Carbohydrate Polymers 86 (2011) 1306–1312

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Hydrogel from crosslinked polyacrylamide/guar gum graft copolymer for sorption of hexavalent chromium ion

E.S. Abdel-Halim[a,b,*], Salem S. Al-Deyab[a]

[a] *Petrochemical Research Chair, Chemistry Department, College of Science, King Saud University, Riyadh 11451, P.O. Box 2455, Saudi Arabia*
[b] *Textile Research Division, National Research Center, Dokki, Cairo, Egypt*

ARTICLE INFO

Article history:
Received 16 May 2011
Received in revised form 6 June 2011
Accepted 13 June 2011
Available online 12 July 2011

Keywords:
Guar gum
Grafting
Hydrogel
Hexavalent chromium ion
Sorption

ABSTRACT

A new sorbent material based on guar gum (GG) was prepared by the polymerization grafting of acrylamide (Aam) onto guar gum, using potassium bromate/thiourea dioxide redox system for initiating the polymerization reaction. The so prepared polyacrylamide/guar gum graft copolymer (PAamGG) was further crosslinked with glutaraldehyde (GA) to obtain the sorbent material in the form of hydrogel. The so-obtained hydrogel was used for removal of hexavalent chromium ion (Cr (VI)) from its aqueous solution. Factors affecting metal sorption, such as pH, sorbent concentration, immersion duration and Cr (VI) solution concentration were extensively investigated. It was found from the study that the sorption of Cr (VI) by the hydrogel is pH-dependent and maximum sorption was obtained at pH 3. The sorption data obeyed Langmuir and Freundlich sorption isotherms. The Langmuir sorption capacity (Q_{max}) was found to be 588.24 mg/g. Freundlish constants, K_F and n, were found to be 55.03 and 2.835, respectively.

1. Introduction

The term hydrogel is given to the polymers which are known to swell in aqueous solutions, forming three-dimensional network. In the swollen state, hydrogels acquire soft and rubbery touch, resembling a living tissue and some possess excellent biocompatibility (Sandolo, Matricardi, Alhaique, & Coviello, 2007). The hydrogel resulting from the modification of natural polymers finds application in many different areas of application fields (Huang, Yu, & Xiao, 2006; Tang, Du, Hu, Shi, & Kennedy, 2007; Vimala, Sivudu, Mohan, Sreedhar, & Raju, 2009; Zhou et al., 2008).

Guar gum, also called guaran, is a galactomannan. It is primarily the ground endosperm of guar beans. Chemically, guar gum is a polysaccharide composed of the sugars galactose and mannose. The backbone is a linear chain of β-1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches (Scheme 1).

Borax or calcium can crosslink guar gum, causing it to gel (Huang et al., 2006). To enhance application spectrum of guar gum, its modification has been reported by several authors through grafting (Abdel-Halim, El-Rafie, & Al-Deyab, 2011; Pandey, Srivastava, Tripathy, & Behari, 2006), derivatization (Trivedi, Kalia, Patel, & Trivedi, 2005), and network formation (Barbucci, Pasqui, Favalorob, & Panariello, 2008). After such modifications the resultant polymers acquire their dominant properties from the individual properties of the incorporated polymers or function groups introduced through the modification process. Based on the above mentioned statement, it is an interesting option to modify guar gum chains to affect its physical properties, chemical properties, its profile including viscosity, water absorption capacity, ion exchange and protein immobilization.

Graft copolymerization of natural polymers with functional synthetic polymers gives modified products having wide range of applications due to combining in one molecule the desired properties of both the natural polymer and the synthetic polymer. Graft copolymerization is an easy method to modify the structure of natural polymers and thus makes them suitable for various applications (Abdel-Halim, Emam, & El-Rafie, 2008a, 2008b; Abdel-Halim, Abdel-Mohdy, Al-Deyab, & El-Newehy, 2010; Abdel-Halim, Fouda, Hamdy, Abdel-Mohdy, & El-Sawy, 2010).

The structure of guar gum can be modified to tailor its properties to be a useful metal sorbent through crosslinking treatment. Earlier, it was shown (Tayal, Pai, & Khan, 1999) that when guar gum is crosslinked with borax, a decrease in viscosity is observed. Rubinstein et al. (Gliko-Kabir, Yagen, Penhasi, & Rubinstein, 2000) have reported guar gum crosslinked with glutaraldehyde and phosphate for applications in colon targeting.

