

Novel TiO₂ NPs Loaded on Activated Carbon as a Green and High Efficient Absorbent: Synthesis, Characterization, Kinetic and Equilibrium Studies

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ABSTRACT

The present study focuses on the development of an effective methodology to obtain the optimum removal conditions assisted by ultrasonic to maximize the simultaneous removal of Bismarck Brown (BB) and Thymol Blue (TB) dyes on to TiO₂ nanoparticles loaded on activated carbon (TiO₂-NPs-AC) in aqueous solution using response surface methodology (RSM). The experimental equilibrium data were fitted to the conventional isotherm models such as Langmuir, Freundlich, Temkin and Dubinin–Radushkevich. The Langmuir isotherm was found to be the best model for the explanation of experimental data. From the Langmuir isotherm, the maximum monolayer capacity (Q_{max}) was found to be 100 and 50 mg g⁻¹ for BB and TB, respectively at optimum conditions. Kinetic evaluation of experimental data showed that the BB and TB adsorption processes followed well pseudo-second-order.

Keywords: TiO₂-NPs-AC; dye; Central composite design; Response surface methodology; Ultrasonicated adsorption

1. Introduction

Dyes as most abundant and hazardous pollutants in high extent presence in wastewater of dye manufacturing, textile and paper industries [1,2]. Their emittance and appearance in water media as associated with some difficultly accurate and safe treatment of such pollutants containing media. Some of accomplished hazards and difficultly from water [3,4]. In the present work, TiO₂ nanoparticles loaded on AC (TiO₂-NPs-AC) as a novel adsorbent was simply synthesized and subsequently characterized by field emission scanning electron microscopy (FE-SEM) (not shown), Fourier transform infrared spectroscopy (FTIR) (not shown).

In dyes removal process, the effects of important variables such as (initial BB and TB concentration, pH, adsorbent mass and sonication time) were investigated and optimized by central composite design (CCD) under response surface methodology (RSM). It was shown that the adsorption of BB and TB follows the pseudo-second-order rate equation. The Langmuir model was found to be applied for the equilibrium data explanation.

2. Experimental

Materials and methods

All chemicals used in this work were of analytical grade and obtained from Merck, Bismarck Brown, Thymol Blue, activated carbon, sodium hydroxide, hydrochloric acid, activated carbon, sodium hydroxide, hydrochloric acid, ethanol and titanium tetra chloride were also from Merck (Germany). To adjust the pH of reaction mixture, a solution of 0.1 mol L⁻¹ KOH was used. All aqueous solutions were prepared with ultrapure water and freshly prepared solutions were used for all chemical procedures.

Measurements of dye uptake

Small central composite design as most applicable type of RSM was applied for modeling and the optimization of effects of concentration of BB (X1) and TB (X2) dyes, PH (X3),

amount of adsorbent (X4) and contact time (X5) on the ultrasonic-assisted adsorption of BB and TB by TiO₂- NPs-AC. Five independent variables were set at five levels at which the R% of BB and TB as response was determined and shown in Table 1.

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

Factors		levels					Star points = 2.0	
		Low (-1)	Central (0)	High(+1)	- α	+ α		
BB Concentration (mg L ⁻¹)		10	15	20	5	25		
TB Concentration (mg L ⁻¹)		10	15	20	5	25		
pH		5.0	6.0	7.0	4.0	8.0		
Adsorbent mass (g)		0.015	0.025	0.0350	0.005	0.045		
Sonication time (min)		2.0	4.0	6.0	2.0	6.0		
Ru	X	X	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

3. Results and discussion

Response Surface Plots

The 3D RSM surfaces corresponding to R%BB and R%TB were depicted and considered to optimize the significant factors and to give useful information about the possible interaction of variables. For example table 3 that the dye removal percentage changes versus the adsorbent dosage. The positive increase in the dye removal percentage with increase in adsorbent mass is seen. Significant diminish in removal percentage at lower amount of TiO₂-NPs-AC is attribute to higher ratio of dye molecules to the vacant sites of the adsorbent.

