Removal of hexavalent chromium by new quaternized crosslinked poly(4-vinylpyridines)

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ABSTRACT

New quaternized crosslinked poly(4-vinylpyridines) prepared by nucleophilic substitution reactions of 4-vinylpyridine: divinylbenzene copolymers of gel and porous structure with halogenated compounds such as benzyl chloride and 2-chloracetone, were used to remove Cr(VI) from the aqueous solution. Batch adsorption studies were carried out to determine the effect of the initial concentration of Cr(VI), pH, temperature and the presence of sulfate anions. The process was found to be pH and concentration dependent. The adsorption capacities increase with the increase of the initial concentration of Cr(VI) and both resins exhibited the degrees of usage of the exchange capacities higher than 90% and good efficiency in the chromium removal. Equilibrium modeling of the process of Cr(VI) removal was carried out by using the Langmuir and Freundlich isotherms. The experimental data obeyed these isotherm models. The thermodynamic parameters (free energy change ΔG, enthalpy change ΔS and entropy change ΔH) for the adsorption have been evaluated and therefore, it was showed the spontaneous and endothermic process of the adsorption of Cr(VI) on the pyridine resins. In the competitive adsorption studies, chromate/sulfate revealed the selectivity of the pyridine adsorbents towards chromium ions. At acidic pH the synthesized pyridine resins offer much greater chromate removal capacities compared to alkaline pH. In the competitive adsorption studies, chromate/sulfate revealed the selectivity of the pyridine adsorbents towards chromium ions due to the formation a sandwich arrangement with the chromium anion and functional groups attached to the quaternary nitrogen atom.

1. Introduction

Metals and metallic compounds are essential for economic growth of any nation. Like many other metallic species chromium also has variety of applications. Several industries such as paint and pigment manufacturing, stainless steel production, corrosion control, leather tanning, chrome plating, wood preservation, fertilizers, textile, photography, etc., discharge effluents containing Cr(VI) [1]. Disposal of untreated industrial effluents is a source of pollution of aquatic systems. Despite a number of alternative technologies suggested to replace chromium, it is particularly difficult to substitute metal finishing industries because of its hardness, bright appearance, corrosion resistance ease of application, and low cost.

Spent chrome liquors and waste from tanneries contain 2900–4500 and 10–50 mg L^{-1} of chromium, respectively [2]. As redox active metal chromium usually exists as Cr(III) and Cr(VI) species in the environment. The hexavalent species may be in the form of dichromate ($Cr_2O_7{}^{2-}$), hydrochromate ($HCrO_4{}^-$) or chromate ($CrO_4{}^{2-}$) in a solution depending on concentration and pH. Due to the repulsive electrostatic interactions these anion species are generally poorly adsorbed by the soil particles in the environment and transfer freely in the aqueous environment. Cr(VI) is reported to be 100 times more toxic than Cr(III) which makes the former a major environmental hazard [3]. Exposure to Cr(VI) causes dermatitis, allergic skin reactions and ulceration of intestine. It is a known carcinogenic agent. The maximum permissible levels of Cr(VI) in potable and industrial wastewater are 0.05 and 0.25 mg L^{-1}, respectively [4]. Installation of a physico-chemical treatment plant to destroy or remove toxic materials is the main method used to treat the wastes generated from electroplating operations. Kinetics of chromium transformations under typical environmental conditions were investigated using batch and column experiments. Some of the investigated reactions such as the reduction of Cr(VI) by Fe(II) under anaerobic conditions were instantaneous and the results followed the stoichiometry of the red-ox equation [5]. The goal of all industry should be the recovery and reuse of the valuable material contained in the generated wastes, and especially in the case of hazardous wastes.

Alternative approaches such as adsorption, reverse osmosis, electrolytic recovery techniques, precipitation, ion exchange and

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liquid–liquid extraction have also been shown to work for treatment of chromium containing effluents and waters. A number of different types of adsorbents such as, including activated carbon [6–11], bioadsorbents [12–17], wine processing [18] and distillery [19] sludges, residual lignin [20], amine modified coconut [21], and synthetic polymers [22–24] were shown to remove chromium from waste water. Solvent extraction is a convenient but expensive technique for the removal of chromate ions from aqueous solutions. Literature data report that the extractants containing tertiary amine group Alamine 336 and Aliquat 336, are effective reagents for the removal of Cr(VI) [25–27]. Among the various treatment techniques available, the most commonly used ones are ion exchange and adsorption.

The main advantages of ion exchange are high degree of metal recovery, selectivity, lesser sludge volume produced and the ability to meet strict discharge specification and reduce dissolved chromate concentration below detectable levels in the water treatment plants.

Ion exchange using synthetic resins is the method of choice for removing toxic contaminants from water or waste water. The anion exchange processes can be used for the removal of chromium from wastewater at alkaline and acidic pH in the presence of a high concentration of chloride, sulfate, bicarbonate and nitrate ions [28,29].

