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# Removal of hexavalent chromium ions from aqueous solution using chitosan/polypyrrole composite

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ABSTRACT

In the present investigation, chitosan/polypyrrole composite (CS/PPy) was synthesized and used as an adsorbent for the first time to remove the Cr(VI) ions from aqueous solution. The CS/PPy composite was characterized using FTIR, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analyzer, and BET. Batch equilibrium experiments were carried out to optimize various parameters for the water treatment process. The optimized conditions revealed that adsorption of Cr(VI) ions onto the CS/PPy composite was highly pH dependent. The maximum Cr(VI) removal capacity of CS/PPy composite was 78.61 mg/g at 303 K. Equilibrium data fitted well with the Freundlich model. Thermodynamic parameters for the adsorption system were calculated and concluded that the nature of sorption was spontaneous and endothermic in nature. The kinetic study reveals that the sorption of Cr(VI) ions by the composite follows the pseudo-second-order and pore diffusion models. The Cr(VI) uptake of CS/PPy composite was mainly governed by electrostatic attraction-coupled reduction.

*Keywords:* Chitosan; Polypyrrole; Adsorption; Reduction; Kinetics

## 1. Introduction

Chromium appears to be one of the major heavy metal pollutants which cause a severe threat to the environment as well as human beings. The current technologies to remove Cr(VI) from water/wastewater include chemical precipitation, adsorption, membrane filtration, etc. Among the numerous techniques, adsorption technique has been extensively studied for the removal of Cr(VI) ions from wastewater due to ease of preparation, low cost, high regenerability, etc. [1,2].

In recent years, biopolymers like chitin, chitosan, cellulose, and its composites have been studied for the water treatment containing heavy metals [1–3]. Among them, chitosan (CS) deserves particular attention, due to unique characteristics such as biodegradability, biocompatibility, biofunctionality, hydrophilicity, and non-toxicity.

Chitosan is a deacetylated form of chitin, possessing higher amino groups and thus used as a better chelating agent than chitin. However, raw chitosan has its own drawbacks such as unsatisfactory mechanical strengths, swelling, and solubility in acidic conditions. In order to overcome these problems, several chemical modifications have been proposed to improve the mechanical strength, stability, pore size, etc. [1–5]. Some new chemically modified chitosan has been prepared and studied for the treatment of water

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containing Cr(VI) ions [4–6]. Although these adsorbents are effective for the removal of heavy metals, they are suffering from the disadvantages such as low sorption capacity, slow kinetics, and practical applications. Therefore, there is still an ongoing need for new materials which are low cost, have excellent sorption capacity, and need a relatively short period of time for the removal of Cr(VI) ions from the aqueous solution.

Recently, the application of polypyrrole (PPy) and its composites have gained much attention for the removal of Cr(VI) ions from the aqueous solution [7–12]. This is because of their non-toxic, high electrical conductivity, good environmental stability, low cost, and ease of preparation. It is reported that the presence of a positively charged nitrogen atom makes PPy a suitable adsorbent for the removal of Cr(VI) ions from the water. In addition, PPy facilitate the spontaneous reduction of toxic Cr(VI) into less toxic Cr(III) through surface chemical reaction which is another interesting and noteworthy factor [9–11]. Although PPy and its composites have been identified as better adsorbents for the removal of Cr(VI) ions from water [12–15], the design and synthesis of new materials are still critical.

In prospect of this, synthesis of bio/conducting polymeric composites, a new class of polymeric composite material has received more consideration for the environmental applications including water treatment. It has been reported in the literature that bio/conducting polymeric composites are very much capable for the removal of Cr(VI) ions from aqueous solution with enhanced sorption capacity [16–20]. However, there are no reports on the removal of Cr (VI) ions from aqueous solution using CS/PPy composite. Hence, in the present work, it is aimed to synthesize and characterize the CS/PPy composite and used as an adsorbent for the removal of Cr(VI) ions from aqueous solution by the batch equilibrium method for the first time. Batch experiments were carried out as a function of parameters such as time, dosage, pH, and effect of co-ions and concentration. Based on the isotherm, thermodynamic and kinetic parameters, the mechanism of Cr(VI) adsorption was established. The mechanism was substantiated with the experimental data from FTIR, X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray analyzer (EDX), and BET.

## 2. Experimental

### 2.1. Materials

Eighty-five percent deacetylated chitosan was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Pyrrole was purchased from Sigma–Aldrich, India. Ammonium peroxydisulfate (APS), potassium dichromate, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Chemical Drug House Ltd., India. The double-distilled water (DD) was used to prepare all the aqueous solutions. All the chemicals were used without further purification.

### 2.2. Synthesis of CS/PPy composite

About 2 g of chitosan was dissolved in 100 mL of 2.0% (v/v) glacial acetic acid and left for 24 h without any disturbance. A certain amount of APS solution (7.0%) was added to the gel and stirred for 2 h at room temperature. Subsequently, under string, different amount of (0.02–0.1 mol/L) pyrrole was added to the above mixture and was continuously stirred. After 12 h, 20 mL of ethanol was added and the resulting nanocomposite was filtered on filter paper, and to separate oligomers and impurities, the composite was washed with DD water until it became colorless. Finally, the resulted CS/PPy composite was washed with acetone and dried at 50˚C for 48 h. The proposed preparation of CS/PPy composite is represented in Scheme 1. For comparison, PPy was also prepared in the presence of APS as previously reported by Bhaumik et al. [13].

