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Chromium(VI) Ion Removal from Solution by Polyaniline/Pumice Composite

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The adsorption of Cr(VI) onto polyaniline/pumice(PAn/Pmc) composite has been investigated by using a batch method at room temperature and its adsorption properties was compared with PAn and Pmc. Cr(VI) adsorption was studied under different conditions (pH, time, initial Cr(VI) ion concentration, adsorbent amount and temperature) on PAn, Pmc and PAn/Pmc. The results of adsorption were fitted to both the Langmuir and Freundlich models and coefficients indicated favourable adsorption of Cr(VI) on the adsorbents. Adsorption of Cr(VI) solution was in order : PAn > PAn/Pmc > Pmc. Data from this study proved that the Cr(VI) adsorption from aqueous solutions amounts by polyaniline and its composite with pumice. The adsorption capacity of Pmc, PAn and PAn/Pmc were found as 0.42, 111.56, 0.77 and 0.05, 0.44, 0.18 for Freundlich and Langmuir adsorption isotherms, respectively. The thermodynamic parameter (free energy change, ΔG) for the adsorption has been evaluated. The sorption of Cr(VI) onto the adsorbents followed reversible first-order rates kinetics.

Key Words: Polyaniline, Adsorption, Chromium(VI), Pumice powder, Composite.

INTRODUCTION

Hexavalent chromium (Cr(VI)) is commonly found in industrial sewage. The major anthropogenic sources of Cr(VI) are the electroplating, electronic, metallurgical, leather tanning and textile industries. The effluent from these industries may contain Cr(VI) at varying concentrations up to hundreds of mg/L. Cr(VI) is considered by the International Agency for Research of Cancer (IARC), as a powerful carcinogenic agent that modifies DNA transcriptions[1]. The two most common oxidation states of chromium found in nature are III and VI. Cr(VI) extremely mobile in the environment, whereas Cr(III) is easily precipitated or adsorbed by a large variety of organic and inorganic substrates at neutral pHs. The compounds of Cr(III) are reported as being 10-100 times less toxic than those of Cr(VI)[2-4].

A number of technologies for the removal of ions from aqueous solutions have been developed over the years. The most important of these techniques include chemical precipitation, filtration, ion-exchange, reverse osmosis, membrane systems, *etc*. However, all these techniques have their inherent advantages and limitations in application. In the last few years, adsorption has shown to be alternative method for removing dissolved ions from liquid wastes[5-7]. In order to minimize processing costs, several recent investigations have focused on the use of low cost adsorbents, *e.g.* agricultural by-products[8], waste materials[9], biosorbents[10], slag[11], polymers[12], clay[13], coal[6,14] and pumice materials[15]. Adsorbents, mainly clay and pumice minerals, are readily available, inexpensive materials and offer a cost-effective alternative to conventional treatment of such mentioned waste streams[16].

Pumice is a light, porous igneous volcanic rock. It has a porous structure and a large surface area and it can be processed easily[17]. It is a valuable scouring, scrubbing and polishing material both powdered form and as a pumice stone. Pumice has been found to be effective for the removal of phosphate ions of water[18,19].

The aim of this study is to investigate the adsorption of Cr(VI) for removal ions onto PAn/Pmc, which is a new adsorbent containing polyaniline and pumice powder which is a low cost adsorbent and to compare the adsorption properties of PAn/Pmc composite with Pmc and PAn.

EXPERIMENTAL

Pumice was obtained from the middle Anatolia region (Nevsehir) of Turkey and its chemical composition was given in Table-1. Aniline was purchased from Aldrich and distilled under pressure before used. Analytical grade $K_2Cr_2O_7$ (Merck) was used without further purification. All experiments employed distilled water.

