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Research Article

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Treatment for phenol-containing wastewater with modified waste tea leaves

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ABSTRACT

The treatment of wastewater containing middle or low concentration of phenol solution is a troublesome environment problem. In this study, tea was modified by $FeCl_3$,$AlCl_3$,$FeSO_4$,and we studied the adsorption performance of modified waste tea leaves on phenol-containing waste water. FeCl3 is the best modifier, the second one is FeSO4, and the last is AlCl3. And the effects of the initial concentration, pH value, adsorption time, particle size, and temperature on adsorption capacity were investigated. Langmuir isotherm model was better to describe the isothermal adsorption of phenol.

Key words: Waste tea leaves; Phenol-containing wastewater; Adsorption

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INTRODUCTION

1.1 Harmfulness of phenol

Phenol and its derivatives are a class of the most important material of organic synthesis,they are widely used in industrial manufacturing[1,2], and they are also common pollutants in water, because of their toxicity, phenol and its derivatives are listed as priority pollutants by Chinese environmental protection department and USA State Environmental Protection Agency[5]. Phenol-containing wastewater complicated composition, the concentration of organic substance is high,it is not only large salinity, colored, flavored,but also contains a large number of material difficult to be biodegraded and inhibition of microbial substances,such as phenol, aniline, nitrobenzene and other aromatic compound. They are not conducive to the direct processing. At present the research of the treatment for phenol-containing wastewater is mainly to study the static adsorption for simulated wastewater[3-5], there is few studies on the dynamic adsorption of simulated wastewater. At present the method of the treatment of wastewater containing phenol are mainly physical adsorption methods[6-8], chemical oxidation methods[9,10] and biological treatment method[11,12]. Usually the adsorption method is used to treat high concentration of phenol-containing wastewater.The commonly used adsorbents are activated carbon, metal oxide adsorbents and non metal oxide adsorbents(such as silicone [13],$AlCl_3$[14], molecular sieve[15], natural clay[16]) and organic polymeric adsorbent(such as macroporous adsorption resin[17,18], activated carbon fiber polymer[19,20]).

1.2 Characteristics of tea

The waste tea leaves is the tea after brewing. After investigation, in Changsha city, waste tea leaves reache 0.1 ton daily.Tea is a kind of porous, large surface area of absorbent. Tea contains more than 500 kinds of compounds, the content of organic matter is very rich, it also contains active groups containing oxygen, nitrogen, phosphorus and sulfur,such as -OH,=NH, >C=C<, >C=O,and polyatomic phenol, these groups react with metal ions under suitable conditions, it can adsorb metal ions on the surface of tea,and polyatomic phenol material can make many kinds of metal ion precipitate.In China the research of the adsorption of tea is only at the beginning stage, tea is used as adsorbent for metal ions has been reported, but the research on adsorption of organic molecules is less.

EXPERIMENTAL SECTION

2.1 Materials and reagents

Experimental reagents:tea(Green tea);NH_4Cl； $NH_3 \cdot H_2O$ (Ammonium Hydroxide)； $K_3[Fe(CN)_6]$ (potassium ferricyanide); 4-Aminoantipyrine,Phenol;$FeCl_3$;$FeSO_4$,Etc. They are analytically pure.

Experimental apparatus: velocity-modulated oscillator(So8-h2), Visible spectrophotometer (T6, Beijing Purkinje General Instrument Co.,Ltd.), pH meter(PHS-3C),circulating water vacuum pump, thermostatic oscillator.

2.2 Experimental method

2.2.1 Preparation of waste tea leaves

Soaked the Green Tea 2 times: first socked it in 90℃ water for 12 hours, filtered the tea, socked it with distilled water for 12 hours, and then filtered the tea again, drying the filtered tea in an oven at 110℃, ground it into powder, classified the waste tea leaves with 100mesh,80mesh,60mesh,40 mesh and 10 mesh respectively. Put the waste tea leaves in a dry dish.

2.2.2 Preparation of modified waste tea leaves

At room temperature added 1g waste tea leaves in 1.5mol/L of modifier,stired it for 1h,had a filtration using a vacuum pump,drying it in an oven at 105℃ for 24h,and we got modified waste tea leaves,then put the waste tea leaves in a dry dish.

