Research on the Adsorption Behaviour of Crystal Violet Simulated Wastewater on Fallen Willow Leaves

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Abstract. The adsorption of crystal violet (CV) simulated wastewater on the fallen willow leaves has been investigated. The effects of adsorption oscillating time, fallen willow leaves dosage, pH value, temperature and so on were examined of CV adsorption on fallen willow leaves, respectively. The result shows that the fallen willow leaves adsorbed the CV simulated wastewater well. The experimental data conformed to the Langmuir and Freundlich isotherm equations. The maximum biosorption capacity is 312.5 mg/g at 298K, which is superior to most reported biosorbents.

1. Introduction
Rapid population growth and industrial development have led to environmental damage. A large number of pollutants were released into the environment over the past few decades. Dye is one of major pollutant, which can’t be completely biodegraded and remains in the effluent of wastewater treatment plant [1]. Crystal violet is a kind of triphenylmethane cationic dye, which has been widely applied in coloring paper, dyeing cottons and wools, etc [2]. Many methods have been used to remove dyes wastewater including chemical oxidation, biological process, adsorption and membrane treatments etc. [3-4]. Aqueous and gas pollutants adsorbed on solid adsorbents can be eliminated effectively and therefore has considerable environmental significance [5]. In the recent years, leaves of neem, poplar, acer monoes, paper mulberry etc. have been used in dye and metal removal [5-8]. Fallen tree leaves are mostly combusted under permission, because other methods are not economical and the effect is general. Fallen leaves could be utilized as an adsorbent for dye adsorption. In addition, fallen leaves can be stored for a long time after being treated [9]. In the present research work fallen willow leaves was used as an economically, efficient and easily available adsorbent for the adsorption of crystal violet.

2. Materials and methods

2.1. Adsorbent and adsorbate
The fallen willow leaves were collected in Liaoning Shihua University campus in November. The leaves were first cleaned with a quantity of water, and then with distilled water. The washed leaves were oven dried at 80 °C until a constant weight and crushed with a pulverizer. The fallen willow leaves powder was stored in dryer.

CV stock solution of 1000mg/L was prepared by dissolving 1g CV in distilled water and diluted to 1 L in volumetric flask. CV dye solution of different concentration used in the experiment was diluted
with the stock solution. The CV residual and adsorption concentration was analyzed by UV 1102 spectrophotometer and then calculated with CV standard curve of each experiment. Solution pH was adjusted using a certain concentration of NaOH and HCl.

2.2. Adsorption experiments
The CV simulated wastewater was mixed with a quantity of the fallen willow leaves powder in constant temperature oscillator at a speed of 170rpm/min at 25 °C (except for the temperature experiments). The effect of adsorption oscillating time, pH value, the fallen willow leaves dosage, experiment temperature and initial dye concentration on CV adsorption has been studied, respectively. The adsorption efficiency dye was calculated by equation (1). The adsorption capacity at equilibrium \(q_e\) was obtained by equation (2).

\[
\text{Crystal violet adsorption efficiency } E(\%) = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \tag{1}
\]

\[
\text{Adsorption capacity } q_e = \frac{(C_0 - C_e) \times V}{M} \tag{2}
\]

Where \(C_0\) and \(C_e\) are the initial and equilibrium concentration of CV solution, mg/L; \(M\) are the fallen willow leaves mass, g; \(V\) are the solution volume, L.

3. Results and Analysis

3.1. Effect of oscillating time on CV adsorption

![Figure 1. Change of E% and qe with oscillating time](image)

The change of E% and \(q_e\) with oscillating time of CV (initial concentration of 80mg/L and 100mg/L) adsorption on fallen willow leaves (dosage of 1.6g/L) is shown in Figure 1. It can be seen that the adsorption of CV on fallen willow leaves is a slow process. The adsorption efficiency and \(q_e\) increased with time increasing, which was obviously within 90min, and then slowly between 120min and 240min. 180min was used as the oscillating time in other experiments.

