Removal of Chromate from Aqueous Solution by a Novel Clinoptilolite-Polyanillin Composite

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ABSTRACT: *Unmodified zeolites show little affinity for anions due to the fact that their surfaces are negatively charged. However modification of zeolites with amines turns their negative surface charge to positive and creating higher adsorption capacity for anions. In this study, polyaniline-clinoptilolite composite was prepared by polymerization of anilinium on the surface of zeolite. The composite was characterized by elemental analysis and X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Fourier Transform InfraRed (FT-IR) techniques. The adsorption capacity of the composite for removal of CrO_4^{2-} from aqueous solutions was studied under different experimental conditions including initial concentration, pH, temperature, and contact time. The maximum adsorption capacity of this adsorbent was higher than the values reported for similar adsorbents. The adsorption process was kinetically fast and the equilibration was attained after 30 minutes. The Langmuir and Freundlich isotherm models were applied to describe the equilibrium adsorption and the Freundlich model agreed well with the experimental data.*

KEY WORDS: *Clinoptilolite, Environment protection, Separation, CrO_4^{2-}, Nanocomposite, Polyaniline.*

INTRODUCTION

Chromium is a redox active metal that exists as either Cr(III) or Cr(VI) in the environment. These two oxidation states have differing toxicity and mobility [1]. Cr(VI) is toxic, readily transported, and a common environmental pollutant, while Cr(III) is immobile above pH=5.5 and rather non-toxic [2-3]. The polluted industries effluents contain both Cr(VI) and Cr(III) in concentrations ranging from tens to hundreds of milligrams per litre. However, the hexavalent form is 500 times more toxic than the trivalent one and human toxicity of Cr(VI) includes skin irritation to lung cancer, as well as kidney, liver, and gastric damage [4]. Chromium is widely used in industries such as electroplating and tanneries. Untreated streams

from such industries pollute ground water with chromium. In the conventional treatment of chromium, precipitation of Cr(III) as $Cr_2O_3xH_2O$ at high pH is followed by the disposal of the dewatered sludge. The major drawback of the method is the high cost of chemicals used. Therefore, extensive research is being performed to find suitable materials for adsorption and immobilization of chromate. Removal of trivalent and hexavalent chromium by seaweed biosorbent has been reported by *David* [5]. Adsorption of chromate from aqueous solutions by MnO_2 has been studied by *Bhutan* [6]. Low cost fertilizer waste materials have been used for adsorption of hexavalent chromium from aqueous solutions [7]. Separation of

Cr(VI) has been carried out by modified zeolites [8]. Biosorption of chromium (VI) by bacterium bacillus thuringiens is has been reported by *Sahin* [9]. Recent studies have shown that modification of zeolites with certain reagents yield sorbents with a strong affinity for many anions [10-11]. Electrochemical removal of the hazardous dyes from industrial effluents has been reported by *Gupta* [12]. Waste carbon slurry has been used for defluorination of wastewaters [13]. Hazardous triarylmethane dye has been treated by waste material adsorbents [14]. Biosorption of nickel onto treated alga has also been investigated [15]. Adsorption of hazardous dye crystal violet from wastewater by waste materials was reported by *Mittal A. et al.* [16]. *Vinod et al.* studied the removl of lead by a synthesized alumina-coated carbonnanotubes[17].

Zeolites are composed of three dimensional framework of aluminosilicate tetrahedral where the aluminium and silicon structure atoms are bound by covalent bonds over shared oxygen atoms to form interconnected cages and channels. Each aluminium (Al^{3+}) atom substitution for silicon (Si^{4+}) in the zeolite framework generates one negative charge on the framework. The negative charges within the pores are balanced by positively charged ions, Therefore natural zeolite are not good adsorbent for negative charged species without modification. The aim of this research, is to modified natural zeolite clinoptilolite with polyaniline to enhance its adsorption capacity for removal of Cr(VI) from aqueous solutions.

EXPERIMENTAL SECTION
Reagents and materials

Natural clinoptilolite was collected from Semnan , Iran deposits in north-east of Iran. The chemicals were purchased from Merck Company and were used as received. Stock solution of Cr(VI) (1000 ppm) was prepared by K_2CrO_4.

