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Advanced Treatment for Chromium-Containing Wastewater with Modified Fly Ash Charcoal-chitosan

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ABSTRACT

In this paper, we used fly ash as the main raw material, under the conditions of the water bath to prepare three kind of modified fly ash: Na-fly ash, K-fly ash and Ca-fly ash, and then we studied their removal of chromium ions and tested the effects of dosage, temperature, mixing time and pH value of modified fly ash on characteristic of composite adsorbent. The experimental results show that: in the three kind of modified fly ash, Ca-fly ash has strong adhesive properties, when it was used to process Chromium-containing wastewater, the removal rate of Chromium ion reached 39.32%, and when the modified fly ash-composite Chitosan was used to process Chromium-containing wastewater, the adsorption rate on Cr (VI) reached 40.67%.

Key words: Modified fly ash, Charcoal-chitosan, Compound absorbent, Chromium- Containing Wastewater

INTRODUCTION

Source, Characteristics and Harmfulness of Chromium-containing wastewater

Chromium and its compounds are widely used in industry, Metallurgy, chemical engineering, mineral engineering, electroplating, chromium plating and a series of industries will produce large amounts of wastewater containing chromium [1-5]. Chromium is a silver white metal, it is non-toxic, and its chemical properties are very stable. Stainless steel contains more than 12% chrome, the stainless steel containing chromium is non-toxic, but the chromium ion in the chromium compound is highly toxic.

Chromium compounds are present in the form of divalent chromium ions, trivalent chromium ions and hexavalent chromium ions [6-7], Chrome can invade the human body through the skin, the digestive tract, and the respiratory tract, Chromium compounds can cause cancer [8-13]. The harm of chromium to the human body has attracted the attention of the world, in China stipulates that the highest concentration of chromium in industrial waste water is defined as 0.5mg/L, so the chromium containing wastewater must be processed before discharge.

Source, Characteristics and Harmfulness of fly ash

Ash Fly is a kind of solid waste produced by coal combustion in power plant, it is a kind of porous, loose, solid composite, its main components are SiO_2, Al_2O_3, Fe_2O_3, FeO, CaO and so on, the morphology and surface structure of the ash fly particles are similar to that of activated carbon, it is porous and it has a larger specific surface area, its porosity is about 75%~60%, its specific surface area can reach 2700 ~ 3500cm^2/g.

Introduction of Chitosan

Chitosan is a kind of natural, safe, non-toxic organic high polymer which has the antibacterial activities, in dilute acid, Chitosan can be hydrolyzed, but it is difficult to dissolve in water when pH value is over 6.5, which limits its application, it is an alkaline polysaccharide in natural polysaccharides, Chitosan has complex chemical properties[14,15], Chitosan has a unique molecular structure, which contains a large number of active functional such as groups amino and hydroxyl groups, usually Chitosan has α,β two isomers, the molecular structure of chitin

and Chitosan is shown in Figure 1.1 :

Figure 1: Molecular structures of chitin and Chitosan

Chitosan as a kind of new natural high polymer flocculants was widely used in water treatment. Compared with other flocculant, Chitosan derived flocculant has the advantages of high adsorption capacity, good selectivity, low cost and easy operation, it has a good prospect in industrial application.

EXPERIMENTAL SECTION

Materials and reagents

Experimental reagents:NaOH,KCl,$CaCl_2$, potassium dichromate, concentrated sulfuric acid(H_2SO_4), concentrated hydrochloric acid(HCl),H_3PO_4,CH_3COOH, acetone(CH3COCH3), Diphenylcarbazide ($C_{13}H_{14}N_4O$), Chitosan.

Experimental apparatus: Visible spectrophotometer(T6, Beijing Purkinje General Instrument Co.,Ltd.), circulating water vacuum pump, digital drier, constant temperature stirring bath, electronic balance, thermostatic oscillator.

Preparation of fly ash

We washed fly ash with distilled water for 3-4 times, and mixed it for 30 minutes and made it precipitate, then removed the upper part of the turbid liquid. Then we dried the fly ash after cleaning in an oven at 105℃ for 24 hours, ground it into powder, cooled it to room temperature, classified it with 200 mesh respectively, and put it in a sealed bag.

