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Removal of Basic Dye Rhodamine-B by Activated Carbon-MnO_2-Nanocomposite and Activated Carbon-A Comparative Study

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Abstract: ***The removal of Rhodamine-B by adsorption on Activated carbon-MnO2-Nanocomposite as well as on Activated carbon under optimized conditions has been studied. The effect of several parameters such as pH, contact time, initial concentration of the adsorbate, adsorbent dosage and temperature has been evaluated. The application of Pseudo first order, Pseudo second order, intra-particle diffusion model and Elovich kinetic models have been calculated. The adsorption on both the Activated carbon and nanocomposite followed Pseudo second order kinetics. Langmuir, Freundlich and Tempkin isotherms were also studied. The equilibrium data fitted well with Langmuir model. Thermodynamic parameters such as free energy change(ΔG°) enthalpy change (ΔH°), and entropy change (ΔS^o) indicate the adsorption process to be endothermic and spontaneous. Adsorbent used in this study are characterized by FT-IR, XRD and SEM analysis. The study revealed that nanocomposite is more effective than activated carbon in removing methylene blue by adsorption.***

Keywords: Rhodamine-B, AC, AC-MnO2-NC, Adsorption isotherm, Kinetics.

1. Introduction

During the last few decades the mobility and distribution of dyes in water have been studied extensively due to their toxic effects to humans, animals, plants and the aquatic organisms. Many of the industries, such as dyestuffs, textile, paper, leather, foodstuffs, cosmetics, rubber and plastics are using enormous quantity of synthetic dyes in order to give color for their products and consume substantial volumes of water. As a result, they generate a considerable amount of colored waste water. Textile and dyeing industry are among important sources for the continuous pollution of the aquatic environment. Because they produce approximately 5% of them end up in effluents. The textile and dyeing industries effluents are discarded into rivers, ponds and lakes; they affect the biological life various organisms [1-3]. Dye-containing effluents are undesirable wastewaters because they contain high levels of chemicals, suspended solids, and toxic compounds [4, 5]. Color causing compounds can react with metal ions to form substances which are very toxic to aquatic flora and fauna and cause many water borne diseases [6-8].

Due to the chemical structure of dye, they are act as a resistant to many chemicals, oxidizing agents, and heat, and are biologically non-degradable. So it is difficult to decolorize the effluents, once released into the aquatic environment. Many of the methods are available for the removable pollutants from water, the most important of which are reverse osmosis, ion exchange, precipitation and adsorption.

Adsorption process has been found to be superior technique for treating dye effluents due to simplicity and insensitivity to toxic substance. Although the activated carbon [9, 10] is most effective for absorption of dye, but it has some disadvantages such as (i) high adsorbent cost, (ii) problems of regeneration and difficulties of separation of powdered activated carbon from waste water for regeneration are expensive and hence increasing need for equally effective but commercially low cost sorbents. A wide variety of materials such as animal bone [11], black tea leaves [12], cocoa [13], almond shell [14], mango leaves [15], saw dust [16], Jambonut [17] and Borassus flabellifer L[18].

The present study is aimed at comparing the effectiveness of both Activated carbon-MnO_2-Nanocomposite and Activated carbon in removing Rhodamine-B 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 pH. The thermodynamic parameters were also evaluated from the adsorption measurements. The Langmuir, Freundlich and Tempkin adsorption isotherms, kinetics, FT-IR, XRD and SEM were also studied. Double distilled water was used throughout the experiment.

2. Results and Discussion

2.1 Effects of agitation time Vs initial dye concentration

Effects of agitation time and initial dye concentration (10, 20, 30 and 40 mg/L) on removal of RHB by both AC-MnO_2-NC and AC was increased with increase in agitation time and reached equilibrium at 90 min. In the AC-MnO_2-NC the percent dye removal at equilibrium decreased from 62.59 to 34.47 as in the case of AC it is 31.39 to 20.42 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.

2.2. Effect of adsorbent dose

The removal of RHB by both AC-MnO_2-NC and AC at different adsorbent doses (10mg to 600mg/50ml) was tested for the dye concentrations 10, 20, 30 and 40 mg/L. With both AC-MnO_2-NC and AC the adsorption increases with increase in adsorbent concentration; this is due to the increase in surface area and availability of more adsorption site. The percentage removal of MB is greatly increases in the range of 10-600mg/50ml after that small change occur. So the optimum adsorbent carbon doses for the experiments were carried out using 100mg/50ml.

2.3 Effect of pH

Effect of pH on the removal of RHB by both AC-MnO_2-NC and AC are calculated. The solution pH is one of the most important factors that control the adsorption of RHB on the adsorbent material. Therefore an increase in pH may cause an increase or decrease in the adsorption capacity. The adsorption capacity can be attributed to the chemical form of RHB in a solution at the specific pH or due to different functional groups on the adsorbent surface. To examine the effect of pH on the percentage removal of RHB gradually increases as the pH increases. The pH value upto 8.95 the percentage removal is up to 45.11 in the case of AC-MnO_2-NC and 31.91 for AC after that suddenly increases. At the solution pH the adsorbent surface negatively charged and favours uptake of cationic dyes due to increased electrostatic force of attraction. Therefore, all the experiments were carried out at the pH 8.95. For 40mg/L dye concentration the percent removal increased from 28.69 to 58.57 in the case of AC-MnO_2-NC and 24.36 to 45.37 for AC. when the pH was increased from 2 to 14 and the percent removal remained almost the same above pH 8.95.

