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Removal of Chromate from Aqueous Solutions by Adsorption onto Commercial Activated Carbon.

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ABSTRACT

The present study is a contribution to the removal of chromate by commercial activated carbon in various conditions. Batch experiments were undertaken to evaluate the effects of adsorbent dose, contact time, chromium concentration and competitive ions. The obtained results show that the chromium sorption process is pH dependent; the maximum removal is observed at $\text{pH} < 5$. The sorption kinetics is in a relation to the solution pH; as the pH increases, the chromium removal is slower. Equilibrium is attained at onset at $\text{pH} < 6$ and after 45min at $\text{pH}=7.5$. The effects of the presence of competitive ions follow the order $\text{Ca}^{2+} > \text{SO}_4^{2-} > \text{Cl}^-$. The maximal sorption capacity obtained at $\text{pH} 3.5$ is about 150mg/g.

Keywords: chromate, activated carbon, sorption, competitive ions.

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INTRODUCTION

Chromium is usually introduced into the environment by industrial activities [1] such as petroleum refining, electroplating, tanning, metallurgy, battery and textile [2]. Among the various inorganic forms of chromium, hexavalent chromium is the most toxic. Nowadays there is a continuously increasing worldwide concern for the development of wastewater treatment technologies. However, the use of activated carbon as adsorbent is always of interest in the treatment of industrial waste waters. In the literature, a variety of materials have been tried as adsorbents for Cr (VI) [3-6] and a number of studies have been reported using activated carbon [7, 8]. However, most of them concern the adsorption in the absence of competitive ions which is not the case in industrial wastewater. The present investigation deals with the application of a commercial activated carbon in the removal of chromium (VI) from aqueous solutions at various conditions and in the presence of foreign ions.

MATERIAL AND METHODS

Characterization of the activated carbon

The activated carbon used in this study is a commercial product supplied by Biochem Company. Titration methods have been used to determine the point of zero charge (PZC) and the iodine index. The estimation of the surface functional groups was performed qualitatively by Infrared spectroscopy and quantitatively by neutralization method using NaOH and HCl solutions.

Chromate sorption experiments

All chemicals reagents used in this study were of analytical grade. All solutions were prepared with distilled water. The stock solutions of chromium were prepared by dissolving sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$) in distilled water. The adsorption experiments were performed in batch system. The effects of activated carbon dose, contact time, chromium concentrations and competitive ions were evaluated.

In all experiments, analyses were performed in solutions obtained after centrifugation and filtration through 0.45 μm membrane. The adsorption progress was measured by using UV-Visible SCHIMADZU 1650 PC spectrophotometer. The removal efficiency was calculated from the difference between the initial and the final concentrations.

RESULTS AND DISCUSSION

Characterization of the activated carbon

In the IR spectrum presented in Figure 1, the bands observed at above 3000cm^{-1} are assigned to hydroxyl group; the peak at 2356.9cm^{-1} is due to $\text{C}\equiv\text{C}$ stretching vibration [9]. The bands observed at 1103.2cm^{-1} is attributed to C-O in esters [10], those observed at 1388.7cm^{-1} and 1527.5cm^{-1} are attributed to the presence of carbonate.

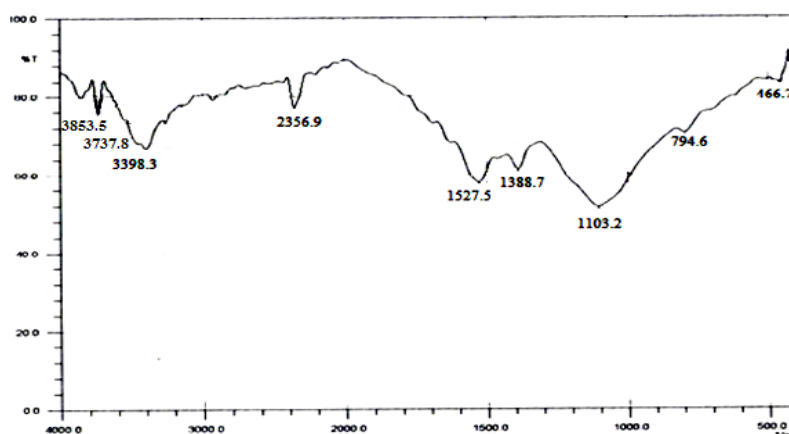


Figure 1: IR spectrum of the activated carbon

The used activated carbon is characterized by pH_{pzc} equal to 7.4; which is in the range cited in the literature [11]. The iodine index is equal to 1148.4mg/g. The total acid and basic functions are estimated to about 1.46 and 1.7 milliequivalent respectively.

