

# Adsorption and reduction: combined effect of polyaniline emeraldine salt for removal of Cr(VI) from aqueous medium

PURNIMA BARUAH and DEBAJYOTI MAHANTA\*

Department of Chemistry, Gauhati University, Guwahati 781014, India

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**Abstract.** In this study, we have reported the removal of Cr(VI) ions by polyaniline (PANI) particles from aqueous medium. PANI in its emeraldine salt (ES) form can interact with Cr(VI), which is present as  $\text{HCrO}_4^-$  in two ways. The adsorption of  $\text{HCrO}_4^-$  ions due to the electrostatic interaction between partially positively charged PANI backbone and Cr(VI) anions causes the major portion of Cr(VI) removal and a small portion of Cr(VI) is reduced to Cr(III) by PANI (ES). The adsorption follows Langmuir adsorption isotherm and second-order kinetic model. It is observed that the removal of Cr(VI) is negligibly effected by the presence of other anions in the aqueous medium. The adsorption capacity of PANI (ES) is found to be  $123 \text{ mg g}^{-1}$ , which is very high compared to activated carbon-based materials. The adsorbed anions can be desorbed by converting PANI emeraldine salt (ES) to PANI emeraldine base (EB). The EB form of PANI can be converted into ES form by treating with acid, which can be reused as adsorbent. It is important to note that the PANI (ES) is oxidized by  $\text{HCrO}_4^-$  ions which decrease the hydrophilicity of the surface of PANI particles. This causes the decrease in adsorption capacity of recycled PANI.

**Keywords.** Adsorption; Cr(VI) ions; polyaniline; kinetics.

## 1. Introduction

The removal of different pollutants from environment becomes a major concern in recent times. Lots of research activities have been carried out for removal of different pollutants from waste water [1–4]. Cr(VI) ion is one of the major industrial wastes as dichromate and chromate ions are extensively used in various industrial applications such as in metal plating, corrosion control agents, leather industries, wood treatment, etc [5–8]. It is also well known that Cr(VI) is toxic and it may cause many diseases such as cancer, epigastric pain, vomiting, nausea and many more [9–12]. For the toxic nature of Cr(VI) in aqueous medium, it becomes a serious environmental issue to remove it from water. Various techniques such as adsorption [13–15], chemical reduction [16], reverse osmosis [17], electrolysis [18], etc. have been employed for Cr(VI) removal from waste water. Among these techniques, adsorption has many advantages such as easy handling, availability of many cost-effective adsorbents and high efficiency [19].

Conducting polymers and their various composite materials have attracted the researchers for their exciting electrical and optical properties [20]. These classes of materials have wide range of applications such as solar cells, light-emitting diodes, field effect transistors, etc [21–24]. Polyaniline (PANI) is one of the most important members of conducting polymer family due to its easy synthesis, high environmental stability, high conductivity and low cost [25]. The

doped form of PANI (emeraldine salt) is formed by the conventional chemical oxidation method [26]. PANI emeraldine salt can be converted into undoped emeraldine base (EB) by simple base treatment. Thus, very simple doping/dedoping is possible in this polymer by acid and base treatment, respectively. PANI is known to be a promising polymeric material for a wide range of applications such as sensors, batteries, actuators, corrosion protection, electrochromic devices, etc [27–31]. PANI has been used for the removal of various dyes from waste water [32–35]. The electrostatic interaction between the positively charged PANI backbone and organic anions in aqueous medium is responsible for high efficiency of adsorption on PANI particles [33].

Many groups have reported the removal of toxic Cr(VI) by PANI and PANI-based composite materials [36–39]. According to these reports, the removal of Cr(VI) is due to the reduction of Cr(VI) to Cr(III) by PANI. In this report, we have shown the efficient removal of Cr(VI) from aqueous medium by bulk PANI (ES) synthesized by chemical oxidation method. We have proposed that the high removal of Cr(VI) is due to dual activity of PANI (ES). It acts both as an excellent adsorbent material and a small amount of Cr(VI) is converted into Cr(III) by PANI (ES). We have investigated the adsorption of Cr(VI) ions ( $\text{HCrO}_4^-$ ) on HCl-doped PANI emeraldine salt. The detailed kinetics of adsorption has been studied in this paper. The adsorption of Cr(VI) on PANI in the presence of other anions in the aqueous medium has also been investigated. The adsorption studies have been carried out in two different temperatures to know the thermodynamic nature of adsorption. The adsorbed Cr(VI) ions can be

