

Modelling and Response Surface Optimisation of Methyl Violet Removal by a Mixture of Titaniferous Sand and Non-Activated Attapulgitite

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Abstract

In recent years, the discharge of dye-laden effluents from the textile industries into the aquatic environment has increased considerably. These industries are among the largest consumers of water. They generate huge amounts of pollutants from their huge discharge of toxic effluents and pose serious public health problems. So, this study focuses on the use of the mixture of titaniferous sand and attapulgitite for the removal of methyl violet by adsorption in discontinuous mode. The different adsorbents were characterized by X-ray fluorescence spectroscopy and their different physico-chemical properties such as pH, zero charge potential, bulk and absolute density, porosity and specific surface area were determined. The response surfaces, through the Box-Behnken model, were used to model and optimize the operating conditions. The different factors studied were the ratio of titaniferous sand and attapulgitite, the initial concentration of methyl violet and the pH. These vary between 1.25 and 8, 20 and 100 mg/L, 4 and 10 respectively. The results obtained after statistical analysis of the data show that the optimum mixture ratio is 2, the optimum concentration is 99.92 mg/L and the optimum pH is 9.88 corresponding to a maximum capacity of 5.52 mg/g and a maximum removal efficiency of 99.56%. The study of the effects of the different factors showed that the initial concentration of methyl violet and the pH significantly influence the adsorption capacity and the removal efficiency of the dye.

Keywords

Adsorption, Surface Response, Titaniferous Sand, Attapulgitite, Methyl Violet

1. Introduction

The increase in domestic and industrial activities is the cause of water pollution. Indeed, industrial effluents often contain significant quantities of chemical pollutants, which may be organic, such as petroleum hydrocarbons and synthetic dyes [1] [2]. The latter, discharged into the aquatic environment in high concentrations, causes enormous problems such as increased toxicity and chemical oxygen demand [3] [4]. Treatment methods for toxic effluents are currently facing enormous difficulties due to the lack of universal treatment methods [5] [6]. Among these effluents, those containing organic pollutants pose enormous disposal difficulties. Several treatment methods have been developed in recent years to eliminate refractory chemical compounds [7] [8]. Among them are biological processes that are widely used in wastewater treatment plants, involving the metabolic activity of microorganisms to degrade the organic matter present in the water [9] [10]. However, these biological processes are ineffective when faced with a biorefractory organic load [11] [12]. Physico-chemical purification processes, on the other hand, only transfer the pollution and subsequently produce sludge that requires further treatment, thus increasing the cost [13] [14]. These major constraints have led to the search for alternative methods that are easier to implement and less costly. Among the various alternative techniques, adsorption is the most widely used method [15] [16]. Activated carbon is currently considered to be one of the most versatile adsorbents and many studies have shown its effectiveness, but its use remains limited due to the problem of regeneration and its high cost [17] [18]. To overcome these drawbacks, the search for other more economical and efficient natural adsorbents is important.

This work is part of a perspective of eliminating coloured organic molecules, in particular methyl violet, using a mixture of natural materials. The materials targeted in this study are titaniferous sand and attapulgite. The study of the effects of different parameters such as the ratio of the two materials, the concentration of the adsorbate and the pH as well as their interactions will be carried out through a Box-Behnken design.

2. Materials and Methods

2.1. Materials

2.1.1. Preparation of 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. The treatment was carried out by bringing it into contact with a sulphuric acid solution of concentration 4 mol/L and a volume of 100 mL. The mixture was stirred for 4 hours to ensure maximum contact with the sulphuric 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 flasks for later use. The other material, namely attapulgite, has not undergone any prior treatment and is used in a raw state in the work.

2.1.2. Adsorbat

In this study, methyl violet with the formula $C_{23}H_{26}N_3Cl$ was used as a pollutant. It is an organic compound belonging to the triphenylmethane family. It is a cationic dye mainly used as a dye in the textile and paint industry. Its structure is given in **Figure 1**.

2.2. Methods

2.2.1. pH Zero Charge Point (Isoelectric Point)

The pH_{pzc} was determined by introducing 0.2 g of adsorbent and 50 mL of a sodium chloride (0.1M) solution into 250 mL Erlenmeyer flasks. 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 stage are recorded. The meeting point of the two curves $pH_{final} = f(pH_{initial})$ and $pH_{final} = pH_{initial}$ gives the isoelectric point [17].

2.2.2. Determination of the Nature of the Adsorbent

The acidic or basic nature of the adsorbent was determined by contacting 1 g of adsorbent with 100 mL of distilled water. The mixture was stirred for 1 h at room temperature and the suspension was filtered to measure the pH of the final solution. This value gives an idea of the acid or basic nature of the adsorbent [19].

2.2.3. Determination of the Specific Surface

The specific surface area of the adsorbents was estimated using the Sear's method. This consists of introducing 0.5 g of adsorbent into a previously prepared salt solution (10 g of NaCl in 50 mL of distilled water) and adjusting the pH to a value of 3 using hydrochloric acid of 0.1N concentration. The reaction mixture is then measured with 0.1N NaOH. The volume V of NaOH to be poured in to raise the pH from 3 to 9 allows the value of the specific surface of the adsorbents to be estimated [20]. It is deduced from the following relationship:

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

2.2.4. Absolute and Bulk Density and Porosity

To determine the absolute density, a 1 litre graduated cylinder was used and filled with a volume V_1 of water. A dry mass of adsorbent M_{ads} is introduced into the test tube, taking care to remove all air bubbles. The new volume V_2 obtained is read. The absolute density is estimated using Equation (2).

$$\rho_{abs} = \frac{M_{ads}}{V_2 - V_1} \quad (2)$$

For the bulk density, a test tube of volume V is filled completely with a dry mass M_{ads} of adsorbent. Thus, the bulk density of the adsorbent was calculated through Equation (3).

$$\rho_{app} = \frac{M_{ads}}{V} \quad (3)$$

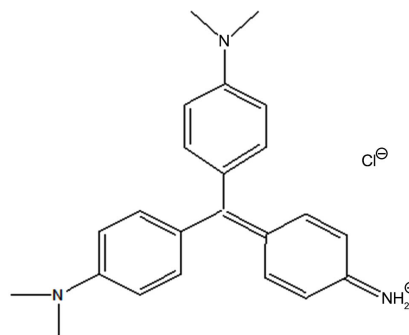


Figure 1. Chemical structure of methyl violet.

