Research on the adsorption treatment of the malachite green simulated wastewater on fallen acer monoes leaves

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Abstract. The adsorption treatment of malachite green (MG) wastewater using fallen acer monoes leaves as adsorbent has been studied. The effects of single factors such as adsorption oscillating time, pH value, fallen acer monoes leaves dosage, temperature, initial MG concentration and salts concentration on MG adsorption on fallen acer monoes leaves have been investigated, respectively. The results show that the major effect factors on adsorption are including adsorption time, adsorbent dosage, pH value and salts concentration. Through the analysis of the orthogonal test, it is confirmed that the effect orders of the MG adsorption rate from master to the secondary were NaCl concentration, pH value, fallen acer monoes leaves dosage, oscillating time. The adsorption efficiency of MG on fallen acer monoes leaves could obtain 95.2% at the optimum condition of acer monoes leaves dosage of 3g/L, oscillating time of 5min, pH value of 7.0, NaCl dosage of 0.08mol/L. Fallen acer monoes leaves have a good effect on the adsorption of MG wastewater.

1. Introduction
A variety of dyes and pigment coloring agents, mostly synthetic, are used in many industries to paint, which leads to the greater content of these substances in industrial wastewater. Colored wastewater, especially organic wastewater, is one of the main wastes of various industries, such as paper making, food, plastics and textile, etc [1]. The cause of water and wastewater pollution is one of the main concerns of researchers in recent years. In actual wastewater, there are many mixtures of different substances, most of which are toxic and must be completely removed from the treated wastewater. Malachite green is a kind of alkaline synthetic dye, which is mainly used for the dyeing of wool, silk, leather, paper and cotton etc [2]. It was used as an antiparasite and antiseptic in aquaculture and fish culture before, it can also be used as a food colorant, food additive, medical disinfectant and insecticide [3]. However, malachite green is very dangerous and highly cytotoxic to mammalian cells, and also acts as a liver tumor-enhancing agent[4]. It is necessary to remove the dye before the discharge of the wastewater. Many methods such as biodegradation [5], photocatalytic degradation [6], membrane separation [7], solvent extraction, adsorption and so on have been used to treat malachite green wastewater [8]. Adsorption is one of the commonly used methods among all these methods in recent years because of the advantages of low cost, effectiveness, simple design and easy operation. To decrease the cost of treatment, attempts have been made to find inexpensive and abundant adsorbents. For instance, agricultural by-products have been widely studied for dye removal [9-11]. In
this work, the biomaterial fallen acer monoes leaves have been tested for its ability to adsorb malachite green from aqueous solution. The fallen leaves could be obtained easily in campuses and city streets.

2. Materials and methods

2.1. Adsorbent and adsorbate
The fallen acer monoes leaves were collected from Liaoning Shihua University in autumn. They were continuously washed with water to remove the surface dirty particles and soluble material, and then washed with distilled water. The washed leaves were dried at 70 °C in an oven for 24h until constant weight. The cooled leaves were crushed and kept in the dryer. Malachite green was purchased from Tianjin Zhiyuan chemical reagent Co., Ltd., and was used without further purification. Stock solutions of MG were prepared by dissolving accurately weighed dyes in distilled water to the desired concentration. The experimental solutions with different initial concentrations were obtained by diluting stock solution in required proportions and their absorbance was read by UV-Vis spectroscopy. After taking the measurements, a calibration curve was made to compute the concentration of each experiment. All other chemicals were analytical grade.

2.2. Experiments of adsorption
To study the effect of parameters like oscillating time, pH, adsorbent dosage, salts concentration, temperature and initial MG concentration for the adsorption of MG, batch experiments were carried out in constant temperature air bath oscillator at a constant speed of 170rpm at 25 °C (except for the temperature experiments). The residual dye concentrations were analyzed by UV 1102 spectrophotometer (Shanghai Techcomp Analytical Instrument Co., Ltd, China) at maximum adsorption wavelength 618nm. The percentage of dye adsorption, the amount of MG adsorbed at equilibrium (q_e, mg/g) was calculated through the following equations, respectively.

\[ \text{Malachite green adsorption rate(E)}\% = \left(1 - \frac{C_e}{C_0}\right) \times 100\% \]

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

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

3. Results and Discussion

3.1. Effect of oscillating time
The effect of oscillating time (2~90min) on the MG adsorption with fallen acer monoes leaves dosage of 4g/L at different initial dye concentration (100mg/L, 120mg/L and 140mg/L) is shown in Figure 1. It shows that the adsorption of MG on fallen acer monoes leaves is a rapid adsorption process. The adsorption rate of MG and fallen leaves adsorption capacity of 80mg/L, 100mg/L and 120mg/L MG were 79.6%, 74.5%, 67.6% and 15.9mg/L, 19.7mg/g, 30.3mg/g, respectively at the oscillating time of 2min. The amount of adsorption changed with time increasing first and then decreased, and the maximum adsorption rate and adsorption capacity of three kinds of MG concentration reached at 4min, 5min and 5min respectively. The oscillating time was used 5min in the following experiments.
3.2. Effect of pH value

Solution pH is one of the most important parameters which can affect the adsorption of dye molecules. The pH of the solution affects not only the surface charge of the adsorbents, the degree of ionization of the pollutants present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry [12]. The effect of solution pH on adsorption of dye on fallen acer monoeyes leaves was studied by varying the pH of initial MG concentration of 120mg/L which is shown in Figure 2. The initial pH of MG solution was adjusted by adding various concentrations of HCl or NaOH. The results show that solution pH significantly affected MG adsorption rate, particularly under basic conditions. MG adsorption rate and $q_e$ increased when pH increased from 1.6 to 2.5, and then decreased after pH 2.5. Because the better adsorption could be obtained in neutral pH, the initial solution pH wasn’t adjusted for other experiments.

