Isotherm and Kinetic Study of Disulfin Blue and Methyl Orange dyes by adsorption onto by Titanium dioxide- NPs loaded onto Activated Carbon : Experimental Design

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ABSTRACT

The applicability of TiO_2 nanoparticles (TiO_2-NPs-AC) for removing Disulfine Blue (DSB) and Methyl Orange (MO) from aqueous solutions has been reported.The influence of nanoparticle loaded on activated carbon (TiO_2-NPs-AC) dosage, pH of the sample solution, individual dye concentration, contact time between the sample and the adsorbent were studied by central composite design(CCD) under response surface methodology(RSM). The kinetic results revealed that the pseudo-second-order equation is the best model to analyze the adsorption mechanism. The isotherm analysis indicated that the equilibrium data are well fitted to the Langmuir isotherm model with maximum adsorption capacities of 100 and 50 mg/g-1 of the adsorbent for removal Disulfine Blue and Methyl Orange respectively.

Keywords: adsorption, methyl orange, Disulfine Blue, Langmuir and Temkin isotherms, response surface methodology.

INTRODUCTION

Hues are widely used in the fabric, paper, plastic, leather, guest-host liquid crystal displays, solar cells, food and mineral processing industries.The effluents containing hues andpigments have been paid great attention in recent years since they can cause environmental problems. The removal methods of hues include physical adsorption, chemical degradation, biological degradation, photodegradation or the synergic therapy of different methods[1–5]. Many methods are accessible for the removal of pollutant scontaminants from water, the most important of which are reverse osmosis, ion exchange, precipitation, and adsorption. Among these methods, adsorption is by far the most versatile and widely used method for the removal of toxic contaminants[6-8] because of its inexpensive nature and ease of operation. Methyl Orange (MO, Fig.1(a),

4-[[(4-Dimethyl amino) phenyl]azo]benzene sulfonic acid sodium salt, C.I. 13025 , chemical formula, MW=327.34 g/mol, λ max= 500 nm. It shows several side effects such as eye and skin sensitivity. Also, inhalation of its dust may cause digestion and respiratory tract burning. Disulfine blue (DSB, Fig. 1(b) is a hazardous dye that is widely used for dyeing of wool and silk, carbon paper, cosmetics, and leather [9,10].
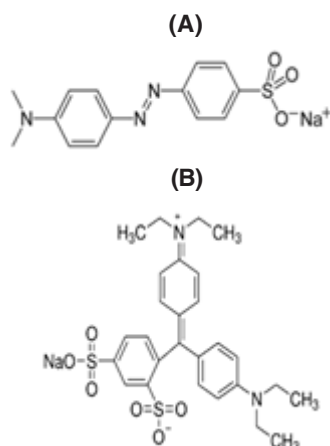
(A)

(B)

Fig. 1. (A) Chemical structure of Methyl Orange (B).Disulfine Blue

EXPERIMENTAL

Apparatus and materials

Hues concentrations were determined using Jasco UV–Vis spectrophotometer model V-530 (Jasco Company, Japan). Disulfine blue, Methyl orange activated carbon, sodium hydroxide, hydrochloric acid, activated carbon, sodium hydroxide, hydrochloric acid, ethanol and titanium tetra chloride were also from Merck & Co. (Germany).

Preparation of TiO$_2$ -NPs-AC

Titanium dioxide nanoparticles was synthesized by the sol–gel process at room temperature directly from titanium tetra chloride and ethanol. 2 ml of titanium tetra chloride was added in 20 ml of dry ethanol drop wise under stirring. Obtain solution was maintained at room temperature for 36 h. to obtain a homogeneous gel which was then was dried in 80ºC and calcined at 500ºC for 2 hours. The titanium dioxide (TiO$_2$) loaded onto AC with a weight ratio 1: 10 in the following manner: AC was thoroughly dispersed in 250 mL of ethanol under sonication for 1h,. Then 0.2 g the titanium TiO$_2$-NPS was added to ethanolic mixture. The suspension

was sonicated for 1 h. and stirred for 20 h at 400 rpm. TiO$_2$ –NP-AC was filtrated by centrifugation and dried for 18 h, at 80ºC.

