Prediction and Verification of the Conditions Governing the Synthesis of Tailored Zeolite a for Heavy Metals Removal

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Abstract

Numerous experimental trials, exhaustive analytical and testing procedures are usually undertaken, to reach the appropriate conditions for synthesis of “Zeolite A”. However, it is possible to come-up with a semi quantitative approach, through modeling and optimization techniques, to define the approximate range of initial conditions governing the preparation of a tailored zeolite with specific characteristics including silica to alumina ratio, particle size, and cation exchange capacity to be used for the removal of heavy metals.

This paper is an attempt to adopt an engineering approach essentially comprising the formulation of a mathematical model relating the characteristics of zeolite A to the synthesis conditions based on numerous experimental published results, optimization to define the synthesis conditions required to produce specific zeolite A , verification of this proposed approach with experimental results for preparation of tailored zeolite A conducted at our laboratories and the assessment of its efficiency for separation of chromium (III). The composition of the synthesized zeolite A has been as anticipated and the removal of chromium (III) has been in agreement with the developed model. These results indicate that is possible to adopt this approach in a generic manner to select the optimum synthesis conditions for the preparation of zeolites having specific performance characteristics.

Introduction

Heavy metals are common pollutants that have become an eco-toxological hazard of prime concern as confirmed by [1]. One of the most pollutive heavy metals is chromium, which finds its way through waste waters from iron and steel manufacturing, chrome leather tanning and other industrial sources as mentioned by Barros, et.al [2]. Also, Barros et. al [3,4] indicated that the ion exchange process has been applied successfully for heavy metals removal. Among the various cation exchangers, zeolites meet the requirements of good selectivity and acceptable capacity, in addition to being environmentally friendly and relatively low cost adsorbents.

Zeolites occur naturally and they have been extensively synthesized in laboratory and industrial conditions. Due to their high cation exchange capacity, zeolites are used as sorbents, catalysts, and cation exchangers [5]. Several investigations on the use of zeolites for heavy metals removal have been reported. In particular, chromium (III) has been successfully removed from contaminated waters using zeolites A[1,2], zeolite X [6,7] and zeolite Y [5]. Other authors [1,8,9] explained the main features of these groups of zeolites that affect their selectivity towards chromium (III) removal. These are: the silica to alumina ration ranging from 2 to 6, the pore diameter ranging from 4.2 to 10 A, cavity diameter ranging from 11.4 to 13 A, the void volume ranging from 0.47 to 0.5 cc/g, the surface area ranging from 600 to 950 m^2/g, and the cation exchange capacity ranging from 3.9 to 5.45 meq/g.

Zeolite characteristics are basically governed by raw material composition & properties, relevant processing and post treatment conditions. Main processing conditions affect zeolite characteristics as follows:

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- The silica to alumina ratio has been found to increase by increasing the aging time and decreasing the aging temperature [10] synthesis temperature and pH [11], initial silica to alumina ratio [12], and synthesis time [13].
- The pore and cavity diameters have been found to increase by increasing the initial silica to alumina ratio, using the sodium as the cation, and by decreasing the aging time [14].
- The crystal size has been found to increase by increasing the aging temperature [13], aging time [15], synthesis time [16,17], synthesis temperature [18], pH [19], silica to alumina ratio [20,21] and seeding [12]. It is also affected by the super-saturation, and, the silicon source [22].

According to numerous investigations, the chromium exchange capacity (CrEC) of zeolite A, X, and Y reaches 5.14, 4.9, and 3.92 meq Cr^{3+}/g respectively as reported by several researchers [2,5,6]. Thus zeolite A has been selected as a model to be investigated in this study.

Thus, in order to prepare a zeolite of specific characteristics for chromium removal, as typical of heavy metal, it is necessary to go through a large number of experiments, exhaustive testing and analysis procedures to reach the optimum synthesis conditions and consequently the required specifications. Theoretical prediction of the synthesis conditions has been attempted by several authors to minimize the number of trials required to prepare zeolite of specific characteristics and performance behaviour.

