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Application of nanodimensional pores of zeolite mordenite and mordenite nanocrystal for phenothyazine dyes removal from the industrial wastewaters

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ABSTRACT

Mordenite and mordenite nanocrystal, were employed as effective adsorbents for new methylene blue (NMB) from aqueous solution. The adsorption kinetics was investigated. The adsorption capacity of mordenite nanocrystal zeolite for NMB dye is more than mordenite zeolite. Kinetic studies indicate that the adsorption follows the pseudo second-order kinetics. The effects of equilibrium time, solution pH and sorption temperature were examined. Solution pH will affect the adsorption behavior of mordenite and mordenite nanocrystal. Higher solution pH results in higher adsorption capacity. The results show that adsorption capacity dye increase in lower temperature.

KEYWORDS

Mordenite nanocrystal;
New methylene blue;
Dye removal;
Adsorption;
Zeolite.

INTRODUCTION

Dyes are extensively used in the textile industry, photocatalytic industry, coating industry and photochemical application. Treatment of colored wastewater from textile or other industries is a serious problem that has attracted the attention of many researchers during last decades. In general, the methods for the treatment of wastewater containing dyes can be divided into two main groups[1]: (I) chemical or physical methods of dye removal, which refer to the process called decoloration and (II) dye removal by means of biodegradation. Physical methods of decoloration include different precipitation methods, adsorption, filtration, reverse osmosis and etc. Among chemical methods of dye removal, there are processes such as reduction, oxidation, compleximetric methods, ion exchange and neutralization. Biological treatment can be conducted in the presence or absence of oxygen[2]. These processes have their disadvantages and limitations, such as high cost, generation of secondary pollutants, and poor removal efficiency. Thus adsorption has been found to be the most effective economic alternative with high potential for the removal and recovery of dyes from wastewater[3,4]. Zeolites have already found many applications because of its high cation-exchange capacity and surface area, etc. Structurally, it is mainly composed of aluminosilicates with a three-dimensional framework structure bearing AlO_4 and SiO_4 tetrahedral that are linked to each other by sharing of their oxygens to form interconnected cages and channels containing mobile water molecules and alkalis and/or alkaline earth[5,6]. Zeolite is a good adsorbent for heavy metal ions from wastewater[7] and for organic dyes[8,9]. Of course, mesoporous materials such as MCM-41 and MCM-22 are widely used as adsorbents for organic dyes. The larger surface area and good adsorption capacity render these materials very interesting for adsorption and catalysis[10,11]. Synthetic zeolites have become increasingly important due to the wide range of their chemical and physical properties and have been used as adsorbents, molecular sieves, membranes, ion exchanger and catalysts in the past decades[10]. Meshko et al.[11] have shown that the granular activated carbon has a higher adsorption capacity than the natural zeolite. But activated carbons have higher cost in production and regeneration. Therefore, other adsorbents such as zeolite with higher surface area can be an alternative. Armagan and co-workers[12,13] examined the ability of natural and modified zeolites to remove reactive dyes from aqueous solutions. The adsorption results indicated that the natural zeolite has a limited adsorption capacity for reactive dyes. Metes et al.[14] investigated several synthetic zeolites for cleaning printing ink wastewater and found that adsorption is independent of pore structure. They showed that ZSM-5 and NH_4-Beta are effective while other zeolites studied Showed a lower efficiency. On the other hand, nanosized zeolites are important in catalytic and adsorptive applications. Smaller crystals of zeolites will have larger surface areas and less diffusion limitations compared to zeolites with micrometer-sized crystal[15]. That was why; we have chosen mordenite nanocrystal zeolite as adsorbent.

In this paper, we report an investigation using mordenite and mordenite nanocrystal as an adsorbent to remove new methylene blue from aqueous solution. The kinetics and adsorption equilibrium of the basic dye on synthetic zeolites were investigated. The results show that, mordenite nanocrystal is an effective adsorbent to remove dye with respect to mordenite.

EXPERIMENTAL PROCEDURES

Adsorbent and dye

Mordenite zeolite was synthesized hydrothermally following standard procedure reported in literature[16].

Mordenite nanocrystal was prepared by a hydrothermal synthesis method based on the published recipe[17]. The chemical composition of the mordenite and mordenite nanocrystals gels were Al_2O_3: $15SiO_2$: $8.5Na_2O$: $1300H_2O$ and Al_2O_3: $30SiO_2$: $6Na_2O$: $780H_2O$ respectively. Then, the reaction mixture were introduced into a stainless-steel autoclave, heated to 170 ºC and kept for a given time until crystallisation was completed. After the autoclave was quenched in cold water, the crystalline products were filtered, washed with water and dried at 110 ºC over night. Then the samples were calcined in a muffle furnace at 540 ºC for 5 h.

