

REMOVAL OF CR (VI) FROM AQUEOUS SOLUTION USING GRAFT COPOLYMER OF CELLULOSE EXTRACTED FROM SISAL FIBRE WITH ACRYLIC ACID MONOMER

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The extraction of cellulose from sisal fiber was done initially using the steam explosion method. Extracted cellulose was grafted with acrylic acid in the presence of ceric ammonium nitrate redox initiator. The grafting phenomenon taking place between cellulose and the acrylic acid was proved by Fourier transform infrared spectroscopy (FTIR). The prepared graft copolymer was used as adsorbent for the removal of Cr (VI) from the aqueous solution. The effect of pH, contact time, and initial adsorbent dosage on the metal ion adsorption capacity was investigated. From the observed results, it was evident that the adsorption of metal ions increased with the increase in contact time and adsorbent dosage. The optimum pH was found to be 5.0 for the removal of Cr (VI) for cellulose-g-acrylic acid copolymer. The experimental data were fitted well to the Freundlich adsorption isotherm for cellulose graft acrylic acid. The correlation coefficient values of cellulose grafted acrylic acid ($R^2=0.99$) in the Freundlich isotherm were higher than the Langmuir isotherm correlation values ($R^2=0.77$). The pseudo second order model was found to explain the kinetics of Cr (VI) adsorption most effectively with good correlations. From the results obtained, it was concluded that the cellulose graft acrylic acid copolymer is an efficient adsorbent for the removal of Cr (VI) under optimum conditions.

Keywords: grafting, cellulose, sisal fiber, acrylic acid, adsorption isotherm

INTRODUCTION

The presence of heavy metals in water bodies for human consumption and in industrial waste water has become a cause of great concern due to their highly toxic nature and their increased discharge.¹ Heavy metal contamination has been a critical problem mainly because metals tend to persist and accumulate in the environment. Serious soil and water pollution was mainly caused by many toxic heavy metals, which have been discharged into the environment as industrial wastes.² The ultimate disposal of treated and untreated waste effluents containing toxic metals as well as metal chelates³ from different industries, e.g. tannery, steel plants, battery industries, thermal power plants etc. cause serious water pollution. The excessive levels of heavy metals have been linked with a wide range of health conditions, including skin disease, birth defects and cancer etc.⁴ In addition, anthropogenic activities like mining, using indiscriminately fertilizers and pesticides

containing heavy metal ions in agriculture also resulted in deterioration of water quality. Plant metabolism is also negatively affected by these heavy metals.⁵ Cr (VI) is the common environmental contaminant in most of the industrial effluents, which causes severe environmental and public health problems. Chromium occurs primarily in (III) and (VI) oxidation states, the most potentially harmful ones,⁶ as all the other oxidation states are not stable in aqueous solutions. Cr (VI) is highly mobile and is considered acutely toxic, carcinogenic and mutagenic to living organisms and more hazardous than other heavy metals. Apart from lung cancer and death, the most common effects of ingestion of chromium (VI) on humans are respiratory problems, genetic alteration, kidney and liver damage, and weakened immune systems.⁷ The tolerance limits for Cr (VI) for discharge into inland surface water and potable water are 0.1 mg/L and 0.05 mg/L,

respectively.⁸ Animal studies show that Cr (VI) is generally more toxic than Cr (III). Ingesting large amounts of chromium (VI) can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. Cr (VI) is a very strong oxidizing agent (therefore very fast in reacting, unlike Cr (III) and likely to form complexes). The hexavalent form is of particular concern because of its greater toxicity. Hence, the removal of Cr (VI) from industrial effluents is important. So the World Health Organization has recommended strict controls on the percentages of various heavy metals in effluent waters. Since metals are non-biodegradable,⁹⁻¹¹ and may be bioaccumulated in living tissues, their removal from wastewater is nowadays legally imposed.¹² Most technologies available for removing metals from industrial waste including precipitation,^{13,14} ion exchange,¹⁵ cementation,¹⁶⁻¹⁸ electrodepositing,¹⁹ membrane separation technology²⁰ etc. do not seem to be economically feasible because of their high cost.²¹ As a result, recent research has been focused on the development of cost effective alternatives. Adsorption processes have been investigated as an efficient, low-cost^{22,23} and easy operation method requiring little use of chemical additives and allowing the possibility to reuse the adsorbent materials.

