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# Study of dark tea residue's high efficiency absorption in treatment of Cr-bearing waste water

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**ABSTRACT**

*As an absorbent dark tea residue can get rid of heavy metal ion effectually and do no harm to the environment. From the dynamic experiment on dark tea residue's absorption of Cr(VI), the absorption dynamic curve and absorption isothermal curve are obtained. The effects of pH value, initial concentration, dosage of residue, adsorption time and other factors on absorption are studied and the result shows that: when the pH value of the waste water is 2,the initial concentration is 100mg/L, the adsorption time is 60min, the dosage of dark tea residue is 1g,the maximum adsorption rate reaches 99.96%.The adsorption conforms with the Langmuir adsorption isotherm, it is a kind of monolayer adsorption, the adsorption kinetics curve conforms with pseudo-second-order equation. In the end discusses the development prospect of dark tea residue.*

**Keywords:** Dark tea, Absorption, Cr-bearing waste water

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## INTRODUCTION

Water is one of the most important and basic natural resources. It is not only a fundament of human survival, but also is a key of social and economic sustainable development. China is not only facing the problem of water shortage, water pollution, and more and more cause for concern and attention. Chromium is an important industrial raw material in the production[1]; there is no alternative in many areas of the material. Chromium emissions from extensive use and unreasonable emissions, resulting in surface water and groundwater pollution.

There are many kinds of technologies in treating the wastewater containing chromium[2-5], including physical method, chemical method, physical and chemical method and biological method. The chemical method is the main one, and it plays a very important role in engineering practice.

Usually chromium-containing wastewater treatment methods are chemical precipitation, electrochemical method, ion exchange, membrane separation, biological and adsorption[6-9]; various methods have advantages and disadvantages. Adsorption is widely used in the treatment of industrial wastewater emissions[10]. Adsorption process is simple, repeated use of renewable sorbent. Finding cheap, good adsorption capacity of adsorbent for wastewater treatment has become a hot research.

## EXPERIMENTAL SECTION

### 2.1 *Materials and reagents*

Experimental reagents: NaOH, HCl, $H_2SO_4$, acetone($C_3H_6O$), $HNO_3$, $K_2Cr_2O_7$, NaCl, dark tea, $H_3PO_4$, $C_{13}H_{14}N_4O$

(DPCI).

Experimental apparatus: //visible spectrophotometer, acidimeter, electric vacuum drying oven, timing oscillator, electronic balance, circulating water vacuum pump.

**2.2.** ***Experimental method***

*2.2.1. Preparation of adsorbent*

Soaked the dark tea 2 times: First, dark tea was soaked with 90℃ tap water, the soaking time is 12h; after being filtered, the dark tea was soaked in distilled water for 12h. After being soaked, it was filtered with gauze, then the filtered tea was baked in an oven, then grinded it, classified the dark tea with 100mesh, 80mesh, 60mesh, 40 mesh and 10mesh respectively.

*2.2.2. Determination of Cr(VI)*

Determined Cr(VI) using the method of diphenylcarbazide spectrometry.

*2.2.3. Adsorption tests*

Took the dark tea residue into a 150mL iodine volumetric flask, added 50mL of known concentration of Cr(VI) solution, adjusted the pH value of the solution with 2.00mol/L of $HNO_3$ or NaOH, then oscillated the iodine volumetric flask in a timing oscillator, at room temperature took the supernatant after a certain amount of adsorption time, filtered it, measured the absorbance and calculated the concentration of Cr(VI).Then calculated the adsorption rate and adsorbing capacity using formula (1) and formula (2)[11].

adsorption rate $$R_e = \frac{C_0 - C_e}{C_0} \quad (1)$$

adsorption capacity $$q = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where $C_0$ is the concentration before adsorption(mg/L), $C_e$ is the concentration upon the adsorption equilibrium(mg/L),V is the volume of a solution(L), Wis the quality of the adsorbent(g), $R_e$ is the adsorption rate, q is the adsorbing capacity（$mg.g^{-1}$）.

