ESJ Natural/Life/Medical Sciences

Modelling and Optimizing the Removal of Methylene Blue by a Mixture of Titaniferous Sand and Attapulgite Using Complete Factorial Design

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Doi:10.19044/esj.2021.v17n40p1

Submitted: 02 August 2021
Accepted: 27 October 2021
Published: 30 November 2021

Cite As:
Ba K., Toure A.O., Diop E. H.M., Sambe M.F., & Diop C.G.M., (2021). *Modelling and Optimizing the Removal of Methylene Blue by a Mixture of Titaniferous Sand and Attapulgite Using Complete Factorial Design.* European Scientific Journal, ESJ, 17(40), 1. https://doi.org/10.19044/esj.2021.v17n40p1

Abstract

This paper focuses on the removal of methylene blue by adsorption using a mixture of titaniferous sand and attapulgite. The different adsorbents were characterized by X-ray fluorescence spectroscopy and their different parameters such as pH, zero charge potential, and specific surface area were determined. The experiments performed were optimized and modeled by a full 2-level and 4-factor design. The four factors are the ratio of titaniferous sand and attapulgite, the concentration of methylene blue, pH, and time. These vary from 4 to 19, 20 to 100 mg/L, 2 to 9, and 30 to 150 min respectively. The study of the effects of the different factors showed that the effect of methylene blue concentration and pH significantly influence the adsorption capacity and removal efficiency of the dye. The optimum parameters (adsorbent ratio, adsorbate concentration, pH and time) obtained for the adsorption capacity through the desirability function are: 19, 100mg/L, 9 and 150min. Those obtained for the yield are: 4, 100mg/L, 9, 150min. The pseudo second order adsorption kinetics gave an equilibrium adsorption capacity qe (calculated) =

7.6863 mg/g which is almost equal to that obtained experimentally qe (exp) = 7.3562 mg/g. This shows that the pseudo second order kinetic model is the adequate mathematical model to describe the methylene blue adsorption phenomenon on the mixture of titaniferous sand and attapulgite. The thermodynamic study showed that the methylene blue adsorption reaction is exothermic, non-spontaneous, and the degree of disorder of the particles at the adsorbing surface decreases.

Keywords: Factorial design, Adsorption, Methylene blue, Titanium sand, Attapulgite

Introduction

Effluents from textile industries contain highly toxic and non-biodegradable coloured organic molecules, which are released into the receiving environment, causing huge problems for the environment and human health (Oladipo et al., 2014; Venkataraghavan et al., 2020). Methylene blue is the most widely used dye in silk and cotton dyeing. Its inhalation and ingestion can cause breathing difficulties and burning sensation respectively (Karim et al., 2010; Taylor et al., 2015). Therefore, it is important to implement treatment methods to remove these dyes. Several remediation techniques have been implemented which includes physical, chemical, biological, conventional oxidation, and membrane processes (Aarfane et al., 2014; El-Sayed, 2011; Gürses et al., 2006). The major challenge of these different methods results on one hand from the difficulty to completely remove some recalcitrant molecules and on the other hand from the high cost of implementing these techniques (Abbaz et al., 2014). In recent years, adsorption on activated carbon seems to be the most studied and used process due to its efficiency and ease of implementation. This is why its disadvantages are mainly related to the problem of energy cost for its calcination and the problem of regeneration (Biophys et al., 2014; Ozer et al., 2012; Salem & El-maazawi, 2000). These major constraints have led to the reorientation of the application of this method with other adsorbents of natural origin, which are easier to handle and less expensive (Benguella & Yacouta-Nour, 2009; Bonetto et al., 2015; Gupt et al., 2020).

In this work, we report the use of full factorial design to carry out the experimental series, to develop more accurate models, and to optimize the different process variables. The adsorption process was optimized by varying four variables, namely the ratio of the two adsorbents, the pH of the solution, the initial concentration of MB, and the contact time. In addition, the study of kinetics and thermodynamics were also carried out to reveal the adsorption mechanism.

 ISSN: 1857-7881 (Print) e - ISSN 1857-7431

Material and Methods

Material

Adsorbate

The target pollutant in this study is methylene blue (MB), which is also known as tetramethylthionine hydrochloride. Methylene blue (**Figure 1**) is a cationic dye with a molecular weight of 319.85 g/mol that belongs to the group of quinone imides in the Thiazine section. They are sulphur dyes in which two benzene rings are joined by a closed ring consisting of one nitrogen atom, one sulphur atom, and four carbon atoms.

