

## REMOVAL OF Cr (VI) FROM AQUEOUS SOLUTION BY POLYMER BASED GUAR GUM-G-POLY (AAM) AND ACTIVATED CHARCOAL ADSORBENTS

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Graft copolymerization of acryl-amide onto guar-gum has been carried out in the presence of potassium per sulphate as a redox initiator. The prepared graft copolymer was characterized by various techniques such as FT-IR, SEM-EDX and TGA-DTA-DTG. Activated charcoal was also studied as the adsorbent in the present study to evaluate their adsorption capacity for Cr (VI) and compared it with indigenously synthesized graft copolymer. The experimental data were fitted well to Langmuir adsorption isotherm for Guar Gum-g-Poly (AAM) as well as activated charcoal. The maximum monolayer adsorption capacities for Guar Gum-g-Poly(AAM) and activated charcoal were 142.8 mg/g and 200 mg/g. Pseudo second order model was found to explain the kinetics of Cr (VI) adsorption most effectively with good correlations ( $R^2 > 0.99$ ) in both cases. Thermodynamic parameters showed that adsorption processes were spontaneous and endothermic for Guar Gum-g-Poly (AAM) and activated charcoal.

**Key words:** adsorption, guar gum-g-poly (AAM), chromium (VI), isotherms.

**Uklanjanje Cr (VI) iz vodene otopine pomoću polimerne baze guar gume-g-poli (AAM) i aktivnog ugljena kao adsorbensa.** Cijepljena kopolimerizacija akril amida na guar-gumu provedena je kalij sulfatom kao redoks inicijatorom. Karakterizacija pripremljenog cijepljenog kopolimera obavljena je različitim tehnikama kao što su FT-IR, SEM-EDX i TGA-DTA-DTG. U ovom radu proučavan je i aktivni ugljen kao adsorbens za procjenu adsorpcijskog kapaciteta za Cr (VI) i uspoređivan sa sintetiziranim cijepljenim kopolimerom. Eksperimentalni podaci su obrađeni primjenom Langmuirove adsorpcijske izoterme za Guar gumu-g-poli (AAM) kao i za aktivni ugljen. Maksimalni kapacitet jednoslojne adsorpcije u za Guar gumu-g-poli (AAM) i za aktivni ugljen iznosio je 142,8 mg/g i 200 mg/g. Kinetički model pseudo drugog reda najbolje opisuje adsorpciju s dobrom korelacijom ( $R^2 > 0.99$ ) u oba slučaja. Termodinamički parametri pokazuju da je adsorpcijski proces spontan i endoterman i za Guar gumu-g-poli (AAM) i za aktivni ugljen.

**Ključne riječi:** adsorpcija, guar guma-g-poli (AAM), krom (VI), izoterme.

### INTRODUCTION

Due to urbanization, a large number of industries are setting up. A few of them based on leather tanning, mining, cement, electroplating, photography, nuclear power plant, metal finishing and textiles are releasing most of heavy metal ions in their effluents. These heavy metal ions are toxic

inorganic contaminants which cannot be degraded and have tendency to accumulate in living bodies [1]. The removal of these heavy metal ions from their effluents is the major requirement for any industry to set up. Cr (VI) is the common environmental contaminant in most of the industrial

effluents which causes severe environmental and public health problems. Chromium exists in (III) and (VI) oxidation states, as all other oxidation states are not stable in aqueous solutions and these oxidation states of chromium are potentially harmful [2]. However, Cr (VI) which is primarily present in the form of chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ) poses significantly higher levels of toxicity than the other valence states [3]. Cr (VI) is highly mobile and is considered acutely toxic carcinogenic and mutagenic to living organisms and more hazardous than other heavy metals [4]. The tolerance limit for Cr (VI) for discharge into inland surface water and potable water are 0.1 mg/L and 0.05 mg/L, respectively [5]. A number of treatment methods for the removal of heavy metal ions from aqueous solution have been reported by several researchers. A few methods among them are: Reduction followed by chemical precipitation, Solvent extraction, Reverse osmosis, Ion exchange, and electrolytic methods. These methods are non-economical and have many disadvantages such as high operational costs, inefficient in treating large quantities, incomplete metal removal, generation of toxic sludge that require disposal or treatment. Adsorption is one of the preferred method for the removal of Cr (VI) from wastewater because of its efficiency and low cost [6]. It is well known that activated charcoal acts as an excellent adsorbent and is widely employed for the removal of heavy metal ions from industrial wastewater due to their large surface area, microporosity and chemical nature of their surface. The high material cost, however limits its use in wastewater treatment.

Much attention has recently been focused on graft copolymer as the adsorbent for the removal of heavy metal ions from wastewater since they have no adverse impact on human or environmental health.

Grafting has been used to modify various physio-chemical properties of the

polymer in which metal ion uptake is one of them. In principle, graft co-polymerization is a method to impart a variety of functional groups onto natural and synthetic polymer to enhance their physical as well as chemical properties. Much of studies on graft copolymerization have been carried out for its wide application in agriculture, biomedical, drug delivery and metal ion uptake etc. Graft copolymerization of vinyl monomers such as acrylamide [7], acrylic acid [8] methyl methacrylate [9] and methacrylic acid [10] onto guar-gum can introduce desired properties and enlarge the field of its applications by incorporating selective side chains. Guar-gum is a rigid, non-ionic natural plant polysaccharide which is cheapest, abundantly available and renewable organic materials produced from the ground endosperm of guar bean seeds.

The backbone is a linear chain of  $\beta$  (1  $\rightarrow$  4) linked mannose to which  $\alpha$  (1  $\rightarrow$  6) galactopyranoside single subunits are attached as side chains and there are nearly 1.5-2 mannose residues for every galactose residue [10]. It has a wide range of applications in various industries such as pharmaceutical, food processing, mining etc. However, due to its low mechanical as well as thermal stability, biodegradability and flexible behavior, the modification of this polymer has received much attention. Among the methods of modification of polymer, grafting is the most preferable and economical method for producing a substantial modification in the polysaccharide properties thereby enlarging the range of its utilization [11].

The graft co-polymerization of different monomer on the polymeric backbone has been achieved by various techniques such as chemical, radiation, photochemical, plasma-induced method and enzymatic grafting. In the present study an attempt has been made to study the behavior of Guar Gum-g-poly (AAm) towards removal efficiency of Cr (VI) from aqueous

solution. In view of above, we have synthesized polymer based adsorbent by free radical polymerization of acrylamide monomer onto guar gum by using potassium persulphate (KPS) as an initiator and N-N'Methylene bis-acrylamide (MBA) as a crosslinker. The prepared graft copolymer has been used as the adsorbent for removal of Cr (VI) from aqueous solution. Activated charcoal has also been employed as the

adsorbent in this study without any chemical modification to explore their potential in removing Cr (VI) ion from aqueous solution and compared their adsorption performance with synthesized graft copolymer on the basis of their adsorption capacity. The adsorption studies were conducted by varying various parameters such as effect of adsorbent dosages, pH, initial concentration of Cr (VI) and contact time.

## MATERIALS AND METHOD

All solutions were prepared using Milli-Q filtered deionized water having conductivity of 14.7  $\mu\text{S}$ . The glassware's were washed with dilute  $\text{HNO}_3$  followed by with double distilled water every time before use. A high precision electrical balance (Afcosct) was used for weighing the amount of adsorbents. pH measurements were made with a pH meter, (Cyberscan-1100, Eutech Instrument). Concentration of the Chromium metal was determined by atomic absorption spectrophotometer (Model AAS 4129, ECIL).

### Chemicals

The analytical grade E-merck chemicals like guar-gum, acryl-amide, N-N'Methylene bis-acrylamide(MBA), potassium persulphate (KPS), acetone, ethanol, nitric acid ( $\text{HNO}_3$ ), hydrochloric acid (HCl), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sodium hydroxide (NaOH) and activated charcoal were used as received in this study.