The selectivity of the commercial polystyrene or polyacrylic based strong or weak base anion exchangers for chromate anions was studied in the pH range of 3–8 [30–41]. The synthesis of the anion exchangers with higher affinity with chromate than the commercially available anion exchangers at neutral to alkaline pH in the presence of other competing anions, namely, sulfate, chloride, bicarbonate, and nitrate was reported [42].

Strong base anion exchangers containing pyridine moieties have shown high selectivity for Cr(VI) and could represent a viable alternative for the selective retention of chromate ions. The previous work focused on the thermodynamic and kinetic studies of Cr(VI) removal from aqueous solutions by the pyridine resins with different lengths of alkyl substituent namely, methyl, ethyl, butyl or amide functional groups at the quaternary nitrogen atom [43–46]. Chromium retention capacity depends on the ionic form of the strong base anion exchangers and the substituent type at the quaternary ammonium atoms. Selectivity of these strong base anion exchangers was influenced by the concentration of chromium, the ionic form of the resin and the substituent type at the quaternary ammonium atoms.

In this paper the primary objective is to synthesize pyridine resins with novel functional groups for selective retention of Cr(VI). The functional groups of the new anion exchange resins namely, benzyl and ketone groups are attached to the quaternary nitrogen atoms by the nucleophilic substitution reactions of the 4-vinylpyridine (4-VP): divinylbenzene (DVB) copolymer of gel and porous structure with halogenated compounds such as, benzyl chloride (BCl) and 2-chloroacetone (ClA). The retention studies of the synthesized pyridine resins towards Cr(VI) were performed for the different conditions, the parameters that influence adsorption are initial chromium concentration, contact time, pH, resin amount, temperature and the presence of sulfate anions as competitive anions.

2. Experimental

2.1. Materials

4-Vinylpyridine supplied from Fluka was purified by vacuum distillation immediately prior to use. Divinylbenzene supplied from Fluka, of technically purity (80%) contains residual mainly 3- and 4-ethyl vinylbenzene.

The starting 4-VP:8%DVB copolymers of gel morphological type was synthesized by aqueous suspension copolymerization of 4-VP with DVB using 1.5 wt. % of benzoyl peroxide as initiator according to [35,36]. To obtain a porous copolymer the copolymerization reaction was carried out in the presence of toluene as the porogenic agent using a dilution, D of 0.2. D = mL toluene/(mL toluene + mL monomers). The copolymerization reaction was allowed to proceed for 10 h at 80 °C and 2 h at 90 °C. After copolymerization, the copolymers in the beads form were separated by filtration and extracted with methanol, in a Soxhlet apparatus to remove traces of residual monomers, linear oligomers of 4-VP and toluene and finally dried at 50 °C for 48 h. The samples were characterized by their nitrogen content as determined by elemental analysis. The experimental nitrogen content is 10% compared to the theoretical one (11%) meaning the most part of 4-VP amount reacted with DVB.

The pyridine strong base anion exchange resins were obtained by nucleophilic substitution reactions of 4-VP:8%DVB copolymer, gel or porous type, with BCl and ClA. The quaternization reactions were performed in methanol with BCl and dimethylformamide with ClA in a glass round bottomed flask equipped with a stirrer, reflux condenser and thermometer. The amounts of BCl and ClA corresponded to nitrogen: halogenated compound molar ratio of 1:1.5 for both halogenated compounds. The reactions were carried out at 60 °C for 48 h. After this, the beads were isolated by filtration and washed with methanol and finally with distilled water.

Samples of anion exchangers were regenerated with 5% NaCl solution, followed by washing with distilled water until complete removal of chloride ions. The final products were characterized by strong base exchange capacities determined by the ion exchange of Cl^- for SO_4^{2-}. The volumetric strong base anion exchange capacity was determined by the elution of Cl^- anions with 5% Na_2SO_4 aqueous solution, the chloride ions being potentiometrically determined using aqueous solutions 0.02 N $AgNO_3$. To calculate the gravimetric exchange capacity, 5 mL samples of the resins were dried at 110 °C to constant weight. All the resins were sieved to separate a fraction with at a particle size of 0.4–0.8 mm. The resins were stored air dried.

The chromate solutions were prepared in distilled water from stock solution of K_2CrO_4 supplied by Aldrich. Na_2SO_4 anhydrous and $AgNO_3$ were analytical reagent grades from Merck.

2.2. Instrumentation

A shaker with thermostat Grant Instrument of OLS 200 model was used for all adsorption experiments.

Atomic absorption spectrometry (AAnalyst 200, PerkinElmer) was used for the chromium analysis. pH was measured by a glass electrode SevenEasy Mettler Toledo model pH meter. Scanning electron microscopy (SEM) studies of the pyridine anion exchangers beads coated with gold were performed using a JEOL Model JMS 6310 microscope. For the cross-section of the beads ×3500 magnification was used.

