

Adsorption of Congo red from Aqueous Solution by a Novel Activated Carbon from *Passiflora foetida* [PAC-MnO₂-NC]: Different Isotherm Studies

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ABSTRACT: Adsorption is of significant importance for the effluent treatment, especially for the treatment of colored effluent generated from the dyeing and bleaching industries. Low cost adsorbents have gained attention over the decades as a means of achieving very high removal efficiencies to meet discharge standards. The present paper reports on batch investigations for color removal from aqueous solutions of Congo red (CR) using *Passiflora foetida* [PAC-MnO₂-NC] as an alternative low cost adsorbent. The performance analysis was carried out as function of various operating parameters, such as initial concentration of dye, adsorbent dose, contact time, particle size of adsorbent and pH. Detailed data analysis indicated that the adsorption of CR followed Langmuir isotherm.

KEYWORDS: Nano composite, Congo Red, Adsorption, Batch mode, Isotherms.

I. INTRODUCTION

Dye is an organic compound that has an ability to impart specific color to the substance to which it is being applied. There is a variety of dyes like; acid dyes, basic dyes, azo dyes, mordant dyes, plastic dyes, etc., Large quantities of dyes are released into water by textile industries possess serious environmental problems [1] due to its persistent nature. The colored effluent has an inhibitory effect [2] on the process of photosynthesis and affecting aquatic ecosystem.

Thus the removal of dyes from colored effluents in textile industry is one of the major environmental problems. There are many colour removal techniques amongst which adsorption process is inexpensive and readily available to control the various pollutants from water and wastewater [3]. The adsorption process [4] has been found to be more effective method overall other treatments.

A wide variety of materials such as animal bone [5], black tea leaves [6], cocoa [7], almond shell [8], mango leaves [9], saw dust [10], Jambonut [11], *Borassus flabellifer* L[12] and *Typha Angustata* L[13]. Hence adsorption is recommended as a viable means for Basic dye removal.

The present study is aimed at comparing the effectiveness of *Passiflora foetida* [PAC-MnO₂-NC] in removing Congo Red by adsorption. In the batch mode studies, the dynamic behavior of the adsorption was investigated on the effect on initial Dye Concentration, temperature, adsorbent dosage and p^H. The Langmuir, Freundlich and Tempkin adsorption isotherms were studied. Double distilled water was used throughout the experiment.

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II. MATERIALS AND METHODS

A. PREPARATION OF ACTIVATED CARBON

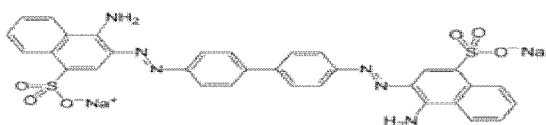
The Passiflora foetida plant materials were collected from local area situated at Thindal, Erode District, Tamilnadu. They were cut into small pieces and dried for 20 days. Finally it was taken in a steel vessel and heated in muffle furnace. The temperature was raised gradually upto 500°C and kept it for half an hour. The carbonized material was ground well and sieved to different particle size. It was stored in a plastic container for further studies. In this study particle size of 0.15 to 0.25mm was used and it was labeled as PAC.

B. PREPARATION OF PAC-MnO₂-NC

Activated Carbon (3gm) was allowed to swell in 15mL of water-free Alcohol and stirred for 2 hours at 25°C to get uniform suspension. At the same time, the Manganese dioxide (3gm) was dispersed into water-free Alcohol (15mL). Then the diluted Manganese dioxide was slowly added into the suspension of activated Carbon and stirred for a further 5 hours at 25°C. To this, 5mL alcohol and 0.2mL of deionised water was slowly added. The stirring was continued for another 5 hours at 25°C and the resulting suspension was kept overnight in a vacuum oven for 6 hours at 80°C. It was labelled as PAC-MnO₂-NC.

C. PREPARATION OF SORBATE

Basic dye used in this study is Congo red purchased from S.d. fine chemicals. MG has molecular formula C₃₂H₂₂N₆Na₂O₆S₂. The dye concentration in supernatant solution was determined at characteristic wavelength [λ_{max} =500nm] by double beam UV-visible spectrophotometer [Systronics 2202]. Congo red is the sodium salt of 3,3'-(1,1'-biphenyl)-4,4'-diyl)bis(4-aminonaphthalene-1-sulfonic acid) (molecular weight: 696.66 g/mol). It is a secondary diazo dye. Congo red is water-soluble, yielding a red colloidal solution. The Chemical structure of Congo red is given below.



