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ISOTHERM STUDIES FOR THE ADSORPTION OF A ACID GREEN DYE BY USING PASSIFLORA FOETIDA ACTIVATED CARBON [PAC-MNO_2-NC] NANOCOMPOSITE

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Abstract: The Removal of Acid Green by adsorption on Activated carbon-MnO_2-Nanocomposite, under optimized conditions has been studied. The adsorption data were analyzed by using adsorption isotherms like Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich and Halsey isotherms were also studied. The study has found that the Nanocomposite adsorbent play an effective role in removing the Acid Green from its aqueous solution.

Keywords: Nanocomposite, Acid Green, adsorption isotherm.

I. INTRODUCTION

Dye waste water is obtained mainly from textile, leather, paper, rubber, plastics, cosmetics, pharmaceutical and food industries. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment [1]. It causes severe environmental pollution and human health hazards if it is not treated properly before discharging into the natural water [2]. Therefore, an increased interest has been focused to find economic and effective methods for removing of such dyes from the contaminated water [3]. The color removal was extensively studied with physicochemical methods such as coagulation, ultra filtration, electrochemical adsorption and photo oxidation. Among these methods, the adsorption process, offers a great potential for treating effluents containing undesirable compounds and renders them safe and reusable [4,5].

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 [6], shells of lentil, wheat and rice [7], Guava leaf powder [8], Jambonut

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[9], Borassus flabellifer L [10] and Typha Angustata L [11] etc, used for removal of dye removal studies.

Nanocomposites are material that are usually created by introducing appropriate nanoparticles into a macroscopic sample material. Research is currently activated being conducted to better understand the advantages of using nanoscale versus micro scale paricles, as well as the fate and transport of nanoparticles once released into the environment. The efficiency of the adsorption process mainly depends on the cost and removal capacity of adsorbents used.

The purpose of the present work is to evaluate the sorption of Acid Green (Cationic dye) from its aqueous solution using Passiflora foetida.

II.MATERIALS AND METHODS

2.1. Preparation of Activated Carbon

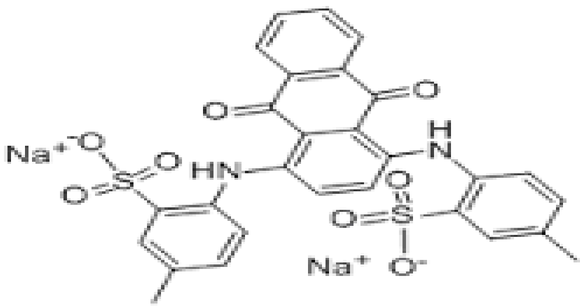
The Passiflora foetida plant materials were collected from local area situated at Thindal, Erode District, Tamilnadu. They were cut into small pieces and dried for 20 days. Finally it was taken in a steel vessel and heated in muffle furnace. The temperature was raised gradually upto 500^0C and kept it 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.

2.2. Preparation of PAC-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.It was labelled as PAC-MnO_2-NC.

2.3. Preparation of sorbate

Acid Green 25 is purchased from S.d. fine chemicals. An anionic dye Acid Green 25 has molecular formula $C_{28}H_{20}N_2Na_2O_8S_2$. The dye concentration in supernatant solution was determined at characteristic wavelength [λmax =622.57nm] by double beam UV-visible spectrophotometer [Systronics 2202]. The Chemical structure of Acid Green is given below.



III. ADSORPTION ISOTHERM

The adsorption isotherm was obtained from the data deduced from the effect on initial dye concentration. These isotherms are generally used to establish the relationship between the amount of dye adsorbed and its equilibrium concentration in solution. The degree of the adsorbent (PAC-MnO_2-NC) affinity for the adsorbate (AG) determines its distribution between the solid and liquid phases. These adsorption isotherms are used as functional expressions capable of simulating favourable adsorption uptake capacity as long as environmental parameters such as pH, initial dye concentration and contact time are carefully controlled during experiments. The Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Halsey isotherm were applied in this study. Although these isotherms shed no light on the mechanism of adsorption, they are useful for comparing results from different sources on a quantitative basis, providing information on the adsorption potential of a material with easily interpretable constants.

3.1 Langmuir Isotherm

Langmuir isotherm [12] is represented by the following equation.

$$\frac{C_e}{q_e} = \frac{1}{Q_O K_L} + \frac{C_e}{Q_O} \qquad \text{………… (1)}$$

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.1). Values of Q_0 and K_L were calculated from the slope and intercept of the linear plot and are presented in Table 1.

