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Study on adsorption of methyl orange by waste tea

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Abstract

The adsorption effect of waste tea leaf on dye methyl orange was studied. The tea after decolorization for 6 h was modified with potassium permanganate, and then the adsorption properties of unmodified and potassium permanganate modified tea to methyl orange were studied. The influence of the optimal pH value, dosage of unmodified and modified tea, initial concentration of methyl orange, adsorption temperature and contact time variables of methyl orange and tea powder on the adsorption performance was obtained in the experiments. Under the optimized conditions, the maximum adsorption rate of potassium permanganate-modified tea leaves was 99.82 %, and the maximum adsorption capacity was 3.9928 mg/g. The kinetics, thermodynamics and adsorption properties of methyl orange by $KMnO_4$ activated tea and unmodified teas were studied. The adsorption kinetics results showed that the adsorption was in accordance with the pseudo-second-order kinetic equation. The adsorption thermodynamics results showed that the adsorption process was exothermic and the entropy decreased. The research results of adsorption isotherms showed that the adsorption process was in accordance with the Freundlich adsorption isotherm. Scanning electron microscopy, X-ray diffraction and infrared spectroscopy were used to characterize $KMnO_4$ activated tea powder samples. This method can adsorb methyl orange, reduce the concentration of methyl orange in wastewater and the damage to the environment.

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1. Introduction

With the rapid development of industry, because the output of the industrial wastewater produced by the factory is too large, the pollution of the environment has reached an alarming level. The treatment capacity for polluted water has already been seriously insufficient, people need to clean up the harmful substances in industrial wastewater through artificial methods to reduce the pressure of industrial wastewater that the environment deals with. Industrial wastewater mainly stems from the discharge of factory waste water, such as papermaking, printing, leather, food and plastic etc. But due for the rapid development of the chemical industry, various kinds of synthetic materials emerge in an endless stream, the composition in the sewage has become complex and diverse and the traditional sewage degradation means is difficult to achieve the effect of degradation [1-3]. The color pollution caused by organic dye in printing and dyeing sewage, with large pollution areas, deep color concentrations and diversified content of harmful substances, was identified as the key treatment object. First in the visual effect, the colorful aqueous solution of the dye can also visually produce unpleasant emotions. Different colors also interfere with the growth of plants and destroy the living space of living organisms in the water, so the pollution of dye wastewater is one of the important murderers of destroying the entire ecosystem [4]. Some dyes themselves are toxic, and serious ones can cause cancer.

The spread of dyes will cause an increased incidence of various non-communicable diseases, such as asthma, hormone disruption, allergies and chronic lung diseases, and a significantly increased incidence of occupational diseases also appears [5-6]. Therefore, it is imperative to treat industrial wastewater and the pollution hazards of industrial wastewater are minimized when the industrial wastewater enters the environment. Single, binary and ternary nanomaterials were synthesized by precipitation, solvothermal, simple solution and impregnation methods to serve as photocatalysts. Photocatalytic degradation performances of all the as-synthesized photocatalysts for methyl orange were investigated under visible light irradiation [7].

Since the discovery of dye wastewater pollution, a variety of dye wastewater treatment technologies have emerged. These methods include physical treatment methods, chemical treatment methods, biological treatment methods, and various methods have their own advantages and disadvantages [8-12]. Some have disadvantages such as expensive instruments or reagents price, inconvenient operation and secondary pollution [13-15]. Biological oxidation and chemical precipitation are the international treatment methods for dye wastewater. However, their disadvantages are obvious. When the colored dye concentration is very low, these treatments means cannot achieve cost-effective purposes. Moreover, for most of the synthetic organic dyes speed of biodegradation is very slow during processing. Therefore, adsorption technology has been found to be cheaper with adsorption materials and the adsorption process does not consume expensive and economical steps, which meets people's requirements for adsorption materials. Therefore, adsorption technology is currently widely used in factories around the world [16-20]. Reverse osmosis, ion exchange, activated carbon adsorption and other technologies, due for their high capital investment and operating costs, are not suitable for investment and construction of small factories, were abandoned by most factories, especially in developing countries. Low cost and easy access materials are the adsorbent materials jointly expected by all plants. Activated carbon, as an important adsorbent, has a high surface area, excellent acid/alkaline stability, and is rich in functional groups such as - OH [21]. Although activated carbon can adsorb certain harmful substances, its initial cost and complexity make it difficult for activated carbon to be widely used as an adsorbent in practical production. In recent years, some new synthetic materials have been able to remove certain dyes [5-6], but the synthesis of new materials requires certain costs. Therefore, it is urgent to develop effective adsorbents with high substitutability [20, 22].

China's annual tea production reaches more than 1.1 million tons, but the waste tea is rarely applied. As a porous material, waste tea has the characteristics of high specific surface area, large aperture, wide source and easy to obtain. The proportion of fresh tea water is as high as 75%, dry substances account for 25%. Fresh tea contains a variety of pigments, which mainly can be divided into two categories: water-soluble pigment and lipid-soluble pigment. Water-soluble pigments mainly include anthocyanins, black tea pigments, flavonoids. Lipid-soluble pigments mainly include chlorophyll and carotenoids, *etc*. The highest pigment of tea is catechin, reaching 12% to 30%, because it still has a large number of acid carboxyl group, which is very easy to be oxidized. Tea yellow is its oxidation component, flavonoids account for low 3% to 5%, presents yellow or yellow green. Other pigment content is low, are the main color components of tea water. Tea adsorption experiment for a long time cooking tea at high temperature is to remove the pigment inside the tea as far as possible, to avoid their own pigment affecting the experimental results. The tea leaves themselves inside has a large number of pores [23], forming a complex and diverse mesh structure and having a huge contact area with the outside material. The specific surface area of tea is very large, which can make the tea fully contact with the adsorbed material and then absorb it into the hole, which is a standard porous material. The surface of the tea leaves is rough, concave-convex uneven. There are many holes, the shape of a single hole is a bread ring, these holes are of great significance for the tea adsorption of dye and other substances. Tea as a porous material is one of the ideal materials to absorb dyes. The removal of harmful dyes has aroused the research interest of scientists. Mohamed *et al.* [24] studied the ability of a new type of biosorbent in acacia leaf powder to remove methylene blue (MB) under different operating conditions. The study showed that acacia leaf powder is rich in functional groups such as - OH, - COOH, - NH_2, and can effectively bind MB molecules. At room temperature, the maximum adsorption capacity can reach 71.43 mg g^{-1}, making it an economically effective biosorbent and easy to obtain. It conforms to the principles of green chemistry and can effectively remove methylene blue from wastewater.

Methyl orange (MO) is either powder or crystalline shape, slightly soluble in water, and insoluble in ethanol. MO acts as an acid-base indicator, its change color range is at pH <3.1 and turns red, at pH > 4.4 turns yellow, and presents orange at 3.1 < pH < 4.4. Methyl orange belongs to a water-soluble acid dye of azo benzenesulfonic acids kind and is a common kind of textile dye. It is mainly used in dyeing the acrylic fibers. The presence of azo-group —N=N— makes methyl orange extremely difficult process and easy to cause environmental pollution, its structure is shown in Figure 1 and its properties are shown in Table 1. Azo dye is a common pollutant in printing and dyeing wastewater, and methyl orange belongs to the water-soluble acid dye of azobenzene sulfonic acids. In order to overcome the shortage of dye wastewater, this paper uses cheap and fine waste tea as the adsorption material and azo dye methyl orange as study object to make adsorption study. By controlling the change of various factors, the best conditions for the adsorption of methyl orange by tea were investigated. The thermodynamic and dynamic properties of adsorption of the dye by tea were discussed. Through tea modification by potassium permanganate, the adsorption capacity of tea to the dye has been enhanced. No studies has been reported in the literature on use of potassium permanganate modified tea material for the adsorption of methyl orange.

