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Efficient Adsorption and Photocatalytic Degradation of Malachite Green Dye Using Bentonite Natural Adsorbent

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Abstract: Removal of dyes which are toxic in nature from industrial wastewaters is currently of great interest. For this purpose, the use of Bentonite for the removal of Malachite green dye from aqueous solutions at different contact times, pH and dye concentration was investigated. Bentonite has a high potential to adsorb reactive dyes from aqueous solutions according to TEM image. The extent of dye removal increased with increasing adsorbent concentration, contact time, pH and dye concentration. The kinetics of the adsorption process was tested for the pseudo-first order and pseudo-second order reaction models. The rate constant of adsorption was obtained for the pseudo-second order kinetic model. The adsorption capacity of the Bentonite is comparable to the other available adsorbents, and it is quite cheaper. It's easily available in market.

Keywords: Bentonite, Malachite green, wastewater.

1 Introduction

Colored dye wastewater occurs as a direct result of the production of the dye and also as a consequence of its use in the textile and other industries. Colored effluents and dyes can cause toxic problems in several type of receiving media and can have acute or chronic effects on exposed organisms [1, 2]. There are many processes available for treatment of dyes: chemical oxidation, flotation, adsorption, electrolysis, chemical coagulation, photo catalysis and biodegradation. Among all these, adsorption has been found to be an efficient method for the removal of dyes from aqueous solutions because it produces high quality treated effluent and also allows kinetic and equilibrium measurements without any highly sophisticated instruments [4, 5].

Different adsorbents have been used for removal of various materials from aqueous solutions, such as dyes, metal ions and other organic materials. These include perlite [1–6], activated carbon [7–11], bentonite [12], silica gels [13], fly ash [14–16], lignite [17], peat [18], silica [19], Montmorillonite [20] etc., In order to minimize processing costs for these effluents, recent investigations have focused on the use of cheaper and easily obtainable low cost unconventional adsorbents. Bentonite, which form an important group of clay minerals, and because of their structural morphology currently used in a number of different applications such as many industrial, catalytic and environmental applications, most of which are similar to those of the more traditional clays. There are different types of bentonite, each named after the respective dominant element, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al). Experts debate a number of classified problems with the classification of bentonite clays.

Bentonite usually forms from weathering of volcanic ash, most often in the presence of water. However, the term bentonite, as well as similar clay called tonstein, has been used to describe clay beds of uncertain origin. For industrial purposes, two main classes of bentonite exist: sodium and calcium bentonite. In stratigraphy and tephrochronology, completely devitrified (weathered volcanic glass) ash-fall beds are commonly referred to as K-bentonites when the dominant clay species is illite. Other common clay species, and sometimes dominant, are Montmorillonite and kaolinite. Kaolinite-dominated clays are commonly referred to as tonsteins and are typically associated with coal [12, 20]. The main uses of bentonite are for drilling mud, binder (e.g., foundry-sand bond, iron ore pelletizer), purifier, absorbent (e.e. pet litter), and as a groundwater barrier. As of around 1990, almost half of the US production of bentonite was used for drilling mud [20, 21].

So, the present study deals with the adsorption abilities for removal of Malachite green dye from wastewater. The influence of several parameters such as pH, temperature and time was explored.

2 Experimental

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Bentonite, is a clay mineral with a unit cell formula (Na, Ca) $_{0.33}$ (Al, Mg)$_2$ (Si$_4$O$_{10}$) (OH)$_2$·nH$_2$O [12] used as an adsorbent heated before using for surface activation. The surface of was characterized by transition electron microscopy which is shown in Fig. 1, TEM micrograph of it, it is observed; that had an irregular, heterogeneous and porous surface, which indicated high surface areas. Bentonite has several adsorption applications due to its channel structure.

The presence and concentration of surface functional groups play an important role in the absorption capacity and the removal mechanism of the adsorbate. The structural form of Malachite green ($C_{23}H_{25}N_2Cl$) [364.911 g/mol] dye is given in Figure 2. The concentrate of it in 250 ml suspension was 50 ml (200 ppm). A 100 mg bentonite absorbent was used to affect in solution at various loading pH ranging from 4 to 9, temperature ~25 °C as well as at different contact times.