2.4 Effect of Temperature

The effect of temperature of adsorption of RHB by both AC-MnO2-NC and AC is Calculated. For concentration 40 mg/L adsorbent was carried out at 30^o,40^o,50^o and 60^oC. The percent removal of dye increased from 13.00 to 55.48 as in the case of AC-MnO2-NC and 10.37 to 48.39 for AC. 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.

3. Adsorption Isotherms

To quantify the adsorption capacity of the absorbent for the removal of dyes, the most commonly used isotherm, namely Freundlich and Langmuir have been adopted.

3.1 Langmuir isotherm

Langmuir isotherm model [19] is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of the Langmuir isotherm equation can be described by

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

Where Ce is the concentration of dye solution (mgl-1) at equilibrium. The constant Q_0 signifies the adsorption capacity (mgg-1) and KL(L/mg) is the Langmuir isotherm constant that relates to the energy of adsorption or rate of adsorption. In order to find out the feasibility of the isotherm, the essential characteristics of the langmuir isotherm can be expressed in terms dimensionless constant separation factor (RL) [20,21]is given by the equation

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{…………….. (2)}$$

Where K_L is the Langmuir isotherm constant and C_0 is the initial dye concentration (mgL-1). The parameter R_L indicate the nature of the adsorption isotherm.

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RL >1 Unfavourable adsorption
0< RL <1 Favourable adsorption
RL =0 Irreversible adsorption
RL =1 Linear adsorption

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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 . Langmuir isotherm constant value indicate the maximum adsorption capacity (Q_0) in 76.9230mg/g as in the case of AC-MnO_2-NC and 66.666mg/g for AC. 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 [22] 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/g) at equilibrium, C_e is the equilibrium dye concentration in solution (mgL-1), k_f is (mg/g(L/mg)) measure of adsorption capacity and 1/n is the adsorption intensity. The magnitude of the exponent 1/n gives an indication of the favourability of adsorption. The value of n > 1 represents favourable adsorption condition [23, 24] or the value of 1/n lying in the range of 1 to 10 confirms the favourable condition for adsorption. The Values of k_f and n were calculated from the intercept and slope of the plot .The Freundlich isotherm parameter indicates that the adsorption capacity is 29.6483 as in the case of AC-MnO_2-NC and 26.1216 for AC. The n value indicates the adsorption is favourable process.

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 (25).A plot of qe versus lnCe enables the determination of the isotherm constants A and B. A is the equilibrium binding constant (1/mol) corresponding to the maximum binding energy and constant B, is related to the heat of adsorption. Compared to the correlation coefficient (R^2) values shows that Langmuir isotherm of AC-MnO_2-NC is found to best.

4. Adsorption Kinetics

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid – solution interface. The kinetics of RHB adsorption on the AC-MnO_2 –NC and AC were analysed using Pseudo first order, Pseudo second order, Elovich and Intraparticle diffusion kinetics models. The confirmity between experimental data and the kinetics models was expressed by the correlation coefficients (R^2) value, the R^2 values close or equal to 1. A relatively high R^2 value indicates that the model successfully describes the kinetics of RHB dye adsorption. So that the adsorption of RHB by both AC-MnO_2-NC and AC is to follow the Pseudo second order kinetic model.

5. Thermodynamic Parameter

The adsorption data indicates that ΔGº were negative at all temperatures. The negative ΔGº confirms the spontaneous nature of adsorption of RHB by both AC-MnO_2-NC and AC. The magnitude of ΔGº suggests that adsorption is physical adsorption process. The positive value of ΔHº were further confirms the endothermic nature of adsorption process. The positive ΔSº showed increased randomness at the solid-solution interface during the adsorption of RHB dye by both AC-MnO_2-NC and AC. This was also further supported by the positive values of ΔSº, which suggest that the freedom of RHB is not too restricted in the adsorbent, confirming a physical adsorption. The ΔGº value increases with increase in temperature is the increase in enhancement of the adsorption capacity of adsorbent may be due to increase or enlargement of pore size and/or activation of the adsorbent surface.

6. Desorption Studies

After activated carbon is saturated with dye molecules, different solvents could be used to regenerate the activated carbon to restore its dye adsorptive capability [26]. Desorption was not satisfactory, which confirms the chemisorptive nature of adsorption.

7. Conclusions

The present investigation showed that AC-MnO_2-NC and AC can be used as adsorbent for removal of Rhodamine-B. The amount of dye adsorbed varied with initial concentration, adsorbent dose, pH and temperature. Removal of dye by both AC-MnO_2-NC and AC was found to obey Langmuir adsorption model. The kinetic parameters fit for Pseudo second order model. Evaluation of thermodynamic parameters showed the process as endothermic and spontaneous. Desorption studies reveals that was not satisfactory desorption taking place confirming chemisorptive nature of adsorption. The study reveals that AC-MnO_2-NC is more efficient than the AC in removing the Rhodamine-B.

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