In recent years, a great deal of interest has been devoted to the applicability of modified polymeric materials for the removal or separation of metal ions from heavy metal contaminated water.²⁴ Several sorbents that can be used for such purposes include fungal biomass, bacteria and algae, aquatic plants,^{25,26} sunflower stalks, yeast,^{27,28} biopolymers, chatoyant and n-carboxyl-methyl chatoyant, *Sphagnum* moss peat,²⁹ *Cladophora* cellulose-polyaniline composite,³⁰ cellulose modified with D-glucose and quaternary ammonium groups,³¹ *Spirulina platensis* extracts,³² maize cob and husk^{33,34} chemically modified and unmodified cassava waste.³⁵

In addition, lignocellulosic fibers have gained special attention, since the cost of these materials is much lower than the cost of commercial adsorbents, such as activated carbon or ion-exchange resins.³⁶ With the help of pulping or steam explosion technology, lignocellulosic biomass materials can be fractionated into

biopolymer constituents. Sisal fiber is one of the natural fibers often used as adsorbent in waste water treatment.³⁷ Sisal fiber belongs to the Agave family (*Agave sisalina*), an environmentally friendly crop. It is a strong, stable, biodegradable and versatile material, which has been recognized as an important source of fiber for composites. Sisal fiber is composed of cellulose (63-64%), hemicelluloses (19%), lignin (5%) and has a moisture content of 10-11%. Cellulose is extracted from sisal fiber using chemical and mechanical treatments (steam explosion method). The steam explosion technique is intended to increase cellulose accessibility. The main aim of this study has been to extract cellulose from sisal fiber using chemical and mechanical treatments and to graft it with acrylic acid monomer in order to use the prepared cellulose-g-acrylic acid as an adsorbent for the removal of Cr (VI) ions. The kinetics, mechanism and thermodynamics of metal ion sorption were evaluated. In addition to this, the optimum parameters affecting the metal ions uptake, e.g. adsorbent dose, pH of the solution and contact time of adsorbent with the adsorbate, were also observed.

EXPERIMENTAL

Materials

The sisal fiber was purchased from local farms. The analytical grade reagents, such as NaOH, acetic acid, sodium hypochlorite and oxalic acid, were obtained from Central Drug House Pvt Ltd. An aqueous stock solution (200 mg/L) of Cr (VI) ions was prepared using potassium dichromate ($K_2Cr_2O_7$) salt. This was used as source of Cr (VI) in the synthetic wastewater. The pH of the solution was adjusted using 0.1 N HCl or NaOH. Fresh dilutions were used for each study. All the chemicals used above were of analytical reagent grade.

Preparation of steam exploded fibers

About 30 g of sisal fibers were chopped into uniform sizes of approximately 10 cm. The chopped fibers were introduced into a beaker and 2% NaOH (fiber to liquor ratio 1:10) was added to them. The mixture was then placed in an autoclave for a period of 1 h under a pressure of 20 lb. After a certain period of time, the pressure was released immediately. The fibers were removed from the autoclave and then washed with water to remove the alkali. The washed fibers were allowed to drain.

Preparation of steam exploded bleached fibers

The bleaching treatment of the steam exploded fibers was carried out using a mixture of NaOH and acetic acid (27 and 78.8 g, respectively) and a mixture

of 1:3 sodium hypochlorite solutions. This treatment was then repeated for approximately six times. After the completion of this process, the fibers were thoroughly washed in distilled water and dried.

Preparation of steam exploded fibers in acidic medium

The steam exploded bleached fibers were placed in an autoclave and treated with different concentrations of oxalic acid, such as 5%, 7%, 9%, and 11%, until a pressure of 20 lb was attained. Then, the pressure was released immediately. The autoclave was again set to reach the pressure of 20 lb, and the fibers were kept under that pressure for 15 min. Then, the pressure was released again and the process was repeated 8 times. After completion of this process, the fibers were taken out and washed well using distilled water.^{38,39}

Mechanical treatment of processed fibers

The acid-treated fibers were suspended in water and then stirred well using a mechanical stirrer type RQ-1.27 Aat a speed of 8000 rpm for 4 h. The suspension was then kept in an oven at 90 °C until it was dry.

