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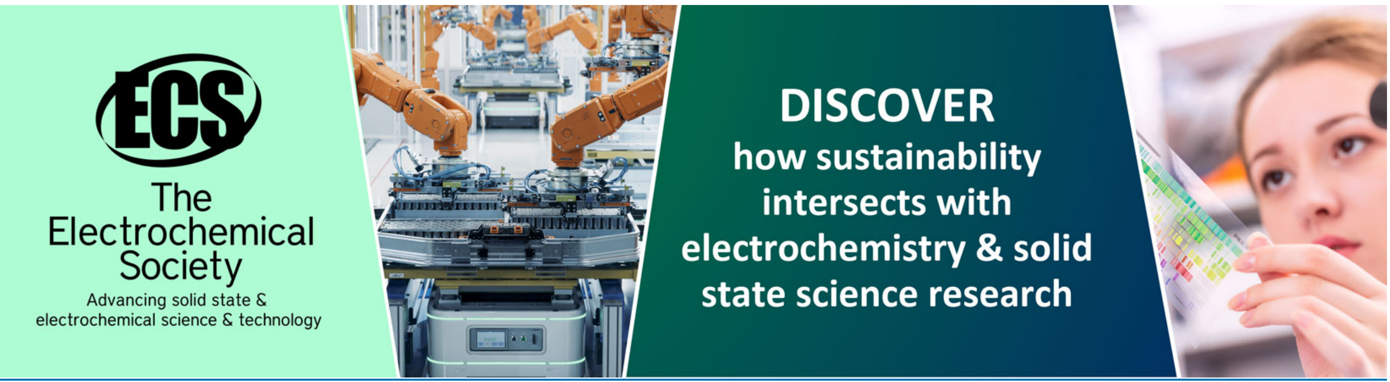

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# Removal of Methylene Blue Dye from Aqueous Solution Using Kaolin

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**Abstract.** Freshwater resources were suffered from the pollution problems that resulted from pollutants of industries such as dyes and colourants. This study utilised a natural adsorbent, kaolin clay to remove pollutants' dye (Methylene Blue) from aqueous solutions. Batch studies were conducted to evaluate the adsorption efficiency for dye removal from aqueous solution under varying conditions such as initial pH (pH), contact time, initial dye concentration on adsorption of dye. The optimum pH was found to be 6. The investigations in this study showed that 83% of dye removal can be achieved at the first 50$^{th}$ min. Meanwhile, 60 min was enough to reach the equilibrium state. Additionally, the results revealed that 100 mg/l of kaolin can lead to increase the 83 mg/g of adsorbed dye amount. The maximum removal was 89 % when the quantity of kaolin dosage increased to be 1.5 g. To sum up it, using kaolin as adsorbent material showed high efficiency to remove the dye which can be another addition for serious water pollution treatment efforts.

## 1. Introduction

Freshwater resources are vital element to continuous life and create smart cities and sustainable societies [1]. It can be seen that all the cities lie near from water resources, which is also driven the all types of industries in the world [2, 3]. Zubaidi et al., [4] mention that different studies were mentioned that the freshwater resources were globally affect by several adversely impacts include climate change [5, 6], socio-economic factors, and pollution [7, 8]. Iraq is one of the countries that its freshwater resources are under stress because of climate change, rapid urbanisation, population growth and water pollution [9]. These impacts led to depilation most of these resources and reduce the accessibility especially in the centre of cities, and increase the uncertainty of decision-makers [10]. Accordingly, these issues raise the motivation of researchers to find solutions that minimise the uncertainty and lead to sustainable development. Various scenarios were applied and one of these is water treatment.

The effluent of industrial and health facilities has adversely impact on the normal function and properties of pure water and led to rising the phenomenon of water pollution in watersheds [11-13]. Colours presence in water can be considered one of the symptoms of water pollution of any water

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body/groundwater [14]. Therefore, colourants (dyes and pigments) have gained relatively more significance as an aquatic pollutant in view of their persistence, bio-magnification and toxicity [15, 16]. Colourants are added to change the colour of a material or its surface. These substances are mainly originated from the textiles industry as well as printing, painting, medical and health laboratories and food colouring activities [17]. These materials are not biodegradable and have a direct effect on human health, it tends to exhibit genotoxicity. It was reported that it causes adverse interactions between DNA and different compounds that produce a hereditable variation in the cell or organism [18]. Due to this, the colourants should be prevented from reaching the natural environment through all feasible and effective measures.