TABLE-1
CHEMICAL COMPOSITION (%) OF Pmc

SiO_2	Al_2O_3	Na_2O	K_2O	CaO
72.11	14.07	3.80	3.90	1.35

Particle dimension of Pmc: < 63 µm

A Perkin-Elmer model AA800 atomic absorption spectrometer (AAS) operating with an air-acetylene flame was employed to measure residual Cr(VI) ion concentrations. The pH of the solution was measured with an Crison Basic20 model pH meter with a glass electrode. A mechanical shaker model a Memmert WB 29 thermostatic shaker was used for shaking the adsorption batches and in temperature experiments. The surface morphology of PAn, Pmc and PAn/Pmc after and before adsorption with Cr(VI) was investigated using JEOL 5600-LV model Scanning Electron Microscopy. FTIR spectra in the range of 4000-400 cm^{-1} with a 4 cm^{-1} spectral resolution were obtained from compressed KBr pellets by a Perkin Elmer BX model IR spectrometer.

PAn and PAn/Pmc were synthesized according to procedure reported before elsewhere[20,21]. Cr(VI) stock solution (1×10^{-3} mol/L) was prepared by dissolving $K_2Cr_2O_7$ salt (from Merck) in distilled water. The stock solution was diluted as required to obtain solutions containing 1×10^{-4}-8×10^{-4} mol/L of Cr(VI).

Adsorption measurements were made by a batch technique at 20 ± 1ºC. 30 mL, 1×10^{-3} mol/L of Cr(VI) solution was used and the initial pH's of the samples were adjusted in the range of 3-8 by using diluted 0.1 N HCl or 0.1 N NaOH solution. Known amounts of PAn, PAn/Pmc and Pmc were added to each bottle. After completion of a pre-selected shaking time (2 h), the flasks containing the sample were withdrawn from shaker, the suspensions were then filtered and the supernatant solution in each flask was analyzed by atomic absorption spectroscopy for its residual Cr(VI) content.

Adsorption isotherms were carried out with different initial concentrations of Cr(VI) while maintaining the PAn, PAn/Pmc and Pmc dosages at constant level. For temperature effects, 30 mL, 1×10^{-3} mol/L of Cr(VI) and PAn, PAn/Pmc and Pmc doses of 100 mg were used from 20 to 65ºC. Kinetic studies were carried out using 30 mL, 1×10^{-3} mol/L of Cr(VI) and 100 mg adsorbent for a 5-2880 min period.

To study the adsorbent dosage, the sample was used at the solution pH and agitated with different dosages of PAn, PAn/Pmc and Pmc at 20 ± 1ºC for 2 h period. In order to correct for any adsorption of Cr(VI) on the container surface, control experiments were carried out in the absence of adsorbents. These experiments indicated that no adsorption by the container walls was detectable.

In addition, all mixing vessels were kept sealed throughout the duration of each isotherm test in order to minimize the release of gaseous species to the atmosphere.

RESULTS AND DISCUSSION

The kinetics of Cr(VI) sorption were studied by varying the contact time from 5 to 2880 min using about 100 mg of PAn, Pmc and PAn/Pmc composite and an initial ion concentration of 1×10^{-3} mol/L (Fig. 1a-c). As Fig. 1(a-c), the Cr(VI) sorption involved within 2 h of contact. The highest Cr(VI) sorption was observed in PAn while the lowest sorption was in

Pmc. Experiments were also directed at an attempt to understand the kinetics of Cr removal by PAn, Pmc and PAn/Pmc composite. It is a well established fact that the adsorption of ions in aqueous system follows reversible first-order kinetics, when a single species is considered on a heterogeneous surface. Using the kinetic equations, the overall rate constant, the forward and backward rate constants were calculated according to the known equation[22,23]. The equilibrium constant K_d, forward and backward rate constants, k_1 and k_2, were calculated (Table-2). From Table-2, it is clear that the forward rate constants for the removal of chromium were much higher than backward rate constants, namely the adsorption process. The sorption of Cr(VI) onto the samples followed reversible first-order rate kinetics. The rate constants of adsorption of PAn/Pmc, PAn and Pmc are compared, PAn/Pmc and PAn have higher rate than that of Pmc. The rate constant of Pmc is lower than those of PAn/Pmc and PAn. From these results it is observed that the adsorption rate constant of Pmc was increased from 0.0119 to 0.0216 modifying with PAn.