The porosity of the adsorbents is deduced from Equations (2) and (3). It is given by:

$$n = 1 - \frac{\rho_{app}}{\rho_{abs}} \quad (4)$$

2.2.5. Adsorption in Batch Mode

The study of the adsorption of methyl violet by the composite material consisting of titaniferous sand and attapulgite is carried out using a response surface design. The design chosen in this study is a Box-Behnken design with 3 factors. The stirring speed, contact time and particle size are kept constant at 750 rpm, 90 min and <100 μm respectively. The mixtures were stirred in batch reactors using 250 mL Erlenmeyer flasks. The ratio of the two adsorbents, the initial concentration of the dye and the pH varied between 1.25 and 8, 20 and 100 mg/L, 4 and 10 respectively. The pH of the methyl violet solution is adjusted using HCl (0.1N) and NaOH (0.1N). When the set time for adsorption is reached, the reaction is stopped and the suspension is centrifuged at 600 rpm for 15 min to obtain a clean supernatant. The residual concentration of methyl violet is analyzed using a UV-visible spectrophotometer at 585 nm. The adsorption capacity and removal efficiency are given by Equation (5).

$$q_e = \frac{(C_i - C_f) * V}{m}, \quad r = \left(\frac{C_i - C_f}{C_i} \right) * 100 \quad (5)$$

where:

- C_i : is the initial concentration (mg/L);
- C_f : is the final concentration (mg/L);
- m : the total mass of the two adsorbents (g);
- V : the volume of the solution (mL).

2.2.6. Description of the Experimental Design

For the modelling of the adsorption process, a three-factor Box-Behnken design with five points in the centre was carried out using the Design expert 8 software. The default model is cubic with seventeen (17) repeated experiments. 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 chosen and is written as Equation (6).

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_{ii}^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} X_i X_j \quad (6)$$

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 .

The number of trials was determined using Equation (7).

$$N = 2k(k-1) + p \quad (7)$$

where:

N : the number of trials.

k : the number of parameters.

p : the number of points in the centre.

3. Results and Discussion

3.1. Physico-Chemical Parameters

The values of the different adsorbent parameters are summarized in **Table 1**.

These values obtained show on the one hand that titaniferous sand treated with sulphuric acid is very dense, somewhat acidic and has a relatively low specific surface area, whereas attapulgite is basic, less dense than titaniferous sand and has a higher specific surface area.

3.2. X-Ray Fluorescence Characterisation

The different values obtained during the characterisation of the titaniferous sand are summarized in **Table 2** and those for attapulgite in **Table 3**. **Figure 2** and **Figure 3** illustrate the fluorescence analyses performed.

Analysis of the titaniferous sand treated with sulphuric acid (**Table 2**) shows that titanium, iron and aluminium are the predominant elements which are present at concentrations of 300,000 ppm, 63423.27 ppm and 18676.65 ppm respectively. This confirms the presence of oxides such as titanium dioxide, iron oxide and alumina, which are essential elements in the adsorption of refractory organic and inorganic compounds. However, for attapulgite, the major elements are silicon and aluminium with concentrations of 408028.69 ppm and 24737.43 ppm respectively (**Table 3**). The literature has revealed a great importance given to these elements in the context of surface adsorption of organic compounds and heavy metals [20] [21].

3.3. Isoelectric Point: pH_{pzc}

The pH zero charge point is the pH value for which the net charge on the surface of the adsorbent is zero. The pH value $_{\text{pzc}}$ of titaniferous sand and attapulgite found is 8.75 (**Figure 4**). For pH values above pH_{pzc} the surface of the adsorbent will be negatively charged by deprotonation of the functional groups on the ad-

sorbent surface. 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. While for pH values below pH_{pzc} the surface of the support is positively charged, adsorption with anionic dyes is much more favoured. Similar results have been reported on the study of methylene blue adsorption on eucalyptus and palm bio-material depending on the particle size [22].

Table 1. Physico-chemical properties of adsorbents.

Physical properties	Titanic sand	Attapulgit
pH	6.4	8.21
pH_{pzc}	8.75	8.75
Absolute density (kg/m^3)	4054	1660
Bulk density (kg/m^3)	2500	455
Porosity (%)	38.33	72.5
External specific surface (m^2/g)	13.4	70.68

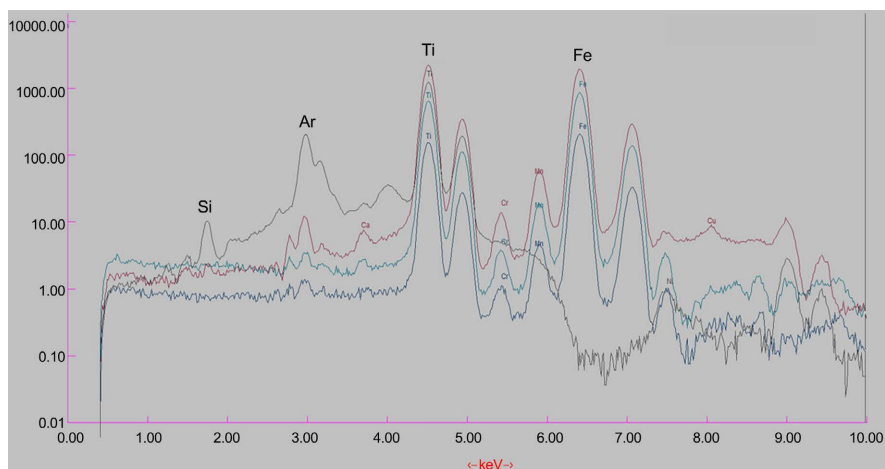


Figure 2. X-ray spectrum of activated titanium sand.

