Research Journal of Chemical Sciences _____ ISSN 2231-606X
Vol. **5(12),** 38-43, December **(2015)** *Res. J. Chem. Sci.*

Removal of Malachite green dye from Aqueous solution using Magnetic Activated Carbon

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Available online at: www.isca.in, www.isca.me
Received 9th November 2015, revised 26th November 2015, accepted 10th December 2015

Abstract

Magnetic activated carbon (MAC) was synthesized by combining aqueous solution of prepared activated carbon (AC) and iron oxide nanoparticles by co-precipitation method. A variety of techniques such as N_2-BET surface area, X ray Diffraction (XRD), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Vibrating Sample Magnetometer (VSM) were used to characterize the structure,morphology and magnetic performance of MAC. The N_2-BET surface area of the MAC (721 m^2g^{-1}) is found lesser than the prepared AC (1900 m^2g^{-1}). The saturation magnetization for MAC was 22.80emu/g it shows super magnetic behaviour. SEM of the MAC shows the presence of different size pores, cracks and crevices. TEM of MAC produce nanoparticles with size in the range of 5-25nm. XRD of MAC indicates the presence of crystalline structure for iron oxide nanopartcles. The adsorption data show that the adsorption capacity was investigated by absorbing Malachite Green (MG) from aqueous solution, which demonstrated an excellent adsorption capacity of MAC (333 mg g^{-1}). A Langmuir kinetic model is fitted well for malachite green adsorption on MAC.

Keywords: Magnetic Activated carbon, chemical co precipitation, Malachite green dye, adsorption and kinetics.

Introduction

Due to rapid industrialization the removal of dyes from industrial waste water is becoming increasingly important as awareness of the environmental impact of such pollutants is fully realized[1,2]. In industries, such dyes precipitating out of solution and coating other materials can have a profound effect on both aqueous and nonaqueous environments[3]. Malachite Green (MG) is dye is basically a cationic dye and these dyes are used in many industries for their coloring agent[4,5]. Activated carbon with high surface area has been widely used in a variety of applications like separation /purification of liquids and gases, removal of toxic substances and organic pollutants from drinking water, recovery of solvents and as catalysts. As environmental pollution is becoming an increasingly serious problem, the need for high surface area activated carbon is growing. It can be prepared from any carbonaceous materials like agriculture waste, coal and ligno-cellulosic materials. Activated carbon is a non graphitic carbonaceous material with high surface area, pore volume and widely used as an adsorbent in chemical and food industry. Most commonly used malachite green dyes removal methods like coagulation, ion exchange, precipitation and adsorption, out of which adsorption is the most widely used because of high efficiency, low cost and easy to handle[6-10]. Activated carbon is considered to be one of the best technologies implanted in water purification systems[11]. Many researchers have investigated activated carbon is expensive price, it uses cheap and efficient alternative to remove dyes from waste water treatment[12]. Recently, magnetic activated carbons have been interested in many researchers and scientists. Nowadays, nanoparticles are not only widely applied in the fields of medicine, molecular biology and bioinorganic chemistry, but they are also well known in environmental science[13]. Magnetic activated carbon adsorbents can easily be separated from a solution using a magnetic separator even if the solution contains a significant concentration of solids. In contrast, traditional adsorbents are removed by screening. Magnetic materials have gained special attention in water treatment, based on their advantage such as easy separation, simple manipulation process, kind operation conditions and easy specifically functional modifications[14-15]. The present work is an attempt to prepare magnetic activated carbon (MAC) by using activated carbon and Fe_3O_4 magnetic nanoparticles by a chemical coprecipitation method for the removal of Malachite Green (MG) dyes from aqueous solution.

Material and Methods

Materials: Nitric acid (HNO_3, 63%), Ferric Chloride ($FeCl_3$), Ferrous chloride ($FeCl_2$), Sodium hydroxide (NaOH) and Malachite green dye (Merck, India) were procured from Nagpur, India.

