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# Evaluation of Cr(VI) adsorption on glutaraldehyde crosslinked chitosan beads using cyclic voltammetry employing gold electrode

Varuna Watwe and Preeti Kulkarni\*

## Abstract

Hexavalent chromium is one of the toxic heavy metals found in wastewaters from industries like electroplating, leather tanning, and steel manufacturing. The Cr(VI) removal and quantitative detection are among the major concerns from an environmental toxicity point of view. In the present work, we report an effective electrochemical technique for Cr(VI) monitoring based on the utilization of gold electrode. The technique developed is user-friendly, non-destructive, and provides real-time monitoring of Cr(VI) from wastewaters in contrast to other spectroscopic and optical techniques. The technique developed was applied in monitoring Cr(VI) removal from synthetic Cr(VI) samples using chitosan cross-linked glutaraldehyde (C + G) beads. The parameter optimization for Cr(VI) removal using C + G beads was done. The experimental data of Cr(VI) adsorption on C + G beads obtained using cyclic voltammetry were further used for kinetic and thermodynamic studies. Kinetic and thermodynamic studies found that Cr(VI) adsorption follows pseudo-second-order kinetics and Modified Langmuir isotherm. The maximum adsorption capacity of C + G beads for Cr(VI) was found to be  $28.65 \text{ mg g}^{-1}$ . These results obtained indicate that the cyclic voltammetric technique using gold electrode can be effectively applied for Cr(VI) analysis from wastewaters.

**Keywords:** Chromium, Chitosan, Glutaraldehyde, Crosslinking, Adsorption, Cyclic voltammetry, Gold electrode

## Introduction

Heavy metals are one of the persistent and most toxic pollutants found in industrial wastewaters. Chromium is one such toxic heavy metal released into freshwater bodies from industries like leather tanning, electroplating, and steel manufacturing (Altun 2019). According to WHO,  $0.05 \text{ mg L}^{-1}$  is the permissible limit of chromium in freshwater. In the literature, various methods like chemical precipitation, ion exchange, membrane separation, coagulation, and advanced oxidation processes

are available for chromium removal (Owlad et al. 2009). Out of all these methods, adsorption serves to be one of the promising methods for removing chromium from wastewaters (Kulkarni et al. 2019) due to advantages like ease of operation, cost-effectiveness, and low secondary sludge generation. Various biodegradable and non-biodegradable materials have been employed for the effective adsorption of chromium from wastewaters in the literature. Chitosan is one such biodegradable polymer abundantly used in the remediation of heavy metals from wastewaters. Chitosan is highly soluble in acidic conditions and cannot be directly employed for chromium removal from wastewaters. To overcome this limitation, chitosan is either cross-linked or combined with other materials to form a composite for chromium remediation from wastewaters.

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The evaluation of Cr(VI) adsorption efficiency on adsorbents can be done using a suitable method of analysis. Analysis of chromium is a challenging task due to its variable oxidation states present in wastewaters. Among all its possible oxidation states, Cr(III) and Cr(VI) are more stable and environmentally relevant states. Cr(III) plays a vital role in biological processes and is essential at trace levels, whereas Cr(VI) is 100–1000 times more toxic (Cespón-Romero et al. 1996). The methods available for the detection and speciation of chromium can be broadly divided into direct and indirect methods. The indirect methods require prior separation of chromium species before analysis; they include methods like extraction, co-precipitation, atomic absorption spectrophotometry, X-ray fluorescence spectrometry, and chromatography (Bhanjana et al. 2019). However, all indirect methods suffer from limitations like Cr(III) interference, large sample volumes, skilled analyst, and recurring cost. Direct detection of chromium is generally carried out using the spectrophotometric method with complexing agents like 1,5-diphenyl carbazide, tetrazolium violet, dibenzyl dithiocarbamate, and methylene blue (Welch et al. 2005). However, spectrophotometric methods are destructive and require the addition of complexing agents before detection.

In contrast, electrochemical methods offer advantages like high sensitivity, small sample volumes, shorter response time, ease of handling, and reliability (Meters et al. 2012). The electrochemical methods are further divided into two categories, potentiometric and potentiostatic. Potentiometric techniques involve the measurement of potential generated by the analyte at the ion-selective membrane. Potentiostatic techniques involve oxidation–reduction of analyte at electrode surface at a controlled potential. Potentiostatic techniques are superior to potentiometric techniques due to advantages like selectivity for electroactive species, low detection limits, low cost of instrumentation, and availability of electrode materials (Jin and Yan 2015). The Cr(VI) determination is reported in the literature using different potentiostatic methods like chronoamperometry, adsorptive stripping voltammetry, differential pulse voltammetry and cyclic voltammetry. Out of all these techniques, adsorptive stripping and cyclic voltammetry techniques are more widely employed for Cr(VI) detection due to their low detection limits and ease of operation. In the adsorptive stripping voltammetric technique, the analyte is adsorbed on the surface of the working electrode and is then oxidized/reduced during the stripping step. Diethylenetriamine pentaacetic acid (Grabarczyk 2008), pyridine modified glass carbon electrode (Carrington et al. 2006), 4-(mercapto-*n*-alkyl)pyridinium monolayer modified gold electrode (Turyan and Mandler 1997) and

poly-L-histidine film-modified screen-printed carbon electrode (Bergamini et al. 2007) have been used in the literature for Cr(VI) detection. The limitation of using adsorptive stripping voltammetry for Cr(VI) detection is that it requires pre-concentration of analyte on electrode before its detection. In this respect, cyclic voltammetric techniques are found to be superior to the adsorptive stripping technique.