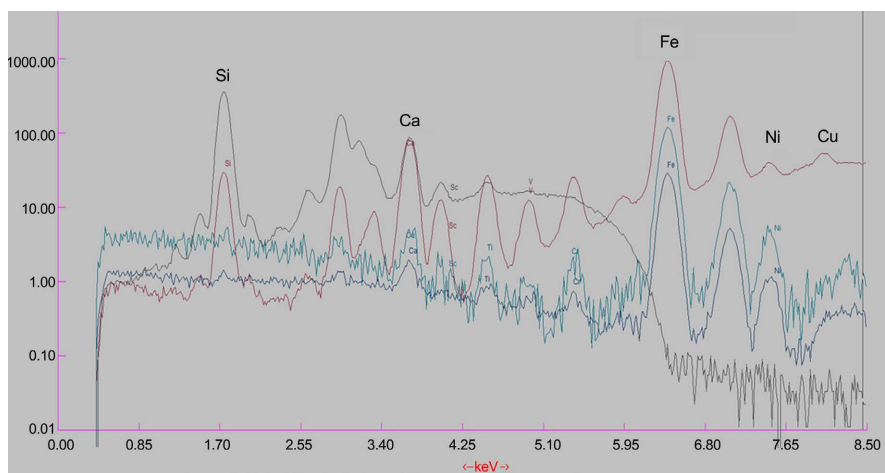


Figure 3. X-ray spectrum of non-activated attapulgite.

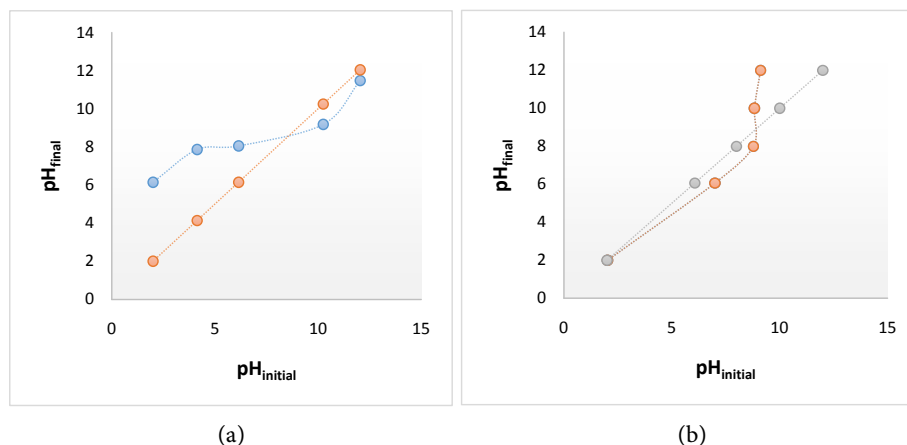


Figure 4. Isoelectric point of attapulgite (a) and titaniferous sand (b).

Table 2. Constituents of titanium sand.

Sample		Units	Ni	Al	Fe	Mn	Ca
Titaniferous sand + H ₂ SO ₄ (4M)		ppm	92.77	18676.65	229129.56	6573.29	2233.36
Si	Zn	V	Zr	Ti	P	Cr	As
63423.27	182	750.3	2421.75	3E+05	1130.31	1116.39	149.35
Se	S	Cl	Sn	Nb	Sr	Au	
15.94	544.35	167.69	28.71	430.57	6.04	105.8	

Table 3. Attapulgite constituents.

Sample	Units	Al	Fe	Mn	Ca				
Attapulgite	ppm	24737.43	17829.26	388.91	11952.21				
Si	Zn	V	Cd	K	Zr	Ti	P	Cr	As
408028.69	101	89.82	4.55	1105	53.61	1303	2159.72	514.58	7.3
Cl	Mo	Nb	Sr	Rb	Bi				
189	12.55	16.89	71.02	14.27	1.63				

3.4. Statistical Analysis Procedure

Table 4 shows the levels of the study factors. Their combination allowed us to obtain 17 experiences illustrated in **Table 5**.

3.5. Analysis of Variance

It then tests the statistical significance of each of the effects by comparing the root mean square to an estimate of the experimental error. Effects with probabilities below the threshold value $\alpha = 0.05$ are significantly different from zero at the 95% confidence interval. The coefficients of determination R^2 indicate that

Table 4. Levels of study factors.

Factor	Name	Units	Minimum	Maximum
<i>A</i>	Ratio		1.25	8.00
<i>B</i>	Concentration	mg/L	20.00	100.00
<i>C</i>	pH		4.00	10.00

Table 5. Experience matrix.