2.3. Experimental methods

Prior to any experiments the resins were converted to the chloride form. The effect of the chromium concentration on the retention capacity was investigated using Cr(VI) solutions in the concentration range of 5–1000 mg L^{-1}. For the exchange equilibrium measurements, a series of swollen resin samples (0.1 g in the dry state) originally completely loaded with Cl$^-$ ions was equilibrated with a 25 mL K_2CrO_4 solution of different concentrations at 30 °C in a thermostatic shaker bath for 4 h. The effect of pH on the removal of chromate ions was investigated by equilibrating 0.1 g resin with 25 mL of chromate solution with concentrations 59, 138 and 270 mg L^{-1}. The solution pH values were controlled using

0.1 M HCl. The kinetic studies were carried out by shaking 0.1 g (dry weight) samples of the resins contacted with 25 mL chromate solution of 13, 22, 59 and 116 mg L^{-1} chromium concentration. The solution pH value was not controlled during the experiments in order to maintain the same ionic strength in the solution using 1×10^{-3} M NaClO$_4$ solution.

The effect of the temperature on the adsorption capacity of resins was studied in the range from 20 to 40 °C for chromium concentrations of 13, 22, 59 and 116 mg L^{-1}.

The competitive adsorption of Cr(VI) was studied at initial chromium concentration of 22, 59 and 138 mg L^{-1} and 1% Na$_2$SO$_4$ concentration. The adsorption experiments were performed by contacting 0.1 g resin with 25 mL of chromate solution containing SO$_4^{2-}$ ions.

In all experiments the resins were separated by filtration and the filtrate was analyzed by AAS spectrometry for total chromium content. The amount Q of chromium adsorbed was calculated using Eq. (1):

$$Q = \frac{(C_i - C_f)V}{m} \qquad (1)$$

where Q is adsorbed amount (mg g^{-1}), C_i and C_f are initial and final concentrations of chromate solutions (mg mL^{-1}), V is the volume of solution (mL) and m is the dry weight of resin (g).

All experiments were conducted in duplicate under the same conditions and the relative error between duplicates was less than 5%. The results were reported as mean values.

3. Results and discussion

3.1. Synthesis of the pyridine resins

Physicochemical characteristics of yielded these resins are presented in Table 1.

From this table it can be seen that both the synthesized strong base anion exchangers have high values of the strong base exchange capacities in comparison with those of the commercial strong base anion exchanger, Amberlite IRA 400, i.e., 4.57 meq g^{-1} and

1.25 meq mL^{-1}. The gel and porous structures of the pyridine resins were evidenced by scanning electron microscopy of the beads cross-section, SEM images clearly show the internal porous structure of PyR2 resin which is attributed to toluene used as porogenic agent during the synthesis of the pyridine polymeric matrix.

3.2. Adsorption studies

Factors influencing the adsorption rate are mainly, among others, the nature and concentration of competing ions, pH, resin amount, shaking time and temperature. Three individual composition variables, the nature of polymer matrix, basicity and steric property of the functional groups of the anion exchanger could have significant influence on the chromate sorption. Apparently, the adsorption is related to the basicity of the pyridine strong base anion exchangers. The adsorption capacity values for the studied resins depend on their exchange capacities and functional groups attached to the quaternary nitrogen atoms from the pyridine rings. The apparent effects of the basicity on Cr(VI) sorption are also believed to be due to the difference in their steric properties of the functional groups.
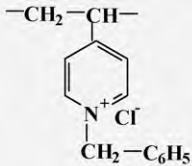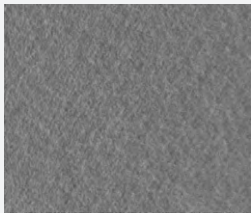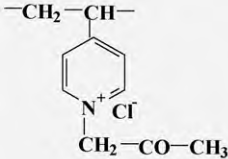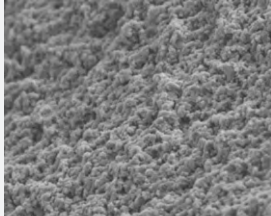
The effect of the initial concentration of Cr(VI) on the adsorption capacity of resins is expressed as the percentage of the maximum exchange capacity in Fig. 1.

As expected the amount of the adsorption of the adsorbed Cr(VI) increases with the increase of the initial amount in the range of 5–1000 mg L^{-1} reaching a plateau at about 1000 mg L^{-1}, which corresponds to 100% use of the ion exchange capacity. At the high concentration of the chromate solutions all the hexavalent chromium species are present in the solution, namely HCrO$_4^-$, CrO$_4^{2-}$ and Cr$_2$O$_7^{2-}$. The functional groups attached to the matrices of the pyridine resins create an favorable environment for adsorption of Cr(VI) oxy-anions.

3.3. Equilibrium isotherms

The relationship between adsorbed dye concentration and concentration of the solution at equilibrium is described by isotherm

Table 1
Strong base exchange capacities of the synthesized pyridine resins.

