

# REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION USING ACTIVATED CHARCOAL

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## INTRODUCTION

Water pollution is a major concern of the world today and governments of numerous countries are trying to find solutions to reduce this problem. The textile industry is one of the largest polluters in the world. The World Bank estimates that almost 20% of global industrial water pollution comes from the treatment and dyeing of textiles. The textile industry is second only to agriculture as the biggest polluter of clean water globally. The effluents from dye manufacturing and consuming industries are highly coloured coupled with high chemical and biochemical oxygen demands and suspended solids. Discharge of such effluents imparts colour to receiving streams which not only affects its aesthetic value but also inhibit the penetration of sunlight, with a consequent reduction in photosynthetic activity. This leads to disturbance in the ecological equilibrium (Bhanuprakash, *et al.*, 2015).

Today, dye pollutants from various industries are important sources of environmental contamination. Some dyes have mutagenic, carcinogenic and teratogenic effects either when inhaled or when in contact with the skin and thus affect human health. Dyes are synthetic aromatic organic compounds, which are normally used for coloration of various substances and are widely used in many industries such as textile, carpet, paper, plastic, leather tanning, pharmaceutical and cosmetic industries (Gercel *et al.*, 2008). Dyes are generally stable to light, oxidizing agents and heat, and their presence in wastewaters offers considerable resistance to their biodegradation, thus upsetting aquatic life (Aksu, 2005). Of current world production of dyestuffs (approximately 10 million kg/year) between 1 and 2 million kg of active dye enter the biosphere, either dissolved or suspended in water, every year (Allen *et al.*, 2003). These dyestuff pollute water bodies and make it unfit for aquatic life and cause human health hazard. Although dyes are recognized easily even at low concentrations, removal and treatment of dyes from wastewater presents a very special challenge because such wastewaters cannot be treated by conventional treatment methods (Geetha and Belagali, 2012). Various treatment methods for removal of colors and dyes are coagulation, ozonisation, membrane separation, anaerobic decolorization, oxidation, flocculation and absorption. Among all these methods, adsorption appears to be the best process for overall treatment of dyes stuff effluents.

Dyes exhibit considerable structural diversity and most of them are known to be non-biodegradable making it difficult to treat them by a single process (Southern, 1995). Since dyes are recalcitrant to the conventional aerobic biological treatment, eco-friendly and economical physical and chemical treatment processes need to be explored. Adsorption process has been found to be an efficient and economic process to remove dyes, pigments and other colorants. It has also been found to be superior to other technique for waste water treatment in terms of initial costs,

## ABSTRACT

Textile industry is the second largest source of water pollution in the world and pollution of water by use of dyes is a widespread phenomenon. Malachite green is a synthetic aromatic dye widely used by the textile industry of India and has been most often associated with aquatic pollution. This paper reports the ability of activated charcoal, a cheaply prepared adsorbent, to remove malachite green from aqueous solutions by varying the amount of adsorbent, pH, temperature, contact time and dye concentration in batch adsorption studies. It was found that adsorption increased with increasing pH upto 8 and temperature up to 50°C and equilibrium was achieved within 90 minutes of contact time between activated charcoal and malachite green. More than 99% of the dye could be removed by using only 500 mg activated charcoal per litre of dye. Adsorption data of malachite green onto activated charcoal could be described by the first order kinetic model and fitted well in the Freundlich adsorption isotherm. Using the Freundlich isotherm, the absorption capacity of activated charcoal was found to be 133.89  $\text{ug}^{1-1/n} \text{ml}^{1/n} \text{g}^{-1}$  at 30°C and hence is a promising low cost material for removal of dyes from waste water.

## KEY WORDS

Malachite green  
Activated charcoal  
Kinetics  
Adsorption isotherm

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simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al.*, 2004). Many adsorbents have been tested on the possibility to lower dye concentrations from aqueous solutions, such as activated carbon, peat, chitin, and others (Tahir and Rauf, 2006). Carbon based adsorbents are the most popular and has been used with great success. This study explores the feasibility of using commercially available activated charcoal as an eco friendly dye removal technology.

