Adsorption of methyl orange by zinc oxide synthesized via a facile precipitation method

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Abstract

The present study deals with the preparation and characterization of zinc oxide for adsorption characteristics of methyl orange (MO). The influence of initial dye concentration, contact time and adsorbent dose on the adsorption capacity were investigated. The equilibrium adsorption was analyzed using Langmuir and Freundlich adsorption models. In order to study the kinetic aspects of the adsorption of MO, pseudo-second order were employed. The results confirm the feasibility of ZnO adsorption process of MO.

Keywords: Adsorption; Methyl orange; Zinc oxide; Precipitation method.

Introduction

Nowadays industrial activities increase the organic pollutants in wastewater. Among the organic pollutants, color wastes were considered to be more harmful substances due to their serious toxic outcome to the environment, and they were difficult to be degraded and existed profoundly and persistently in nature. So far, most attention has been devoted to the study of different types of low cost and high removal efficiency materials to remove the pollutants from aqueous solution. Up to date, different materials such as activated carbon [1], silica-gel[2], aluminum oxide[3], zeolites[4], resins [5], and silver nanoparticles decorated carbon microspheres[6], have been used to adsorb contaminant from wastewater. Among these material in terms of price, zinc oxide is a possible

sorbent. In this study, we synthesized via facile co-precipitation method for eliminating the MO from aqueous solution. The methyl orange was used as model pollutants to investigate the adsorption characteristics of zinc oxide in agues system. Furthermore, the recyclability of the ZnO was evaluated. The results showed that the zinc oxide could be used as a good adsorbent for environmental remediation.

Materials and methods

All chemicals used in this study were analytical grade and were used without further purification.

Preparation of adsorbent

ZnO was prepared with co-precipitation method. In a typical procedure, 0.5 M aqueous solution of zinc acetate [$Zn(AC)_2 \cdot 2H_2O$] and 1.0 M aqueous solution of ammonia were separately prepared in 100 mL distilled water. 100 mL of ammonia was added dropwise into zinc solution at 70◦ C with constant stirring. The solution was centrifuged at 4000 rpm to obtain precipitated ZnO. White solid was washed with distilled water and ethanol then dried in air atmosphere at about 100 ◦C for 4 h.

Characterization of adsorbent

Scanning electron microscopy (SEM) analysis of as-prepared sample was carried out using Tescan MIRA3 scanning electron microscope to examine the surface morphology. Xray diffraction patterns for adsorbent was obtained using Philips X'pert Pro diffractometer with 2q range of 10 to 60 and step size of 0.05. The amount of residual dye in the solution was traced by UV-vis spectra

(ShimadzuUV-1700), and the dye concentration was calculated by the absorbance at the maximum absorption.

Batch adsorption studies

The effect of initial dye concentration on the adsorption capacity was investigated in a range from 10 to 100mg L^{-1} of MO with adsorbent dosage of 1 $g.L^{-1}$ at 25°C. The effect of adsorbent dosage on the dye removal efficiency was evaluated in a range from 50 to 400 mg at 100 mL of MO (100 $mg.L^{-1}$) at 25°C. The effects of contact time was also investigated with 1 $g.L^{-1}$ of adsorbent and dye initial concentration of 200 $mg.L^{-1}$. The recyclability of the sample was conducted in the 100 mL of 100 $mg.L^{-1}$ MO solution with 0.01 g of as-prepares sample at room temperature. The dye removal and adsorbed amount were determined according to the following:

$$\text{Dye removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100$$

$$Q_e = \frac{(C_0 - C_e)V}{m}$$

where Q_e is the adsorbed amount of MO per unit weight of adsorbent ($mg.g^{-1}$), C_0 and C_e ($mg.L^{-1}$) are the initial and equilibrium concentration of MO, respectively; V (L) is the volume of the dye solution and m (g) is the dry mass of the adsorbent.

Results and discussion

Characterization

The representative SEM (Fig. 1) image revealed that sample has nano sheet like structures in the surface and was porous.

