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Adsorption of Rhodamine-B by using Citrus peel powder: Influence of operating parameters

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Rhodamine-B (RB) is widely used for different purposes in industries such as printing and dyeing in paints, paper, leathers, textiles, etc. and may remain in high concentrations in surface water used as drinking water sources. In this study removal of RB from aqueous solution using Citrus peel powder (CPP) has been investigated. The influence of various factors such as the amount of a concentration of RB (20, 40, 60, 80 mg/L), adsorbent (CPP) dosage (0.5, 1.0, 1.5, 2.0, 2.5 g/L), pH (3, 5, 7, 9, 11), agitation speed (100, 200, 300 rpm) and temperature (40, 50, 60°C) were studied. It has been found that maximum adsorption is occurring at 2 g/L amount of adsorbent, dye the concentration of 20 mg/L, pH of 3, agitation speed 300 rpm at 60°C. Equilibrium data were fitted to Langmuir and Freundlich isotherms and the equilibrium data were best described by the Langmuir isotherm model with 125 mg/g at 60°C. The values of their corresponding constants were determined from the slope and intercepts of their respective plots. The results of this study indicate that the adsorption is favorable and suggested that natural adsorbents can be utilized as adsorbent materials, because of their selectivity for the removal of RB from aqueous solutions.

Keywords: Rhodamine-B, Citrus peel powder, adsorption isotherms, process parameters.

Introduction

Colour removal from wastewater/effluents is of great importance. Various industries such as textile, paper, carpet, leather, distillery, and printing are responsible for the discharge of wastewater containing dyes into rivers and natural water streams, these dyes prove to be toxic to the aquatic life and damage the ecosystem[1,2]. This toxic wastewater that is polluted due to chemicals worsens the water and soil quality after mixing with rivers, natural streams, and its dependent habitat and environment[3]. As a consequence of such high quantities of effluent and dye-bearing wastewater, these industries are now facing major problems in environmental pollution[4].

In many of the cases, effluent wastewater from such industries is directed towards the natural stream of water and thus poses a severe hazard to the environment and local flora and fauna[4]. Wastewater effluents discharged from industries and containing even small amounts of dyes is of high priority matter of concern as it causes a change in properties and color of water and has a long term damaging effect on aquatic life[5]. Due to the fact that this dye bearing wastewater imposes severe health harm to humans, there is a strong need for developing an eco-friendly, robust, and cost-effective method to treat the dye contaminated wastewater[6].

There are various technologies available for the treatment of wastewater like ozonation, coagulation, reverse osmosis, photocatalytic degradation, oxidative degradation, nano-filtration, membranes, etc. Although, many of the treatment methods are not at all practically applicable either in terms of performance standards or cost of usage. However, the adsorption method is an eco-friendly, easy to use, cost-effective and efficient technique to remove the noxious pollutants present in the wastewater effluent[7–9].

In the light of these realities, the present research work is focused on the adsorption of RB dye using Citrus peel powder (CPP) as adsorbent. The batch adsorption study of RB dye onto the CPP was carried out as a function of the initial concentration of dye, adsorbent dose, temperature, pH, and agitation speed to generate isotherm data.

Table 1. Characteristics of the CPP

Typical properties	
Total pore volume (cm^3/g)	0.29
Average pore diameter	33.21
Bulk density (g/cm^3)	0.58
Proximate analysis	
Moisture (%)	8.19
Volatile matter (%)	86.54
Fixed carbon (%)	0.29
Ash content (%)	4.98
Ultimate analysis (%)	
C (%)	36.63
H (%)	5.89
N (%)	1.62
S (%)	0.12
O (by difference)	55.74

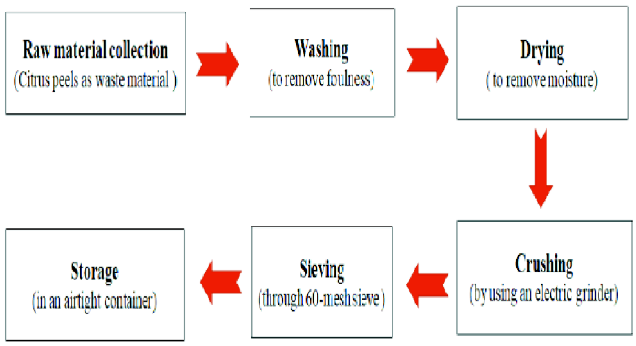


Fig. 1. Schematic diagram for the processing of waste Citrus peels.