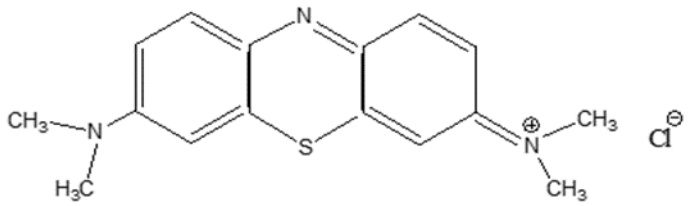

Figure 1. Structure of Methylene Blue

Adsorbents

The adsorbents used in this work are titaniferous sand and attapulgite. The titaniferous sand is a residue of a mining industry located in Senegal. Its treatment was carried out by putting it in contact with a sulphuric acid solution of concentration 4M. The mixture was stirred for 4 hours to ensure maximum contact with the acid. At the end of the operation, the sand is recovered and washed several times with distilled water until a pH close to neutrality is obtained. It is then dried in an oven for 24 hours and placed in tinted glass bottles for later use. The other material, namely attapulgite, has not undergone any prior treatment and is used in a raw manner in the work.

Methods

Determination of Isoelectric Point

The pHpzc was determined by introducing into 250mL Erlenmeyer flasks a 2g of adsorbent, and 50mL of a sodium chloride solution (0.1M). These solutions were adjusted to pH values between 2 and 12 using NaOH and HCl (0.1M) solutions. The suspensions were kept under constant agitation for 24 hours at room temperature. The pH values corresponding to the final step are recorded. The meeting point of the two curves $pH_{final} = f(pH_{initial})$ and $pH_{final} = pH_{initial}$ gives the isoelectric point (El-Sayed, 2011).

Determination of the Nature of the Adsorbent

The acidic or basic nature of the adsorbent was determined by mixing 1g of the adsorbent with 100mL of distilled water. The mixture was stirred for 1hour at room temperature and the suspension was filtered to measure the pH of the final solution. This value gives an idea about the acidic or basic character of the adsorbent (Das, 2014).

Determination of the Specific Surface

The specific surface area of the adsorbents was estimated using the Sear's method. This consists of introducing 0.5g of adsorbent into a previously prepared salt solution (10g of NaCl in 50mL of distilled water) and adjusting the pH to a value of 3 using 0.1N chloridric acid. The reaction mixture is then measured with 0.1N NaOH. The volume (V) of NaOH is to be poured in to raise the pH from 3 to 9 so as to allow the value of the specific surface of the adsorbents to be estimated (Bhattacharyya & Gupta, 2007). It is deduced from the following relationship:

$$S\ (m^2/g) = 32V - 25 \qquad (1)$$

Adsorption in Batch Mode

Batch adsorption experiments were performed in glass reactors containing 50 mL of MB solution of given concentration to which an appropriate ratio of adsorbents was added. The reactors were stirred at a constant speed of 750 rpm in a multi-stage stirrer. The operating parameters such as ratio, initial MB concentration, pH, and contact time were studied and optimized for maximum MB removal based on the screening design methodology. After the experiment was completed, the residual MB concentration was measured using a UV-Vis spectrophotometer (Agilent technologies Cary 60) at a wavelength of 653 nm which corresponds to the maximum absorbance of the MB dye. The adsorption capacity (mg.g-1) and removal efficiency (%) were determined using **equations 2 and 3** respectively:

$$q_e = \frac{(C_i - C_f) * V}{m} \qquad (2)$$

$$r = \left(\frac{C_i - C_f}{C_i}\right) * 100 \qquad (3)$$

Where:

C_i : The initial concentration (mg/L);

C_f : The final concentration (mg/L);

m : The total mass of the two adsorbents (g) ;

Full Factorial Design Modeling

The study of the effects of different adsorption parameters by conventional methods remains tedious and time consuming. However, in order to better understand the effects of different factors such as ratio, initial dye concentration, pH and time, as well as their interactions, a 2^k factorial design was carried out. These two levels are called high and low and have the values +1 and -1 respectively. The letter k represents the number of factors. The design of this factorial plan allows on one hand the reduction of the number of experiments to be carried out and on the other hand to avoid carrying out a series of independent studies. The significance of the independent variables and their interactions were tested by analysis of variance (ANOVA). To express the observed response as a function of the experimental factors, the second-order polynomial model was selected and is written as follows:

$$Y = \beta_0+\sum_{i=1}^{k}\beta_i X_i+\sum_{i3=1}^{k}\beta_{ii} X_{ii}^2+\sum_{i=1}^{k}\sum_{i\neq j=1}\beta_{ij} X_i X_j \quad \textbf{(4)}$$

Where β_0 is the constant, β_i and β_{ii} are the linear and quadratic coefficients of the input variable X_i respectively, and β_{ij} is the interaction coefficient of the input variables X_i and X_j. Furthermore, the experimental design, the regression coefficients of the models, the analysis of variances, and the graphs were determined using the software called Statgraphics Centurion XV (**version 16.2**).