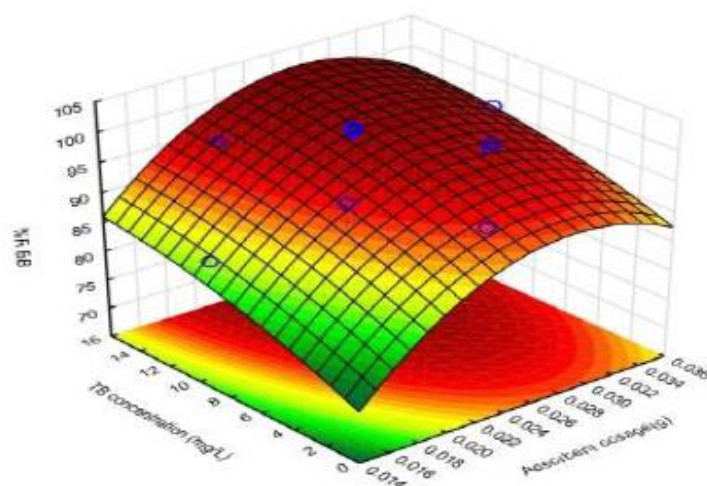


Fig 1: Response surfaces for the BB dye removal: initial TB concentration– adsorbent dosage.

Adsorption Equilibrium Study

The experimental adsorption equilibrium data was evaluated for studying the mechanism of BB and TB dyes adsorption onto TiO₂-NPs-AC using different models such as Langmuir, Freundlich, Temkin, Dubinin– Radushkevich isotherms [5, 6, 7] in their conventional linear form. Subsequently, their corresponding constants were evaluated from the slopes and intercepts of respective lines (Table 2). , It was concluded that the Langmuir isotherm is the best model to explain the BB and TB dyes adsorption onto TiO₂-NPs-AC.

Table 2: The resultant values for the studied isotherms in connection to BB and TB dyes adsorption onto TiO₂-NPs-AC.

Isotherm	parameters	Value of parameters ForBB	Value of parameters for TB
Langmuir	$q_m/(mg\ g^{-1})$	100	50
	$b/L\ mg^{-1}$	0.487	1.53
	R^2	0.998	0.997
Freundlich	$1/n$	0.55	0.24
	$p/ (L\ mg^{-1})$	4.09	3.66
	R^2	0.982	0.985

Kinetic Study

The kinetic of reactions in adsorption process is strongly influenced by several parameters related to the state of the solid and to the physico-chemical conditions under which sorption is occurred. To investigate the sorption processes of TB and BB dyes onto the adsorbent, different kinetics models such as pseudo-first order and pseudo-second-order models (Tables 2 and 3) [8], As a result, the adsorption fits to the pseudo-second-order better than the pseudo-first-order kinetic model for both dyes.

Table 3: The resultant values for the studied Kinetic in connection to BB and TB dyes adsorption onto TiO₂-NPs-AC.

Model	parameters	Value of parameters for BB	Value of parameters for TB
pseudo-First-order kinetic	$k_1/(min^{-1})$	0.987	1.43
	$q_e / (calc) (mg\ g^{-1})$	17.92	10.155
	R^2	0.95	0.95
pseudo-Second-order kinetic	$k_2 / (min^{-1})$	0.154	0.507
	$q_e (calc) (mg\ g^{-1})$	56.15	53.46
	R^2	0.999	0.999

4. Conclusions

1. Ultrasound assists the whole adsorption time leading to omit undesirable effects.
2. Combined ultrasound-assisted/nanoparticles adsorption as an efficient dye removal method. Experimental design based response surface methodology was used for optimization.
3. We demonstrate a methodology for simultaneous dyes removal from aqueous solution.
4. Nanoparticles shows considerable advantages on the removal yield of dyes.

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