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Original Research Article

Removal of Malachite Green from Aqueous Solutions by Adsorption Using Low Cost Boisorbent Neem Leaf *(Azadirachta Indica)*

Kassa Belay* and Mesfin Abebe

Adigrat University, Department of Chemistry, P.O. Box 50, Adigrat, Ethiopia

***Corresponding Author email: kassa.belay1@gmail.com**

Abstract

Removal of dyes from waste water is a major ecological problem. Colorants present in dye house effluent are responsible for environmental pollution. Removal of malachite green from its aqueous solution by Neem tree has been investigated by means of a batch system. The effects of contact time, initial concentration of dye, particle size of adsorbent and adsorbent dosage on the adsorption of malachite green by Neem tree were studied. The results showed that adsorption of the dyes were found to increase as the adsorbent dosage increases, but decreases as initial concentration of adsorb ate increases, this is due to the active site of the adsorbent can absorb a certain concentration of the dye. The removal of adsorb ate by activated Neem bark leaves adsorption is investigated in present study.

Keywords: Spectrophotometer, Malachite green, Neem tree leaf

INTRODUCTION

Environmental pollution due to industrial effluents is the major concern. Because of their toxicity and threat for human life and the environment (Amren and Zulfikar, 2010). Adsorption has been found to be an efficient and inexpensive method for removal of dyes, pigments and other colorants and for controlling the biochemical oxygen demand (Crini, 2006). Dyes are chemicals, which on binding with a material will give color to them. Dyes are ionic, aromatic organic compounds with structures including aryl ring, which have delocalized electron system (Chatterjee et al., 2009).

Removal of colour from dye-bearing wastewaters is one of the major environmental problems because of difficulty in treating such waste waters by conventional treatment methods, as most of the dyes are stable to light and oxidizing agents (Han et al., 2008). The presence of even minimum quantities of colouring substance makes it unsuitable for drinking or other recreational purposes due to its undesirable appearance. The most commonly used methods for the removal of colour from dyestuffs are chemical precipitation and biological oxidation (Al-Asheh et al., 2003). Photo-catalytic oxidation and ozone treatment are the other alternative technologies commonly employed. However, these methods are effective and economic only when the solute concentrations are relatively high.

The colors of provided by the presence of a chromospheres group, that is radical configuration consisting of conjugated double bonds containing benzene, naphthalene or anthracites ring is part of a chromate chromospheres structure along with an axon chrome due to low biodegradation of dyes are not very

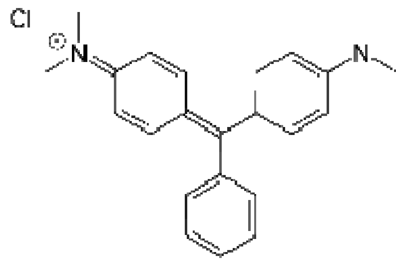

Figure 1. Molecular structure of malachite green

effective in treating a dyes waste water (Naseem and Tahir, 2001) .Activated carbon, inorganic oxides mineral and natural adsorbents have been extensively used as adsorbents to treat waste water (Wang and Wang, 2008).

This activated carbon is the most popular adsorbent for removal of dye stuff from waste water. However, there problems are associated with the use of carbon for the adsorption of pollutants. Its relatives high cost, regeneration and re use are difficult and it is limited to the removal of non polar materials (Oke et al., 2008). Therefore there is a need to find locally available low cost and effective materials for dyes waste water treatment (Patil and Shrivastava, 2010; Namasivayam and Kavitha, 2002).

Study on the adsorption of malachite green from low cost biosorbent Neem leaf is important for the removal of absorbent from the aqueous solution (Zhang et al., 2002). The adsorption and effects of agitation time, initial dye concentration, particle size, contact time, adsorbent dosage on the adsorption of malachite green were investigated (Binupriya et al., 2008).

Dyes are the most visible pollutants in which presented in effluents discharged from different industries, textile, paper, and dye manufacturing (Mumin et al., 2007). The color of dye provided by the presence of chromospheres group, where the chromospheres are a radical configuration consisting of conjugated double bond containing benzene ring s, due to have low cost biodegradation of dyes are not very effective in treatment of waste water (Vimoneses et al., 2009).

Malachite green is an organic compound that is used as a dyestuff and has emerged as a controversial agent in aquaculture. Malachite green is traditionally used as a dye for materials such as silk, leather, and paper. Although called *malachite green*, the compound is not related to the mineral malachite the name just comes from the similarity of color (Reddy, 2006; Rajamohan, 2009). (Figure 1)

Malachite green is classified in the dyestuff industry as a triarylmethane dye and also using in pigment industry. Formally, Malachite green refers to the chloride salt $[C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl$, although the term Malachite green is used loosely and often just refers to the colored cation. The oxalate salt is also marketed. The chloride and oxalate anions have no effect on the color. The intense green color of the cation results from a strong absorption band at 621 nm (Jayaraj et al., 2011).