D. 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 PAC-MnO₂-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 500 nm. The amount of CR adsorbed per unit mass was calculated from the following equation:

$$q_t = \frac{(C_o - C_t)V}{W} \dots\dots\dots (1)$$

Where q_t is the amount of dye adsorbed per unit weight of adsorbent (mg/g); C_o the initial concentration of CR (mg/L); C_t the concentration of CR 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 CR 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.

III. RESULTS AND DISCUSSION

A. 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 CR are presented in Fig.1. The percent removal of CR increased with increase in agitation time and reached equilibrium at 150 min. The percent dye removal at equilibrium decreased from 71.01 to 54.41 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.

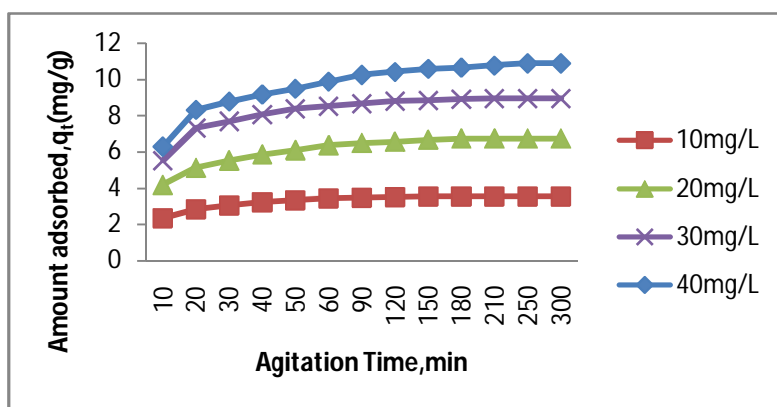


Fig.1. Effect of agitation time and concentration of Congo Red on removal of PAC-MnO₂-NC

B. EFFECT OF ADSORBENT DOSE

The removal of CR by PAC-MnO₂-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.

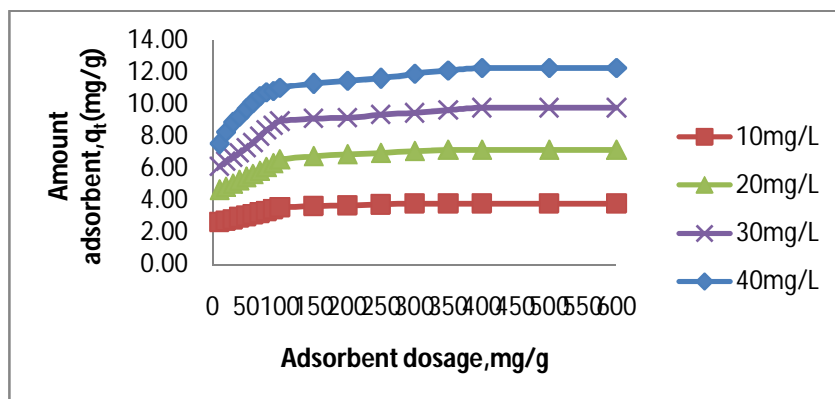


Fig.2. Effect of adsorbent dosage on removal of Congo Red by PAC-MnO₂- NC

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C. EFFECT OF PH

Effects of pH on the removal of CR by PAC-MnO₂-NC are shown in Fig.3. Dye adsorption decreases with increase of pH from 2 to 5 and no remarkable change thereafter. Low pH favors the adsorption, as decrease of pH the surface become more protonated and acquire positive charge which makes it easier for the anionic dyes to bind with carbon. Poor adsorption of CR at higher pH value is due to the competition between the negatively charged hydroxyl ions and anionic dye for the sorption sites.