The use of low-cost adsorbents has been investigated as a replacement for costly current methods. Natural materials or vast products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost.

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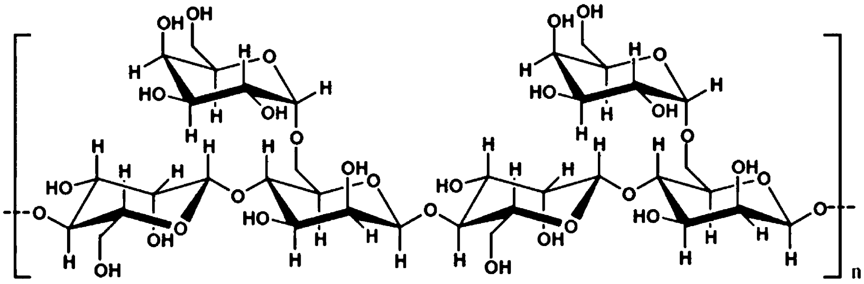
* Corresponding author at: National Research Center, Dokki, Cairo, Egypt. Tel.: +20 108113477.
E-mail address: essamya@yahoo.com (E.S. Abdel-Halim).

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.06.033



Scheme 1. Chemical structure of guar gum.

Heavy metals are often discharged by a number of industries, such as metal plating facilities, mining operations and tanneries, this can lead to the contamination of freshwater and marine environment (Aguado, Arsuaga, Arencibia, Lindo, & Gascón, 2009). Heavy metals are not biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders (Ju et al., 2009). It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, and cadmium they are significantly toxic to human being and ecological environments (Mohan & Sreelakshmi, 2008). Numerous techniques are available for water purification and metal recovery operations from wastewaters. Many of these are established methods, while others are still in the experimental stage. Generally, the techniques employed for heavy metal removal include precipitation, ion exchange, adsorption, filtration, electrodeposition and reverse osmosis (Miretzky, Saralegui, & Cirelli, 2006). The above mentioned techniques are used to concentrate waste streams and remove the heavy metals. Activated carbon is effective in reducing hexavalent chromium, mercury, and many metals complexed by organic ligands. Similarly, various ion-exchange resins have been found to be effective in removing metal ions from solution. Interest has risen recently in removing heavy metals from solution by binding with agricultural materials such as waste wool, nut wastes, tree barks, modified cotton and sawdust. Many agricultural and industrial by-products have little or no economic value, and some, such as short fibers from jute processing, and sawdust, which are produced in large quantities, are often present a disposal problem. If these by-products could be used, as sorbents, contaminated water streams would be cleaned, and a new market would be opened for these by-products (Vinodh, Padmavathi, & Sangeetha, 2011). Precipitation methods are particularly reliable but require large settling tanks. The precipitation of voluminous alkaline sludge and a subsequent treatment is needed. Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated. Adsorption on solid–solution interface is an important means for controlling the extent of pollution due to heavy metal ions. The use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs (Cao, Tan, Che, & Xin, 2010). This has encouraged research into discovering materials that are both efficient and cheap. Interest has recently arisen in the investigation of some unconventional methods and low cost materials for scavenging heavy metal ions from industrial wastewaters (Abdel-Halim, Abou-Okeil, & Hashem, 2006; Abdel-Halim & Al-Deyab, 2011; Hashem, Abdel-Halim, El-Tahlawy, & Hebeish, 2005; Hashem, Sokkar, Abdel-Halim, & Gamal, 2005; Hashem, Abdel-Halim, & Sokker, 2007; Hashem, Abdel-Halim, Maauof, Ramadan, & Abo-Okeil, 2007; Sokkar, Abdel-Halim, Aly, & Hashem, 2004). The suitably modified biosorbents are also appropriate choice for heavy metal removal from their aqueous solutions. Some of the biosorbents include modified chitosan (Wang et al., 2008), alginates (Abdel-Halim et al., 2011; Jeon, Yoo, & Hoell, 2005), starches and dextrins (Xie, Shang, Liu, Hu, & Liao, 2011), carboxymethyl cellulose (Ibrahim, Adel, Abd El-Wahab, & Al-Shemy, 2011), *Fucus serratus* (Ahmady-Asbchin, Andres, Gerente, & Le, 2008), newspaper pulp (Chakravarty, Pimple, Chaturvedi, Singh, & Gupta, 2008), natural gum (Sharma & Lalita, 2011) and mimosa tannin gel (Sengil and Ozacar, 2008). There exists structure/property relationship in various biosorbents as a study of marine brown alga, terrestrial moss and birch wood (Grimm, Zanzi, Bjornbom, & Cukierman, 2008) revealed that the latter was the least effective. The influence of the degree of crosslinking on the adsorption properties of chitosan beads was studied (Osifo et al., 2008). They reported that the performance of the biosorbent was related to its water contents.