\* Author for correspondence (debam@gauhati.ac.in)

desorbed from PANI (ES) particles by converting PANI (ES) into PANI (EB) by treating with 1 (M)  $\text{NH}_4\text{OH}$  solution. The reusability of the adsorbent has been investigated. It was noted that there may be structural change of surface PANI polymer chains due to partial oxidation, which decreases the hydrophilicity of the PANI surfaces, which is responsible for decrease in adsorption after few recycles. The mechanism of Cr(VI) adsorption on PANI particles has also been proposed in this paper.

## 2. Experimental

### 2.1 Materials

Aniline (Merck, India) was purified by distillation before use. Ammonium persulfate (APS), hydrochloric acid (HCl), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), sodium chloride (NaCl), sodium acetate ( $\text{CH}_3\text{COONa}$ ), *N*-methyl-2-pyrrolidone (NMP), ammonia solution and acetone are bought from Merck, India, and used as received. Distilled water was used for all the experiments.

### 2.2 Synthesis of polyaniline

Polyaniline emeraldine salt (PANI (ES)) was synthesized by chemical oxidative polymerization method. In this method, 5 g aniline was dissolved in 150 ml of 1 HCl and stirred in an ice bath for 1 h. 12.25 g APS was dissolved in 50 ml of 1 M HCl and kept in an ice bath. APS solution in 1 M HCl was taken in a burette and added to aniline solution under constant stirring. The temperature of the reaction mixture was maintained at 0–5°C by slow addition of APS. It was taken 45 min for complete addition of APS. The reaction mixture was stirred at room temperature for 6 h. The product was washed with distilled water for several times and finally washed with acetone to remove low-molecular-weight oligomers. The final green product (PANI (ES)) was dried in air and kept in a desiccator. PANI (EB) was synthesized by stirring 1 g PANI (ES) in 1 M  $\text{NH}_4\text{OH}$  solution for 6 h. The blue product was washed with distilled water for several times and dried in air, then kept in a desiccator.

### 2.3 Adsorption experiments

A series of adsorption experiments have been performed to study the equilibrium and kinetics of adsorption. Different amounts of PANI samples have been added to a 250 ml conical flask containing 100 ml of Cr(VI) solution with different concentrations. The solution containing PANI particles as adsorbent was stirred with magnetic stirrer in a constant stirring rate. Same conditions of stirring were maintained for all the adsorption experiments. Small amounts of solution from the conical flask were removed at different time intervals. The solutions were filtered just after removal from the conical flask, where the adsorption experiment was performed to remove the PANI particles from the collected samples. Concentration of Cr(VI) ions in the reaction mixture at different times can be determined by using UV/Vis

spectroscopy. A calibration curve was obtained from known concentrations of Cr(VI) solutions.

The PANI samples before and after the adsorption of Cr(VI) ions were characterized by UV/Vis spectroscopy (UV 1800-Shimadzu) and XRD analysis was done on Phillips X'pert pro diffractometer with  $\text{CuK}\alpha$  radiation at the scanning rate of  $1^\circ \text{min}^{-1}$ .

