

## Research Article

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## Synthesis and modification by ion exchange of the composite Core-Shell

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### Abstract

Zeolites are a large family of inorganic compounds with particular properties that have resulted in several important industrial applications; ion exchange has the first industrial application in the field of water treatment. The exchange by aqueous route is the most used method in the case of this type of micro-porous materials and it is that technique which will be used in the present work, this study aims to "Purification". The objective of this work is to find performance materials for recovery and the incorporation of heavy metals such as lead and cadmium. The study is to compare the ion exchange properties of different zeolite Na-X and Na-A, their physical mixture and a composite called LTA/FAU formed by zeolites A (LTA) and zeolite X (FAU). Indeed, several syntheses of different zeolites X and A were performed, then a core-shell model was designed to form the composite LTA/FAU. Finally, the study of ion exchange on the different zeolite materials formed are thus achieved. The cations are exclusively tested for lead and cadmium, toxic elements harmful to health and to the environment as well.

**Keywords:** Zeolite LTA, Zeolite FAU, Ion exchange, Composite core shell, Exchange capacity, Purification.

### Introduction

We are living in a time and in a world heavily polluted. In the list of the great dangers awaiting the man can be placed on top of the list pollution by heavy metals: lead, mercury, cadmium.

Fatigue, Depression, Thyroid disorder, Alzheimer's, Parkinson's, Cancer, are some of the health problems caused by heavy metal pollution. The environmental protection has long since become a major political and economic issue. Among the priorities include safeguarding water resources. All countries of the world are concerned either because they lack water or because they pollute it. <sup>1</sup> There are several ways to remove these heavy metals, ion exchange by zeolites is one of these ways, which our work is based on [2]. <sup>2</sup>

Zeolites were among the main clean up materials either by adsorption<sup>3-4</sup>, ion exchange<sup>5</sup> and catalysis<sup>6</sup> Lead and cadmium, heavy metals, is one of the main dangers fulminate the flora and fauna of our small planet<sup>7</sup>, so many resources are deployed to remedy them. The elimination of lead and cadmium by ion exchange has been extensively studied.<sup>8</sup> However, exchange capacity of more and larger formed a major challenge for researchers and industry.

## Materials and Methods

### Zeolitic materials, synthesis and characterization

The method of synthesis of the zeolite X (Part: Core) was performed according to the protocol established by the International Association of IZA zeolites<sup>9</sup> with slight modifications<sup>10</sup>. From a molar composition of the starting gel type:  $3.5\text{Na}_2\text{O} : 1\text{Al}_2\text{O}_3 : 2.9\text{SiO}_2 : 150\text{H}_2\text{O}$ , a first solution (A) was prepared with sodium aluminate  $\text{NaAlO}_2$  (Carlo Ereba) and  $\text{NaOH}$  (99%, Prolabo). A second solution (B) is prepared by dissolving sodium silicate  $\text{Na}_2\text{SiO}_3$  (Merck product, 63%  $\text{SiO}_2$ , 19%  $\text{H}_2\text{O}$ , 18%  $\text{Na}_2\text{O}$ ), stirred with a medium heat. The water used is deionized water. The two solutions A and B are mixed under agitation for 40 min. The mixture thus formed is placed in a polypropylene bottle and then heated to  $90^\circ\text{C}$  for 20 hours. After heating, the product is filtered and washed several times with distilled water to  $\text{pH} < 9$ ; it is then dried in an oven at  $100^\circ\text{C}$ .<sup>1</sup>

The zeolite surface (Part: Shell) is formed mainly by a nano-crystals of zeolite A. The procedure to seed formation of zeolite A from the stoichiometry of the starting gel as follows:  $3.165\text{Na}_2\text{O} : 1\text{Al}_2\text{O}_3 : 1.926\text{SiO}_2 : 128\text{H}_2\text{O}$ . Was dissolved  $\text{NaOH}$ , sodium hydroxide (99 %, Prolabo) in water and then this solution is divided into two equal amounts. As the zeolite of the core, two solutions A and B were prepared; the first contains sodium aluminate  $\text{NaAlO}_2$  Carlo Erba, the second sodium silicate Merck. The second solution is quickly added to the first, the mixture is homogenized for 90 min to 03 hours, and then cured at a temperature ranging from  $25^\circ\text{C}$  to  $70^\circ\text{C}$ . The crystallization is done at temperatures below  $100^\circ\text{C}$  low temperatures for a time, which varies between 4 and 42 hours. The washing is performed with distilled water to  $\text{pH} < 9$  and drying at  $80^\circ\text{C}$  in an oven.<sup>11</sup>

The composite zeolite / zeolite of the core-shell model is to introduce crystals core zeolite X obtained in a gel composition similar to that of zeolite A, previously aged at  $70^\circ\text{C}$  with agitation. The mixture gel + crystals are homogenized, then heated to temperatures below  $100^\circ\text{C}$ .