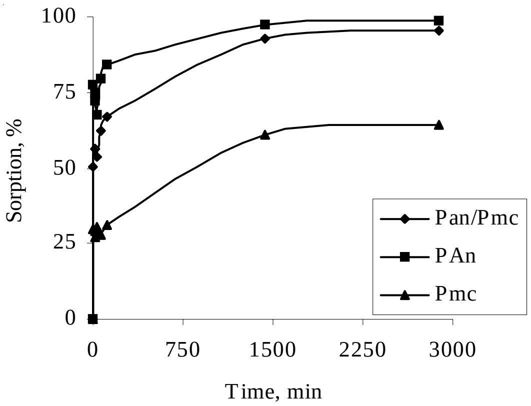


Fig. 1. Effect of contact time on the sorption of Cr(VI) by adsorbents (adsorption conditions: initial concentration of Cr(VI), 1 × 10^{-3} M; adsorption time, 5-2880 min; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; temperature, 20 ± 1ºC)

TABLE-2
RATE CONSTANTS FOR THE REMOVAL OF Cr(VI) WITH PAn/Pmc, PAn AND Pmc SYSTEM

Adsorbent type	Overall rate constant ($K_d = k_1 + k_2$ (h^{-1}))	Forward rate constant k_1(h^{-1})	Backward rate constant k_2 (h^{-1})
PAn/Pmc	0.0227	0.0216	0.0011
PAn	0.0242	0.0239	0.0003
Pmc	0.0184	0.0119	0.0065

Concentrations of Cr(VI): 1.10^{-3} mol/L

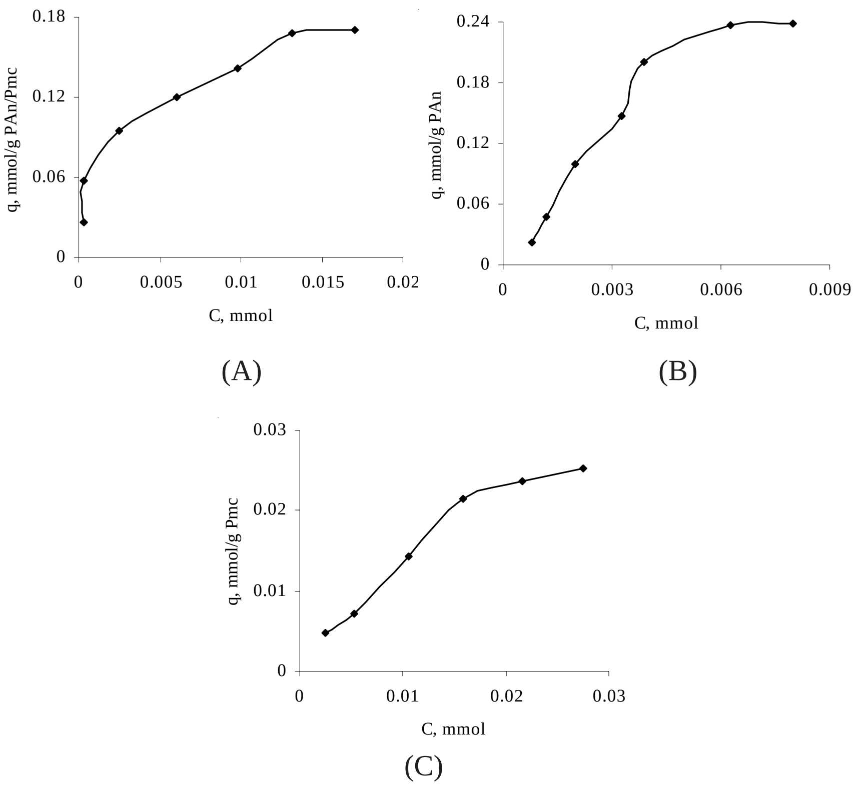
Sorption Equilibrium

The concentration of Cr(VI) on a medium is calculated as the difference between the original concentration in the solution and the concentration in solution, after contact. The mass balance may be expressed as:

$$q = [V(C_o-C_e)]/m \qquad (1)$$

where q and C_e are, respectively, the adsorbent phase chromium concentration (mmol/L) and solution phase concentration at equilibrium (mmol/L), C_o the initial Cr(VI) concentration (mmol/L), V the solution volume (L) and m the mass of adsorbent (g)[24].

