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Adsorption study on removal of Cr(VI) ions by polyaniline composite

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ABSTRACT

The polyaniline composite composed of 0.2 mol L^{-1} aniline and 2% w/v polyvinyl alcohol was prepared by *in situ* polymerization technique. When this polyaniline/polyvinyl alcohol (PANI/PVA) composite was used as an adsorbent, it removes Cr(VI) ions from water effectively. Further investigations using FTIR, SEM-EDX, and XRD reveal that this composite has a unique structure and morphology, which favors higher Cr(VI) ion adsorption with the maximum sorption capacity of 111.23 mg of Cr(VI)/0.1 g of adsorbent. Subsequently, results from a batch adsorption system suggest that it requires relatively less contact time (60 min) at pH 4 with the initial concentration range of Cr(VI) ions (200 mg L^{-1}). Adsorption of Cr(VI) by PANI/PVA composite obeys Freundlich isotherm. Furthermore, the nature of Cr(VI) sorption is found to be spontaneous and endothermic which does not require any pre-treatment. It follows the pseudo-second-order kinetics and resembles pore diffusion model. Overall, the Cr(VI) removal by composite is driven by the adsorption-coupled reduction. Considering all these unique characteristics, the composite can be considered for potential removal of Cr(VI) from aqueous solution on a larger scale.

Keywords: Polyaniline; Polyvinyl alcohol; Chromium; Adsorption; Freundlich

1. Introduction

Chromium is one of the top priority metal pollutants in the environment. A certain amount of chromium is naturally identified in fresh water (0.1–117 μg L^{-1}) and soil (5–3,000 mg kg^{-1}) samples worldwide. Besides, it is also released to the environment from industrial wastewater generated during anthropogenic process, such as chromium plating, leather tanning, and wood preserving, and manufacturing of steel and other alloys, bricks, dyes, and pigments [1]. Chromium exists in the environment as trivalent [Cr(III)] and hexavalent [Cr(VI)] forms. It seems that Cr(III) is about 1,000 times less toxic than Cr(VI) and in contrast it is recognized as a supplementary mineral for human health. On the other side, Cr(VI) is reported to be highly toxic and causes lung cancer, skin rashes, upset stomachs and ulcers, respiratory problems, weakened immune systems, kidney and liver damage, and alteration of genetic material [2]. Subsequently, world environmental organization and world health organization (WHO) set the maximum permissible limits of Cr(VI) in potable water, inland surface water, and industrial wastewater as 0.05, 0.1, and 0.25 mg L^{-1}, respectively [3].

In fact, Cr(VI) exists in different anionic forms with respect to pH and concentration. For instance, Cr(VI) exists mostly in the form of $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions at pH values between 2 and 6, whereas under alkaline

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conditions ($pH > 8$), Cr(VI) exists predominantly as chromate (CrO_4^{2-}) ion. Hence, removal of Cr(VI) from aqueous solution in its native pH is a challenging task.

Several conventional methods are in practice for the removal of Cr(VI), they include chemical precipitation, solvent extraction, filtration, ion exchange, oxidation/reduction, membrane separation, electrochemical coagulation, adsorption, and biosorption [4–6]. However, these methods have their own advantages and limitations as well. Among all these methods, adsorption is the most widely used, feasible technique due to its low cost, high efficiency, and regeneration ability. In general, adsorbents such as chitosan, zeolite, activated carbon, clay, and metal oxides are widely studied for the removal of Cr(VI) ions [7,8]. Though these adsorbents assist the removable of Cr(VI) ions, they lack in specific functional groups which led to low sorption capacity, slow adsorption kinetics, and other practical difficulties. Hence, there is a sustained demand for an environmentally friendly material that can effectively and rapidly remove Cr(VI), and also regains its removal efficacy of the cost-effective regeneration process.

In recent years, polyaniline (PANI) a conducting polymer is the most promising candidate for the removal of toxic ions, especially Cr(VI) ions from water/wastewater [9–14]. The presence of larger amounts of amine and imine functional groups in PANI exhibits strong affinity towards heavy metal ions including Cr(VI). Unfortunately, PANI shows a typical recalcitrant processability, it cannot be directly utilized for commercial applications, especially in water/wastewater treatments. Alternatively, PANI can be blended with some additives, such as PVA, cellulose, chitosan, polypyrrole, and humic acid to gain better processability as well as function effectively in adsorption processes [11,12].

PVA is a water soluble, synthetic polymer material containing large number of reactive hydroxyl groups. Recently, PVA is reported to improve biocompatibility, mechanical strength, and chemical stability of various preparations including membrane synthesis and composites for heavy metal removal. Additionally, PVA is a non-toxic polymer, abundantly available, and cheap [15]. Consequently, PVA can be considered as one of the suitable additives to enhance the Cr(VI) adsorption efficiency of PANI [14]. Meanwhile, addition of PVA with PANI reported to increase electrical conductivity as well as mechanical strength. Presumably, the large number of amino groups in PANI form hydrogen bonds with hydroxyl groups present in PVA and eventually results higher electrical conductivity and better mechanical strength [14,16–19].