Tatlier, et.al., [23] used artificial neural networks for the estimation of zeolite molar compositions and hence the zeolite phases that may be obtained from certain reaction mixture composition for zeolites A, X, Y, HS, mordenite, and analcime. The results indicate that using artificial neural network methods may decrease significantly the number of experiments to be performed to discover new synthesis compositions. Lechert [24] proved the possibility of predicting the silica alumina ratio of the produced zeolite from the starting ratio for faujasite zeolite and other different zeolite types.

This paper addresses the development of a simple approach for the prediction of zeolite synthesis with defined specifications. A model developed on the basis of published data has been successfully verified by experimental preparations conducted in our laboratory and evaluation of results comprising zeolite characterization and (Cr^{3+}) removal in view of other reported data.

Approach & Methodology

Compilation of data

Published data comprising starting molar ratios, synthesis conditions, and results of synthesis has been compiled and analysed. All the data used in this study has been obtained from conventional synthesis experiments using similar reactants. Data from several references [1,2,4,8,9,25-28] and others have been used.

Compiled data has been firstly analyzed for consistency and reliability and database has been then formulated for ease of retrieval.

Formulation of empirical models

The analyzed data has been correlated by applying relevant analysis methods, such as multiple non linear regression software and curve fitting to formulate the mathematical empirical models governing the synthesis of zeolite A for chromium removal. Typical software used for the purpose includes Labfit (V.7.2.37) and Microsoft Excel.

Determination of optimum conditions for synthesis of zeolite of specific characteristics

BOX Complex Routine [29] has been used to define the optimum synthesis conditions through minimization of an objective function comprising the squares of discrepancy between the target specification of zeolite product, which is zeolite Si/Al molar ratio, and the corresponding value calculated by the developed model. The optimization problem is constrained with the range of validity of the independent parameters governing the synthesis conditions. These parameters include: feed Si/Al, water to alumina, soda to alumina molar ratios, crystallization time (h), and crystallization temperature (^{o}C). Other dependent specifications have been then estimated, comprising: zeolite crystal size, pore diameter (A), cavity diameter (A), cation exchange capacity (CEC) (meq/g), and Cr^{3+} exchange capacity (CrEC) (meq/g).

Experimental verification of predicted conditions

Synthesis

According to the procedure reported by several authors, for example [8, 27], zeolite has been synthesized following the predicted synthesis conditions and the starting molar ratios. The synthesis materials have been aluminum hydroxide (Panareac Quimicasa), sodium meta silicate (Arabic Laboratory Equipment Co. GPR), and sodium hydroxide (Modern Lab). First, the alumina trihydrate has been dissolved in a sodium hydroxide solution under boiling while retaining constant volume. The silicate solution has been prepared similarly.

The synthesis gel has been then prepared by addition of the silicate solution to the aluminate solution at 65°C, and mixing at 500 rpm for 1 h, with seeding of previously prepared zeolite of about 7.5 wt%. For comparison, two samples have been prepared one with aging of the synthesis gel at room temperature for 64 h (sample designated as I) and another one without aging (sample designated as II).

Crystallization has been then conducted at 98°C, and continuous mixing at 250 rpm, for 2 h with constant solution volume. After crystallization and cooling, the mother liquor has been separated from the product using a G^3 sintered glass filter. The product has been washed repeatedly with distilled water to pH 10.25, then, dried at 110-120°C for 6.5 h.

Another sample (designated as III) has been prepared using another mode of addition of the reactants, where the prepared aluminate solution has been added very slowly to the silicate solution over 1.5 hours after the addition of seeds. All the other steps have been completed as for sample II.

