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Elaboration and Characterization of Solid Materials of Types Zeolite NaA and Faujasite NaY Exchanged by Zinc Metallic ions Zn^{2+}

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Abstract

The present work deals with the elaborated of NaA and faujasite NaY solid materials according to a hydrothermal crystallization of amorphous gels composed of solutions of silicon, aluminum and sodium. The process elaboration has been achieved in autoclaves made of steel lined in Teflon under different operating conditions of temperature of heating, time of contact and stirring. After crystallization, the samples were characterized by different techniques such as X ray diffraction, scanning electronic microscopy, infrared spectroscopy, thermal analysis, and chemical analysis. Pure solid materials NaA and NaY zeolites were obtained and were impregnated by (Zn^{2+}) ions by ion exchange process. The effects of various parameters such as initial metal concentration, pH, solid-liquid ratio (R) and temperature on the exchange percentage are studied. The equilibrium isotherms of zinc ions sorption are also evaluated using Langmuir and Freundlich models. Thermodynamic parameters, i.e. enthalpy of adsorption ΔH_{ads}° , entropy change ΔS_{ads}° and Gibbs free energy ΔG_{ads}° for the sorption of zinc ions on NaA and NaY zeolites were examined.

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1. Introduction

Zeolites are a large group of different natural minerals and numerous elaborated forms [1-2]. NaA and NaY zeolites are proven ion exchange materials where Na^{+} cations are not fixed rigidly to the hydrated aluminosilicate structure and are readily exchanged with other cations in aqueous solutions [3-4]. Zeolites are a suitable choice as they have a large cation exchange capacity and an affinity for heavy metals. Many toxic heavy metals like Fe^{3+} , Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} have been discharged into the environment as industrial wastes, causing serious soil

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and water pollution [5]. The most commonly employed treatment method for heavy metal removal is chemical precipitation, ultra filtration, phytoextraction, electro dialysis, reverse osmosis and ion exchange [6]. This method has the decided advantage of minimal associated waste generation, process simplicity, and ease of maintenance. Zinc exchange from aqueous media using both synthetic and naturally zeolites has been reported [6-7]. The liquid phase concentrations of metal are generally, measured by atomic absorption spectrophotometry (AAS) as reported in literature [8-9]. The aim of this work is to examine the application of NaA and NaY with high surface areas for the remove of zinc (II) from aqueous solutions using an in situ method to monitor the exchanged sodium Na^+ ions by ion selective potentiometric method [10]. The effects of various parameters such as initial metal concentration, pH, solid-liquid ratio (R) and temperature on the exchange percentage were investigated. The equilibrium isotherms of zinc ions sorption are also evaluated using Langmuir and Freundlich models. Thermodynamic parameters, i.e. enthalpy of adsorption $\Delta H^{\circ}_{\text{ads}}$, entropy change $\Delta S^{\circ}_{\text{ads}}$ and Gibbs free energy $\Delta G^{\circ}_{\text{ads}}$ for the sorption of zinc ions on NaA and NaY zeolites were examined.

2. Materials and methods

2.1. Zeolite preparation

NaA and faujasite NaY zeolites were prepared from gels with respectively molar compositions 1.1 Na_2O : 1 Al_2O_3 : 1.26 SiO_2 : 92 H_2O 1 Al_2O_3 : 1.26 SiO_2 : 92 H_2O and 4.8 Na_2O : 1 Al_2O_3 : 3.8 SiO_2 : 224 H_2O . A typical preparation for NaY was performed as follows. Distilled water (21.6 g) and a solution of sodium hydroxide (2.1 g) were added to 1.23 g of fumed silica. After stirring for 2 h, 2.2 g of isopropoxylaluminium ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$) was gradually added under continuous stirring. Finally, the whole mixture was stirred for another 2 h and kept over 24 h for incubation. The preparation of NaA zeolite was performed in the same conditions. The gels were hydrothermally reacted in Teflon-lined stainless steel autoclaves at 100°C for 24 h. Thereafter, the products were recovered by filtration, washed with distilled water and dried at 100°C overnight. The as-prepared forms of zeolites were calcined by heating from room temperature to 600°C during 6 h in air.