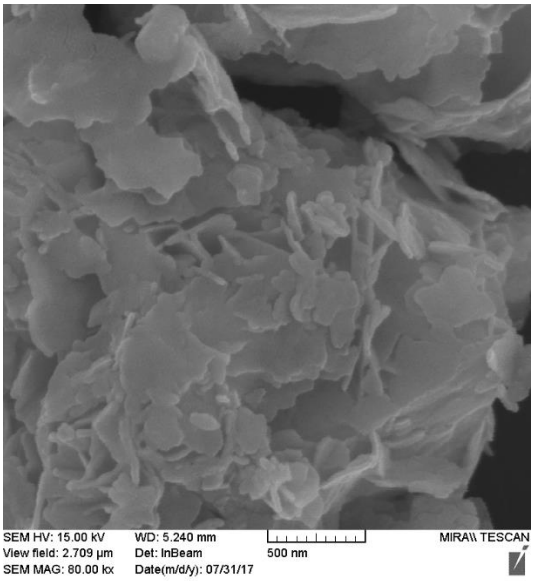

Fig. 1. SEM image of adsorbent

XRD patterns of zinc oxide was shown in Fig. 2. XRD pattern of ZnO showed diffraction peaks at the position of 31.5662◦, 34.4421◦, 36.2844◦, 47.6271◦, 56.6759◦, 65.2949◦ and 72.1416◦ which were in good agreement with the standard JCPDS file No. 30-1451 for zinc oxide.

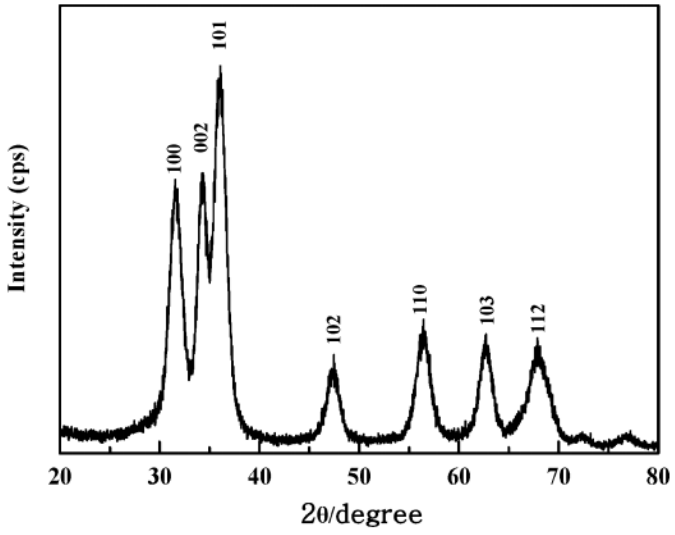

Fig. 2. XRD pattern of as-prepared sample

Effect of initial dye concentration on MO adsorption

The dye adsorption capacities onto adsorbent increased with the increase of the concentration of dye solutions (Fig. 3). The removal efficiencies for MO initially increased and then decreased which might be due to the fact that large numbers of vacant active sites were available for the adsorption at a lower initial concentration, and then saturated sites were difficult to capture the dye molecules [7].

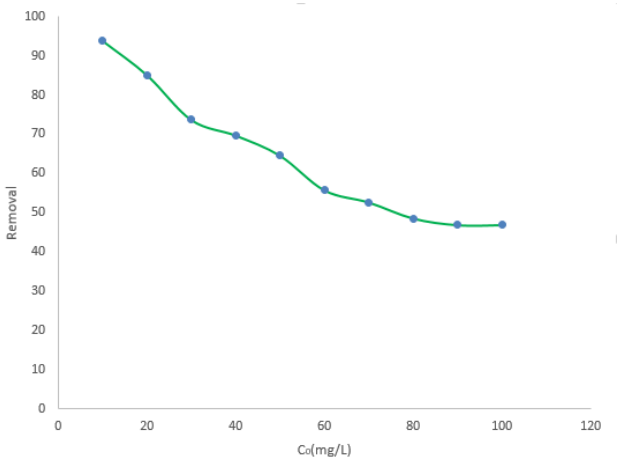

Fig. 3. Effect of initial dye concentration on MO adsorption

Effect of adsorbent Dosage

Fig. 4 show the effect of adsorbents on the percentage of removal and specific uptake of dye with respect to time. The dye removal efficiency increased dramatically with increasing the adsorbent dosage, which was due to the increase of available adsorption sites in adsorbent [8].