The influences of initial Cr(VI) concentration on the adsorption efficiency at an initial solution using PAn, Pmc and PAn/Pmc are shown in Fig. 2(a-c), respectively. The amount of adsorbent was kept at 100 mg and the contact time of 2 h was employed in this study. The sorption was found to increase with the initial Cr(VI) concentration, then it reached equilibrium[23].



(A) (B)

(C)

Fig. 2. Sorption isotherms of Cr(VI) ion on PAn/Pmc(A), PAn(B) and Pmc(C)(adsorption conditions : initial concentration of Cr(VI), 1×10^{-4} - 8×10^{-4} M; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; adsorption time, 2 h; temperature, 20 ± 1ºC)

Langmuir and Freundlich isotherm models were fitted to the adsorption data and their constants were evaluated. Satisfactory conformity between experimental data and the model-predicted values was expressed by the correlation coefficient (R^2).

The experimental results obtained for the adsorption isotherms of PAn/Pmc were found to obey the Langmuir adsorption isotherms. The maximum adsorption capacity from the Langmuir isotherm equation was found to be 0.98 mmol/g for PAn/Pmc whereas R^2 of PAn/Pmc for Freunlich isotherm was 0.87 mmol/g.

The Langmuir isotherm is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{Q_o b} \tag{2}$$

where C_e (mmol/L) is the equilibrium concentration, q_e (mmol/L) is the amount of Cr(VI) sorbed at equilibrium, Q_o and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively[24-27]. Q_o and b were determined from the slope and intercept of the Langmuir plot and are presented in Table-3.

TABLE-3
FREUNDLICH AND LANGMUIR ADSORPTION ISOTHERM PARAMETERS OF PAn/Pmc, PAn AND Pmc

Freundlich Isotherm				Langmuir Isotherm			
Adsorbents	k	n	R^2	Q_0	B	R^2	R_L
PAn/Pmc	0.7679	2.7701	0.8700	0.1841	517.3172	0.9790	0.6591
PAn	111.5578	0.8588	0.9600	0.4427	164.8807	0.8608	0.8585
Pmc	0.4199	1.3278	0.9900	0.0542	34.4477	0.8602	0.9667

k and Q_o: mmol/g adsorbent; R^2: correlation coefficient; n and b: constants

The essential feature of the Langmuir equation can be given in terms of a dimensionless separation factor, R_L, defined as

$$R_L = 1/(1 + b\,C_o) \tag{3}$$

where C_o is the highest initial solute concentration. The value of R_L indicates the shape of the isotherm to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In this work, the values of R_L obtained are listed in Table-3.

The Freundlich isotherm is the most widely used non-linear sorption model and is given by the general form:

$$q = kC^{1/n} \tag{4}$$

where k relates to the sorption capacity and n to sorption intensity[5,23,24,27]. The logarithmic form of eqn. 4 given below is usually used to fit data from batch equilibrium studies:

$$\log q = \log k + 1/n \log C \quad (5)$$

eqns. 2 and 5 are usually used for the analysis of equilibrium batch experiment data assuming Langmuir and Freundlich isotherms parameters given in Table-3 for Cr(VI), respectively. The equilibrium data was fitted very well to both sorption isotherms.

Influence of pH

The pH value of the solution is an important factor that controls the sorption of Cr(VI). Fig. 3(a-c) show the extent of removal of Cr(VI) as a function of pH for initial concentration of 1×10^{-3} mol/L. It can be seen that the adsorption is maximum at pH 3. At pH values higher than 3, the adsorption of Cr(VI) has been decreased for PAn, Pmc and PAn/Pmc. The highest adsorption among adsorbents at pH 3 has been shown in PAn. The effect of pH on adsorption of Cr(VI) onto PAn can be interpreted with the help of the structure of the sorbent and the speciation of chromium. PAn has a $NH_3^+Cl^-$ group acting as an anion exchanger. Thus, in PAn and PAn/Pmc, exchange of Cl^- to anions takes place on treatment with solution containing anions.