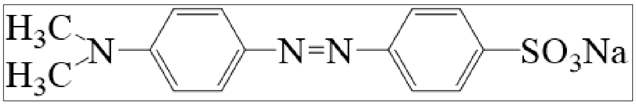


Fig 1: Structural diagram of methyl orange

Table 1: Basic physical properties of methyl orange

Type	Example
Molecular Formula	$C_{14}H_{14}N_3NaO_3S$
Molecular Weight	327.33 g/mol
Density boiling point melting point water-solubility toxicity	1.28 g/cm^3, solid state easy to decompose greater than 300 °C solute in water low in poison

2. Experimental

2.1. Reagents and materials

Adsorbate: Methyl Orange (MO), was purchased from Suzhou Qihang Biotechnology Science and Technology Co., Ltd, China. Adsorbent: tea (West Lake Longjing) was sold by market and purchased from shopping mall in Changchun University of Science and Technology, China. Potassium permanganate, was purchased from Jinan Huijing Chuanshang Trading Co., Ltd, China. All reagents of phosphoric acid, boric acid, acetic acid, sodium hydroxide, hydrochloric acid, sodium chloride and calcium chloride were purchased from Beijing Chemical Plant, China. pH = 2.0 tri-acid (phosphoric acid + boric acid + acetic acid) - sodium hydroxide buffer: 5.0 mL 0.20 mol/L sodium hydroxide solution was added to 100 mL tri-acid (phosphoric acid, acetic acid, boric acid concentration was 0.04 mol/L). The reagent purity was analytical purity. The experimental water was deionized water. The experimental results were an average of 3 parallel measurements.

2.2. Instrument

Determination of methyl orange was performed on a type 722 spectrophotometer (Shandong Gaomi Rainbow Analysis Instrument Co., Ltd., China). Powder X-ray diffraction (XRD) was done for phase analysis on a D5005 type X-ray diffractometer (Siemens, Germany), using Cu-Kα target, $\lambda = 1.540560 Å$, operating voltage (tube voltage) of 50 kV, operating current (tube current) of 150 mA. The 2θ value was from 10 - 80 ° with a step length of 0.2°. Scanning electron microscopy (Scanning electron microscopy, SEM) photographs were taken on a type Philips XL30 field emission scanning electron microscope with an operating voltage of 20 kV. Fourier transform infrared spectrum (FT-IR) was determined on Vertex 70 (Brooke, Germany) with KBr tablet. 32 scan, scan range 400-4000 cm^{-1}, and resolution 4 cm^{-1} was selected. The N_2 adsorption-desorption isotherms were measured at -196 °C on a sorption instrument (ASAP2020M, Micromeritics Instruments Corporation, USA). The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method.

2.3. Experimental method

2.3.1. Preparation of adsorbent waste tea and potassium permanganate activated tea and their adsorption of methyl orange

2.3.1.1. Preparation of waste tea leaves. First 100 mL water was taken and added to a 250 mL beaker. A heat collecting magnetic mixer was used to set the temperature to 95 °C, and the beaker was heated. When the temperature reached the setting value, 2.0 g of fresh tea was added. 2 h was continuously heated and then the tea was filtered. The filtered tea was again put into a 95 °C beaker for heating. After repeating 3 times, the tea was nearly colorless and was filtered. The filtered tea was taken and put into a blast loft drier. The temperature was adjusted to be 60 °C for dry for 6 h. The preparation of waste tea was accomplished. Part was used for the preparation of potassium permanganate activated tea, part of the waste tea was ground in a mortar into powder shape. It was filtered by 60 mesh (300 nm) sieve, and the powder was used for the adsorption experiments of methyl orange by waste tea.

2.3.1.2. Modifier selection

10% (V/V) phosphoric acid and hydrochloric acid (V/V), 10% (W/W) potassium permanganate, sodium chloride, sodium hydroxide and 1 % (W/W) sodium hydroxide were prepared, respectively, to modify tea, adsorption of methyl orange. Compared with the adsorption effect of waste tea, potassium permanganate activation tea had the best effect and the adsorption rate was improved, and no enhanced adsorption effect for other.

2.3.1.3. Preparation of potassium permanganate-activated tea leaves

90 mL water was added to a 250 mL beaker and 10.0 g potassium permanganate was dissolved in the beaker. 40 mL standard solution of 10 % (W/W) potassium permanganate was placed in an autoclave. 1.0 g of dry waste tea was weighed and added to the reactor. The oven temperature was adjusted to 120 °C. After reaching the setting value, the reactor was put in the oven and the reactant was activated 120 °C for 6 h. After the reactor was taken at rest, the temperature dropped to room temperature and the reactor was opened. The potassium permanganate activated tea was taken out and water was added for sucking filtration until the solution became colorless. The activated tea was put into a blast loft drier, the temperature was adjusted to be 60 °C and the product was dried for 6 h. The dried modified tea was ground in a mortar and sifted by a 60 mesh (300 nm) screen mesh, and the powder was used for adsorption experiments of methyl orange by potassium permanganate activated tea.

2.3.1.4. Adsorption of methyl orange by waste tea and potassium permanganate activated tea

0.050 g (conditional experiment: 0.03, 0.05, 0.10, 0.30, 0.50, 0.80 g) waste tea and potassium permanganate activated tea was accurately weighed and placed in 50 mL conical flask, 10 mL concentration of 20 μg/mL (conditional experiment: 10, 20, 30, 40, 60, 100 μg/mL) methyl orange was added and pH = 2.0 (conditional experiment pH: 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 6.0, 8.0, 10.0) tri-acid (H_3PO_4-HAc-H_3BO_3)-sodium hydroxide buffer was respectively added and the volume was controlled to be 20 mL. At room temperature 25 ± 1 °C, magnetic stirring was made for 100 min (conditional experiment: 20, 40, 60, 80, 90, 100, 110, 120, 150, 180 min). After the mixture was centrifuged for 20 min at 8000 r/min, the upper supernatant was taken, poured into a cell and measured with a spectrophotometer. The absorbance was determined at 463 nm.

2.3.2. Conditional optimization experiments

2.3.2.1. pH optimization

Nine portions of 0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 6.0, 8.0, 10.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 ml (pH 1.0 system was controlled and regulated by 0.1 mol/L hydrochloric acid solution medium). The mixture was stirred for 110 min (unmodified material, the same below) and 100 min (modified material, the same below) at room temperature 25±1 ℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

2.3.2.2. Optimization of waste tea and $KMnO_4$ activated tea amount. 0.030, 0.050, 0.10, 0.30, 0.50, 0.80 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 mL. The mixture was stirred for 110 min and 100 min at room temperature 25 ± 1 ℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

2.3.2.3. Optimization of methyl orange concentration. Six portions each of 0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 10, 20, 30, 40, 60, 100 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 mL. The mixture was stirred for 110 min and 100 min at room temperature 25±1 ℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

2.3.2.4. Optimization of contact time. Ten portions each of 0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 mL. The mixture was stirred for 20, 40, 60, 80, 90, 100, 110, 120, 150, 180 min at room temperature 25±1 ℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

2.3.2.5. Temperature optimization. Ten portions each of 0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 ml. The mixture was stirred for 110 min and 100 min at temperature 25, 35, 45±1℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

2.3.3.6. Ionic strength optimization. Four portions each of 0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 mL. Calcium chloride or sodium chloride were added to the solution with a final concentration of 1 mol/L, 0.1 mol/L, respectively. The mixture was stirred for 110 min and 100 min at room temperature of 25 ± 1℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance.

Data were calculated as follows

Spectrophotometer measures absorbance of the different concentrations of methyl orange at the maximum absorption wavelength of 463 nm to obtain the methyl orange working curve:

$$A = 0.3690\ C + 0.0003 \qquad (1)$$

$$C = (A - 0.0003)/0.3690 \qquad (2)$$

Where

A is absorbence, and

C is a methyl orange solution concentration (μg/mL).

$R^2 = 0.9992$, and R is the regression coefficient.

The methyl orange concentration after adsorption can be calculated.

The equilibrium adsorption amount q_e of methyl orange and the adsorption amount q_t at the time t can be found by formula (3) (4):

$$qe = (C0 - Ce)\bullet V/m \qquad (3)$$

$$qt = (C0 - Ct)\bullet V/m \qquad (4)$$

Where C_0 is the initial adsorption concentration of adsorbate (μg/mL), C_e is equilibrium sorption concentration (μg/mL), C_t is the concentration at t time, V is solution volume (mL) and m is adsorbent mass (g).