3.2. Effect of pH value
The solution pH disturbs the nature and surface charge of the adsorbent material, and is responsible for the attraction of dye molecules to the adsorbent material [10]. The change of E% and qe with initial solution pH of crystal violet (100mg/L) adsorption on fallen willow leaves is shown in Figure 2. It can be seen that the pH affect CV adsorption obviously at the lower pH value. When the pH value increased from 1.5 to 3.6, the adsorption efficiency increased from 80.2% to 90.0% and reached the best at pH value of 3.6. After that, the adsorption efficiency decreased slightly with pH value increasing. Because the pH value of CV solution itself was close to neutral and the adsorption effect of CV was also better under neutral conditions, the solution pH was not regulated in other experiments.

3.3. Effect of willow leaves dosage

The change of E% and qe with fallen willow leaves dosage on CV adsorption is shown in Figure 3. The fallen willow leaves dosage was from 0.8 to 4 g/L and mixed with 100mg/L CV for 180min. The results show that E% increased and qe decreased with willow leaves dosage increasing. When the dosage of fallen willow leaves increased from 0.8g/L to 2g/L, the adsorption efficiency of CV increased from 80.6% to 90.7%. But at higher adsorbent dosage, the increase was not significant. The
q_e has been decreasing from 100.8 mg/g to 22.4 mg/g. Considering the adsorption efficiency and q_e, the fallen willow leaves dosage of 1.6 g/L was used as the adsorbent dose in this experiment.

3.4. Effect of temperature

Figure 4. Change of E% and q_e in different initial CV concentration from 25 °C to 40 °C

The change of E% and q_e in different initial CV concentration from 25 °C to 40 °C is shown in Figure 4. It can be seen that E% decreased and q_e increased with the increase of the initial CV concentration. The initial concentration of CV influenced the adsorption capacity. q_e of fallen willow leaves absorbing CV increased with initial CV concentration increasing at the same temperature. The higher the temperature was, the bigger the adsorption efficiency and q_e was in the same initial CV concentration. High temperature was beneficial to the adsorption of CV on fallen willow leaves. q_e of CV (180 mg/L) on fallen willow leaves was 101.9 mg/g at 40 °C.

3.5. Adsorption isotherms

Langmuir isotherm model (3) and Freundlich isotherm model (4) were used to linearly fit the adsorption equilibrium data of 100 mg/L CV on 1.6 g/L fallen willow leaves at 298K~313K. Fitting curves are shown in Fig. 5 and Fig. 6, and related parameters have been calculated.

\[
\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}
\]

\[
\ln q_e = \ln k + \frac{1}{n} \ln C_e
\]

Where b is the Langmuir constant related to the affinity of binding sites, L/mg; q_m is the theoretical saturation capacity of the monolayer, mg/g. The q_m and b values can be calculated from the linearized form of equation (3). k and 1/n are the Freundlich constants, which correspond to the adsorption capacity and the adsorption intensity of the adsorbent, respectively.
The results show that the adsorption of CV fits with both Langmuir and Freundlich adsorption isotherm equations. The maximum adsorption capacity of CV on fallen willow leaves during 298K–313K was 312.5 mg/g, 303.0 mg/g, 256.4 mg/g and 222.2 mg/g, respectively. The values of 1/n can be calculated from the slope of the logarithmic plot of lnq_e versus lnC_e. The value of 1/n determines the magnitude of adsorption in Freundlich isotherm. The values of the empirical parameter 1/n during 298K–313K were 0.7938, 0.8231, 0.7778 and 0.6766, respectively, which represents a favorable adsorption.

4. Conclusion
The biosorption of CV simulated wastewater on the fallen willow leaves has been studied. The suitable adsorption conditions of CV adsorption on fallen willow leaves were time of 180 min, adsorbent dosage of 1.6 g/L and pH value of 3.6. While the adsorption effect of CV was also better under neutral condition, the solution pH of was not regulated in other experiments. Higher temperature was advantage for CV adsorption. The experimental data was fitted to the Langmuir and Freundlich isotherm equations. The maximum biosorption capacity was 312.5 mg/g obtained at 298K, which was superior to most reported biosorbents.
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