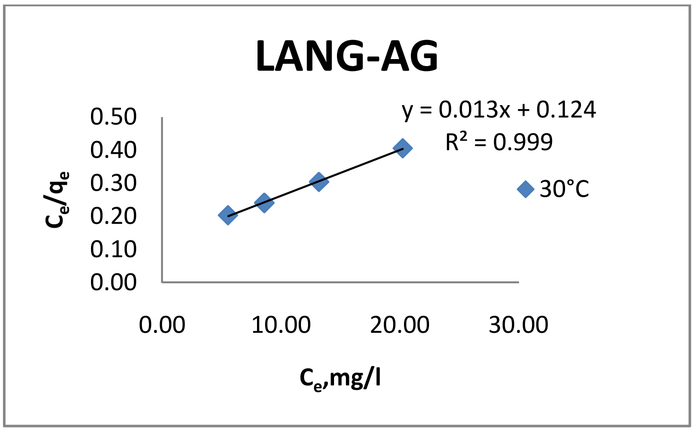


Fig.1: Langmuir plot for the adsorption of Acid Green onto PAC-MnO_2-NC

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

$$R_L = \frac{1}{1 + K_L C_0} \qquad \ldots\ldots\ldots\ldots\ldots(2)$$

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 76.923mg/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.

3.2 Freundlich Isotherm

The Freundlich isotherm [13] was also applied for the adsorption of the dye. This isotherm is represented by the equation

$$\log q_e = \left(\frac{1}{n}\right)\log C_e + \log k_f \quad \text{……….(3)}$$

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.2. Values of k_f and n were calculated from the intercept and slope of the plot and are presented in Table.1.

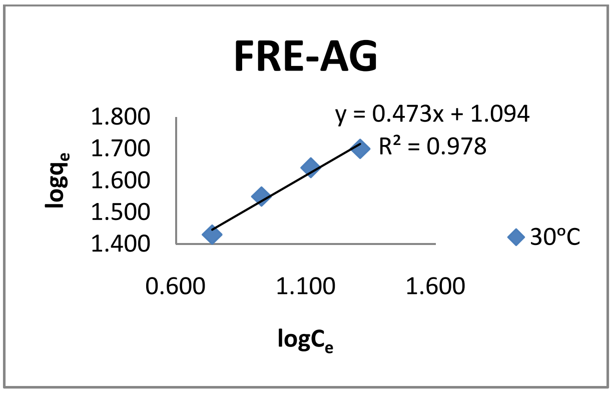


Fig.2. Freundlich plot for the adsorption of Acid Green onto PAC-MnO_2-NC

3.3. 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 [14] Tempkin isotherm is represented by the following equation:

$$q_e = RT/b \ \ln(AC_e) \quad \text{……………..(4)}$$

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

$$q_e = RT/b \ \ln A + RT/b \ \ln C_e$$

$$q_e = B \ \ln A + B \ln C_e \quad \text{…………….(5)}$$

Where B=RT/b

The adsorption data can be analyzed according to equation (5). 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.3. 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.3 for Acid Green adsorption on PAC-MnO_2-NC and values of the parameters are given in Table.1.

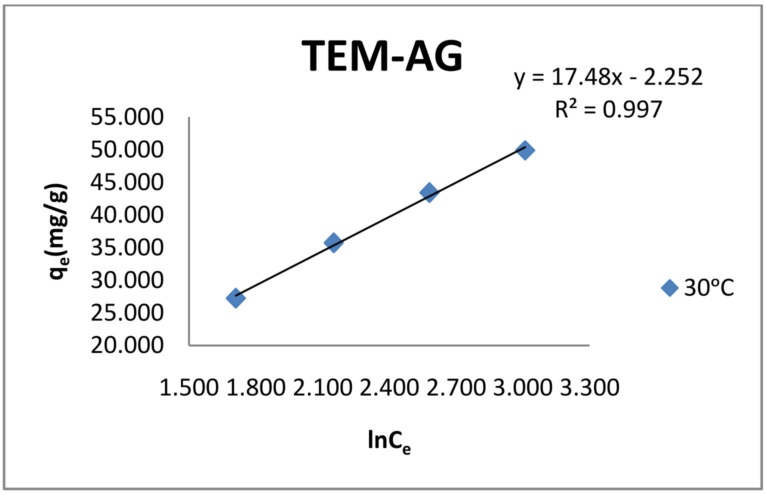


Fig.3. Tempkin plot for the adsorption of Acid Green onto PAC-MnO_2-NC

3.4 Dubinin-Radushkevich (D-R) Isotherm

The (D-R) isotherm this model is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. This model has often successfully fitted high solute activities and the intermediate range of concentration data well. This model is applied to the data in order to deduce the heterogeneity of the surface energies of adsorption (physical or chemical) and the characteristic porosity of the adsorbent [15]. The linear form of the D-R isotherm is given in