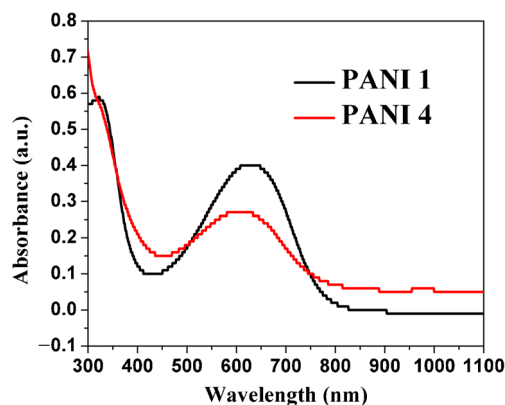
## 3. Results and discussion

### 3.1 UV-spectral study

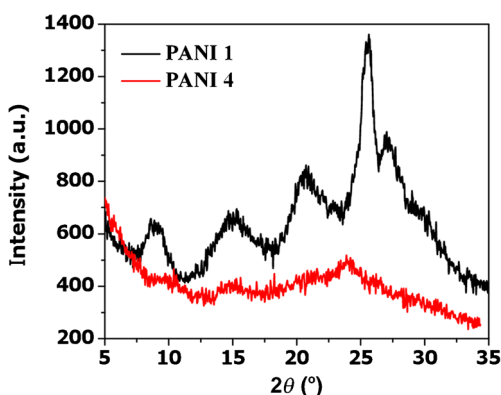
The UV/Vis spectra of PANI samples before Cr(VI) adsorption (PANI 1) and after Cr(VI) adsorption (PANI 4) are shown in figure 1. All spectra were recorded by dissolving the samples in NMP. In PANI, two absorption peaks were observed, one at around 630 nm and another at 320 nm. The absorption peak at 320 nm was due to  $\pi \rightarrow \pi^*$  transition. The molecular excitation associated with quinone diimine structure was responsible for the broad absorption peak at 630 nm. These were characteristic peaks of PANI (EB) [40]. It is already known that PANI (ES) on dissolving in NMP gets converted into undoped form PANI (EB) [41,42]. A slight blue shift of the absorption peak at 630 nm was observed in the case of PANI 4. This is due to partial oxidation of emeraldine form into pernigraniline form [43]. As the shift is very small the conversion of emeraldine to pernigraniline is very small and most of Cr(VI) ions are adsorbed rather than involving in the oxidation of PANI emeraldine form. This phenomenon is supported by XRD analysis and desorption experiments, where adsorbed Cr(VI) ions can be got back in the aqueous solution by treating with 1 M  $\text{NH}_4\text{OH}$ . The Cr(VI) ion concentration desorbed from PANI particles is less than the adsorbed Cr(VI) ion concentration. It indicates that some Cr(VI) ions are involved in oxidation of PANI emeraldine form into pernigraniline form.

### 3.2 XRD studies

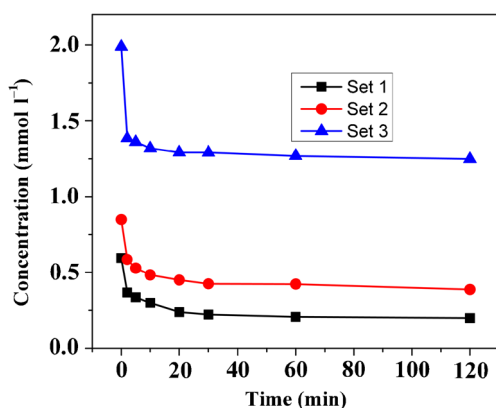
The XRD patterns of PANI samples before adsorption (PANI 1) and after adsorption of Cr(VI) ions (PANI 4) are shown in



**Figure 1.** UV/Vis spectra of PANI before Cr(VI) adsorption (PANI 1) and after Cr(VI) adsorption (PANI 4).



**Figure 2.** XRD of PANI samples before (PANI 1) and after Cr(VI) adsorption (PANI 4).

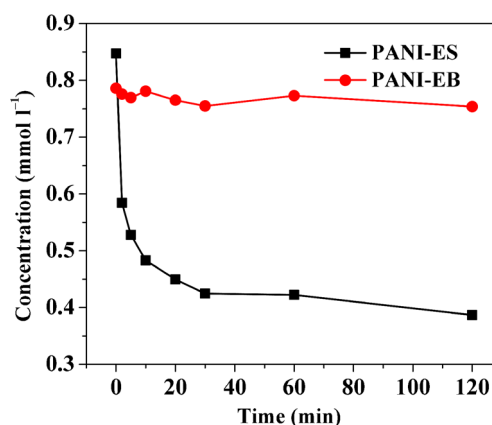


**Figure 3.** Concentration profile of Cr(VI) ion with different initial concentrations in the presence of PANI (ES).

figure 2. The powder diffraction patterns of PANI (ES) show four characteristic features of four reflection at  $2\theta = 9.4, 15.1, 20.5$  and  $25.5^\circ$ . The diffraction pattern is in agreement with values reported by several groups [44,45]. After adsorption of Cr(VI) the sample shows amorphous nature. This can be explained by the partial oxidation of emeraldine form into pernigraniline form. The partial oxidation has reduced the intramolecular hydrogen bonding in the PANI matrix, which is responsible for the reduction in crystalline nature of the polymer.