Though there are many composites reported in literature for Cr(VI) removal, attaining maximum level of adsorption while at higher initial concentration ($>100\ mg\ L^{-1}$) of Cr(VI) and also at a wide pH range (2–10) is observed to be difficult [11,12]. In fact, Cr(VI) adsorption efficiency of a composite is directly derived from the core material (e.g. Activated carbon and PANI) and additive (e.g. Polypyrrole, humic acid, zeolite and PVA) supplemented with it, and also it depends on the polymerization process that how the composite is prepared. Therefore, selecting a synergistic candidate of core and additive material and their composite synthesis process are very important to achieve a high level of Cr(VI) adsorption. In the literature, there are only a few papers noticed on composite preparation using PANI with PVA (Mw~72,000) [20,21], and the combination of maleic anhydride and PVA for water treatment [14,22]. Normally, the concentration of Cr(VI) in natural water as well as in industrial effluent varies drastically, and at the same time in most cases the native pH of aliquots cannot be controlled. Therefore, a suitable composite is necessary to achieve a significant level of Cr(VI) removal and that should typically function with a high initial concentration ($>100\ mg\ L^{-1}$) of Cr(VI) in a wide pH range (2–10).

In this study, a composite of PANI with PVA (Mw 89,000–98,000) is prepared by using ammonium persulfate as a free radical initiator in the hydrochloric acid (HCl) medium. Batch studies were carried out to evaluate the effect of pH, contact time, dosage, and initial concentration for the removal of Cr(VI) ions from the aqueous solutions. The adsorption characteristics including isotherm, kinetics, thermodynamics, and mechanism were investigated in detail.

2. Experimental procedure

2.1. Materials

Aniline and polyvinyl alcohol were purchased from Sigma-Aldrich, India. Ammonium peroxydisulfate (APS), potassium dichromate, 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. The stock solution ($1{,}000\ mg\ L^{-1}$) of Cr(VI) ions was prepared by dissolving 2.829 g of potassium dichromate in 1,000 mL of DD water.

2.2. Preparation of PANI/PVA composite

In a typical experiment to prepare PANI/PVA composite, 4 g of PVA was added into the beaker containing APS, where APS ($0.25\ mol\ L^{-1}$) was

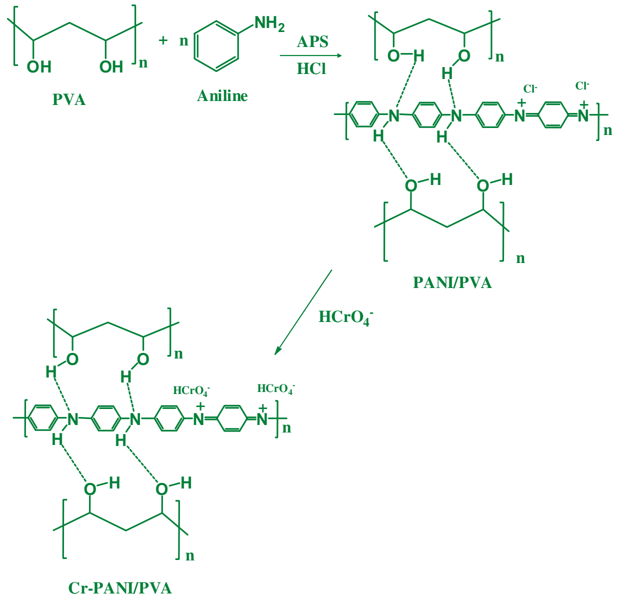

Fig. 1. Schematic illustration shows the synthesis of PANI/PVA composite followed by its Cr(VI) adsorption.

prepared in 50 mL of HCl (1 M) and stirred for 15 min. Then, 0.2 mol L^{-1} of aniline dissolved in 50 mL of HCl (1 M) was added drop wise to the above mixture and kept at 0–4˚C without any disturbance. This led to *in situ* polymerization of aniline (PANI) with PVA in presence of APS. After 24 h, the resulting composite of PANI/PVA was filtered on a filter paper and to separate oligomers and impurities, product was washed with 1 M HCl solutions followed by DD water until the filtrate became colorless. Finally, the resulting PANI/PVA composite was washed with acetone and dried at 50˚C for 48 h. Synthesis route scheme for PANI/PVA composite is represented in Fig. 1. Similarly, PANI was synthesized by the same procedure without PVA.

2.3. Characterization techniques

The functionality present in the prepared PANI/PVA composite before and after treatment with Cr(VI) was characterized using Fourier transform infrared spectroscopy (FT-IR) (JASCO-60 plus). The PANI/PVA composite (0.05 g) and KBr (0.15 g, IR Grade, Merck, India) were thoroughly mixed and this mixture was pressed to form a tablet which was used for FT-IR analysis. Scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX) (VEGA3 TESCAN) was used to characterize the surface morphology of the composite. X-ray diffraction measurements were obtained to determine the crystalline phases present in the sorbent.

2.4. Sorption experiments

All sorption studies were carried out by the batch equilibration method. Initially, a stock solution containing 1,000 mg L^{-1} of Cr(VI) was prepared by dissolving 2.829 g of potassium dichromate in 1,000 mL of DD water. Later, it was diluted appropriately with DD water to attain expected initial concentration in the adsorption study. In a typical study, 0.1 g of PANI/PVA composite was added to a conical flask contained 50 mL of 200 mg L^{-1} of Cr(VI) as initial concentration. The adsorption experiments were conducted at pH 4.12 under room temperature with the agitation speed of 200 rpm. After 60 min of adsorption, the reaction mixture was filtered and the filtrate was analyzed for non-adsorbed Cr(VI). To optimize conditions for Cr(VI) removal, and also to evaluate the adsorption capacity of PANI/PVA composite, the adsorption reactions were conducted at a wide pH range (pH 2–10), contact time (15–90 min), initial concentration (50–250 mg L^{-1}), and adsorbent dose (0.025–0.150 g). The working solution pH was adjusted by adding 0.1 M of HCl/NaOH.