Adsorption ratio, R, can be obtained by formula (5):

$$R = (C0 - Ce)/C0\times 100\% \qquad (5)$$

Where R is the adsorption rate, C_0 is the initial adsorption concentration of adsorbate (μg/mL), and C_e is the equilibrium adsorption concentration (μg/mL).

2.4. Desorption

0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 ml. 0.1 mol/L calcium chloride, sodium chloride, 1 mol/L of calcium chloride, sodium chloride, was added, respectively. The mixture was stirred for 110 min and 100 min at room temperature of 25±1℃. After it was separated for 20 min at 8000 r/min by centrifugation, the sample for the study of desorption was prepared. 20 mL 0.1 mol/L HCl, 1 mol/L HCl, 1 mol/L NaOH, 1 mol/L

CH_3COOH was respectively added to the prepared sample, and magnetically stirred for 30, 60, 120, 150 min at room temperature 25±1 °C. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance. The-desorption ratio was calculated.

2.5. Adsorption kinetics

0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 10, 20, 40, 60 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3) -NaOH buffer solution was respectively added and the volume was controlled to be 20 ml and the temperature was controlled to be 298.15 K. The mixture was stirred for some time to equilibrium state. The mixture was poured into centrifuge tube, after it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and the absorbance was measured. The concentration of methyl orange was calculated. The adsorption amount at equilibrium was calculated, and the adsorption kinetics figure was drawn.

2.6. Adsorption thermodynamics

0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 20 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3)-NaOH buffer solution was respectively added and the volume was controlled to be 20 ml. The mixture was stirred for some time to equilibrium state at 298.15, 308.15, 318.15, 328.15 K. The mixture was poured into centrifuge tube, after it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and the absorbance was measured. The concentration of methyl orange was calculated. The adsorption amount at equilibrium was calculated, and the thermodynamic equation figure was drawn.

2.7. Adsorption isotherm

0.050 g waste tea and $KMnO_4$ activated tea were accurately weighed and respectively placed in 50 mL conical flask. 10 mL methyl orange solution of 10, 20, 40, 60 μg/mL was added, respectively, and pH = 2.0 tri-acid (H_3PO_4-HAc-H_3BO_3) -NaOH buffer solution was respectively added and the volume was controlled to be 20 mL. The mixture was stirred for some time to equilibrium state at 298.15, 308.15, 318.15, 328.15 K. The mixture was poured into centrifuge tube, after it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and the absorbance was measured. The concentration of methyl orange was calculated. The adsorption amount at equilibrium was calculated, and Langmuir adsorption isotherm and Freundlich adsorption isotherm was drawn.

3. Results and Discussion

3.1 Modifier agent selection

Phosphoric acid, hydrochloric acid, potassium permanganate, sodium chloride and sodium hydroxide served as modified agents to modify the waste tea and adsorb methyl orange. The experimental results showed that compared with the adsorption effect of waste tea, potassium permanganate activated tea is the best, the others had no enhanced adsorption effect. The adsorption ratio and capacity of unmodified tea were 98.51 % and 3.9404 mg/g, The adsorption ratio and capacity of potassium permanganate modified tea were 99.82 % and 3.9928 mg/g, increased by 1.31 % compared with that of unmodified tea.

3.2 Optimum adsorption condition

(1) pH optimization result

As can be seen from Fig. 2, waste tea and potassium permanganate activated tea accompanied with the increase of pH, adsorption ratio and adsorption capacity showed a trend, raise first and then decrease. Both reached the highest adsorption ratio and adsorption capacity at pH 1.0. However, it is thought that when pH is 1.0, the buffer is hydrochloric acid and high concentration hydrochloric acid is unfavorable to the environment. Because the results are slightly lower than those at pH 2.0, pH is selected to be 2.0. Under over-alkali conditions, the buffer will react with methyl orange molecules, resulting in reducing solution methyl orange concentration and decreasing adsorption results.

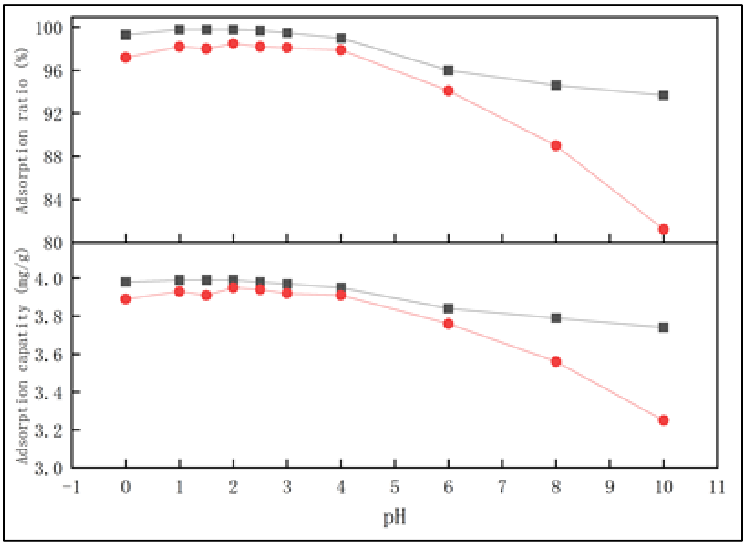


Fig 2: Effect of pH on the adsorption result for potassium permanganate activated tea and waste tea (Adsorbent dosage: 2.5 g/L, methyl orange concentration: 10 μg/mL, temperature: 25 °C, contact time for unmodified tea and potassium permanganate modified tea: 110, 100 min) (-■- Potassium permanganate modified tea -●-Unmodified Tea)

(2) Optimization results of potassium permanganate activated tea and waste tea dosage

It can be seen from Fig. 3 that with the increase of waste tea and potassium permanganate activation tea dosage, the adsorption ratio curve showed a trend of rising first and then decreasing. When the adsorption ratio of waste tea and potassium permanganate activation tea dosage was 0.05 g, the highest point was reached. The adsorption capacity curve showed a downward trend. It can be seen that the suitable amount of waste tea and potassium permanganate activation tea was 0.05 g. In this system, adsorbent dosage was 2.5 g/L.

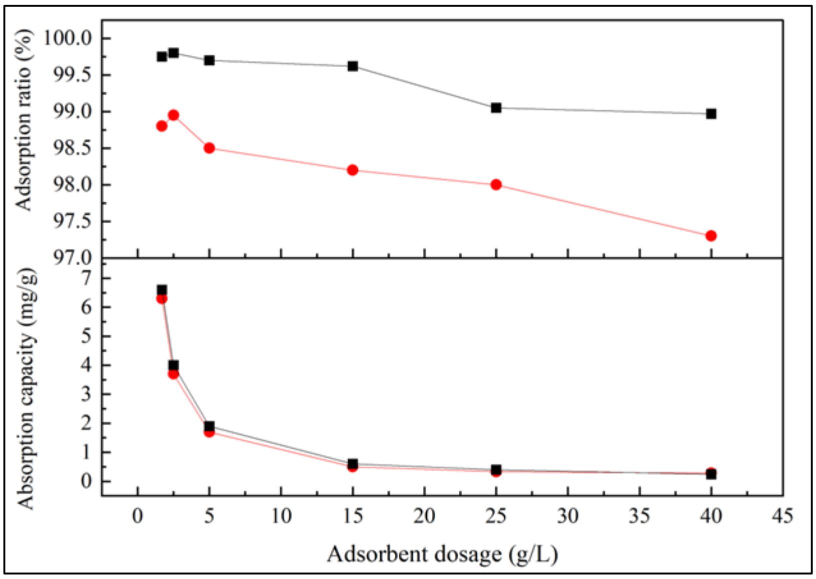


Fig 3: Effect of potassium permanganate activation tea and waste tea adsorbent dosage on the adsorption result (pH: 2.0, methyl orange concentration: 10 μg/mL, temperature: 25 ℃, contact time for unmodified tea and potassium permanganate modified tea: 110, 100 min) (-■-Potassium permanganate modified tea -●-Unmodified Tea)

(3) Optimization result of initial concentration of methyl orange

As can be seen from Fig. 4, for waste tea and potassium permanganate activated tea with increase in the initial concentration of methyl orange the adsorption ratio curve showed first increase and then decrease trend. The adsorption ratio was the highest when the concentration reached 10 μg/mL. The adsorption capacity increased with increase in concentration increase, and it was the highest when the concentration reached 10 μ/mL. The appropriate initial concentration of methyl orange was 10 μg/mL under the premise that other condition was remained unchanged.

