

Uptake of Cd^{2+} by Synthesized Zeolite from Thermally Activated Tunisian Kaolinite

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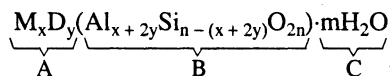
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Thermal activated Tunisian kaolinite (CEC = 10 meq/100 g of calcined clay) was used to synthesize a molecular sieve by hydrothermal treatment in alkaline medium. The obtained zeolite corresponds to the A type. The cation exchange capacity of this new material reaches 340 meq/100 g of calcined zeolite. The uptake of Cd^{2+} on zeolite-A was studied using cation exchange measurement. The effect of pH on the uptake has been reported.

Key Words: Uptake, Cd^{2+} , Zeolite, Activated Tunisian kaolinite.

INTRODUCTION

The presence of metal in aquatic environments has been known to cause several health problems to animals and human beings. The heavy metals levels in waste water, drinking water, and water used in agriculture must be reduced to maximum permissible concentration. Precipitation, solvent extraction, adsorption in the activated carbon and ion exchange are the conventional methods for the removal heavy metal ions from aqueous solutions. Clay minerals and zeolite^{1,2} can be used as cation exchangers, but the cation exchange capacities of zeolite are much higher than clay. Clay is the layered bi-dimensional aluminosilicate but zeolite is a three-dimensional crystalline hydrated aluminium silicate whose structure contains channels and/or cages filled with exchangeable cations and which is of the general formula³:



A : exchange cations

B : three-dimensional framework

C : intra-crystalline water

The purpose of the work is to use a kaolinite clay as the principal source of silicon and aluminium to synthesise a zeolite and then the application of molecular sieve type-A to remove heavy metals (Cd^{2+}) from aqueous solutions.

The sample was a natural kaolinite from Touila deposit (Tabarka, Tunisia) containing near 33% impurities (18% quartz and illite 15%)⁴.

The chemical analysis of crude and purified samples (wt %) is given below.

	Crude	Purified
SiO ₂	58	47.1
Al ₂ O ₃	23	31.8
Fe ₂ O ₃	2.1	2.7
CaO	0.3	0.3
MgO	0.4	0.5
Na ₂ O	0.35	0.6
K ₂ O	1.25	1.35
TiO ₂	0.8	0.9
(Lost at 1000°C)	12.9	14.9

EXPERIMENTAL

X-ray patterns were obtained from the original and treated material using a Philips PW 1900 with CuK_α Radiation. Infrared spectra were obtained by using KBr pellets and were recorded with a Perkin-Elmer apparatus type 783 from 4000–400 cm⁻¹.

Cation exchange capacities: Ammonium acetate saturation (AMAS)⁵, methylene blue adsorption (MBA)⁶ and copper ethylenediamine complex (EDAC) methods⁷ are used to determine the cation exchange capacities (CEC).

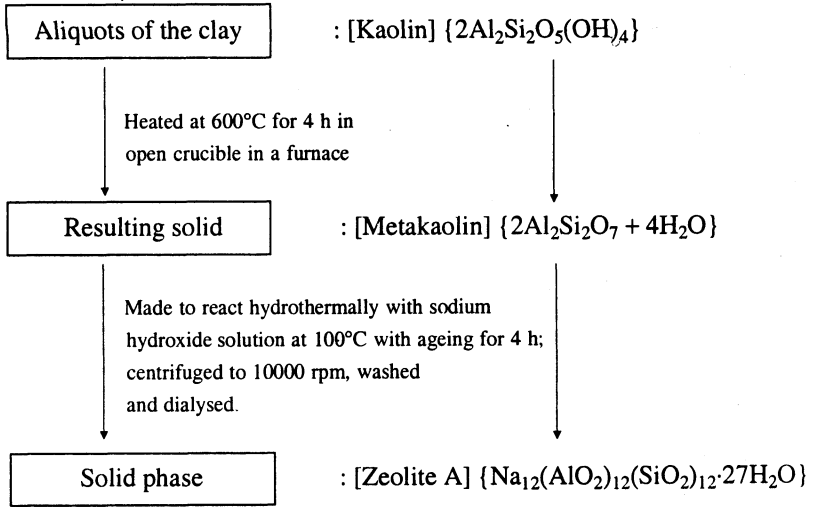
Adsorption of heavy metals: Cd²⁺ solution was prepared by dissolution of Cd(NO₃)₂ in distilled water. pH values of the solution were adjusted to 1, 2, 3.15 and 5.5 by adding 0.1 N HCl or 0.1 N NaOH. Batch adsorption experiments were conducted using 100 mg of the adsorbent with 50 mL of solution containing heavy metal ions of the desired concentration at room temperature. After contact time the suspensions were filtered and solutions were analysed for heavy metal ions by atomic adsorption method.