Materials and methods

Chemicals:

The chemical nature of adsorbate has a profound effect on the adsorption characteristics[10]. The dye chosen in the present study was Rhodamine-B (RB). Distilled water was used for the preparation of various solutions and the glassware was washed with distilled water. For varying the pH of the solution, 0.1 *N* hydrochloric acid (HCl), and 0.1 *N* sodium hydroxide (NaOH) was used respectively. Citrus peel powder was used as an adsorbent that was used. Analytical grade chemicals were used for experimentation.

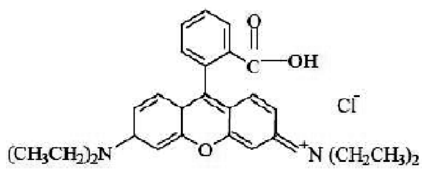
Preparation and characterization of Citrus peel powder adsorbent:

In the present study, Citrus peels as waste material was used as an alternative zero-cost adsorbent for the elimination of hazardous RB dye from water. Citrus peel was collected from local fruit vendors and then thoroughly washed to remove foulness. This peel was dried in sunlight for 3–4 days then converted to powder. This powder was further kept in a tray drier for 6 h at 70°C to remove the complete moisture content of the powder. CPP powder was passed through sieving through a 60-mesh sieve to maintain the uniformity of particle size and stored in a container that is airtight for further analysis. Fig. 1 represents the schematic diagram for the processing of waste Citrus peels and Table 1 show the characteristics of adsorbent (CPP).

Preparation of solution and characteristics of Rhodamine-B:

The synthetic dye RB is used in this study. It is used mainly in the paper and printing industries. It is also used in medicine and cosmetics, in addition to this. This dye is also extremely toxic on the other hand. Prolonged exposure can lead to nausea and vomiting; increased exposure can result in unconsciousness. The solution of 20, 40, 60, and 80 mg/L of RB was prepared for batch study. The Table 2 shows the molecular structure and other properties of RB.

Table 2. Characteristics of Rhodamine-B dye

Symbol	RB
Appearance	Red to violet powder
Solubility in water	50 g/L
Chemical structure	
Molecular formula	$C_{28}H_{31}ClN_2O_3$
Molar mass	479.02

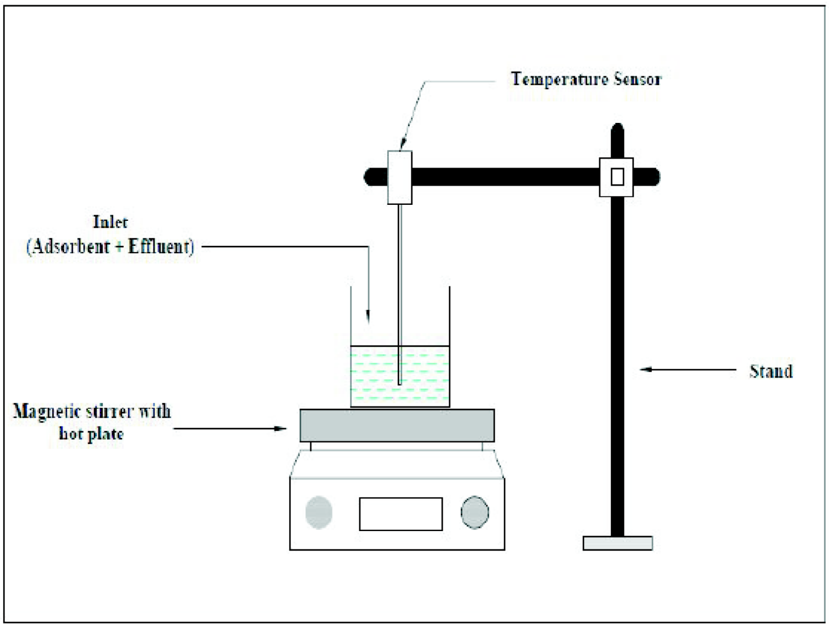


Fig. 2. Schematic representation of batch adsorption experimental setup.