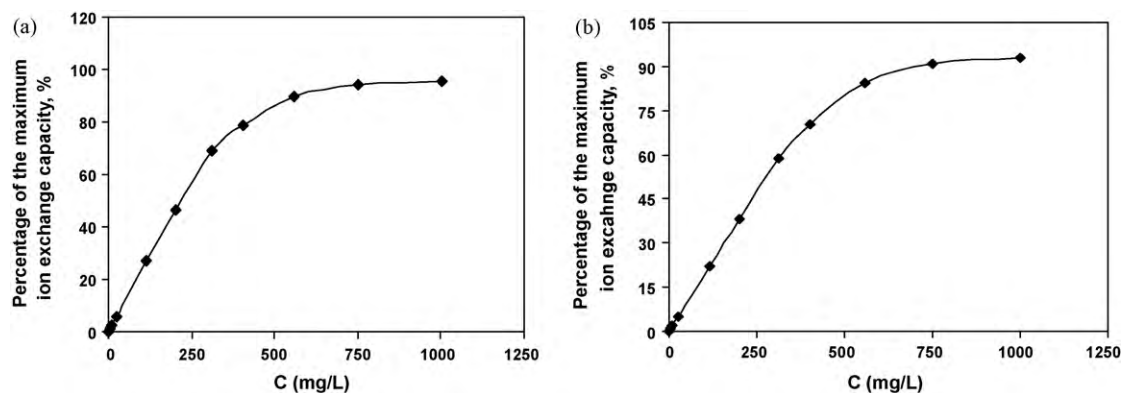| Sample code	Structural unit	Strong base anion exchange capacity		SEM image of the bead cross-section
		meq g^{-1}	meq mL^{-1}	
PyR1	—CH$_2$—CH— ... N$^+$ Cl$^-$ CH$_2$—C$_6$H$_5$	3.30	1.90	—— 5 μm
PyR2	—CH$_2$—CH— ... N$^+$ Cl$^-$ CH$_2$—CO—CH$_3$	4.20	1.60	—— 5 μm

Fig. 1. Degree of usage of the exchange capacity for PyR1 (a) and PyR2 (b) resins (adsorption conditions: amount of resin 0.1 g; volume of solution 25 mL; temperature 30 °C).

models, of which Langmuir and Freundlich are the most widely used equations.

Langmuir equation was basically derived for the sorption of gases on the solid surface. Nevertheless, it has been extended to include the sorption of solute at solid–liquid interface. The Langmuir isotherm is valid for monolayer adsorption onto the surface containing a finite number of identical sites and the standard mathematical representation is

$$\frac{C_e}{q_e} = \frac{1}{Q^0 \times b} + \frac{C_e}{Q^0} \qquad (2)$$

where C_e is the equilibrium concentration of chromium in the solution ($mg\,L^{-1}$); q_e is the amount of the retained chromium ($mg\,L^{-1}$); Q^0 is the maximum adsorption capacity ($mg\,g^{-1}$) and b is the Langmuir constant related to the affinity of the binding sites. The values of Q^0 were calculated from the slope and intercept of the straight-line plots of C_e/q_e versus C_e with a correlation coefficient higher than 0.99. Another essential characteristics of the Langmuir isotherm equation can be expressed in terms of a dimensionless constant known as separation factor or equilibrium parameter, R_L which can be evaluated by the Eq. (3):

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

where C_0 is the initial concentration of the chromate solution ($mg\,L^{-1}$).

The Freundlich isotherm model assumes multilayer adsorption and it is applicable to adsorption of metal ions occurs on a heterogeneous adsorbent surface. Freundlich equation is expressed as Eq. (4):

$$\log \frac{Q}{m} = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

where Q is the amount of the retained chromium ($mg\,L^{-1}$); m is the amount of the resin ($g\,L^{-1}$); C_e is the concentration at equilibrium ($mg\,L^{-1}$); K_F and n are Freundlich constants determined by slopes and intercepts of the straight-line of $\log Q/m$ versus $\log C_e$.

The Langmuir and Freundlich adsorption parameters are determined by plotting the experimental data based on Eqs. (2) and (4), respectively. The parameters that were determined and their corresponding correlation coefficients (R^2) are listed in Table 2.

The parameter calculated from Eq. (3) clearly indicate a favorable adsorption of chromate ions by the resins studied, the adsorption curves fit very well both Langmuir and Freundlich isotherm models. The R_L values obtained in the present case are much less than 1 and very close to 0 and therefore, indicates also a favorable adsorption [47].