## MATERIALS AND METHODS

### Materials used in the experiment

Among many classes of synthetic dyes used in the textile and dyeing industries, triphenyl methane group of dyes such as malachite green is the largest and most versatile. Malachite green is not approved by the US Food and Drug Administration and has been nominated by it to be a priority chemical for carcinogenic testing by the National Toxicology Program in 1993 and is highly cytotoxic to mammalian cells and also acts as a liver tumor enhancing agent. Malachite Green (MG) used in the experiment is a dye commonly used in the Eastern part of Uttar Pradesh in textile and carpet industries. The dye was obtained from Ranchem, a branch of Ranbaxy Industries Limited, with a product code M0050, Batch No. G022H04 and adsorption maxima between 616 and 620 nm. The dye is identified as Basic Green 4 and is commercially known as Malchite Green and is identified by the IUPAC name as 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N, N-dimethyl aniline and empirical formula is  $C_{23}H_{25}N_2Cl$ ; molecular weight 365 and structure depicted herein. We scanned the wavelength in the visible region and found that the adsorption maximum was 615. Henceforth all experiments using malachite green was measured at 615 nm.

Activated carbon is a crude form of graphite with a random or amorphous structure, which is highly porous, exhibiting a broad range of pore sizes, from visible cracks, crevices and slits of molecular dimensions and finds widespread use as an adsorbent because of a large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity. Activated charcoal used in the experiment was obtained from HiMedia chemicals company and was used as received having atomic weight 12.01, CAS No. 7440-440 having traces of iron, chloride and sulphate.

### Determination of parameters affecting dye removal

The effect of adsorbent concentration, initial dye concentration, time of contact, pH and temperature was investigated as per methods suggested by Ram *et al.* (2012) and Bhanuprakash, *et al.*, (2015). The optimum pH for greatest removal efficiency was found out by equilibrating 50 mg of activated charcoal for 120 minutes on a rotary shaker with a rotation speed of 120 rpm with 50 mg L<sup>-1</sup> MG at different pH (2, 3, 4, 5, 6, 7, 8, 9, 10 and 11). The optimum contact time was found by equilibrating 50 mg of activated charcoal for 10, 20, 30, 40, 60, 90, 120 and 180 minutes with 60, 80 and 100 mg L<sup>-1</sup> MG and the effect of temperature on the adsorption process was investigated at 30, 40, 50 and 60 °C. In order to determine the optimum adsorbent concentration, increasing amounts of activated charcoal (25, 50, 100, 200, 300 and 400 mg) was equilibrated for 120 minutes on a rotary shaker with a rotation

speed of 120 rpm with 60 mg L<sup>-1</sup> MG. The influence of dye concentration on removal efficiency was investigated with 500 mg of activated charcoal shaken at 30°C for 90 minutes at 120 rpm with 100 mL of MG varying in strengths from 25 to 500 mg l<sup>-1</sup> respectively. The amount of dye removed was calculated and the percentage of dye removed was found out from the ratio of the amount of dye removed and the amount of dye added, multiplied by 100 and reported as %.

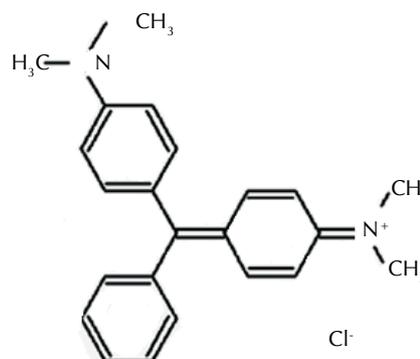
## RESULTS AND DISCUSSION

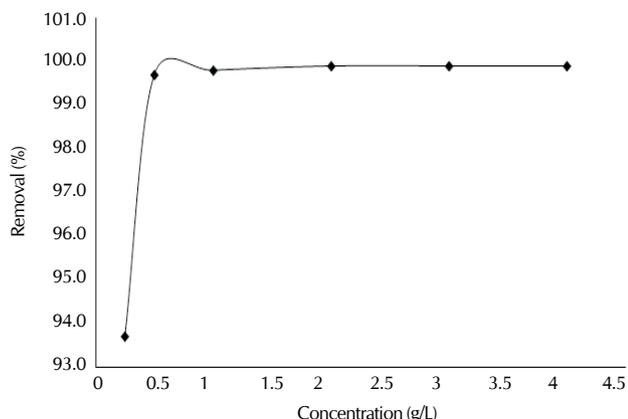
### Influence of adsorbent dose on adsorption

