



ORIGINAL ARTICLE

Synthesis and characterization of polyaniline/zeolite nanocomposite for the removal of chromium(VI) from aqueous solution



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Received 27 November 2011; accepted 1 January 2012

Available online 9 January 2012

KEYWORDS

Oxidative polymerization;
Adsorption;
Metal ion

Abstract The synthesis, characterization and capacity studies of ion exchange resin capable of coordinating with metal ion are reported. Zeolite was modified with conducting polyaniline by the polymerization of anilinium cation in and out side of zeolite channels and a nanocomposite of polyaniline/zeolite (PANI/zeolite) was obtained by the oxidative polymerization of anilinium cation with the zeolite structure. The product was characterized by UV–visible, FTIR, ¹H NMR, XRD, SEM and TGA techniques. From FTIR studies it was obtained that the composite has a high content of PANI. SEM pictures in the present study show that the diameter of the PANI/zeolite nanocomposite is between 300 and 600 nm.

Batch adsorption experiments were used to investigate the effect of various experimental parameters on the equilibrium adsorption of chromium(VI) on PANI/zeolite nanocomposite. The adsorption characteristics of the composite toward Cr(VI) in dilute aqueous solution were followed spectrophotometrically. The effect of contact time, size of the sorbent and the concentration of Cr(VI) in solution on the metal uptake behavior of the composite were studied. It has been observed that the capacity of chromium adsorption on PANI/zeolite increases with initial metal concentration, the metal ion adsorption on surfactant is well represented by the Freundlich isotherm.

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1. Introduction

Environmental contamination by metals is a widespread problem, with sources of pollution arising from industrial activities. Many toxic metal ions that are highly toxic for animals and human beings have been discharged into the environment as industrial wastes, causing serious soil and water pollution (Lin and Junang, 2002). These metals are of significant importance as they are non-biodegradable and once released into the environment, they can only be diluted or transformed, not destroyed (Tramontina et al., 2001).

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Various methods have been proposed to remove heavy metal ions from sea water and waste waters using ion-exchange resin, adsorption (Fugiang and Baojiao, 2006; Li et al., 2005, 2009, 2010), electrolyte or liquid extraction, electrodialysis (Qdais and Moussa, 2004), chemical precipitation (Karabulut et al., 2002), membrane filtration (Saliba et al., 2000), Biosorption (Rao et al., 2002). Ion exchange/adsorption methods do offer the most direct method for producing the highest quality treated water (Ko et al., 2000).

Zeolite is a crystalline aluminosilicate with 3-dimensional, open anion framework consisting of oxygen sharing TO_4 , Tetrahedral, where T is Si or Al. Their framework structure contains interconnected voids that are filled with cations usually from group IA or IIA which can be exchanged with other cations (such as anilinium cations) (Olad et al., 2010; Ramos et al., 2008). Due to their unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion exchange, etc.) zeolites have been used as heavy metal adsorbents, as chemical sieves and as water softeners (Zeng et al., 2010; Hong, 2009; Sulimenko et al., 2001).

The main objectives of this study are to develop inexpensive and effective metal ion adsorbents, also to explore the feasibility of using zeolite nanocomposite for the removal of toxic heavy metals from waste waters.

2. Experimental

2.1. Instrumentation

Fourier Transform Infrared Spectrometer (FTIR) was used for the determination of functional groups in PANI/zeolite using KBr pellets. The pellets were analyzed with FTIR Spectrometer (Shimadzu 8400S) in transmittance (%) mode in the range $4000\text{--}400\text{ cm}^{-1}$.

UV-visible spectra were taken on T80 double beam spectrophotometer. The morphology of the prepared materials was examined on Inspect™ S50-scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed using Shimadzu TGA 60, measurements were carried out in N_2 atmosphere under 50 ml/min flow rate and a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ from room temperature to $800\text{ }^\circ\text{C}$. X-ray diffraction pattern was measured on XRD 7000 Shimadzu X-ray diffractometer.

2.2. Materials

Aniline, ammonium persulfate were purchased from Merck. Aniline was distilled under reduced pressure and stored at $5\text{ }^\circ\text{C}$. Zeolite was obtained from Aldrich.

