

Study on the Adsorption of Methylene Blue from Dye Wastewater by *Humulus Japonicus* Leaves

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Abstract: This paper took the objective of preparing high-performance, low-cost biological adsorbent for printing and dyeing wastewater, and the adsorption experiment of dyestuff wastewater with high chromaticity and high biodegradability was studied. The Methylene Blue was adsorbed by the prepared *Humulus Japonicus* Leaves (HJ), the effects of adsorption time, pH, dosage of adsorbent, initial Methylene Blue concentration and temperature on the adsorption process were investigated, and the adsorption mechanism was described by adsorption isotherm, adsorption thermodynamics and adsorption kinetics, and the results showed that: when HJ was added 0.15g and pH was 7, the temperature was 30°C (303K), adsorption was carried out for 20min, simulated dye wastewater, adsorption efficiency of Methylene Blue of 100mg/l were excellent, adsorption rate reached up to 92%, the equilibrium adsorption rate was positively correlated with the initial concentration of CV dye. *Humulus* leaves adsorption CV Gibbs free energy of $\Delta G < 0$, $\Delta H > 0$, $\Delta S > 0$ showed spontaneous adsorption process, the adsorption process Methylene Blue was more suitable for the Freundlich isothermal adsorption equation, the adsorption kinetics accorded with the quasi two level kinetic model, the adsorption of the Methylene Blue dye molecule by the HJ was chemically adsorbed as the rate control step, the Methylene Blue molecule was mainly adsorbed on the surface of the *Humulus* leaves; the model of internal diffusion kinetics showed that there was membrane diffusion and internal diffusion of the HJ in the process of Methylene Blue adsorption. The experimental results showed that HJ as adsorbent can effectively remove Methylene Blue from dye wastewater, and the research results provide a new method and idea for biological treatment of dye wastewater.

1 Introduction

China is the world's largest dye production, trade volume, and consumer country. Dye production accounts for more than 60% of the world's total production. However, due to technical reasons, there is a loss of more than 10% of the dyes used during the printing and dyeing process. Dye wastewater is immeasurable, and dyes enter the environment with wastewater [1-2]. Because most dyes have a benzene ring structure, their metabolites are toxic, and have potential carcinogenic, sudden, and allergenic effects, which are very harmful to the environment. [3-5]. Methylene blue [6] is a very commonly used phenothiazine-based basic dye. It is a major organic pollutant in printing and dyeing wastewater. It can be used for the dyeing of hemp, silk fabric, paper and the coloring of bamboo and wood. Greatly reduce the amount of light transmitted, affect the photosynthesis of organisms, and it is difficult to be effectively degraded by organisms. The treatment of dye wastewater decolorization is the key point. In recent years, the adsorption method has been widely used and paid attention due to its excellent adsorption performance and good workability [7-11].

Biosorption materials are compared with traditional materials in terms of material preparation cost and adsorption capacity. Adsorption materials have significant advantages. The search for high-performance, cheap and easily available biomass adsorption materials for dye wastewater treatment has become a research hotspot in recent years [12-14].

Humulus [15] (*humulus japonicus*), a perennial vine herb, is mainly used as feed for herbivores. *Humulus* leaves are rich in plant cellulose, lignin, protein and other active polymer compounds, and the raw materials are very cheap and abundant. They are distributed in Xinjiang and Qinghai, and other provinces and regions in China, and can be seen everywhere. There are few reports on the application of *Humulus humulus* leaves or its derivative modified substances as adsorption materials for the adsorption of methylene blue from dye wastewater and other adsorption applications. In this study, the crushed *humulus* leaf was used as the matrix adsorption material, and the dye wastewater methylene blue adsorption process was directly studied without modification. The adsorption kinetics and thermodynamic behavior were described, and the structure was characterized and analyzed, hoping to be the actual industry of *humulus* leaf. The application provides theoretical reference and provides a new method

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and idea for the biological treatment of dye wastewater.

2 Materials and methods

2.1 Main reagents and instruments

Methylene blue, concentrated hydrochloric acid, and sodium hydroxide (flake), all of analytical grade (Chengdu Kelon Chemical Co., Ltd.), deionized water (>18.2MΩ.cm, self-made).

Electric heating blast drying oven (Shanghai Jianheng Instrument Co., Ltd. CS101-10EB), analytical balance (Mettler-Toledo ME104E), sealed laboratory sample preparation crusher (China Building Materials Inspection and Certification Group (Shaanxi) Co., Ltd. YHGJ-1), UV-VIS spectrophotometer (Thermo Fisher Scientific UV-VIS Evolution-220A), pH meter (Shanghai INESA Scientific Instrument Co., Ltd. PHS-3E), centrifuge (Hunan Xingke Scientific Instrument Co., Ltd. TGL-18-B), SEM (Phenom ProX, Phenom ProX), FT-IR (SENSOR-27, Bruker, Germany).

2.2 Adsorption test

2.2.1 Biomass adsorbent Humulus leaf treatment

Wash the collected humulus leaves (HJ) with deionized water several times to remove the dust and water-soluble components attached to the surface, and place them in a 70°C blast drying oven for 6 hours, and then crush them. The machine is crushed and sieved (80 mesh) for later use.

