

Removal of Cr (VI) from aqueous solution using *Camellia oleifera* abel shell-based activated carbon

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Abstract: The possible use of activated carbon (COASAC) prepared from *Camellia oleifera* abel shells (COAS) by phosphoric acid activation as a biosorbent in the removal of Cr (VI) from aqueous solution was demonstrated. The effect of different parameters such as initial concentration of Cr (VI), dose of adsorbent, pH and temperature on Cr (VI) adsorption were investigated. The results showed that the maximum uptake of Cr (VI) was up to 165.0 mg/g at pH of around 2.0, under the initial Cr (VI) concentration of 250 mg/L and the temperature of 293K. The adsorption kinetics was found to follow a pseudo-second order kinetic model. The extent of the Cr (VI) removal increased with increasing initial Cr (VI) concentration and the equilibrium data fitted well to the Freundlich model.

Introduction

Heavy metal pollution has been represented as an important environmental problem due to its toxic effects and accumulation throughout the food chain and the human body. Furthermore, heavy metals are nonbiodegradable and tend to posing health hazards if their concentrations exceed allowable limits^[1]. Hexavalent chromium is a highly toxic metal that may result to cancer in humans if prolonged inhalation, and it is toxic to aquatic life at relatively low concentrations.

For the removal of Cr(VI) from contaminated water, several methods such as membrane filtration, coagulation, adsorption, oxidation, ion exchange and precipitation have been investigated. Adsorption with activated carbon is highly efficient for the removal of numerous trace elements from water, but the high cost inhibits its large-scale use as adsorbent^[2-5].

Camellia oleifera abel shells (COAS) is a genus of *Camellia* family which is widely distributed in the southern China. The annual production in 2014 was 383 700 tons and this production generates a huge amount of shells as waste material.

In this work, we demonstrated that activated carbon prepared from COAS was an effective adsorbent in the removal of Cr(VI) from aqueous solutions. The effects of pH, adsorbent dosage, temperature and initial concentration on the adsorption of dye were studied. The analysis of adsorption isotherms of Cr(VI) over COASAC was investigated as well.

Experimental

Materials

The activated carbons (COASAC) was prepared from COAS by phosphoric acid activation at an impregnation ratio of 1:3. The mixture was maintained at room temperature for 24 h to incorporate all the chemicals in the interior of the particles, and then evaporated to dryness at 105 °C. The sample was heated from room temperature to 873 K at a heating rate of 5 K/min. The sample was activated at 873 K for a holding time of 90 min. The specific surface area of COASAC is about 1102 m²/g.

Chemicals

All the chemicals used in this work were AR grade and ion-free distilled water was used throughout. The stock solutions of Cr(VI) were prepared by dissolving appropriate quantities of $K_2Cr_2O_7$ in distilled water. The pH values of the solutions were adjusted with 0.1M HCl or 0.1M NaOH. Fresh dilutions were made before each experiment.

Batch equilibrium studies

Batch adsorption experiments were carried out in 250 ml Erlenmeyer flasks by transferring 100 ml Cr (VI) solutions, and a known weight of COASAC particles. The mixtures were shaken on an orbital shaker at 200 rpm in tightly stopped flasks at a fixed temperature for a known period of time. The suspensions were filtered through Whatman filter paper (No.42) and the concentration of Cr(VI) in the filtrate was measured on a Varian AA240 atomic absorption spectroscopy (AAS), from which the adsorption capacity (q) and the strain away rate (R) were calculated according to the following equations:

$$q = \frac{c_0 - c_e}{m} * v \quad (1) ; \quad R = \frac{c_0 - c_e}{c_0} * 100\% \quad (2)$$

Where c_0 (mg/L) is the initial concentration of Cr (VI), c_e (mg/L) is the concentration of Cr (VI) at equilibrium, v (ml) is the volume of the solution, and m (mg) is the weight of COASAC.

Results and discussion

Effect of temperature

The effect of temperature on the percentage of adsorption and Cr (VI) biosorption capacity of the adsorbent were performed at different temperatures of 293, 303 and 313 K (conditions: $C_0=250$ mg/L, $T=293$ K, $pH=2.0$, $W/V = 0.1$ g/100 mL).