Instrumentation

X-ray diffraction patterns were taken by Bruker, D8ADVANCE X-ray diffractometer using Cu-Kα radiation to study the crystallinity of the composite. FT-IR spectra of the samples were taken in the range of 4000–400 cm^{-1} by a Nicolet 400Dspectrometer using KBr pellet. A scanning electron microscope (Philips, XL30) was used to study the surface morphology of the samples. Cr(VI) concentration was measured by Shimadzu Carry 100 Scan UV-Vis spectrophotometer (Japan).

Composite preparation

To introduce anilinium cation into the zeolite structure, the exchange between Na$^+$ (in clinoptilolite) and anilinium ion (in solution) was applied. 1.0 g of clinoptilolite was dispersed in 50 mL of 0.2 M aniline solution. The mixture was acidified with sulfuric acid and stirred for 48 hours at room temperature. It was then filtered and washed with excess of double distilled water in order to remove free anilinium ions. The resulting wet solid was dispersed in 50 mL of 0.3 M sulfuric acid solution containing 0.16 g ammonium persulfate as oxidizing agent. To polymerize the anilinium cation, the mixture was kept at room temperature for 24 hours under magnetic stirring. The resulting composite was filtered, washed with double distilled water and dried in vacuum oven at 80°C.

Adsorption experiments

To study the adsorption behavior of the composite, 0.2 g of the adsorbent was in contact with 50 mL of chromate solution. The mixture was stirred for 30 min at room temperature. After equilibration, the solid phase was separated. The pH of the solution changes both the surface charge of the adsorbent and the relative abundance of different species of Cr (IV). To keep the solution pH constant, known amount of borax was added to the solution and the pH was adjusted on 9.00. Cr(VI) concentration was measured at λmax=375nm. The amount of adsorbed chromate was calculated by Eq. (1).

$$a = \left(\frac{C_0 . C}{C_0}\right) \times 100 \tag{1}$$

Where C and C_0 are respectively equilibrium and initial concentrations of Cr(VI) in the solutions (mol/L). The effect of different experimental conditions on adsorption of Cr(VI) was studied and optimized.

RESULTS AND DISCUSSION
Characterization of composite

In the XRD pattern of the natural sample the main characteristic line of clinoptiloite were observed at 10,0, 22.1, 23.2, 26.2, 28.1 and 30.0 (Fig. 1a). This indicated
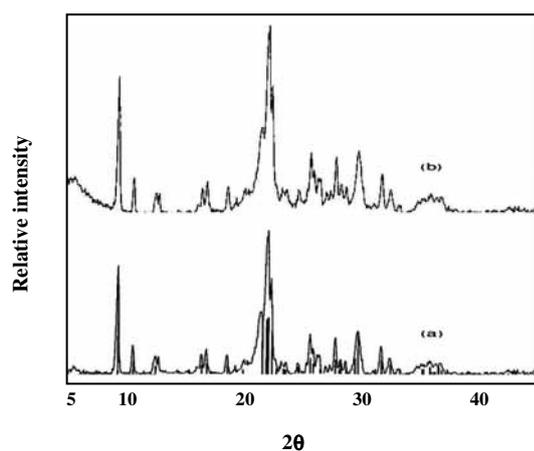
Fig. 1: X-ray diffraction patterns of natural clinoptilolite (a) and polyaniline-clinoptilolite nanocomposite(b).

Fig. 2: FT-IR spectra of clinoptilolite (a), aniline-clinoptilolite (b), and polyaniline-clinoptilolite nanocomposite(c).

that the main phase of the mineral was clinoptilolite. The line position and the line intensity of the composite were similar to those of clinoptilolite indicating that the structure of zeolite remained intact during the course of polymerization (Fig. 1b). This also confirmed that polymerization was taken place in the channels of the host zeolite without changing thier dimensions.

The FT-IR spectra of the samples are represented in (Fig. 2). The characteristic absorption bands of polyaniline and clinoptilolite which were observed in the spectra indicated that both components were present in the composite structure. The bands appeared around 1066-1086 and 700-800 were respectively related to   stretching vibration of TO (T=Si,Al). The strong band about 470 was attributed to the bending vibration of the TO. The adsorption bands around 3700 and 1600 were related to the water molecules. In the FTIR of aniline/ clinoptilolite (Figs. 2a and 2b), the stretching vibrations of CH were observed around 2800-3000 cm^{-1}. The stretching vibration and bending vibration of NH were observed respectively around 3450 and 1650 cm^{-1}. This indicated the polymerisation of aniline in the pores of zeolite.

