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Molecular weight effect on chromium(VI) retention by poly (N-octyl-4-vinylpyridinium bromide) copolymers

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ABSTRACT

Copolymers containing poly(4-vinylpyridine) (P4VP) quaternized with octylbromide (C_8Br) were synthesized. The rate of quaternization was determined using conductivity measurements and confirmed by ^1H NMR spectroscopy. We describe the effect of P4VP molecular weight on the retention ability of hexavalent chromium (Cr(VI)). The retention of Cr(VI) was investigated by batch equilibrium procedure, and this study was monitoring by UV–vis spectrophotometry and FTIR spectroscopy. Empirical equation expressing the adsorbent amount as a function of molecular weight was proposed for the retention of Cr(VI). Four P4VP samples were considered in a wide interval of molecular weights: 7.5×10^3–9.4×10^5 g/mol. The retention efficiency increases with copolymer molecular weight of P4VP then remains constant for long chain from $M_w = 3.8 \times 10^5$ g/mol. The adsorption kinetic experiments reveal that the adsorbed amount of Cr(VI) continuously increases with the time and reaches saturation after 10 min, independently to the molecular weight. P4VP-C_8Br showed fairly good results in total chromium removal kinetics.

Keywords: Quaternized poly(4-vinylpyridine); Molecular weight; Octylbromid; Chromium(VI); Retention

1. Introduction

The presence of heavy metals in the environment is of major concern because of their toxicity to many life forms [1]. Most heavy metals never degrade completely and accumulate in organisms. For this reason, their concentrations must be reduced and monitored.

Chromium (Cr) compounds are widely used in industry such as electroplating, metal finishing, leather tanning, pigments, etc. The predominant use of chromium in industry unfortunately introduces an environmental concern. Chromium exists almost exclusively in the Cr(III) oxidation state or in the Cr(VI) oxidation state. In the environment, Cr(III) is typically not a problem, its relative toxicity is low. In contrast, Cr(VI) compounds are toxic chemicals and genotoxic carcinogens [2]. Thus, the presence of Cr(VI) ions in the environment is posing serious problems and causing great public concern [3,4]. Currently, the United States Environmental Protection Agency has set a maximum contaminant level for chromium at 0.1 ppm in drinking water [5]. The increasing concern with Cr(VI) pollution, significantly motivates the investigation and development of new and improved

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materials to address the problems. A wide range of technologies have been investigated for the removal of Cr(VI) from water [6–9].

Wastewaters containing relatively low chromium concentrations are usually treated with expensive ion-exchange resins [10]. Adsorption is an effective method for the retention of heavy metals. In the recent years, interest has been focused on removal of chromium(VI) from aqueous solutions using adsorption method [11–14]. Naturally available adsorbents like wool [15] and dead fungal biomass [16] were used for chromium removal. However, many of these naturally available adsorbents have low chromium removal capacities and slow process kinetics. Thus, there is a need to develop innovative low-cost adsorbents with affinity toward metal ions for the removal of chromium from aqueous solution within a short time.

A system of bentonite/poly(4-vinylpyridinium) was used to remove hexavalent chromium. The retention process depends on the various interactions: bentonite/P4VP (poly(4-vinylpyridine), bentonite/Cr(VI), P4VP/Cr(VI) and P4VP/Cr(VI) complex bentonite [17,18]. A quaternized and crosslinked P4VP have been used to remove hexavalent chromium Cr(VI). It exhibited the degrees of usage of the exchange capacities higher than 90% with a time of saturation equal to two hours [19]. Toral et al. [20] carried out the retention of Cr(VI) onto P4VP N-alkyl quaternized at P4VP of $M_w = 6 \times 10^4$ g/mol but did not consider large domain of molecular weight.