2.2. Zeolite characterization

NaA and faujasite NaY zeolites were characterization by X-ray powder diffraction (Philips PW 1800, using $\text{CuK}\alpha$ radiation), scanning electronic microscopy (Philips XL 30), infrared spectroscopy (Philips PU 9800), thermogravimetry and differential thermal analysis (M2 BDL-Setaram) and energy dispersive spectroscopy (EDS) for chemical analysis.

2.2. Reagents

Inorganic chemicals were supplied by Merck as analytical grade reagents and distilled water was used. For zeolite preparation, the reagents used were NaOH (98%, Merck), isopropoxylaluminium ($[(\text{CH}_3)_2\text{CHO}]_3\text{Al}$) (98%, Aldrich) and fumed silica (100%, Merck). The metal ions studied were Zn^{2+} . We prepared a synthetic stock solution of zinc using ZnCl_2 salt.

2.3. Batch adsorption studies

The ion exchange of zinc metal on NaA and faujasite NaY zeolites was carried out using the batch method. Batch adsorption experiments were conducted using different amounts of powder adsorbent with 100 ml of solution containing zinc metal ions. The particle size of the samples is 4 μm for NaA and 3 μm for NaY. The exchanged sodium Na^+ ions were measured by ion selective potentiometric method using a sodium and Ag/AgCl reference electrodes and Radiometer potentiometer model. The zinc ions were determined using the following equilibrium: $\text{Zn}^{2+}_{(\text{solution})} + 2\text{Na}_{(\text{zeolite})} \leftrightarrow \text{Zn}_{(\text{zeolite})} + 2\text{Na}^+_{(\text{solution})}$. The amount of zinc (II) was calculated (E_q, I) from the difference between the initial (C_i) and the determined final (equilibrium) concentration (C_{eq}) in the solution respectively.

$$C_{adsorbed} = C_i - C_{eq} \text{ (mg/L)} \tag{1}$$

The adsorption percentage (*Eq.2*) was calculated by using the following equation:

$$\text{Adsorption (\%)} = (C_i - C_{eq}) 100 / C_i \tag{2}$$

where C_i and C_{eq} are the initial and the determined final (equilibrium) concentration of studied metal ion in its aqueous solution at the beginning and at the end of adsorption experiments respectively.

The uptake distribution factor K_D (*Eq.3*) is defined as the concentration of the species adsorbed per gram of the adsorbent divided by its concentration per ml in the liquid phase [11] :

$$K_D = (C_i - C_{eq})V / C_{eq}m \text{ (ml/g)} \tag{3}$$

Where V is the volume of the solution in ml and m is the mass of adsorbent in g.

3. Results and discussion

3.1. Characterization of elaboration zeolites

The product of the two syntheses was zeolites NaA and NaY with almost identical XRD patterns, as shown in Fig.1 with no detected contaminated phases. Thus, zeolites were obtained with high purity and a good crystallinity. These results are in good agreement with those reported in the literature [12]. After indexation of XRD patterns of prepared zeolites, all diffraction planes (hkl) correspond to NaA and NaY phases.

Scanning electronic micrographs (Fig.2) show that NaA and NaY crystallize as rather fine particles with cubic shape with average size of 4 and 3 μm respectively. The chemical analysis gives molar Si/Al ratios of 1.2 for NaA and 3.2 for NaY which are lower than the ratios used initially as raw materials.