Scanning Electron Microscopy (SEM) was used to investigate the surface morphology of the samples (Fig. 3). The surface of zeolite treated with aniline turned to white indicating that aniline had been deposited on the zeolite surface (Fig. 3.b). After polymerization, aggregation of polyaniline on the surface of the composite was clearly observed (Fig. 3.c).
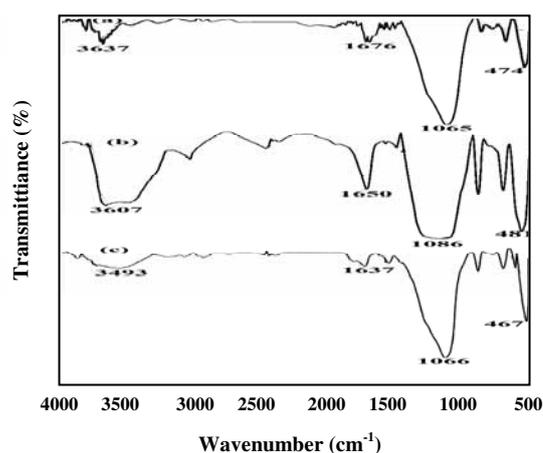
Adsorption Experiments
Effect of pH

The higher adsorption capacity of the composite at lower pH can be explained by the presence of negative species of Cr and the positive charge of the adsorbent surface. In acidic pH, the predominant species are $Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$ and the surface of the adsorbent becomes highly protonated and favors the uptake of negatively charged anionic species. At pH above 8, the only stable anion is CrO_4^{2-} and the degree of protonation gradually decreases and hence adsorption is again lowered, (Fig. 4) [11]. Furthermore, at higher pH, the concentration of negatively charged hydroxyl ions is high and the surface is less positive. However, the CrO_4^{2-} concentration is maximal at pHs higher than 8 and the aim of this research was removal of this anion, the adsorption experiments were conducted at pH=9.0.

Effect of initial concentration

The influence of initial concentration on the uptake of Cr(VI) is illustrated in (Fig. 5). As the initial concentration of Cr(VI) varied from 20.0 to 150.0 ppm, the adsorption capacity of the composite increased from 2.4 to 23.0 mg/g and beyond that, the adsorption is leveled off. Adsorption of chromate have been investigated by some other natural adsorbents [7,18]. The adsorption capacity of the adsorbent of this work was higher than the earlier works.

Fig. 3: SEM images of clinoptilolite (a), aniline-clinoptilolite (b), and polyaniline-clinoptilolite nanocomposite(c).
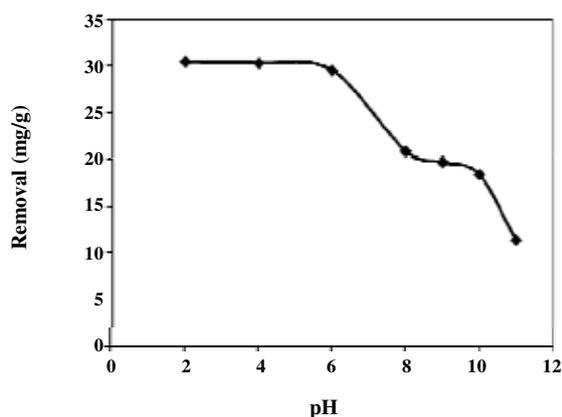

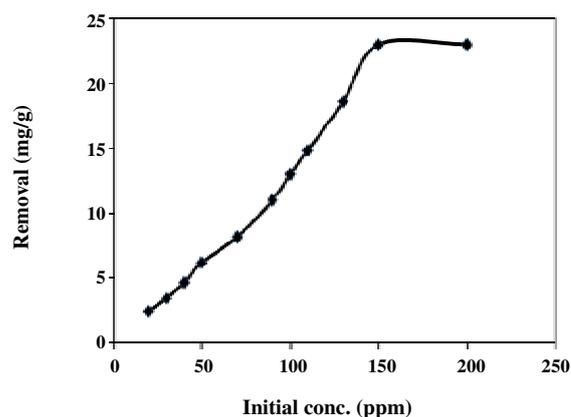**Fig. 4: Effect of pH on the removal of chromium (VI), initial conc. =150 mg/L, temp. =25°C.**

Fig. 5: Effect of initial concentration on the removal of chromium (pH=9.0 and temp. =25°C).