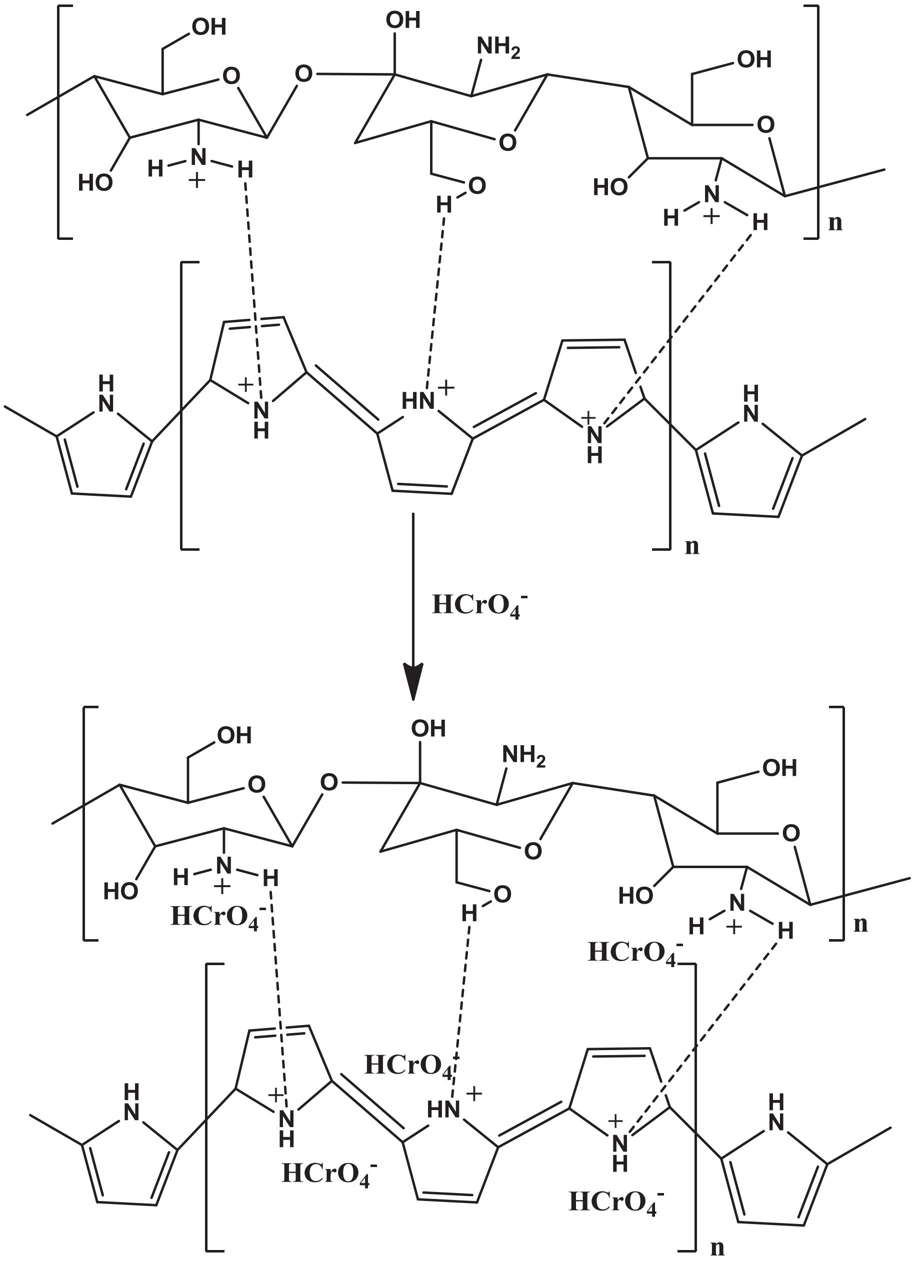
### 2.3. Adsorption experiments

The adsorption experiments were performed in a 100-mL conical flask equipped with thermostated shaker rotating at a speed of 200 rpm. It should be noted that all the experiments were carried out at solution of pH 4.2. In a typical case, a desired amount of sorbent was added to 50 mL of Cr(VI) ions solution of initial concentration of 100 mg/L and the mixture was kept at room temperature for desired time. After treatment, the mixture was filtered, and the filtrate was analyzed for the Cr(VI) ions by UV-VIS spectrophotometer (Pharo 300 Merck) using 1,5-diphenyl carbazide method at the wavelength of 540 nm.

The adsorption capacities were calculated using Eq. (1):

$$\text{Sorption capacity (SC)}\, q_e = (C_0 - C_e)V/W \tag{1}$$

where $q$ is the adsorption capacity of CS/PPy composite (mg Cr(VI) ion/g adsorbent), $V$ is the volume of Cr(VI) ions solution (L), $C_0$ is the initial concentration of Cr(VI) ions before adsorption (mg/L), $C_e$ is the final



Scheme 1. Mechanism of Cr(VI) ion removal by CS/PPy composite.

concentration of Cr(VI) ions after adsorption (mg/L), and *W* is the weight of adsorbent (g). The Cr(VI) ion percentage removal was calculated as follows:

$$\%\ \text{removal} = C_0 - C_e/C_0 \times 100 \tag{2}$$

## 2.4. Instrumentation

Fourier transform infrared (FTIR-JASCO-60 plus) spectra of the composite before and after treatment were recorded in the range between 400 and 4,000 $cm^{-1}$. Surface morphologies of the CS/PPy composite before and after water treatment were monitored using SEM (VEGA3 TESCAN). Quantitative detection and localization of elements in the composite were obtained using an EDX during SEM observations. XRD measurements were obtained to determine the crystalline phases present in the sorbent. BET surface area of the CS/PPy composite was measured by $N_2$ adsorption—desorption using a Micromeritics Gemini V-2380 surface area analyzer.

### 2.5. Isotherm studies

The three most widely used isotherms namely Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) isotherm models have been adopted to describe the adsorption characteristics of CS/PPy composite for the removal Cr(VI) ions from the aqueous solutions. Adsorption isotherm data were obtained by conducting experiments at 303, 313, and 323 K with three different initial concentrations.

The linear form of isotherm is represented as follows,

Freundlich isotherm

$$\log q_e = \log k_F + 1/n \log C_e \tag{3}$$

Langmuir isotherm

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \tag{4}$$

where $q_e$ is the amount of Cr(VI) adsorbed per unit weight of the sorbent (mg/g), $C_e$ is the equilibrium concentration of Cr(VI) in solution (mg/L), $k_F$ is the measure of adsorption capacity, and $1/n$ is the adsorption intensity. $Q^0$ is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent, and $b$ (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, $R_L$ [21].

$$R_L = 1/1 + bC_0 \tag{5}$$

where $b$ (L/mg) is Langmuir isotherm constant and $C_0$ (mg/L) is initial Cr(VI) ions concentration.