The results presented in Fig.2.indicated that the removal of Cr (VI) by adsorption on COASAC was found to be accelerated from 293 to 313 K. The fact that the adsorption of Cr (VI) is in favor of temperature indicates that the mobility of the Cr (VI) molecule increases with a rise in the temperature, then the Cr(VI) molecule interacts more effectively with the sorbent surface. The increase in adsorption capacity with increasing temperature suggests that the process of removal of Cr (VI) by COASAC is endothermic in nature and activated process.

It can be also seen from the Fig.2 that the adsorption of Cr (VI) onto COASAC increases significantly within the first 160 min. The rapid Cr (VI) uptake stage was likely to be large surface of COASAC due to its highly porous and mesh structure and the abundant availability of active sites on the surface. The adsorption process attained equilibrium within 10 h. Therefore, all further studies were carried out for 10 h.

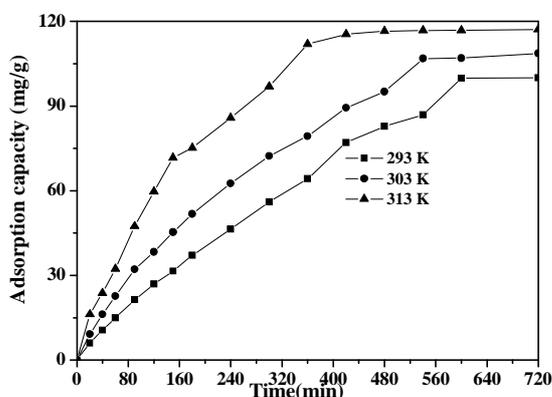


Fig.1 Effect of temperature on the adsorption to Cr (VI) by COASAC

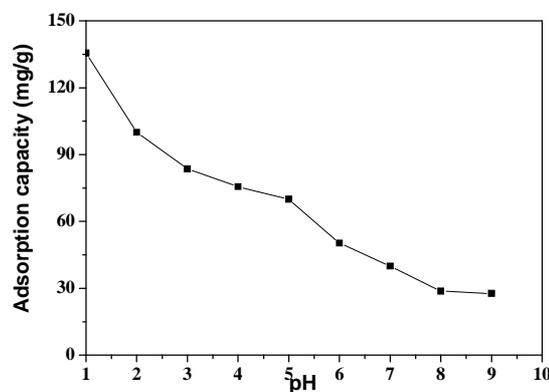


Fig.2 Effect of pH on the adsorption to Cr(VI) by COASAC

Effect of pH

The effect of pH on Cr(VI) ion removal of this study were conducted at vary of pH ranging from 1.0 to 9.0 on COASAC($C_0 = 250$ mg/L, $T=293$ K, $W/V = 0.1$ g/100 mL, $t = 10$ h). The results presented in Fig.3 showed that the removal ratios of Cr(VI) were decreased as the pH increased. When the pH=1 and pH=9, the maximum removal ratio of Cr(VI) were 54.2%, 11.1 %, respectively. So the optimum adsorption of Cr(VI) by camellia oleifera Abel shell was observable at pH=1.0.

Effect of initial concentration of Cr(VI)

A series of experiments were performed at different initial concentration ($T=293$ K, $pH=2$, $W/V = 0.1$ g/100 mL, $t = 10$ h).