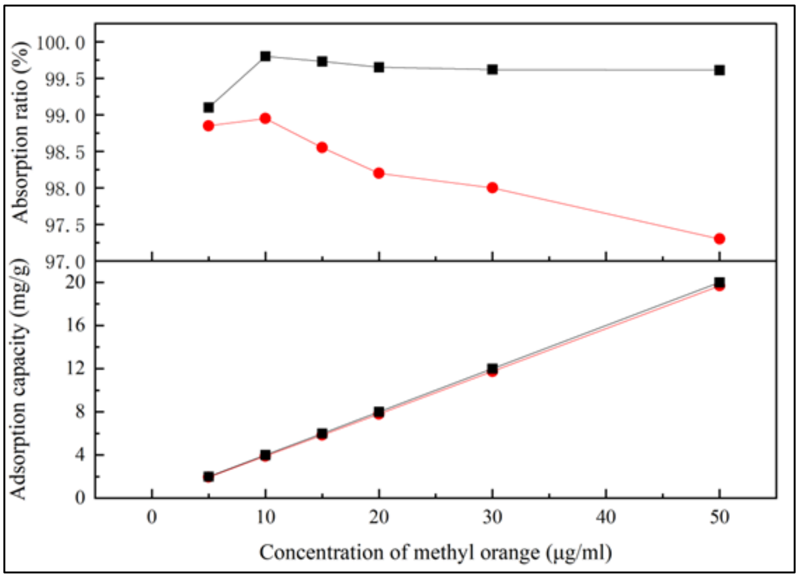


Fig 4: Effect of initial concentration on adsorption result for potassium permanganate activation tea and waste tea (pH: 2.0, sorbent dosage: 2.5 g/L, temperature: 25 ℃, contact time for unmodified tea and potassium permanganate modified tea: 110,100 min) (-■-Potassium permanganate modified tea -●-Unmodified Tea)

(4) Optimization result of contact time

As can be seen from Fig. 5 that for waste tea and potassium permanganate activated tea with increase in time, the adsorption ratio and adsorption capacity showed an upward trend. The adsorption ratio and adsorption capacity reached the highest value when the adsorption was at 100 min for potassium permanganate activated tea. The adsorption ratio and adsorption capacity reached the highest value when the adsorption was at 110 min for unmodified tea. The surface of potassium permanganate activated tea and waste tea contains the adsorption site combined with methyl orange molecule. With the growth of adsorption time, methyl orange gradually occupies the adsorption site of waste tea and potassium permanganate activated tea surface. With the decrease of adsorption site, the adsorption speed of methyl orange solution gradually decreases until the adsorption site reaches saturation and the solution concentration reaches equilibrium.

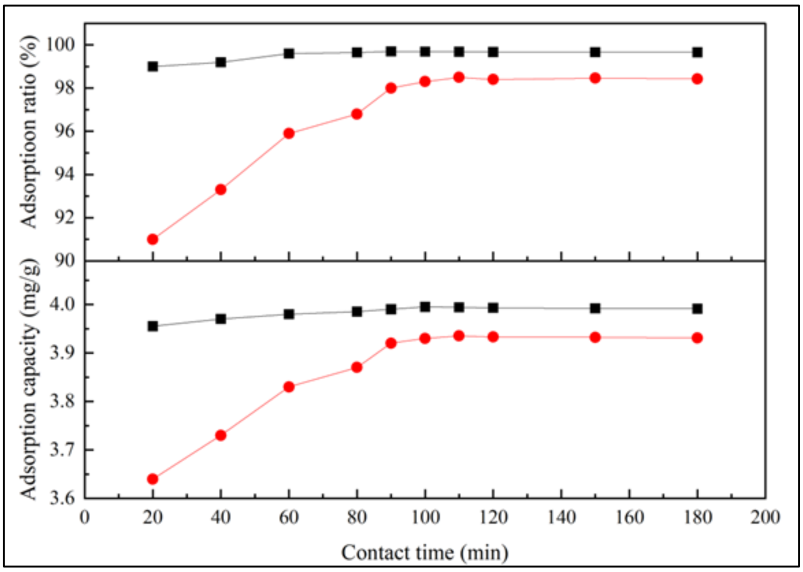


Fig 5: Effect of the contact time on the adsorption result for potassium permanganate activation tea and waste tea (pH: 2.0, adsorbent dosage: 2.5 g/L, methyl orange concentration: 10 μg/mL, temperature: 25 ℃) (-■- Potassium permanganate modified tea -●-Unmodified tea)

(5) Temperature optimization results

As can be seen from Fig. 6, for waste tea and potassium permanganate activated tea together with increased temperature, the adsorption ratio and adsorption capacity show the trend of rising first and then decreasing. The adsorption ratio and adsorption capacity reach the highest value at 30 ℃. It can be concluded that the adsorption 20-30 ℃ is an endothermal reaction and 30-45 ℃ is an exothermal reaction.

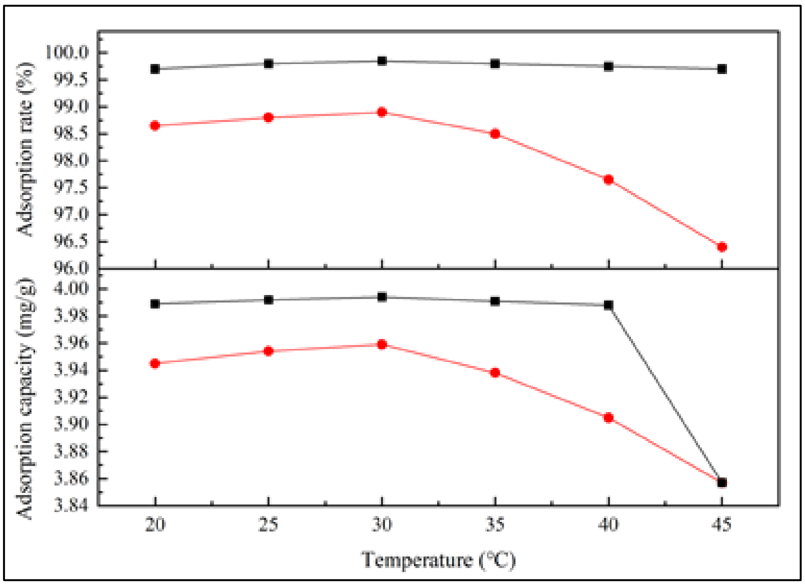


Fig 6: Effect of temperature on the adsorption result for potassium permanganate activated tea and waste tea (pH: 2.0, sorbent dosage: 2.5 g/L, methyl orange concentration: 10 μg/mL, contact time for unmodified tea and potassium permanganate modified tea: 110,100 min) (-■-Potassium permanganate modified tea -●-Unmodified tea)

(6) Effect of ion strength on adsorption

The effect of salinity ion Na^+ and Ca^{2+} that are commonly seen in solution on the adsorption of methyl orange by waste tea and potassium permanganate activated tea were studied in the experiment. The initial concentration of methyl orange is 10 μg/mL, the result is as shown in Figure 7. The presence of four salinity ions affected the adsorption, reducing the adsorption ratio of tea toward methyl orange. The influence results of different salinity ions on adsorption is different. In the range of four salinity ions experimental concentrations, Ca^{2+} is more influential than Na^+, and the influence of high-valent salt ions on the adsorption process of methyl orange is greater than low-valent salt ions. Moreover, the change value of the adsorption ratio is within 10%, therefore, in the case of not too high salt, the tea biological adsorption of methyl orange still has a better effect.