Adsorbent dose is an important parameter influencing sorption processes since it determines the sorption capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. It was found that the removal efficiency of malachite green increased from 93.7% to 99.9% with increase of adsorbent dose from 0.25-4.0 g L<sup>-1</sup> (Fig.1). This is attributed to the increase in surface area resulting from the increase in adsorbent mass, and the resulting increase in number of active adsorption sites (Nasuha *et al.*, 2010). The equilibrium adsorption capacity for MG and the amount of dye adsorbed per unit mass of adsorbent decreased with increasing adsorbent mass. This may be due to the decrease in total and effective adsorption surface area available to dye molecules resulting from overlapping or aggregation of adsorption sites (Crini *et al.*, 2007). Thus with increasing adsorbent mass, the amount of dye adsorbed onto unit mass of adsorbent gets reduced, resulting in decrease of equilibrium value with increasing adsorbent mass concentration. The maximum dye removal (99.9%) was observed at 4 g L<sup>-1</sup>, but this value was not very much different from the maximum removal obtained at 99.7% with an adsorbent dose of 0.5 g L<sup>-1</sup>. This is due to the binding of almost all dye molecules to activated charcoal surfaces and the establishment of equilibrium between the dye molecules on the adsorbent and in the solution at 0.5 g L<sup>-1</sup> and hence was considered to be optimal for removal of malachite green dye. A similar trend has been reported for adsorption of MG by sawdust (Garg *et al.*, 2004), clayey soil (Saha *et al.*, 2010), cyclodextrin based adsorbent (Crini *et al.*, 2007), sugar cane stalks (Hameed and Khaiary, 2008), bentonite (Ram *et al.*, 2012) and coral tree wood legume (Bhanuprakash, *et al.*, 2015).

