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RESEARCH ARTICLE

ADSORPTION, ISOTHERM STUDIES ON THE REMOVAL OF CATIONIC DYE FROM AQUEOUS SOLUTION BY THE USE OF ACTIVATED CARBON-MnO_2-NANOCOMPOSITE

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ABSTRACT

The use of activated carbon-MnO_2 nano composite for the removal of Bismarck Brown Y, a most widely used basic dye has been studied. The effect of several parameters such as adsorbent dose, contact time, initial dye concentration, pH and temperature has been evaluated. The adsorption data were analysed by using adsorption isotherms like Langmuir, Freundlich and Tempkin isotherms. The study has found that the nano composite adsorbent play an effective role in removing the Bismarck Brown Y from its aqueous solution.

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INTRODUCTION

Textile industry uses large volumes of water in wet processing operations and there by generates substantial quantities of waste water containing large amounts of dissolved dyestuffs from dyeing units and other products such as dispersing agents, dye bath carriers, salts, emulsifiers, leveling agents and heavy metals form textile processing units (Khaled *et al.*, 2009). Majority of this dyes are synthetic in nature and are usually composed of aromatic rings in their structure, inert and non-biodegradable when discharged into waste streams. Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical and commercial importance (Bulut *et al.*, 2007). Coloured waste water containing even 1% of dye is unsuitable for human purposes. Discharge of such colored waste water into the water bodies without proper treatment causes irreparable damage to the surrounding eco system. It interfaces light penetration and reduces aquatic photosynthetic activities. Several commonly used dyes or their metabolites have toxic effects as carcinogenic, mutagenic, genotoxic and teratogenic effects on aquatic biota and humans (Culp *et al.*, 1999). Therefore, the colored waste water should be decolorized before released into to the pristine water bodies. Conventional biological treatment processes and use of bio mass materials as absorbers to remove biochemical oxygen demand (BOD) and Chemical oxygen demand (COD) of water were found to be inadequate to decolorize the water containing dissolved dyestuff and to meet more increasingly stringent regulations and laws (Chen *et al.*, 2011) and using biomass to adsorb dyes (Kurniawan *et al.*, 2011). Reports are available on various studies made to remove color and other contaminants using various types of methods that include adsorption, coagulation, nano-filtration and ozonalysis, membrane filtration, oxidation process etc., in which adsorption is most useful due to its efficiency and versatility. The use of low cost, easy obtained, high efficiency and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from waste water. These adsorbents were prepared from natural materials such as plant roots, leaf and seed like neem leaf powder (Wang *et al.*, 2006), Shells of lentil, wheat and rice (Aydm *et al.*, 2008), Guava leaf powder (Ponnusami *et al.*, 2008), Jambonut (Kumar 1991), Fire clay (Rathinavelu *et al.*, 2016), Passiflora foetida (Sathya *et al.*, 2017) etc., used for removal of dye removal studies. Nanocomposites are materials that are usually created by introducing appropriate nanoparticles into a macroscopic sample material Research is currently actively being conducted to better understand the advantages of using nanoscale versus microscale particles, as

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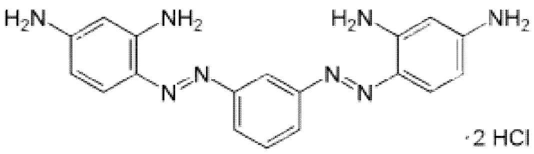
well as the fate and transport of nano particles once released into the environment. In the present study, flower of Typha Angustata L plant Carbon with MnO_2 nano Composite was used as a novel adsorbent. This is further indicated in this report as Activated Carbon- MnO_2-Nano Composite [AC-MnO_2-NC].

