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Adsorption of methylene blue from aqueous solutions using natural clay

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Abstract
In this study, natural clay was used as an adsorbent for the removal of methylene blue from an aqueous solution. The influence of the initial dye concentration, contact time, pH temperature, and dosage of biosorbent was investigated in batch experiments. This clay was characterized according to the following technique: scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX).

Keyword: Natural clay, dye, metylene blue, adsorption.

1. Introduction
Textile industry plays an important role in the economic development in non-oil and gas sector of many developing countries. Apart from its significant role, however, textile industry also creates serious problems to environment, particularly disposal of colored dye wastewater. Dye contaminated wastewater contains colored compound from residues of dyes and various chemical additives. Reactive dyes are extensively used in dyeing processes for coloring yarn or fabric due to their high reactivity and good color resilience [1]. However, they are harmful to aquatic environment especially for aquatic livings if they discharge via inadequate treatment [2].
Dye molecules present a considerable structural diversity, allowing them to reclassify by several manners: either according to their chemical structures or their applications with suitable type of fiber. They can also be classified with respect to their solubility in water [3] .Cationic dyes are synthetic pigments, commonly known as basic dyes and are widely used in textile industry. Basic dyes are used in several processes such as acrylic, nylon, silk, and wool dyeing [4]. Basic Yellow 2 (BY2), a yellow dye, (4, 4 dimethylaminobenzophenonimide) and its hydrochloride salt are used in the coloring of paper, textiles and leather. Acid, basic, reac-tive and direct dyes are soluble dyes, while dispersed pigments and oxidized dyes are insoluble in water [5]. Cationic dyes have been intercalated into clay interlayers and various chromatic effects based on the intercalation reactions have been induced by the formation of aggregates through intermolecular interactions such as static interactions with the clay surfaces or by protonation [6].
The removal of low levels of such compound is difficult. Several treatment methods have been developed for decontamination purposes including coagulation, chemical oxidation, membrane separation, electrochemical processes, and adsorption techniques. The last one has been recognised as a cost-effective process to remove dyes from aqueous solution and it has been tested with many adsorbents; activated carbon has been the most commonly used adsorbent because of its high adsorption capacity. However, the operating cost of activated carbon adsorption is high, though some strategies to reduce costs were also proposed [7, 8, 9, 10, 11, and 12]. Problems of regeneration and difficulty in separation from the wastewater after use are the two major concerns of using this material. Other commonly-used adsorbents are chitin [8], fly ash [13], silica gels [14], peat [15, 16], and more recently, heteropoly blue-intercalated layered double hydroxide [17]. A wide compilation of the different considered strategies can be found in a review of [18]. However, the amount of adsorbed dye by these methods is not very high. To improve the efficiency of the adsorption processes, it is essential to develop more effective and cheaper adsorbents.
Clays have a high adsorption capacity due to their lamellar structure which provides high specific surface areas [19] and possibility to adsorb ions and polar organic molecules on particle external site and in interlayer positions [20,21]. Adsorption and desorption of organic molecules in the clays are primarily controlled by surface properties of the clay and the chemical properties of the molecules [22]. Natural clay exhibits a negative

charge of structure which allows it to adsorb positively charged dyes but induces a low adsorption capacity for anionic dyes. Thus literature mostly reports on cationic dye adsorption by clay and very few studies have been devoted to anionic dye adsorption onto natural clay [23, 24, 25,26]or treated clay see e.g., [27, 28].
The present study undertaken to evaluate the efficiency of natural clay as an adsorbent for the removal of MB dye from aqueous solutions.
The effect of adsorption parameters such as initial dye concentration, temperature, pH, adsorbent dose, contact time has been studied.

2. Materials and methods

2.1 Preparation of adsorbents

The clay sample was treated before using in the experiments as follows: a distilled water suspension of the clay was dispersed for approximately 4 h and then cleaned several times with de-ionized water.
The fine fraction of clay was collected by repeated dispersion, sedimentation and siphoning techniques. The solid sample was dried at 105 °C for 24 h, ground sieved by 140 μm sieve.

2.1.1 Dye and chemicals

All chemicals used were of analytical reagent grade and supplied by Merck
Germany. Stock solutions of the test reagents were made by dissolving Methylene Blue {3, 9-bis dimethyl-aminophenazo thionium chloride}, in doubly distilled water. The structure of this dye is shown in *Fig. 1*.

