

Utilization of Egyptian kaolin for Zeolite-A Preparation and Performance Evaluation

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Abstract—Zeolite-A was synthesized from Egyptian kaolin through metakaolinization and zeolitization. Metakaolinization targeted the thermal activation of kaolin, while zeolitization involved alkaline attack of thermally activated, amorphous kaolin (metakaolin) and its transformation into crystalline Zeolite-A. Effect of various controlling parameters on Zeolite-A preparation was investigated. These include temperature and time of metakaolinization, solid to liquid (S/L) ratio, NaOH concentrations and processing time of zeolitization. Zeolite-A was prepared on both laboratory and pilot scales. Metakaolin and prepared Zeolite-A were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM). The sorbent removal of chromium (III) from synthetic 5 mg/l solution was investigated in batch mode using raw kaolin, and Zeolite-A prepared on lab and pilot scales. Results indicated that the produced Zeolite-A samples are well-developed crystals with almost uniform particle size distribution. Adsorption results indicated that the maximum were chromium adsorption capacities obtained 3.30 mg/l, 9.98 mg/l and 11.10 mg/l for raw kaolin, and Zeolite-A prepared on lab and pilot scales, respectively.

Keywords: Egyptian clay, Zeolite-A, Preparation, Removal, Chromium.

I. INTRODUCTION

Zeolites have grown to an estimated \$1.6-1.7 billion industry since their successful introduction as commercial molecular sieves in 1954 [1], with the largest part (68%) being consumed in the detergents industry (zeolites A and X). Natural as well as synthetic zeolites are also known to show high selectivity towards extracting trace amounts of heavy metals from wastewater [2-4].

With increasing demand of fresh water, there is a need to reuse secondary waters of marginal quality. It is expected that the adsorbate market will significantly expand to accommodate huge quantities of zeolites.

Traditionally, zeolites are commonly produced from the hydro gels of sodium aluminate and silicate [5]. However, production of zeolites from clays, as a source of alumina and silica has been and is still continuously investigated, with positive results [5-7]. Cost considerations may shift consumers to clay based zeolites especially as sorbents for water treatment.

Zeolite-A of average composition $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}\cdot 216\text{H}_2\text{O}$ has been produced using clay minerals. Kaolin is ideally

suited for this purpose [1-4 & 8]. Hydroxysodalite appears to be the main product whenever raw kaolinite is reacted with NaOH of sufficient concentration, independent of the kaolinite used [9].

The synthesis of Zeolite-A from kaolinite comprises two steps: metakaolinization and zeolitization. The first step involves the thermal activation of the clay in the temperature range of 500–900°C whereby dehydroxylation takes place giving an amorphous more reactive product (metakaolinite). The thermally activated, amorphous kaolin (metakaolin) with an overall $\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ composition, when attacked with the alkaline solution is transformed into $\text{Na}_{12}[\text{Al}_{12}\text{Si}_{12}\text{O}_{48}]$ crystalline zeolite, after an induction period [10-13]. The transformation conditions are governed by the synthesis temperature, duration, alkali concentration as well as the origin and conditions of kaolin calcination. Accordingly, the lowest and highest calcination temperatures are crucial for Zeolite-A formation. If the temperature is too low, hydroxysodalite is formed whereas for higher temperatures (>900°C), zeolite NaP is formed [14, 13 and 15].

Zeolites prepared from kaolin have proved high efficiency for heavy metals removal as mentioned in previous investigations. Zeolite-A prepared from cheap Egyptian kaolin removed copper and nickel from waste solution with removal efficiency of 33 mg/g and 20 mg/g, respectively [16]. It was reported also that Zeolite-A prepared from Kalabsha kaolin removed copper and zinc completely from waste solution [17]. Lead was also removed from waste solution with an adsorption capacity of 100 mg/g using Zeolite-A prepared from Jordanian kaolin [18].

