Chromium removal by adsorption onto activated carbon

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The aim of this study was to investigate the effectiveness of granular activated carbon for adsorption of hexavalent chromate ion Cr (VI) from aqueous solution. The results are best fitted with Langmuir isotherm with maximum adsorption capacity of 1.381mg.g^{-1} and pseudo-second order kinetic model.

I. Introduction

Out of the various toxic pollutants chromium and its derivatives are considered as the most dangerous inorganic water pollutants [1]. Typically in environmental waters Chromium comes from industrial pollution sources, including tanning factories, steel works, wood preservation and artificial fertilizers. [2] Because of the toxicity of Cr (VI) even at low concentrations less than 0.05 mg.L^{-1} and its consequences on the human health, it is important to remove it from water. There are many developed techniques for removing Cr (VI) ions from water [3]. Several metal ions removal techniques have been targeted as possible solutions. Ion exchange, reduction, chemical precipitation, polymer based membrane separation, adsorption, electrochemical precipitation, solvent extraction, cementation and electro kinetic remediation are among the available methods which may be used to reduce the metal concentrations in aqueous effluents [4]. Adsorption is widely used to remove heavy metals from industrial waste waters [5]. In the present paper, a commercial activated carbon was used for sorption of Cr (VI) from aqueous solution.

II. ExperimentalMaterials and Methods

A commercial activated carbon (AC) purchased from (BDH, Prolabo) was used for hexavalent chromium removal from synthetic aqueous solution. A stock solution of chromium ions was prepared (50 mg.L^{-1}) by dissolving the required amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water. The stock solution was diluted with distilled water to obtain desired concentration ranging from 1 to50mg.L^{-1}.

III. Adsorption Experiments

Adsorption experiments were carried out in a batch system to determine the effect of contact time, and initial concentration of chromium on adsorption capacity. Effect of contact time was studied by stirring 0.3g of AC and 10 ml of potassium dichromate solutions (10mg.L^{-1}). At predetermined time the samples were withdrawn from the shaker and the solution was separated from the adsorbent and filtered through Whatman No. 1 filter paper. Equilibrium experiments were carried out by contacting 0.3g of AC with 10 mL of different initial chromium solution concentrations (1-50mg.L^{-1}). The agitation was run for 24 h, a sufficient time to achieve equilibrium. The residual concentration was measured by the reaction of chromium (VI) with 1,5diphenylcarbazide which formed a complex of purplish coloration. The absorbance of the formed complex was measured at a wavelength of 540 nm [6]. Figures 1 represent a calibration range of increasing and known concentrations of chromium of 0-0.5 mg.L^{-1}. The adsorption capacity at equilibrium q_e (mg.g^{-1}) was obtained as follows:

$$q_e = \frac{(C_0 - C_e) * V}{m} \qquad (1)$$

with C_0 (mg.L^{-1}) and C_e (mg.L^{-1}) the initial anion and the equilibrium concentrations, respectively; V (L) the volume of solution and m (g) the mass of adsorbent.
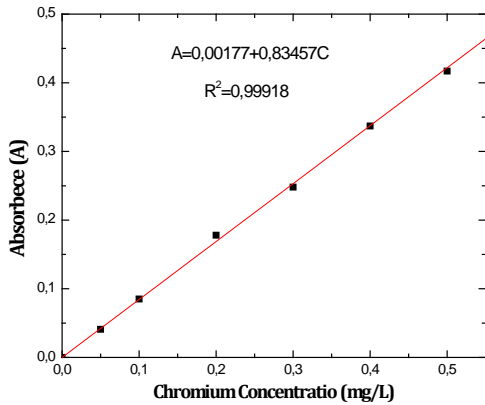
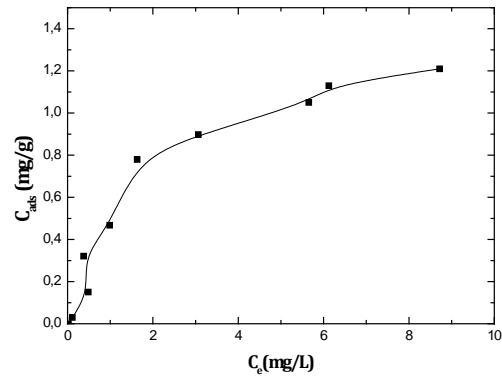**Figure1.** Calibration curve for determination of total chromium using DPC method.

Figure2. Effect of initial concentration of chromium on adsorption; (adsorbent dose: 30g.L^{-1}, contact time – 24h).

IV.   Equilibrium adsorption isotherm models

The best known isotherms models of Langmuir [7] and Freundlich [8] were used in this study to investigate the chromium ions adsorption from aqueous solutions:

Table 1. Isotherm model equations

	Langmuir	Freundlich
Isotherm equation	$q_e = \dfrac{q_{max}K_L C_e}{1 + K_L C_e}$	$q_e = K_F C_e^n$
Linear form	$\dfrac{C_e}{q_e} = \dfrac{1}{q_{max}K_L} + \dfrac{C_e}{q_{max}}$	$Ln\ q_e = Ln K_F + n\ Ln C_e$

