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Removal of toxic hexavalent chromium from aqueous solution by nickel ferrite-polyaniline nanocomposite

Sonal Agrawal, N.B. Singh*

Research and Technology Development Centre, Sharda University, Greater Noida 201306, India, emails: nbsingh43@gmail.com (N.B. Singh), osho.sonal@gmail.com (S. Agrawal)

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ABSTRACT

Cr(III) and Cr(VI) are toxic metal ions and available in trace amounts in aquatic system. These ions can easily enter into the human body and particularly Cr(VI) can cause serious health problems. As per government regulations, it is necessary that all the industries, before discharging the effluents containing chromium, should reduce the level below the allowable limit. A number of methods have been developed to remove chromium ions particularly Cr(VI) from aqueous solutions. In this paper, we prepared $NiFe_2O_4$–PANi nanocomposite and used it for the removal of Cr(VI) from the aqueous solution of $K_2Cr_2O_7$. The process of adsorption was studied by varying pH of the solution, adsorbent dose, metal ion concentration, and contact time. The adsorption studies were also made using PANi alone as an adsorbent. The results showed that the nanocomposite gave good results. The removal of Cr(VI) was maximum at pH ~2.0. The adsorption isotherm was verified on the basis of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherm models. Langmuir adsorption model provided the best fit of the data. It was found that pseudo-second-order equation fitted the kinetic data. The mechanism of adsorption has been discussed and a model is proposed.

Keywords: Nickel ferrite; Nanocomposite; Chromium; Adsorption; Polyaniline

1. Introduction

Due to rapid industrialization, a large amount of industrial wastewater containing heavy metals, which are toxic in nature and cannot be degraded, are discharged into the environment [1–4]. The wastewater containing highly toxic chromium if discharged causes serious environmental problems [5,6]. Chromium is the seventh most abundant element on the earth and twenty-first most abundant element in the rocks [7,8]. Chromium is released from different industrial operations, including metallurgy, leather tanning, paint, textile industries, chemical manufacturing, pulp production, ore and petroleum refining, metal corrosion, electroplating, and the manufacture of products for corrosion protection [9–11]**.** Chromium exists in two oxidation states Cr(III) and Cr(VI). Cr(III) is considered to be an essential nutrient [12], whereas Cr(VI) is highly toxic [13]. Cr(VI) can cause severe damages to the human health [14–16] and therefore its concentration is required to be reduced to an acceptable level before being discharged into environment.

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*Corresponding author.

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The maximum permissible limit of Cr(VI) for discharge into inland surface water and potable water is 0.1 and 0.05 mg L^{-1}, respectively [17]. A number of methods have been used for the removal of chromium from aqueous solutions [18]. Among various methods, adsorption is considered to be the simplest, most economical, and efficient method in reducing Cr(VI) concentration below the acceptable level from wastewater.

Existing physiochemical methods for removal of toxic elements from water suffer from higher operational cost, lower efficiency, and huge sludge production. Recent researches have shown that nanomaterials and nanofiltration can be helpful in purification of water and resolving issues related to the quality of water [19,20]. Among the available adsorbents, nanosized metal oxides are considered as the promising materials for heavy metals removal from aqueous systems [21–23]. This is partly because of their large surface areas and high activities caused by the size quantization effect [24,25]. Recent studies have suggested that many nanometaloxides exhibit very favorable sorption to heavy metals in terms of high capacity and selectivity, which would result in the removal of toxic metals to meet increasingly strict regulations [26]. However, it is difficult to separate the nanoparticles from water after removal of metal ions. In order to overcome these problems, polymeric nanocomposites/composites have been used as adsorbents for the removal of toxic metal ions from wastewater [27–29]. These polymeric nanocomposites/composites are expected to display new properties and present relatively high metal ion adsorption capacities.

In recent years, considerable attention has been given to conducting polymers for the removal of toxic elements from wastewater system. The conducting polymers such as polyaniline (PANi) and polypyrrole (PPy) are being used for water purification. Polyaniline contains imine and amine groups which can chelate metal ions and also can adsorb metal species through electrostatic or hydrogen bonding. As such, polyaniline was found to be a good adsorbent for removing heavy metal ions from aqueous solution [30]. However, pure polyaniline particles are generally aggregated in solution and lower the adsorption process. Therefore, polyaniline nanocomposites have been widely used as adsorbents for the removal of pollutants from aqueous solutions [31–34]. In this paper, $NiFe_2O_4$–PANi nanocomposite is used for the removal of chromium ions from aqueous solution of $K_2Cr_2O_7$ under different conditions and the removal efficiency is discussed.

