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# Removal of the heavy metal ion Cr(VI) by soybean hulls in dyehouse wastewater treatment

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ABSTRACT

The preparation and properties of soybean hulls are studied. The efficiency of chromium ions removal by soybean hulls from aqueous solutions is investigated. The experiment results showed that the quality of the dyehouse treated wastewater can meet the national requirements of the first grade of integrated wastewater discharge standard (GB 8978–1996) through this treatment. The experiment results indicated that the initial concentration of the metal ions, pH solutions, contact time, soybean hulls of different molecular weight could affect the efficiency of heavy metal ions removal. With soybean hulls of 2 g $l^{-1}$ for 20 min, the removal rate of Cr(VI) was 91.991% at 30°C pH 2–3. The soybean hulls could be used repeatedly because the desorption rate of Cr(VI) was 95.01%. Soybean hulls are safe and environmentally-friendly natura1 products. The treating system could be managed conveniently and operated reliably.

*Keywords:* Soybean hulls; Heavy metal ions; Adsorptive property; Desorption; Removal rate; Adsorbent dosage

## 1. Introduction

Chromium pollution is mainly from a great number of modern industries such as electroplating wastewater, chromium minerals processing, leather tanning, metal surface treatment, printing and dyeing, photographic materials and so on [1–3]. Chromium concentration is higher in untreated chromium liquid that is several or even thousands of times more than the national emission standard. Heavy metals cannot be biodegraded and enrich in organisms through the food chain, eventually accumulated in human body which is harmful [4,5]. The Cr(VI) ions can bring highest toxicity among chromium compounds, which cause teratogenesis, carcinogenicity and mutagenic effect and are absorbed in human body, ultimately accumulate and lead to liver cancer. Therefore, it is particularly significant to manage chromium in the electroplating wastewater [6–8].

The main methods currently be used for removing the heavy metal ions from wastewater are chemical precipitation, activated carbon adsorption, solvent extraction and ion exchange adsorption methods. The problem is that the adsorption efficiency of these methods is not very well and the treated water cannot be directly drunk. Cellulose is the most abundant natural macromolecular substance in nature, which is not only rich in nature but is a renewable resource. Cellulose molecule contains plenty of the hydrophilic groups—hydroxyl, and is a kind of fibrous and capillary natural macromolecule [9]. It has porous and high specific

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surface characteristics that it can be used as an ion adsorbent for a certain adsorption. More and more modern researches are focused on the new, more efficient absorbents made of cellulose base material especially to agricultural waste. Natural adsorbents such as sheet jelly of Cocoa, coconut shells, chestnut endothelial, lignin and chitosan are specially observed [10].

Soybean hulls are the byproducts of oil industry, accounting for the entire soybean weight of 8%. They contain high cellulose content and can be made as natural polymer adsorbent [11]. In this study, soybean hulls are considered as raw material directly, to treat wastewater containing heavy metal ion Cr (VI) [12,13]. The effects of pH, contact time, amount of soybean hulls, initial concentration of Cr(VI) on adsorption activity and desorption rate of Cr(VI) were studied.

## 2. Experimental

### 2.1. Materials

Soybean hulls were provided by Shandong New Jiahua Group, the chrome standard solution with concentration of 1 g $l^{-1}$ was provided by National Standard Material Research Center. Before using, filtering dilution to required quality concentration. Heavy chromic acid potassium, sodium hydroxide, hydrochloric acid were analysis pure reagents.

### 2.2. Instruments

Z-2000 240 V atomic absorption spectrophotometer, SHZ-88 A reciprocating water-bath thermostatic oscillators, PHS-3 C Precision pH dollars, KDC-40 low speed centrifuge.

### 2.3. Procedures

#### 2.3.1. Simulation to the preparation of heavy metal wastewater

A certain amount of $K_2Cr_2O_7$ was weighed, which was equipped with a 10 mg $l^{-1}$ Cr(VI) solution, as the simulated heavy metal wastewater.