D–R isotherm [22]

$$\ln q_e = \ln X_m - K_{DR}\varepsilon^2 \tag{6}$$

where $X_m$ is the adsorption capacity (mg/g) and $k$ is the constant related to adsorption energy (mol$^2$/kJ$^2$). $\varepsilon$ is Polanyi potential and can be calculated by the equation:

$$\varepsilon = RT \ln(1 + 1/C_e) \tag{7}$$

where $T$ is the temperature (K) and $R$ is the gas constant (8.314 Jmol$^{-1}$ K$^{-1}$). The value of $k$ is used to calculate the mean of free energy $E$ (kJ/mol) of the sorption,

$$E = -(2k)^{-0.5} \tag{8}$$

#### 2.5.1. Chi-square analysis

In order to identify the suitable isotherm model for the removal of Cr(VI) ions using CS/PPy composite, chi-square analysis has been carried out [23]. The mathematical expression for chi-square analysis is as follows;

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{9}$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and $q_e$ is experimental data on the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, $\chi^2$ will be a small number, while if they differ, $\chi^2$ will be a bigger number.

#### 2.5.2. Thermodynamic treatment of Cr(VI) ions sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change ($\Delta G^0$), standard enthalpy change ($\Delta H^0$), and standard entropy change ($\Delta S^0$) were calculated as follows;

The change in free energy of sorption is given by:

$$\Delta G^0 = -RT \ln K_0 \tag{10}$$

where $K_0$ is the sorption distribution coefficient, $\Delta G^0$ is the standard free energy change of sorption (kJmol$^{-1}$), $T$ is the temperature in $K$, and $R$ is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$). The sorption distribution coefficient $K_0$ was determined from the slope of the plot ln ($q_e/C_e$) against $C_e$ at different temperatures and extrapolating to zero $C_e$ according to Khan and Singh method [24].

The sorption distribution coefficient can be expressed in terms of $\Delta H^0$ and $\Delta S^0$ as a function of temperature:

$$\ln K^0 = \Delta S^0/R - \Delta H^0/RT \tag{11}$$

where $\Delta H^0$ is the standard enthalpy change (kJ mol$^{-1}$) and $\Delta S^0$ is standard entropy change (kJ mol$^{-1}$K$^{-1}$).

The values of $\Delta H^0$ and $\Delta S^0$ can be obtained from the slope and intercept of a plot of ln $K^0$ against $1/T$.

## 3. Results and discussion

### 3.1. Characterization

Fig. 1(A) showed FTIR spectra of CS, CS/PPy, and Cr–CS/PPy composite in the range of 400–4,000 $cm^{-1}$. For the CS/PPy composite, a broad band at 3,388 $cm^{-1}$ is due to overlapping of the stretching bands of both primary amine and –OH groups present in CS moiety. A stretching vibration peak of C=O in –NHCO– in CS occur at 1,623 $cm^{-1}$. The peak located at 2,921 $cm^{-1}$ indicates the –CH stretching vibration in –CH and –$CH_2$ [4]. The peaks at 1,552 $cm^{-1}$ and 1,481 $cm^{-1}$ are assigned to C=C and C–N asymmetric and symmetric vibration of the pyrrole ring, respectively. A band at 781 $cm^{-1}$ could be attributed to C–H ring-wagging vibration of the pyrrole ring [25–27]. These results confirmed the presence of PPy moieties in the prepared composite. Interestingly, in the chromium-sorbed CS/PPy composite, a slight shifting of the band from 3,388 $cm^{-1}$ to 3,446 $cm^{-1}$ has been occurring, and this may be taken as an indicative of electrostatic adsorption between the sorbent and the chromium. The band at 536 $cm^{-1}$ confirms the formation of $Cr(OH)_3$ in the chromium-sorbed CS/PPy composite which suggests the reduction of Cr(VI) to Cr(III) [4,6,28].

XRD pattern of CS and CS/PPy composite are shown in Fig. 1(B). A broad peak found at $2\theta = 25^\circ$ in CS/PPy composite is attributed to the characteristic peak of PPy polymer [12], and chitosan showed characteristic peaks at $2\theta = 10.3^\circ$, 20.3°, 26°, and 42° [2,4]. Thus XRD analysis confirmed that both CS and PPy moieties existed in the prepared composite. It was evident from the Fig. 1(B) that prepared composite has more or less amorphous in nature with small crystalline area between $2\theta = 15$ and 20 = 30°.

The surface morphology of CS/PPy before and after treatment is explored in Fig. 1(C) and (D). It was evident from Fig. 1(C) that after polymerization with PPy, the surface of the chitosan becomes highly porous as PPy uniformly covers the chitosan surface. This may be attributed to the growth of nitrogen-containing functional groups on the surface of chitosan, which is responsible for the removal of Cr(VI) ions. After the treatment, the porous structure of the composite was demolished which is shown in Fig. 1(D). This may be due to the adsorption of Cr(VI) ions onto the surface of composite.

Adsorption of chromium onto CS/PPy composite was verified with EDX. The EDX spectra of CS/PPy composite before and after treatment are depicted in Fig. 1(E) and (F). The presence of chromium peak in the EDX spectrum of chromium-sorbed CS/PPy composite shown in Fig. 1(F) confirms the sorption of chromium. The quantitative elemental compositions of the composite are given in their respective figures. The surface area of the synthesized CS/PPy composite is calculated as 3.066 $m^2/g$.

### 3.2. Optimization of pyrrole concentration

The effects of pyrrole concentration on the removal of Cr(VI) ions by CS/PPy composite were investigated and are shown in Fig. 2(A). It is clear from the graph that the SC of the composites increases as the pyrrole concentration was increased from 0.01 to 0.1 mol/L, as expected. The enhancement of the SC with increasing pyrrole concentration is due to the entry of more number of –NH groups to the CS/PPy composite which facilitate the higher removal of Cr(VI) ions. On the whole, 0.1 mol/L of pyrrole-added CS/PPy composite has obtained more SC than other CS/PPy composite materials, and hence, the CS/PPy composite prepared with 0.1 mol/L was used for further adsorption studies.