In the literature, various working electrodes like glassy carbon, modified glassy carbon, platinum, boron-doped diamond, mercury, gold, and modified gold electrodes have been reported for Cr(VI) determination using cyclic voltammetry technique (Ge et al. 1992; Faldini et al. 1990; Cox and Kulesza 1983). Due to Cr(VI) corrosive environment, its detection using glassy carbon and boron-doped diamond electrodes is limited and shows the irreversible reaction at electrode surface. Mercury electrodes are found best for Cr(VI) determination in the entire pH range (Harzdorf 1987), but their use is limited due to the toxicity of mercury. Hence, gold and modified gold electrodes are found to be superior for Cr(VI) detection over all other working electrodes. Burke et al. have reported Cr(VI) determination using gold and platinum electrode, and reduction of Cr(VI) took place at lower potentials on the gold electrode as compared to platinum electrode (Burke and Nugent 1997). Welch and Compton have reported Cr(VI) reduction using polycrystalline gold electrode (Welch et al. 2005). However, to the best of our knowledge, no studies for quantitative monitoring of Cr(VI) using the cyclic voltammetry method during adsorption have yet been reported.

In the present work, a cyclic voltammetric technique using gold as a working electrode was developed for the quantitative and real-time monitoring of Cr(VI). The technique developed was used in analysis of Cr(VI) removal from synthetic wastewaters using C + G beads. Kinetics and thermodynamics of Cr(VI) adsorption on C + G beads were done using cyclic voltammetric data.

## Materials and methods

### Apparatus

UV–visible spectrophotometer (T60, PG instruments) was used for all absorbance measurements. 600E potentiostat (CH Instruments, DST-FIST laboratory at AGC, Pune) was used for all cyclic voltammetric experiments. Gold electrode (CH Instruments) was a working electrode for cyclic voltammetry experiments. A digital pH meter (Labtronics, India) was used for all pH adjustments.

## Chemicals

All the chemicals used in the present study were of analytical grade and were used as received without any further purification. Chitosan powder (deacylated up to 85%) was obtained from Loba Chemie (India). Glutaraldehyde used for cross-linking studies was obtained from Merck (India). 1,5 Diphenyl carbazide (DPC), potassium dichromate ( $K_2Cr_2O_7$ ), acetic acid, acetone, NaOH, and HCl were purchased from Loba Chemie (India). All solutions were prepared in deionized water using Milli-Q ultrapure.

## Methods

### Preparation of chitosan beads

A 1.3% w/v solution of Chitosan was prepared by dissolving 1 g chitosan powder in 75 mL 5% acetic acid solution. The chitosan solution obtained was ultrasonicated for 1 h to get a homogeneous solution. Further, this solution was taken into a 1-mL syringe with a diameter of 0.3 mm and added dropwise to 500 mL 0.5 N NaOH solution with continuous stirring at 180–200 rpm. The beads formed were stirred in NaOH solution for 2 h and then were filtered and rinsed using deionized water till residual solutions pH was neutral.

### Crosslinking of chitosan beads with glutaraldehyde

10 g wet chitosan beads (C) were added to 200 mL 10% glutaraldehyde solution. The glutaraldehyde solution with beads was stirred at 100–120 rpm for 2 h. After 2 h, chitosan beads cross-linked with glutaraldehyde were filtered and rinsed with deionized water to remove excess glutaraldehyde adhered to the surface of chitosan beads. The chitosan beads cross-linked with glutaraldehyde were then stored in deionized water in an airtight container till further use. The chitosan beads cross-linked with glutaraldehyde are referred to as C + G beads.

## Characterization

C, C + G + Cr beads were characterized using FTIR in the range of 4000–400  $cm^{-1}$  by AMETEK STS-1900 FT. Surface morphology of C, C + G + Cr beads were studied using a field emission scanning electron microscope by FEI NOVANO SEM-450. Cr(VI) mapping in C + G beads were done using Bruker energy-dispersive X-ray spectrometer (XFLASH-6I30).

### Swelling degree and porosity

The swelling degree of C and C + G bead was investigated to scrutinize the interaction between beads and the aqueous medium. The weight of a single C and C + G bead was recorded as  $W$  g. Both the beads were then allowed

to dry in a desiccator till all water evaporated. The weight of the dry bead was recorded as  $W_d$ . The swelling degree of C and C + G bead was then calculated using Eq. (1),

$$\text{Degree of swelling (\%)} = \frac{W - W_d}{W} \times 100 \quad (1)$$

Further porosity of C and C + G bead was calculated using Eq. (2),

$$\text{Porosity (\%)} = \frac{W - W_d}{\rho_w - V} \times 100 \quad (2)$$

where  $\rho_w$  is the density of deionized water, and  $V$  is the C and C + G bead volume, respectively.

### Batch adsorption studies

Stock solution of 1000  $mg\ L^{-1}$  of Cr(VI) was prepared by dissolving 2.83 g of potassium dichromate in 1 L of distilled water. This stock solution was further used to prepare different concentrations of Cr(VI) in the range 20–100  $mg\ L^{-1}$ . For parameter optimization studies, amount of Cr(VI) adsorbed on C + G beads was measured spectrophotometrically using 1,5-Diphenyl carbazide method as reported in our previous work (Kulkarni et al. 2017). pH optimization studies were carried out in the range of 2–8 by adjusting pH of Cr(VI) solution using 0.1 M HCl and 0.1 M NaOH. Effect of adsorbent weight was studied in the range of 0.25–1.5 g by keeping other parameters same. Effect of concentration was studied in the range of 20–100  $mg\ L^{-1}$ . All experiments were performed in triplicates, and average results were reported.

The adsorption capacity of C + G beads at a given time was calculated using Eq. (3),

$$q_t = \frac{(C_0 - C_t) \times V}{M} \quad (3)$$

where  $q_t$  represents a milligram of Cr(VI) adsorbed per gram of C + G beads at any given time  $t$ ,  $V$  represents the volume of Cr(VI) solution in a liter,  $M$  is mass of dry C + G beads in grams,  $C_0$  and  $C_t$  represent the initial and residual concentration of Cr(VI) in solution, respectively.