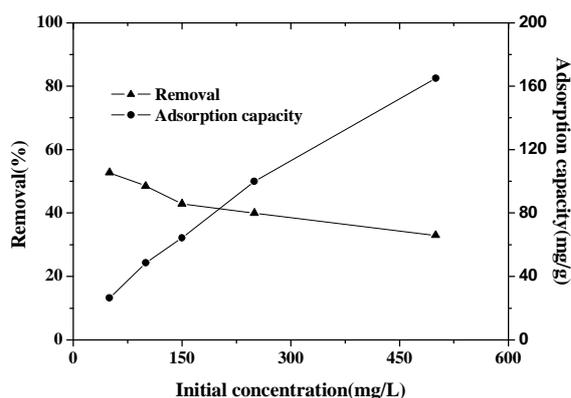


Fig.3 Effect of initial concentration on the adsorption to Cr(VI) by COASAC

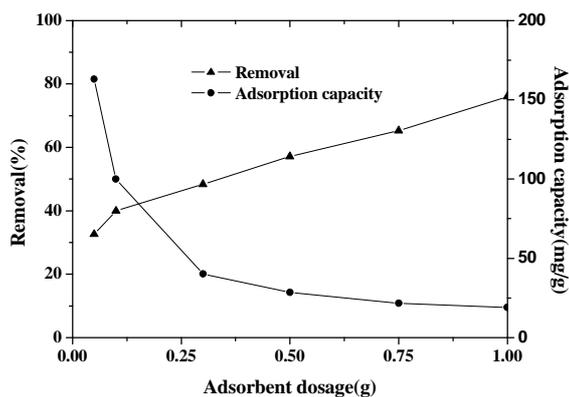


Fig.4 Effect of dosage on the adsorption to Cr(VI) by COASAC

It could be seen from the Fig.4 that when the initial Cr(VI) concentration increased from 50 to 500 mg/L, the removal ratio of Cr(VI) decreased from 52.7% to 33.0 % and the Cr(VI) biosorption capacity of the biomass increased from 26.4 mg/g to 165.0 mg/g, this was probably the higher concentration of Cr(VI) led to faster and more binding sites compared to lower initial Cr(VI) concentrate ion at the same dose of adsorbent. Moreover, higher initial concentration of Cr(VI) increased driving force to overcome the mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between the adsorbates and adsorbents.

Effect of adsorbent dosage

The trend of adsorption at varying doses of adsorbent is shown in Fig.5 ($C_0 = 250$ mg/L, $pH=2.0$, $T=293$ K, $t = 10$ h).

The percentage of Cr(VI) adsorbed increased rapidly with increasing sorbent concentration due to the greater availability of the exchangeable sites or surface area. The Cr(VI) adsorption capacity of the adsorbent decreased from 163.0 to 19.0 mg/g when the adsorbent dosage increased from 0.5 to 10g/L. The decrease in Cr(VI) uptake at higher adsorbent concentration might be attributed to the competition of Cr(VI) ions for the adsorption sites available (S.S. Baral, et al., 2008). Further agglomeration of the adsorbent particles resulted in a decrease in total adsorbent surface area available to Cr(VI) and an increase in diffusion path length, which could be another reason for the decrease in uptake.

Adsorption kinetics

The linear form of the pseudo-first-order model for the adsorption of Cr(VI) onto COASAC is expressed as the plot of $\lg(q_e - q_t)$ versus t . The plot of t/q_t versus t shows a linear relationship for the applicability of the second-order kinetic model. The values of rate constants and correlation coefficients for each model are shown in Table 1.

The R^2 value for the pseudo-second-order model was higher than that of the pseudo-first-order model. These results illustrated that the pseudo-second-order model gives a better fit than the

pseudo-first-order model, and that adsorption may be the rate limiting step involving valence forces through sharing or exchange of electrons between adsorbent and sorbate.

T/k	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	k_0 /g/mg/min	q_e / mg/g	R^2	$K_1 * 10^3$ /g/mg/min	q_e / mg/g	R^2
293K	0.0115	422.8	0.6498	0.0054	222.2	0.9298
303K	0.0005	319.7	0.9594	0.0139	175.4	0.9842
313K	0.0005	325.0	0.8425	0.0321	158.7	0.9841

Table 1 Kinetic parameters for the adsorption of Cr(VI) ions onto COASAC at different initial temperatures

Adsorption isotherms

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms and their respective coefficients are presented in Table 2.

As seen from Table 2, Freundlich modelling exhibited a better fit to the data for Cr(VI) ($R^2=0.9975$ for Freundlich model, and $R^2=0.9585$ for Langmuir model, respectively).

Freundlich			Langmuir		
$1/n$	k	R^2	$b/(L/mg)$	$q^o/(mg/g)$	R^2
1.4467	0.2004	0.9975	0.0038	285.7	0.9585

Table 2 The imitation parameters of adsorption isotherm

Conclusions

The results of this study reveal that COASAC can be converted into an adsorbent with good adsorption capacity of Cr(VI) from aqueous solution. The maximum uptake of Cr (VI) was up to 165.0 mg/g at a pH of around 2.0, under the initial Cr (VI) concentration of 250 mg/L and the temperature of 293K. The sorption kinetics was found to follow a pseudo-second order kinetic model. The extent of the Cr (VI) removal increased with increasing initial Cr (VI) concentration and the equilibrium data fitted well to the Freundlich model.

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