

# An Efficient Removal of Toxic Cr(VI) from Aqueous Solution by MnO<sub>2</sub> Coated Polyaniline Nanofibers: Kinetic and Thermodynamic Study

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## Abstract

The present study explored the removal of toxic Cr(VI) ions by MnO<sub>2</sub> coated polyaniline nanofibers (MPNF) adsorbent by batch mode technique. The MnO<sub>2</sub> coated polyaniline nanofibers were synthesized by *in-situ* oxidative polymerization of polyaniline by rapid mixing technique and were employed for the removal of Cr(VI) ions from aqueous solution. The synthesized adsorbent was characterized by various techniques to elucidate the structure, composition, and morphology. The effects of pH, initial Cr(VI) concentration, adsorbent dose, temperature and operating time on adsorption were investigated. The maximum adsorption removal efficiency was observed at low pH i.e., 1.0. Spectrophotometric method was used to examine the Cr(VI) concentration in the filtrate after batch adsorption studies. The equilibrium adsorption capacity and adsorption kinetics followed Freundlich isotherm and pseudo-second-order respectively, with a capacity of 39.3 mg/g. The thermodynamic study parameters like:  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  revealed that the adsorption process is spontaneous and endothermic at high temperature.

**Keywords:** Adsorption; Isotherms; Pseudo second order kinetics; Thermodynamic studies

## Introduction

Increased population has been shown to manifest the increased industrialization to satisfy human needs. This leads to increased discharge of large amount of waste water containing non degradable, toxic heavy metals into water, which causes serious health problems to human being, aquatic life and environment as well [1]. Therefore, it is imperative to treat the waste water in order to remove or bring it to permissible level concentration by various techniques. Among such, ion exchange, precipitation, electrodialysis, osmosis, chemical precipitation, coagulation techniques are notable. [2], which already grabbed the interest as various removal techniques adopted in the past decades. Due to high cost, operation difficult, sludge formation drawbacks of the above methods [3], adsorption technique finds the place in overcoming the difficulties with its technical feasibility and high efficiency.

Most commonly, chromium exists in two different oxidation states in nature viz., Cr (III) and Cr(VI). Among these Cr(VI) is soluble, mobile, toxic, carcinogenic and is 500 times harmful in compared to Cr (III) [4], but Cr (III) is very essential nutrient for regulating the function of insulin in the human body. The World Health Organization recommends a 0.05 mg L<sup>-1</sup> maximum contaminant level of Cr(VI) in drinking water [5], while total chromium should be discharged below 2 mg L<sup>-1</sup> according to USEPA regulations [6]. The industries like leather, electroplating, dyes and pigments, metal finishing, battery manufacturing etc. are the main sources of the Cr(VI) ion effluent discharge [7].

The recent literature survey uses the various polyaniline (PANI) based adsorbents to remove toxic Cr(VI) ions from aqueous solution. This is due to the formation of chemical bonding or electrostatic force of attraction between Cr(VI) ions with amine and imine functional groups of PANI [8]. But, due to aggregation of PANI adsorbent in aqueous solution as a drawback, adsorption capacity decreases. This made the researchers to looking into PANI based nano composites.

Madi et al. reported an 95% Pb removal efficiency was achieved

by polyaniline (PANI) nanofiber composites mixed with polyvinyl alcohol or polystyrene [9]. Mahmud et al. reported that polypropylene-polyaniline nanofibers were used as an effective adsorbent material for various heavy metals from aqueous solution [10]. Zhou et al. reported polyaniline/acid treated neutral silica as a potential adsorbent in removal of Cr(VI) and PO<sub>4</sub> (III) ions from aqueous solution [11]. Ahmed and Mondal, reported that photodegradation of methylene blue by a mechanism of OH<sup>-</sup> radicals and its intermediates by polyaniline-titanium dioxide nanocomposites (PANI/TiO<sub>2</sub>) [12]. While, Bhaumik et al. performed that, selective adsorption of Cr(VI) ions from aqueous solution was achieved in the presence of other co-existing ions using polypyrrole-polyaniline (PPy-PANI) nanofiber with maximum adsorption capacity of 227 mg/g [13]. Gemeay et al. reported the, PANI-MnO<sub>2</sub> composites have been used as catalysts for the removal of textile dyes from aqueous solutions [14]. Shyaa et al. reported an *in-situ* polymerization method to synthesize PANI/zeolite nanocomposite and its application in removal of Cr(VI) ions from aqueous solution [15]. Chen et al. reported that, MnO<sub>2</sub> nanofiber alone was found to possess high adsorption capacities for heavy metal ions such as, arsenic and lead in water due to its high specific surface area and high surface activity [16]. Chen et al. have also documented that, MnO<sub>2</sub> nanofibers outperformed commercial MnO<sub>2</sub> as oxidant for As(III) to As(V) conversion and it was also an outstanding adsorbent for both As(V) and Pb(II) [17]. The adsorption of metal ions by manganese oxides depends on the nature of the metal ions, whereas heavy metals and transition elements are adsorbed by specific adsorption and selective adsorption [18].