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

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

where q is the adsorption capacities of PANI/PVA 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^{-1}), C_e is the final concentration of Cr(VI) ions after adsorption (mg L^{-1}), and W is the weight of adsorbent (g). The Cr(VI) ion percentage removal was calculated by Eq. (2):

$$\text{Percentage removal} = C_0 - C_e/C_0 \times 100 \quad (2)$$

2.4.1. Desorption and regeneration studies

Desorption experiments were carried out at room temperature to regenerate the adsorbent so that it could be reused for Cr(VI) removal in subsequent batches. For the desorption study, 0.1 g of the adsorbent was added to 50 mL of Cr(VI) ions solution of initial concentration of 200 mg L^{-1} for 2 h, at pH 4. After the adsorption process, desorption of metal from PANI/PVA was carried out by treating the composite with NaOH (0.2 N) and HCl (2 M). Afterwards, the adsorbent was thoroughly washed with DD water. Similarly, to estimate the reusability of PANI/PVA composite for Cr(VI) removal, the adsorption and desorption process were repeated for five consecutive batches.

2.5. Analytical methods

The concentration of Cr(VI) ion was measured by a UV-spectrophotometer (Pharo 300 Merck) using 1,5-diphenyl carbazide method at the wavelength of 540 nm. The pH measurement was carried out with the expandable ion analyzer EA 940 with pH electrode.

2.6. Adsorption isotherms

Adsorption isotherm was conducted at 303, 313, and 323 K with three different initial concentrations (200, 225, and 250 mg L^{-1}) of Cr(VI). The most widely used isotherms namely Freundlich and Langmuir models were adopted to describe the adsorption characteristics of PANI/PVA composite for the removal of Cr(VI) from aqueous solution.

The linear form of isotherm is represented by Eqs. (3) and (4).

Freundlich isotherm [23]:

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

Langmuir isotherm [23]:

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

where q_e is the amount of Cr(VI) adsorbed per unit weight of the sorbent (mg g^{-1}), C_e is the equilibrium concentration of Cr(VI) in solution (mg L^{-1}), 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^{-1}) and gives the maximum sorption capacity of sorbent and b (L mg^{-1}) 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 [24].

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

where b (L mg^{-1}) is Langmuir isotherm constant and C_0 (mg L^{-1}) is initial Cr(VI) ions concentration.

2.6.1. Chi-square analysis

Chi-square analysis was carried out to identify the suitable isotherm for sorption Cr(VI) ions onto PANI/PVA composite. The mathematical expression for chi-square analysis is expressed by equation,

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{6}$$

where $q_{e,m}$ is equilibrium capacity obtained from the model (mg g^{-1}) and q_e is equilibrium capacity (mg g^{-1}) estimated from the experiment. Typically, if the data from model correlate with experimental results, χ^2 values a small number or else it values a larger number.

2.6.2. Thermodynamic treatment of Cr(VI) ions sorption process

Thermodynamic parameters associated with the adsorption, viz. standard free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated by Eqs. (7) and (8).

The change in free energy of sorption is given by:

$$\Delta G^\circ = -RT \ln K_0 \tag{7}$$

where K_0 is the sorption distribution coefficient, ΔG° is the standard free energy change of sorption (kJ mol^{-1}), T is the temperature in K, and R is the universal gas constant ($8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$). 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 [25].

The sorption distribution coefficient can be expressed in terms of ΔH° and ΔS° as a function of temperature:

$$\ln K^\circ = \Delta S^\circ/R - \Delta H^\circ/RT \tag{8}$$

where ΔH° is the standard enthalpy change (kJ mol^{-1}) and ΔS° is standard entropy change ($\text{kJ mol}^{-1}\ \text{K}^{-1}$). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of ln K_0 against $1/T$.

3. Results and discussion

3.1. Optimization of parameters for Cr(VI) adsorption by PANI/PVA composite

3.1.1. Effect of contact time

Though several parameters influence Cr(VI) ion adsorption, the contact time between adsorbent and Cr(VI) is noticed to impact the sorption capacity to a larger extent [13]. Fig. 2(A) shows the Cr(VI) sorption profile by PANI and PANI/PVA composite with respect to time. Adsorption of Cr(VI) increases with