Characterization

The chemical formula, phases formed, crystallite size, and the degree of crystallinity have been characterized by X-ray diffraction analysis (XRD) using a computer controlled X-ray diffractometer (made by Diano Corporation, USA) of a measuring range (2θ) from -20° to +150° target X-ray tube operated at 45 kV and 6 mA

The prepared samples have been also analysed by X-ray fluorescence analysis (XRF) using AXIOS, WD-XRF Sequential Spectrophotometer (Panalytical, 2005) for determination of the Si/Al molar ratio.

The prepared zeolite particle size and morphology have been determined by using Scanning Electron Microscope (SEM) images Model JEOL: JXA-840A Electron Probe Micro-analyzer Coupled with Energy Dispersive Analysis by X-ray (EDEX). All samples were gold coated prior to measurement.

Transmission Electron Microscope (TEM) images have been taken using JEOL: JEM-1230 electron microscopy, 120kV. The samples were dispersed in distilled water and ultrasonicated for 15 minutes. Subsequently, the dispersed solution was dropped on a copper grid pre-covered with a very thin amorphous carbon film.

Performance Assessment

The adsorbents (0.1 g) was left in contact with 100 ml of the chromium nitrate solutions of 320-1000 ppm with initial pH values ranging from 3-4. The test was carried out at room temperature for 1 hour under constant shaking. The filtered solution was then analyzed to determine the final chromium concentration using DR 2000 Spectrophotometer. The adsorption capacity is expressed as the meq Cr^{3+}/g zeolite.

Results & Discussion

1-Compilation & formulation

Acknowledging the range of validity of the analysed screened data and in view of the predictive nature of the developed approach, the following empirical equations have been developed:

$$S/A_Z = 6.87*10^{-09} * S/A_F^{-2.223} * H/A_F^{-1.016} * \\ *N/A_F^{\ 2.409} * C_t^{\ -0.063} * C_T^{\ 4.452} \quad (1)$$

$$Cs = 1.0392 * C_t + 0.1541 \quad (2)$$

$$P_D = -32.9 * S/A_Z^{\ 4} + 251.7 * S/A_Z^3 - 690.8 * \\ *S/A_Z^2 + 802 * S/A_Z -325 \quad (3)$$

$$C_D = 10.07 * \exp(((P_D +5.2)^2) / 903) \quad (4)$$

$$CEC = 21.3-0.44* S/A_Z^2+0.074* P_D^2-0.13* C_D^2 \quad (5)$$

$$CrEC = 3.05* S/A_Z^{\ 3.61} \quad (6)$$

Where S/A_Z : zeolite Si/Al molar ratio, S/A_F : feed Si/Al molar ratio, H/A_F : feed water to alumina molar ratio, N/A_F : feed soda to alumina molar ratio, C_t : crystallization time (h), C_T : crystallization temperature (°C), C_S : average crystal size (μ), P_D: pore diameter (A), C_D : cavity diameter (A), CEC: cation exchange capacity (meq/g), CrEC: chromium exchange capacity (meq/g).

Tables (1) and (2) represent the calculated values using the developed empirical models as compared to the compiled data from various published reports. The range of validity as obtained from the original source has been given for each parameter in the corresponding equation. The % error and the correlation coefficient R^2 have been also mentioned for each formulated equation.

Table (1) shows that the calculated S/A_Z manifests zero error in the investigated range while table (2) shows that the calculated C_S manifests minor error in the -6 to +5% ranges. Moderate error in the range from -14 to 16% is observed for the calculated zero error in the PD values. The shown % error ranges seems acceptable in the prediction stage. The calculated C_D, CEC and CrEC values manifest minor error % as compared to original values.

Moreover, verification of the efficiency of the developed equations is illustrated by a parity plot for Cs. Figure (1) represents a parity plot for equation (2) where the original and calculated Y values (average crystal size) are plotted against the original X values (crystallization time).