In the present work, laboratory and pilot-scale preparation of zeolite-A were investigated using Egyptian kaolin. The produced zeolite was utilized for the removal of water hazardous pollutants.

II. MATERIALS AND METHODS

A. Materials

Sodium hydroxide pellets (98.6% NaOH) and natural, poorly crystalline kaolin (Abu Zeneima), which has been selected for economic considerations, were used in this work for zeolite preparation. The mineralogical and chemical composition of the used kaolin is shown in Table 1. Chromium (III) was supplied as chromium nitrate (PRS Panareac Quimica Sa). Stock solutions were prepared by

dissolving weighed amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in distilled water.

B. Experimental Investigations

1) Laboratory-Scale preparation of Zeolite-A from Kaolin

Kaolin was calcined and converted to metakaolinite at 800°C for different time durations ranging between 4-12 hrs. The resulting metakaolin was then scanned by XRD. The metakaolin was reacted with 3.0 M aqueous NaOH solution in 100 ml covered Teflon beakers. The solid/ liquid ratios respectively were 0.5-2.0:5.0 (for metakaolin to alkali solution). The mixture was treated in an electric oven at 100°C for different time durations of 1 to 5 hrs. The reaction product was washed to remove excess alkalinity and then centrifuged several times with distilled water for solid- liquid separation. The solid powder was dried overnight at 80°C and collected in dry, clean plastic containers for phase-characterization. In all the treatments, the yield percentage of the dried product was calculated in relation to the actual product yield as well as the 100% theoretical yield based on the metakaolinite to Zeolite-A transformation equation $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}$ [19].

2) Pilot-Scale preparation of Zeolite-A from Kaolin

Guided by the laboratory scale experiments, Zeolite-A was prepared under the following conditions:

- The kaolin samples were calcined for metakaolin transformation at 800°C for 6 and 8 hrs in a Pilot Scale Calciner (Naber Industrie Ofenbau-Germany).
- Zeolite-A production was carried out using a 30 liter pilot reactor heated with an electric coil and provided with a temperature controller and a multiple speed mixer.

TABLE I. CHEMICAL AND MINERALOGICAL ANALYSIS OF THE USED KAOLIN

Chemical composition of kaolin		Mineralogical composition	
Oxides	Conc Wt%	Mineral	(%)
SiO_2	50.00	Kaolinite	56.0
Al_2O_3	30.31	Quartz	38.5
TiO_2	1.65	Anatase	5.5
Fe_2O_3	4.61		
MgO	0.20		
$\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{MnO}$	0.96		
L.O.I	11.30		

- The alkali-concentration effect on the evolution of zeolite-A were tested at both high (6.0M) and low (3.0M) NaOH concentrations.
- The reaction was conducted at 90°C for 3hrs. The product in each pilot experiment was filtered using Pilot Nutsche Vacuum Filter and dried overnight at 100°C . The dry powder was then collected and preserved in a clean, dry container for product characterization.

C. Characterization

The X-Ray Diffraction (XRD) identification for freshly, dry prepared zeolite-A powder was carried out using BRUKER apparatus, Axs, D8-ADVANCE (Germany 2001) by

applying Cu-K α radiation. The patterns of all synthesized phases were compared to the JCPDS data, Card No.97-002-0294. The microstructure of the prepared zeolite samples were investigated using Scanning Electron Microscope (SEM) model Philips XL30 attached with EDX unit, with accelerating voltage 30 K.V., magnification 10x up to 400,000x and resolution for W (3.5nm).

