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Removal of methylene blue from water using zeolites prepared from Egyptian kaolins collected from different sources

Doaa M. EL-Mekkawi[a,*], Fatma A. Ibrahim[b], Mohamed M. Selim[a]

[a] Physical Chemistry Department, National Research Centre, NRC, 33 EL Bohouth st., Dokki, P. O. 12622, Giza, Egypt
[b] Physical Chemistry Department, Faculty of women for Art, Science and Education, Ain Shams University, Egypt

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ABSTRACT

Na-Y Zeolites prepared from local Egyptian kaolins were investigated as adsorbents to remove methylene blue (MB) from aqueous solutions. Three Egyptian kaolins, KS, KD and KK were collected from Saint Catherine, Dehessa and Kalabsha, respectively. The influences of the chemical composition of kaolin ores and the surface properties of the prepared zeolites on the adsorption processes have been studied. The effects of various parameters such as surface area, particle size, initial MB concentration, contact time, adsorbent concentration and successive adsorption cycles were examined. Comparison with previous studies show satisfactory removal performance for MB as compared to other reported zeolites. The adsorption capacities of zeolite toward MB are mainly influenced by the particle size of zeolites rather than the zeolitic content. Zeolite samples with small particle size and high external surface area are recommended for the removal of MB.

1. Introduction

Adsorption techniques have currently become the most common solution for the removal of many classes of organic pollutants from wastewater [1]. The deep blue dye, methylene blue (MB), has been widely considered as undesired pollutant in the industrial wastewater [2]. Although commercial activated carbon is a preferred adsorbent for color removal, its widespread use is restricted due to its relatively high cost. This led to the researches on alternative non-conventional and low-cost adsorbents [3]. However, adsorption of organic dyes using clays has been reported as a cost effective method for wastewater purification [3,4]. Many studies addressed the relatively cheap synthetic zeolites as a promising adsorbent. Zeolites are good scavenger of pollutants from water through ion exchange and adsorption. Zeolites, have already found many applications because of their high cation-exchange capacity and surface area, etc. [5–10]. Zeolites are considered as a good adsorbent for heavy metal ions from wastewater and for organic dyes.

Zeolites are aluminosilicates with a three-dimensional framework structure. It is composed of AlO_4 and SiO_4 tetrahedra that are linked to each other by sharing all of their oxygens to form interconnected cages and channels. Zeolites are characterized with the existence of mobile cations inside their cages and channels [4]. The adsorption of the cations is ascribed to the negative charge of zeolites derived from isomorphous substitution of Si by Al [11]. Previously, it has been concluded that the relatively mobile Na^+ ions as extra framework cation favours the incorporation of MB^+ into the zeolite channels. It was found that MB^+ was incorporated in zeolites with Na^+ as an extra framework cation, but it failed for zeolites with Ca^{2+} and K^+ as an extra framework cation [12].

Zeolite Y is characterized by high surface area; uniform pore size distributions with pore sizes in the range 0.9–1.2 nm and high thermal stability. Zeolite Y is one of the most important zeolites in terms of the volume of research activity and the scale of commercial use. The major approach to prepare zeolite Y is hydrothermal synthesis, which is similar to the naturally occurring.

Clay minerals have been used as a combined source for $A1_2O_3$ and SiO_2 for the synthesis of zeolites. Kaolinite ($A1_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) with a Si/A1 ratio of 1, is the principal mineral in clay and is ideally suited for the synthesis of zeolites [13].

The use of local Egyptian kaolinite ores in the production of synthetic zeolites deserves more attention. The easy availability, low cost and high abundance of kaolinite ores in the Egyptian lands would make the synthetic kaolin-based zeolite a promising low cost adsorbent. A simplified feasibility study on the cost of kaolin-based zeolite Y production according to our preparation method has been previously introduced [14]. The study indicated that the

* Corresponding author. Fax: +202 33370931.
E-mail addresses: doaa_egypt@yahoo.com, doaa_egyptian@yahoo.com (D.M. EL-Mekkawi).

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price of the prepared zeolite is around 200 $ per ton which is approximately 15 times cheaper than the commercially available zeolites in the Egyptian markets. Further, zeolites are much cheaper than many of the other widely used adsorbents. The low price of zeolites makes them more attractive than the other adsorbents. For example, the cost of activated carbon in the Egyptian markets is about 1800–3000 $ per ton, depending on the quality.

In earlier studies, we examined synthetic Na-Y zeolites prepared from Egyptian kaolins collected from different sources on the removal of lead. The zeolite contents in the prepared samples were proportional to the kaolinite contents in the corresponding raw kaolins. The order of Pb^{2+} loading was proportional to the zeolitic contents in each zeolite sample. These results suggest that one should choose the kaolin of high kaolinite content in the preparation of zeolite for efficient removal of Pb^{2+} [14].