Results and Discussion

Adsorbents and Adsorbate Parameters

The values of the various parameters of the adsorbents and adsorbate as well as the results of the X-ray fluorescence characterization are recorded in **Tables 1 and 2** respectively.

Table 1. *The Different Parameters of the Adsorbents and the Adsorbate*

Adsorbents/Adsorbate	Titaniferous Sand	Attapulgite	Methylene Blue
pH	6.4	8.21	6.21
pHpzc	8.75	8.75	-
Specific surface area (m^2/g)	13.4	70.68	-

Sample	Units	Ni	Al	Fe	Mn	Ca
Titaniferous sand+H_2SO_4 (4M)	ppm	92.77	18676.65	229129.56	6573.29	2233.36
Raw titaniferous sand	ppm	66.4	22695.45	272074.78	8107.22	2450.83
Attapulgite	ppm	< LOD	24737.43	17829.26	388.91	11952.21

 ISSN: 1857-7881 (Print) e - ISSN 1857-7431

Table 2. X-ray Fluorescence Analysis of Samples

Si	Zn	V	Cd	K	Zr	Ti	P	Cr	As
63423.27	182	750.3	< LOD	< LOD	2421.75	3E+05	1130.31	1116.39	149.35
82240.62	211	852.2	< LOD	< LOD	2407.55	3E+05	1631.17	1142	187.54
408028.69	101	89.82	4.55	1105	53.61	1303	2159.72	514.58	7.3

Se	S	Cl	Ba	Sn	Ag	Mo
15.94	544.35	167.69	< LOD	28.71	< LOD	< LOD
19.29	457.9	168.52	193.57	51.59	50.68	14.21
< LOD	< LOD	189	< LOD	< LOD	< LOD	12.55

Nb	Sr	Rb	Bi	Au	Co
430.57	6.04	< LOD	< LOD	105.8	< LOD
570.32	14.04	< LOD	44.58	139.88	414.64
16.89	71.02	14.27	1.63	< LOD	< LOD

The elemental analysis of the raw and activated titaniferous sand (**Table 2**) shows that titanium, iron, and aluminium are the predominant elements present at concentrations of 300,000 ppm, 63423.27 ppm and 18676.65 ppm respectively, followed by silicon. This confirms the presence of oxides such as titanium dioxide, iron oxide, and alumina which are essential elements in the adsorption of refractory organic compounds. Elements such as manganese, calcium, zircon, phosphorus, and chromium are present in a minority. Furthermore, silicon is the predominant element in the case of non-activated attapulgite, followed by aluminium, iron, and calcium. It also shows the presence of silica, alumina, and iron oxide respectively. In addition, activation of the titaniferous sand with a sulphuric acid solution resulted in a considerable reduction in the content of iron, aluminium, silicon, and manganese.

pH Zero Charge Point: pHpzc

The pH zero charge point is the pH value at which the net charge on the surface of the adsorbent is zero. The pH_{pzc} value for titaniferous sand and attapulgite found from **Figure 2** is 8.75. For pH values above pH_{pzc}, the surface of the adsorbent will be negatively charged by deprotonation of the functional groups on the surface of the adsorbent. Under these conditions, the support is ready to attract any cationic compound resulting in an increase in the electrostatic force between the negative charge of the adsorbent and the positive charge of the dye. For pH values below pHpzc, the surface of the support is positively charged and adsorption with anionic dyes is much more favoured. Similar results have been reported on the study of methylene blue

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adsorption on eucalyptus and palm biomaterial which depends on the particle size (Abdallah et al., 2016; El-Sayed, 2011).