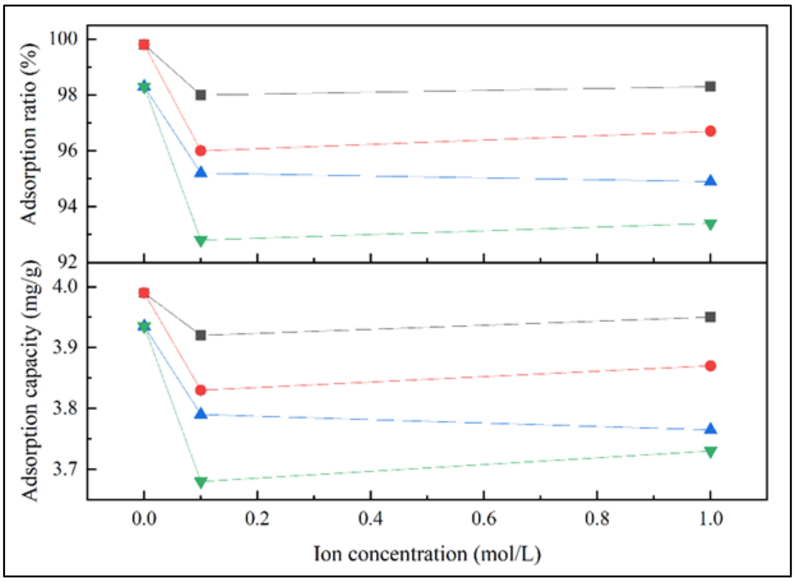


Fig 7: Effect of ion strength on adsorption result for potassium permanganate activated tea and waste tea (adsorbent dosage: 2.5 g/L, pH value: 2.0, temperature: 25 ℃, contact time for unmodified tea leaves and potassium permanganate modified tea leaves: 110, 100 min) (-■-potassium permanganate activated tea + NaCl -●-potassium permanganate activated tea + $CaCl_2$ -▲-waste tea plus + NaCl ▼ -waste tea + $CaCl_2$)

The best adsorption conditions obtained were that when the unmodified tea solution pH is 2.0, 30 ℃, solution methyl orange concentration is 10 μg/mL, tea adsorbent dosage is 2.5 g/L, adsorption time of 110 min, the maximum adsorption ratio is 98.51% and the maximum adsorption capacity is 3.9404 mg/g. After 10% potassium permanganate (W/W) modified the faded tea, the removal of methyl orange was significantly improved. We therefore used potassium permanganate-activated tea leaves in this study. At solution pH value of 2.0, temperature of 30 ℃, concentration of methyl orange 10 μg/mL and amount of potassium permanganate-activated tea adsorbent 2.5 g/L, adsorption 100 min, the maximum adsorption was reached. The maximum adsorption ratio is 99.82% and maximum adsorption capacity is 3.9928 mg/g.

3.3 Desorption result

Using 0.1 mol/L HCl, 1 mol/L HC1, 1 mol/L NaOH, 1 mol/L CH_3COOH as desorption agent, magnetic stirring was made for 30, 60, 120, 150 min at room temperature of 25±1 ℃. After it was separated for 20 min at 8000 r/min by centrifugation, the upper supernatant was taken and poured into a cell and measured with a spectrophotometer to measure its absorbance. The data showed that only 1 mol/L HCl and 1 mol/L NaOH had desorption effect. The best desorption time for 1 mol/L HCl and 1 mol/L NaOH were 120 min, and the desorption ratio were 35.6% and 43.6%, respectively.

3.4 Property of adsorption system

3.4.1 Adsorption kinetics

Quasi-first-order kinetic model [25-28]

$$\lg(q_e - q_t) = \lg q_e - k_1 t \qquad (6)$$

Where q_e represents the adsorption amount (μg/g) of methyl orange when realizing adsorption equilibrium, while q_t represents the adsorption amount (μg/g) possessed by methyl orange at t min, k_1 (min^{-1}) represents a quasi-first order kinetic rate constant, and t is the adsorption contact time (min).

Quasi-second-order kinetic model [17, 29-31]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (7)$$

Where t is the adsorption contact time (min), k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) is a quasi-second order kinetic rate constant, q_t represents the adsorption amount (μg/g) of methyl orange at the t minute, while q_e represents the adsorption amount (μg/g) of methyl orange when adsorption equilibrium is realized. Based on the measured time and concentration data linear fit was made quasi-first order kinetic equation figure (Figure 8) and quasi-second order kinetic equation figure (Figure 9) was drawn, the relevant kinetic data are listed in Table 2 and Table 3, where q_{e1}, q_{e2} is the theoretical q_e obtained respectively from the quasi-first-order kinetic equation and quasi-second-order kinetic equation and R_1^2, R_2^2 is the correlation coefficient obtained from the quasi-first-order and quasi-second-order kinetic equations respectively. The relevant parameters show that for the quasi-second-order adsorption kinetic equation, the correlation coefficient is greater than 0.99 and the theoretical q_e is very close to the actual q_e, which shows that the use of the quasi-second-order kinetic equation can show the adsorption process of methyl orange by potassium permanganate activated tea and waste tea. [24, 32-33].

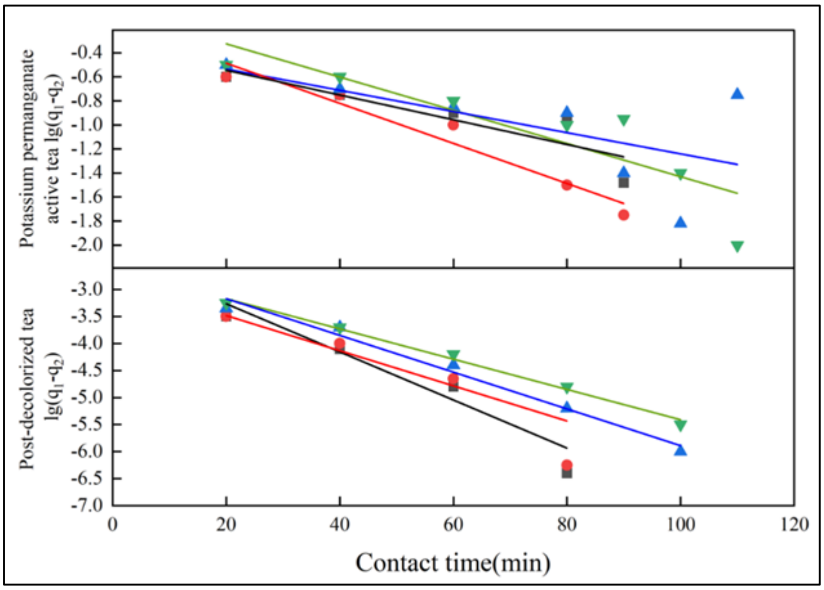


Fig 8: Quasi-first-order kinetic equation for potassium permanganate activation tea and waste tea (adsorbent dosage: 2.5 g/L, pH value: 2.0, temperature: 25 ℃) （-■-5 μg/mL -●-10 μg/mL -▲-20 μg/mL -▼-30 μg/mL).

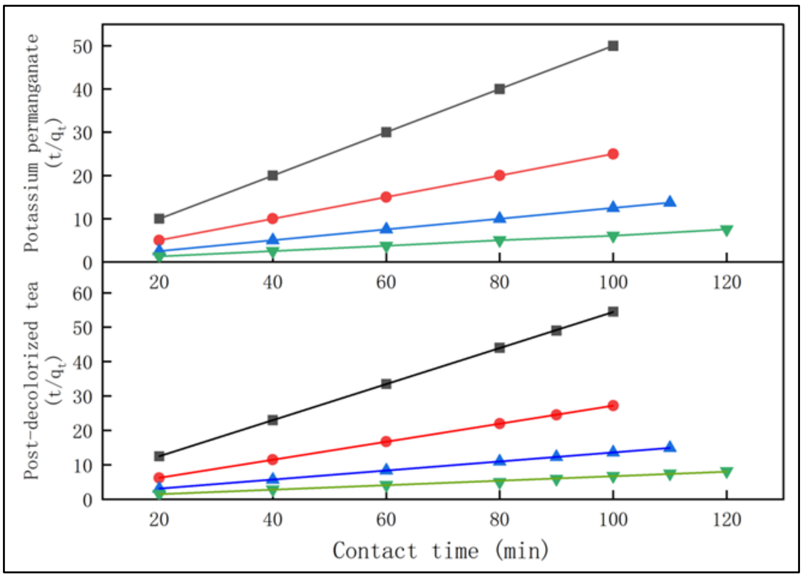


Fig 9: Quasi-second-order kinetic equation for potassium permanganate activation tea and waste tea (adsorbent dosage: 2.5 g/L, pH value: 2.0, temperature: 25 ℃) (-■-5 μg/mL -●-10 μg/mL -▲-20 μg/mL -▼-30 μg/mL)