Batch adsorption study:

In this experiment, a batch adsorption method was used. In order to investigate the effects process parameters such as the concentration of RB (20, 40, 60, 80 mg/L), adsorbent (CPP) dosage (0.5, 1.0, 1.5, 2.0, 2.5 g/L), pH (3, 5, 7, 9, 11), agitation speed (100, 200, 300 rpm) and temperature (40, 50, 60°C) at different time intervals were measured. The solutions were then subjected to magnetic stirrer for proper adsorption[11]. At different intervals the samples were removed from the stirrer. Then the adsorbents were separated from the sample by using the centrifuge. The RB concentration was analyzed with a wavelength of 554 nm using UV-Visible spectrophotometer. Fig. 2 shows that the schematic representation of batch adsorption experimental setup. The amount of dye adsorbed per gram of adsorbent is determined using the equation in equilibrium, q_e (mg/g)[12] :

$$q_e = \frac{(C_i - C_e)V}{X}$$

where, q_e = adsorbed dye per unit adsorbing mass (mg/g), C_i = initial concentration of dye (mg/L), C_e= final concentration of dye (mg/L), V = volume of solution (ml), X = dose of adsorbent (CPP) used (g/L).

Results and discussion

Influence of operating parameters:

The evaluations of various operating parameters such as the effect of concentration of RB, effect of the adsorbent dose, the effect of pH, effect of agitation speed and effect of temperature is of vital importance in the design of any adsorption system. The effect of these operating parameters studied for the removal of RB dyes by using CPP adsorbent.

Effect of concentration of dye (RB):

The results are shown in Fig. 3 represents the adsorption data for removal of Rhodamine-B versus contact time at different concentrations of RB. The experiments were carried out at a fixed adsorbent dose (2 g/L) and the different initial RB concentrations (20, 40, 60, 80 mg/L). The concentration of RB increased from 20 to 80 mg/L the percentage removal of RB decreased. With the increase in contact time the percent removal of dye (RB) is increased and remained constant after a time of equilibrium has been reached. The explanation for this observation was that almost every RB molecule was very rapidly adsorbed to the external surface at lower concentration but further increase in the first RB concentration led to the fast saturation of the CPP surfaces and thus to a slow RB adsorption within the pores.

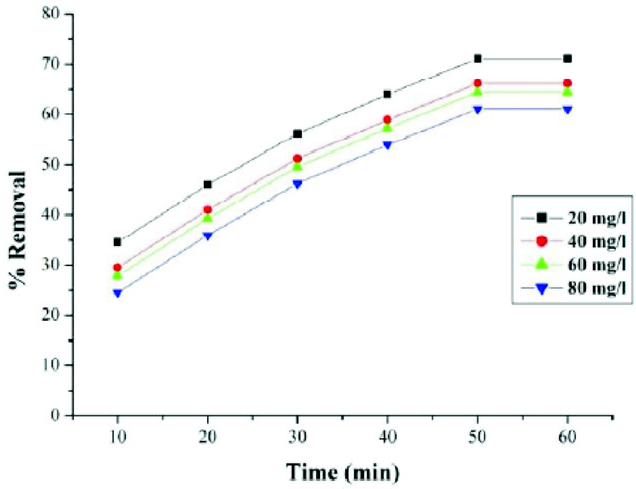


Fig. 3. Effect of concentration of RB on CPP.

Effect of adsorbent (CPP) dose:

The dosage of adsorbents is an integral parameter as this defines the adsorbent's capacity for a certain adsorbent concentration[13]. The adsorption of RB was evaluated by taking the different adsorbent doses (0.5, 1.0, 1.5, 2.0, 2.5 g/L). The effect of the adsorbent dose (CPP) on RB removal is shown in Fig. 4. The percentage removal of RB also increases with rising adsorbent dosages. With a concentration of 0.5 to 2.5 g/L, the percentage of the dye removal is higher. Equilibrium at low concentrations was shown to be reached more easily. However, from the Fig. 4, it is observed that for adsorption of percentage RB removal was increased up to an adsorbent dosage of 2 g/L and then it remains almost constant. This could be due to a higher adsorption dose that increases the adsorption area available to improve the availability of additional sites. Therefore all the adsorption experiments onto CPP were carried out at an adsorption dose of 2 g/L.

