Chromium (VI) removal from wastewater by acid-treated pyrolytic char derived from used rubber tires

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Introduction

Hexavalent chromium is a highly toxic pollutant of aquatic environment coming from a wide variety of industries, including textile, leather, tanning, electroplating and metal finishing. Thus, the removal of Cr (VI) from waters and wastewaters, is of significant importance for the protection of human health and natural environment. Adsorption has been long used as an effective technique for the removal of organic pollutants and heavy metals, such as chromium, from industrial wastewater due to its relatively low cost, operational simplicity and reuse potential of adsorbents (Zhao, 2005). Activated carbon has been widely used as an adsorbent to remove organic pollutants and Cr(VI) from aqueous solutions because of its high specific surface area. However, expensive running costs for the production of activated carbon have restricted its wide application (Wang, 2014). Low cost adsorbents from industrial and agricultural wastes and by-products could be the alternatives for large scale purification process. Pyrolysis is an established process, including thermal decomposition of waste tires at high temperatures under oxygen-free atmosphere which results in the recovery of valuable products such as oil and a gas fraction for energy, plus the carbonized soli residue, the pyrolytic tire char (Miguel,1998).

In the present study, acid (HNO_3)-treated pyrolytic tire char has been used as a low-cost adsorbent of Cr(VI) from aqueous solutions. The objective of this work is to assess the ability of acid-treated pyrolytic tire char for Cr(VI) removal from aqueous solutions, to evaluate the adsorption characteristics of Cr(VI) on the basis of equilibrium and kinetic studies and determine the thermodynamic parameters of Cr(VI) adsorption.

Experimental: Char was derived from the pyrolysis of used rubber tires at 450 ^{o}C in oxygen-free atmosphere under vacuum for 4 hours. For the purification of as-received pyrolytic tire char, 10 g of char were suspended in 250 mL of a HNO_3 2M solution and refluxed for 48 h under vigorous stirring. The as-refluxed pyrolytic char suspension was washed several times with distilled water until pH reaches the value of pH=7 and was labeled as 'char-purified'**.**

Kinetic experiments were carried out to find out the equilibrium time on the adsorption process according to the experimental procedure: a series of 200 mL conical flasks was prepared with the addition of 10 mg of char-purified adsorbent in 100 mL aqueous solutions of Cr(VI) with initial concentration of 10 mg L^{-1}. The suspensions were kept in the dark and stirred for 180 min at 600 rpm (25 ^{o}C). The adsorption performance of char-purified was evaluated by adsorption isotherm experiments. Five mg of adsorbent were suspended in 50 mL of aqueous solutions at varying concentrations ($C_{Cr(VI)}$ =5, 10, 20, 50, 100 mg L^{-1}) at different pH values. The suspensions were kept under dark and stirred for 60 min at 600 rpm (25 °C), to reach adsorption equilibrium. At specific time aliquots (≈ 2 mL) were withdrawn and filtered through a 0.45μm filter (HVLP, Millipore).

The concentration of Cr(VI) was determined using an ultraviolet UV–visible spectrophotometer (Hitachi U-2000) at the maximum wavelength (λ_{max}) of 540 nm.

Results

The adsorption kinetics of Cr(VI) onto purified char was fast as shown in Fig. 1. The equilibrium time was found to be 60 min. The pseudo- first order, pseudo-second order, intraparticle diffusion and Elovich kinetic models were assayed to describe the experimental data. The kinetic experimental data were better fitted by the pseudo-second order model (R^2 = 0.9998) indicating that the rate-limiting step may be the surface adsorption interactions and also, adsorption capacity is proportional to the number of active sites of pyrolytic char (Table 1).

Fig. 2 presents the adsorption equilibrium isotherms for Cr(VI) on Char purified under pH values of 4, 7 and 10.

