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Removal of toluidine blue by manganese/graphene coated titaniferous sand and optimization of decoloration process via Box-Behnken design

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Abstract: An adequate modification of a titaniferous sand fraction by manganese/graphene coating (GMnTS) was carried out. Indeed, the surface of titaniferous sand (TS) with a particle size less than 100 µm was functionalized by chemical precipitation of manganese oxide on which were coated graphene oxide nano-sheets. Modified Hummer method was used to produce a stable suspension of graphene oxide. In this study, the adsorption affinity was tested using toluidine blue (BT) as an aquatic contaminant. According to the Langmuir model, GMnTS has an adsorption capacity about 12 times higher than that of unmodified titaniferous sand. This is a coating rate of about 0.73 ± 0.02 %. The response surface methodology based on Box–Behnken design was applied to optimize the linear and interactive effects of four factors (BT concentration, pH, solid/liquid ratio and KCl concentration) influencing the discoloration process by GMnTS.

Keywords: titaniferous sand; manganese/graphene coating; affinity; toluidine blue; Box–Behnken.

Introduction

Different types of sand, which include quartz or silica sand, iron sand, gypsum have traditionally been tested in filter beds for the physicochemical separation of a wide variety of organic and inorganic contaminants. However, several studies have found that sands have insufficient adsorbent properties for dyes retention from aqueous solutions [1]. Recently, surface modifications of the sand grains have been done by a chemical method, which can significantly enhance the removal efficiency. Graphene Oxide (GO) has attracted great attention and research interest in many fields, particularly in water treatment due to their remarkable properties. GO was used as a surface modifier to improve the adhesion or provide an active functional group for further reaction. Indeed, GO is a two-dimensional nanomaterial and hexagonal carbon ring, but with many functional groups, such as carboxyl (-COOH), hydroxyl (-OH) and epoxy (>O) groups [2], and readily disperses in water to form a stable colloidal suspension [3]. For example, Gao et al.[4] used GO functionalized by diazonium chemistry to coat silica sand surfaces and the GO-enabled sand retains at least 5-fold higher concentration of mercuric ions and Rhodamine B than unmodified sand. Similarly, a variety of organosilanes (KH550, KH570, and HMDS[5]) were grafted at the surface of the sand grains in order to improve the level of interactions with the functional groups of GO (generation of covalent bonding) for the removal of organic contaminants from water. Sand-based superhydrophobic surfaces were easily achieved by coating sand particles with octadecyltrichlorosilane [6]. Other approaches have been used to modify a grain surface with a polymeric coating [7,8,9,10]. Nevertheless, coating technology using organosilane coupling agents and polymer is often costly which greatly limits their applications in water treatment.

Based on this idea, we have developed a simple coating process of Titaniferous Sand (TS) with a high content of hematite. Characterization data of TS are provided in the supplementary information (Appendix A.). The surface modification of TS was made by chemical precipitation of manganese oxide (MnO_2) used as a coupling agent, and then the surface functional groups of TS were reacted with GO nano-sheets. In order to investigate the feasibility of using GMnTS for dye retention from aqueous solution, Toluidine Blue (TB) or basic blue 17 (Fig. 1) (CAS number: 92-31-9; C.I. = 52040; Chemical formula: $C_{15}H_{16}N_3SCl$; Molar mass = 305.85 g/mol; λmax = 635 nm) has been used as a water contaminant. Response surface methodology based on four variables and three-level Box–Behnken design was employed to optimize the parameters for maximum retention efficiency. The factors studied are the TB concentration, pH of the aqueous solution, solid/liquid ratio and KCl concentration.