### 3.3. Effect of contact time

Fig. 2(B) shows the effect of time on the residual Cr(VI) concentration using PPy and CS/PPy composite. When holding other parameters such as concentration, pH, and dosage as constant, the residual Cr(VI) concentration decreased constantly with the increase in contact time. There was not much decrease in the residual Cr(VI) concentration when the contact time was longer, which implies that the equilibrium adsorption was obtained after 60 min. Therefore, the optimum contact time for the removal of Cr(VI) ions by CS/PPy composite was fixed as 60 min for the further adsorption studies.

### 3.4. Effect of initial pH of Cr(VI) ion solution

Fig. 2(C) shows the adsorption performance of CS/PPy composite for Cr(VI) ions at different pH levels (2–12). pH measurements were carried out with the expandable ion analyzer EA 940 with pH electrode. The pH of the working solution was adjusted by adding 0.1 M HCl/NaOH solution. The maximum percentage removal of the composite of Cr(VI) ions was found to be at lower pH levels. This could be explained by the facts that at lower pH values, the amino groups present in the composite are protonated

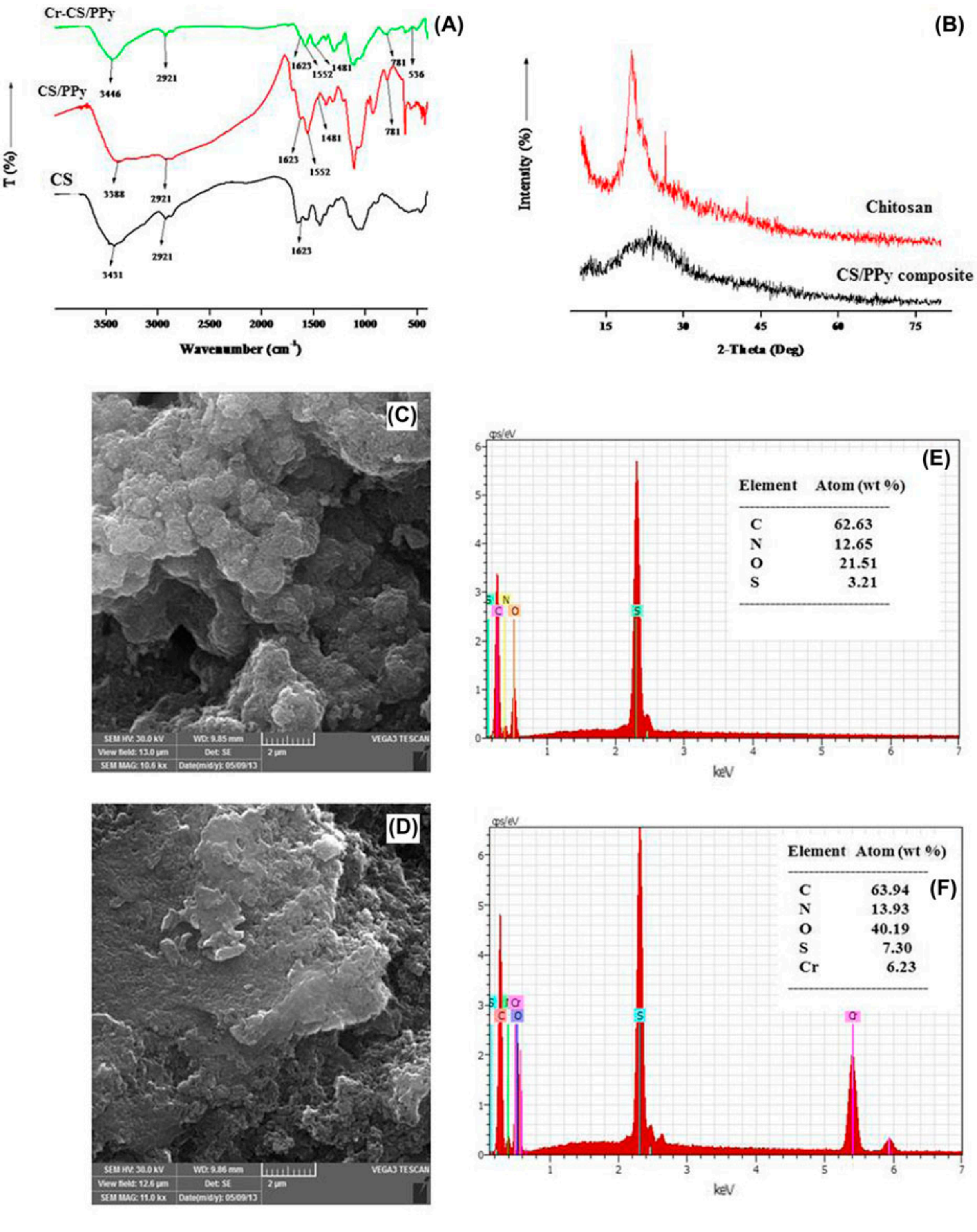


Fig. 1. (A) FTIR spectra of CS, CS/PPy, and Cr–CS/PPy composite, (B) XRD pattern of CS and CS/PPy composite, (C and D) SEM micrographs of CS/PPy and Cr–CS/PPy composite, and (E and F) EDX spectra of CS/PPy and Cr–CS/PPy composite.

