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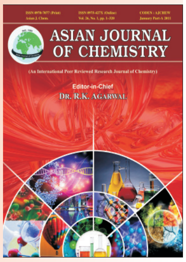

Removal of Hexavalent Chromium from Aqueous Solution by Adsorption on Treated Cole Straw†

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In this paper, cole straw was thermochemically modified with citric acid as biosorbent and characterized by FTIR spectra and CHN analysis. The adsorption properties of modified cole straw for Cr(VI) were determined. At room temperature, the removal efficiency of 0.2 g modified cole straw under 10 h vibration time for Cr(VI) solution with condition of 100 mL, 10 mg/L and pH 2 can be up to 100 %. The adsorption data were fitted well by Langmuir isotherm, adsorption capacity was found to be 28.2 mg/g of adsorbent at Cr(VI) concentration in the effluent being 5 mg/L, $\Delta G = -0.57$ kJ/mol. The negative value of ΔG indicates the feasibility and spontaneous nature of adsorption. The presence of Cr(III) proved that the adsorption of Cr(VI) coexists with the redox process in acidic condition. The modified cole straw is a potential biosorbent which could be used in treatment of chromium contaminated wastewater.

Keywords: Cr(VI), Cole straw, Modification, Adsorption.

INTRODUCTION

With the development of modern industry, the pollution of heavy metals has become one of the severe water pollution. The methods to deal with the pollution of heavy metals are varied, adsorption is widely accepted by the researchers because of the low cost materials and the good effect. Absorbent is the key of adsorption. In recent years, dealing with heavy metal ions by agricultural wastes has received extensive attention[1]. In Anhui province located in the midland of China, cole straw (CS) is a very common and abundant. It is a fibrous material and the presence of compounds such as cellulose, hemicellulose, lignin and silica in this material, with binding sites capable to take up metals. The aims of the present investigation are to detect the performance of modified cole straw (MCS) on Cr(VI) removal from aqueous solution, to evaluate the effect and to obtain adsorption isotherms and thermodynamic parameters.

EXPERIMENTAL

Analytical grade reagents were used in all cases. The stock solution of Cr(VI) (1 mg/mL) was prepared by dissolving the exact quantities of $K_2Cr_2O_7$ (AR grade) in distilled water.

All working concentrations were obtained by diluting the stock solution with distilled water.

Preparation of modified cole straw: The air-dried cole straw was obtained from a local farm and was passed through different sieve size. Cole straw was washed several times with distilled water and was dried for 2 h at 100 ºC. The chemical modification of cole straw was made according to the similar method described by Wing[2].

Adsorption experiments: Batch Cr(VI) adsorption studies were performed by mixing requisite quantity of modified cole straw with 100 mL of solution of varying Cr(VI) concentrations. Initial pH was adjusted using 0.1 mol/L HCl or 0.1 mol/L NaOH. The adsorption of Cr(VI) was carried out in a shaking machine at room temperature. The solution was intermittently sampled and centrifuged at 8000 rpm for 8 min. The supernatant was collected for Cr(VI) and total Cr concentration measurements.

Analysis: The absorbance of Cr(VI) in aqueous phase was measured by the 1,5-diphenyl carbazide method[3]. Total Cr concentration was determined by ammonium persulfate method[4]. The removal percentage (E %) of Cr(VI) was calculated according to the following equation:

$$E(\%) = \frac{(C_i - C_f) \times 100}{C_i}$$

where C_i is the initial Cr(VI) concentration (mg/L); C_f is the final concentration (mg/L).

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RESULTS AND DISCUSSION

Characterization of adsorbent: The percent of C, H and N element in the modified and unmodified cole straw were presented in Table-1. The increase in the O content was due to the adsorption of citric acid on to cole straw surface.

TABLE-1
ELEMENTAL COMPOSITION OF (A) COLE STRAW (B) MODIFIED COLE STRAW

Sample	C (%)	H (%)	O (%)
(A) Cole straw	43.53	6.11	47.36
(B) modified cole straw	43.56	5.54	52.77

The FTIR spectrum of cole straw, modified cole straw and chromium loaded modified cole straw were shown in Fig. 1. The absorption peaks and there wave numbers are quite consistent in three curves. The intensity of the band at 1734 cm^{-1} increased due to the increase in the aliphatic carbon content in modified cole straw, which in turn is due to the adsorption of citric acid on to cole straw surface. No change in the spectrum was observed for the chromium loaded modified cole straw.