3.4. Adsorption kinetics

It is a well-established fact that the adsorption of ions from aqueous solutions is reversible and follows reversible first-order kinetics when a single species is considered on a heterogeneous surface. Kinetics of sorption describing the solute uptake rate which in turn govern the residence time of sorption reaction is one of the important characteristic defining the efficiency of sorption.
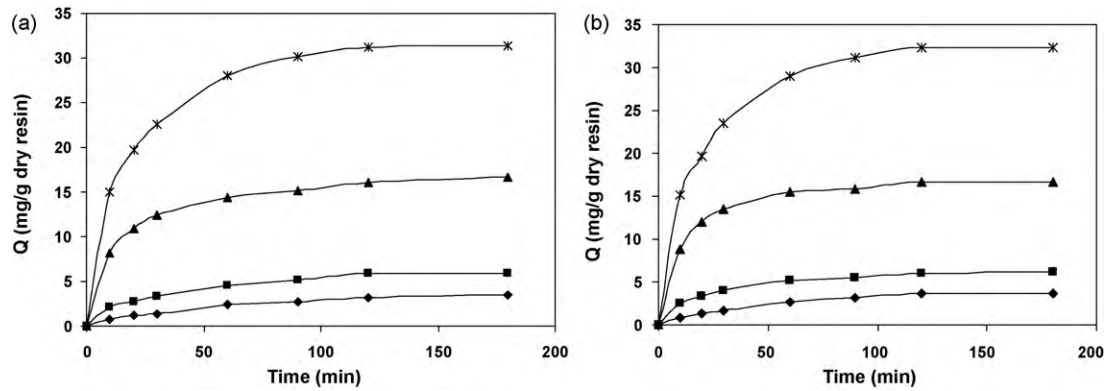
The progress of the adsorption process monitored at different time intervals is shown in Fig. 2.

The adsorption kinetics experiments reveal that the adsorbed amount of Cr(VI) continuously increases with increasing time reaching saturation after 2 h. It is also notable that the rate of adsorption remains almost constant up to 1 h. In each case, the decreasing concentration of chromium ions remaining in the solution indicates that chromium was adsorbed strongly by all the pyridine resins. The Cr(VI) adsorption with respect to time curves is smooth and continuous leading to saturation showing monolayer coverage of metal ion on the surface of the resins.

The chromium concentration in these experiments had a pronounced effect on the adsorption rate showing that when the chromium concentration increased the adsorption rate also increased. Such a concentration effect has also been reported by Chanda and Rempel for the sorption of uranyl sulfate on a reactive polymer-coated gel. Such a concentration effect is not consistent with predictions from the ordinary particle diffusion control model but it is in accord with the shell–core or reacted-layer diffusion control model [48].

In order to analyze the sorption rate, the kinetic data were modeled using Lagergren pseudo-first-order [49,50] and pseudo-second order [51,52] equations.

$$\text{Lagergren first-order}: \quad q_t = q_e(1 - e^{-k_1 t}) \qquad (5)$$

Table 2
Values of Langmuir and Freundlich constants for the adsorption of Cr(VI).

Resin code	Langmuir constants				Freundlich constants		
	R_L	Q^0 ($mg\,g^{-1}$)	K_L ($L\,g^{-1}$)	R^2	n	K_F ($L\,g^{-1}$)	R^2
PyR1	0.003	113.63	14.11	0.9973	3.18	33.11	0.9998
PyR2	0.008	142.85	22.17	0.9989	4.02	45.48	0.9998

Fig. 2. Effect of the contact time on the sorption capacity of Cr(VI) by PyR1 (a) and PyR2 (b) (adsorption conditions: concentration of Cr(VI) (♦) 13 mg L^{-1}; (■) 22 mg L^{-1}; (▲) 59 mg L^{-1}; (*) 116 mg L^{-1}; amount of resin 0.1 g, volume of the solution, 25 mL, temperature 30 °C, stirring time 140 rpm, initial solution pH).

Table 3
Kinetic parameters derived from pseudo-first-order and pseudo-second-order plots for Cr(VI) adsorption by PyR1 resin.

Initial concentration C_0 (mg L^{-1})	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_t (cal) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_t (cal) (mg g^{-1})	R^2
13	0.117	40.15	0.987	0.055	40.42	0.991
22	0.118	79.20	0.986	0.025	78.54	0.999
59	0.201	115.05	0.989	0.024	115.90	0.999
116	0.202	130.10	0.989	0.028	130.06	0.999

Pseudo-second-order : $q_t = \dfrac{k_2 q^2 e^t}{1 + k_2 q_e t}$ (6)

where, q_t and q_e are the amounts of Cr(VI) adsorbed (mg g^{-1}) at time t and at equilibrium, respectively, and k_1 (min^{-1}) and k_2 (mg g^{-1} min^{-1}) are the rate constants of pseudo-first-order and pseudo-second-order adsorptions, respectively. Values of q_t, k_1, and k_2 are calculated by the non-linear regression analysis using ORIGIN program, version 7.5 (Tables 3 and 4). The correlation coefficient ($R^2 > 0.999$) values of the pseudo-second-order equation for the selected concentration range (13–116 mg L^{-1}) suggest that

adsorption kinetics can be well described by the pseudo-second-order equation.