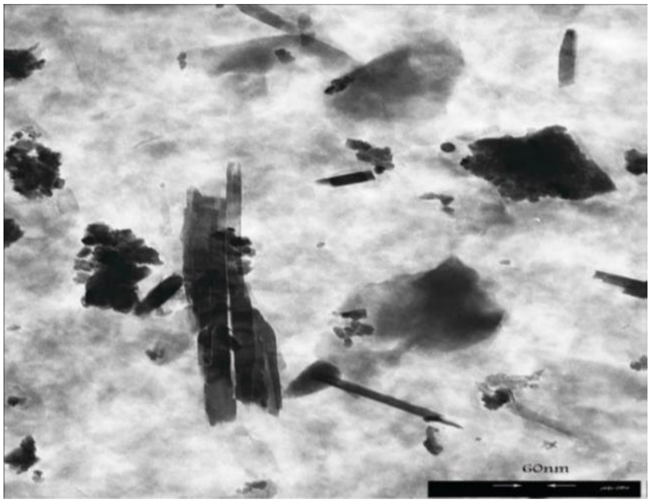

Figure 1. Transition Electron Microscopy Image of Bentonite

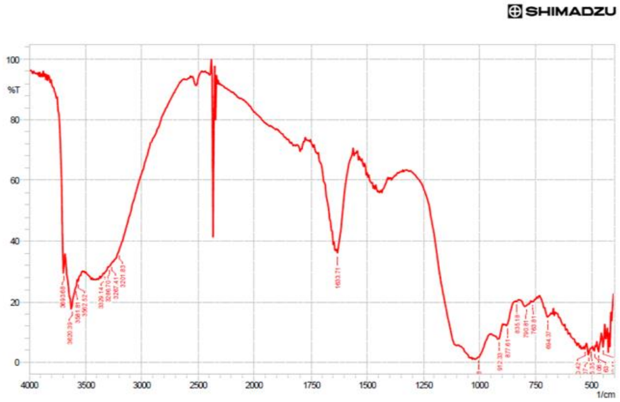

Fig. 2 IR Spectra of Bentonite Clay

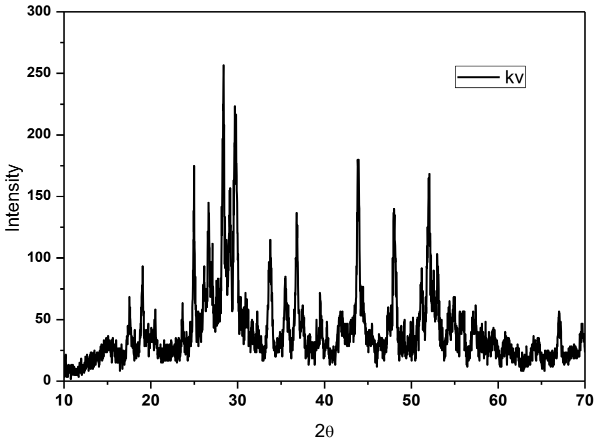

Fig. 3 X-Ray diffraction (XRD) of Bentonite clay

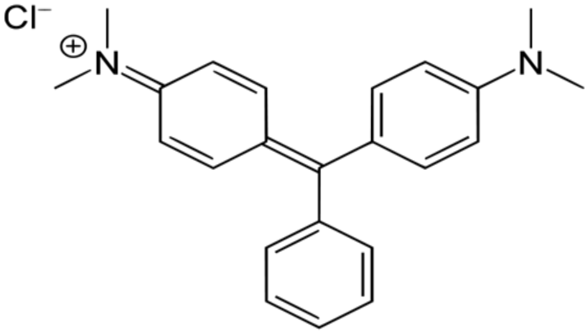

Figure 4. Structure of Malachite Green

3 Result and Discussion

3.1 The Effect of pH on Adsorption

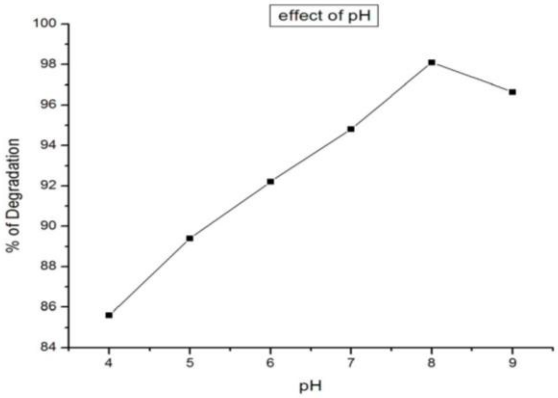

Figure 5. The Effect of pH on Adsorption at 25 ^{0}C and 100 mg Bentonite on 50 ml 200 ppm Malachite green Solution

The pH of the solution was found to influence the adsorption of the adsorbate on adsorbent. The studies were conducted at a fixed concentration of adsorbate (200 mg/l), contact time (75 min) and adsorbent dose 0.100 g/l at 298 K. pH was adjusted by adding either 0.1M HCl or 0.1M NaOH and the change in adsorption of the dye was studied over a pH range of 4-9.