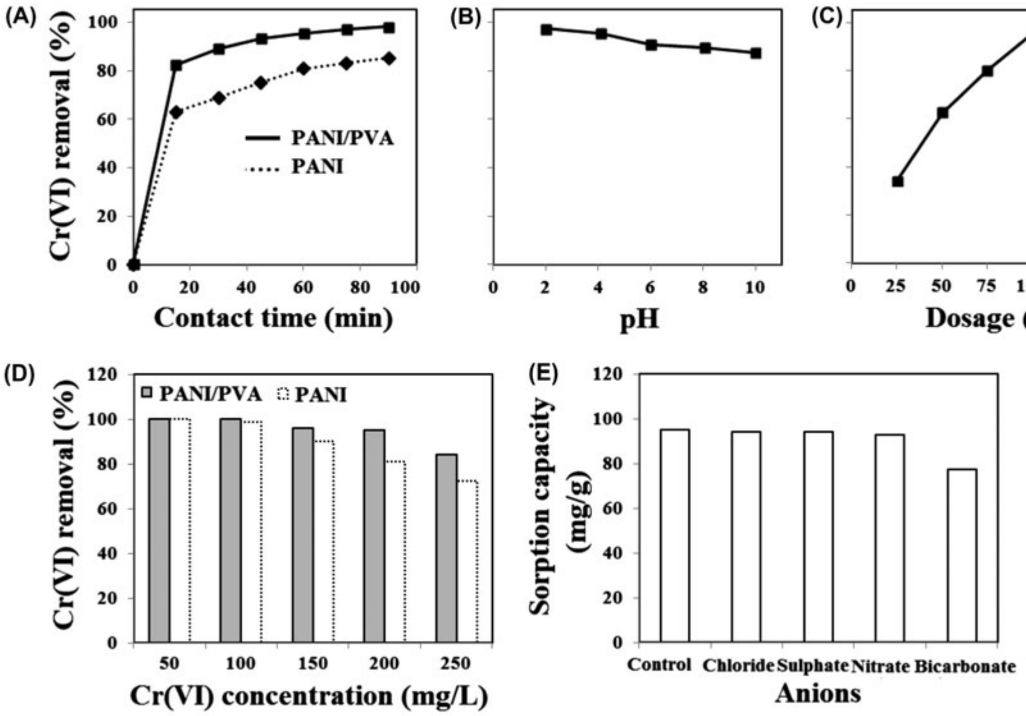

Fig. 2. Optimization of parameters contact time (A), pH (B), dosage (C), initial concentration of Cr(VI) (D) and interference of anions (E) for Cr(VI) adsorption by PANI/PVA composite.

the increase of contact time. It is observed that PANI/PVA sorption capacity is about 1.3 times higher than that from PANI. However, in both the cases, adsorption equilibrium was attained at 60 min. Whereas, composites prepared from PANI/humic acid and substituted PANI/chitosan required about 120 and 240 min, respectively, to reach equilibrium in Cr(VI) sorption [11,26]. Noticeably, PANI/PVA composite requires much less contact time (60 min), and the addition of PVA enhances the sorption capacity without changing the sorption pattern of PANI.

3.1.2. *Influence of pH*

In an adsorption process, pH can significantly control the electrical properties of adsorbent and adsorbate. Subsequently, sorption capacity would vary according to the pH condition in reaction. To know the pH effect on Cr(VI) sorption by PANI/PVA, pH of the solution was adjusted between pH 2–10. Cr(VI) sorption by PANI/PVA is observed higher (90–100 mg g^{-1}) at an acidic pH region (pH 2–6) than that from the alkaline region (pH 8–10) (Fig. 2(B)). The reason could be at lower pH levels, the Cr(VI) ions exist as $HCrO_4^-$ or $Cr_2O_7^{2-}$ depending on their concentration and the adsorbent acquires a positive charge due to protonation of amine groups present in PANI/PVA composite which removes $HCrO_4^-$ or $Cr_2O_7^{2-}$ anions by electrostatic attraction. At acidic condition (pH 2–6), PANI presence in PANI/PVA composite acquires its reduced form which can spontaneously transfer electrons with Cr(VI). Similar to PANI/PVA in the literature, other composites PANI/polypyrrole and PANI/polystyrene are reported with high Cr(VI) sorption capacity at acidic region [10,27]. Further, the electron rich groups like oxygen and nitrogen present in the composite reduce the sorbed Cr(VI) ions into less toxic Cr(III) ions [12,28–30]. At higher pH levels, sorption capacity was found to be low and this could be attributed to the competition between CrO_4^{2-} ions and OH^- ions for the sorption sites of the adsorbent surface.

3.1.3. *Effect of adsorbent dosage*

To examine the effect of the dosage on the percentage removal of Cr(VI) ions, studies were conducted with varied adsorbent dosage ranging from 0.025 to 0.150 g. Fig. 2(C) illustrates the Cr(VI) ion removal from the aqueous solutions based on different dosage of PANI/PVA composite. It shows that the removal of Cr(VI) ions increases with increase in PANI/PVA composite dosage which is due to the increase in the number of adsorption sites available for the adsorption. The removal percentage was increased from 34 to 100% (equivalent to 2.5 g L^{-1}) at a dose of 0.025–0.125 g of PANI/PVA composite. From the investigation, 0.1 g of the adsorbent was found to be the optimum dosage for the removal of 95% of Cr(VI) ions and hence in subsequent experiments the dosage of PANI/PVA was fixed to 0.1 g. Similar studies were reported in many research groups in the literature [13,31–33], to achieve a complete removal (100%) of Cr(VI) ions from the aqueous solutions, a wide range of adsorbent dosage (2–20 g L^{-1}) was utilized. However, in case of PANI/PVA, the Cr(VI) removal (100%) requires only 2.5 g L^{-1} which is advantageous.

