Removal of methylene blue dye from wastewater using ZnONPs in the dark and light

Elhossein A. Moawed, Talaat A. Hegajy, Tamer R. Kosbar and Mai S. Eissa

Abstract—. In this work, the efficiency of ZnO nanoparitcles for the removal of methylene blue dye from wastewater was studied through a sorption process. The effects of various parameters such as solution pH, initial dye concentration, contact time and temperature were examined. Sorption kinetics followed Pseudo second order and sorption isotherms followed Freundlich, assuming to chemisorption process. Thermodynamic parameters indicated spontaneous and exothermic sorption process.

Index Terms—ZnO, methylene blue, removal, wastewater, isotherm, kinetic, thermodynamics.

1 Introduction

Dyes are widely used in several industries such as textile, printing, paper, rubber, cosmetics, plastics and dying industries. Dyes become water pollutants due to their presence in the effluents of dye manufactures [1]. Approximately 15% of the Dyestuffs were estimated to be lost in industrial effluents during the manufacturing process [2]. Dyes and their breakdown products are toxic, carcinogenic and can cause several damages to the environment and human health. Therefore, there is a general need to remove dyes before it is released into the water streams [3].

Methylene Blue (MB) is a cationic dye widely used in dyeing cotton, wool, and silk. The dye structure makes it easily accumulate and highly soluble in water even when low concentrations cause harmful effects [4]. In addition, MB can cause eye burns, breathing difficulties, convulsions, tachycardia, irritation to the skin and its long exposure can cause vomiting, nausea, anemia and hypertension, diarrhea and mental confusion [5].

Due to the environmental concerns related to wastewater effluents, different separation techniques have been investigated in the removal of dyes [6]. Various physico-chemical methods, including adsorption, oxidation, filtration and photo-degradation have been used for the treatment of dye wastewater. Adsorption is the top effective separation technique due to its ease of operation, availability over a wide range of sorbents [5].

Application of nanomaterials for water treatment has attracted intense attention in recent years. Nano-sorbents offer significant performances that may be due to their unique characteristics such as high surface area, small size and availability [7]. ZnO is an effective sorbent due to its low cost, high chemical stability, eco-friendly nature, and non-toxic synthesis route, promoted it to be suitable for the sorption of organic and inorganic compounds [8].

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The ability of ZnONPs to remove Methylene blue (MB) dye was investigated using batch sorption procedures. The ZnONPs were prepared using a direct precipitation method. The physico-chemical conditions for the removal of MB were investigated in the dark and light. Kinetics, isotherm models and thermodynamic studies were tested to evaluate the experimental data. ZnONPs were applied under the optimum conditions to remove MB dye from wastewater samples

2 Experimental

2.1 Preparation of ZnONPs

Zinc oxide nanoparticles were obtained by direct controlled precipitation method as shown [9]. Aqueous solution of NH_4OH (7 mol/L) was added to a solution of $ZnSO_4.7H_2O$ (0.5 mol/L) drop wise with continuous stirring at room temperature. Then, a solution of $NaHCO_3$ (3 mol/L) was added under stirring to form a colloid of zinc hydroxy carbonate (ZCH). Then the reaction mixture was heated up to 60 ^oC and stirred for 30 min. The precipitate was then filtered and washed with distilled water and ethanol. Finally, the powders were dried at 100 °C overnight, calcined at 400 ^oC for 2 h and grounded into fine particles.

2.2 Characterization

Morphology of ZnONPs was investigated using a JEOL (JSM-6510LV, USA) scanning electron microscope. The SEM image of ZnONPs at magnifications of 1000 X reveals that the particles are spherical (fig. 1). In the higher resolution SEM image the agglomeration of particles is observed.

FT-IR spectra were performed by a JASCO (FTIR-410 spectrometer) in the 4000-400 cm-1 spectral range (fig. 2). A broad-band from 3730 to 2660 cm^{-1} and peaks at 1639 and 1393 cm^{-1} are characteristic of the hydroxyl group resulting from the hygroscopic nature of ZnO [10]. The characteristic peaks of ZnO were observed at 829, 604 and 446 cm^{-1}.

The absorbance measurements were performed using a JASCO (V-630 UV-VIS Spectrophotometer, Japan). UV-Vis absorption spectrum of ZnONPs was recorded in the solid state (Fig. 3). An absorption band at 350-370 nm due to surface plasmon resonance confirmed the formation of ZnO nanoparticles [11] and it also attributed to the band gap of semiconductor ZnO nanoparticles [12].