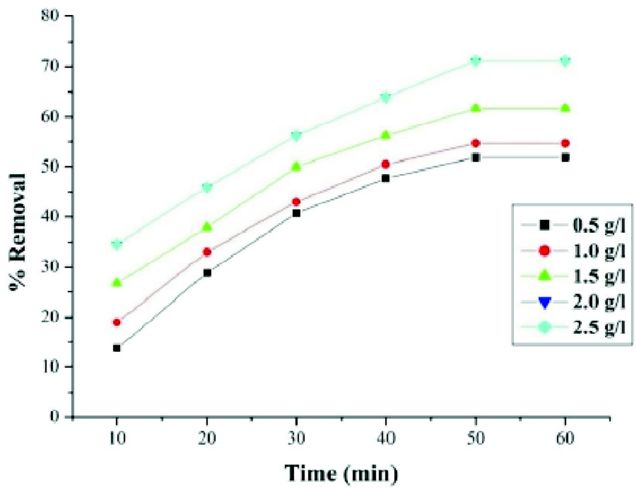


Fig. 4. Effect of adsorbent (CPP) dose on the removal of RB.

Effect of change in pH of the solution:

In the entire adsorption process and in particular on the adsorption power, pH of the RB solution plays an important role, influencing the surface charge of the adsorbing material, the degree to which this solution ionizes the material and the separation of working groups in an adsorbent's active sites[14]. In order to study the effect of pH on the removal of RB, experiments were carried out at various pH values, ranging from 3, 5, 7, 9, 11 for RB concentration (20 mg/L) and CPP dose 2g/L. The effect of pH on removal of RB on the adsorbent CPP dose (2 g/L) is shown in Fig. 5. The pH was controlled and tested using a pH meter, using 0.1 *N* NaOH and 0.1 *N* HCl solutions. It has been observed that the percentage of removal RB was observed by decreasing pH. The maximum removal of RB was observed to be at pH 3.

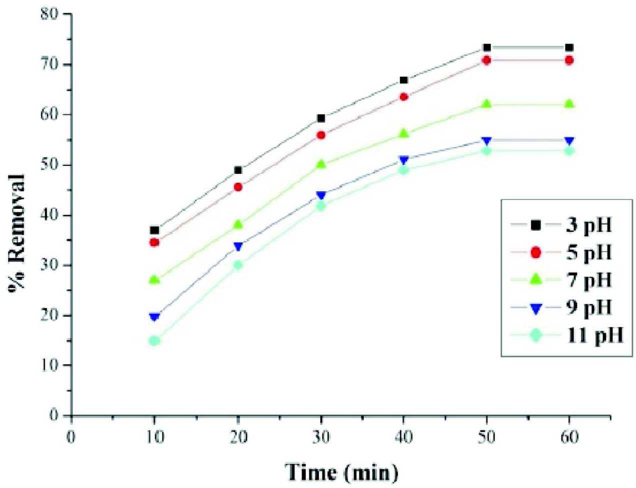


Fig. 5. Effect of pH on removal of RB.

Effect of temperature:

The adsorption studies were carried out at three different temperatures of 40°, 50° and 60°C with the dye (RB) concentrations of 20 mg/L and the results of the experiments are shown in Fig. 6. As the temperature increased from 40°C to 60°C, the percentage removal of RB also increased. The potential of the adsorption increases with the temperature due to an increase in the rate in which molecular adsorption diffuses over the external boundary and the internal pores of

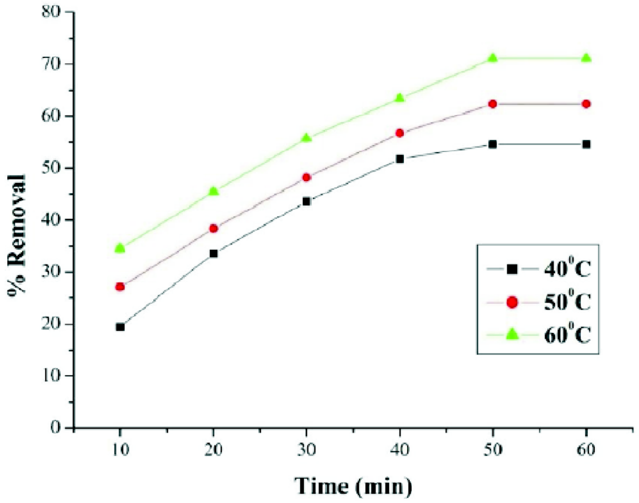


Fig. 6. Effect of temperature on removal of RB.

the adsorbent particle. In addition, the adsorbent's balance potential for a certain adsorbent varies as temperature changes. The maximum percentage removal RB was observed at 60°C.