D. Batch adsorption studies

A specified quantity of the prepared zeolite (0.25g), with particle size <75 microns, was left in contact with 500 ml of chromium nitrate solution of 5 mg/l with an initial pH values of about 4.5-5 and 3.5-4 for lab and pilot scale samples, respectively. Dilute nitric acid and sodium bi-carbonate were used for pH adjustment. The experiments were carried out at room temperature. Stirring was kept first at 250 rpm for 2 min., followed by 70 rpm for 2 hrs. Settling was performed for 30 min. followed by filtration through Whatman filter paper no. 40. The filtered solution was then analyzed to determine the final chromium concentration using an atomic absorption flame spectrometer (GBC Avanta). The amount of ions adsorbed per unit mass of adsorbent (q_e in milligrams of metal ions per gram of adsorbent) was evaluated using the following expression:

$$q_e = \frac{C_o - C_e}{m} * V \quad (1)$$

Where C_o is the initial metal ion concentration (mg/l), C_e the equilibrium metal ion concentration (mg/l), V the volume of the aqueous phase (l), and m the amount of adsorbent used (g). Removal efficiency of Cr(III) ions by the adsorbent is calculated by:

$$\text{Removal efficiency (\%)} = \frac{C_o - C_e}{C_o} * 100 \quad (2)$$

III. RESULTS AND DISCUSSIONS

A. Laboratory-Scale Investigations

1) Thermally Treated Kaolin

“Fig. 1” shows the XRD results of the thermally activated kaolinite where a broad featureless hump extends between 2θ of 15 to 38° with a maximum d-spacing at about 3.9 \AA indicating the transformation of kaolinite to an amorphous phase. A sharp peak of anatase impurity could be seen at 3.50 \AA . The presence of secondary phases, quartz and anatase, is a reflection of the low- grade nature of the kaolin. The appearance of quartz peaks indicates the presence of some of the silica in the form of free quartz. In the same trend, the Anatase presence is a common feature of most calcined kaolins as a reflection of the TiO_2 crystallization at the high temperature of calcinations [20]. The key point is that, the presence of both secondary minerals (quartz and anatase) is not affecting the crystallization of zeolite-A [20]. All the calcined kaolin samples show the same features whatever the time taken in their thermal treatment. Thus, only the samples heated at the least and longest times are presented.

2) Characterization

a) Effect of reaction time

“Fig. 2” shows the diffraction pattern of zeolite product obtained from the metakaolin samples calcined at 800°C, treated with alkali solution of 3.0 M NaOH and heated at 100°C, for different time durations. The results indicate that, zeolite-A is the main phase produced after 3hrs and 5 hrs of treatment, accompanied with some secondary mineral phases, namely quartz and anatase.

As previously mentioned, the reaction product is contaminated by quartz and anatase as a reflection of the low grade parent kaolin [19] but their presence is not affecting the crystallization of zeolite-A. It is observed in this synthesis that hydroxysodalite-zeolite mineral is absent, the presence of which is a direct indication of high alkalinity and structural similarity to Zeolite-A [19]. Hydroxysodalite has the same composition of zeolite-A, but with much less pore volume and zero channel direction.

The previous result shows that the S/L ratio of 1:5 is appropriate for Zeolite-A crystallization. Furthermore, the 3-hrs duration depicts the best crystallization time for zeolite development. As indicated, the strong peak intensities recorded on the XRD chart after 5 hrs, are almost identical to their 3-hrs counter parts “Fig. 2”.

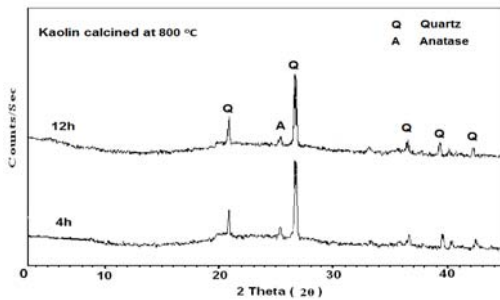


Figure 1. XRD patterns of the kaolin calcination for 4hrs and 12hrs at 800°C.