The zeolite X of the core, nano-crystals of zeolite A and the composite formed are characterized by X-ray powder (Philips PW 1820), the crystals were examined on a scanning electron microscope type Joel and elements Na, Si and Al determined by electron microprobe the same device electron microscopy.

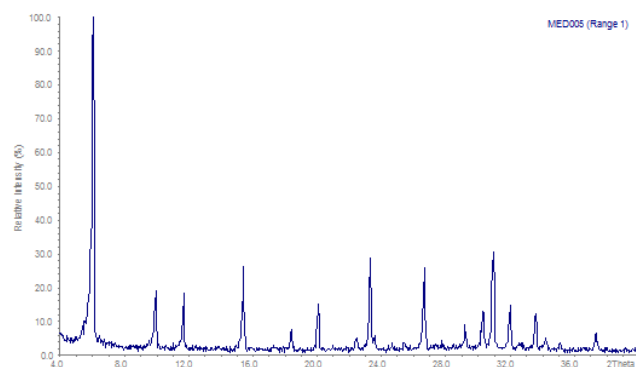
### Ion Exchange

The ion exchange is carried out by hydrothermal way of preparing the saline solutions containing lead acetate,  $\text{Pb}(\text{CH}_3\text{COOH})_2 \cdot 3\text{H}_2\text{O}$  and cadmium chloride, Merck  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$  at different concentrations  $10^{-3}\text{M}$ ,  $5 \cdot 10^{-3}\text{M}$ ,  $10^{-2}\text{M}$ ,  $5 \cdot 10^{-2}\text{M}$ , then introducing an amount of 500 mg of zeolite (the zeolite X, zeolite A, or the composite). In the case of physical mixture of zeolite A and zeolite X, it is sufficient to introduce an amount of 250 mg of each zeolite. The whole solution-zeolite is subjected to agitation at  $25^\circ\text{C}$  for six hours. For the  $60^\circ\text{C}$  temperature, the exchange is performed in a system to reflux for a period of three hours.

The contents of  $\text{Na}^+$ ,  $\text{Pb}^{++}$  and  $\text{Cd}^{++}$  were measured by atomic absorption Perkin Elmer. The exchanged solids are controlled by X-ray diffraction of powder (Philips PW1820).

## Results and Discussion

Analysis by X-ray diffraction of the solids zeolite X obtained shows a diffraction pattern (Figure 1) in accordance with the Record ICDD, very intense lines mean that the product is well crystallized.<sup>2</sup> Indeed, the degree of crystallinity, measured from the diffraction X-ray, is equal to 100%.<sup>3</sup>



**Figure 1:** X-ray diffraction patterns of core crystals-zeolite X (FAU)

The crystals have a surface area relatively high for such zeolite (measured by the BET method) of  $800\text{ m}^2 \cdot \text{g}^{-1}$ , which could explain the high purity of the product.<sup>4</sup>

**Table 1:** The Chemical composition of crystals core zeolite X (FAU)

Molar ratio (zeolite) Si/ Al	% Na Na/Al (mass)	% Al (mass)	% Si (mass)	
1.3	0.9	13.2	17.2	23.2

Chemical analysis by electron microprobe crystals (Table 1) shows that the Si/Al ratio is 1,3. This value confirms that we are in the presence of zeolite X (FAU) and no Y zeolite (FAU).<sup>4</sup>

In order to optimize the conditions for the formation of nano-crystals of zeolite A, we are offered to control the speed of agitation to promote nucleation against growth. Indeed, for samples MED001, MED008 and MED014, the stirring time varies from 1h 30min to 3 hours at 25°C and