Measurements of dye uptake

In accordance with the experiments layouted method, in their binary solution Hues onto TiO2-NPs-AC was carried out in a batch system as follows: 50 ml of binary hues solution with certain hues concentrations was prepared. After the adjustment of test solution pH 6.5.0 added into 50 ml Erlenmeyer flask containing 0.03 g of TiO$_2$-NPs-AC. The experiments were performed at room temperature and predetermined sonication time (3 min.) in ultrasonic bath. Finally, the sample solution was immediately centrifuged. The final concentration of hues by using a UV–Vis spectrophotometer set at a wave-length of 500 and 639 nm for MO and DSB, respectively. The removal percentage of each dye (R% MO and DSB) and the capacity for the adsorption of each dye (qi, mg g^{-1}) was determined as:[11,12]

$$\% \text{ dye removal} = \frac{(C_o\text{-}C_t)}{C_o} \times 100 \qquad (1)$$

Where $C.$(mg^{L-1}) and C_t(mg^{L-1}) is the concentration of target at initial and after time t respectively.

$$q_e = \frac{(C_o\text{-}C_e)V}{W} \qquad (2)$$

RESULTS AND DISCUSSIONS

Textural and chemical characterization *of TiO$_2$-NPs-AC*

The FT-IR spectra of TiO$_2$-NPs-AC were shown in Fig. 2. The absorption band at 533 cm^{-1} may be attributed to angular deformation and Ti–O stretching modes of TiO$_2$-NPs. In the range of 1500–3500 cm^{-1}, water has three dominant peaks. Absorption band at 1733 cm^{-1} corresponding to the stretching vibration of carbonyl groups. The broad peaks at 1029 cm^{-1} could be assigned to C–O stretching from phenolic, alcoholic, etheric groups and to C–C bonds. The morphological features of the samples studied by SEM are shown in Fig. (3).

Central composite Design (CCD)

ANOVA was performed to obtain information on the most important variables and their possible interactions (Table 2). The "Lack of Fit F-value" of 3.611 and 2.239 for DSB and MO respectively and the corresponding p-value implied

Table.1 : Matrix for the central composite Design(CCD)

Factors			levels			Star pointa = 2.0	
		Low (-1)	Central (0)	High(+1)	$-\alpha$	$+\alpha$	
DSB Concentration (mg L^{-1}) (X_1)		10	15	20	5	25	
MO Concentration (mg L^{-1}) (X_2)		10	15	20	5	25	
pH(X_3)		5.0	6.0	7.0	4.0	8.0	
Adsorbent mass (g) (X_4)		0.0150	0.025	0.0350	0.005	0.045	
Sonication time (min) (X_5)		2.0	4.0	6.0	2.0	6.0	

| Run	X1	X2	X3	X4	X5	R %$_{DSB}$	R %$_{MO}$
1	10	20	7	0.035	2	98	100
2	15	15	4	0.025	4	95	95
3	20	20	7	0.035	6	97.9	99.4
4	25	15	6	0.025	4	98	100
5	15	15	6	0.025	4	94.45	94.87
6	10	10	7	0.015	2	88	88
7	10	10	7	0.035	6	100	100
8	15	15	8	0.025	4	97.5	95.77
9	15	15	6	0.025	4	95	95
10	15	15	6	0.025	4	94.7	95
11	20	10	7	0.015	6	95	95
12	10	10	5	0.035	2	100	100
13	15	15	6	0.025	4	95	95
14	15	5	6	0.025	4	97	99
15	10	20	5	0.035	6	100	100
16	15	15	6	0.025	4	95	95
17	20	20	5	0.015	6	73	81.8
18	15	15	6	0.005	4	70	78.8
19	20	10	5	0.015	2	80	96.47
20	20	10	7	0.035	2	99.69	100
21	10	20	5	0.015	2	88.5	90
22	20	20	5	0.035	2	100	98.45
23	15	25	6	0.025	4	95	95
24	15	15	6	0.045	4	100	100
25	15	15	6	0.025	8	99.48	98.52
26	10	10	5	0.015	6	99.33	100
27	5	15	6	0.025	4	100	100
28	10	20	7	0.015	6	100	96
29	15	15	6	0.025	4	94.57	94.7
30	20	20	7	0.015	2	80	81.7
31	20	10	5	0.035	6	100	100
32	15	15	6	0.025	4	95	95

the significance of this model for the prediction of experimental data. Data analysis gave a semi-empirical expression applies to model the removal percentage (R %) of for DSB and MO respectively:

$$R\%_{DSB} = 95.709 - 2.1767X_1 - 1.0258X_2 + 0.94833X_3 + 6.3233X_4 + 2.0955X_5 - 1.4350X_1X_2 + 1.3388X_1X_3 + 2.9638X_1X_4 - 1.1638X_1X_5 + 0.69000X_2X_3 + 1.0650X_2X_4 - 1.3900X_2X_5 - 1.6612X_3X_4 + 1.4612X_3X_5 - 1.9138X_4X_5 + 0.66726X_1^2 + 0.91726X_2^2 - 0.020244X_3^2 - 2.8327X_4^2 - 0.41595X_5^2$$