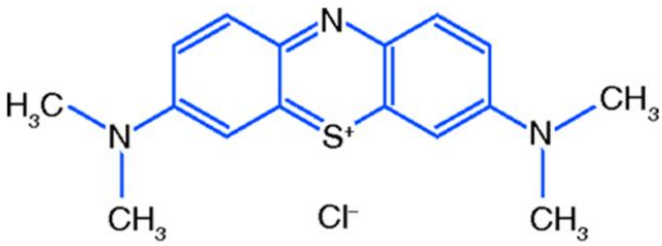


Figure 1*:* The structure of methylene blue

2.2 Surface characterisation

Surface morphology and chemical constitution of both the adsorbent were studied by Scanning electron Microscopy (SEM) (model: FEI Quanta 450FEG) and Energy dispersive X-ray spectroscopy (EDX).

2.3 Adsorption studies

Adsorption studies were performed by the batch technique to obtain rate and equilibrium data. Various Methylene Blue solutions with different initial concentrations, in the range of 100 - 900 mg L−1, were prepared by diluting stock dye solution (1g L^{-1}). Equilibrium experiments, to determine the adsorption capacity of clay, were conducted using 125mL centrifuge tubes where 0.1 g of clay and 50 ml of the above dye solution were added and shaken for 2 h at 2 5 °C. Absorbance of 10 mg/l was determined at different wavelengths using Equiptronics single beam u.v. visible spectrophotometer to obtained a plot of absorbance verses wavelength.
The wavelength corresponding to the maximum absorbance (λmax = 665nm) as determined from the plot, was noted and this wavelength was used for measuring the absorbance of residual concentration of MB. PH of solutions were adjusted using 1M HCl and 1M NaOH.
Equiptronics pH- meter was used to adjust the pH of MB solution as per the requirement. By conducting batch mode experimental model experimental studies the efficiency of the adsorbent was evaluated Specific amount of adsorbent were shaken in 50ml. aqueous solution of dye of varying concentration for different time period at natural pH and temperature. At the end of pre-determined time intervals, adsorbent was removed by centrifugation at 10000 rpm and supernatant was analysed spectrophotometrically for the residual concentration of MB, at 665nm was wavelenght. The value of amount of dye adsorbed calculated using following relationships:
Amount adsorbed = (C_i-C_f) m/v
Where, C_i = Initial concentration (mg/l).
C_f = Final concentration (mg/l).
m = Mass of adsorbent (g).
V is the volume of dye solution (ml).

2.3.1 Effect of initial dye concentration

Initial MB concentration of 100,200, 300 ,400,500,600,700,800,900were used in conjunction with adsorbent dose 0.1g , contact time 120min, Ph solution , agitation speed= 60rpm, temperature 25°C.

2.3.2 Effect of pH

Initial pH of MB solutions were adjusted to 2,5 ,7 ,10,11for 100mg/l concentration .contact time 120min , adsorbent 0.1g speed 600rpm , temperature 25°C.

2.3.3 Effect of temperature

10°C, 20°C, 30°C, 40°Cand 50 °C temperature were used in conjunction with 100mg/l the MB concentration contact time 120min, adsorbent 0.1g, agitation speed 600rpm.

2.3.4 Effect of adsorbent dose

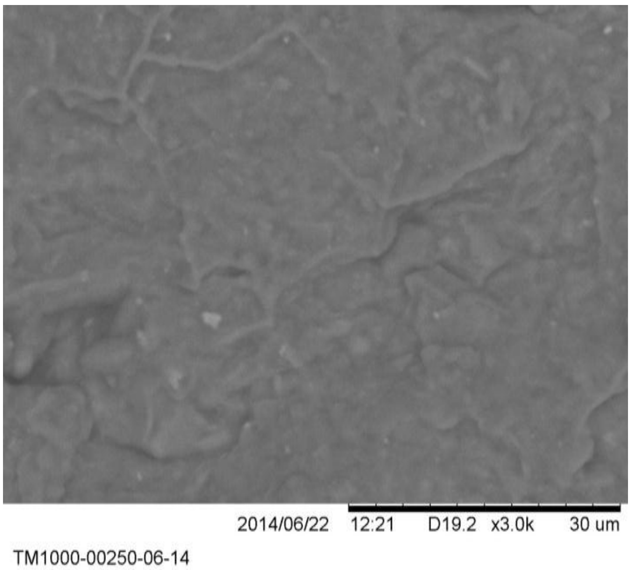
Initial of adsorbent dose 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 g. Contact time 120 min, agitation speed 600 rpm, temperature 25°C.