2.2.2 Adsorption test method

Put a certain quality of Humulus leaves into an Erlenmeyer flask containing 100mL of a certain initial concentration of methylene blue solution. By changing the experimental conditions such as adsorption time, dosage of Humulus leaves, pH, temperature and initial

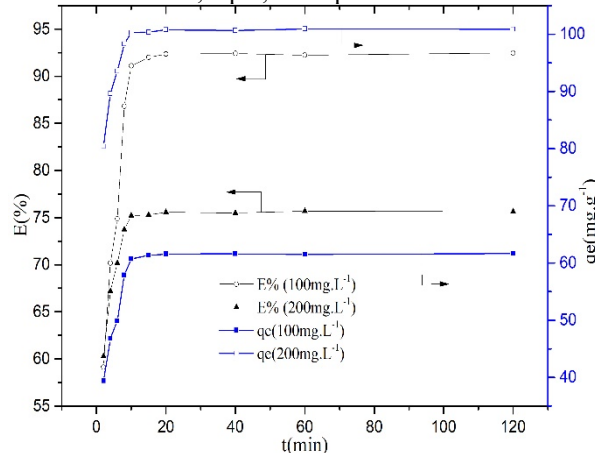


Fig 1. The effect of time value on the adsorption of Methylene Blue

The results show that the adsorption rate of humulus leaves to methylene blue is relatively fast, and the adsorption rate of methylene blue dye can reach more than

concentration of methylene blue, Perform oscillating static adsorption in a constant temperature oscillator with the corresponding temperature. After the adsorption test is completed, the sample solution is centrifuged at 4000r/min for 20 minutes, and the supernatant is taken to determine the methylene blue concentration (the methylene blue is made with deionized water 1000mg/L stock solution, diluted to a certain standard series concentration, use UV-VIS instrument at methylene blue maximum absorption wavelength $\lambda=665\text{nm}$, measure the corresponding absorbance A value to make a standard curve; take the supernatant after solid-liquid separation and determine Solve the corresponding methylene blue concentration value through the standard curve, unit mg/L). The CV adsorption rate (E, %) and the humulus leaf (HJ) adsorption capacity (q_e , mg/g) can be calculated according to formula (1) and formula (2) respectively.

$$E(\%) = (C_0 - C_e) \div C_0 \times 100\% \quad (1)$$

$$q_e = (C_0 - C_e) \times V \times m^{-1} \quad (2)$$

In the above formula: C_0 is the initial CV concentration (unit: mg/L); C_e is the CV concentration after adsorption equilibrium (unit: mg/L); V is the volume of the adsorption solution (unit: L); m is the humulus leaf (HJ) Dosing amount (unit: g).

3 Results and discussion

3.1 The effect of adsorption time on methylene blue adsorption

At 303K, 0.15g Humulus leaves and methylene blue solution (initial concentrations are 100mg/L and 200mg/L respectively), within 0-120min, measure the methylene blue adsorption rate and adsorption capacity in the corresponding state at intervals, and the results are shown in the Figure1-2.

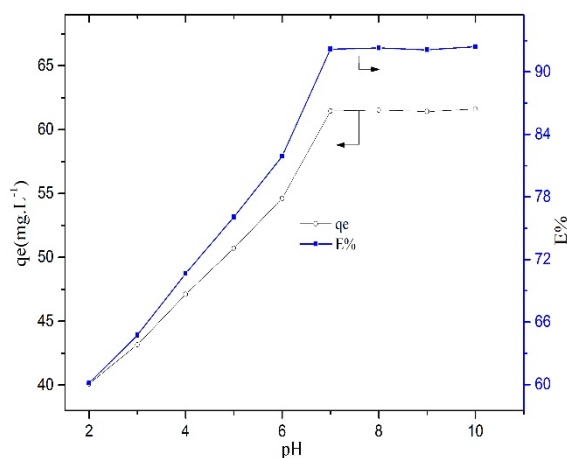


Fig 2. The effect of pH value on the adsorption of Methylene Blue

92% in about 8 minutes. The adsorption of methylene blue by humulus leaves adsorbent may mainly occur on the surface of adsorbent HJ. HJ is the adsorption in the initial

stage. Occurrence provides a huge surface area, and the opportunity and probability of effective contact between the methylene blue dye molecule and the numerous active adsorption sites of the adsorbent is great. The adsorption rate and adsorption capacity have a tendency to rise slowly from 8min to 20min. After 20min, the adsorption reaches equilibrium, and the adsorption rate and adsorption capacity basically no longer change. At this time, most of the active adsorption sites on the surface of *Humulus humulus* leaves have been occupied. The probability of contact with the adsorption site is greatly reduced, and the adsorption site can only be found by diffusion inward, and the adsorption process becomes slow. Some scholars believe that this adsorption model with faster early stage and late stage slowdown is caused by the concentration difference. When the adsorbent is added, the concentration of the adsorption system is large, the driving force of mass transfer is large, and the adsorption rate is fast; as the adsorption progresses, the adsorbent surface and adsorption The concentration difference between the masses gradually decreases, and the decrease in the driving force of mass transfer causes the adsorption to balance [17-18]. Choose 20min as the oscillation time for the subsequent adsorption test.

