IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

PREPARATION, CHARACTERIZATION AND BIOSORPTION BEHAVIOR OF IRON IMPREGNATED ACACIA ARABICA - A LOW COST ADSORBENT

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ABSTRACT

Water pollution is being a major threat to the existing environment due to contamination from natural and anthropogenic origins. Various treatment techniques are being reported by the researchers, of which adsorption has gained more importance in removing colour, odour, toxic gases, heavy metals etc. from waste water. Activated carbon is the commonly used adsorbent well known for its high porosity and larger surface area. Various biomaterial wastes are being converted to activated carbon for the treatment of waste water because it not only solves the problem of waste disposal but can be used as a valuable raw material for pollution abatement. Acacia Arabica, a locally available tree is widely used as biosorbent . The present investigation was done using iron impregnated Activated carbon synthesized from Acacia Arabica bark for the removal of malachite green dye from aqueous solution. AC from Acacia Arabica and iron impregnated AC were characterized using FTIR and SEM micrograph . Batch mode of adsorption studies were performed for optimizing control parameters such as pH, contact time, initial dye concentration, adsorbent doses. The experimental data were fitted using Langmuir and Freundlich isotherm models. The potential of Acacia Arabica and Iron impregnated Acacia Arabica are compared.

Keywords: Acacia Arabica, Activated Carbon, Biosorbent, Isotherms, Malachite Green

I INTRODUCTION

Synthetic dyes are more widely used in industries such as textiles, paper and pulp, plastics, tanneries , printing, cosmetics, pharmaceuticals, color photography and petroleum. This generates huge amounts of coloured effluents that are directly discharged into the nearest water bodies. These effluents are characterized to be ecotoxic to aquatic organisms and human beings. Malachite Green dye is one of the direct dyes used for silk, wool, jute, cotton, leather and paper[1]. It is also used in animal food and in aquaculture[2]. However, the dye effluents are reported to cause carcinogenesis, mutagenesis, chromosomal fractures, teratogenecity and respiratory toxicity[3]. Thus removal of malachite green dye has been chosen for study.

Several biosorbents have been used to remove dyes[4-5] from aqueous solutions for its good adsorption behavior and easy recovery of sorbent for further treatment. The surface characteristics of an activated carbon makes it a versatile adsorbent in treatment of dyes. This research work illustrates the modification in surface morphology of Acacia Arabica[6-8] to increase the adsorption capacity towards the dye. The activated carbon synthesized from Acacia Arabica was oxidized using KMnO4 followed by iron impregnation[9] to increase the number of active sites.

II EXPERIMENTAL

2.1 Material

AR grade of potassium permanganate($KMnO_4$) and ferrous sulphate($FeSO_4.7H_2O$) were purchased from Qualigens Fine chemicals, Mumbai and sodium bicarbonate($NaHCO_3$) were purchased from Sigma Aldrich.

2.2 Preparation of Adsorbent

Barks of Acacia Arabica were obtained from local grounds and were washed well with tap water to remove dust and other impurities. It was then sun dried and cut into small and uniform sized pieces. Dried bark pieces were chemically activated using 1:1 sulfuric acid[10] kept overnight. After decanting the acid the remains were washed with deionised water thoroughly several times to remove excess acid. It was then subjected to thermal activation at 600^oC for about 90 mimutes in muffle furnace. The obtained carbonized material is cooled to room temperature and finely ground and sieved using 125 micron sieve. 2g of powdered AAAC was stirred with 1 M $KMnO_4$ solution for 30 min at 300 rpm. The so obtained AC was then stirred with 1M $FeSO_4.7H_2O$ for 6 hr at 300 rpm. The suspension was filtered, washed with 1% $NaHCO_3$ several times and filtered again. The FeAAAC that was formed was dried well in the hot air oven at 110^oC [9].

2.3 Preparation of Adsorbate

The stock solution of the dye malachite green(AR Grade) purchased from Loba Chemie Ltd., Mumbai was prepared by dissolving 100 mg of the dye in 1 litre deionised water. To optimize dye concentration, a number of standard solutions were prepared of different concentrations ranging from 10 to 50 mg/l. The absorbance corresponding to residual amount of dye were recorded at 617 nm spectrophotometrically using UV/vis spectrophotometer.

