Acta Polytechnica **56**(5):373–378, 2016
doi:10.14311/AP.2016.56.0373

EXPERIMENTAL INVESTIGATION ON CHROMIUM(VI) REMOVAL FROM AQUEOUS SOLUTION USING ACTIVATED CARBON RESORCINOL FORMALDEHYDE XEROGELS

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Abstract. The adsorption of chromium(VI) metal ion in aqueous solutions by activated carbon resorcinol formaldehyde xerogels (ACRF) was investigated. The results showed that pore structure, surface area and the adsorbent surface chemistry are important factors in the control of the adsorption of chromium(VI) metal ions. The isotherm parameters were obtained from plots of the isotherms and from the application of Langmuir and Freundlich Isotherms. Based on regression analysis, the Langmuir isotherm model was the best fit. The maximum adsorption capacity of ACRF for chromium (VI) was 241.9 mg/g. The pseudo-second-order kinetic model was the best fit to the experimental data for the adsorption of chromium metal ions by activated carbon resorcinol formaldehyde xerogels. The thermodynamics of Cr(VI) ions adsorption onto ACRF was a spontaneous and endothermic process.

Keywords: Adsorption, Chromium(VI) ion, Langmuir isotherm, Freundlich isotherm, Activated carbon resorcinol formaldehyde xerogels (ACRF).

1. Introduction

Chromium is used in various industries such as the metallurgical industry (steel, ferro- and nonferrous alloys), refractories (chrome and chrome-magnesite), and in the chemical industry (pigments, electroplating and tanning) [1]. As a result of these industrial processes, large amounts of chromium compounds are discharged into the environment. These compounds are toxic and have negative effects on humans and the environment. Persistent exposure to Cr(VI) causes cancer in the digestive tract and lungs, and may cause other health problems, for instance skin dermatitis, bronchitis, perforation of the nasal septum, severe diarrhoea, and haemorrhaging [2, 3]. The maximum level for chromium in drinking water permitted by the World Health Organization (WHO) is 0.05 mg/L [4].

Cr(III) and Cr(VI) species are the two stable forms of chromium present in the environment. They have different chemical, biological and environmental characteristics. The most toxic form of chromium is Cr(VI), which exists with oxygen as chromate ${CrO_4}^{2-}$ or dichromate ${Cr_2O_7}^{2-}$ oxyanions. Cr(VI) compounds are highly soluble and mobile. Cr(III) is less mobile, less toxic and is mainly found bound to organic matter in soil and aquatic environments [5].

Typical methods for the removal of dissolved heavy metals from aqueous solution include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange, electrochemical treatment and application of membrane technology. However, these processes have some major drawbacks, which include incomplete metal removal, requirements for expensive equipment and monitoring system, high reagents and energy requirement and generation of toxic sludge with special disposal requirements, especially with the application of low cost adsorbents [6].

Adsorption can be an effective method for the removal of chromium from aqueous solution, especially in combination with suitable regeneration steps, which resolves the problems associated with sludge disposal and makes the process more economically viable [6]. Previous studies on the removal of Cr(VI) using activated carbons produced from coconut shells [7], clays [8], wheat bran [9], rice husk [10], tyres and sawdust [11], etc. have been reported in the literature.

This study investigates the adsorption of chromium(VI) onto activated carbon resorcinol formaldehyde xerogels using the Langmuir and Freundlich isotherms. The kinetics of adsorption was fitted with pseudo-first-order and pseudo-second-order and the controlling rate of adsorption described by intra-particle diffusion.

2. Material and methods

2.1. Material

All chemical reagents and materials used were of analytical grade. Deionised water (18.0 Ω) was used as solvent in the preparation of stock solutions of chromium metal ions by dissolving 2.828 g of potassium dichromate in 1 dm^3 of deionised water.

