Methylene Orange dye removal in aqueous solution using synthesized $CdO-MnO_2$ nanocomposite: kinetic and thermodynamic studies

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Water pollution problems by dyes is one of the dangerous pests facing the environment, especially those dyes that cause health problems. In this study, $CdO-MnO_2$ Nanocomposite have been successfully synthesized by simple chemical method. The crystallite size and morphology of the Nano-synthesized powders were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). The SEM result revealed that, the average particle sizes was 31.56 nm with particles shape as a Zero dimension. The $CdO-MnO_2$ Nano-synthesized behave as an attractive adsorbent for Methylene orange (M.O) dye in aqueous solution by various temperature (25, 35, 45 and 55˚C). The thermodynamic parameters (ΔS, ΔH, ΔG) and Kinetic (order of the adsorption process) were calculated. The results show that the application of nanocomposite $CdO-MnO_2$ would be promoted by high adsorption capability and selectivity for dye solutions (M.O). $CdO-MnO_2$ can considered as a friend of the environment and Nano powder as advanced adsorbent materials.

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1. Introduction

During this era, nanoscience advancements, covering almost any research area as well as nanotechnology, make life even simpler [1-10]. Science and technology describe nanomaterials as important materials an increasing area of research because of the configuration of their atoms on the 1-100 nm scale, this includes structures, instruments and mechanisms with unique morphologies [11-18].

Synthetic dyes are nowadays widely used during many areas for example in the textile, paper, plastic, rubber, leather and printing industries, etc. [19], wastewater from the industries has increasingly become an important problem for the environment. Dyes are particularly toxic and dangerous to aquatic organisms in waste water [20]therefore, these organic dyes must be removed from the wastewater before they are released through the environment. Most organic dyes, unfortunately cannot be degraded in traditional wastewater treatment due to the aromatic structures. After that, the adsorption process became promising for efficient pigment removal, simple design, adaptability, and ease of use[21],various sorbents have been developed to remove pigments. Recently, nanomaterials made of metals or metal oxides have been extensively studied as highly developed adsorbent materials in environmental treatment [22].

Nanocomposites are type of nanomaterials with crystalline solids formed of many phases, with any of the phases that have nanoscal dimensions or structures having a nanoscale repeat distance used to removed dye in water treatments,binary metal oxides of Cdo and MnO prepared with different methods [23-25].

Here, one of the most economically appropriate and effective techniques is adsorption.The use of nanocomposites for dyes removal recently have attracted great researchers interest and has been increasingly utilized in recent years [26-28], due to the dispersion of adsorbent particles in the solution, adsorbents are essential in promoting their isolation from adsorption suspension as well as solutions containing the appropriate pollutant therefore nanocomposites have at present

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gained a lot of attention in removing dyes and heavy metals from aqueous solution [29-33]. In this study, Laboratory synthesized binary CdO-MnO_2 Nanocomposite with a high surface area were used and applied in removing the methylene orange dye from their aqueous solution.

2. Experimental

2.1. Materials

All chemicals were analytical grades of reagents and were used from Sigma-Aldrich, without further purification.

2.2. Synthesis of CdO-MnO_2 nanocomposite

In a simple chemical method, CdO-MnO_2 nanocomposite was synthesized with high purity. 25 ml, 0.03 mole of Manganese(II) Chloride Tetra hydrate was added to 25 ml, 0.03 mole Cadmium Chloride with magnetic stirring at 40 °C for 10 minutes. Then, (1% w/v) PVP was slowly added (drop by drop) to the mixture. the PH was adjusted to 9.5 by adding about 15 ml gradually of 0.06 M potassium hydroxide solution (KOH) with stirring at 100 °C for 2 hours. The solution product was separated and washed several times with deionized water, then dehydrated at 120 °C then calcinated for 3 hours at 450 °C. a black-brown precipitate of cadmium-manganese oxide nanocomposite was obtained.