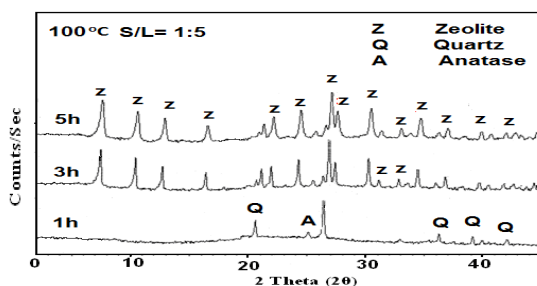


Figure 2. Zeolite formation from metakaolin heated at 800°C/12hrs and then treated at 100°C for different durations and constant Solid/Liquid ratio of 1:5.

The SEM micrographs of “Fig. 3” show the evolution of zeolite-A characteristic cubes from the extensively reacted metakaolin platelets at different durations. After 3 hrs, the cubes show minute crystals with rounded-edges of 1.0 to 3.0µm (cube edge) which then grew with time to bigger euhedral-cubes reaching up to 5.0 µm in size at the expense of the original platelets. At the later stages of crystallization,

the well-defined crystals of perfect cube edges of 6.0-8.0 µm are abundant along with very small amounts (<5 %) of the metakaolin debris indicating the final stage of zeolite-A crystallization.

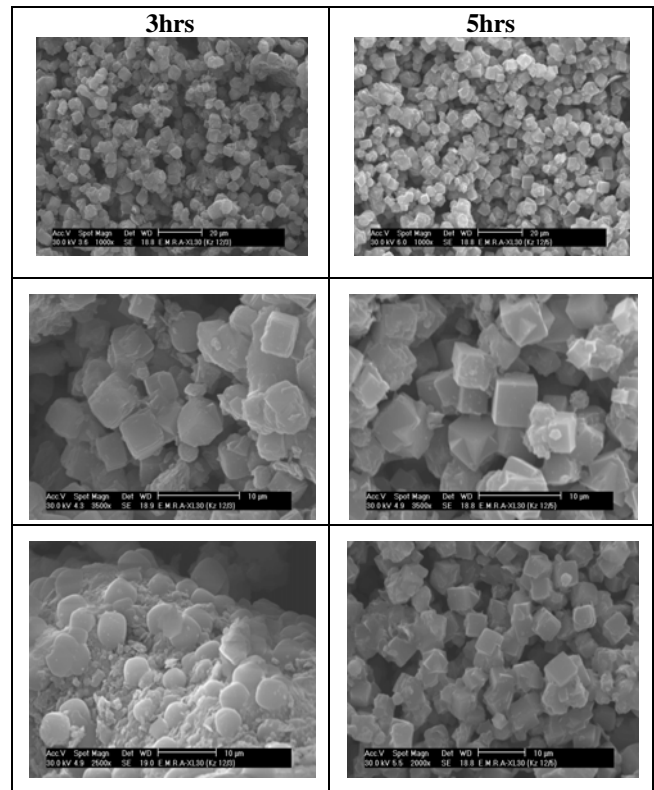


Figure 3. SEM Micrographs of Zeolite-A produced from metakaolinite samples (S/L=1:5) reacted with 3.0M NaOH and heated at 100°C /3hrs and 5hrs under hydrothermal conditions.

b) Effect of Solid/Liquid Ratio (S/L)

To improve cost effectiveness, a set of experiments were conducted using different S/L ratios of 0.5, 1.0, 1.5 and 2: 5 prepared by adding varying amounts of metakaolin (which could be converted to Zeolite-A) to a specific amount of alkali solution. It was found that the conversion of metakaolinite into zeolite is effective in the whole range of S/L ratios except that of 2:5, as zeolite peaks were absent at this ratio.

The XRD pattern of “Fig. 4” shows the effect of increasing the solid/liquid ratio to 1.5:5, where Zeolite-A is developed after 3hrs. The observed result is not only indicating the dependency of metakaolin conversion into zeolite on the S/L ratio, but also confirms the previously mentioned result of considering the 3h as the most optimum time for the crystallization of zeolite-A from Egyptian kaolin (metakaolinized) at 100 °C.

