Adsorption and Separation of Chromium from Electroplating wastewater with Banana Stem Adsorbent

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Abstract. The preparation process of waste banana stem adsorbent and the conditions of removing Cr were studied. The experiment results showed that the saturated adsorption capacity of banana stem adsorbent with phosphoric acid reached 5.84mg/g, over 95% of Cr(VI) and 70% of total Cr can be removed from water with banana stem adsorbent at 20~30 °C and pH=2~3. When used for cleaning model electroplating wastewater, it was found that the removal effect of Cr with banana stem adsorbent was apparently higher than the commercial activated carbon. The concentration of heavy metals can meet the emission standard of electroplating wastewater after treated with banana stem adsorbent.

Introduction

Banana is the most popular fruit, because a banana tree can only grow one ear of fruit , so the waste banana trees were always produced with the harvest of banana, and the weight of waste banana trees were almost equal to the weight of banana . At present, these waste banana trees were mainly discarded in the field randomly, it often take a very long time for corrosion and degradation of banana trees under natural conditions, the process will not only pollute environment, but also cause serious insect pest. On the other hand, banana trees are also valuable resource containing natural fiber, which have been widely used for paper industry, spinning, polymer reinforcing material[1]. Nevertheless, the recycling of banana in these fields requires complicated technologies and equipment, so their industrial applications were greatly limited in past time. Recently, research on preparation of low-cost wastewater cleaning agent with agricultural and forest wastes has become an important development direction of high-efficiency utilization of agricultural and forest wastes. Various agricultural wastes[2], such as corn stalks, straw, wheat-straw and bagasse are most common raw materials preparing wastewater cleaning and adsorbing agents. Research[3] pointed out banana tree is mainly composed of cellulose, hemicellulose and lignin. Total content of these three components exceeds 90%. Stem of banana trees is actual cauloid formed with multilayer tile-shaped sheath overlapping. It has loose and porous internal structure, so it is the ideal raw material to prepare adsorbing materials. In this study, preparations of adsorbent with banana trees were studied and its effect in processing electroplate discharged wastewater was studied.

Materials and Methods

Leaves were removed from banana stems. After most water was eliminated by an extractor, further was dried for 2h at 105˚C , and then grinded into particles (diameter<0.1mm), the model electroplating wastewater used in this study was prepared according the composition of real electroplate discharged wastewater. All reagents used in this study were analytical pure.

50g of banana stem powder was put into a beaker and reacted with aqueous solution of modifier for 24h. then powder were filtered and rinsed to neural with distilled water , finally dried for 2h at 105˚C, banana stem adsorbent was prepared. .

10g of banana stem adsorbent was put in a 250ml conical flask, then 100mL water containing Cr(VI) was also added and the mixture was oscillated in thermostatic waterbath for 2h. According to

GB7467-87 and GB7466-87, Cr(VI) and total Cr concentration in the aqueous solution were tested by the color rendering method of diphenyl carbonyl dihydrazide.

Results and Discussions

Preparation of Adsorbent

The banana stem adsorbent unmodified was applied directly to adsorb metal ions. It is not only has a smaller adsorption capacity, but also pectin, humic acid and lignin in banana stem are easy to be dissolved into water, thus deepening the water color and increasing organic concentration, this will cause secondary pollution. Modifiers like acid, alkali and amine can facilitate crosslinking, stabilization and functionalization of adsorbent, thus improving the adsorption performance. Processing effects of different chemical modifiers are shown in Table 1.

Table 1 Modified experimental results of banana stem-based adsorbent

Modifiers	Phosphoric acid	Sulfuric acid	Nitric acid	Ethylenediamine	Sodium hydroxide
Growth rate of adsorption capacity [%]	22.54	13.32	8.06	6.78	12.43
Dissolving of color components	Few	Few	Few	Many	Many

Experimental results demonstrated that after processed by 0.10 mol/L phosphoric acid, sulfuric acid, nitric acid or 1.00% sodium hydroxide and ethylenediamine, the adsorpton capacity of adsorbent is increased obviously. Among them, phosphoric acid has the best effect. Dissolving content of color components declines dramatically and stability is enhanced sharply. Therefore, phosphoric acid is a relatively appropriate modifier. 0.1mol/L phosphoric acid and solid-to-liquid ratio was 1:5.The isothermal adsorption curve of banana stem adsorbent at 25˚C is shown in Fig.2.
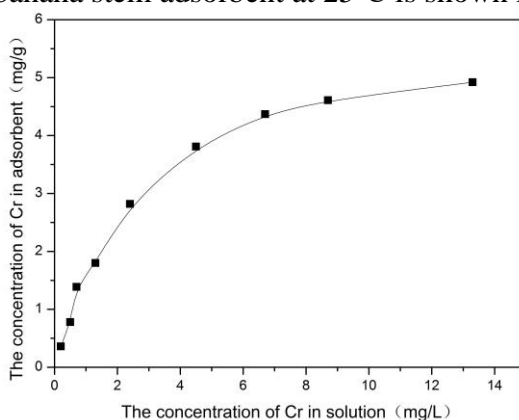