The results obtained are presented in Fig. 3, which show that adsorption of malachite green increases with increase in pH from 4.0 to 8.0 and on further increase in pH the solution become colorless. Malachite green (Pka = 10.3) becomes protonated in the acidic medium and deprotonation takes place at higher pH. Consequently, the positive charge density would be more on dye molecules at low pH and these accounts for the higher uptake on the negatively charged surface for adsorbent.

3.2 The Effect of Different Contact Time on Adsorption

A series of experiments was performed to optimize the adsorption time at an initial dye concentration of 200 mg/L. The effect of contact time on the adsorption rate of dye is presented in Figure 4, the effect of contact time for the removal Malachite green dye by bentonite showed rapid adsorption of dye by increasing the contact time. This was caused by strong attractive forces between the dye molecules and the adsorbent; fast diffusion onto the external surface was followed by fast pore diffusion into the intra particle matrix to attain rapid equilibrium.

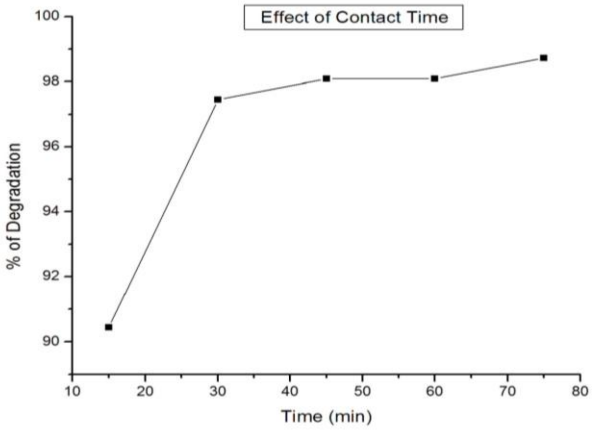

Figure 6. The Effect of Contact Time on Adsorption Rate on 50 ml 200 ppm Malachite green Solution with 100 mg Bentonite.

3.3 The Effect of Various Loading Adsorbent on Adsorption

For this study, pH~8, temperature~ 25 °C and time~ 75 min, choose with different amount of adsorbent ranging from 25 to 100 mg to 50 ml Malachite green solution at an initial dye concentration of 200 mg/L which is shown in Figure 5, as expected by increasing adsorbent the adsorption increased. It has been stated that increasing in the ionic strength of the solution increases adsorption at pH values below the isoelectrical point and decrease adsorption at pH values above the isoelectrical point.

A cause of increasing of adsorption in increasing ionic strength is that increasing in the ionic strength increases the positive charge of the surface below the isoelectrical point, resulting in greater attraction of anions, and increases the negative charge on the surface above the isoelectrical point, resulting in greater repulsion of anions.

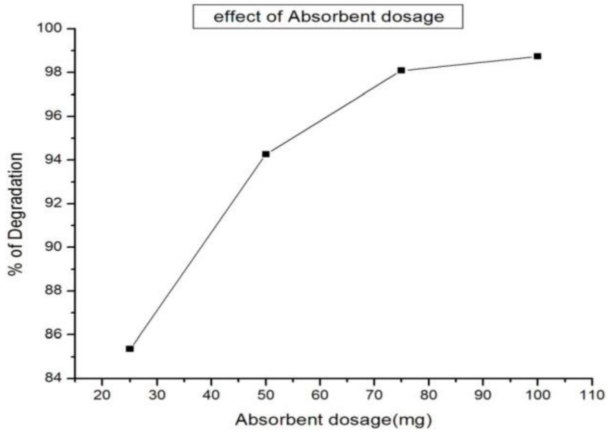

Figure 7. The Effect of Various Loading on Adsorption Rate with 50 ml 200 ppm Malachite green Solution