### Preparation of Cr (VI) solution

Synthetic stock solution (1000  $\text{mg}/\text{dm}^3$ ) of Cr (VI) was prepared by

dissolving required quantity of  $\text{K}_2\text{Cr}_2\text{O}_7$  in deionized water. For adsorption experiments, working solutions of Cr (VI) having concentration in between 2 to 10  $\text{mg}/\text{dm}^3$  were prepared by serial dilution using micropipette. The pH of the prepared solutions were maintained at 6.

### Synthesis of polymer based adsorbent

The 15 ml of solvent (Deionized water) was taken in a 100 ml beaker and (1g) of guar-gum powder was added to it followed by the addition of 0.051 g of potassium persulphate (KPS) which was used as an initiator, 0.95 g of acryl-amide (AAm) used as a monomer and 0.1 g of N-N'Methylene bis-acrylamide (MBA) as a crosslinker. The whole mixture was stirred gently throughout the reaction by mechanical stirrer. The reaction was carried out at 333K in an oven for 210 minutes. The product obtained was cooled at room temperature and washed with deionized water. The synthesized material as shown in the Fig.2 was then dried in the oven at 343K for 5 hours. The dry material obtained was grounded with grinder into fine powder and sieved to 500  $\mu\text{m}$  with standard sieve.

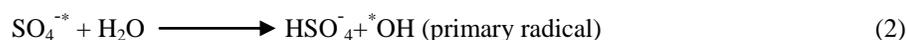
## Mechanism of Graft copolymerization

Free radical polymerization was the mechanism for the formation of cross linked graft co-polymer. The  $-OH$  groups on the backbones of guar-gum as showed in the chemical structure (Fig.1) acts as the active sites for the formation of GG-cl-poly (AAM). Initially per sulphate dissociate to give  $SO_4^{\cdot-}$  (primary radical) which further reacts with water molecule to give  $OH^{\cdot}$  (primary radical) [12-13]. Then  $SO_4^{\cdot-}$

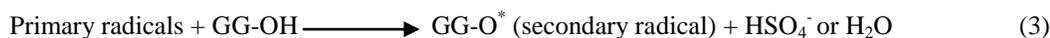
and  $OH^{\cdot}$  generate active free radical site (secondary radical) by abstracting hydrogen atom from the  $-OH$  group of the polymer guar-gum. Secondary radical formed could then react with double bond of the monomer (acrylamide), resulting in a covalent bond between the monomer (acrylamide) and guar-gum to propagate the chain [10]. The reaction mechanism of the graft copolymerisation was described below:

### Initiation

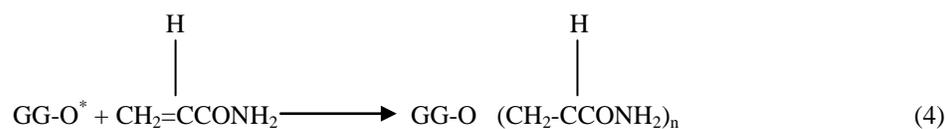
1. Formation of primary radicals as initiator



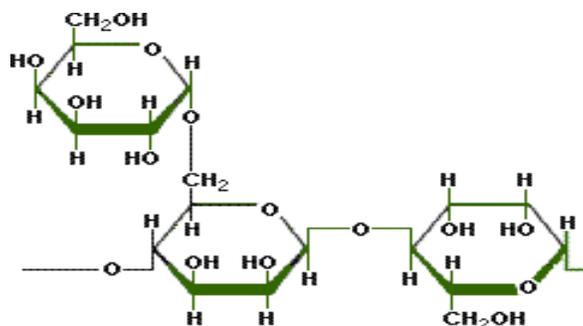
2. Formation of secondary radical on the guar-gum backbone



### Propagation



Where  $\text{GG-O}^{\cdot}$  was the guar-gum backbone free radical



**Figure 1.** Chemical Structure of Guar-Gum

**Slika 1.** Kemijska struktura guar-gume



**Figure 2.** Synthesized Guar Gum-g-Poly (AAM) used as the adsorbent  
**Slika 2.** Umjetna guar guma-g-poli (AAM) korištena kao adsorbens

## EXPERIMENTAL

0.2, 0.4, 0.6, 0.8 and 1.0 g each of both Guar-Gum-g-poly (AAM) and activated charcoal adsorbents were taken in five 250 cm<sup>3</sup> conical flasks separately and numbered as 1 to 5. The pH of the chromium solutions were maintained from 1 to 12 either with 1 N HCl or with NaOH solutions. 50 cm<sup>3</sup> of 10 mg/dm<sup>3</sup> stock solutions of chromium were then added to each flask with the help of pipette.

The conical flasks were uniformly shaken at optimum speed using a Electric wrist action shaker for fixed time intervals of 30 to 180 minutes at a temperature of 303±1K. The solutions were then filtered through A-grade Whatman No.1 filter paper with the help of vacuum pump and the filtrates were preserved for residual

chromium ion concentration determination by AAS at the wavelength of 357.8 nm.

The amount of Chromium metal adsorbed in (mg/g) at time (t) was calculated by using the following equation:

$$q_t = \frac{(C_i - C_t)V}{m} \quad (5)$$

$C_i$  and  $C_t$  were the Cr (VI) concentrations in (mg/dm<sup>3</sup>) initially and at a given time  $t$ , respectively.  $V$  was the volume of the Cr (VI) solution in (cm<sup>3</sup>);  $m$  was the weight of the adsorbent in (g). The percent removal of Cr (VI) ion in solution was calculated as

$$\text{Removal (\%)} = \frac{(C_i - C_t)}{C_i} \times 100 \quad (6)$$

## RESULTS AND DISCUSSION

### Analysis and Characterization of Graft Copolymer

**SEM:** In order to understand graft copolymerization SEM photographs of guar-gum as well as Guar Gum-g-Poly (AAM) were shown in Fig.3 (a) and (b). There was clear cut difference in crystal structure of the

synthesized product as compared to guar-gum. Sharp edged crystalline structure with variation in particle size was observed in the SEM photograph of Guar Gum-g-Poly (AAM) as shown in the Fig.3 (b).

**EDX:** EDX spectrum analysis of graft co-polymer confirmed some prominent peaks due to Carbon (33.82%), Oxygen

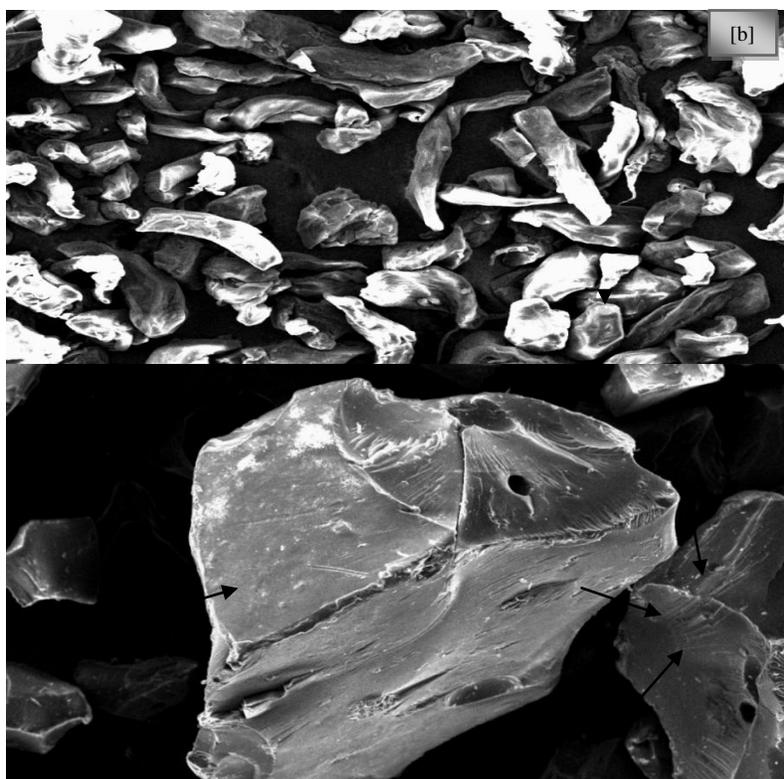
(64.66%), Fe (4.89%) Nitrogen (3.92%), Sulphur (0.67%) and Potassium (0.12%) elements as shown in Fig.4. The chemical composition of Guar Gum-g-Poly (AAM) in atomic, weight and compound form were represented in the Table 1. The presence of these elements may produce opposite charge on the surface and enhance electrostatic attraction with adsorbate present in the form of  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$  in the aqueous solution.