2. Material and methods

2.1. Materials

Nickel sulfate (Fisher Scientific), ferric nitrate (Qualikems), ammonia solution, sodium hydroxide, potassium dichromate, aniline (Lobachemie), benzene (Fisher Scientific), and copper sulfate (Qualigens) were used without further purifications. Stock solutions of test reagents were prepared in distilled water.

2.2. Preparation of adsorbent

$NiFe_2O_4$ of nanodimension was prepared in a manner as described earlier [35]. Nickel sulfate and ferric nitrate were mixed in 1:2 M ratio in water. Ammonium hydroxide solution was added to this solution drop by drop till nickel hydroxide and ferric hydroxide co-precipitated. The precipitate thus obtained was washed with water, dried, and calcined at 300˚C/500˚C for 3 h, to get $NiFe_2O_4$ of nanosize.

Polyaniline (PANi) was prepared by oxidative polymerization of aniline at room temperature using $CuSO_4$ solution [35]. In a separate experiment, 5.0 wt% $NiFe_2O_4$ was mixed thoroughly during the polymerization process (*in situ*) where $NiFe_2O_4$–PANi nanocomposite was formed.

2.3. Materials characterization

$NiFe_2O_4$, PANi, and 5% $NiFe_2O_4$–PANi were characterized by powder X-ray diffraction, SEM, TG, and FTIR spectroscopic techniques as described earlier [35].

2.4. Adsorption experiments

Potassium dichromate solution of different concentrations was prepared and UV–vis spectra of the solutions were recorded. From the spectra, λ_{max} was found out to be 560 nm. A calibration curve between the concentration and the absorbance was plotted. Ten milliliter solution of 10 ppm concentration of Cr(VI) (pH ~2.0) was taken in two different bottles. 0.2 g powders of $NiFe_2O_4$–PANi nanocomposite and PANi were dispersed separately in each solution and stirred magnetically. After every 10 mins, the absorbance of Cr(VI) solutions containing the two adsorbents was recorded at $\lambda_{max} = 560$ nm and from the calibration curve the concentration of Cr(VI) adsorbed was determined. The experiments were conducted in the pH range 1–7. The pH variations were done using suitable volumes of 0.1 N HCl/0.1 N NaOH solutions. The adsorption was studied as a function of time (up to 90 min) and adsorbent dose (0.05–0.5 g). Percent Cr(VI) removal (adsorption efficiency) was calculated using Eq. (1).

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 is the initial concentrations of Cr(VI) in mg/L and C_e is the equilibrium concentration of Cr(VI) in mg/L.

Eq. (2) was used to determine the equilibrium sorption capacity.

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where q_e is the amount of Cr(VI) adsorbed per unit mass of adsorbent (mg/g) at equilibrium, V is the sample volume, and m is the mass of adsorbent dosage in (g). Kinetics of adsorption was studied by mixing 0.20 g of adsorbent with 10 ml of Cr(VI) solution at room temperature (35˚C). The amount of Cr (VI) adsorbed was calculated using Eq. (3):

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{3}$$

where q_t is the amount of Cr(VI) adsorbed per unit mass of the adsorbent (mg/g) at any time t, C_t is the bulk-phase Cr(VI) concentration (mg/L) at any time t, and m is the mass of adsorbent (g).

3. Results and discussion

3.1. Preparation of $NiFe_2O_4$–PANi nanocomposite

The formation of Nickel ferrite is represented in Fig. 1. PANi can exist in three different forms (Fig. 2) [36]. The conducting form can be obtained by oxidative doping of Leucoemeraldine Base (LB) or by protonation of Emeraldine Base (EB), i.e. doping with protonic acids (Fig. 3). *In situ* polymerization gave $NiFe_2O_4$–PANi nanocomposite. The formation of nanocomposite is represented by Fig. 4.

3.2. Characterization of nanocomposite

The characterization of nanocomposite has been discussed elsewhere [35]. X-ray diffraction patterns of PANi, $NiFe_2O_4$, and PANi/$NiFe_2O_4$ composite are shown in Fig. 5. The diffraction pattern of pure $NiFe_2O_4$ suggests that the spinel is crystalline in nature and the broadening in the line suggests that particles are of nanodimension. The diffraction pattern of PANi suggests poorly crystalline character. However, the diffraction pattern of PANi-5% $NiFe_2O_4$ suggested that the nanocomposite retained almost all the peaks of both the components with less crystalline character. The SEM pictures (Fig. 6) show that all the materials are of nanodimension.