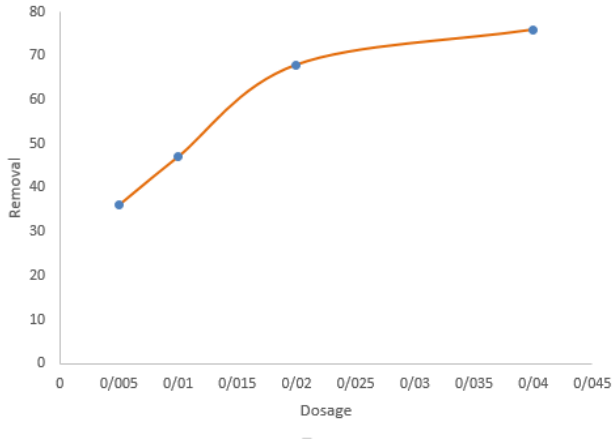

Fig. 4. Effect of adsorbent Dosage

Effect of Contact Time

The contact time between adsorbate and the adsorbent is of significant importance in the wastewater treatment by adsorption. The obtained results (Fig. 5) for as-prepared sample show that the dye could be removed rapidly in the first 40 min.

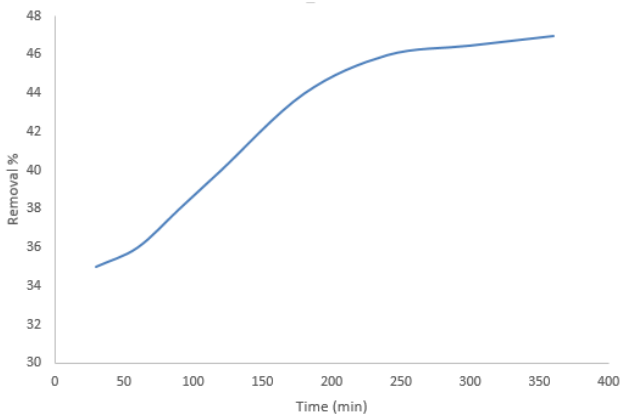

Fig. 5. Effect of Contact Time

Adsorption isotherms

Isotherm models are of high importance because they give a correlation between Pollutant concentration and adsorption value at equilibrium condition. In the present study, three different isotherm models including Langmuir and Freundlich models were used. The linear form of Langmuir isotherm is presented in following Eq:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_l q_m C_e}$$

Where qe (mg/g) is the adsorption value at equilibrium condition, and qm (mg/g) is the maximum adsorption capacity of the adsorbent. Ce (mg/ L) is the equilibrium dye concentration in solution, and KL, Langmuir constant (L/mg) is related to the affinity of binding sites and the free energy of sorption. Langmuir isotherm is useful to both chemical and physical adsorptions.

The linear form of Freundlich equation is presented in following Eq:

$$L_n(q_e) = L_n(K_f) + \frac{1}{n} L_n(C_e)$$

Where K_F is Freundlich constant ((mg/g) (L/mg)1/n) and 1/n is the heterogeneity factor. One can deduce the values of KF and n from the intercept and slope of the plot of ln (qe) versus ln (Ce).

Like Langmuir isotherm, Freundlich isotherm is applicable to both chemical and physical adsorptions.

Each of the tow above-mentioned isotherm models was fitted to the experimental data.According to the results, R square values of Langmuir and Freundlich isotherms are 0.993, 0.891, respectively. Therefore, Langmuir isotherm is the most suitable model which describes the adsorption process. Adsorption value of ZnO followed by its low cost can introduce this adsorbent as an industrial choice for MO removal from waste solutions.

Adsorption Kinetics

To further investigate the adsorption mechanism, pseudo-first-order kinetic model and pseudo-second-order kinetic model were employed. The constants of both kinetic models were calculated using following Eq respectively:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e}$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t, respectively. k1 (min-1) and k_2 (g /mg.min) are the rate constants of pseudo-first-order and pseudo-second-order, respectively. Results showed that the values of R^2 for MO obtained from the pseudo-second-order kinetic model were found to be over 0.994, making them higher than those of the pseudo-first-order kinetic model. The results indicated that the adsorption of MO onto the adsorbents was well described by the pseudo-second-order kinetic model.

The reusability of adsorbent

In order to evaluation of applicability of zinc oxide, the desorption-adsorption cycles were performed. Desorption studies were carried out using distilled water and ethanol solution. Results showed that ample still retained adsorption capacity for MO even after four cycles of reuse.

Conclusion

In summary, zinc oxide was successfully synthesized by a co-precipitation method. A little amount of prepared ZnO was employed for the elimination of MO dye from aqueous solutions in high concentrations. These results indicate that his type of adsorbent with nanosheet structure is reasonable and affordable in the wastewater treatment.

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