2.2. Synthesis of activated carbon resorcinol formaldehyde xerogels

Activated carbon obtained from the synthesis of resorcinol formaldehyde xerogels (ACRF) was used for the adsorption studies [12]. The RF xerogels were synthesised from the polycondensation of resorcinol, $C_6H_4(OH)_2$ (R), with formaldehyde HCHO (F) according to the method proposed by Pekala et al. [13, 14], RF solutions were prepared by mixing resorcinol (R), formaldehyde (F), sodium carbonate Na_2CO_3 (C) and distilled water. The solution was mixed vigorously for 45 min. The resorcinol/formaldehyde ratio R/F was fixed at 0.5, while the molar ratio of R/C and the ratio of R/W (g/cm) were varied. The homogeneous clear solution was then poured into sealed glass vials to avoid water evaporating during the gelation process. The sealed vials were then placed in an oven set at 25 °C for 24 h. Oven temperature was then increased to 60 °C for 48 h, and then finally it was increased to 80 °C for an additional 24 h to complete the curing process. The wet gels were then removed from the oven and allowed to cool to room temperature. In order, to remove water from the pores of the gels, the gels were immersed in acetone for solvent exchange at room temperature for three days. After the third day, the acetone was poured out and the gels were placed in a vacuum oven for drying. The gels were dried in a vacuum oven at 64 °C for 3 days.

2.3. ADSORPTION STUDIES

All adsorption experiments were carried out with batch reactors (glass bottles and beakers). Stock solutions (1000 ppm) of Cr(VI) metal ions were prepared. Different concentrations of standard solutions (25, 50, 100, 150, 200 and 250 ppm) were prepared by appropriate dilutions of the stock solutions with deionised water. Chromium (VI) concentrations were analysed at 540 nm wavelength using HACH-DR-2800 UV visible spectrophotometer with 1, 5-diphenylcarbazide reagent. The reagent was prepared by using 250 mg of 1, 5-diphenylcarbohydrazide which was dissolved in 50 ml of methanol (HPLC-grade). 250 ml of H_2SO_4 solution (contains 14 ml of 98 % H_2SO_4) was added into the above solution, which was then diluted with deionised water to 500 ml.

2.4. ADSORPTION ISOTHERMS

Experimental data obtained from the batch tests were analyzed using the Langmuir and Freundlich isotherms to determine the isotherm model that described the experimental data more accurately.

Langmuir Isotherm. The Langmuir isotherm assumes a monolayer, uniform, and finite adsorption site and therefore saturation is reached, beyond which no further adsorption takes place. It is also based on the assumption that there is no interaction between the molecules adsorbed on neighbouring sites [15]. The model developed by Langmuir (1916) is given by:

$$q_e = \frac{q_{max} b C_e}{1 + bC_e} \tag{1}$$

The very important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless constant called the separation factor [6, 16]:

$$R_L = \frac{1}{1 + bC_o} \tag{2}$$

Freundlich Isotherm. The Freundlich isotherm is an empirical equation for multilayer, heterogeneous adsorption sites [17]. The Freundlich isotherm is given by:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. EFFECT OF INITIAL PH

The effect of pH on the adsorption of the Cr(VI) metal ions was studied with the pH varied from 2.0–11.0. The studies were performed with constant initial metal ions of 100 ppm, adsorbent dose of 1 g/L solution and contact time of 72 h.

The adsorption of chromium(VI) (Fig. 1) increases with the pH to a maximum at pH 3, and thereafter decreases with further increase in pH. This shows that adsorption of chromium ions is pH dependent. The maximum adsorption at pH 3 may be attributed to the existence of chromium ions as $HCrO_4^-$ which is the dominant form of Cr(VI) at pH 3. The high adsorption of Cr(VI) at pH 3 might be a result of electrostatic attraction between positively charged groups of the ACRF surface and $HCrO_4^-$. This can also be attributed to fact that the surface charge on the ACRF. The pH_{zpc} of ACRF is at 9.19 and below this pH, the surface charge of the ACRF is positive. Hence, adsorption of Cr(VI) might also be due to electrostatic attraction between positively charged adsorbent and negatively charged $HCrO_4^-$ [18]. As the pH increased, the overall surface charge on the adsorbents became negative and adsorption decreased [19]. The decrease in removal at higher pH may be due to the abundance of OH^- ions which compete with the negatively charged Cr(VI) species for the active sites on the ACRF.

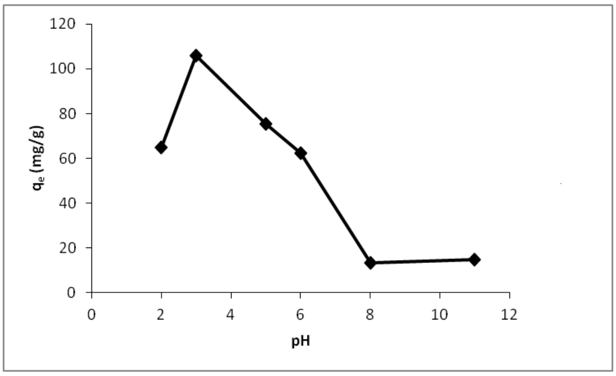

FIGURE 1. Effect of pH on adsorption of Cr(VI) ions

3.2. Effect of initial chromium(VI) concentration on ACRF

The effect of initial chromium metal ion concentration on the adsorption was studied at optimum the pH of 3 which was observed from a previous study. The experimental data for the adsorption of Cr(VI) onto activated carbon resorcinol formaldehyde xerogels were fitted to the Langmuir and Freundlich isotherms using non-linear regression analysis. The isotherm parameters are given in Table 1. Langmuir isotherm (Fig. 2) was seen to have a better fit based on non-linear regression analysis.