### Adsorption studies using cyclic voltammetry

The cyclic voltammetry method was used for residual Cr(VI) monitoring in the C + G beads system. For monitoring with CV, a potentiostat with three electrodes was used. The gold electrode (GE) (CH Instruments) was used as a working electrode, platinum wire as a counter electrode, and Ag/AgCl (CH instrument) was used as the reference electrode. GE electrode surface was polished with alumina after every scan. All CV experiments were

carried out in a 20 cm<sup>3</sup> glass cell, sealed with a Teflon cap at room temperature–pressure conditions.

For monitoring residual Cr(VI) in the C+G beads system at different time intervals, a calibration curve of Cr(VI) in the concentration range of 20–100 mg L<sup>-1</sup> was constructed using a potentiostat. The monitoring of residual Cr(VI) concentration in the C+G beads system was done periodically till 48 h. For measurement of Cr(VI) concentration in C+G beads system, cyclic voltammogram of residual Cr(VI) solution was recorded in the potential range of 0.0 to 0.6 V versus Ag/AgCl as reference electrode, with a scan rate of 0.1 V s<sup>-1</sup> and sensitivity of 0.001 A V<sup>-1</sup>. The effect of scan rate on CV measurements of Cr(VI) concentration in C+G beads system was done by varying scan rate at 0.01, 0.05, 0.1, 0.25, and 0.5 V s<sup>-1</sup> in the potential range of 0.0 to 0.6 V and sensitivity of 0.001 A V<sup>-1</sup>.

### Kinetics and thermodynamic studies

For kinetic studies, a 100-mL glass beaker containing 25 mL 60 mg L<sup>-1</sup> Cr(VI) solution of pH 2 along with 0.5 g wet C+G beads was taken. The residual Cr(VI) concentration in the C+G beads system was monitored at the time interval of 3, 6, 9, 28, and 48 h using the CV method described in “Adsorption studies using cyclic voltammetry” section.

For thermodynamic studies, five identical 100-mL glass beakers were taken. To these beakers, 25 mL of 20, 40, 60, 80, and 100 mg L<sup>-1</sup> of Cr(VI) solution of pH 2 was added, respectively. Further, 0.5 g of wet C+G beads was added to each of these beakers and kept until complete adsorption of Cr(VI) on C+G beads was achieved. The residual Cr(VI) concentration from all five beakers was monitored periodically using the CV method mentioned in “Adsorption studies using cyclic voltammetry” section. From residual Cr(VI) concentration values, equilibrium adsorption capacity ( $q_e$ ) of C+G beads was calculated using Eq. (3). The  $q_e$  values obtained from Eq. (3) were used to study Cr(VI) and C+G beads interaction using adsorption isotherms. Further from adsorption isotherm constant ( $K$ ) Gibbs free energy ( $\Delta G^\circ$ ) of the system was calculated using Eq. (4),

$$\Delta G^\circ = -RT \ln K \quad (4)$$

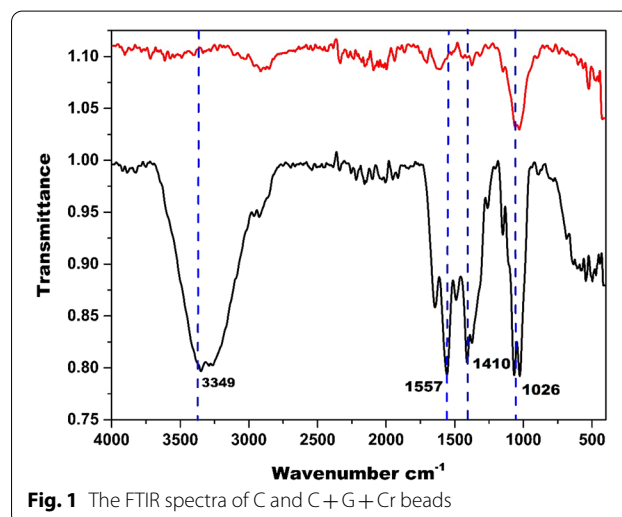
## Results and discussion

### Swelling degree and porosity

Chitosan tends to swell in an aqueous medium. The swelling degree obtained for pristine chitosan bead is 95.4%, whereas after cross-linking chitosan with glutaraldehyde, the swelling degree of the C+G bead is found to be 87%. The swelling degree of chitosan bead decreases after cross-linking with glutaraldehyde. This decrease can

**Table 1** Swelling degree and porosity of C and C+G beads in aqueous medium at neutral pH

Type of beads	Swelling degree (%)	Porosity (%)
Pristine chitosan (C)	95.4 ± 2.3	6.2 ± 0.1
Chitosan cross-linked glutaraldehyde (C+G)	87 ± 1.8	5.9 ± 0.1