Single factor experiment on modified fly ash

Test the effects of dosage of NaOH on characteristic of fly ash:

Took 5g of fly ash in six 250ml erlenmeyer flasks, added 20ml、40ml、60ml、80ml、100ml、120ml of NaOH solution, their mass ratio of fly ash and NaOH were 6.25:1,3.13:1, 2.08:1,1.56:1,1.25:1 and 1.04:1,heated them in water-bath at a temperature of 100℃ for 2 hours, cooled it to room temperature, and added HCl, filtrated them, and washed them with deionized water, dried them at a temperature of 110℃for 2 hours, and we got Natrium-modified fly ash. Added 0.5g of Natrium-modified fly in 25ml Chromium-containing wastewater, and detected the removal rate of chromium ions.

Test the effects of dosage of KCl on characteristic of fly ash:

Took 5g of fly ash in six 250ml erlenmeyer flasks, added 5ml, 10 ml,15 ml, 20 ml, 25 ml and30 ml of KCl solution, their mass ratio of fly ash and KCl were 13.5:1, 6.6:1, 4.5:1, 3.4:1, 2.7:1 and 2.2:1:1, heated them in water-bath at a temperature of 100℃ for 2 hours, cooled it to room temperature, and added HCl, filtrated them, and washed them with deionized water, dried them at a temperature of 110℃for 2 hours, and we got Potassium-modified fly ash. Added 0.5g of Potassium-modified fly in 25ml Chromium-containing wastewater, and detected the removal rate of chromium ions.

Test the effects of dosage of $CaCl_2$ on characteristic of fly ash:

Took 5g of fly ash in six 250ml erlenmeyer flasks, added 5ml, 10 ml, 15 ml, 20 ml, 25 ml and30 ml of KCl solution, their mass ratio of fly ash and $CaCl_2$ were 8.93:1, 4.50:1, 3.00:1, 2.25:1, 1.80:1 and 1.50:1, heated them in water-bath at a temperature of 100℃ for 2 hours, cooled it to room temperature, and added HCl, filtrated them, and washed them with deionized water, dried them at a temperature of 110℃ for 2 hours, and we got Calcium-modified fly ash. Added 0.5g of Calcium-modified fly in 25ml Chromium-containing wastewater, and detected the removal rate of chromium ions.

Test the effects of heating time on characteristic of fly ash:

Took 5g of fly ash in six erlenmeyer flasks, added 20ml of $CaCl_2$, heated them in water-bath at a temperature of 100℃ for 60 min, 90 min, 120 min, 150 min, 180 min and 210 min, cooled it to room temperature, and added HCl, filtrated them, and washed them with deionized water, dried them at a temperature of 110 ℃ for 2 hours, and we got Calcium-modified fly ash. Added 0.5g of Calcium-modified fly in 25ml Chromium-containing wastewater, and detected the removal rate of chromium ions, then we can got the optimum heating time on characteristic of modified

fly ash.

Test the effects of temperature on characteristic of fly ash:
Took 5g of fly ash in six erlenmeyer flasks, added 20 ml of $CaCl_2$, heated them in water-bath at a temperature of 60 ℃, 70 ℃, 80 ℃, 90 ℃, 100 ℃ and 110 ℃ for 120 min, cooled it to room temperature, and added HCl, filtrated them, and washed them with deionized water, dried them at a temperature of 110 ℃ for 2 hours, and we got Calcium-modified fly ash. Added 0.5g of Calcium-modified fly in 25ml Chromium-containing wastewater, and detected the removal rate of chromium ions, then we can got the optimum temperature on characteristic of modified fly ash.

Experiment of modified fly ash-Chitosan
Test the effects of dosage of modified fly ash on characteristic of composite adsorbent:
Weighed 1g of Chitosan, added right amount of 1% acetic acid solution, mixed it, added 5g,10g,15g,20g,25g and 30g of optimum modified fly ash, their mass ratio of fly ash and $CaCl_2$ were 5:1, 10:1, 15:1, 20:1, 25:1 and 30:1,mixed them for 2 hours, dried them at a temperature of 110 ℃ for 2 hours, ground them and classified them with 200 mesh respectively, then we can get modified fly ash composite Chitosan adsorbent. Added 0.5g of Calcium-modified fly in 25 ml Chromium- containing wastewater, and detected the removal rate of chromium ions, then we can got the optimum dosage on characteristic of modified fly ash.