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The present study synthesized MnO<sub>2</sub> coated polyaniline nanofibers via in-situ chemical oxidative polymerization of PANI by simple rapid mixing method. The synthesized MnO<sub>2</sub> coated PANI nanofibers were characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) techniques, point of zero charge (pH<sub>PZC</sub>) and sorption of Cr(VI) ions from aqueous solution was examined.

## Materials and Methods

### Materials

Potassium permanganate (99.9%), potassium dichromate (99.9%), aniline (99.5%), sulphuric acid (98%), hydrochloric acid (99%), ammonium peroxydisulfate (98%) were purchased from Merck, India and methanol (99.9%), 1,5-diphenylcarbazide (98%) were purchased from Sigma Aldrich, USA and were used as such without further purification. Stock solution of Cr(VI) (1000 ppm) was freshly prepared by dissolving 2.282 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 1000 ml of deionized water and is diluted for desired Cr(VI) concentration. 0.1M NaOH and 0.1M HCl were used to maintain the desired pH.

### Method

#### Synthesis of MnO<sub>2</sub> coated polyaniline nanofibers

One ml of pure aniline monomer was taken in 100 ml of 1M HCl. One equivalent of ammonium peroxydisulfate in 10 ml of 1M HCl was poured rapidly into the above mixture and stirred vigorously for 30 seconds. The mixtures were left undisturbed for 24 h. The obtained mixtures were thoroughly washed with 5.0 mM HCl followed by distilled water and methanol to obtain PANI nanofibers. Later it is dried in hot air oven at 60°C for 2 h. The obtained PANI nanofibers were further treated with 0.06 mg KMnO<sub>4</sub> in 100 ml distilled water, which favours oxidation of nanofibers in turn of reduction of Mn(VII) to Mn(IV) resulting in MnO<sub>2</sub> coated PANI nanofibers. The above mixture is stirred for 30 min. Then it is filtered and further washed with distilled water several times to reach neutral pH. Finally, the obtained product is dried at 60°C in the oven for 4 h.

#### Sorption experimental procedure of Cr(VI) ions

The percent removal efficiency of Cr(VI) ions were carried out by taking 50 ml of 10 ppm Cr(VI) ion solution in 250 ml Erlenmeyer flask with 10 mg/50 ml adsorbent dose at 250 rpm rotating speed at temperature 298 K in a constant water bath shaker. After regular time intervals, about 2 ml of Cr(VI) ion solution was drawn, centrifuged and the residual concentration of Cr(VI) ions was determined spectrophotometrically using 1,5-diphenylcarbazide as complexing agent at 540 nm absorption wavelength.

The percent removal efficiency was calculated by the following equation:

$$\% \text{ Removal} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

The adsorption capacity (q<sub>e</sub>) was evaluated by the following equation:

$$q_e = \frac{(C_o - C_e) V}{m} \quad (2)$$

Where, 'C<sub>o</sub>' and 'C<sub>e</sub>' are the initial and equilibrium concentration

of Cr(VI) ions in mg/L, 'V' is the volume of Cr(VI) ion concentration in litre and 'm' is the mass of adsorbent in grams. All the experiments were carried out in triplicate and were used for calculation.

#### Determination of point zero charge of MPNF

The pH<sub>PZC</sub> (point of zero charge) is the pH when the charge on the surface of adsorbent is zero i.e., the pH above which the total surface of the adsorbent is negatively charged and the pH below of which the adsorbent surface is positively charged [19]. The procedure of pH<sub>PZC</sub> drift method [20] could be described as follows: To a series of 250 mL conical flasks, 50 mL of 0.01N NaCl was added. Then, the initial solution pH values (say pH initial) were adjusted in the range between 1-9 with pH intervals of one, using 0.01N HCl solutions and 0.01N NaOH. After constant value of pH initial is reached, 0.010 g of MPNF sample was added into each conical flask and capped them immediately. Then, shook them for 12 h to reach equilibrium. After 12 h, pH of solution was measured and noted as pH<sub>final</sub>. The pH<sub>PZC</sub> of MPNF sample is the point when pH<sub>initial</sub> = pH<sub>final</sub>.

#### Characterization

FTIR spectra of MPNF adsorbent before and after adsorption were recorded using KBr pellet using IR Prestige (BRUKER TENSOR 27 FTIR, Nicolet) in the 400-4000 cm<sup>-1</sup> range. X-Ray diffraction pattern were recorded using CuKα radiation in 2θ range with 10-80°. SEM micrograph and EDAX analysis were done by using JEOL-JSM-5600 LV Japan, Scanning electron microscope. Chromium analysis was done by using Elico-159 spectrophotometer.

## Results and Discussion

### X-Ray diffraction

The XRD spectra of MPNF adsorbent was shown in Figure 1. The two characteristic resolved peaks at 2θ angle of 36.9° and 66.3° indicate the presence of MnO<sub>2</sub>. The same MnO<sub>2</sub> phase is correlating with JCPDS No. 42-1317 [21]. The observed low intensity peaks is due to poor crystallinity of MnO<sub>2</sub>, Zhang et al. reported the similar results [22]. The ideal diffraction peaks at 14.6°, 19.1° and 27.5° are corresponding to interaction of PANI and MnO<sub>2</sub> [23]. This shows the MnO<sub>2</sub> nanofibers may successfully coated over PANI.