The aim of this work is to describe the effect of the molecular weight on the retention capacity of hexavalent chromium in aqueous solutions by P4VP quaternized with octyl-bromid. In our previous work [21], we have study the equilibrium isotherms and kinetics parameters of the Cr(VI) adsorption on N-octyl quaternized P4VP. In this work, we have considered four P4VP samples in a wide interval of molecular weights: 0.75×10^4–94×10^4 g/mol. As far as we know, in the literature, there are no studies reporting the use of P4VP with different molecular weight for Cr(VI) retention.

This study is monitoring by UV–vis spectrophotometry including the characterization of the copolymers in the absence and in the presence of Cr(VI) through infrared spectroscopy (FTIR).

2. Experimental

2.1. Materials and methods

Octyl bromide, chloroform, hexane, methanol, and ethyl acetate were supplied by Aldrich (analytical grade) and used without further purification. Potassium chromate was purchased from Biolab

2.1.1. Preparation and characterization of the linear P4VP

P4VP (Fig. 1) was prepared by radical polymerization, using AIBN or benzoyle peroxide as initiators, in toluene at 60˚C. Detailed procedures were described earlier [22–24]. P4VP samples were fractionated by successive dissolution/precipitation in the following solvents: chloroform/hexane or methanol/ethylacetate. Fractionation has provided four P4VP fractions, P4VP1 to P4VP4.

M_w was determined by light scattering in ethanol by classical treatment. M_v of each sample was measured in absolute ethanol (distilled on calcium oxide CaO) by an Ubbelhode-Schott Gerat AVS400 viscosimeter using the empirical power law $[\eta] = 2.35 \times 10^{-5} \mathrm{Mv}^{0.90}$ for long chains and for short chains $[\eta] = 6.08 \times 10^{-4} \mathrm{Mv}^{0.61}$ [21]. Measurements were conducted at 25˚C in a thermostatic bath. Table 1 shows different M_v and M_w values of P4VP.

^{1}H NMR spectra for both samples of P4VP ($CDCl_3$, δ ppm): (8.31; –N–C–H), (6.37; –N–C–C–H), (1.51–2.37; –CH_2–CH–). ^{1}HNMR spectra were measured with a Bruker (400 MHz) spectrometer. $CDCl_3$ was used as solvent.

The retention of chromium in aqueous solutions was determined using UV–vis (Perkin Elmer Lambda 800 UV–vis spectrophotometer, Tlemcen, Algeria). The

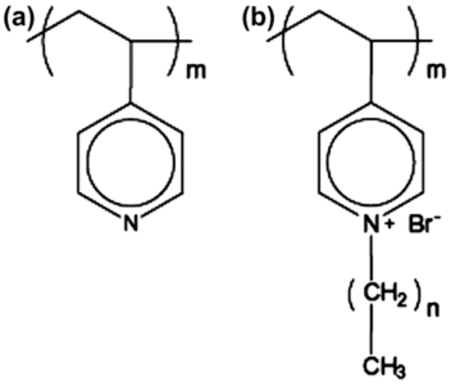

Fig. 1. Structural unit of P4VP and P4VP-C_8Br (a) P4VP, (b) P4VP-C_8Br with $n = 7$.

Table 1
Values of M_w and M_v

Polymers	M_w 10^{-4} g/mol	M_v 10^{-4} g/mol
P4VP1	94.00	52.70
P4VP2	31.00	19.87
P4VP3	6.00	3.27
P4VP4	0.75	0.36

concentrations of the residual chromium(VI) was determined by 1,5-diphenylcarbazide method [25].

2.1.2. Synthesis of poly(N-octyl-4-vinylpyridinium bromide) copolymers [P4VP-C_8Br]

The quaternization was performed by refluxing P4VP with octyl-bromide in ethanol. The reactions were carried out under nitrogen in a thermostated water bath (±0.1 K). The quaternization rate was obtained by conductivity measurements using a Mettler DL 40 RC titrator with a silver electrode [26–28]. The solution was then poured into diethylether to obtain a solid which was washed with diethylether repeatedly, filtered and dried under vacuum at room temperature to constant weight. P4VP-C_8Br quaternization rate was confirmed by ^{1}H NMR spectroscopy. The copolymers were named P4VP1-C_8Br, P4VP2-C_8Br, P4VP3-C_8Br, and P4VP4-C_8Br, respectively. The values of quaternization maxima rate are given in Table 2.