Fig.1 Isothermal adsorption curve of adsorbent (25˚C)

According to experimental results (Fig.1), the isothermal adsorption curve of banana stem adsorbent agrees well with that of the first type. It can be calculated by following Langmuir equation[4]:

$$\frac{C_e}{q_e} = \frac{1}{Q_m \times b} + \frac{C_e}{Q_m}$$

where.

q$_e$ is equilibrium adsorption capacity (mg/g),

c$_e$ is equilibrium concentration (mg/L),

Q$_m$ is saturated adsorption capacity of monomolecular layer (mg/g).

A straight line of Ce was gained based on $\frac{Ce}{Qm}$. It can be calculated from intercept ($\frac{1}{Qm} \times \frac{1}{b}$) and slope ($\frac{1}{Qm}$) of the straight line that Q$_m$=4.89 mg/ g, r$_1$ = 0. 97976, and q$_e$= 5.84mg/g

The effect of adsorption conditions on the removal rate of Cr

pH and temperature are main influencing factors on adsorption efficiency. In this experment, 10g adsorbent and 100mL 1mg/L Cr(VI) water were added into a 250ml conical flask. Solution pH was

adjusted to the set value with 0.1mol/L sulfuric acid and NaOH solution. Next, the solution was oscillated in water bath at the set temperature for 2h. The experimental results of separating Cr from water are shown in Fig.2.
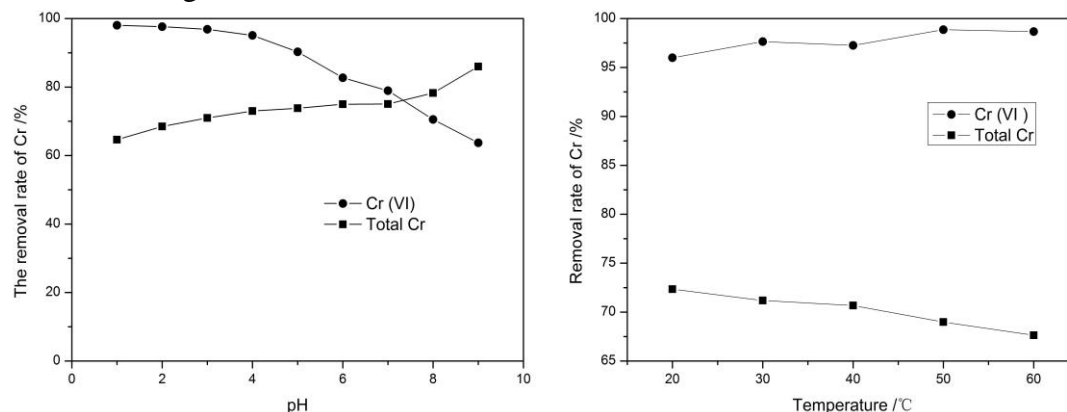

Fig.2 Influences of adsorption conditions on removal rate of Cr

In Fig.2, it can be founded that pH can significantly influence the removal rate of Cr(VI). With the increase of pH, the removal rate of Cr(VI) reduces quickly. This is mainly because most of Cr(VI) in solution exists as $HCrO_4^-$ under strong acid conditions, and $HCrO_4^-$ can form covalent bonds with hydroxyls and carboxyls of the banana stem adsorbent, so it is a chemical adsorption process. As pH further increases, some of $HCrO_4^-$ will turn into $Cr_2O_7^{2-}$,which has larger radius. The affinity between functional groups of adsorbent and $Cr_2O_7^{2-}$ is weaker than that of affinity between functional groups of adsorbent and OH^-, so reducing adsorption capacity of Cr(VI). Therefore, high pH is disadvantageous for removal of Cr (VI). The affects trend of temperature on the removal rate of Cr(VI) is different from pH, the removal rate of Cr(VI) is positively related with temperature. The removal rate of Cr(VI) increases with temperature, but high temperature is generally unbeneficial of adsorption process, indicating that reduction of Cr (VI) concentration in aqueous solution is not only caused by adsorption of banana stem adsorbent.