A typical dye, new methylene blue (NMB), was selected for adsorption tests. It was obtained from sigma chemical. A stock solution with concentration at 10^{-4} M was prepared and the solution for adsorption test was prepared from the stock solution to the desired concentration (10^{-5}).

Adsorbent characterization

Powder X-ray diffraction patterns of the samples were recorded using a X'pert diffractometer with Cu K_α radiation ($\lambda = 1.54$ ºA).

UV-visible absorption spectra were recorder using a Shimadzu 1600 PC in the spectral range of 190-900 nm.

The specific surface area and pore volume of the samples were measured using a Sibata Surface Area Apparatus 1100. All of the samples were first degassed at 250 ºC for 2 h.

The pH of samples was measured as follows: 0.1 g of samples were mixed with 10 mL of distilled water and shaken for 24 h at 25 ºC. After filtration, the pH of solution was determined by a pH meter.

Sorption tests

Adsorption kinetics and isotherm experiments for all samples were undertaken using a batch equilibrium technique. The adsorption of dye was performed by shaking 0.05 g of adsorbent in 200 mL of dye solution with an initial concentration of 1.00×10^{-5} M at 100 rpm at different temperatures. The determination of dye concentration was done spectrophotometrically on a Shimadzu 1600 PC in the spectral range of 190-900 nm, by measuring absorbance at λ_{max} of 632 nm for NMB.

The data obtained from the adsorption tests were then used to calculate the adsorption capacity, q_t (mol g^{-1}), of the adsorbent by a mass-balance relationship, which represents the amount of adsorbed dye per amount of dry adsorbent,

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

Where C_0 and C_t are the concentrations of dye in solution (M) at time t = 0 and t = t, respectively, V is the volume of the solution (dm^3), and W is the mass of the dry absorbent used (g).

RESULTS AND DISCUSSION

Material characteristics

Figure 1 presents the XRD patterns of mordenite and mordenite nanocrystal zeolite. The XRD profiles of mordenite and mordenite nanocrystal show quite well with patterns that is given in literatures[15-18] which allowed up to identify the product as crystalline mordenite zeolite.

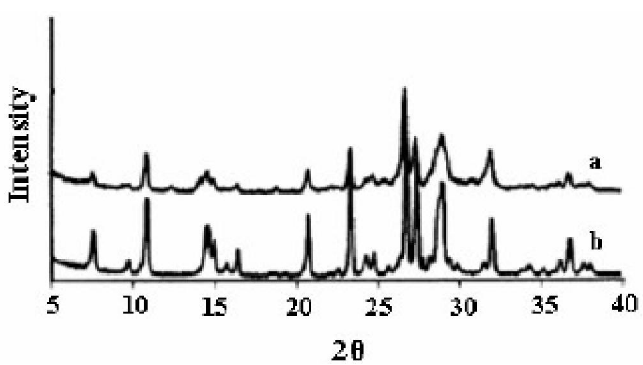

Figure 1 : XRD patterns of (a) mordenite nanocrystal zeolite (b) mordenite zeolite.

The specific surface area and pore volume of the mordenite and mordenite nanocrystal are presented in TABLE 1.

TABLE 1 : Physico-chemical properties of mordenite and mordenite nanocrystal zeolite.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g) (micro)	Pore volume (cm^3/g) (total)	Si/Al ratio	pH
mordenite	240	0.14	0.16	6	6.5
Mordenite nanocrystal	379	0.18	0.208	15	6.5

It is seen that mordenite nanocrystal zeolite has a surface area of 379 $m^2 g^{-1}$ while the mordenite zeolite only has 240 $m^2 g^{-1}$ (TABLE 1). The pore volume of two adsorbents also demonstrates that mordenite nanocrystal is a porous material having a pore volume of 0.18 $cm^3 g^{-1}$ with micropores. It is seen that mordenite nanocrystal zeolite has much higher adsorption than mordenite. The pH of the solid solution indicates that mordenite and mordenite nanocrystal zeolite exhibits acidic properties.

Comparison of new methylene blue on adsorbents

Figure. 2 presents the dynamic adsorption of NMB on mordenite and mordenite nanocrystal at initial concentration of 1.00×10^{-5} M and 25 ºC. The equilibrium adsorption for NMB on mordenite and mordenite nanocrystal zeolite were 8×10^{-5} and 1.2×10^{-4} mol g^{-1}, respectively. From TABLE 1, it is seen that mordenite nanocrystal zeolite has higher surface area and pore volume, which results in the higher adsorption capacity. On the other hand, large pores are larger than NMB molecular size[19] and are all available for NMB adsorption, resulting in higher adsorption capacity. But it is close to NMB molecular size in mordenite zeolite.