Table 1. Correlation coefficients (R^2) values for the applied kinetic models

Kinetic Models	**R^2**
Pseudo-first order	0.9773
Pseudo-second order	**0.9998**
Intraparticle diffusion	0.4016
Elovich	0.5694

It is clearly showed that as the pH value decreases, the Cr(VI) removal ratio increases. It is indicated that the pH value of Cr(VI) solution plays a key role in adsorption capacity of the acid-treated pyrolytic tire char. The experimental data were fitted by the Langmuir and Freundlich isotherm equations. All parameters derived for the two isotherm models and their correlation coefficients (R^2) are listed in Table 2. The results have shown that Langmuir isotherm model better fits the experimental data compared with Freundlich isotherm. This indicates that the adsorption of Cr(VI) on Char purified is of monolayer type. Langmuir monolayer adsorption capacity (Q_m) and correlation coefficients (R^2) ranged from 5.12 mg g^{-1} to 10.98 mg g^{-1} and from 0.9816- 0.9121 for the Char purified with pH =10 to pH= 4, respectively (Table 2).

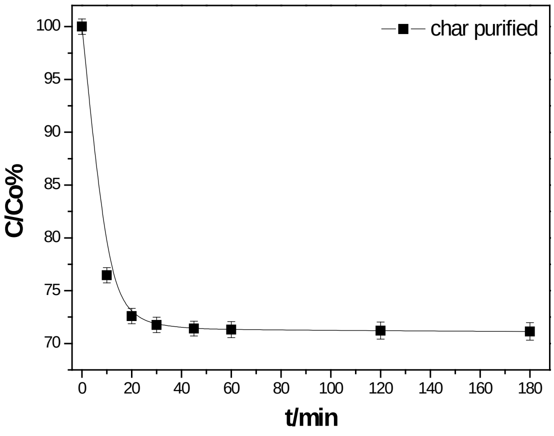

Fig. 1. Adsorption kinetics of Cr(VI) on purified char.

Table 2. Isotherm constants for Cr(VI) on Char purified.

Char purified	Freundlich			Langmuir		
	K_f (mg g^{-1})	1/n (mg L^{-1})	R^2	Q_m (mg g^{-1})	k_L (L mg^{-1})	R^2
pH=4	1.31	0.43	0.7692	10.98	0.049	0.9121
pH=7	0.73	0.43	0.9061	6.43	0.042	0.9864
pH=10	0.38	0.51	0.9176	5.12	0.033	0.9816

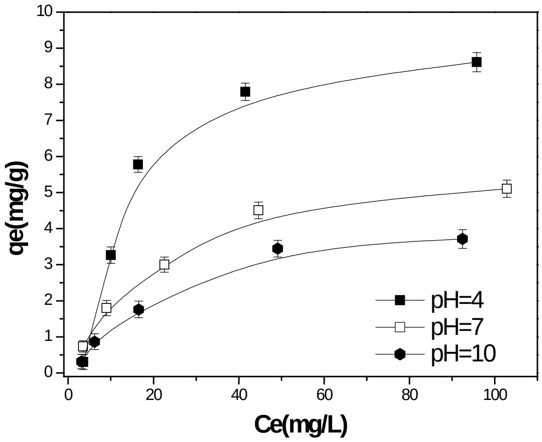

Fig 2. Adsorption isotherm of Cr(VI) on purified char at pH values of 4, 7 and 10.

- Thermodynamic parameters were calculated and are shown in Table 3. The negative values of ΔG^o at various temperatures indicate the spontaneous nature of the adsorption process. Cr(VI) adsorption onto char purified showed a negative enthalpy, indicating that the process is exothermic. The negative value of entropy exhibits the decrease of randomness at the solid-solute interface during the adsorption process.

Table 3. Thermodynamic parameters of Cr(VI) on Char purified.

	ΔH^o (kJ/mol)	ΔS^o (kJ/mol)	ΔG^o (kJ/mol)			R^2
			288 K	298 K	308 K	
Cr(VI)	-35.22	-0.038	-24.51	-24.13	-24.05	0.9791

Conclusions

- This study concludes that acid-treated pyrolytic tire char is considerably efficient for the removal of Cr(VI) from aqueous solutions. Adsorption kinetics follows pseudo-second order model while Langmuir model described better the adsorption isotherms. The adsorption process was found spontaneous ($\Delta G < 0$) and exothermic ($\Delta H < 0$).

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