The present work reports the synthesis of glutaraldehyde crosslinked hydrogel from PAamGG. The graft copolymer was prepared by grafting Aam onto GG using potassium bromate/thiourea dioxide redox system as an initiator. The so-obtained hydrogel was used to remove Cr (VI) from wastewater.

2. Experimental

2.1. Chemicals

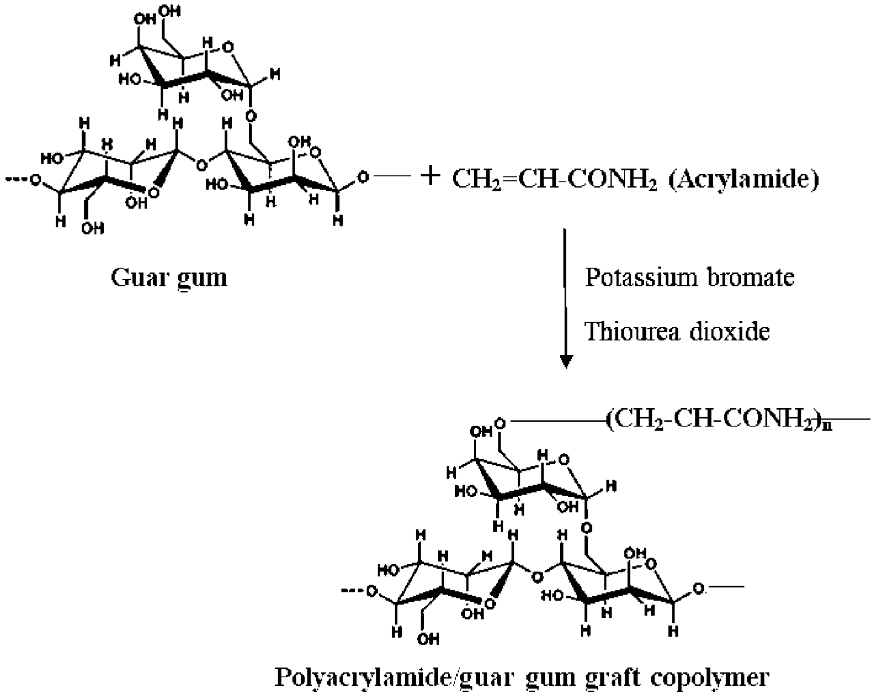
GG was supplied by Fluka and Aam was supplied by Aldrich. Sodium laurel sulphate, GA (25%, w/v), light liquid paraffin, hexane, potassium bromate, thiourea dioxide, sulphuric acid, potassium iodide, sodium thiosulphate and all other chemicals used in this study were laboratory grade reagents.

2.2. Preparation of PAamGG

Twenty grams of GG was dissolved in 100 ml water and pH 2–2.5 was adjusted using dilute sulphuric acid. Ten grams Aam, dissolved in 20 ml water was added to the guar gum solution and the temperature of the reaction medium was raised to 60 °C under continuous stirring. At this end, potassium bromate (6 mmole/100 g GG) and thiourea dioxide (6 mmole/100 g GG) were added and the polymerization reaction was allowed to proceed for 120 min. PAamGG was separated from the homopolymer (polyacrylamide) via precipitation using ethyl alcohol (Abdel-Halim et al., 2008a, 2008b; Abdel-Halim et al., 2011). The graft copolymer was washed thoroughly with alcohol, dried, ground and its graft yield was estimated by determining the nitrogen content according to standard Kjeldhal method. The preparation reaction of PAamGG is represented in Scheme 2.