#### 2.3.2. Adsorption experiment

A certain amount of soybean hulls was put into 100 ml simulated heavy metal wastewater. According to the research performance requirement, Change experimental conditions and adsorb. Then centrifugalized with centrifugal sedimentation centrifugal separation, take for 1 ml supernatant fluid which was determined the concentration of Cr(VI) with atomic absorption spectrophotometer. According to the concentration of Cr(VI) around the adsorption, the unit adsorption quantity of the absorbent *Q* (mg $g^{-1}$) and the removal rate of Cr(VI)(or absorption) *R*% were calculated by Eqs. (1) and (2):

$$Q = V \times (\mathrm{Co} - \mathrm{Ce})/M \tag{1}$$

$$R = (\mathrm{Co} - \mathrm{Ce})/\mathrm{Co} \times 100\% \tag{2}$$

where *Q* is the unit adsorption capacity of the absorbent (mg $g^{-1}$), *R* is the removal rate (%), *V* is the volume of adsorption liquid (l), Co is initial quality concentration of Cr(VI) in untreated solution (mg $l^{-1}$), Ce is quality concentration of Cr(VI) in adsorbed solution (mg $l^{-1}$), *M* is the amount of the adsorbent.

#### 2.3.3. Desorption experiment

Under the condition of 30°C, pH = 2–3 and soybean hulls of 2 g $l^{-1}$ for 30 min, 100 ml 120 mg $l^{-1}$ Cr(VI) solution was adsorbed to make soybean hulls fully adsorb Cr(VI). Then soybean hulls were filtered, and detect the content of Cr(VI) in the filtrate. What's more, soybean hulls were put into 0.5 mol $l^{-1}$ HCL for 24 h in order to desorb. Adsorption and desorption solution were adjusted for 100 ml, detecting the content of Cr(VI) in the filtrate. The desorption rate *D*(%) was calculated by Eq. (3):

$$D = \mathrm{Ct}/(\mathrm{Co} - \mathrm{Ce}) \tag{3}$$

where Co is initial quality concentration of Cr(VI) in untreated solution (mg $l^{-1}$), Ce is quality concentration of Cr(VI) in adsorbed solution (mg $l^{-1}$), Ct is quality concentration of Cr(VI) in desorbed solution (mg $l^{-1}$).

## 3. Results and discussion

### 3.1. Effect of the time of adsorption

The experiments were conducted with solutions of Cr(VI) concentrations of 10 mg $l^{-1}$ at pH 2.6. The amount of 0.2 g soybean hulls was weighed and added into 100 ml Cr(VI) solution in 250 ml iodine number flask at 30°C. Fig. 1 showed the Cr(VI) adsorption on the soybean hulls in solutions at different adsorption time.

The typical experimental result of adsorbed Cr(VI) on the soybean hulls versus time was shown in Fig. 1. The soybean hulls had high adsorption capacities for Cr(VI) adsorption. The adsorption equilibrium was reached at about 20 min, and the adsorption rate reached at 84.96%. The adsorption of Cr(VI) on the soybean hulls may be considered to consist of two processes: (a) the removal rate increased rapidly in 20 min, and (b) the adsorption in the late stage (20–120 min) slowed down.

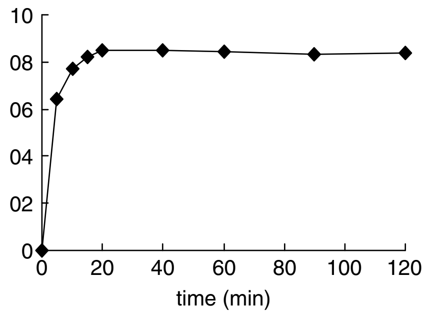


Fig. 1. Effect of the time of adsorption.

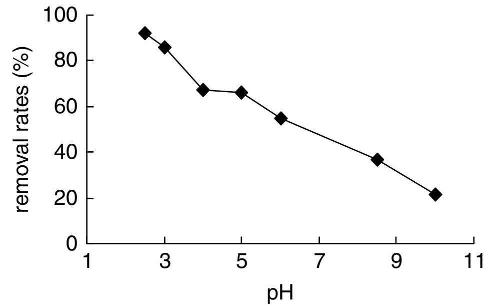


Fig. 2. Effect of initial pH on adsorption.

In the initial fast adsorption stage, the surfaces of the beads were relatively free of Cr(VI) and the Cr(VI) that arrived at the soybean hulls' surfaces may attach instantly to the sites of the surface. The sufficient transport of Cr(VI) from the bulk solution to the surface of the soybean hulls may be dominated by a higher initial Cr(VI) concentration and the number of active adsorption sites on the surface of the soybean hulls. Hence, the big initial adsorption rate was shown.

In the late stage of Cr(VI) adsorption, the experimental data indicated that other factors started to play an important role on controlling the adsorption. At that time, the adsorption rate was determined mainly by the ions which is diffused in the interior of adsorbent, so the adsorption rate was reduced.

Fast adsorption of heavy metal ion by adsorbent was attributed to chemical reaction and surface diffusion mechanism, while slow adsorption was related to the process in which the metal ions diffuses from a higher to a lower energy states and surface precipitation.

