

Adsorption of Methylene Blue from Aqueous Solution on the Surface of Znapso-34 Nanoporous Material

B. Abbad, A. Lounis, and Tassalit Djilali

Abstract—The effects of equilibrium time, solution pH, and sorption temperature of cationic methylene blue (MB) adsorption on nanoporous metallosilicoaluminophosphate ZnAPSO-34 was studied using a batch equilibration method. UV–VIS spectroscopy was used to obtain the adsorption isotherms at 20° C. The optimum period for adsorption was 300 min. However, MB removal increased from 81,82 % to 94,81 %. The equilibrium adsorption data was analyzed by using Langmuir, Freundlich and Temkin isotherm models. Langmuir isotherm was found to be the better-fitting model and the process followed pseudo second-order kinetics. The results showed that ZnAPSO-34 could be employed as an effective material and could be an attractive alternative for the removal of dyes and colors from aqueous solutions.

Keywords—Adsorption, Dye, Metallosilicoaluminophosphate, Methylene Blue.

I. INTRODUCTION

RAPID industrialization and urbanization has resulted in the deterioration of water, air, and land quality. Dye contaminated wastewater originates from a number of industries, such as textile, metal plating, packaging, and paper industry [1]-[2]. During the past three decades, several physical, chemical and biological methods are used to remove dyes from effluents. Among the physical methods available of dye removal, adsorption is found to be the most effective treatment for the removal of colour from wastewater and gives the best results as it can be used to remove different types of colouring materials [3]-[4]. In wastewater treatment, zeolite is commonly applied as an adsorbent, ion exchange, or molecular sieve medium. Physical adsorption occurs through phenomena such as Van der Waals forces between solute and adsorbent surface. Zeolites are predominantly used in a wide spectrum of water and wastewater treatment processes in which the presence of heavy metal and ionic contaminants is inherent, although in some cases, organic contaminants can be removed as well [5-7].

In this work, initial dye concentration, contact time, adsorbent dosage, pH and kinetic studies were carried out to evaluate the adsorption capacity ZnAPSO-34 nanoporous material for the removal of MB from aqueous solutions.

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II. EXPERIMENTAL

A. Preparation of Zeotype for Laboratory Experiments

ZnAPSO-34 was synthesized by following previously reported procedure [8]. The typical synthesis of gel with a molar composition of: 0.8SiO₂:0.8Al₂O₃:1P₂O₅:1TEAOH:0.4Zn:225H₂O was prepared in 120 ml Teflon-lined autoclave. Isopropoxyde of alumina (Fluka) and ortho-phosphoric acid (Merck 85%) were used as aluminum and phosphorus sources, respectively; the divalent metal was introduced as an acetate (zinc acetate, Fluka p.a.), other reactants were fumed silica (Aerosil 200, Serva), tetraethylammonium hydroxide (20% aqueous solution, Fluka) and deionized water. Product crystallization was carried out under static conditions in an oven at 180-200°C over a 24h period. The autoclaves were cooled down to room temperature using running water. The product was recovered by centrifugation, washed and dried overnight at 80 - 100°C. The final product was in the form of a white powder.

B. Preparation of Basic Dye Solution

We used an analytical reagent grade of Methylene Blue supplied by BIOCHEM Chemopharma (MW=319.86g, Absorption max (water):663 - 667 nm). Stock solutions of the test reagent were made by dissolving Methylene Blue, (3,9-bis dimethyl- aminophenazo thionium chloride), in distilled water. The structure of this dye is shown in Fig. 1.

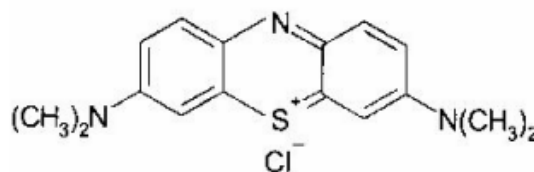


Fig. 1 The structure of methylene blue

All the other chemicals used in the preparation were of analytical reagent grade and were purchased from Merck (Germany)

C. Adsorption Studies

The adsorption experiments were performed in a batch mode. Kinetic experiments were carried out by stirring 250 mL of dye solution of known initial dye concentration with 0.05 g of ZnAPSO-34 at room temperature (20°C) at 400 rpm in different 500 mL PE flasks. At different time intervals, samples were drawn out and then centrifuged at 3500 rpm for 10min. The concentration in the supernatant solution was analyzed using a UV spectrophotometer SHIMADZU 1800 by measuring absorbance at $\lambda_{max} = 664$

nm and pH = 6. Adsorption isotherms were carried out by contacting 0.05 g of ZnAPSO-34 with 250ml of methylene blue over the concentration ranging from 2 to 10 mg l⁻¹.