2.3. Synthesis of polyaniline/zeolite nanocomposite

PANI/zeolite nanocomposites were synthesized via an in situ oxidative polymerization (Marjanovic et al., 2009), in which the natural zeolite was ground and sieved with $100\text{ }\mu\text{m}$ of sieve. Then 1.5 g of zeolite was vigorously stirred in 200 mL of 1 M HCl for 24 h. Ten grams (107.5 mmol) of aniline was dispersed in matures of HCl and zeolite with

continuous stirring for 24 h. Ammonium persulphate (67 mmol) was dissolved in 1 M HCl (200 ml) and dropped into the Beaker. The mixture was kept at constant stirring and the solution is placed inside an ice bath maintaining stirring for another 24 h. When the reaction was completed, the dark green precipitate resulting from the polymerization reaction was filtered and washed with distilled water, acetone and methanol sequentially in order to remove the excess of initiator, monomer, and oligomer. The precipitate was then dried overnight in vacuum oven at $60\text{ }^\circ\text{C}$.

2.4. Adsorption experiments

The Cr(VI) solutions were prepared in different concentrations that ranged from 20 to 100 ppm by diluting K_2CrO_4 stock solution (1000 ppm) appropriately as necessary.

To determine the conditions that achieve the maximum amount of metal ion removal, adsorption experiments were done. Reaction isotherm and kinetics were also conducted in this study.

Various amounts of PANI/zeolite powder were introduced into a 100 ml volumetric flasks and 50 ml Cr(VI) solution of different concentrations were added. The adsorption tests were conducted in thermostated water bath shaker at a fixed temperature of $30\text{ }^\circ\text{C}$.

The efficiency of Cr(VI) removal was calculated as follows:

$$\text{Removal efficiency} = 100 \frac{C_i - C_f}{C_i}$$

where C_i and C_f are the initial and final concentrations in ppm, respectively.

If q is the amount of metal adsorbed per specific amount of adsorbent (mg/g). The sorption capacity of time t , q_t (mg/g) was obtained as follows:

$$q_t = \frac{v(C_i - C_f)}{m}$$

where C_i and C_f (ppm) were the liquid phase concentrations of solutes at initial and given time t , v was the solution volume and m is the mass of PANI/zeolite (g).

3. Results and discussion

3.1. Characterization of PANI/zeolite nanocomposite

Zeolite was modified through the polymerization of aniline monomer inside and outside of zeolite channel, where the exchangeable cations were replaced by anilinium ions. The polymerization of aniline is achieved only in an acidic medium in the presence of hydrochloric acid where aniline exists as anilinium cations. Peroxy disulfate was used as an oxidant for the anilinium ion due to the higher solubility in water of its ammonium salt. To minimize the presence of residual aniline and to obtain the best yield of PANI, 1.25 peroxydisulfate/aniline ratio is recommended (Fu and Elsenbaumer, 1994), the oxidation of aniline is exothermic so the temperature of the reaction mixture can be used to monitor the progress of the reaction (Hong, 2009; Sulimenko et al., 2001). In this study, polyaniline was

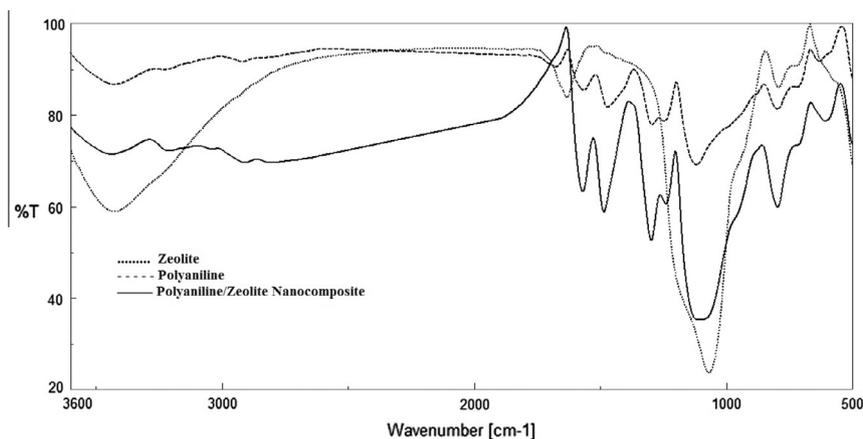
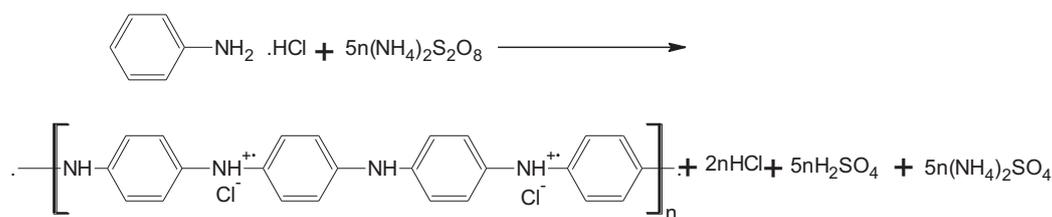


