Removal of Azo Benzidine Reactive Dye From Aqueous Solution By Adsorption onto ZnO Surface

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Abstract

In this study, the adsorption of azo benzidine reactive dye was carried out by using ZnO surface. Various parameters such as pH, adsorbent weight, initial dye concentration and contact time were studied in terms of their effect on the adsorption process. Furthermore, Lagergren's equation was used to determine adsorption kinetics. It is observed that high removal of dye was obtained at pH=5. Removal of dye was increased by increasing initial dye concentration and contact time. High removal of dye was at the time equivalent of 90 min and reached equilibrium. Increasing of adsorbent weight leads to decrease dye adsorption where 0.1gm was the best weight. For kinetics the reaction onto ZnO followed pseudo-second order Lagergren's equation.

Keywords: Azo benzidine; Adsorption; Dye; Removal.

الخلاصة:

تم في هذا البحث دراسة امتزاز صبغة الآزو بنزدين على سطح اوكسيد الخارصين. وقد درست العديد من العوامل المؤثرة في سرعة التفاعل منها: الدالة الحامضية، وزن السطح الماز، التركيز الابتدائي للصبغة وزمن التماس. بالإضافة الى ذلك تم استخدام معادلة Lagergren لتحديد حركيات الامتزاز. لقد لوحظ ان اعلى ازالة للصبغة كانت عند الدالة الحامضية pH=5 حيث ان ازالة الصبغة كانت تزداد مع زيادة التركيز الابتدائي للصبغة وزمن التماس والذي وصل الى الاتزان عند (90 دقيقة). كما أدت زيادة وزن السطح الماز الى تقليل الامتزاز حيث ان أفضل وزن كان (0.1 gm). أما بالنسبة الى حركيات الامتزاز فان التفاعل كان من الدرجة الثانية الكاذبة على سطح اوكسيد الخارصين.

1. Introduction

Many industries often use dyes and pigments to color their products. Most dyes are inert and non-toxic at the concentration discharged into the receiving water, however, they impart color undesirable to the water user. Color removal from textile effluents is a major environmental problem because of the difficulty to treating such streams by conventional physicochemical and biological treatment methods(1). Liquid-phase adsorption has been shown to be an effective way for removing suspended solids, odors, organic matter, and oil from aqueous solutions. Nassar and El-Geundi(2) evaluated the cost of dye removal using natural clay, bagasse pith, and maize cob. While many physical and chemical methods including adsorption, coagulation, precipitation, filtration and oxidation have been used for the treatment of dye-containing effluent, adsorption appears to offer the best prospects over all the other treatments(3).

Wastewater from textile industries creates a great problem of pollution due to the dyes contained therein. The disposal of coloured wastes such as dyes into receiving waters causes damage to the environment as they are toxic to aquatic life(4).

Benzidine (BZ)-based azo dyes are widely used in the dye manufacturing, textile dyeing, color paper printing, and leather industries(5,6). In 1980, the National Institute for Occupational Safety and Health published a survey of the data on the carcinogenicity of BZ-based dyes from tests with experimental animals and epidemiological studies of workers exposed to the dyes(5). Whereas BZ itself has long been recognized as a human urinary bladder carcinogen(7) and tumorigenic in a variety of laboratory animals(8), the National Institute for Occupational Safety and Health review declared BZ-based dyes to be carcinogenic as well, due to their biotransformation to BZ. Since BZ is used as a reactant in dye synthesis, workers could be directly exposed to the carcinogen.

Benzidine derivatives, as a kind of non-natural organic pollutant, could be generated from tannery wastewaters containing large amounts of dyes and pigments after illumination, heating or biological treatment. The compounds are highly toxic, carcinogenic, mutagenic, teratogenic, stable in water, almost non-biodegradable and irremovable with conventional water treatment technology, thus internationally recognized as priority pollutants[9,10].

The purpose of this work was to investigate the ability of ZnO for adsorption of azo benzidine reactive dye (ABZ), a toxic dye. Adsorption characteristics of ABZ were investigated by pH, adsorbent weight, dye concentration, contact time and kinetic study.