Effect of agitation speed:

Agitation, which affects the formation of the external boundary film and the distribution of the solution in the broad solution, is the key parameter in adsorption[15]. The effect of agitation speed in RB removal on the CPP was investigated by varying agitation speed from 100 to 300 rpm, with constant concentration, pH, temperature and other parameters. The results obtained are shown in Fig. 7 and it can be seen that equilibrium RB concentration in the solid phase was affected by low agitation speed. These results indicated that the removal of RB dye increases with an increase in rotational speeds from 100 to 300 rpm.

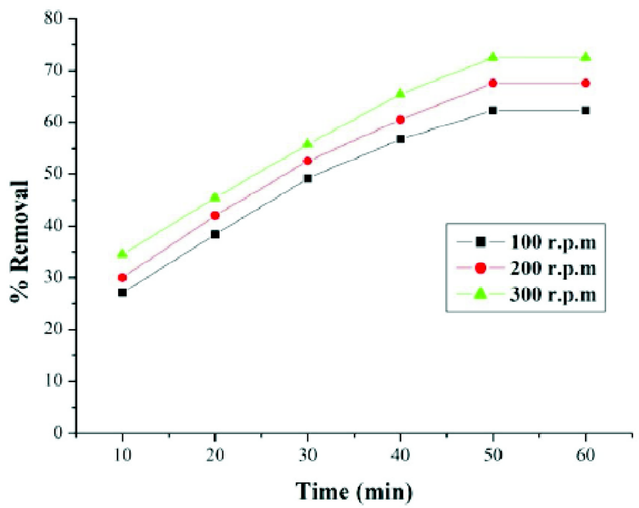


Fig. 7. Effect of agitation speed on removal of RB.

Adsorption isotherm:

When the adsorption process reaches an equilibrium state the adsorption molecules are distributed between a solid state and liquid state which is indicated by adsorption isotherm. Langmuir and Freundlich are two well-known isotherms on which an adsorption study was carried out at different temperatures. In many monolayer adsorption processes, the adsorptions occur at specific homogeneous sites on the adsorbent is successfully used and it assumes by the Langmuir model. The Freundlich model endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy levels of adsorption[16]. The applicability of the isotherm equation is compared by judging the correlation coefficients, R^2.

Langmuir isotherm:

Langmuir isotherm has been used extensively by many authors for the adsorption of heavy metals, dyes, organic pollutants onto adsorbents[17]. The Langmuir isotherm model estimates the maximum adsorption capacity produced from complete monolayer coverage on the adsorbent surface. The linear form of the Langmuir model is given:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L}$$

where, C_e = equilibrium concentration of dye (RB) solution (mg/L), q_e = equilibrium capacity of dye (RB) on the adsorbent (mg/g), q_{max} = adsorption capacity of the adsorbent (CPP) (mg/g), KL = Langmuir adsorption constant (L/mg) and is related to the free energy of adsorption.

The equilibrium data for adsorption of RB onto CPP was analyzed using the Langmuir model. The plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) gives linear relationship as shown in Fig. 8 with a coefficient of correlation (R^2) is 0.99 which confirms the applicability of the Langmuir model indicating the homogeneous nature of CPP adsorbents, i.e. each dye molecule/adsorbent adsorption has equal adsorption activation energy. From the graph, the slope was found which gives us the value of $1/(q_{max}KL)$. The equation is $y = mx + c$. The y-axis intercept gives the

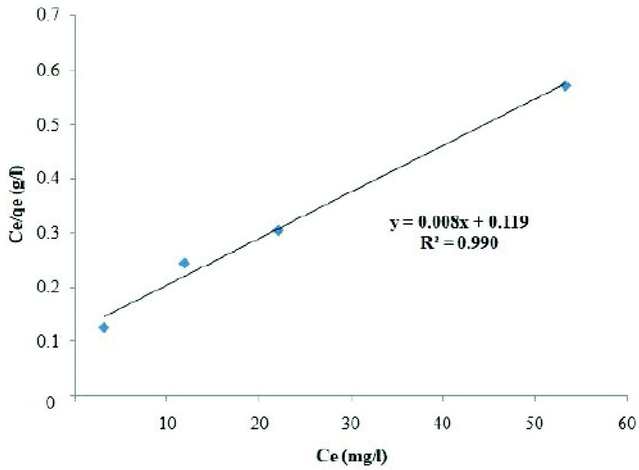


Fig. 8. Langmuir isotherm for the adsorption RB onto CPP.