### Scanning Electron Microscope

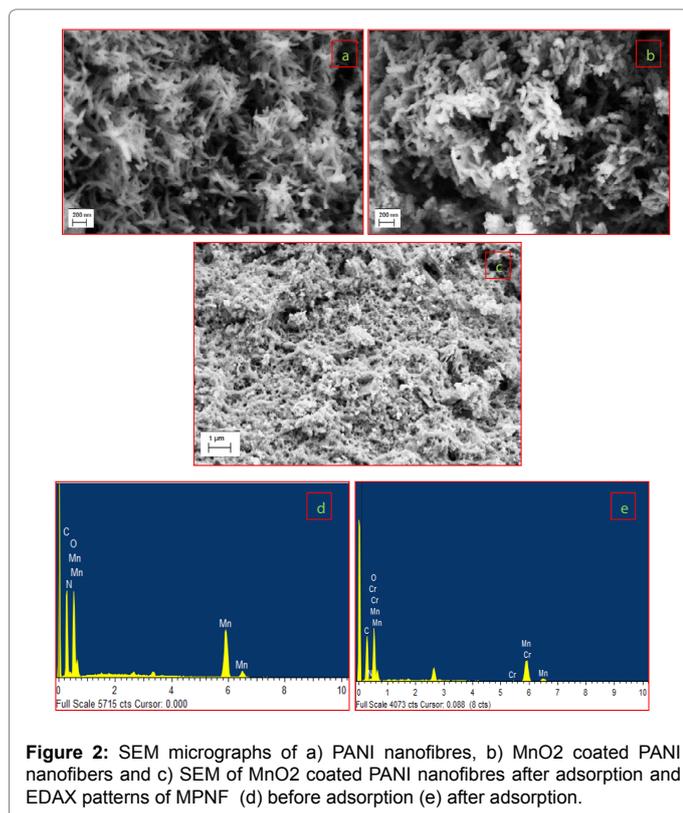
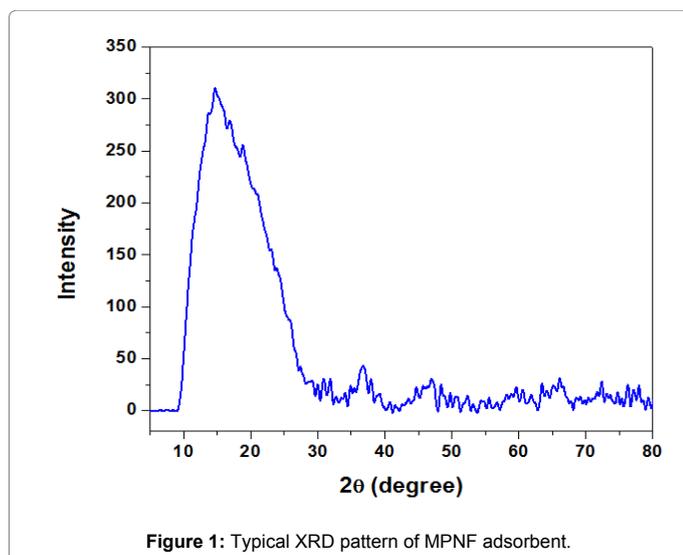
Figures 2a-2c illustrates the scanning electron microscopy images of PANI nanofibers and MnO<sub>2</sub> Coated PANI nanofibers. Uniform nanofibers can be observed in as prepared PANI and MnO<sub>2</sub> coated PANI. The nanofibers were found to have an average length of around 250-300 nm. No considerable change in morphology of nano adsorbent was observed before and after adsorption process, indicating considerable stability of as synthesized hybrid MnO<sub>2</sub> coated PANI adsorbent material.

### EDAX analysis

The chemical composition of MnO<sub>2</sub> Coated PANI nanofibers before and after adsorption of Cr(VI) was investigated by EDAX analysis (Figures 2d and 2e). Figure 2d, clearly indicating the presence of Mn, O as major constituents and slight amount of N and C impurities. In Figure 2e, Chromium peaks were clearly observed and indicating that Cr(VI) is adsorbed on MnO<sub>2</sub> Coated PANI nanofibers.

### FTIR studies

FTIR spectra of MPNF adsorbent before and after adsorption of



Cr(VI) was shown in the Figure 3. The characteristic peaks at 1579 cm<sup>-1</sup> and 1490 cm<sup>-1</sup> were relate to the stretching vibration of quinoid (-N=C<sub>6</sub>H<sub>4</sub>=N-) ring and benzenoid ring (-C<sub>6</sub>H<sub>4</sub>-) respectively [24]. The peak at 508 cm<sup>-1</sup> indicating stretching vibration the Mn-O bond and also an additional typical peak at 835 cm<sup>-1</sup> is observed and attributed to stretching of 1,4-substituted phenyl ring indicating the backbone of mesoporous PANI-MnO<sub>2</sub> nanocomposite [23]. The peaks at 1305 cm<sup>-1</sup> and 1579 cm<sup>-1</sup> correspond to the C-N and C=N bonds, are the emerging of characteristic absorption bands of PANI/MnO<sub>2</sub> composite indicating the existence of both components in the nanofibers. The shifting of the band from 2985 cm<sup>-1</sup> to 2920 cm<sup>-1</sup> may be as an indicative of electrostatic adsorption between adsorbent and Cr(VI) ions [25].