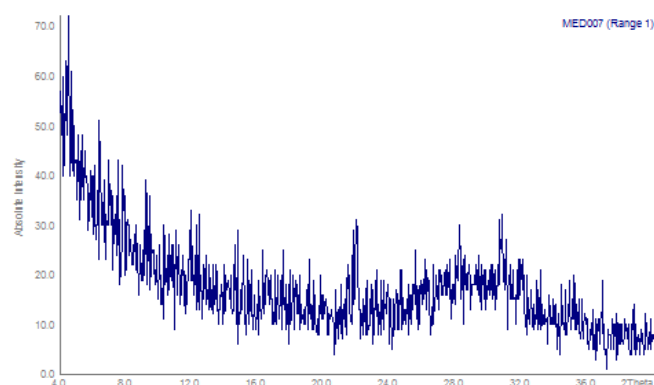
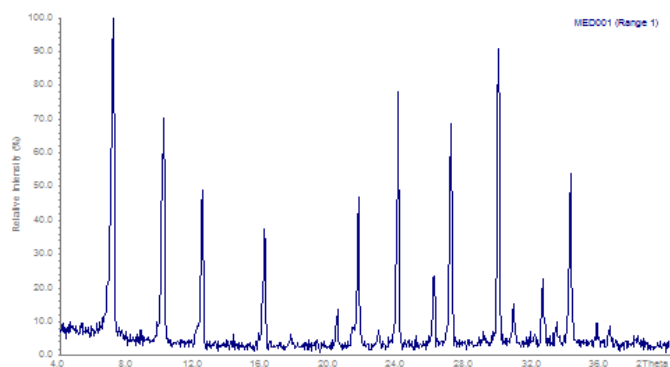
crystallization is followed by static method at 100°C and 70°C. Whereas, for the sample MED007, crystallization took place only in dynamic mode at 70°C. The synthesis conditions and the results are summarized in Table 2.

Diffractograms of the various samples are shown in Figures 2, 3, 4 and 5.

Table 2 is a summary of the conditions and the results of synthesis of nano-crystals of the zeolite LTA.

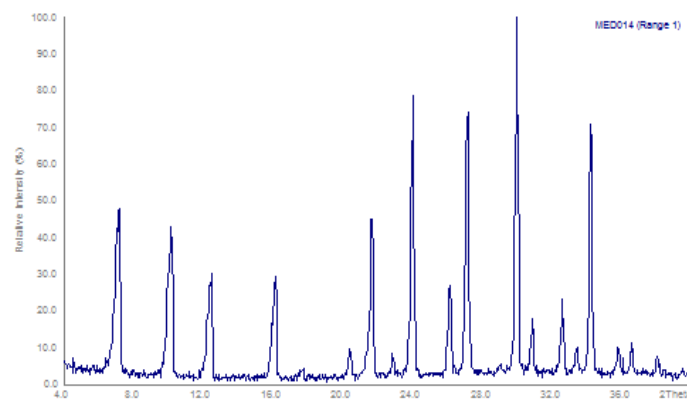
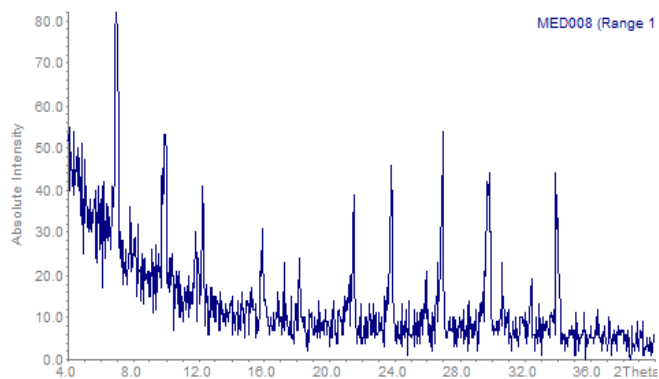
**Table 2:** Conditions and results of synthesis of nano-crystals of zeolite A

Samples	Crystallization				Phase obtained
	Stirring		Static		
	Duration	Temperature	Duration	Temperature	
MED001	1h 30mn	25°C	4h	100°C (stove)	Zeolite LTA pur large crystals
MED007	4 h	70°C (bath marie)	-	-	Beginning formation of small crystals of zeolite LTA, almost amorphous
MED008	1h 30mn	25°C	24h	70°C (bath marie)	Beginning formation of small crystals of zeolite LTA
MED014	3h	25 °C	42h	70°C	Small crystals of zeolite LTA