Preparation of grafted co-polymer

The cellulose extracted from the sisal fiber (1 g) was added to 100 ml of water and stirred well to form a homogeneous suspension. 1ml of acrylic acid monomer dissolved in 20 ml of water was then added to that homogenous solution. To initiate the polymerization process in the above mixture the redox initiator ceric ammonium nitrate (0.5 g of CAN in 10 ml of 1N HNO₃) was added. Then, the above mixture was heated to 70 °C. Simultaneously, this hot solution was stirred using a magnetic stirrer for approximately 30 minutes. After a certain period of time, the above solution was poured into excess sodium hydroxide (2N) solution to precipitate the graft copolymer. Finally, the obtained graft copolymer precipitate was filtered, dried and weighed.

The grafting parameters, such as the grafting percentage, grafting efficiency and grafting yield, were defined and calculated as follows:

$$GE(\%) = \frac{Wt \text{ grafted polymer}}{Wt \text{ grafted polymer} + Wt \text{ homopolymer}} \times 100 \quad (1)$$

$$GY(\%) = \frac{Wg - Wi}{Wa} \times 100 \quad (2)$$

$$GP(\%) = \frac{Wpa}{Wa} \times 100 \quad (3)$$

where W_i = W_t of ungrafted polymer, W_{pa} or W_g = W_t of grafted polymer, W_a – weight of monomer.

Experimental process of Cr (VI) removal

Investigation was done to study the extent of adsorption with different concentrations of K₂Cr₂O₇ using the batch adsorption technique. The extent of removal of the metals was examined separately by changing the solution pH, adsorbent dosage, and time of shaking of the adsorbent metal solution mixture.

About 1 g of cellulose-g-acrylic acid copolymer was treated with 100 ml of the prepared K₂Cr₂O₇ solution.

These solutions were introduced into stoppered bottles and then agitated at 30 °C using an orbital shaker at a fixed rate of 160 rpm. The adsorbent was separated by filtration using Whatman filter paper and the aqueous phase concentration of the metal was determined by the atomic adsorption technique. A similar procedure was carried out at various time intervals, adsorbent doses and pH. When using the sodium hydroxide or the hydrochloric acid the pH of each solution was adjusted to different values.

The ability of removing Cr (VI) from aqueous solution depends on the fraction of the side chains of the copolymers. The main chain of cellulose shows poor Cr (VI) adsorption due to lack of desirable properties. Modification by graft copolymerization provides one of the best ways to affect the physical and chemical properties of cellulose, to combine the advantages of both natural cellulose and synthetic polymers and to use cellulose for various purposes like metal removal etc. In the current study, the acrylic acid functional group was incorporated onto the cellulose backbone to increase the physical and chemical properties, including high metal adsorption etc.

