

ADSORPTION OF CR(III) FROM AQUEOUS SOLUTIONS BY POLYACRYLAMIDE-GRAFTED RUBBERWOOD FIBRE: KINETICS, EQUILIBRIUM, AND THERMODYNAMIC STUDIES

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Cr(III) ions were adsorbed onto polyacrylamide-grafted rubberwood fibre, and effects of aqueous conditions were evaluated. The adsorbent was prepared via graft copolymerization of acrylamide (Am) onto rubberwood fibre (RWF), using ceric ammonium nitrate as an initiator. Fourier transform infrared spectroscopy was used to confirm the formation of PAm-g-RWF. Various variables affecting the adsorption capacity such as the pH of the solution, adsorption time, initial metal ion concentration, and temperature were investigated. The Cr(III) was up to 92% removed by PAm-g-RWF from an initial concentration of 10 mg/L at pH 5.0. Kinetic data fitted very well to a pseudo-second-order rate expression and less well to a pseudo-first-order equation. The equilibrium parameters for adsorption isotherms of the metal ions on the grafted fibre were obtained using Langmuir and Freundlich models, and the Langmuir model was found to be in better correlation with the experimental data with a maximum adsorption capacity of 18.24 mg/g. Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°), and entropy change (ΔS°) were calculated; the adsorption process was spontaneous and endothermic.

Keywords: Cr(III) adsorption; Rubberwood fibre; Grafted; Equilibrium

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INTRODUCTION

Water pollution is one of the most serious environmental problems facing modern society. Toxic metals constitute a serious environmental problem because they are not biodegradable and can accumulate in living tissues, causing various diseases and disorders (Pehlivan et al. 2008). Chromium ion is one of the heavy metals considered especially toxic to humans and aquatic life. Accumulation of Cr(III) ions can inhibit various enzyme systems of living organisms and also affect the ecology of the environment when it is present in large amounts (Anirudhan and Radhakrishnan 2007). A long-term exposure to trivalent chromium is known to cause allergic skin reactions and cancer (Tangjuank et al. 2009). The toxicity of chromium compounds depends on the oxidation state of the metal. The Cr(VI) species is more toxic and carcinogenic than Cr(III); however, it is possible that Cr(III) may be oxidized to Cr(VI) under suitable conditions, and in such cases the toxicity of Cr(VI) manifests itself. Cr(III) is readily oxidized to the hexavalent state at high pH (Nik Malek and Mohd Yusof 2007).

Chromium solutions are widely used in many industrial processes such as chrome plating, wood preserving, textile dyeing, pigmentation, Cr chemical production, pulp and

paper production, and tanning. The wastewater resulting from these processes can contain high amounts of chromium metal, which is harmful to the environment and human health (Esmaeili et al. 2005). The necessity to reduce the amount of Cr(III) ions in wastewater streams of industries, as well as subsequent possible reuse of the metal ions, has led to an increasing interest in selective adsorbents. There are various methods for the removal of toxic metals from aqueous solution, such as chemical precipitation, evaporation, ion-exchange, adsorption, and reverse osmosis (Kurniawan et al. 2006). Adsorption has attracted considerable interest in recent years as a wastewater treatment process (Crini 2006). Fibrous adsorbents, which have large specific surface areas and high adsorption rates, are increasingly used in removal of toxic metal ions and enrichment recovery of traces of elements from aqueous solution. Chemical modifications on fibre adsorbents have shown great promise in improving their physical and chemical properties and also in significantly increasing their adsorption capacity and selectivity by forming many reactive groups upon the polymer chains (O'Connell et al. 2008). Rubberwood is a natural polymer that has gained special importance because it is cheap and plentiful. Chemical compositions of this wood have shown that its main components are cellulose (67.0%) and lignin (26.0%). Cellulose fibre of rubberwood, a linear-chain polymer with a large number of hydroxyl groups, is a highly abundant natural resource. Cellulose as a bioaffinity carrier, exhibits good chemical stability, mechanical strength, recoverability, high reproducibility, and low cost (Klemm et al. 2002). In the present study, a new adsorbent material has been prepared from rubberwood fibre for the removal of Cr(III) from aqueous solutions. Rubberwood fibre was modified with acrylamide to introduce amide functional groups in order to enhance its adsorption ability for metal ions. The main objective of this study is to assess the effectiveness of PAm-g-RWF in the removal of Cr(III) by determining the maximum adsorption capacity. Langmuir and Freundlich adsorption isotherm models were used to fit the equilibrium isotherm. The adsorption kinetics were determined using pseudo-first-order and pseudo-second-order models. The thermodynamics of Cr(III) adsorption and adsorption mechanisms were also considered.