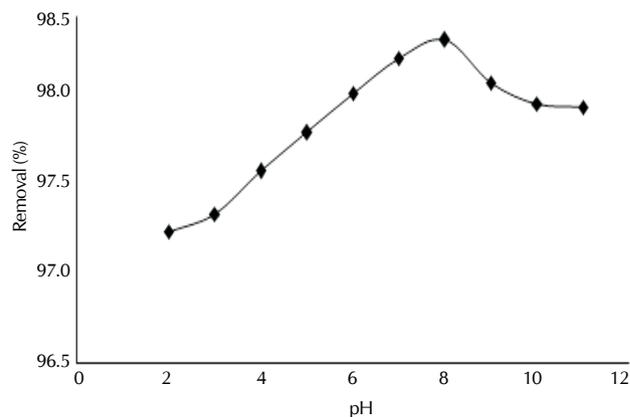
### Influence of pH on adsorption

The pH of an aqueous solution is an important monitoring

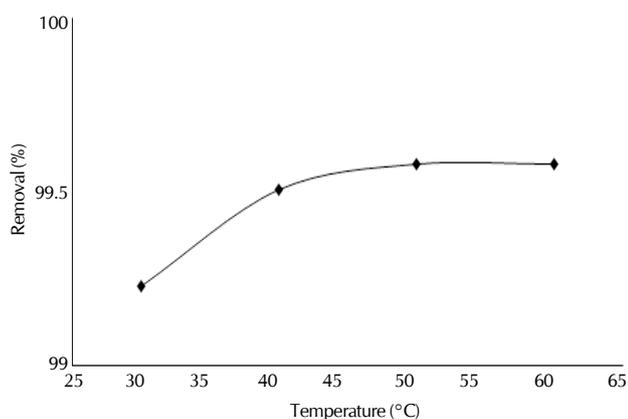




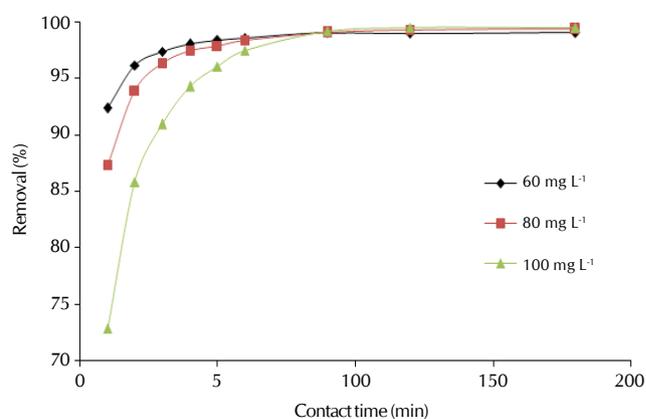
**Figure 1:** Influence of activated charcoal concentration on removal of malachite green from aqueous solution.



**Figure 2:** Influence of pH on the removal (%) of dye from aqueous phase.



**Figure 3:** Influence of temperature on the removal of dye from aqueous phase.



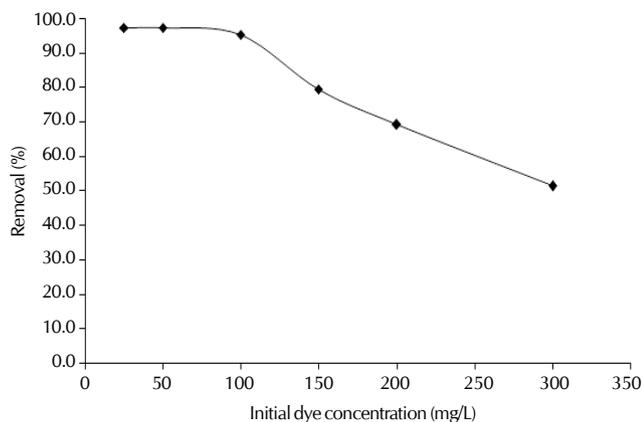
**Figure 4:** Influence of initial dye concentration and contact time on removal of dye from aqueous solution by activated charcoal.

parameter in dye adsorption, as it affects the surface charge of the adsorbent material and the degree of ionization, structural stability and colour intensity of the dye molecule. In this study, changes of pH of MG solution increased the adsorption capacity of activated charcoal (Fig. 2.). At pH 2 the dye removal was 97.3% which increased to 98.1% at pH 8.0. MG is a cationic dye, which exists in aqueous solution in the form of positively charged ions. As a charged species, the degree of its adsorption onto the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the solution pH. At low pH values, the adsorption was less because protonation of the functional groups present on the adsorbent surface easily takes place which restricts the approach of positively charged dye cations to the surface of the adsorbent resulting in lower adsorption of dye in acidic solution. With decrease in acidity of the solution, the functional groups on the adsorbent surface become de-protonated resulting in an increase in the negative charge density on the adsorbent surface, which facilitate the binding of dye cations (Mungapati *et al.*, 2010). The increase in dye removal capacity at higher pH may also be attributed to the reduction of H<sup>+</sup> ions, which compete with dye cations at lower pH for appropriate sites on the adsorbent surface. However with increasing pH, this competition weakens and dye cations replace H<sup>+</sup> ions bound to the adsorbent surface

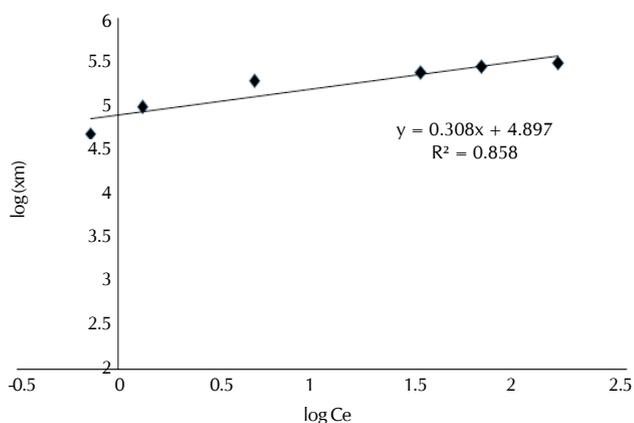
resulting in increased dye uptake. Similar observation has been reported for sorption of MG onto degreased coffee bean (Baek *et al.*, 2010) and rice husk based activated carbon (Sharma, 2011). The further decrease in adsorption above pH 8 observed in this study could probably be due to competition of dye molecule on adsorbent surface or reduction in negative surface charges on the surface of the adsorbent. Pradeep Sekhar *et al.*, (2009) also observed decrease in adsorption of malachite green on a biopolymer adsorbent at pH above 7.2.