The chromium concentration had a pronounced effect on the rate of adsorption, when the chromium concentration increased the adsorption rate also increased. When the chromium concentration increased, the collision numbers between the sorption site and the chromium species increase; this increased the adsorption rate. As a result, the time needed to reach the equilibrium was shortened. Since the resins beads are constantly agitated during the adsorption process, it is reasonable to assume that the rate is not limited by the external mass transfer from the bulk liquid to the beads external

Table 4
Kinetic parameters derived from pseudo-first-order and pseudo-second-order plots for Cr(VI) adsorption by PyR2 resin.

Initial concentration C_0 (mg L^{-1})	Pseudo-first-order			Pseudo-second-order		
	k_1 (min^{-1})	q_t (cal) (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_t (cal) (mg g^{-1})	R^2
13	0.109	38.15	0.987	0.051	38.42	0.991
22	0.108	74.20	0.986	0.021	74.54	0.999
59	0.205	111.05	0.989	0.018	111.10	0.999
116	0.208	123.10	0.989	0.015	123.06	0.999
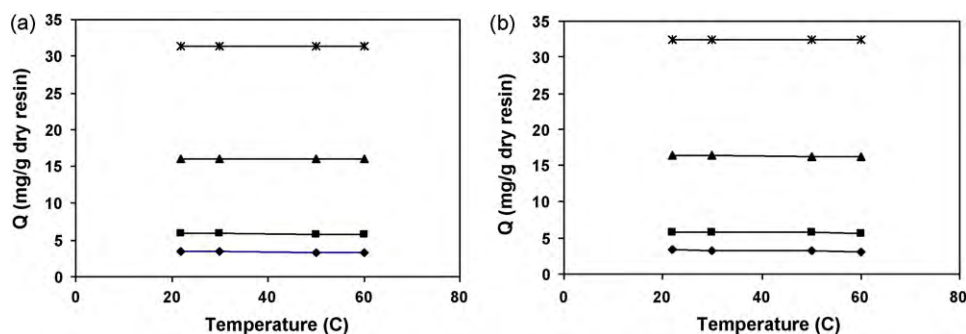
Fig. 3. Influence of temperature on the adsorption of Cr(VI) for PyR1 (a) and PyR2 (b) resins at different concentrations of the chromate solutions (adsorption conditions: concentration of Cr(VI) (♦) 13 mg L^{-1}; (■) 22 mg L^{-1}; (▲) 59 mg L^{-1}; (*) 116 mg L^{-1}; amount of resin 0.1 g, volume of the solution, 25 mL, stirring time 140 rpm, contact time, 24 h, initial solution pH).

Table 5
Thermodynamic parameters for the adsorption of Cr(VI) on pyridine resins.

T (K)	PyR1			PyR2		
	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (KJ K^{-1} mol^{-1})	ΔG (KJ mol^{-1})	ΔH (KJ mol^{-1})	ΔS (KJ K^{-1} mol^{-1})
293	−8.35	−5.76	0.029	−9.15	−4.22	0.038
303	−8.89	−5.76	0.029	−9.35	−4.22	0.038
313	−8.99	−5.76	0.029	−9.54	−4.22	0.038
293	−8.35	−5.76	0.029	−9.15	−4.22	0.038
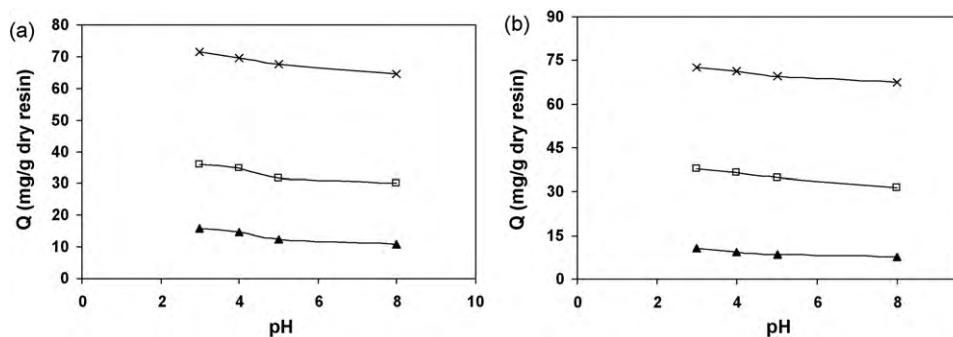
Fig. 4. Effect of pH on the adsorption Cr(VI) for PyR1 (a) and PyR2 (b) resins at different concentrations (adsorption conditions: concentration of Cr(VI) (▲) 59 mg L^{-1}; (□) 138 mg L^{-1}; (*) 270 mg L^{-1}; amount of resin 0.1 g; volume of solution, 25 mL; stirring time 140 rpm; contact time, 24 h; temperature 30 °C.

surface. One might suggest that the rate-limiting step may be either film or intraparticle diffusion.

3.5. Effect of temperature

Temperature is a significant parameter controlling adsorption of species in a system.

The effect of temperature on the adsorption has been studied by performing adsorption experiments in the temperature range of 20–40 °C for different concentrations of chromium solution (Fig. 3).