*FT-IR*: Infrared spectroscopic studies of pure guar gum and after graft copolymerization of guar gum were carried out to evaluate the evidence of graft copolymerization. The broad band centered at  $3435\text{cm}^{-1}$  was ascribed to (Bonded  $-\text{OH}$  groups),  $2157\text{cm}^{-1}$  (alkynated carbon stretching),  $2924\text{cm}^{-1}$  ( $>\text{C}-\text{H}$  asymmetric stretching, aliphatic chain),  $1647\text{cm}^{-1}$  ( $>\text{C}=\text{C}<$  stretching),  $1453\text{cm}^{-1}$  ( $-\text{CH}_3$  bend) and some prominent peaks in between  $1000$  and  $1160\text{cm}^{-1}$  were assigned to ( $>\text{C}-\text{O}$  stretching vibrations) for the infrared spectral analysis of pure guar-gum which indicated that hydroxyl and  $>\text{C}-\text{H}$  groups were abundantly available on the back bone of pure guar gum as shown in the Fig.5 (a) while the prominent band at  $1664\text{cm}^{-1}$  for ( $>\text{C}=\text{O}$  of amide groups),  $1543\text{cm}^{-1}$  and  $810\text{cm}^{-1}$  due to ( $>\text{N}-\text{H}$  out of plane bending),  $690\text{cm}^{-1}$  ( $>\text{C}-\text{H}$  out of plane bend,

aromatic),  $1458\text{cm}^{-1}$  ( $-\text{CH}_3$  bend),  $1268$  and  $1301\text{cm}^{-1}$  ( $>\text{C}-\text{N}$  amine groups) and weak band centered at  $3434\text{cm}^{-1}$  due to (Bonded  $-\text{OH}$  groups) were observed for Guar-Gum-g-Poly (AAM) as shown in Fig.5 (b). The prominent bands due to  $>\text{C}=\text{O}$  (Amide groups),  $>\text{N}-\text{H}$ ,  $>\text{C}-\text{N}$  groups and weak band due to  $>\text{C}-\text{O}$  (alcohol groups),  $-\text{OH}$  groups for Guar Gum-g-Poly (AAM) confirmed that grafting took place on the backbone of guar gum due to the free radical initiation reaction of (monomer, acrylamide) with the preferably available free hydroxyl groups.

*TGA/DTA/DTG*: Thermal behavior of the backbone and candidate polymer was investigated on TGA/DTA 6300, SII EXSTAR 6000 in air at heating rate of  $283\text{K}/\text{min}$ . As shown in the Fig.6 and Table-3 guar-gum exhibited initial decomposition temperature (IDT) at  $376.7\text{K}$  and final decomposition temperature (FDT) at  $738.4\text{K}$ . Two exothermic peaks at  $584.7\text{K}$  ( $67.3\mu\text{V}$ ) and  $737.9\text{K}$  ( $123.7\mu\text{V}$ ) were obtained in case of DTA of guar-gum.

DTG of guar-gum showed decompositions with  $6.61$  and  $1.04\text{mg}/\text{min}$ . weight loss at  $577\text{K}$  and  $736.7\text{K}$ , respectively. In case of Guar Gum-g-Poly (AAM), IDT was observed at  $359.5\text{K}$  and FDT has been found to be  $873.9\text{K}$  which was higher than FDT of guar-gum  $738.4\text{K}$ .



**Figure 3.** SEM micrographs of [a] pure Guar-Gum [b] Guar Gum-g-Poly (AAM)  
**Slika 3.** SEM mikrografije [a] čista guar-guma [b] guar guma-g-poli (AAM)

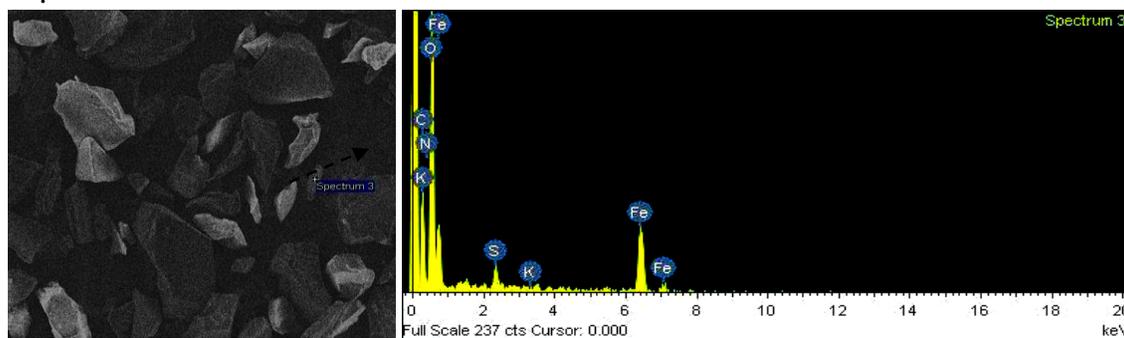
It showed that rate of decomposition of cross linked polymer with respect to temperature was less than that of guar-gum. Hence, grafting and cross linking of guar-gum with (AAM)-MBA increased the stability towards the thermal decomposition significantly as compared to starting material. The results were further supported

#### Effect of adsorbent dosage

The effect of amount of Guar Gum-g-poly(AAM) and activated charcoal on the removal of Cr (VI) were shown in Fig.7. Amount of adsorbents were varied from 0.2 to 1.0 g and equilibrated for 60 min. at an initial Cr (VI) ion concentration of  $10 \text{ mg/dm}^3$ . The percent removal of Cr (VI) increased with the increase in the amount of Guar-Gum-g-Poly (AAM) and activated charcoal.

by DTA studies in which endothermic and exothermic peaks at 358.6 K ( $-19.5 \mu\text{V}$ ) and at 850.9 K ( $104.1 \mu\text{V}$ ) were observed for Guar Gum-g-Poly (AAM). In DTG curve of Guar Gum-g-Poly (AAM), weight loss rate of 0.472 mg/min at 354.9 K and 0.9772 mg/min at 850.2 K were observed, respectively.

The maximum removal efficiencies for Cr (VI) by Guar Gum-g-Poly (AAM) and activated Charcoal were 96% and 86% for an amount of 1g. It might be due to availability of more adsorbent sites initially at the time of contact [14-15]. The percent removal of Cr (VI) beyond 0.6 g for Gum-g-Poly (AAM) and 0.4g for activated charcoal were subsequently becomes constant which can be attributed due to the competition of the Cr (VI) ions for the sites available.