3.2 The effect of initial pH on the adsorption process

Figure 2 The test results show the trend graph of the influence of humulus leaves on the adsorption rate and capacity of methylene blue under different pH (2~9) under 0.15g adsorbent dosage, 20min adsorption time, 100mg/L methylene blue initial concentration. It can be seen from the figure that both the adsorption capacity and the adsorption rate increase rapidly when the pH rises from 2 to 7, and the methylene blue adsorption rate can rise to more than 92% when the pH is near the neutral range; the adsorption rate can still be achieved in the alkaline system Maintained at a high level, but the adsorption rate tends to be flat, and there is no upward trend. In the process of adsorption and removal of dyes, pH is closely related to the existence of the adsorbed dye molecules in the wastewater system, solubility, color status, the charging status of the adsorption matrix material, and the number of adsorption active sites, which affect the final adsorption effect [20-22]. As a basic dye ($pK_a=0.8$), methylene blue has a cationic valence in solution. The effect of pH on the biosorption of methylene blue dye is based on the isoelectric point of the surface of the humulus leaf. Under conditions, the protonation/deprotonation effect on the

surface of the adsorbent of *Humulus humulus* leaves changes the binding ability of the dye molecules to the active sites of the adsorbent. The surface of HJ is negatively charged. When the pH is low, a large amount of H^+ in the solution will form a competitive active site with methylene blue. At this time, there is an inhibitory effect on the adsorption of methylene blue molecules by HJ. As the initial pH increases, the adsorption on the humulus leaf adsorbent The surface potential of the anion increases, and when the pH value is 7, the adsorption amount does not change significantly, indicating that electrostatic effect is not the only factor that controls adsorption. With the decrease of H^+ in the solution, the adsorption capacity of the adsorbent for methylene blue is continuously improved. This change rule has also appeared in the research reports on the adsorption of methylene blue by other biomass materials [12-14]. *Humulus humulus* leaves had better adsorption of methylene blue under neutral conditions, and pH=7 was chosen as the initial pH condition for subsequent adsorption experiments.

3.3 The effect of humulus leaf dosage on the adsorption of methylene blue

The effect of different dosages (0.05g~0.4g) of HJ adsorbent on the adsorption of methylene blue was investigated. The test results are shown in Figure 3. It can be seen from the figure that when the adsorbent increases within the range of 0.05g~0.15g, the adsorption efficiency of methylene blue dye increases significantly. The reason is that the increase of the adsorbent within a certain range provides more active adsorption sites for the adsorption system, and at this time The dosage of HJ is low, and the distance between the active adsorption sites is large. Each active site will help more methylene blue molecules to gather, which is beneficial to the effective surface adsorption or ion exchange between HJ and methylene blue.; When the dosage of humulus leaves exceeds 0.15g, the methylene blue adsorption rate begins to decrease. The possible reason for this trend is that the shielding effect is formed around the high concentration of adsorbent [18,21], adsorbent and adsorbate The binding capacity is weakened, and the steric hindrance caused by the accumulation of excessive adsorbents between the adsorbents, the available active adsorption points are reduced, and the effective surface adsorption or ion exchange effect is also weakened. The dosage of humulus leaf adsorbed methylene blue dye molecule is set at 0.15g.

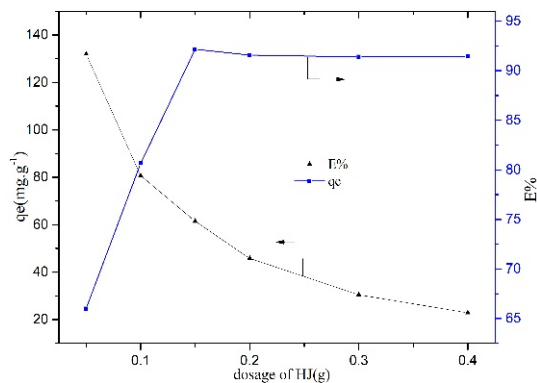


Fig 3. The effect of dosage value on the adsorption of Methylene Blue

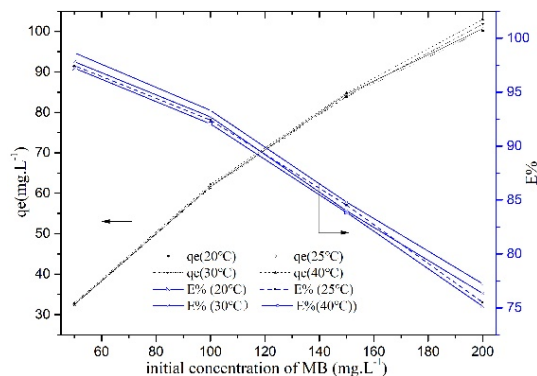


Fig 4. The effect of initial concentration value on the adsorption of Methylene Blue

3.4 The effect of initial methylene blue concentration and temperature on adsorption

The effect of different initial concentrations of methylene blue (50~300mg/L) on the adsorption of methylene blue by humulus leaves at 20°C, 25°C, 30°C and 40°C constant temperature system was investigated. The results are shown in Figure 4. It can be seen from the figure that under the same temperature conditions, the adsorption capacity q_e of humulus leaves for methylene blue increases with the increase of the initial concentration of methylene blue, showing a positive correlation. Under the same initial concentration conditions, as the temperature increases, the adsorption rate E and the adsorption capacity q_e of methylene blue increase slightly. Increasing the temperature is conducive to the progress of the adsorption reaction. As the temperature rises, the mobility of the dye molecules increases, and the molecules The intensified inter-collision provides more opportunities for the combination of methylene blue molecules and the active sites of the HJ adsorbent, and the effective contact and binding force will increase. The adsorption test effect is better at 30°C. When the initial concentration of methylene blue is low, the adsorption rate of methylene blue by Humulus humulus leaves changes with temperature more obviously than when the concentration is high.

When Humulus humulus is added with 0.15g, pH is 7, temperature is 30°C (303K), adsorption is 20min, and the initial concentration of 100mg/L methylene blue, the adsorption effect is better, and the adsorption rate can reach more than 92%.

