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## **Montmorillonite as Efficient Nanoclay for Removal of Aniline Blue Dye: Optimization, Isotherm and Kinetic Study**

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### **Abstract**

In this study, montmorillonite clay was used as the adsorbent for the removal of Aniline Blue dye, from aqueous solution by the batch adsorption technique under different conditions. The maximum removal of aniline blue dye for initial dye concentration 20 mg/L was more than 95% at optimum conditions (pH=4.5, contact time=30 min, and adsorbent dosage=2 g/L). The data of this study were fitted with Langmuir and Freundlich isotherms. Also, kinetic adsorption study showed that for initial dye concentration 50 mg/L, pseudo-second-order kinetic is more favorable. More than 90% removal for Aniline Blue dye showed that this adsorbent is an effective natural compound and also inexpensive for treatment processes. Hence, using this technique and process was recommended for dye pollutants removal from aqueous environments. High removal, simplicity and high adsorption capacity of adsorbent are the main advantages in this method.

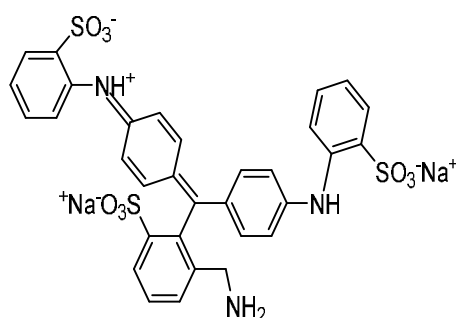
**Keywords:** Aniline Blue Dye, Adsorption kinetics, Equilibrium isotherm, Montmorillonite.

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## Introduction

Dyes are compounds that are widely used in textile, paper, plastic and cosmetic industries and are easily recognized as pollutants [1]. Many dyes and their breakdown products are toxic, carcinogenic and teratogenic for living organisms [2]. The presence of the dye in natural water systems inhibits sunlight diffusion into the water, consequently reducing the photosynthetic process of the aquatic plant. Hence, the remediation of the dye from wastewaters before discharge into the water environment is essential [3]. There is difficulty in removing dyes from the aqueous system using conventional methods such as precipitation, solvent extraction, membrane filtration, and biological. However, adsorption has been proven to be an excellent method of removing dyes from aqueous solutions because of its significant advantages like effective for any concentration, cheap, easy availability, most profitable, ease of operation and no sludge formation, over the conventional methods from the economic and environmental point of view [4,5]. Aniline blue (AB) dye (Figure 1) is toxic and carcinogenic. The different adsorbents have been employed by the scientist in an attempt to remove AB dye from aqueous solutions such as Kaolinite clay [6] Rice Husk Carbon [7] Prosopis Juliflora carbon [8]. Naturally occurring clays are bellowing to low-cost materials with good adsorption ability [9]. This ability comes from their high specific surface area, chemical and mechanical stability, layered structure and high cation exchange capacity [10]. Many reports showed that Montmorillonite (MMT) displayed a comparatively high-adsorption capacity for toxic dyes [11-14].

The present work aims to study a convenient and economical method for AB dye (Figure 1) removal from water by adsorption on MMT as low cost, eco-friendly and available adsorbent. The effects of initial AB dye concentration, contact time, pH and amount of adsorbent on AB dye removal have been evaluated.



**Figure 1.** The chemical structure of Aniline blue (AB) dye.

## Experimental

### *Chemicals and instruments*

All chemicals used were analytical grade and doubled distilled water was used throughout. Montmorillonite (MMT) clay was supplied from the F.F.C company in China. Aniline blue dye was purchased from Merck Germany. A stock solution of AB dye (1000 mg/L) was prepared by dissolving 0.50 g of Aniline blue dye in water and diluting to 500 mL in a volumetric flask. The AB dye concentration evaluation was carried out using a spectrophotometer UV–Vis model Lambda 35 (Perkin Elmer, American) at a wavelength of 601 nm. The pH measurements were carried out using pH meter model F-11 (HORIBA, Japan).

