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Use of chabazite, a naturally abundant zeolite, for the investigation of the adsorption kinetics and mechanism of methylene blue dye

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ABSTRACT

Chabazite, one of the common types of zeolite, was used in our study to remove methylene blue (MB) dye from aqueous solutions. The characterization of chabazite was performed using scanning electron microscope (SEM), Fourier Transform infrared (FTIR), X ray diffraction (XRD), and thermogravimetric-differential thermal analyses TG/DTA. During the experimental study, the effects of some parameters, such as contact time, adsorbent dosage, pH, stirring speed, and concentration, on the removal efficiency of chabazite were taken into consideration. To evaluate the experimental data, Langmuir, Freundlich, and Tempkin isotherm models were used. The experimental data were well fitted to the Langmuir isotherm model, with a correlation coefficient of 0.95. The adsorption kinetics of MB dye on chabazite could be described by a pseudo second-order model.

1. Introduction

Chabazite beds have been observed in the north-western part of Tuzgölü area, which is the largest interior basin in central Anatolia in the eastern Mediterranean [1]. The chabazite beds are found either with other zeolite minerals, e.g., clinoptilolite, erionite, and rarely erionite, as nearly pure zeolite mineral in different percentages in the groundmass, and/or as a replacement for feldspars [1,2]. The thicknesses of nearly pure chabazite beds vary from 1 cm to 50 cm, and laterally range from 5 to 20 m.

Among many different pollutants released from industrial applications, dyes are important due to their environmental impact, especially their toxicity to aquatic organisms. Dyes are mainly discharged into wastewaters from various industries, such as the dye manufacturing, textile, printing, food, cosmetic, and leather manufacturing industries [3,4]. Wastewaters containing biologically non-degradable dyes are difficult to treat due to their stability against light and heat [5–7]. Therefore, the removal of dyes from aqueous solutions is an extremely important application.

Conventional methods, such as sedimentation, filtration, membrane separation, oxidation, and reverse osmosis, are used for the removal of dyes from water and wastewater [8,9]. However, adsorption, which refers to a process wherein a material is concentrated at a solid surface from its liquid or gaseous surroundings, is effectively applied for the treatment of wastewaters. Adsorption has some advantages when compared to the aforementioned conventional techniques in terms of cost, flexibility and simplicity, especially if the adsorbent is inexpensive and readily available [4,6]. A good adsorbent should generally possess a porous structure (resulting in high surface area), and the time required for adsorption equilibrium should be as small as possible so that it can be used to remove dye wastes in a shorter amount of time.

Many adsorbents have been tested to reduce dye concentrations from aqueous solutions. Active carbon is an efficient adsorbent, but it is expensive, due to its high cost of manufacturing, and regeneration; as a result, other naturally occurring alternative adsorbents have been discovered and applied. Therefore, in addition to the commercially available adsorbents, natural coal [10], peat [11], chitin, chitosan [12,13], fly ash [14], wood sawdust [15], rice husk [16], and red mud [17] have been used as natural adsorbents for the removal of dyes from wastewaters.

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Natural zeolites, which are low-cost and easily available adsorbents with high adsorption capacities, are also abundant [18,19] and a few have been studied before for dye removal including zeolites X [20], P [21] and A [7]. These low-cost sources are crystalline hydrated aluminosilicates with a framework structure containing pores occupied by water, alkali, and alkaline earth cations [20,22–24]. Due to their high cation-exchange ability and to their molecular sieve properties, natural zeolites have been widely used as adsorbents in separation and purification processes [25,26]. Chabazite, a tectosilicate mineral of the zeolite group, is one of the most porous natural zeolites, having a high surface area. Structurally, chabazite consists of stacked, double six-membered ring prisms, interconnected through four rings, in a cubic, close-packed array [27,28]. Chabazite is a small-pore zeolite that can be used as an ion exchanger for the removal of pollutants from effluents due to its physicochemical property, such as cation exchange and sorption, and it can be found in significant quantities worldwide [29,30].

In the last one-to-two decades, several hundred technical papers and scientific articles, including a few reviews, have been devoted to (waste)water treatment by natural zeolites from different deposits [31–33]. However, the ion exchange on chabazite has been the subject of very few works. In this study, the main goal was to investigate the adsorption performance of chabazite for methylene blue (MB) removal. Towards this goal, the changes in adsorption efficiency were measured with respect to the effects of contact time, adsorbent dosage, stirring speed, concentration, and pH.

2. Materials and method

2.1. Chabazite and its characterization

The naturally abundant adsorbent chabazite (CHA) sample was obtained from southwest of Ankara, Turkey. This natural zeolite was used without any need for pretreatment. The oxide contents, trace element, and loss on ignition values were determined using ICP-MS and EAS in ACME Laboratories (Canada). When chemical composition of CHA was taken into consideration, its high content of SiO_2 was found to be 57.40%. Moreover, this highly abundant zeolite is comprised of some exchangeable cations, such as Na, Ca, and K.