2.3. Adsorption experiments

Batch adsorption experiments were accomplished using the dye solutions of 0.0159 g Methylene orange (M.O) $C_{16}H_{18}N_3SCl$ dye was purchased from Sigma-Aldrich were prepared with deionized water. Kinetic experiments were performed out by adding 0.01 g of nanocomposite together with 50 mL of (M.O) solution with various time intervals (0-300 min.) in each 30 min. At various temperatures (25, 35, 45, 55 °C), the glass tubes were placed on a shaker (HZQ-C) and shaker for (300 minutes). The absorbance values was examined by Uv-Visble spectroscopy at 665 nm wavelength before and after the adsorption experimental. The adsorbed-dye quantity in the solution was calculated using equation 1 [34].

$$Q_e = \frac{(C_O - C_e)V_{sol}}{M} \qquad (1)$$

where Q_e represents the equilibrium capacity of adsorption (mg / g), C_o is the initial methylene orange concentration (mg / L), Ce represent the equilibrium concentration of dye (mg / L), V is the volume of the solution (L) and M is the amount of the nanocomposite (g).

3. Results and discussion

3.1. X-ray diffraction of CdO-MnO_2 nanocomposite

The powder XRD pattern of binary metal oxides was illustrates in Figure (1), relative peak intensities and peaks position of CdO-MnO_2 are in a good agreement with JCPDS card No. [00-05-0640] and [00-24-0735] for Cadmium oxide and Manganese(IV) oxide respectively. CdO exhibits peaks at 28.90˚, 32.59˚ and 67.60˚ correspond to (111), (200) and (311) lattice reflection planes respectively, whereas peaks at 36.10˚, 44.46˚, 56.03˚, 60.16˚ and 64.78˚ correspond to (101), (111), (211), (220) and (310) lattice reflection planes respectively of MnO_2 phase.

In addition, average crystallite sizes (D) had been calculated using Debye-Scherer (equation 2) from main diffraction peaks where (λ) is the wavelength of Cu Kα radiation, (k) is a constant equal to 0.9, (FWHM) the full width at half maximum of the diffraction peak expressed in radians and θ is the Bragg angles of the main planes [35,36]. From Debye-Scherer equation (D) was (20.12) nm.

$$D = \frac{K\lambda}{B\ COS\theta} \qquad \text{Equation (2)}$$

Strong and wide diffraction peaks of the crystalline pattern and reduced crystal size revealed that nanostructure synthesis has a good product.

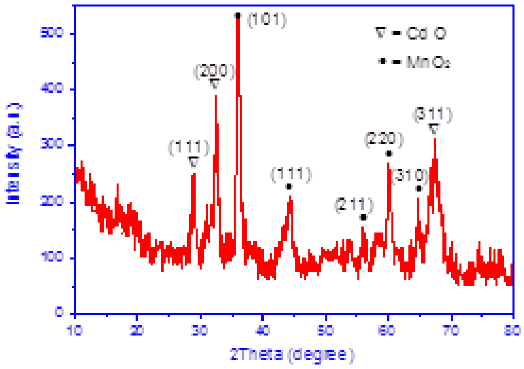

Fig. 1. XRD pattern of CdO-MnO_2 nanoparticles.

3.2. FE-SEM images of CdO-MnO_2

Fig. 2 FE-SEM composite images revealed spherical particles composed of a small (11-29) nm range of nanoparticles with aggregate formation as comparatively wide ~(42-69) nm spherical nanoparticles with an average grain size of (31.56) nm nanoparticles.

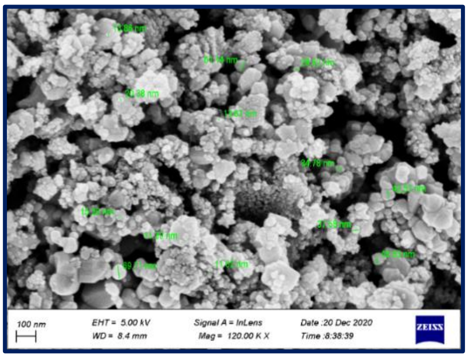

Fig. 2. FE-SEM image CdO-MnO_2 nanoparticles.