RESULTS AND DISCUSSION

Evidence of grafting by FT-IR spectral analysis

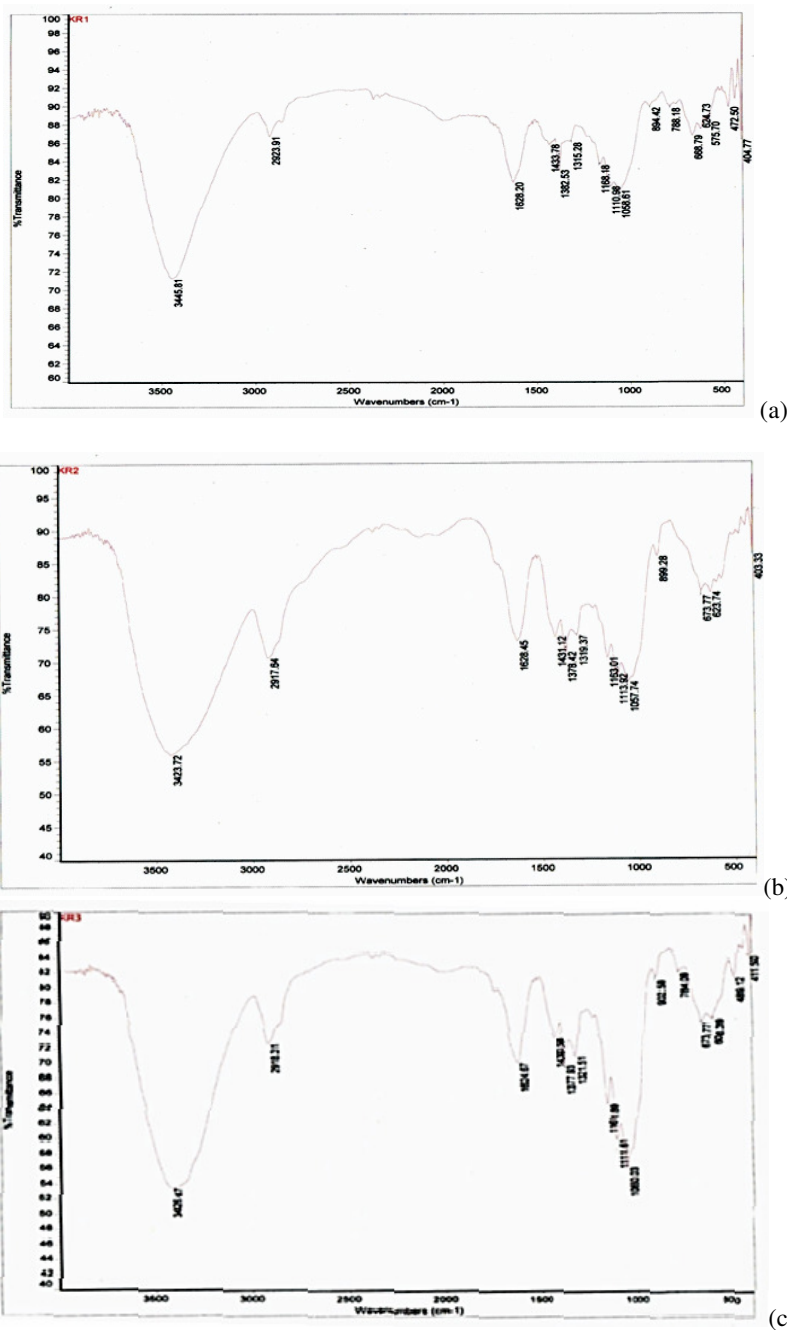
Figure 1(a-e) shows the FT-IR spectra recorded during the four treatment stages of the fibers and graft copolymer. The IR spectra of the steam exploded fibers (Fig. 1 (a)) indicate a prominent peak at 3445.81 cm⁻¹ corresponding to OH stretching. The peak at 2923.91 cm⁻¹ corresponds to CH₂ stretching. The peak obtained at 1628.20 cm⁻¹ is due to C=O stretching. The peaks at 1168.18 cm⁻¹, 1110.98 cm⁻¹ and 1058.61 cm⁻¹ are attributed to C-O stretching, C-H in plane bending and C-O-C stretching, respectively. Similar results were observed in stages 2 to 4 (Fig. 1(b-d)). Comparing the FTIR spectral results of steam exploded fibers with those obtained for the other stages, it was found that the area of the peak at 1628.45 cm⁻¹ increased successively. The increase in peak intensity at 1628.45 cm⁻¹ in sisal fiber is due to the bonded acetyl group. From the successive increase in the peak area, it was concluded that the cellulose content increased during the mechanical treatment of the processed fibers (stage 4) with the removal of lignin, hemicelluloses etc. The grafted copolymers thus prepared were characterized by FTIR spectral analysis. The spectra of the grafted copolymer showed the existence of a moderate peak at 2500 cm⁻¹, as observed in Figure 1(e) corresponding to

the acid group (COOH), which is an evidence of grafting. These additional peaks confirm that the grafting took place effectively.

Effect of pH

Fig. 2 shows the effect of pH on the removal of Cr (VI) from aqueous solution using the cellulose-g-acrylic acid copolymer. The effect of

the initial pH value on the Cr (VI) cellulose-g-acrylic acid copolymer was investigated within the pH range of 4-8 by taking into account the precipitation pH value of metal ions. From Fig. 2, it is evident that Cr (VI) removal initially increases with the increase in the pH value, but thereafter it decreases.