Figure 1 FTIR spectra of zeolite (a), polyaniline (b), and polyaniline/zeolite nanocomposite.

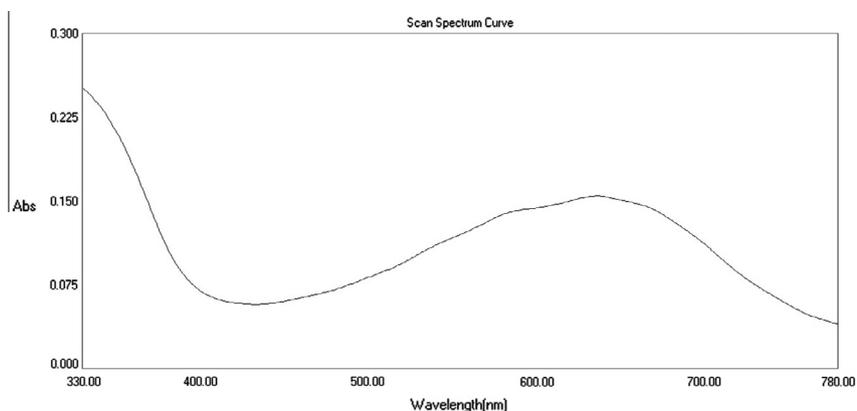


Figure 2 UV-visible spectra of the polyaniline/zeolite nanocomposite in N-methyl-2-pyrrolidone.

polymerized by oxidative coupling using $\text{K}_2\text{S}_2\text{O}_8$ in acidic aqueous medium as given below (Trchová et al., 2006):

In comparison the FTIR spectra of polyaniline/zeolite nanocomposites with those of pure PANI (Fig. 1), the intense band in 3423 cm^{-1} which is due to the stretching frequency of amino group (N-H) in the doped polyaniline (Olad et al., 2010) are shifted to 3452 cm^{-1} in PANI/zeolite nanocomposites. The peaks observed at 1563 and 1471 cm^{-1} corresponding to quinone and benzene for PANI band are slightly shifted to higher wave number values (1570 and 1486 cm^{-1}) in nanocomposites. The band at 1294 cm^{-1} belongs to C-N stretching of secondary aromatic amine strengthened by the protonation of PANI, and is also present in spectra of all composites with slight shifting. The strong band at 1120 cm^{-1} is considered to be a measure of the degree of electron delocalization in PANI chains and thus is a characteristic peak related to PANI conductivity,

it is evident that the intensity of this peak increases with increasing PANI content in the composites, the wave number value of this peak decreases from 1120 cm^{-1} for pure PANI to 1093 cm^{-1} in PANI/nanocomposites. Noticeable changes were observed for bands which are related to the structural OH vibrations in the region between 3500 and 3700 cm^{-1} related to the bridging OH groups in $\equiv\text{Al}-\text{OH}-\text{Si}\equiv$ and other hydrogen atom on different oxygen atoms in the frame work of zeolite (Doula, 2007).

The UV-visible spectra of PANI/zeolite nanocomposite show two absorption maxima at 320 and 630 nm (Fig. 2), in N-methyl-2-pyrrolidone as a solvent. The band at 340 nm has been assigned to the $\pi \rightarrow \pi^*$ electronic transition, this band is known to be sensitive to the number of aniline units the excitation band at 630 nm can be used as a measure of the oxidation state of PANI which could be attributed to the standard emeraldine base (Quillard et al., 1994).