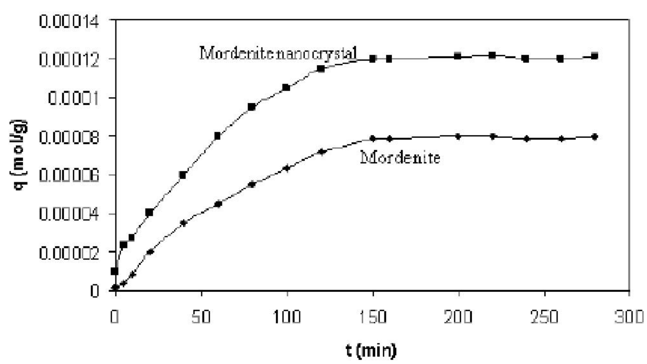

Figure 2. Comparison of dynamic adsorption of NMB on mordenite nanocrystal and mordenite zeolite. Absorption conditions: 0.05 g adsorbent in 200 mL NMB initial concentration 1.00×10^{-5} M, temperature: 25 ºC, pH = 6.5.

Effect of solution pH

Figure. 3 shows the dynamic adsorption of NMB on mordenite nanocrystal at three different initial pH values at initial dye concentration of 1.00×10^{-5} M and 25 ºC. It is seen that the amount of adsorption increase as the pH is increasing. The adsorption increase from 1.2×10^{-4} M to 2.4×10^{-4} mol g^{-1}, when solution pH is changed from 3 to 9. Several investigations also have shown that dyes adsorption have higher adsorption at higher pH values[20-22]. For cationic dyes, lower adsorption of NMB at acidic pH is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye (NMB) and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption.

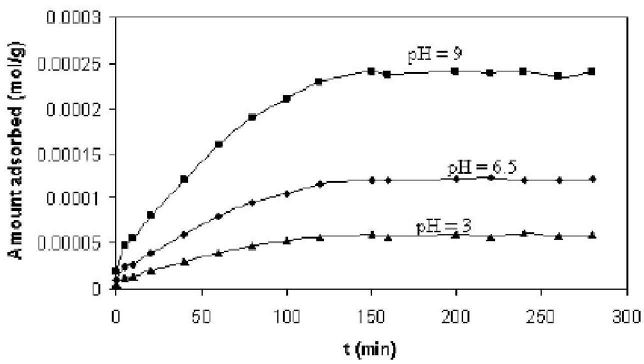

Figure 3 : Effect of solution pH on NMB adsorption on mordenite nanocrystal zeolite. Adsorption conditions: 0.05 g adsorbent, NMB initial concentration: 1.00 × 10^{-5} M, temperature: 25 ºC.

Influence of temperature on NMB adsorption

Figure. 4 shows the effect of temperature on the adsorption of NMB onto mordenite nanocrystal and mordenite zeolite. As seen from the figures, temperature has effect on NMB adsorption in zeolite. The decrease in dye adsorption capacity with increasing temperature might be due to the dye desorbed of zeolite. Juang et al. have reported similar results[23].

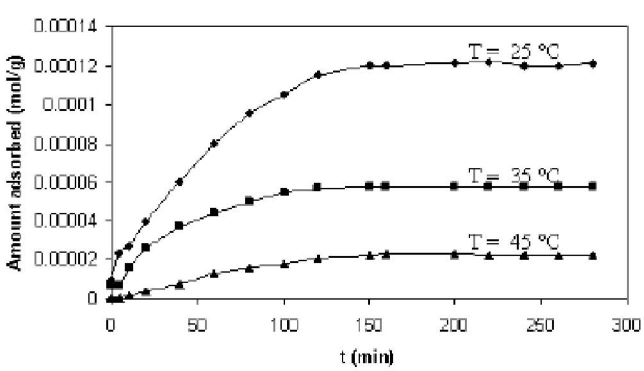

Figure 4 : Effect of solution temperature on NMB on mordenite nanocrystal zeolite. Adsorption conditions: NMB initial concentration: 1.00 × 10^{-3} M, pH = 6.5.