3.5 Adsorption isotherm

Use Langmuir adsorption isotherm (assuming that the adsorbent has a uniform surface and a monolayer without interaction with adsorbate molecules) and Freundlich adsorption isotherm (assuming that the adsorbent is a non-uniform surface multi-layer adsorption) The model simulates the adsorption process [20], and the experimental data obtained through model fitting describes the adsorption process of humulus leaf adsorption crystal violet. The Langmuir adsorption isotherm and Freundlich adsorption isotherm equations are shown in the following equations (3) and (4), respectively.

$$\text{Langmuir: } C_e \cdot q_e^{-1} = C_e \cdot q_{ml}^{-1} + (b \cdot q_{ml})^{-1} \quad (3)$$

$$\text{Freundlich: } \ln q_e = \ln k_F + n^{-1} \ln C_e \quad (4)$$

In the formula: b is the adsorption rate constant (unit: L.min-1); q_{ml} is the saturated adsorption capacity of the monolayer (unit: mg/g); k_F is the Freundlich constant representing the adsorption capacity (unit: mg/g); n is the Freundlich constant representing the adsorption strength; q_e is the equilibrium adsorption capacity (unit: mg/g); C_e is the CV concentration at the adsorption equilibrium (unit: mg/L).

Humulus humulus leaf dosage is 0.15g, pH=7, adsorption for 20min, measured at 20°C~40°C, and calculated the corresponding equilibrium concentration and adsorption capacity. The adsorption data obtained is subjected to the Langmuir equation model ($C_e \cdot q_e^{-1} - C_e$ plot) And Freundlich equation model ($\ln q_e - \ln C_e$ mapping) for linear fitting, the fitting results are shown in Figures 2-5 and 2-6; the fitted data are calculated according to equations (3) and (4) to calculate the Langmuir and Freundlich equation isothermal For line constant, the data is summarized in Table 2-1.

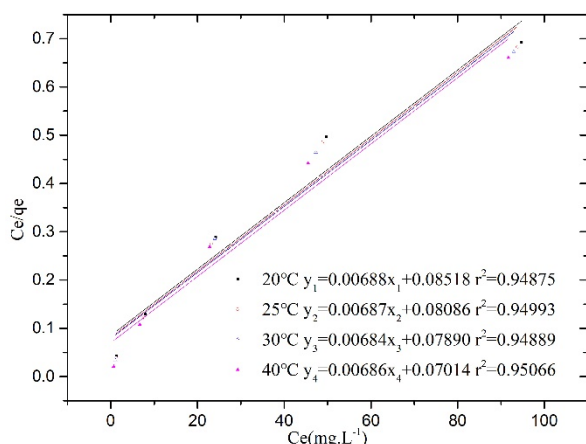


Fig 5. Langmuir adsorption isotherms of Methylene Blue by HJ

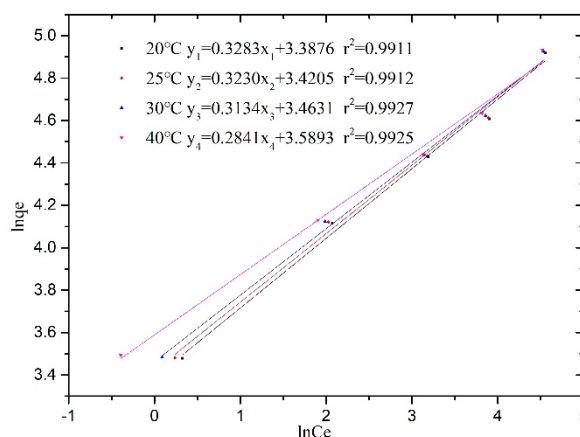


Fig 6. Freundlich adsorption isotherms of Methylene Blue by HJ

Table1. Constants of adsorption isotherms of Methylene Blue on HJ at different temperature

°C	Langmuir			Freundlich		
	q _{ml} /(mg.g ⁻¹)	b/(mg ⁻¹ .L)	Modulus r ²	K _F /(mg.g ⁻¹)	1/n	Modulus r ²
20	145.35	0.081	0.94875	29.59	0.33	0.9911
25	145.56	0.085	0.94993	30.58	0.32	0.9912
30	146.20	0.087	0.94889	31.91	0.31	0.9927
40	145.77	0.098	0.95066	36.21	0.28	0.9925

From Figures 5-6, and Table 1, it can be seen that the correlation coefficient r² of the Langmuir isotherm adsorption model is between 0.94875 and 0.95066, and the correlation coefficient r² of the Freundlich isotherm adsorption model is greater than 0.99, which is better than the Langmuir isotherm adsorption model. A better correlation coefficient indicates that the Freundlich isotherm adsorption model can better describe the isotherm adsorption effect of Humulus humulus leaves on methylene blue. According to the Freundlich adsorption isotherm model theory [20] when the Freundlich constant n-1 of adsorption strength ranges from 0 to 1 The adsorption on the surface is easy to proceed. Humulus leaves adsorb methylene blue in the range of 20°C~40°C (293K~313K). The adsorption intensity constant n-1 is between 0.28~0.33, which indicates that the surface of the adsorbent is non-uniform and has multilayer adsorption. There is an interaction force between Humulus humulus leaves and methylene blue, and adsorption is easy.