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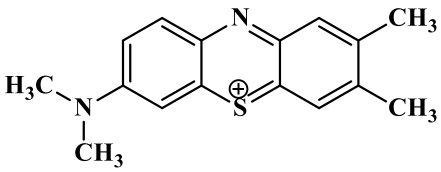

Figure 1. Chemical structure of TB

Experimental and methods

Preparation of manganese/graphene coated titaniferous sand (GMnTS)

Preparation of graphene oxide (GO)

GO was prepared by the chemical oxidation of graphite powder according to improved Hummers method [11,12]. Typically, 90 mL of sulphuric acid and 10 mL of phosphoric acid (9:1) were mixed and stirred for 10 min. Then, 3g of graphite powder and 9g $KMnO_4$ were slowly added into mixing solution under stirring condition. This mixture was stirred for 2 days until the solution became dark brown. Later, the resulting mixture was added to a beaker containing flaked ice and 4 mL H_2O_2 solution was added to stop the oxidation process by permanganate ion, and the color of the mixture changed to bright yellow, indicating a high oxidation level of graphite. The exothermic reaction occurred and let it cool down. 10 ml of hydrochloric acid and 30 ml of deionized water was added and centrifuged using at 2000 rpm for 10 min. Finally, the supernatant was decanted away and the residuals were then rewashed again with HCl and deionized water for 3 times. The washed GO solution was dried using the oven at 90 °C for 24 hours.

Preparation of GMnTS

TS of grain size 80 - 100 µm was collected in Taghazout beach (North-East of Agadir, Morocco) and washed repeatedly with distilled water and 10 % HCl to remove all earthen impurities, followed by oven drying at 105 °C (designated as unmodified TS). A boiling solution containing 5.10 - 4.0 M KMnO4 was poured over dried unmodified TS placed in a beaker, and 1 M HCl (37.5%) solution was added dropwise to the solution [13]. After stirring for 2 h, the media was filtered, washed several times with distilled water, dried at room temperature, and stored in polypropylene bottle for future use (designated as MnTS). Mass of 20 g of MnTS was put in a petri dish, with 100 ml/100 mg of GO/ deionized water dispersion, and heated up to 150 °C in a vacuum oven for two hours. The percentage of grafting reached to 0.73 ± 0.02 %, calculated by the following equation:

$$\%\ \text{grafting} = \frac{\text{GMnTS/g-Unmodified TS/g}}{0.1} \times 100 \qquad (1)$$

Batch adsorption process

Batch adsorption studies were carried out by contacting a known amount of adsorbent with 25 mL of dye solution of known initial dye concentration in 30 mL stoppered conical flask. This mixture was agitated in a temperature controlled shaking water bath at a constant speed of 80 rpm. The initial pH of the solution was adjusted by addition of dilute aqueous solutions of HCl or KOH (0.1 M). The effect of ionic strength on the removal efficiency of dye onto adsorbent was discussed over the KCl concentration range from 0.0 to 1 mol/l. Adsorption isotherm was carried out at different initial concentrations of dye at 25 ± 1.0 °C. The contact was made for 5 h, which is more than sufficient time (predetermined) to reach equilibrium. At the end of adsorption experiments, the dye solutions were separated from the adsorbent by syringe filter (0.45 µm pore size, Whatman). After, the dye concentration was determined at λmax, using UV spectrophotometer (Jenway Model 6800) and then applying Beer-Lambert law. The adsorption capacity was calculated using the following equation:

$$q = \frac{(C_0 - C_e)}{m} \times V \qquad (2)$$

Where C_0 and Ce are the initial and equilibrium concentrations of TB (mg/l), respectively, V is the volume of solution (l) and m is the weight of adsorbent (g). The percentage removal of dye was calculated using the following relationship:

$$\%\ \text{dye removal} = \frac{(C_0 - C_e)}{C_0} \times 100 \qquad (3)$$

Experimental design

The 3-levels (low (-1), basal (0) and high (+1)) Box-Behnken experimental design, with five replicates at the center point, was used for optimization of decoloration process by GMnTS and to investigate the significance effects of four parameters, that leading to 29 runs. TB concentration (A, mg/l), initial pH (B), Solid/liquid ratio (C, g/l) and KCl concentration (D, mol/l) are the independent process variables input parameters (Table 1), while dye concentration of 100 mg/l was kept as a constant input parameter.

