

Adsorption of uranium-containing wastewater by Sugarcane Stalks

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Abstract. The new sorbent—sugarcane stalks on the adsorption of uranium-containing wastewater was studied by static adsorption experiments in this research. Its feasibility and adsorption capacity as a biological adsorbent was verified through modification experiments. The influence of adsorbents dosage, adsorption time and temperature, adsorption solution pH, initial concentration on the adsorption of uranium after the modification was studied and the adsorption mechanism of uranium adsorption by sugarcane stalks was discussed. The experimental results showed that adsorption efficiency increased about 50% after modification by ZnCl_2 and NaOH , and the maximum adsorption efficiency was 86.6% and the maximum adsorption capacity was 2.5 mg/g at 303 K, pH = 3, the time was about 90 mins, modification was feasible. Warming was conducive to the adsorption. The amount of adsorbent to the optimum volume of the solution was 8 g/L. The results indicated that sugarcane stalks can be used as the good uranium-containing wastewater decontamination biosorbent.

Introduction

With global demand for nuclear fuel increasing, especially for uranium, more and more uranium-containing wastewater was released. Uranium-containing wastewater was radioactive and chemically toxic, so that all countries attached great importance to the treatment processing of uranium-containing wastewater[1] and developed a variety of treatment methods and techniques[2]. A promising new method—biosorption has many advantages[3], came into being. In recent years, researchers in this area had also been studied and tried a variety of adsorbents, such as corn cobs[4], *Saccharomyces*[5], they have made some progress. China, as the world's third largest sugar cane producing countries, will produce a large number of post-squeezed sugar cane residue, which was burned or discarded directly, resulting in a great waste of resources and environmental pollution.

Materials and Methods

Instruments and reagents. pH-3C Precision pH meter (Shanghai Lei magnetic Instrument Factory); SHC-C.constant temperature water bath oscillator (Jiangsu Jiangnan Instrument Factory); FA1104 electronic balance (accuracy of 0.0001 g), Shanghai Ryohei Instrument Co., Ltd.; ZKF040 Vacuum oven (Shanghai experimental Instrument Co., Ltd.). Reagents: 1 g/L uranium standard solution; hydrochloric acid (HCl), sodium hydroxide (NaOH) and zinc chloride (ZnCl_2) were analytical grade.

Materials. Cane stalks were purchased in around market and sugar cane bagasse was washed by distilled water after juicing, then it was grounded into powder after drying and dried to constant weight at 80 °C, it through 40 mesh sieve, put it in the oven to cool and then at dry place after bagging sealed.

Methods. a(non-modified): Take 1 g/L uranium standard solution, add distilled water to a solution of different concentrations, and the pH was adjusted with HCl(aq) and NaOH(aq) , 25 ml pipette with uranium standard solution was added 250 ml conical flask, a certain amount of the adsorbent was added thereto, it was placed in a thermostatic water shaker shaking adsorption certain time at a temperature, taking appropriate supernatant after filtration, remaining uranium

concentrations in solution was measured by $\text{TiCl}_3/\text{NH}_4\text{VO}_3$ titration[6], calculation adsorption performance parameters. b(modified): Weigh a quantity of the adsorbent and put into two 250 ml Erlenmeyer flasks, 100 ml of 50% $\text{ZnCl}_2(\text{aq})$ and 0.1 mol/L $\text{NaOH}(\text{aq})$ were added. Filtration after oscillating adsorption 12 h, wash and drying. The sorbent modified by ZnCl_2 was used in other experimental groups. The amount of the adsorbent Q (mg/g) to U(VI) and the removal rate R (%) were calculated by the following equations:

$$Q = (C - C_e) V/m \quad (1)$$

$$R = (C - C_e) \times 100\% / C \quad (2)$$

Formula: C = initial uranium concentration (mg/L); C_e = uranium concentration in solution at equilibrium (mg/L); V = volume of solution adsorption (L); m = dry weight (g) of the adsorbent;

Results and Discussions

Effect of adsorbent dose on adsorption of uranium(VI). At room temperature, the adsorbents(a group: 0.05 g, 0.10 g, 0.15 g, 0.20 g, 0.25 g, 0.30 g; b group: 0.12 g, 0.16 g, 0.20 g, 0.24 g) were added to 25 ml solution the concentration 20 mg/L to oscillate adsorption 12 h. The results of effect of adsorbent dosage on the adsorption of U(VI) were shown in Figure 1.

