Depuration of Chromium Wastewater with Coal*

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ABSTRACT The purpose of this paper is to explore a new method of chromium pollution disposal. The best adsorption conditions, such as acidity and temperature etc., have been obtained. In the aqueous solution, coal adsorption to Cr(Ⅵ) is chiefly physical process, and conforms to the Freundlich experiential formula. The relationship between adsorption capacity (m) and time (t) is following: $m = 3.70t(1+2.06t)^{-1}$.

KEYWORDS coal; adsorption / chromium wastewater

0 Introduction

The chromium pollution is mainly from the industrial wastewater including leather processing, chromium-plating and manufacturing chromic compounds (such as chromic anhydride and potassium dichromate). The pollution endangers seriously man's health and growth of plant[1,2], and its harmness is latent and long-term. After the accumulation of ion state chromium reaches a certain amount, it will cause various illnesses, including cancer. Thus, chromium pollution disposal becomes imperative. In this paper, we use coal to depurate draining chromium wastewater from chemical plant at the aim of finding the most appropriate pH value and temperature of the solution during the adsorption process.

1 Experiment

The wastewater was supplied by the chemical plant producing chromic anhydride and potassium dichromate, and the content of Cr(Ⅵ) is about 2000 $mg \cdot dm^{-3}$. The wastewater was pretreated with H_2O_2 at $pH = 12$ before disposal. The concentration of Cr(Ⅵ) is determined by means of titration and 721 spectrophotometry.

Coal A and coal D (anthracite) are from 20112 coal tunnel, Baijiao Coal Mine, Gong County, Sichuan Province. Coal A is sampled from the edge of outburst site. The distance between sampling site of coal A and that of coal D is about 20 meters. Table 1 lists industrial analysis data, porosity

* 收文日期 1996-07-14
重庆大学曾川优秀青年教育基金(97062)和国家教委博士点基金(9461107)资助项目

(φ_{Hg}) and apparent density (ρ_{Hg}) of coal. Coal samples are groud into powder of -80 mesh. Activated carbon is chemical agent.

Table 1　Industrial analysis, porosity and apparent density of coals　%

sample	M_{ad}	A_d	V_{daf}	φ_{Hg}	ρ_{Hg}/g · cm^{-3}
coal A	0.37	24.49	11.15	4.65	1.552
coal D	0.36	28.40	11.14	3.84	1.612

* M_{ad}——content of water; A_d——content of ash; V_{daf}——content of volatiles

Apsorption capacity of adsorbent is calculated by equation (1):

$$m = \frac{C_0 - C}{W} V \tag{1}$$

Where m is the adsorption capacity of coal or activated carbon (mmol · g^{-1}), C_0 and C are respectively concentration of $Cr_2O_7^{2-}$ before and after adsorption (mol · dm^{-3}), W is the mass of adsorbent (g), and V is the volume of the wastewater (cm^3). The coal samples and activated carbon must be weighed by analytical balance.

The effect of various factors on adsorption capacity have been studied. The factors include the ratio of adsorbent mass to wastewater volume (SW, mg/10cm^3), temperature, acidity, time (t, h) and concentration of Cr(Ⅵ). Volume of wastewater is 50 cm^3 when the effect of the solution's concentration is considered, and it is 40 cm^3 at other cases.

2 Results and Discussion

2.1 The effect of SW on adsorption capacity

SW is the giving mass (milligram) of coal or activated carbon in 10 cm^3 original wastewater. The adsorption experiments of coals and activated carbon have been finished in various SW. The experiment conditions are ambient temperature, pH = 1 and t = 1 hour. The results are shown in Fig. 1.

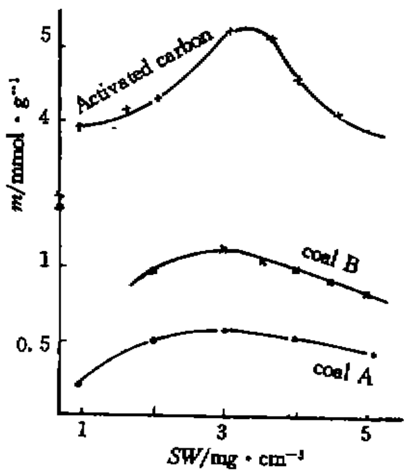

Fig. 1　The effect of SW on m

As seen in Fig. 1, the adsorption capacity of activated carbon and two pieces of coal reached the maximum when SW is 30 mg/10cm^3. Thus, the following experiments are completed in SW = 30. It is quite evident that the adsorption ratio increases with the increase of SW. The adsorption capacity of activated carbon is much larger than that of coal due to the great difference in specific surface areas of two types of adsorbents.