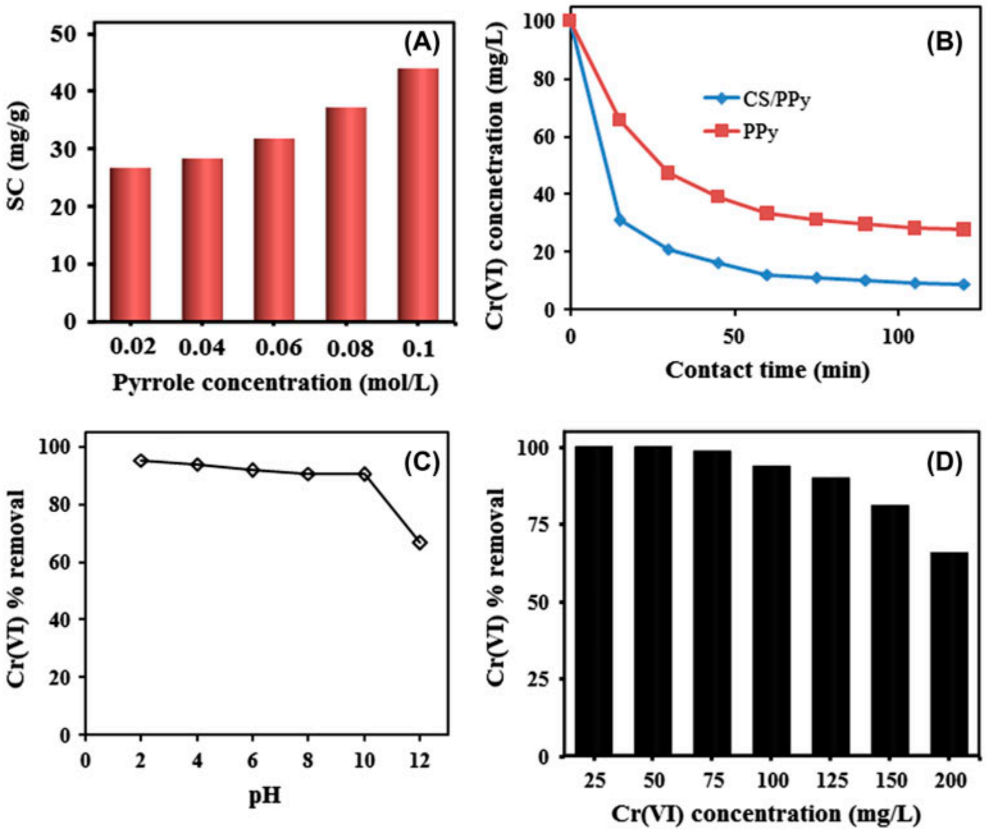


Fig. 2. Optimization of various parameters for the removal of Cr(VI) ions by CS/PPy composite (A) Effect of pyrrole concentration, (B) Effect of contact time, (C) Influence of pH, and (D) Effect of initial concentration.

due to the increase in $H^+$ ion concentration. The protonated amino groups of the composite remove chromate/dichromate anions by means of electrostatic attraction which contribute to higher removal of Cr(VI) ions. Another interesting factor is that the spontaneous reduction of Cr(VI) to Cr(III) also occurs under acidic medium due to high redox potential (1.3 V) [8,29]. Moreover, according to hard acid–soft base principle, the nitrogen present in the composite act as a hard base while $HCrO_4^-$ act as a soft acid and thus leads to the formation of strong surface complexation between the composite and $HCrO_4^-$ [30,31]. The decrease in the adsorption capacity in the alkaline media could be attributed to two factors: the first one is electrostatic repulsion between the composite and $CrO_4^{2-}$ ions, and the other one is competition between the $OH^-$ ions and $CrO_4^{2-}$ for exchange. Hence, all further experiments were carried out without adjusting the stock solution pH, that is 4.2, which has shown considerable percentage removal of Cr(VI) (93%). The possible mechanism of chromium removal is represented in Scheme 1.

### 3.5. *Effect of initial concentration*

The effect of initial concentration on the removal percentage of Cr(VI) ions from aqueous solution is shown in Fig. 2(D). It is observed that the removal percentage decreased with an increase in the initial concentration from 25 to 200 mg/L, as expected. A similar trend was observed in terms of SC by Bhaumik et al. [8] and Lei et al. [29]. Cr(VI) ions were not completely removed at higher concentrations, and this may be due to saturation of sorption sites or non-availability of sorbent surface. Hence, for further studies, the initial Cr(VI) ion concentration was fixed at 100 mg/L.

### 3.6. *Sorption isotherms*

The values of isotherm parameters of the Freundlich, Langmuir, and D–R models were calculated from the slope and intercept (log $q_e$ vs. log $C_e$—for Freundlich, $C_e/q_e$ vs. $C_e$—for Langmuir, and ln $q_e$ vs. $\varepsilon^2$—for D–R) and are given in Table 1. Fig. 3(A) and (B) are

Table 1
Freundlich, Langmuir, and D–R isotherms of CS/PPy composite

| | | Temperature | | |
|---|---|---|---|---|
| Isotherms | Parameters | 303 K | 313 K | 323 K |
| Freundlich | $1/n$ | 0.179 | 0.160 | 0.161 |
| | $n$ | 5.570 | 6.249 | 6.186 |
| | $k_F$ (mg/g) (L/mg)$^{1/n}$ | 35.87 | 46.19 | 53.76 |
| | $r$ | 0.998 | 0.998 | 0.999 |
| | SD | 0.008 | 0.009 | 0.0009 |
| | $\chi^2$ | 0.008 | 0.013 | 0.0001 |
| Langmuir | $Q^0$ (mg/g) | 78.61 | 86.13 | 92.16 |
| | $b$ (L/g) | 0.236 | 0.503 | 0.974 |
| | $R_L$ | 0.020 | 0.009 | 0.005 |
| | $r$ | 0.997 | 0.997 | 0.998 |
| | SD | 0.030 | 0.020 | 0.009 |
| | $\chi^2$ | 79.32 | 82.12 | 85.59 |
| Dubinin–Radushkevich | $k_{DR}$ (mol$^2$/J$^2$) | 1.58E-06 | 2.29-07 | 7.25E-08 |
| | $X_m$ (mg/g) | 68.80 | 75.60 | 80.57 |
| | $E$ (kJ/mol) | 0.562 | 1.476 | 2.626 |
| | $r$ | 0.940 | 0.938 | 0.941 |
| | SD | 0.106 | 0.127 | 0.140 |
| | $\chi^2$ | 0.284 | 0.470 | 0.641 |