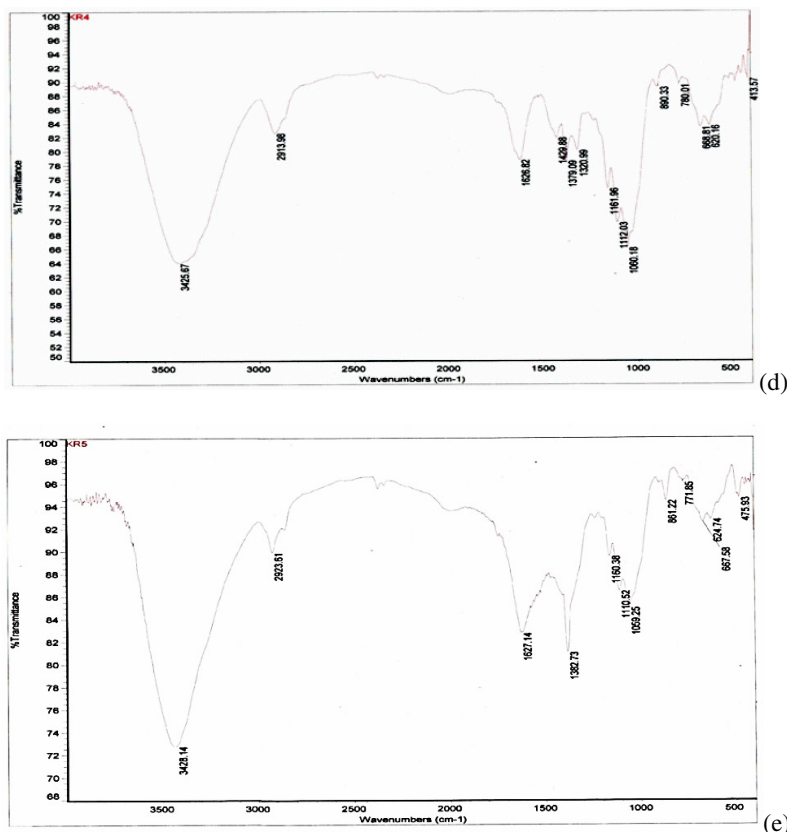


Figure 1: FT-IR spectra of steam exploded fiber (a), steam exploded bleached fiber (b), steam exploded bleached fiber in acidic medium (c), mechanically treated processed fiber (d), cellulose-g-acrylic acid (e)

At a low pH value, large amounts of H⁺ might compete with the metal ions for the binding sites, resulting in a decrease of divalent metal ions binding.⁴⁰ The optimum pH was observed to be 5. It was noticed that when the pH value was higher than 5, the amount of adsorption decreased, which may be attributed to the fact that heavy metal ions started precipitating, leading to a reduction of the metal ions in the aqueous solution.⁴¹ The prepared cellulose graft acrylic acid showed a maximum adsorption of 79% at pH 5.

Effect of adsorbent dose

The adsorption of Cr (VI) from aqueous solution onto the cellulose-g-acrylic acid copolymer was studied by varying the amount of adsorbent from 1 to 6 g, while keeping other parameters (pH and contact time) constant. Fig. 3 presents the effect of adsorbent dose on the removal of Cr (VI) from the aqueous solution using cellulose-g-acrylic acid copolymer. From this figure, it is evident that the adsorption of Cr (VI) increases rapidly with an increase in the amount of adsorbent at first, but after it reaches an

optimum dosage it remains constant. The rapid uptake reveals a high affinity between the heavy metals and the adsorbent, which is directly attributed to the character of the adsorbent. The positively charged adsorbent dispersed evenly in the solution after grafting, which was favorable to the rapid contact between heavy metals and the active sites. However, further addition of the adsorbent beyond 4 g did not cause any significant change in the adsorption, which may be due to the overcrowding of the adsorbent particles.⁴² Thus, it was observed that at the dosage of 6 g the maximum adsorption of Cr (VI) onto Ce-g-acrylic acid occurred and it was 78%.

Effect of contact time

Fig. 4 clarifies the effect of contact time on the adsorption of Cr (VI) ions onto the cellulose grafted acrylic acid. The adsorption of Cr (VI) was measured at five different contact time periods from 60 min to 360 min. From the results of Fig. 4, it is evident that the removal of Cr (VI) increased with the increase in the contact time and reached a maximum at 360 min. The higher rate

of adsorption initially was mainly due to the availability of more active sites, as the adsorption process is dependent on the surface morphology.⁴³ After a certain point, further increase in contact time did not bring about any improvement, which

may be due to a quick exhaustion of the adsorption sites.^{44,45} Studying the effect of contact time, it was found that at 360 min the maximum adsorption of Cr (VI) occurred on Ce-g-acrylic acid and it was 75%.