*2.2.4. Adsorption isotherm*

Studying on adsorption isotherm is the primary work, it is described using Langmuir and Freundlich adsorption isotherm commonly, through processing the experimental data, some constants can be obtained in the isotherm, these constants can reflect the absorption mechanism, the structure of the adsorbed layer and the surface structure of the adsorbent.

The linear Langmuir equation is shown as formula (3)[11]:

$$c_e/q_e = 1/(aq_m) + c_e/q_m \quad (3)$$

where parameter ce is the equilibrium concentration $(mg.L^{-1})$ ,parameter $q_e$ is the equilibrium adsorption capacity $(mg.g^{-1})$, parameter $q_m$ is the saturated adsorption $(mg.g^{-1})$ ,parameter a is Langmuir constant. Constant a is determined by the adsorption equilibrium constant, it is related with the adsorption heat, the greater the value of constant a is, at low concentration the isothermal curve is more close to the absorption axis, the slope of the isotherm is greater.

The linear Freundlich equation is shown as formula (4):

$$\ln q_e = \ln k + (1/n)\ln c_e \quad (4)$$

Where parameter $c_e$ is the equilibrium concentration $(mg.L^{-1})$; parameter $q_e$ is the equilibrium adsorption capacity $(mg.g^{-1})$; 1/n is the adsorption exponent $(mg.g^{-1})$; parameter K is the Langmuir constant. K is a parameter related to adsorption capacity, n is a parameter related to the strength of surface adsorption.

*2.2.5. Adsorption kinetics*

Adsorption kinetics is the study of adsorption rate and adsorption mechanism, it affects the size of the adsorption equipment and the control of parameters directly, usually. Adsorption kinetics can be fitted with pseudo-first-order equation, pseudo- second-order equation, intra-particle diffusion equation[12].

pseudo-first-order equation: $1/q_t = 1/q_e + K_1/(q_e t)$,

pseudo-second-order equation: $t/q_t = 1/(K_2 q_e^2) + t/q_e$,

intra-particle diffusion equation: $q_t = K_i t^{0.5}$.

where $q_t$ is the adsorption quantity at time t $(mg.g^{-1})$, $q_e$ is the equilibrated adsorption capacity $(mg.g^{-1})$, $K_1$ is the pseudo-first-order constant(min), $K_2$ is the pseudo- second-order constant $(g.mg^{-1}\,min^{-1})$, $K_i$ is the intra-particle diffusion constant $(mg.g^{-1}.min^{-0.5})$ [9].

## RESULTS AND DISCUSSION

### 3.1. *Adsorption of chromium ion*

*3.1.1. Effects of adsorption time on adsorption rate*

Added 1g 60mesh of dark tea residue into 6 groups of 50ml, concentration of 100 mg/L simulated wastewater respectively, adjusted their pH values to 2, put them in a oscillator, at room temperature shocked them for 15min,30min,45min,60min,90min, 120min respectively, took their supernatant after filtering, after adding chromogenic agent, determined its absorbance using a spectrophotometer. Then draw the curve of adsorption time and adsorption rate.

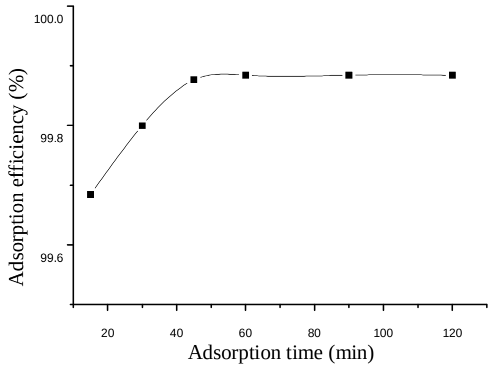


**Figure 1. Effects of adsorption time on adsorption rate**

Figure 1 shows, with the increase of oscillation time, adsorption effect is getting better. In 0~60min adsorption quantity increases obviously, after 60min, the adsorption reaction flattens out, this shows that after 60min the adsorption reaction tends to saturation state, so the best adsorption time is 60min.After 15min, the adsorption rate reaches 99.68%,this shows that the adsorption rate is very high, it is a rapid process.