Preparation of Magnetic activated carbon (MAC): The magnetic activated carbon was prepared by combining aqueous solution of prepared activated carbon (AC) and prepared iron oxide nanoparticles Fe_3O_4 by co-precipitation method. First to prepare magnetic iron oxide nanoparticles Fe_3O_4 were carried out in co-precipitation method. A suspension of 20 g $FeCl_3$ and 10g $FeCl_2$ per 400ml of deionised water was stirred for 1h. After

stirring by adding 2M NaOH solution at 40^0C under the presence of N_2 gas. These suspension keep at 70^0C for 12h. Finally Fe_3O_4 was cooled at room temperature, washed with deionised water until pH neutral. In the next step some amount of Activated carbon were impregnated with nitric acid using ultrasonic bath without stirring for 2 hours at 100^0C. This impregnated activated carbon was filtered and dried at room temperature. Then Activated carbon mixed with prepared Fe3O4 nanoparticles in 200ml aqueous solution for 1.5 h at 100^0C. Then these samples were filtered and dehydrated in an oven at 100^0C for 1h. Then these samples were heated in muffle furnace at 750°C for 3h under the presence of N_2 gas. The product washed with deionised water to remove excess NaOH and dried at 70^0C.

Method for Adsorption Isotherm and Kinetics study: To evaluate adsorption equilibrium data for Malachite Green (MG) experiments were performed in a batch system. 100mL of MG solution of known concentration was placed in 300 ml BOD bottles and accurately 0.1 gm Magnetic activated carbon (MAC) were added into each bottle. The BOD bottles were placed on a mechanical shaker with shaking speed of 600+-20 rpm and stirred for 72 hours. After equilibrium reached, solutions from each bottle were withdrawn and adsorbate concentration, C_e was determined by UV/visible spectrophotometer (Model Lambda 35, Perkin Elmer UV/VIS spectrophotometer) with wavelength 615 nm.

Kinetics study, a cylindrical vessel of 5L capacity fitted with 8 baffles was used. 2gm of accurately weight prepared magnetic activated carbon was introduced into 2L of malachite green solution of known concentration with constant stirring. The adsorbate was taken out from the vessel at following time period and the concentration was determined with the help of UV/visible spectrophotometer.

Results and Discussion

Characterization of prepared MAC: To determine Microporous structure of the MAC, iodine number was determined as per ASTM D4607-94 (1999) and the surface area and pore volume of prepared MAC were determined by SMARTSORB 92/93 N_2- BET surface area analyzer**.** The iodine number of AC; 1650 mg g^{-1} is more than that of MAC; 670 mg $g^{-1}$and N_2BET and pore volume of AC are 1900m^2 g^{-1} , 0.5420 cm^3 g^{-1} and MAC are 721 m^2 g^{-1} ,0.3459 cm^3 g^{-1} respectively shown in Table-1. The lesser surface area of the MAC is due to partially filling of pores of AC with iron oxide nanoparticles. It reveals that magnetization processes reduce the Iodine value, surface area and the pore volume. Micro porosity development is substantially reduced in MAC.

Table-1
Characteristics of AC and MAC

Adsorbent	Iodine number (mg/g)	N_2-BETsurface Area (m^2/g)	Pore volume (cm^3/g)
MAC	670	721	0.3459
AC	1650	1900	0.5420

X-ray diffraction (XRD) analyses of prepared magnetic activated carbon sample were carried out with X-ray Diffractometer model (PANalyticalX'pert Pro). XRD patterns are given in figure-1. The XRD pattern shows a crystalline structure and indicates the amorphous character of the carbon matrix in which iron oxide nanoparticles is impregnated. The X-ray diffraction patterns for MAC show a number of sharp peaks which are compatible with the presence of $Fe(OH)_2$, $Fe(OH)_3$ and Fe_2O_3.