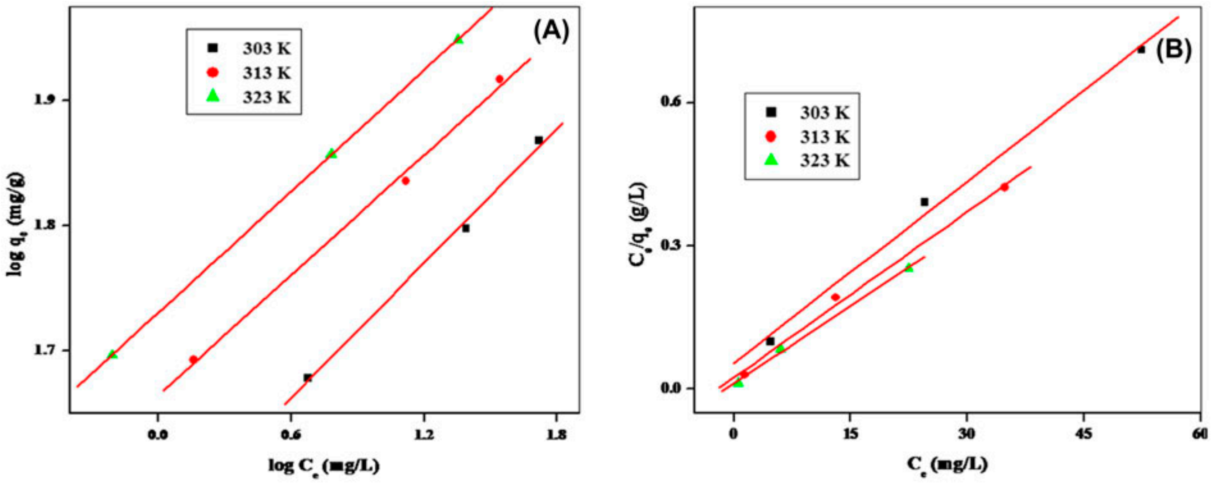


Fig. 3. (A) Freundlich adsorption isotherm model. (B) Langmuir adsorption isotherm model.

the isotherms of the Freundlich and Langmuir models. The value of $k_F$, $Q^0$, and $b$ increased with the increase in temperature suggesting that the Cr(VI) uptake by CS/PPy composite is an endothermic process. The $R_L$ values of Langmuir and the magnitude of the exponent $1/n$ of Freundlich lie between 0 and 1 that indicates the favorable conditions for the adsorption. The values of $X_m$ obtained from D–R increased with a rise in temperature, further confirming the endothermic nature of chromium sorption. The values of $E$, obtained in this study lying between 1 and 8 kJ/mol, indicate that the chromium removal was governed by electrostatic interaction.

The values of $q_e$ obtained by the Freundlich isotherm model were close to experimental values at given experimental conditions. Moreover, the higher $r$ value obtained by the Freundlich over Langmuir and D–R isotherm models, suggested that the Freundlich

Table 2
Thermodynamic parameters of CS/PPy composite

| Thermodynamic parameters | | CS/PPy |
|---|---|---|
| $\Delta G^{o}$ (kJ mol$^{-1}$) | 303 K | −8.11 |
| | 313 K | −6.77 |
| | 323 K | −5.66 |
| $\Delta H^{o}$ (kJ mol$^{-1}$) | | 45.29 |
| $\Delta S^{o}$ (kJ mol$^{-1}$ K$^{-1}$) | | 0.12 |

isotherm model was more fitted to the sorption process than the other two isotherm models, namely Langmuir and D–R.

### 3.6.1. Chi-square analysis

The $\chi^2$ values for CS/PPy composite are calculated and tabulated in Table 1. The lower $\chi^2$ values obtained by Freundlich than Langmuir and D–R isotherm models confirm the applicability of Freundlich isotherm model as best-fitting model for the Cr(VI) ions sorption.

### 3.6.2. Thermodynamic parameters

The values of $\Delta H^0$ and $\Delta S^0$ can be obtained from the slope and intercept of a plot of ln $K_0$ against $1/T$. The calculated values of thermodynamic parameters are shown in Table 2. The negative values of $\Delta G^0$ at three different temperatures confirm the spontaneous nature of Cr(VI) ions sorption onto the CS/PPy composite. The positive value of $\Delta H^0$ and $\Delta S^0$ indicates that the sorption process is endothermic and increased the randomness at the solid/liquid interface during Cr(VI) ion sorption. The value of $\Delta H^0$ may give the information about the type of adsorption. The magnitude of $\Delta H^0$ for physisorption is 2.1–20.9 kJ/mol and for chemisorption is 20.9–418.4 kJ/mol [31]. The $\Delta H^0$ for the present study was found to be 45.29 kJ/mol as shown in Table 2, indicating that the adsorption process was chemisorption/electrostatic adsorption.

## 3.7. Sorption kinetics

Two main types of sorption kinetic models, viz., reaction-based and diffusion-based models, were employed in order to investigate the adsorption process of Cr(VI) ions on to CS/PPy composite.

### 3.7.1. Reaction-based models

The most commonly used pseudo-first-order kinetic model [32] is given as

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303 \tag{12}$$

where $q_t$ is the amount of phenol on the surface of the resins at time $t$ (mg/g) and $k_{ad}$ is the equilibrium rate constant of the pseudo-first-order sorption (min$^{-1}$). The linear plots of log $(q_e - q_t)$ against $t$ give straight line indicate the applicability of pseudo-first-order model. The slope of the straight line plot of log

Table 3
Kinetic parameters of CS/PPy composite with different temperatures with different initial concentrations