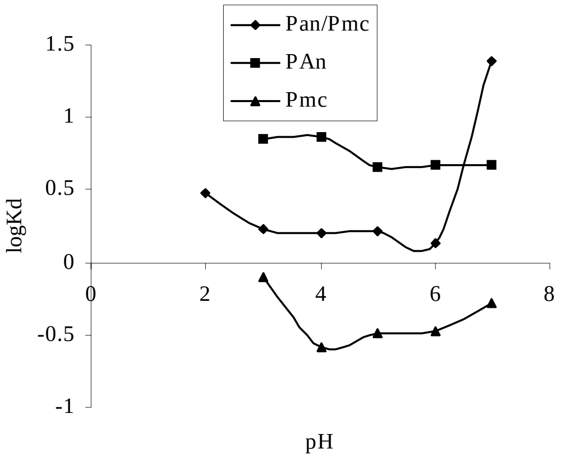


Fig. 3. The distribution coefficients of Cr(VI) metal on the adsorbents as a function of pH (adsorption conditions : initial concentration of Cr(VI), 1×10^{-3} M; amount of adsorbent, 100 mg; volume of adsorption medium, 30 mL; adsorption time, 2 h; temperature, 20 ± 1ºC)

The variation in adsorption can be explained by taking into account the affinities of the PAn and PAn/Pmc for different species of Cr(VI) coexisting at acidic pH ($Cr_2O_7^{2-}$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, $Cr_4O_{13}^{2-}$)[18]. Above pH 8, only CrO_4^{2-} is stable and as the pH decreases into the pH region 3-6 the equilibrium shifts to dichromate according to the overall equilibrium.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

The perusal of the Pourbaix diagram[28] clearly indicates that the pH of the highest sorption efficiency (pH 3), the dominant species were $HCrO_4^-$. It can thus be suggested that the $HCrO_4^-$ and $Cr_2O_7^{2-}$ species are most easily exchanged with Cl^- from peripheral $–NH_3^+Cl^-$ group contained in PAn and PAn/Pmc. This mechanism is in agreement with the finding of previous studies on other adsorbents, such as those used by Leyva-Ramos *et al.*[29] and Shukla *et al.*[30]. Pmc also exhibited the highest adsorption at pH 3 because it form the positively charged surface. But at this pH, its adsorption capacity is lower than PAn and PAn/Pmc. As a result of this, it has been seen that adsorption of Cr(VI) onto Pmc increased with entering PAn to Pmc structure.

Effect of amount of adsorbent

In order to investigate the effect of mass of adsorbent on the adsorption of Cr(VI), a series of adsorption was carried out with different adsorbent amount at initial Cr(VI) concentration of 1×10^{-3} mol/L. Fig. 4 is a plot of Cr(VI) sorption (%) *vs.* adsorbent dosage. The adsorption of Cr(VI) increased with increase in adsorbent amount. This may be attributed to increased adsorbent surface area and availability of more adsorption sites resulting from the increase amount of the adsorbent. It is apparent that the equilibrium metal ion concentration decreases with increasing adsorbent dosage for a given initial Cr(VI) concentration[23,24,27,28]. This is to be expected because, for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area or adsorption sites. The maximum

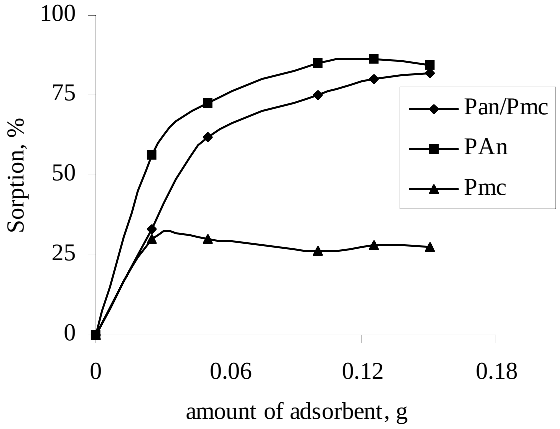


Fig. 4. The effects of the amount of adsorbents for Cr(VI) from aqueous solutions (adsorption conditions : initial concentration of Cr(VI), 1×10^{-3} M; amount of adsorbent, 25-125 mg; volume of adsorption medium, 30 mL; adsorption time, 2 h ; temperature, 20 ± 1ºC)

adsorption of Cr(VI) was seen at adsorbent amount of 100 mg. Thus, in all experiments adsorbent amount was selected as 100 mg. The results also clearly indicated that the removal efficiency increases up to the optimum dosage beyond which the increase in removal efficiency is negligible. The sorption order for adsorbents is PAn > PAn/Pmc > Pmc.