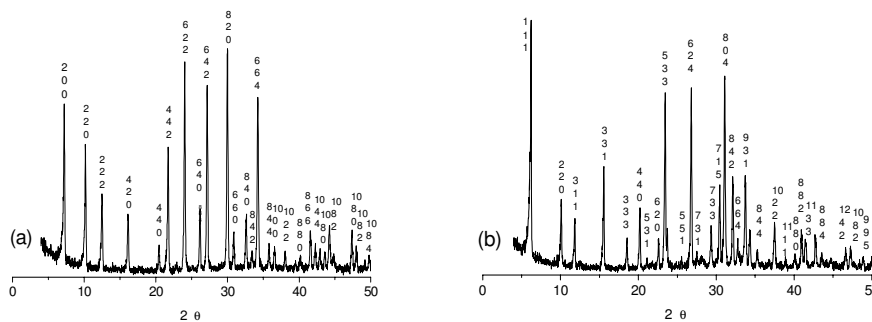


Fig.1. XRD patterns of as-elaborated (a) NaA and (b) faujasite NaY zeolites

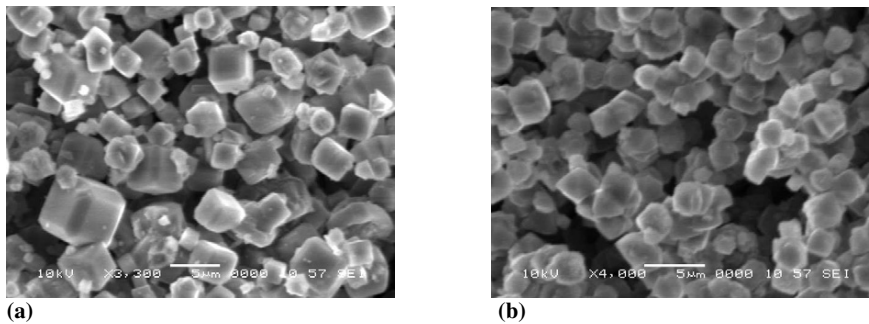


Fig.2. Scanning electronic micrographs of elaborated (a) NaA and (b) faujasite NaY zeolites

Fig.3 shows FT-IR spectra of elaborated NaA and faujasite NaY zeolites. The bands at 1200 to 450 cm^{-1} are known to assignable to Si-O-Al, Si-O-Si, Si-O, Si-Al and T-O species [13]. In the other hand, the bands at 3750 to 3450 cm^{-1} are attributed to Si-OH, Si-OH-Al and -OH hydroxyl groups. The band at 660 cm^{-1} is known to assignable to Si-O-M where M is the exchangeable Na^+ ion metal species [14]. When closed examined, the absorption band at 660 cm^{-1} in NaA is large and visible which is incorporated with Na atoms in the zeolite framework.

TG characterization of prepared NaA and NaY in air flow show total weight losses at 900°C of 35 wt.% and 27 wt.% respectively. DTA profiles of NaA and NaY show a large peaks at 145°C which are ascribed to desorption of water located in the zeolite channels. The second peak appears at 265°C and is due to the decomposition of organic template used as aluminium reagent during the preparation of zeolites. The surface areas of NaA and NaY zeolites are 260 and 350 m^2/g respectively and therefore allow high exchange surfaces where Na^+ cations are available in hydrated aluminosilicate.

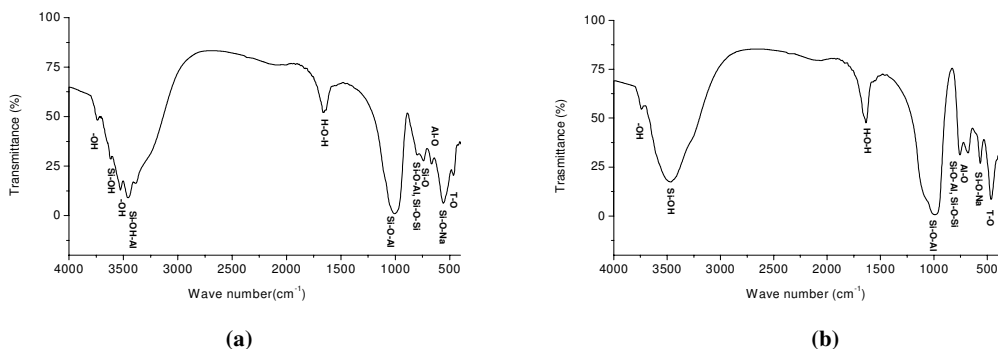


Fig.3. FT-IR spectra of elaborated (a) NaA and (b) faujasite NaY zeolites

3.2. Adsorption of zinc ions on NaA and NaY zeolites

In the subsequent investigations, experiments were performed at solution pH value of 6 to avoid any possible hydroxide precipitation [15-16]. The adsorption of Zn^{2+} ions onto NaA and NaY as a function of the initial zinc (II) concentrations was studied at 25°C by varying the metal concentration from 5 to 50 mmol/l . All other parameters were kept constant. The results in Fig.4 showed that the percentage adsorption of zinc (II) decreases with an increase in the solution concentration indicating that fewer favourable sites become involved when solution concentration rises.

The variation of distribution factor K_d as function of initial zinc concentration is illustrated in Fig.4. The K_d values decreases for both NaA and NaY with an increase of initial concentration of zinc indicating that less favourable media become involved when solution concentration increases. The maximal levels of exchange reached for both zeolites NaA and NaY was 75 and 67 %.