Effect of contact time

In order to evaluate the requisite time for equilibration of the process, 0.2g of composite was exposed to 50mL of chromate solution for known period of time. It was concluded that the adsorption process is kinetically fast and the equilibration time for adsorption is about 30 minutes (Fig. 6). The results showed that the adsorption process by the adsorbent of this research was kinetically faster than the earlier work [7].

Effect of temperature

The effect of temperature on the adsorption process is shown in (Fig. 7). It was observed that adsorption decreased with increase in temperature and was found to reach a maximum at 25°C. The temperature effect is the net effect of temperature on the Cr(VI)-oxide bond, the water-polyaniline bond, the Cr(VI)-Cr(VI) interactions and the water-Cr(VI) interaction. The water-polyaniline bond is important, as adsorption of Cr(VI) probably involves concomitant displacement of water molecules from the polyaniline surface [11].

Desorption experiment

Desorption chromate was performed by using NaOH solution. The adsorbed chromate was completely desorbed by 2M NaOH solution. Furthermore, the regenerated adsorbent retained more than 94% of its original capacity after six successive regenerations (Fig. 8).

Equilibrium modeling:

Two isotherms were tested for their ability to describe the experimental results, namely the Langmuir isotherm, and the Freundlich isotherm. The Langmuir adsorption model is based on the assumption that the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, with no lateral interaction between the adsorbed molecules [17]. The linear expression of the Langmuir model is given by Eq. (2).

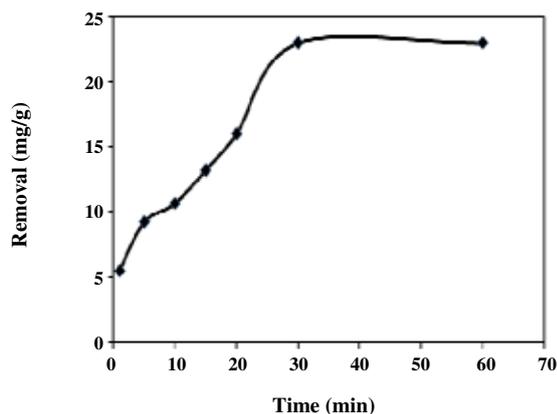$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \left(\frac{1}{Q_0}\right) C_e \tag{2}$$

Fig. 6: Effect of contact time on the removal of chromium (pH=9.0, initial conc. =150 mg/L, temp. = 25°C).
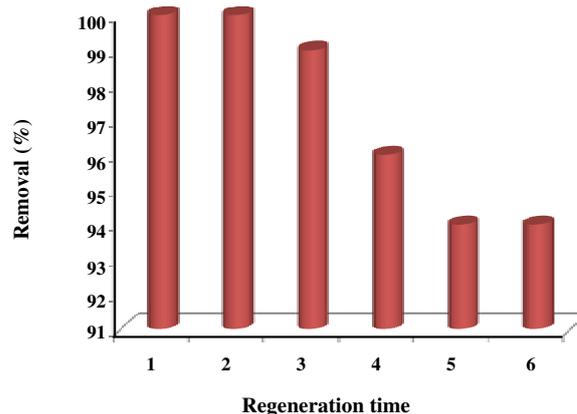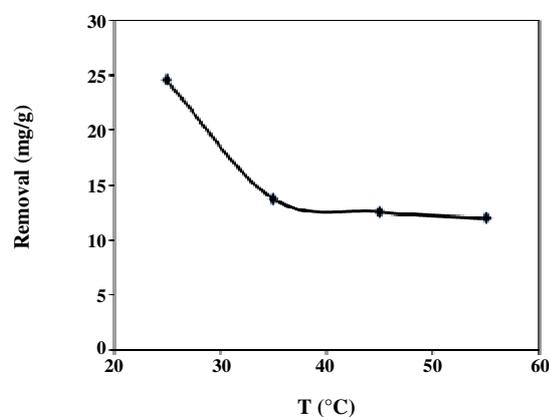

Fig. 8: Regeneration of adsorbent by 2M NaOH.