2.3. Preparation of PAamGG crosslinked hydrogel

Crosslinked PAamGG was prepared by a water-in-oil (w/o) emulsification method according to reported method (Kumaresh, Soppirnath, & Aminabhavi, 2002). Briefly, 20 ml of 5.0% (w/v) PAamGG was prepared and acidified with 5 ml dilute sulphuric acid. In order to crosslink PAamGG, 7.5 ml of 25% (w/v) GA solution was added to PAamGG solution. This solution was then emulsified into 100 ml of light liquid paraffin with 2% (w/v) sodium laurel sulphate using an Eurostar high-speed stirrer (IKA Labortechnik,

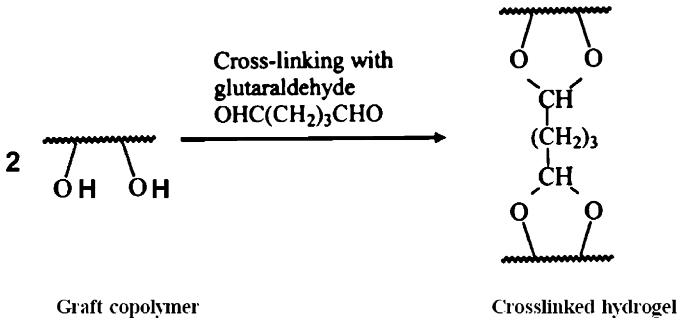


Scheme 2. Graft copolymerization of acrylamide onto guar gum.

Germany) at 600 rpm for 5 h at room temperature. Hardened hydrogel microspheres were filtered and washed repeatedly with hexane and water to remove liquid paraffin, unreacted GA and any adhered sodium laurel sulphate. The hydrogel microspheres were then dried under vacuum at 40 °C overnight and kept in a desiccators until further use. The crosslinking reaction is represented in Scheme 3.

2.4. Adsorption studies

The Cr (VI) solution was prepared by dissolving 1.5 g of potassium dichromate ($K_2Cr_2O_7$) in certain volume of distilled water. The solution was diluted to 1 l with distilled water to yield a stock solution containing 1500 mg/l. The stock solution was further diluted to obtain standard solutions with certain concentrations. The pH's of the solutions were adjusted by using 0.1 M sulphuric acid or 0.1 M NaOH. A 100 ml of Cr (VI) solution of known concentration was poured in a 125 ml Erlenmeyer flask containing certain weight of the hydrogel (sorbent). The hydrogel was immersed in the Cr (VI) solution for different time intervals. At the end of immersion duration, Cr (VI) ion solutions were separated from the hydrogel by filtration. Blank experiments were simultaneously carried out without the hydrogel.



Scheme 3. Crosslinking of polyacrylamide/guar gum graft copolymer with glutaraldehyde.

2.5. Determination of percent Cr (VI) removal

The Cr (VI) ions remaining in the solution after sorption by the hydrogel (C_e) or that in the blank solution (C_o) were determined by direct titration of known volume of these solutions against standard thiosulphate solution (Vogel, 1961). The percentage removal of Cr (VI) was calculated as follows:

$$\%\text{Removal of Cr(VI)} = \left[\frac{C_o - C_e}{C_o}\right] \times 100$$

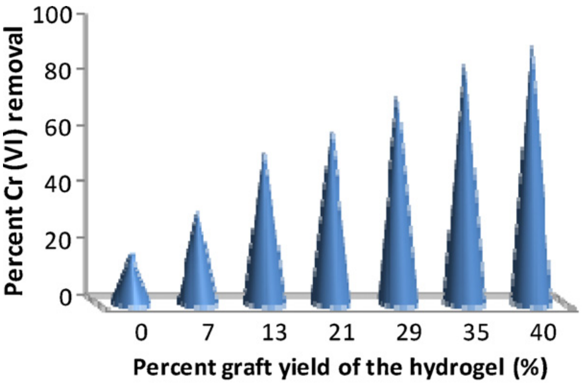
where C_o and C_e are the initial and remaining Cr (VI) concentrations, respectively.

3. Results and discussion

3.1. Effect of graft yield on Cr (VI) sorption

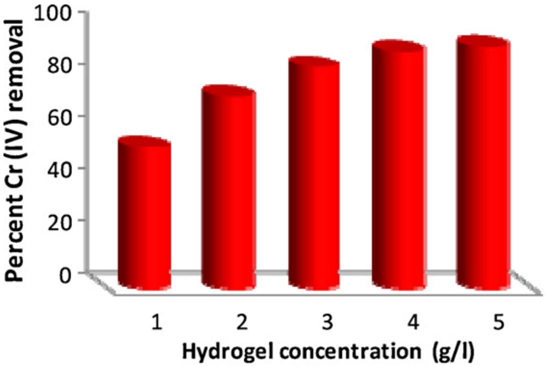
Carbohydrate polymers which are composed of repeated anhydroglucose units are considered ideal for heavy metals and dye removal. The structure of these carbohydrate polymers contains active functional groups for metal ion complexation. The linkage between the functional group and the metal ion is mainly of the coordination type. According to the nature of hydrogels, they have capacity to absorb metal ions from their aqueous solution into the gel phase resulting in ion sorption. Depending on the structure of the hydrogel and the functional groups it has, sorption is a combination of ion exchange processes and simple adsorption processes (Sharma & Lalita, 2011).