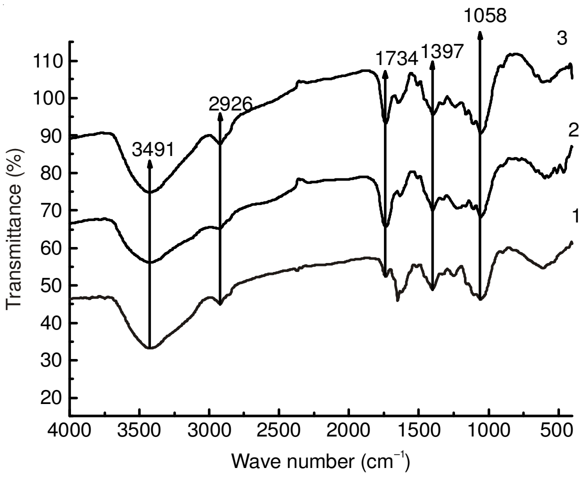

Fig. 1. FTIR of (1) cole straw, (2) modified cole straw and (3) adsorbent after Cr(VI) adsorption

Effect of initial solution pH: The pH of aqueous solution has been known as the most important variable affecting Cr(VI) adsorption onto biosorbents. Fig. 2 clearly shows that maximum removal efficiency was observed at pH 2 and hence it was taken as the optimal pH value. There was a sharp decline in per cent removal efficiency with increase in pH of the aqueous solution. The removal efficiency was 60 % under same standard conditions by using cole straw (no presented in Fig.).

The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups present on the adsorbent and the metal chemistry in solution[5]. These phenomena may be explained by that at low pH the surface of corncob are protonated so that the net surface charge is positive, which enhances the adsorption of the negatively charged oxyanionic Cr(VI) ($HCrO_4^-$) species. As the pH increases, the surfaces are increasingly deprotonated so that the net surface positive charges are decreasing, leading to a reduction in Cr(VI) adsorption[6]. It has also been postulated that under acidic conditions, Cr(VI) could be reduced to Cr(III) in presence of an adsorbent.

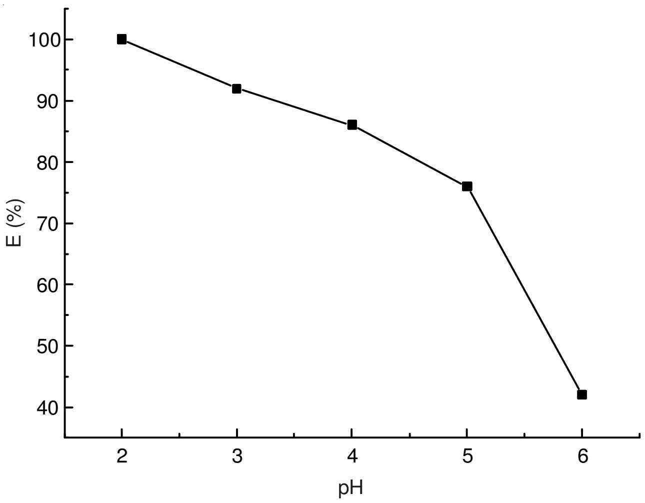

Fig. 2. Effect of initial solution pH on Cr(VI) removal efficiency: dosage = 2 g L^{-1}, C_i = 10 mg L^{-1}, T = 298 K and t = 10 h

Dichromate ion ($Cr_2O_7^{2-}$) under acidic conditions get reduced to Cr^{3+},

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

Effect of initial Cr(VI) concentration: The effect of initial Cr(VI) concentration on the sorption of Cr(VI) at pH 2 was presented in Fig. 3. The removal rate of Cr(VI) decreased with increase in initial chromium concentration, while the actual amount of chromium adsorbed per unit mass of the adsorbent was increased with increase in chromium concentration in the test solution.