**Figure 4.** SEM-EDX micrograph and Spectrum of Guar-g-poly (AAM)

**Slika 4.** SEM-EDX mikrofotografije i spektar guar-g-poli (AAM)

**Table 1.** Chemical composition of elements detected in the EDX Spectra of Guar-g-poly (AAM)

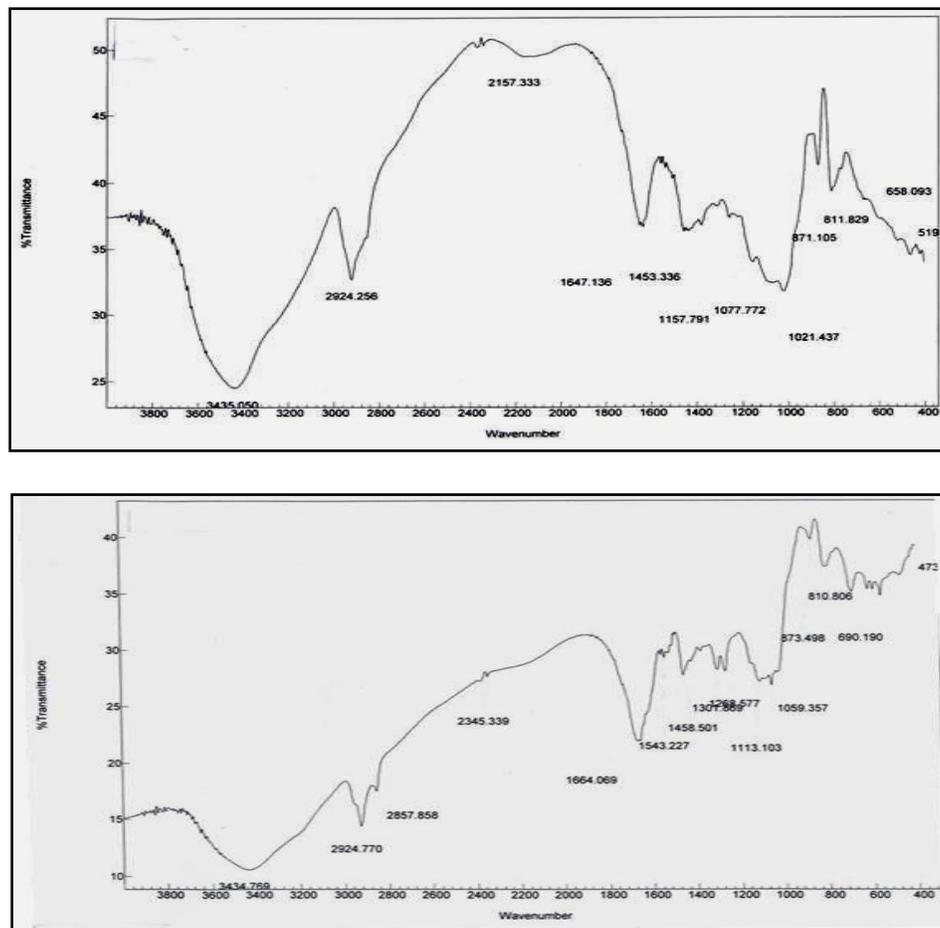
**Tablica 1.** Kemijski sastav elemenata određen EDX spektrom za guar-g-poli (AAM)

Element	Weight (%)	Atomic (%)	Compound (%)
C	1.35	33.82	4.95
N	0.18	3.92	0.71
O	3.44	64.66	4.95
Fe	0.91	4.89	1.17
K	0.02	0.12	0.02
S	0.07	0.67	0.18

**Table 2.** Functional groups and their interpretation

**Tablica 2.** Funkcionalne grupe i njihova interpretacija

Guar-Gum		Guar-Gum-g-Poly(AAM)	
Wavelength (cm <sup>-1</sup> )	Functional groups	Wavelength (cm <sup>-1</sup> )	Functional groups
3435	-OH (Bonded)	3434	-OH(Bonded)
2924	-C-H (Asymmetric stretching)	1664	>C=O (Amide groups)
1647	>C=C<(Stretching)	1543 and 810	-N-H Out of plane bending
1021	>C-O(Stretching vibrations)	1268 and 1301	>C-N
1453	-CH <sub>3</sub> Bend	1059 and 1113	>C-O(Stretching vibrations)
2157	Alkynated carbon stretching	1458	-CH <sub>3</sub> Bend



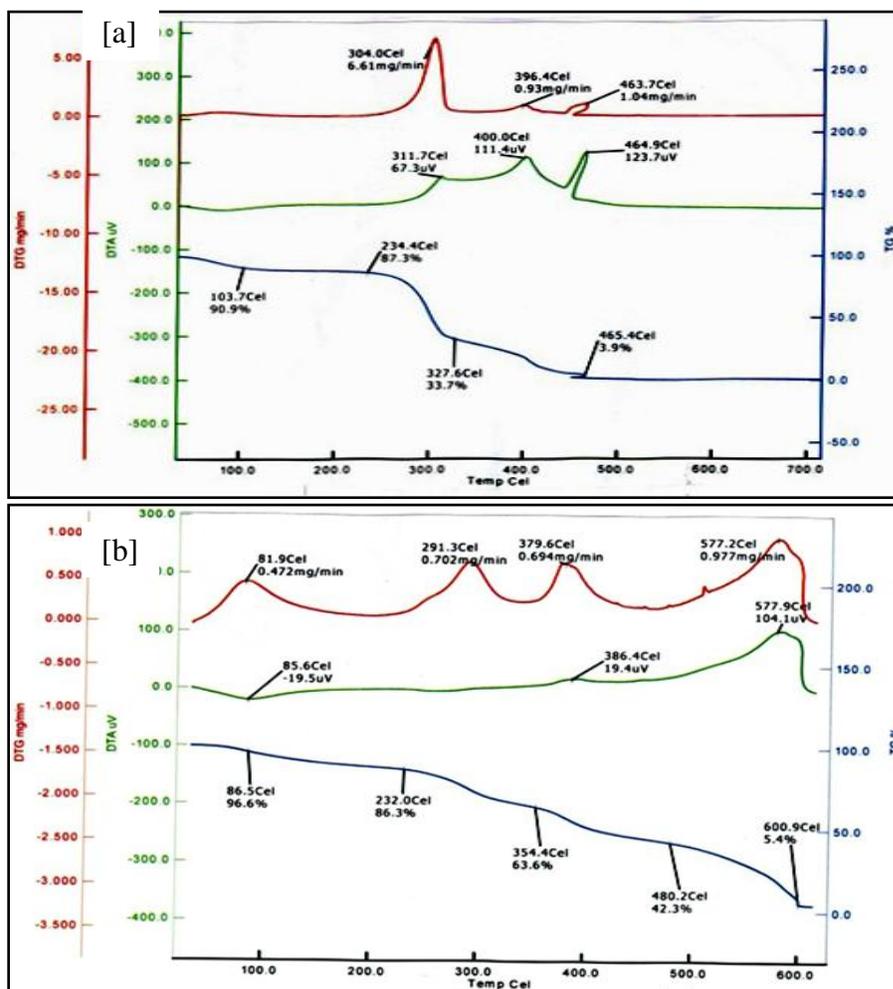
**Figure 5.** FT-IR Spectrum of [a] Guar-Gum[b] Guar Gum-g-Poly (AAM)

**Slika 5.** FT-IR spektar [a] guar-gume [b] guar gume-g-poli (Aam)

**Table 3.** Interpretation of TGA/DTA/DTG data for Guar-Gum and Guar Gum-g-Poly (AAM)

**Tablica 3.** Interpretacija TGA/DTA/DTG podataka za guar-gumu i guar gumu-g-poli (AAM)

Sample	TGA		DTA		DTG	
	Initial Decomposition temperature in K & (% wt. loss) (IDT)	Final Decomposition temperature in K & (% wt. loss) (FDT)	Exothermic peaks at different decomposition Temperature, K ( $\mu$ V)		Decomposition Temperature, K (Rate of wt. loss rate in (mg/min)	
			1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>
Guar-Gum	376.7 (90.9%)	738.4 (3.9%)	584.7 (67.3)	737.9 (123.7)	577 (6.61)	736.7 (1.04)
Guar Gum -g- Poly (AAM)	359.5 (96.6%)	873.9 (5.4%)	358.6	850.9 (104.1)	354.9 (0.472)	850.2 (0.9772)