Conversion of sodium zeolite to hydrogen form: The aliquots of sodium zeolite were added to 50 mL of acidic solutions (pH range 1–5.25). After stirring and separation the released Na⁺ was analysed in the supernatant by spectrophotometer method.

Synthesis

Zeolite synthesis from clay involves two steps.⁸

In the first step, clay samples are heated at 600°C for 4 h in open crucibles in a furnace and then after cooling the heated sample is made to react hydro-thermally with sodium hydroxide solution at 100°C with ageing for 20 h. The final mixture was centrifuged to 10000 rpm. The solid phase was washed several times with distilled water until pH 9, dialysed and dried at 80°C. The solid was then ground and sieved to 40 μm.



X-ray Diffraction

Fig. 1 gives X-ray patterns for crude clay (A), heated at 600°C (B) and hydrothermal alkaline treated.

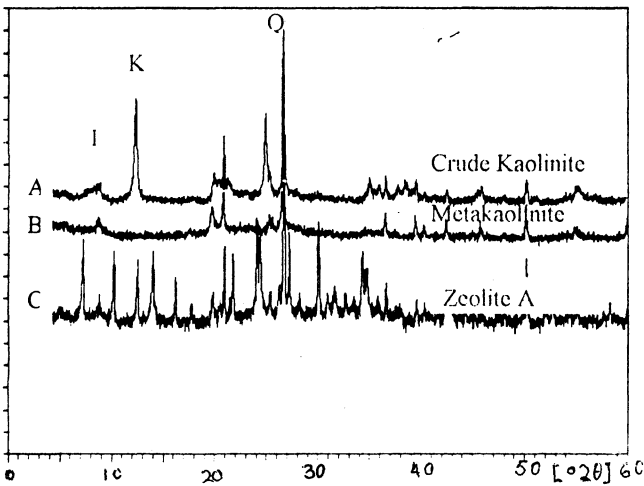


Fig. 1. XRD of crude kaolinite, metakaolinite and zeolite-A.

The X-ray patterns show:

- (A) The kaolinite (d_{001} and d_{002} reflections at 7.16 and 3.56)
 - traces of illite (d_{001} reflection at 10 Å)
 - the quartz (d_{101} reflection at 3.35 Å) is the major impurity.
- (B) After thermal treatment the reflections of kaolinite disappear.
- (C) After calcination and hydrothermal treatment in alkaline medium, the new reflections appeared at (12.29, 8.71, 7.11 and 5.51 Å), corresponding to zeolite A phase.

Infrared spectra

The spectrum (A) shows some bands indicating the presence of kaolinite⁹:

- OH stretching, hydroxyl sheet at 3695, 3670, 3655 and 3622 cm^{-1}
- SiO stretching at 1110, 1035 and 1030 cm^{-1}
- OH deformation at 935 and 912 cm^{-1}
- Mixed SiO deformations and octahedral sheet vibrations at 650, 540, 470 and 430 cm^{-1}

After heating, the characteristic bands of kaolinite disappear indicating the destruction of this material and its transformation to metakaolinite (spectrum B).