### *Method*

In the experiment, AB dye with a concentration of 20 mg/L and intended pH was prepared in a 50 mL volumetric flask, and then it was added to a 100 mL Erlenmeyer flask, containing 0.1 g of MMT. The Erlenmeyer flasks were placed on a shaker at 100 rpm, for 30 minutes. After filtration, the obtained solutions were analyzed, with a spectrophotometer at  $\lambda_{\max} = 601$  nm. The same procedure was done on blank without the presence of AB dye. The resulted adsorption was achieved through a calibration curve for AB dye in the concentration range of 0.5 to 25.0 mg/L. It was then changed to concentration and the percentage of dye removal was calculated from the equation (1):

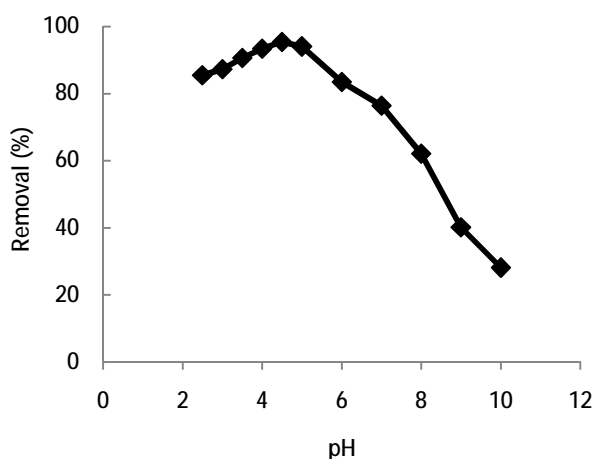
$$\text{Removal(\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

Where  $C_e$  and  $C_o$  are the equilibrium and initial concentrations of dye (mg/L).

## Result and discussion

### *Effect of pH*

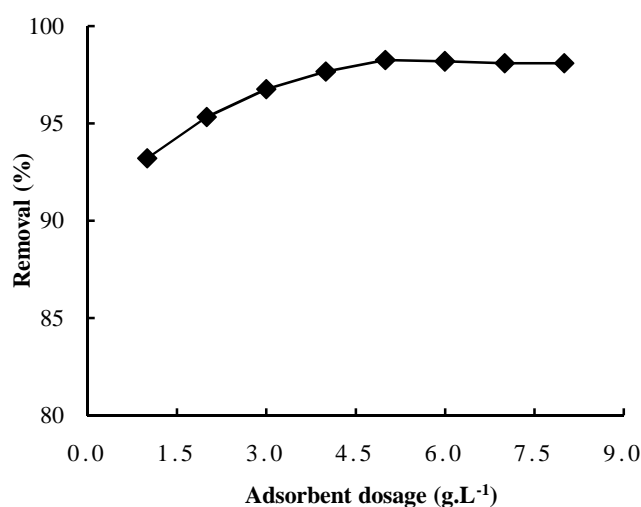
The solution pH was very effective in the adsorption process. The effect of pH on the removal of AB dye was studied over a pH range of 2.5-10.0. The dilute  $\text{HNO}_3$  and  $\text{NaOH}$  solutions were used to adjust the pH of the solutions. The removal was maxima in  $\text{pH}=4.5$  (Figure 2). The sulfonate ( $-\text{SO}_3^-$ ) and amine groups ( $-\text{NH}$ ) in AB dye were protonated completely in pH 4.5, thus the electrostatic interaction between negatively Montmorillonite and positively charged protonated AB dye was facilitated, and as a result, AB dye was removed from water samples.



**Figure 2.** Effect of pH on removal of AB dye (Experimental conditions: dye concentration=20 mg/L; dosage MMT=2 g/L; contact time= 30 min; stirring speed=100 rpm).