Effect of temperature on adsorption

The adsorption mechanism, (*i.e.*, chemical or physical) is often an indicator to describe the type and level of interactions between the adsorbate and adsorbent. If adsorption decreases with increasing temperature, it may be indicative of physical adsorption and the reverse is generally true for chemisorption. However, there are a number of contradictory cases in the literature[25,28,31,32]. In this system, the increase in adsorption with increasing temperature suggested the presence of chemical adsorption. Nevertheless, this alone is not sufficient to determine the type of adsorption. The type of adsorption may be also determined through free energy of adsorption (ΔG).

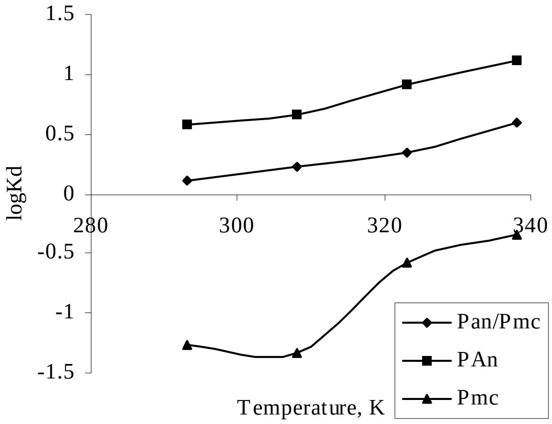


Fig. 5. The equilibrium constants of Cr(VI) on the adsorbents as a function of temperature (adsorption conditions : initial concentration of Cr(VI), 1×10^{-3} M; amount of adsorbent, 25-125 mg; volume of adsorption medium, 30 mL; adsorption time, 2 h; temperature, 20 ± 1ºC)

The isotherms for adsorption of Cr(VI) ions are presented in Fig. 5 for four different temperatures (293.15, 308.15, 323.15 and 338.15 K). Equilibrium constants (K_d) for the adsorption of Cr(VI) ion onto PAn, Pmc and PAn/Pmc were high and adsorption increased with increasing temperature (from 293.15 to 338.15 K). The standard free energy change ΔG, was calculated using the equation

$$\Delta G = -RT \ln K_d \tag{6}$$

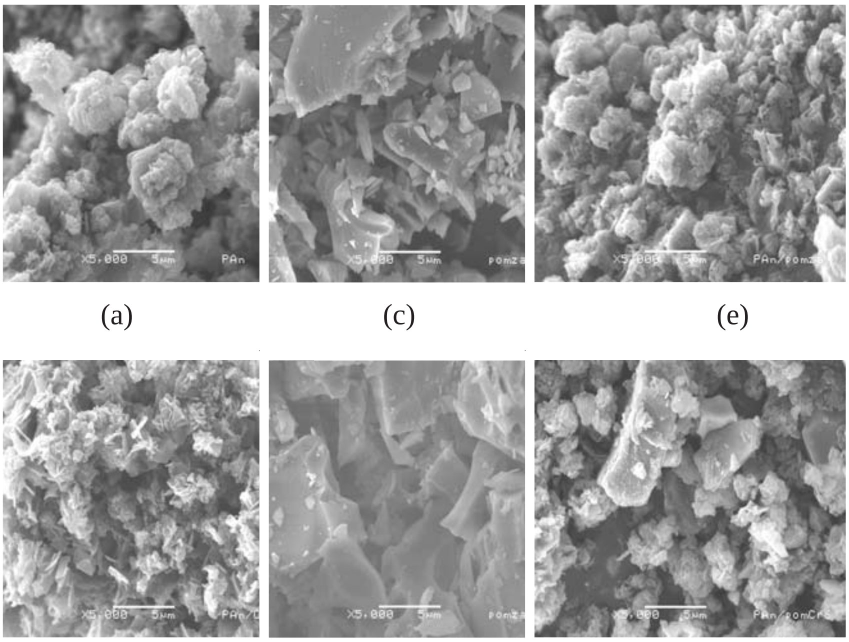
The negative values of ΔG of PAn and PAn/Pmc (Table-4) indicate the feasibility of the process and indicate the spontaneous nature of adsorption whereas positive ΔG value of Pmc shows lower adsorption according to PAn and PAn/Pmc.