## Effect of pH

pH is an important parameter that affects the surface charge of an adsorbent and speciation of heavy metal ions at different pH in the adsorption process [26]. The equilibrium concentrations of Cr(VI) ions from aqueous solution as a function of pH is shown in the (Figure 4). From the (Figure 4), it is observed that, there is a decreased adsorption tendency of Cr(VI) ions with increase in pH indicating that pH is significantly affecting the adsorption process. The sharp declining of percentage removal of Cr(VI) from 98% to 12% at corresponding pH 1-9. In the pH range of 1.0-6.0, chromium ions co-exists in different forms such as Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, HCrO<sub>4</sub><sup>-</sup>, Cr<sub>3</sub>O<sub>10</sub><sup>2-</sup>, Cr<sub>4</sub>O<sub>13</sub><sup>2-</sup> of which HCrO<sub>4</sub><sup>-</sup> predominates. As the pH of the solution increases, the predominant species are then CrO<sub>4</sub><sup>2-</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> [27]. The pH<sub>PZC</sub> of the MPNF adsorbent was found to be 3.8 (Figure 5), as a result of this the pH<sub>PZC</sub> > pH of the solution indicating that the surface of MPNF adsorbent is positively charged. So electrostatic force of attraction exists between positively charged surfaces with negatively charged hydrogen chromate ions (Figure 6). The gradual decrease in adsorption is observed above pH 3, is attributed to decreased surface positive charge upon increase in pH. At above pH 7, development of competitiveness between oxyanions of chromium and hydroxyl ions of the solution.