#### *Effect of adsorbent dose on dye removal*

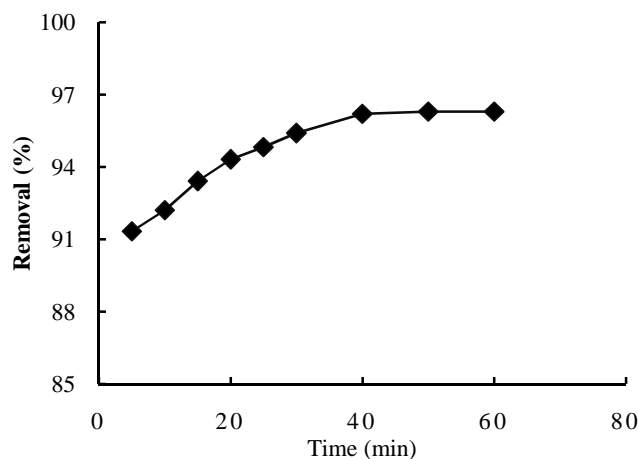
In order to achieve the minimum amount of adsorbent for the removal of AB dye, the adsorbent dose was optimized. The results showed (Figure 3) that an adsorbent dose of 6 g/L for a concentration of 20 mg/L can remove more than 98 % of the dye. It is well to mention that the adsorbent dose of 2 g/L can remove about 96 %. Therefore, an adsorbent dose of 2 g/L was selected for further experiments. Whenever the dosage of adsorbent gets increases, the efficiency of adsorbent also gradually increases; this is due to the increase in the number of available sites on the adsorbent surface.



**Figure 3:** Effect of adsorbent dosage on removal of AB dye (Experimental conditions: dye concentration= 20 mg/L; contact time= 30 min; stirring speed=100 rpm; pH = 4.5).

*Effect of contact time on dye removal*

The effect of contact time on dye sorption was carried out at a time interval 5-60 min (Figure 4). Removal of dye was increased by increasing contact time and reached equilibrium before 60 min although dye removal was very high at initial contact time. At contact time equal 5 min, 91 % of AB dye was removed. It can be concluded that MMT has a high capacity for the removal of AB dye. The contact time equal 30 min was selected as optimum time because removal was more than 95 %.



**Figure 4.** Effect of contact time on removal of AB dye (Experimental conditions: dye concentration=20 mg/L; dosage MMT=2 g/L; stirring speed=100 rpm; pH = 4.5).

*Effect of initial concentration on dye removal*

The effect of the initial dye concentration on the removal using the above optimum concentrations was investigated. The results showed that the optimization condition was applicable for concentrations 5-500 mg/L. This is a relatively large range (5-500 mg/L) and the percentage of removal in this range was significant.

*Interference study*

The effect of various ions as potential interference on the removal of AB dye was also investigated. Known concentrations of potential interfering ions were added to a solution containing 20 mg/L of AB dye and the solution was analyzed by the proposed method. Each of the ions in different concentrations was investigated. The results showed that  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Na^+$ ,  $Mg^{2+}$ ,  $CH_3COO^-$ ,  $Cd^{2+}$ ,  $K^+$ ,  $Cl^-$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Ca^{2+}$ ,  $Ba^{2+}$ , and  $Co^{2+}$  are tolerable up to 20 mg/L. The interference of some dyes was also studied. The results showed that some dyes such as Crystal violet, Congo Red, Rhodamine B, and Alizarin Red-S are tolerable up to 20 ppm. The tolerance levels of some metal ions and dyes are suitable for the removal of AB dye from the real sample.

### *Isotherms of Adsorption*

In this study, Langmuir [15] and Freundlich [16] isotherms were employed for the study of the adsorption of AB dye on MMT. The isotherms were achieved for an initial concentration of 30-350 mg/L in the previous optimization condition time 120 and a temperature of  $25 \pm 2$  °C. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. In order to study of Langmuir Isotherm, a plot of  $C_e/q_e$  versus  $C_e$  was drawn. The  $q_e$  is the adsorption capacity in equilibrium;  $C_e$  is the equilibrium concentration of dye. The Langmuir constants are presented in Table 1. To study Freundlich isotherm,  $\log q$  was plotted versus  $\log C_e$  and then data were presented in Table 1.