The effect of initial concentration on Cr(VI) adsorption is represented in figure2.The adsorption capacity increased from 0.02958 to 1.1292 mg.L^{-1} with increasing initial concentration from 1 to 40mg.L^{-1}. This was due to the fact that a higher initial concentration enhanced the driving force between the aqueous and solid phases and increased the number of collisions between metal ions and adsorbents [9]. In this study both Freundlich and Langmuir isotherms had been used to describe equilibrium data (Table1; Figure 3-4). It was found that the Langmuir model fitted the data better than the Freundlich model, indicating that the adsorption of Cr(VI) on AC was a monolayer sorption type [10].
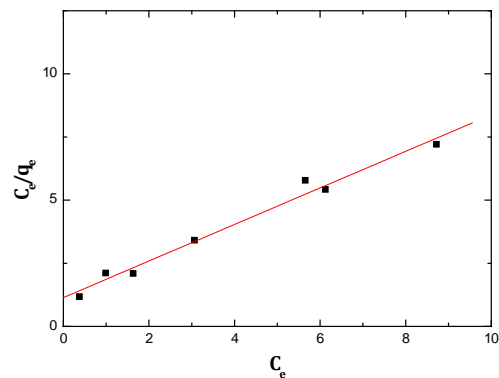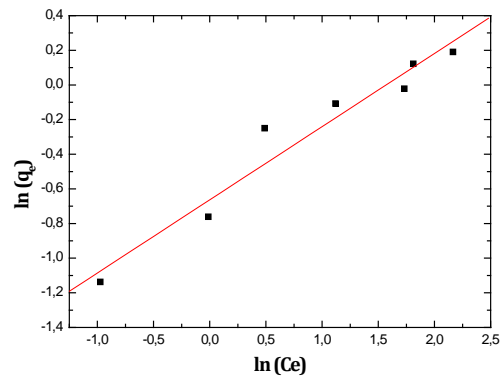

Figure3. Langmuir isotherm model

Figure4. Freundlich isotherm model

Table2. Isotherm model parameters for sorption of Cr(VI) by AC

Langmuir parameters			Freundlich parameters		
K_L	q_{max}	R^2	K_F	n	R^2
0.635	1.381	0,98194	1.940	0,42236	0,94851

V. Adsorption kinetics

The pseudo-first and second order models were applied to study the kinetics of Cr(VI) ions adsorption.

Table 3. Kinetic parameters for sorption of Cr(VI) by AC

	Kinetic equation	R^2	Ref
Pseudo-first order model	$\ln(q_e - q_t) = \ln q_e - k_1 t$	0,49567	[11]
Pseudo-second order model	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^{\,2}} + \left(\dfrac{1}{q_e}\right)t$	0,99553	[12]

The effect of contact time on Cr (VI) adsorption was represented in Figure5. It can be observed that adsorption of Cr(VI) increased with the increasing time and reached equilibrium after 360 min. It can be seen that pseudo-second-order kinetic model was able to properly describe the kinetic behavior of Cr(VI) on AC with correlation coefficients (R^2) above 0.99 [13].
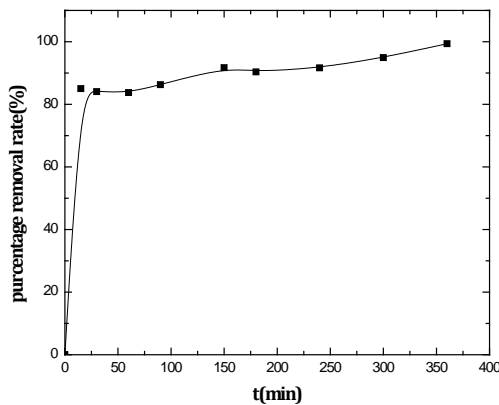

Figure5. Effect of contact time on the Cr(VI) adsorption onto AC (adsorbent dose :30g.L^{-1} , different concentrations (0-50 mg.L^{-1}).
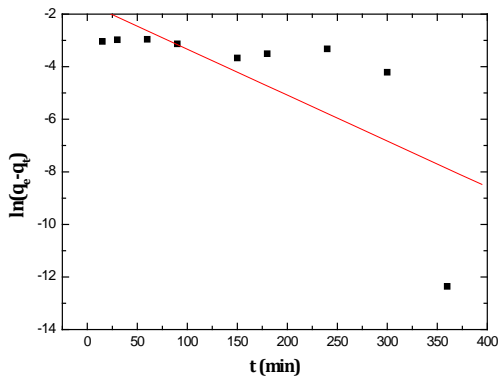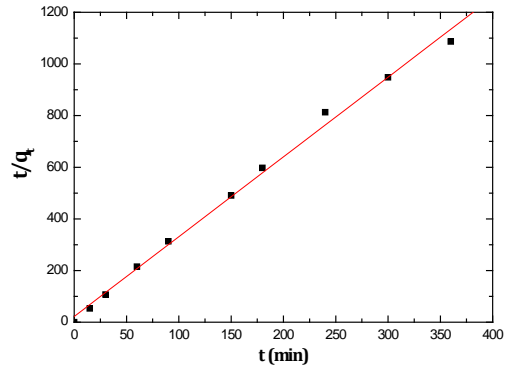

Figure6. pseudo-first order model

Figure7. pseudo-second order model

VI. Conclusion

In this study, the adsorption of hexavalent chromium onto activated carbon (AC) was investigated. Langmuir isotherm model best represented the experimental data with adsorption capacity of 1.381mg.g^{-1}. It was found that 360 minutes was sufficient to attain adsorption equilibrium. The adsorption process followed a pseudo-second-order kinetic model.

Used symbols

AC: Activated Carbon.
Cr (IV): Hexavalent chromium.
$K_2Cr_2O_7$: potassium dichromate.
DPC: 1.5 Diphenylcarbazide.
V: Volume of aqueous solution
q_e: amount of adsorbent.
C_e:equilibrium concentration of the adsorbate (mg.L^{-1})
C_0: concentration of pollutant.
q_{max}: maximum surface coverage (formation of monolayer) of sorbent (mg.g^{-1}).
K_L: adsorption energy constant of Langmuir adsorption isotherm (L.mg^{-1}).
K_F: Freundlich constant.
R: coefficient correlation.
t: time.
h: hour.
Ref: Reference

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