3.1.4. Effect of initial Cr(VI) ions concentration

The effect of different initial concentration onto the removal percentage of Cr(VI) ions was carried out using solutions containing 50–250 mg L^{-1} of Cr(VI) ions. At optimum pH and contact time (pH 4.12 and 60 min, respectively), 0.1 g of adsorbent was added to 50 mL of Cr(VI) ion solution with different initial concentration. Fig. 2(D) shows the influence of initial concentrations on the Cr(VI) ion removal by PANI and PANI/PVA composite. It was observed that at higher concentration levels, the removal percentage was found to be less and this may be attributed to saturation of the sorption sites where sorption takes place. Similar behavior is observed (in terms of SC) in most of the adsorption processes. The maximum removal percentage of Cr(VI) ions by the PANI/PVA composite at different initial concentration was from 100 to 84.14%, respectively.

3.1.5. Effect of competitive anions

Drinking water contains several common anions, such as Cl^-, SO_4^{2-}, HCO_3^-, and NO_3^-, along with Cr(VI). These common anions may compete with the Cr(VI) ions for the sorption sites during the adsorption process. Hence, the removal of Cr(VI) ions by PANI/PVA composite was investigated in the presence of common anions. The experiments were carried out in the presence of common anions with affixed initial concentration of 200 mg L^{-1} by keeping 200 mg L^{-1} as Cr(VI) ion initial concentration. Fig. 2(E) shows the effect of common anions on the adsorption capacity of PANI/PVA composite under given experimental conditions. As it is seen from Fig. 2(E), the anions such as Cl^-, SO_4^{2-}, and NO_3^- did not negatively influence the Cr(VI) ions for the sorption sites, whereas HCO_3^- has competed with Cr(VI) ions; hence, the sorption capacity of PANI/PVA composite was decreased. This is probably due to the competition among the anions for the sites on the adsorbent surfaces, and this was decided by the concentration, charge, and size of the anions.

3.2. Sorption isotherms

Fig. 3(A) and (B) shows the isotherms of the Langmuir and Freundlich models. The values of isotherm parameters of the Freundlich and Langmuir models are calculated from the slope and intercept (log q_e vs. log C_e—for Freundlich and C_e/q_e vs. C_e—for Langmuir) and are given in Table 1. The value of k_F, Q^0, and b increases with increase in temperature suggesting that the Cr(VI) uptake by PANI/PVA composite is an endothermic process. The R_L values and the magnitude of the exponent $1/n$ of the Langmuir isotherm lies between 0 and 1, indicating the favorable conditions for the adsorption. A linear plot and the correlation coefficient $(r) > 0.9$ of both the isotherms indicate the applicability of both Freundlich and Langmuir isotherm models.

3.2.1. Chi-square analysis

The χ^2 values for PANI/PVA composite are calculated and tabulated in Table 1. The lower χ^2-values of

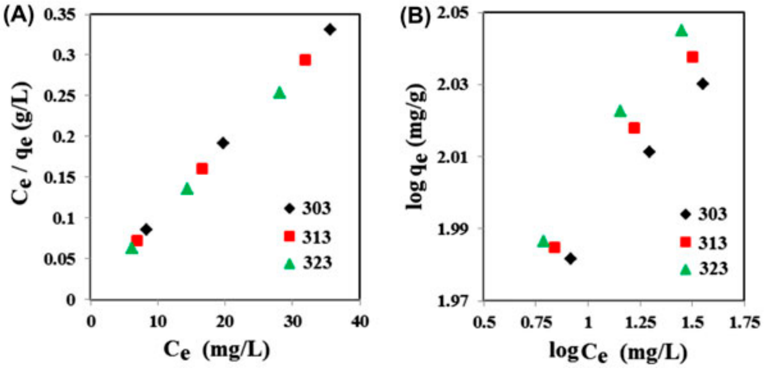

Fig. 3. Adsorption isotherms for Cr(VI) ions removal by PANI/PVA composite Langmuir (A) and Freundlich (B).

Table 1
Freundlich and Langmuir isotherm parameters of PANI/PVA composite for the removal of Cr(VI) ions

Isotherms	Parameters	Temperature 303 K	313 K	323 K
Freundlich	$1/n$	0.077	0.083	0.088
	$k_{F(\mathrm{mg/g})\ (\mathrm{L/mg})^{1/n}}$	81.801	82.695	83.416
	r	0.995	0.946	0.980
	sd	0.003	0.012	0.008
	χ^2	0.007	0.043	0.023
Langmuir	Q^0(mg g^{-1})	111.23	113.12	115.47
	b (L g^{-1})	0.725	0.841	0.863
	R_L	0.005	0.004	0.004
	r	0.999	0.999	1
	sd	0.001	0.001	0.00005
	χ^2	136.53	138.91	140.20

the Freundlich than Langmuir isotherm suggest the better applicability of Freundlich isotherm for the Cr(VI) ions sorption on PANI/PVA composite.

3.2.2. Thermodynamic parameters

The values of ΔH° and ΔS° 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 ΔG° and the positive value of ΔS° at three different temperatures confirm the spontaneous nature of Cr(VI) ions sorption onto the PANI/PVA composite. The positive value of ΔH° indicates that the sorption process is endothermic.