3.6 Adsorption kinetics

In order to describe the adsorption kinetics of humulus leaves on methylene blue (including reaction pathways and rate control steps), a quasi-first-order kinetic model, a quasi-second-order kinetic model, and an internal diffusion kinetic model were used for different initial concentrations of methylene blue. (50mg/L, 100mg/L, 200mg/L, 300mg/L) adsorption data for fitting.

$$\text{Quasi-first: } \lg(q_e - q_t) = \lg q_e - \frac{k_1 t}{2.303} \quad (5)$$

$$\text{Quasi-two: } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$\text{Internal diffusion: } q_t = k_3 t^{0.5} + C \quad (7)$$

In the formula: q_t is the adsorption capacity at time t (unit: mg/g); k₁ is the rate constant of the quasi-first-order kinetic equation (unit: min⁻¹); k₂ is the rate constant of the quasi-second-order kinetic equation (unit: mg⁻¹.g.min⁻¹); k₃ is the internal diffusion rate constant (unit: mg.g⁻¹.min^{-0.5}); q_e is the equilibrium adsorption capacity (unit: mg/g); C is the dimensionless constant.

The dosage of Humulus humulus leaves was 0.15g, pH=7, and 30°C. The adsorption behavior was investigated under different initial concentrations of methylene blue. The corresponding equilibrium concentration and adsorption capacity were determined and calculated. The adsorption data obtained were subjected to the quasi-first order kinetic model equation (lg (q_e-q_t)-t plotting), quasi-two-stage kinetic model equation model (t.q_t-1-t plotting) internal diffusion kinetic model (q_t-t^{0.5} plotting) for linear fitting, three The fitting results of these models are shown in Figures7 to 9; the fitted data are calculated according to formulas (5), (6) and (7) respectively. The quasi-first-order equation model and the quasi-second-order equation of humulus leaf adsorption methylene blue The kinetic constants of the model and the internal diffusion equation model are

summarized in Table 2.

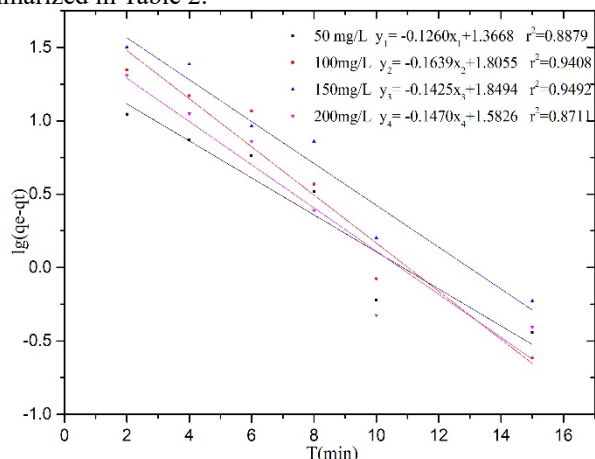


Fig 7. Pseudo-first-order model of Methylene Blue by HJ

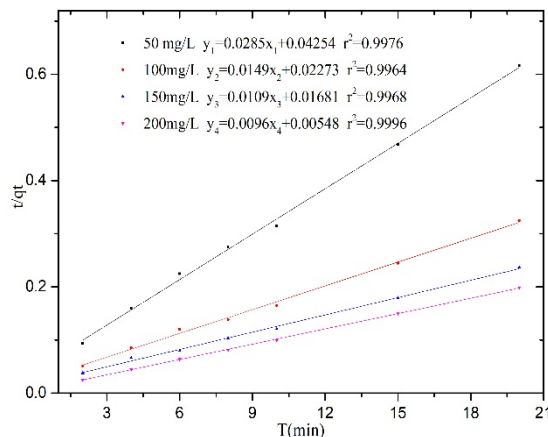


Fig 8. Pseudo-second-order model of Methylene Blue by HJ

The correlation coefficient fitted by the quasi-first-order kinetic model data is between 0.8711 and 0.9492. The theoretical equilibrium adsorption capacity (q_e cal) of the Humulus humulus leaf adsorbent is far from the actual equilibrium capacity (q_e exp); quasi-second-order kinetics. In the data fitted by the model, the q_e cal and q_e exp of adsorption under different initial methylene blue initial concentration conditions are very close, and the correlation coefficients are all above 0.99, indicating that

the quasi-second-order kinetic model is more suitable for describing humulus than the quasi-first-order kinetic model. In the kinetic process of grass leaf adsorption of methylene blue, chemisorption plays a dominant role in rate control. The methylene blue dye molecule mainly chemically adsorbs with active groups of Humulus humulus leaf and adsorbs on the surface of Humulus humulus leaf.

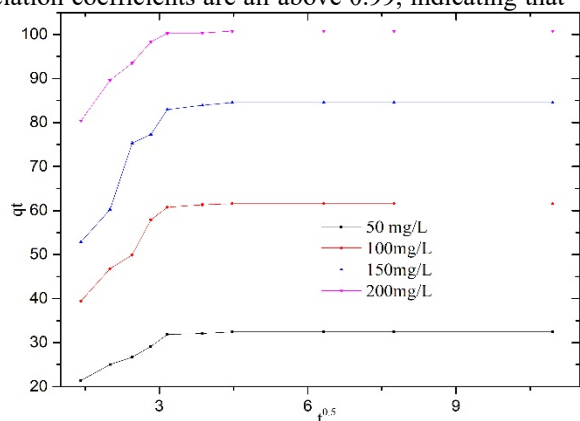


Fig 9. Intraparticle diffusion model of adsorption of Methylene Blue by HJ

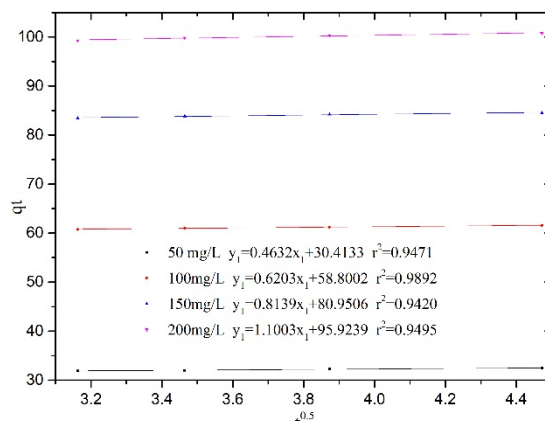


Fig 10. Practical intraparticle diffusion model of adsorption of Methylene Blue by HJ