*3.1.2. Effects of pH value on adsorption rate*

Added 1g 60mesh of dark tea residue into 6 groups of 50ml,concentration of 100 mg/L simulated wastewater respectively, adjusted their pH values to 2,3,4,5,6,7,8 respectively, at room temperature shocked them for 60min, took their supernatant after filtering, after adding chromogenic agent, determined its absorbance. Then draw the curve of pH value and adsorption rate.

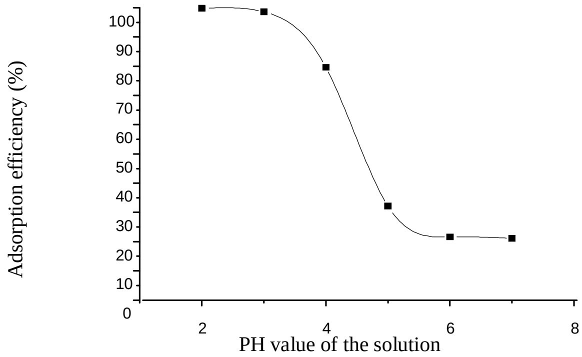


**Figure 2. Effect of initial pH value on adsorption**

Figure 2 shows, the acidity of the solution has great influence on the adsorption effect of dark tea residue, it shows obvious chemical characteristics. The acidity of the solution influences the state of the solute (molecules, ions, complex) and it influences the charge characteristics and chemical characteristics of surface of the adsorbent, thus affect the adsorption effect. When the pH value is in the range of 2-3, The adsorption effect is the best. Dark tea residue has the characteristics of porous, large surface area, so there is physical adsorption, but the adsorption mechanism is complex, it needs to be studied further.

*3.1.3. Effects of dosage of dark tea residue on adsorption rate*

Added 0.1g,0.3g,0.5g, 0.7g,1g 60mesh of dark tea residue into 5 groups of 50ml, concentration of 100mg/L simulated wastewater respectively, adjusted their pH values to 2, at room temperature shocked them for 60min, took their supernatant after filtering, after adding chromogenic agent, determined its absorbance. Then draw the curve of dosage of dark tea residue and adsorption rate.

Figure 3 shows, increasing the dosage of adsorbent is conducive to the adsorption. When dosage of dark tea residue is greater than 0.8g, the adsorption curve starts smoothly, the adsorption reaction is in equilibrium.

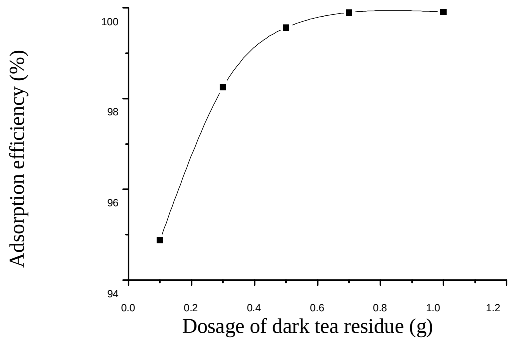


**Figure 3. Effect of dosage of dark tea residue on adsorption**

*3.1.4. Effects of initial concentration of chromium ions on adsorption rate*

Added 1g 60mesh of dark tea residue into 5 groups of 50ml, concentration of 50mg/L, 100mg/L,150mg/L, 200mg/L, 250mg/L simulated wastewater respectively, adjusted their pH values to 2, at room temperature shocked them for 60min, took their supernatant after filtering, after adding chromogenic agent, determined its absorbance. Then draw the curve of initial concentration of chromium ions and adsorption rate.