## Effect of adsorbent dose

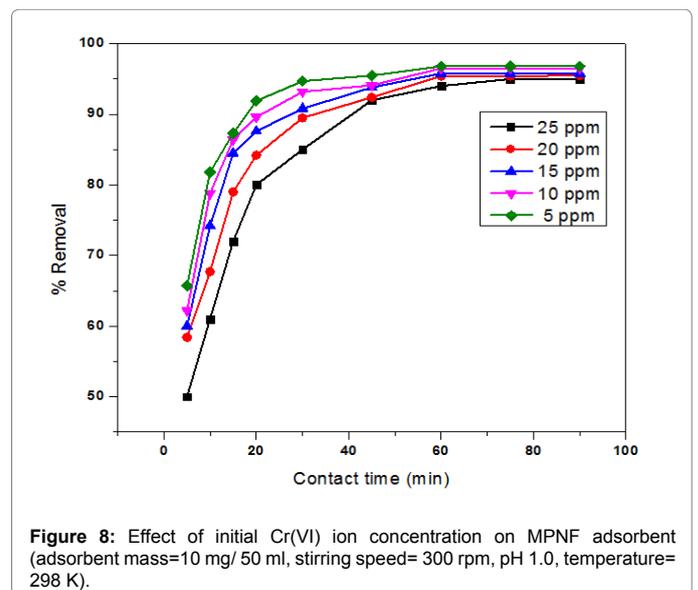
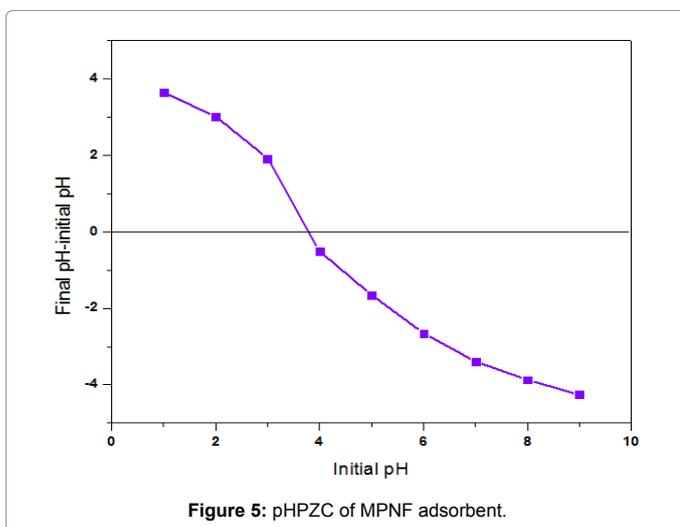
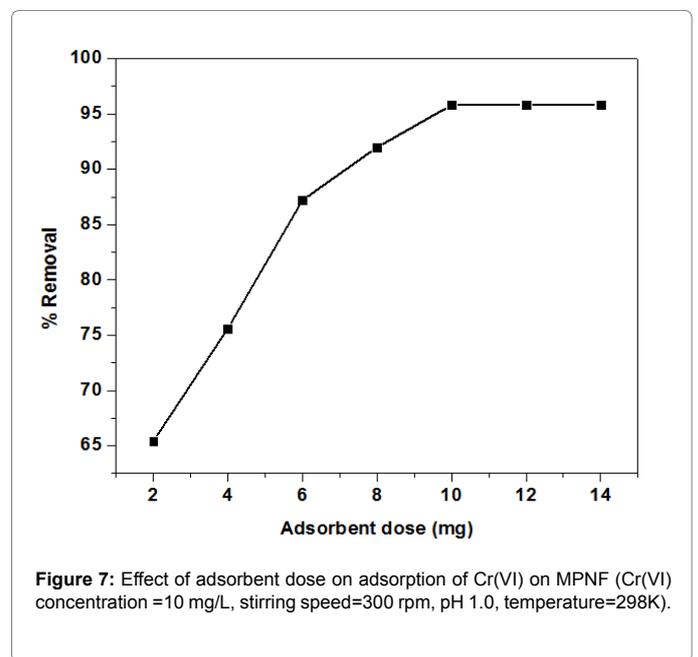
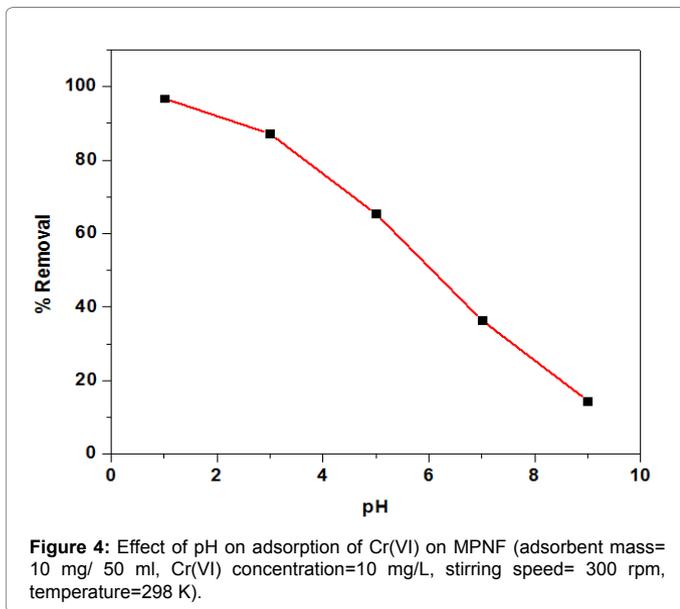
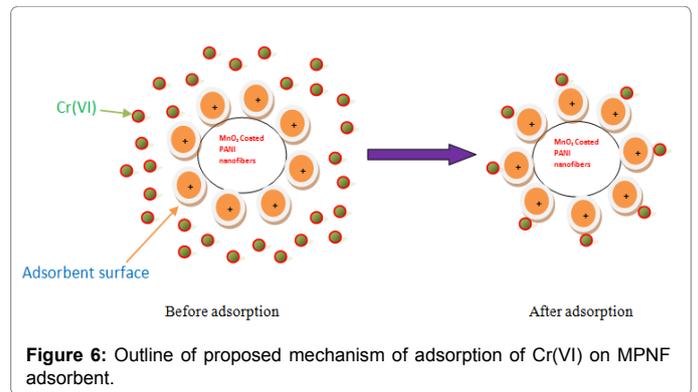
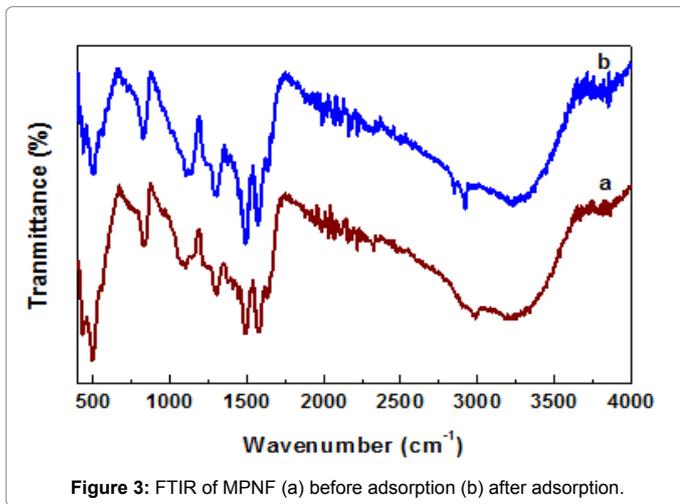
To evaluate the influence of adsorbent mass on percentage removal of Cr(VI) ions from aqueous solution was investigated and shown in (Figure 7). The corresponding Cr(VI) ion removal efficiency from 65.4 to 95.8% was observed upon varying adsorbent mass from 10 mg/50 ml to 14 mg/50 ml resulting an gradual increased removal efficiency with increase in adsorbent mass. It is attributed to increased adsorbent mass leads to increased surface area and number of active sites. Based on the above results, the optimum removal efficiency can be achieved at an adsorbent mass concentration of 20 mg /100 ml after 60 min of contact time. There is no significant percentage removal efficiency was observed beyond 200 mg/L of adsorbent mass is may be due to saturation of adsorption sites.