The surface morphology of MAC was studied by scanning electron microscopy (SEM) with a JEOL JSM-6380 model Scanning Electron Microscope. Figure-2 shows SEM image of MAC, in the picture it appears that Fe_3O_4 particles composed of small particle.

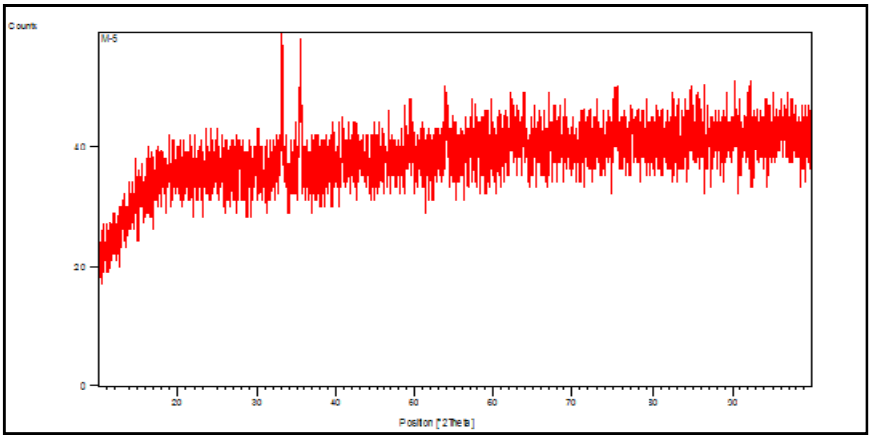

Figure-1
XRD of MAC

The size and shape of nanoparticles of MAC were observed by Transmission electron microscopy (TEM) and high resolution TEM (HRTEM) on a JEOL JEM-2010F. TEM micrographs for the prepared MAC and are shown in figure- 3 (a-b). From these micrographs it is observed that the particle size of the nanoparticles lie in the range of 5-20 nm. Fe_3O_4 nanoparticles with a cubic structure are clearly visible in the micrographs. The particles formed tend to cluster as they are magnetic in nature. Recording of higher resolution images of the carbon might be quite difficult owing to its highly disordered structure[16].

Vibrating Sample Magnetometer (VSM) was used to characterize the structure; morphology and magnetic performance of MAC.The VSM analysis was carried out using Lakeshore vibrating sample magnetometer (VSM) 7410 at room temperature are shown in figure-4. VSM shown hysteresis loop by plotting a graph between magnetic moment and magnetic field[17]. The saturation magnetization for MAC was 22.80emu/g it shows super magnetic behavior.