Influence of adsorbent amount used on NMB adsorption

In order to obtain the optimum zeolite amount required for adsorption at pH 6.5, a series of experiments were undertaken with different amounts of adsorbents in 200 mL of 1.00 × 10^{-5} M NMB solutions. The NMB concentration was tasted after 2 h of shaking at 25 ºC. The zeolite amounts added against adsorbed NMB (mol g^{-1}) are shown from Figure. 5. Examination of this figure revealed that the amount of adsorbed dye per amount of adsorbent (mol g^{-1}), increases with increasing amount of zeolites, because of the necessity of additional filtration to lower turbidity to required levels, the amount of 0.05 g/200mL has been found as the optimum.

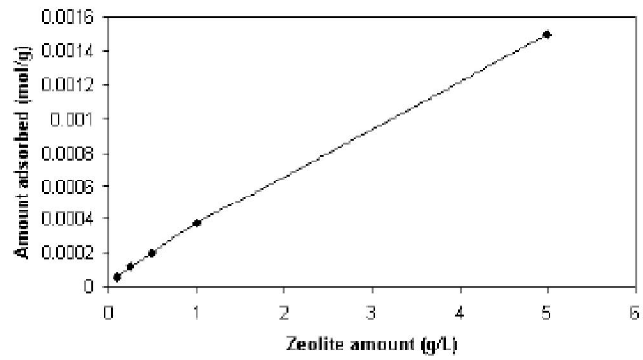

Figure 5 : Influence of mordenite nanocrystal zeolite amount on the adsorption amount of NMB.

Adsorption kinetics

A study of adsorption kinetics is desirable as it provides information about the mechanism of adsorption, which is important for optimising the efficiency of the process. Adsorption kinetics can be modelled by several models, the pseudo-first-order Lagergren equation[24] and pseudo-second-order rate equation[25] given below in non-linear form:

$$q_t = q_e\,(1-e^{-K_1 t}) \qquad (2)$$

$$q_t = \frac{q_e^2 K_2 t}{(1 + q_e K_2 t)} \qquad (3)$$

Where K_1 is the rate constant of pseudo-first-order adsorption (h^{-1}), K_2 (g mol^{-1} h^{-1}) the rate constant of pseudo-second-order adsorption, q_e and qt are the amount of dye adsorbed on the adsorbent (mol g^{-1}) at equilibrium and at time to respectively.

We used the above two non-linear equations for curve fitting by employing a commercially available software Sigma Plot. The parameters of kinetic models of NMB adsorption on mordenite and mordenite nanocrystal zeolites are presented in TABLE 2. The first-order model seems to be not good in modelling the kinetics of whole adsorption process and the regression coefficients are less than the ones obtained from the second-order-kinetics (TABLE 2). From the results, it is also seen that the equilibrium adsorption from the pseudo-second-order model are closer to the experimental data than the ones from the pseudo-first-order kinetics, suggesting the better fit of the second-order kinetics.

TABLE 2 : Parameters of kinetic models of NMB adsorption on zeolites

Adsorbent	T (ºC)	pseudo- K_1 (h^{-1})	first-order q_e ($molg^{-1}$)	model R^2	pseudo- K_1 (h^{-1})	second-order q_e ($molg^{-1}$)	model R^2
mordenite	25	0.255	6.90×10^{-5}	0.891	1347.7	7.90×10^{-5}	0.992
	35	0.122	3.18×10^{-5}	0.953	1228.9	3.65×10^{-5}	0.989
	45	0.06	1.40×10^{-5}	0.912	1197.5	1.22×10^{-5}	0.989
mordenitenaocrystal	25	0.442	1.02×10^{-5}	0.933	2587.2	1.18×10^{-4}	0.991
	35	0.235	5.10×10^{-5}	0.892	2223.8	5.70×10^{-5}	0.987
	45	0.198	2.00×10^{-5}	0.883	1988.2	2.20×10^{-5}	0.992

From TABLE 2, one can also see that the rate constant for mordenite nanocrystal zeolite is more than mordenite zeolite.

CONCLUSION

Mordenite nanocrystal zeolite is an effective adsorbent for new methylene blue with respect to mordenite zeolite. The adsorption capacity for NMB in mordenite nanocrystal and mordenite zeolite was 1.2×10^{-4} and 8×10^{-5} mol g^{-1} at 25 ºC, respectively.

Solution pH affects the adsorption behaviour of mordenite and mordenite nanocrystal zeolite. Adsorption capacity increases with increasing solution pH. The dye adsorption decrease with increasing temperature and optimum temperature was 25 ºC. Kinetic analyses show that adsorption of dyes on mordenite nanocrystal and mordenite zeolite follows pseudo-second-order kinetics. The rate constant for mordenite nanocrystal zeolite was more than mordenite zeolite.

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