(3)

$$R\%_{MO} = 95.775 - 0.88250X_1 - 1.3383X_2 - 0.21167X_3 + 4.6367X_4 + 1.2054X_5 - 1.7575X_1X_2 + 0.33625X_1X_3 + 1.0550X_1X_4 - 1.1513X_1X_5 + 1.2700X_2X_3 + 1.7388X_2X_4 - 0.21750X_2X_5 + 0.53250X_3X_4 + 1.4887X_3X_5 - 0.98000X_4X_5 + 0.94960X_1^2 + 0.94960X_2^2 - 0.20415X_3^2 - 1.7004X_4^2 - 0.12982X_5^2$$

(4)

Table. 2: Analysis of variance (ANOVA) for CCD.

Source of variation	Df	DSB				MO			
		Sum of square	Mean square	F-value	P-value	Sum of square	Mean square	F-value	P-value
Model	20	1920.3	96.013	11.161	0.00011	977.95	48.898	8.4833	0.000412
X_1	1	113.71	113.71	13.218	0.003918	18.691	18.691	3.2428	0.099187
X_2	1	25.256	25.256	2.9359	0.11463	42.987	42.987	7.4579	0.019546
X_3	1	21.584	21.584	2.509	0.1415	1.0753	1.0753	0.18655	0.67415
X_4	1	959.63	959.63	111.55	< 0.0001	515.97	515.97	89.516	< 0.0001
X_5	1	74.495	74.495	8.6597	0.013382	24.653	24.653	4.277	0.062979
X_1X_2	1	32.948	32.948	3.83	0.076198	49.421	49.421	8.5741	0.013736
X_1X_3	1	28.676	28.676	3.3335	0.095127	1.809	1.809	0.31385	0.58655
X_1X_4	1	140.54	140.54	16.337	0.001942	17.808	17.808	3.0896	0.10655
X_1X_5	1	21.669	21.669	2.5189	0.14079	21.206	21.206	3.6791	0.081416
X_2X_3	1	7.6176	7.6176	0.88551	0.3669	25.806	25.806	4.4772	0.057977
X_2X_4	1	18.148	18.148	2.1096	0.1743	48.372	48.372	8.3921	0.014525
X_2X_5	1	30.914	30.914	3.5936	0.084568	0.7569	0.7569	0.13132	0.72394
X_3X_4	1	44.156	44.156	5.1329	0.044651	4.5369	4.5369	0.78711	0.39396
X_3X_5	1	34.164	34.164	3.9714	0.071677	35.462	35.462	6.1524	0.030552
X_4X_5	1	58.599	58.599	6.8119	0.024259	15.366	15.366	2.6659	0.13079
X_1^2	1	12.981	12.981	1.509	0.24493	26.291	26.291	4.5613	0.056021
X_2^2	1	24.53	24.53	2.8515	0.1194	26.291	26.291	4.5613	0.056021
X_3^2	1	0.011948	0.011948	0.001389	0.97094	1.2151	1.2151	0.21081	0.65508
X_4^2	1	233.96	233.96	27.196	0.000288	84.299	84.299	14.625	0.002822
X_5^2	1	2.9101	2.9101	0.33829	0.57254	0.28347	0.28347	0.049179	0.82856
Residual	11	94.627	8.6025			63.404	5.764		
Lack of Fit	5	71.027	14.205	3.6115	0.074721	41.28	8.2561	2.2391	0.17741
Pure Error	6	23.6	3.9334			22.123	3.6872		0.000412
Cor Total	31	2014.9				1041.4			0.099187
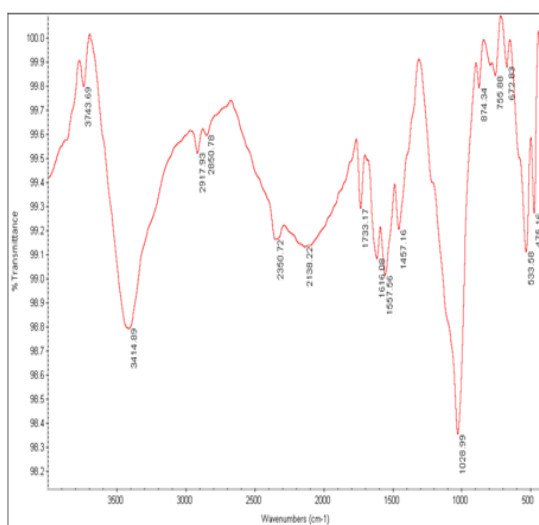
Fig. 2. FT-IR spectrum of TiO$_2$ -NPs-AC.
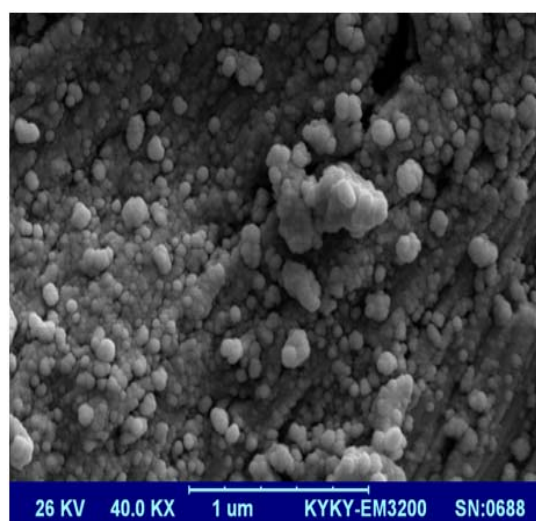
Fig. 3. SEM image of TiO$_2$ -NPs-AC.