Table 2
Values of molar quaternization maxima rate (τ_{max})

Copolymers	$\tau_{max\ (\%)}$
P4VP1-C_8Br	82.0
P4VP2-C_8Br	75.7
P4VP3-C_8Br	70.0
P4VP4-C_8Br	64.0

2.2. Retention procedure for Cr(VI) in P4VP-C_8Br

The Cr(VI) solutions were prepared in different concentrations by diluting K_2CrO_4 stock solution appropriately as necessary. To determine the conditions that achieve the maxima amount of metal ion removal, adsorption experiments were done. The kinetic studies were carried out by shaking 200 mg of P4VP-C_8Br copolymer (dry weight) with 100 mL of chromate solution at different concentrations. NaOH 0.1 mol/L was added to achieve pH 8.5 ± 0.2. In fact, Cr(VI) is very soluble in aqueous solutions and solubility increases with pH; therefore, it was practical to employ copolymers at solution pH values of 8 and below [21].

In all experiments, the copolymers were separated by filtration. The filtrate was analyzed by liquid and solid UV–vis spectrophotometry.

2.3. Characterization of solid phase

The characterization of the solid phase was performed for P4VP-C_8Br in the absence and in the presence of Cr(VI). The solid phase was filtered and analyzed by infrared spectroscopy FTIR (SHIMADZU TFIR-8300, Tlemcen, Algeria).

3. Results and discussion

3.1. Studies of retention of Cr(VI) on P4VP-C_8Br

3.1.1. Effect of P4VP-C_8Br molecular weight on Cr(VI) absorbance in liquid phase

P4VP1-C_8Br, P4VP2-C_8Br, P4VP3-C_8Br, and P4VP4-C_8Br were used for the retention of Cr(VI). The solid copolymers were added to chromate solutions (concentration = 10^{-4} mol/L at pH = 8.5). The absorbance of the liquid phase was measured after 0, 10, and 30 min.

Figs. 2–4 represent the UV–vis spectra of Cr(VI) remaining in the solution after the addition of P4VP-C_8Br copolymers with various molecular weights. The results show that the absorbance of Cr(VI) decreases in the aqueous solution according to the time of agitation. They confirm that the Cr(VI) ions were well adsorbed on P4VP-C_8Br copolymers. The absorbance decreases when the molecular weight increases. The retention efficiency increases with the copolymer molecular weight.

3.1.2. Effect of P4VP-C_8Br size chains on the absorbance of Cr(VI) ions in solid phase

The retention ability was also determined in the solid phases P4VP-C_8Br at Cr(VI) concentration equal to 8×10^{-6} mol/L. For these experiments, the solid phases were agitated with copolymer of different size (P4VP1-C_8Br, P4VP2-C_8Br, P4VP3-C_8Br, and P4VP4-

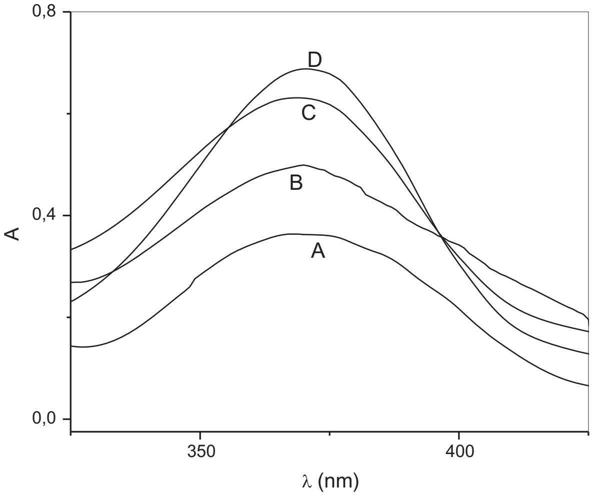

Fig. 2. Spectra of Cr(VI) remaining in the solution from first contact. A: P4VP1-C_8Br, B: P4VP2-C_8Br, C: P4VP3-C_8Br, D: P4VP4-C_8Br.