Run	<i>A</i> : Ratio	<i>B</i> : Concentration mg/L	<i>C</i> : pH	Capacity mg/g	Yield %
1	8.00	20.00	7.00	1.06	95.90
2	1.25	100.00	7.00	5.51	99.27
3	4.63	20.00	4.00	1.07	96.71
4	8.00	60.00	10.00	3.27	98.34
5	4.63	20.00	10.00	1.07	96.91
6	4.63	60.00	7.00	3.29	98.78
7	8.00	60.00	4.00	3.14	94.29
8	4.63	100.00	4.00	5.37	96.67
9	1.25	60.00	10.00	3.29	98.74
10	4.63	60.00	7.00	3.29	98.74
11	4.63	100.00	10.00	5.50	99.06
12	4.63	60.00	7.00	3.28	98.66
13	1.25	60.00	4.00	3.29	98.83
14	4.63	60.00	7.00	3.29	98.70
15	8.00	100.00	7.00	5.23	94.31
16	1.25	20.00	7.00	1.07	96.46
17	4.63	60.00	7.00	3.29	98.77

the cubic model used is very reliable in predicting the responses and also explains 100% of the variability in capacity (**Table 6**) and 99.98% of the variability in yield (**Table 7**). The actual and predicted values of the responses are shown in **Figure 5** for the capacity and **Figure 6** for the removal yield. The actual values are those obtained through experimentation while the predicted values are derived from the mathematical model. The adjusted coefficients of determination (R^2_{adjusted}) for both responses show a perfect correlation between the actual and predicted values. These results are in agreement with those found by [23].

The mathematical models that relate the two responses to the various factors involved in adsorption are given below.

$$\begin{aligned} \text{Capacity} = & +3.29 - 0.041 * A + 2.18 * B + 0.034 * C - 0.067 * AB \\ & + 0.035 * AC + 0.033 * B * C - 0.036 * A^2 - 0.032 * B^2 \\ & - 2.988E-003 * C^2 - 0.027 * A^2 * B \\ & - 6.282E-004 * A^2 * C - 0.029 * A * B^2 \end{aligned} \quad (8)$$

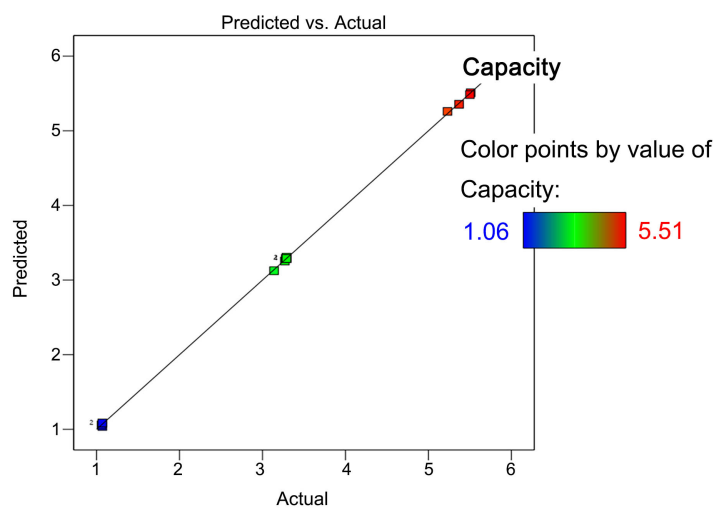
$$\begin{aligned} \text{Yield} = & +98.74 - 1.23 * A + 0.53 * B + 0.65 * C - 1.10 * A * B \\ & + 1.04 * A * C + 0.55 * B * C - 1.02 * A^2 - 1.23 * B^2 \\ & - 0.17 * C^2 - 0.23 * A^2 * B + 0.35 * A^2 * C - 0.15 * A * B^2 \end{aligned} \quad (9)$$

Table 6. Adsorption capacity anova.

	Sum of		Mean	F	p-value
Source	Squares	df	Square	Value	Prob > F
Model	37.66	12	3.14	1.194E+006	<0.0001 significant
<i>A</i> -Ratio	6.752E-003	1	6.752E-003	2567.91	<0.0001
<i>B</i> -Concentration	19.02	1	19.02	7.235E+006	<0.0001
<i>C</i> -pH	4.545E-003	1	4.545E-003	1728.67	<0.0001
<i>AB</i>	0.018	1	0.018	6917.58	<0.0001
<i>AC</i>	4.782E-003	1	4.782E-003	1818.86	<0.0001
<i>BC</i>	4.253E-003	1	4.253E-003	1617.59	<0.0001
<i>A</i> ²	5.592E-003	1	5.592E-003	2126.74	<0.0001
<i>B</i> ²	4.214E-003	1	4.214E-003	1602.74	<0.0001
<i>C</i> ²	3.758E-005	1	3.758E-005	14.29	0.0194
<i>ABC</i>	0.000	0			
<i>A</i> ² <i>B</i>	1.406E-003	1	1.406E-003	534.57	<0.0001
<i>A</i> ² <i>C</i>	7.892E-007	1	7.892E-007	0.30	0.6129
<i>AB</i> ²	1.735E-003	1	1.735E-003	659.86	<0.0001
<i>AC</i> ²	0.000	0			
<i>B</i> ² <i>C</i>	0.000	0			
<i>BC</i> ²	0.000	0			
<i>A</i> ³	0.000	0			
<i>B</i> ³	0.000	0			
<i>C</i> ³	0.000	0			
Pure Error	1.052E-005	4	2.629E-006		
Cor Total	37.66	16			
Std. Dev.	1.622E-003	R-Squared	1.0000		
Mean	3.26	Adj R-Squared	1.0000		
C.V. %	0.050	Pred R-Squared	N/A		
PRESS	N/A	Adeq Precision	3138.100		

Table 7. Anova of removal efficiency.