International Journal of Advance Research in Science and Engineering
Vol. No.6, Issue No. 03 , March 2017
www.ijarse.com
IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

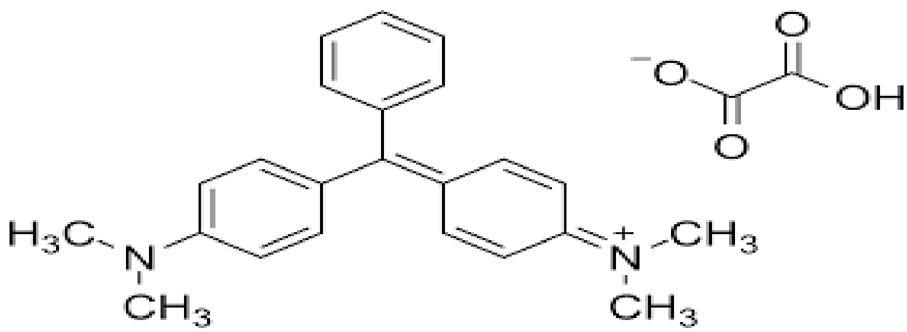

Figure 1. Molecular structure of malachite green dye

2.4 Batch Mode Adsorption Studies

Batch mode experiments were carried out to investigate the adsorption efficiency at varied initial concentration (10,20,30,40,50 mgL^{-1}), pH(3.0,4.0,5.0,6.0,7.0,8.0), adsorbent dosage(0.01,0.02,0.03,0.04,0.05g) and contact time(30,60,90,120,150 min.). All the experiments were performed at room temperature of 29±1^oC [11]. Batch mode experiments were carried out in 100 ml conical flask with 50 ml of the test solution and shaken in Benchtop incubator cum orbital shaker(Model: NEOLAB OSI 261). At the end of required time interval, the samples were removed from the shaker and filtered using Whatman No. 42 filter paper The unadsorbed dye was recorded using UV/vis spectrophotometer. The amount of dye adsorbed at equilibrium was calculated from the equation[12] (1):

$$q_e = \frac{(C_0 - Ce)V}{(m)} \quad (1)$$

where C_e (mgL^{-1}) is the concentrations of dye at equilibrium

C_0 (mgL^{-1}) is the initial concentration of the dye in solution

V is the operating volume of the solution (L)

m is the mass of dry adsorbent (g).

The removal percentage of the dye was calculated using equation (2):

$$\text{Removal efficiency,\%} = \frac{(C0 - Ce)}{(C_0)} \times 100 \quad (2)$$

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www.ijarse.com
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III RESULTS AND DISCUSSION

Characterisation of the adsorbent: The Scanning electron microscope images of the material serve as the direct tool n understanding the surface morphology of the adsorbent. The nano tubular and porous structure of Acacia Arabica indicates large surface area for better adsorption. The adsorption capacity is further increased by oxidation and iron impregnation of activated Acacia Arabica.

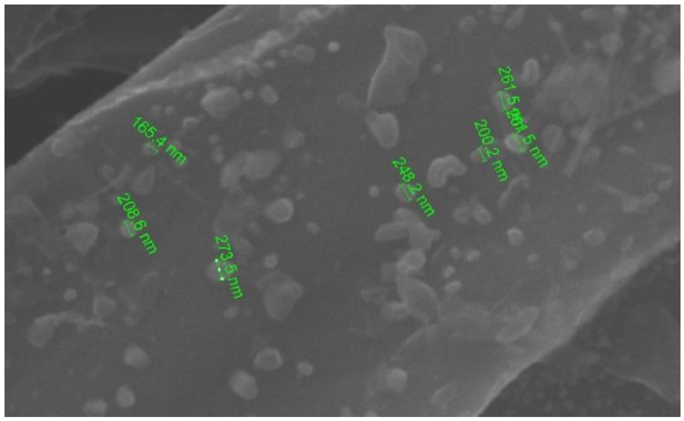
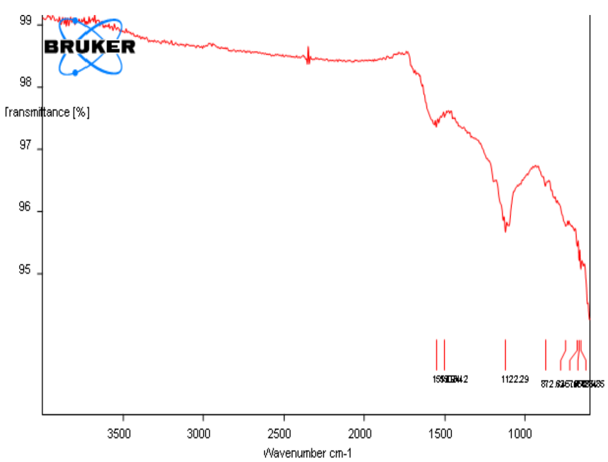