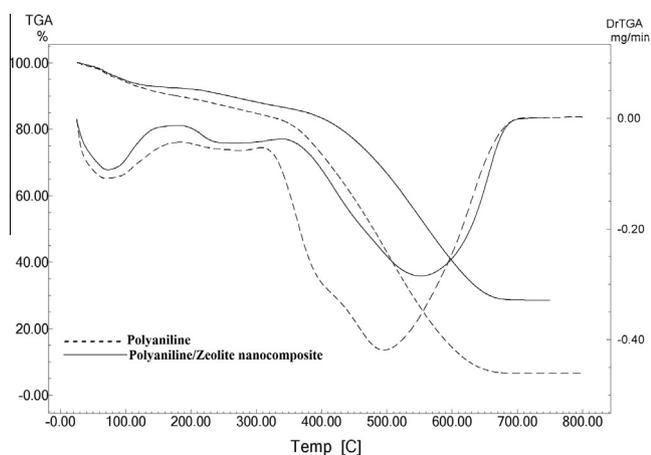


Figure 3 TGA curve of polyaniline/zeolite nanocomposite.

The H NMR spectrum of the PANI sample was recorded by dissolving the sample in DMSO- d_6 solvent. The H NMR spectrum of the functionalized PANI chain exhibits peaks near 7.6 ppm due to the aromatic protons of the quinoid ring and the peaks of benzenoid protons.

Fig. 3 shows the thermogravimetric analysis (TGA) of polyaniline and PANI/zeolite nanocomposite. The weight loss at 30–200 °C corresponds to the removal of water molecules (Duval, 1963). Also, the weight ratio of PANI/zeolite could also be determined from the TGA graph taking into account that the residual weight at 680 °C refers to the content of zeolite in the composite. The thermograph shows that the extent of decomposition of PANI/zeolite nanocomposite (560 °C) is less than that of polyaniline (490 °C) which can be explained by the strong interaction of between PANI and zeolite which restricts the thermal motion of PANI chains.