These figures show the minor effect of temperature on the adsorption capacity of pyridine strong base anion exchangers.

Thermodynamic studies are used to explain any reaction in a better way. In this paper also, thermodynamic parameters namely, ΔG^0, ΔH^0 and ΔS^0 were determined at 20, 30 and 40 °C. The values of these parameters have been given in Table 5.

The negative, ΔG^0 values indicate the process for pyridine resin to be spontaneous in nature of adsorption. Values of energy change decrease slightly by increasing the temperature which revealed the improvement of the adsorption by increase the temperature.

Positive values of entropy change and enthalpy change also indicate the endothermic nature of adsorption of Cr(VI) on pyridine strong base anion exchange resin. ΔS^0 can be used to describe the randomness at the resin–solution interface during the adsorption.

Increase in the solution temperature has not effect on the adsorption. Therefore, a general temperature range is suggested to be 20–40 °C.

3.6. Effect of pH

The effect of pH was studied at temperature of 30 °C by varying the pH pf the solution from 3 to 8 for initial concentrations of 59, 138 and 270 mg L^{-1} (Fig. 4).

At chromium concentrations lower than 1 g L^{-1} the adsorption capacity at acidic pH is higher than at alkaline pH since the major species at lower pH is HCrO$_4^-$, which allows removing more chromium atoms per exchange site than CrO$_4^{2-}$ which is the main species at alkaline pH. That is why acidic pH operation is universal practice in treating wastewater and contaminated groundwater for Cr(VI) removal. Although in our experiments the adsorption capacity of resins had the same trend, but they showed good adsorption capacity by Cr(VI) at alkali pH as well as at acidic pH. At low concentration of Cr(VI) the pyridine strong base anion exchanger offer much greater chromate removal capacity at acidic pH compared to alkaline pH. At the pH decrease, the ionic strength of the solution increases and as a consequence, the effectiveness of Cr(VI) adsorption onto pyridine resin with functional groups attached to the quaternary nitrogen atoms increased.
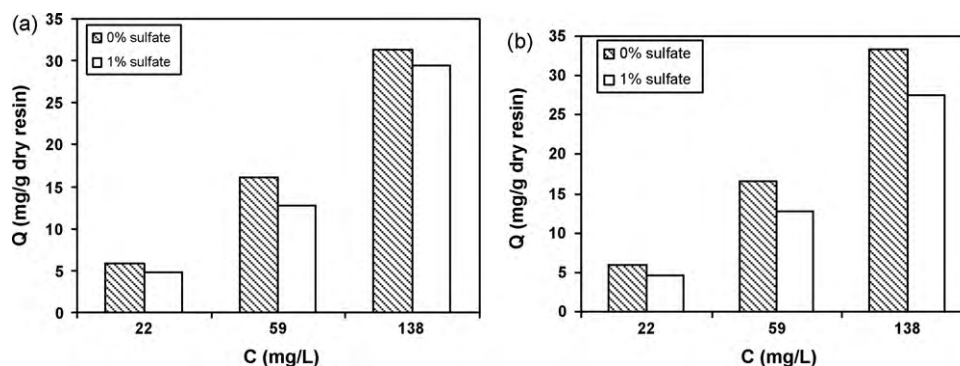
Fig. 5. The effect of sulfate anions on the adsorption capacity of PyR1 (a) and PyR2 (b) resins (adsorption conditions: concentration of Cr(VI) 22 mg L^{-1}; 59 mg L^{-1}; 138 mg L^{-1}; amount of resin 0.1 g; volume of solution, 25 mL; stirring time 140 rpm; contact time, 24 h; temperature 30 °C; concentration of Na$_2$SO$_4$, 1 wt.%).

3.7. Effect of the SO_4^{2-} ions

Addition of inorganic salts to the adsorption system is an effective way of influencing adsorption. In fact, added salts affect adsorption via two mechanisms: (i) either by screening the coulombic potential between the adsorbing ion and changed adsorbents, or (ii) by adsorbing preferentially on the active site of the adsorbent. In open recirculating cooling water systems, sulfuric acid is normally added to make-up water to avoid build-up of scale-forming bicarbonate ions. Sulfate is therefore the most predominant anion in cooling water followed by chloride and this was the main reason to investigate the adsorption of hexavalent chromium its presence (Fig. 5).

The results presented in Fig. 5 show that high selectivity of the pyridine resins towards Cr(VI) is not significantly affected by the competing sulfate ion even at high excess of the latter in solution.

It is well known that the adsorption selectivity for the common anions on the commercially styrene anion exchangers is as follows $SO_4^{2-} > I^- > CrO_4^{2-} > Br^- > Cl^-$. In our case the synthesized resins have a reversal of the order, selectivity namely, $CrO_4^{2-} > SO_4^{2-} > Cl^-$ for the concentration range of Cr(VI) between 22 and 119 mg L^{-1}.