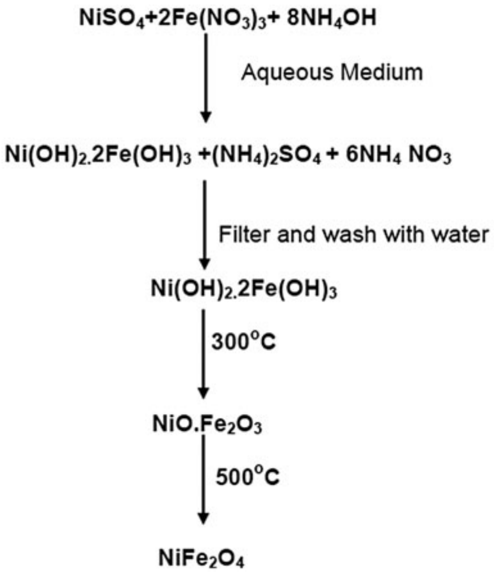

Fig. 1. Formation of $NiFe_2O_4$.

3.3. Effect of adsorbent dose

The effect of adsorbent dose on chromium(VI) removal at fixed initial chromium(VI) concentration (10 ppm) is shown in Fig. 7. It shows that the adsorption efficiency of chromium(VI) from the solution increases rapidly with an increase in the adsorbent dose from 0.05 to 0.5 g/10 mL; a marginal increase was observed on further increase in the adsorbent dose for both PANi and $NiFe_2O_4$–PANi. With an increase in the adsorbent dose, available surface for adsorption increased resulting into an increase in the removal efficiency of chromium(VI) [37,38]. The removal efficiency was higher in the presence of nanocomposite as compared to that of PANi.

3.4. Effect of pH on adsorption

The solution pH has a significant effect on the uptake of metal ions since it determines the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate. Adsorption behavior

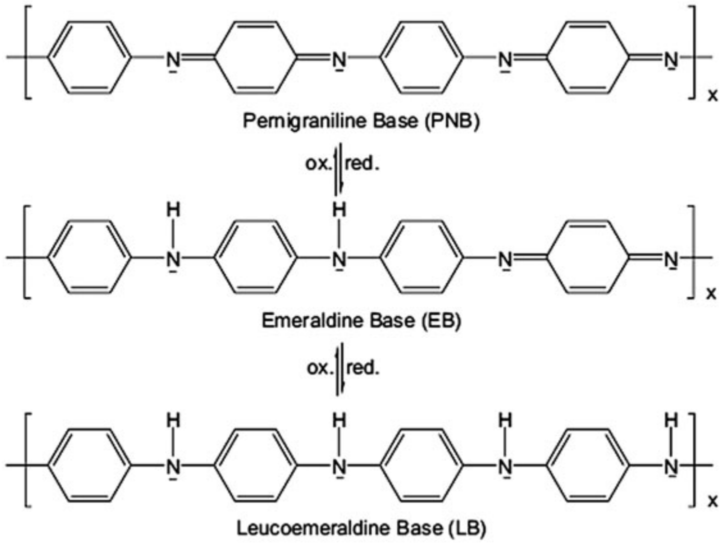

Fig. 2. Different forms of polyaniline.

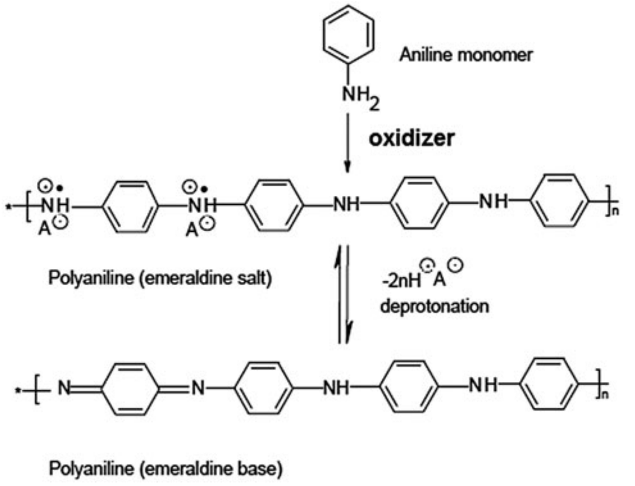

Fig. 3. Formation of polyaniline from aniline and its two forms.