**Figure 6.** TGA/DTA/DTG Spectrum of [a] Guar-Gum [b] Guar-Gum-g-Poly (AAM)  
**Slika 6.** TGA/DTA/DTG spektar [a] guar-gume [b] guar gume-g-poli (AAM)

### Effect of Contact time

The equilibrium time for the adsorption of Cr (VI) by Guar Gum-g-poly (AAM) and activated charcoal were also studied. The variation in percent removal of Cr (VI) with the time has been shown in Fig.8 which showed 31% removal of Cr (VI) in first 30 minutes which increased up to 81% for Guar Gum-g-poly (AAM). In case of activated charcoal the initial removal rate was 48% and at 180 minute percent removal of Cr (VI) reached to 95%.The removal rate of Cr (VI) increased with the increase of the

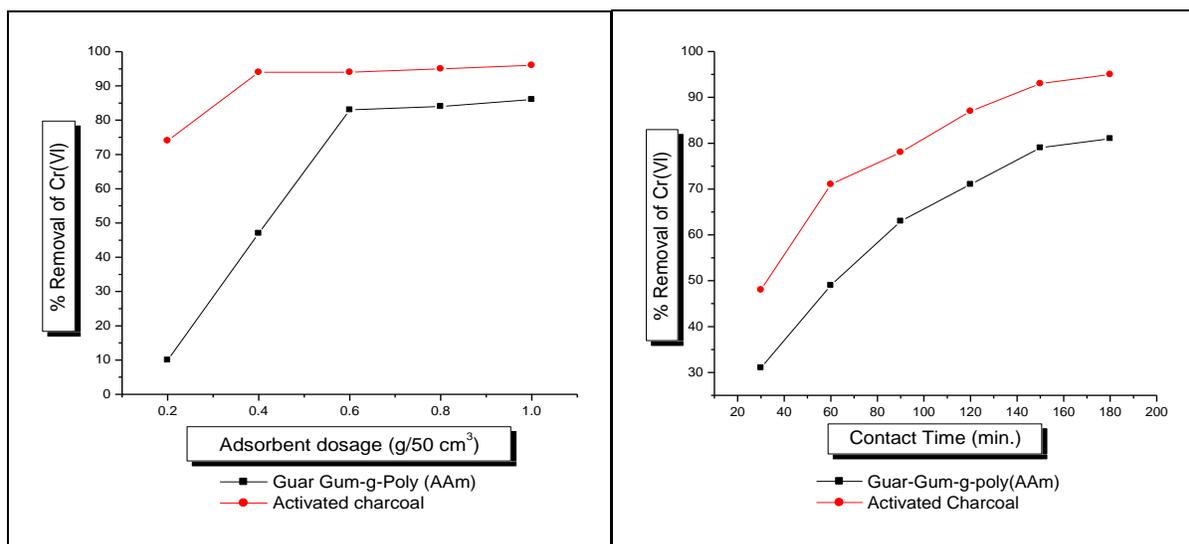
adsorption time. The rate of adsorption was higher in the beginning and become declined slightly with increase in contact time.

It might be due to larger surface area having large number of vacant sites available for adsorption at initial time and after a few minutes, the remaining vacant surface sites were difficult to be occupied due to repulsive forces between Cr (VI) adsorbed on the surface of the adsorbents and in solution in the form of  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$  etc [16].

## Effect of pH of solution

The effect of pH on the adsorption of Cr (VI) ions by Guar Gum-g-Poly (AAM) and activated charcoal were shown in Fig.9. The adsorption studies at different pH values were conducted in the pH range of 1 to 12. Maximum adsorption of Cr (VI) ions by Guar Gum-g-Poly (AAM) and activated charcoal were observed between pH 3-6

which sharply decreased by increasing the pH value beyond 6. At lower pH, the surfaces were positively charged due to protonation which leads to electrostatic attraction with anionic species of chromium in the solution exists in  $\text{HCrO}_4^-$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and other chromium oxyanion states.



**Figure 7.** Effect of adsorbent dose on adsorption of Cr (VI)

**Slika 7.** Utjecaj količine adsorbensa na adsorpciju Cr (VI)

**Figure 8.** Effect of Contact time on adsorption of Cr (VI)

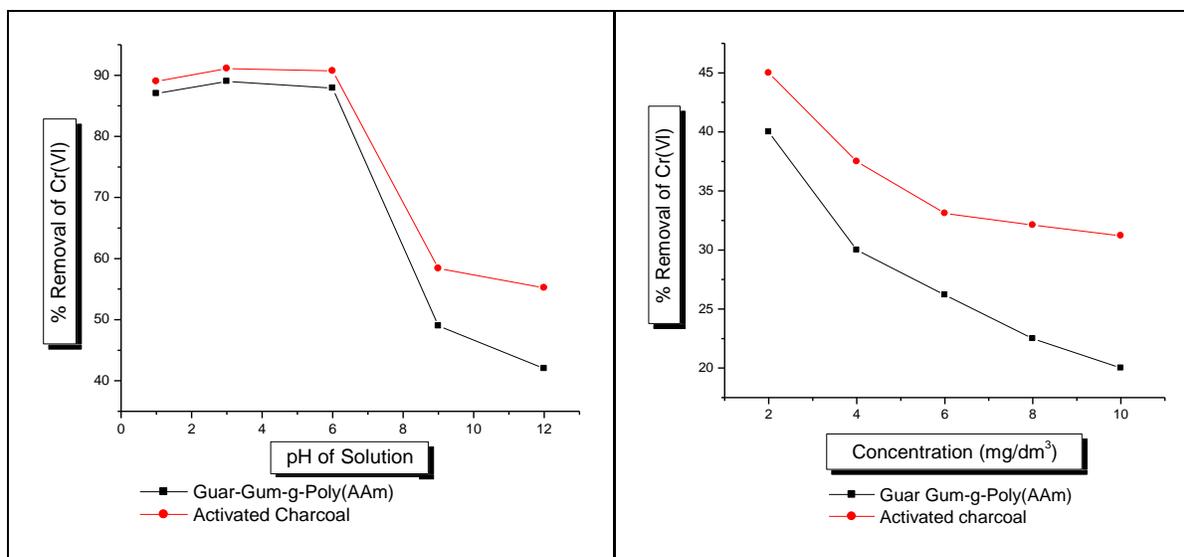
**Slika 8.** Utjecaj vremena kontakta na adsorpciju Cr (VI)

As the pH increased, there were little increases in the percent of adsorptions from pH=1 to pH=3 and become constant between pH 3 and 6. When the pH was further increased above pH 6, sharp decreases in percent of adsorptions were observed.

The decrease in the adsorptions beyond pH=6 might be due to occupation of the adsorption sites by anionic species like  $\text{HCrO}_4^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{CrO}_4^{2-}$  which retards the

approach of such ions further towards the surfaces [17-19].

Hence the weakening of electrostatic attractions between the oppositely charged adsorbate and adsorbents ultimately reduce the percent adsorption of Cr (VI). The decreases in the percent adsorptions at high pH values can be attributed due to the competitiveness of the oxyanions of chromium and  $\text{OH}^-$  ions in the bulk.