2.2.3 *Adsorption tests*

At room temperature,took a certain amount of modified waste tea leaves, added it in a conical flask with a certain concentration of phenol solution, adjusted its pH value, shake the solutionin a constant temperature oscillator until it teached the adsorption equilibrium,took 3 copies of supernatant, did the parallel experiments,and determinated the concentration of phenol solution using the method of diphenylcar-bazide spectrometry(λ=510nm).

Then calculated the adsorption rate and adsorbing capacity using formula (1) and formula (2)[11].

adsorption capacity : $Q=V(C_0-C)/m$ (1)

adsorption rate: $\eta=(C_0-C)\times 100\%/C$ (2)

where Q is the adsorption capacity(mg/g);V is the volume of phenol solution (ml),C_0 is the concentration before adsorption(mg/L),C is the concentration after adsorption (mg/L),m is the quality of the adsorbent(g).

2. 2. 4 Determination of the concentration of phenol solution

Determinated the concentration of phenol solution using the method of diphenylcar-bazide spectrometry.

RESULTS AND DISCUSSION

3.1 Choice of modifier

Took 50mL phenol concentration of 40mg/L solution,added 1g particle size of 100 mesh modified waste tea leaves,studied the effect of different modifiers on adsorption capacity,where the concentrations of modifiers are 1.5mol/L,we did three groups of parallel experiments,and the results are shown in table 1.

Table 1. Modifier experiment

Modifier (mg/L)	$FeCl_3$	$AlCl_3$	$FeSO_4$	Without modifier
Adsorption capacity (mg/g)	0.271	0.176	0.215	0.098

It can be seen from table 1 that, after adding modifier the adsorption performance has improved, in three kinds of modifiers, the modification effect of $FeCl_3$ is the best,and the modification effect of $FeSO_4$ is the worst.This is because in modifier,the factors play a major role is metal ions, metal ions can react with hydroxyl and polyphenols in tea,among the ions of Al^{3+},Fe^{3+} and Fe^{2+}, the complexing ability of Fe^{3+} is the most strongest,so $FeCl_3$ is the best modifier, so in the following experiments we choosed modified waste tea leaves as the adsorbent.

3. 2 Effects of particle size of waste tea leaves on adsorption capacity

Added 1g 200mesh, 100mesh, 80mesh,60mesh, 40mesh ,10mesh of modified waste tea leaves into 6 groups of 50ml, concentration of 100mg/L simulated phenol-containing wastewater respectively, adjusted their pH values to 2,

at room temperature shocked them for 60min,took their supernatant after filtering,after adding chromogenic agent, determinated their absorbance. Then draw the curve of the particle size of modified waste tea leaves on adsorption capacity.The results are shown in Figure 1.

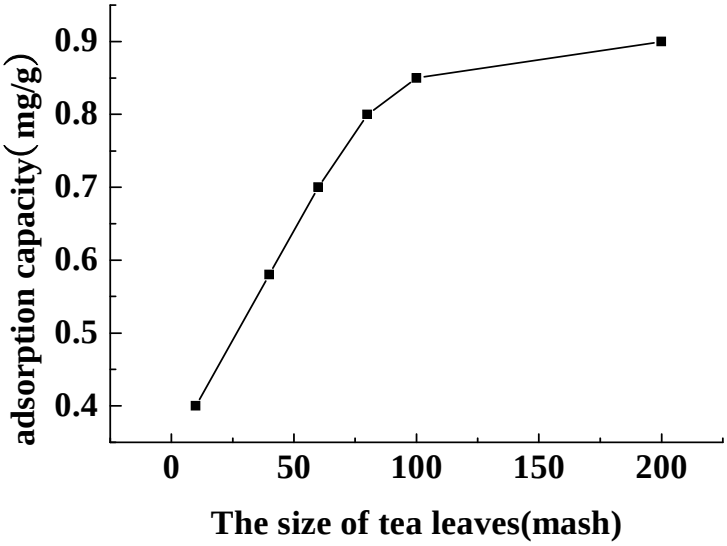

Figure 1. Effects of the particle size of modified waste tea leaves on adsorption capacity

Figure 1 shows that,the adsorption capacity of phenol increases with the decreasing of particle size of modified waste tea leaves, when the particle size of modified waste tea leaves is less than 100 mesh, the adsorption capacity changes little,so we choosed 100 mesh of modified waste tea leaves as the adsorbent.