Table1. Box-Behnken design levels of chosen variables.

Variables	Factors	Low level (-1)	Middle level (0)	High level (+1)
TB concentration (mg/l)	A	5	20	40
Initial pH	B	2,5	6	10
Solid/liquid ratio (g/l)	C	10	20	30
KCl concentration (mol/l)	D	0	0,5	1

The statistical results of the experimental design were studied and interpreted by Design-Expert 8 program software including ANOVA to estimate the response of the dependent variable. TB/water decoloration efficiency (Eq. 3) was considered as a dependent factor (response Y (%)).

Results and discussion

Adsorption isotherm

Different initial dye concentrations were investigated to appreciate the interaction between TB and adsorbent. Fig. 2 depicts the amount of TB adsorbed against the equilibrium concentrations. According to Giles classification [14], The isotherms are of L-type (or Langmuir isotherm) which reflects a relatively high affinity between the GMnTS and TB and there is no strong competition of the solvent for the active sites of adsorption. The maximum adsorption of TB was 0.38, 1.02 and 5.32 mg/g on unmodified TS, MnTS, and GMnTS, respectively. The difference in binding affinity may be attributed to the difference in the nature of functional groups carried by the three adsorbents. The fairly low grafting efficiency (0.73 ± 0.02 %) and the low TB retention are probably attributed to the low specific surface area of unmodified TS, typically not exceeding 0.8 m^2/g (Appendix A.). The maximum adsorption capacity of GMnTS for TB retention is similar to other modified adsorbents reported in the literature (Table 2) for dye removal from aqueous solution.

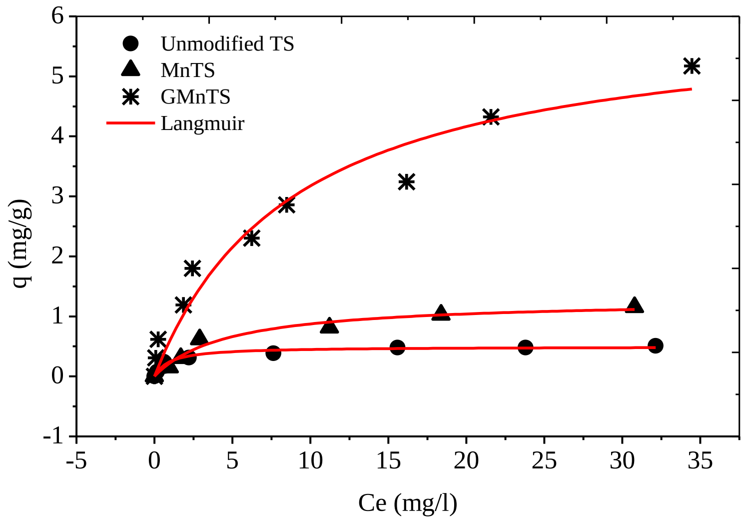

Figure 2. Adsorption isotherms of TB from aqueous solution on unmodified TS, MnTS, and GMnTS. Curves represent the non-linear fitting of the experimental data to the Langmuir equation.

Table 2 Comparison of adsorption capacities of various modified materials for dye from aqueous solution.

Dye	Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Methylene Blue	modified zeolite	8.3	15
Reactive Blue	modified wheat straw (MWS)	4.22	16
Congo Red	Chitosan-Coated Quartz Sand	3.56	17
Toluidine Blue	GMnTS	5.32	This work

Optimization of decoloration process by GMnTS

The aim of this study is to optimize and to evaluate the interaction effects of four process factors on TB retention by GMnTS. Response surface methodology (RSM) based on Box-Behnken design, compared with classical methods, has proved to be a suitable method to optimize the best-operating conditions to maximize the dye removal. This method is based on an adequate mathematical model taking into account of all possible combinations of the two factors. Table 3 shows the results of 29 experiments carried out according to Box-Behnken design matrix with the measured responses Y (%).