Source	Sum of Squares	df	Mean Square	F Value	p-value	
Model	42.81	12	3.57	1507.63	<0.0001	significant
<i>A</i> -Ratio	6.08	1	6.08	2567.91	<0.0001	
<i>B</i> -Concentration	1.12	1	1.12	475.23	<0.0001	
<i>C</i> -pH	1.67	1	1.67	706.29	<0.0001	
<i>AB</i>	4.86	1	4.86	2052.70	<0.0001	
<i>AC</i>	4.30	1	4.30	1818.86	<0.0001	
<i>BC</i>	1.20	1	1.20	506.33	<0.0001	
<i>A</i> ²	4.36	1	4.36	1842.36	<0.0001	
<i>B</i> ²	6.34	1	6.34	2678.17	<0.0001	
<i>C</i> ²	0.12	1	0.12	48.65	0.0022	
<i>ABC</i>	0.000	0				
<i>A</i> ² <i>B</i>	0.10	1	0.10	43.61	0.0027	
<i>A</i> ² <i>C</i>	0.24	1	0.24	101.20	0.0005	
<i>AB</i> ²	0.044	1	0.044	18.75	0.0124	
<i>AC</i> ²	0.000	0				
<i>BC</i> ²	0.000	0				
<i>BC</i> ²	0.000	0				
<i>A</i> ³	0.000	0				
<i>B</i> ³	0.000	0				
<i>C</i> ³	0.000	0				
Pure Error	9.466E-003	4		2.366E-003		
Cor Total	42.82	16				
Std. Dev.	0.049	R-Squared	0.9998			
Mean	97.60	Adj R-Squared	0.9991			
C.V. %	0.050	Pred R-Squared	N/A			
PRESS	N/A	Adeq Precision	117.241			

**Figure 5.** Design-expert plot: Predicted versus actual for adsorption capacity.

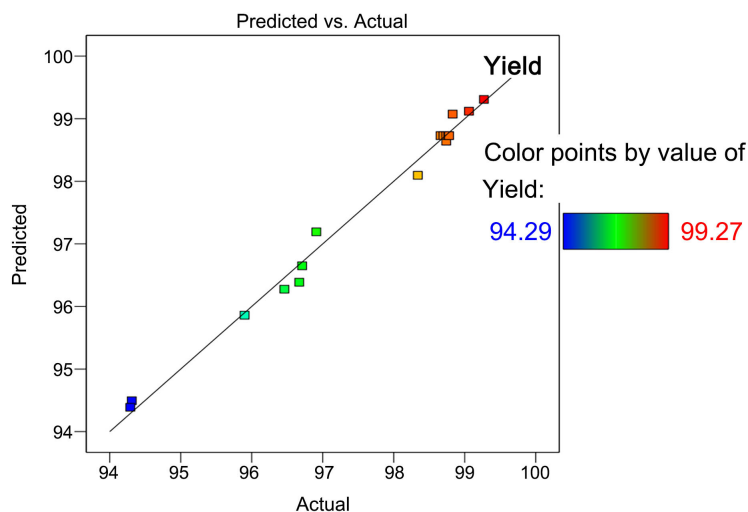


Figure 6. Design-expert plot: Predicted versus actual for removal efficiency.

3.6. Effects and Interactions of Key Factors

The response surface method was used to estimate the effect of the three factors on methyl violet removal. The effects of the different variables such as ratio, concentration and pH were investigated using the perturbation plot for the capacity and removal yield. This graph allows the effect of all factors on the responses at a particular point in the design space to be studied. From **Figure 7**, the effect of initial dye concentration ($p < 0.0001$) is more influential on the adsorption capacity compared to the effects of dye ratio and pH which are less pronounced. On the other hand, the effects of ratio ($p < 0.0001$), initial dye concentration ($p < 0.0001$) and pH ($p < 0.0001$) have a strong influence on the removal efficiency which is justified by the strong curvature of these different factors (**Figure 8**). However, for the study of the different types of interactions, a three-dimensional representation was used for two selected types of factors. The interactions AB (ratio and concentration), AC (ratio and pH) and BC (concentration and pH) all have a very significant influence on the adsorption capacity. The interactions between these different factors are shown in **Figure 9**. These same interactions, namely AB ($p < 0.0001$), AC ($p < 0.0001$) and BC ($p < 0.0001$), have a highly significant influence on the removal efficiency because their probabilities are lower than the threshold value $\alpha = 5\%$ (**Figure 10**).

3.7. Desirability

The corresponding desirability of the optimal torque is 1 (**Figure 11**). Based on the observed responses, the best results were obtained for test 2. The maximum adsorption capacity predicted by the model is 5.52 mg/g under the following optimal conditions: ratio of 2, concentration of 99.92 mg/L and at pH 9.88. The confirmation test showed an adsorption capacity of 5.4905 mg/g. The optimal yield predicted by the model is 99.56% under the same optimal conditions. The confirmation test showed a removal efficiency of 98.90%.

Factor Coding: Actual

Capacity (mg/g)

Actual Factors

A = 4.625

B = 60

C = 7

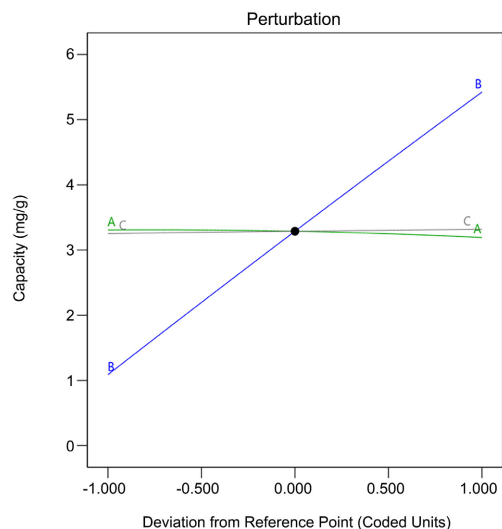


Figure 7. Capacity disturbance graphs.