**Figure 9.** Effect of pH of solution on adsorption of Cr (VI)

**Slika 9.** Utjecaj pH otopine na adsorpciju Cr (VI)

**Figure 10.** Effect of Concentration of Cr (VI) on adsorption of Cr (VI)

**Slika 10.** Utjecaj koncentracije Cr (VI) na adsorpciju Cr (VI)

### Effect of Initial Concentration of Cr (VI)

The adsorption of Cr (VI) by Guar Gum-g-Poly (AAM) and activated charcoal at different initial concentrations (2-10 mg/dm<sup>3</sup>) of Cr (VI) were investigated and shown in Fig.10. The maximum adsorption by both Guar Gum-g-Poly (AAM) and activated charcoal 45% and 40% were took place at lower concentration of Cr (VI) at an optimized pH=3 and contact time of 180 minutes. It can be attributed to the fact that at lower concentration, more adsorption sites

were available for Cr (VI) and all free Cr (VI) in solution were adsorbing on the available adsorbent surfaces. As the initial concentration of Cr (VI) increased from 2 to 10 mg/dm<sup>3</sup> the percent adsorption of Cr (VI) ions decreased from 40 to 20% for Guar-Gum-g-Poly (AAM) and from 45% to 31.2% in case of activated charcoal. It might be due to the unavailability of no more free surfaces of the adsorbents for Cr (VI) adsorption.

### Adsorption Isotherm

Adsorption studies were carried out with a fixed initial adsorbent dose (1.0 g), pH =3 and by varying adsorbate concentration. The Langmuir and Freundlich isotherm models were used to describe the adsorption equilibrium of Guar Gum-g-poly (AAM) and activated charcoal over entire

concentration range studied. The adsorption equilibrium studies were carried out at room temperature 303±1K. The Freundlich isotherm model proposes a monolayer adsorption with a heterogeneous energetic distribution of active sites. The general form of this model was [20].

$$q_e = k_f C_e^{1/n} \quad (7)$$

Where the adsorption capacity and adsorption intensity, were denoted by  $k_f$  and  $n$ , respectively. A linear form of the Freundlich isotherm can be obtained by taking the logarithmic of Eq.(7):

$$\text{Log}q_e = \text{Log}k_f + \frac{1}{n}\text{Log}C_e \quad (8)$$

The Linear plots of  $\text{Log}q_e$  vs.  $\text{Log}C_e$  were plotted for Guar Gum-g-poly (AAM) and activated charcoal as shown in the Fig. 12(a) and 12(b).The values of  $k_f$  and  $n$  as calculated from the slope and intercept of the given plots for Guar Gum-g-poly (AAM) were 0.19 and 2.08 while 0.20 and 1.65 were the values  $k_f$  and  $n$  in case of activated charcoal, respectively. The values of  $n$  greater than one for Guar Gum-g-poly (AAM) and activated charcoal adsorbents indicated that adsorption process were favourable in both cases. The correlation coefficient values of Guar Gum-g-poly (AAM) and activated charcoal ( $R^2=0.987$  and  $0.964$ ) in Freundlich isotherm were lower than Langmuir isotherm correlation values ( $R^2=0.998$  and  $0.993$ ) as given in Table-4.The Langmuir model described that uptake of solute occurs on a homogeneous surface by monolayer sorption. The linear form of Langmuir isotherm was represented in the following equation [21]:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} b} + \frac{C_e}{q_{max}} \quad (9)$$

The linear plot of  $C_e/Q_e$  vs  $C_e$  in case of Guar Gum-g-poly (AAM) and activated charcoal for uptake of chromium were represented in Fig. 11(a) and 11(b).The values of  $q_{max}$  and  $b$  as calculated from the slope and intercept of the plots were found to be 148.8 mg/g and  $0.33 \text{ dm}^3/\text{mg}$  for Guar Gum-g-poly (AAM) and  $200 \text{ mg/g}$  and  $0.29 \text{ dm}^3/\text{mg}$  for activated charcoal, respectively. The linear correlation coefficients of Langmuir isotherm proved that Langmuir isotherm model exhibit better fit to an experimental data as compared to Freundlich isotherm model for Guar Gum-g-poly (AAM) as well as activated charcoal which indicated that monolayer adsorption took place on the homogeneous surface of the adsorbents and there were significant interactions among the solute molecules. In addition, the model confirmed uniform energies of adsorption onto the surface and no transmigration of the adsorbate. In order to determine the nature of adsorption process whether favourable or unfavourable, the dimensionless constant separation term ( $R_L$ ) was investigated and expressed as

$$R_L = \frac{1}{(1+bC_0)} \quad (10)$$

$R_L$  values indicated the

$R_L$ values
$RL > 1$
$RL = 1$
$0 < RL < 1$
$RL = 0$

In the present

**Table 4.** Equilibrium isotherm parameters for Cr (VI) adsorption  
**Tablica 4.** Ravnotežni izotermni parametri za adsorpciju Cr (VI)

Adsorbent	Langmuir Isotherm				Freundlich Isotherm		
	$q_{max}(\text{mg/g})$	$b (\text{dm}^3/\text{mg})$	$R_L$	$R^2$	$n$	$K_f$	$R^2$
Guar Gum-g- Poly(AAM)	142.8	0.33	0.23	0.998	2.08	0.19	0.987
Activated Charcoal	200	0.29	0.25	0.993	1.65	0.20	0.964

## Kinetics of adsorption

In the present studies, Pseudo first order, Pseudo second order and Intraparticle diffusion kinetic models were analyzed to understand the mechanism of Cr (VI) adsorption on Guar-Gum-g-Poly (AAM) and activated charcoal.

### Pseudo first order equation

The Lagergren equation was considered to be the most widely used rate equation in liquid phase adsorption. The linear form of pseudo first order equation was given as [39]

$$\text{Log}(q_e - q_t) = \text{Log } q_e - \frac{k_1}{2.303} t \quad (11)$$

Where  $q_t$  and  $q_e$  were the adsorption capacities at time  $t$  and at equilibrium (mg/g) while  $k_1$  ( $\text{min}^{-1}$ ) was the pseudo first order rate constant for the adsorption process. The pseudo first order rate constant  $k_1$  and amount of chromium adsorbed  $q_e$  (mg/g) can be obtained from the slope and intercept of the linear plot between  $\log(q_e - q_t)$  vs.  $t$  as shown in Fig.14. The calculated  $k_1$  ( $9.0 \times 10^{-3}$  and  $1.6 \times 10^{-2}$ ) values and corresponding linear correlation coefficients of Guar Gum-g-Poly (AAM) and activated charcoal were shown in Table 5.

### Pseudo second order equation

The pseudo second order adsorption rate equation was expressed as [40]

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (12)$$

Where  $h$  (mg/g. min.) was the initial adsorption rate i.e.

$$h = k_2 q_e^2$$

Where  $k_2$  (g/mg. min.) was the equilibrium rate constant of pseudo second order equation.  $q_e$  and  $q_t$  were the adsorption capacities at equilibrium and at time  $t$  (mg/g), respectively. The constants  $k$  and  $h$  were computed from the slope and intercept of the plot. The pseudo second order rate constant  $k_2$ , and the corresponding linear correlation coefficient values  $R_2^2$  were outlined in Table-5. The linear plots of  $t/q_t$  vs.  $t$  for Guar Gum-g-poly (AAM) and activated charcoal were shown in Fig.15. The plot for pseudo second order model yields very good straight lines and the correlation coefficients ( $R_2^2 > 0.99$ ) were found to be higher for both Guar Gum-g-poly (AAM) and activated charcoal adsorbents. The higher  $R_2^2$  values confirmed that the experimental data were well represented by pseudo second order kinetic model and supports that the adsorption were due to chemisorption process in both Guar Gum-g-poly (AAM) as well as activated charcoal.

### Intraparticle diffusion equation

The adsorbate species were most probably transported from the bulk of the solution onto the solid phase through an intraparticle diffusion process, which was often the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was determined by using the intraparticle diffusion equation expressed as follows [41]:

$$q_t = k_{id} t^{1/2} + C \quad (13)$$

Where,  $C$  was the intercept and  $K_{id}$  (g/mg.min<sup>1/2</sup>) the intraparticle diffusion rate constant. The linear Plots of  $q_t$  vs.  $t^{1/2}$  were shown in Fig.16. The values of  $k_{id}$ ,  $C$ , and the corresponding linear correlation coefficients  $R_3^2$  were given in Table 5.