3.3. Sorption dynamics

Adsorption kinetics were conducted at 303, 313, and 323 K with three different initial concentrations (200, 225, and 250 mg L^{-1}) of Cr(VI). Samples were drawn at regular time interval and analyzed for Cr(VI) adsorption. The sorption kinetic models such as reaction and diffusion based models were employed to investigate the adsorption process of Cr(VI) over PANI/PVA composite.

Table 2
Thermodynamic parameters of PANI/PVA composite for the removal of Cr(VI) ions

Thermodynamic parameters		PANI/PVA
ΔG° (kJ mol^{-1})	303 K	−7.64
	313 K	−7.68
	323 K	−7.52
ΔH° (kJ mol^{-1})		9.42
ΔS° (kJ mol^{-1} K^{-1})		0.01

3.3.1. Reaction-based models

The most commonly used linear forms of the pseudo-first-order and the pseudo-second-order kinetic models are represented by Eqs. (9) and (10).

Pseudo-first order [34]:

$$\log(q_e - q_t) = \log q_e - k_{\mathrm{ad}}\, t/2.303 \tag{9}$$

Pseudo-second order [35]:

$$t/q_t = 1/h + t/q_e \tag{10}$$

where $q_t = (q_e^2 kt)/(1 + q_e kt)$ is the amount of Cr(VI) on the surface of the composite at any time t (mg g^{-1}), q_e is the amount of Cr(VI) ion adsorbed at equilibrium (mg g^{-1}), k_{ad} is the equilibrium rate constant of the pseudo-first-order sorption (min^{-1}), and h is the initial sorption rate, $h = k\, q_e{}^2$ (g mg^{-1} min^{-1}).

The values of the pseudo-first-order rate constant (k_{ad}) and r are calculated from the intercept and slope of the graph between log ($q_e - q_t$) vs. t at three different concentrations and temperatures. The values obtained are reported in Table 3. The value of q_e, k, h, and r of the pseudo-second-order model were obtained from the plots of t/q_t vs. t at all the studied conditions are presented in Table 3. The values of q_e increase with increase in temperature indicating Cr(VI) ion sorption increases with the rise in temperature. Moreover, the calculated q_e values are very well agreed with the experimental data. The higher correlation coefficient (r) values obtained by the pseudo-second-order model than the pseudo-first-order model suggest the applicability of the pseudo-second-order model for the Cr(VI) ions sorption onto the PANI/PVA composite.

3.3.2. Diffusion-based models

In 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 and intraparticle diffusion sorption process are given in Eqs. (11) and (12).

Particle diffusion controlled sorption process [23].

$$\ln(1 - C_t/C_e) = -k_p t \tag{11}$$

Table 3
Kinetic parameters of PANI/PVA composite for the removal of Cr(VI) ions

		303 K			313 K			323 K		
Kinetic models	Parameters	200 mg L^{-1}	225 mg L^{-1}	250 mg L^{-1}	200 mg L^{-1}	225 mg L^{-1}	250 mg L^{-1}	200 mg L^{-1}	225 mg L^{-1}	250 mg L^{-1}
Pseudo-first-order	k_{ad} (min^{-1})	0.086	0.076	0.065	0.143	0.142	0.064	0.096	0.082	0.053
	r	0.870	0.892	0.994	0.803	0.799	0.964	0.949	0.962	0.984
	sd	0.443	0.349	0.062	0.960	0.972	0.161	0.288	0.212	0.088
Pseudo-second-order	q_e (mg g^{-1})	109.17	116.95	120.33	109.76	118.34	121.80	110.37	119.61	122.85
	k (g/mg min)	0.0009	0.0008	0.001	0.0009	0.0008	0.0009	0.001	0.001	0.001
	h (mg/g min)	10.826	11.603	14.896	11.713	12.459	14.088	12.95	14.71	17.44
	r	0.998	0.998	0.999	0.999	0.999	0.999	0.999	0.999	0.998
	sd	0.012	0.011	0.004	0.008	0.008	0.009	0.003	0.005	0.010
Particle diffusion	k_p (min^{-1})	5.478	2.833	2.612	4.160	2.779	4.110	4.826	3.103	1.689
	r	0.762	0.871	0.909	0.853	0.915	0.787	0.872	0.937	0.958
	sd	2.971	0.992	1.140	1.380	0.712	2.782	1.658	0.735	0.362
Intraparticle diffusion	k_i (mg/g $min^{0.5}$)	34.97	37.360	45.65	37.17	39.88	46.07	39.57	45.08	56.32
	r	0.993	0.990	0.977	0.988	0.992	0.995	0.976	0.976	0.992
	sd	1.704	2.188	3.401	2.334	2.089	1.567	3.308	3.483	1.773

Intraparticle diffusion sorption process [36].

$$q_t = k_i t^{1/2} \tag{12}$$

where k_p is the particle rate constant (min^{-1}), k_i is the intraparticle rate constant (mg/g $min^{0.5}$)

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 standard deviation (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 intra particle diffusion model than the particle diffusion model for PANI/PVA composite indicate the possibility of sorption process is being controlled by intra particle diffusion process.