**Table 1.** Equilibrium constants for Langmuir and Freundlich Isotherms.

<b>Isotherm</b>	<b>b</b>	<b><math>q_m</math> (mg/g)</b>	<b>n</b>	<b><math>k_f</math>(<math>\text{mg}^{1-n} \text{L}^n / \text{g}</math>)</b>	<b><math>R^2</math></b>
Langmuir	-228.8	238.1	-	-	0.9664
Freundlich	-	-	1.43	12.11	0.9969

Both of the isotherms are well adapted with the adsorption of AB dye on MMT (Table 1). The coefficients of correlation were high ( $R^2 = 0.9664$  for Langmuir isotherm and  $R^2 = 0.9969$  for Freundlich isotherm) showing good linearity. This means that the adsorption of AB dye on MMT is both monolayer and reversible, and it also practically shows that adsorption develops appropriately. The maximum adsorption capacity for this adsorbent is very better than other adsorbents [7, 17, 18].

### *Kinetic modeling*

The kinetic models were used to predict the variation of adsorbed AB dye with time using MMT. The rate constants of chemical adsorption were determined using the equations of the pseudo-first-order and pseudo-second-order models. The pseudo-first order model is one of the most widely used procedures for the adsorption of a solute from the aqueous solution. The Pseudo-first order kinetic model of Lagergren is given as follows:

$$\ln(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

Where  $q_e$  and  $q_t$  are the amounts of dye adsorbed onto MMT (mg/g) at equilibrium and at time  $t$ , respectively and  $K_1$  ( $\text{min}^{-1}$ ) is first-order rate constant for adsorption. The rate constant,  $K_1$ , can be calculated from the plots of  $\log (q_e - q_t)$  versus  $t$ . Pseudo-second order kinetics may be expressed as the following equation:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2} q_e^2 \quad (6)$$

where  $K_2$  is the rate constant of the second-order adsorption (g/mg/min). The straight-line plots of  $t/q_t$  against  $t$  have been tested to obtain rate parameters [19]. The pseudo-first-order and pseudo-second-order kinetic models for AB dye removal by MMT were investigated using the above equations. The rate constants and correlation coefficients for both models are presented in Table 2. The correlation coefficients for the second-order kinetic model were higher than 0.99 indicating the applicability of this kinetic model of the adsorption process of dye on MMT. The results also indicate that the adsorption of dye on MMT and is not fitted to a first-order model.

**Table 2.** Kinetic parameters for the adsorption of concentration 50 mg/L AB dye onto MMT.

Pseudo-First-order equation				Pseudo-second-order equation			
$q_e(\text{Exp})$	$K_1(\text{min}^{-1})$	$q_e(\text{mg/g})$	$R^2$	$q_e(\text{Exp})$	$K_2(\text{min}^{-1})$	$q_e(\text{mg/g})$	$R^2$
6.31	0.046	47.19	0.9286	47.39	0.019	47.19	0.9995

### Comparison with literature

The performance of the proposed method has been compared with other adsorbents. As is seen in Table 3 the contact time, adsorbent dosage and  $q_{\text{max}}$  for the proposed method in comparison with other adsorbents are preferable and superior to the works of literature which show satisfactory removal performance for AB dye as compared to other reported adsorbents.

**Table 3.** comparison for the removal of AB dye by different adsorbents.

Adsorbent	Adsorbent dosage (g/L)	contact time (min)	$q_{\text{max}}$	Ref.
Aspergillus niger	2.7	24	17.58	[17]
Soy meal hull	0.70	1440	109.8	[18]
Rice Husk carbon	10	120	71.1	[7]
Nano clay	2	30	238.1	Present study

### Conclusion

Nanoclay Montmorillonite is environmentally friendly and cheap material that could be used as a potential adsorbent for the removal of aniline blue dye from aqueous solution and polluted water. The MMT is a very effective adsorbent for the removal of aniline blue dye from aqueous solution because it removed dye quantitative (more than %90) at very short time (5 min) and very low dose (0.1 mg/g). It can be concluded from this study that montmorillonite is a good adsorbent for compounds having amine groups because the amine groups are protonated in acidic medium and have good interaction with montmorillonite. The most prominent advantages of this method include

the use of environmentally friendly absorbent, low cost, high efficiency of adsorbent and short process times.

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