### 3.3 Cr(VI) adsorption experiments

All Cr(VI) adsorption experiments were carried out for 2 h duration. It was observed that after 2 h, there was no significant ion adsorption by PANI (ES). In figure 3, the change of Cr(VI) concentration with the contact time with different initial concentrations of Cr(VI) is shown. All experiments were carried out for 100 ml Cr(VI) solution with different initial concentrations and 20 mg PANI (ES) as adsorbent. From this concentration profile, it was observed that the amount of Cr(VI) ion adsorption at equilibrium increases with the increase in initial Cr(VI) ion concentration. But there is a



**Figure 4.** Comparison of concentration profiles of Cr(VI) ion in the presence of PANI (ES) and PANI (EB).

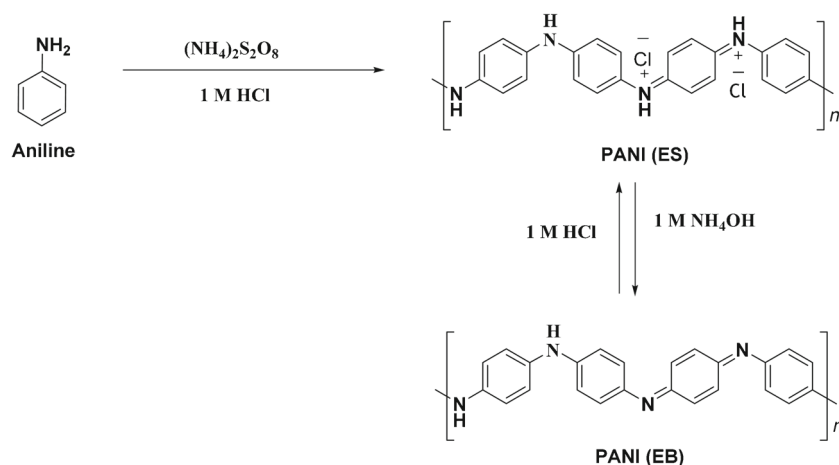
maximum limit for a particular amount of adsorbent above which it cannot adsorb with increase in initial concentration of adsorbate.

In figure 4, the comparison of concentration profiles of Cr(VI) ions in presence of 20 mg PANI (ES) and 20 mg PANI (EB) is shown. It was observed that PANI (EB) shows negligible Cr(VI) ion adsorption in comparison to PANI (ES). This is due to the structural difference between PANI (ES) and PANI (EB). PANI (ES) has partial positive charge in its chain, while PANI (EB) is neutral as shown in scheme 1. The positively charged PANI (ES) can adsorb the Cr(VI) anions due to electrostatic interaction, which does not occur in the case of PANI (EB).

The effect of adsorbent amount on the Cr(VI) ion removal is shown in figure 5. In all cases, the volumes of Cr(VI) ion solutions and their initial concentrations were same. It is observed that Cr(VI) ion adsorption increases with increase in amount of adsorbent. With increase in amount of adsorbent, the number of active sites of adsorption also increases, where the Cr(VI) ions can be adsorbed by simple electrostatic interaction.

Temperature is known to be a very important parameter which affects the adsorption phenomenon. The effect of temperature on Cr(VI) ion adsorption is shown in figure 6. It was observed that temperature has a very little effect on adsorption in this case. But the adsorption increases with increase in temperature. These results indicate that the adsorption of Cr(VI) ion on PANI (ES) is slightly endothermic.