The purpose of this work to evaluate the adsorption capacity of activated carbon prepared from Typha Angustata L with MnO_2 nano composite on adsorption of Bismarck Brown Y, basic dye as a model one. Bismarck Brown is a diazo dye. Its molecular formula and molecular weight are $C_{18}H_{18}N_8.2HCL$ and 419.3 g/mol respectively. It has maximum absorbance at 516nm wavelength. C.I.No is 21000. The structure of Bismarck Brown Y is Activated Carbon (3gm) was allowed to swell in 15mL of water-free Alcohol and stirred for 2 hours at 25^0C to get uniform suspension. At the same time, the Maganese dioxide (3gm) was dispersed into water-free Alcohol (15mL). Then the diluted Maganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 hours at 25^0C. To this, 5mL alcohol and 0.2ml of deionised water was slowly added. The stirring was continued for another 5 hours at 25^0C and the resulting suspension was kept overnight in a vacuum oven for 6 hours at 80^0C.



MATERIALS AND MATHODS

Preperation of AC-MnO_2-NC

Activated Carbon (3gm) was allowed to swell in 15mL of water-free Alcohol and stirred for 2 hours at 25^0C to get uniform suspension. At the same time, the Maganese dioxide (3gm) was dispersed into water-free Alcohol (15mL). Then the diluted Maganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 hours at 25^0C. To this, 5mL alcohol and 0.2ml of deionised water was slowly added. The stirring was continued for another 5 hours at 25^0C and the resulting suspension was kept overnight in a vacuum oven for 6 hours at 80^0C.

Adsorbate

A stock solution containing Bismarck Brown Y (1000 mgL^{-1}) was prepared by dissolving required amount of dye in deionised water which was later suitably diluted to solutions of four different concentrations (10, 20, 30 and 40mgL^{-1}). Solution pH was adjusted by adding either 0.1N HCl or 0.1N NaOH as required. The chemicals used were of AR Grade. In this study it is further indicated as BBY.

Batch Adsorption studies

Batch method was followed by agitating 50 ml of four different dye solutions (10, 20, 30 and 40 mgL^{-1}) at their natural pH with 100 mg of AC-MnO_2-NC in 150 ml stoppered conical flasks at room temperature (30±2°C) in a temperature controlled water bath shaker at 140 rpm. The samples were withdrawn from the shaker at predetermined time intervals and the dye solution was separated from the adsorbent by centrifuging at 10,000 rpm for 10 min. The absorbance of supernatant solution was measured using UV-VIS spectrophotometer (Cyber Lab, 100) at wave length 516 nm. The amount of BBY adsorbed per unit mass was calculated from the following equation:

$$q_t = \frac{(C_o - C_t)V}{W} \qquad \text{................(1)}$$

Where q_t is the amount of dye adsorbed per unit weight of adsorbent (mg/g); C_o the initial concentration of BBY (mg/L); C_t the concentration of BBY solution at time t (min); V the volume of working solution (mL); W is the adsorbent dosage (mg). Blanks with only the adsorbate in 50 ml of distilled water were conducted simultaneously at similar conditions to account for adsorption in using glass containers. It was found that no adsorption of BBY by container walls occurred. The experimental parameters studied are adsorbent dosage, contact time, initial dye concentration, pH and temperature. Langmuir, Freundlich and Tempkin isotherms were employed to study the adsorption capacity of the adsorbent.

RESULTS AND DISCUSSION

Effects of agitation time and initial dye concentration of dye on adsorption

Effects of agitation time and initial dye concentration (10, 20, 30 and 40 mg/L) on removal of BBY are presented in Fig.1. The percent removal of Bismarck Brown Y increased with increase in agitation time and reached equilibrium at 250 min. The percent dye removal at equilibrium decreased from 67.90 to 61.04 as the dye concentration was increased from 10 to 40 mg/L. It is clear that the removal of dye depends on the initial concentration of the dye. The removal curves are single, smooth and continuous leading to saturation.