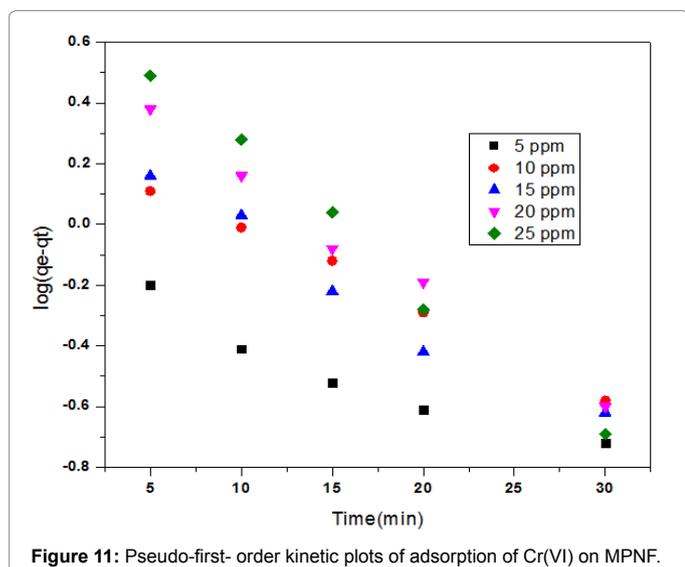
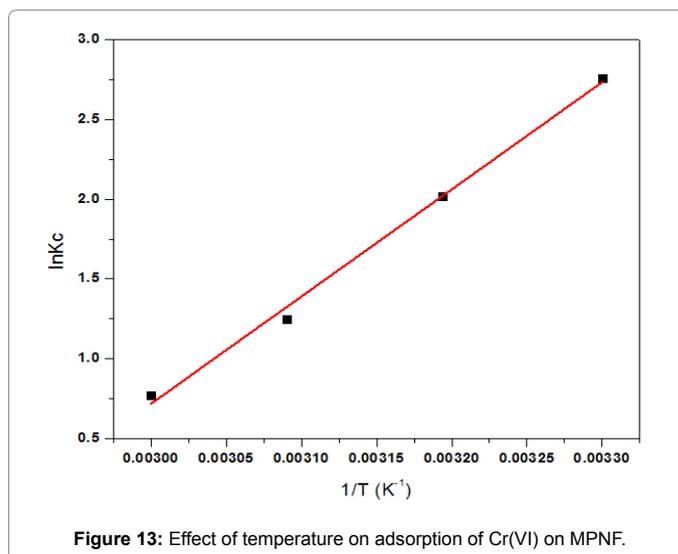
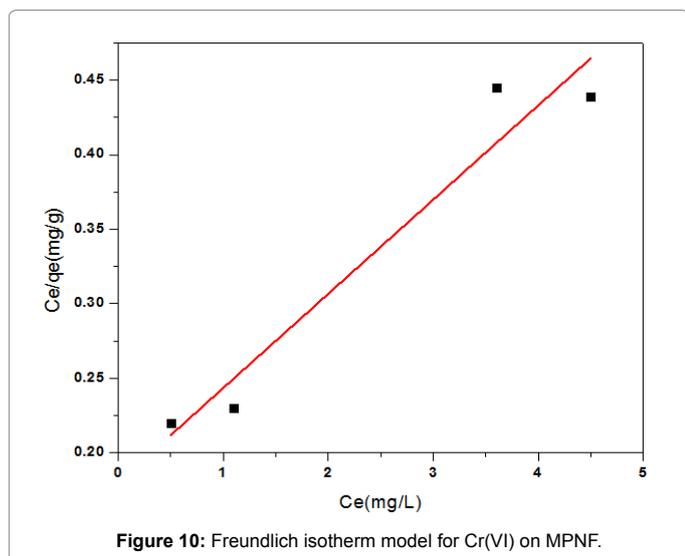
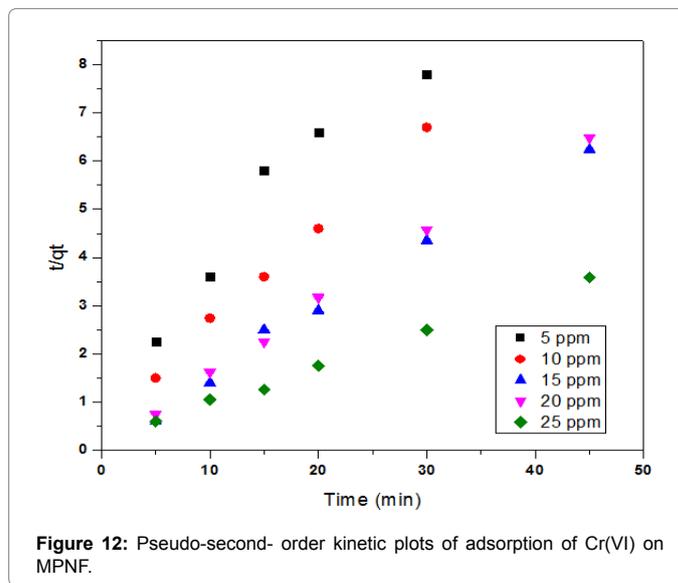
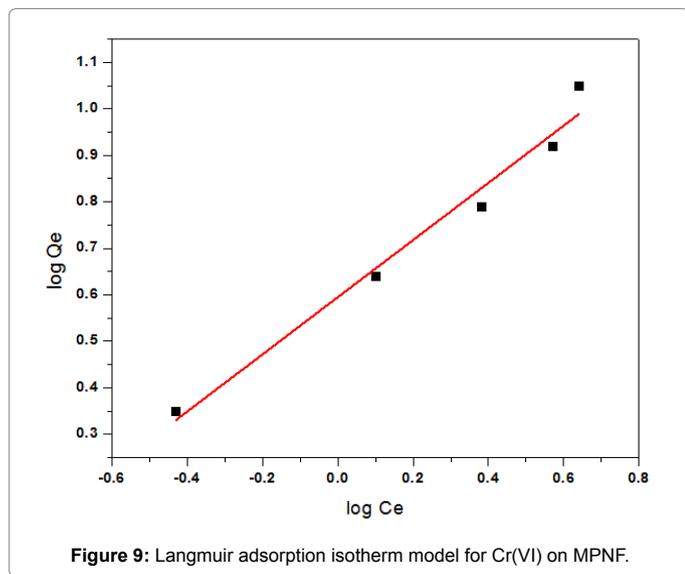
## Effect of initial Cr(VI) ion concentration