Reusability of an adsorbent is a very important issue for its practical application. To examine the reusability of PANI (ES), 10 mg PANI (ES) was used as adsorbent for 100 ml of  $1.4 \text{ mmol l}^{-1}$  Cr(VI) solution for 2 h duration. The amount of Cr(VI) ion adsorption was determined by UV/Vis spectroscopy as discussed earlier. After adsorption, the adsorbent containing the Cr(VI) ions was separated and washed with distilled water and then stirred with 100 ml 1 M  $\text{NH}_4\text{OH}$  solution to convert the PANI (ES) to PANI (EB). The PANI (EB) has neutral structure as shown in scheme 1. The PANI (EB) cannot hold the negatively charged Cr(VI) ions on it



Scheme 1. Chemical oxidative polymerization of PANI (ES) and PANI (EB).

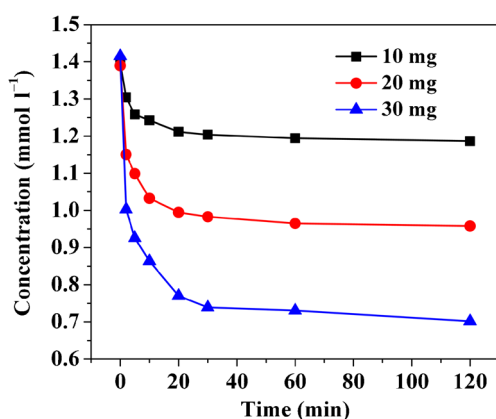


Figure 5. Concentration profile of Cr(VI) ion with different amounts of adsorbent.

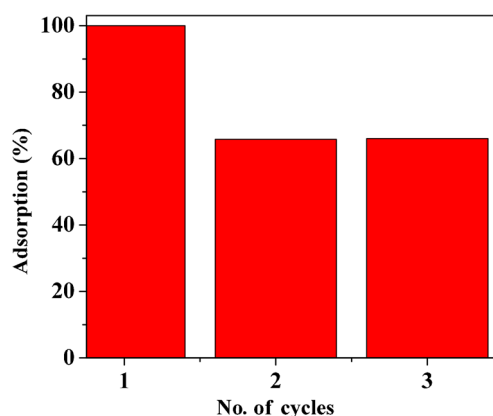


Figure 7. Adsorption of Cr(VI) ion with recycled PANI (ES).

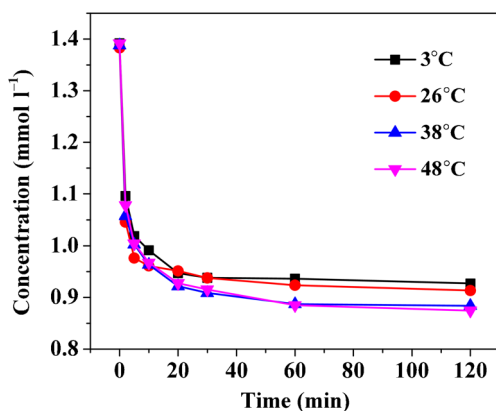


Figure 6. Effect of temperature on Cr(VI) ion adsorption by PANI (ES).

and hence desorption occurs. Each desorption experiment was continued for 2 h duration. After 2 h, the PANI (EB) was separated and washed with distilled water. Then the PANI (EB) sample was stirred with 100 ml 1 M HCl solution for 2 h to convert PANI (EB) to PANI (ES). The recycled PANI (ES)

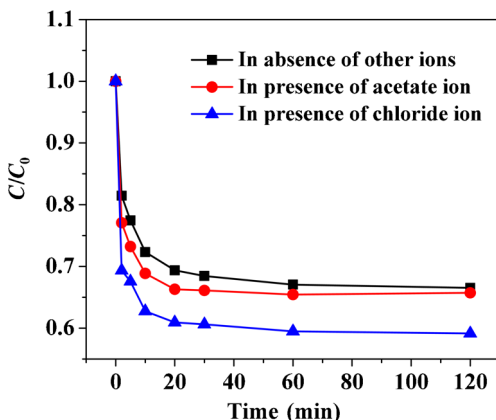
sample was washed and dried. The sample was then ready for 2nd cycle of Cr(VI) ion adsorption experiment under identical conditions as mentioned above. The PANI (ES) was recycled and its equilibrium adsorption was determined after each cycle. It was observed that the equilibrium adsorption of the recycled PANI (ES) sample decreases to 65% of 1st cycle. This may be due to two reasons. The partial oxidation of PANI particle surfaces by Cr(VI) ions introduces hydrophobicity to the surface, which reduces the Cr(VI) adsorption on recycled PANI particles in aqueous medium. Moreover, the incomplete desorption of Cr(VI) ions may be another reason for lower adsorption by recycled PANI samples. Some Cr(VI) ions may diffuse into the pores of PANI (ES) particles. These entire pores occupied Cr(VI) ions may not desorb in 2 h on the addition of 1 M NH<sub>4</sub>OH base solution. Adsorption of Cr(VI) ion with PANI (ES) after different numbers of recycle steps are shown in figure 7.