2. Materials and methods

2.1. Material

The molecular structure of ABZ in non-hydrolyzed form is illustrated in Fig.1. Initial maximum absorbance of ABZ solution was measured at 600 nm wavelength.

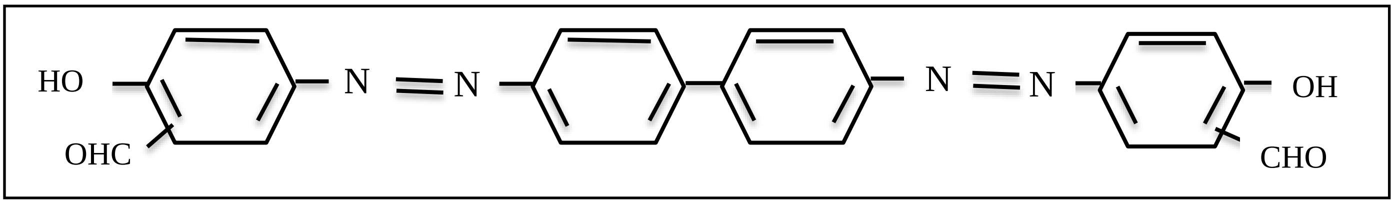

Fig.1 Chemical structure of ABZ in non-hydrolyzed form

Methods

2.1.1. Experimental Procedure

Azo benzidine reactive dye was dissolved in dioxane solvent to prepare a stoke solution (1000 ppm), and then a practical solutions were prepared from a stock solution in an appropriate concentration (100, 200, 300, 400, 500) ppm. For the experiments, 50 ml of dye solution was added to a given amount of ZnO, with a magnetic stirrer. At a predetermined time interval, the sample was taken and after filtration (Wathman), the final concentration of dye was determined by using UV/VIS spectrophotometer (model 1700, Shimadzu Japan) at a maximum absorbance wavelength (λ_{max}) of 600 nm for ABZ and calibration curve as in Fig.2.

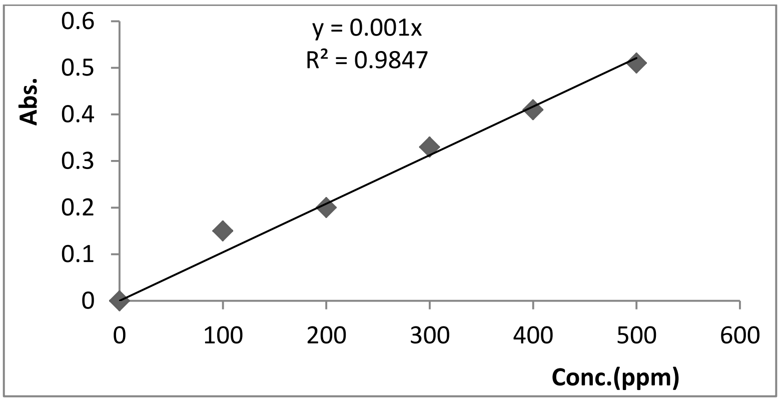

Fig.2 Calibration curve for aqueous solution of ABZ

2.1.2. Kinetics and Equilibrium Study

To investigate adsorption kinetics, (50 mg/L) of ABZ solution was added to (0.1 g) of ZnO surface, then the mixture was agitated at room temperature for (90 min) with a magnetic stirrer.

Amount of dye adsorbed on ZnO surface was calculated as following equation:[11]

$Q_e = (C_o – C_e) V/ m$ (1)

Where Q_e : the amount of dyes adsorbed (mg/g).

C_o and C_e : the initial and equilibrium concentrations (mg/L) of the adsorbate dye in solution , respectively.

V : the volume of solution (L) and (m) the mass of adsorbent(g).

3. Results and Discussion

3.1. Effect of Contact Time

The removal of dye was investigated at time intervals of 15, 30, 45, 60, 75 and 90 min from initial time. Results showed that by lapse of time, dye removal was increased and reached equilibrium point at (90 min). Fig.3 shows the effect of contact time on dye removal.