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \text{ --------(6)}$$

Where q_e is the amount of dye adsorbed in the adsorbent at equilibrium (mg/g), q_D is the D-R constant representing theoretical saturation capacity (monolayer adsorption capacity) (mg/g), and B_D is the D-R isotherm constant of the sorption energy (mol^2/ KJ^2), which is related to the (E) average energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from an infinite distance in the solution [16]. The parameter ε is the Polanyi [17] potential, which can be obtained by

$$\varepsilon = RT \ln\left(1+\frac{1}{C_e}\right) \text{ ------- (7)}$$

where T is the solution temperature(K) and

R is the gas constant, which is equal to 8.314 J/mol K.

The average energy, E (kJ/mol), can be calculated by using the D-R parameter B_D:

$$E= \frac{1}{\sqrt{2B_D}} \text{ --------------- (8)}$$

The adsorption data were analyzed according to linear form of the D-R isotherm equation. The plot of $\ln q_e$ against ε^2 is shown in Fig.4. and the constants q_D and B_D were calculated from the slope and intercept respectively. The D-R isotherm parameters are given in Table.1.This plot also indicated from the regression parameter (R^2). If the value of E lies between 8 and 16kJ/mol the sorption process is a chemisorptions one, while values of below 8kJ/mol indicates a physical adsorption process [18]. The high value q_D show high adsorption capacity. The values of the apparent energy of adsorption also depict chemisorption process.

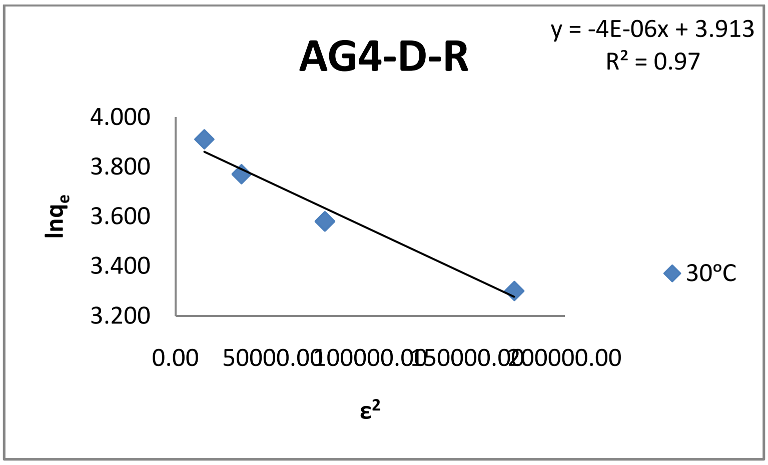


Fig.4. Dubinin-Radushkevich plot for the adsorption of Acid Green onto PAC-MnO_2-NC

3.5 Halsey Isotherm

Halsey proposed an expression for condensation of a multi layer at a relatively large distance from the surface [19],

$$q_e = \left[\frac{K_H}{C_e}\right]^{1/n} H \text{ --------------------(9)}$$

This can be linearised as:

$$\ln q_e = \frac{1}{n_H \ln K_H} - \frac{1}{n_H \ln C_e} \text{ --------(10)}$$

This equation is suitable for multilayer adsorption. Especially, the fitting of the experimental data to this equation attests to the hetero porous nature of the adsorbent. The plot of $\ln q_e$ vs $\ln C_e$ is shown in Fig.5. and the constants K_H and n_H were calculated from the slope and intercept respectively.

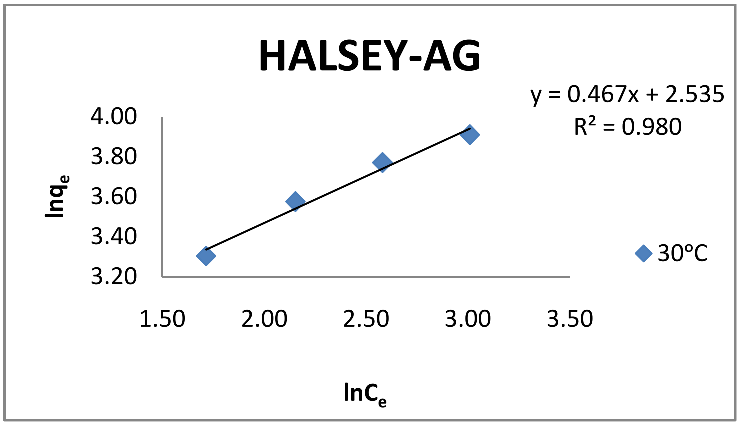


Fig.5. Halsey plot for the adsorption of Acid Green onto PAC-MnO_2-NC

Table 1: Results of various isotherms plots for the adsorption of AG onto PAC-MnO_2-NC

