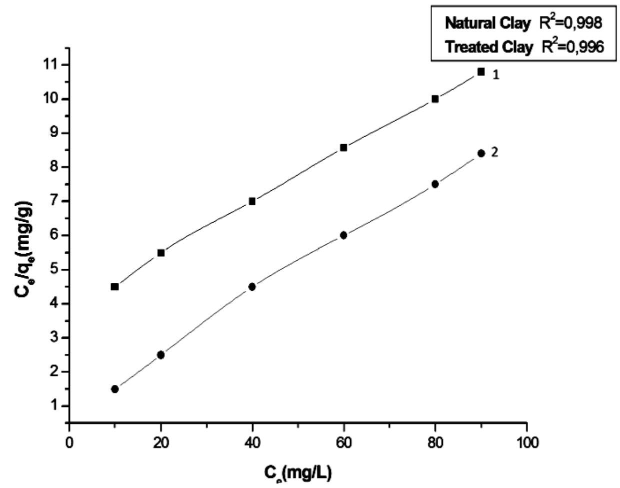

Fig. 6. Langmuir isotherms for Zn^{2+} adsorption on treated (1) and natural (2) clay. Clay concentration 0.6 g/100ml; solution volume 100 ml; initial concentration zinc ion 100 mg/l; contact time 5 h; pH 7; temperature 293 K

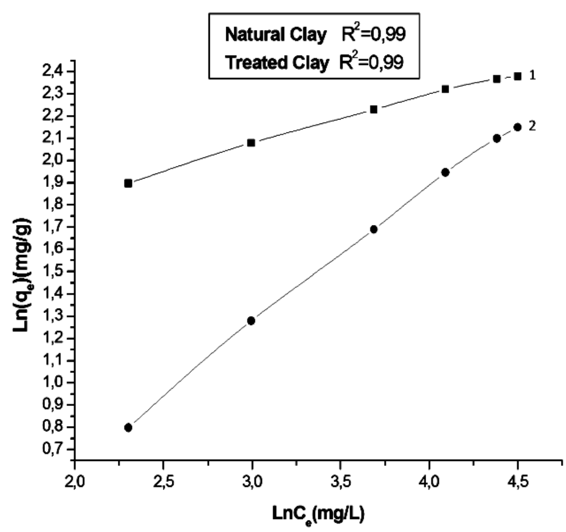

Fig. 7. Freundlich isotherms for Zn^{2+} adsorption on treated (1) and natural (2) clay. Clay concentration 0.6 g/100ml; solution volume 100 ml; initial concentration zinc ion 100 mg/l; contact time 5 h; pH 7; temperature 293 K

Table 3

Adsorption isotherm model constants for Zn^{2+} adsorption on natural and treated clay

	The Langmuir isotherm constants			The Freundlich isotherm constants		
	q_0, mg/g	b, l/mg	R^2	K_f	$1/n$	R^2
Natural clay	11.79	0.1	0.996	0.58	0.6	0.9926
Treated clay	12.92	0.02	0.998	4.05	0.21	0.9921

3.6. Kinetics of Adsorption

The adsorption mechanism and above-mentioned characteristics are explained using the adsorption kinetics.

It is possible to verify from Fig. 5 that equilibrium is reached after 300 min.

The monolayer capacity, q_0, for treated and natural clay was 12.92 and 11.79 mg/g, respectively. The higher b value of natural clay compared with that of treated clay showed that the adsorption of Zn^{2+} ions on the raw clay required more energy. The value of correlation coefficient (R^2 = 0.99) is also good for treated and natural clay. It can be said that Freundlich model suitable for adsorption natural and treated clay.

3.7. Thermodynamic Parameters

Thermodynamic parameters for the adsorption of zinc ions by natural and treated clay can be calculated from the maximum variation in adsorption with temperature using the thermodynamic relationships [26].