### *3.2. Effect of initial pH on Cr(VI) adsorption*

To study the effect of solution pH on Cr(VI) adsorption on soybean hulls, Cr(VI) solutions with an initial concentration of 10 mg $l^{-1}$ were prepared by diluting the standard Cu solution with DI water, and the pH values of the solutions were adjusted to a value in the range of 2–11 with 0.1 M NaOH or 0.1 M $HNO_3$. The amount of approximate 0.2 g soybean hulls was weighed and added into a number of 250 ml iodine number flask. Each bottle contained 100 ml of the Cr(VI) solution of a different pH (2–11) at 30°C. The pH of the solutions in each flask was not controlled during the adsorption process.

After 20 min, samples were taken from the flasks for the determination of the final Cr(VI) concentrations in the solutions, the effect of solution pH on Cr(VI) adsorption on soybean hulls was studied.

Fig. 2 showed the Cr(VI) adsorption on the soybean hulls in solutions with initial pH values from 2 to 11 (initial Cr(VI) concentration in the solution: 10 mg $l^{-1}$).

In general, the removal rates decreased with the increase of the solution pH values for soybean hulls. The maximum removal rate reached about 91.99% at about pH 2. The removal rate reached 54.81% at about pH 6, while it reached 21.67% at about pH 10, because the existent form of Cr(VI) was closely related with different pH value.

Cr(VI) is presented as the form of $CrO_4^{2-}$ at pH ≥ 7, while Cr(VI) is presented as the forms of $HCrO_4^-$ and $CrO_4^{2-}$ at pH (5–6). Cr(VI) is presented as the form of $HCrO_4^-$ and $Cr_2O_7^{2-}$ at pH (3–4), while Cr(VI) is presented as the form of $Cr_2O_7^{2-}$ at pH not more than two.

When pH value is low, the attachment of $HCrO_4^-$, $CrO_4^{-2}$ and $Cr_2O_7^{-2}$ to the protonation adsorption sites through electrostatic attraction is much easier. More hydrogen ions on the surfaces of the adsorbent, larger removal rate of heavy metal ion Cr(VI) by soybean hulls, especially at pH (2–3). $Cr_2O_7^{2-}$ is common, and the amount of Cr(VI) is about 2 times more than the other forms of Cr.

The maximum removal rate of heavy metal ion Cr(VI) by soybean hulls reached at pH 2 to 3. With the increasing pH value, the surface of the adsorbent appeared to have electronegativity, and the repulsive electrostatic interaction may result in the reduction of the absorption capacity. So pH 2 to 3 is the optimum pH value for the maximum removal rate of heavy metal ion Cr(VI) by soybean hulls.

### *3.3. Effect of adsorbent dosage*

Adsorbent dosage study was conducted with solution of Cr(VI) at the concentration of 10 mg $l^{-1}$ and pH 2 to 3. A series of different amount of the soybean hulls was weighed and added into 100 ml Cr(VI) solution in 250 ml iodine number flask at 30°C. Effect of the quantity of adsorbent (Fig. 3) on adsorption results were follows:

The removal rates of heavy metal ion Cr(VI) by the soybean hulls improved significantly with the increase of adsorbent dosage. It is mainly due to the increase in the surface area and the adsorption sites of

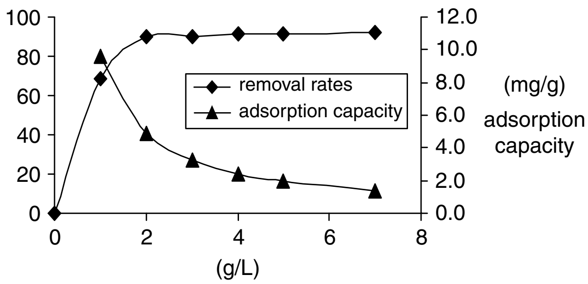


Fig. 3. Effect of the quantity of adsorbent.

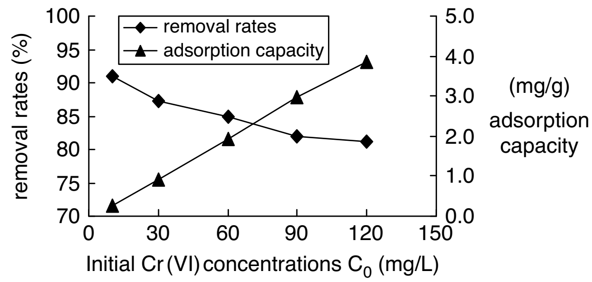


Fig. 4. Effect of initial Cr(VI) concentration.

the adsorbent. The metal ions increased access to the adsorption sites which led to the increased adsorption capacity of adsorbent. When the adsorbent dosage increased from 1 to 2 g $l^{-1}$, the removal rates increased drmatically from 68.82% to 89.8%.