3.3. Adsorption of pollutants on CdO-MnO_2 nanoparticles

The experimental data for Methylene orange (M.O) dye adsorption from their solution can be modeled by the Langmuir and Freundlich isothermal[37].

The Langmuir isotherm is given by equation (3)

$$\frac{C_e}{Q_e} = \frac{1}{a} + \frac{b}{a} C_e \qquad (3)$$

where Qe represents the quantity of adsorption correlated to monolayer coverage, a and b are the Langmuir constants, and Ce is (M.O) concentration at equilibrium. The Langmuir equation was used to measure the adsorption curves of (M.O) dye in their solutions, as seen in the relationship between (Ce) versus (Ce/Qe) in Figure (3A), and the results show that they are susceptible to the Langmuir adsorption equation, which is ideal for surface monolayer sorption with a small number of corresponding sites and uniform adsorption energies.

The Freundlich equation [37], equation (4)

$$\log(Q_e) = \log(k_f) + \left(\frac{1}{n}\right) log\,(C_e) \quad (4)$$

The Freundlich constants, which are the capacity of adsorption and the intensity of adsorption, were indicated by K_F and *n*. The Freundlich equation was developed on heterogeneous surfaces for adsorption, the capability of the monolayer adsorption is not mentioned, however. In solutions, the adsorption curves of (M.O) dye (figure 3 B) were modified to the Freundlich equation as seen in the relation between (ln Q_e) versus (ln C_e) and the results show that they do not undergo adsorption on this equation(4).

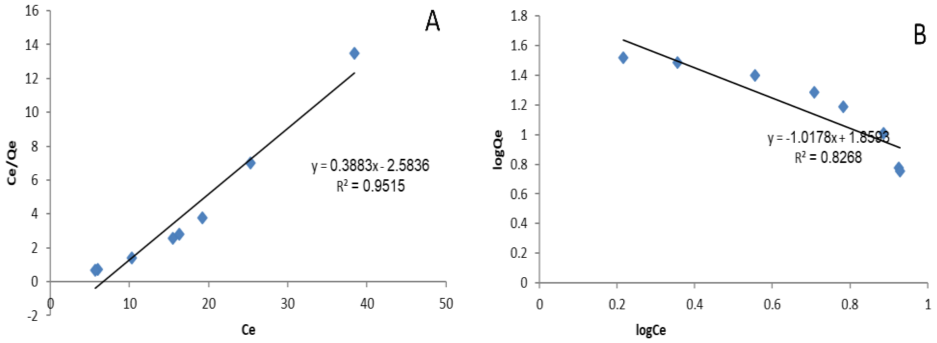

Fig. 3. Adsorption equation of (A) as Langmuir isotherm, (B) Freundlich isothermal, at 298 K.

3.4. Thermodynamic parameter

The effect of temperature on the (M.O) dye adsorption on the surface CdO-MnO_2 nanoparticles was studied at various temperatures (25, 35, 45, and 55 °C). The experimental results demonstrate that with the rise in temperature, the amount of adsorbed dye increases, which indicates that the adsorption process seems to be endothermic as well as the mean value of ΔH is positive. This is indicative of processes of absorption and adsorption, where temperature changes lead to increases in the speed of diffused surfactant adsorption within the pores on the surface and indicates a strong bond that binds between the adsorbate and the adsorbent, which would be consistent with several research[38][39]. The thermodynamic parameters supply inclusive information relating to the inherent energetic changes connected with adsorption, therefore, they must be assessed appropriately. The free energy changes (ΔG), enthalpy (ΔH), and entropy (ΔS) of adsorption were estimated in this study using equations (5 , 6) to anticipate the process of adsorption [40].

$$\log x_m = \frac{-\Delta H}{2.303R} + \frac{\Delta S}{R} \quad (5)$$

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

where X_m is the greatest amount of Adsorbate (mg/g), R is the gas constant (8.314 J/mol K), T is the temperature (K). ΔH was determined from the slope of the van't Hoff plots of log (Xm) versus 1/T, and (ΔS) was determined from the y intercept, as shown in Fig. 4.