**Table 5.** Kinetic parameters for the adsorption of Cr (VI)**Tablica 5.** Kinetički parametri za adsorpciju Cr (VI)

Adsorbent	Pseudo first order			Pseudo second order			Intraparticle diffusion		
	$\text{Log } q_e$	$k_1$	$R_1^2$	$k_2$	$h$	$R_2^2$	$ki_d$	$C$	$R_3^2$
Guar-Gum-g- Poly(AAm)	0.42	$9.0 \times 10^{-3}$	0.988	$7.1 \times 10^{-6}$	7.19	0.993	31.67	1.61	0.973
Activated charcoal.	0.41	$1.6 \times 10^{-2}$	0.986	$1.4 \times 10^{-5}$	14.7	0.995	28.89	108.9	0.952

### Thermodynamics studies on adsorption of Cr (VI)

Thermodynamic parameters were evaluated to predict the nature of adsorption of chromium on the Guar Gum-g-poly (AAm) as well as activated charcoal adsorbents. Gibbs free energy ( $\Delta G$ ), enthalpy change ( $\Delta H$ ) and entropy change ( $\Delta S$ ) were some of the important thermodynamic parameters that were calculated in the present study. The values of thermodynamic constants; entropy change ( $\Delta S$ ) and enthalpy change ( $\Delta H$ ) were computed from the slope and intercept of the linear plots of  $\text{Log } k_c$  vs  $1/T$  as shown in Fig.17. The values of  $\Delta S$  and  $\Delta H$  were calculated using following relation:

$$\text{Log } k_c = \frac{\Delta S}{R} - \frac{\Delta H}{2.303} RT \quad (14)$$

Where  $k_c$  was the equilibrium constant of the adsorption process. The Gibbs free energy of the adsorption process was obtained from equation:

$$\Delta G = -RT \ln(k_c) \quad (15)$$

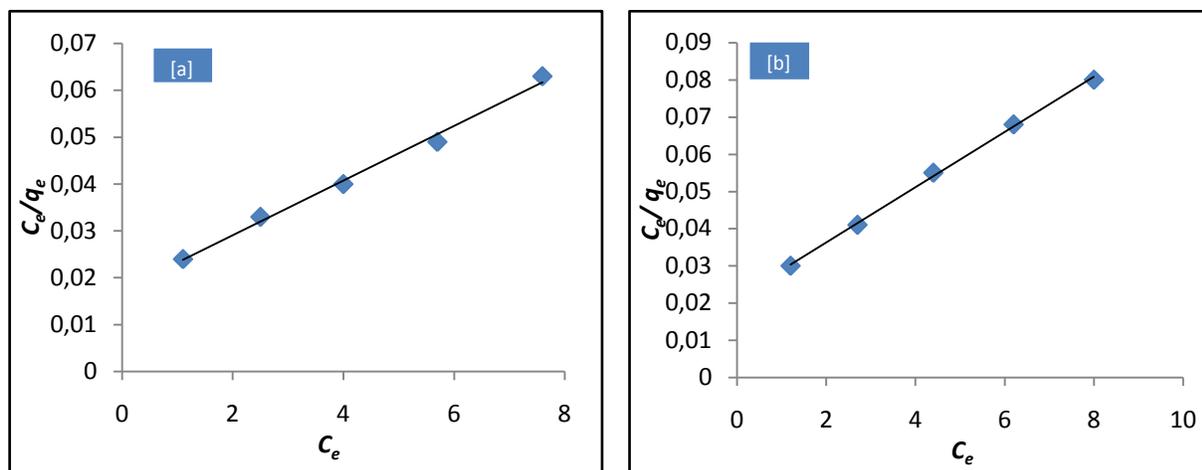
Where  $\Delta G$  was the Gibbs free energy change (kJ/mol),  $T$  was the absolute temperature (K),  $R$  was the universal gas constant (8.314J/K.mol).

The Gibbs free energy of the adsorption process at all temperatures were negative and decreased with the rise in temperature from 303K to 343K in both cases that means the adsorption process was spontaneous and feasible for Guar Gum-g-poly (AAm) as well as for activated charcoal. The positive values of  $\Delta S$  suggest increase in the randomness at the solid/solution interface during the adsorption of Cr (VI) ions onto both Guar Gum-g-poly (AAm) and activated charcoal. Positive values of  $\Delta H$  indicated the endothermic nature of the adsorption process.

The thermodynamic parameters for the adsorption of Cr (VI) by Guar Gum-g-poly (AAm) and activated charcoal were given in Table 6.

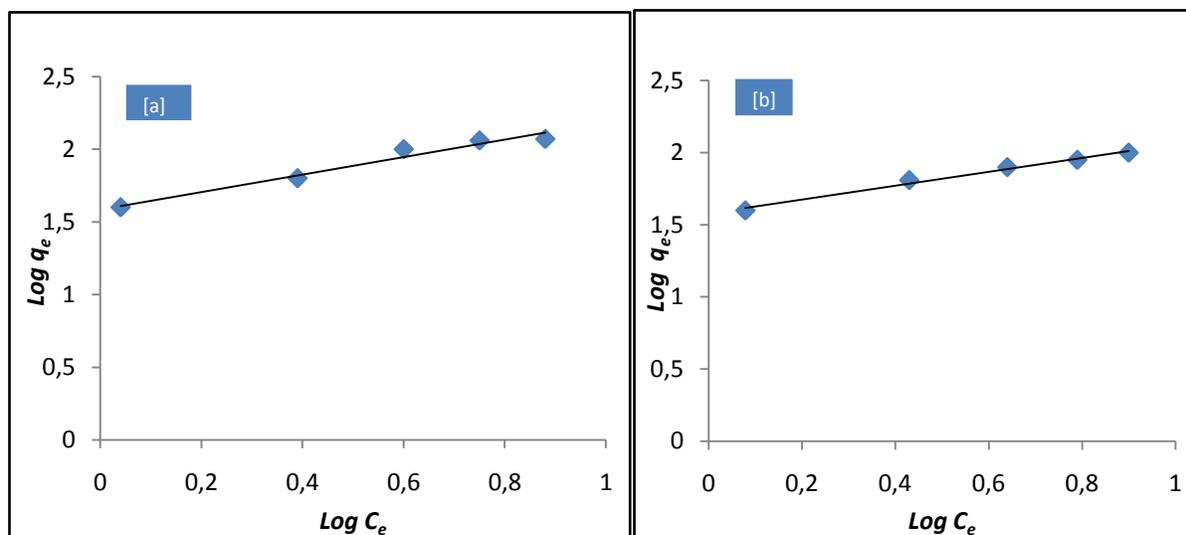
**Table 6.** Thermodynamic parameters for Cr (VI) adsorption**Tablica 6.** Termodinamički parametri za adsorpciju Cr (VI)

Adsorbent	$\Delta S$ (KJ/mol.K)	$\Delta H$ (KJ/mol)	$\Delta G$ (KJ/mol)				
			303	313	323	333	343
Guar-Gum-g-poly(AAm)	0.056	0.0017	-0.32	-1.37	-2.75	-4.37	-5.95
Activated charcoal	0.060	0.0417	-0.88	-1.95	-3.08	-4.17	-6.95