The crystallinity was determined using an XRD Brucker D8 diffractometer equipped with a Cu Kα radiation (λ=1.5418 Å) with 40 kV voltage and 40 mA current. The XRD patterns of ZnONPs showed strong and narrow diffraction peaks (Fig. 4), referring to a good crystallinity of the nanoparticles [13]. The particle size (D) was calculated using the Debye-Scherrer equation, $D = K\lambda/\beta \cos\theta$, where θ is the Bragg diffraction angle, K is equal to 0.97, λ is the X-ray wavelength (0.15418 nm) and β is the width of the half peak height in radian. The average particle size of ZnONPs is found 17.24 nm.

Surface area and Pore size were determined by BET and BJH techniques using a NOVA 3200 (USA). The N_2 adsorption-desorption isotherms of ZnONPs was matched a type-IV curve which related to porous sorbents. ZnONPs showed a BET surface area 31.5 m^2/g, BJH pore diameter 18.6 nm and mesoporous volume 0.13 cm^3/g.

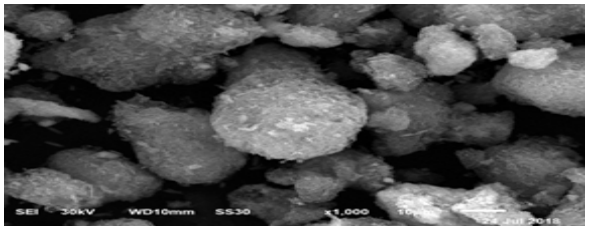
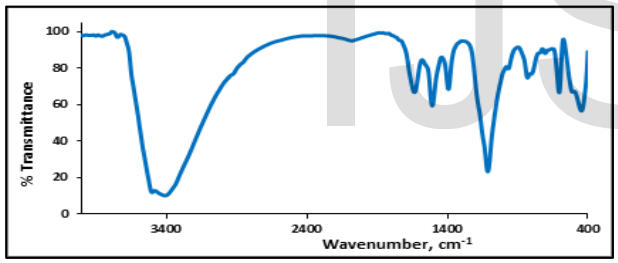


Fig.1 SEM of ZnONPs



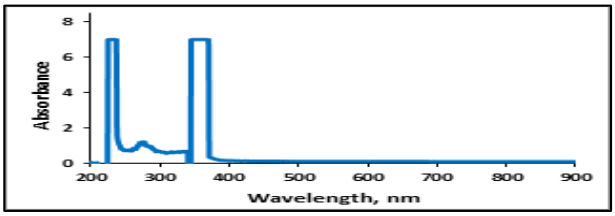


Fig.3 UV-Vis spectra of ZnONPs

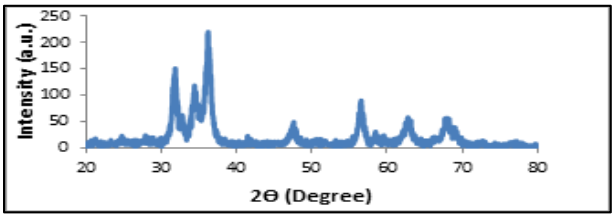


Fig.4 XRD of ZnONPs

2.3 Recommended procedures

The sorption of MB ($C_{16}H_{18}ClN_3S$, 319.85 g/mol) onto ZnONPs was investigated using a batch experiments. 0.1 g of ZnONPs, was added to 25 mL of the MB dye solution, then the solution was shaken, filtered and the remaining dye concentration in solution was analyzed at λ_{max}= 670 nm. The effects of pH, contact time, initial dye concentration and temperature were further investigated in the dark and light.

The percentage of dye removal (%E) and sorption capacity (Q) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$Q = C_o\, E\, V/m \quad (2)$$

Where, C_o is the initial dye concentration, C_e is the concentration of dye in solution at equilibrium, V is the volume of dye solutions and m is the mass of sorbent.

3 Results and Discussion

3.1 Optimum conditions for MB removal using ZnONPs

3.1.1 pH

The effect of the pH on the removal of MB (8 mg/L) using ZnONPs was studied in the dark and light (fig. 5). The removal rates of MB onto ZnONPs increases from 62% to 90% in the dark and from 71% to 93% in light by increasing the pH values from 3 to 11. While ZnO can easily dissolve at pH 1 and 13 due to it is amphoteric nature [14].