| | | 303 K | | | 313 K | | | 323 K | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Kinetic models | Parameters | 100 mg/L | 150 mg/L | 200 mg/L | 100 mg/L | 150 mg/L | 200 mg/L | 100 mg/L | 150 mg/L | 200 mg/L |
| Pseudo-first-order | $k_{ad}$ (min$^{-1}$) | 0.065 | 0.040 | 0.057 | 0.070 | 0.050 | 0.062 | 0.080 | 0.060 | 0.064 |
| | $r$ | 0.951 | 0.894 | 0.940 | 0.859 | 0.931 | 0.903 | 0.884 | 0.916 | 0.865 |
| | SD | 0.287 | 0.278 | 0.284 | 0.575 | 0.270 | 0.400 | 0.581 | 0.358 | 0.511 |
| Pseudo-second-order | $q_e$ (mg/g) | 54.555 | 68.166 | 84.246 | 55.340 | 75.244 | 94.161 | 56.242 | 80.645 | 99.009 |
| | $k$ (g/mg min) | 0.0013 | 0.0012 | 0.0009 | 0.0014 | 0.0012 | 0.0007 | 0.0014 | 0.0010 | 0.0008 |
| | $h$ (mg/g min) | 4.152 | 5.593 | 6.496 | 4.459 | 7.078 | 6.869 | 4.682 | 6.845 | 8.039 |
| | r | 0.999 | 0.995 | 0.998 | 0.999 | 0.999 | 0.999 | 0.999 | 0.999 | 0.998 |
| | SD | 0.010 | 0.041 | 0.019 | 0.023 | 0.015 | 0.012 | 0.003 | 0.007 | 0.018 |
| Particle diffusion | $k_p$ (min$^{-1}$) | 4.752 | 3.754 | 2.565 | 5.947 | 4.565 | 3.184 | 6.586 | 4.752 | 3.659 |
| | r | 0.853 | 0.747 | 0.835 | 0.798 | 0.779 | 0.818 | 0.846 | 0.817 | 0.799 |
| | SD | 1.965 | 3.002 | 1.991 | 2.351 | 2.940 | 2.097 | 1.909 | 2.153 | 2.210 |
| Intraparticle diffusion | $k_i$ (mg/g min$^{0.5}$) | 19.125 | 28.742 | 28.828 | 20.868 | 32.915 | 31.742 | 21.204 | 31.615 | 39.129 |
| | $r$ | 0.977 | 0.996 | 0.929 | 0.969 | 0.981 | 0.964 | 0.967 | 0.977 | 0.987 |
| | SD | 1.579 | 0.692 | 4.652 | 1.823 | 1.761 | 3.574 | 1.950 | 2.220 | 1.958 |

$(q_e - q_t)$ against $t$ at three different temperatures, viz., 303, 313, and 323 K, gives the value of the pseudo-first-order rate constant ($k_{ad}$) and $r$ of CS/PPy composite and are listed in Table 3, respectively.

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [23] and the most popular linear form is

$$t/q_t = 1/h + t/q_e \tag{13}$$

where $q_t = (q_e^2 kt)/(1 + q_e kt)$, the amount of Cr(VI) ions on the surface of the composite at any time, $t$ (mg/g), $k$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$), $q_e$ is the amount of Cr(VI) ion sorbed at equilibrium (mg/g) and the initial sorption rate, and $h = k\, q_e^2$ (g mg$^{-1}$ min$^{-1}$). The value of $q_e$ (1/slope), $k$ (slope$^2$/intercept), and $h$ (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting $t/q_t$ against $t$. The values of $q_e$, $k$, $h$, and $r$ of the pseudo-second-order model were obtained from the plots of $t/q_t$ against $t$ for Cr(VI) ion sorption at three different temperatures, viz., 303, 313, and 323 K and are presented in Table 3, respectively. The values of $q_e$ increase with increase in temperature, indicating Cr(VI) ion sorption increases with the rise in temperature. The higher $r$ values obtained for the pseudo-second-order model than the pseudo-first-order model suggesting the applicability of the pseudo-second-order model for the Cr(VI) ions sorption onto the CS/PPy composite.

### 3.7.2. *Diffusion-based models*

For a solid–liquid sorption process, the solute transfer is usually characterized either by particle diffusion or by intraparticle diffusion control.

A simple equation for the particle-diffusion-controlled sorption process [16] is given as follows,

$$\ln(1 - C_t/C_e) = -k_p t \tag{14}$$

where $k_p$ is the particle rate constant (min$^{-1}$), the value of particle rate constant is obtained by the slope of the plot ln $(1 - C_t/C_e)$ against $t$.

The intraparticle diffusion model used here refers to the theory proposed by Weber and Morris [33] and its equation is

$$q_t = k_i t^{1/2} \tag{15}$$

where $k_i$ is the intraparticle rate constant (mg/g min$^{0.5}$). The slope of the plot of $q_t$ against $t^{1/2}$ will give the value of intraparticle rate constant. The values of particle rate constant, $r$ and standard deviation (SD) obtained from the slope of the plot ln $(1 - C_t/C_e)$ against $t$ are reported in Table 3. The value of intraparticle rate constant, $r$, and SD obtained from the slope of the plot of $q_t$ against $t^{1/2}$ are reported in Table 3. The higher correlation coefficient ($r$) values obtained by the intraparticle diffusion model than the particle diffusion model for CS/PPy composite indicate the possibility of sorption process is being controlled by intraparticle diffusion process.

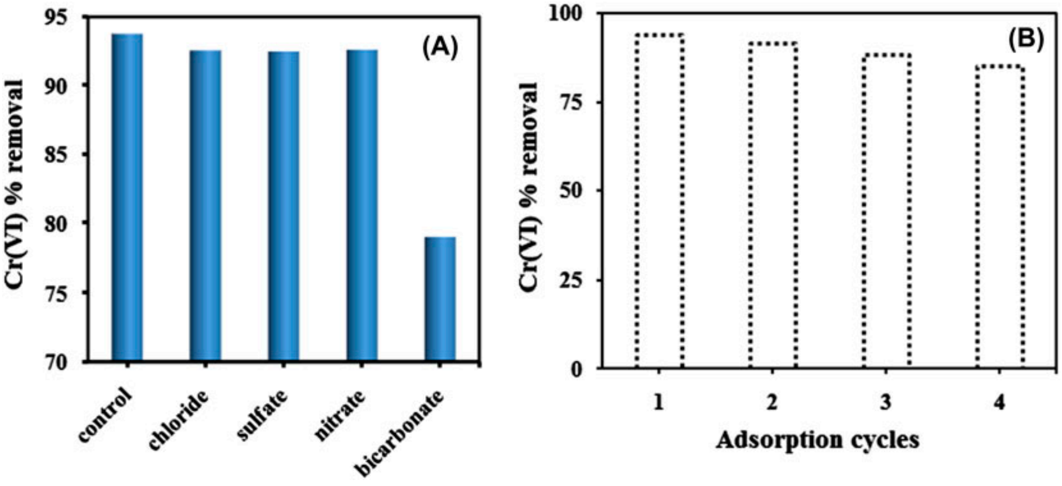


Fig. 4. (A) Effect of co-anions on the removal of Cr(VI) ions by CS/PPy composite and (B) Desorption–regeneration cycles.