To investigate the role of graft yield in improving the sorption capacity of the hydrogel, crosslinked PAamGG samples with different graft yield percents (0–40%) were tried in Cr (VI) sorption. It was found (Fig. 1) that percent Cr (VI) sorption increases as the graft yield increases. This is due to the fact that as grafting increases, the density of sorption sites for metal ions are increased due to increased functional groups of the introduced polyacrylamide graft chains. Polyacrylamide chains contain poly-pendent amide groups which have complexation ability towards metal ions through the



Hydrogel concentration, 1 g/l; Cr (VI) solution concentration, 700 mg/l; pH 3; immersion duration, 120 minutes at 30°C

Fig. 1. Effect of percent graft yield on Cr (VI) sorption.



Cr (VI) solution concentration, 300 mg/l; initial pH 3; immersion duration, 120 minutes at 30°C

Fig. 3. Effect of hydrogel concentration on Cr (VI) sorption.

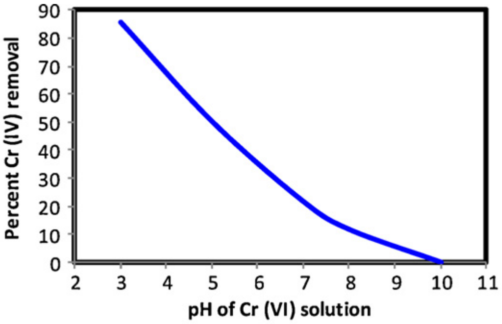
formation of coordination bond, this is in addition to the physical adsorption forces.

3.2. *Effect of adsorbate solution pH*

The pH value of the metal ion solution is an important factor that controls the uptake of the metal ions by the sorbent. To study the effect of pH of Cr (VI) solution on its sorption capacity by the hydrogel, sorption experiments were carried out at a pH range of 3–10. The Cr (VI) concentration in solution was 300 mg/l. It is clear from Fig. 2 that the percent removal of Cr (VI) significantly decreases upon increasing the pH value from 3 to 10. That the percent removal is higher in acidic than in alkaline medium. This is in accordance with previous studies (Kobya, 2004) and can be explained as follows: at acidic pH, the predominant species of Cr (VI) are $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-}. Under acidic conditions, the surface of the sorbent becomes more protonated and attracts anionic species of Cr (VI). As the pH increases, the protonation of the sorbent surface decreases leading to reduction in the electrostatic attraction between the Cr (VI) species and the sorbent surface, with a consequent decrease in the percentage removal of Cr (VI).

3.3. *Effect of sorbent concentration*

To investigate the effect of sorbent concentration on the amount of sorbed Cr (VI), the sorbent concentration was changed in the range (1–5 g/l), keeping constant adsorbate concentration (700 mg/l) and keeping other sorption parameters, like pH, temperature and immersion duration constant. It can be seen from the sorption data given in Fig. 3 that the percent removal of Cr (VI) increases by increasing the sorbent concentration. That is, the percent removal increased from 54 to 93% as the hydrogel dose increased from 1 g/l to 5 g/l. This can be associated with higher available surface area, and more available sorption sites at higher sorbent doses.



Hydrogel concentration, 1 g/l; Cr (VI) solution concentration, 300 mg/l; immersion duration, 120 minutes at 30°C

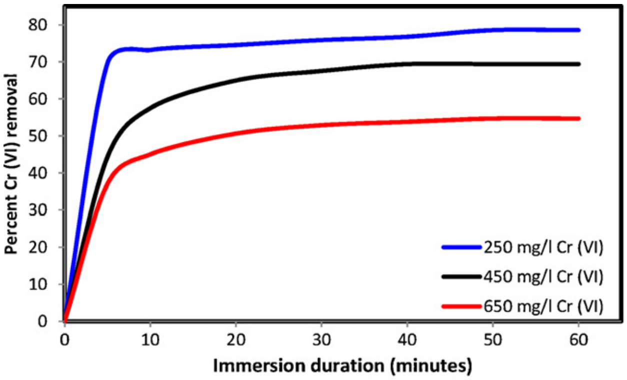
Fig. 2. Effect of Cr (VI) solution pH on Cr (VI) sorption.