To assess the effect of initial Cr(VI) ion concentration, the concentration range 5 mg/L -25 mg/L was taken at 298K, at pH 1.0, 250 rpm speed, and 20 mg/100 ml of adsorbent dose and the results are shown in Figure 8, it is inferred that the removal efficiency of Cr(VI) ions for lower concentrations was achieved in shorter contact time and increases with increase in concentration. This may be due to the sufficient availability of adsorption sites for Cr(VI) ions for lower concentration and thereby increased number of Cr(VI) ions upon increase in concentration of Cr(VI) to 25 mg/L at constant adsorbent mass of 0.2 g/L. At higher concentrations of Cr(VI), an aroused competition between adsorbate molecules and active sites of adsorbent surface. This brought in consequent decrease in adsorption process with increase in concentration results [28].

## Point of zero charge

The pH<sub>PZC</sub> of MPNF adsorbent was found to be 3.8. Ajith et al. reported that, the pH point of zero charge (pH<sub>PZC</sub>) for manganese dioxide was between pH 3 and 4 [29], indicates the predominance of positively charged surface of the MPNF adsorbent [30]. From Figure 5, it is observed that the pH<sub>PZC</sub> of the MPNF adsorbent was found to be 3.8, revealing that the surface is possessing positive charge and hence it attracts the predominating hydrogen chromate ions species at pH 1.0 from aqueous solution.





### Adsorption isotherms

The mathematical form of sorption equilibrium clearly explains the surface properties and affinity of adsorbent at a given pH and temperature. In betterment understanding up of adsorption mechanism between adsorbate molecules and adsorbent surface at equilibrium, isotherm models, namely, Langmuir and Freundlich models were used to fit the adsorption equilibrium data.

### Langmuir isotherm

The Langmuir equation is probably the best known and most widely applied sorption isotherm [31]. The Langmuir equation is based on the assumption of monolayer adsorption between adsorbent surface and adsorbate containing an identical with finite number of active sites and is energetically equivalent. The linear expression of Langmuir equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

Where  $C_e$  (mg/L) is the equilibrium concentration of Cr(VI) ions in solution,  $q_e$  (mg/g) is the amount of Cr(VI) adsorbed on adsorbent at equilibrium,  $q_{max}$  is the amount of Cr(VI) adsorbed at complete monolayer (mg/g),  $K_L$  is the Langmuir constant related to the binding site (L/mg). A plot of  $C_e/q_e$  vs.  $C_e$ , a straight line with slope  $q_e$  and intercept  $K_L$  is obtained and is shown in (Figure 9).

An essential characteristics of the Langmuir isotherm, which is commonly known as separation factor or equilibrium parameter ( $R_L$ ) and it can be obtained as:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

Where  $b$  is the Langmuir constant and  $C_0$  is the highest initial concentration of Cr(VI) ions (mg/ L). The value of  $R_L$  indicates adsorption nature to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ) [32]. The high regression constants ( $R^2 > 0.90$ ) for both Langmuir and Freundlich isotherms indicating that the adsorption is well fitted with experimental data and the observed  $R_L$  value of 0.46 indicating it lies in between 0-1 proved to be favorable adsorption (Table 1). But it is better fit for the Freundlich isotherm model than Langmuir. The overall experimental data indicated that the adsorption sites are heterogeneous with multilayer adsorption is occurred at equilibrium [33-34].

### Freundlich isotherm

In order to describe the interaction between Cr(VI) ions and the adsorbent surface and to fit the adsorption equilibrium data [35], a linear form of Freundlich expression is as follows:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (5)$$

Where  $K_f$  and  $n$  are the isotherm constants of the Freundlich equation and the regression coefficients ( $R^2$ ) were calculated from the plot of  $\log q_e$  and  $\log C_e$  depicted in Figure 10.

From Freundlich adsorption isotherm model, the obtained values of  $n$  is greater than 1 (Table 1) represents the adsorption is favourable with high correlation coefficient value ( $R^2 = 0.9703$ ) in compared to Langmuir isotherm model. Therefore the adsorption process is best obeyed Freundlich isotherm model than Langmuir [15].

### Kinetic modelling

In order to analyze the adsorption equilibrium kinetic data of Cr(VI) ions from aqueous solutions on adsorbent surface, Lagergren first-order [36] and pseudo second-order [37] rate equations were used.