The effect of pH was observed by studying the adsorption of dye over a pH range of 2 - 10. The initial pH of the dye solution was adjusted by the addition of 0.1 N solution of hydrogen chloride (HCl) or sodium hydroxide (NaOH). The sorption kinetic studies were also carried out at different temperatures, i.e., 20, 30, and 40 °C, to determine the effect of temperature.

The amount of dye adsorbed per unit weight of adsorbent; q_t (mg.g.l⁻¹) was calculated using the mass balance equation given by:

$$q_t = \frac{(C_0 - C_t)V}{m} \quad (1)$$

Where, C_0 (mg/l) is the initial dye concentration, C_t (mg/l) the liquid phase concentrations of dye at any time, V the volume of the solution (l) and m the mass of dry adsorbent used (g).

D. Characterization Techniques

The as-synthesized product was characterized initially by X-ray powder diffraction using a diffractometer (Miniflex2, RIGAKU) equipped with a linear position sensitive detector (CuKα1 radiation, $k = 1.5406 \text{ \AA}$). The morphology and average size of the crystals were determined by scanning electron microscopy (SEM) using a HITACHI S4800 microscope.

III. RESULTS AND DISCUSSION

A. Characterisation of the Adsorbent

The crystallinity of the sample and the phase identification were evaluated from XRD patterns (Fig. 2). Examination of the powder data of the sample revealed the existence of one phase only, which corresponds to Chabazite structure [9].

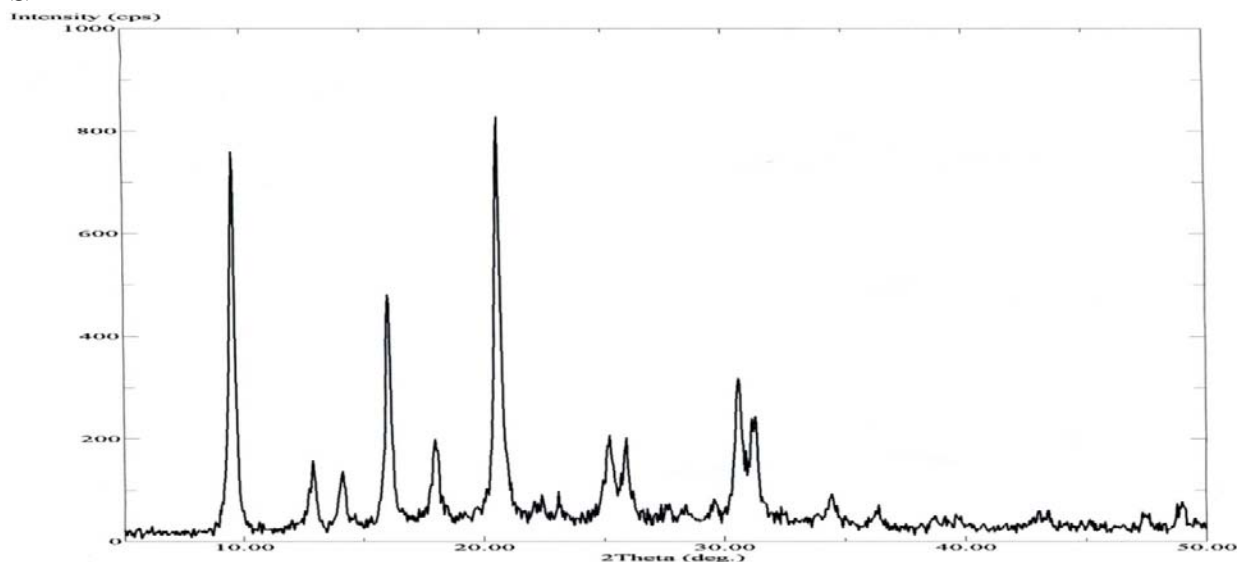


Fig. 2 X-ray powder diffraction of as calcined sample at 500°C

We have examined the sample by SEM, to investigate the morphology of the crystals. SEM images of the calcined samples are provided in Fig. 3. The sample prepared shows

the typical chabazite morphology: cubic crystals are well-developed in the size range of 3–10 μm.