3.4. *Effect of immersion duration*

Fig. 4 shows the effect of immersion time on the percent removal of Cr (VI) by the hydrogel at 30 °C using a sorbent concentration of 1 g/l at pH 3 and also using different Cr (VI) concentrations. It is obvious that the increase in immersion duration from 0 to 10 min is accompanied by an increase in the percentage removal of Cr (VI). Further increase in the immersion duration over 10 min has a negligible effect on Cr (VI) % removal. Fig. 4 also shows that equilibriums are attained in about 10 min, within the concentration range studied. It is also observed that the removal curves are smooth and continuous, which indicates the possibility of the formation of monolayer coverage of Cr (VI) ion on the hydrogel available surface.

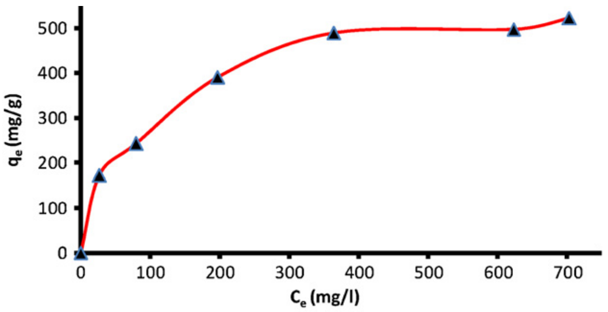
3.5. *Sorption isotherm*

The sorption isotherm shows how the adsorbate molecules are distributed between the liquid phase, C_e (mg/l) and the solid phase,



Hydrogel concentration, 1 g/l; pH 3; immersion at 30°C

Fig. 4. Effect of duration on Cr (VI) sorption.



Hydrogel concentration, 1 g/l; pH 3; immersion duration, 120 minutes at 30°C

Fig. 5. Sorption isotherm of Cr (VI) by the hydrogel.

q_e (mg/g). Fig. 5 shows the equilibrium curve plateau, which indicates the maximum sorption capacity of Cr (VI) ion by the hydrogel. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purposes.

3.6. Langmuir isotherm

The Langmuir model (Langmuir, 1918) assumes that the uptake of Cr (VI) ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linear form of Langmuir isotherm is given by Eq. (1),

$$\frac{C_e}{q_e} = \left(\frac{1}{Q_{\max}} * b\right) + \left(\frac{C_e}{Q_{\max}}\right) \tag{1}$$

where C_e is the equilibrium concentration of adsorbate (mg/l), q_e is the amount of the Cr (VI) ion sorbed by the hydrogel at equilibrium (mg/g), and $Q_{\max}$ (mg/g) and b (l/mg) are the Langmuir constants related to the sorption capacity and energy of sorption, respectively. The linear plot of C_e versus C_e/q_e (Fig. 6a) shows that the sorption obeyed Langmuir isotherm model ($R^2 > 0.98$). $Q_{\max}$ and b were determined from slope and intercept of the plot and were found to be 588.24 mg/g and 2.5177×10^{-4}, respectively. According to Hall, Eagleton, Acrivos, and Vermevlem (1966), the essential characteristics of Langmuir isotherm can be explained in terms of dimensionless constant separation factor (R_L), which is defined by Eq. (2),

$$R_L = \frac{1}{1 + (b * C_o)} \tag{2}$$

where b (l/mg) is the Langmuir constant related to the energy of adsorption and C_o (mg/l) is the initial concentration of Cr (VI) ion. The parameter, R_L shows the type and shape of isotherm and is shown in Table 1.

It is clear from Table 2 that all R_L values lie between 0 and 1 indicating the favorable sorption of Cr (VI) by the hydrogel.

Table 1
Effect of separation factor, R_L on isotherm shape.

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 2
R_L Values based on Langmuir equation for Cr (VI) sorption by the hydrogel.