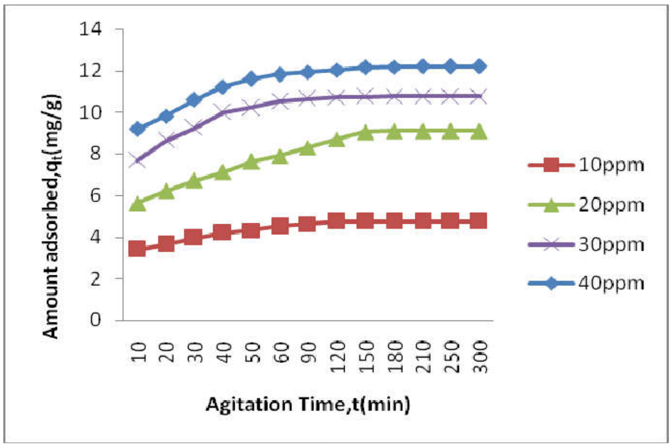


Fig. 1. Effect of agitation time and concentration of Bismarck Brown Y on removal of AC-MnO_2-NC

Effect of adsorbent dose

The removals of Bismarck Brown Y by AC-MnO_2-NC at different adsorbent doses are presented in Fig.2. (10mg to 600mg / 50ml) was tested for the dye concentrations 10, 20, 30 and 40 mg/L. Increase in adsorbent dose increased the percent removal of dye which is due to the increase in surface area of the adsorbent.

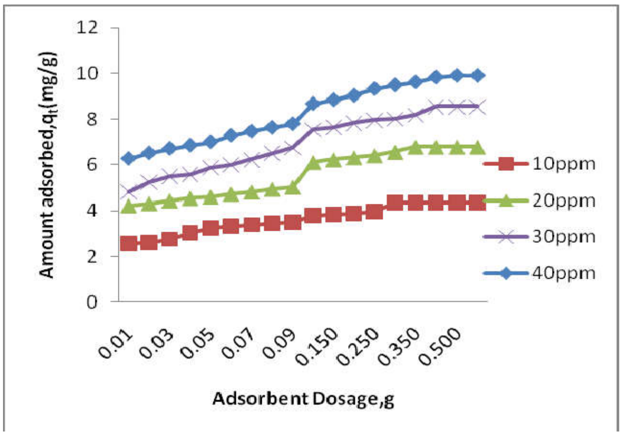


Fig.2. Effect of adsorbent dosage on removal of Bismarck Brown Y by AC-MnO_2- NC

Effect of pH

Effect of pH on the removal of Bismarck Brown Y is shown in Fig.3. For 40 mg/L dye concentration the percent removal increased from 36.79 to 62.73 when the pH was increased from 2 to 14 and the percent removal remained almost the same above pH 9. As the pH of the dye solution becomes higher, the association of dye cations on solid will take place more easily.

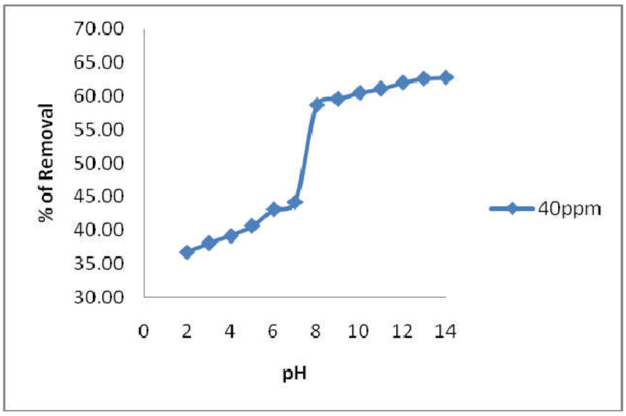


Fig.3. Effect of pH on removal of Bismarck Brown Y by AC-MnO_2-NC

Effect of Temperature

The effect of temperature of adsorption of Bismarck Brown Y (Fig.4) for concentration 40 mg/L adsorbent was carried out at 30°, 40° and 50°C. The percent removal of dye increased from 17.13 to 67.58. This indicates that increase in adsorption with increase in temperature may be due to increase in the mobility of the large dye ions. Moreover, increasing temperature may produce a swelling effect within the internal structure of the adsorbent, penetrating the large dye molecule further.