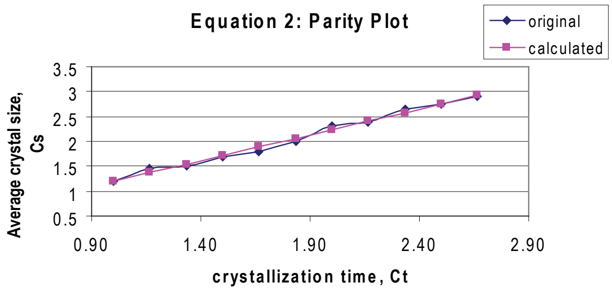


Fig. 1. A Parity Plot for Equation (2)

In general, the calculated Y values in both tables (1) and (2) demonstrates the reliabilities of equations 1-6 as sound predictive tools of zeolite A synthesis conditions.

It should be emphasized that the developed models should be used as integrated predictive set within the indicated validity range.

2- Prediction & optimization

BOX COMPLEX routine has been adopted to find the values of the synthesis conditions that would minimize the following objective function:

$$(\min (S/AZ - 1)^2)$$

where S/A_Z is defined by equation (1).

The objective function is subject to the following constrains:

$$0.9 < S/AF < 1.21,$$
$$80 < H/AF < 124,$$
$$3.4 < N/AF < 4.23,$$
$$0.5 < Ct < 2.67,$$
$$85 < CT < 98.$$

Consequently, equations (1 to 6) have been used to calculate other parameters using the defined optimum for the independent variables. Results are presented in table (3).

It is noted that, the predicted values are in agreement with the characteristics of zeolite A as shown in tables (1) and (2) and with the specifications of zeolite A prepared within the scope of this work .

Table 1.

Original & Calculated Experimental Data-Equation 1

Y value			X values					Equation number	R^2	Reference
Original	calc	% Error	S/A_F	H/A_F	Na/Al_F	C_t	C_T			
S/A_Z										
Range of validity 0.53-1			Range of validity 0.9-1.21	80-124	3.4-4.23	0.5-2.67	85-98			
0,90	0,90	0,00	0,90	80,00	3,60	0,50	85	1	1	[9,28]
1,00	1,00	0,00	0,95	100,00	3,40	1,00	98			
0,81	0,81	0,00	0,97	100,00	3,40	2,00	95			
0,69	0,69	0,00	1,21	124,00	4,23	1,17	95			
0,53	0,53	0,00	1,21	124,00	4,23	1,50	90			

Table 2.

Original & Calculated Experimental Data- Equations 2-6

Original	calc	% Error				number	R^2	Reference
C_s			C_t			2	0,99	{27]
Range of validity 1.2-2.9			Range of validity 0.5-2.67					
1,2	1,19	-0,56	1.00					
1,45	1,37	-5,76	1.17					
1,5	1,54	2,65	1.33					
1,7	1,71	0,76	1.50					
1,8	1,89	4,78	1.67					
2	2,06	2,97	1.83					
2,3	2,23	-2,93	2.00					
2,4	2,41	0,24	2.17					
2,65	2,58	-2,68	2.33					
2,75	2,75	0,08	2.50					
2,9	2,93	0,87	2.67					
P_D			S/A_Z			3	0,93	[1,2,8]
Range of validity 4.2-10			Range of validity 0.53-1					
4,2	4,211	0,26	1					
7,4	8,6117	16,37	1.233					
10	8,6061	-13,94	1.24					
7,4	7,6473	3,34	1.37					
3,5	3,2029	-8,49	1.67					
2,6	2,8365	9,10	1.7					
2,6	2,624	0,92	2.1					
7,4	7,4239	0,32	2.429					
C_D			P_D			4	0,99	[1,2,4,7]
Range of validity 11.4-13			Range of validity 4.2-10					
11,4	11,105	-2,59	4.2					
12	12,005	0,04	7.4					
13	13,006	0,04	10					
CEC			S/A_Z	P_D	C_D	5	0,94	{1-4,6-8]
Range of validity 3.9-6.47			Range of validity 0.53-1	4.2-10	11.4-13			
6,00	6,16	2,72	1,00	4,21	11,11			
6,00	6,16	2,72	1,00	4,21	11,11			
6,01	6,04	0,51	1,24	8,61	12,44			
5,96	5,85	-1,92	1,37	7,65	12,09			
5,86	5,60	-4,43	1,50	5,75	11,50			
5,55	5,44	-1,97	1,75	2,32	10,72			
5,08	5,12	0,73	2,00	1,81	10,63			
4,45	4,37	-1,78	2,25	4,66	11,22			
3,90	4,07	4,47	2,43	7,44	12,02			
CrEC			S/A_Z			6	0,89	[1,2,7]
Range of validity 3.05-5.18			Range of validity 0.95-1.13					
3,05	3,05	0,00	1					
4,3	4,5917	6,78	1.12					
5,18	4,7415	-8,47	1.13					