Spectrum C shows new bands corresponding to formation of zeolite A. Two type of bands appear:

- Asymmetric stretch at 1090, 1050 and 995 cm^{-1}
- Symmetric stretch at 740, 705 and 660 cm^{-1}
- Double rings at 550 cm^{-1}
- T—O Bend at 464 cm^{-1}

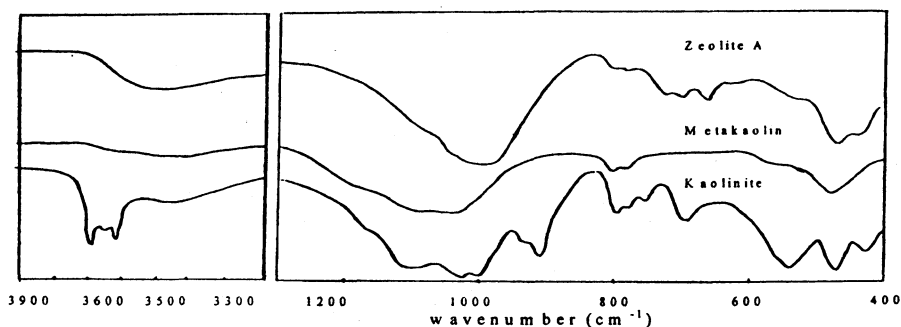
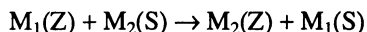


Fig. 2. Infrared spectra of kaolinite, metakaolinite and zeolite-A.

Cation Exchange Capacities

Cation exchange capacity (CEC) is an important property of zeolite. CEC results from the presence of loosely bound cations of alkaline and alkali earth elements, often called exchangeable cations in the structure of the zeolites. These loosely bound cations are easily exchanged when zeolites are in contact with saturating ion solutions.

The exchange reaction between a zeolite and an ionic solution is described as:



M_1 is the exchangeable cation present in zeolite Z,

M_2 is the saturating ion in solution S.

The results of cation exchange capacities (meq/100 g of calcined samples) is given in the following table:

	AMAS	MBA	EDAC
Crude kaolinite	15	9.37	10.6
Metakaolinite	12	10.00	9.3
Zeolite	336	24.00	24.5

The MBA and EDAC methods are not suitable for zeolites because the size and the projected plan areas of the MB and EDC molecules are usually greater than the size of the zeolitic channels. Only the ammonium acetate method gives the true results for this determination. Zeolite A can display a double ion sieve active. Only small cations can penetrate the 6 rings into the β cage.

Ion exchange isotherms of Cd^{2+} : Ion exchange isotherms of Cd^{2+} on synthesised zeolite at four initial pH (zeolite referred to 1000°C) are given in Fig. 3. The results show an increase of adsorbed cations when the initial pH increases. This phenomenon is explained by competition between proton and metallic cation at different pH. Two distinct regions for all curves appear. In the first region the slope of the isotherm approaches unity, This indicates practically all Cd^{2+} added was taken up. In the second region Cd^{2+} uptake depends on the initial pH of the suspension.

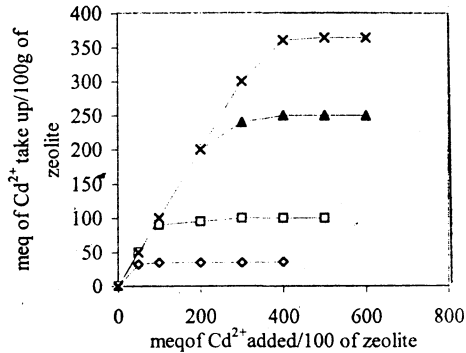


Fig. 3. Uptake of Cd^{2+} by zeolite.

Transformation of zeolite A to its hydrogen form: Fig. 4 shows Na^+ released as function of initial pH. At pH less than 1, the total Na^+ in exchange position is liberated in solution and the zeolite is transformed to its hydrogen form. This result can be used to generate the active zeolite from the contaminated heavy metal zeolite.

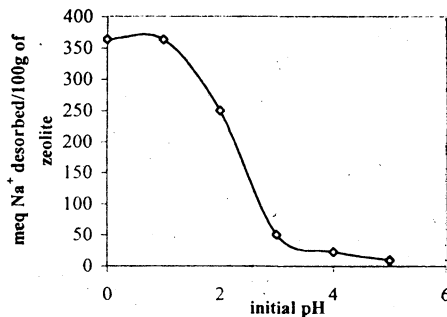


Fig. 4. Effect of pH to desorb cation exchange of zeolite.

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