EXPERIMENTAL

Materials

Rubberwood fibre (RWF) was kindly supplied by Merbok MDF Sdn. Bhd. Kedah, Malaysia with average length of 2.36 mm. RWF was washed with hot distilled water and acetone several times to remove dust and any other impurities. It was then dried in an oven at 60 °C to constant weight. Acrylamide (Am) monomer and ceric ammonium nitrate ((NH₄)₂Ce(NO₃)₆), were purchased from Fluka, Chemie, Switzerland. Aceton and nitric acid were obtained from BDH, UK. Chromium (III) chloride was purchased from Fluka.

Graft Copolymerization of Acrylamide onto RWF

Grafting was carried out by adding 5 g of fibre to distilled water (80 mL) and mixing with solutions of 15 g of acrylamide (Am) in 50 mL distilled water and 0.5 g ceric ammonium nitrate in 1 mL dilute nitric acid. The solution was stirred at 50 °C for 4

hours. After grafting, the sample was filtered, washed with distilled water for several times, and air dried. Finally, this dried sample was extracted with distilled water in a soxhlet apparatus for 48 hours to dissolve the formed homopolymer. After extraction, the sample was washed with distilled water to remove impurities and air-dried.

FTIR Analysis

The change in chemical structure of rubberwood fibre as a result of graft copolymerization with acrylamide monomer and functionalization was characterized using FTIR spectroscopy. The infrared spectra of the polymer was recorded by model 100 series Fourier Transform IR(FTIR) spectrophotometer using universal ATR sampling accessory technique in the range 280-4000 cm^{-1} .

Adsorption Experiments for Cr(III)

The stock solution of 1000 mg/L Cr(III) was prepared by dissolving a weighed quantity of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in distilled water. All the required working solutions were prepared by diluting in distilled water. Batch experiments were conducted to determine the effects of pH, contact time, initial Cr(III) concentration, and temperature on the adsorption of Cr(III). The effect of pH on adsorption was investigated in the pH range 2 to 5 at 30°C. The pH adjustment was done by adding H_2SO_4 or NaOH into the solutions with known initial metal ion concentrations. For Cr(III) adsorption kinetics studies, 0.1 g of adsorbent was contacted with 25 mL of Cr(III) solution of varying concentrations in a flask and stirred continuously in a water bath maintained at different temperatures (30, 50, and 70 °C). At the end of the pre-determined time intervals, the adsorbent was filtered through a paper filter. The residual concentration of Cr(III) in the filtrate was determined using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) model Perkin Elmer 1000. Adsorption isotherm experiments were also carried out by contacting 0.1 g of the adsorbent with 25 mL of varying concentrations of Cr(III) from 5 to 250 mg/L. The mixtures were agitated in a flask for 2 h, which was sufficient time to reach adsorption equilibrium at various temperatures (30, 50, and 70 °C). The pH of the solution was adjusted to an optimum pH 5. After stirring for 2 h, the adsorbent was separated by filtration, and the residual Cr(III) concentration in the filtrate was determined using ICP-AES.

RESULTS AND DISCUSSION

Adsorbent Characterization

Infrared spectra of fibre and grafted fibre are shown in Fig. 1. The adsorption bands found at 670 cm^{-1} were from the β -glucosidic linkage. Compared with the ungrafted RWF (Fig. 1a), a sharp peak appeared in PAm-g-RWF at 1650 cm^{-1} (Fig. 1b), corresponding to the stretching of the carbonyl (C=O) of the amide group in acrylamide. For the grafted polymer a new band at 828 cm^{-1} was also observed, which indicates the (C-H) stretching vibrations in the acrylamide molecule. The presence of the peak at 1736 cm^{-1} in the RWF spectrum could be due to the carbonyl (C=O) stretching vibration of the carboxyl groups of hemicellulose and lignin in the fibre (Abu-Ilaiwi et al. 2004). The

ratio of the band intensity at 1650 cm^{-1} to the band intensity at 1215 cm^{-1} increased by grafting because of the increase due to incorporation of CONH_2 groups onto the fibre. Both IR spectra of the ungrafted and the grafted RWF exhibited absorption band at 3400 cm^{-1} due to hydroxyl group stretching vibrations from the RWF structure. The relative absorbance of the OH band at 3400 cm^{-1} was increased by grafting due to the reaction of acrylamide monomer with the OH of fibre (Nada et al. 2007). And also, the relative absorbance of C-O-C band at 1215 cm^{-1} decreased by grafting. This means that some degradation of RWF occurred through grafting.