3.3 Effects of initial concentration on adsorption capacity

Prepared 50mL 40.0mg/L , 60.0mg/L,80.0mg/L,100.0mg/L,150.0mg/L,200.0mg/L,300.0mg/L and 500.0mg/L concentration of phenol solution ,adjusted their pH values to 2, added 1g 100 mesh of modified waste tea leaves into the 8 groups of simulated phenol-containing wastewater respectively, at room temperature shocked them for 60min, took their supernatant after filtering,after adding chromogenic agent,determinated its absorbance.Then draw the curve of initial concentration of waste water on adsorption capacity. The results are shown in Figure 2.

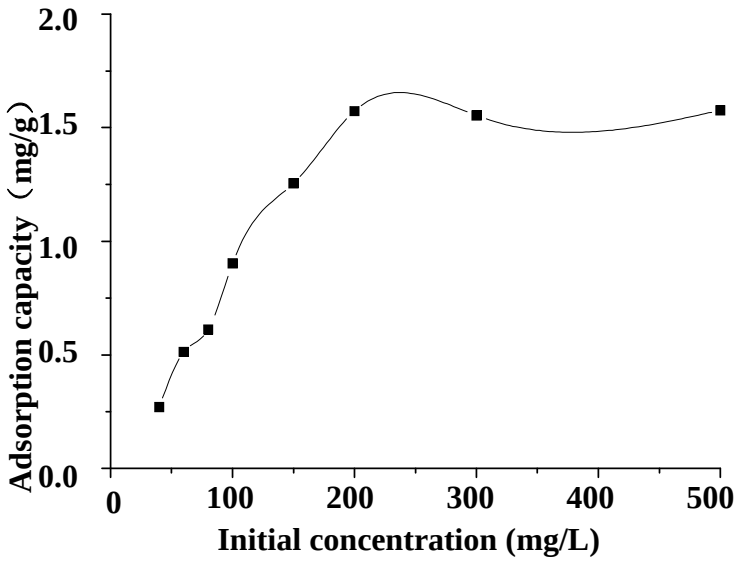

Figure 2. Effects of the initial concentration on adsorption capacity at room temperature

Figure 2 shows that,at room temperature the adsorption capacity of phenol increases with the decreasing of the initial concentration of phenol solution, when the initial concentration was higher than 200mg/L, the adsorption capacity changes little, this shows that the initial concentration reachs 200mg/L, the adsorption of modified waste

tea leaves reachs saturation. so we choosed the initial concentration of 200mg/L phenol solution as the adsorption solution.

3.4 **Effects of the pH value of waste water on adsorption capacity**

Prepared 6 groups of 50mL concentration of 200mg/L phenol solution ,adjusted their pH values to 3,5,7,9,11 and 12, added 1g 100mesh of modified waste tea leaves into the 6 groups of simulated phenol-containing wastewater respectively, at room temperature shocked them for 60min, took their supernatant after filtering,after adding chromogenic agent,determinated its absorbance.Then draw the curve of pH value of waste water on adsorption capacity. The results are shown in Figure 3.

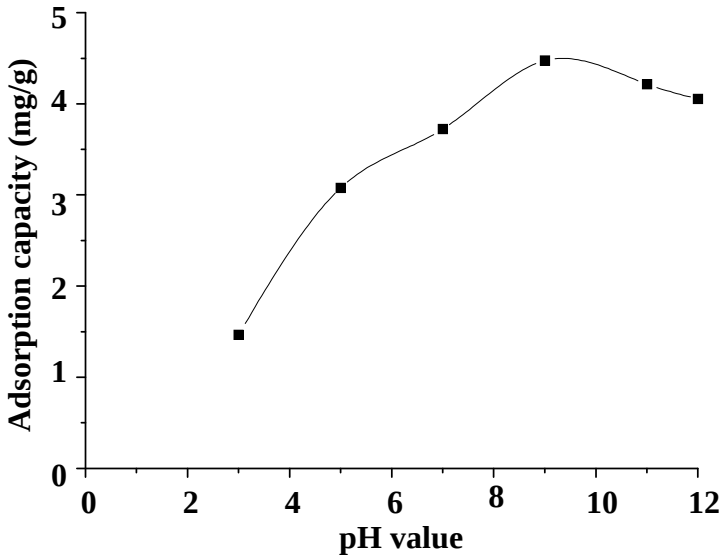

Figure 3. Effects of pH value of waste water on adsorption capacity in the initial concentration of 200mg/L