As shown in Fig. 1, the adsorption capacity of coal A is less than that of coal D. It may be explained as follows. Mercury intrusion experiments[3] show that specific surface areas of ink bottle model for coal A and coal D are 0.909 $m^2 \cdot g^{-1}$ and 0.652 $m^2 \cdot g^{-1}$ respectively. It means that the pores of ink bottle in coal A are more than those in coal D. Because the CO_2 apparent surface area (S_{CO_2}) of coal A is the largest of 9 samples in the same seam[3], the amount of micropores in coal A is more than that in coal D. Owing to the relatively large space structure of $Cr_2O_7^{2-}$, it is difficult that Cr(Ⅵ) enters into the micropore or ink bottle pore and is adsorbed by these pores. Thus, adsorption ability of coal D is stronger than that of coal A.

2.2 The effect of pH on adsorption capacity

The adsorption capacity of coal A to Cr(Ⅵ) under different acidity condition (adsorption time is 1 hour) is shown in Fig. 2. It's seen in Fig. 2 that the adsorption capacity reaches the maximum while the initial pH of wastewater is about 1.2. It is consistent with the result of Liu[4].

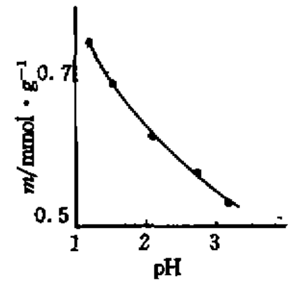

Fig. 2 Relationship between pH and m

2.3 Relationship between adsorption capacity and temperature

In order to inspect the relationship between the adsorption capacity and the solution temperature, adsorption experiments in different temperatures have been finished. The results include the adsorption capacity, the adsorption ratio and rate constant of coal D are summarized in Table 2. The adsorption ratio (X) in the Table 2 is calculated with equation (2)

$$X = \frac{C_0 - C}{C_0} \times 100\% \tag{2}$$

and the rate constant (k) by using equation (3)

$$\ln \frac{C_0}{C} = kt \tag{3}$$

Table 2 The effect of temperature on m

T/K	293	313	333	353
X/(%)	25.6	32.2	37.6	43.1
m/mmol · g^{-1}	1.417	1.787	2.085	2.338
k/h^{-1}	0.310	0.392	0.496	0.586

As shown in Table 2, rate constant increases with the increase of temperature. The straight line relationship between $\ln k$ and T^{-1} is shown in Fig. 3. It indicates that the effect of temperature on the rate constant obeys the Arrhenius experiential formula:

$$\ln k = \ln k_0 - \frac{E_a}{RT} \tag{4}$$

where k_0 is apparent preexponential factor (h^{-1}), E_a is the apparent activation energy ($J \cdot mol^{-1}$) and T is the thermodynamical temperature (Kelvin). Using the One Variable Linear Regression method, we obtained the following results: $k_0 = 13.758\ h^{-1}$, $E_a = 9.245\ kJ \cdot mol^{-1}$ and correlation coefficient $r = 0.99933$.

As we know, the activation energies for most of chemical reactions are 50～250 $kJ \cdot mol^{-1}$. But E_a of coal adsorbing Cr(Ⅵ) is only 9.245 $kJ \cdot mol^{-1}$. Thus, it might be thought that the adsorbing action to Cr(Ⅵ) on coal is mainly physical process. Of course, it doesn't mean that there is no chemical reaction between coal and Cr(Ⅵ) in the aqueous solution. In fact, coal may be oxidated by $Cr_2O_7^{2-}$ while the metamorphism degree of coal is less than that of this coal sample for studying, the content of Cr(Ⅵ) is relatively large and the pressure of the system is high (such as 7 MPa).