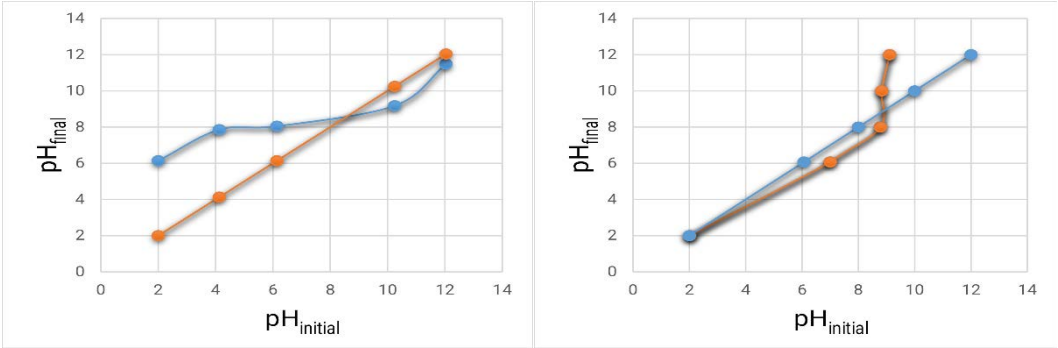

Figure 1. Isoelectric Point of Attapulgite (a) and Titaniferous Sand (b)

Contact Time

In order to study the effect of contact time on the efficiency of the adsorption process, batch adsorption experiments were carried out with a fixed adsorbent ratio of 5 (a 0.5g mass of titaniferous sand combined with a 0.1g mass of attapulgite) and at an initial MB concentration of 100 $mg.L^{-1}$ while varying the contact time from 30 to 240 min. Samples were taken at predetermined time intervals to analyze the residual MB concentration in the solution. The amount of methylene blue adsorbed by attapulgite increases very rapidly with time up to 60 min, and then decreases slowly to reach equilibrium with effective adsorption after an optimum time of 150 min. A slight increase in the adsorbed amount of methylene blue is noted up to 140 min with the composite material, and the corresponding equilibrium time is 150 min. Furthermore, the amount adsorbed by the titaniferous sand evolves weekly to reach the equilibrium from 150 min (**Figure 3**).

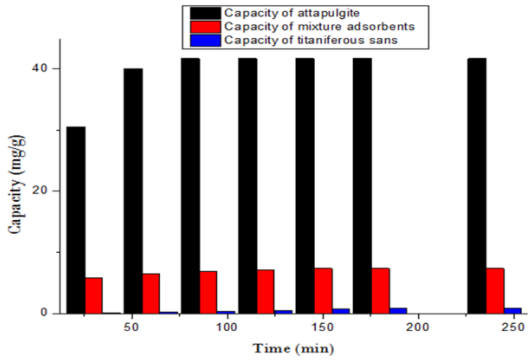

Figure 2. Evolution of the Adsorption Capacity of Attapulgite, the Mixture of the Two Adsorbents and Titaniferous Sand as a Function of Time **(pH =6.21, C_{MB} =100 mg/L, V=50 mL, T=25°C, $m_{attapulgite}$ = 0.1g and m_{sable} =0.5g).**

Description of the Experimental Plan

For the design of the adsorption process, a complete two-level and four-factor design (2^4) was performed. The high and low levels of the different variables in this study including ratio, concentration, pH and time are 4 and 19, 20 and 100 mg/L, 2 and 9, and 30 and 150 min respectively. The levels of the parameters studied and the different tests carried out are summarized in **Tables 3 and 4** respectively:

Essay	*bloc*	*Ratio*	*Concentration*	*pH*	*Time*	*Capacity*	*Yield*
			mg/L		**mn**	**mg/g**	**%**
1	1	4.00	20.00	2.00	30.00	0.11	43.75
2	1	19.00	100.00	9.00	30.00	1.19	95.34
3	1	19.00	20.00	2.00	150.00	0.07	28.41
4	1	4.00	100.00	9.00	150.00	1.12	90.00
5	2	4.00	100.00	2.00	30.00	0.38	30.66
6	2	19.00	20.00	9.00	30.00	0.13	52.50
7	2	19.00	100.00	2.00	150.00	0.85	67.73
8	2	4.00	20.00	9.00	150.00	0.19	78.64
9	3	19.00	100.00	2.00	30.00	0.49	39.02
10	3	4.00	20.00	9.00	30.00	0.19	75.79
11	3	4.00	100.00	2.00	150.00	0.36	29.25
12	3	19.00	20.00	9.00	150.00	0.09	37.95
13	4	19.00	20.00	2.00	30.00	0.19	76.70
14	4	4.00	100.00	9.00	30.00	1.03	82.50
15	4	4.00	20.00	2.00	150.00	0.08	32.73
16	4	19.00	100.00	9.0	150.00	1.05	84.11