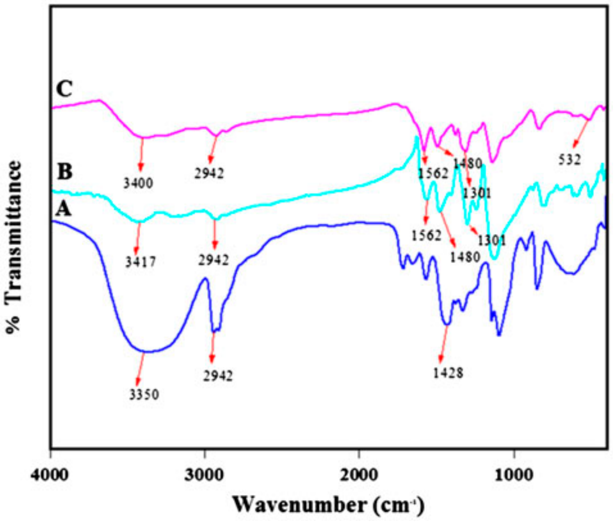

Fig. 4. FTIR spectra for (A) PVA, (B) PANI/PVA and (C) Cr-PANI/PVA composite.

3.4. Characterization of the adsorbent

FTIR spectra of PVA, PANI/PVA, and Cr-sorbed PANI/PVA composite have been recorded and represented in Fig. 4. A broad band observed in the range from 3,200 to 3,400 cm^{-1} in all the stages, corresponding to stretching of –OH from PVA. $-CH_2$ groups present in PVA showed a band at 2,942 cm^{-1} and a band at 1,428 cm^{-1} is related to the –OH deformation of PVA [37]. The bands range 1,562–1,581 cm^{-1} corresponds to the characteristic peaks of nitrogen quinone (*Q*), the bands range 1,480–1,492 cm^{-1} relate to the benzene ring present in the PANI. The bands at 1,301 cm^{-1} related to the stretching peaks of C–N and C=N. In Fig. 4(C), a slight shifting of the band from 3,417 to 3,400 cm^{-1} has been occurring and this may be taken as an indicative of electrostatic adsorption between the composite and chromium. A new band ranges at 530–540 cm^{-1} confirms the formation of $Cr(OH)_3$ in the

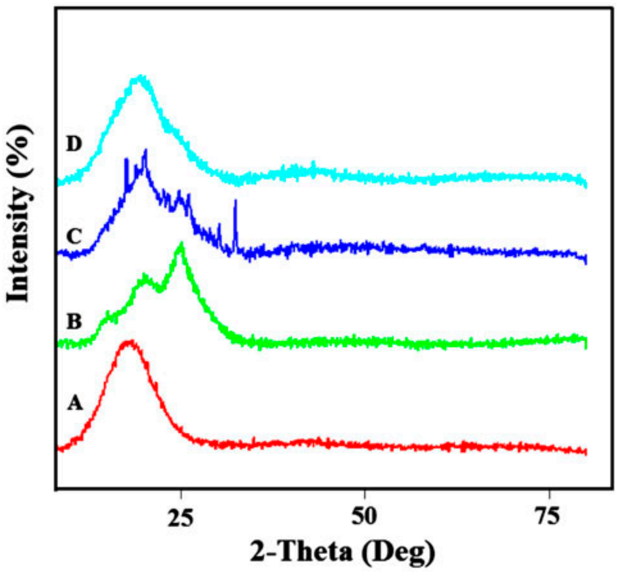

Fig. 5. XRD pattern obtained for (A) PVA, (B) PANI, (C) PANI/PVA and (D) Cr-PANI/PVA composite.

Cr(VI) ion-sorbed PANI/PVA composite which suggests the reduction of Cr(VI) to Cr(III) [28,38,39].

X-ray diffraction pattern of crystalline structure of PVA, PANI, and PANI/PVA composite before and after adsorption of Cr(VI) ions are shown in Fig. 5. From Fig. 5(A), a sharp crystalline peak at $2\theta = 19.6^\circ$ and a shoulder at $2\theta = 23.0^\circ$, typical of crystalline PVA are observed [40]. In Fig. 5(B), the peaks at $2\theta = 17.5^\circ$, 20°, and 25.4° are the characteristic peak of PANI. The characteristic peaks appeared at 17.5°, 20°, and 25.4° corresponding to (0 1 1), (0 2 0), and (2 0 0) crystal planes of PANI confirm that PANI is retaining its crystalline structure [41]. Thus, XRD analysis confirmed that both PANI and PVA moieties existed (Fig. 5(C)) in the prepared composite. As it is evident from the Fig. 5(D) that the crystalline structure of the composite is slightly decreased after the adsorption of Cr(VI) ions. This may be due to the adsorption of Cr(VI) ions onto the surface of the composite.

In Fig. 6(A)–(C), SEM images of PANI, PANI/PVA, and Cr-sorbed PANI/PVA composite is shown. It is evident from the SEM images that the presence of PVA, the rod shapes of PANI are converted into clusters in the prepared composite. The change in the SEM micrographs of the sorbent before and after chromium treatment indicates the structural change in the sorbent. It is evident that the surface of the composite is porous in nature before adsorption which has been blocked after sorption of Cr(VI) ions that indicates the structural changes in the composites. The chromium peak present in the EDX spectra of the chromium sorbed PANI/PVA composite depicted in Fig. 6(E) confirms the adsorption of chromium. Subsequently, the elements carbon (C), nitrogen (N), oxygen