3-Experimental verification

Prepared samples, according to predicted set, have been subjected to experimental verification using the initial data set shown in table (3). The characterization and performance data are outlined below.

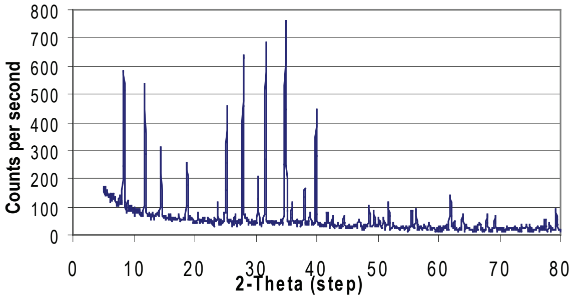
Table 3.
Predicted Variables

Para-meter		Predicted Value
I. Independent Variables		
S/AF	Feed Si/Al molar ratio	0.96
H/AF	Feed water to alumina molar ratio	120.7
N/AF	Feed soda to alumina molar ratio	3.8
Ct	Crystallization time (h)	2.0
CT	Crystallization temperature (°C)	98
II. Dependent Variables		
S/AZ	Zeolite Si/Al molar ratio	1.0
Cs	Average crystal size (µm)	2.23
PD	Pore diameter (A)	4.2
CD	Cavity diameter (A)	11.4
CEC	Cation exchange capacity (meq/g)	5.2
CrEC	Chromium exchange capacity (meq/g)	3.05

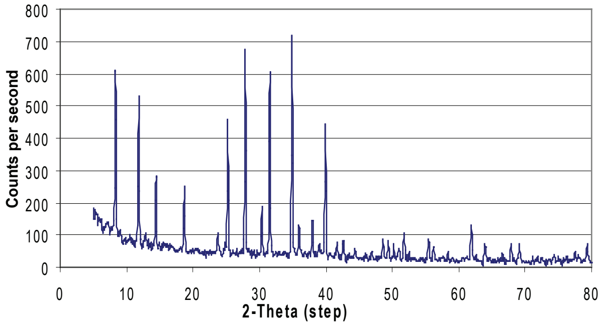
Characterization

X- ray diffraction (XRD)

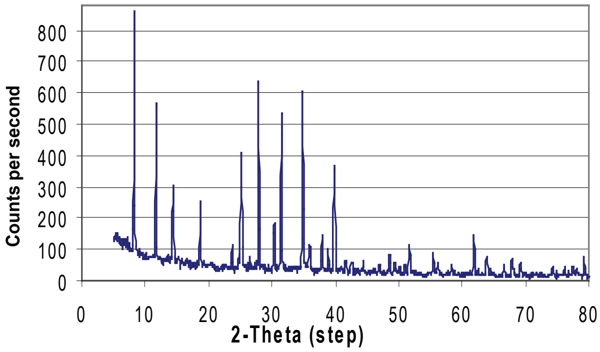
Figure 2 represents XRD charts for the prepared samples



a) I



b)II



c) III

Fig. 2. XRD charts a) sample I, b) sample II, c) sample III

The XRD charts of the three samples show sharp peaks of high intensity indicating highly crystalline and pure zeolite A with the following composition and characteristics

Product name: $Na1_2Al1_2Si1_2O_{48}(H_2O)_{27}$—Sodium aluminum silicate hydrate (Zeolite LTA), molecular weight: 2191.06

System: cubic with unit cell parameter a=24.61.