Factor Coding: Actual

Yield (%)

Actual Factors

A = 4.625

B = 60

C = 7

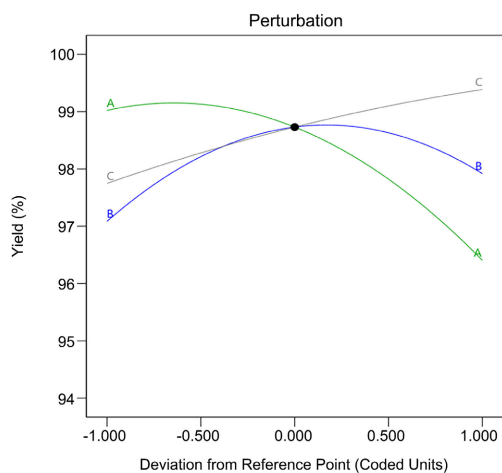


Figure 8. Removal efficiency disturbance graphs.

Factor Coding: Actual

Capacity (mg/g)

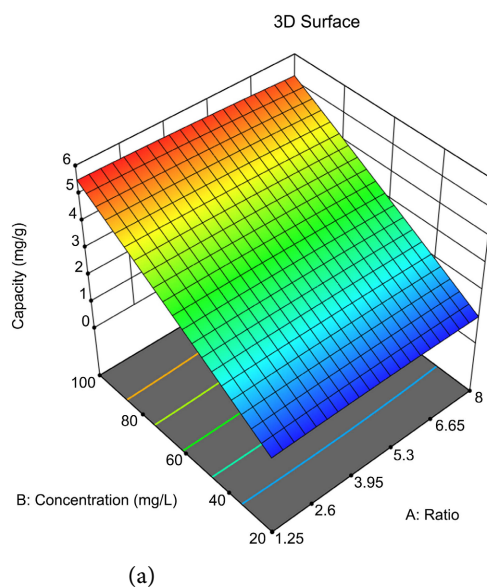
1.06 5.51

X1 = A

X2 = B

Actual Factor

C = 6.04



(a)

Factor Coding: Actual

Capacity (mg/g)

Design Points:

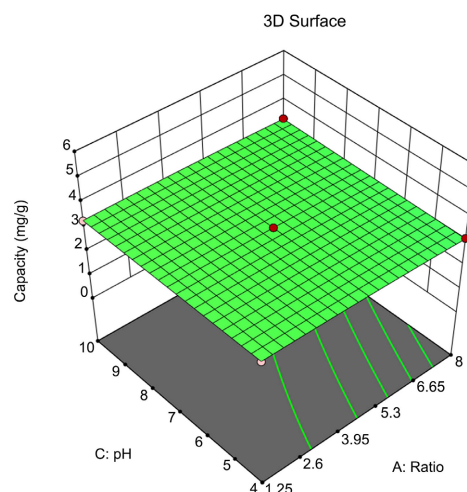
- Above Surface
- Below Surface
- 1.06 5.51

X1 = A

X2 = C

Actual Factor

B = 60



(b)

Factor Coding: Actual

Capacity (mg/g)

Design Points:

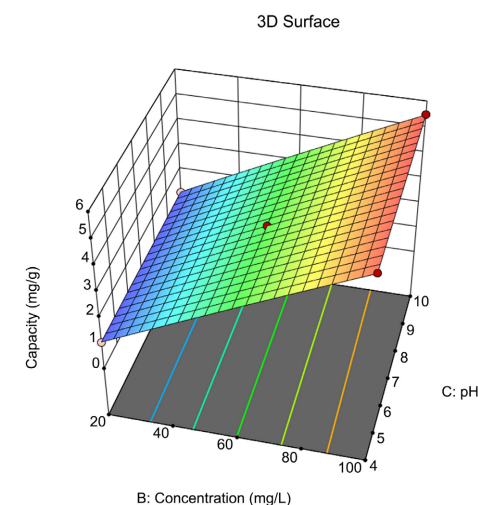
- Above Surface
- Below Surface
- 1.06 5.51

X1 = B

X2 = C

Actual Factor

A = 4.625



(c)

Figure 9. Three-dimensional plots of the interactions between ratio and concentration (a), ratio and pH (b), initial concentration and pH (c) on the capacity.

Factor Coding: Actual

Yield (%)

Design Points:

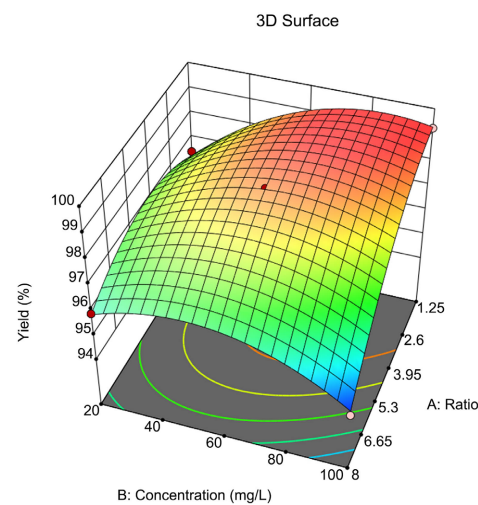
- Above Surface
- Below Surface
- 94.29 99.27

X1 = A

X2 = B

Actual Factor

C = 7



(a)