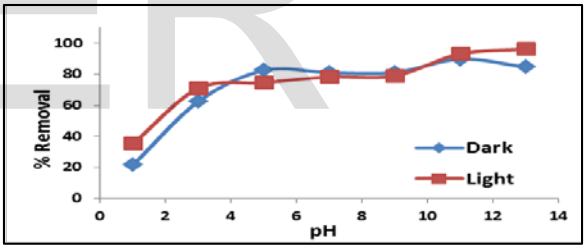


Fig.5 Effect of pH on MB removal using ZnONPs in dark and light

3.1.2 Contact time

The effect of contact time on MB (8 mg/L) removal using ZnONPs was investigated in the dark and light (fig. 6). The removal rates of MB were initially rapid, where 83%-79% of the total amount MB was removed within 1 min. Then the rates become slower with increase in time until reaching 98%-81% of the dark and light at 25 min.

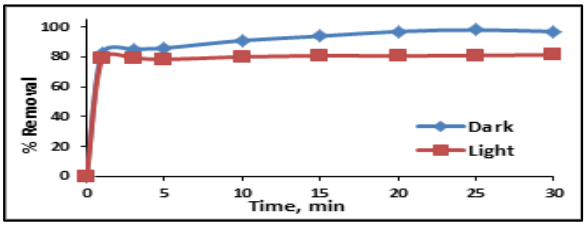


Fig.6 Effect of time on MB removal using ZnONPs in dark and light

3.1.3 Initial dye concentration

The effect of initial dye concentration was studied for different MB concentrations in the dark and light (fig. 7). The removal rates of MB using ZnONPs increased with increase in MB concentration within a range from 2 to 12 mg/L. The maximum sorption capacities of ZnONPs are found 2.14 and 2.24 mg/g in the dark and light.

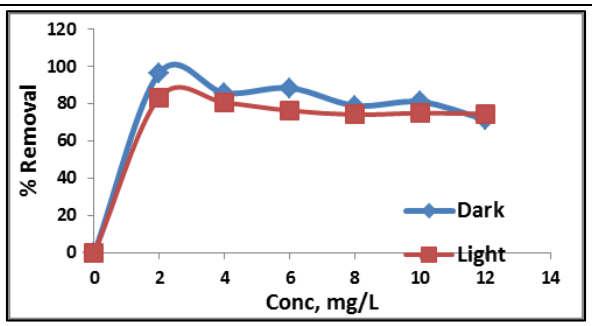


Fig.7 Effect of initial dye concentration on MB removal using ZnONPs in dark and light

3.1.4 Temperature

The effect of temperature on the sorption of MB onto ZnONPs was investigated in the dark and light (fig. 8). The removal rates of MB were decreased gradually with increasing temperature from 25°C to 62°C in the dark and light. The removal rates of MB using ZnONPs were decreased from 86% to 49% in the dark and from 75% to 61% in the light with increasing temperature.

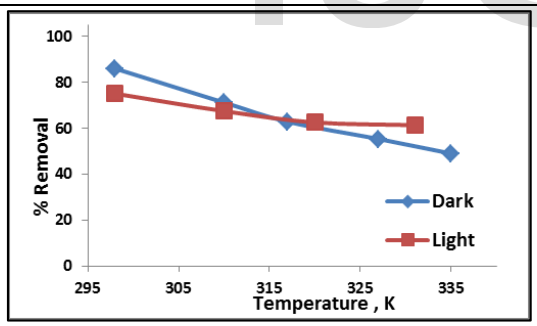


Fig.8 Effect of temperature on MB removal using ZnONPs in dark and light

3.2 Kinetic studies

. The pseudo first-order (3)and pseudo second-order (4) were used to investigate the mechanism of sorption and the rate controlling steps involved in the sorption.

$$\log(Q_e - Q_t) = \log Q_e - (K_1 t/2.303) \quad (3)$$

$$t/Q_t = \left(1/K_2 {Q_e}^2\right) + t/Q_e \quad (4)$$

Where Q_e and Q_t is the sorption capacity at equilibrium and at time t. K_1 and K_2 are the pseudo first rate constant and the pseudo second order rate constant. The half-life time ($t^{1/2}$) of Pseudo first order was calculated from $t_{1/2} = 0.693/K_1$, while that of second order was calculated from $t_{1/2} = 1/Q_e K_2$.