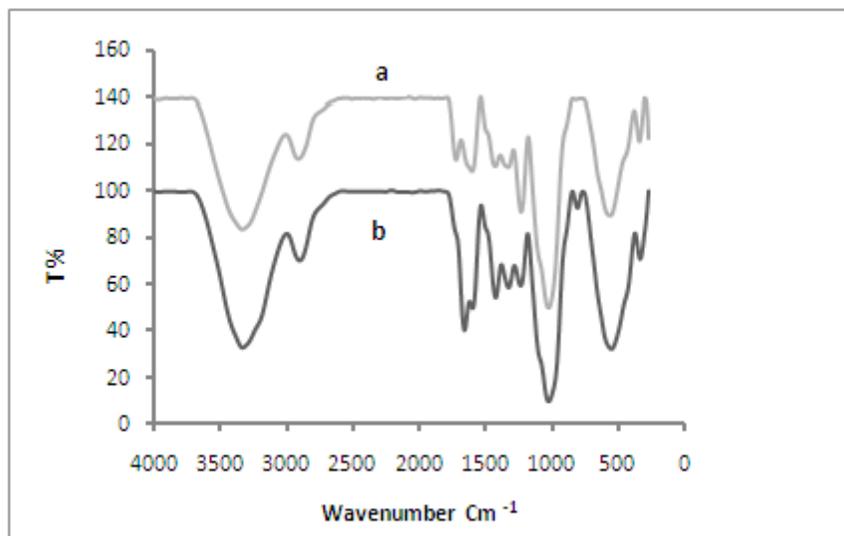


Fig. 1. Infrared spectra of (a) ungrafted and (b) grafted RWF

Effect of pH on Cr(III) Adsorption

The solution pH is one of the most important factors that control the adsorption of metal ions. The effect of pH on the adsorption capacity of Cr(III) by PAm-g-RWF was evaluated within the pH range of 2 to 5, as shown in Fig. 2. The amounts of chromium adsorbed at pH 2, 3, 4, and 5 were 0.05, 0.4, 0.92, and 1.15 mg/g, respectively. It can be observed that the adsorption of chromium increased with increasing pH, and the percentage of adsorption increased from 4% at pH 4 to 92% at pH 5 at 30°C . The increase of chromium removal with pH may be explained by the increase in negative charge at the surface of the adsorbent, which makes the adsorption of the positively charged Cr(III) easier. The electrostatic attraction force between the adsorbent surface and adsorbate ions increases. At lower pH values, there is excessive protonation of the adsorbent surface, resulting in a decrease in the adsorption of chromium ions. According to Reddy et al. (1997) above pH 5, chromium starts to precipitate as $\text{Cr}(\text{OH})_3$ due to the high concentration of OH^- ions in the solution, so the adsorption experiments at these pH values could not be performed well. Therefore, experiments were carried out in the pH range 2 to 5. Figure 2 also shows that at pH 5 the percentage removal of Cr(III) by the grafted fibre was almost doubled in comparison to that of ungrafted fibre.

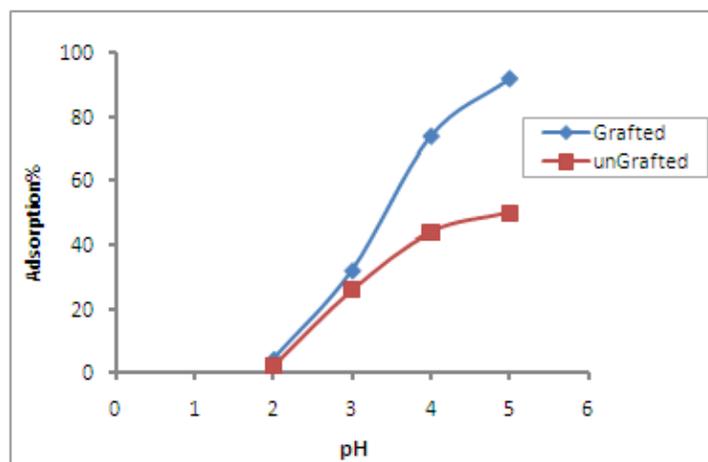


Fig. 2. Effect of initial pH on the adsorption of Cr(III) by PAm-g-RWF and ungrafted fibre. Concentration, 5 mg/L; Temperature, 30 °C; Adsorbent dose, 0.1 g/25 mL; Contact time, 2h