Test the effects of mixing time on characteristic of composite adsorbent
Weighed 1g of Chitosan, added right amount of 1% acetic acid solution, mixed it, took six 250 ml erlenmeyer flasks, and added fly ash and Chitosan solution according to the best quality ratio, mixed these 6 erlenmeyer flasks 60 min, 90 min, 120 min, 150 min, 180 min, 210 min respectively, dried them at a temperature of 110 ℃ for 2 hours, ground them and classified them with 100 mesh respectively, then we can get modified fly ash composite Chitosan adsorbent. Added 0.5g of Calcium-modified fly in 25ml Chromium- containing wastewater, and detected the removal rate of chromium ions, then we can got the optimum mixing time on characteristic of modified fly ash.

Effects of various factors on treatment of chromium containing wastewater by using composite adsorbent
Effects of dosage on treatment of chromium containing wastewater
Made up 1000 ml of concentration of 1mg/L chromium containing wastewater, added 25 ml of chromium containing wastewater in 6 erlenmeyer flasks, then added 0.05g, 0.15g, 0.25g, 0.35g, 0.45g, 0.55g of composite adsorbent, carried out them in a water bath at a temperature of 25℃ for 2 hours, precipitated them for 30min, and detected the removal rate of chromium ions.

Effects of mixing time on treatment of chromium containing wastewater
Made up 1000 ml of concentration of 1mg/L chromium containing wastewater, added 25 ml of chromium containing wastewater in 6 erlenmeyer flasks, then added 0.25g of composite adsorbent, carried out them in a water bath at a temperature of 25 ℃ for 30 min, 60 min, 90 min, 120 min, 150 min, 180 min, precipitated them for 30 min, and detected the removal rate of chromium ions.

Effects of temperature on treatment of chromium containing wastewater
Made up 1000 ml of concentration of 1mg/L chromium containing wastewater, added 25 ml of chromium containing wastewater in 6 erlenmeyer flasks, then added 0.25g of composite adsorbent, carried out them in a water bath at the temperature of 15℃, 20℃, 25℃, 30℃, 35℃, 40℃ for 90 min, precipitated them for 30 min, and detected the removal rate of chromium ions.

Effects of pH value on treatment of chromium containing wastewater
Made up 1000 ml of concentration of 1mg/L chromium containing wastewater, added 25ml of chromium containing wastewater in 6 erlenmeyer flasks, then added 0.25g of composite adsorbent, adjusted the pH value of waste water to 1, 3, 5, 7, 9, 11 by using NaOH and HCl, carried out them in a water bath at the temperature of 25℃ for 90 min, precipitated them for 90 min, and detected the removal rate of chromium ions.

RESULTS AND DISCUSSION

Experimental results and analysis
Experimental results and analysis of modified fly ash
The curve of removal effect of chromium ion by three kinds of modified fly ash was drawn, it is shown in Figure 3:

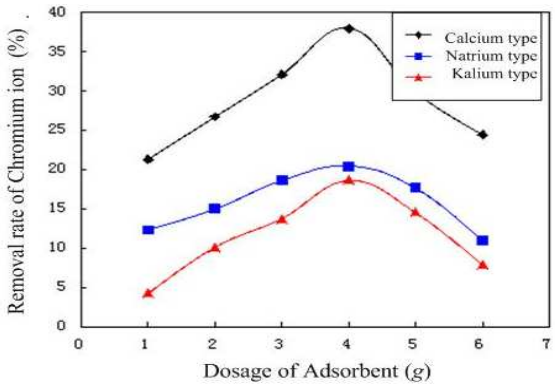

Figure 2: Removal rate of chromium ion by three modified ash fly

Effects of dosage of NaOH on characteristic of fly ash

Figure 3.2 shows that, with the increase of the amount of NaOH, the removal rate of chromium ion by modified ash fly increases first and then decreases, when the dosage of NaOH is 80ml, the removal rate of chromium ions by Na-modified ash fly reaches the maximum value, it is 20.45%, when the amount of NaOH was increased, the removal rate decreased gradually. This is because NaOH can stimulate the activity of SiO_2 and fly in ash Al_2O_3, it improved the activity of ash fly greatly. When the dosage of NaOH is too high, the ash fly will plug the adsorption pore, so the adsorption capacity decreased. So the weight ratio of ash fly and NaOH should be 1.56:1.

Effects of dosage of KCl on characteristic of fly ash

Figure 2 shows that, with the increase of the amount of KCl, the removal rate of chromium ion by modified ash fly increases first and then decreases, when the dosage of KCl is 20ml,the removal rate of chromium ions by K-modified ash fly reaches the maximum value, it is 18.65%, when the amount of KCl was increased, the removal rate decreased gradually. This is because with the increase in the amount of KCl, the active ingredient of modified fly ash is superfluous, KCl will deposit gradually, and close pores of fly ash, so the adsorption capacity decreased. So the weight ratio of ash fly and KCl should be 3.4:1.