Malachite green is prepared by the condensation of benzaldehydeand dimethylaniline to give leuco malachite green (LMG):

$C_6H_5CHO + 2\ C_6H_5N(CH_3)_2 \rightarrow C_6H_5CH(C_6H_4N(CH_3)_2)_2 + H_2O$

Second, this colorless leuco compound, a relative of triphenyl methane, is oxidized to the cation that is MG:

$C_6H_5CH(C_6H_4N(CH_3)_2)_2 + HCl + 1/2\ O_2 \rightarrow [C_6H_5C(C_6H_4N(CH_3)_2)_2]Cl + H_2O$

A typical oxidizing agent is manganese dioxide.

Normally, colorants are water soluble, which is dispersible organic compounds that are capable of being absorbed in to the substrate destroying the crystal structures of the substrates (Chatterjee et al., 2009; Chatterjee et al., 2010). Adsorbents are substances that attract other particles to its surface and also that adsorbents are substances in which have an ability to adsorb such as activated charcoal and, clay (Chen and Wang, 2005). (Figure 2)

Many adsorbent materials have been developed and evaluated, but none has emerged as being economically life. However, adsorbents have a capable adsorption called adsorptive substances. Adsorption of the dyes were found to increase as adsorbent dosage increased, but decreases as initial concentration of adsorbate increases this due to the fact that active site of the adsorbent can adsorbed a certain concentration of the dye (Isene et al., 2007).

However, there has so far been no study reported in academic literature related to the use of powdered leaf Neem leaf as an adsorbent for removing the absorbent from aqueous solution (Smarenda et al., 2011). Therefore the main aim of this study is the use of powdered Neem bark leaf as adsorbent material for removal of malachite

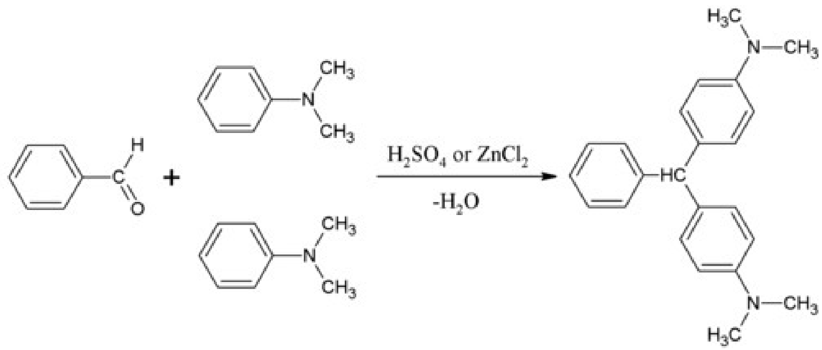

Figure 2. Preparation of malachite green

green from the aqueous solution (Chen and Zhao, 2009). Hypothesis shows that Neem tree would be an efficient adsorbent for removal of dyes from aqueous solution.

So that the objectives of this study were:

- To study the malachite green removal efficiency of thermally treated Neem tree leave from aqueous solutions.
- To study the effect of operating parameters (initial adsorbent concentration, adsorbent dosage, contact time and particle size)

METHODOLOGY

Apparatus

Centrifugation, Uv-visible spectrophotometer Crucible, Test tube, Cuvvat, Beam balance, Drying oven, Thermometer, Volumetric flask, Measuring cylinder, whatt man filter paper, Mortar and pestle.

Chemicals and reagents

The chemicals used during the experiment are: Sodium bi carbonate ($NaHCO_3$), Sulfuric acid (H_2SO_4) and Malachite green ($[C_6H_5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl$)

Experimental Site

Neem leaf sample was collected from Adigrat agricultural cultivation roads and from forest tree during work time which is located in the northern part of Ethiopia, Tigray region 898km far from Addis Ababa and 120km away from north of Mekelle city, which is capital city of Tigray regional state.

Biosorption Study

Neem tree leaf collection and preparation

The Neem leaf was collected from Adigrat agricultural cultivation roads and from forest tree using plastic bags and washed with tape water to remove surface adsorption then dried at 105 °C for 1 h in a convection oven and socked with H_2SO_4 solution 1:1 ratio weight per volume for overnight to increase adsorption efficiency.