Effect of Contact Time and Initial Cr(III) Concentration

A series of contact time experiments for adsorption of Cr(III) were carried out at different concentrations. The obtained results concerning the influence of time on the rate of Cr(III) uptake at various concentrations 5, 15, 25 mg/L, at 30 °C are shown in Fig. 3. It was found that the adsorption capacity of Cr(III) on the adsorbent increased and achieved a constant value at the time about 2 h. As contact time increased, metal uptakes increased initially and then became almost constant. The first phase is related to external surface adsorption of chromium, which occurs instantaneously. The second phase is the gradual adsorption stage before the chromium uptake reaches equilibrium. The rapid metal uptakes were certainly related to the availability of active sites on adsorbent surfaces (Bhattacharya and Gupta 2006).

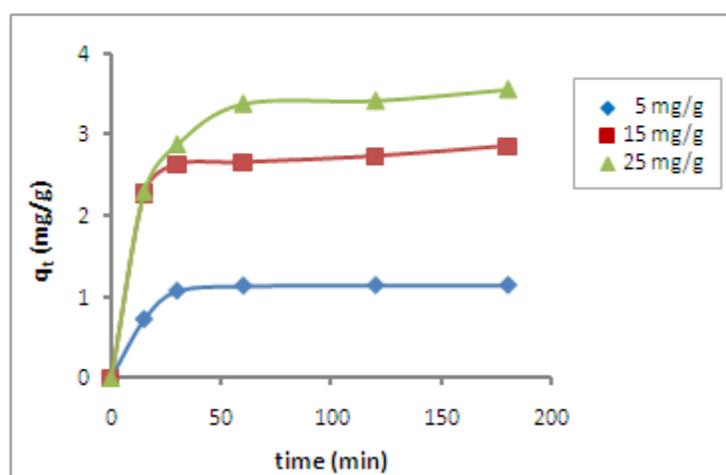


Fig. 3. Effect of various initial concentrations on adsorption of Cr(III) by PAm-g-RWF: Temperature, 30 °C; pH, 5.0; Adsorbent dosage, 0.1 g/25 mL.

It is clear from Fig 3 that the adsorption of Cr(III) increased from 1.14 to 3.62 mg/g with an increase in initial concentration from 5 to 25 mg/L. This is attributed to the fact that the driving force, which depends on the concentration gradient, increases with the increasing initial Cr(III) concentration (Noeline et al. 2005).

Adsorption Kinetic Studies

Adsorption kinetics describes the relationship of solute uptake rate of the adsorption and the adsorption time. The results obtained for adsorption of Cr(III) onto PAm-g-RWF at different concentration and contact time were analyzed by using the first-order Lagergren equation and the pseudo-second-order rate equation, which are shown below as equations (1) and (2), respectively (Wua et al. 2009; Ho and McKay 2000).

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

In these equations q_e and q_t are the amounts of metal ion adsorbed (mg/g) at equilibrium and at time t , respectively. The parameter k_1 (min^{-1}) is the rate constant of the pseudo-first-order adsorption process, and k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) is the rate constant of the pseudo-second-order adsorption process. Kinetic parameters of these models for different concentrations were calculated from the slope and intercepts of the linear plots of $\ln(q_e - q_t)$ versus t and t/q_t versus t (not shown), and are given in Table 1. These parameters at different temperature were also calculated and are given in Table 1. Table 1 shows that the values of the coefficient of determination R^2 for the pseudo-second-order model were above 0.998 at different concentrations and different temperatures, so this model provided the best agreement with the experimental data for the adsorption of Cr(III) ion. In addition, the calculated q_e values from the pseudo-second-order kinetic model were much closer to the experimental values of q_e than that of the pseudo-first-order model. So the pseudo-second-order kinetic model fits the experimental data for adsorption of Cr(III) by PAm-g-RWF better than the pseudo-first-order model in this study.