Response surface methodology

The 3D RSM surfaces was developed by considering all the significant interactions in the CCD to optimize the critical factors and describe the nature of the response surface in the experiment. Fig (4a, b) show that the removal percentage changes versus the adsorbent dosage. The positive increase in the dye removal percentage with increase in adsorbent amount is seen. Fig (4c) that the removal percentage changes *versus* the adsorbent dosage. The positive increase in the dye removal percentage with increase in adsorbent mass is seen.

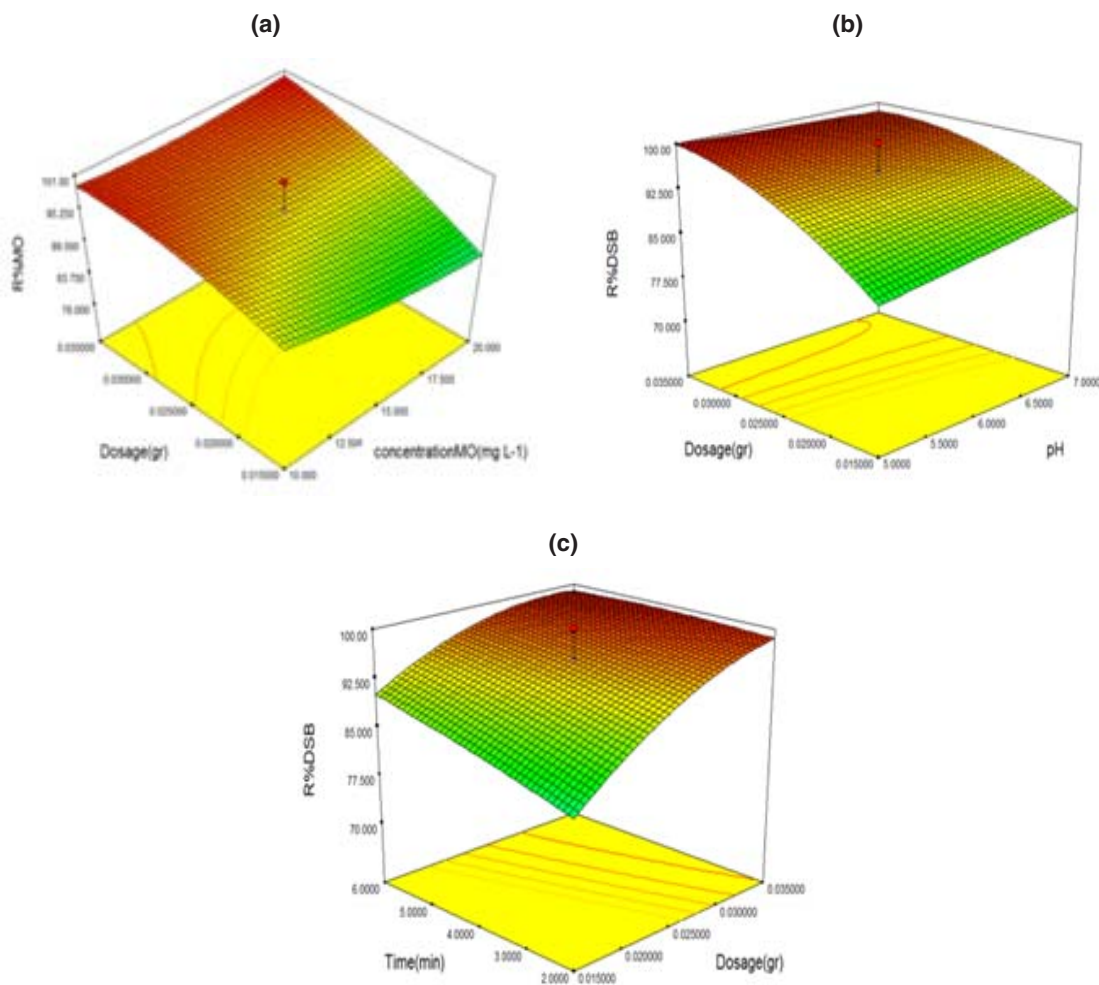**(a)**   **(b)**

(c)

Fig. 4. Response surfaces for the hues removal: (a) pH- adsorbent dosage, (b) Time- adsorbent dosage, (c) Time-concentration DSB, Dosage-concentration MO

Adsorption isotherms

An adsorption isotherm is characterized by certain constant amounts, which express the surface properties of the adsorbent and so on the function of initial concentration of MO and DSB hues are given in table the 3. Based on the linear form of Langmuir isotherm model[13-21] .indicating that the Langmuire adsorption of MO and DSB onto TiO_2 -NPs-AC are favorable.

Study kinetic

The prediction of batch adsorption kinetics is necessary for the layout of industrial adsorption columns. Such kinetic models including pseudo first and second-order, Elovich and intraparticle diffusion were investigated to study the rate and mechanism of an adsorption process[22-27]. Table 4 summarized the properties of each model with the experimental adsorption. higher values of R^2 were

obtained for pseudo-second-order adsorption rate model indicating that the adsorption rates of both dyes onto the TiO2-NPs-AC can be more appropriately described by using the pseudo-second order rate. This means that the rate of the surface adsorption depends on the rate of the chemical adsorption process as the rate-determining step.