Effects of dosage of $CaCl_2$ on characteristic of fly ash

Figure 2 shows that, with the increase of the amount of $CaCl_2$, the removal rate of chromium ion by modified ash fly increases first and then decreases, when the dosage of $CaCl_2$ is 20ml, the removal rate of chromium ions by Ca-modified ash fly reaches the maximum value, it is 37.97%, when the amount of CaCl2 was increased, the removal rate decreased gradually. This is because with the increase in the amount of $CaCl_2$, the active ingredient of modified fly ash is superfluous, $CaCl_2$ will deposit gradually, and close pores of fly ash, so the adsorption capacity decreased. So the weight ratio of ash fly and $CaCl_2$ should be 2.25:1.

Figure 2 shows that, with the increase of the amount of NaOH, KCl and $CaCl_2$, the removal rate of chromium ion by modified ash fly increases first and then decreases, and the removal effect of chromium ion by Ca-modified ash fly is the best, it reaches 37.97%,the removal rate of Na- modified ash fly was 20.45% and the removal rate of K-modified ash fly was only 18.65%,so Ca-modified fly ash is the best reagent for treatment of chromium containing wastewater.

Effects of heating time on characteristic of fly ash

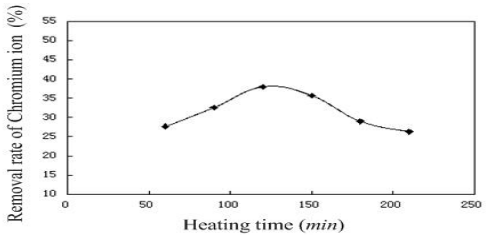

Figure 3: Effects of heating time on characteristic of Ca-modified fly ash

Figure 3 shows that, with the increase of heating time, the removal rate of chromium ion by Ca-modified ash fly increases first and then decreases, when the heating time was 60min to 120min, the removal rate of chromium ion by Ca-modified ash fly increased ,when the heating time was 120min to 210min, the removal rate was not increased,

but decreased, when the heating time was about 120min, the removal rate of chromium ion by Ca-modified ash fly reached the highest, and the removal rate was 37.96%. This is because during the period of 60min to 120min, Chromium ions adsorbed on the surface of ash fly, so the adsorption rate was fast; when the heating time is over 120min, the chromium ion will be absorbed after entering the interior through the pores of the ash fly surface, so the optimal heating time for preparing Ca-modified ash fly was 120min.

Effects of temperature on characteristic of modified fly ash

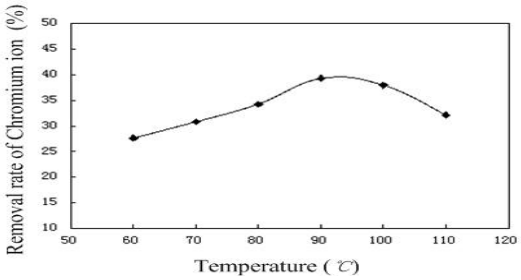

Figure 4: Effects of temperature on removal rate of chromium ion

Figure 4 shows that, with the increase of temperature, the removal rate of chromium ion by Ca-modified ash fly increases first and then decreases, when the temperature was 90℃, the removal rate of chromium ion by Ca-modified ash fly reached the highest, and the removal rate was 39.32%.when the temperature was over 90℃, the removal rate of chromium ion decreased gradually, this is because properly raising the temperature will make the hole in the modified ash fly fully open, and it makes the adsorption increase, but when the temperature is too high, **t**he adsorption pore will collapse or be blocked, it make the specific surface area of ash fly decrease, and it makes the adsorption decrease, so the optimal temperature for preparing Ca-modified ash fly was 90℃.