The identified Si/Al molar ratio agrees with the value predicted from the model as depicted in table (3). Also results are in agreement with the published work as mentioned by several authors [2,4,8].

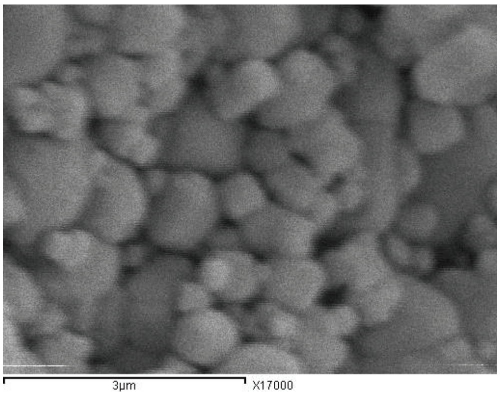
The close resemblance of the XRD charts for the prepared samples clearly indicates the negligible influence of both the aging time [15] and the mode of reactants addition.

X- Ray Fluorescence (XRF)

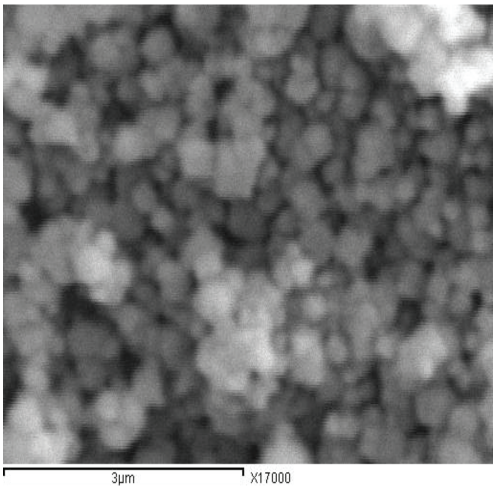
XRF was also used to emphasize the performed zeolite structure. It resulted in Si/Al ratio of 1.01, 1.03 and 1for samples I, II and III respectively, which agrees with the XRD identified Si/Al molar ratio. It also agrees with the value predicted from the model as depicted in table (3).

Scanning Electron Microscopy (SEM)

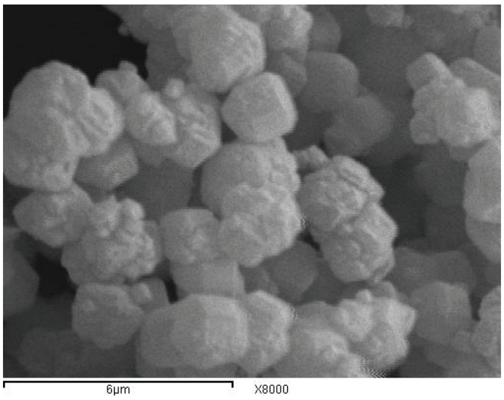
The synthesized zeolite samples have been characterized by (SEM) as shown in figure 3.



a) I



b) II



c) III

Fig. 3. SEM images for :a) sample I, b) sample II, c) sample III

The SEM images show well defined highly crystalline small crystals with the characteristic cube shape LTA zeolite. The images have been analysed by image analysis software and they show that the small zeolite particles formed range in size from a minimum of 0.2 to a maximum of 1.2 μ for sample I, 0.6 μ for sample II, and 2 μ for sample III respectively.

The maximum observed particle size almost agrees with that predicted from the model as depicted in table (3). The particle size in sample III may be affected by the mode of addition of the reactants.