Table. 3: The resultant amounts for the studied isotherms in connection to MO and DSB hues adsorption onto TiO$_2$-NPs-AC

Isotherm	parameters	MO	DSB
Langmuir	q_m /(mg g^{-1})	50	100
	b/L mg^{-1}	1.53	0.487
	R^2	0.997	0.998
Freundlich	1/n	0.24	0.55
	p/ (L mg^{-1})	3.66	4.09
	R^2	0.985	0.982
Tempkin	b_1	5.76	14.15
	K_T/ (L mg^{-1})	56.723	6.855
	R^2	0.98	0.978
Dubinin-Radushkevich (DR)	q_s (mg g^{-1})	29.66	39.64
	B	-4	-1
	E (kj mol^{-1})	3546	2237
	R^2	0.95	0.963

Table. 4: Kinetic parameters for MO and DSB hues adsorption onto TiO$_2$-NPs-AC

Concentration (mg/l)	Model	parameters	Value of parameters for DSB	Value of parametersfor MO
10	Pseudo-first-order kinetic	k_1/(min^{-1})	1.43	0.987
20				
30				
40				
50		R^2	0.95	0.95
60				
10	Pseudo-second-order kinetic	k_2 /(min^{-1})	0.507	0.154
20				
30				
40				
50		R^2	0.999	0.999
60				
10	Intraparticle diffusion	K_{diff}/ (mg g^{-1} min$^{-1/2}$)	4.59	8.05
20				
30				
40				
50		R^2	0.94	0.97
60				
10	Elovich	β/(g mg^{-1})	1.379	0.609
20				
30				
40				
50		R^2	0.94	0.98
60				

CONCLUSIONS

In this study, TiO_2 nanoparticles loaded onto carbon activated were produced and tested as adsorbents for the removal of Disulfine Blue and Methyl Orange dyes from aqueous samples. The results of this work show TiO_2 -NPs-AC under the sonication is an efficient, fast and sentient adsorption method for the removal of DSB and MO. Results showed that the Langmuir isotherm model was fitted well with adsorption data. Kinetic data for both dyes were appropriately fitted to a Pseudo-second-order adsorption rate.

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