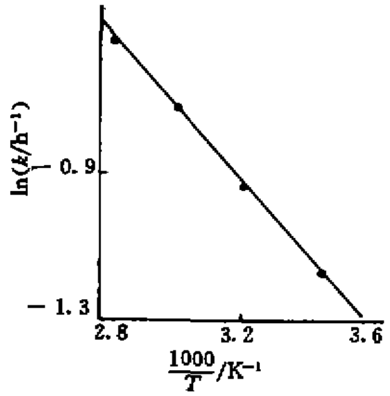

Fig. 3 Relationship between $\ln k$ and T^{-1}

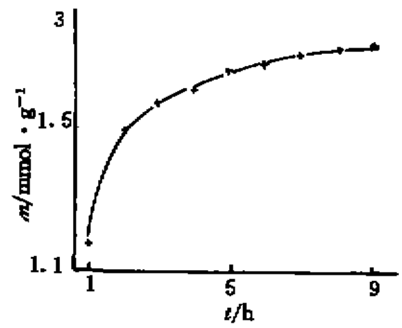

Fig. 4 The effect of t on m

2.4 The effect of the adsorption time on the adsorption capacity

The relation between the adsorption capacity of coal D and the adsorption time is shown in Fig. 4. It's seen from Fig. 4 that the time of reaching adsorption equilibrium is about 5 hours.

The curve in Fig. 4 is very similar to that of adsorption capacities v_s pressures in Langmuir isothermal adsorption, so we use equation (5) to describe relationship between m and t

$$m = \frac{At}{1 + Bt} \tag{5}$$

where A and B are experiential constants. After rewriting equation (5) as: $t/m = 1/A + Bt/A$, the regression results are the following: $m = \frac{3.70t}{1+2.06t}$ and the correlation coefficient $r = 0.99989$. Equation (5) is actually the kinetics equation of adsorption.

2.5 The relationship between the adsorption capacity and the concentration of Cr(Ⅵ)

In the various concentrations of wastewater, the adsorption ratio and the capacity of coal A are listed in Table 3. Because adsorbing solute from solution on solid obeys Freundlich formula, we use equation (6) to study the relation between m and C

$$\frac{m}{m^\theta} = A\left(\frac{C}{C^\theta}\right)^n \qquad (6)$$

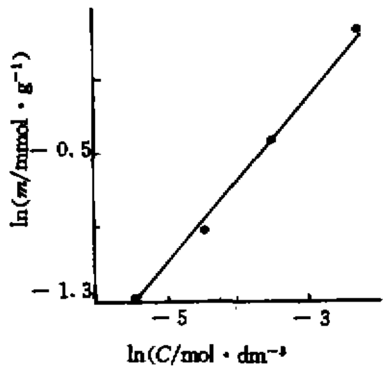

Fig. 5 Adsorption isotherm

where A and n are experiential constants, m^θ (1 mmol · g^{-1}) and C^θ (1 mol · dm^{-3}) are respectively standard adsorption capacity and concentration. The plot of $\log\left(\frac{m}{m^\theta}\right)$ v_s $\log\left(\frac{C}{C^\theta}\right)$ is shown in Fig. 5. The straight line shown in Fig. 5 yields $A = 18.432$ and $n = 0.4818$ with a correlation coefficient of 0.9945.

As seen in Talbe 3, the adsorption ratio decreases with the increase of concentration. When the concentration of $Cr_2O_7^{2-}$ in the wastewater is 3.526×10^{-5} mol · dm^{-3}, the adsorption ratio of coal A is 88.9% and that of coal D is 92.8%.

Table 3 Adsorption capacity of coal A in various concentration of Cr(Ⅵ)

$10^4\ C_0$/mol · dm^{-3}	52.89	5.289	1.058	0.353
$10^4\ C$/mol · dm^{-3}	43.290	3.189	0.366	0.038
X/%	17.20	39.70	65.40	88.92
m/mmol · g^{-1}	1.502	0.349	0.113	0.052

3 Conclusions

In this paper, we have studied the various effective factors on the adsorption capacity of coal to Cr(Ⅵ), and obtain the following conclusions.

1) The suitable adsorption conditions are SW of 30 mg/10cm^3, pH of 1 and the adsorption time of 5 hours.

2) In Cr(Ⅵ) aqueous solution, the adsorption of coal to Cr(Ⅵ) is chiefly physical process, and activation energy of adsorption is 9.245 kJ · mol^{-1}. Kinetics equation of adsorption is following:

$$m=\frac{3.70t}{1+2.06t}$$

3) When the concentration of the wastewater is comparatively low, the adsorption ratio reaches 90% or so.

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煤对含铬废水的净化

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摘　要　用煤对含铬废水进行了净化，得到了最佳的固液比、酸度等吸附条件，考察了温度对净化的影响。在水溶液中，煤对Cr(Ⅵ)的吸附主要为物理过程，并遵从Feundlich经验公式；吸附量与时间的定量关系为：$m=3.70t(1+2.06t)^{-1}$.

关键词　煤；吸附／含铬废水

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