Figure 3 shows that,the acidity of the solution has great influence on the adsorption effect of modified waste tea leaves,it shows obvious chemical characteristics.When the initial concentration of phenol solution is 200mg/L,and the pH value is in the range of [1.0,9.0], the adsorption capacity of phenol increases with the increasing of pH value,when the pH value is higher than 9.0, the adsorption capacity of phenol decreases,this is because the pH value is too high,the Fe^{3+} on the surface of modified waste tea leaves generates Fe $(OH)_3$ precipitate,and the precipitate affects the adsorption.So the optimum pH value is 9.0,and we choosed the pH value of 9.0 phenol solution as the adsorption solution.

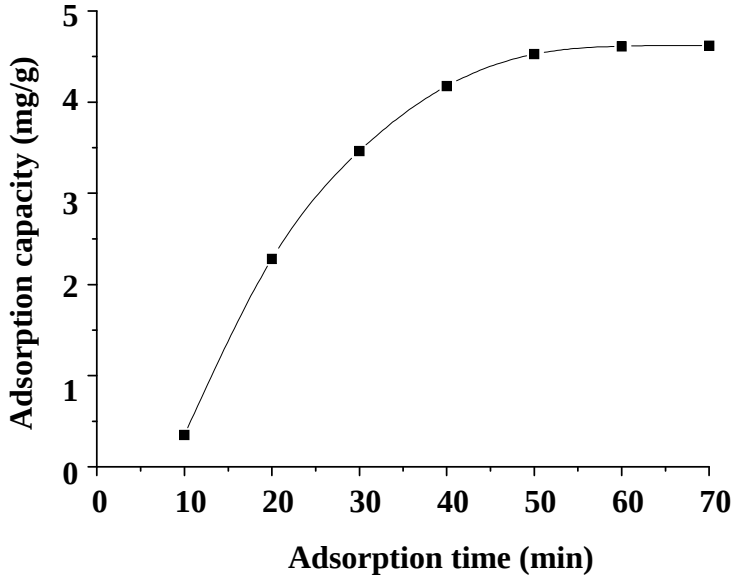

Figure 4. Effects of the adsorption time on adsorption capacity

3.5 *Effects of adsorption time on adsorption capacity*

Prepared 7 groups of 50mL concentration of 200mg/L phenol solution ,adjusted their pH values to9.0, added 1g of modified waste tea leaves into the 7 groups of simulated phenol-containing wastewater respectively, put them in a oscillator, shocked them for 10min,20min,30 min,40 min,50 min, 60min and 70 min respectively, took their supernatant after filtering,after adding chromogenic agent, determinated its absorbance using a spectrophoto-meter. Then draw the curve of the adsorption time on adsorption capacity. The results are shown in Figure 4.

Figure 4 shows that, when the initial concentration of phenol solution is 200mg/L,and the pH value is 9.0, the adsorption capacity of phenol increases with the increasing of adsorption time, after 60min, the adsorption reaction flattens out. Initially,because phenol is adsorpted on the surface of modified waste tea leaves, so the adsorption reaction is fast, with the increasing of adsorption time,phenol gradually got into the pore of modified waste tea leaves,the resistance of the adsorption reaction increases, the adsorption rate increased with the increasing of adsorption time slowly until it reached the adsorption equilibrium. So the optimum adsorption time is 60min.

3.6 **Effects of the dosage of modified waste tea leaves on adsorption capacity**

Prepared 8 groups of 50mL concentration of 200mg/L phenol solution ,adjusted their pH values to 9.0,added 0.5g,1g,1.5g,2g,2.5g,3g,4g,5g of modified waste tea leaves into the 8 groups of simulated phenol-containing wastewater respectively,put them in a oscillator, shocked them for 60min, took their supernatant after filtering,after adding chromogenic agent, determinated its absorbance using a spectrophoto-meter.Then we studied the effect of the dosage of modified waste tea leaves on adsorption capacity,the results are shown in Figure 5.