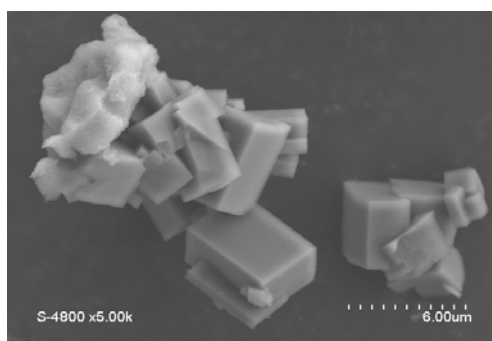


Fig. 3 SEM image of characteristic ZnAPO-34 crystals

B. Effect of Contact Time and Initial Dye Concentration

Equilibration time is an important parameter for economical wastewater treatment. The effects of contact time and initial dye concentration on removal are shown in Fig. 4. Equilibrium adsorption was established within 300 min for all concentrations. These results show that the contact time required for maximum uptake of the dye by ZnAPSO-34 was

strongly dependent on initial methylene blue concentration. The results also show that the amount of methylene blue adsorbed increased with an increase in initial dye concentration.

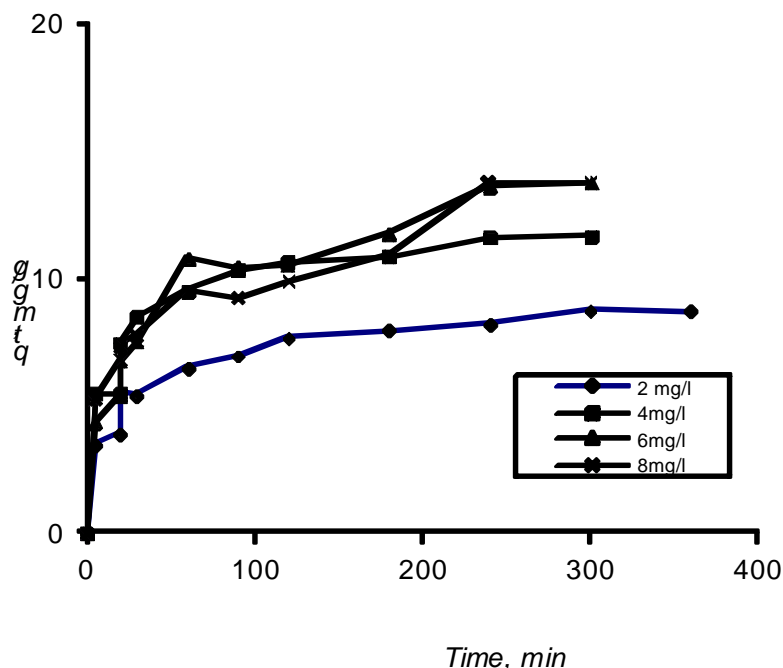


Fig. 4 Effect of initial dye concentration and contact time on the adsorption of Methylene Blue onto ZnAPSO-34

C. Effect of Adsorbent Dosage

The effects of adsorbent dosage on MB removal are presented in Fig. 5. Removal efficiency increased from 85.05% to 94.08% with an increase in the dosage from 0.05 to 0.1 g l⁻¹, and then remained almost constant. This was caused by the fact that, with increasing adsorbent dosage, more adsorption sites are available. However, increasing the sites had little effect on removal efficiency at high adsorbent dosage because of the establishment of equilibrium at an extremely low adsorbate concentration in

the solution before reaching saturation. It can also be seen from Figure 5 that the MB removal efficiency changed slightly from 85.05% to 96.5% with an increase in adsorbent dosage from 0.1 to 0.25 g l⁻¹. This result is mainly because the adsorption sites were more or less saturated by MB at low adsorbent doses (<0.1 g l⁻¹), but unsaturated at high doses (>0.25 g l⁻¹). The adsorbent dosage was fixed at 0.05 g l⁻¹ for the remaining experiments.