Figure 2: Sem photograph of activated acacia arabica bark

The scanning electron microscope image of activated acacia Arabica reveals a rod like structure with nano sized pores that make available a larger surface area for adsorption. Further the surface is modified by oxidation and iron impregnation to increase the adsorption capacity. The IR spectrum of AAAC and FeAAAC are shown below.



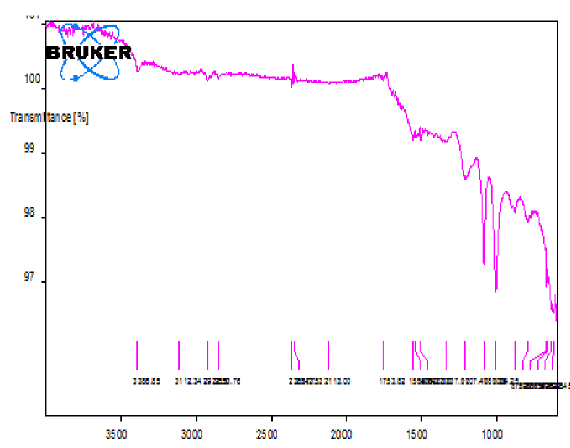


Figure 3: IR image of AAAC **Figure 4: IR image of FeAAAC**

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In fig. 3, Two intense bands are observed, one at 1560-1530 cm^{-1}correspond to secondary amide and N-H bending and a band at 1122 cm^{-1} correspond to C-N stretching vibrations [13].

In fig. 4, a band at 3386 cm^{-1} correspond to N-H stretching and a band at 1560-1530 cm^{-1}correspond to secondary amide and N-H bending which was observed in IR image of AAAC too. A band at 1207 cm^{-1} correpond to C-N stretching as in AAAC, a sharp band at 1083 cm^{-1} ascribes to CO stretching and at 1004 cm^{-1} belongs to =C-H bending.

3.1 Effect of Initial Dye Concentration

The initial dye concentration influences the adsorbent behavior of the system. The dye uptake was high at lower dye concentrations and gradually decreased at higher concentration. All dye molecules at lower concentration interact well with the binding sites. A dye removal efficiency was calculated as follows:

Table 1: Effect of initial concentration on dye removal

Initial Concentration, ppm	Equilibrium Concentration, ppm	Removal Efficiency,%
10	0.65	93.5
20	2.15	89.25
30	5.35	82.17
40	8.25	79.38
50	13.5	73

It can be concluded that every adsorbent has a saturation limit of adsorption at certain concentration of the dye[14] beyond which dye uptake will decrease. The amount of dye adsorbed at different dye concentrations is given below.