Different chemical and physical methods were employed to remove dyes from the aquatic system. Among other most common practice in the dye elimination is the adsorption approach. This Physico-Chemical approach has been widely used due to its simplicity and economic performance [19]. In general, for removal dyes using adsorbents, the most common adsorbent is the activated carbon [16]. However, still, there is a concern about its cost. For this reason, the search about non-toxic, sustainable, and feasible alternative adsorbents should be continued. In recent years, a wide range of biodegradable adsorbents such as agricultural residues and biomaterials have applied for dyes treatment from wastewaters as an economical option. For instance, coconut coir [20], cauliflower leave [21], chitosan [22] banana fibre, and sawdust bagasse [19], wood wastes [23], fruit shell [24] and many more have been studied to be effective and safe adsorbents.

The present study aims to investigate the utilisation of natural adsorbents as a viable route for the removal of dyes from wastewaters. Kaolin clay was used in the adsorption study because it is commercially available, cheap and eco-friendly waste. The suggested adsorbent was examined to verify their efficiency in Methylene Blue (MB) dye removal from the water via application adsorption process under different laboratory conditions.

## 2. Material and methods

In this study the natural adsorbent, kaolin clay, was used to adsorb methylene blue dye from synthetic wastewater. This material was used in the adsorption process without any pre-treatment or modification process. The kaolin was obtained from the local market. This adsorbent was grained and sieved using (100-200) µm sieves. Methylene blue dye (CI52015, MF C16 H18 N3 SCl, MW: 319.85, λ 664nm) was used as the adsorbate. The dye was purchased from (R & M chemicals, UK) and used directly without purification. A stock solution was prepared by dissolve 1g of methylene blue dye (99.9% pure) in distilled water to get1000 mg/L stock solution. Then, stock solutions of methylene blue in the range of 20 to 100 mg/l were prepared to perform the experiments. The pH was modified using sodium hydroxide (NaOH) and hydrochloric acid (HCl). The experiments were carried out at constant test laboratory conditions such as the oven temperature of drying (60ŗc), employed the shaker rotation 150 rpm, centrifugal 3000 rpm, the room temperature approximately (25ŗc).

A specific amount of kaolin (0.5 g mass dosage) was immersed in 100 ml of methylene blue solutions with concentrations of 20, 40, 60, 8, and 100 mg/l in 250 ml conical flasks of. The optimum pH was set for each adsorbent and the temperature was $25^{o}$C. The amount of dye removal was measured using UV Spectrophotometer (Shamizu, Japan) at the maximum wavelength was 663nm. The time of the experiment was 150 minutes; the dye removal was tested at each 10 minutes. The optimum pH was investigated by taken several pH values ranging from 2-11. 50mg/l concentration of methylene blue was selected to evaluate the impact of contact time of the adsorption of methylene blue was measured each 10 minutes. In this study the dosage of adsorbent was examined by setting the methylene blue dye concentration to 50 mg / l. 100 ml sample was prepared with optimum pH. The effect of the initial concentration of methylene

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blue on adsorption rate has been studied by testing concentrations ranging from 20 mg/l to 100 mg/l of methylene blue. All other parameters of the experiment are kept constant.

## 3. Results and discussion

The pH of the solution has a significantly affected in the adsorption process because it can control the charge of the adsorbent surface, the ionization degree of the pollutants and structural stability of methylene blue [21]. The variation in adsorption of methylene blue dye with the initial pH change of kaolin solution was studied in the adsorption of methylene blue and ranged from 3 to 10. The percentages of dye removal based on the pH value of the kaolin solution are depicted in Figure 1. The experiments revealed the optimum pH of treatment solution was found to be equal 6 which resulted in the maximum dye removal. Therefore, this value of pH is employed in the followed experiments that were aimed to study the other parameters to ensure the maximum amount of adsorption.