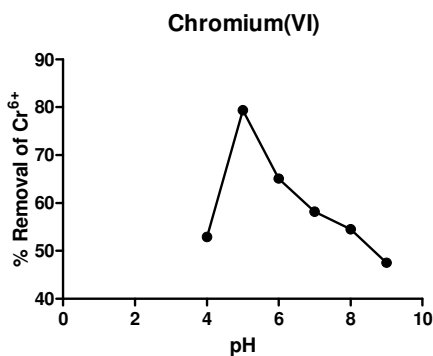


Figure 2: Effect of pH on the removal of Cr (VI) from aqueous solution using the cellulose-g-acrylic acid copolymer

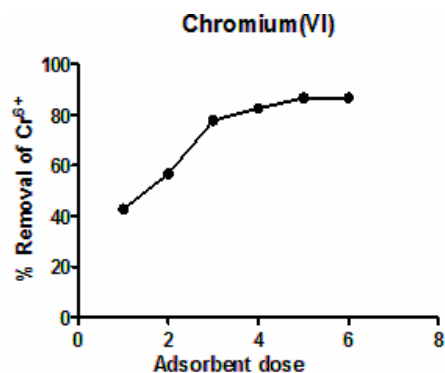


Figure 3: Effect of adsorbent dose on the removal of Cr (VI) from aqueous solution using the cellulose-g-acrylic acid copolymer

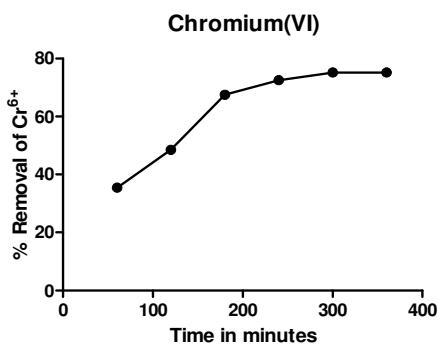


Figure 4: Effect of contact time on the removal of Cr (VI) from aqueous solution using the cellulose-g-acrylic acid copolymer

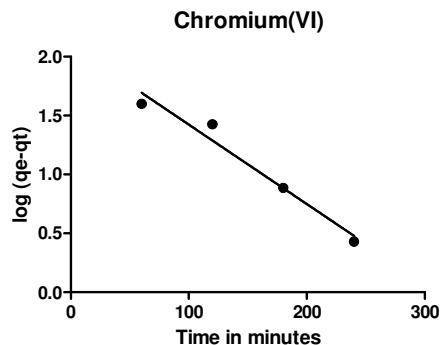


Figure 5: Pseudo first order kinetics for Cr (VI)

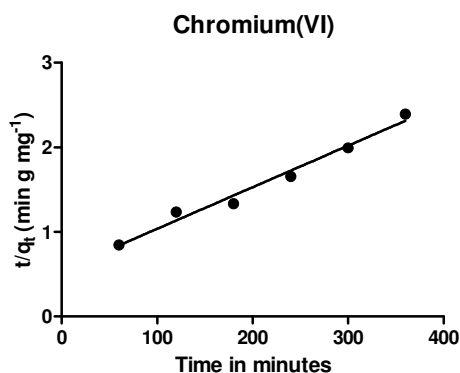


Figure 6: Pseudo second order kinetics for Cr (VI)

Table 1

Comparative results of pseudo first order and pseudo second order kinetic models for Cr (VI)

Sample	Metal ion	Pseudo-first-order kinetic model			Exp. value	Pseudo-second-order kinetic model		
		q _e (mg/g)	k ₁ (min ⁻¹)	R ²		q _e (mg/g)	q _e (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)
	Cr(VI)	310.99	0.006743	0.9646	160	110.72	0.004917	0.9797

Kinetic studies of adsorption

The examination of the controlling mechanism of the adsorption process, such as mass transfer and chemical reaction, was done by the pseudo first order and pseudo second order kinetic models. These pseudo first order and second order kinetic models were used to test the experimental data.⁴⁶ The pseudo first order equation is given below:

$$\log(q_e - qt) = \log q_e (k_1 + 2.303)t \quad (4)$$

where q_e and q_t are the amounts of Cr (VI) adsorbed onto the adsorbent (mg/g) at equilibrium and at time t, respectively, k₁ is the rate constant of first order adsorption with min⁻¹ as the unit. The straight line plot of log (q_e - q_t) against t was used to determine the rate constant k₁, and correlation coefficient R² values of Cr (VI) under different concentration ranges. These values were calculated from the plots shown in Fig. 5.