Transmission Electron Microscopy (TEM)

The synthesized zeolite samples have been characterized by (TEM) as shown in figure 4.

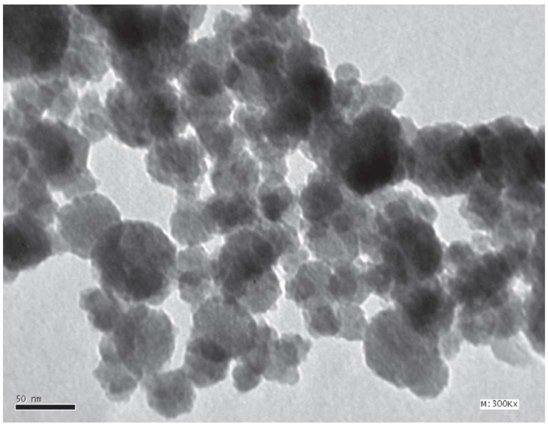
The TEM figures show high crystalline small zeolite crystallites formed ranging from 15- 63 nm for sample I, 28- 86 nm for sample II, and 28- 62 nm for sample III. The latter sample is characterized by relatively minimum crystallite size range as compared to samples I & II.

Performance Assessment

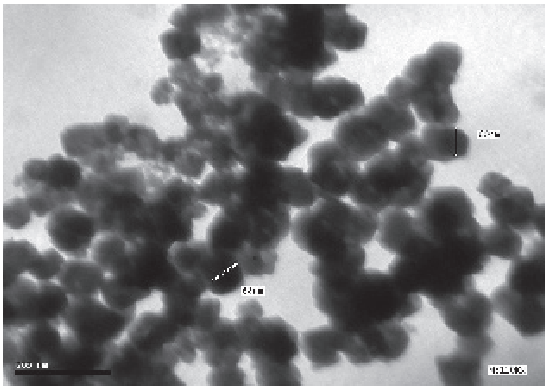
The average Cr^{3+} adsorption capacity of the prepared zeolites in the tested range has been found to be 2.5 meq Cr^{3+}/g for sample I, 2.84 meq Cr^{3+}/g for sample II, and 2.9 meq Cr^{3+}/g for sample III. These values are relatively close and comparable with the predicted value of 3.05 meq Cr^{3+}/g for chromium exchange capacity as presented in table (3). Thus the experimental adsorption results tend to confirm the validity of the adopted prediction approach within the investigated range of validity.

Conclusions

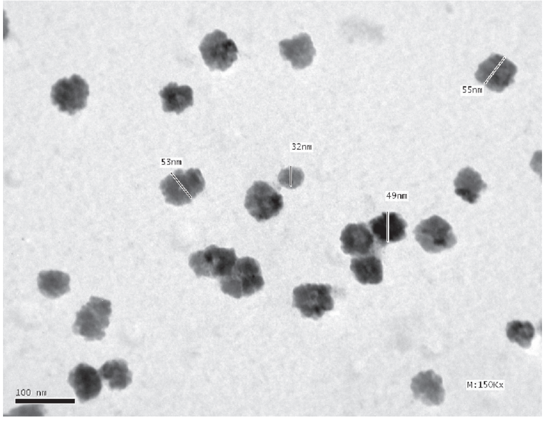
The formulated rational scheme has proved to be a powerful tool for the prediction of synthesis conditions required to prepare the zeolite A, with specific tailored characteristics, for Cr^{3+} removal. The prepared samples were characterized using XRD, XRF, SEM and TEM. Further, the adsorption capacity of Cr^{3+} for several prepared samples has been assessed. The results are in agreement with the predicted values from the model. Further work shall include the development of the prediction scheme for other zeolite types and other heavy metals with expanded validity range. The formulated predictive scheme will support the development of target zeolite with minimum experimental trials.



a) I



b) II



c) III

Fig. (4): TEM figures :a) sample I, b) sample II, c) sample III

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