Table 2 Relevant parameters of adsorption kinetics for potassium permanganate-activated tea leaves

Concentration (μg/mL)	Actual measure, q_e (mg/g)	Quasi-first-order adsorption dynamics equation			Quasi-second-order adsorption dynamics equation		
		k_1(min^{-1})	q_{e1}	R_1^2	k_2 (g·mg^{-1}·min^{-1})	q_{e2}	R_2^2
5	1.9924	0.1096	0.0984	0.9312	2.2701	1.9948	1.0000
10	3.9916	0.1020	0.0954	0.9173	2.1399	3.9936	1.0000
20	7.9912	0.0755	0.0738	0.9853	1.8855	7.9936	1.0000
30	11.9904	0.0670	0.0801	0.9803	1.8304	11.9904	1.0000

Table 3: Relevant parameters of adsorption kinetics for waste tea leaves

Concentration (μg/mL)	Actual measure, q_e (mg/g)	Quasi-first-order adsorption dynamics equation			Quasi-second-order adsorption dynamics equation		
		k_1(min^{-1})	q_{e1}	R_1^2	k_2 (g·mg^{-1}·min^{-1})	q_{e2}	R_2^2
5	1.9536	0.0251	0.7615	0.8228	0.0855	2.0288	0.9971
10	3.9588	0.0371	0.8407	0.9668	0.1063	4.0388	0.9978
20	7.9496	0.0331	0.9111	0.8011	0.0880	8.0257	0.9989
30	11.9408	0.0315	0.9599	0.9672	0.0808	12.0912	0.9998

3.4.2 Adsorption thermodynamics

The Gibbs free energy variation (ΔG^0), enthalpy variation (ΔH^0), entropy variation (ΔS^0) during the process of reaction is obtained by formula (8-10) [34-35]:

$$Kd = qe/Ce \tag{8}$$

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

$$\Delta G0 = \Delta H0- T\Delta S0 \tag{10}$$

Where K_d is the temperature-dependent adsorption equilibrium constant, q_e (μg/g) is the equilibrium adsorption amount of methyl orange, C_e (μg/mL) is the concentration of methyl orange in supernatant at equilibrium, ΔS^0 is the adsorption entropy variation value [J/(moL·K)], R is the ideal gas constant (8.314 $J \cdot moL^{-1} \cdot K^{-1}$), ΔH^0 is the enthalpy variation value (kJ/moL) of the adsorption process, T is absolute temperature (K), ΔG^0 is the free energy variation value of the adsorption process (kJ/moL).

The calculation results of related parameters of adsorption thermodynamic are listed in Table 4. According to Table 4 it can be known that $\Delta G^0{}_{modification} < 0$ at room temperature and above (298.15 - 328.15 K), indicating that this adsorption process can be performed spontaneously. The value of the $\Delta G^0{}_{modification}$ is between 0 and -20 kJ/mol, indicating that this is a physical adsorption process [34]. $\Delta H^0{}_{modification} = -17.2301$ kJ/mol < 0 indicates that the process of potassium permanganate-activated tea for methyl orange adsorption is an exothermal process. $\Delta S^0{}_{modification} = -8.251$ J/(mol·K) < 0 , indicates that the adsorption is an entropy reduction process. $\Delta G^0{}_{waste} < 0$, indicates that this adsorption process can be performed spontaneously. The value of the $\Delta G^0{}_{waste}$ is between 0 and -20 kJ/mol, indicating that this is a physical adsorption process. $\Delta H^0{}_{waste} = -8.0681$ kJ/mol < 0, indicates that the process of potassium permanganate activated tea adsorption of methyl orange is an exothermal process. $\Delta S^0{}_{waste} = -4.111$ J/(mol·K) < 0, indicates that the adsorption is an entropy reduction process.

Table 4: Relevant parameters of adsorption thermodynamics

T (K)	**ΔG^0 original (kJ/mol)**	**ΔH^0 original (kJ/mol)**	**ΔS^0 Original (J/(mol·K))**	**ΔG^0 Modification (kJ/mol)**	**ΔH^0 Modification (kJ/mol)**	**ΔS^0 Modification [J/(mol·K)]**
298.15	-6.8426	-8.0681	-4.111	-14.770	-17.2301	-8.251
308.15	-6.8015			-14.688		
318.15	-6.7604			-14.605		
328.15	-6.7193			-14.523		

3.4.3 Adsorption isotherm

Langmuir equation, the adsorption equilibrium belongs to the dynamic equilibrium. Its equation is shown in formula (11) [36-41]:

$$Ce/qe = 1/(qmaxb) + Ce/qmax \tag{11}$$

Where C_e (μg/mL) is the concentration of methyl orange in supernatant at equilibrium, q_e (μg/g) is the equilibrium adsorption amount of methyl orange, Q_0 (μg/g) is theoretical maximum monolayer adsorption capacity, b (mL/μg) is the constant related with adsorption ability.

Freundlich adsorption isotherms is an empirical equation without hypothetical conditions, its equation is as follows [23, 42-43]:

$$\ln qe = \ln KF + \ln Ce/n \tag{12}$$

Where C_e (μg/mL) is the concentration of methyl orange in supernatant at equilibrium, q_e (μg/g) is the equilibrium adsorption amount of methyl orange. K_F and n are the Freundlich constant. K_F is the Freundlich adsorption isothermal constant, indicating the adsorption degree, while 1/n indicates the adsorption strength. 1/n is generally less than 1.

Langmuir adsorption is a relatively ideal adsorption model, while Freundlich adsorption is an adsorption model closer to the actual experiment, so the scope of Freundlich adsorption model application is more widely used. Fig. 10, Fig. 11, Table 5 and 6 show the research results of adsorption of methyl orange by two adsorbent. The Freundlich model fitting diagram results are closer to the experimental data than the Freundlich model fitting diagram results. Also, all R^2 values of the Freundlich model fitting are near or higher than 0.990, while R^2 values of the Langmuir model fitting are lower obviously than 0.990, which can not reflect the real experimental situation. Therefore, the Freundlich model is more suitable. Hence, this adsorption process meets the Freundlich adsorption isotherm.

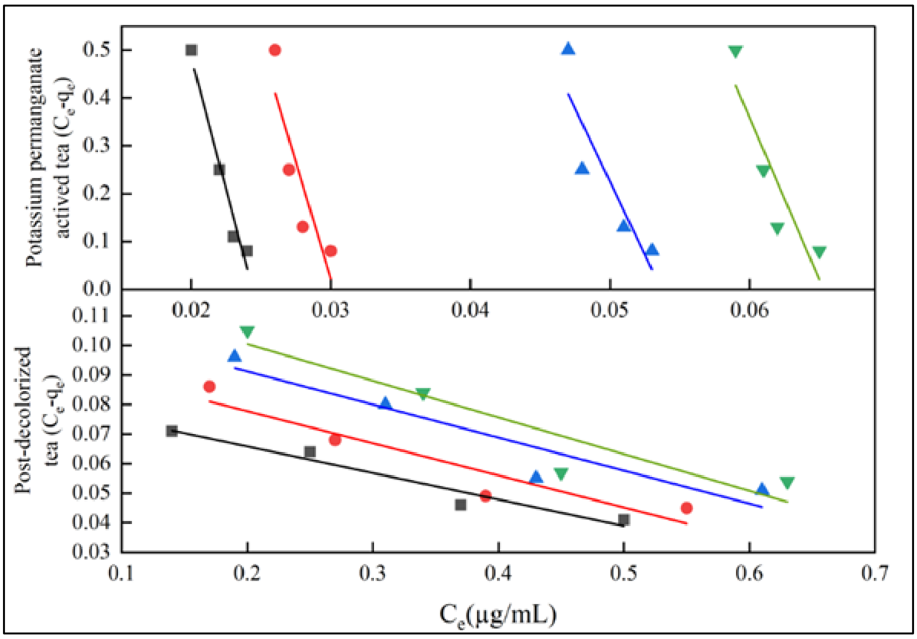


Fig 10: Langmuir adsorption isotherm of potassium permanganate activated tea and waste tea (adsorbent dosage: 2.5 g/L, pH value: 2.0) (-■-298.15K -●-308.15K -▲-318.15K -▼-328.15K)