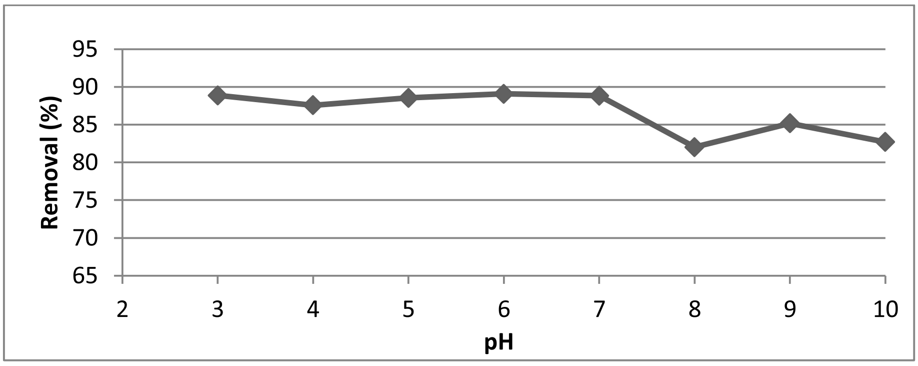


**Figure 1.** Effect of pH on dye removal.

The efficiency of the adsorption procedure was investigated according to the contact time between dye molecules and the adsorbent. During the adsorption different data of time have been used till the equilibrium time. Throughout the experiment, 100 ml of dye with initial dye concentration was 50mg/l of methylene bleu has been investigated with 0.5g of each adsorbent. The optimum pH of the adsorbent has been dedicated. It is clear that the adsorption of methylene blue was rapidly increased with the time increment and then slowed on equilibrium as showed in Figure 2. It can be seen that the adsorption rate of dye with kaolin showed a dramatic increase in the first 50 minutes, whereas the adsorbed amount of dye has been jumped from 10 mg/g at the 3ed minute to be 83 mg/g at the 50$^{th}$ minute. Meanwhile, it kept a steady level after the 60$^{th}$ minute. This might be attributed to the availability of the adsorption surface area on the adsorbent particles which is responsible for the rapid adsorption of methylene blue [25]. It concluded that the adsorbed amount of dye the required approximately one hour to reach the equilibrium state that represents the maximum adsorption capacity for the kaolin.

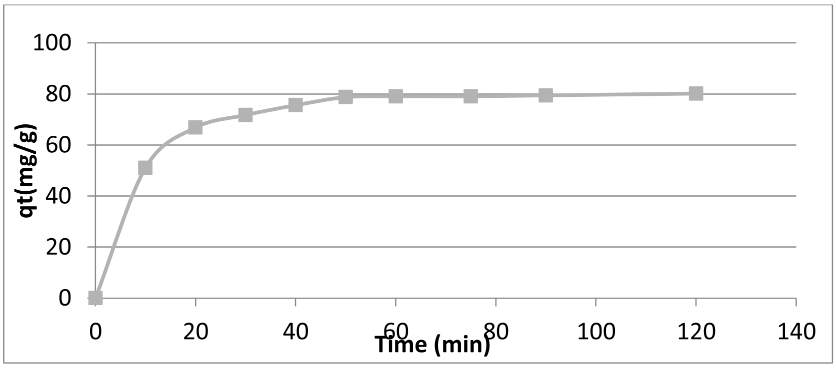


**Figure 2.** Contact time effect on adsorption of Methylene Blue.

One of the factors that were assess in this research is the initial concentration of dye. The Initial concentration is an indicator to identify whether the adsorption process of dye happens in multilayers or monolayer [16]. Five levels of initial concentrations of methylene blue were employed in this study 20, 40, 60, 80, and 100 mg/l at a fixed adsorbent dose which was 0.5 g. All solutions were incubated in 25$^o$C and shake with 150 rpm for 3 hours and the time with intervals every 10 minutes. The filtrate samples were collected with the help of syringe for spectrophotometrically absorbance test. As seen in Figures 3, it can be observed that amount adsorbed at any contact time of adsorption ($q_t$) of methylene blue using the adsorbents (kaolin) was increased by increasing the concentration of adsorbate, the corresponding adsorption capacity also increases and reaches a maximum at a point where the adsorption remains constant. Figure 4 shows that increasing the concentration of dye 20 mg/l to 100 mg/l led to increasing the amount of adsorbed dye, qe (mg/g) from 13 to 83 mg/g, respectively. The changing in the amount removed is attributed to the high mass transfer force of the initial dye concentration which overawed the resistance of mass transfer for molecules between the solid phases and aqueous solution [26].