Table 3. Levels of the Different Adsorption Parameters

Factors	*Low level (-1)*	*High level (+1)*
A: Ratio	4.0	19.00
B: Concentration (mg/L)	20.00	100.00
C: pH	2.00	9.00
D: Time (min)	30.00	150.00

Table 3. The Different Tests with the Actual Values

Analysis of Variance (ANOVA)

The ANOVA tests show the statistical significance of each of the effects by performing a comparison between the root mean square versus an experimental error estimate. Effects with probabilities that are less than the threshold value $\alpha = 0.05$ are significantly different from zero at a 95.0% confidence interval. The coefficient of determination R^2 indicates that the fitted model explains 98.2246% of the variability in capacity and 90.445% of the variability in yield **(Table 5).** In addition, it indicates that the regression is

statistically significant. The mathematical models (**equation 5 and 6**) that relate the two responses to the different factors involved in adsorption are obtained through the statgraphics software after performing the ANOVA.

Capacity (mg/g) = -0.0425343 + 0.00484747*Ratio + 0.000927297*Concentration + 0.0211225*pH - 0.000184983*Time + 0.000158499*Ratio*Concentration - 0,00173837*Ratio*pH + 7.89103E-7*Ratio*Time + 0.000837561*Concentration*pH + 0.0000122958*Concentration*Time - 0.0000799853*pH*Time **(5)**

Yield (%) = 54.5181 + 1.31561*Ratio - **0.681916*Concentration** + 3.36134*pH - 0.155272*Time + 0.0185701*Ratio*Concentration - 0.315476*Ratio*pH - 0,00601011*Ratio*Time + 0.0710228*Concentration*pH + 0.00246331*Concentration*Time + 0.00493775*pH*Time **(6)**

 ISSN: 1857-7881 (Print) e - ISSN 1857-7431

Table 4. ANOVA Table of Adsorption Capacity and Removal Efficiency of Methylene Blue

Analysis of Variance for Capacity

Source	Sum of Square	DDL	Quadratic mean	F Repor	Proba
A:Ratio	0.021	1	0.0213226	1.34	0.3309
B:Concentration	1.834	1	1.83364	115.19	0.0017
C:pH	0.382676	1	0.382676	24.00000	0.016200
D:Time	0.000856	1	0.000856	0.050000	0.831500
AB	0.036175	1	0.036175	2.270000	0.228800
AC	0.033316	1	0.033316	2.090000	0.243800
AD	0.000002	1	0.000002	0.000000	0.991700
BD	0.013933	1	0.013933	0.880000	0.418500
CD	0.004514	1	0.004514	0.280000	0.631300
Blocs	0.315568	3	0.105189	6.610000	0.077600
Total error	0.047754	3	0.015918		
Total (corr.)	2.68976	15			

R-square = 98.2246 percent (s)
Mean absolute error = 0.0448153

Analysis of Variance for Yield

Source	Sum of Square	DDL	Quadratic Mean	F Repor	Proba
A:Ratio	21.285	1	21.2855	0.070	0.802
B:Concentration	530.570	1	530.570	1.860	0.266
C:pH	3862.340	1	3862.340	13.540	0.0350
D:Time	140.7460	1	140.7460	0.490	0.5330
AB	496.5810	1	496.5810	1.740	0.2790
AC	1097.270	1	1097.270	3.850	0.1450
AD	117.0330	1	117.0330	0.410	0.5670
BC+bloc	527.290	1	527.2900	1.850	0.2670
BD	559.2160	1	559.2160	1.960	0.2560
CD	17.203500	1	17.20350	0.060	0.8220
Blocs	325.0240	2	162.5120	0.570	0.6170
Total error	855.4550	3	285.1520		
Total (corr.)	8952.970	15			