Table 1. Kinetic Parameters for the Adsorption of Cr(III) by PAm-g-RWF

Variable	$q_e \text{ exp}$ (mg/g)	Pseudo-first order			Pseudo-second order		
		K_1 (min^{-1})	$q_e \text{ cal}$	R^2	K_2 (g/mg min)	$q_e \text{ cal}$	R^2
Conc (mg/L)							
5	1.14	5.1×10^{-2}	0.58	0.884	27.3×10^{-2}	1.16	0.998
15	2.87	2.1×10^{-2}	1.06	0.828	9.86×10^{-2}	2.89	0.999
25	3.62	1.8×10^{-2}	1.74	0.862	4.42×10^{-2}	3.69	0.999
Temp ($^{\circ}\text{C}$)							
30	3.63	5.2×10^{-2}	3.43	0.973	3.17×10^{-2}	3.78	0.999
50	4.62	2.4×10^{-2}	1.85	0.902	6.57×10^{-2}	4.67	0.999
70	4.75	4.1×10^{-2}	2.94	0.872	7.64×10^{-2}	4.80	0.999

Adsorption Isotherms

The adsorption isotherm provides a relationship between the concentration of metal ions in solution and the amount of metal ions adsorbed onto the adsorbent when both phases are at equilibrium (Kara et al. 2004). The distribution of metal ions between liquid and solid phases is generally described by using the Langmuir, Freundlich, and Dubinin-Radushkevich adsorption isotherm models. Among these, the Langmuir and Freundlich adsorption models are commonly used to analyze and fit experimental data. The Langmuir adsorption isotherm is based on an assumption of monolayer coverage of the adsorbate on the surface of adsorbent, and the Freundlich isotherm is based on multilayer adsorption and applicable to highly heterogeneous surfaces. These relationships can be expressed by the following equations,

$$\frac{C_e}{q_e} = \frac{1}{Q_m b} + \frac{C_e}{Q_m} \quad (\text{Langmuir equation}) \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Freundlich equation}) \quad (4)$$

where q_e (mg/g) is the amount of chromium adsorbed at equilibrium, C_e (mg/L) is the equilibrium concentration of adsorbate, Q_m (mg/g) and b (L/mg) are the Langmuir constants related to the maximum sorption capacity of metal ions and energy of adsorption. The K_F and $1/n$ are Freundlich constants related to adsorption capacity and intensity of adsorption, respectively. The Langmuir and Freundlich isotherm parameters were calculated from the slope and intercept of linear plots of C_e/q_e versus C_e and $\ln(q_e)$ versus $\ln(C_e)$ (not shown), and are given in Table 2.

The Langmuir model fit better than the Freundlich isotherms, which is evident from the fact that the values of R^2 for the Langmuir model were higher than for the Freundlich model. In addition, the adsorption capacities calculated from the Langmuir isotherm were much closer to the experimental values of q_e than that of Freundlich isotherm, which indicate that the Cr(III) adsorbed by PAm-g-RWF formed a monolayer coverage on the surface of the adsorbent.

The type of the Langmuir isotherm can be predicted in terms of an equilibrium parameter (R_L), which is defined by the following equation, according to Hall et al. (1966),

$$R_L = \frac{1}{(1 + bC_0)} \quad (5)$$

where b (L/mg) is the Langmuir constant and C_0 (mg/L) is the initial concentration of Cr(III). The value of R_L indicates the conditions of favourable adsorption, $0 < R_L < 1$; unfavourable adsorption, $R_L > 1$; linear adsorption, $R_L = 1$; and whether the adsorption process is irreversible if $R_L = 0$. The calculated values of the dimensionless factor R_L for chromium ions adsorption onto PAm-g-RWF, indicating favourable adsorption of chromium due to all the values obtained were less than 1, and greater than 0 for the initial

chromium concentration range from 5 to 250 mg/L. According to Mohanty et al. (2006) if the value of n from the Freundlich isotherm is greater than 1, it indicates favourable adsorption of metal ion on the surface of adsorbent. The values of n obtained in this study are given in Table 2, indicating that Cr(III) ions are favourably adsorbed by PAm-g-RWF.