Fig. 7: Effect of temperature on the removal of chromium (pH= 9.0, initial conc. = 150 mg/L, exposure time = 30 minutes)..
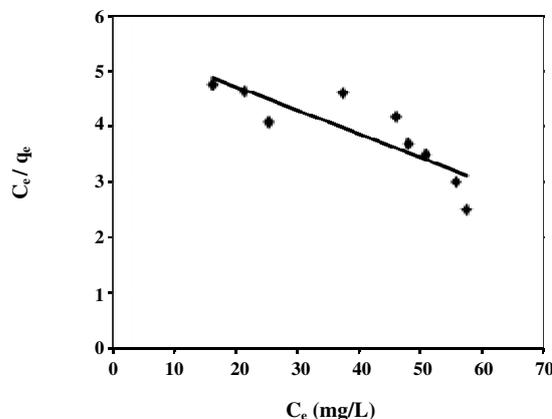

Fig. 9: Langmuir isotherm for adsorption of Cr (VI) by nanocomposite.

Where q_e (mg/g) and C_e (mg/g) are the amount of adsorbed Cr(VI) per unit mass of adsorbent at equilibrium respectively. Q_0 is the maximum amount of Cr(VI) per unit mass of adsorbent to form a complete monolayer on the surface of the adsorbent, and b is a constant related to the affinity of the binding sites (L/mg). The plot of specific adsorption (C_e / q_e) against the equilibrium concentration (C_e) shows that the adsorption obeys the Langmuir model (Fig. 9). The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot and are presented in Table 1. The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. The linear expression of the Freundlich model is given by Eq. (3) (Fig. 10).

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \qquad (3)$$

K_F (mg/g(L/mg)$^{1/n}$) is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption. Values of n>1 represent favorable adsorption conditions [19] . Values of K_F and n are calculated from the intercept and slope of the plot (Fig. 9) and listed in Table 1. From the data in the table it is concluded that the Freundlich isotherm fits the experimental data very well. The fitness of the experimental result is attributed to the homogeneous distribution of active sites on the nanocomposite surface [20]. The homogeneity of the surface is evidenet from the SEM image (Fig. 3.b).

CONCLUSIONS

Clinoptilolite itself has little affinity for chromate adsorption. Its modification with polyaniline sharply

Table 1: Isotherm parameters for adsorption of Cr (VI) on nanocomposite.

Isotherms		Parameters
Langmuir	Q_o (mg/g) =23.0	B (L/mg) =7.78×10^{-3}
	R^2=0.721	
Freundlich	K_F =1.942	n=0.276
	R^2=0.951	
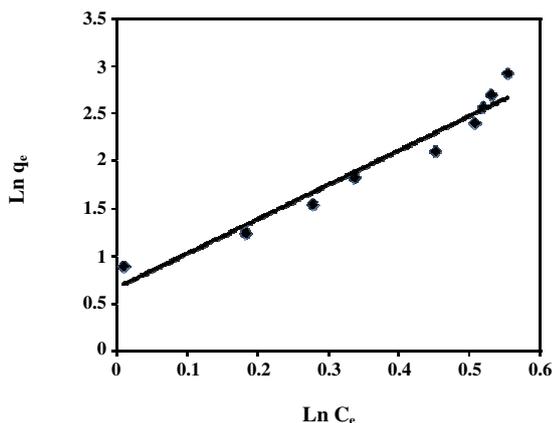
Fig. 10: Freundlich isotherm for adsorption of Cr (VI) by nanocomposite..

increased the adsorption capacity of the zeolite. Introduction of polyaniline on clinoptilolite surface, its polymerization was performed at ambient temperature. The adsorption was found to be strongly dependent on pH, contact time, initial Cr(VI) concentration and temperature. The chromate removal decreased with increasing temperature, showing the exothermic nature of the adsorption. The uptake of Cr(VI) was maximal at pH=9. The Langmuir and Freundlich isotherm models were applied to describe the equilibrium adsorption and the Freundlich model agreed very well with the experimental data.

At the optimized conditions, the adsorbent showed desirable capacity for the chromate. Since the adsorption process was kinetically fast, the adsorbent, the adsorbent could be considered for column operation.

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