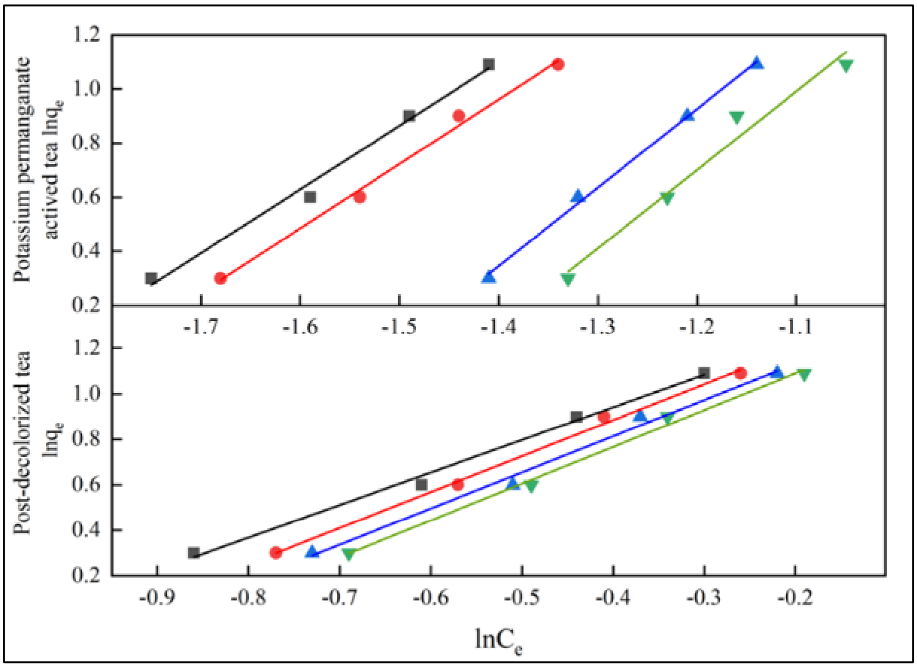


Fig 11: Freundlich adsorption isotherm of potassium permanganate activated tea and waste tea (adsorbent dosage: 2.5 g/L, pH value: 2.0) (-■-298.15K -●-308.15K -▲-318.15K -▼-328.15K)

Table 5: Relevant parameters of adsorption isotherm of waste tea leaves

T/K	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_m (mg/g)	b (L/mg)	R^2	K_F (mL/g)	1/n	R^2
298.15	-12.4532	-0.9701	0.9509	31.9889	1.4407	0.9932
308.15	-9.2081	-1.0838	0.8601	32.0037	1.5747	0.9903
318.15	-8.8810	-0.9903	0.8821	26.9401	1.5795	0.9911
328.15	-8.1833	-0.9831	0.8851	25.7810	1.3270	0.9924

Table 6: Relevant parameters of adsorption isotherm of potassium permanganate activated tea

T/K	Langmuir adsorption isotherm			Freundlich adsorption isotherm		
	q_m (mg/g)	b (L/mg)	R^2	K_F (mL/g)	1/n	R^2
298.15	-0.6472	-40.7884	0.8965	49.567	2.5602	0.9932
308.15	-0.5483	-32.5682	0.7978	22.877	2.4237	0.9903
318.15	-0.3905	-18.5164	0.8900	23.823	2.8806	0.9911
328.15	-0.1249	-16.3229	0.8972	23.142	3.0503	0.9924

3.5. Material characterization

The X-ray diffraction results of the prepared materials (Figure 12) can be seen that the peak of fresh tea, decolorized tea and the decolorized tea after adsorption of methyl orange did not change, indicating that neither the decoloration of fresh tea nor decolorized tea adsorption methyl orange reduces the diffraction order, and the pore structure of tea leaves still existed. After the modification tea leaves of potassium permanganate and its adsorption of methyl orange, the maximum peak disappearance of decolored tea was obviously observed, indicating that in the process of modification of potassium permanganate to decolored tea, the degree of order of tea pore became lower and the structure of tea was damaged.

Scanning electric images mainly reflects the appearance and particle size of sample. As can be seen from Figure 13, the surfaces of fresh tea and decolored tea and potassium permanganate activated tea are porous. The porous structure is the main adsorption site of decolored tea and potassium permanganate activated tea as the adsorbent with methyl orange. A large number of pore structure provides a good foundation for adsorption. The electric images of potassium permanganate activated tea after the adsorption of methyl orange can be significantly observed with a large number of methyl orange accumulation on the surface of the modified tea, indicating that the adsorption was very successful.

From the infrared spectrum in Figure 14, it can be concluded that the broad spectral absorption peak at 3425 cm^{-1} in the FT-IR spectra of fresh tea, decolorized tea, modified tea, post adsorption of decolorized tea, and post adsorption of modified tea may be caused by the O-H stretching vibration of carboxylic acids. The stretching vibrations observed at 2923 and 2853 cm^{-1} may be assigned to C-H bonds. Peaks observed at 1748 cm^{-1} and 1630 cm^{-1} are due to esterified C=O group and COO- asymmetric stretching vibrations of a carboxylic acids. COO- symmetric stretching vibration is shown by the peak at 1400 cm^{-1}. The peak at 1355 cm^{-1} is due to C-H stretching vibration. The peak at 1052 cm^{-1} may be assigned to C=O stretching vibration of carboxylic acids. The maximum absorption of tea peak changed, but the wavenumber of the maximum absorption peak did not change significantly. The tea framework and main functional group did not change after decolorization and its adsorption of methyl orange. Decolored tea after adsorption of methyl orange and tea modified by potassium permanganate showed some characteristic peaks of methyl orange, indicating the successful load adsorption of methyl orange.

As can be seen from the isotherm of adsorption and desorption in Figure 15, typical H3-type hysteresis rings appear in tea and modified tea samples, which are layered pores. The H3 hysteretic ring is typical of non-rigid aggregates of lamellar particles, and the sample does not exhibit adsorption saturation in the region of high relative pressure. It can be seen from the figure that the adsorption and desorption curves do not coincide, which is mainly due to the cavitation effect, resulting in that the lower limit of the desorption branch usually located at the P/P_0 pressure point caused by the cavitation. It can be seen from the pore size distribution diagram of the sample (Figure 16) that the pore size of the sample after potassium permanganate modification becomes larger, and the pore size of the sample after adsorption of methyl orange becomes gradually smaller, which can prove that the tea sample has been successfully modified and can be used for the adsorption of methyl orange.

Due to the high porosity of tea, it can be seen from Table 7 that the BET specific surface area of tea modified by potassium permanganate also increases significantly.