3.3. Effect of adsorbent dosage

The adsorbent dosage is also an important parameter in the determination of adsorption capacity of an adsorbent at the operating conditions. Amount of fallen acer monoeyes leaves was varied from 1 to 8 g/L and equilibrated for 5min at an initial MG concentration of 120mg/L. It can be seen in Figure 3 that the adsorption rate of MG increased first and then decreased, while the adsorption capacity $q_e$ decreased continuously. When the adsorbent dosage was 1g/L, the MG adsorption rate was 70.9%.
The appropriate adsorbent dosage was in the range of 2~4g/L, because the MG adsorption rate was above 92%, and the adsorption capacity was also relatively higher.

![Graph showing MG adsorption rate and capacity under different dosages of Acer monoies leaves.](image)

Figure 3. Effect of fallen Acer monoies leaves dosage on MG adsorption

3.4. Effect of temperature

![Graph showing the effect of temperature on MG adsorption.](image)

Figure 4. Effect of temperature on MG adsorption with different initial dye concentration

The fallen Acer monoies leaves (4g/L) was mixed with initial MG concentration range of 80~180mg/L at different temperatures of 25°C, 30°C, 35°C and 40°C, respectively. It can be seen in Figure 4 that the adsorption rate and qₑ increased with initial dye concentration increasing. The effect of the temperature on MG adsorption is irregular. The higher the initial MG concentration is, the higher qₑ is. The amount of MG adsorption is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface [11]. The adsorption capacity of MG on fallen Acer monoies leaves can reach 42.5mg/g at 25°C.

3.5. Effect of salts concentration

Salt ions were always presence in actual dyestuff effluents. Sodium chloride (NaCl) and calcium chloride (CaCl₂) was used as salts to alter the ionic strength of the solution mixture in the investigation. The results indicate that both Na⁺ and Ca²⁺ had positive effects on MG adsorption onto fallen Acer monoies leaves. The adsorption rate and qₑ changed little when NaCl and CaCl₂ concentration exceeded 0.16mol/L and 0.04mol/L, respectively. As Ca²⁺ had more contribution to ionic strength and...
more positive charge than Na⁺, the effect of Ca²⁺ on adsorption was stronger than Na⁺ in the same mole concentration.

![Figure 5. Effect of salts concentration on MG adsorption](image)

3.6. Orthogonal test

Table 1. Orthogonal test factor level table

| Level | Factor A | Factor B | Factor C | Factor D |
|-------|----------|----------|----------|----------|
| 1     | 2        | 5        | 2.5      | 0        |
| 2     | 3        | 15       | 4.0      | 0.08     |
| 3     | 4        | 30       | 7.0      | 0.16     |

Table 2. Orthogonal test scheme and results

| Test number | Factor A | Factor B | Factor C | Factor D | Index E (%) |
|-------------|----------|----------|----------|----------|-------------|
| 1           | 1        | 1        | 1        | 1        | 75.8        |
| 2           | 1        | 2        | 2        | 2        | 90.1        |
| 3           | 1        | 3        | 3        | 3        | 90.9        |
| 4           | 2        | 1        | 2        | 3        | 92.8        |
| 5           | 2        | 2        | 3        | 1        | 84.7        |
| 6           | 2        | 3        | 1        | 2        | 86.7        |
| 7           | 3        | 1        | 3        | 2        | 95.0        |
| 8           | 3        | 2        | 1        | 3        | 84.8        |
| 9           | 3        | 3        | 2        | 1        | 82.7        |
| k₁         | 85.60    | 87.87    | 82.43    | 81.07    |
| k₂         | 88.07    | 86.53    | 88.53    | 90.60    |
| k₃         | 87.50    | 86.77    | 90.20    | 89.50    |
| R²         | 2.467    | 1.334    | 7.767    | 9.533    |
According to the results of the single factor series of experiments mentioned above, considering the adsorption rate of MG, the factors which had great influence on the adsorption effect were adsorption time, adsorbent dosage, pH value and salts concentration. The level of each control factor was determined and the orthogonal test was carried out by four factor three level L9 (3⁴) (shown in Table 1). Sampling according to the Table 2, the MG concentration was fixed at 120mg/L at temperature 25°C. Analysis of the result of orthogonal test, it was found that pH value and NaCl concentration had obvious effect on MG adsorption rate. The primary and secondary subsequence of factors affecting the adsorption rate of MG was NaCl concentration (D), pH value (C), adsorbent dosage (A) and oscillating time (B). The optimal scheme was A₂B₁C₃D₂, which is the condition of the adsorbent dosage of 3g/L, oscillating time of 5min, pH 7.0 and NaCl concentration of 0.08mol/L. The experimental results show that the adsorption rate of the MG on fallen acer monoes leaves could reach 95.2% under the above conditions, which was higher than the MG adsorption rate under various test conditions in Table 2.

4. Conclusion
The adsorption of MG simulated wastewater on the fallen acer monoes leaves has been investigated to obtain better effect. The best MG adsorption rate obtained at 5min. The lower pH was benefit for MG adsorption. The appropriate adsorbent dosage was in the range of 2~4g/L. salts addition were advantage for MG adsorption. The primary and secondary subsequence of factors affecting the adsorption rate of MG was NaCl concentration, pH value, adsorbent dosage and oscillating time by orthogonal test. The adsorption rate of MG on the fallen acer monoes leaves could get 95.2% at the optimal scheme of the adsorbent dosage of 3g/L, oscillating time of 5min, pH 7.0 and NaCl concentration of 0.08mol/L.

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