B. Pilot Scale Investigation

1) Results of kaolin calcinations

The raw kaolin prepared on the pilot-scale (pilot-kaolin) was calcined at 850°C/ for 6hrs and 8hrs. Compared to the

lab-scale samples heated at 800°C for 12hrs, the pilot-scale samples were calcined at a higher temperature (850°C) but for lower time duration (6 hrs & 8 hrs) to compensate for the effect of temperature difference (50°C higher) by lowering the calcinations time (by 6 and 4hrs). It has been noted that increasing the time of calcination resulted in the slight reduction of quartz –peak intensities as well as the absence of anatase (favorable result) . The previous result marks the apex of the calcination process for the sample heated for the longer time of 8h. Hence, the metakaolin which resulted at 850°C and 6 and 8 hrs was chosen as the precursor for zeolite-A preparation in the pilot-scale experiments.

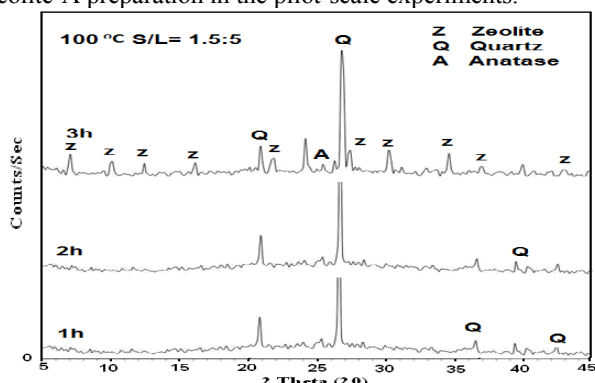


Figure 4. Zeolite formation from metakaolin calcined at 800°C/12hrs, reacted with 3.0M NaOH and heated at 100°C for different durations and constant Solid/Liquid ratio of 1.5:5.

2) Results of Zeolite-A production

“Fig. 5” shows the diffraction pattern of zeolite product obtained from the metakaolin samples calcined at 850°C for 8 hrs, and those treated with alkali solution of 3.0 M NaOH at solid/liquid ratio of 1.5:5, as well as those heated at 90°C for 3 hrs. The results show that zeolite-A is crystallized as the sole zeolite phase in the reaction product obtained after 3 hrs of treatment, and is accompanied with some secondary mineral phases, namely; quartz and anatase. As previously mentioned, the reaction product is contaminated by quartz and anatase as a reflection of the low grade kaolin [19].

For comparing results of the reaction product, another pilot experiment has been carried out using the same previous conditions but with higher alkali concentration of 6.0M NaOH. At this high alkalinity (data not shown), the reaction product contains hydroxysodalite as the main zeolite phase.

This is attributed to the instability of Zeolite-A in the 4.0 to 8M NaOH medium leading to its conversion into Hydroxysodalite (HS) in the end product [20].

The size and morphology of the synthesized product developed from attacking metakaolin by 3.0M NaOH and heated at 90°C for 3 hrs in the pilot-scale are observed in the SEM of “Fig. 6”. The characteristic cubic-shaped Zeolite-A crystals, having ~5µm (cubic edge) in size are seen clearly in the scanned area of “Fig. 6a & b” as the sole zeolite present, indicating suitable reaction conditions. The crystals are well-defined, embedded sometimes in some partially unreacted metakaolinite platelets with no hydroxysodalite crystals.

“Fig.6” represents the well edged euhedral zeolite cubes of different sizes coexisting with a very small amount of metakaolinite debris. The developed product showed a wide crystallite- size ranging between 2.0 to 10.0 µm indicating a continuous crystallization process through the whole range of time and different generations of crystals. This result agrees well with the result given by Bonaccorsi and Proverbio, (2007) [21] who attributed the co-presence of differently sized crystals in the same product to the (20 °C/min) which allow the nucleation to continue for nearly all the process duration.