The second order equation may be expressed as:^{47,48}

$$\frac{t}{qt} = \frac{1}{h} + \frac{t}{q_e} \quad (5)$$

where h = k₂ q_e² (mg g⁻¹ min⁻¹), which can be regarded as the initial adsorption rate as t tends to 0 and k₂ is the rate constant of second order adsorption (g mg⁻¹ min⁻¹). The straight line plots of t/q_t against t have been tested to obtain rate parameters, suggesting the suitability of this kinetic model to fit the experimental data (Fig. 6).

Table 1 lists the computed results obtained from both the first order and second order kinetic models.

Based on the calculated correlation coefficients, it has been concluded that the adsorption of Cr (VI) follows the second order kinetics. In most cases, the first order equation does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption process. The second order equation correlates well to the adsorption behavior in many cases, which may involve valency forces through sharing of electrons between metal cations and adsorbent.

Adsorption isotherm

The distribution of the adsorbate species among liquid and solid phases was described by the adsorption isotherm (mathematical models). The adsorption isotherm mainly describes the interaction between the solute and the adsorbent and so it is critical in optimizing the use of adsorbent.⁴⁹ The Langmuir equation has been frequently used to give the sorption equilibrium.⁵⁰ The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The linearized Langmuir isotherm allows the calculation of adsorption capacities and Langmuir constant by the following equation:

$$C_{ads} = \frac{K_L C_{eq}}{1 + b C_{eq}} \quad (6)$$

The linearized form of the Langmuir isotherm:

$$\frac{C_{eq}}{C_{ads}} = \frac{b C_{eq}}{K_L} + \frac{1}{K_L} \quad (7)$$

$$C_{max} = K_L / b \quad (8)$$

where C_{ads} = amount of Cr (VI) ion adsorbed (mg·g⁻¹); C_{eq} = equilibrium concentration of Cr (VI) ion in solution (mg·dm⁻³); K_L = Langmuir constant (dm³·g⁻¹); b = Langmuir constant (dm³·mg⁻¹); C_{max} = maximum metal ions adsorbed.

The constants “b” and “K_L” can be obtained from the linearized form of Langmuir equation (7). With the help of the slope and intercept of the linear plot of C_{eq}/C_{ads} against C_{eq}, the Langmuir constants K_L and b can be calculated. Positive sorption results in the removal of the solute from the bulk solution and the concentration at the surface of the solid in a solid liquid system. At equilibrium, there is a defined distribution of the solute between the liquid and the solid phases, which can generally be expressed by one or more isotherms. The isotherm of the sorption of Cr (VI) ions by cellulose graft acrylic acid copolymer is represented in Fig. 7. The isotherm is characterized by the initial region, which is represented as being concave to the concentration axis. The isotherm is close to reaching a plateau, which can typically be described by the Langmuir isotherm.

The data derived from the adsorption of Cr (VI) ions by the cellulose graft acrylic acid copolymer adsorbent over the entire concentration range are described by the Langmuir equation. A plot of C_{eq}/C_{ads} vs. C_{eq} yielded a straight line (see Fig. 7), confirming the applicability of the Langmuir adsorption isotherm. The calculated results of the Langmuir isotherm constants and C_{max} are given in Table 2.

From the above results, it was concluded that the adsorption of Cr (VI) onto cellulose g acrylic acid copolymer correlates with the Langmuir equation. The essential features of the above equation can be expressed in terms of the dimensionless parameter R_L . A dimensionless constant separation factor or equilibrium parameter, R_L is used to predict whether the adsorption system is “favourable” or “unfavourable”. The separation factor R_L is defined by:

$$R_L = \frac{1}{1 + bC_f} \tag{9}$$

where C_f is the final Cr (VI) concentration (mg/dm^3) and b is the Langmuir adsorption equilibrium constant (dm^3/mg).