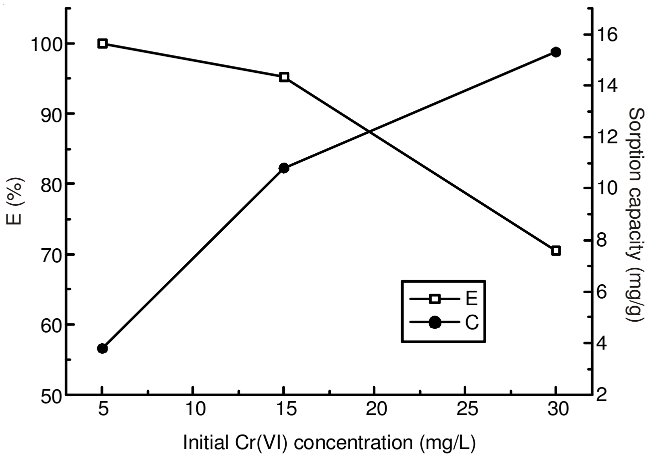

Fig. 3. Effect of initial Cr(VI) concentration on Cr(VI) removal efficiency: dosage = 2 g L^{-1}, pH 2 and T = 298 K

This phenomenon maybe explained: at lower initial concentrations, sufficient adsorption sites are available for the sorption of Cr(VI). And the increased Cr(VI) concentrations provide the maximum driving force to overcome all the mass transfer resistances of metal ions from the aqueous phase to solid phase resulting in higher probability of collision between metal ions and the active sites[7], so the adsorption capacities is increased when adsorbent is constant.

Effect of adsorbent dose: The removal efficiency of Cr(VI) was studied at different adsorbent doses (Fig. 4). The results showed that with increase in the adsorbent dose, the removal efficiency of chromium was increased and the removal

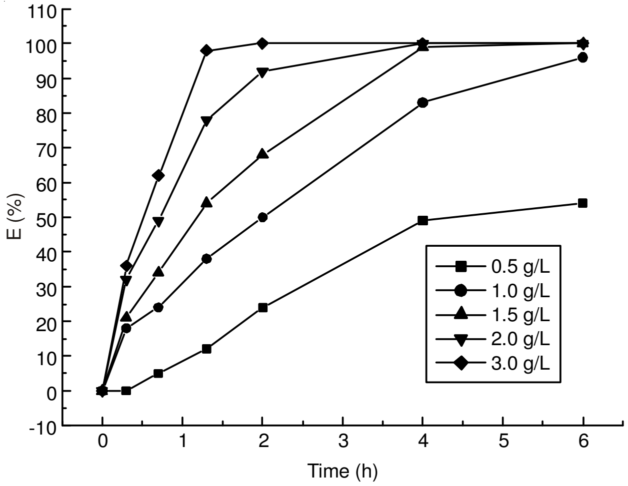

Fig. 4. Effect of adsorbent dose on Cr(VI) removal efficiency: $C_i = 5$ mg L^{-1}, T = 318 K and pH = 2

reaction equilibrium time was shorter. It may be due to the increase in adsorbent surface area and availability of more adsorption sites.

Effect of temperature: Temperature may play an important role in the process of Cr(VI) removal. The variation of sorption with temperature was studied at 298, 308 and 318 K under the optimized conditions selected and the data were shown in Fig. 5. Increasing temperature can finitely enhanced the Cr(VI) removal rate and the adsorption process of Cr(VI) on modified cole straw was endothermic.

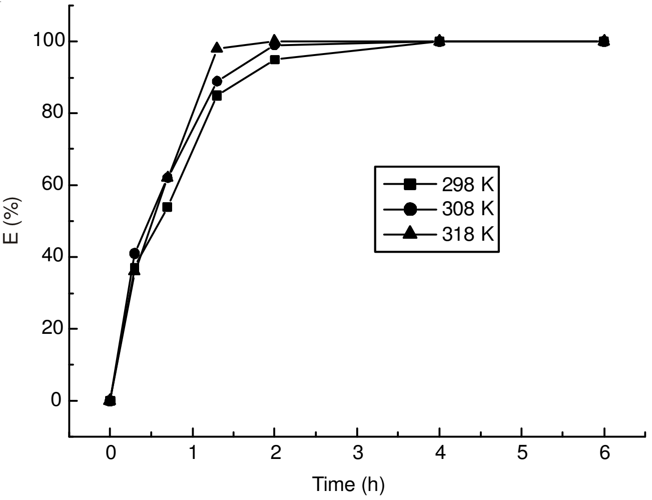

Fig. 5. Effect of temperature on Cr(VI) removal efficiency: dosage = 3 g L^{-1}, $C_i = 5$ mg L^{-1} and pH = 2

Adsorption isotherms and thermodynamic parameters: The Langmuir isotherm was applied to estimate the adsorption capacity of adsorbents used and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules.