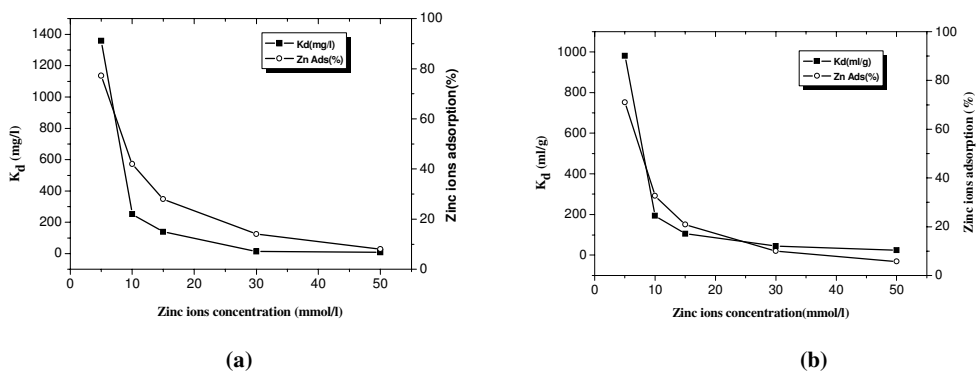


Fig.4. Variation of adsorption uptake of zinc (II) ions and K_d on (a) NaA and (b) faujasite NaY zeolites with the initial concentration. $m = 250$ mg, $V = 100$ ml, $pH = 6$ and $t = 2$ h.

The adsorption of zinc ions onto NaA and NaY zeolites at different temperatures increases sharply during the 10 min, and then keeps increasing slowly until equilibrium is reached as shown in Fig.5. The equilibrium time was found to be 40 min for NaA and 30 min for NaY. We also noticed that the initial concentration and solid liquid ratio varied in the same way. Fig.5 shows that the adsorption percentages decrease with the increase in temperature. This indicates an exothermic nature of the process and the adsorption of zinc (II) ions onto NaA and NaY is favoured at low temperature.

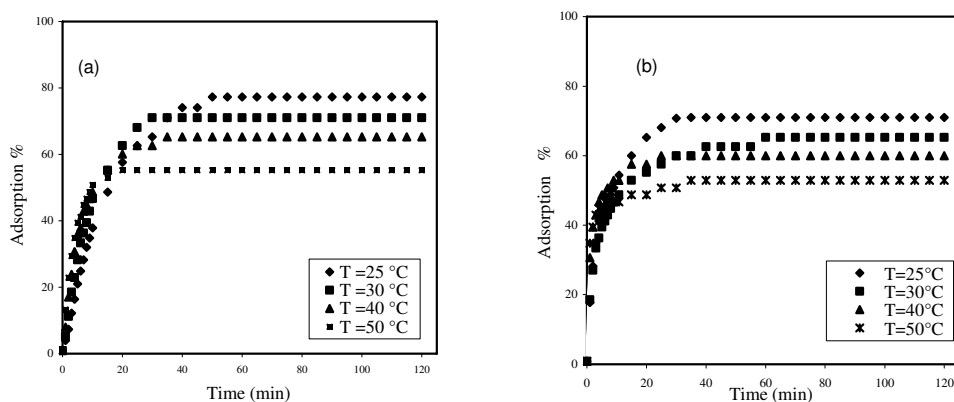


Fig.5. Effect of temperature on the percentage of adsorption of zinc (II) from aqueous solutions onto zeolites (a) NaA and (b) NaY. $m = 250$ mg, $V = 100$ ml, $[Zn^{2+}] = 5$ mmol/l and $pH = 6$.

3.3. Equilibrium isotherms

The study of equilibrium isotherms is fundamental in supplying the essential information required for the design and the sorption process. In this investigation, Langmuir and Freundlich isotherm models were used to analysis the equilibrium data within NaA and faujasite NaY sorbents. Langmuir (4) and Freundlich (5) isotherm models can be expressed by following equations [17-18]:

$$q_e = Q_0 b C_e / (1 + b C_e) \quad (4)$$

$$q_e = K_f C_e^{1/n} \quad (5)$$

Where q_e is the equilibrium uptake (mg/g), C_e is the equilibrium zinc ions concentration (mg/L), Q_0 (mg/g) (saturated monolayer sorption capacity) and b (L/g) (sorption equilibrium constant) are the Langmuir constants, K_f (L/g) and n are Freundlich constants.