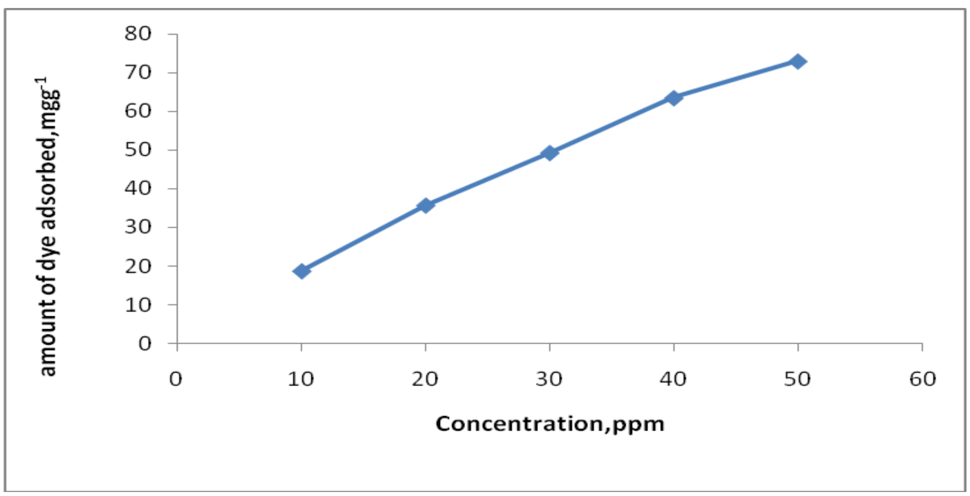

Figure 5: Effect of initial dye concentration on the dye removal

International Journal of Advance Research in Science and Engineering
Vol. No.6, Issue No. 03 , March 2017
www.ijarse.com
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ISSN (O) 2319 - 8354
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3.2 Effect of Adsorbent Dose

The dye removal was investigated as the function of adsorbent dose. With the subsequent increase in adsorbent dose, dye uptake was found to increase. Table 3 shows the data for different doses of adsorbent. As the amount of carbon increased the dye adsorption also increased upto the addition of 0.04g. This is due to the availability of more surface sites at higher amounts of carbon. Earlier literature have reported 99% for 0.5 g/100 ml carbon dose at 80°C for 100 mg/l initial concentration of the dye[5]. It is reported in However, there is a dip at 0.05 g because all the dye molecules get bonded to the adsorbent establishing equilibrium between dye molecules on the adsorbent and in the solution[15]. Thus further adsorption is not possible.

Table2: Effect of adsorbent dose on dye removal

Adsorbent dose,g	Initial Concentration,ppm	Equilibrium concentration,ppm	Removal efficiency,%
0.01	100	25.25	74.75
0.02	100	21.0	79
0.03	100	17.25	82.75
0.04	100	13.75	86.25
0.05	100	15.5	84.5

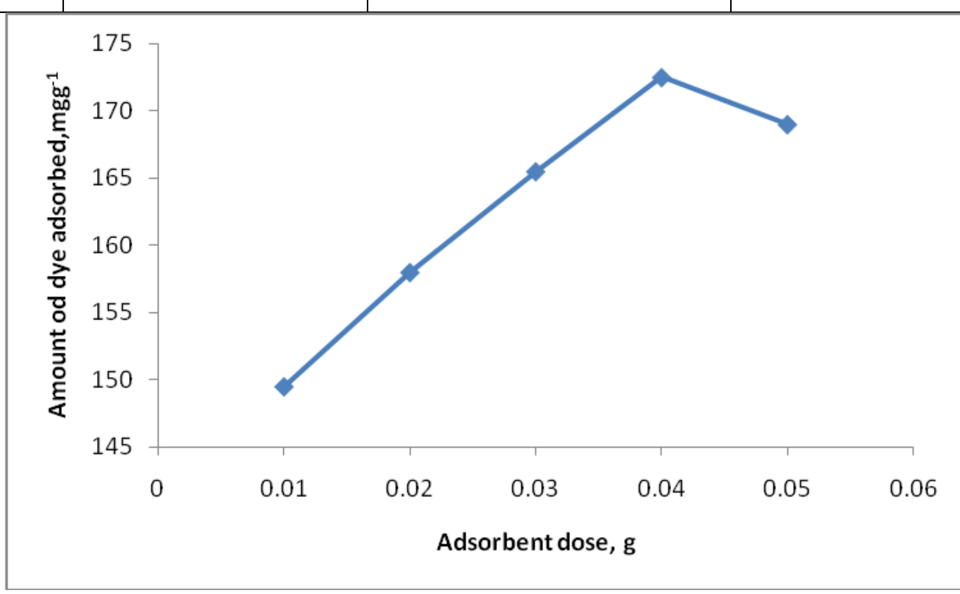

Figure 6: Effect of adsorbent dose on the dye removal

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Vol. No.6, Issue No. 03 , March 2017
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3.3 Effect of pH

The pH of the solution has been found to control adsorption capacity. At pH 2 and 9, the colour of the dye disappeared partially which revealed that the dye is self fed[16]. From pH 4 to 8, adsorption behavior gradually improved and showed better adsorption at pH 8. Table 4 and the graph below shows the removal efficiency with variation in pH.