To find out the mechanistic parameters associated with metal ion adsorption, the result was analyzed by Langmuir isotherms. The mathematical expression of the Langmuir isotherm is,

$$\frac{C_e}{Q_e} = (Q_0 b)^{-1} + \frac{C_e}{Q_0}$$

where C_e is the equilibrium concentration of the adsorbate in solution (mg/L), Q_e the equilibrium loading of sorbate on sorbent (mg g^{-1}), Q_0 and b are the Langmuir constants related to maximum adsorption capacity (mg g^{-1}) and the relative energy of adsorption (L mg^{-1}), respectively.

The equation was $C_t/Q = 0.0041 + 0.0354C_t$, $R^2 = 0.9952$. As indicated by the adsorption coefficients computed from above equation, the adsorption isotherms of modified cole straw well fitted the Langmuir model. Using the slope and the intercept of this line, Q_0 and b were found to be:

$$Q_0 = 28.2 \text{ mg g}^{-1}, \ b = 8.65 \text{ L mg}^{-1}.$$

Gibbs free energy change, ΔG, is an important criterion for spontaneity of a chemical reaction. Value of ΔG can be determined from the following equation:

$$\Delta G = -RT \ln b$$

The values of ΔG obtained -0.57 kJ/mol at 318 K. It is clear the values of was negative suggesting that the adsorption process involved was spontaneous.

Cr(VI) reduction: It was suggested that Cr(VI) was removed from aqueous solutions through a reduction process by biosorbent[8]. The Cr(VI) and total Cr concentration in the filtered solution were measured, respectively and was shown in Fig. 6. Cr(III) concentration was obtained the difference between total Cr and Cr(VI) concentration. It is natural that Cr(VI) can be easily and spontaneously reduced to Cr(III) by contact with the electron-donor groups carboxyl groups of the biomaterial that have lower reduction potential values than that of Cr(VI).

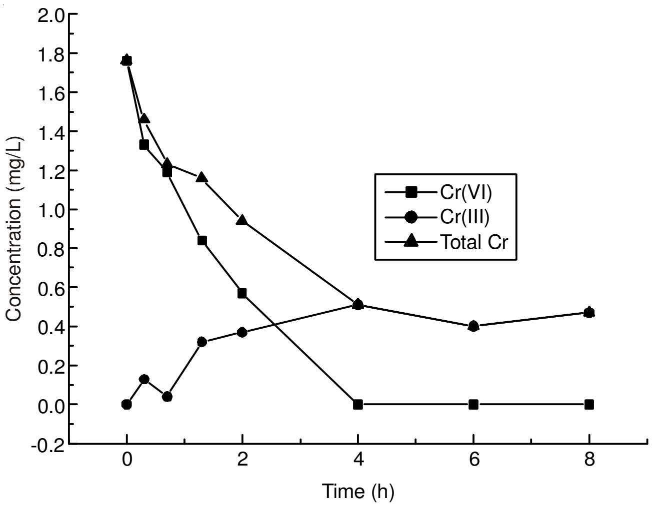

Fig. 6. Test of Cr(VI) reduction

Conclusion

Citric acid was used to modify the surface of cole straw. Chromium removal was substantially greater for modified cole straw than for raw cole straw. The optimal initial pH was 2 and the Cr(VI) removal rate increased with decreased Cr(VI) concentration and the adsorbent dose and with increased temperature. Equilibrium was achieved in about 4h under standard conditions. The reduction of Cr(VI) to Cr(III) also took place during adsorption process. Isotherm studies showed that the sorption of chromium onto the modified cole straw generates monolayer formation. The studies indicated that cole straw, as low cost biomaterial which had high chromium uptake capacity (28.2 mg Cr/g) should be seriously considered for the disposal of chromium from water and wastewater.

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