Table 2. Kinetic model parameters for adsorption of Methylene Blue by HJ at different initial concentration

CVC ₀ /(mg. L ⁻¹)	Quasi-first-level dynamic model parameters			Quasi-two kinetic model parameters				Intra-particle diffusion parameters		
	q_e cal/(mg.g ⁻¹)	k_1 /(min ⁻¹)	r^2	q_e cal/(mg.g ⁻¹)	q_e exp/(mg.g ⁻¹)	k_2 /(mg ⁻¹ .g.min ⁻¹)	r^2	k_3 /(mg.g ⁻¹ .min ^{-0.5})	C	r^2
50	3.92	0.29	0.8879	35.08	32.45	0.019	0.9976	0.46	30.41	0.9471
100	6.08	0.38	0.9408	67.11	61.57	0.010	0.9964	0.62	58.80	0.9892
200	6.36	0.33	0.9492	91.74	84.52	0.007	0.9968	0.81	80.95	0.9420
300	4.87	0.34	0.8711	104.17	100.76	0.017	0.9996	1.10	95.92	0.9495

In the adsorption kinetics, the quasi-first and quasi-second-order kinetic models cannot determine the mechanism of diffusion, and the mechanism of diffusion

is the largest influencing factor in each limiting step in the kinetics [20]. The internal diffusion kinetic model is used to analyze Humulus. The internal diffusion mechanism of

leaf adsorption of methylene blue. Figure 9 shows the internal diffusion kinetic model diagram under different initial concentrations of methylene blue. There are three linear curves in the figure: the rapidly rising part, the slow rising part and the stable part. The three curves will not pass through the origin, indicating that there are multiple diffusion mechanisms for the adsorption of methylene blue on humulus leaves and multiple rate-limiting steps [20]; The main mechanism of the rapid rise is the rapid adsorption and diffusion of the dye molecules and the membrane layer on the surface of Humulus humulus leaves, which is membrane diffusion; the slow rise part of the mechanism is that when the active sites on the surface of the adsorbent are saturated with adsorbates, the adsorbates move towards The internal diffusion of the adsorbent particles (intra-particle diffusion) seeks the opportunity of contact adsorption. Figure 10 shows the fitting data diagram of the kinetic model of partial internal diffusion of the particles. The relevant kinetic parameters are calculated and summarized in Table 2-2. From the chart It can be seen that the fitted correlation coefficient r2 is between 0.9420 and 0.9892, indicating that the internal diffusion kinetic model can better describe the mechanism of this stage. The intra-particle diffusion rate constant k3 and C value increase with the increase of the initial concentration, indicating The internal diffusion rate is positively correlated with the initial concentration of the dye [21]. A higher initial concentration produces a larger concentration difference and can provide a greater driving force for adsorption and mass transfer [17].

3.7 Adsorption thermodynamics

In order to describe the thermodynamic behavior of the humulus leaf methylene blue adsorption process, Van,t Hoff equation and Gibbs-Helmholtz equation [19] were used to calculate the entropy change, enthalpy change, and Gibbs free energy of adsorption equilibrium at different initial concentrations and different temperatures.

Table3. Thermodynamic parameters of MB adsorption by HJ

CV initial C0/(mg.L-1)	$\Delta H/(\text{kJ.mol}^{-1})$	$\Delta S/(\text{J.mol}^{-1}.\text{K}^{-1})$	$\Delta G/(\text{kJ.mol}^{-1})$			
			293K	298K	303K	313K
50	28.77	123.77	-7.67	-8.03	-8.56	-10.11
100	7.02	40.96	-4.98	-5.19	-5.38	-5.79
150	2.75	20.56	-3.02	-35.38	-3.39	-3.43
200	2.57	31.34	-1.71	-5.79	-3.43	-2.12

It can be seen from Figure 11 that the data with a linear correlation coefficient of $\ln K_d-1/T$ fitting between 0.9343 and 0.9995 has good reliability. Table 3 shows that the ΔG at different temperatures will be less than zero. As the temperature of the adsorption system increases, the ΔG becomes smaller, indicating the adsorption process of methylene blue by HJ in the range of 293K~313K (20°C~40°C) It is a spontaneous process. The higher the temperature, the greater the degree of spontaneous progress. This is consistent with the conclusion drawn

$$\Delta G^0 = -RT \ln(Kd) \tag{8}$$

$$\ln(Kd) = \Delta S^0 / R - H^0 / RT \tag{9}$$

In the formula: ΔG^0 is the adsorption Gibbs free energy (unit: kJ.mol^{-1}); H^0 is the enthalpy change (unit: kJ.mol^{-1}); ΔS^0 is the adsorption entropy change (unit: $\text{J.mol}^{-1}.\text{K}^{-1}$); Kd is the adsorption distribution constant ($Kd=q_e/C_e$); T is the temperature (unit: K); R is the gas constant 8.314 (unit: $\text{J.mol}^{-1}.\text{K}^{-1}$).