#### Influence of temperature on adsorption

The effect of temperature on adsorption was investigated in the temperature range of 30 to 50°C (Fig. 3) using MG concentration of 50 mgL<sup>-1</sup> and equilibration time of 90 minutes. It was found that the adsorption capacity increased with increase in temperature from 30° to 50°C indicating that high temperature may favour the removal of MG and the adsorption process is exothermic in nature. Gupta and Suhas (2009) reported that of removal of a number of dyes is an exothermic processes. Saha *et al.* (2010) and Chowdhury and Saha (2010) reported that adsorption process is exothermic and at high temperature the thickness of the boundary layer decreases due to increased tendency of the dye molecules to escape from the adsorbent surface to the solution phase, which results in a decrease in the adsorption capacity as temperature is



**Figure 5: Influence of initial dye concentration on removal of MG by activated charcoal**

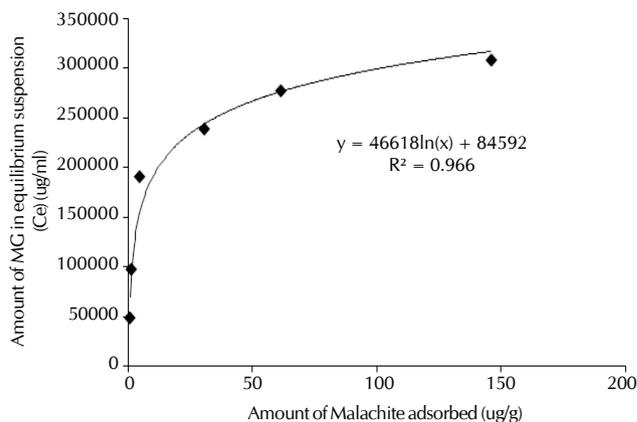


**Figure 7: Freundlich adsorption isotherm of malachite green on activated charcoal**

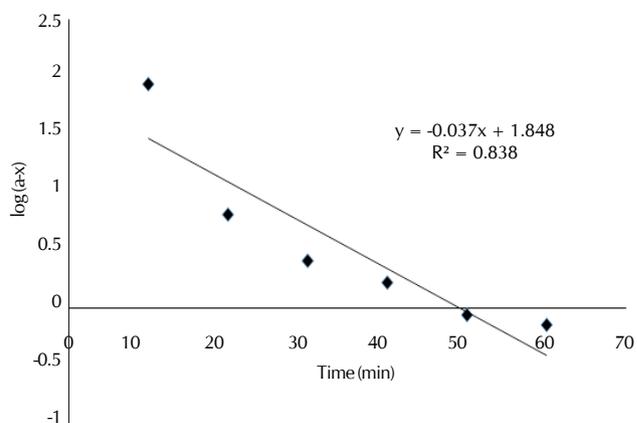
increased.

#### Influence of contact time on adsorption

The time dependant adsorption capacity and the removal efficiency of malachite green by activated charcoal was measured by varying the equilibrium time between three concentrations of malachite green viz., 60, 80 and 100 mg L<sup>-1</sup> and 50 mg adsorbent in the range of 10 to 180 minutes at 30°C (Fig. 4). Adsorption was found to be more at lower initial concentration than at higher initial concentration at small equilibration times but these differences levelled off as the equilibration times increased and equilibrium was attained at 90 min and remained so till 180 min. Similar findings for malachite green adsorption onto other natural adsorbents have been reported by other investigators (Ahmed and Kumar, 2010; Garg *et al.*, 2003; Hamdaoui *et al.*, 2008). Three consecutive steps are involved in the removal of dye from water by a porous adsorbent (Tahir and Rauf, 2006). At first, the adsorbate species migrate from the bulk liquid phase to the outer surface of adsorbent particles (film diffusion). Secondly, the dye species move within the micro and macropores of adsorbent particles (pore diffusion). Thirdly, the reaction of adsorbate-adsorbent species takes place on the surface. The fast adsorption rate at the initial stage may be explained by an increased availability in the number of active