Chromate adsorption

Effect of activated carbon dose

The results of the influence of activated carbon dosage (Figure 2) reveal that the optimal amount for the removal of chromium VI increases with the increase in chromium concentration. Activated carbon dosages of 1g/L, 2g/L and 2.5 g/L are necessary to obtain a total removal of chromium at pH 6 for chromate concentrations 5mg/L, 10mg/L and 25mg/L respectively.

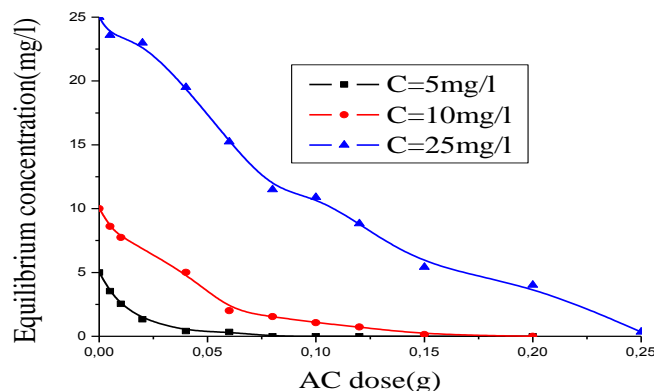


Figure 2: Evolution of chromate adsorption -Effect of the activated carbon dose (t:1h; pH:6)

Effect of pH

It can be seen in Figure 3 that the chromate removal efficiency is quite high in acidic pH. It reaches 100% at $pH < 5$. Thereafter, it decreases sharply with increasing pH to attain 22% at pH 7.5. At solution $pH < pH_{ZPC}$, the surface charge of the activated carbon is positive favoring electrostatic attraction with the anionic Cr(VI) ions, which exists in different anionic forms in solution, such as $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} . At $pH > pH_{ZPC}$ the negative charge of the activated carbon surface induces electrostatic repulsion. At alkaline pH, the chromium ions compete with OH^- for the available adsorption sites.

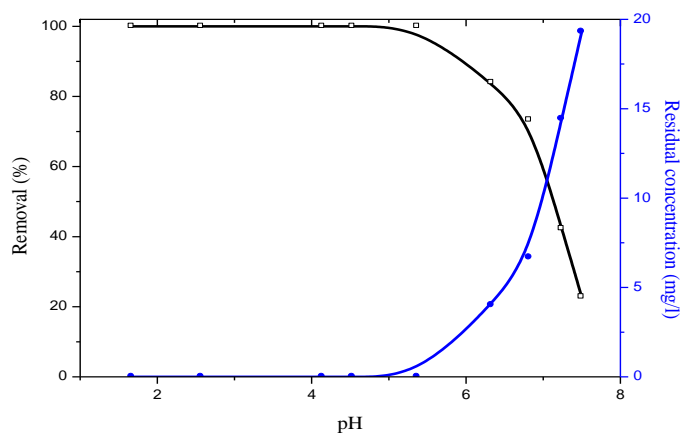


Figure 3: Evolution of chromate adsorption -Effect of pH (C₀:25mg/L; activated carbon dose: 2g/L; t:1h)

Effect of contact time - Kinetic study

The effect of contact time on Cr (VI) removal by the used activated carbon is shown in Figure 4. It suggests that the evolution of chromium uptake is pH dependent; as pH increases the processes becomes slower. At pH<6, the chromium sorption capacity increases rapidly with time. A quick sorption process occurs at pH 3.9 and 5.6. At pH 6.5 and 7.5, the chromium removal follows two steps; a rapid first one followed by a second slower.