R-square = 90.445 percent (s)
Mean absolute error = 6.25284

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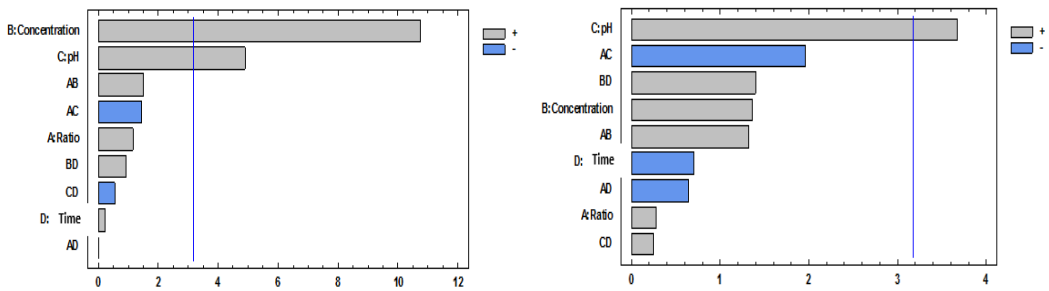
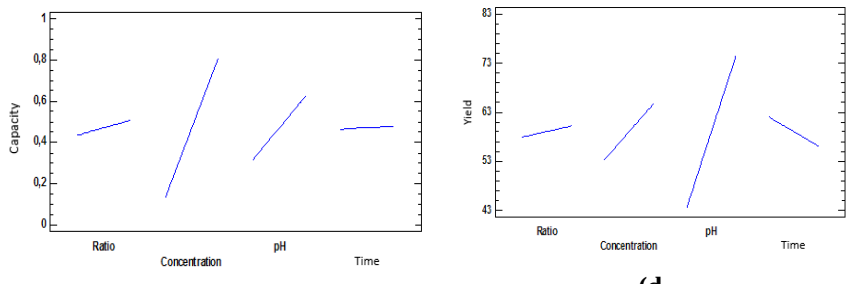
Study of the Effect of Factors and their Interactions

The Pareto chart **(Figure 4)** ranks the effects from the largest absolute value to the smallest absolute value. When the effect has a value greater than the threshold probability value, it is insignificant. The probabilities of the different effects are given in **Table 5**. For capacity, the effect of pH and dye concentration are the two effects that are significant. For yield, the effect of pH is the only significant effect. The interactions AB (interaction between ratio and concentration), BD (interaction between concentration and time), and AD (interaction between ratio and time) are not significant but they influence the capacity positively, while the interactions AC (interaction between ratio and pH) and CD (interaction between pH and time) influence the capacity negatively. However, for the yield, the interactions AB, BD, and CD are not significant but they also contribute positively on the dye removal yield while the interactions AC and AD influence the yield negatively (**Figure 6**). The effect of the ratio of the different adsorbents and the effect of the time of the treatment process are not significant for both responses (**Figure 5**).



(a) **(b**

Figure 4. Pareto Diagram of Capacity (a) and Yield (b)



(c

Figure 3. Graph of Direct Effects of Capacity (c) and Efficiency (d)

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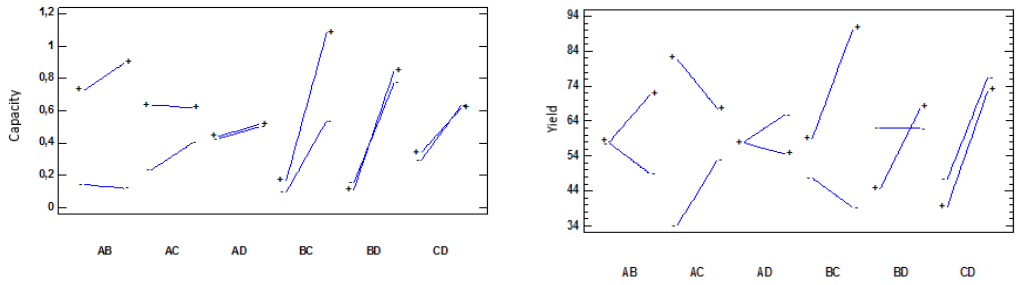

(e) **(f)**

Figure 6. Diagram of Interactions between Capacity (e) and Yield (f)

Desirability

The desirability function simultaneously determines the optimal parameters of the input variables that can determine the optimal performance levels for one or more responses. It consists of converting each response (yi) into a desirability function (di) varying between $0 \leq di \leq 1$. The value 0 is assigned when the factors lead to an unacceptable response. The value 1 is assigned when the response represents the maximum performance desired by the factors (Mourabet, El Rhilassi, El Boujaady, Bennani-Ziatni & Taitai, 2017).

$$D = (d_1 * d_2 * \ldots\ldots\ldots d_n)^{1/n} \quad (7)$$

n: The number of responses in the measure

The desirability for each pair of factors is given in **Table 6**. Based on the observed responses, the best results were obtained for trial 2 and based on the responses predicted by the fitted model, the best results were obtained for trial 4. The maximum uptake capacity predicted by the model is 1.14105 mg/g under the following optimum conditions: at the ratio=19, concentration =100 mg/L, pH= 9, and time=150 min. The confirmation test showed an adsorption capacity of 1.1028 mg/g under the same conditions. The optimal yield predicted by the model is 98.55% under the following optimal conditions: ratio=4, concentration =100 mg/L, pH= 9, and time =150 min. The confirmation test showed a removal efficiency of 97.09% under the same conditions.