The value of the separation factor, R_L, determines the type of isotherm either to be favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavourable ($R_L > 1$) or irreversible ($R_L = 0$) [20]. The low value of R_L (0.000049) showed that the adsorption of chromium(VI) onto ACRF was favourable (Table 1).

3.3. Effect of temperature on chromium(VI) adsorption

The effect of temperature on the adsorption of metal ions was carried out with the temperature varied from 20 °C (293 K) to 60 °C (333 K), with initial concentration of 25–250 ppm, adsorbent dosage of 1 g/L and optimal pH. The adsorption of Cr(VI) ions was found to increase with an increase in temperature range 20–60 °C (Fig. 3). This increase in adsorption capacity of ACRF is an indication of an endothermic process [21]. This might be a result of complexation and reduction reactions [22]. Also, diffusion is an endothermic process and an increase in temperature increases the diffusion rate of the adsorbate molecules across the external boundary layers and into the pores of ACRF. Similar results were observed with adsorption of Cr(VI) onto activated carbon [23].

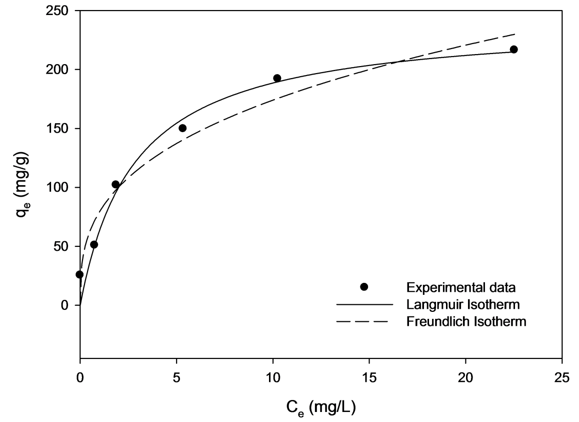

Figure 2. Application of Langmuir and Freundlich Isotherms to adsorption of Cr(VI) ions

Langmuir Isotherm	Freundlich Isotherm
$q_{max} = 241.9$	$K_F = 79.06$
$b = 0.3529$	$1/n = 0.3426$
$R_L = 0.000049$	$R^2 = 0.9441$
$R^2 = 0.9740$	

Table 1. Isotherm parameters for Cr(VI) adsorption onto ACRF

3.4. Effect of contact time

The effect of contact time on the adsorption of Cr(VI) was studied by varying the contact time from 0–420 min under pH of 3. In Fig. 4, it was seen that the uptake of the metal ions increased with increasing contact time until equilibrium was reached. The adsorption of Cr(VI) ions initially increased rapidly and then reached equilibrium. The optimum chromium removal was 74.86 % at 60 min for 25 ppm and 77.21 % at 240 min for 200 ppm; it was 100 % at 420 min for 25 ppm and 83 % at 420 min for 200 ppm.

3.5. Adsorption kinetics

The pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit the experimental data for the different initial chromium ion concentrations. The results of pseudo-second-order kinetics observed in this study are supported by the findings of Bhattacharya [8]. The values of the second

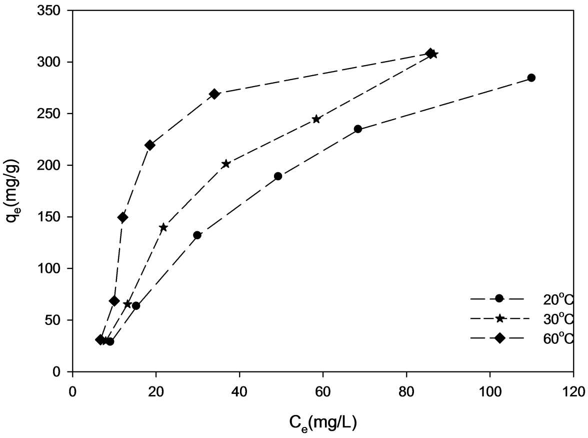

Figure 3. Effect of temperature on the adsorption of Cr(VI)