Table 1 Effect of contact time on adsorption ABZ dye by ZnO surface

Time (min)		15	30	45	60	75	90
C_o =100 ppm	C_e (mg/l)	42.000	36.000	26.000	20.000	16.000	16.000
	Q_e (mg/g)	14.500	16.000	18.500	20.000	21.000	21.000

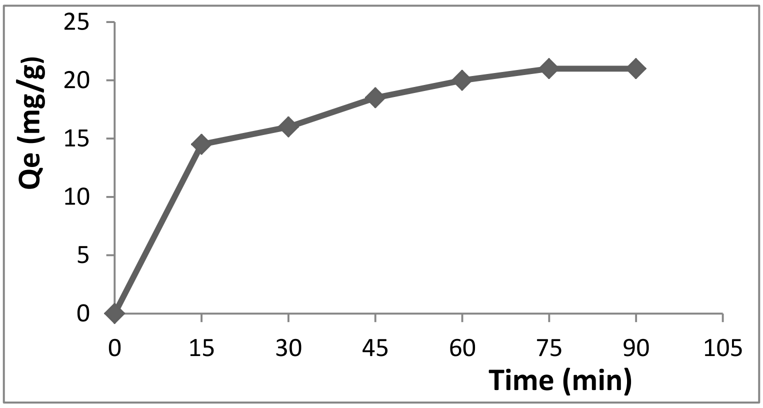

Fig.3 Effect of contact time on adsorption ABZ dye by ZnO surface

3.2. Effect of Initial ABZ Dye Concentration

ABZ solution of (100, 200, 300, 400 and 500) mg/L was used for the study of initial dye concentration on removal efficiency. It is observed that initial dye concentration has a significant effect on dye removal (Fig.4). The results showed that by increases in the initial dye concentration, the removal efficiency was increased. The reason for the effect of the initial dye concentration can be explained by the chemical structure of dye where active sites were increased with ABZ concentration increasing.

Table 2 Effect of initial ABZ dye concentration by ZnO surface

C_o (mg/l)	C_e (mg/l)	Q_e (mg/g)
100	16.000	21.000
200	103.000	24.25
300	177.000	30.75
400	185.000	53.75
500	245.000	63.75

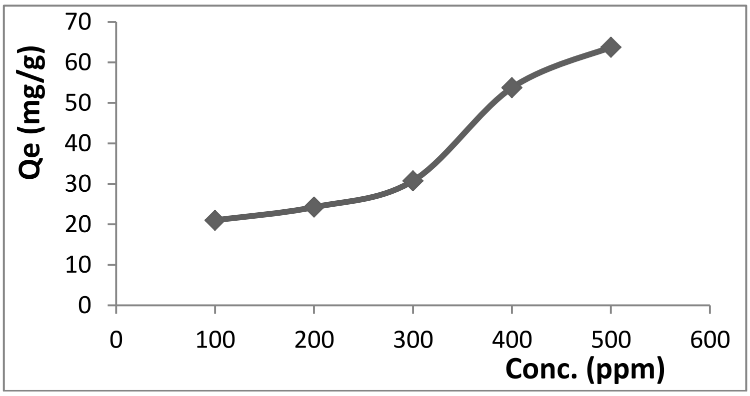

Fig.4 Effect of initial ABZ dye concentration by ZnO surface

3.3. Effect of Adsorbent Weight

The effect of adsorbent weight was investigated by adding different weights of ZnO surface (0.1, 0.3, 0.5, 0.7 and 0.9)gm. into (50 ml) of dye solution; respectively. The results showed that by increasing the adsorbent weight, dye removal was decreased (Fig.5). So removal efficiency can be decreased. The reason for this case was that accumulated some particles of the surface above others so the pores and active sites of surface can be closed and leads to decrease dye adsorption(12).