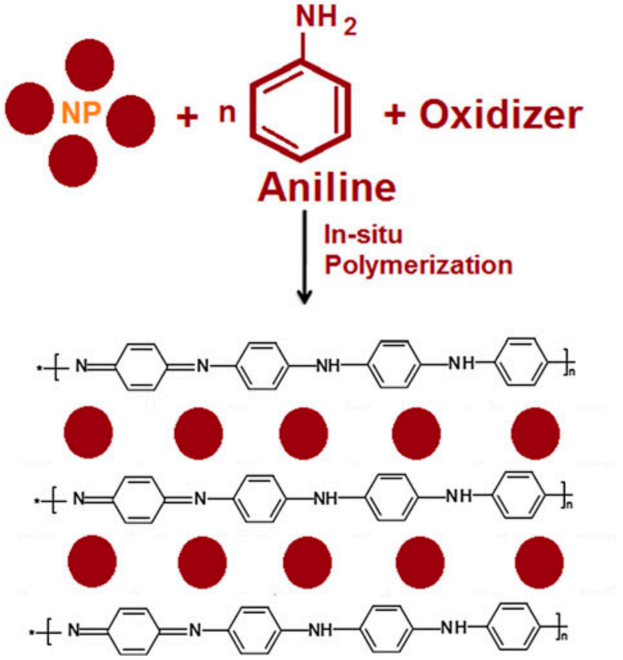

Fig. 4. Formation of $NiFe_2O_4$–PANi nanocomposite.

of Cr(VI) on the surfaces of PANi and $NiFe_2O_4$–PANi at different pH of the solution is shown in Fig. 8. Results showed that Cr(VI) adsorption on $NiFe_2O_4$–PANi decreased with an increase in the pH values of the solution. The maximum Cr(VI) adsorption by $NiFe_2O_4$–PANi was found at pH 2. It can be inferred that the lower pH of the solution may cause the surface of the adsorbent to be highly protonated, leading to a strong attraction between oxyanions of Cr(VI) and positively charged surface of the adsorbent. On the other hand, at high pH but less than 7, there will be less positive charge on the surface i.e. less protonation but after pH 7, abundance of negatively charged hydroxyl ions in the aqueous solution causing hindrance in adsorption [39]. The mechanism of adsorption on the surface of nanocomposite is represented in Fig. 9. However, in the presence of PANi, there is a slow increase in adsorption with pH, indicating that there is a different mechanism of adsorption on the surface of PANi or it may be random due to agglomeration. The variation of concentration of Cr(VI) in solution with pH is already reported (Fig. 10) [18].

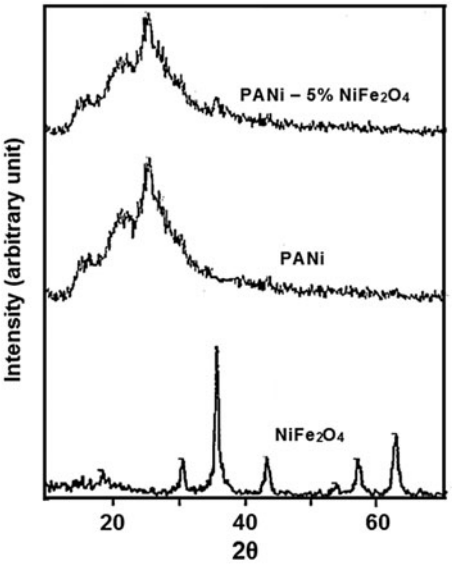

Fig. 5. X-ray diffraction pattern.

3.5. Adsorption isotherms

Adsorption isotherms describe the equilibrium adsorption process at a constant temperature and pH [40]. In this study, four adsorption isotherm models (Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich) have been tested for the adsorption of Cr(VI) on $NiFe_2O_4$–PANi nanocomposite and PANi. The variation of amount adsorbed (q_e) vs. concentration (C_e) is plotted in Fig. 11.