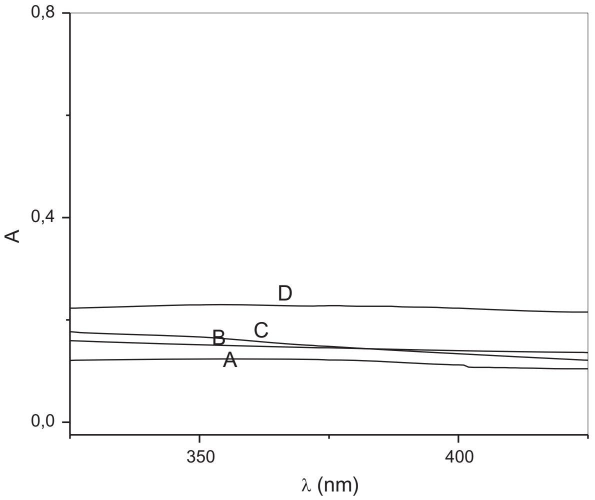

Fig. 3. Spectra of Cr(VI) remaining in the solution after 10 min. A: P4VP1-C_8Br, B: P4VP2-C_8Br, C: P4VP3-C_8Br, D: P4VP4-C_8Br.

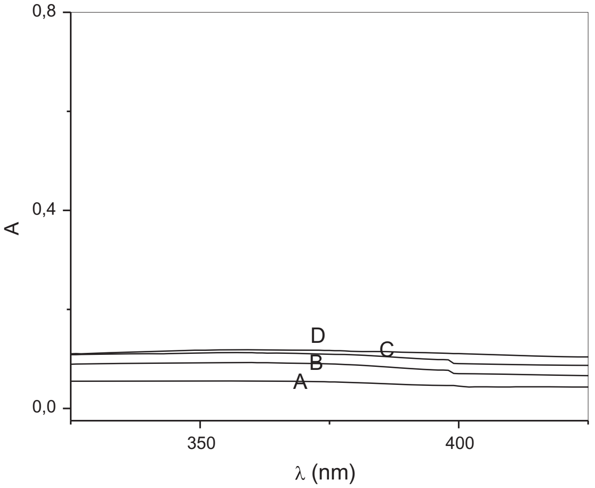

Fig. 4. Spectra of Cr(VI) remaining in the solution after 30 min. A: P4VP1-C_8Br, B: P4VP2-C_8Br, C: P4VP3-C_8Br, D: P4VP4-C_8Br.

C_8Br) for 10 min in all cases. Fig. 5 illustrates that the absorbance of Cr(VI) existing in the copolymer of long chain is higher than that of smaller chain. The spectra bands show that the adsorption corresponds to an interaction between P4VP-C_8Br and chromate.

3.1.3. Kinetics of Cr(VI) retention

The adsorbed amounts of chromium on copolymers were determined through a spectroscopic method. The species of Cr(VI), presumed to be present in aqueous solution, are the bichromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ions; besides chromic acid (H_2CrO_4) that apparently exists in concentrated acid media. The proportion of the different ionic species was determined as a function of pH [29] and predominance of the Cr(VI) species:

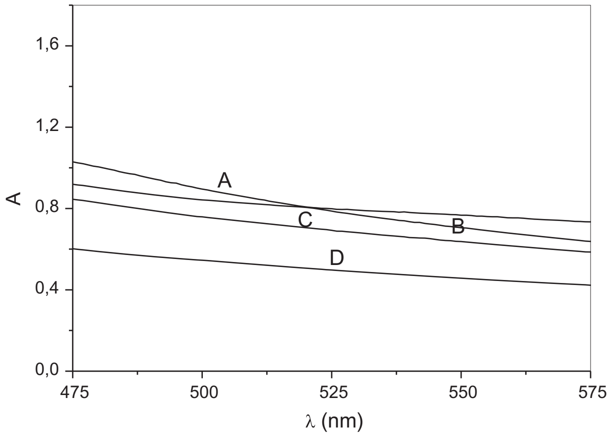

Fig. 5. Spectra of Cr(VI) adsorbed on the solid phase for $[Cr(VI)] = 8.10^{-6}$ M A: P4VP1-C_8Cr(VI), B: P4VP2-C_8Cr(VI), C: P4VP3-C_8Cr(VI), D: P4VP4-C_8Cr(VI).

- H_2CrO_4 exists at significant concentrations only in solutions with $pH < 1$;
- $HCrO_4^-$ predominates in the pH range 1–6.9 except that, above a certain Cr(VI) concentration (about 10^{-3} mol/l), it coexists with $Cr_2O_7^{2-}$;
- At pH above 8, Cr(VI) only exists as CrO_4^{2-}.

The adsorbed amount was analyzed by measuring the amount of Cr(VI) adsorbed at various times of equilibrium according to the following relation:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \tag{1}$$

where C_0 and C_t (mg/L) are the initial and time t Cr(VI) concentrations, respectively; V and m are the liquid volume (L) and the weight of dried used adsorbent (g).

Fig. 6 illustrates the variation of the amount of Cr(VI) adsorbed on copolymers according to the time at pH = 8.5 at 25°C.

The equilibrium adsorption capacity was attained after only 10 min and we did not observe significant fluctuation of the adsorbed quantity after 10 min until 3 h. The time chosen to carry out all the retention experiments was 10 min. Similar behaviors were observed during the retention of hexavalent chromium by the P4VP3 quaternized with C_6Br, C_8Br, and $C_{10}Br$ [20]. An equilibrium time of 30 min was observed for the retention of Cr(VI) by P4VP-bentonite composites [18]. A reaction time of 50–350 h was

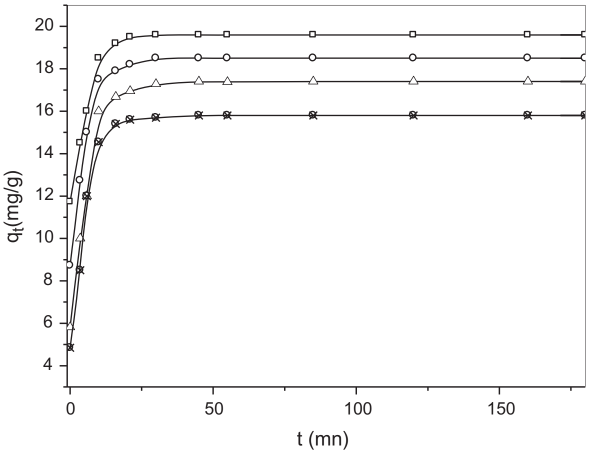

Fig. 6. Kinetics of adsorption of ions Cr (VI) on copolymers at pH = 8.5. □: P4VP1-C_8Br, ○: P4VP2-C_8Br, Δ: P4VP3-C_8Br, ⊗: P4VP4-C_8Br.

observed for the chromium retention by the fungal biomass *Aspergillus niger* with an initial chromium concentration of 25–200 mg/L [30]. Equilibrium time of 2 and 5 h were reported for total chromium removal (initial concentrations 3 and 10 mg/L by iron hydroxide-loaded sugar beet pulp and polyvinylpyridine-coated silica gel, respectively [31,32]. P4VP-C_8Br copolymers are good adsorbents for the hexavalent chromium anions.