By analyzing the concentration of total Cr and Cr^{3+} in adsorbed solution, it was found that the removal rate of Cr (VI) exceeds 98% and the removal rate of total Cr can only reach 60~70% under conditions of pH=2~3 and at 30˚C. This reflects that reduction of some Cr (VI) in solution is not contributed by adsorbent, but is the consequence of conversion into Cr^{3+}. Cr^{3+} is are very difficult to form covalent bonds with adsorbent, it is separated by mainly ion exchange and physicl adsorption. Although low pH is beneficial for removal of Cr (VI), protonation of tannin in banana tree will occur if the acidity of solution is too high, which will weaken the static attractions between Cr^{3+} and adsorbent, and reduce ion exchange between tannin molecules and Cr^{3+}. Therefore, pH=2~3 is appropriate for adsorption separation of Cr (VI) and Cr^{3+}. At the conditions, the removal rate of Cr(VI) reaches over 95% and the removal rate of total Cr is higher than 70%. On the other hand, although high pH is disadvantangeous for adsorption separation of Cr (VI), it is conducive for Cr^{3+} to form precipitation of Cr (OH)$_3$ with the increase of OH^- concentration. Thus, Cr^{3+} can be removed by increasing pH of solution when there's few Cr(VI) amount.

Based on above analysis, Cr(VI) removal from water by banana stem absorbent includes two processes: one is adsoption separation through covalent bonds between anions (e.g. $HCrO_4^-$ and $Cr_2O_7^{2-}$) and functional groups of adsorbent. The other is Cr (VI) reduction into Cr^{3+} by reducibility matters in adsorbent. Since Cr^{3+} can't be adsorbed completely, some parts of them will stay in aqueous solution. Both processes are chemical exothermic process. Therefore, removal rate of Cr(VI) increases with the increase of temperature. Although Cr^{3+} toxicity is far lower than Cr(VI), it still remains quite high toxicity, so Cr^{3+} must also be removed from water as much as possible. According to experimental results on the effect of temperature and pH on removal rate, it is beneficial for removal of Cr (VI) at lower pH range and beneficial for precipitation separation of Cr^{3+} at higher pH range. Therefore, after adsorption separation under 20~30˚C and pH=2~3, followed by a precipitation , over 80% of total Cr and 95% of Cr (VI) can be successfully removed from water by

banana tree adsorbent.

Adsorption experiment of electroplating wastewater

Heavy metals are main pollutants of electroplating wastewater. Generally, they are treated by restoring, flocculation and precipitation. Due to the existence of reaction equilibrium, heavy metal concentration in wastewater discharged from electroplating factory still exceed the emission standard. Therefore, before this kinds of wastewater discharge into the environment, an additional adsorption operation is necessary in the end of treating process. At present, the most commonly adsorbent used for electroplating wastewater is active carbon. Although active carbon has very high adsorption capacity, it is very expensive. Substitute low-cost agricultural and forest waste adsorbent for active carbon, it not only can reduce cost of treating wastewater, but also can further reduce the concentration of Cr (V) by reducibility component in adsorbent. In this study, a banana stem adsorbent was used for treating modell electroplating wastewater. pH of the wastewater was adjusted to about 2 with sulfuric acid. Next, 10L water was suppled by the adsorption separation tube (diameter=2cm and height=20 cm) filled with banana tree adsorbent. Heavy metal concentration of wastewater from the bottom of adsorption column is shown in Table 2.

Table 2 Adsorption experimental results of electroplating wastewater [mg/L]

Heavy metal	Cr(V)	Total Cr	Pb	Ni	Cu	Zn	Chromaticity
Inflow	1.34	2.87	0.75	0.98	1.06	3.45	34
Outflow(banana stem)	0.06	0.28	0.11	0.39	0.34	0.57	42
Outflow(active carbon)	0.104	0.37	0.14	0.36	0.23	1.08	26
Emission limit *	0.1	0.5	0.2	0.5	0.5	1.5	<40

*this is emission limit of heavy metal ion concentration in electroplating wastewater in non-Pearl River Delta of Guangdong Province (DB 44/1597-2015).

Because heavy metal concentrations in electroplating wastewater pre-processed are relatively low, no precipitation operation was arranged. Experimental results in Table 2 demonstrated that the banana stem adsorbent can not only adsorb Cr, but also can remove Pb, Ni, Cu and Zn well. The total removal effect is equal to active carbon. The removal rate of Cr (V) is significantly greater than that of active carbon. Experiment data revealed that the water volume treated by banana stem adsorbent get about 80% of that by active carbon at the same adsorption conditions, heavy metal concentration in effluent from banana stem adsorbent is apparently greater than that from active carbon. Since the banana stem adsorbent is far cheaper than active carbon, it still possesses promising economic benefits to substitute banana stem adsorbent for active carbon.

Conclusions

(1) The adsorption capacity of Cr(V) of the banana stem absorbent prepared reaches 5.84mg/L. The appropriate adsorption conditions are pH=2~4 and 20~30˚C.

(2) The prepared banana stem absorbent is equivalent to active carbon in term of cleaning of electroplating wastewater. Heavy metal ion concentration in model electroplating wastewater treated with banana stem absorbent can meet the emission requirements of electroplating factory .

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