Then washed with distilled water till it attained neutral P^H and treated 2% $NaHCO_3$ over night in order to remove excess of acid present then it was washed with distilled water to remove dirt and boiled to remove color and dried at oven at 105C^o for 1 hours and activated in muffle furnace at 450C^o for an 2 hours.

Finally allowed to pass through 0.5, 1 and 2 mm sieves. Then the powdered Neem leaf was washed with distilled water to remove dirt and boiled to remove color (Selvaraj et al., 2003).

Preparation of adsorbate solutions

A solution was prepared by dissolving 12.5 mg of malachite green in one litter water and centrifuged with 50 rpm at room Temperature. Then Neem leaf will be removed after 12 hours and residual concentration of malachite green will be determined by uv spectrophotometer and evaluate the initial absorbance value by use it.

Batch Adsorption Studies

Batch mode adsorption studies for malachite green were carried out using 250 ml Erlenmeyer flask. The effects of different parameters such as adsorbate concentration, adsorbent dose, contact time and effect of particle size

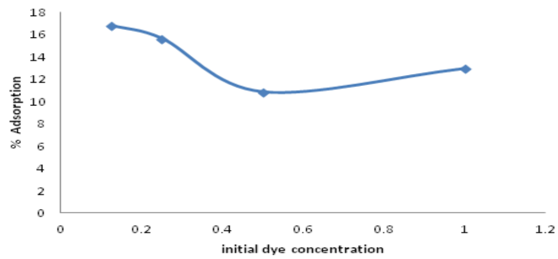

Figure 3. Effect of initial dye concentration on removal malachite green

were studied. The Erlenmeyer flasks were pretreated with the respective adsorbate for 24 hours to avoid adsorption of the adsorbate on the container walls. Standard solutions of the dye were mixed with the Neem tree leave and agitated at different agitation rate on a mechanical shaker. This was carried out by varying the dye concentrations, and the mass of Neem tree leave used for adsorption. Finally, the resulting suspension of the dye was filtered using a Whatman No.1 filter paper and the filtrate was analyzed for the corresponding dye concentration. Removal efficiency was finally calculated by using the relationship.

Adsorption (%) = $((C_o - C_f)/C_o) \times 100$

Where C_o = the initial concentration (mg/L) and C_f = final concentration (mg/L) of the dye being studied. The adsorption capacity of the Neem leave is the concentration of the dye on the adsorbent mass and was calculated based on the mass balance principle.

Effect of adsorbent dosage

The effect of adsorbent dosage was studied by using 0.125, 0.25, 0.5, and 1g of Neem leave in 250 ml Erlenmeyer flask with dye concentration of 12.5 mg/l and the adsorption efficiency for different dose was determined by keeping other parameters constant.

Effect of initial concentration of dye

This step determines the effect of malachite green concentration on malachite green removal efficiency of adsorbent. The effect of malachite green concentration were determined using different concentrations of malachite green (5, 10, 15, 20 mg/L) and keeping other parameters constant.

Effect of contact time

Contact time is one of the most important parameters for the assessment of practical application of sorption process (Selvaraj et al., 2003). For the determination of the rate of dye biosorption by the Neem leave from 12.5 ml of standard solutions, the quantity of dye adsorbed was determined by varying the contact time: 5,10,15,20 min. Other parameters were kept constant.

Effect of particle size

The effect of adsorbent particle size was studied by using 5, 10, 15 and 20 g of adsorbent after passing with 0.5mm, 1.0mm, 0.20mm sieve and evaluate it's absorbance by using spectrophotometer by keeping the other parameters constant.

RESULT AND DISCUSION

Effect of initial dye concentration

During determination of 2.5g of Neem leaf by varying dye concentration single, 10mg/L, 15 mg/l, and 20mg/L,) of malachite green dye at constant agitation speed 50rpm. (Figure 3)

The percentage of malachite green removal at room temperature is decreased. This is due to increased in the initial concentration provides an important driving force to overcome all resistance of the dye.

Effect of particle size of Adsorbent

Determination of the effect of particle sizes on sorption was conducted using samples of four different average particle sizes (5 mm, 10mm, 15mm, and 20mm) at

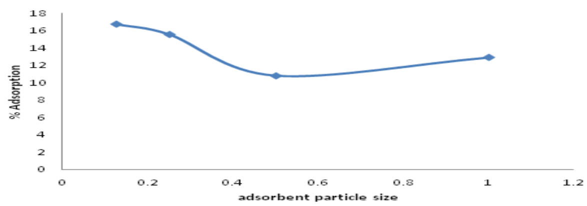

Figure 4. Effect of particle size low cost neem leaf on the removal of malachite green Variation of particle size of neem leaf is statistically has significant effect on the removal of malachite green.