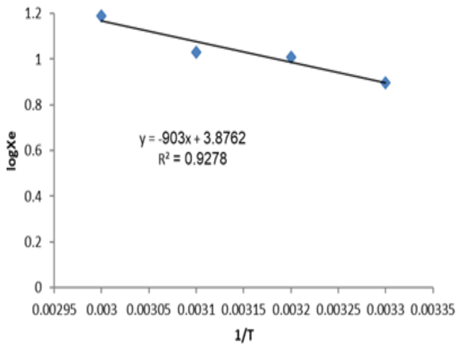

Fig. 4. The relation between log X_e and 1/T for the adsorption of MO.

The corresponding ΔH from the slope was 17.289 kJ/mol and ΔS from the y-intercept was 32.225 J/(mol·K) ΔH indicates that the adsorbed molecules are still in constant motion on the surface this is attributed both to absorption and adsorption [40]. It is stated that dye adsorption is accelerated by a temperature lower. The ΔG for the adsorption was determined as 7.689 kJ/mol at 298 K and this means that the adsorption was non spontaneous.

3.5. Dynamics parameter

The dynamics of dye adsorption on the CdO-MnO_2 adsorbents are decisive in the implementations of CdO-MnO_2 adsorbents. The dispersion state of nanocomposite has greatly affected the dynamics. The well-dispersed nanocomosite pollutants very quickly [41] Herein, this study found that the time of adsorption reaches equilibrium approximately (240 min) for 0.01 g of CdO-MnO_2 adsorbents. However, classical kinetic models have been used to describe the adsorption data above as follows [41]:

The pseudo-first-order model:

$$\ln(q_e - q_e) = \ln(q_e - K_1 \ t) \tag{7}$$

The pseudo-second-order model:

$$1/\mathrm{q_t} = 1/\mathrm{k_2}\, q_e + t/q_e \tag{8}$$

where qe and qt represent the (M.O) dye adsorbed amount (mg / g) at equilibrium time (min), respectively, and the k1 or k2 are the kinetic rate constants. The kinetic data could be explained accurately by the pseudo-second-order model Fig. 5 with a high correlation coefficient (R^2 = 0.9001).

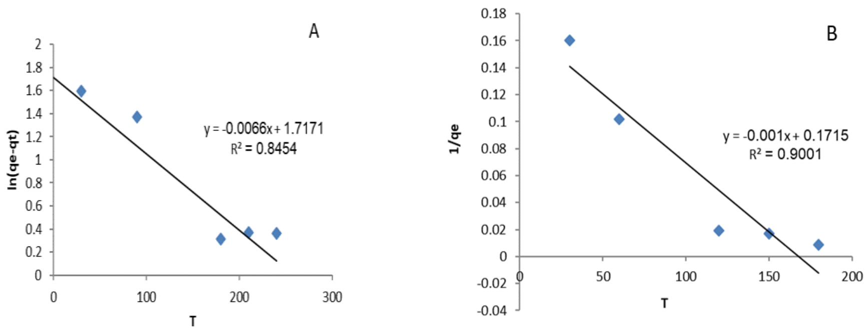

Fig. 5. Dynamic of dye adsorption (A) pseudo-first-order (B) pseudo-second-order.

4. Conclusions

The $CdO-MnO_2$ nanocomposite could be seen as an alternative adsorbent to remove MO or many other anionic dyes in aqueous solutions. The maximum adsorption capacity after (240 minutes) of contact time and temperature 25 ℃ was 7.363 mmol g1 of adsorbent. Experiments have shown that $CdO-MnO_2$ nanoparticles could be successfully used for the quantitative elimination of methylene orange in remediation processes. $CdO-MnO_2$ composite considered as a low-cost material, the adsorption method using nanomaterials tends to be economical process.

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