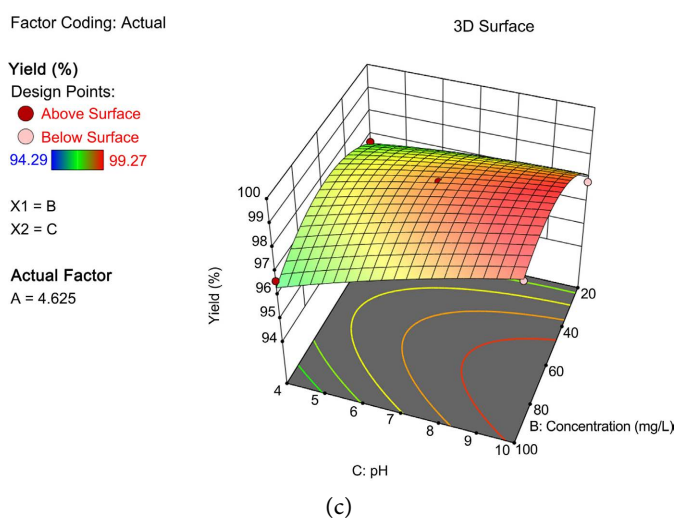
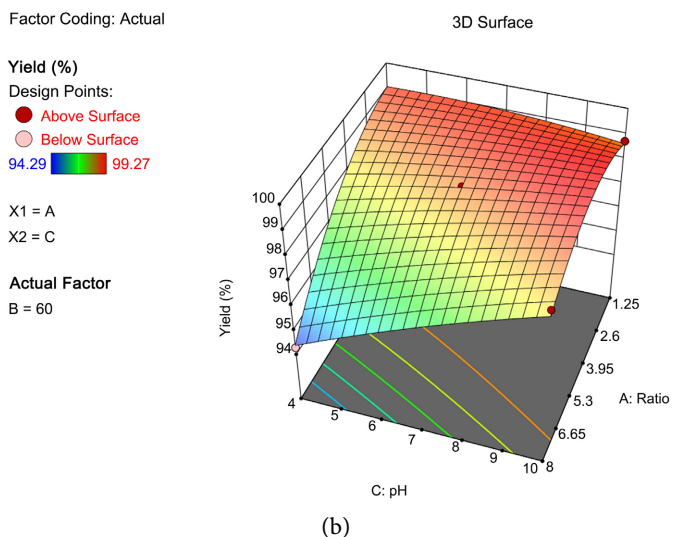


Figure 10. Three-dimensional plots of the interactions between ratio and concentration (a), ratio and pH (b), initial concentration and pH (c) on yield.

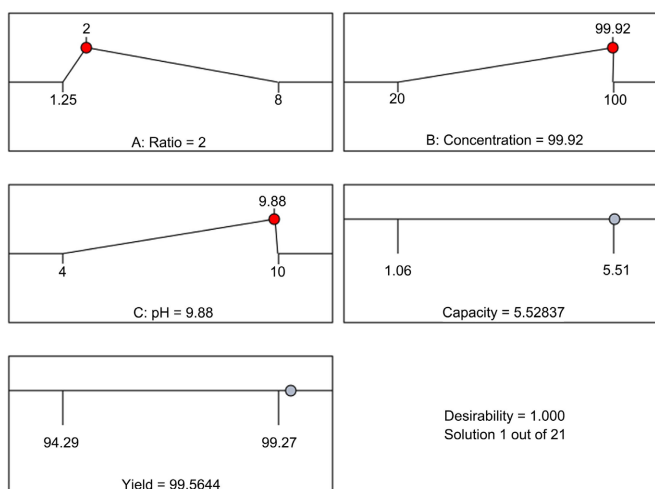


Figure 11. Desirability graph corresponding to the optimal couple: ratio = 2, concentration 99.92 mg/L and pH = 9.88.

4. Conclusion

The objective of this study was to investigate the removal of methyl violet in aqueous media using a mixture of titaniferous sand and attapulgit. The response surface method was used to optimize the operating conditions of the experiment. The analysis of the perturbation curves of the different parameters showed that the effect of the initial concentration of the dye and the initial pH was much more influential on the adsorption capacity while for the removal efficiency, these three factors notably the ratio, the initial concentration and the pH influence it significantly. The results of the optimization through desirability showed that the optimal conditions of the experiment are: 2 for the ratio, 99.92 mg/L for the initial concentration and 9.88 for the dye pH. The maximum adsorption capacity and the maximum removal efficiency of the dye corresponding to the optimal parameters are 5.52 mg/g and 99.56% respectively.

Data Availability

All data supporting the findings are adequately included within the article.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Abbaz, M., et al. (2014) Removal of Methylene Blue from Aqueous Solution Byadsorption onto the Sand Titaniferous. *Journal of Materials and Environmental Science*, **5**, 2418-2425.
- [2] Auta, M. and Hameed, B.H. (2011) Optimized Waste Tea Activated Carbon for Adsorption of Methylene Blue and Acid Blue 29 Dyes Using Response Surface Methodology. *Chemical Engineering Journal*, **175**, 233-243.
<https://doi.org/10.1016/j.cej.2011.09.100>
- [3] Cheruiyot, G.K., Wanyonyi, W.C., Kiplimo, J.J. and Maina, E.N. (2019) Adsorption of Toxic Crystal Violet Dye Using Coffee Husks: Equilibrium, Kinetics and Thermodynamics Study. *Scientific African*, **5**, e00116.
<https://doi.org/10.1016/j.sciaf.2019.e00116>
- [4] Bingöl, D., Veli, S., Zor, S. and Özdemir, U. (2012) Analysis of Adsorption of Reactive Azo Dye onto CuCl₂ Doped Polyaniline Using Box-Behnken Design Approach. *Synthetic Metals*, **162**, 1566-1571. <https://doi.org/10.1016/j.synthmet.2012.07.011>
- [5] Karaoğlu, M.H., Doğan, M. and Alkan, M. (2010) Kinetic Analysis of Reactive Blue 221 Adsorption on Kaolinite. *Desalination*, **256**, 154-165.
<https://doi.org/10.1016/j.desal.2010.01.021>
- [6] Singh, K.P., Gupta, S., Singh, A.K. and Sinha, S. (2011) Optimizing Adsorption of Crystal Violet Dye from Water by Magnetic Nanocomposite Using Response Surface Modeling Approach. *Journal of Hazardous Materials*, **186**, 1462-1473.
<https://doi.org/10.1016/j.jhazmat.2010.12.032>
- [7] Wazir, A.H., Waseem, I., Qureshi, I. and Manan, A. (2020) Saccharum Arundinaceum Leaves as a Versatile Biosorbent for Removal of Methylene Blue Dye from