Adsorption isotherms

Langmuir Isotherm

Langmuir isotherm (Langmuir, 1918) is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_o K_L} + \frac{C_e}{Q_o} \quad \text{............ (2)}$$

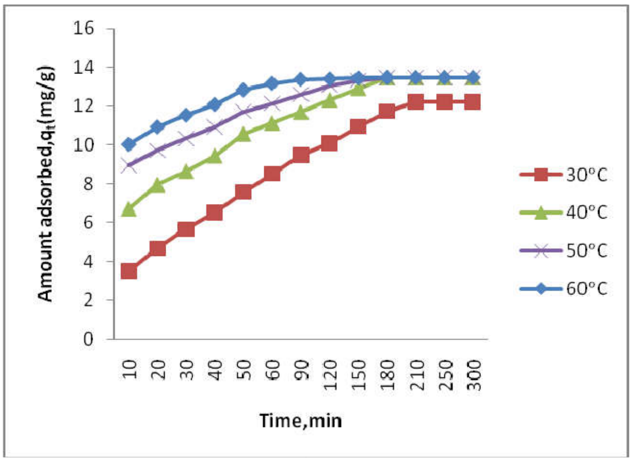


Fig.4. Effect of temperature on removal of Bismarck Brown Y by AC-MnO_2-NC

Where C_e is the concentration of dye solution (mgl^{-1}) at equilibrium. The constant Q_0 signifies the adsorption capacity (mgg^{-1}) and b is related to the energy of adsorption (Lmg^{-1}). The linear plot of C_e/q_e vs C_e shows that adsorption follows a Langmuir isotherm (Fig.5). Values of Q_0 and K_L were calculated from the slope and intercept of the linear plot and are presented in Table 1.

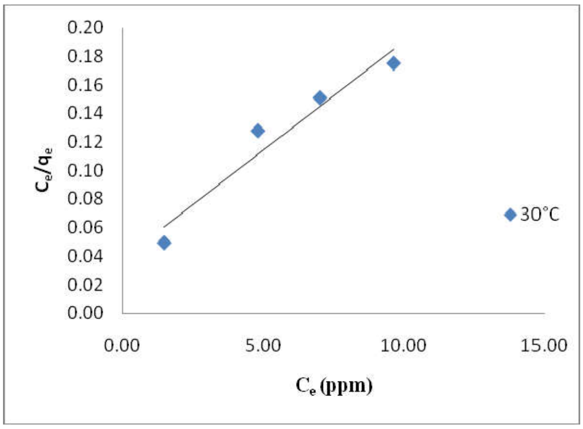


Fig.5. Langmuir Adsorption Isotherm

The essential characteristics of Langmuir isotherm can be expressed by a dimensionless constant called equilibrium parameter, R_L defined by

$$R_L \quad \frac{1}{1 + K_L C_0} \quad \text{................(3)}$$

Where K_L is the Langmuir constant and C_0 is the initial dye concentration (mgL^{-1}). R_L value between 0 to 1 indicates favourable adsorption.

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$R_L >1$Unfavourable adsorption
$0< R_L <1$Favourable adsorption
$R_L =0$Irreversible adsorption
$R_L =1$Linear adsorption

……

The R_L values between 0 to 1 which indicates favourable adsorption. Values of Q_0 and K_L were calculated from the slope and intercept of the linear plot and are presented in

Table 1. Langmuir, Freundlich and Tempkin constants for adsorption of BBY by AC-MnO_2-NC

Initial dye concentration mg/L	Langmuir				Freundlich			Tempkin			
	Q_0 (mg /g)	K_L (L/g)	R^2	R_L	K_f (mg/g/ (L/g))	N	R^2	A	b	B	R^2
60	66.666	0.394	0.941	0.4405	25.1188	3.1446	0.934	6.0254	196.010	12.64	0.884
80				0.3306							
100				0.3247							
120				0.2206							

Table 1. From the Table 1 it is clear that the Langmuir isotherm constant value indicate the maximum adsorption capacity (Q_0) is 66.666mg/g. The Langmuir isotherm can also be expressed in terms of a dimensionless constant separation factor (R_L). The R_L values lies in between 0 to 1 indicate the adsorption is favourable for all the initial dye concentration.