Table 3: Effect of pH on dye removal

pH	Initial conc,ppm	Equilibrium conc,ppm	Removal efficiency,%
3	30	11.65	61.17
4	30	11.0	63.33
5	30	10.20	66.0
6	30	8.30	72.33
7	30	6.15	79.5
8	30	3.45	88.5

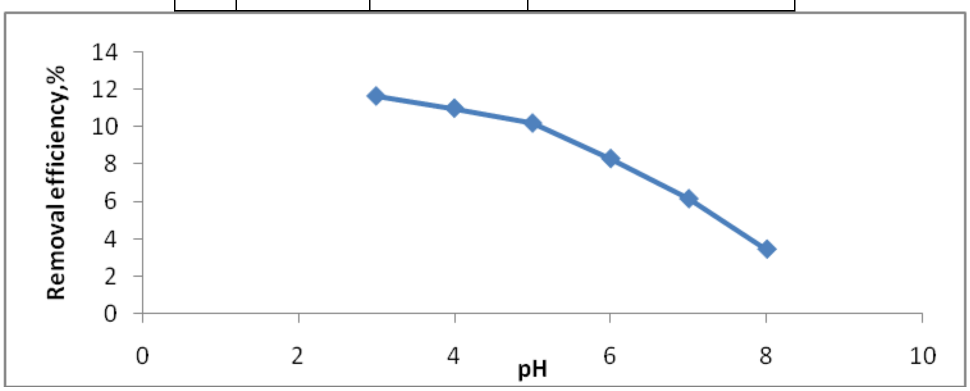

Figure 7: Effect of pH on dye removal

At lower pH protonation of the dye repel the positively charged surface sites[17]. Thus adsorption is less. As pH increases there is an electrostatic attraction of the negative charge density on the dye towards the surface sites that increases the adsorption characteristics.

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ISSN (O) 2319 - 8354
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3.4 Effect of Contact Time

The significance of contact time on adsorption was studied at various time interval.

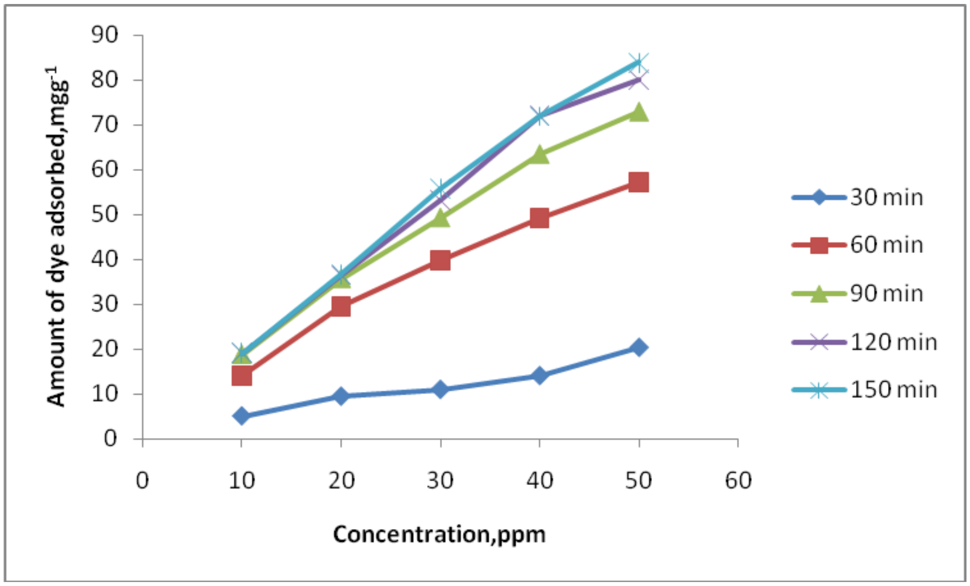

Figure 8: Effect of contact time on the dye removal

Fig. 8 indicates that as contact time increases dye uptake increases. At higher time interval there is no notable change in dye removal. This is due to equilibrium established between dye and adsorbent sites and further extension of time is not required.

3.5 Adsorption Isotherms

The experimental data were modeled using Langmuir and Freundlich isotherms[18].