Preparation of modified fly ash charcoal-chitosan adsorbent
Effects of quality ratio of modified fly ash on adsorption of the composite adsorbent

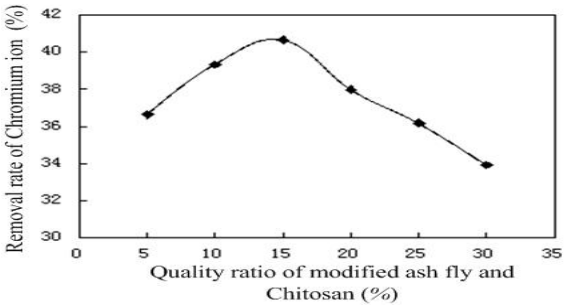

Figure 5: Effect of quality ratio of modified ash fly and Chitosan on the removal rate of chromium ions

Figure 5 shows that, with the increase of quality ratio of modified ash fly and Chitosan, the removal rate of chromium ion by Ca-modified ash fly increases first and then decreases, when the quality ratio of modified ash fly and Chitosan was 15:1, the removal rate of chromium ions by Ca-modified ash fly charcoal-chitosan adsorbent reached the highest, and the removal rate was 40.67%.This is because the surface of the compound is uneven, and a part of chitosan got into the internal of Ca-modified ash fly, it makes the specific surface area increased exponentially, and Ca-modified ash fly turns into coagulant aid, it is conducive to the increase of the flocculation and settlement, so the optimal quality ratio of modified ash fly and Chitosan was 15:1.

Effects of mixing time on Adsorption of the composite adsorbent

Figure 6 shows that, with the increase of mixing time, the removal rate of chromium ion by Ca-modified ash fly increases first and then decreases, when the mixing time was 120min, the removal rate of chromium ion by Ca-modified ash fly charcoal-chitosan adsorbent reached the highest, and the removal rate was 41.87%.When the mixing time was 0 to 120 min, the adsorption of the composite adsorbent gradually increased, this is because it make Chitosan and Ca-modified ash fly fully composite through mixing, when the mixing time was over 120 min, the adsorption decreased ,this is because a part of composite adsorbent has decomposed, so the optimal mixing time was 120 min.

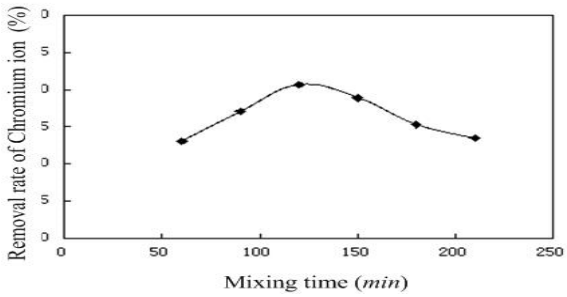

Figure 6: Effects of mixing time on Adsorption of the composite adsorbent

Results and analysis of treatment of chromium containing wastewater by composite adsorbent

Effects of dosage on treatment of chromium containing wastewater by composite adsorbent

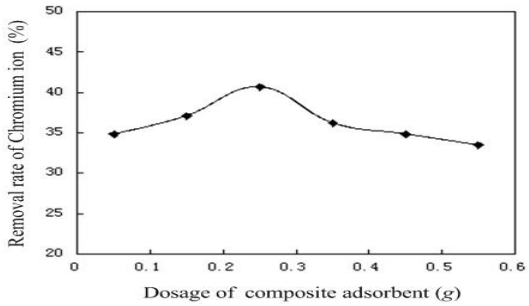

Figure 7: Effects of dosage on treatment of chromium containing wastewater by composite adsorbent

Figure 7 shows that, with the increase of the amount of composite adsorbent, the removal rate of chromium ion by modified ash fly increases first and then decreases, when the dosage of composite adsorbent is 0.25g,the removal rate of chromium ions by Ca-modified ash fly reaches the maximum value, it is 40.67%, The treatment of chromium containing wastewater mainly depends on the adsorption(Physical adsorption and chemical adsorption), under normal circumstances, physisorption and chemisorption may proceed at the same time. When the dosage of composite adsorbent was from 0.05g to 0.25g, the removal rate of chromium ions increased very rapidly, the removal of chromium ions mainly depended on adsorption, flocculation effect was not obvious. Friction between Ca-modified ash fly particles increased with increase of the amount of the dosage of adsorbent, a lot of adsorbed chromium ion returned to the solution, and the removal rate decreased. So the optimal dosage of composite adsorbent was 0.25 g/20 ml that is 12.5 g/L.