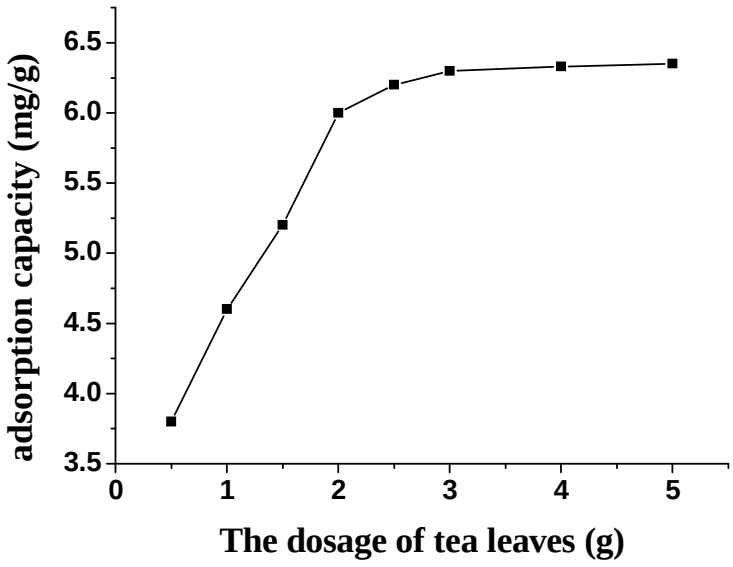

Figure 5. Effects of the dosage of modified waste tea leaves on adsorption capacity

Figure 5 shows that, the adsorption capacity increases with the increasing of the dosage of modified waste tea leaves,when the dosage is more than 2.5g,the adsorption capacity changes little,this shows that the adsorption capacity reachs saturation.So the optimum dosage of modified waste tea leaves is 2.5g.

3.7 **Effects of the temperature of waste wateron adsorption capacity**

Prepared 6 groups of 50mL concentration of 200mg/L phenol solution ,adjusted their pH values to 9.0,added 0.5g,1g,1.5g,2g,2.5g,3g,4g,5g of modified waste tea leaves into the 8 groups of simulated phenol-containing wastewater respectively, put them in temperature of 20℃, 30℃, 40℃, 50℃, 60℃ and 70℃ oscillators respectively,added 2.5g modified waste tea leaves in them respectively. Then we studied the effect of temperature on adsorption capacity and draw the curve,the results are shown in Figure 6.

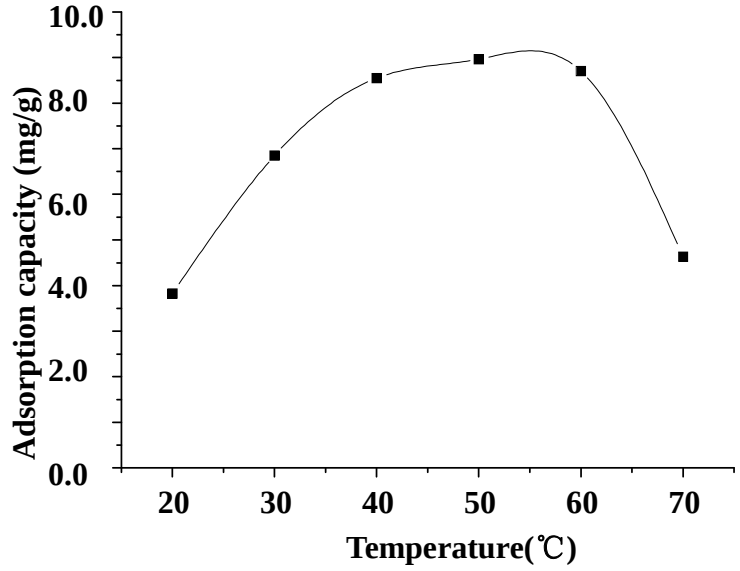

Figure 6. Effects of the temperature of waste wateron adsorption capacity

Figure 5 shows that, the adsorption capacity increases with the increasing of temperature under the condition of low temperature,thia is because heating leads to the fiber inside modified waste tea leaves expansion.When the temperature is higher than 50℃, the adsorption capacity decreases with the increasing of temperature,this is because the high-temperature damage to the surface of modified waste tea leaves, and high temperature accelerated the movement of ions, it makes the phenol on the surface of modified waste tea leaves dissolve into the solution.So the optimum temperature is 50℃.