Table 5. Capacity and Performance Desirability

	Observed	***Planned***	***Observed***	***Planned***	***Observed***	***Planned***
Essay	***Capacity***	***Capacity***	***Yield***	***Yield***	***Desirability***	***Desirability***
1	0.109	0.102	43.750	46.426	0.189	0.198
2	1.191	1.135	95.341	82.835	1.000	0.886
3	0.071	0.161	28.409	34.324	0.068	0.150

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4	1.125	1.098	90.000	93.915	0.935	0.952
5	0.383	0.390	30.659	27.983	0.164	0.116
6	0.131	0.187	52.500	65.006	0.244	0.336
7	0.846	0.756	67.727	61.812	0.662	0.583
8	0.196	0.223	78.636	74.722	0.396	0.400
9	0.487	0.544	39.023	51.528	0.293	0.425
10	0.189	0.196	75.795	73.119	0.380	0.375
11	0.365	0.392	29.250	25.335	0.138	0.000
12	0.094	0.005	37.954	32.039	0.150	0.071
13	0.192	0.135	76.704	64.199	0.385	0.295
14	1031	1.024	82.500	85.176	0.844	0.860
15	0.082	0.055	32.727	36.642	0.109	0.122
16	1.051	1.141	84.114	90.028	0.863	0.941

Adsorption Kinetics

The representation of the linear equations of the first-order adsorption, second-order adsorption, intraparticle diffusion, and Elovich kinetic models is given in **Figure 7**. As shown in **Table 7,** the pseudo second order kinetics is the most adequate model to describe the phenomenon of adsorption of methylene blue on the composite material consisting of the mixture of titaniferous sand and attapulgite. The equilibrium adsorbed amount calculated from the pseudo-second order mathematical model is close to that obtained experimentally (Azoulay et al., 2020). The graphical representation of the intraparticle diffusion model does not pass through the origin. Therefore, this shows that the adsorption is controlled by a molecular diffusion film. These same results were found by Xiaoyu Chen, Song and Sun (2016).

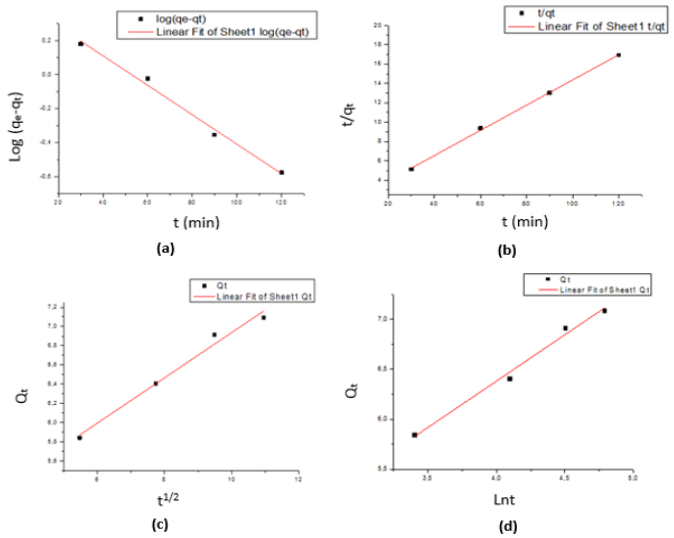

Figure 7. Kinetic Models: Pseudo-First Order (a), Pseudo-Second Order (b), Intraparticle Diffusion *(c)*, Elovich Equation (d)

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Table 6. Kinetic Model Parameters for MB Adsorption on the Mixture of Adsorbents Thermodynamic Study

Linear Equations	Parameters	Titaniferous sand/Attapulgite
Linear equation of pseudo-first order kinetic $\log(q_e-q_t) = -K_1+\log q_e$ (8) (Xi Chen et al., 2020; Mekatel et al., 2015)	R^2	0.987
	K_1 (mn^{-1})	0.008
	q_e (cal) (mg/g)	1.577
Linear equation of pseudo-second order kinetic $\frac{t}{q_t}=\frac{1}{K_2 q_e^2}+\frac{1}{q_e}t$ (9) (Bonetto et al., 2015; Salehi et al., 2020)	K_2 ($g.mg^{-1}.mn^{-1}$)	0.012
	R^2	0.998
	q_e (cal) (mg/g)	7.686
	q_e (exp) (mg/g)	7.356
Elovich equation $Q_t=\frac{1}{b}\ln(ab)+\frac{1}{b}\ln t$ (10) (Xiaoyu Chen et al., 2016)	R^2	0.985
	a ($mg.g^{-1}.mn^{-1}$)	16.560
	b ($g.mg^{-1}$)	1.078
Intraparticle diffusion $Q_t=K_d t^{1/2}+C$ (11) (Xiaoyu Chen et al., 2016; Jayasantha Kumari et al., 2017).	R^2	0.975
	K_d ($mg.g^{-1}.mn^{-0,5}$)	0.235
	C	4.580