3. Results and discussion

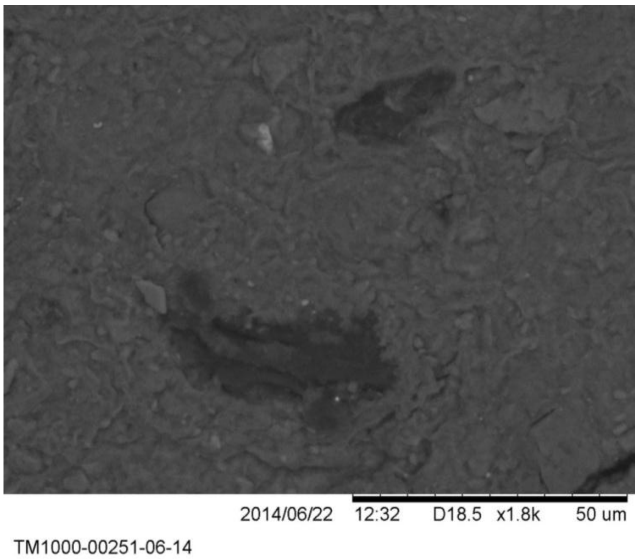
3.1 Characterization of adsorbent

3.1.1 Scanning electron microscopy

Surface morphology of adsorbent was analyzed by scanning electron microscopy.
The surface of natural clay was analyzed by scanning Electron Microscopy (SEM) before and after adsorption of BM molecules from aqueous solution.
Figure1a. Shows the SEM micrographe of clay before adsorption and figure 1.b shows the SEM micrograph of clay surface after adsorption of MB.
SEM images show different structural features with uneven surface (figure1) .After adsorption the adsorbed molecules remain as aggregates on the clay surface as show in figure [29].



SEM micrograph of clay before adsorption
(a)



SEM micrograph of clay after adsorption
(b)

Figure 1: (a), (b): scanning electron micrographs of natural clay.

3.1.2 Energy dispersive x-ray spectroscopy (EDX).

The chemical constitution of the adsorbent was studied by EDX .EDX spectrum is shown in figure 2 elemental constitution is represented in table 1.

Tableau 1: Characterization *of natural clay using EDX.*

Elément	*% massique*
Aluminium	*23.4*
Silicium	*61.0*
Potassium	*15.6*

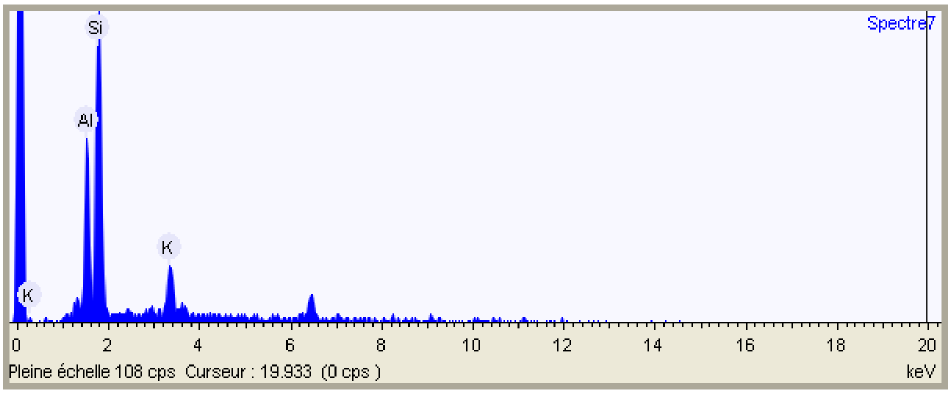


Figure 2: *EDX Spectrum of natural clay.*

3.2 Effect of contact time

For the evaluation of adsorption as a function of time, amount of dye adsorbed per gram (Q_e).
The resultat showed that the rate of adsorbed MB onto natural clay was initially rapid and then it slowed down gradually until equilibrium was attained as figure 3 illustrate, uptake attained equilibrium at 20 min.

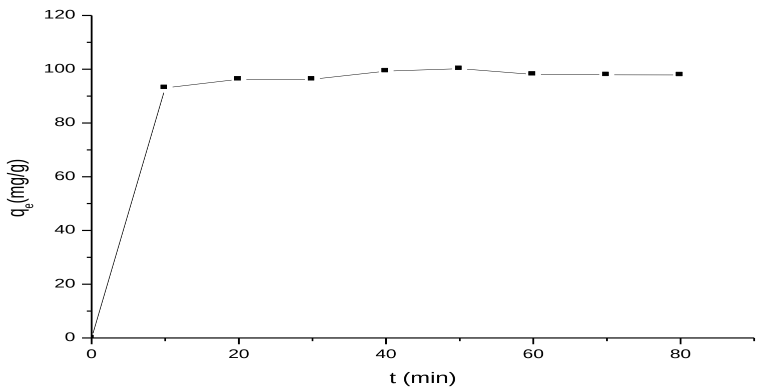


Figure 3: Effect of contact time on BM adsorption on natural (Temperature = 25°C, rotations per minute=600rpm, Concentration of dye= 100 mg/L, equilibrium time = 2hr).