As the pollutants are present as mixture of many components, it is important to investigate the adsorption of Cr(VI) ions by PANI (ES) in the presence of other anions. We examine the adsorption profile of Cr(VI) ion solution in the presence of equimolar amount of NaCl and CH<sub>3</sub>COONa and

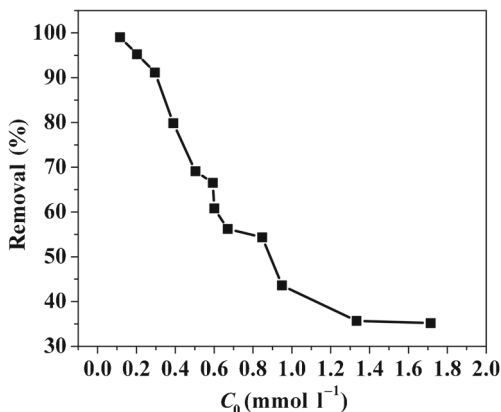
the results are shown in figure 8. It was observed that the presence of these two ions have a negligible effect on the adsorption of Cr(VI) ions from the aqueous solution.

### 3.4 Equilibrium adsorption studies

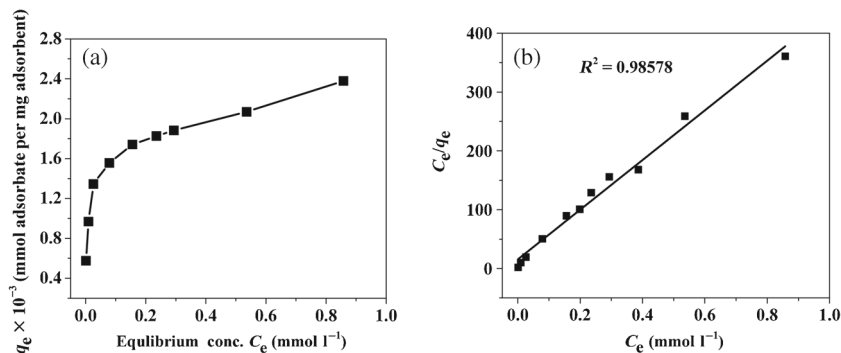
The equilibrium adsorptions of Cr(VI) ions on 20 mg PANI (ES) have been determined with different initial Cr(VI)



**Figure 8.** Adsorption profile of Cr(VI) ions by PANI (ES) in the presence of other anions.



**Figure 9.** % Cr(VI) ion removal as a function of initial concentrations.



**Figure 10.** (a) Variation of equilibrium amount adsorbed with equilibrium concentration and (b) linear variation of  $C_e/q_e$  with  $q_e$ .

concentrations. It has been observed that the obtained data were best fit on Langmuir adsorption isotherm.

The percentage removal of dye was calculated by using the formula:

$$\text{Percentage removal} = 100 \frac{C_0 - C_e}{C_0}$$

The % of removal was 100% for low  $C_0$ . It decreases with increase in initial concentration of Cr(VI) ions in the solution. The effect of initial Cr(VI) ion concentration on the % of removal of the ion from aqueous solution is shown in figure 9.

The equilibrium uptake was calculated as

$$q_e = \frac{(C_0 - C_e)V}{W}$$

In the above equation,  $q_e$  is the amount of Cr(VI) ions adsorbed by PANI at equilibrium,  $C_0$  the initial concentration of the Cr(VI) solution and  $C_e$  the equilibrium concentration of the Cr(VI) solution in  $\text{mmol l}^{-1}$ .  $V$  is the volume of the solution in litre and  $W$  the mass of PANI in milligrams for the experiments. The variation of  $q_e$  with  $C_e$  is shown in figure 10a.