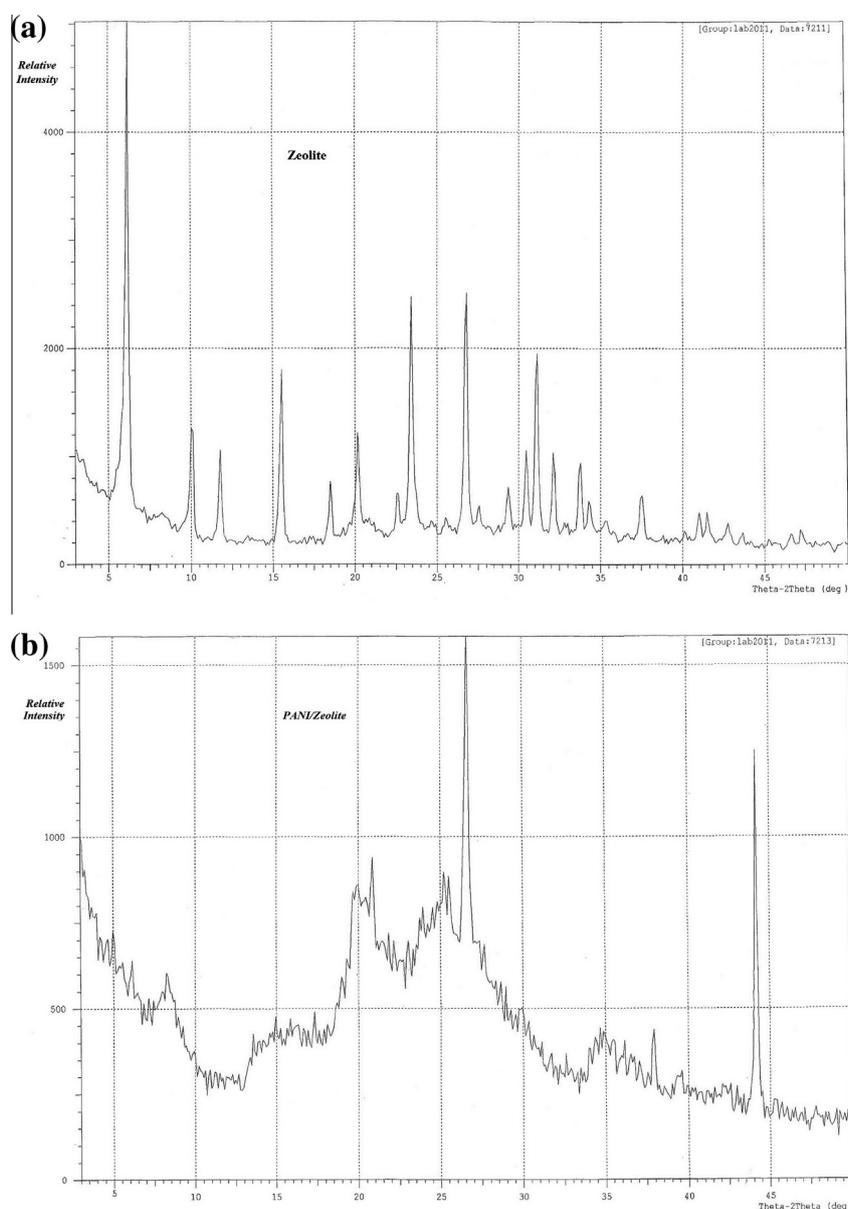


Figure 4 XRD pattern of zeolite and PANI/zeolite nanocomposite.

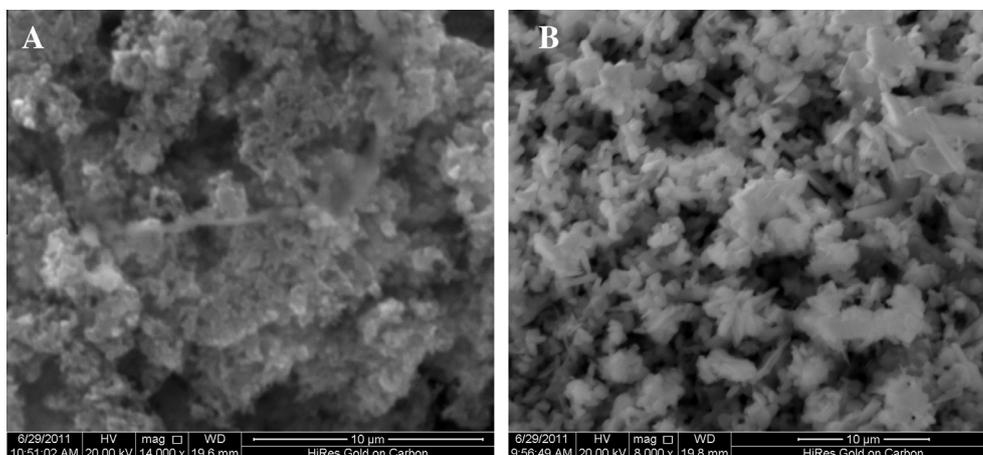


Figure 5 SEM images of (A) pure PANI and (B) PANI/zeolite nanocomposite.

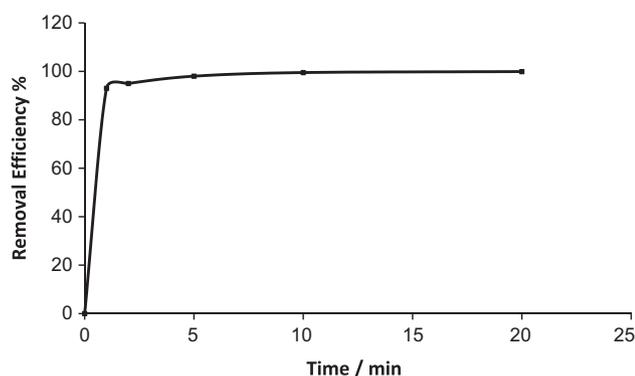


Figure 6 The effect of contact time on the removal efficiency (the initial concentration, volume of solution and amount of adsorbent were 50 ppm, 50 mL and 0.2 g, respectively).

The X-ray diffraction patterns were recorded for zeolite, polyaniline/zeolite nanocomposite as shown in Fig. 4. From XRD patterns, the well ordered polymer within the zeolite matrix having high crystallinity is clearly evident. The peaks centered around $2\theta = 20$ and 25 may be ascribed to the periodicity parallel and perpendicular to the polymer chain, respectively. The peak at around 2θ is 15, 20, 25 are assigned to the emeraldine structure (Sui et al., 2004; Pouget et al., 2004; Li et al., 2008).