Langmuir isotherm: $$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \qquad (3)$$

Freundlich Isotherm: $$\text{Log } q_e = \log K_F + (1/n) \log C_e \qquad (4)$$

where C_e is the dye concentration at equilibrium

q_e is the amount of dye adsorbed per g of biosorbent

q_m is the monolayer adsorption capacity

K_L is Langmuir adsorption constant

n is Freundlich constant

K_F is Freundlich Coefficient

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IJARSE
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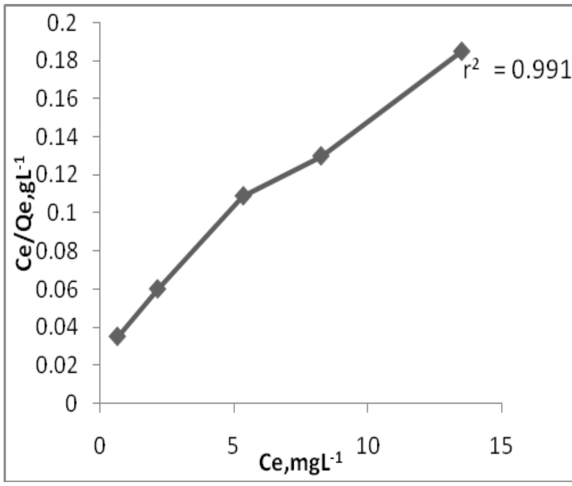

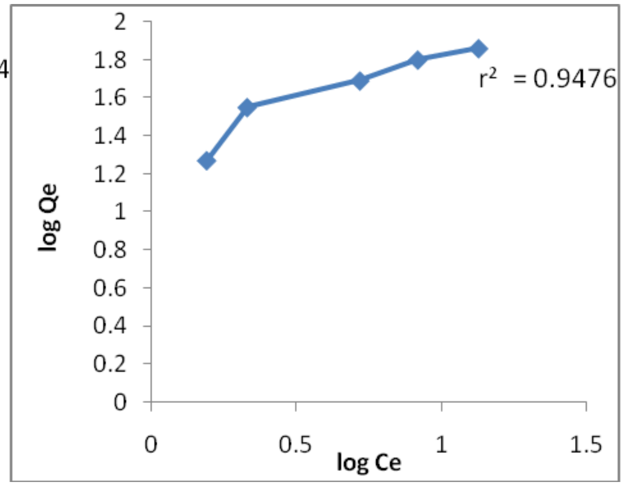

Figure 9: Langmuir plot for different concentration at 90 mins

Figure 10: Freundlich Isotherm plot for different dye concentrations at 90 mins

Langmuir plot gives a good fit to adsorption of malachite green dye onto FeAAAC which is supported by r^2 = 0.9914. This indicates that adsorption follows a monolayer interaction on the homogeneous surface. This is further proved from a dimensionless constant separation factor, R_L which is given by:

$$R_L = 1/(1+K_LC_e)$$

The R_L values indicate the feasibility of the isotherm model. For isotherm to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$)[19]. From the above Langmuir plot R_L values were found to lie between 0.833 and 0.194 which confirms that adsorption is favourable.

Whereas Freundlich plot shown in figure 7 did not indicate a good fit for adsorption of malachite dye onto FeAAAC. The correlation coefficient, r^2 = 0.9476 and Freundlich constant n > 1 indicate adsorption of malachite green on FeAAAC unfavourable and did not follow Freundlich model.

Table 4: Isotherm constants for adsorption of malachite green dye onto FeAAAC

Langmuir constants			Freundlich constants		
q_m(mg/g)	K_L(L/mg)	r^2	K_f	1/n	r^2
90.9	0.3055	0.9914	18.2	1.75	0.9476

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IV CONCLUSION

Activated carbon was prepared from Acacia Arabica bark by chemical followed by thermal activation. To improve the adsorption property of the activated carbon, the surface was modified by oxidation followed by iron impregnation. Batch mode adsorption study was carried out using FeAAAC and the influence of control parameters on adsorption reaction was investigated. The experimental data were fitted using the classical adsorption isotherms namely Langmuir and Freundlich models. It was found that Langmuir isotherm fits best than Freundlich model thereby proving monolayer adsorption of malachite green dye on FeAAAC.

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