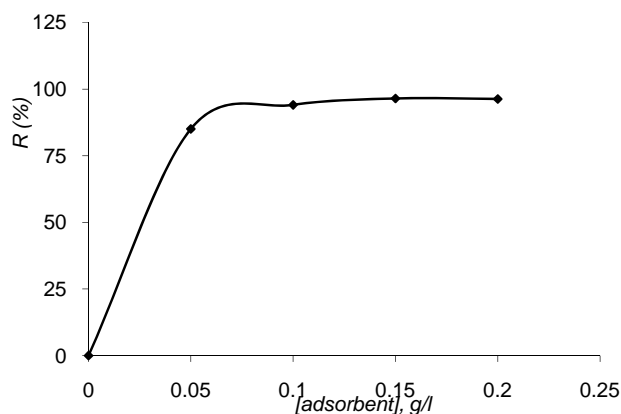


Fig. 5 Effect of adsorbent dosage on the adsorption of Methylene Blue onto ZnAPSO-34 (dye concentration: 2 mg^l⁻¹ temperature: 20°C; contact time: 300 min) pH: 6

D. Effect of pH

The pH of the dye solution is an important factor controlling the adsorption processes. The effect of pH on the

uptake of Methylene Blue by ZnAPSO-34 is shown in Fig. 6. The percentage uptake increased from 81% to 95% with an increase in pH from 1 to 11.

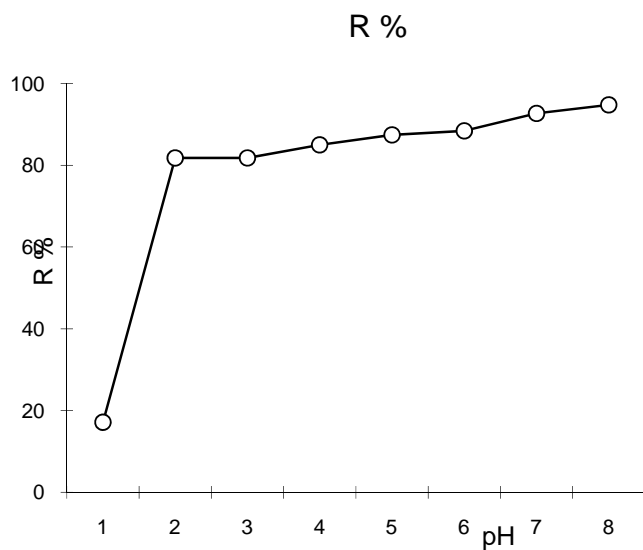


Fig. 6 Effect of pH on the adsorption of MB on ZnAPSO-34 (Initial dye concentration: 2 mg

E. Adsorption Isotherms

The adsorption isotherm of Methylene Blue onto ZnAPSO-34 is presented in Fig. 7. The isotherm showed the shape of type 'L' according to the classification of Giles et al. [10]. The L or Langmuir shape of the isotherms means that there is no

strong competition between the solvent and the adsorbate to occupy the adsorbent sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface.

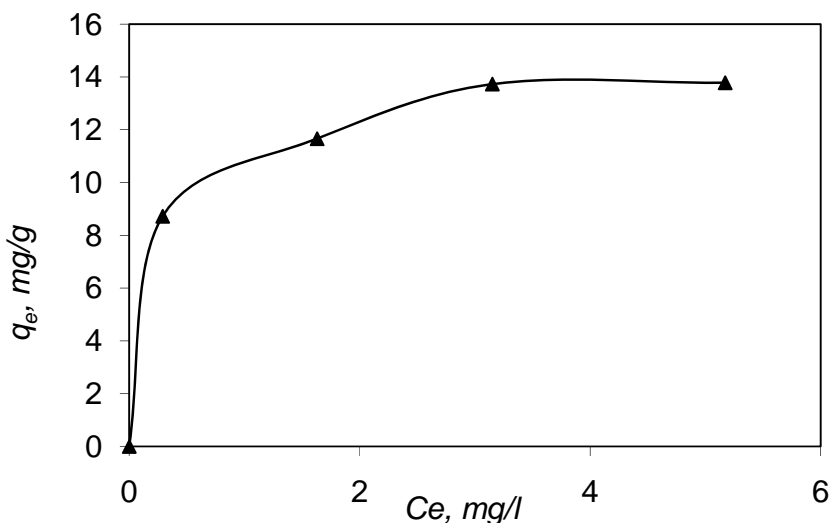


Fig. 7 Equilibrium isotherm of Methylene Blue onto ZnAPSO-34

IV. CONCLUSION

The ability of ZnAPSO-34 to remove Methylene blue from aqueous solution was investigated. The conditioning time of 3h was found to be sufficient for reaching equilibrium. The results showed that the process follows pseudo second-order kinetics. The low values of maximum adsorption capacities obtained from Langmuir model, confirm that the molecule of MB is not strongly adsorbed inside the pores because of its size. Only the surface functions are responsible for adsorption.

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