3.6 *Adsorption isotherm*

Prepared 25mL 40.0mg/L, 60.0mg/L,80.0mg/L,100.0mg/L,150.0mg/L,200.0mg/L,300.0mg/L and 500.0mg/L concentration of phenol solution ,adjusted their pH values to 9.0, added 1g modified waste tea leaves, shocked them for 60min,draw the curve of adsorptive capacity(mg/g) and equilibrium concentration(mg/L),got the adsorption isotherm line(shown in figure 7).

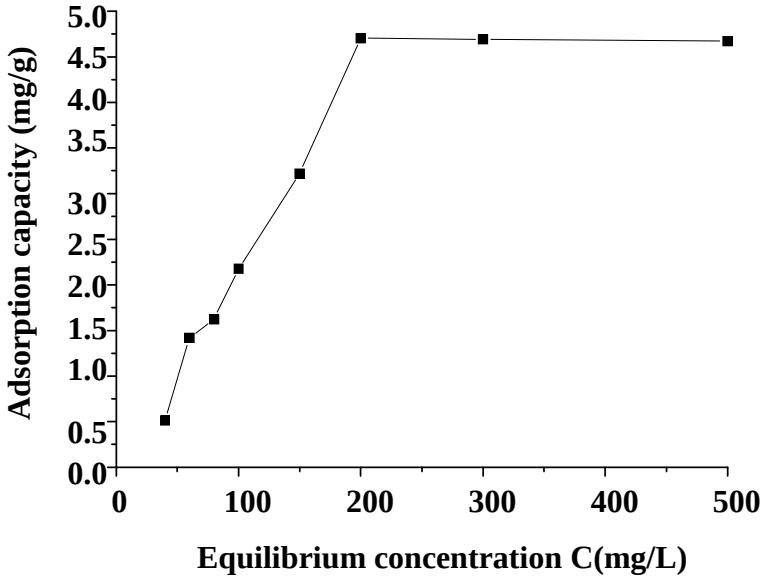

Figure 7. Adsorption isotherm

Figure 7 shows that the equilibrium concentration of phenol increases with the increasing of equilibrium mass concentration,when the concentration reachs 200mg/L,the adsorption capacity increases slowly,and soon it reachs saturation.

The Langmuir isothermal adsorption equation is shown as formula (3):

$$\frac{C}{Q}=\frac{C}{Q_m}+\frac{1}{kQ_m} \tag{3}$$

where parameter C is the equilibrium mass concentration(mg/L), parameter Q is the equilibrium adsorption capacity(mg/g), Q_m is the maximum adsorption capacity(mg/g), parameter k is a adsorption equilibrium constant.

The data in figure 6 was fitted using Langmuir adsorption isotherm model,the results are shown in figure 8.

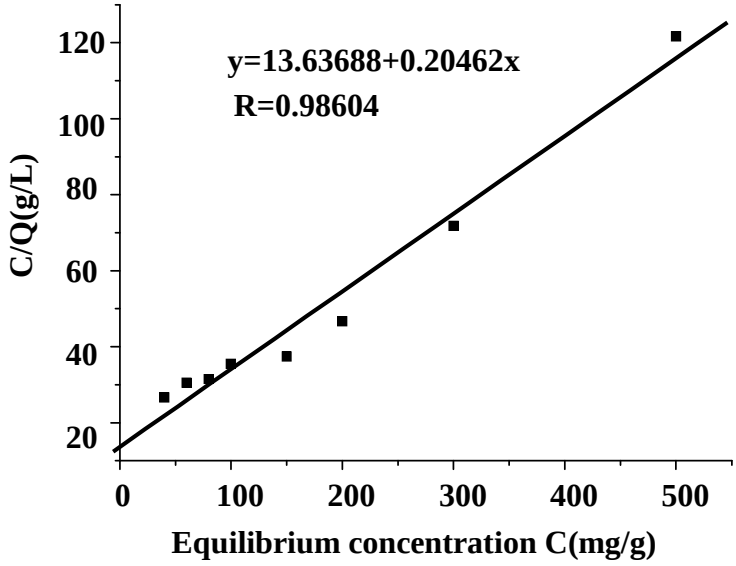

Figure8. Langmuir Adsorption isotherm

The Freundlich isothermal adsorption equation is shown as formula (4):