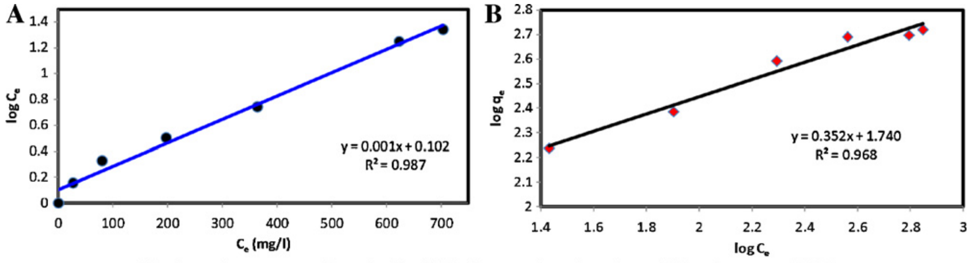
Cr (VI) concentration (mg/l)	R_L value
50	0.9880
100	0.9754
200	0.952
400	0.9085
600	0.8687
700	0.8502

3.7. Freundlish isotherm

Freundlish isotherm assumes that the uptake of metal ions occurs on a heterogeneous surface by multilayer sorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration (Freudlich, 1907). Freundlish isotherm is represented by Eq. (3),

$$\log q_e = \log K_F + \left(\frac{1}{n \log C_e}\right) \tag{3}$$

where q_e is the amount of adsorbate adsorbed per unit weight (mg/g) of hydrogel, C_e is the equilibrium concentration of Cr (VI), mg/l and K_F (mg/g) and n are Freundlish constants related to the capacity of sorption and favorability of sorption, respectively. Linear plots of $\log q_e$ versus $\log C_e$ give a straight line with the slope and intercept of which correspond to $1/n$ and $\log K_F$, respectively. Freundlish isotherm of Cr (VI) ion adsorption by the hydrogel is shown in Fig. 6b. The values of Freundlish constants K_F and n were calculated and found to be 55.03 and 2.835, respectively. The value of n (2.835) for Cr (VI) ion adsorption by hydrogel ($0 < n < 10$) indicates that the sorption of Cr (VI) ion by the hydrogel is favorable. The correlation coefficient, R^2 value of Cr (VI) sorption by hydrogel was over 0.968 indicating that the sorption of Cr (VI) ion by the hydrogel fitted also well on Freundlish isotherm (obey the Freundlish isotherm). It is clear from Fig. 6a that Langmuir isotherm proved to be a better mathematical fit for equilibrium data than Freundlish model (Fig. 6b), based on the higher R^2 value.



Hydrogel concentration, 1 g/l; pH 3; immersion duration, 120 minutes at 30°C

Fig. 6. Langmuir (A) and Freundlich (B) isotherms for Cr (VI) sorption by hydrogel.

4. Conclusion

Acrylamide was grafted onto guar gum through graft copolymerization reaction using potassium bromate/thiourea dioxide redox system for initiating the polymerization reaction. The copolymer resulting from the graft copolymerization reaction was further treated with glutaraldehyde to obtain crosslinked hydrogel. The so-prepared crosslinked hydrogel was used as a new sorbent material for removal of Cr (VI) from its aqueous solutions. Factors affecting the sorption process such as pH, sorbent concentration, immersion duration and Cr (VI) ion concentration were extensively investigated. It was found from the study that sorption of Cr (VI) by the hydrogel is affected by the extent of grafting of polyacrylamide onto guar gum. Also it was found that the sorption process is pH-dependent and maximum sorption was obtained at pH 3. The sorption studies were carried out using different Cr (VI) concentrations for different lengths of time. It was found that the extent of Cr (VI) sorption increases upon increasing Cr (VI) concentration within the range studied. Regarding the effect of sorption duration, It is found that the increase in the immersion duration from 0 to 10 min is accompanied by remarkable increase in the sorption of Cr (VI) by the hydrogel. Further increase in the immersion duration over 10 min has a negligible effect on Cr (VI) sorption. The sorption data was found to obey both Langmuir and Freundlich sorption isotherms but Langmuir isotherm proved to be a better mathematical fit for equilibrium data than Freundlish model, based on the higher R^2 value. The Langmuir sorption capacity ($Q_{\max}$) was found to be 588.24 mg/g. Freundlish constants, K_F and n, were found to be 55.03 and 2.835, respectively.

Acknowledgement

The authors extend their appreciation to the Deanship of Scientific Research at King Saud University for funding the work through the research group project No. RGP-VPP-029.

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