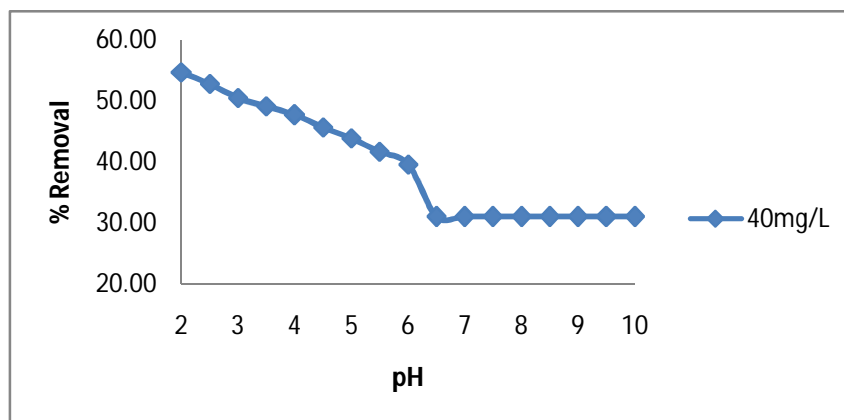


Fig.3. Effect of pH on removal of Congo Red by PAC-MnO₂-NC

D. EFFECT OF TEMPERATURE

The effect of temperature of adsorption of Congo Red (Fig.4) concentration 40 mg/L adsorbent was carried out at 30°, 40° and 50°C. The percent removal of dye increased from 20.66 to 64.53. 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.

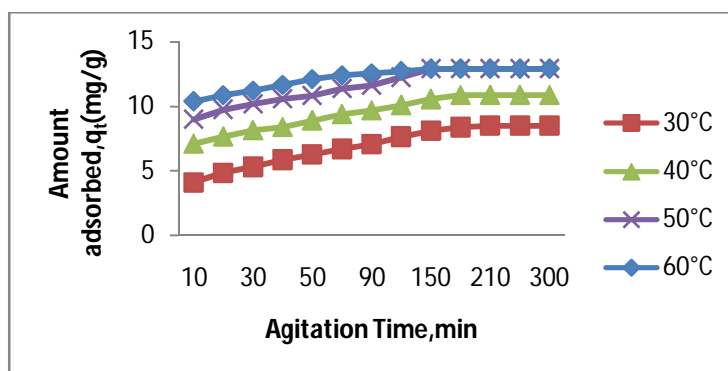


Fig.4. Effect of temperature on removal of Congo Red by PAC-MnO₂-NC

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IV. ADSORPTION ISOTHERMS

A. LANGMUIR ISOTHERM

Langmuir isotherm [14] is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \quad \dots\dots\dots (2)$$

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.

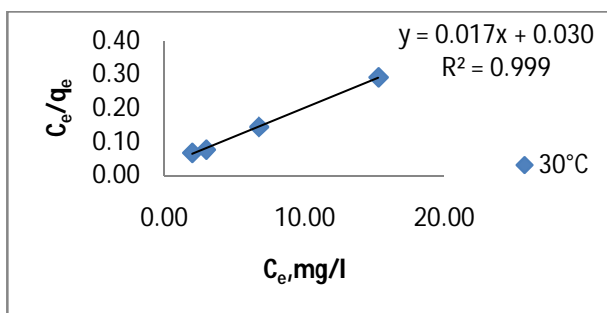


Fig.5 Langmuir Adsorption Isotherm

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

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots\dots\dots(3)$$

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.

-
- | | |
|---------------------------------------|--------------------------------|
| $R_L > 1$ | 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. From the Table.1 it is clear that the Langmuir isotherm constant value indicate the maximum adsorption capacity (Q_0) is 58.8235mg/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.

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B. FREUNDLICH ISOTHERM

The Freundlich isotherm [15] was also applied for the adsorption of the dye. This isotherm is represented by the equation

$$\log q_e = \left(\frac{1}{n}\right) \log C_e + \log k_f \quad \dots\dots\dots(4)$$

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.

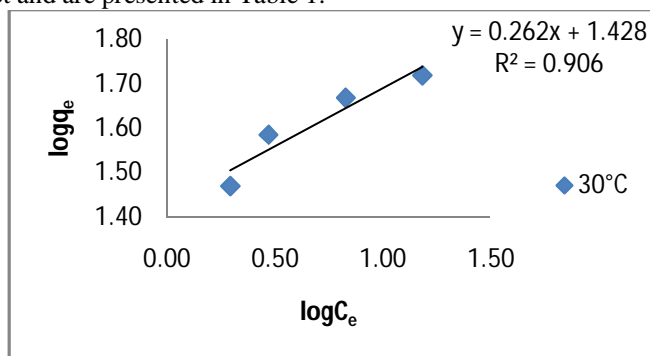


Fig.6.Freundlich Adsorption Isotherm

C. 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 [16].

Tempkin isotherm is represented by the following equation:

$$q_e = \frac{RT}{b} \ln(A C_e) \quad \dots\dots\dots(5)$$

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

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e$$

$$q_e = B \ln A + B \ln C_e \quad \dots\dots\dots(6)$$

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 on PAC-MnO₂-NC and values of the parameters are given in Table (1).