Table 3 Effect of adsorbent weight for adsorption ABZ by ZnO surface

Wt. (gm)	C_e (mg/l)	Q_e (mg/g)
0.1	245.000	63.75
0.3	86.000	20.70
0.5	70.000	12.90
0.7	68.000	9.257
0.9	57.000	7.383

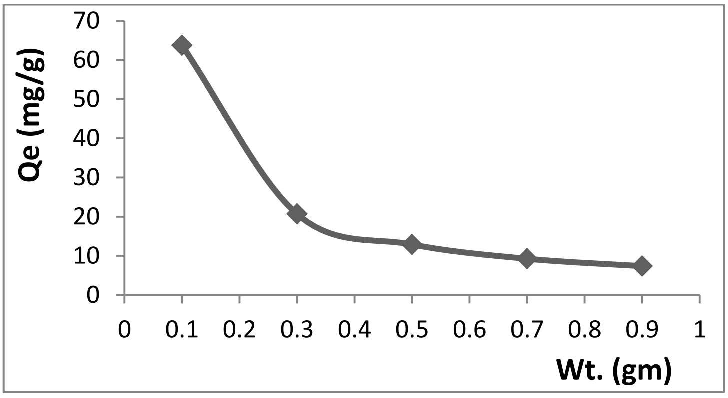

Fig.5 Effect of adsorbent weight for adsorption ABZ by ZnO surface

3.4. Effect of pH

To determine the optimum pH, pH was changed in the range of (5, 7 and 9). Fig.6 shows the effect of pH solution on dye removal. In view of this figure, it is clear that the pH of the solution has a significant effect on dye removal. In ZnO surface, high removal occurred at pH= 5, while low removal occurred at pH= 9. The reason was that in acidic pH the surface was fraught with a positive charge while in basic pH the surface was fraught with a negative charge.

Table 4 Effect of pH for adsorption ABZ by ZnO surface

pH	C_e (mg/l)	Q_e (mg/g)
5	48.000	22.80
7	65.000	20.25
9	111.000	13.35

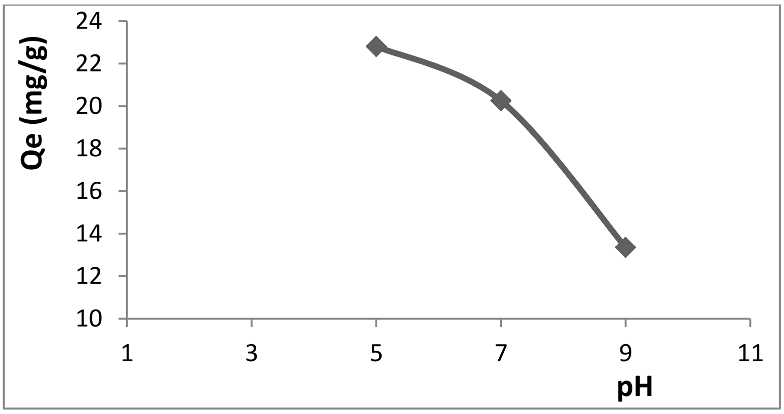

Fig.6 Effect of pH for adsorption ABZ by ZnO surface

3.5. Adsorption Kinetics

The adsorption kinetics of ABZ onto ZnO surface was investigated to determine the order of reaction. To investigate sorption characteristics of ABZ, two kinetic equations were applied: pseudo- first order and pseudo-second order. Two kinetic equations can be expressed as follows:[13]

Pseudo-first order Lagergren's equation:

$$\log (q_e - q_t) = \log q_e - \frac{K_1}{2.303}\, t \qquad (2)$$

Pseudo- second order Lagergren's equation:

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

where q_e and q_t (mg/g) are the amount of adsorbed ABZ at equilibrium and time t, respectively. K_1 and K_2 are the first order rate constant (min^{-1}) and the second order rate constant (g/mg. min), respectively.

To determine the order of reaction the pseudo-first order Lagergren's equation and the pseudo- second order Lagergren's equation were applied then the theoretical q_e was found and compared with the experimental q_e whichever was fitted or approximated that's mean the reaction had that order.

The results showed that the theoretical q_e obtained from pseudo-first order Lagergren's equation was (14.487) and its far on the experimental q_e onto ZnO surface was that (21.000). While When applying pseudo-second order Lagergren's equation the results showed that the theoretical q_e was that (23.980) and its nearby the experimental q_e onto ZnO surface was that (21.000). as illustrated in Fig.7& 8. That's mean the reaction had pseudo- second order for ZnO surface.