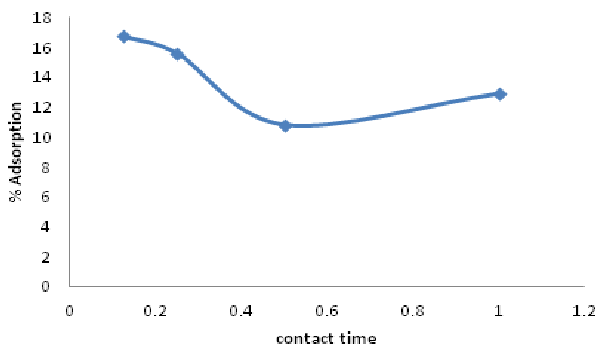

Figure 5. Effect of contact time on removal malachite green decreases as the minimum contact time, but increases the percentage of adsorption as increasing the contact time.

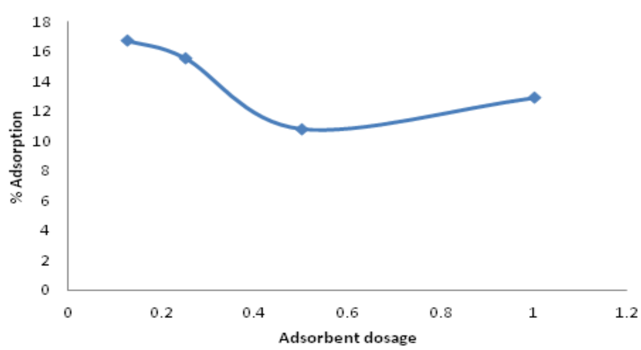

Figure 6. Effect of adsorbent dosage on removal efficiency of malachite green

constant temperature for 80 minutes. The result is show as follow: (Figure 4)

Effects of contact time of low cost Neem leaf

The effect of contact time for malachite green adsorption, 12.5 mg/L solution of dye was added into 2 g of Neem tree leaf adsorbent and agitated by varying the contact time from 5 to 35 minutes at 5 minutes interval. The results obtained are given in Figure 5.

Effect of adsorbent dosage on sorption process

The effect of the adsorbent dose was studied at room temperature by varying the adsorbent amounts from 0.125 to 1 g. For all these runs, initial concentration of dye, agitation speed and contact time was kept constant. Figures 6 show the adsorption efficiency of different doses of the biosorbent. Adsorption efficiency increased with adsorbent dose in the range from 0.125- 1g and showed little variation with further increment. This is due to limited availability of adsorbate species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is reasonable that with higher dosage of adsorbent there would be greater number of exchangeable sites for metal ions (Adina et al., 2008). Therefore, the maximum removal efficiency of malachite green was obtained at an adsorbent dose of 1 g. (Figure 6)

As the variation of the removal of malachite green decreases as the percentage of removal increases as the effect of adsorbent dosage increases. Which is due to the increases in absorbent surface area of the adsorbent.

CONCLUSIONS AND RECOMMENDATION

Conclusion

In this study, batch adsorption experiments for the removal of malachite green from aqueous solutions have been carried out using Neem tree leaf as a low cost, readily available adsorbent. The adsorption characteristics have been examined at different initial dye concentrations, contact time, particle size and adsorbent dosages. The obtained results can be summarized as follows

MG exhibited a fast biosorption rate during the first 5 minutes of contact time due to a great availability of surface area/binding sites or large number of vacant surface sites is available for dye molecules to be biosorbed. Generally, MG anions will bind to all the active sites until they are fully occupied or until it attains equilibrium. Hence with time, fewer active sites are available and thus reduce the amount of dye being adsorbed or after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases.

When the initial concentration increases the removal efficiency decreases. This is probably due to high driving force for mass transfer. The reduction of dye removal as a function of its concentration can be explained by the limitation of available free sites for adsorption of dye with the increase in dye concentration in bulk solution for a fixed mass of adsorbent, as well as by the increase in intraparticular diffusion.

As the dosage of adsorbent increases the adsorption increases proportionately. The increase of dosage increases adsorbent sites thus surface area of contact with the dyes increases. Therefore the amount of dye uptakes increases and consequently leads to a better adsorption. This observed trend is mainly due to the increase in absorptive surface area and availability of more adsorption site. The removal efficiency was high at smaller particle size of adsorbent material because as the particle size decreases the surface area increases and this leads to high removal efficiency.

RECOMMENDATION

The following recommendations are made in order to benefit those who need to intervene with the result of the study under consideration.

- The adsorbent should characterized by using FT-IR.
- The use of adsorbent for removal of other toxic heavy metals should be studied.
- Other factors such as P^H, temperature and kinetic isotherm should be studied.

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