Mineralogical analyses of the chabazite was performed at Hacettepe University (Ankara, Turkey) on randomly oriented samples using XRD (Rigaku D/MAX 2200 PC, Cu-Kα radiation source with a tube voltage and a current of 40 kV and 40 mA, respectively) at a scanning speed of 2°/min over the angular range from 2 to 70° 2θ. The total abundances of the major oxides of the sample was determined by ACME Laboratories (Vancouver, British Columbia, Canada) using inductively coupled plasma optical emission spectrometry and mass spectrometry (Spectro ICP-OES USA). Samples (0.1 g) were fused in Li-metaborate/tetraborate and then digested with nitric acid. The loss on ignition (LOI) was determined as the weight difference after ignition at 1000 °C.

The sizes and morphological features of the submicroscopic chabazite minerals and their interrelations with other minerals were determined using scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS) was used for determining the elemental composition. These analysis were performed at Afyonkarahisar Kocatepe University (LEO 1430VP). To identify the mineral composition, the SEM was equipped with EDS and BSE was used with the following parameters: the accelerating voltage was in the range of 15–20 kV, the probe current was 15 mA, and the spot size was 5 μm. Measurements of IR absorption were performed using a Perkin Elmer 1600 Fourier Transform infrared (FTIR, UK) spectrophotometer at Selcuk University (Konya, Turkey) at a wave number range of 400–4000 cm^{-1}. KBr heated for 16 h at 150 °C was admixed with the samples at a ratio of approximately 1/200 and then made into pellets by being subjected to a pressure of 10 tons/cm^2. The samples were heated for 16 h at 120 °C.

Thermogravimetric-differential thermal analyses were performed using a SII Exstar 600 TG/DTA 6300 (Netzsch, Germany) derivatograph using sample of mass of 30–40 g that were dried overnight at 60 °C within a temperature range from 20 to 1000 °C in the air atmosphere at continuous 10 °C/min heating rates. The analyses were performed at the laboratories of the Mineral Research & Exploration General Directorate (Ankara, Turkey).

The specific surface area and the micropore volume of the chabazite samples were measured according to N_2 absorption-desorption data collected at −198 °C using a Micromeritics Gemini VII 2390 V1.03 (USA) model surface area instrument. The samples were subjected to the degassing process, which was conducted at 300 °C under vacuum for 3 h, to attain a constant weight. The surface area values were determined via the BET equation [34] using P/Po within a range between 0.06 and 0.30 of the branch of the isotherm, and the pore size distribution was determined from the desorption branch of the isotherms. The degassing of the HEU/CLI-rich powder samples was performed under vacuum (10^{-2} Torr) at temperatures in the range from 100 to 300 °C.

2.2. Adsorbate

In this study, a basic dye (cationic) MB was chosen because of its known strong adsorption onto solids. The adsorbate MB (chemical formula: $C_{16}H_{18}ClN_3S$, MW: 319.85 g/mol, λ_{max}: 663–667 nm) was supplied by Acros (USA) as a green fine crystalline powder. Concentrations of MB dye were determined by determining the absorbance at the characteristic wavelength using a double beam UV-visible spectrophotometer (Hach Lange DR 2800 UV-Visible spectrophotometer). Calibration curves were plotted between the absorbance and the concentration of the MB dye solution.

2.3. Batch experiments

Batch experiments were performed to investigate the effects of various parameters on the removal process. For each experimental run, 50 ml of MB dye of known concentration and pH as well as the known amount of CHA were placed into a 100-ml stoppered conical flask. This mixture was agitated with a temperature controlled shaker at 200 rpm at 25 °C. After appropriate time intervals, the samples were filtered through cellulose acetate filters, and then the supernatant liquid was analyzed for the remaining dye concentration by using the UV-spectrophotometer. Experiments were performed at initial pH values in the range from 3 to 9, which was controlled by the addition of 0.1 M HCl or 0.1 M NaOH solutions.

The percentage of removal of dyes and the equilibrium adsorption uptake were calculated using the following equation:

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (1)$$

where q_e is the value of mg-adsorbate/g-adsorbent, C_0 is the initial sorbate concentration (mg/L), C_e is the equilibrium sorbate concentration (mg/L), V is the volume of the solution (L), and w is the mass of the adsorbent (g) [6].

To determine the optimum amount of CHA per unit mass adsorbate, a 30-ml dye solution was agitated with different amounts of CHA until equilibrium. The kinetics of adsorption were determined by analyzing the adsorptive uptake of the dye from aqueous solution at different time intervals. For adsorption isotherms, dye solutions of different concentrations were agitated