. **Table 5** Experimental data of pseudo-first order Lagergren's equation of adsorption ABZ onto ZnO surface

C_o = 100 ppm	Time (min)	15	30	45	60
K_1=0.041 min^{-1}	Log ($q_e - q_t$)	0.812	0.698	0.397	0.000

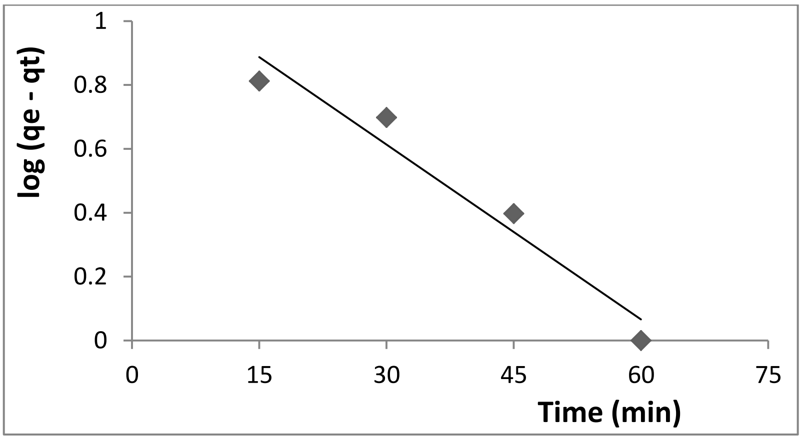

Fig.7 pseudo-first order Lagergren's equation of adsorption ABZ onto ZnO surface

Table 6 Experimental data of pseudo-second order Lagergren's equation of adsorption ABZ onto ZnO surface

C_o = 100 ppm	Time (min)	15	30	45	60	75	90
K_2= 0.003 g/mg. min	t/q_t (min.g/mg)	1.034	1.875	2.432	3.000	3.571	4.285

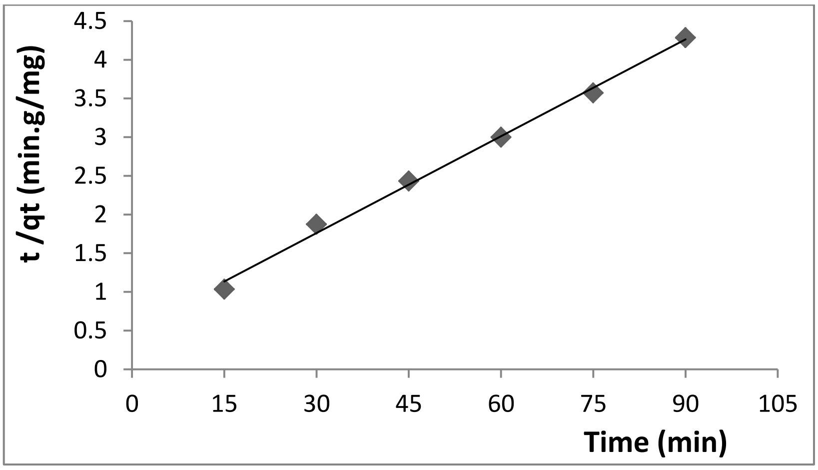

Fig.8 pseudo-second order Lagergren's equation of adsorption ABZ onto ZnO surface

4.

5. Conclusions

This work was one of the applications of adsorption for the effective removal of ABZ dye from aqueous solution. The following are the main results:

1. In this study dye adsorption reached to equilibrium point at (90 min) for ZnO surface.
2. Increasing the initial dye concentration leads to increase adsorbed amount so increasing removal efficiency, where the best dye concentration was (500 mg/L).
3. Adsorbent weight has significant effect in adsorption process, its observed that by increasing the adsorbent weight;adsorption was decreased, where the best adsorbent weight was(0.1gm).
4. High removal for ABZ dye from aqueous solution was obtained at pH=5.
5. The order of reaction for ZnO surface was that pseudo- second order.

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