Freundlich Isotherm

The Freundlich isotherm (Freundlich, 1906) was also applied for the adsorption of the dye. This isotherm is represented by the equation

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log k_f \qquad \text{………(4)}$$

Where q_e is the amount of dye adsorbed (mg) at equilibrium, C_e is the equilibrium dye concentration in solution (mgL^{-1}) and k_f and n are constants incorporating all factors affecting the adsorption process, adsorption capacity and intensity of adsorption. Linear plot of $\log q_e$ vs $\log C_e$ shown in the Fig. 6. Values of k_f and n were calculated from the intercept and slope of the plot and are presented in Table 1.

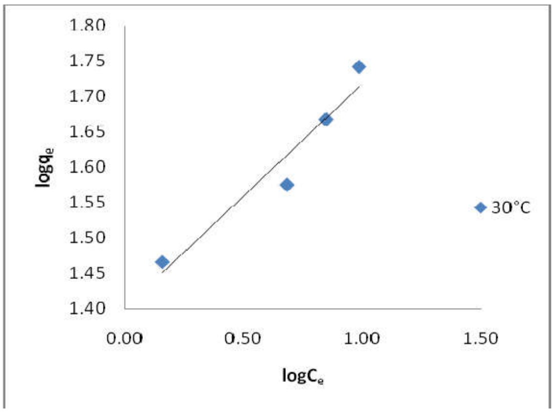

Fig.6. Freundlich Adsorption Isotherm

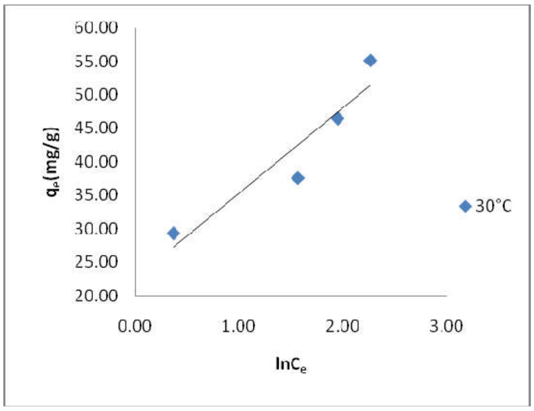

Fig.7. Plot of Tempkin adsorption isotherm

Tempkin isotherm

Tempkin isotherm contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. This isotherm assumes that: (1) The heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate interactions, and (2) Adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy (Temkin *et al.*, 1940).

Tempkin isotherm is represented by the following equation:

$$q_e = RT/b\ln(AC_e) \qquad \text{……………..(5)}$$

equation (5) can be expressed in its linear form as:

$$q_e = RT/b \ln A + RT/b \ln C_e$$
$$q_e = B\ln A + B\ln C_e \qquad \text{…………….(6)}$$

Where B=RT/b

The adsorption data can be analysed according to equation (6). A plot of q_e versus $\ln C_e$ enables the determination of the isotherm constants A and B and it is shown in Fig.7. A is the equilibrium binding constant (1/mol) corresponding to the maximum binding energy and constant B, is related to the heat of adsorption. This isotherm is plotted in Fig (8) for Bismarck Brown Y adsorption on AC-MnO_2-NC and values of the parameters are given in Table (1).

From this Table (1) the correlation co-efficient (R^2) show that Langmuir model is well fitted and which shows that mono layer adsorption was predominate.

Conclusion

The present study shows that AC-MnO_2-NC is an effective adsorbent for the removal of Bismarck Brown Y from aqueous solution. Adsorption is followed by Langmuir isotherms. The adsorption capacity was found to be 66.666 mgg^{-1}. Complete removal of the dye can be achieved using an appropriate dosage of the adsorbent and pH for waste waters. The results would be useful for the fabrication and designing of waste water treatment plants for the removal of dye. Since the raw material is freely available in large quantities the treatment method, seems to be economical.

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