Effects of mixing time on treatment of chromium containing wastewater by composite adsorbent

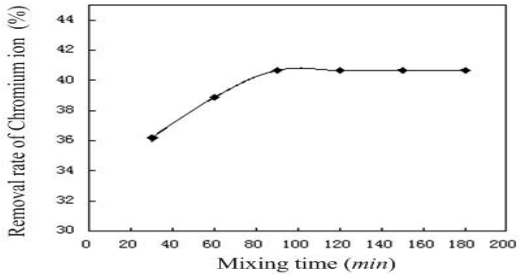

Figure 8: Effects of mixing time on treatment of chromium containing wastewater by composite adsorbent

Figure 8 shows that, the removal rate increased rapidly at the beginning of the period, and then it slowly decreased, this is because when the adsorbent was added in chromium containing waste water, the concentration gradient between the adsorbent and the solution chromium ions was the largest, the resulting adsorption driving force was also the largest, with the increase of mixing time, the concentration gradient between the adsorbent and the solution chromium ion became low gradually, and adsorption also became low. And with the increase of mixing time, the amount of flocs increased, when the mixing time reached 90min, flocs subsided, the removal rate reached 40.67%, adsorption also reached equilibrium.

Effects of temperature on treatment of chromium containing wastewater by composite adsorbent

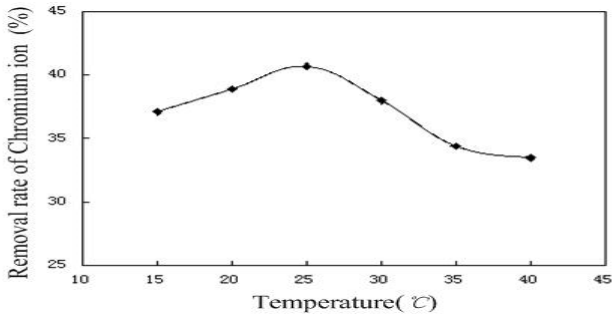

Figure 9: Effects of temperature on treatment of chromium containing wastewater by composite adsorbent

Figure 9 shows that, with the increase of mixing temperature, the removal rate of chromium ions increases first and then decreases, when the temperature reached 25℃,the removal rate reached 40.67%, when the temperature is over 25℃, the removal rate stopped growing and even decreased, this is because properly raising the temperature will fully open the hole in the composite adsorbent, and it makes the adsorption increase, but when the temperature is too high, the adsorption pore will collapse or be blocked, and the adsorption decreased, so the optimal mixing temperature was 25℃.

Effects of pH value on treatment of chromium containing wastewater by composite adsorbent

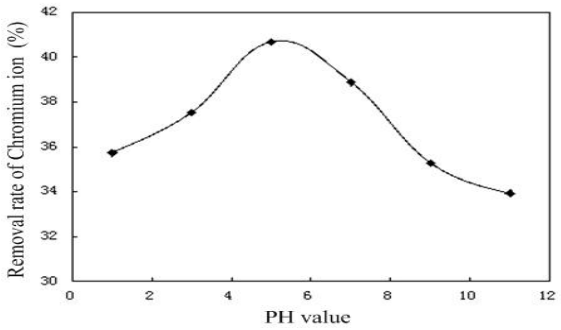

Figure 10: Effects of pH value on treatment of chromium containing wastewater by composite adsorbent

Figure 10 shows that, when the PH value is 5, the removal rate of chromium ions is 40.67%, the removal rate of the compound adsorbent on chromium ions was the largest, with the increase of PH value, the removal efficiency of chromium ions was getting worse, there are two reasons:

(1) Under acidic condition, a chemical reaction occurred between H^+ and Al_2O_3、Fe_2O_3 in the adsorbent, it generated Al^{3+},Fe^{3+},they are inorganic flocculants, it produced flocculation sedimentation, but also increased the surface area of ash fly,it improved the adsorption.

(2) Chitosan can only be dissolved under acidic conditions, when pH is greater than 5, Chitosan can not completely dissolve, positive charge of adsorbent reduced, this leads to adsorption capacity greatly reduced.

CONCLUSION

(1).In Na-modified fly ash, K-modified fly ash, Ca-modified fly ash, the optimum modified fly ash is Ca-modified fly ash, its optimal preparation conditions are: the weight ratio of ash fly and $CaCl_2$ should be 2.25:1,the heating time is 120min,the temperature is 90℃, the removal rate of chromium ion by Ca-modified ash fly reached 39.32%.

(2) The optimal conditions of preparation of modified fly ash charcoal-chitosan adsorbent are: the quality ratio of modified ash fly and Chitosan was 15:1,the mixing time is 120min.

(3) The optimal conditions of treatment of chromium containing wastewater by composite adsorbent are: the dosage of composite adsorbent is 0.25g； the mixing time is 90min,the temperature is 25℃, the PH value is 5,the removal rate was 40.67%.

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