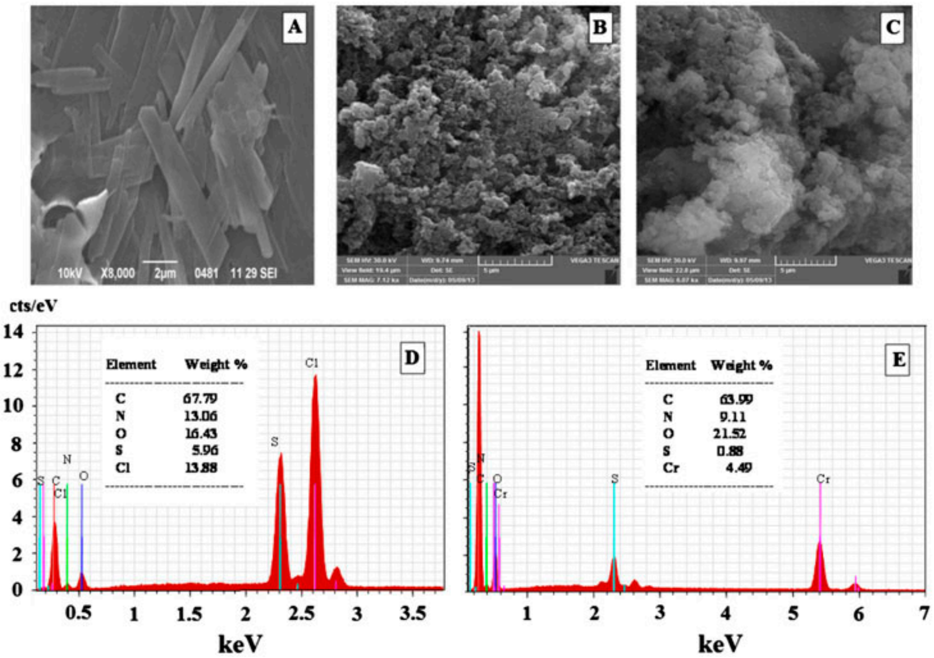

Fig. 6. SEM micrographs obtained for (A) PANI, (B) PANI/PVA, and (C) Cr-PANI/PVA composite and EDX spectra for (D) PANI/PVA and (E) Cr-PANI/PVA composite.

(O), and chromium (Cr) present in the composite were estimated using EDX analysis (Fig. 6). Besides, sulfur is also predicted in the EDX spectra, presumably it comes from APS, which was the free radical initiator in the polymerization reaction.

3.5. Cr(VI) desorption and regeneration studies

Nowadays, desorption and regeneration experiments were carried out to develop the cost effective adsorbent for the removal of Cr(VI) ions. The desorption experiments were carried out as metal-loaded adsorbent was added to 50 mL of 1 N NaOH solution, stirred for 2 h, and then filtered. The filtrate was examined for residual Cr(VI) ion concentration and the solid residue was washed with DD water several times to remove the desorption medium present in the material. Only 27.8% of Cr(VI) ions were released from the first cycle of desorption. Due to the presence of electron rich groups in the composite, the remaining Cr(VI) ions which were reduced into Cr(III) were released in the presence of 2 M HCl solution, where the sorption sites were also regenerated [12]. The sorption efficiency of the regenerated material was calculated over five consecutive adsorption–desorption cycles and is given in Fig. 7. As it was evident from the figure, that the sorption efficiency of the first two cycles remains unchanged and was about 94%. From the third cycle onwards, the sorption efficiency was found to be reduced. Therefore, the composite can be reused for the first two adsorption–desorption cycles without loss of its original sorption capacity.

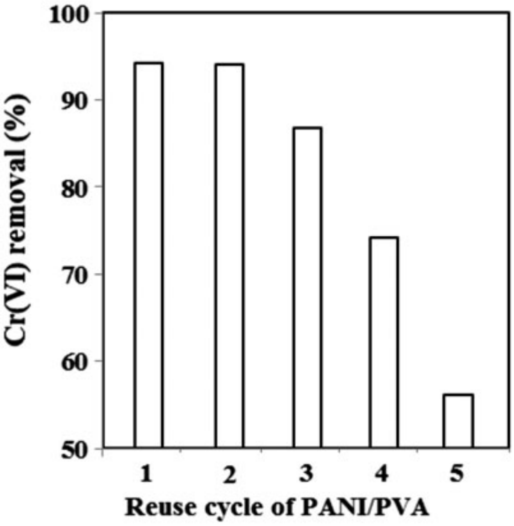

Fig. 7. Recycle of PANI/PVA composite for Cr(VI) removal.

4. Conclusions

The adsorption process for the removal of Cr(VI) ions by PANI/PVA composite was studied in detail. The pH of the reaction was found to play a major role in the Cr(VI) removal process, and the optimum pH for the removal of Cr(VI) was pH 4.12. The results obtained for Cr(VI) sorption successfully fit the Freundlich isotherm model than the Langmuir model. The values (ΔG°, ΔH°, and ΔS°) of thermodynamic parameters support that the Cr(VI) adsorption by PANI/PVA composite was spontaneous and endothermic in nature. Subsequently, the kinematic data fit to pseudo-second-order model and the sorption process was controlled by the pattern of intraparticle diffusion. Overall, the removal of Cr(VI) ions by PANI/PVA composite was driven by electrostatic adsorption coupled reduction. Based on these results, the prepared PANI/PVA composite can be considered as potential adsorbent to remove Cr(VI) ions effectively from natural ground water and industrial effluent.

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