3.3 Effect of pH

PH is one of the most important factors in controlling the adsorption process. To evaluate the effect of pH on the adsorption process, the adsorption of the dye with pH value from 2-11 were studied keeping all other variables constant. It was observed after analyzing Fig 4 for methylene blue the amount of dye adsorbed per unit weight of adsorbent (Qe) increased with increasing pH values. As the pH of the solution increases, the surface charge density decreases and the electrostatic repulsions between the adsorbent and the positively charged basic dyes is less, thereby increasing the extent of adsorption. Similar results have been reported elsewhere [30].

3.4 Effect of Temperature

The effect of temperature on the equilibrium adsorption capacity of MB onto clay are show in figure 5 The resultats obtained indicated that the change in temperature in the specified range has amost no effect on the adsorption capacity of metylene blue .for this reason a room temperature of 25°C throughout this work[31].

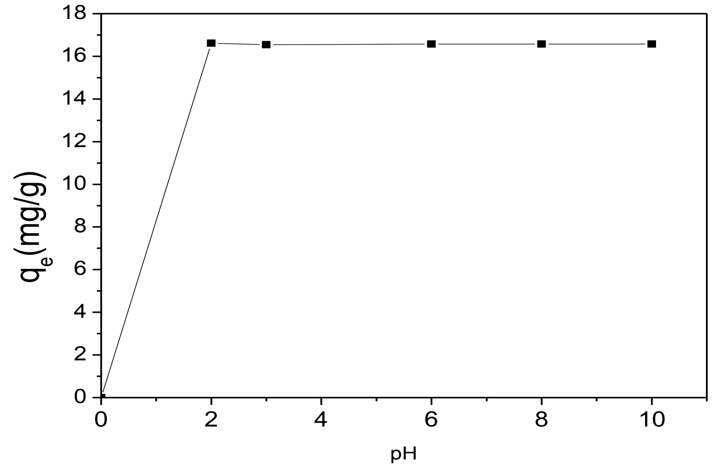


Figure 4: Effect of pH on the amount of dye adsorbed per unit weight (Qe) for the adsorbent the MB (Temperature = 25°C, rotations per minute=600rpm, Concentration of dye= 100 mg/L, equilibrium time = 2hr).

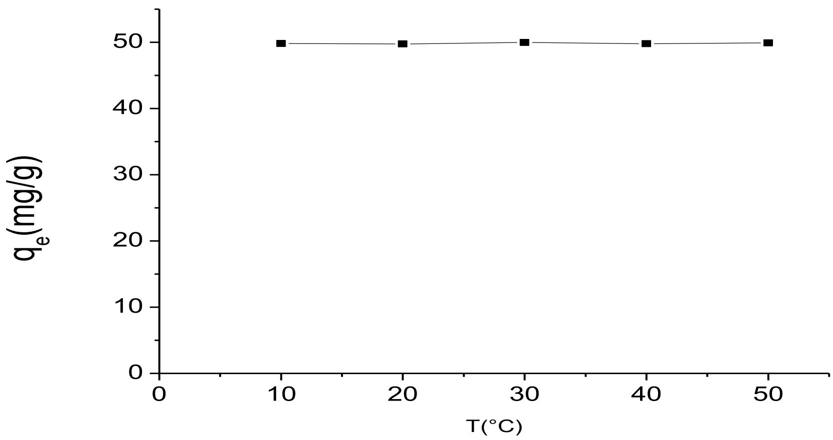


Figure 5: Effect of temperature on MB removal by natural clay (rotations per minute=600rpm, Concentration of dye= 100 mg/L, equilibrium time = 2hr).

3.5 Effect of adsorbent dose

The adsorbent dose is an important parameter in adsorption studies because it determines the capacity of adsorbent for a given initial concentration of dye solution .fig 6 shows effect of dosage on the adsorption capacity of MB onto natural clay. From obtained data it was observed that with increasing amount of adsorbent, amount of the dye adsorption also decrease accordingly because maximum surface area is available for adsorption which increases exchangeable number of sites on the surface of the adsorbent. However, a decrease in the value of Qe was observed from 50mg/g to 4.98 mg/g, for MB [32].The decrease in the amount of dye adsorbed per gram of the adsorbents (Qe) with increase in the adsorbent dose is mainly because of instauration of adsorption sites through the adsorption process [33].