When the observed R_L values are in the range of $0 < R_L < 1$, then the cellulose-g-acrylic acid

copolymer is a favourable adsorbent. The values of R_L were calculated for different initial Cr (VI) concentrations. Since the calculated R_L values were obtained in the range of $0 < R_L < 1$, it was concluded that the adsorption of Cr (VI) onto cellulose-g-acrylic acid copolymer is favourable.

Another very frequently used isotherm to determine the adsorption parameters is the Freundlich isotherm, which was first developed by Herbert Freundlich in the year 1906. The widely used empirical Freundlich equation based on a heterogeneous surface is given by:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{10}$$

where K_F and n are constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity of adsorption. A plot of $\log q_e$ versus $\log C_e$ gives a straight line of slope $(1/n)$ and an intercept of $\log K_F$. The Freundlich constants K_F and n are calculated with the help of the slope and intercept. The linear regression plot of the Freundlich isotherm for Cr (VI) uptake by the cellulose graft acrylic acid copolymer is presented in Fig. 8. The calculated results of the Freundlich adsorption isotherm constants are presented in Table 3.

Table 2
 C_{max} value and Langmuir constants for Cr (VI)

Metal ions	Langmuir constants		
	K_L (dm^3/g)	b (dm^3/mg)	C_{max} (mg/g)
Cr(VI)	2.842	0.009333	304.51

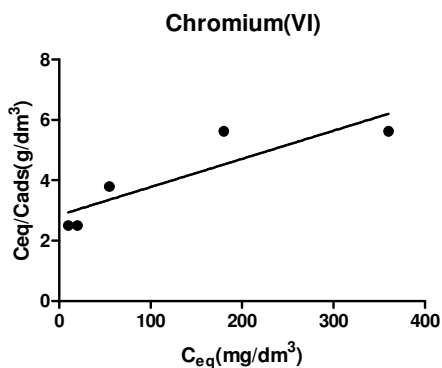


Figure 7: Langmuir isotherm plot for Cr (VI)

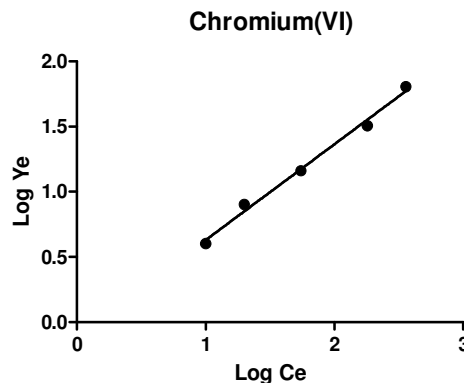


Figure 8: Freundlich isotherm plot for Cr (VI)

Table 3
Freundlich constants and correlation coefficients for Cr (VI)

Adsorbent	Metal ions	Freundlich constants		
		K_f	n	R^2
Cellulose-g-acrylic acid	Cr (VI)	0.7838	1.3605	0.9924

Table 4
Comparison of Langmuir and Freundlich isotherm parameters for Cr (VI)

Sample	Metal ions	Langmuir constants			Freundlich constants			
		K_L (dm ³ /g)	b (dm ³ /mg)	C_{max} (mg/g)	R^2	K_f (dm ³ /g)	n (dm ³ /mg)	R^2
Cr(VI)		2.842	0.009333	304.51	0.7750	0.7838	1.3605	0.9924

A comparison between the Langmuir and Freundlich isotherm models is tabulated in Table 4. From the observed K_f , n and R^2 values, it may be concluded that the Freundlich model better describes the adsorption process when compared to the Langmuir model.

CONCLUSION

The extracted cellulose was grafted with the acrylic acid monomer, using ceric ammonium nitrate as an initiator. The evidence of grafting has been ascertained from the FTIR spectra analysis. The prepared cellulose graft acrylic acid copolymer was subjected to adsorption studies and the results showed that the adsorbent dose, contact time, and pH had a marked effect on the removal of Cr (VI) ions from the metal solution. An atomic adsorption study was carried out to examine the extent of adsorption of Cr (VI) by the prepared graft copolymer. The adsorption isotherm could be well fitted by the Freundlich equation. The adsorption process could be best described by the second order equation. From the above observed results, it can be concluded that the extracted cellulose graft acrylic acid copolymer is an effective low cost adsorbent for the collection of metal ions, such as Cr (VI), from waste water at an industrial level.

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