With the further addition of the adsorbent beyond the concentration of 2 g $l^{-1}$, the change of the removal rate of heavy metal ion Cr(VI) is small. It suggested that the optimum concentration of adsorbent was 2 g $l^{-1}$.

The shape of the survey curve of the adsorption capacity indicated that the adsorption capacity of heavy metal ion Cr(VI) was gradually reduced with the increase of adsorbent dosage. When the adsorbent dosage increased from 1 to 4 g $l^{-1}$, the adsorption capacity reduced from 9.60 to 2.44 mg $g^{-1}$. The absorption speed of heavy metal ion Cr(VI) on the adsorbent surface in solution have a faster increase with the increase of adsorbent dosage, which lead to lower-value of the Cr(VI) concentration. When the adsorbent dosage is higher, but the adsorption sites on the adsorbent surface has not obtained saturation, so the adsorption capacity is lower.

### 3.4. *Effect of initial Cr(VI) concentration*

The experiment was conducted with the Cr(VI) solution concentrations ranging from 10 to 120 mg $l^{-1}$ at pH (2–3). The amount of 2.5 g soybean hulls was added to a 100 ml Cr(VI) solution in 250 ml iodine number flask at 30°C. The mixtures in the bottles were stirred for 20 min. The adsorption capacities and the removal rates of Cr(VI) on the soybean hulls at various initial Cr(VI) concentrations (initial solution pH 2–3) were studied. The experimental adsorption data of Cr(VI) on the soybean hulls was shown in Fig. 4.

The soybean hulls have obvious absorbability on chromium in wide initial concentration, and the removal rate can reach above 80%. With the increase of initial concentration, the equilibrium adsorption capacity increased linearly and the removal rates dropped off. When the initial Cr(VI) concentration was 30 mg $l^{-1}$, the adsorption capacity was 0.90 mg $g^{-1}$ and the removal rate was 91.04%. When the initial Cr(VI) concentration was 120 mg $l^{-1}$, the adsorption capacity was 3.85 mg $g^{-1}$ and the removal rate was 81.25%.

Initial concentration of chromium had a great driving force to overcome mass transfer resistance between liquid and solid phases in adsorption system. The driving force which can overcome mass transfer resistance was increased which led to the decreasing of adsorption resistance with the increase of initial concentration. In addition, the adsorption of Chromium on the surfaces of the soybean hulls increases, leading to the increase of the adsorption capacity. However, when initial concentration is lower, the ratio of Cr(VI) ions to the available adsorption unit sites of adsorbent is lower It may lead to a better removal rate and a higher removal rate. When the initial concentration is higher, the available adsorption unit sites of adsorbent is relatively small. It may lead to the decreased removal rate of Cr(VI) ions.

### 3.5. *Desorption character of the soybean hulls*

The experimental results demonstrated that the removal rate reached 91.99%, but desorption rate reached 95.01%. It indicated that the soybean hulls had a good desorption effect, and this novel process of metal removal provides a sustainable way of managing contaminated waste water with Cr(VI).

## 4. Conclusions

1. Cr(VI) removal of the absorption of Cr(VI) by soybean hulls was observed to be optimum at 20 min adsorption time at 30°C for pH 2–3 at the concentration of 2 g $l^{-1}$, and the maximum removal rate reached 91.99%.
2. The adsorption effect was significantly influenced by the factors that included adsorption time, pH, dosing quantity of the adsorbent, initial concentration of heavy mental ion and so on. Adsorption process was divided into rapid phase and slow phase, and adsorption equilibrium could reach in 20 min. The optimal pH was 2–3. With pH increasing, the adsorption rate reduced. The removal rate of Cr(VI) increased and

the adsorption quantity decreased, with the dosing quantity of soybean hulls increasing. Soybean hulls which was in a wider range of the initial concentration had obvious effect on adsorption of Cr(VI), and all of the removal rate was above 80% under the condition that the initial concentration was 10–120 mg $l^{-1}$.

3. The desorption effect of soybean hulls was good and desorption rate reached as high as 95.01%. It indicated that the soybean hulls provided a sustainable way of managing contaminated Cr(VI) waste water.
4. Soybean hulls could be used to eliminate heavy metal Cr(VI) ions in waste water, and be utilized to treat drinking water.

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