Table 4
A few chitosan-based materials used for the removal of Cr(VI) ions

| Materials | Sorption capacity (mg/g) | pH | Isotherm | Reference |
|---|---|---|---|---|
| Chitosan/silica gel composite | 3.5 | 4 | – | [4] |
| La(III) loaded Chitosan/silica gel composite | 240.0 | 4 | Langmuir | [4] |
| Chitosan/alumina composite | 8.62 | 4 | D–R | [5] |
| Chitosan/nano-hydroxyapatite composite | 3.45 | 4 | Freundlich | [32] |
| Fe0-nanoparticles-chitosan composite | 35.97 | | Freundlich | [34] |
| Chitosan/ceramic alumina | 153.85 | 4 | Freundlich | [35] |
| Chitosan/montmorillonite | 41.67 | 4 | – | [36] |
| Chitosan/perlite | 153.8 | 4 | Langmuir | [37] |
| Chitosan/cellulose | 13.05 | | Langmuir | [38] |
| Magnetic chitosan | 69.40 | 4 | Langmuir | [39] |
| Magnetic cyclodextrin–chitosan/graphene oxide composite | 67.66 | - | Langmuir | [40] |
| Chitosan-coated fly ash | 33.27 | 5 | Langmuir | [41] |
| Chitosan/clay nanocomposite | 357.14 | 3 | Langmuir | [42] |
| N-2-hydroxypropyl trimethyl ammonium chloride chitosan bentonite nanocomposite | 22.17 | – | Langmuir | [43] |
| Fe-crosslinked chitosan | 295 | 4.7 | Langmuir–Freundlich | [44] |
| Protonated chitosan beads | 3.2 | 4 | Langmuir | [6] |
| Carboxylated chitosan beads | 3.6 | 4 | Langmuir | [6] |
| Grafted chitosan | 4 | 4 | Langmuir | [6] |
| Chitosan flakes | 0.63 | 4 | – | [5] |
| Cross linked chitosan | 215 | 4 | Langmuir | [45] |
| Metal ion imprinted chitosan | 51 | 5.5 | Langmuir | [46] |
| Chitosan crosslinked with epichlorohydrin | 52.3 | 5.5 | Langmuir | [46] |
| Amino terminated polyamidoamine functionalized chitosan beads | 185 | 4 | Freundlich | [47] |
| PNMANI/Ch-HCl composite | 192.4 | 4.2 | Freundlich | [19] |
| P2EANI/Ch-HCl composite | 148.7 | 4.2 | Freundlich | [19] |
| PNEANI/Ch-HCl composite | 229.8 | 4.2 | Freundlich | [19] |
| Chitosan–Fe(III) complex | 173.1 | 5 | Langmuir–Freundlich | [48] |
| Chitosan/polypyrrole composite | 78.61 | 4 | Freundlich | Present study |

### 3.8. *Influence of co-anions*

Normally, drinking water contains common anions such as chloride, sulfate, bicarbonate, and nitrate in significant concentration along with Cr(VI). The influence of these common anions on the removal percentage of Cr(VI) ions by CS/PPy composite was established and given in Fig. 4(A). The experiments were carried out in the presence of common anions with a fixed initial concentration of 200 mg/L, 100 mg/L of Cr(VI) initial concentration, and 60 min contact time with 0.1 g of CS/PPy composite. From the figure, it is observed that percentage removal of Cr(VI) ions was not significantly altered in the presence of chloride, sulfate, and nitrate, but in the case of bicarbonate, the percentage removal of Cr(VI) ions was decreased by 13%. This may be due to either competition of bicarbonate with Cr(VI) ions for the sorption sites or the increment in the pH of the solution due to the addition of bicarbonate.

### 3.9. *Desorption and reusability experiments*

In order to evaluate the cost-effectiveness of the adsorption process, the synthesized CS/PPy composite should be tested for regeneration and reusability. For this purpose, 0.1 M NaOH and 0.5 M HCl were used as desorption and regeneration medium. After adsorption, the Cr(VI)-adsorbed CS/PPy composite was added into 50 mL of 0.1 M NaOH and agitated for 2 h to desorb the adsorbed Cr(VI) ions. As a result of which, only 62.5% of the adsorbed Cr(VI) ions was released, and the remaining Cr(VI) (already reduced into Cr(III) by surface chemical reaction) was released as Cr(III) upon treatment with 50 mL of 0.5 M HCl. In addition, as soon as the composite was treated with 0.5 M HCl, the sorption sites were also regenerated by doping with chloride anions. The reusability of the CS/PPy composite was also checked for Cr(VI) ions, and the results are shown in Fig. 4(B). It is clear from the figure that even after fourth cycle, the removal efficiency of the CS/PPy composite remains almost same as 85%. The small decrease in the removal efficiency of each cycle could be due to handling loss of the adsorbent. Therefore, the CS/PPy composite could be reused as an efficient adsorbent for successive adsorption cycles.

### *3.10. Comparison of Cr(VI) ion removal with a few different chitosan-based adsorbents reported in the literature*

The adsorption capacity of CS/PPy composite was compared with other chitosan-based materials and is given in Table 4. It can be seen from Table 4 that the Cr(VI) ion removal capacity of CS/PPy composite is superior than the reported values in many cases. Hence, it can be concluded that the prepared CS/PPy composite is used as an effective adsorbent for the removal of Cr(VI) ions from aqueous solutions.

## 4. Conclusions

- CS/PPy composite was successfully prepared, characterized, and evaluated as an adsorbent for the removal of Cr(VI) ions from aqueous solution.
- Based on the batch experiments, it is confirmed that the removal of Cr(VI) ion is highly pH dependent and requires 60 min as contact time to remove 93.77% of 100 mg/L of Cr(VI) ions with the dosage of 2 g/L of CS/PPy composite.
- The adsorption kinetics and isotherms were discussed in detail. The equilibrium data well fitted to Freundlich isotherm model. The maximum adsorption capacity of CS/PPy composite for Cr(VI) was 78.61 mg/g at 303 K.
- The results of thermodynamic parameters revealed that the adsorption process was spontaneous and endothermic in nature. The high positive value of $\Delta H^0$ implies that the chemisorption/electrostatic adsorption was involved in the Cr(VI) ion adsorption process.
- The kinetic study reveals that the adsorption process follows the pseudo-second-order and pore diffusion patterns.
- The CS/PPy composite could be reused for four consecutive cycles.

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