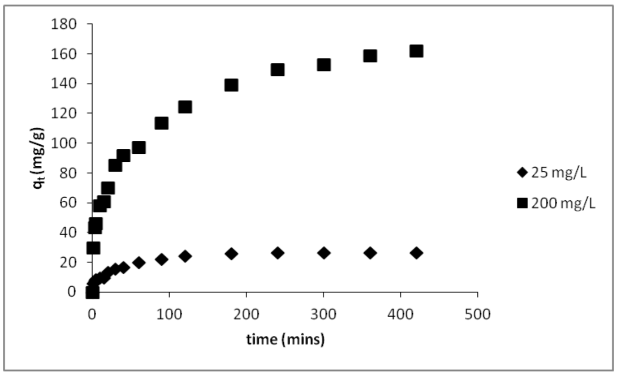

Figure 4. Effect of contact time on the adsorption of Cr(VI).

C_o (mg/L)	Pseudo-first-order		Pseudo-second-order			Intra-particle Diffusion	
	k_1	R^2	k_2	h	R^2	k_i	R^2
25	0.1705	0.9768	0.0136	3.2938	0.9743	1.5737	0.7411
50	0.0935	0.9742	0.0041	3.3706	0.9833	2.2374	0.7888
150	0.0706	0.9138	0.0015	8.3693	0.9647	3.0394	0.7584
200	0.0530	0.9499	0.0010	5.7566	0.9864	3.3937	0.8209

TABLE 2. Kinetic models and parameters of adsorption of Cr(VI)

order rate constants (k_2) were found to decrease from 0.0136–0.0010 g mg^{-1} min^{-1} as the initial concentration increased from 25–200 mg/L. This indicated that the process is highly concentration dependent [24].

3.6. MECHANISM OF ADSORPTION

As seen in Fig. 5, the ACRF spectra displayed a change of intensity and shift of the carbonyl stretching band around 1630 cm^{-1} after the contact with chromium solution. This is a result of the complexation of the carbonyl group with chromium. Another shift can be observed as a result of complexation of the oxygen from the carboxyl C−O bond at wave numbers 1166 and 1066 cm^{-1}. The O−H (3434 cm^{-1}) and C−O (2390 and 2361 cm^{-1}) band absorption peaks are observed to shift when ACRF is loaded with chromium. Two new peaks were observed in FTIR spectra of Cr(VI)-loaded sorbents, which is attributed to Cr−O and Cr=O bonds of chromate anions, and which confirms the sorption of Cr(VI) onto the activated carbon resorcinol formaldehyde xerogel (ACRF) at 719 and 910 cm^{-1} [25].

The mechanism of chromium(VI) adsorption from aqueous solution is attributed to physical adsorption by electrostatic attraction between positively charged adsorption sites in the adsorbent and the negatively charged Cr(VI) species.

It can be seen that carboxyl groups are involved in the removal mechanism, as shown with the FTIR results [26]. Other functional groups may also be involved in metal ions adsorption. From the SEM (Figure 6a (Unloaded ACRF)), it can be seen that ACRF has a large surface area. The chromium metal ions were adsorbed onto the pores and surfaces of adsorbent as shown by the SEM image (Figure 6b (loaded ACRF)). The EDX analyses of ACRF before adsorption were: C: 97.48 %; O: 2.31 %; Na: 0.21 %. The EDX analyses for Cr(VI)-loaded ACRF were: C: 39.56 %; O: 3.0 %; Na: 0.05 %; Cr: 57.38 %.

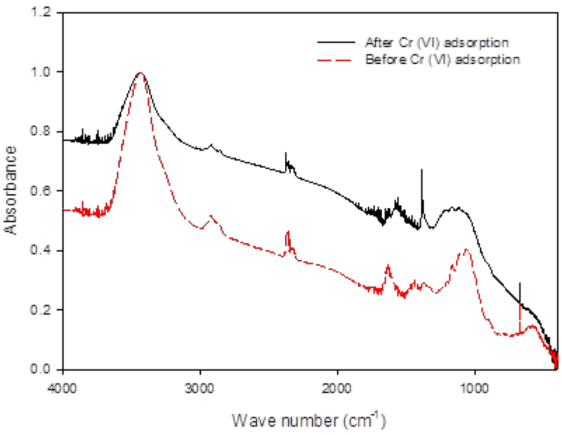

FIGURE 5. FTIR spectra of ACRF adsorbent (A) before and (B) after Cr(VI) adsorption.