TABLE-4
THERMODYNAMIC PARAMETERS OF PAn/Pmc, PAn AND Pmc

Adsorbent type	$\Delta G_{293.15}$ (J mol^{-1})	$\Delta G_{308.15}$ (J mol^{-1})	$\Delta G_{323.15}$ (J mol^{-1})	$\Delta G_{338.15}$ (J mol^{-1})
PAn/Pmc	-597.9035	-1301.3932	-2126.0445	-3830.0261
PAn	-3244.8608	-3880.4176	-5601.9146	-7230.1164
Pmc	7078.3076	7891.1927	3628.7765	2225.4034

SEM and FTIR analysis results

Figs. 6 and 7 show SEM and FTIR results, respectively for PAn, Pmc and PAn/Pmc composite after and before Cr(VI) adsorption. Both results supported to each other and they have shown that Cr(VI) has been adsorbed by these samples[33]. The most changing in morphologies was seen in SEM



(a) (c) (e)

(b) (d) (f)

Fig. 6. SEM micrographs of PAn(a), PAn/Cr(VI)(b); Pmc(c), Pmc/Cr(VI)(d); PAn/Pmc(e), PAn/Pmc/Cr(VI) (f) before and after adsorption

micrograph of PAn (Fig. 6a-b). Moreover, the FTIR bands of PAn, especially bands of benzenoid and quinoid rings at 1502 and 1580 cm^{-1}, were not affected from $K_2Cr_2O_7$ oxidizing aniline monomer (Fig. 7). According to this result it is suggested that there is not reduction of Cr(VI) to Cr(III) in the presence polyaniline.

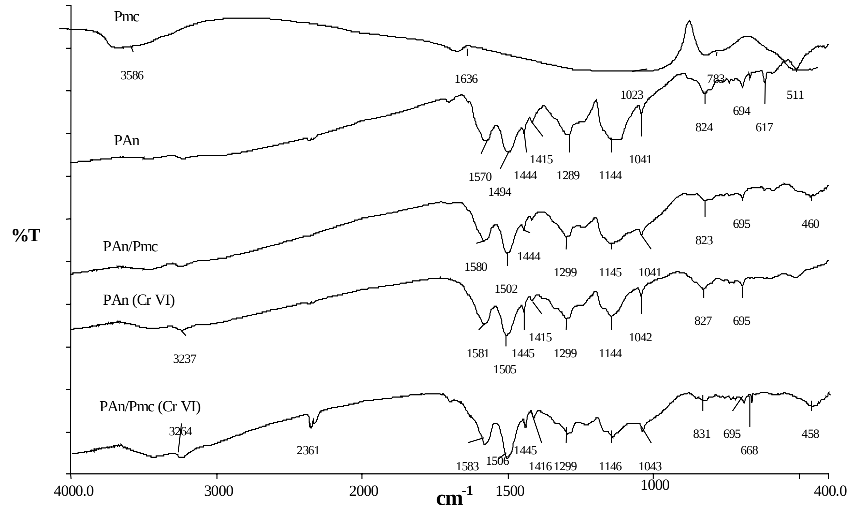


Fig. 7. FTIR spectra of adsorbents (PAn, Pmc, PAn/Pmc), before and after adsorption

Conclusions

The adsorption of Cr(VI) from aqueous solution onto pumice, polyaniline and polyaniline/pumice composite has been studied. Adsorption capacity of pumice, as a natural and cheap product, was increased preparing composite with polyaniline. The adsorption of Cr(VI) ions is dependent on the initial concentrations of adsorbent, sorbent amount, pH and time of contact. Isothermal data of Cr(VI) on adsorbents can be modeled by both Freundlich and Langmuir isotherms. As a result, the proposed method is excellent with respect to simplicity, sensitivity, precision and stability of adsorbent and suggested that polyaniline/pumice powder could be employed as adsorbent for removal of Cr(VI).

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