Investigate the adsorption effect of different initial concentrations of methylene blue (50mg/L~300mg/L) in the temperature range of 293K-313K, and calculate the adsorption partition constant Kd under the corresponding conditions from the measured and calculated C_e and q_e data, and use $\ln Kd$ to $1/T$ is linearly fitted, and the adsorption entropy change and enthalpy change are solved according to equation (9). Figure11 shows the fitted $Kd-1/T$ curve of the adsorption of methylene blue on Humulus humulus leaves. The values of the thermodynamic functions of the adsorption process at different initial concentrations of methylene blue at different temperatures are shown in Table3.

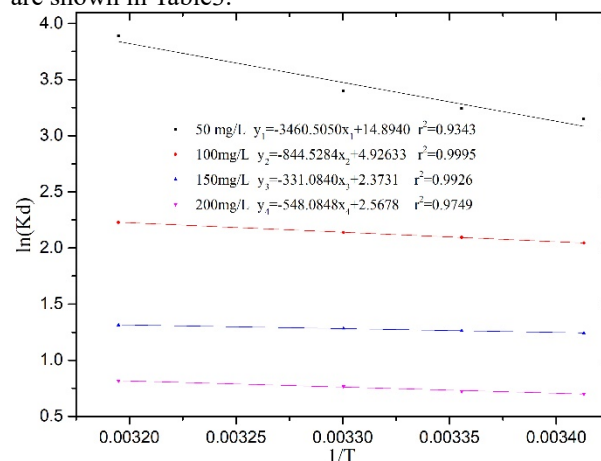


Fig 11. $Kd-1/T$ of Methylene Blue adsorption by HJ

from the aforementioned isotherm adsorption curve and temperature on the adsorption of methylene blue; the adsorption process $\Delta S > 0$ indicates that the system becomes More chaotic, it is a process of increasing entropy degrees of freedom that is conducive to the compensation of adsorption thermodynamics. The adsorption process is driven by entropy. Humulus humulus leaves have an affinity for methylene blue adsorption [17-20]. ΔH is positive at different initial concentrations of methylene blue. Compared with the

adsorption process of high concentration, the ΔH value of the adsorption process of low initial concentration is larger, indicating that the adsorption process is a result of multiple adsorption. The adsorption process of low concentration of methylene blue is chemically Adsorption dominates, and physical adsorption may dominate the adsorption process of high concentration of methylene blue. In general, the adsorption of humulus leaves (HJ) to methylene blue is a spontaneous endothermic process, and high temperature has a positive effect on the adsorption process.

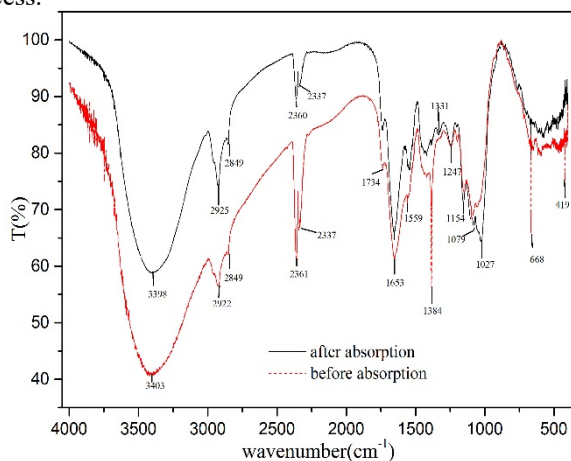


Fig 12. FT-IR of HJ (before and after absorption of MB)

It can be seen from the figure that there is a strong and broad absorption peak at 3403cm^{-1} , indicating that there are -OH and -NH stretching vibrations on the surface of Humulus leaves, which may be caused by the numerous hydroxyl or amino groups in the cellulose of Humulus leaves; 1734cm^{-1} , 1653cm^{-1} , there is the characteristic stretching vibration absorption peak of C=O in carboxyl and ketone groups; there is an asymmetric stretching vibration peak of -CH₃ at 2922cm^{-1} , and the symmetric stretching vibration peak of CH at 2849cm^{-1} ; 1027cm^{-1} and the nearby peaks are mainly caused by the bending vibration of -OH and the stretching vibration of COC; the absorption peaks in the range of wavenumber less than 1000cm^{-1} may be the heterocyclic aromatic substances from Humulus leaves. Humulus leaves after adsorption of methylene blue appeared, disappeared or red shifted and blue shifted at 3403cm^{-1} , 1559cm^{-1} , 1331cm^{-1} , 1027cm^{-1} , 1734cm^{-1} , etc., the original phenomenon of adsorption of methylene blue as Humulus leaves. The oxygen-containing functional groups and amino groups are deprotonated and ion-exchanged with positively charged dye molecules. This result is consistent with the results of the aforementioned adsorption kinetic model fitting results, which are mainly controlled by chemical adsorption. Active functional groups such as -OH, -NH, amino, C=O, and C-O play important functions in the

3.8 Infrared spectrum analysis

The adsorption mechanism mode on plant materials is attributed to the active functional groups and bonds existing inside. In order to clarify the change mechanism of these active groups before and after adsorption, the adsorbent before and after the dye methylene blue was adsorbed was compressed with KBr, and FTIR was performed at $400\text{-}4000\text{cm}^{-1}$ test. The results are shown in Figure 12-13.