The study of methylene blue removal efficiency as a function of temperature was carried out between 303K and 333K. This variation is given in **Figure 8i**. The adsorption of methylene blue decreases with increasing temperature. This indicates that the adsorption of methylene blue is favored at low temperatures. The variation of the free energy of the adsorption process is related to the equilibrium constant K_d by the following relation:

$$\Delta G^0=-RT\ln K_d \quad \text{(Kavak, 2009; Saravanan et al., 2020)} \qquad \textbf{(12)}$$

$$\ln K_d=\frac{\Delta S^0}{R}-\frac{\Delta H^0}{RT} \qquad \textbf{(13)}$$

$$K_d=\frac{q_e}{c_e} \qquad \textbf{(14)}$$

Where:
R: Constant of perfect gases,
T: Absolute temperature of the system in (K),
K_d: Adsorption equilibrium constant,
q_e: The equilibrium adsorbed amount (mg/g),
Ce: The equilibrium concentration (mg/L).

 ISSN: 1857-7881 (Print) e - ISSN 1857-7431

The graphical representation of $\ln K_d$ as a function of 1/T is a linear line whose slope is $-\Delta H^0/R$ and the intercept $\Delta S^0/R$ (**Figure 8j**). The different thermodynamic parameters are given in **Table 8**. The negative value of the enthalpy ΔH^0 shows that the adsorption reaction of methylene blue on the support is exothermic. In addition, the negative value of the entropy ΔS^0 corresponds to a decrease in the degree of disorder of the adsorbing particles. The positive values of the free energy ΔG^0 at 303 K, 313K, 323K, and 333K indicate that the adsorption reaction is non-spontaneous.

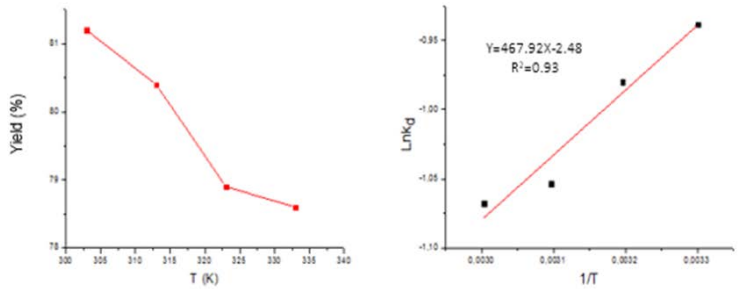

Figure 8. Variation of the Yield as a Function of the Temperature Evolution (i) and the Van't Hoff Curve (j)

Table 8.Thermodynamic Parameters of Methylene Blue Adsorption on the Composite Material

Température (K)	K_d	ΔGº (kJ/mol)	ΔHº (kJ/mol)	ΔSº (kJ/mol K)
303	0.391	2363.720		
313	0.375	2550.170		
323	0.348	2829.680		
333	0.343	2956.370	-3890.270	-20.640

Conclusion

In this study, a mixture of natural adsorbents was used for efficient removal of MB. The efficiency of the composite material was significantly influenced by the pH of the solution and the initial concentration of MB. Full factorial design methodology involving the design of a screening design was used to investigate the influence of the four selected independent variables and to determine the optimal adsorption conditions. The study of the direct effects of the factors show that the percentage removal of the MB molecule increases by increasing the initial dye concentration and pH. The optimized values, at which the maximum removal rate (98.55%) was achieved, are obtained at ratio

4, initial MB concentration (100 mg.L^{-1}), pH=9, and time 150min. The kinetic data suggest that the adsorption process of MB on the composite material is governed by the pseudo-second order adsorption mechanism (R^2 = 0.998). The thermodynamic study showed that the adsorption process was non-spontaneous and exothermic in nature. Therefore, this mixture of adsorbents can be used as stable, environmentally friendly, and effective adsorbents for wastewater treatment.

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