The Langmuir isotherm model [41] is applicable to monolayer adsorptions and can be expressed by Eq. (4):

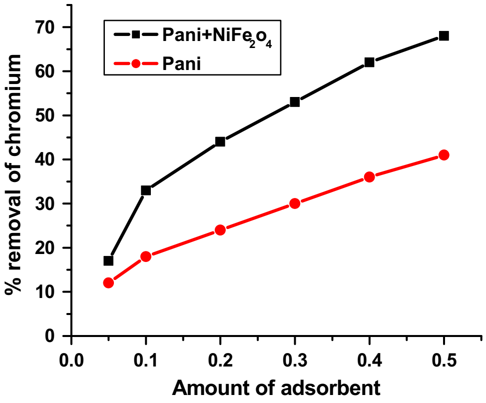

Fig. 7. Effect of adsorbent dose on % removals of chromium.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \tag{4}$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount of adsorbed at equilibrium (mg/g), and q_m and b are Langmuir constants related to adsorption capacity and energy of adsorption.

The Langmuir equation is based on the following assumptions [42]:

(1) Molecules are adsorbed at a fixed number of well-defined localized sites;
(2) each site can hold one adsorbate molecule;
(3) all sites are energetically equivalent;
(4) there is no interaction between molecules adsorbed on neighboring sites.

$NiFe_2O_4$ PANi $NiFe_2O_4$-PANi

Fig. 6. SEM pictures.

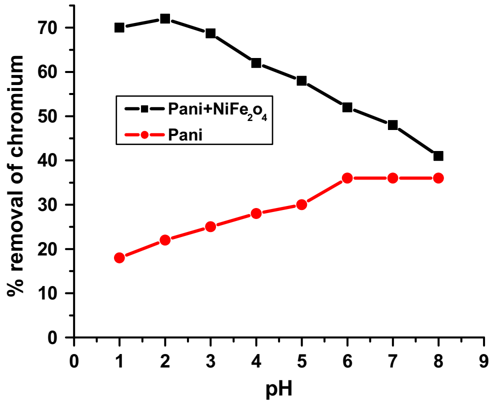

Fig. 8. Variation of % removal of Cr(VI)in presence of PANi and NiFe$_2$O$_4$–PANi at different pH.

The validity of Eq. (4) was tested by plotting a graph between $1/q_e$ against $1/C_e$, where straight lines are obtained (Fig. 12).

Compared with the Langmuir isotherm model, the Freundlich isotherm model describes adsorption process on heterogeneous surfaces and is suitable to describe adsorption in a narrow range of solute concentration [43]. Freundlich equation (Eq. (5)) can be rearranged to the linearized form.

$$\log q_e = \log K_F + 1/n \log C_e \tag{5}$$

where K_F is a Freundlich constant and n is related to the magnitude of the driving force for sorption and to energy distribution of sorption sites [44]. When $0 < 1/n < 1$, the adsorption is favorable; when $1/n = 1$, the adsorption is irreversible; and when $1/n > 1$, the adsorption is unfavorable [45]. The validity of Freundlich isotherm is shown in Fig. 13. The values of $1/n$ (Table 1) suggest that Freundlich isotherm is not favorable.

The Temkin adsorption isotherm model is based on the assumptions that the adsorption energy decreases linearly with the surface coverage, which is due to the adsorbent–adsorbate interactions. The Temkin isotherm model is expressed by Eq. (6).

$$q_e = B \ln A + B \ln C_e \tag{6}$$

and

$$B = RT/b \tag{7}$$

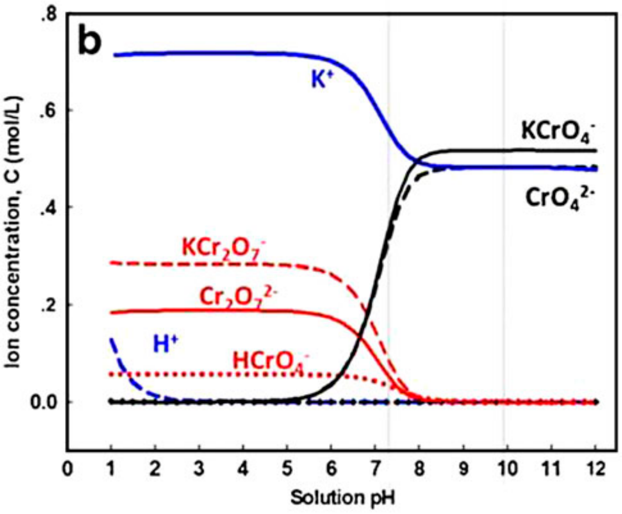

Fig. 10. Cr(VI) species distribution in solution of different pH.