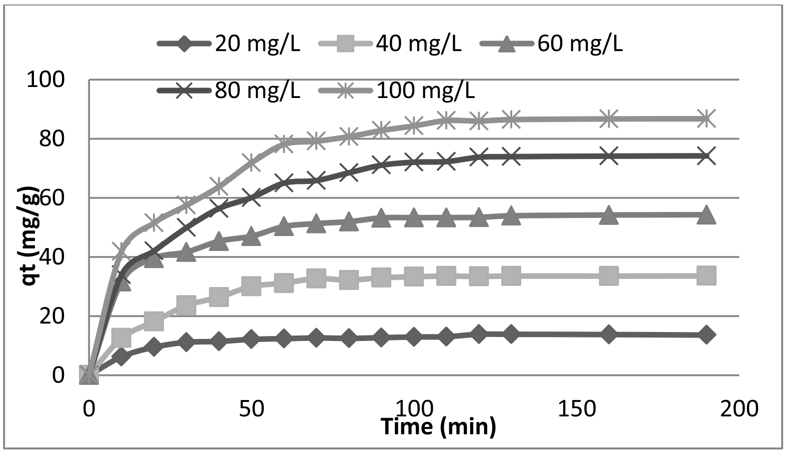


**Figure 3.** Impact of initial methylene blue concentration for adsorption on kaolin.

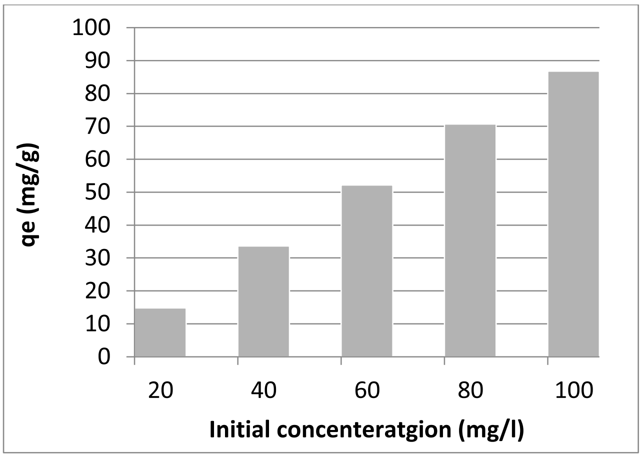


**Figure 4.** Impact of the initial concentration of MB on adsorption rate.

The adsorption of dyes from the aqueous solution can be significantly influenced by the adsorbent dose. Hence, the elevated of variation of adsorbent dosage effect was detected at the environment of pH= 6 that included a fixed concentration of methylene blue (50 mg/l), 150 rpm, and 25$^{o}$C till equilibrium time. Figures 5 and 6 illustrate the results of removed dye at equilibrium and the percentage of dye removal, respectively. The outcomes present that there is an increase of dye removal by increasing the adsorbent dosage which can be seen in Figure 6. By the same token, the amount of dye removal was 63.3% using kaolin dosage 0.25g. It is easy observe that the dye removal showed proportional increase behaviour with adsorbent concentration increment. This removal was reached the maximum to 89 % when the quantity of kaolin dosage increased to be 1.5 g.

## 4. Conclusions

This work illustrated the kaolin powder, which is natural clay, is a high efficiency that can be utilised as an adsorbent to remove the pollutant dye (methylene blue) from synthetic aqueous solution. The adsorbed dye quantity varied with, pH, initial solution concentration, contact time, and adsorbent dose. The amount of dye uptake has been found to increase with the increase in the initial dye solution concentration and contact time, and it has been found to decrease with an increase in adsorbent dosage but the percentage of removal increases. For further studies, the continuous flow experiments using the kaolin suggested being carried out to conclude breakthrough curves and investigate the adsorption kinetic.

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