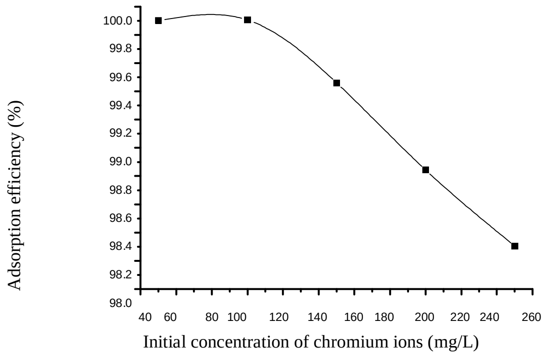


**Figure 4 . Effects of initial concentration of chromium ions on adsorption rate**

Figure 4 shows, when using a certain doses of dark tea residue, the concentration is in the range of 50-100mg/L, the adsorption efficiency increased, but the difference is not big, this shows the dark tea residue has high $Cr^{6+}$ adsorption efficiency in a wide range of concentration.

*3.1.5. Effects of particle size of dark tea residue on adsorption rate*

Added 1g 100mesh, 80mesh,60mesh, 40mesh ,20mesh of dark tea residue into 5 groups of 50ml, concentration of 50mg/L,100mg/L,150mg/L,200mg/L,250mg/L simulated wastewater respectively, adjusted their pH values to 2, at room temperature shocked them for 60min,took their supernatant after filtering, after adding chromogenic agent, determined its absorbance. Then draw the curve of the particle size of dark tea residue and adsorption rate.

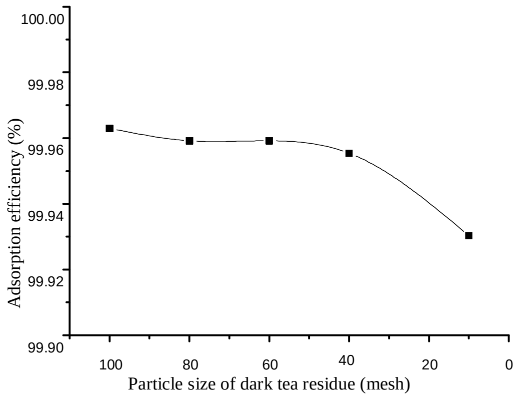


**Figure 5. Effects of particle size of dark tea residue on adsorption rate**

Figure 5 shows, the adsorption rate is related to the particle size of dark tea residue, the smaller the particle size, the higher the adsorption rate. But the adsorption rate is at 99.93%~99.96%, this shows that the particle size of dark tea residue is not the main factors influencing the adsorption efficiency of chromium ion.

**3.2. Adsorption isotherm and adsorption kinetics of chromium ion**

*3.2.1. Adsorption isotherm*

Under the same experimental conditions as 3.14, draw the curve of adsorptive capacity（$mg.g^{-1}$) and equilibrium concentration（$mg.L^{-1}$) , got the adsorption isotherm line(shown in figure 6).

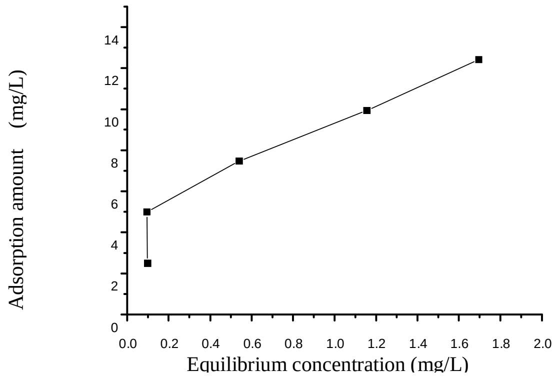


**Figure 6. The adsorption isotherm of Cr(VI)**

Figure 6 shows that, the slope of the initial segment of the isotherm is large, when the concentration increases to a certain value, the adsorption quantity increases slowly, this shows it is conducive to adsorb low concentration of Cr(VI),and it is a kind of preferential adsorption isotherm. The data in figure 6 was fitted using Langmuir Adsorption isotherm and Freundlich adsorption isothermal model, the results are shown in figure 7,figure 8 and table 1.