Table 2. Isotherm Constants for the Adsorption of Cr(III) by PAm-g-RWF

Temp(°C)	Langmuir isotherm			Freundlich isotherm		
	Q_m (mg/g)	b (L/mg)	R^2	K_F (mg/g)	n	R^2
30	13.15	4.30×10^{-2}	0.976	1.62	2.65	0.824
50	14.85	6.09×10^{-2}	0.989	2.32	2.85	0.941
70	18.24	7.71×10^{-2}	0.999	2.75	2.87	0.917

Comparison of PAm-g-RWF with Various Adsorbents

The comparison of adsorption capacity for Cr(III) using PAm-g-RWF with other reported adsorbents is given in Table 3. The Langmuir isotherm maximum adsorption capacity Q_m of Cr(III) adsorbed by PAm-g-RWF was found to be 18.24 mg/g, which is higher compared to the capacities of some other adsorbents, as reported earlier. Therefore, considering the low cost of this natural adsorbent, it can be used as a potential adsorbent for treatment of wastewater containing chromium.

Table 3. Comparison of Maximum Adsorption Capacity of Cr(III) with other Adsorbent

Adsorbent	Maximum adsorption capacity (mg/g)	Reference
Seaweed biomass	68.12	Cossich 2002
Spirulina sp	34.6	Michalak et al. 2007
Lewatit	20.28	Gode and Pehlivan 2006
Natural moss	18.9	Lee et al. 1995
Rubberwood fibre	18.24	This work
Sorghum straw	6.96	Bernardo 2009
Agave lechuguilla biomass	11.31	Romero-Gonzalez et al. 2006
Agave bagasse	10.84	Bernardo 2009
Brown seaweed	11	Yun 2001
Wood pulp	4.7	Nada et al. 2007

Effect of Temperature and Estimation of Thermodynamic Parameters

The effect of temperature on the adsorption characteristics of Cr(III) was investigated by determining the adsorption isotherms at 30, 50, and 70 °C to obtain the thermodynamic parameters, which were evaluated using the Van't Hoff equation,

$$\ln k_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (6)$$

where ΔS° and ΔH° are entropy (J/mol K) and enthalpy (J/mol) change of adsorption, respectively, R is the universal gas constant (8.314 J/mol K), T is the absolute temperature (K), and K_d is a equilibrium constant obtained by multiplying Langmuir constants Q_m and b (L mol^{-1}). The enthalpy change (ΔH°) and the entropy change (ΔS°) can be calculated from the slope and intercept of the linear Van't Hoff plot of $\ln K_d$ versus $1/T$ (not shown). The Gibbs free energy change (J/mol) of the adsorption process is related to the equilibrium constant by the classical Van't Hoff equation:

$$\Delta G^\circ = -RT \ln k_d \quad (7)$$

The calculated thermodynamic parameters ΔH° , ΔS° , and ΔG° are given in Table 4.

Table 4. Thermodynamic Parameters of Cr(III) Adsorption by PAm-g-RWF

Temp (K)	ΔH° (kJ/mol ⁻¹)	ΔS° (J/mol ⁻¹ K ⁻¹)	ΔG° (kJ/mol ⁻¹)
303	12.64	105.6	-19.43
323			-21.65
343			-23.66

At equilibrium the amounts of Cr(III) adsorbed after treatments at 30, 50, and 70 °C were 3.63, 4.62, and 4.75 mg/g, respectively, for an initial Cr(III) concentration of 25 mg/L. The value of ΔH° was found to be positive, and also the adsorption capacity of adsorbent increased with increasing temperature, which shows the adsorption reaction of Cr(III) on PAm-g-RWF was endothermic. The positive ΔS° value corresponds to an increase in the degrees of freedom of the adsorbed species. The negative values of ΔG° indicate that the adsorption process is feasible and spontaneous at all temperature studied. The decrease in the value of ΔG° with increasing temperature shows that the reaction is favorable at higher temperature (Haron et al. 2009).

CONCLUSIONS

1. Rubberwood fibre can be converted into an adsorbent with good adsorption capacity by grafting with acrylamide monomer.
2. The Cr(III) adsorption increases as the solution pH is increased from 2 to 5.
3. The adsorption equilibrium for Cr(III) can be well described by Langmuir isotherms with maximum capacities of 18.24 mg/g at 70 °C.
4. The kinetic data fit very well to the pseudo-second-order kinetics model.
5. The positive values of the change in enthalpy suggest an endothermic nature of the process, and the negative values of the change in free energy indicate the feasibility and spontaneous nature of the process.

6. Acrylamide-grafted rubberwood fibre could be successfully used as low-cost adsorbents for the removal of Cr(III) ions from aqueous solutions.

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