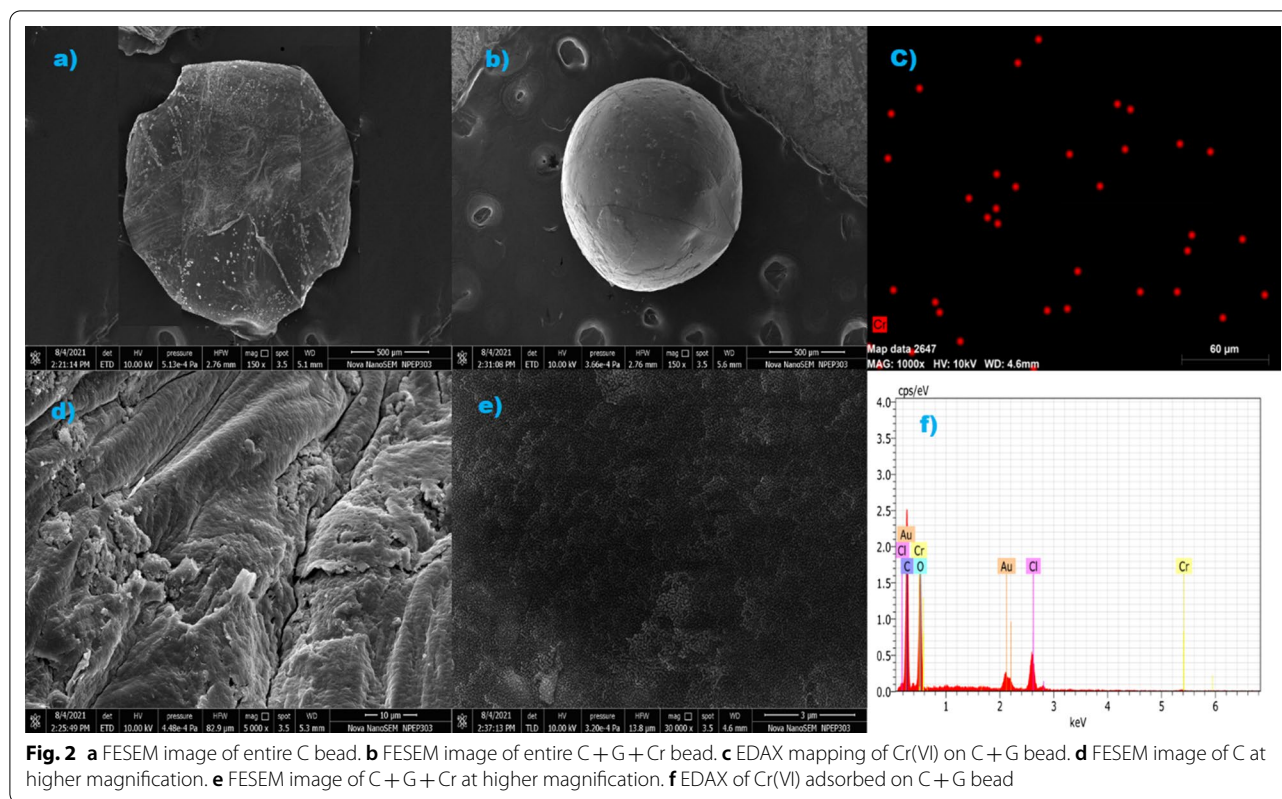
**Fig. 1** The FTIR spectra of C and C+G+Cr beads

be attributed to a decrease in the number of free NH<sub>2</sub> groups present in Chitosan for hydrogen bonding due to imine formation with glutaraldehyde after cross-linking (Khan and Ranjha 2014). However, there is not much difference between C and C+G beads in terms of porosity. Table 1 shows values of swelling degree and porosity of C and C+G beads.

### Characterization

Figure 1 shows FTIR spectra of pristine C and C+G beads after adsorption of Cr(VI). Pristine C shows broad peak at 3349 cm<sup>-1</sup> which corresponds to N–H bond in chitosan. Peak at 1026 cm<sup>-1</sup> corresponds to C–O vibration. Peak at 1410 cm<sup>-1</sup> indicates presence of C–H bending. Peak at 1066 cm<sup>-1</sup> corresponds to alkyl amine present in chitosan. In the case of C+G+Cr beads peak at 3349, 1066 cm<sup>-1</sup> disappeared indicating crosslinking with glutaraldehyde, and binding with Cr(VI) via free NH<sub>2</sub> group.

Figure 2 shows FESEM images of C and C+G+Cr beads where 2a and 2b show images of entire C and C+G+Cr beads, respectively, (d) and (e) show images of C and C+G+Cr at higher magnification. From image (e), crosslinking in C+G+Cr beads can be seen. Figure 2c shows mapping of Cr(VI) on C+G bead, and Fig. 2f shows EDAX peak of Cr(VI) in C+G bead. From



**Fig. 2** **a** FESEM image of entire C bead. **b** FESEM image of entire C + G + Cr bead. **c** EDAX mapping of Cr(VI) on C + G bead. **d** FESEM image of C at higher magnification. **e** FESEM image of C + G + Cr at higher magnification. **f** EDAX of Cr(VI) adsorbed on C + G bead

FESEM and EDAX of C and C+G beads, crosslinking and adsorption of Cr(VI) is confirmed.

#### Batch adsorption studies

The batch adsorption experiments for Cr(VI) adsorption on C+G beads were done as reported in our earlier work on Cr(VI) adsorption on C+G films (Kulkarni et al. 2017). The pH studies indicated that at pH 2, Cr(VI) adsorption on C+G beads is maximum. This follows from literature studies on Cr(VI) removal from aqueous medium using chitosan and chitosan cross-linked beads. Acidic pH favors Cr(VI) adsorption on C+G beads because amine groups present in Chitosan protonates as  $\text{NH}_3^+$  and  $\text{HCrO}_4^-$  from bulk Cr(VI) solution binds with  $\text{NH}_3^+$  by the electrostatic force of attraction. Hence, all further Cr(VI) adsorption experiments were carried out at pH 2. Along with the pH of Cr(VI) solution, the weight of C+G beads and concentration of Cr(VI) solution were optimized to 0.5 g and 60 mg  $\text{L}^{-1}$ , respectively, from batch experiments.