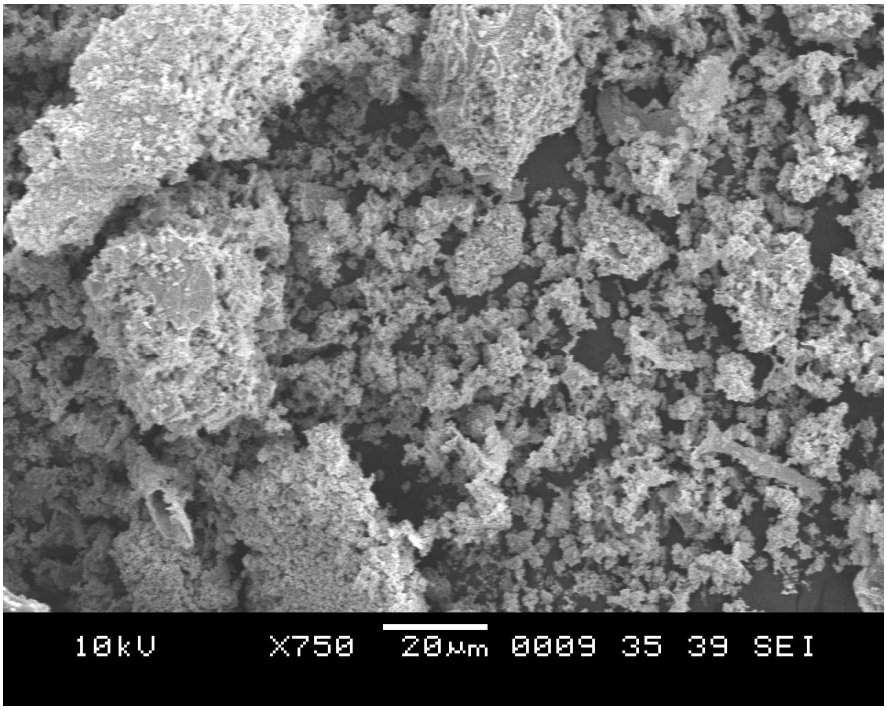

Figure-2
SEM image of MAC

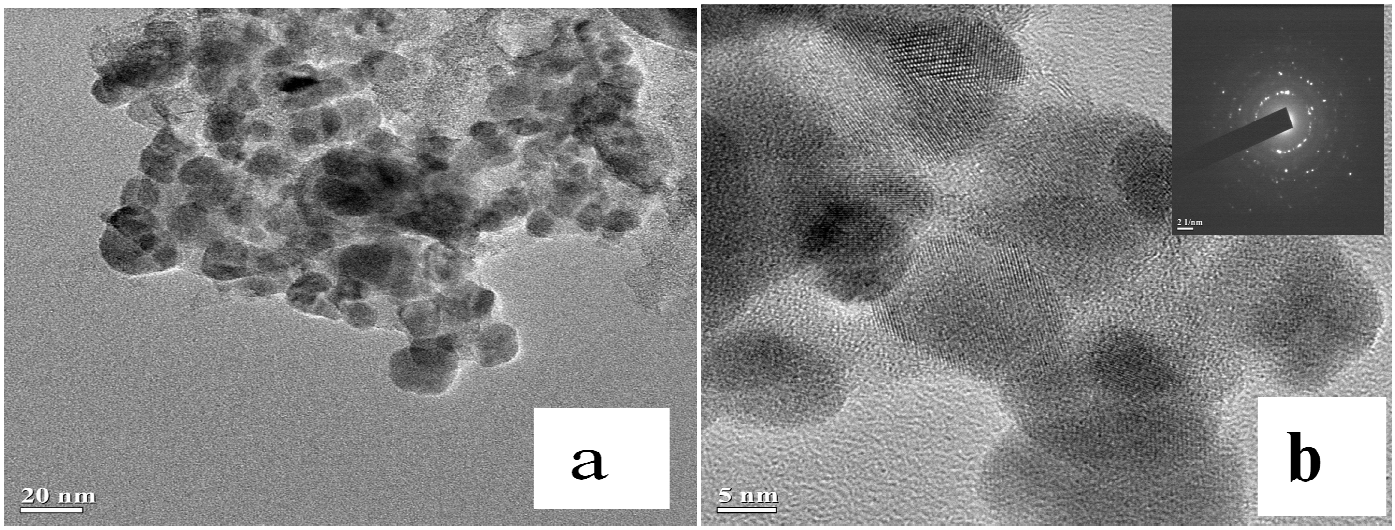

Figure-3 a, 3b
TEM images of MAC

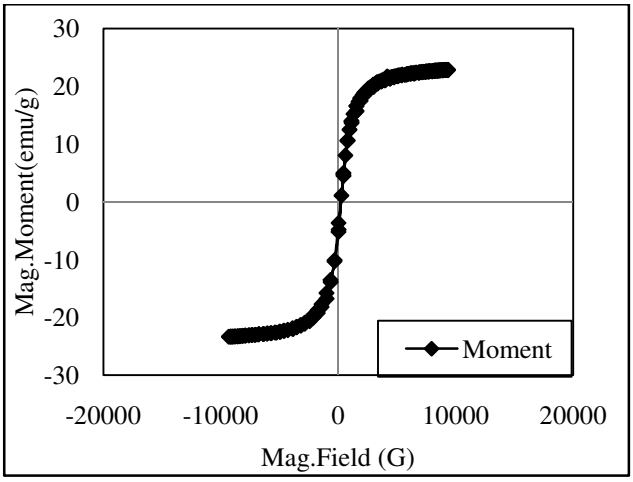

Figure-4
VSM Magnetisation Curve of MAC

Adsorption isotherms: Adsorption isotherms study was performed by various ways, in these study Langmuir adsorption isotherm, Freundlich adsorption isotherm and BET adsorption isotherm were used.

The precise quantity of MG adsorbed was calculated from the following equation;

$Qe = (C_0 - C_e) \times V/W$

Where Qe is the adsorption amount of malchite green (mg/g) in the solid at equilibrium, C_0 and C_e are initial concentration of Malachite Green (mg/L) respectively; V is volume (L) of aqueous solution of Malachite green and W is the weight (g) of magnetic activated carbon. The plot of Qe (mg/g) verses the equilibrium concentration of adsorbate in solution Ce (mg/L) in figure-5.

The Langmuir adsorption isotherm has been used by many authors for the adsorption of inorganic and organic substances. The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the sorbed molecules[18]. The linear form of the Langmuir isotherm is given by the following equation:

$1/Q_e = (1/Q_0) + (1/Q_0 b) \times 1/C_e$

Where Q_e is the maximum amount of the Malachite Green (MG) adsorbed per unit weight of the adsorbent at equilibrium, Q_0 is the monolayer capacity of adsorbent, C_e is the concentration of adsorbate at equilibrium, and b is a Langmuir constant. Langmuir parameters Q_0 and b were calculated from the slope and intercept of the linear plots of $1/Q_e$ vs. $1/C_e$ as given in figure-6 and value shown in table-2.

The adsorption data for Malachite green (MG) was also analyzed by the Freundlich adsorption model. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems[19]. The linear form of Freundlich adsorption model is as follows:

$\text{Log } (Q_e) = \text{Log}K_f + 1/n \text{ Log } (C_e)$

Where, K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The value of K_f and 1/n are obtained from the slope and intercept of the linear Freundlich plot of Log Qe vs. Log Ce in figure-7 and the values shown in table-2.

The BET adsorption model can be derived similar to the Langmuir adsorption model, but by considering multilayered gas/solid molecule adsorption, where it is not required for a layer to be completed before an upper layer formation starts. The Langmuir adsorption isotherm is usually better for chemisorptions and the BET adsorption isotherm works better for physisorption for non-micro porous surfaces. The BET adsorption equation can represented as:

$C_e/Q_e(C_s - C_e) = 1/Q_0 z + (z - 1/Q_0 z) * C_e/C_s$

Where C_e, Q_e, Q_0, have the same meaning as in Langmuir model, C_s is the saturated concentration of the adsorbate and z is BET constant. BET parameters Q_0 and z were calculated from the graph Plotted between C_e/C_s vs C_e/Q_e $(C_s - C_e)$ in figure-8.The values shown in Table-2