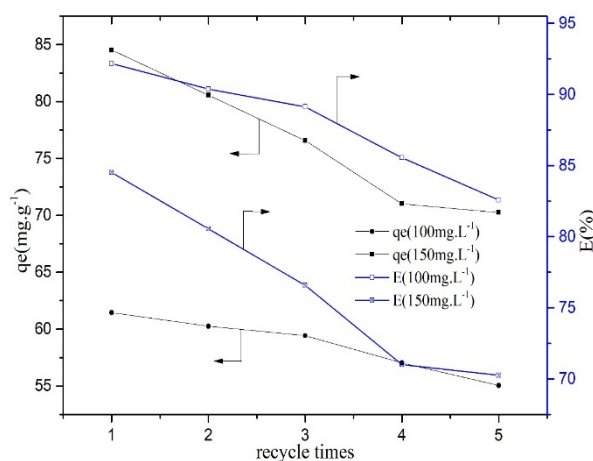


Fig 13. Trends in the repeated use of methylene blue adsorbed by HJ

adsorption process.

3.9 Reusability of adsorbent

Add 0.15g Humulus humulus sorbent each time, pH=7, adsorb for 20min, 25°C , under the conditions of 100mg/L and 200mg/L initial MB concentration respectively, to investigate the reusability of the sorbent. Before each cycle, the adsorbent in the previous cycle was immersed in 1M hydrochloric acid for 2 hours, filtered and dried, and the adsorption performance was investigated in the next cycle according to the previous steps. The result is shown in Figure 2-13. It can be seen from the graph that after 5 cycles, for the initial MB concentration of 100mg/L , the adsorption rate remained above 80%, and the adsorption capacity reached 55mg/g ; the initial MB concentration of 150mg/L , both the adsorption rate and adsorption capacity decreased by 16.88% And 16.88%, indicating that Humulus humulus adsorbent has excellent repeatability and can be recycled.

3.10 SEM analysis

Figure14 and Figure15 are respectively the SEM images of Humulus leaf before and after adsorption.

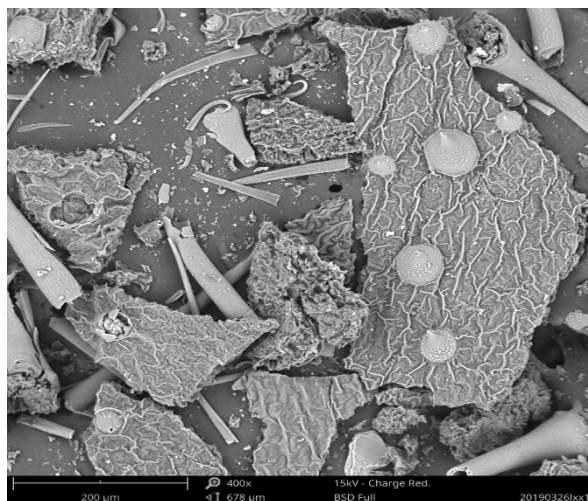


Fig 14. SEM of HJ (before absorption of MB)

From Figure 14, it can be seen that the surface of Humulus leaves is irregular and lamellar, with many folds on the surface, and there are many rough voids at the cross section, and the surface area is large. This substructure is conducive to the adsorption of methyl blue; there are many pores after the adsorption of methylene blue. The part becomes smooth, which is caused by the adhesion of the adsorbed methylene blue to the channels.

4 Conclusion

The adsorption behavior of methylene blue in dye wastewater with Humulus humulus as adsorbent was studied. When the dosage of humulus leaves is 0.15g, pH=7, temperature 30°C (303K), 100mg/L methylene blue simulated dye wastewater under the condition of 20min adsorption, the adsorption effect is better, the adsorption rate can reach 92%, and the equilibrium adsorption capacity is The initial concentration of methylene blue dye is positively correlated; $\Delta G < 0$, $\Delta H > 0$, $\Delta S > 0$ of humulus leaves adsorbing methylene blue indicate a spontaneous endothermic process. Humulus leaves have an affinity for methylene blue adsorption. The higher the temperature, the spontaneous progress. The greater the degree; the adsorption process is more in line with the Freundlich-type adsorption isotherm equation, the surface of the humulus leaf adsorbent is non-uniform, there are multilayer adsorption phenomena, the interaction force between the humulus leaf and methylene blue is easy to adsorb; the adsorption kinetics is more accurate The second-level kinetic model. The adsorption of methylene blue dye molecules by Humulus leaves is based on chemical adsorption as the rate control step. Methylene blue molecules are mainly adsorbed on the surface of Humulus leaves; the study of internal diffusion kinetic model shows that the adsorption process of HJ on methylene blue exists. Membrane diffusion and internal diffusion; FT-IR test results show that: -OH, -NH, amino, C=O, CO and other active functional groups play important functions in the adsorption process; through SEM test, the surface of Humulus leaves presents a rough porous structure. It can provide more adsorption sites for

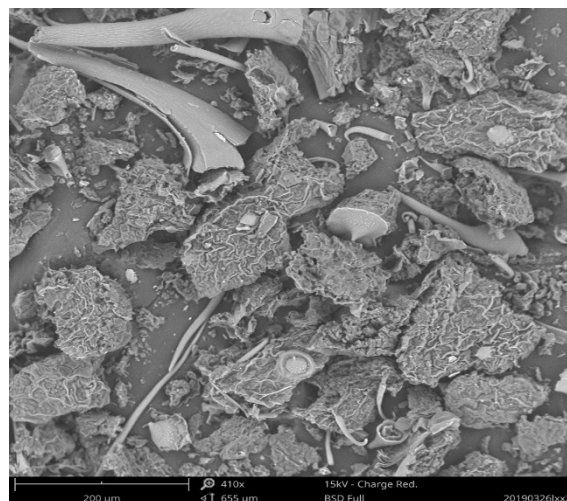


Fig 15. SEM of HJ (after absorption of MB)

the adsorption of methylene blue. The test results show that Humulus japonicus (HJ) as an adsorbent can effectively remove methylene blue in dye wastewater.

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