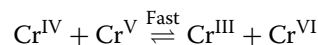
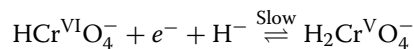
#### Adsorption studies using cyclic voltammetry

##### Cr(VI) measurement using a gold electrode

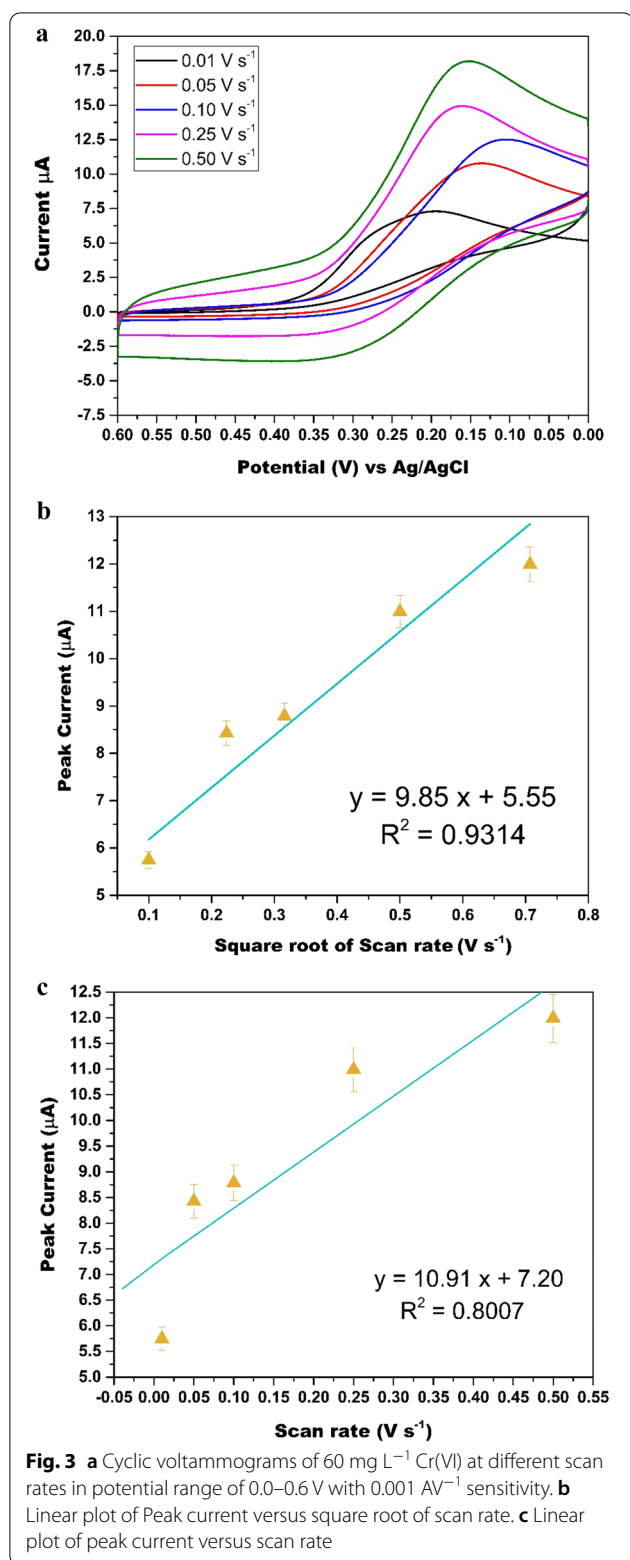
In electrochemical quantitative analysis of Cr(VI), the highly corrosive conditions for voltammogram

measurements and passivation of electrodes serve as a barrier. It is suggested that the nature of the electrode surface highly influences the reduction rate of Cr(VI) in acidic solution. According to the literature, a gold electrode is thought to be stable toward a corrosive environment, and the passivation of the electrode being a noble metal (Danilov and Protsenko 1998). Hence, in the present work gold electrode was employed as a working electrode for the quantitative determination of Cr(VI) from the C+G beads system.

At pH 2, residual Cr(VI) from bulk solution undergoes reduction to Cr(V) at the gold electrode surface. The reduction follows one electron and one proton transfer reaction. Further, followed by Cr(VI) reduction to Cr(V), fast reduction of Cr(V) to Cr(III) takes place by disproportionation of Cr(IV) species (Welch et al. 2005). This gives rise to a single sharp reduction peak of Cr(VI) at 0.15 V against Ag/AgCl as a reference electrode.



The cyclic voltammetric response of 60 mg  $\text{L}^{-1}$  Cr(VI) solution was recorded at different scan rates using linear



sweep voltammetry at the gold electrode (Fig. 3a). The cyclic voltammograms are either diffusion-limited or kinetically controlled. If a redox process is diffusion

limited, then peak potentials are generally independent of scan rate. However, if redox process is kinetically controlled, then peak potentials depend on scan rate. From Fig. 3a, it can be observed that with an increase in scan rate from 0.01 to 0.5 V s<sup>-1</sup>, there is only a slight shift in peak potentials of Cr(VI) from 0.15 to 0.18 V, indicating that reduction of Cr(VI) at the gold electrode surface is electrochemically reversible and diffusion controlled. Figure 3b shows a linear plot of Cr(VI) reduction peak currents versus the square root of scan rate. This plot shows good fitting with an  $R^2$  value equal to 0.9314, indicating the diffusional nature of the Cr(VI) at the gold surface.