The linearized forms of Langmuir and Freundlich equations are:

$$C_e/q_e = 1/Q_0 b + C_e / Q_0 \quad (6)$$

$$\text{Log } q_e = \text{Log } K_f + 1/n \text{ Log } C_e \quad (7)$$

The Langmuir and Freundlich model parameters and the statistical fits of the sorption data to these equations are given in Table 1. The results show that Langmuir model describes the sorption data with R^2 values > 0.996 . According to the saturated monolayer sorption capacity Q_0 (mg/g) and b (L/g), sorption on prepared zeolites is produced as following faujasite NaY $>$ NaA. On the other hand, the equilibrium data were analyzed using Freundlich isotherm model and R^2 values were estimated as 0.856 and 0.956 for NaA and faujasite NaY respectively. The value of $1/n < 1$ generally indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the zeolites by the zinc ions; thus infinite surface coverage is predicted and indicating multilayer adsorption on the surface [18]. When the two isotherm models are compared, values of coefficient of determination showed that Langmuir has better performance than Freundlich for representing the equilibrium data.

3.4. Thermodynamic parameters

Thermodynamic parameters (heat of adsorption ΔH° , entropy change ΔS° , and free energy ΔG° for the sorption of zinc ions on NaA and faujasite Y zeolites were calculated using the following equations:

$$\ln K_d = (\Delta S^\circ / R) - (\Delta H^\circ / RT) \quad (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (9)$$

The values of ΔH° and ΔS° are obtained from the slope and the intercept of each plot ($\ln K_d$ against $1/T$ for two prepared zeolites), which were estimated by a curve-fitting program. The values of thermodynamic parameters for the sorption of zinc ions on NaA and faujasite Y zeolites are given in Table 2. The values of thermodynamic parameters show that Gibbs free energy $\Delta G^\circ_{\text{ads}}$ become less negative with increasing temperature indicating that sorption is less favourable at high temperatures. The negative values of $\Delta H^\circ_{\text{ads}}$ and $\Delta S^\circ_{\text{ads}}$ indicate that the sorption of zinc (II) ions on prepared zeolites is exothermic process and the sorbate (Zn^{2+}) ions are stable on the solid surface.

Table 1. Characteristic parameters and determination coefficient of the experimental data according to the Langmuir and Freundlich equations

Zeolite sorbents	Langmuir constants			Freundlich constants		
	Q ₀ (mg/g)	b (L/g)	R ²	K _f (L/g)	1/ n	R ²
NaA	118.906	0.021	0.996	85.541	0.338	0.856
faujasite NaY	106.382	0.033	0.998	77.239	0.395	0.956

Table 2. Thermodynamic parameters for adsorption of zinc ions on NaA and faujasite NaY zeolites as function temperature

Zeolite sorbents	ΔH° (KJ/mol)	ΔS° (J/mol K)	ΔG° (KJ/mol)			
			298 K	303 k	313 k	323 k
NaA	-30.667	-43.256	-17.777	-17.761	-17.128	-16.696
faujsite NaY	-23.690	-22.560	-16.967	-16,854	-16.628	-16.403

4. Conclusion

In the present work, we report the preparation and characterization of two sorbent zeolites such as NaA and faujasite NaY used in the adsorption of zinc (II) ions from aqueous solutions. The results obtained allowed the following conclusions.

The use of hydrothermally method allowed to obtaining of pure solid materials NaA and NaY zeolites. The materials are thermally stable up to at least 900°C. The maximum percentage of adsorption was estimated as 80 and 70 % for NaA and faujasite NaY respectively. The Langmuir and Freundlich equations were used to describe the sorption isotherms of these processes. The experiments showed that linear form of the Langmuir model has better performance than Freundlich for representing the equilibrium data. The values of thermodynamic parameters show that ΔG° become less negative with increasing temperature indicating that sorption is less favourable at high temperatures. The negative values of ΔH° and ΔS° indicate that the sorption of zinc (II) ions on prepared zeolites is exothermic process and the sorbate (Zn^{2+}) ions are stable on the solid surface. The exchange of zinc (II) ions as results of adsorption is ascribed to a decrease in the degree of freedom of adsorbate ion which results in the entropy change.

These results show that NaA and NaY zeolites can used effectively for the removal of zinc metal ions from aqueous solutions or wastewater.

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