The intensity of the XRD pattern peaks can be influenced by crystallinity or by polyaniline chains order in the nanocomposite structure. Fig. 4 shows the XRD pattern of polyaniline that suggests that it has a relatively amorphous structure, but by the encapsulation of polyaniline in the zeolite channel, the alignment and arrangement of polyaniline chain significantly improved as a result. The intensity of these peaks related to the nanocomposite was increased.

SEM pictures show that the diameter of the PANI zeolite are between 300 and 600 nm, we suggest aggregation of the single PANI chains as it emerges out of the zeolite layers, it is reported that one zeolite layer contains lots of PANI chains (Frisch et al., 2001). The SEM image of PANI/zeolite nanocomposite in Fig. 5 shows the presence of polyaniline on the layered surface of zeolite. This image shows that the formation

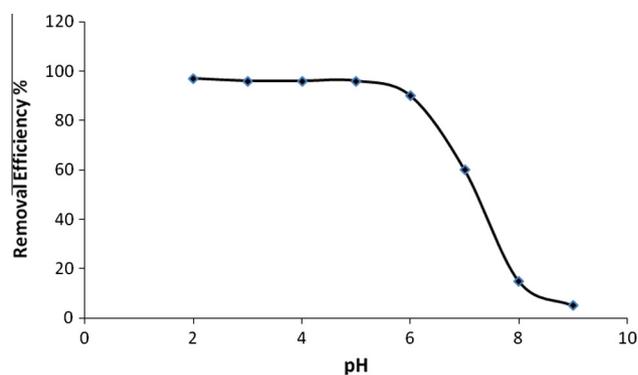


Figure 7 The effect of pH on the removal efficiency of Cr(VI) on (the initial concentration, volume of solution and the amount of adsorbent were 50 ppm, 50 mL and 0.2 g, respectively).

of polyaniline takes place not only in the zeolite channels but also on the zeolite outside surfaces, this is due to the adsorption of anilinium cations both inside the pores' surfaces and on the outside of zeolite layer by cation exchange processes between anilinium cations and the mineral cations existing inside and outside of the zeolite channels.

3.2. Metal ion uptake study

3.2.1. Effect of contact time

The saturation time of PANI/zeolite nanocomposite was obtained by plotting the removal efficiency of Cr(VI) against time (Fig. 6). For a concentration less than 50 ppm Cr(VI) the maximum was reached in a short period of time and the composite adsorbed approximately 100% of the metal ion. The kinetics of the uptake is related to the specificity of the interaction between the metal ion and the polymeric matrix.

3.2.2. Effect of pH

The effect of pH on the adsorption process is presented in Fig. 7, where the adsorption was determined over the pH range 2–9, using 0.2 g PANI/zeolite nanocomposite and 50 ppm

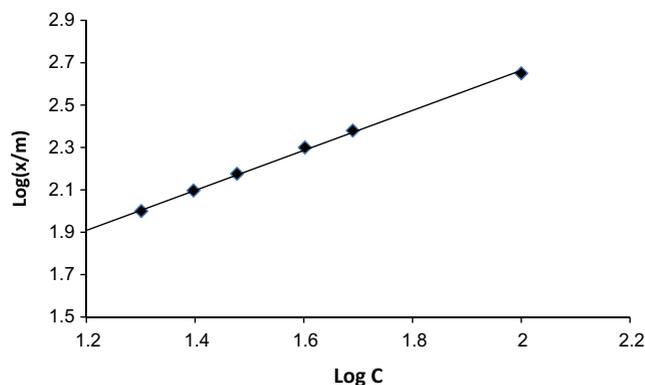


Figure 8 Freundlich sorption isotherm (50 ml volume of solution and contact time of 10 min).

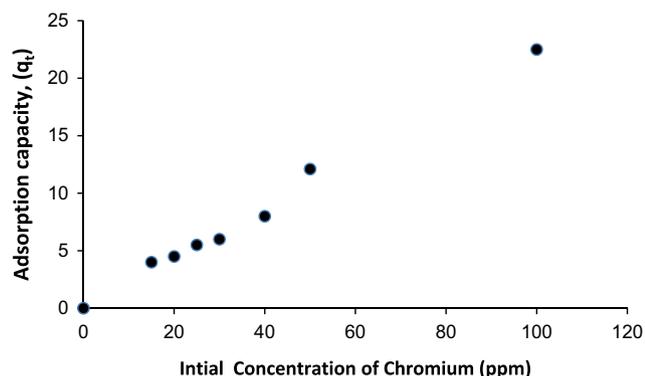


Figure 9 The effect of initial concentration on the adsorption capacity (50 ml volume of solution and contact time of 10 min).

chromium solution. It is clear that the maximum adsorption of Cr(VI) occurred at pH 2–6, and decreased at higher pH values. In this study, the pH of prepared Cr(VI) solutions were adjusted to pH 2.