This model assumes that the uptake of adsorbate ions occurs on the homogeneous surface of the adsorbent by monolayer adsorption. This indicates that

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_2 q_m}$$

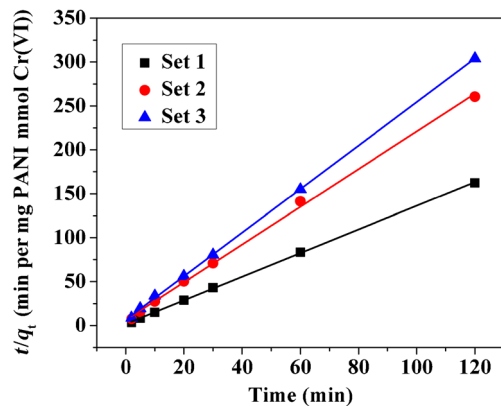
where  $k_2$  is the Langmuir adsorption constant in litre per mmol and  $q_m$  the adsorption capacity in mmol adsorbate per mg adsorbent. Thus, a plot of  $C_e/q_e$  vs.  $C_e$  should be linear as shown in the figure 10b. The values of  $k_2$  and  $q_m$  are  $2.62 \times 10^{-2} \text{ l mmol}^{-1}$  and 2.4 mmol Cr(VI) per mg PANI (123 mg Cr(VI) per g PANI), respectively.

### 3.5 Kinetic studies

Figure 3 shows the concentration profile of Cr(VI) ions with different initial concentrations in presence of 20 mg PANI as

adsorbent. A rapid uptake of Cr(VI) ions by PANI indicates maximum efficiency and this occurs in physical adsorption or strong chemisorption. A second-order model for adsorption indicates

$$\frac{dq_t}{dt} = k_s(q_e - q_t)^2,$$



**Figure 11.** Second-order kinetic plots for removal of Cr(VI) ions with different initial concentrations by PANI.

where  $k_s$  is the rate constant and  $q_t$  the amount adsorbed at time  $t$  in mmol Cr(VI) per mg PANI. The above equation can be integrated with initial condition of  $q_t = 0$  at  $t = 0$ ,

$$\frac{t}{q_t} = \frac{1}{k_s q_e^2} + \frac{1}{q_e} t.$$

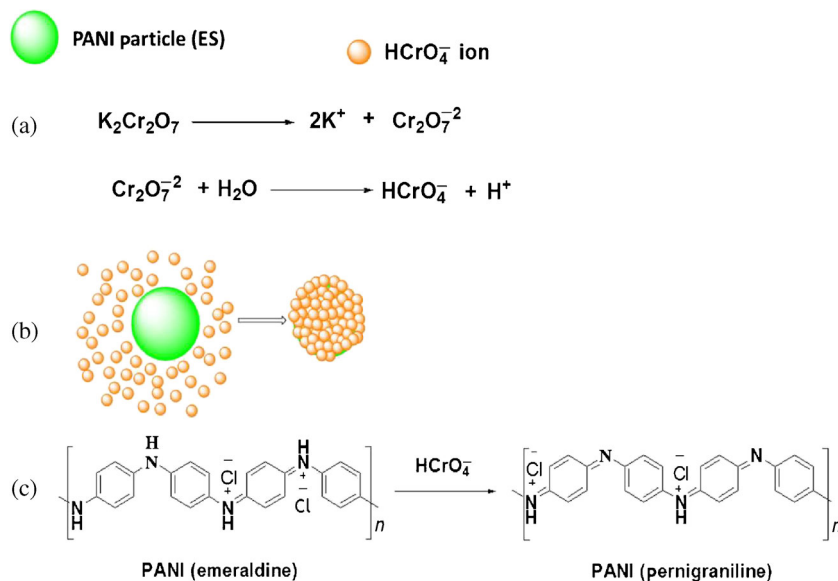
The plot of  $t/q_t$  vs.  $t$  is shown in figure 11. The values of  $q_e$  and  $k_s q_e^2$ , for different initial concentrations of Cr(VI) are determined from the slope and intercept of the plots. These values are given in table 1.

