Study on Adsorption of Chromium (VI) by Activated Carbon from Cassava Sludge

Jinhui Yang¹, Chuanshu Li¹, Bin Yang², Sijun Kang¹ and Zhen Zhang³

¹School of Civil Engineering, University of South China, Hengyang, China
²University of South China Nuclear Sanli Company, Hengyang, China
³School of Civil Engineering, Anhui University of Technology, Maanshan

Corresponding author: 15656534862@163.com

Abstract. In this paper, a new type of adsorbent prepared by waste sludge from alcohol production industry was used to adsorb Cr (VI) in activated carbon from cassava sludge. A series of static adsorption experiments were carried out on the initial concentration of solution Cr (VI), pH value of solution, adsorption time and dosage of adsorbent. The results of single factor experiments show that the removal rate of Cr (VI) increases with the initial concentration of Cr (VI), while the adsorption amount is opposite. When the pH value of the solution is low, the adsorption effect of activated carbon is better. The adsorption time should be controlled within 40-60 min. When the activated carbon dosage is increased, the removal rate increases but the adsorption capacity decreases.

1. Introduction

Chromium is a metallic substance widely found in nature. It is found that Chromium exists in in FeCr²O₄ and PbCrO₄, at present. There are a variety of Chromium oxide in nature and the ionic valences of Chromium exist 0 to 6 valence, the most common ionic valences are Cr⁶⁺ and Cr³⁺ that they have a mutual transformation in certain condition[¹]. Cr (VI) usually exists in aqueous solution by CrO₄²⁻, HCrO₄⁻, HCr₂O₇²⁻, Cr₂O₇²⁻[³] and so on. Every form of being is affected by pH, temperature, hardness, redox potential and the concentration of Chromium in aqueous solution. At present, there are several common treatment methods of the chromium containing wastewater: ion exchange, membrane separation, barium salt method, reduction neutralization method, biological method and adsorption method. The adsorption method has its unique advantages, because of the adsorption material selectivity, low cost, the saturation capacity of the adsorbent, and adsorbent renewable, it not only solves the expensive problem of chemical method, but also overcomes the disadvantages of limited adsorption capacity of biological process.

The mechanism of the treatment of the wastewater containing chromium by activated carbon adsorption or reduction according to the different pH value of aqueous solution. When the solution pH value is between 4 to 6.5, Cr (VI) direct interact with activated carbon and it is adsorbed on the surface by activated carbon in wastewater; when the pH value was less than 3, the activated carbon has reduction. It can reduce the Cr (VI) in the solution to Cr (III); when the oxygen is sufficient, amolecular oxygen, hydrogen ions and anions adsorbed on the surface of active carbon reacts to generate hydrogen peroxide. With the strong reduction of hydrogen peroxide, Cr (VI) is reduced to Cr (III). The reaction equation as follows:

\[ 3C + 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ = 3\text{CO}_2 + 4\text{Cr}^{3+} + 8\text{H}_2\text{O} \]
2. Experimental materials and methods

2.1. Experimental Reagent and Equipment

The main reagents used in the experiment: zinc chloride, sodium chloride, diphenylcarbazide, potassium dichromate, sodium hydroxide, acetone, concentrated hydrochloric acid and concentrated sulfuric acid; The reagent levels are all analysis pure; National drug group chemical reagents Co., Ltd.

| Table 1. The main equipment |
|-----------------------------|
| Name                      | Model / type       | Manufacturer                  |
| Oven                      | Electric blast     | Shanghai Yiheng Scientific Instrument |
| Ultraviolet spectrophotometer | UV               | Beijing Ruili Analytical Instrument Co. |
| Water bath                | HWS24             | Shanghai Yiheng Scientific Instrument |
| Thermostatic oscillator   | SHA-B             | Guohua Enterprises             |
| Concrete mixer            | MY3000-6BRSL      | Qianjiang Mei Yu Instrument Co., Ltd. |
| Electronic balance        | FA2004N           | Shanghai precision instrument factory |