The rate equations have been widely used for estimation of adsorption rates and to predict characteristic of possible reaction mechanisms. Based on the agreement between experimental ( $q_e(\text{exp})$ ) and theoretical ( $q_e(\text{theor})$ ) uptake values and linear correlation coefficient ( $R^2$ ) values the best fit model was selected.

The linear form of pseudo-first-order kinetic equation is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

where  $q_e$  and  $q_t$  are the sorption capacity at equilibrium (mg/g) and

any time  $t$ , respectively, and  $k_1$  is the rate constant of pseudo-first-order ( $\text{min}^{-1}$ ) kinetics.

The linear form of pseudo-second-order kinetic equation is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

and  $k_2$  is the rate constant of the pseudo second-order adsorption process ( $\text{mg}^{-1} \text{min}^{-1}$ ). This model was based on the quantity of adsorbate is present on the adsorbent surface. The linearized pseudo-first-order and second-order kinetics models were shown in (Figure 11 and Figure 12) respectively and the corresponding constant values and correlation coefficients ( $R^2$ ) are shown in (Table 2). The regression coefficients for the pseudo second order model ( $R^2 > 0.99$ ) were greater than pseudo first order [11] indicate the experimental adsorption kinetic data is best obeyed the pseudo-second-order kinetics.

### Thermodynamic studies

In the present study, the extent of adsorption of Cr(VI) ions on the adsorbent upon variation in temperature between 303 K-333 K, has been explained based on values of experimentally obtained thermodynamic parameters viz. changes in standard free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ). The thermodynamic parameters were calculated using the thermodynamic equation shown below [38];

$$\Delta G^\circ = -RT \ln K_c \quad (8)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (9)$$

Where,  $R$  is the ideal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ),  $T$  is the absolute temperature (K), and  $K_c$  is the thermodynamic equilibrium constant.  $\Delta H^\circ$  and  $\Delta S^\circ$  values were obtained by from slope and intercept of the plot  $\ln K_c$  vs.  $1/T$ , a temperature dependent adsorption isotherm (Figure 13).

The values of the thermodynamic parameters were presented in Table 3. Positive  $\Delta H^\circ$  values at different temperatures suggested the endothermic nature of the adsorption process; Negative  $\Delta G^\circ$  values indicated that the sorption of metal ions was feasible and spontaneous under the conditions applied [39]. The negative values of entropy indicated the decreased randomness at the solid/solution interface, while positive values of entropy showed an increased randomness during metal ions adsorption. Study carried out by Panadare et al. on Cu (II) removal by waste sweet lime peel, showed similar results [40].

The positive value of  $\Delta H^\circ$  and negative value  $\Delta S^\circ$  suggests that the process is endothermic because the hydration of each ion is endothermic [41] and less disordered at the adsorbate and adsorbent during the process.

### Conclusions

MnO<sub>2</sub> coated PANI nanofibers were found to be an effective adsorbent for removal of Cr(VI) ions from aqueous solutions. The adsorption process is highly pH dependent and the values of thermodynamic parameters revealed that the sorption of Cr(VI) ions was spontaneous and endothermic in nature. Dynamic experimental data is well obeyed pseudo-second-order kinetics in compare to pseudo-

Metal ion	Langmuir			Freundlich		
Cr (VI)	$K_L$ (L/mg)	$R_L$	$R^2$	$K_f$ (mg/g)	$n$	$R^2$
158.2	0.35	0.16	0.9204	39.3	1.62	0.9703

Table 1: Adsorption isotherm model parameters for sorption of Cr(VI) on MPNF adsorbent.

C <sub>0</sub> (mg/L)	Experiment	Pseudo-first –order model			Pseudo-second –order model		
	q <sub>e</sub> (mg/g)	q <sub>e</sub> (mg/g)	k <sub>1</sub> (min <sup>-1</sup> )		q <sub>e</sub> (mg/g)	k <sub>2</sub> (g. mg <sup>-1</sup> . min <sup>-1</sup> )	R <sup>2</sup>
5	44.98	6.691	0.0451	0.8901	44.33	0.0317	0.9003
10	51.34	18.528	0.0641	0.9435	48.90	0.0751	0.9975
15	69.24	20.341	0.0751	0.9596	69.66	0.1949	0.9901
20	75.29	35.393	0.0885	0.9898	71.70	0.1333	0.9960
25	130.54	55.159	0.1113	0.9931	134.28	0.0232	0.9968

Table 2: Kinetic parameters for Cr(VI) adsorption onto MPNF adsorbent.

Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/kmol)
303	-6.945	+6.715	-19.42
313	-5.259		
323	-3.354		
333	-2.137		

Table 3: Thermodynamic parameters of Cr(VI) adsorption on MPNF.

first-order kinetics. The equilibrium experimental data were analyzed using linearized Langmuir and Freundlich adsorption isotherms and the maximum multilayer adsorption tendency found at pH 1 for Freundlich isotherm. The mechanism of adsorption was occurred mostly on electrostatic forces of attraction between MPNF surface and Cr(VI) ions. Based on the above results, MnO<sub>2</sub> coated PANI nanofibers were considered to be a potential adsorbent for removal of Cr(VI) ions from aqueous solution.

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