The data showed that the R^2 of the Pseudo second order is higher than that of the first order, whether in the dark or light (Table 1). Also, higher rate constant and faster half-life time suggests that the sorption is followed Pseudo second order which controlled by chemisorption mechanism and depended on both MB and ZnONPs [15].

Table 1
The Kinetic parameters for removing of MB using ZnONPs in the dark and light

Method	Pseudo first order			Pseudo second order		
	R^2	k_1 (min^{-1})	$t^{1/2}$ (min)	R^2	k_2 (g/mg min)	$t^{1/2}$ (min)
Dark	0.935	0.13	5.22	0.9996	0.89	0.56
Light	0.879	0.09	7.65	1.0000	4.98	0.12

3.3 Equilibrium studies

Langmuir (5) and Freundlich (6) isotherms were applied to study the removal behavior MB dye using ZnONPs.

$$C_e/Q_c = (1/K_L b) + (C_e/K_L) \quad (5)$$

$$Log\ Q_c = Log\ K_F + 1/n\ Log\ C_e \quad (6)$$

Where Q_c is the amount of dyes adsorbed at equilibrium and C_e is the dye concentration at equilibrium. K_L and b are Langmuir constants, while K_F and n are Freundlich constants.

The results showed that the R^2 of Freundlich is higher than that of Langmuir, whether in the dark or light (Table 2), suggesting for multilayer sorption over heterogeneous surfaces. Also, the values of 1/n are less than 1, referring to a favorable chemisorption process [16].

Table 2
The equilibrium parameters for removing of MB using ZnONPs in the dark and light

Method	Langmuir		Freundlich	
	R^2	R_L	R^2	1/n
Dark	0.938	0.05	0.941	0.40
Light	0.825	0.24	0.993	0.73

3.4 Thermodynamic studies

The thermodynamic parameters such as Gibbs free energy change (ΔG), enthalpy (ΔH), and entropy (ΔS) were evaluated using the following equations.

$$Ln\ K = -\Delta H/RT + \Delta S/R \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

Where K is the equilibrium constant for sorption, R is the gas constant (8.314 J/mol K) and T is the temperature (K). The equilibrium constant was calculated from $K = C_a/C_e$ where C_a and C_e is the equilibrium dye concentration on the sorbent and in the solution.

The values of ΔH and ΔS were determined from the slope and intercept of Ln (K) plots versus 1/T and (ΔG) was calculated (Table 3). The negative value of ΔG indicates that spontaneous

nature of the removal process. The negative value of ΔH reveals the exothermic nature of the removal process. The negative ΔS value suggests a decrease in randomness during the removal process [17].

Table 3
Thermodynamic parameters for removing of MB using ZnONPs in dark and light conditions

Methods	ΔH (kJ/mol)	ΔS (kJ/mol)	ΔG (kJ/mol)	R^2
Dark	-41.07	-0.12	-4.14	0.965
Light	-16.38	-0.05	-2.59	0.926

4 Application

ZnONPs was applied for the removal of MB dye from real wastewater samples. The samples were collected from Damietta (Egypt), including Nile wastewater, industrial wastewater and washing wastewater. The samples were spiked with MB (8 mg/L), and then 25 ml of samples was shaken with 0.1 g of ZnONPs for 25 min at room temperature in the dark. The final MB dye concentrations in the solution were determined. The average removal rates of MB dye using ZnONPs are 73% with average RSD% values of 2 % (and n= 5), which is acceptable for real samples (<10%). The result promotes ZnONPs as an efficient sorbent for MB dye removals.

5 Conclusion

ZnONPs were successfully prepared as identified by SEM, XRD, BET, FTIR and UV-Vis spectroscopy. ZnONPs were tested for the removal of methylene blue (MB) dye in the dark and light. The maximum sorption capacities of ZnONPs are found 2.14 and 2.24 mg/g in the dark and light within 25 min over a wide pH range (3-11). The kinetic studies were followed by pseudo-second-order model. The equilibrium isotherms showed that Freundlich model was having a good fit to the experimental data. Thermodynamic parameters demonstrate the spontaneous and the exothermic nature of sorption process. ZnONPs proved its efficiency in the removal of methylene blue from wastewater under optimum conditions.

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