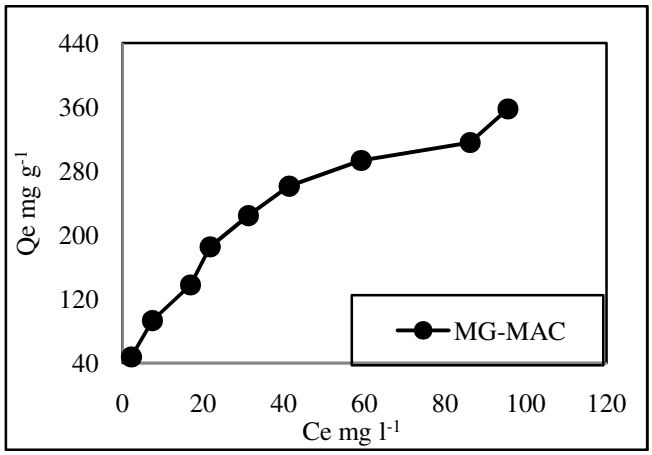

Figure-5
General Adsorption graph of MAC

Kinetic study for MAC: A simplified interpretation of the rate expression based on Langmuir theory has also been used to evaluate the adsorption rate constant using Langmuir kinetic model[10]. Kinetic data were evaluated using following Langmuir Kinetic equations,