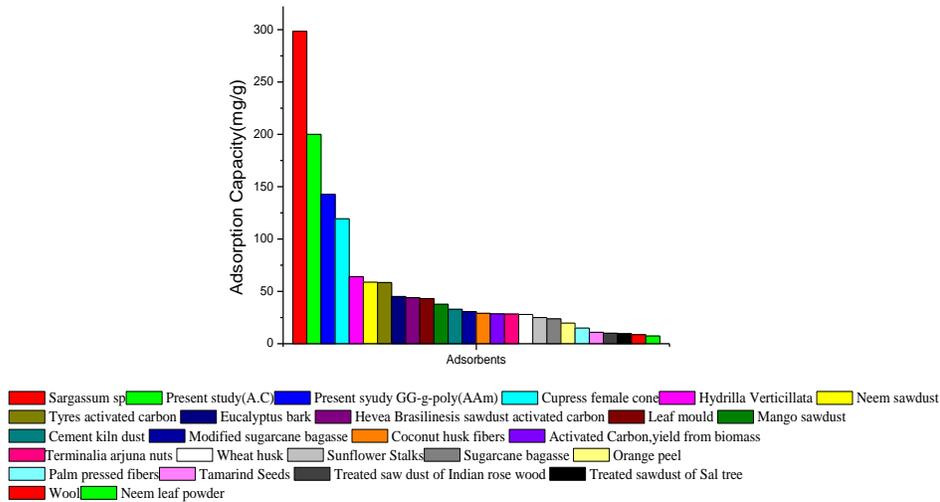
**Figure 11.** Langmuir Isotherms for Cr (VI) adsorption on [a] Activated charcoal [b] Guar Gum-g-Poly (AAM)

**Slika 11.** Langmuirova izoterma za adsorpciju Cr (VI) na [a] aktivnom ugljenu [b] guar-gumi-g-poli (AAM)



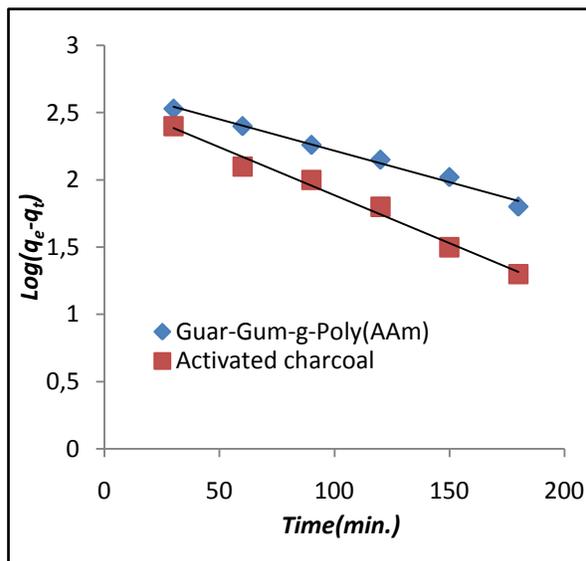
**Figure 12.** Freundlich Isotherms for Cr (VI) adsorption on [a] Activated charcoal [b] Guar Gum-g-Poly(AAM)

**Slika 12.** Freundlichova izoterma za adsorpciju Cr (VI) na [a] aktivnom ugljenu [b] guar-gumi-g-poli (AAM)



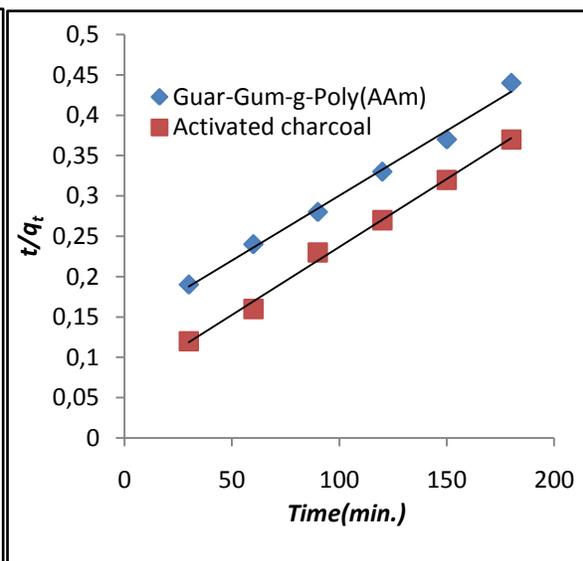
**Figure 13.** Adsorption capacities for chromium removal by various other adsorbents. Ref. (22-38)

**Slika 13.** Kapacitet adsorpcije za uklanjanje kroma pomoću različitih adsorbensa. Lit. (22-38)



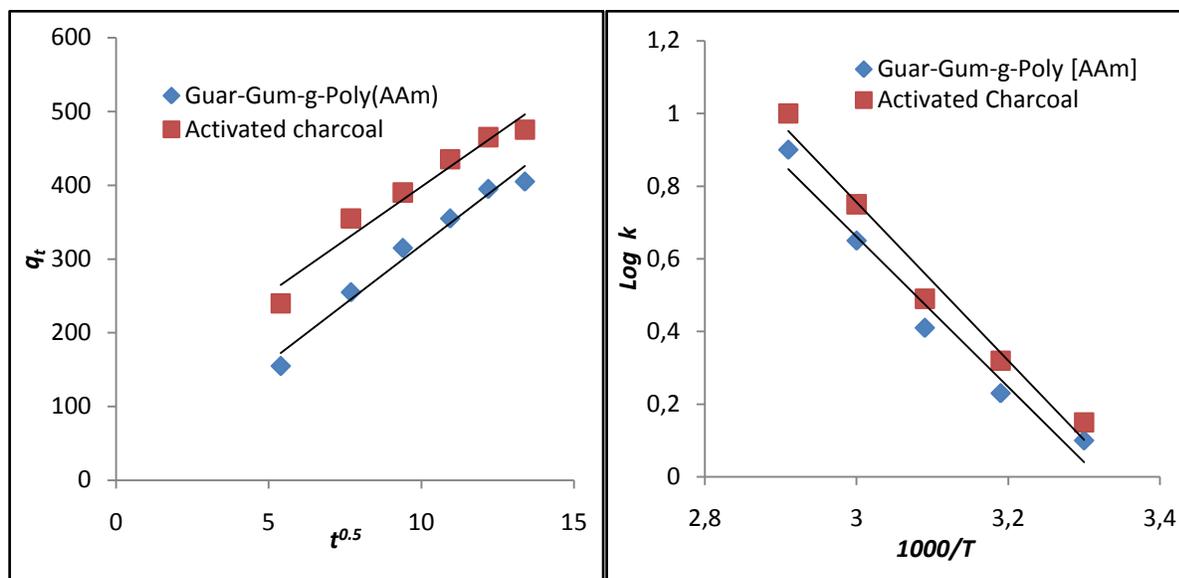
**Figure 14.** Pseudo-first order reaction kinetic plot for adsorption of Cr (VI)

**Slika 14.** Dijagram kinetike reakcije pseudo prvog reda za adsorpciju Cr (VI)



**Figure 15.** Pseudo second order reaction kinetic plot for adsorption of Cr (VI)

**Slika 15.** Dijagram kinetike reakcije pseudo drugog reda za adsorpciju Cr (VI)



**Figure 16.** Intraparticle diffusion plot for the adsorption of Cr (VI)

**Slika 16.** Dijagram unutarčestične difuzije za adsorpciju Cr (VI)

**Figure 17.** Effect of temperature on the adsorption of Cr (VI)

**Slika 17.** Utjecaj temperature na adsorpciju Cr (VI)

## CONCLUSION

The present study revealed that Guar Gum-g-poly(AAm) synthesized by graft copolymerization of guar-gum by free radical initiation method can be used as a valuable adsorbent for the removal of chromium due its low cost and eco-friendly nature as compared with activated charcoal. Maximum adsorptions were observed in the acidic medium between pH=3-6 with an optimum time period of 180 minutes for both Guar Gum-g-Poly (AAM) and activated charcoal. The adsorption parameters showed

that Langmuir isotherm was the best fit model for both Guar Gum-g-poly (AAM) and activated charcoal. The adsorption kinetics follows the pseudo second order rate and Intraparticle diffusion was not only the rate determining step for the adsorption process in both the cases. As the guar-gum (a natural gum) was easily available in the Indian subcontinent regions, their utility as the adsorbent after chemical modification will be economical for the treatment of wastewater.

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