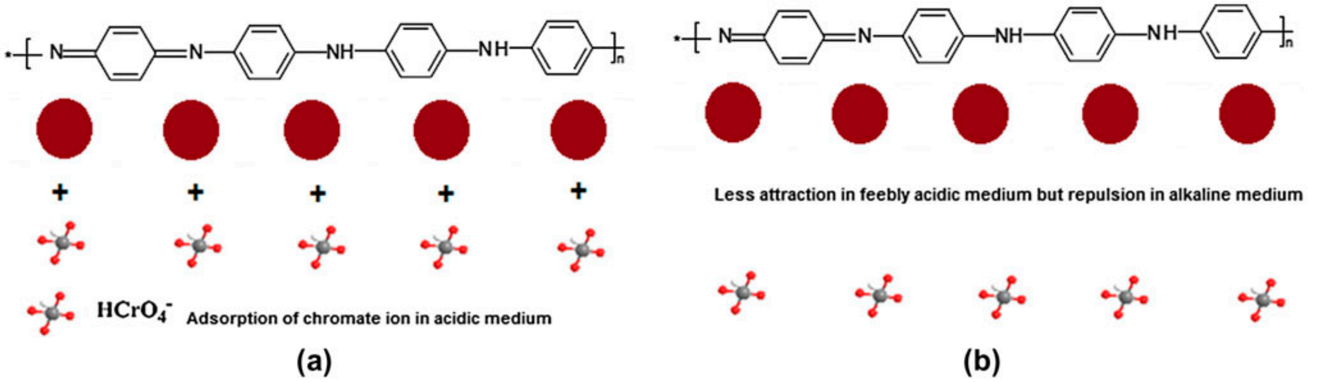

Fig. 9. (a) Adsorption of chromate ion (HCrO$_4^-$) on NiFe$_2$O$_4$–PANi surface in acidic medium and (b) less attraction in feebly acidic medium bur repulsion of chromate ion (HCrO$_4^-$) on NiFe$_2$O$_4$–PANi surface in basic medium.

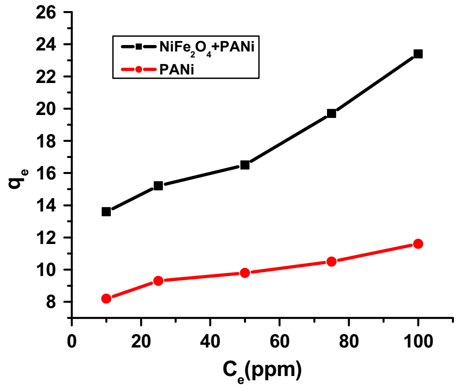

Fig. 11. Variation of amount adsorbed (q_e) with concentration (C_e).

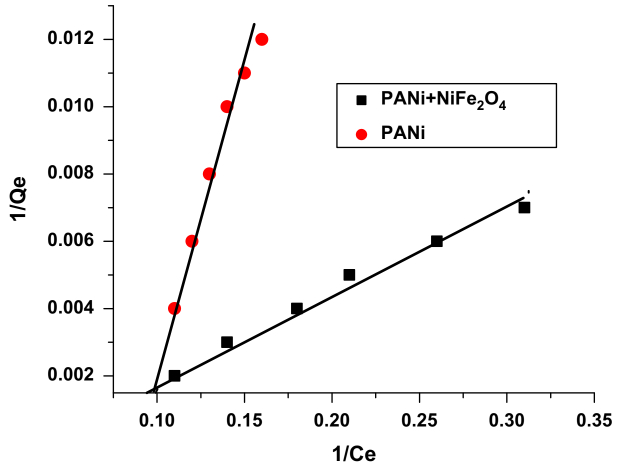

Fig. 12. Langmuir isotherm for Cr(VI) removal.

where q_e is the adsorbed amount (mg/g), A (L/g) is Temkin isotherm constant, b (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 J/mol K), and T the absolute temperature (K) [46]. Validity of Eq. (6) was tested by plotting a graph between Q_e and $\ln C_e$ (Fig. 14). The data were scattered. The values of constants were calculated and are given in Table 1.