3.4 The Effect of Different Dye concentration:

The effect of initial concentration of malachite green between the ranges of 50 to 250 mg/l was carried out to observe the absorption efficiency at various temperatures ranges from 298 K with fixed adsorbent dosage (100 mg/l). The contact time was kept 75 min. The results of the studies are shown in Fig. 6 which depicts that dye uptake increases with increase in initial malachite green concentration from 50 to 250 mg/l and thereafter equilibrium is achieved in dye uptake efficiency at 298 K. The increment in sorption capacity may be due to the increase of dye concentration which resulted in higher concentration gradient of the dye, thus leading to higher sorption capacity.

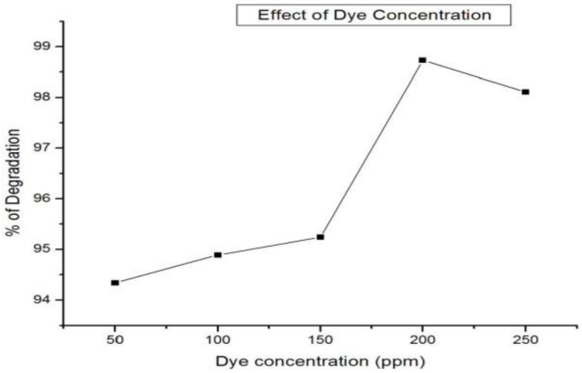

Figure 8. The Effect of Dye Concentration on Adsorption Rate at 25 ^{0}C on 100 mg Bentonite

3.5 Adsorption Kinetic Study

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. Several kinetic models are available to understand the behavior of the adsorbents and to examine the controlling mechanism of the adsorption process. In the present investigation, the adsorption data were analyzed using two different kinetic models, namely the pseudo-first-order and pseudo-second order which are shown in Figures 7 and 8.

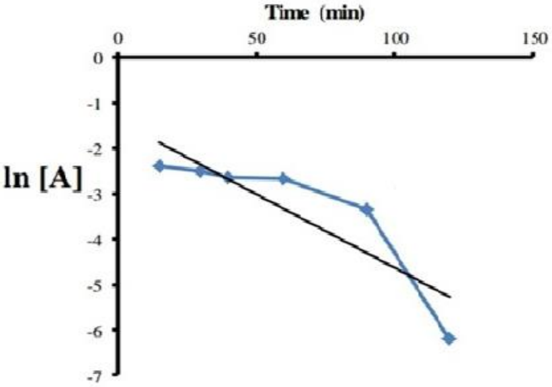

Figure 9. Kinetic Model of Pseudo- First Order for Bentonite on 50 ml Malachite green Solution

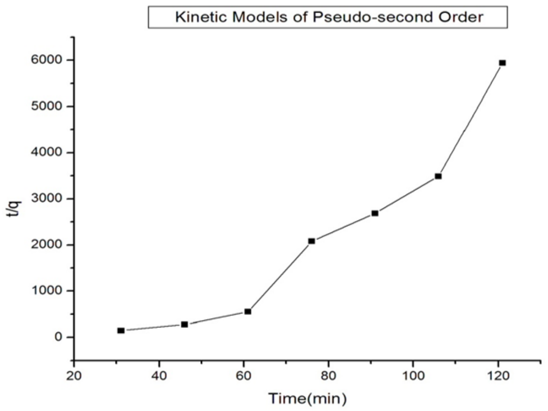

Figure 10. Kinetic Models of Pseudo- Second Order for Bentonite on 50 ml Malachite green Solution

4 Conclusions

- Batch adsorption studies were conducted to evaluate the effect of various parameters Such as pH, adsorbent effect, different contact time and effect of various dye concentration on the removal of Malachite green. According to results these conclusions were obtained
- The pH of the dye solution strongly affected the chemistry of both the dye Molecules and adsorbents in aqueous solutions. The optimum conditions for this Study were pH 8.
- The amount of dye uptake was found to increase with increase in contact time
- The kinetic data may be useful for environmental technologist in designing treatment plants for color removal from wastewaters enriched with Malachite green.
- The results showed that these adsorbents could potentially be used as a low-cost material for the removal of the reactive dyes in aqueous solutions.
- During the experiments we conclude that, when increases the dye concentration also required the more dosage of absorbent.

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