#### Calibration curve of Cr(VI) using cyclic voltammetry

According to the Randles–Sevcik equation, current ( $I_{\text{peak}}$ ) generated during cyclic voltammetry scan is directly proportional to the concentration of species analyzed.

$$I_{\text{peak}} = 2.69 \times 10^5 n^{\frac{2}{3}} D^{\frac{1}{2}} C A V^{\frac{1}{2}} \quad (5)$$

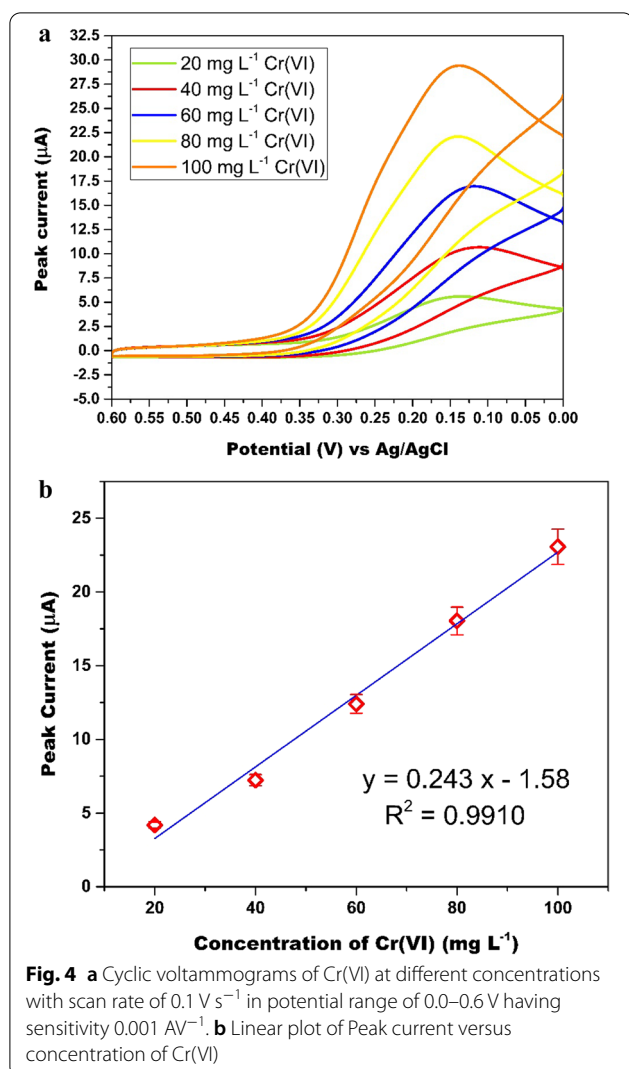
where  $n$  represents the number of electrons transferred during the reaction,  $D$  is diffusion coefficient (cm<sup>2</sup> s<sup>-1</sup>),  $A$  is the area of the electrode (cm<sup>2</sup>),  $C$  is the concentration of analyte (mol dm<sup>-3</sup>), and  $V$  is the potential sweep scan rate (V s<sup>-1</sup>).

Hence for measuring residual Cr(VI) concentration in the C+G beads system, the calibration curve of Cr(VI) concentration versus current generated ( $I_{\text{peak}}$ ) was plotted. Figure 4a shows cyclic voltammetry scans of Cr(VI) in the concentration range of 20–100 mg L<sup>-1</sup>. From scans, it can be observed that as Cr(VI) concentration increases, the peak height of current at 0.15 V against Ag/AgCl electrode also increases. Figure 4b shows a linear plot of peak current ( $I_{\text{peak}}$ ) at 0.15 V versus different concentrations of Cr(VI) with a regression value ( $R^2$ ) of 0.991. This plot indicates that the concentration of Cr(VI) is directly proportional to  $I_{\text{peak}}$  at 0.15 V in the concentration range of 20–100 mg L<sup>-1</sup>.

For measuring unknown residual Cr(VI) at different time intervals in C+G beads system,  $I_{\text{peak}}$  of residual Cr(VI) was measured using CV method described in “Adsorption studies using cyclic voltammetry” section (Fig. 5) and, then converting  $I_{\text{peak}}$  into concentration using Eq. (6),

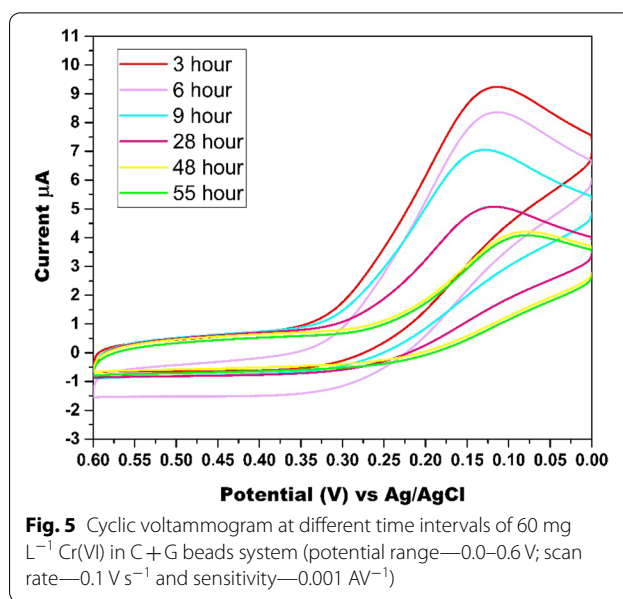
$$\frac{I_{\text{peak } 60}}{I_{\text{peak unknown}}} = \frac{C_0}{C_t} \quad (6)$$

where  $I_{\text{peak } 60}$  represents current generated by reduction of Cr(VI) having a concentration of 60 mg L<sup>-1</sup>,  $I_{\text{peak unknown}}$  represents current generated by reduction of Cr(VI) in C+G beads system at any time  $t$ ,  $C_0$  represents initial Cr(VI) concentration in mg L<sup>-1</sup>, and  $C_t$  represents



residual Cr(VI) concentration in C+G beads system at any time  $t$ .

The  $C_t$  values obtained from Eq. (6) for Cr(VI) in the C+G beads system at different time intervals were then substituted in Eq. (3) for calculating absorption capacity  $q_t$ . The  $q_t$  values obtained were further used for kinetic and thermodynamic studies of Cr(VI) adsorption on C+G beads. The advantage of measuring residual Cr(VI) concentration by CV was that no prior separation, the addition of complexing agent, or supporting electrolyte was needed. This is because the optimum pH for maximum adsorption of Cr(VI) on C+G beads was 2, and at pH 2, HCl in the reaction system used to adjust pH served as a supporting electrolyte.