$\ln [(C_t - C_e)/(C_t + a)] = -kC_e t + \ln[(C_0 - C_e)/(C_0 + a)]$

Where, $a = (C_0/kC_e)$ and $K = k/k'$

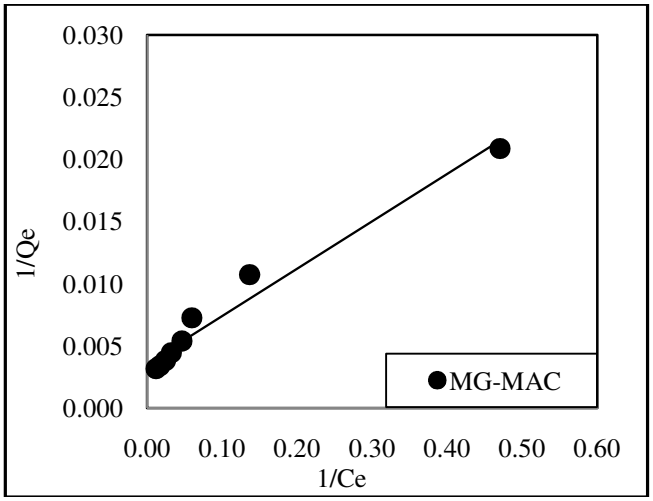

Figure-6
Langmuir Adsorption graph of MAC

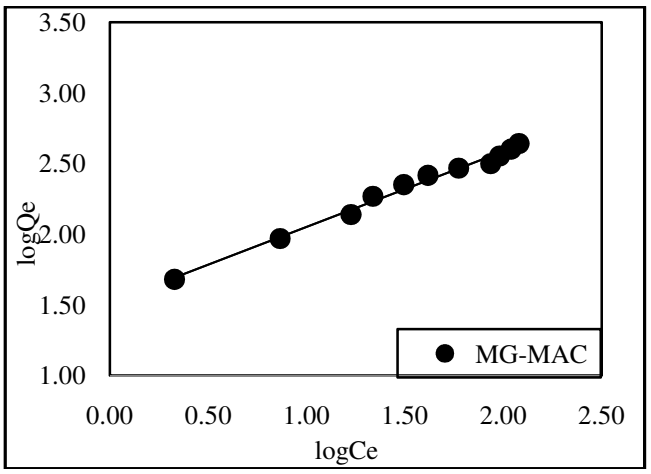

Figure -7
Freundlich Adsorption graph of MAC

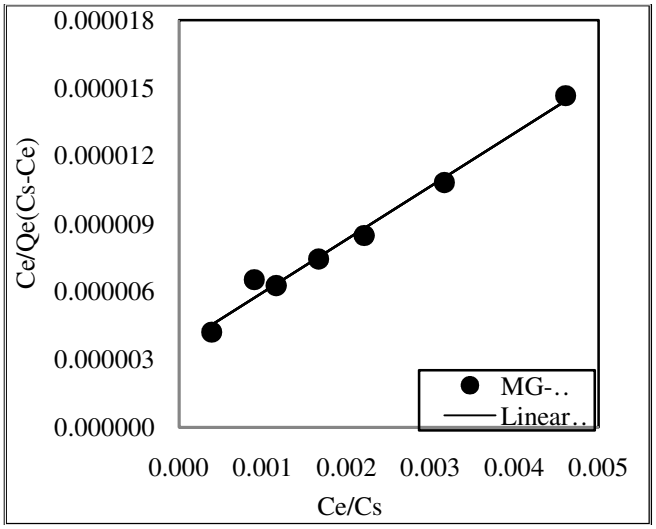

Figure-8
BET Adsorption graph of MAC

The rate of adsorption in kinetics of MAC is more at initial time intervals represented in figure-9. The adsorption and desorption rate constants were thus evaluated by plotting $\ln[(C_t-C_e)/(C_t+a)]$ against t, figure-10. Table-2 reports the value of adsorption and desorption rate constants for MAC.

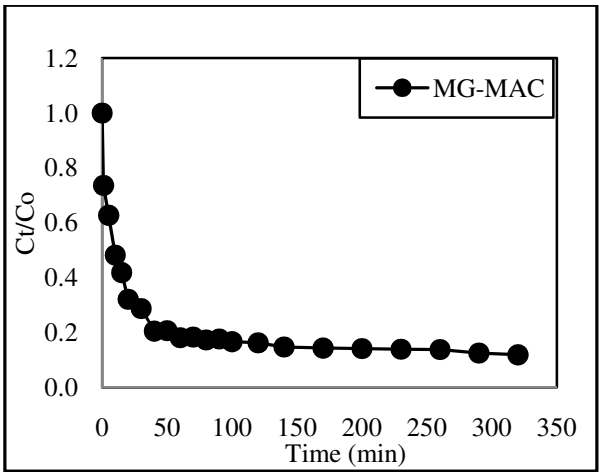

Figure-9
General Kinetics graph of MAC

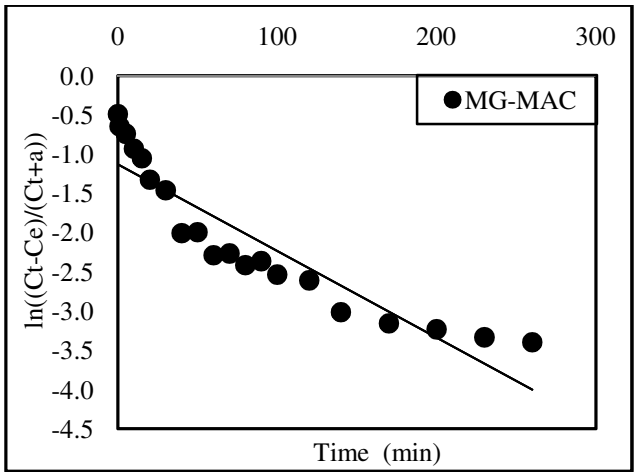

Figure-10
Langmuir kinetics graph of MAC

Conclusion

Magnetic activated carbon (MAC) were prepared, characterised and evaluated for removal of malachite green from aqueous waste. SEM of MAC shows the dispersion of Fe_3O_4 nanoparticles. These magnetic adsorbents have very good adsorption efficiency for Malachite Green (MG) contaminants in water. The XRD of MAC shows a number of sharp peaks which are compatible with the presence of $Fe(OH)_2$, $Fe(OH)_3$ and Fe_2O_3 .This illustrates that domain of iron species exists which is crystalline in the MAC sample. The TEM of MAC shows Fe_3O_4 nanoparticles of size 5-20 nm and cubic in nature. VSM analysis of MAC is 22.80 emu/g, which display magnetic properties under external magnetic field.

Table-2
Adsorption isotherm and Kinetic data for MAC

Adsorbent	Adsorbate	Langmuir Constant		Freundlich Constant		BET Constant		Langmuir Kinetic Constant	
MAC	MG	Q^o	b	K_f	1/n	Q^0	z	Ka	Kd
-	-	333	0.0946	32.80	0.534	457	570	167.16	0.0048

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