**Figure 2:** X-ray diffraction patterns of crystals of sample MED001

**Figure 3:** X-ray diffraction patterns of crystals of sample MED007

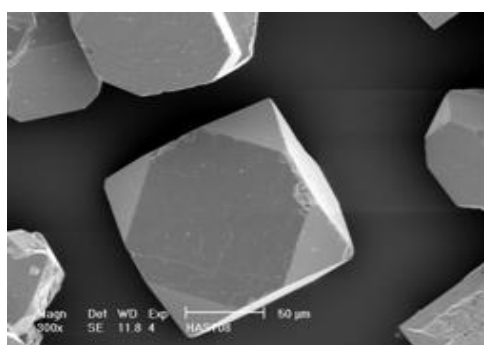


**Figure 4:** X-ray diffraction patterns of crystals of sample MED008

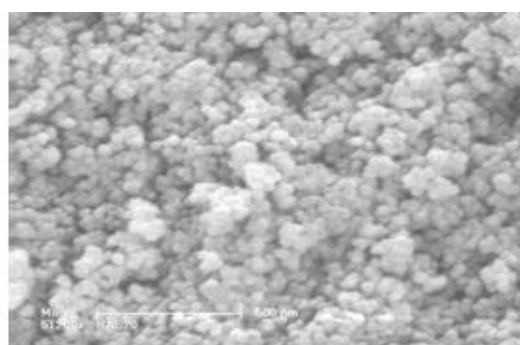
**Figure 5:** X-ray diffraction patterns of crystals of sample MED014

LTA phase in all cases except for Sample MED007 where a large amount of the amorphous phase coexists with the crystal of zeolite A.

We also note that the diffraction peaks of zeolite LTA present in the diffractograms of samples MED008 and MED014 are enough wide, which constitute evidence of the existence of nano-crystals (Sherrer effect).<sup>6, 7</sup> In contrast, the peaks of the diffractogram MED001 sample are acute which proves the existence, rather, large crystals. To confirm these findings we took SEM pictures of samples MED001 and MED014 and are presented in Figures 6a and 6b.



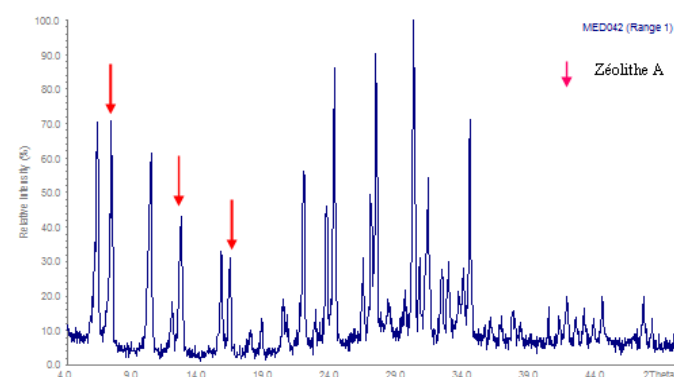
(a)



(b)

**Figure 6:** SEM images of the samples: (a) MED001, (b) MED014

Zeolites A (LTA) and X (FAU) do not have the same structural type, but their structures have in common the sodalite cage. Good compatibility between these two zeolites seems possible with a good inter growth therefore good adhesion. In addition, their chemical compositions are almost equivalent. The processing conditions were varied to obtain crystallization in the reaction medium. For this, the mixture underwent stirring at room temperature for 3 hours; the temperature was set at 70°C to promote the nucleation and formation of zeolite A, the synthesis time was 42 hours.

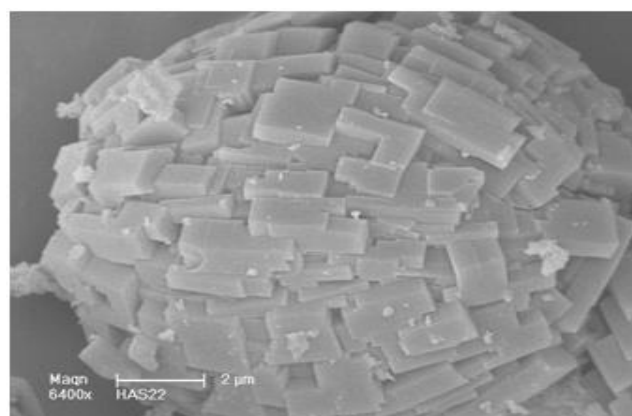


**Figure 7:** X-ray diffractogram on powder of crystals of zeolite X (FAU) with seeds zeolite A adsorbed on their surface

SEM pictures confirm that the zeolite crystals A passes a size 50µ ridge to a few nanometers in passing a stirring time of 1h30 mn to 3h. As for the crystallization of a lasted 4 hours to 42 hours and a temperature of 100°C to 70°C. This result is expected since the agitation promotes the nucleation process against growth.