**Figure 6: Adsorption isotherm of malachite green on activated charcoal**



**Figure 8: Kinetics of malachite green adsorption onto activated charcoal at 100 mg L<sup>-1</sup> dye concentration**

binding sites on the adsorbent surface whereas at the later stages, sorption is likely an attachment-controlled process due to less available sorption sites.

#### Influence of dye concentration on adsorption

The effect of initial dye concentration on the adsorption of MG on activated charcoal was studied at 0.5 g L<sup>-1</sup> and the initial MG concentration of 25 to 500 mg L<sup>-1</sup> (Fig. 5). As the initial dye concentration increased from 25 mg L<sup>-1</sup> to 100 mg L<sup>-1</sup>, the adsorption capacity of AC also increased slightly. As a rule, increasing the initial dye concentration results in an increase in the adsorption capacity because it provides a driving force to overcome all mass transfer resistances of dyes between the aqueous and solid phase which is also evident from increasing equilibrium sorption. The increase in equilibrium sorption generally continues till the sorbent saturation is achieved (Baek *et al.*, 2010). However the dye removal percentage decreased thereafter from 97.4 % to about 51.3 %. It can be explained that the adsorbent has a limited number of active sites, which becomes saturated at a certain concentration. This indicates that the adsorption capacity will increase with the increase of initial dye concentration mainly due to the rise in the mass transfer from the concentration gradient. However, the concentration will have inversely impacted on the adsorption frequency because of the limited

adsorption sites available for the uptake of cationic dye. Similar observations have been reported by Chowdhury *et al.*, (2011) and Zhang *et al.*, (2008).

### Adsorption and Kinetic studies

Plotting the solid phase concentration against liquid phase concentration, graphically it is possible to represent the equilibrium adsorption isotherm (Fig 6). The isotherm yields certain constants whose values express the affinity and surface properties of the adsorbent. Our adsorption data could be described by the linearised form of Freundlich adsorption equation viz.,  $\log(x/m) = \log K + 1/n \log C_e$ , where K and 1/n are constants associated with the affinity of activated charcoal for malachite green and the degree of curvature of the isotherm respectively. The correlation coefficient of the data was greater than 0.86, suggesting a good fit of the experimental data. The value of K and n for adsorption of malachite green on activated charcoal was estimated by linear regression of the logarithmically transformed data (Fig. 7) and were  $133.89 \text{ ug}^{-1/n} \text{ ml}^{1/n} \text{ g}^{-1}$  and 4.9 g l<sup>-1</sup> respectively. The magnitude of K expresses the adsorption capacity whereas 1/n values provide an idea of the intensity of adsorption.

The chemical kinetic describes reaction pathways, along times to reach the equilibrium whereas chemical equilibrium gives no information about pathways and reaction rates. In recent years, adsorption mechanisms involving kinetics-based models have been reported. We investigated the first order kinetic model to investigate the mechanism of adsorption and found that the plot of  $\log(a-x)$  versus time, where a, is the initial concentration and x, the equilibrium concentration at time t, to be linear within the first 60 minutes (Fig 8).

Huge amount of organic wastes are produced in our country that could be easily converted into activated charcoal. Such low cost locally produced activated charcoal could be readily used as an adsorbent for the removal of malachite green from aqueous solution. Adsorption of the dye was studied by batch technique and it was observed that >99% of dye removal was achieved by using 0.5 g of activated charcoal. The adsorption increased with increasing pH upto 8 and temperature upto 50°C. Equilibrium was achieved within 90 minutes and the kinetics of adsorption developed can be used to achieve low levels of dye from aqueous solutions utilizing activated charcoal. The adsorption data follows the Langmuir isotherms and has a linear kinetic behaviour in the first 60 minutes.

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