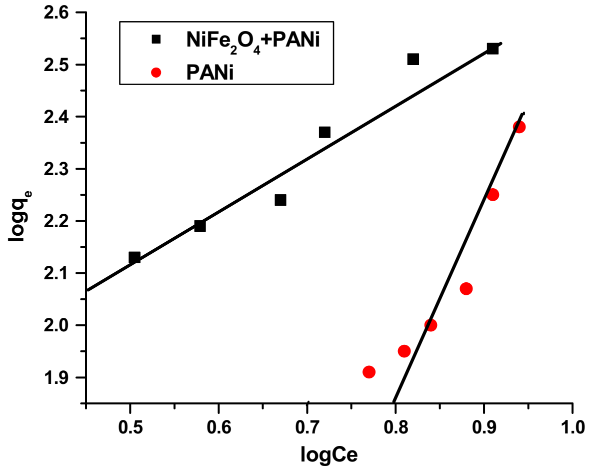

Fig. 13. Freundlich isotherm for Cr(VI) removal.

Dubinin–Radushkevich (D–R) adsorption isotherm model predicts that the adsorption process follows a pore-filling mechanism and is expressed by a semi-empirical equation. The assumptions of the model are that the adsorption has a multilayer character involving van der Waals forces [47]. The D–R isotherm model is presented linearly by Eq. (8).

$$\ln q_e = \ln X_m - \beta\varepsilon^2 \tag{8}$$

where q_e is the adsorbed amount (mg/g), X_m is Dubinin–Radushkevich monolayer capacity, β is the activity coefficient related to mean sorption energy, and ε is Polanyi potential which is given by Eq. (9).

$$\varepsilon = RT\ln(1 + 1/C_e) \tag{9}$$

The mean energy of sorption, E (kJ/mol), is calculated by Eq. (10):

$$E = 1/\sqrt{2\beta} \tag{10}$$

A plot of $\ln q_e$ vs. ε^2 enables the determination of the isotherm constants X_m and β from the slope and

Table 1
Isotherm model coefficient for the adsorption of Cr(VI) on $NiFe_2O_4$–PANi and PANi nanocomposite at 308 K

	Freundlich isotherm			Langmuir isotherm			D–R isotherm			Tempkin isotherm		
Adsorbent	$1/n$	K	R^2	Q_o	b	R^2	X_m	β	R^2	A	B	R^2
PANi-$NiFe_2O_4$	1	2.06	0.948	12.19	2.48	0.9880	5.9	0.000004	0.8907	1.35	233	0.938
PANi	3.3	0.8	0.902	11.76	0.425	0.9761	5.8	0.00002	0.9025	5.05	250	0.839

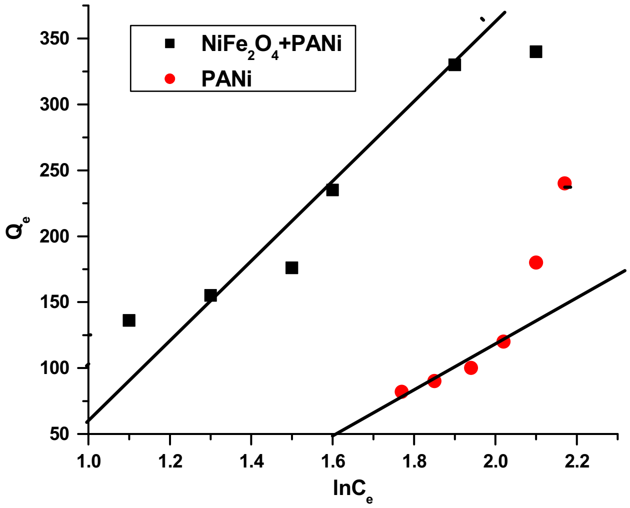

Fig. 14. Temkin isotherm for Cr(VI) removal.

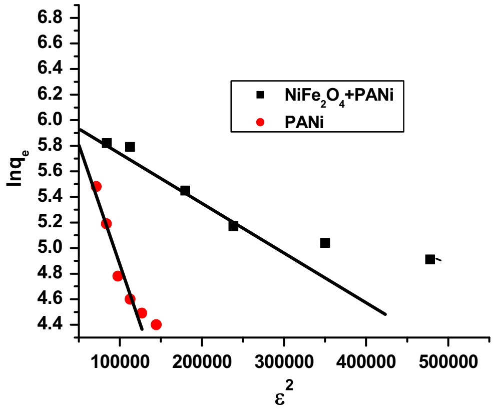

Fig. 15. Dubinin–Radushkevich isotherm for Cr(VI) removal.

intercepts (Fig. 15). Values of constants and other parameters are given in Table 1. Based on the average values of the statistical parameters for each isotherm, it can be concluded that Langmuir isotherm provides the best representation of the experimental equilibrium data and the next is Freundlich model. The results suggested that $NiFe_2O_4$–PANi nanocomposite can be considered as a promising adsorbent for the removal of Cr(VI) from aqueous solution.