3) Performance assessment

Chromium adsorption capacities for some selected representative samples are represented in “Fig. 7”. It is clear that the adsorption capacity of chromium onto raw kaolin (sample K) was much lower than all the other zeolite samples. This agrees with previous investigations on comparisons between the adsorption capacities of different heavy metals onto kaolin and the synthesized zeolites [18, 22].

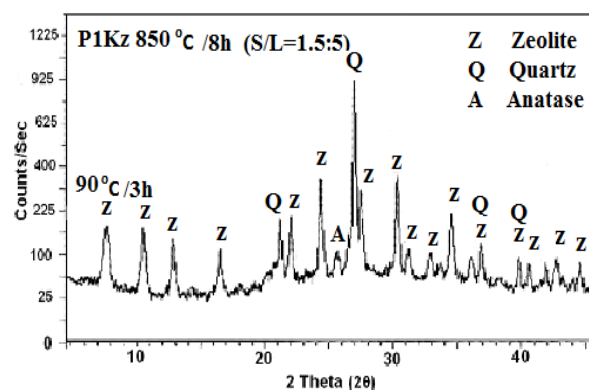
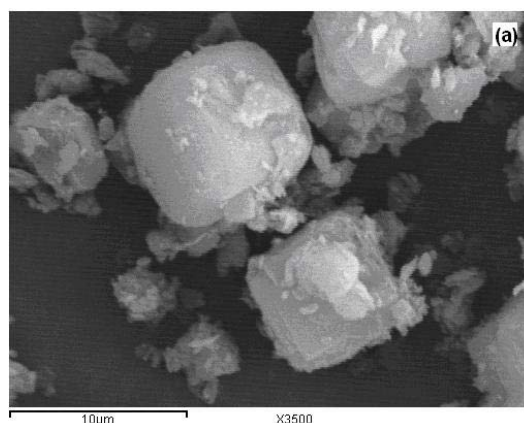


Figure 5. XRD pattern for zeolite-A obtained from metakaolin calcined at 850°C/ 8 h, reacted with the solid/liquid ratio of 1.5:5 in alkali solution of 3.0M NaOH at 90°C / 3 hrs.



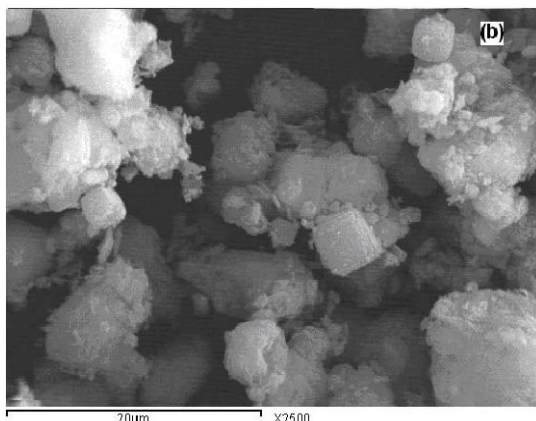


Figure 6. Micrographs of the crystalline product obtained on the pilot-scale process for zeolite-A production from metakaolin reacted with 3.0M NaOH at 90°C, 3h; different magnifications.

Based on the interpretation of the synthesis conditions effect on the produced zeolite, it was concluded that the S/L ratio of 1.5:5 is considered more cost-effective. Consequently, samples Z1, 2, 3 were chosen for performance comparison on the laboratory scale using the same S/L ratio of 1.5:5 and varied processing time (2, 3 and 4 h, respectively). It is clear from “Fig.7” that sample Z2 has the highest chromium adsorption capacity of 10 mg/g as compared to Z1 and Z3 (8, 7.5 mg/g respectively) indicating that the 3 h processing time is optimum for zeolite formation.

Chromium adsorption capacity has increased from 10.6 mg/g for pilot sample calcined at 850°C for 6 h with 1:5 S/L ratio, 6M NaOH and 3 h processing time (sample Z4) to 11.06 mg/g for the other pilot sample calcined at 850°C for 8 h with 1.5:5 S/L ratio, 3M NaOH and 3 h processing time (sample Z5) as shown in “Fig. 7”. This indicates that using lower alkalinity and 1.5/5 S/L ratio contributes to the enhancement of the chromium adsorption capacity.