In order to correctly evaluate the adequacy and the significance of a mathematical model (Linear, interactive 2FI, quadratic and cubic models) with respect to the experimental data, several statistical tests using analysis of variance (ANOVA) must be taken into account, such as the P-value and the regression coefficient (R-Squared) values. ANOVA results for four models are listed in Table 4. Sequential model and lack of fit showed that the p-values were lower than 0.05 for a quadratic model with a high value of the coefficient of determination (Adjusted R-Squared = 0.926 and Predicted R-Squared = 0.793). However, the cubic model was found to be aliased.

Table 3. Box-Behnken design matrix and experimental results for TB retention.

Trial No.	Coded variable				Natural variable				Y (%)
	X1	X2	X3	X4	A (mg/l)	B	C (g/l)	D (mol/l)	
1	0	0	1	1	22,5	6,25	30	1	82,4
2	0	0	0	0	22,5	6,25	20	0,5	90,21
3	1	0	0	1	40	6,25	20	1	52,54
4	-1	0	0	1	5	6,25	20	1	97,7
5	0	0	0	0	22,5	6,25	20	0,5	93,8
6	-1	0	-1	0	5	6,25	10	0,5	84,41
7	0	0	-1	1	22,5	6,25	10	1	62,56
8	0	0	1	-1	22,5	6,25	30	0	99,1
9	0	1	-1	0	22,5	10	10	0,5	82,23
10	0	0	0	0	22,5	6,25	20	0,5	91,47
11	0	0	0	0	22,5	6,25	20	0,5	90,85
12	0	0	-1	-1	22,5	6,25	10	0	71,04
13	-1	-1	0	0	5	2,5	20	0,5	92,458
14	0	-1	0	1	22,5	2,5	20	1	77,08
15	0	1	0	1	22,5	10	20	1	82,56
16	1	-1	0	0	40	2,5	20	0,5	70,47
17	1	0	1	0	40	6,25	30	0,5	75,12
18	0	1	1	0	22,5	10	30	0,5	97,06
19	-1	0	0	-1	5	6,25	20	0	99,74
20	0	-1	0	-1	22,5	2,5	20	0	88,64
21	0	1	0	-1	22,5	10	20	0	99,28
22	-1	0	1	0	5	6,25	30	0,5	96,66
23	1	0	0	-1	40	6,25	20	0	79,86
24	0	0	0	0	22,5	6,25	20	0,5	92,76
25	1	0	-1	0	40	6,25	10	0,5	33,65
26	1	1	0	0	40	10	20	0,5	73,38
27	0	-1	-1	0	22,5	2,5	10	0,5	64,63
28	0	-1	1	0	22,5	2,5	30	0,5	88,56
29	-1	1	0	0	5	10	20	0,5	94,75

Table 4. Significance of the models tested according to ANOVA.

Model	Sequential p-value	Lack of Fit p-value	Adjusted R-Squared	Predicted R-Squared	Test F	Prob>F	Judgment
Linéaire	< 0.0001	0,0015	0,7235	0,6583	19,31	< 0.0001	
2FI	0,4174	0,0014	0,7281	0,5547	1,07	0,4174	
Quadratique	0,0001	0,016	0,9264	0,7932	13,12	0,0001	Suggested
Cubique	0,0938	0,0305	0,9663	0,141	3,08	0,0938	Aliased

Table 5. ANOVA of the postulated model.

	Sum of squares	df	Mean square	F-test	Prob>F	Judgment
Model	6466,19	14	461,87	26,16	< 0.0001	
A-C	2720,98	1	2720,98	154,1	< 0.0001	Highly significant
B-pH	187,4	1	187,4	10,61	0,0057	Significant
C-R	1642,21	1	1642,21	93	< 0.0001	Highly significant
D-KCl	571,6	1	571,6	32,37	< 0.0001	Highly significant
AB	0,095	1	0,095	5,41E-03	0,9424	
AC	213,45	1	213,45	12,09	0,0037	Significant
AD	159,77	1	159,77	9,05	0,0094	Significant
BC	20,7	1	20,7	1,17	0,2972	
BD	6,66	1	6,66	0,38	0,5491	
CD	16,89	1	16,89	0,96	0,3446	
A2	430,32	1	430,32	24,37	0,0002	Highly significant
B2	2,34	1	2,34	0,13	0,7215	
C2	624,2	1	624,2	35,35	< 0.0001	Highly significant
D2	55,49	1	55,49	3,14	0,098	
Residual	247,2	14	17,66			
Lack of Fit	238,74	10	23,87	11,29	0,016	Significant
Pure error	8,46	4	2,11			
Cor total	6713,39	28				