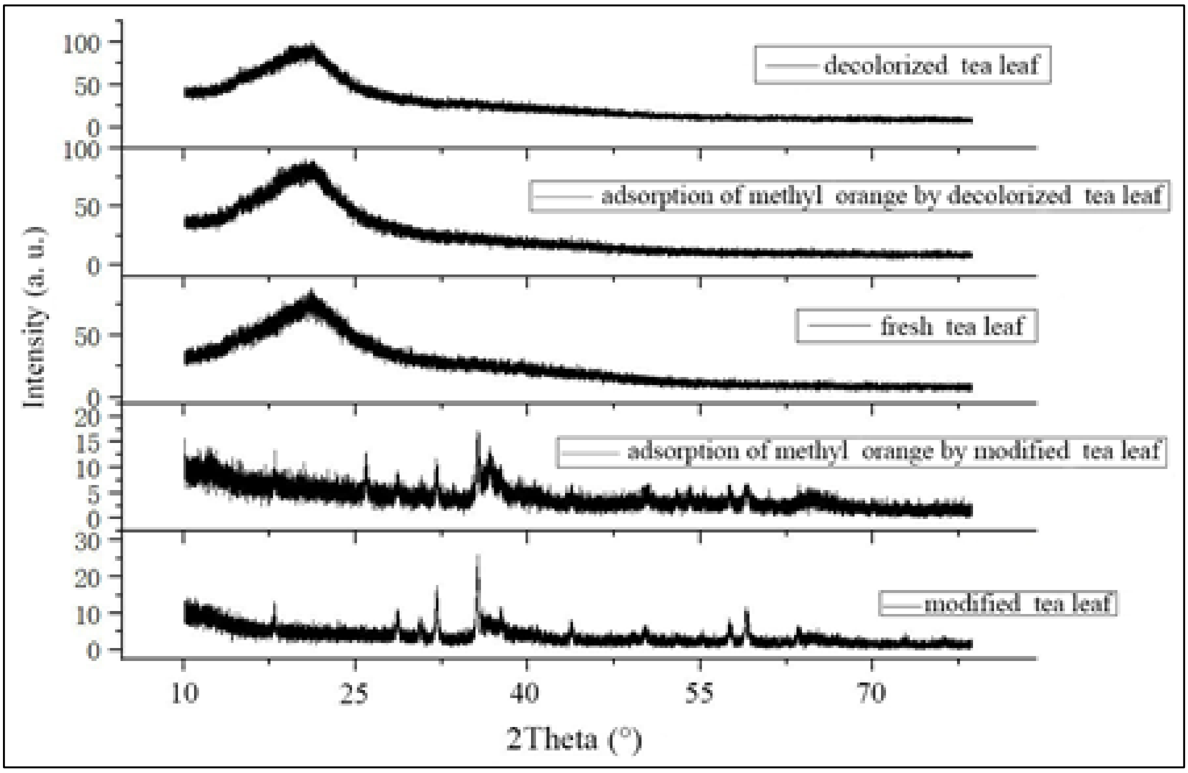
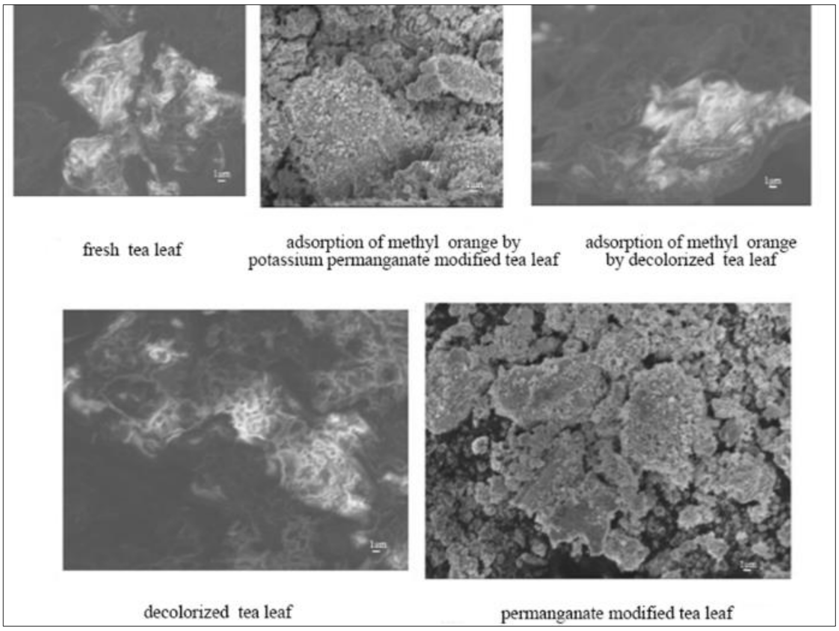


Fig 12: X-ray diffraction diagram



fresh tea leaf

adsorption of methyl orange by potassium permanganate modified tea leaf

adsorption of methyl orange by decolorized tea leaf

decolorized tea leaf

permanganate modified tea leaf

Fig 13: Scanning electric microscopic diagram

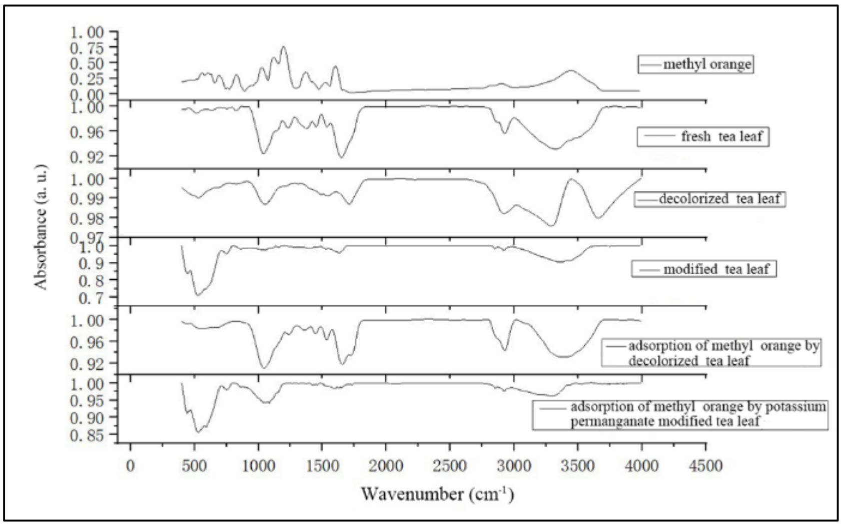


Fig 14: Infrared spectra

3.6. Comparison of adsorption capacity of adsorption system

Here, we compares the adsorption capacity of different adsorption systems, and the results show that (Table 7) this adsorption system has a relatively good adsorption capacity and has a good potential application value.

Table 7: Comparison of adsorption ability of various adsorbents: adsorption for orange methyl from aqueous medium

Adsorbent	pH, initial concentration (mg/L)	Adsorption capacity (mg/g)	Reference
Activated carbon derived from waste orange and lemon peels	2.0, 100	33	[44]
Immobilized chitosan-montmorillonite composite	2.5, 20	8.70	[45]
Mesoporous Fe_3O_4–SiO_2–TiO_2	2.5, 20	2.5	[46]
Amino-crosslinked hypromellose	3.0, 20	1.55	[47]
Rectorite/iron oxide nanocomposites	3.0, 1.0	0.36	[48]
$KMnO_4$ modified waste tea leaves	2.0, 10	3.99	Present study

4. Conclusions

(1) The structure of the tea leaves was not fundamentally changed after waste tea and the decolored tea modified by potassium permanganate adsorbed methyl orange and potassium permanganate modified the tea leaves and absorbed the methyl orange. Both the modified tea and decolored tea have a high adsorption ability of methyl orange, and its adsorption effect is better than the unmodified waste tea. Potassium permanganate has a good modification effect of tea.

(2) The process of adsorption of methyl orange of waste tea and potassium permanganate activated tea complies with the quasi-second order kinetic equation. The process of adsorption of methyl orange for two tea leaves is an

exothermal process and the entropy reduction process, consistent with the Freundlich adsorption isotherm.

(3) After potassium permanganate modified the faded tea leaves, decolor ability of methyl orange by tea was significantly improved. When solution pH is 2.0, temperature is 30 ℃, the concentration of solution methyl orange is 10 μg/mL, the adsorbent dosage of tea activated by potassium permanganate is 2.5 g/L and the adsorption is carried out for 100 min, the maximum adsorption was reached. The maximum adsorption rate is 99.82% and the maximum adsorption capacity is 3.9928 mg/g.

Declarations

Supplementary Information Not applicable.

Competing interests The author declares no competing interests.

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Author Contribution Statement Xiao-Dong Li and Qing-Zhou Zhai conceived and designed the experiments. The experiments were performed by X.-D. Li and Q.-Z. Zhai. Data was analyzed by X.-D. Li and Q.-Z. Zhai. The manuscript was written by X.-D. Li and Q.-Z. Zhai. The manuscript was reviewed and corrected by Q.-Z. Zhai. All authors read and approved the final manuscript.

Data Availability Statement The data used or analyzed during the current study are available in the article.

Ethics approval and consent to participate Not applicable.

Consent for publication All authors have read this manuscript and consent for publication in XXX.

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