<table>
<tr><td rowspan="2">Isotherm Models</td><td rowspan="2">Initial dye concentration</td><td colspan="4">Parameters and their results</td></tr>
<tr><td>R_L</td><td>b</td><td>Q_o(mg/g)</td><td>R^2</td></tr>
<tr><td rowspan="4">Langmuir</td><td>60</td><td>0.1372</td><td rowspan="4">0.1048</td><td rowspan="4">76.923</td><td rowspan="4">0.999</td></tr>
<tr><td>80</td><td>0.1065</td></tr>
<tr><td>100</td><td>0.0871</td></tr>
<tr><td>120</td><td>0.0736</td></tr>
<tr><td rowspan="5">Freundlich</td><td>Initial dye concentration</td><td>n</td><td colspan="2">K_F (mg/g(L/mg)$^{1/n}$)</td><td>R^2</td></tr>
<tr><td>60</td><td rowspan="4">2.1141</td><td colspan="2" rowspan="4">12.4165</td><td rowspan="4">0.978</td></tr>
<tr><td>80</td></tr>
<tr><td>100</td></tr>
<tr><td>120</td></tr>
<tr><td rowspan="5">Temkin</td><td>Initial dye concentration</td><td>B_T</td><td>A_T</td><td>b_T</td><td>R^2</td></tr>
<tr><td>60</td><td rowspan="4">17.48</td><td rowspan="4">0.8791</td><td rowspan="4">141.737</td><td rowspan="4">0.997</td></tr>
<tr><td>80</td></tr>
<tr><td>100</td></tr>
<tr><td>120</td></tr>
<tr><td rowspan="5">Dubinin-Radushkevich</td><td>Initial dye concentration</td><td>B_D</td><td>q_D</td><td>E</td><td>R^2</td></tr>
<tr><td>60</td><td rowspan="4">$4X10^{-6}$</td><td rowspan="4">50.0488</td><td rowspan="4">0.1767</td><td rowspan="4">0.970</td></tr>
<tr><td>80</td></tr>
<tr><td>100</td></tr>
<tr><td>120</td></tr>
<tr><td rowspan="5">Halsey</td><td>Initial dye concentration</td><td>n_H</td><td colspan="2">K_H</td><td>R^2</td></tr>
<tr><td>60</td><td rowspan="4">2.141</td><td colspan="2" rowspan="4">0.8317</td><td rowspan="4">0.980</td></tr>
<tr><td>80</td></tr>
<tr><td>100</td></tr>
<tr><td>120</td></tr>
</table>

IV. ANALYSIS OF ISOTHERM

4.1 Langmuir isotherm

In the present study Q_o value is 76.923. The separation factor R_L values in between 0 to 1 indicate the favourable adsorption. The R^2 value is close to unity which reached to good fitting into Langmuir isotherm.

4.2 Freundlich isotherm

The values of n were between 1 to 10 indicates cooperative adsorption [20]. The R^2 value is is close to unity which reached to good fitting into Freundlich isotherm.

4.3 Temkin isotherm

B_T – Temkin constant is related to the heat of adsorption. This B_T value is 17.48 indicates temperature of adsorption increased. The Temkin parameter A_T value give on idea about nature of adsorption [14]. In our present study the A_T value is 0.8791 which indicate the adsorption is chemical nature. The R^2 value is low.

4.4 Dubinin-Radushkevich isotherm

The activation energy E value is 15.284 and B_D value is $2X10^{-3}$ indicates the chemisorption. The R^2 value is is close to unity which reached to good fitting into D-R isotherm.

4.5 Halsey isotherm

The R^2 value is low compared to other isotherms.

In general the fitting data in isotherm equation were in the following order:Langmuir> Temkin >Halsey > Freundlich> Dubinin-Radushkevich.

V. CONCLUSION

This study shows that PAC-MnO_2-NC can be used effectively for the removal of Acid Green dye from aqueous solution. The adsorption equilibrium data well described by the following order: Langmuir> Temkin >Halsey > Freundlich> Dubinin-Radushkevich.This isotherm constant predicted that the mono layer and multi layer adsorption.

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