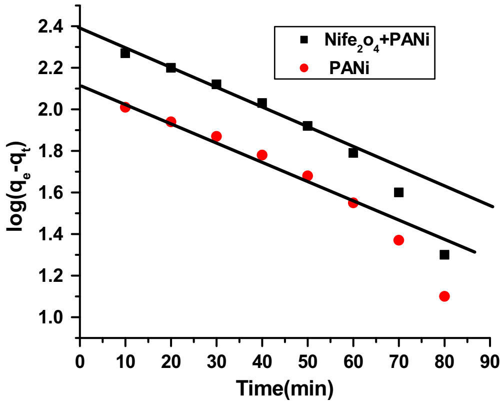

Fig. 16. Kinetic data for pseudo-first-order adsorption rate.

3.6. Sorption kinetics

Pseudo-first-order and pseudo-second-order models were used to test the kinetic data. The pseudo-first-order assesses different adsorption situations, including (i) systems close to equilibrium; (ii) systems with time-independent solute concentration or linear equilibrium adsorption isotherm; and (iii) special cases of more complex systems [48]. On the other hand, pseudo-second-order equation assumes that the sorption rate is proportional to the number of active sites occupied onto the sorbent [49]. The pseudo-first-order and pseudo-second-order equations are given by Eqs. (11) and (12), respectively:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{11}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{12}$$

where q_t is Cr(VI) uptake at time t, and k_1 and k_2 are the pseudo-first-order and second-order rate constants, respectively. The validity of Eqs. (11) and (12) was tested (Figs. 16 and 17). From the plots, the rate

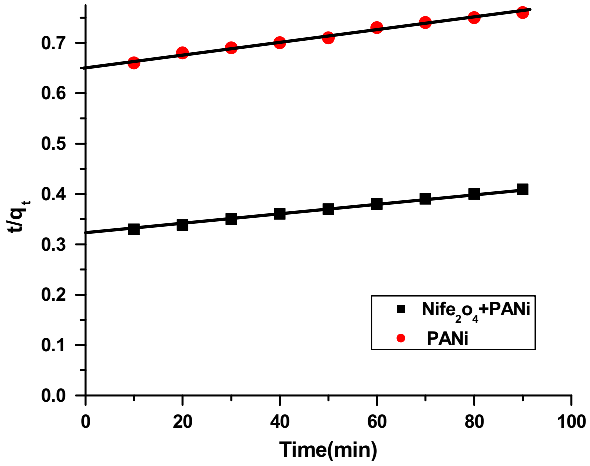

Fig. 17. Kinetic data for pseudo-second-order adsorption rate.

Table 2
Kinetic parameters for Cr(VI) adsorption onto PANi-$NiFe_2O_4$ nanocomposite and PANi

		Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
Adsorbent	C_0 (mg/l)	q_e (mg/g)	K_1 (1/min)	R^2	q_e (mg/g)	K_2 (g/mg/min)	R^2
PANi-$NiFe_2O_4$	10	2.4	.0460	0.9350	1,000	3×10^{-5}	0.998
PANi	10	2.1	.0230	0.9389	500	6×10^{-5}	0.992

constants were determined and are given in Table 2. The correlation coefficient values are also given in Table 2. Higher values of correlation coefficients indicated that the pseudo-second-order model fitted the data for Cr(VI) adsorption.

4. Conclusions

$NiFe_2O_4$–PANi nanocomposite was synthesized *in situ* by chemical polymerization process and used as an adsorbent for the removal of Cr(VI) from aqueous solution of $K_2Cr_2O_7$. The adsorption efficiency of $NiFe_2O_4$–PANi nanocomposite was found to depend on the solution pH. The adsorption decreased with increase of pH and the maximum removal of Cr(VI) by $NiFe_2O_4$–PANi nanocomposite was found at pH 2.0. Langmuir isotherm and pseudo-second-order kinetic models fitted the data well. The efficiency of PANi alone as an adsorbent for the removal of Cr(VI) was much lower as compared to that of $NiFe_2O_4$–PANi nanocomposite. The results indicated that the nanocomposite can be considered as a better adsorbent for the removal of Cr(VI) from aqueous solution as compared to that of PANi. However, further investigations are needed to assess the cost effectiveness of the material for industrial wastewater treatment.

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