3.7. ADSORPTION THERMODYNAMICS

The thermodynamics parameters such as Gibbs free energy, enthalpy change and entropy change were obtained using the following equations [6]:

$$K_c = \frac{q_e}{C_e}, \tag{4}$$

$$\Delta G^o = -RT \ln K_c, \tag{5}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT}. \tag{6}$$

The value of ΔH^o and ΔS^o are obtained from the slope and intercept of the linear Van't Hoff plot of $\ln K_c$ versus $1/T$ (6). Table 3 shows the calculated values of the thermodynamic parameters for the adsorption of Cr(VI) on ACRF.

The negative values of ΔG^o at various temperatures indicate the spontaneous nature of the adsorption process. The increase in ΔG^o with temperature clearly indicates a more favourable adsorption at high temperature. The positive value of ΔH^o indicates the adsorption process is endothermic. More so, the positive value of ΔS^o indicates the degree of randomness of the system solid-solution interface during the adsorption process. Similar results were reported for Cr(VI) adsorption [6, 27]. As reported by Malkoc

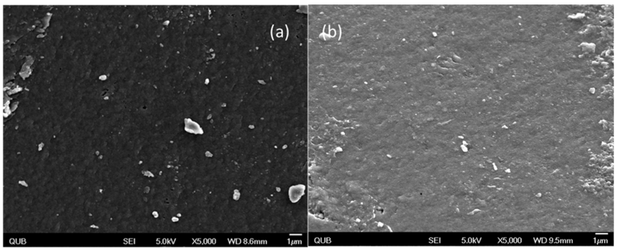

FIGURE 6. SEM images of ACRF (a) before Cr(VI) adsorption and (b) after Cr(VI) adsorption.

T	K_c	ΔG^o	ΔH^o	ΔS^o
293	3.0398	−2.71	7.51	0.0355
303	4.0450	−3.52		
333	4.6185	−4.24		

Table 3. Thermodynamics parameters for Cr(VI) adsorption onto ACRF

and Nuhoglu [27], the positive value of ΔS^o reflects the affinity of the adsorbent for Cr(VI) ions and suggests some structural changes in chromium and the adsorbent.

4. Conclusions

The effect of initial Chromium(VI) metal ion concentration on the adsorption on ACRF was studied at optimum pH observed from a previous study. The Langmuir isotherm was seen to have a better fit based on non-linear regression analysis. The maximum adsorption capacity of ACRF for Chromium(VI) was 241.9 mg/g. The pseudo-second-order kinetic model was the best fit to the experimental data for the adsorption of chromium (VI) metal ions by activated carbon resorcinol formaldehyde xerogels. The optimal removal was 74.86 % at 60 min for 25 ppm and 77.21 % at 240 min for 200 ppm. Different mechanisms were responsible for Chromium(VI) metal ion adsorption. The results showed that the adsorption of Cr(VI) is a result of electrostatic attraction, ion exchange/complexation and reduction reactions. The thermodynamic analysis showed that the Chromium adsorption process was endothermic and spontaneous in nature.

List of symbols

q_e	Amount of solute adsorbed per unit weight of adsorbent [mg/g]
C_e	Equilibrium concentration of solute in the bulk solution [mg/L]
b	Constant related to the free energy of adsorption [L/mg]
q_{max}	maximum adsorption capacity [mg/L]
C_o	initial Cr(VI) concentration [mg/L]
K_F	Freundlich constant [mg/g]
$1/n$	Heterogeneity factor [mg/L]
k_1	pseudo-first-order rate constant [$\mathrm{min^{-1}}$]
k_2	pseudo-second-order rate constant [g/mg min]
k_i	Intra-particle diffusion constant [$\mathrm{mg\,g^{-1}\,min^{-0\,5}}$]
R_L	Separation factor
T	Temperature [K]
R	Universal gas constant, 8.314 $\mathrm{J\,mol^{-1}}$
K_c	Equilibrium constant
ΔH	Enthalpy change [$\mathrm{kJ\,mol^{-1}}$]
ΔS	Entropy change [$\mathrm{kJ\,mol^{-1}K^{-1}}$]
ΔG^o	Gibbs free energy change [$\mathrm{kJ\,mol^{-1}}$]
R^2	Coefficient of determination

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