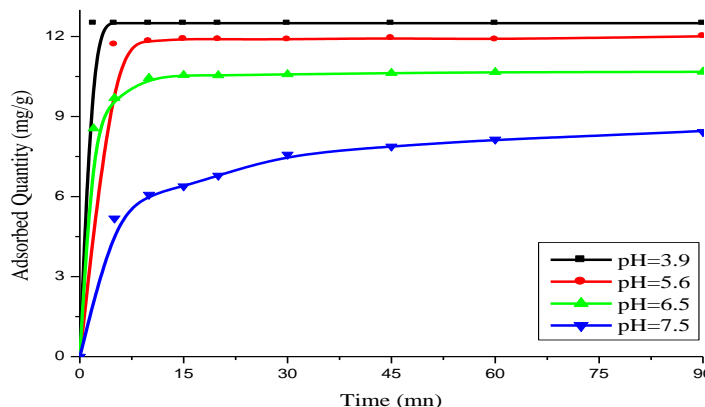


Figure 4: Evolution of chromate adsorption - Effect of time

(C₀:25mg/L; t:1h; activated carbon dose: 2g/L)

In the presence of sulfate and calcium ions which coexist usually with Cr(VI) in wastewater, the adsorption capacity of the activated carbon via chromium decreases (Figure 5). Ca²⁺ exhibits the largest competing effect followed by SO₄²⁻. No effect is observed in the presence of chloride ions. This can be attributed to the fact that Cl⁻ which is a monovalent ion has no competition for adsorption sites. Whereas, SO₄²⁻ is polyvalent ion and has similar structure and size with Cr₂O₇²⁻, HCrO₄⁻ and CrO₄²⁻ [12].

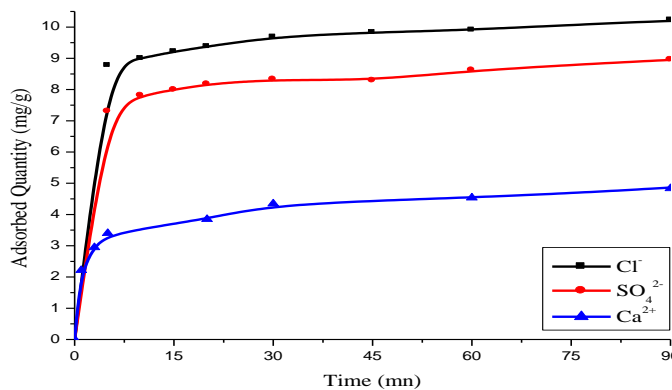


Figure 5: Evolution of chromate adsorption - Effect of competitive ions

(C₀: 25mg/L; C_{ions}: 50mg/L; activated carbon dose: 2g/L; t: 1h; pH: 6)

Five kinetics models are applied to the experimental data: pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models. The corresponding parameters are summarized in Table 1. The calculated correlation coefficients (R) show that the chromium uptake kinetics is better described by the pseudo second order model either in the absence or in the presence of competitive ions. The equilibrium adsorbed quantities calculated by the equation of the second order model are closer to the experimental ones. It has been found that this model describes well the chromium sorption in several studies using various activated carbon [13, 14]. As the pH increases from 5.6 to 7.5, the kinetics constant decreases from 0.57

$\text{g.mg}^{-1}.\text{mn}^{-1}$ to $0.02 \text{ g.mg}^{-1}.\text{mn}^{-1}$. In the presence of foreign ions this constant decreases in the order $\text{Cl}^- < \text{Ca}^{2+} < \text{SO}_4^{2-}$.

Table 1: Kinetic parameters for the chromate removal by activated carbon – Effect of pH

Model	Parameters	pH		
		5.6	6.5	7.5
Pseudo first order model $\text{Ln}(Q_e - Q_t) = \text{Ln}Q_e - K_1 t$	$K (\text{mn}^{-1})$	0.4934	0.4325	0.0438
	$Q_e (\text{mg.g}^{-1})$	7.04	7.42	3.79
	R	0.938	0.985	0.995
Pseudo second ordre model $t/Q_t = 1/(K_2 Q_e^2) + 1/Q_e \cdot t$	$K (\text{g.mg}^{-1}.\text{mn}^{-1})$	0.57	0.15	0.02
	$Q_e (\text{mg.g}^{-1})$	12.01	11	8.84
	R	0.999	0.999	0.999
Intra-particle diffusion $Q = K_d \sqrt{t} + C$	$K_d (\text{mg.g}^{-1}.\text{mn}^{1/2})$	0.1281	1.1115	0.4429
	R	0.999	0.955	0.958
Elovich $Q = K_3 \text{Ln}t + C$	K	0.19	1.21	1.17
	R	0.999	0.991	0.993