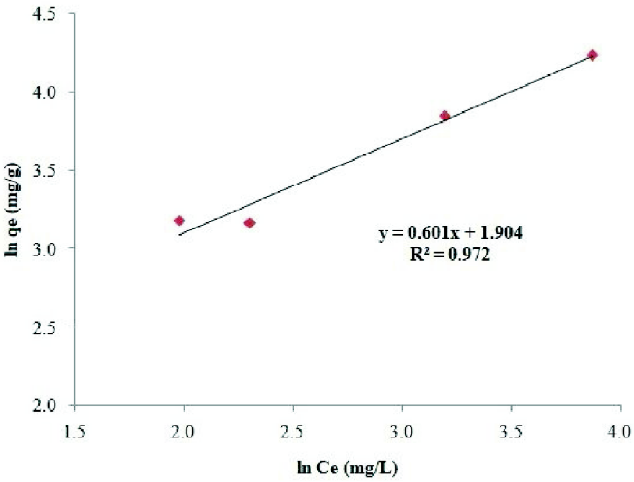


Fig. 9. Freundlich isotherm for the adsorption RB onto CPP.

$1/q_{max} = m$. The results also demonstrate the formation of monolayer coverage of dye molecule at the outer surface of adsorbent (CPP) studied. The maximum monolayer capacity q_{max} for RB onto CPP adsorbent obtained from the Langmuir model is 125 mg at 60°C.

Freundlich isotherm:

The Freundlich model is based on the assumption that metal ions are adsorbed on a heterogeneous surface and is not restricted to formation of monomolecular layer[18]. Freundlich model can be represented by the linear form as follows:

$$\ln q_e = \ln q_e K_F + \frac{1}{n} \ln C_e$$

where, K_F and n (dimensionless constants) are the Freundlich adsorption isotherm constants, which indicate the capacity and intensity of the adsorption, respectively. The equilibrium data for adsorption of RB onto CPP was analyzed using the Freundlich equation. Fig. 9 represents the plot of ln q_e versus ln C_e, which is a straight line, with the intercept value of ln K_F and the slope of $1/n$ and is presented in Table 3. The correlation coefficients (R^2), obtained from the Freundlich model indicates that the experimental data can be fitted to the Freundlich model and $n > 1$, indicating that the adsorption of RB onto CPP is a favorable adsorption process. However, based on the R^2 value, the Freundlich isotherm appears to be less applicable than Langmuir isotherm models.

Table 3. Langmuir and Freundlich constant for the adsorption of RB on

Langmuir model	
Constants	Magnitude
K_L (L/mg)	0.055
q_{max} (mg/g)	125
R^2	0.99
Freundlich	
Constants	Magnitude
K_F (mg g^{-1}) (mg^3/g)$^{1/n}$	6.74
n	1.66
R^2	0.972

Conclusion

This study examined the potentials of natural materials (CPP) as adsorbents for the removal of RB from aqueous solution in a batch reactor. The result from the equilibrium study gave the adsorption capacity of 125 mg/g at 60°C, while the isotherm models tested conform well with the experimental data, although Langmuir demonstrated a better fitting. Thus, CPP is a cost-effective and efficient adsorbent for the removal of RB from wastewater. Future work will focus on the studies of adsorption thermodynamic and kinetic as a second part of the present study.

Abbreviations

RB	Rhodamine-B
CPP	Citrus peel powder

q_e	Amount of dye adsorbed per unit mass of adsorbent (mg/g)
C_i	Initial concentration of dye (mg/L)
C_e	Final concentration of dye (mg/L)
V	Volume of solution (ml)
X	Dose of adsorbent (CPP) used (g/L)
q_{max}	Adsorption capacity of the adsorbent (CPP) (mg/g)
K_L	Langmuir adsorption constant (L/mg)
K_F	Freundlich adsorption constants (mg g^{-1}) (mg^3/ g)$^{1/n}$
n	Dimensionless constants

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