From the results shown in Fig. 6, it appears that at the beginning of contact the adsorbed amount (q_t) of Cr(VI) anions increases with the molecular weight of copolymer. After 10 min of agitation, a plateau of Cr(VI) adsorb amount (q_t) was reached. The length of the macromolecular chains has a determining influence on the retention of Cr(VI). The amount of hexavalent chromium ions adsorbed on copolymer of high molecular weight after 10 min was 18.6 and 14.0 mg/g on copolymer of low molecular weight starting with initial concentration of Cr(VI) equal to 19.4 mg/L. The adsorbed amount increases with copolymer molecular weight. The kinetic of retention is very fast in comparison with the other adsorbents. Ten minutes is enough to reduce Cr(VI) anions for all copolymers. The removal percentage using copolymer of long macromolecular chain is 95.8 and 72.3% using copolymer with small macromolecular chain.

This effect of P4VP molecular weight can be explained by the hydrophobic/hydrophilic balance of the copolymer. Indeed, when the hydrophobic character of the copolymer increases, the copolymer acquires a compact structure [33,34]. Moreover, copolymer in contact with the aqueous phase interacts with chromate forming a pair of ions. It is clear that the interaction between the polyelectrolytes and Cr(VI) is mainly of electrostatic nature and it depends on the rate of quaternization.

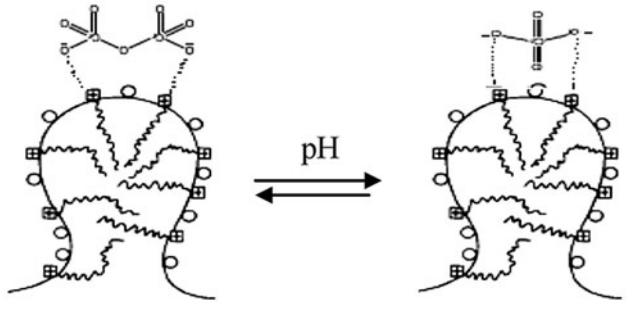

Fig. 7. Model proposed of interaction between copolymer and Cr(VI).

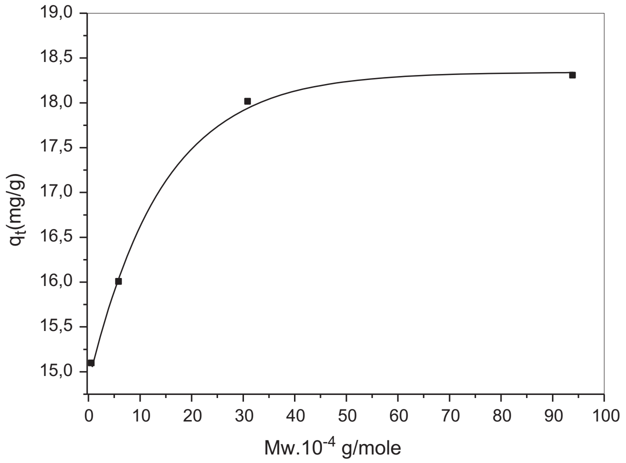

Fig. 8. Variation of Cr(VI) adsorbed amount from aqueous solution as function of copolymers weight.

Fig. 7 represents the model suggested for the interactions between copolymer and Cr(VI).

Fig. 8 illustrates the variation of adsorbed Cr(VI) amount versus the molecular weight of P4VP.

Fig. 8 permits to propose an empiric equation describing the effect of P4VP molecular weight on hexavalent chromium adsorption capacity:

$$q_t = 18.34 - 3.45\, e^{\left(\frac{-M_w}{14.36}\right)} \quad R^2 = 0.999 \tag{2}$$

where q_t and M_w represent adsorbed amount in the liquid phase and polymers molecular weight (g/mol), respectively. Fig. 8 shows that the adsorbed amount increases with the molecular weight of P4VP then remains constant for longer macromolecular chain from $M_w = 3.8 \times 10^5$ g/mol.