### 3.6 Mechanism

The mechanism of Cr(VI) adsorption on PANI (ES) is similar to the anionic dye adsorption mechanism by PANI (ES) reported in previous studies. As the  $\text{HCrO}_4^-$  ion is an oxidizing agent, a small amount of Cr(VI) ions were involved in oxidation of PANI (ES) which is not occurring in the case of dye adsorption on PANI (ES) [33,34]. The mechanism of Cr(VI) removal from aqueous solution is proposed as shown in scheme 2. Potassium dichromate is dissociated into potassium ion ( $\text{K}^+$  ion) and  $\text{HCrO}_4^-$  ion as shown in scheme 2a. When PANI (ES) powder was added to the

**Table 1.** Kinetic parameters for the removal of Cr(VI) by PANI (ES).

Initial Cr(VI) concentration ( $C_0$ )	$q_e$ (mmol Cr(VI) per mg PANI)	$K_s q_e^2$ (mmol Cr(VI) per mg PANI per min)
2 mmol	0.743	0.572
0.84 mmol	0.466	0.16
0.6 mmol	0.403	0.15



**Scheme 2.** Mechanism for adsorption of Cr(VI) ions on PANI (ES). (a) Dissociation of potassium dichromate in water medium, (b) adsorption of  $\text{HCrO}_4^-$  on PANI particles and (c) oxidation of PANI emeraldine form into PANI pernigraniline form.

**Table 2.** Adsorption capacity values of Cr(VI) adsorption by some adsorbents.

Adsorbents	Adsorption capacity (mg g <sup>-1</sup> )
PANI (ES)	123.21
Activated carbon (coconut tree saw dust) [46]	3.46
Wool [47]	41.17
Olive cake [47]	33.44
Saw dust [47]	15.82
Chemically activated <i>syzygium jambolanum</i> nut carbon (CHSJC) [48]	100
<i>Hevea brasiliensis</i> (rubber wood) saw dust-activated carbon [49]	44.04
Nitric acid oxidized commercial activated carbon [50]	15.47
Orange peel (white inner skin) [50]	125
Irish sphagnum moss peat [50]	119
PEI wool [50]	330.9

aqueous solution of potassium dichromate,  $\text{HCrO}_4^-$  ions get adsorbed on the surface of PANI particles due to electrostatic interaction (scheme 2b). As  $\text{HCrO}_4^-$  ions are good oxidizing agents, a small portion of these ions are involved in oxidation of PANI emeraldine form into more oxidized PANI pernigraniline form as shown in scheme 2c. Although doped form of both PANI emeraldine and pernigraniline forms have same number of positive sites per repeating unit, pernigraniline form has less number of  $-\text{NH}$  groups in its backbone. It reduces the intermolecular hydrogen bonding in the more oxidized pernigraniline form of PANI, which is responsible for decrease in crystallinity of PANI sample after Cr(VI) adsorption. Thus, this mechanism is supported by the results obtained from UV/Vis spectral analysis, XRD analysis and desorption experiments.

### 3.7 Comparison of adsorption capacity with some other adsorbents

The adsorption capacity of PANI (ES) for Cr(VI) adsorption was compared with some common adsorbents like activated carbon-based materials from literature in table 2. It was observed that the adsorption capacity of PANI (ES) is among the adsorbents with very high Cr(VI) uptake capacity reported in the literature. The adsorption capacity of the material is higher than the activated carbon-based materials.

## 4. Conclusion

We have studied the application of PANI (ES) for adsorption of Cr(VI) ions from aqueous solution. It was found that the adsorption follows the Langmuir adsorption isotherm and second-order kinetics. The adsorption of Cr(VI) ions on PANI particles is slightly endothermic. The effect of other anions on the adsorption of Cr(VI) ions was observed to be very negligible. It shows the selectivity of Cr(VI) adsorption on PANI surface. The recycled PANI particles were found with lower adsorption capacity. This may be due to

the increase in hydrophobicity on PANI surface due to partial oxidation of PANI emeraldine form into PANI pernigraniline form by  $\text{HCrO}_4^-$  ions. There is a possibility of use PANI or PANI-based composite materials for adsorption of negatively charged species from aqueous medium.

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