3.5 Effect of initial concentration

The effect of the initial dye concentration factor depends on the immediate relation between the dye Concentration and the available binding sites on an adsorbent surface [34]. The effect of the initial MB concentration, on the adsorption capacity, is shown in Fig.7. The amount of MB adsorbed increased with the increase in the concentration MB. This means, when the initial concentration increased from 100 to 800 mg/L.

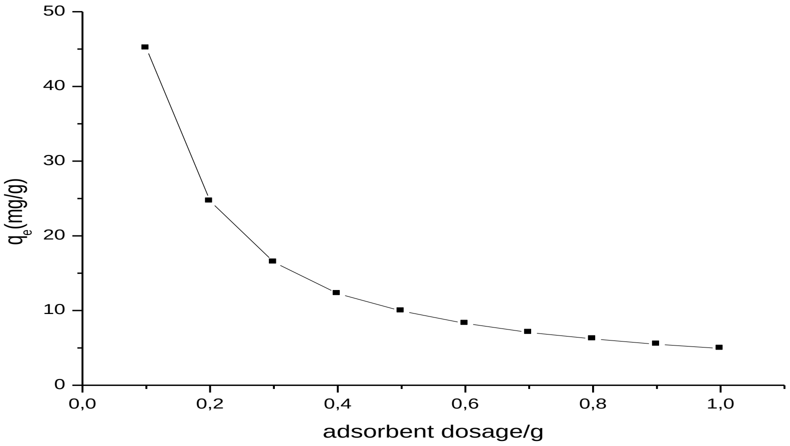


Figure 6: Effect of adsorbent dose on the amount of dye adsorbed per unit weight (Qe) for the MB. (Temperature = 25°C, rotations per minute=600rpm, Concentration of dye= 100 mg/L, equilibrium time = 2hrs pH=6.0 for MB).

It was because the initial concentration plays an important role which provided the necessary driving force to overcome the resistances to the mass transfer of MB between the aqueous and the solid phases [35]. The interaction between adsorbate and adsorbent was also found to enhance with the increase in the initial concentration. Thus, it can be concluded that higher initial concentration enhances the adsorption uptake of MB.

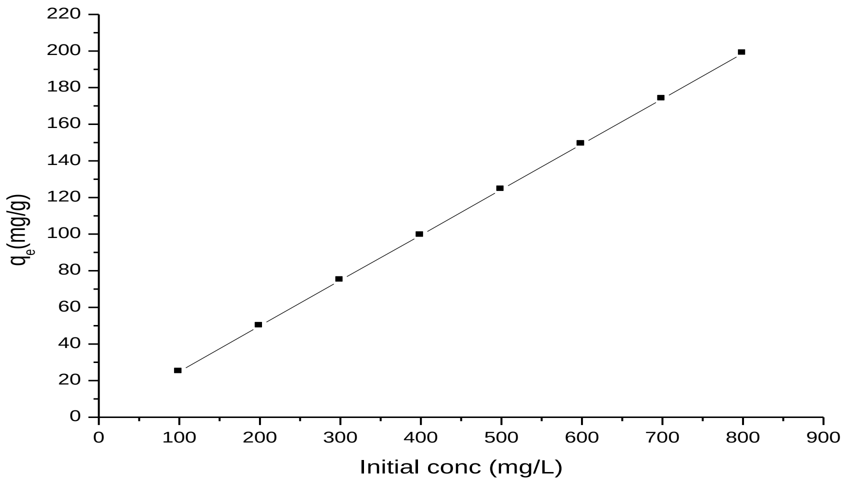


Figure 7: Effect of initial dye concentration on the amount of dye adsorbed per unit weight (Qe) for MB. (Temperature = 25°C, rotations per minute=600rpm, adsorbent dose= 0.1g, equilibrium time = 2hrs pH=6.0 for MB).

Conclusion

Adsorption of basic dye metylene blue was investigated using clay natural. From this study can be represented as follow

1. It was alsow concluded that pH of the solution has a marked effected on the adsorption and adsorption increased with the increase in pH value.
2. It was found that adsorbent dose and initial concentration of dye has a significant effect on the adsorption of dye.
3. The present study shows that about 100mg of MB adsorbed per g of natural clay in20min at 25°C.

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