According to Eqs.(7) and (8) the thermodynamic parameters are the change of enthalpy (ΔH^0), free energy of Gibbs (ΔG^0) and entropy (ΔS^0).

$$K_{ads} = Q_e \frac{\left(\frac{m}{u}\right)}{\left[C_0 - C_e\left(\frac{m}{u}\right)\right]} \quad (6)$$

$$\Delta G^0 = RT \ln K_{ads} \quad (7)$$

$$\Delta S^0 = \frac{(\Delta H^0 - \Delta G^0)}{T} \quad (8)$$

where R is the gas constant, R=8.314·10^{-3} kJ/mol·K; K_{ads} is the equilibrium constant; T is the absolute temperature, K; ΔG^0 is the change of free energy, kJ/mol; ΔH^0 is the change in enthalpy, kJ/mol; ΔS^0 is the change in entropy, kJ/mol; u is the solution volume, ml; m is the weight of the clay sample, g; C_0 and C_e are the initial and equilibrium concentrations.

According to Eq. (8), the mean value of the enthalpy change due do the adsorption of Zn^{2+} by natural and treated clay within the studied temperature range can be determined graphically by the linear plotting of $\ln K_{ads}$ against $1/T$ using the least squares method (Fig. 8). The calculated thermodynamic parameters are summarized in Table 4. Within the temperature range of 293–323 K, the values of ΔG^0 for Zn^{2+} are negative indicating that adsorption is spontaneous. The adsorption capacity of Zn^{2+} adsorption on treated clay is higher than on natural clay because the lower the value of ΔG^0, the more spontaneous and favorable is the adsorption.

The ΔH^0 values for Zn^{2+} were found to be positive indicating that the adsorption process is endothermic; hence, the increase in temperature increases the metal adsorption capacity.Positive values of ΔS^0 mean that there is the increase in the disordered character at the solid-solution interface of zinc ions on natural and treated clay [27].

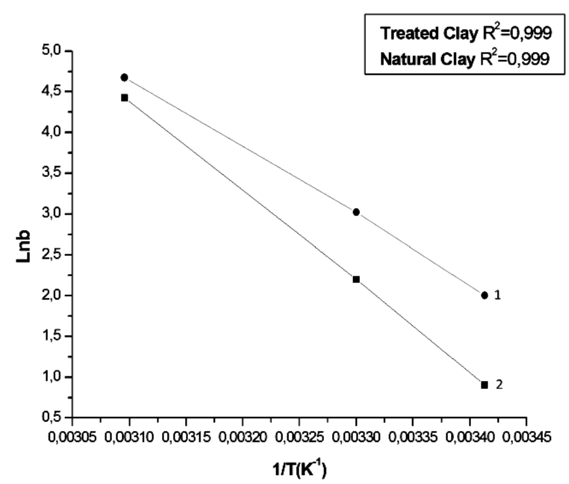

Fig. 8. Van't Hoff plots of Zn^{2+} adsorption on treated (1) and natural (2) clay

Table 4

Thermodynamic parameters for Zn^{2+}ion adsorption on natural and treated clay

	Temperature, K	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0, kJ/mol
Natural clay	293	-2.25	69.8	25.79
	303	-5.47		
	323	-11.90		
Treated Clay	293	-4.95	92.13	32.23
	303	-7.50		
	323	-12.60		

4. Conclusions

Zn^{2+} was removed from the solutions by natural clay from Algeria. Treated clay increased the adsorption capacity. The adsorption reached the maximum at pH 8.5 and increased with the increase in temperature. The isotherms could be described by the Langmuir model. The monolayer capacity for treated and natural clay was found to be 12.92 and 11.79 mg/g, respectively. The adsorption process was spontaneous and endothermic. The amount of Zn^{2+} adsorbed by natural clay is lower compared with treated clay.

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АДСОРБЦІЯ ЙОНІВ ЦИНКУ У ВОДІ НА ПРИРОДНИХ ТА АКТИВОВАНИХ ГЛИНАХ

Анотація. *Досліджено адсорбцію йонів цинку у воді на природних та активованих глинах. За допомогою методів ТГА/ДТА та хімічного аналізу визначено характеристики природної глини до і після активації. Досліджено вплив різних параметрів, таких як вихідна концентрація, температура, pH, час контакту та концентрація адсорбенту. Показано, що активована глина є кращим адсорбентом для видалення йонів* Zn^{2+} *у порівнянні з природною і може використовуватися замість дорогих адсорбентів. Розраховані термодинамічні параметри, які показали, що адсорбція* Zn^{2+} *на природній та активованій глині є ендотермічним процесом.*

Ключові слова: *активована глина, ізотерма адсорбції, термодинамічні параметри, монтморилоніти, ендотермічний, екзотермічний.*