Taking into account the operating conditions, we conclude that the agitation alone at 70°C for 4 hours is not sufficient for a complete crystallization.

The X-ray diffraction revealed no alteration of the crystallinity of the zeolite X, in addition, the presence of zeolite A as a second phase is also detected.<sup>2, 3</sup> In all cases the presence of zeolite of LTA type is confirmed by X-ray diffraction. Peaks characteristic of this phase are pointed by arrows in the X-ray diffractogram (Figure 7).<sup>8</sup> This remains insufficient to confirm or not the formation of core-shell composite. However, the observation by scanning electron microscopy confirms the formation of the composite (Figure 8).



**Figure 8:** SEM Photographs of seeds zeolite A adsorbed on the surface of zeolite crystals X

In this photograph it can be seen clearly that the small crystals which surround a sphere may be the X zeolite crystals whose presence is confirmed by the X-ray diffraction.

Ion exchange of  $Pb^{2+}$  and  $Cd^{2+}$  on the zeolite X, the zeolite A, the physical mixture A + X and the composite core-shell formed, previously saturated with solutions of sodium was determined by flame atomic absorption which is a very good way analyzing both its selectivity by its sensitivity. We admit that after saturation of sodium, all sites are occupied by  $Na^+$ . We have gathered the results under form variation of the CEC according to various materials, concentrations and temperature in Figure 9 (case of  $Cd^{2+}$ ) and Figure 10 (case of  $Pb^{2+}$ ).

The cation exchange capacity, of a zeolite denoted CEC is the amount of cations that it can retain its complex adsorbent at a given pH. CEC is milli equivalents per 100 grams (meq/100 g) of zeolite.<sup>12</sup>

Case of exchange with  $Cd^{++}$ : For the zeolite Na-A, the amounts of  $Cd^{++}$  and the remaining  $Na^+$  released are too low for the concentration  $C_0=0.001$  M, the values of CEC are not determined.

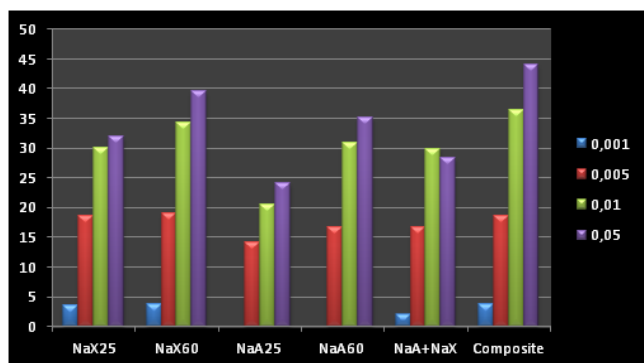


Figure 9: The variation of the CEC based on various materials, concentrations and temperature

The results of the figure show that the CEC increase with the initial concentration. This result, not expected, could be explained by the choice of too low concentrations (0.001M and 0.005M) where the amount of  $Cd^{++}$  do not even constitute 30% of the quantity of sodium present in the zeolite. What was offset by relatively higher concentrations (0.01M and 0.05M). Best CEC are obtained for the concentration  $C_0 = 0.05$  M.

However, the effect of temperature, performed to Na-X and Na-A only, is entirely consistent with the theory. Increasing the temperature of the active system and the CEC are best obtained for the temperature 60°C.<sup>4</sup>

Moreover, the results presented above show that 25°C and  $C_0=0.05$ M, the CEC to 32 meq for zeolite X, 24 meq only for Na- A, 28 meq for the physical mixture (Na-X + Na-A) and 44 meq for the composite LTA / FAU. At 60°C two swaps were performed on zeolite X alone and zeolite A. For the zeolite Na-X, the CEC observed is 39 meq. While for Na-A the CEC=35 meq.