Table 5 shows the ANOVA study of the postulated model. F-test and Prob>F were used to estimate the statistical significance of all terms of the model within 95% confidence interval. As it can be seen from Table 5, the P-value values (with a low F-test) obtained for the AB, BC, BD, and CD interactions are greater than 0.05, except for AC and AD interactions where Prob>F is 0.0037 and 0.0094, respectively. Thus, the interaction effect between (TB concentration - solid/liquid ratio) and (TB concentration - KCl concentration) was found to be significant. Similarly, we also note the presence of quadratic effects of A^2 and C^2. To optimize the postulated model, the terms of the polynomial model with p-values greater than 0.05 have been eliminated. Based on these results, the response Y (%) in terms of natural variables was expressed by the second-order polynomial equation:

$$\mathbf{Y(\%) = 47{,}30 - 0{,}220\times A + 1{,}054\times B + 3{,}930\times C + 2{,}45\times D - 0{,}02476\times A.A - 0{,}0925\times C.C + 0{,}0417\times A.C - 0{,}722\times A.D} \quad (4)$$

The 3D response surface curves and their respective 2D contours plot against any two independent variables while keeping the third independent variable at constant value are given in Fig. 3. As shown in Fig. 3a, the discoloration efficiency by GMnTS increases with increase in solid/liquid ratio, whereas it decreases with increase in TB concentration. Moreover, for R > 27 g/l, the variations of the Y (%) response become almost constant, that may be related to the limited adsorption sites.

Finally, Fig. 3b and Fig. 3c, show the effect of initial pH and KCl concentration by keeping solid/liquid ratio constant on the elimination of toluidine blue dye, respectively. Discolouration efficiency Y (%) increases with increase in initial pH whereas it greatly decreased especially in the presence of KCl salt. This can be explained by a competitive effect between H^+, K^+ and TB molecules onto the active GMnTS adsorption sites. The increase in the amount of adsorbed dye suggests that the electrostatic interactions contribute to the adsorption process [18]. At lower KCl concentrations, more than 92% TB removal efficiency by GMnTS could be achieved at constant solid/liquid ratio of 27g/l with pH values higher than 5 for TB concentration varying from 5.0 to 26 mg/l.