## Kinetic and thermodynamic studies

### Kinetic studies

The experimental data of the adsorption capacity of C+G beads for Cr(VI) were obtained by CV scans of residual Cr(VI) concentration in the C+G beads system. These data were fitted into pseudo-first-order, second-order (Azizian 2004), and pseudo-mixed-order kinetic (Marczewski 2010) equations as stated below

Pseudo first order,

$$q_t = q_e(1 - \exp(-k_1 t)) \quad (7)$$

Pseudo second order,

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (8)$$

Pseudo mixed order,

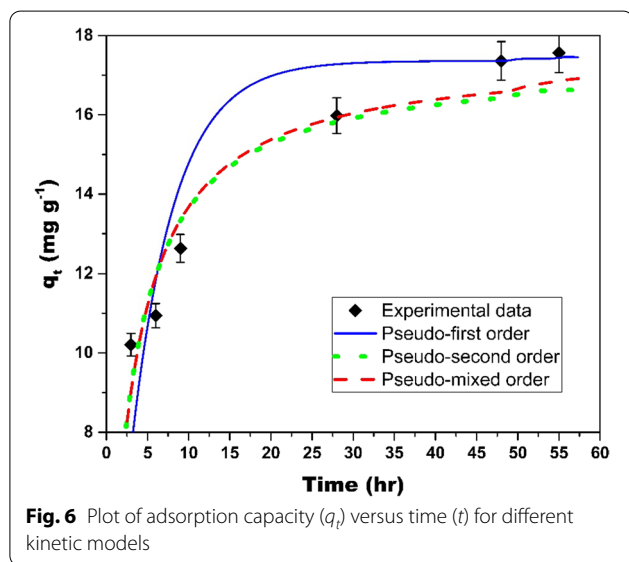
$$q_t = q_e \left( \frac{1 - \exp(-k_{1,2} t)}{1 - f_2 \exp(-k_{1,2} t)} \right) \quad (9)$$

where  $q_t$  is adsorption capacity in  $\text{mg g}^{-1}$  of C+G beads at any time  $t$ ,  $q_e$  is adsorption capacity in  $\text{mg g}^{-1}$  of C+G beads at equilibrium,  $f_2$  is mixed order kinetic constants,  $k_1$ ,  $k_2$ , and  $k_{1,2}$  are pseudo-first, second-, and mixed-order kinetic constants, respectively.

Table 2 shows kinetic parameters obtained for Cr(VI) adsorption on C+G beads monitored by CV. From Table 2, it is observed that the pseudo-second-order model fits better as compared to the pseudo-first and mixed-order model, indicating that the adsorption process of Cr(VI) is dependent on the concentration of

**Table 2** Parameters of kinetic models obtained using CV for adsorption of Cr(VI) on C + G beads

Kinetic model	$k_1$ ( $\text{h}^{-1}$ )	$k_2$ ( $\text{mg g}^{-1} \text{h}^{-1}$ )	$k_{1,2}$ ( $\text{h}^{-1}$ )	$q_e$ ( $\text{mg g}^{-1}$ )	$f_2$	$R^2$
Pseudo first order	$0.191 \pm 0.029$			17.36		0.9362
Pseudo second order		$0.021 \pm 0.002$		17.36		0.9909
Pseudo mixed order			$0.008 \pm 0.0005$	17.36	0.97	0.9814

**Fig. 6** Plot of adsorption capacity ( $q_t$ ) versus time ( $t$ ) for different kinetic models

Cr(VI) in equilibrating solution as well as on the number of adsorption sites on C + G beads. Figure 6 shows a plot of  $q_t$  versus time, it can be seen from this plot that initially, adsorption of Cr(VI) is fast till 12 h, and after that  $q_t$  values slowly increase, and equilibrium is reached within 48 h. The slow increase in  $q_t$  values after 12 h can be attributed to a decrease in the number of adsorption sites on C + G beads.

### Adsorption isotherm studies

Adsorption isotherm studies help in understanding the mechanism of adsorption and interactions between adsorbate and adsorbent. Classical Langmuir and Freundlich isotherms are the most commonly employed isotherms for understanding adsorbate–adsorbent interactions in the literature. However, these isotherms were designed to study

the adsorption of gas molecules on homogenous solid surfaces and hence have certain limitations when applied to the adsorption of solids onto heterogeneous surfaces (Kulkarni et al. 2021). In the present work, instead of classical Langmuir isotherm, modified Langmuir (Azizian et al. 2018), modified Langmuir–Freundlich (Azizian et al. 2018), and Freundlich (Basha et al. 2008) isotherms were employed for Cr(VI) adsorption on C + G beads. Equations of these isotherms are as stated below

Modified Langmuir isotherm,

$$q_e = \frac{q_m K_{ML} C_e}{(C_s - C_e) + K_{ML} C_e} \quad (10)$$

Freundlich isotherm,

$$q_e = K_F (C_e)^{\frac{1}{n}} \quad (11)$$

Modified Langmuir–Freundlich isotherm,

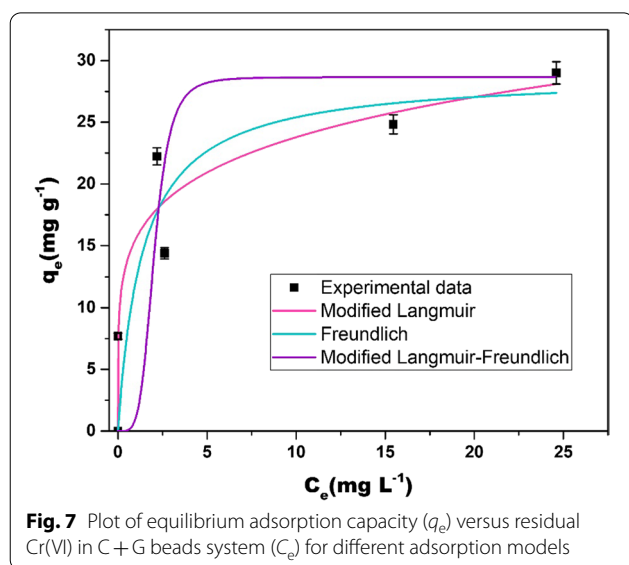
$$q_e = \frac{q_m (K_{MLF} C_e)^n}{(C_s - C_e)^n + (K_{MLF} C_e)^n} \quad (12)$$