3.2. Characterization of P4VP-C_8Cr by FTIR

Figs. 9 and 10 represent the FTIR spectrum of P4VP-C_8Br in the absence and in the presence of chromium ions, respectively, at pH = 8.5 ± 0.2 for

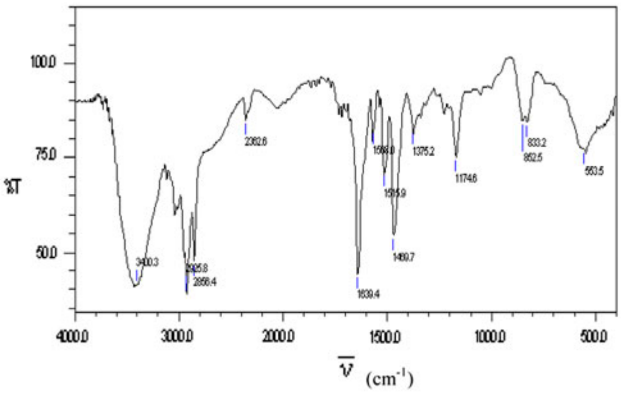

Fig. 9. Infra-red spectrum of P4VP-C_8Br.

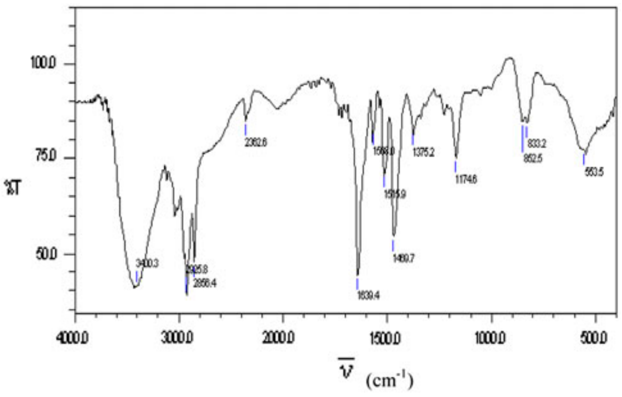

Fig. 10. Infra-red spectrum of P4VP-C_8Cr.

10^{-3} mol/L of Cr(VI). In the IR spectrum of P4VP-C_8Br (Fig. 9), alkylation leads to complete disappearance of the bands corresponding to the valence oscillations in pyridine rings at 1,597 and 1,415 cm^{-1}, and to the appearance of the new ones corresponding to the valence oscillations in the quaternized pyridine rings at 1,465 cm^{-1} [35,36].

Fig. 10 shows a characteristic signal between 950 and 770 cm^{-1} corresponding to CrO_4^{2-}. Besides, a band of low intensity can be observed around 780 cm^{-1}, which suggests the existence of $Cr_2O_7^{2-}$ because some dichromate exists even at this pH (8.5 ± 0.2).

4. Conclusion

The effect of molecular weight of P4VP on the hexavalent chromium removal from aqueous solution was investigated. The results showed that the molecular weight plays a major role on the adsorptive properties of poly(N-octyl-4-vinylpyridinium bromide). The synthesized P4VP-C_8Br copolymers exhibited high retention ability towards Cr(VI) from aqueous solution.

P4VP-C_8Br copolymers present fast kinetics of retention with respect to Cr(VI) and are good adsorbents for Cr(VI) anions comparing with different natural and synthetic adsorbents. More the molecular weight increases, more the retention capacity is higher. The adsorbed Cr(VI) amount on the copolymer of high molecular weight was 18.6 mg/g. Instead the copolymer with a smaller molecular weight shows a retention amount of 14.0 mg/g. An Empiric equation expressing the adsorbent amount as function of M_w was proposed for the retention of Cr(VI). The molecular effect disappears when M_w over pass 3.8×10^5 g/mol. The necessary time to remove the Cr(VI) anions is 10 min, and it is independent on the molecular weight.

Based on these results, we can conclude that P4VP-C_8Br at different molecular weights have a strong potential to be employed in analytical chemistry and/or in the environmental Cr(VI) treatments.

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