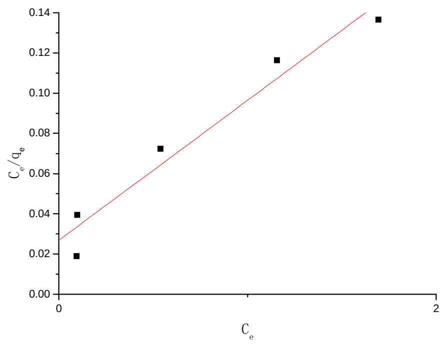


**Figure 7. Langmuir Adsorption isotherm**

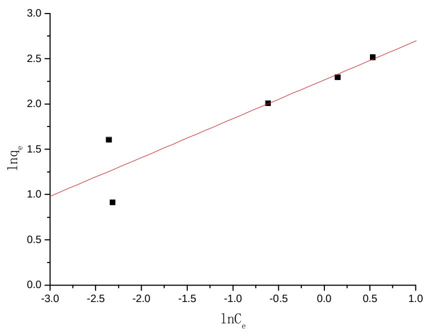


**Figure 8. Freundlieh Adsorption isotherm**

**Table 1. The fitting results of adsorption isotherm**

| adsorption isotherm | Formula | parameter |
|---|---|---|
| Langmuir | $C_e/q_e=0.06957C_e+0.02683$ | $a=2.593,q_m=14.374,r=0.9768$ |
| Freundlich | $lnq_e=0.3290lnC_e+0.4759$ | k=9.64,1/n==0.4286,r=0.91725 |

According to figure 7, figure 8 and Table 1, we can draw the following conclusions:

(1)There is good correlation between the data and Langmuir adsorption isothermal model or Freundlich adsorption isothermal model, the correlation coefficient is 0.9768 and 0.9173,They can be described the adsorption, but

Langmuir isothermal adsorption model follows this pattern better than Freundlich model, this shows the adsorption of dark tea residue on chromium ion is a single molecular adsorption.

(2) From the Langmuir adsorption isotherm parameters we can determine that there is a maximum adsorption capacity in the process of adsorption, the value is 14.37mg/g.

(3) In the Freundlich adsorption isotherm, the parameter n is 2.333, the parameter n is between 2~10, this shows the adsorption reaction is easy to happen and because n>l, this is a preferential adsorption process.

*3.2.2. Adsorption kinetics*

Under the same experimental conditions as 3.11, draw the curve of the adsorptive capacity（$mg.g^{-1}$) and the adsorption time(min),and we got the adsorption isotherm line(shown in figure 9).

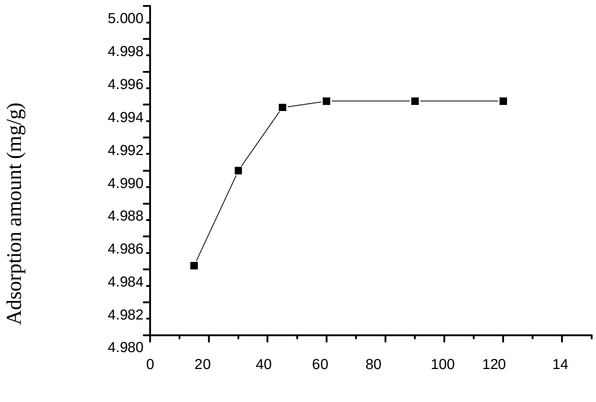


**Figure 9. kinetic curve for Cr(VI)**

Figure 9 shows that, in 45 minutes the adsorption capacity of dark tea residue on chromium ion increases quickly, as the adsorption reaction, adsorption quantity increases slowly, the adsorption reaction reached a balance after 60 min. In short time, The dark tea residue has a good adsorption on Cr (VI), the adsorptive capacity reaches 4.994（$mg.g^{-1}$) ,this shows that, dark tea residue has strong combination on chromium ions.

The data was fitted using pseudo-first-order equation, pseudo-second-order equation and intra-particle diffusion equation, they are shown in Figure 10,Figure 11,Figure 12,the fitting results of adsorption kinetics are shown in table 2.