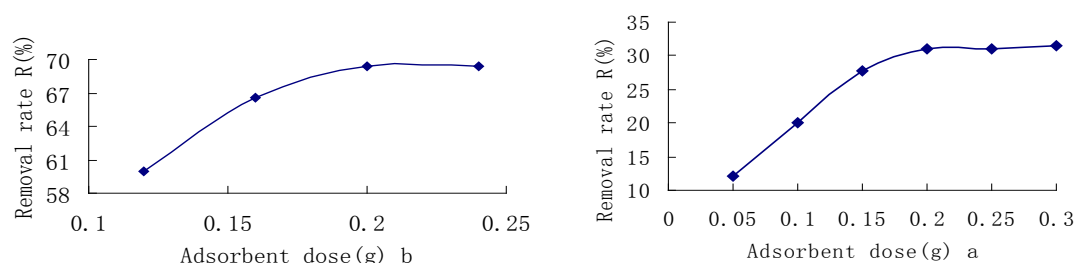


Fig.1 Effect of adsorbent dose on adsorption of uranium(VI)

Figure 1 showed that before and after the modification, the removal rate of U(VI) ions gradually increased with the addition of adsorbent, it reached a maximum at 0.20 g and then tended to stabilize. The adsorption sites increased as adsorbent was added, so that the removal rate of U(VI) ions increased. Maybe there was a U(VI) concentration equilibrium between solution and within the adsorbent with further increasing of the amount of adsorbent and adsorption came to stabilized[7]. Therefore the best adsorbent amount to solution volume ratio is 8.0 g/L.

Effect of initial pH value on adsorption of uranium(VI). At room temperature, adding 0.20 g adsorbent to 25 ml concentration of 20 mg/L uranium-containing solution and oscillating adsorption 12 h. Changing the initial solution pH (a group: 1,2,3,4,5,6,7; b group: 2,3,4,5,6) to study the effect of pH on the adsorption of U(VI), the results were shown in Figure 2.

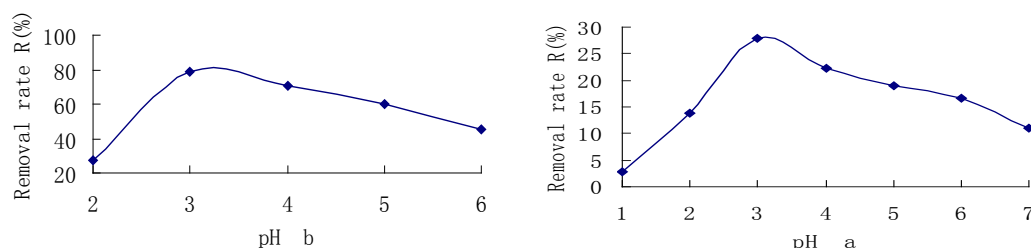


Fig.2 Effect of initial pH value on adsorption of uranium(VI)

Figure 2 showed that before and after modification, the removal rate of U(VI) changed with the pH changing, first to rise then to decrease, which has a maximum in the vicinity of pH=3, the adsorption efficiency decreased faster when the $\text{pH} < 3$ compared to $\text{pH} > 3$ and the maximum removal rate was about 86% after the significant modification. It explained the removal rate of U(VI) ions was greatly affected by pH. This was because the pH of the solution had a significant impact on the adsorption sites of activity and UO_2^{2+} ions in the presence of the state. Under strongly acidic conditions, the solution with H^+ ions combined with adsorption sites and it impacted the

adsorption of UO_2^{2+} ions. UO_2^{2+} ions were hydrolyzed to produce other ions resulting in the adsorption capacity decreasing when acidic weakened.

Effect of time on adsorption of uranium(VI). At room temperature, adding 0.20 g sorbent to the 25 ml concentration of 20 mg/L uranium-containing solution to oscillate adsorption within the certain time(2h) (a group interval of 10 mins; b group interval 20 mins within 2h). The results of effect of adsorption time on the adsorption of U (VI) were shown in Figure 3.

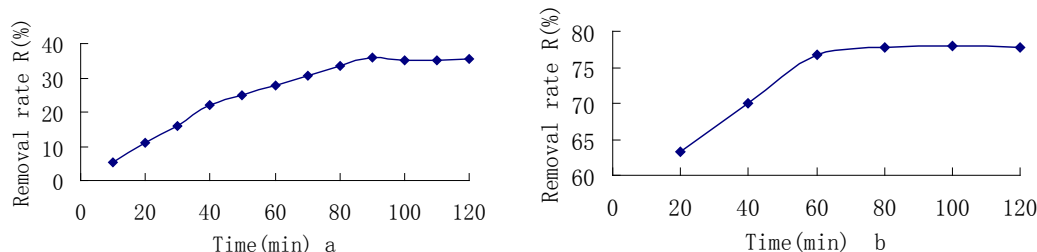


Fig.3 Effect of time on adsorption of uranium(VI)

Figure 3 showed that U(VI) ions removal rate increased with the adsorption time before and after modification, the removal rate of rapid growth within 90 mins generally tended to adsorption equilibrium about 90 mins, increasing the adsorption efficiency of about 40%.