3.2.3. Effect of metal ion concentration

The effect of metal ion concentration on the uptake behavior of the nanocomposite was studied in the concentration range 20–100 ppm of the metal ion (Fig. 8). Increasing the concentration enhanced the percentage of loading. The adsorption coefficient, K_{ad} , of the composite for the adsorption of Cr(VI) was computed from the Freundlich adsorption isotherm (LeVan and Vermeulen, 1981).

$$\log \left(\frac{x}{m} \right) = \log K_{ad} + 1/n \log C$$

where, C is the equilibrium concentration of the metal ion in ppm, m is the weight of the resin in g, x is the quantity of the metal ion adsorbed by the resin in ppm and n is the constant.

Freundlich adsorption isotherms within the concentration range 20 to 100 ppm lead to linear relationships with high regression coefficients of 0.9985 (Fig. 8). The values of the constants n and K_{ad} , determined from the Freundlich plot are 1.06 and 5.97, respectively. The n value between 0.0 and 1.0 indicates favorable adsorption (Arfaoui et al., 2008), while the rel-

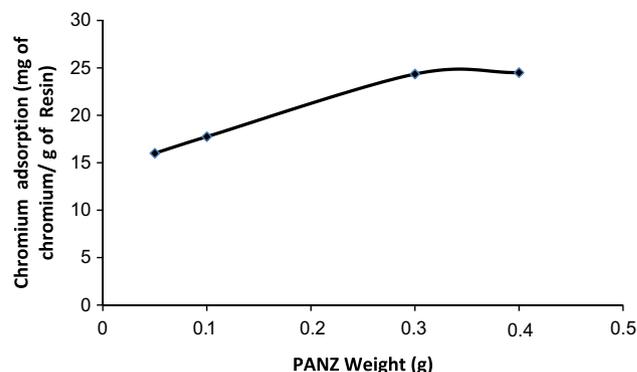


Figure 10 The effect of amount of PANI/zeolite on the removal efficiency (the initial concentration, volume of solution and contact time were 50 ppm, 100 mL and 10 min, respectively).

atively low K_{ad} value suggests that a lesser number of active sites are available.

The effect of changing the initial concentration of chromium ion on the adsorption capacity is illustrated in Fig. 9. The adsorption capacity was found to be increasing with increase in the initial concentration of Cr(VI). The higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in a higher probability of collision between Cr(VI) ions and sorbents. This results in higher metal uptake (Isa et al., 2008).

The variation of the mass of Cr(VI) removed from solution per unit mass of PANI/zeolite with the initial concentration of Cr(VI) species indicates that the adsorption process can be identified as type II isotherm (Fig. 9) according to IUPAC classification (Donohue and Aranovich, 1998). This suggests that the adsorption on PANI/zeolite nanocomposite shows strong adsorbate–adsorbent interactions.

3.2.4. Effect of PANI/zeolite dosage on the sorption of Cr(VI)

The effect of sorbent dose was also investigated (Fig. 10). Different amounts (0.01–0.5 g) of sorbent were suspended in 100 mL Cr(VI) solution (100 ppm) under optimized conditions. It was observed that the adsorption percentage of Cr(VI) onto the PANI/zeolite increased rapidly with increasing adsorbent concentration. This result is expected because the increase of adsorbent dose leads to greater surface area.

4. Conclusion

The preparation of PANI/zeolite nanocomposite was successfully performed by in situ polymerization method and the incorporation of the polyaniline in the zeolite channels was confirmed by FTIR and XRD studies. SEM images of PANI/zeolite nanocomposite confirmed the nanometer size range of polyaniline chains in zeolite channels. Adsorption performance of PANI/zeolite nanocomposite is studied for the removal of hexavalent chromium. The adsorption capacity of Cr(VI) increases with initial metal concentration. The experimental data were fitted when analyzed using Freundlich isotherm.

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