Table 2: Kinetic parameters for the chromate removal by activated carbon in the presence of foreign ions

Models	Parameters	Ions		
		Cl^-	SO_4^{2-}	Ca^{2+}
Pseudo first order model $\text{Ln}(Q_e - Q_t) = \text{Ln}Q_e - K_1 t$	$K (\text{mn}^{-1})$	0.0271	0.0196	0.0186
	$Q_e (\text{mg.g}^{-1})$	1.76	1.83	2.34
	R	0.987	0.971	0.955
Pseudo-second-ordre model $t/Q_t = 1/kQ_e^2 + 1/Q_e t$	$K (\text{g.mg}^{-1}.\text{mn}^{-1})$	0.0456	0.0363	0.0415
	$Q_e (\text{mg.g}^{-1})$	10.46	9.3	5.26
	R	0.999	0.999	0.996
Intra-particle diffusion $Q = K_d \sqrt{t} + C$	$K_d (\text{mg.g}^{-1}.\text{mn}^{1/2})$	0.1812	0.1941	0.2669
	R	0.981	0.972	0.958
Elovich $Q = k_3 \text{Ln}t + C$	K	0.5166	0.5493	0.5756
	R	0.995	0.979	0.981

Effect of chromate concentration-isotherms

The evolution of chromate uptake in function of equilibrium concentrations is illustrated in Figure 6. The solution pH has a significant effect on the adsorption capacity of the used activated carbon. The experimental data have been modeled by Langmuir, Freundlich, and Temkin equations. The calculated isotherms parameters are resumed in Table 3. The correlation coefficients of the three models are closer, showing that the chromium uptake is due to physical and chemical sorption. At pH 3.5 and using the Langmuir equation, the adsorption capacity is estimated to about 150mg/g. It falls to about 50mg/g at pH 5.5. The adsorption capacity at pH 3.5 is greater than those obtained in several studies cited in the literature [8, 13, 14, 15].

Table 3: Isotherm parameters of chromate removal by activated carbon

Isotherms	Parameters	pH		
		3.5	4.5	5.5
Langmuir $Q = Q_{\text{max}} K_L C_e / (1 + K_L C_e)$	$Q_{\text{max}} (\text{mg mg}^{-1})$	150.8	86.88	50.94
	K_L	1.03	0.59	1.11
	R	0.998	0.993	0.986
Freudlich $Q = K_f C_e^{1/n}$	K_f	63.78	31.7	19.95
	n	2.3	2.53	2.62
	R	0.919	0.994	0.999
Temkin $Q = b + a \text{Ln}C$	a	76.23	35.51	16.49
	R	0.988	0.993	0.999

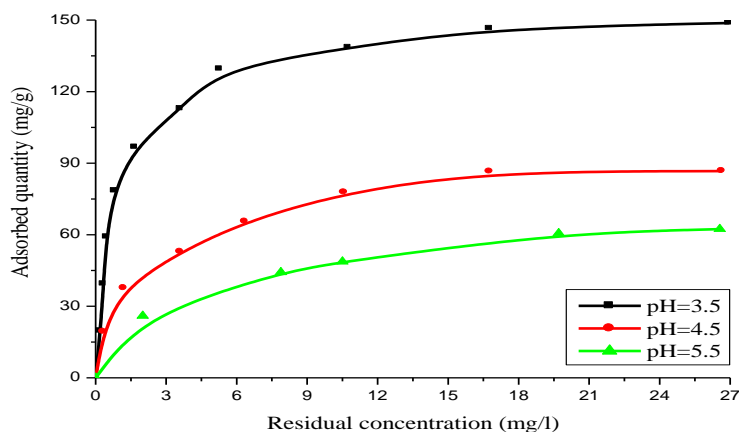


Figure 6: Evolution of chromate adsorption - Effect of concentration
(activated carbon dose: 2g/L; t:1h)

CONCLUSION

The present work evaluates the use of a commercial activated carbon for the elimination of Cr (VI) from aqueous solutions in the absence and in the presence of competitive ions. The obtained results show that the used activated carbon is more effective to remove chromium at acidic pH. The presence of competitive ions implies a decrease in both the velocity and the efficiency of the removal.

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