Effect of temperature on adsorption of uranium(VI). Adding 2.0 g sorbent to 25 ml concentration of 20 mg/L uranium standard solution to oscillate adsorption 90 mins at 20 °C, 30 °C, 40 °C, 50 °C, 60 °C, the results of impact of temperature on adsorption of U(VI) were shown in Figure 4.

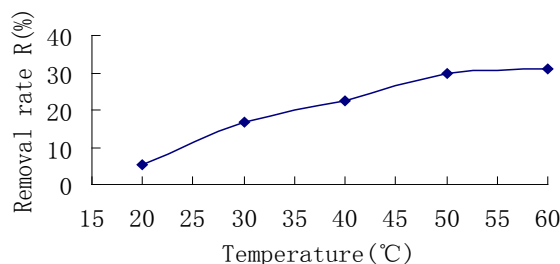


Fig.4 Effect of temperature on adsorption of uranium(VI)

Figure4 showed that U(VI) ions removal rate increased with increasing temperature. 50 °C previous rapid growth and stabilizing at around 50 °C as indicated warming adsorption. It was because the temperature accelerated the diffusion rate of ions in solution and formed some new adsorption sites in the sorbent to improve the adsorption efficiency.

Effect of initial concentration on adsorption of uranium(VI). At room temperature, adding 0.20 g of modified adsorbent in 25 ml concentration of 10 mg/L, 20 mg/L, 30 mg/L, 50 mg/L, 100 mg/L uranium-containing solution and shaking adsorption 12 h; the results of influence of the initial concentration on adsorption of U (VI) were shown in Figure 5.

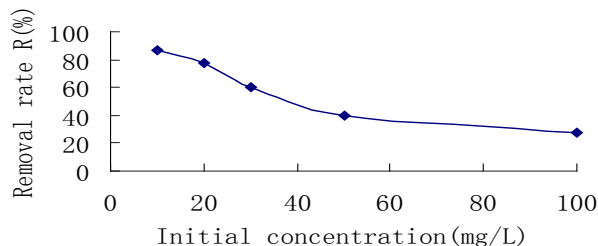


Fig.5 Effect of initial concentration on adsorption of uranium(VI)

As can be seen from Figure 5, U(VI) ions removal rate increased with the decrease of initial concentration, it was because when the uranium concentration in the solution was low and the adsorption sites could be sufficiently contacted with the ions, which had a high removal rate; With concentration of ions in solution increasing, a large number of adsorption sites came to saturated and it resulted in other ions only free in solution, so that the removal rate declined[8].

Adsorption Mechanisms

Natural uranium does not exist as the form of ions and mainly in the positive tetravalent and hexavalent positive coexistence with metal compounds or oxides, U(IV) with inorganic form stable complexes precipitated, and U(VI) often participate in the adsorption process. Uranyl ions, most of the uranium in the solution is adsorbed in the form of UO_2^{2+} ions.

Cell wall is the main place for the accumulation of metal ions, chemical analysis found that sugar cane stalks containing about 45% cellulose, 28% hemicellulose, 18% lignin. By infrared spectroscopy, we found it contained the functional groups[10] of carbon-carbon double bond, carboxyl group, carbonyl group, ether group, aryl group, phenolic hydroxyl group. For one thing, UO_2^{2+} ions diffused to the reaction interface during adsorption process and reacted esterification, etherification, chelating with functional groups to form a complex or complexes, the most important of which was hydroxyl group and carboxyl group. For another, UO_2^{2+} ions further spreaded within the modified material to exchange reaction[11]. The adsorption efficiency of modified sugar cane stalks increased significantly because its surface of the cells post-treatment contained lignin, cellulose, hemicellulose, and other structures were exposed, these structures provided UO_2^{2+} ions with organic functional groups to occur complexing ligands and to improve the adsorption efficiency[12].

Conclusions

The results showed that before the modification, the adsorption equilibrium time was 90 mins, the maximum removal rate was about 35% and the maximum adsorption capacity reached to 1.2 mg/g; an optimum pH was 3 and the optimum adsorption temperature was about 50 °C, heating was conducive to the adsorption and the optimum amount of adsorbent to the solution volume ratio was 8.0 g/L.

The adsorbent have better adsorption effect after ZnCl_2 feasible modified; maximum removal rate of U(VI) ions was about 86%, the maximum adsorption capacity reached to 2.5 mg/g, adsorption equilibrium time and optimal pH were substantially identical before and after modification. Adsorption efficiency decreased with the increasing of initial concentration of U(VI) and adsorption efficiency increased with adsorbent dosage increasing under certain initial concentration.

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