Thus, the first observation is that the zeolite X has a larger exchange capacity than that of A. In fact, for two temperatures considered, the CEC of the zeolite X is always greater than that of zeolite A. This exchange capacity is predicted from the structure of the zeolite NaX containing multiple sites of cations sodium 87 for 12 to sodiums zeolite A.<sup>13, 14</sup>

The second remark concerns the fact that the physical mixture (zeolite A + zeolite X) has a slightly lower than the CEC zeolite X. Taking into account the errors of the experiment closely, we can consider that it is practically the same CEC is observed for the zeolite X and to the mixture (A + X). This leads us to assume that it is the X zeolite determines the exchange phenomenon, since the zeolite Na-A does not allow the exchange rate at that temperature.

The third point concerns the composite LTA / FAU. We noticed a CEC 44 meq at 25°C, significantly higher than that of zeolite X alone at the same temperature (CEC=32meq) and its CEC reaches only about 40 when going from 25°C to 60°C.

Case exchange with  $Pb^{++}$ : To the mixture of the two zeolites, exchange is carried out at 25°C only. The amounts of  $Pb^{++}$  and the remaining  $Na^+$  released are too low for the concentration  $C_0=0.001$ M, the values of CEC are not determined. Similarly to the composite, the values of quantities of  $Pb^{++}$  and  $Na^+$  remaining released could not be determined for  $C_0 = 0.001$

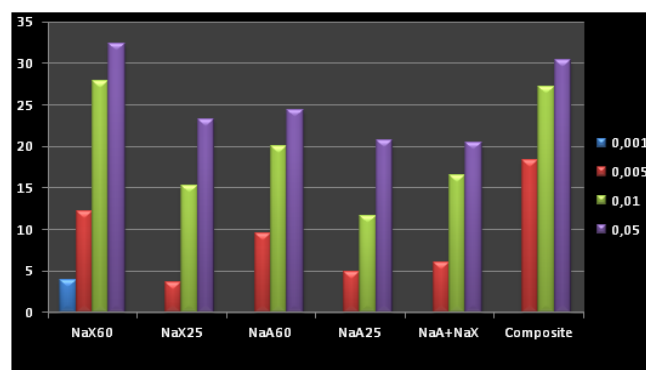


Figure 10: The variation of the CEC based on various materials, concentrations and temperature

From the results presented above, we observed essentially the same variation observed in the case of cadmium.

First we note lower CEC than those observed in the case of cadmium. This is likely due to the size of cation  $Pb^{++}$  comparing with cadmium and acetate anion which causes a reduction in the capability exchange in zeolites.

As before, we noticed that the CEC observed increases with the initial concentration. This was explained by the choice of too low concentrations where the amount of  $Pb^{++}$  was not enough compensation for amounts of sodium present in the zeolite. Best CEC are obtained for the concentration  $C_0=0.05$  M.

At 25°C for  $C_0=0.05$ M. CEC reached 23meq for the zeolite X, 20meq to zeolite A. So zeolite X has a CEC greater than zeolite A, this is predictable because of the structure of Na-X zeolite containing sodium multiple sites (87 to cations toward sodium 12)<sup>13, 14</sup> At 60°C, we notice an increase in CEC has reached 32.5meq for zeolite X and 24mEq for zeolite A.<sup>4, 15</sup>

Similarly, we observed that the physical mixture has a CEC approaching that of zeolite X. Here, we can say that the exchange capacity of the zeolite X, outweighs that of zeolite A in the mixture.<sup>16</sup>

Unlike the case of cadmium, we noticed a slight decrease in exchange capacity CEC in the composite (30.4meq) comparing with zeolite X at 60°C (32.4meq). However a significant improvement in the ability for the composite exchange compared with zeolite X at 25°C (23.2meq).

## Conclusion

The purpose was to design a model of zeolite - zeolite composite in order to, improve the performance of each zeolite taken apart. Indeed, based on the core-shell model, we developed the LTA/FAU composite comprising the zeolite X coated nano-crystals of zeolite A.

To prepare this material, large crystals of zeolite X pure and well crystallized were obtained. In addition, small crystals of nanometer size are also obtained by increasing the crystallization time and temperature decreases. Finally, the composite is obtained by crystal growth of nano - crystals of zeolite A on the surface of the zeolite X crystals in a clear solution.

The composite material LTA/FAU prepared by core-shell model, exhibits satisfactory performance ion exchange for

lead and cadmium compared to zeolite X (FAU) zeolite A (LTA) or even physical mixing.

Thus, exchange capacities for both metals are achieved in the presence of composite that could not be achieved at high temperatures.

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