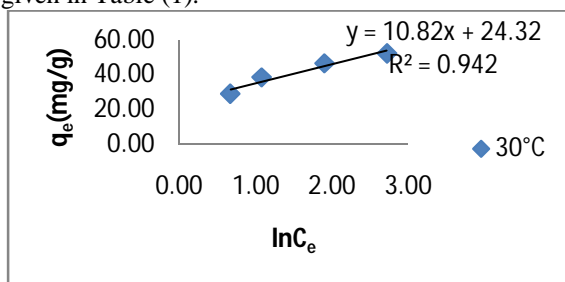


Fig.7. Plot of Tempkin adsorption isotherm

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Table 1: Langmuir, Freundlich and Tempkin constants for adsorption of CR by PAC-MnO₂-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	58.823	0.566	0.999	0.0285	26.7916	3.8167	0.906	9.4649	228.980	10.82	0.942
80				0.0215							
100				0.0173							
120				0.0144							

From this Table (1) the correlation co-efficient (R²) show that Langmuir model is well fitted and which shows that mono layer adsorption was predominate.

V.CONCLUSIONS

The present study shows that PAC-MnO₂-NC is an effective adsorbent for the removal of Congo Red from aqueous solution. Adsorption is followed by Langmuir isotherms. The adsorption capacity was found to be 58.8235mg/g. 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.

REFERENCES

- [1] G.Mcmullan, C.Meehan, A.Conneely, N.Kirby, and T.Robinson, "Microbial decolourization and degradation of textile dyes", Appl Microbiol Biotechnol, 56, 81-87, 2001.
- [2] P.Nigam, G.Armour, I.M.Bonant, D.Singh, and R.Marchant, "Physical removal of textile dyes and solid state fermentation of dye-adsorbed agricultural residues", Bioresour Technol,72, 219-226, 2000.
- [3] S.K.Krishna, M.Sathya, "Usage of nanoparticle as adsorbent in adsorption process-A Review", International Journal of Applied Chemistry ,Volume 11, Number 2,pp. 221-227, 2015.
- [4] S.D. Khatri, M.K. Singh, "Colour removal from synthetic dye waste water using a biadsorbent", Water Air Soil Pollut,120,283-294,2000.
- [5] M. El Haddad, R. Mamouni, N. Saffaj, and S. Lazar, Global J.Human Soc. Sci.
- [6] M.Abul Hossain, R.M.Afiqur, Orbital Elec. J. Chem. Campo Grande, 4(3),187-201,2012.
- [7] C.Theivarasu, S.Mylsamy, Int. J. Eng .Sci.Technol,2(11),6284-6292,2010.
- [8] M.Aliabadi, I.Khazari, M. Hajiabadi, and F.Shahzad, J. Bio & Env. Sci, 2(9), 39-44,2012.
- [9] T.A.Khan, S. Sharma, and I.Ali, J. Toxicol. Environ. Health Sci, 3(10), 286-297, 2011.
- [10] A.Witek-Krowiak, M.Mittek, K. Pokomeda, R.G. Szafran, and S.Modelsk, Chem. Process Eng,31, 409-420, 2010.
- [11] P.E.Kumar, "Studies on characteristics and Fluoride removal capacity of Jambonut Carbon", M.Phil., Disseration: Bharathiar University, Coimbatore, Tamilnadu, India. 1991.
- [12] P.E.Kumar, V.Perumal, "Novel Adsorbent Derived from the Inflorescence of Palmyra (Borassus flabellifer L.) Male Flowers". Nature Environment and Pollution, 9 [3], 513-518, 2010.
- [13] M. Santhi, P.E. Kumar, and B. Murlidharan, "Removal of Malachite Green Dyes By Adsorption onto Activated Carbon -MnO₂-Nanocomposite -Kinetic Study and Equilibrium Isotherm Analyses", J. Appl. Chem, 8, 33, 2015.
- [14] I. Langmuir, "The Adsorption Of Gases On Plane Surfaces Of Glass, Mica and Platinum", Chem Soc, 40(9),1361-1403, 1918.
- [15] H. Freundlich, "Adsorption Solution", Z Phys Chemie, 57, 384,1906.
- [16] M.J.Temkin, V. Pyzhev, "Kinetics of ammonia synthesis on promoted iron catalysts", Acta Physiochim URSS,12[54],217-22,1940.