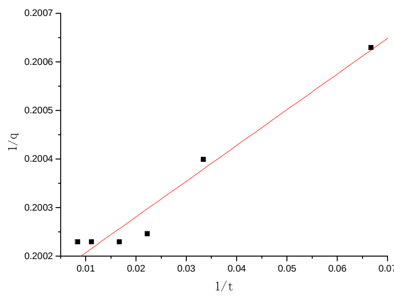


**Figure 10. The curve of pseudo-first-order equation**

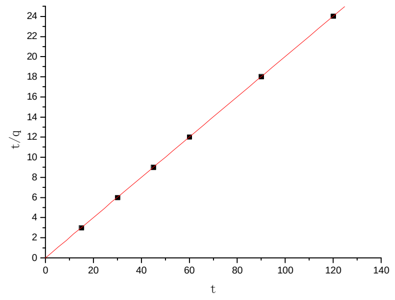


**Figure 11. The curve of pseudo-second-order equation**

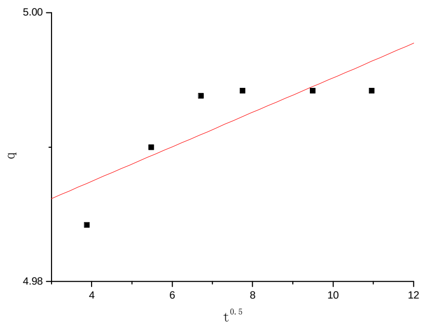


**Figure 12. The curve of intra-particle diffusion equation**

Figure 10, Figure 11 and Figure 12 show that, the linear characteristics of Figure 11 is the best, it is more suitable to describe the experimental results using a pseudo- second-order equation.

**Table 2. The fitting results of adsorption kinetics**

| type of adsorption kinetics | Formula | parameter |
|---|---|---|
| pseudo-first-order equation | $l/q_t$=0.20013/t+0.00735 | $k_1$=0.0367 $q_e$=4.997 r=0.98036 |
| pseudo-second-order equation | $t/q_t$=0.01037t+0.19992 | $k_2$=3.8542 $q_e$=5.0020 r=1 |
| intra-particle diffusion equation | $q_t=0.00128t^{0.5}+4.98232$ | $k_i$=0.00128 r=0.82112 |

Table 2 shows that ,in the fitting results of three kinetic equation, the correlation coefficient of pseudo-second-order equation is 1,it is higher than the correlation coefficient of pseudo-first-order equation and intra-particle diffusion equation, this shows that the adsorption process fits the pseudo-second-order equation, the adsorption rate is influenced by the concentration of Cr (VI), in order to ensure higher adsorption rate, the best adsorption time is 60 min.

## CONCLUSION

(1).The optimum conditions of treatment of wastewater containing chromium using dark tea residue is: the pH value of waste water is 2,the initial concentration of Cr(VI) is 100mg/L, the adsorption time is 60 min, the dosage of dark tea residue is 1 g, the maximum adsorption rate can reach 99.96%.

(2).The adsorption isotherm of dark tea residue on Cr(VI) is a preferential adsorption isotherm, the adsorption conforms with the Langmuir adsorption isotherm, it is a kind of monolayer adsorption, the regression equation is $C_e / q_e = 0.06957C_e + 0.02683$, the correlation coefficient is 0.97679, the saturated adsorption in theory is 14.37mg/g.

(3).The adsorption kinetics curve conforms with pseudo-second-order equation, the pseudo-second-order equation is $t / q_t = 0.01037t + 0.19992$ ,its pseudo-second-order constant is 3.8542g/mg•min, the equilibrated adsorption capacity is 5.0020mg/g, the linear correlation coefficient (r) is 1, it can be supposed that, the adsorption is mainly controlled by the chemical mechanism.

(4).The output of dark tea residue is very high, it can be used in wastewater treatment, and reduce the cost.

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