- Wastewater. *Environmental Engineering Science*, **37**, 737-745.
<https://doi.org/10.1089/ees.2020.0075>
- [8] Pajak, M. and Dzieniszewska, A. (2020) Evaluation of the Metallurgical Dust Sorbent Efficacy in Reactive Blue 19 Dye Removal from Aqueous Solutions and Textile Wastewater. *Environmental Engineering Science*, **37**, 509-518.
<https://doi.org/10.1089/ees.2019.0410>
- [9] Hadjel, K.K., Benyoucef, M.C.R., Sciences, L., De, F., Technologie, D. and Boudiaf, M. (2005) Etude De L'Adsorption Du Bleu De Methylene Par Materiaux Aluminosilicates D'Origine Algerien Etude Cinetique Et Thermodynamique.
- [10] Karim, A.B., Mounir, B., Hachkar, M., Bakasse, M. and Yaacoubi, A. (2010) Removal of Basic Dye "Methylene Blue" in Aqueous Solution by Safi Clay. *Revue Des Sciences De L'Eau*, **23**, 375-388. <https://doi.org/10.7202/045099ar>
- [11] Banat, F., Al-asheh, S., Zomaout, R. and Qtaishat, B. (2015) Photodegradation of Methylene Blue Dye Using Bentonite as a Catalyst. *Desalination and Water Treatment*, **5**, 283-289.
- [12] Biophys, J.P.C., Aa, O. and Aj, O. (2014) Kinetic Study of Decolorization of Methylene Blue with Sodium Sulphite in Aqueous Media: Influence of Transition Metal Ions. *Journal of Physical Chemistry & Biophysics*, **4**, Article ID: 1000136.
<https://doi.org/10.4172/2161-0398.1000136>
- [13] Salem, I.A. and El-maazawi, M.S. (2000) Kinetics and Mechanism of Color Removal of Methylene Blue with Hydrogen Peroxide Catalyzed by Some Supported Alumina Surfaces. *Chemosphere*, **41**, 1173-1180.
[https://doi.org/10.1016/S0045-6535\(00\)00009-6](https://doi.org/10.1016/S0045-6535(00)00009-6)
- [14] Ozer, C., Imamoglu, M. and Turhan, Y. (2012) Removal of Methylene Blue from Aqueous Solutions Using Phosphoric Acid Activated Carbon Produced from Hazelnut Husks. *Toxicological & Environmental Chemistry*, **94**, 1283-1293.
<https://doi.org/10.1080/02772248.2012.707656>
- [15] Chen, X., et al. (2020) Efficient Adsorption of Methylene Blue by Xanthan Gum Derivative Modified Hydroxyapatite. *International Journal of Biological Macromolecules*, **151**, 1040-1048. <https://doi.org/10.1016/j.ijbiomac.2019.10.145>
- [16] Bonetto, L.R., Ferrarini, F., De Marco, C., Crespo, J.S., Guégan, R. and Giovanela, M. (2015) Removal of Methyl Violet 2B Dye from Aqueous Solution Using a Magnetic Composite as an Adsorbent. *Journal of Water Process Engineering*, **6**, 11-20.
<https://doi.org/10.1016/j.jwpe.2015.02.006>
- [17] El-Sayed, G.O. (2011) Removal of Methylene Blue and Crystal Violet from Aqueous Solutions by Palm Kernel Fiber. *Desalination*, **272**, 225-232.
<https://doi.org/10.1016/j.desal.2011.01.025>
- [18] Shakoor, S. and Nasar, A. (2018) Adsorptive Decontamination of Synthetic Wastewater Containing Crystal Violet Dye by Employing *Terminalia arjuna* Sawdust Waste. *Groundwater for Sustainable Development*, **7**, 30-38.
<https://doi.org/10.1016/j.gsd.2018.03.004>
- [19] Das, S. (2014) Characterization of Activated Carbon of Coconut Shell, Rice Husk and Karanja Oil Cake. Thesis, National Institute of Technology, Rourkela, No. 110, 1-42.
- [20] Bhattacharyya, K.G. and Sen Gupta, S. (2007) Adsorptive Accumulation of Cd(II), Co(II), Cu(II), Pb(II), and Ni(II) from Water on Montmorillonite: Influence of Acid Activation. *Journal of Colloid and Interface Science*, **310**, 411-424.
<https://doi.org/10.1016/j.jcis.2007.01.080>
- [21] Benguella, B. and Yacouta-Nour, A. (2009) Elimination des colorants acides en so-

lution aqueuse par la bentonite et le kaolin. *Comptes Rendus Chimie*, **12**, 762-771.
<https://doi.org/10.1016/j.crci.2008.11.008>

- [22] Abdallah, M., Hijazi, A., Hamieh, M., Alameh, M., Toufaily, J. and Rammal, H. (2016) Treatment of Industrial Wastewater Using a Natural and Biodegradable Adsorbent Based on Eucalyptus. *Journal of Materials and Environmental Science*, **7**, 4036-4048.
- [23] de Luna, M.D.G., Flores, E.D., Genuino, D.A.D., Futralan, C.M. and Wan, M.W. (2013) Adsorption of Eriochrome Black T (EBT) Dye Using Activated Carbon Prepared from Waste Rice Hulls-Optimization, Isotherm and Kinetic Studies. *Journal of the Taiwan Institute of Chemical Engineers*, **44**, 646-653.
<https://doi.org/10.1016/j.jtice.2013.01.010>