Herein, among various kaolin based zeolites, the suitable characteristics of zeolites for the most efficient removal of methylene blue were determined. In the present study, comparative analyses of the MB loading capacities of Na-Y zeolite samples prepared from different Egyptian kaolins was introduced. Surface properties of zeolites, the influence of the zeolite dose, the initial MB concentrations and the number of loading cycles on loading of MB from aqueous solution by each zeolite were investigated.

2. Experimental and methods

2.1. Zeolites preparation

Three Egyptian kaolins, KS, KD and KK, were obtained from three different areas in Egypt. KS and KD were collected at the north east from Saint Catherine and Dehessa, respectively. On the other hand, KK was collected from Kalabsha at the Upper Egypt. All kaolins were used as received. The three different kaolins show different physico-chemical properties as shown later. The corresponding Y zeolites; ZK, ZD and ZS; were prepared by hydrothermal treatment of the heated Egyptian kaolins with alkali solution and sodium silicate at 100–120 °C for 8 h according to the submitted Egyptian patent no. (165/2008).

2.2. Zeolites characterization

Particle size distributions of zeolite samples were examined by dynamic light scattering (DLS) using Particle Sizing System (PSS) Nicomp 380, USA.

The surface characteristics, namely specific surface areas (SBET), total pore volume (Vp) and average pore radius ($\acute{r}$) of the various zeolites were determined from nitrogen adsorption isotherms measured at −196 °C using a Quantachrome NOVA 2000 automated gas-sorption apparatus model 7.11 (USA). All zeolites were degassed at 350 °C overnight under a reduced pressure of 1.3 mPa before taking the measurements.

Kaolin and zeolite structures were investigated using the scanning electron microscope (JEOL JXA 840).

2.3. Adsorbate

Methylene blue (MB), 96%, provided by Riedel-De Haen, was used as received. An accurate weighed quantity of MB was dissolved in distilled water to prepare a stock solution. The solutions for adsorption tests were prepared from the stock solution to the desired concentrations by successive dilutions. After taking the measurements by UV–visible spectrophotometer (Jasco V-550, Japan), a curve was made to calculate the concentration of each experiment. This curve was used to convert absorbance data into concentrations for kinetic and equilibrium studies.

2.4. Adsorption experiments

The MB adsorption experimental studies were conducted using synthetic solutions prepared from dye dissolved in distilled water. A stock solution of 1000 mg/l MB was prepared and the solutions for adsorption experiments were prepared from the stock solution to the desired concentrations. The adsorption of MB on the three prepared zeolites was carried out using the batch method at room temperature (25 ± 0.1 °C) in 150-ml glass bottles. The bottles containing a mixture of 100 ml of 10 mg/l MB and 0.1 g of each zeolite were stirred from 5 min to 24 h.

The influence of zeolites dose on adsorption of MB at the constant initial MB concentration—10 mg/l (MB) was studied with the following protocol: in 25 ml of MB solution, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035 and 0.040 g of either ZD, ZS, or ZK zeolite was added and the mixtures were shaken at room temperature for 2 h.

To study the effect of the initial MB concentrations, 0.025 g of each zeolite was mixed with 25 ml of aqueous solutions, containing various initial concentrations of MB (2–30 mg/l) for a period of 2 h.

The distribution of MB dyes between the zeolite-solution interface equilibrium was described by the Langmuir Eq. (1) [15].

$$1/q_e = C_e/q_m b + 1/C_e q_m \qquad (1)$$

where q_e (mg/g) and C_e (mg/l) are the amounts of adsorbed MB per gram of zeolite and unadsorbed MB concentration in solution at equilibrium, respectively. q_m is the maximum amount of adsorbed MB per gram of zeolite to form a complete monolayer on the surface at high C_e, and b is a constant related to the affinity of the binding sites (l/mg).

On the other hand, Freundlich model describes the highly heterogeneous surfaces [16] as given in Eq. (2):

$$\log q_e = \log K_F + 1/n \log C_e \qquad (2)$$

where, K_F refers to the relative adsorption capacity and 'n' represents adsorption intensity under different experimental conditions.

All the results together with the standard deviations (SD) of Langmuir and Freundlich parameters are summarized in Table 3.

Another series of adsorption experiments dealing with the effect of repetition on the adsorption behavior of zeolite Y for MB has been carried out. The initial concentration of MB solution is 10 mg/l and fresh salt solution is used for each repetition.

In all adsorption experiments, after the reaction time, suspensions were centrifuged 2 times at 5500 rpm for 10 min to separate the solution and solid. The initial and non-adsorbed concentrations of MB in supernatants were determined by UV–visible spectrophotometer at appropriate wavelength corresponding to the maximum absorption of MB (i.e., 664 nm). In all adsorption experiments, at least two runs with each zeolite were performed to evaluate the reproducibility of the measurements.

3. Results and discussion

3.1. Characterization of the prepared zeolites

XRF and XRD analyses of both raw kaolins and corresponding zeolites have been recorded previously [14]. The analyses indicated the formation of Na-Y zeolites. In addition, it was found that the zeolitic content in each prepared zeolite is proportional to the kaolinite content in the corresponding raw kaolin. The data for KS