By comparing between the performance of laboratory and pilot scale samples represented by laboratory scale sample Z2 and pilot scale sample Z5 prepared under almost the same conditions, it is observed that the chromium adsorption capacity of sample Z5 (11.06 mg/g) was higher than that of sample Z2 (10 mg/g) by about 10%.

“Fig. 8” illustrates the chromium removal efficiencies of the previously mentioned samples. It is observed that sample Z2 has the highest removal efficiency among the laboratory prepared zeolite, while sample Z5 has the highest removal %, approaching 100%, among the laboratory and pilot prepared zeolite samples. It is clear that zeolite production from Egyptian kaolin is highly reproduced on the pilot scale.

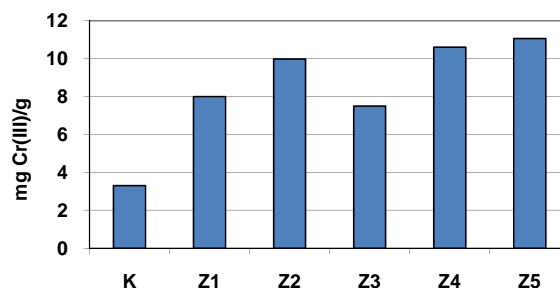


Figure 7. Chromium adsorption capacities for selected samples

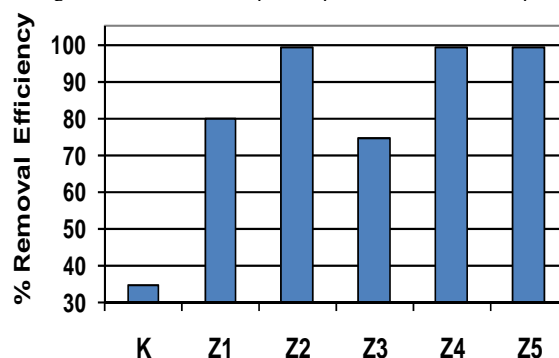


Figure 8. Chromium removal efficiency for selected samples

IV. CONCLUSIONS

- The lab-scale formation of zeolite-A from the Egyptian kaolin was successful under the following conditions: 800°C/12h for the kaolin calcination, 100°C/3h for the reaction time and temperature, 0.5-1.5: 5 for the solid/liquid ratio and: 3.0 M NaOH for the alkali concentration.
- The 1.5:5 ratio seems to be more cost-effective and is recommended for zeolite-A formation from Egyptian kaolin (metakaolinized) based on laboratory and pilot scale investigations
- Generally, zeolite-A product obtained through the whole stages of synthesis in this study shows well-developed crystals with almost uniform particle size distribution.
- The economically important zeolite-A was successfully produced from the Egyptian low-grade kaolin of Abu-Zeneima area (Sinai).
- Compared to the lab-scale, zeolite-A preparation on the pilot plant scale was carried out at 850°C/8 hrs and 90°C/3 hrs for metakaolin production and zeolite-production, respectively. The successful production of zeolite-A, as confirmed by both XRD and SEM, under such conditions indicates the suitability of the selected reduced pilot-scale conditions for zeolite-A production.
- The reduced conditions in terms of less energy consumption, along with using the low-grade Egyptian kaolin in terms of lowering costs were the

main economic interest and priority for the current study.

- Chromium adsorption capacity of the prepared zeolites is higher than raw kaolin.
- Highest chromium adsorption capacity (11.06 mg/g) has been obtained by a sample prepared on the pilot scale by calcining kaolin at 850°C for 8 h with 1.5:5 S/L ratio, 3M NaOH and 3 h processing time.
- Zeolite-A prepared from Egyptian kaolin is promising for treatment of heavy metals polluted wastes.

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