Application of nanodimensional pores of zeolite mordenite and mordenite nanocrystal for phenothiazine 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. © 2009 Trade Science Inc. - INDIA

KEYWORDS

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

INTRODUCTION

Dyes are extensively used in the textile industry, photocatalytic industry, coating industry and photo-chemical 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 groups11: (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 oxygen12. 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 wastewater3,4. 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 AlO4 and SiO4 tetrahedral that are linked to each other by sharing of their oxygens to form interconnected cages and channels containing mobile
Zeolite mordenite and mordenite nanocrystal

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 \(\text{Al}_2\text{O}_3: 15\text{SiO}_2: 8.5\text{Na}_2\text{O}: 1300\text{H}_2\text{O}\) and \(\text{Al}_2\text{O}_3: 30\text{SiO}_2: 6\text{Na}_2\text{O}: 780\text{H}_2\text{O}\) respectively. Then, the reaction mixture were introduced into a stainless-steel autoclave, heated to 170 °C 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 °C over night. Then the samples were calcined in a muffle furnace at 540 °C 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\(_\alpha\) radiation \((\lambda = 1.54 \text{ Å})\). 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 °C 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 °C. 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 \(1.00 \times 10^{-5}\) 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 \(\lambda_{\text{max}}\) 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,

\[
q_t = \frac{(C_0 - C_t) V}{W}
\]

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.

**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 °C. It is seen that mordenite nanocrystal zeolite has higher adsorption capacity. 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 °C. 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.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{BET} ) (m(^2)/g)</th>
<th>Pore volume (cm(^3)/g) (micro)</th>
<th>Pore volume (cm(^3)/g) (total)</th>
<th>Si/Al ratio</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mordenite</td>
<td>240</td>
<td>0.14</td>
<td>0.16</td>
<td>6</td>
<td>6.5</td>
</tr>
<tr>
<td>Mordenite nanocrystal</td>
<td>379</td>
<td>0.18</td>
<td>0.208</td>
<td>15</td>
<td>6.5</td>
</tr>
</tbody>
</table>

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.
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 \cite{23}. 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 \cite{24} and pseudo-second-order rate equation \cite{25}, given below in non-linear form:

\begin{equation}
q_t = q_e (1-e^{-K_1t})
\end{equation}

\begin{equation}
q_t = \frac{q_e^2K_2t}{1 + q_eK_2t}
\end{equation}

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 $q_t$ are the amount of dye adsorbed on the adsorbent (mol g$^{-1}$) at equilibrium and at time $t$ 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

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 $\times$ 10$^{-3}$ M NMB solutions. The NMB concentration was tasted after 2 h of shaking at 25 $^\circ$C. 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.
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 ad sorption 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.

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 $1.2 \times 10^{-4}$ and $8 \times 10^{-5}$ 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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