where  $q_m$  is the maximum adsorption capacity of C + G beads in  $\text{mg g}^{-1}$  and  $n$  is heterogeneity constant.  $C_s$  is saturation concentration of Cr(VI) in water at 298 K, and  $K_{ML}$ ,  $K_F$ , and  $K_{MLF}$  are adsorption isotherm constants of modified Langmuir, Freundlich, and modified Langmuir–Freundlich, respectively.

Table 3 shows adsorption isotherm parameters obtained after fitting experimental adsorption data of Cr(VI) measured using CV. From Table 3, it is observed that modified Langmuir isotherm fits best to Cr(VI) adsorption on C + G beads. This indicates that monolayer adsorption of Cr(VI) takes place on C + G beads surface. The  $\text{NH}_3^+$  groups present on the surface of the C + G bead serve as active sites for  $\text{HCrO}_4^-$  adsorption from bulk Cr(VI) solution. The modified Langmuir adsorption

**Table 3** Parameters of isotherm models obtained using CV at 298 K for adsorption of Cr(VI) on C + G beads

Isotherm model	$q_m$ ( $\text{mg g}^{-1}$ )	$K_{ML}$	$K_F$ ( $\text{L g}^{-1}$ )	$n$	$K_{MLF}$	$n_{MLF}$	$R^2$
Modified Langmuir	28.65	$110.1 \pm 5.3$					0.9854
Freundlich			$15.54 \pm 0.45$	5.4			0.8422
Modified Langmuir–Freundlich	28.65				$73.71 \pm 2.36$	4.5	0.7408



constant  $K_{ML}$  was further used to calculate Gibbs free energy using Eq. (4). The Gibbs free energy obtained using  $K_{ML}$  is found to be  $-11.65 \text{ kJ mol}^{-1}$  indicating adsorption of Cr(VI) on C+G beads is spontaneous in nature. Figure 7 shows the fitting of Cr(VI) adsorption data to adsorption isotherm models mentioned above.

#### Mechanism of Cr(VI) adsorption on C + G beads

The amino group present in chitosan protonates as  $\text{NH}_3^+$  at acidic pH resulting in electrostatic attraction of  $\text{HCrO}_4^-$  ion, showing higher efficiency for Cr(VI) removal. However, chitosan beads dissolve in acidic solution. In basic pH, Cr(VI) removal efficiency of chitosan beads decreases as hydroxyl ion competes with  $\text{CrO}_4^{2-}$  ions (Kulkarni et al. 2017). To increase the strength and stability of chitosan beads in acidic solution, its crosslinking with glutaraldehyde is essential. Aldehydic group in glutaraldehyde reacts with amino group in chitosan to form imine linkage, which gives rise to network like structure as shown in Fig. 2e. Due to extensive network-like structure, C + G beads show higher stability in acidic pH while maintaining Cr(VI) removal efficiency.

#### Conclusions

In the present work, cyclic voltammetry equipped with gold electrode was utilized for real time and efficient detection of Cr(VI) from synthetic chromium wastewater sample. The technique developed was employed for monitoring of Cr(VI) removal from wastewater using C + G beads. The FTIR, FESEM, and EDAX analysis of C and C + G beads indicated that network like structure is formed in C + G beads due to crosslinking, making C + G beads more stable in acidic pH maintaining

Cr(VI) removal efficiency of C beads. Measurement of residual Cr(VI) from the C + G beads system at different time intervals was recorded using a gold electrode due to its non-corrosive nature in an acidic environment. From optimization experiments, it was found that pH 2, the concentration of Cr(VI)  $60 \text{ mg L}^{-1}$ , 0.5 g of wet C + G beads, and 48 h of equilibration time are the parameters for maximum uptake of Cr(VI) using C + G beads. The CV method used for measurement of residual Cr(VI) in C + G beads system was found better over existing electrochemical and non-electrochemical techniques due to advantages like non-destructive nature, no addition of complexing agents, no prior separation, and no addition of secondary electrolytes. The data obtained from CV measurements of residual Cr(VI) at different time intervals and at different concentrations were fitted into pseudo-first-, second-, and mixed-order kinetic models and modified Langmuir, Langmuir–Freundlich, and Freundlich isotherm models. Kinetics and adsorption isotherm studies indicated Cr(VI) adsorption on C + G beads follows the pseudo-second-order kinetic model and modified Langmuir model with a maximum adsorption capacity of  $28.65 \text{ mg g}^{-1}$ . Thermodynamic studies showed adsorption process is spontaneous with Gibbs free energy equal to  $-11.65 \text{ kJ mol}^{-1}$ . From the present work, it can be concluded that CV can be used as a quantitative technique for Cr(VI) monitoring.

#### Abbreviations

Cr(VI): Hexavalent chromium; C: Pristine chitosan beads; C + G: Chitosan cross-linked glutaraldehyde beads; GE: Gold electrode; CV: Cyclic voltammetry.

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#### Authors' contributions

Both authors contributed equally in planning of work, experimental work, interpretation of data, and manuscript writing. Both authors read and approved the final manuscript.

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#### Availability of data and materials

All the data and materials can be made available if required.

#### Declarations

#### Competing interests

The authors declare that they have no competing interest.

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