2.2. Preparation of Cassava Sludge Activated Carbon

The sludge was from Ma'anshan Taixing Jin Jiang Chemical Industry Co. Ltd. (alcohol manufacturer). The cassava sludge was dehydrated and dried under natural conditions, then it was dried in a constant temperature drying oven at 105 centigrade, grinding with mortar, 20-50 mesh sieve, The particle size was guaranteed to be between 0.355-0.887mm. Weighed 10g the grinding sludge in 200ml beaker and residual sludge was placed in a sealed bag and stored. Weighed 10.2041g zinc chloride solid dosage in 50ml beaker, 40ml distilled water was poured into the beaker and mixed with zinc chloride, and then completely dissolved with glass rods to get 20% concentration of zinc chloride solution. The prepared solution was poured into a beaker contained 10g sludge and mixed with it in a constant temperature water bath. The temperature of the water bath was set at 60 centigrade and activated for 12 hours. After activated for 12 hours, the beaker sludge was transferred to the 100ml size of the crucible, and then placed in a muffle furnace, carbonized for 60 minutes at high temperature of 500 centigrade. Then cooled it and ground with mortar, added 1mol prepared hydrochloric acid pickling. Then washed to pH greater than 5. Finally, dried in a constant temperature drying oven at 105 centigrade, and the drying solid was the cassava sludge activated carbon that was stored in the sealed bag for stand-by using.

The concentration of Cr (VI) in water was determined by two benzoyl two hydrazine spectrophotometry (GB7467-87).

3. Results and analysis

3.1. The Effect of pH on Adsorption of Cr (VI)

The effects of pH=2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 on the removal of Cr (VI) were experimentally investigated. The specific experimental process is as follows: Weigh 1.0g activated carbon in 800mL the beaker, prepare the 500mL of 10mg/L concentration potassium dichromate solution, and the pH value is adjusted as the required size. Pour into the beaker and stir it by the blender for 3h, the temperature is at normal temperature, and the stirring speed is 150r/min. After 3h using the fast filter paper filter, and the spectrophotometric value of each water sample was measured and the removal rate was calculated. The effect of pH value on the removal of Cr (VI) by activated carbon adsorption is shown in figure 1:

It can be seen from the diagram that with the increase of initial pH value of the solution, the removal of Cr (VI) by cassava sludge activated carbon is obviously decreased. When the pH value

\[ 3\text{H}_2\text{O}_2 + \text{Cr}_2\text{O}_7^{2-} + 8\text{H}^+ = 3\text{O}_2↑ + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \]
increased from 2 to 12, the adsorption removal rate decreased from 98.43% to 1.53%, and the reasons were as follows: Analysis from the perspective of adsorbate: in aqueous solution, Cr (VI) mainly exists in three forms of CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$ and HCrO$_4$$^{-}$[5]. With the change of solution pH, the form of will change accordingly. When the solution is acidic, Cr (VI) is mainly distributed in the form of HCrO$_4$$^{-}$, the study found that HCrO$_4$$^{-}$ can form stable compounds[6] with adsorbent. In the acidic conditions, the oxidation of Cr (VI) is very strong, the oxidation and reduction on the removal of Cr (VI) to make a contribution. Therefore, the removal rate is high under acidic conditions. When the pH of the solution increases gradually, the Cr (VI) in the solution begins to be dominated by CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$; With the concentration of OH$^{-}$ increases, and the competitive adsorption of with Cr (VI) results in inhibition of the adsorption of Cr (VI). So under acidic conditions, the removal rate of Cr (VI) is higher than that under alkaline condition.

3.2. the Effect of Activated Carbon Dosage on Adsorption of Cr (VI)

The dosages of activated carbon respectively are 0.2g, 0.6g, 1.0g, 1.5g, 2.0g and 2.5g; The concentration of Cr (VI) solution is 10mg/L; the temperature is at room temperature; the stirring intensity is 150r/min; the adsorption time is 120min; the solution pH is 1. The effect of activated carbon dosage on removal of Cr (VI) is shown in figure 2.

In the picture, it can be seen that when the activated carbon dosage increased from 0.2g to 2.5g, the removal rate of Cr (VI) increased from 15.32% to 95.44%, showed a rising trend. Analysts believe that with the increase of the amount of activated carbon, the available adsorption sites in the contact reaction increased correspondingly[9]. The amount of Cr (VI) adsorbed by activated carbon increased, which showed that the removal rate increased with the increase of dosage. It is also found that the amount of adsorption decreases with the increase of dosage[11]. The reason is that the dosage increases and the specific surface area increases, so more Cr (VI) is adsorbed on the surface of activated carbon, but the unit surface utilization of adsorbent decreases. Thus, the amount of activated carbon is not the more the better. Combined with Figure 2 and the above analysis, 1.5g/L was selected as the best dosage for removing of Cr (VI).
Figure 2. The effect of activated carbon dosage on removal of Cr (VI)

3.3. the Effect of Adsorption Time on the Adsorption of Cr (VI)