$$\lg Q = \lg k + \frac{1}{n}\lg C \tag{4}$$

where parameter Q is the equilibrium adsorption capacity(mg/g), parameter k and parameter n are adsorption equilibrium constants.The data in figure 6 was fitted using Freundlich adsorption isothermal model,the results are shown in figure 9.

Figure 8 and figure 9 show that, there is good correlation between the data and Langmuir adsorption isothermal model, the corresponding parameters are shown in table 2.

Table 2. The fitting results of adsorption isotherm

Adsorption	Formula	Parameter
Langmuir	C/Q=13.63688+0.20462C	Q_m=4.887 $Q_{实}$=4.28 k=0.015 R=0.98604
Freundlich	lgQ=0.34562+0.3878lgC	1/n=0.3878 k=2.216 R=0.91782

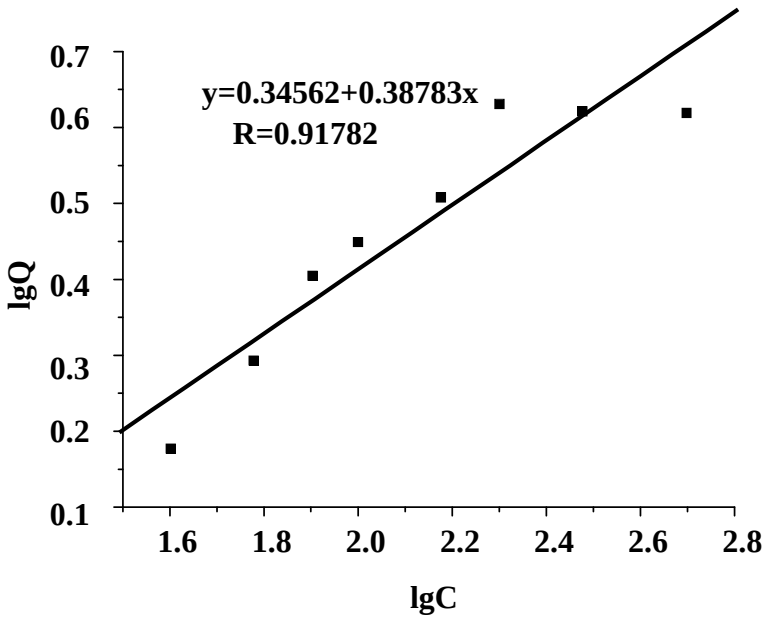

Figure 9. Freundlieh Adsorption isotherm

Compared the two fitting results of Langmuir isothermal adsorption model and Freundlich isothermal adsorption model, we can found that Langmuir isothermal adsorption model follows this pattern better than Freundlich model, the correlation coefficient R is greater than 0.98,the theoretical maximum adsorption capacity Qm is similar to the experimental value Q,this means that the adsorption of modified waste tea leaves on phenol belongs to monolayer adsorption.In Freundlich isothermal adsorption model, parameter n=2.57,it is in the range of 2~10, this shows that the adsorption is easy to occur, and n>l, the adsorption of modified waste tea leaves on phenol is a single molecular adsorption.

CONCLUSION

(1) The waste tea leaves modified by $FeCl_3$ has strong adsorption capability on phenol, the effect of adsorption is mainly affected by pH value and temperature. the adsorption conforms with the Langmuir adsorption isotherm,it is a kind of monolayer adsorption.

(2) The optimum conditions of treatment of phenol-containing wastewater using modified waste tea leaves is: the pH value of wastewater is 9.0,the initial concentration of phenol is 200mg/L,the adsorption time is 60 min,the dosage of dark tea residue is 2.5g,the maximum adsorption capacity can reach 8.5mg/g.

(3)The output of waste tea leaves is very high, and the waste tea leaves can reduce the cost of treatment for wastewater.

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