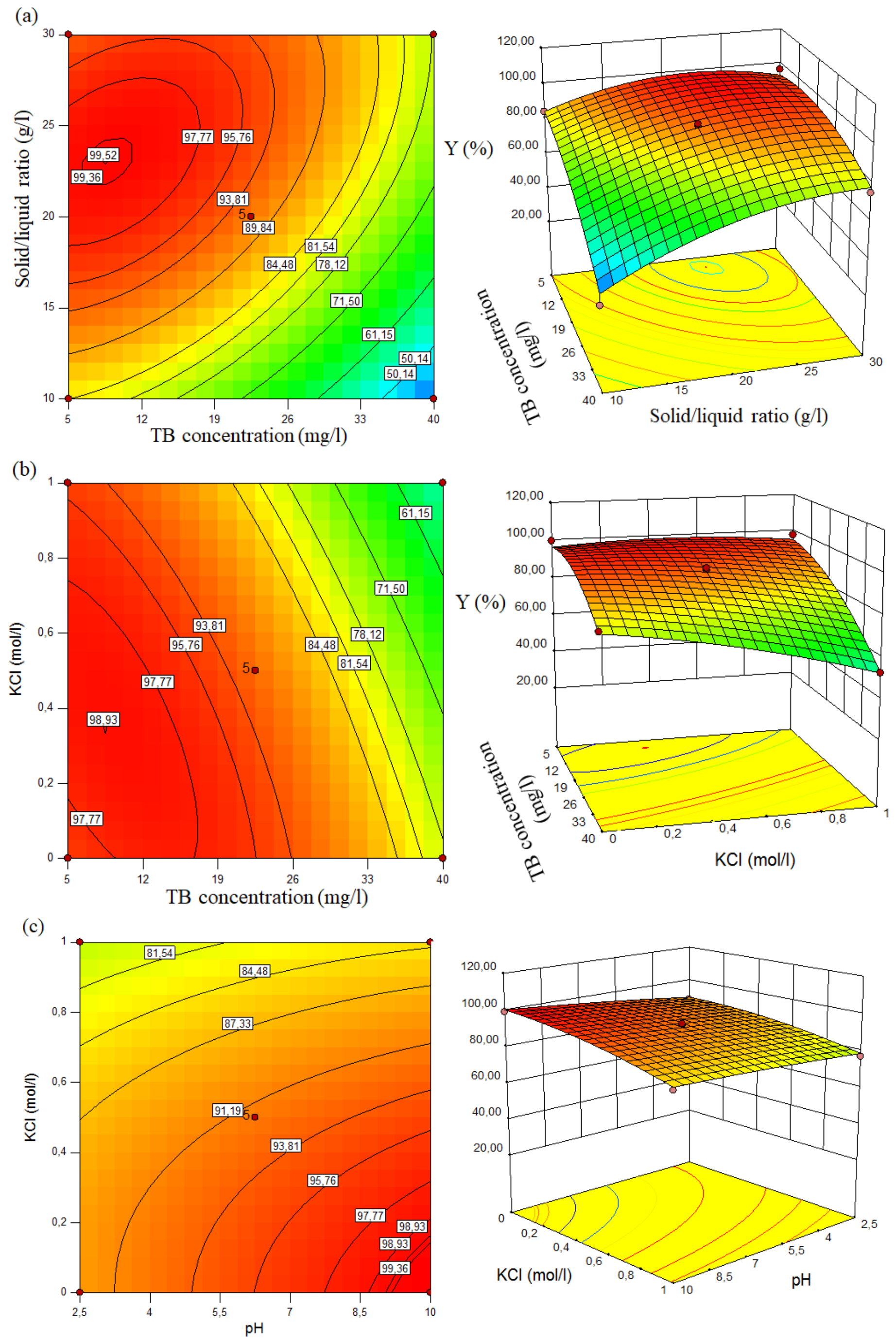

Figure 3. Response surface curves and contour plots showing interactive effect of (a) TB concentration and solid/liquid ratio (b) KCl and TB concentration (c) KCl concentration and pH on the decolouration process.

Conclusion

This investigation shows that manganese/graphene coated titaniferous sand (GMnTS) can be successfully used for the adsorption of Toluidine Blue (TB) as the toxic dye from aqueous solution. According to the Langmuir isotherm, the adsorption capacity of TB for unmodified TS, MnTS, and GMnTS is 0.38, 1.02 and 5.32 mg/g, respectively. Four-variables/three-level Box-Behnken design has been applied to determine the optimal experimental conditions. A quadratic model could properly interpret the experimental data with a coefficient of adjusted and predicted R-squared values of 0.926 and 0.793, respectively and an F-test of 26.16. Graphical response surface and contour plot were used to locate the optimum point. Maximum dye removal (> 92 %) was observed at the lowest level of KCl concentration (< 0.4 mol/l) and at higher pH levels. The electrostatic attractions are the main driving force for the adsorption process.

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Conflict of Interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Supplementary data associated with this article can be found online at:
http://revues.imist.ma/index.php?journal=JACEP&page=article&op=view&path%5B%5D=11285
http://revues.imist.ma/index.php?journal=AJEES&page=article&op=view&path%5B%5D=8559

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