Setting time in experiment were 5, 10, 15, 20, 30, 40, 50, 60, 70, 90, 120, 150 and 180 minutes, respectively. The experimental conditions were as follows: potassium dichromate solution with 10mg/L concentration, adsorbent dosage of 1g, room temperature, stirring speed of 150r/min, solution pH of 1. According to figure 3 shows that the adsorption capacity increased with adsorption time, finally gradually balanced. The adsorption process can be divided into three stages, the rapid adsorption stage, slow adsorption stage and adsorption equilibrium stage. The first stage is the initial adsorption, at this time, the concentration gradient of Cr (VI) between the solution and the surface of the activated carbon is larger, which accelerates the diffusion of Cr (VI) from the solution to the surface of activated carbon, and promote the speed of Cr (VI) adsorption. At the same time, the activated carbon surface can provide sufficient active adsorption sites, so the amount of Cr (VI) adsorbed by activated carbon increased rapidly at this stage. With the adsorption reaction to the second stage, the surface adsorption sites using activated carbon gradually reduced, the concentration gradient of Cr (VI) ion between the solution and the surface of activated carbon decreases and the surface of the activated carbon Cr (VI) and solution Cr (VI) repulsive interaction\(^{[12]}\) to make the adsorption sites on the adsorbent surface are less likely to be occupied, so the adsorption rate is slow and the adsorption capacity of Cr (VI) increased slowly. After the adsorption reaction of 150min, the available adsorption sites of activated carbon are almost completely occupied, and the adsorption capacity is difficult to increase again to reach equilibrium.

Figure 3. The effect of adsorption time on the adsorption of Cr (VI)
3.4. the Effect of Initial Concentration on Adsorption of Cr (VI)
This experiment set the initial concentrations of Cr (VI) were 1, 3, 5, 7, 10, 15, 20, 30mg/L, respectively. The experimental conditions were as follows: adsorbent dosage of 1g, room temperature, stirring speed of 150r/min, solution pH of 1, the adsorption time 120min.

First of all, from the aspect of removal rate, the removal rate decreased with the increase of initial concentration. When the initial concentration of water was 1mg/L, the removal rate was as high as 99.25%; when the concentration increased to 30mg/L, the removal rate is only 28.13%. Analysts believe that this may be due to the initial concentration of Cr (VI) is small, the surface of the activated carbon with positively charged functional groups and active adsorption sites were excessive, it can adsorb a large amount of Cr (VI) in a short period of time, which makes the adsorbent have a high removal rate of Cr (VI) at low concentration; With the initial concentration of Cr (VI) increasing, the active sites on the adsorbent surface are continuously squeezed, while the excess Cr (VI) can only be dissociated in the solution, resulting in the adsorption of Cr (VI) removal rate decreased. From the aspect of adsorption capacity, the adsorption capacity increases with the initial concentration of solution, and the adsorption amount increases from 0.99mg/g to 8.44mg/g. This is because the pore structure of cassava sludge activated carbon is well-developed, and the active adsorption sites are distributed inside and outside the pores. When the initial concentration of Cr (VI) is low, the adsorption point on the outer surface of pores is occupied by Cr (VI) firstly, and at this time the adsorption point provided by the activated carbon surface is enough to adsorb Cr (VI) in the solution. When the concentration of Cr (VI) in aqueous solution is higher, the concentration gradient of Cr (VI) between the solution and the activated carbon surface will increase, which can promote the migration of Cr (VI), and promote the movement of Cr (VI) to the inner channel of activated carbon, and eventually be removed with the adsorption point of the internal surface[14]. As more adsorption sites are utilized, the amount of adsorbent increases with the increase of initial concentration.

![Figure 4](image-url)

**Figure 4.** the effect of initial concentration on adsorption of Cr (VI)

4. Summary
In this study, the feasibility and effect of cassava activated carbon as an adsorbent for Cr (VI) was basically understood through a series of experiments. In terms of single factor experiment results, the removal rate of Cr (VI) by activated carbon increased with the increase of initial concentration of Cr (VI), while the adsorption amount showed an opposite trend. For the effect of pH, when the solution pH is low, the adsorption effect of activated carbon is better under acidic condition; Stirring time control in 40-60min, the removal of Cr (VI) by activated carbon can reach a good level in this time period; When the dosage increased, the adsorption capacity decreased, the results reflect the dosage of 1.5g/L is the best dosage. The whole study not only obtain a lot of important conclusions, but also reflect many problems that need to be improved. In the experiment, the cassava sludge activated carbon
has certain removal effect of Cr (VI), comparing to the actual project, the influence factors in the experiment can be effectively controlled, but the various factors in the actual project hybrid is difficult to control, the experiment results lack of the practical engineering inspection.

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