The origin of this rather remarkable selectivity towards hexavalent chromium over sulfate anion is probably due to the interaction between the transition metal anion adsorption on the π bonds of the pyridine ring, and formation a sandwich arrangement with the chromium anion and functional groups namely, benzyl and ketone groups, attached to the quaternary nitrogen atom.

4. Conclusions

Nucleophilic substitution reaction of 4-VP:DVB copolymers of gel and porous type with benzyl chloride and 2-chloracetone as halogenated compounds led to the novel pyridine strong base anion exchange resin with benzyl and ketone functional groups attached to the quaternary nitrogen atoms. These resins exhibited good values of the strong base exchange capacity in comparison with the commercial strong base anion exchange resin, Amberlite IRA 400.

Adsorption study of hexavalent chromium on new performed resins showed a good efficiency of the chromium ions. At high concentration of the chromate ions there are all types of chromium in the solution and functional groups attached to the matrices of the pyridine resins create an appropriate environment to ensure the ion exchange for a counter ion with no smaller equivalent volume and the high diameter of their hydrated forms. Pyridine resins have the degrees of usage of the strong base exchange capacities higher than 90% which it means a very good efficiency in the removal of Cr(VI) as the pyridine resin with quaternary ammonium and amide functional groups presented in the recent literature. A comparison of Cr(VI) uptakes by different natural and synthetic adsorbents presented in the literature shown that the activated carbon, synthetic anion exchange resins based on styrene: divinylbenzene matrices or imidazole functionalized adsorbents have the highest removal capacities i.e., 97.4%, 91.1% and 92.31%, respectively [53].

Temperature has a small effect on the Cr(VI) adsorption capacity essentially depending upon pH and concentration. The adsorption of chromium ions took place by the ionic mechanism and no possibility to formation of some coordinate type of bond between chromium atom and electron donor atoms belong to the functional groups attached to the quaternary nitrogen atom.

At low concentration of Cr(VI) the pyridine strong base anion exchanger offer much greater chromate removal capacity at acidic pH compared to alkaline pH. At the pH decrease, the ionic strength of the solution increases and as a consequence, the effectiveness of Cr(VI) adsorption onto pyridine resin with amide functional groups increased.

The yielded pyridine strong base anion exchange resins are selective towards chromium anions in the chromium/sulfate binary sorption experiment. The pyridine resins exhibited the higher selectivity for Cr(VI) in the presence of sulfate anions as competitive counter ions than the commercial strong base anion exchange resins based on styrene: divinylbenzene copolymer.

It is evident to note that in the present experiments the morphology of the macromolecular support of the pyridine resins had not an influence on the kinetic and thermodynamic of the adsorption process of Cr(VI).

Because the pyridine strong base anion exchange resins offer much higher resistance to oxidation than conventional strong base polystyrene anion exchange resins could be considered as the new alternatives for the retention of chromate ions from the aqueous solutions.

References

[1] K. Kannan, In Fundamentals of Environmental Pollution, S. Chand & Co., New Delhi, 1995.
[2] S.M. Chattopadhyay, H.C. Arora, V.P. Sharma, Characteristics of feasibility of chrome tannery wastes, Int. J. Environ. Health 15 (1973) 208–213.
[3] J.O. Niragu, A silent epidemic of metal poisoning, Environ. Pollut. 50 (1988) 139–161.
[4] EPA Control and Treatment Technology for the Metal Finishing Industry Sulfide Precipitation; EPA-625/8-80-003; U.S. Environmental Protection Agency: Cincinnati, OH, 1980.
[5] F.Y. Salem, T.F. Parkerton, R.V. Lewis, J.H. Huang, K.L. Dickson, Kinetics of chromium transformations in the environment, Sci. Total Environ. 86 (1–2) (1989) 25–41.
[6] S.J. Park, Y.S.J. Jang, Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr(VI), Colloid Interface Sci. 249 (2002) 458–463.
[7] K. Srinivasan, N. Balasubramanian, T.V. Ramakrishan, Studies on chromium removal by rise husk carbon, Ind. J. Environ. Health 30 (40) (1988) 376–387.
[8] J. Fang, Z. Gu, D. Gang, C. Liu, E.S. Ilton, B. Deng, Cr(VI) removal from aqueous solution by activated carbon coated with quaternized poly(4-vinylpyridine), Environ. Sci. Technol. 41 (13) (2007) 4748–4753.
[9] H. Hasar, y. Cuci, Removal of Cr(VI), Cd(II), and Cu(II) by activated carbon prepared from almond husk, Environ. Technol. 21 (12) (2000) 1337–1342.
[10] N.R. Bishnoi, M. Bajaj, N. Sharma, A. Gupta, Adsorption of Cr(VI) on activated rice husk carbon and activated alumina, Bioresour. Technol. 91 (3) (2004) 305–307.
[11] C. Selomulya, V. Meeyoo, R. Amal, Mechanisms of Cr(VI) removal from water by various types of activated carbons, J. Chem. Technol. Biotechnol. 74 (2) (1998) 111–122.
[12] D. Sidlauskiene, R. Klimaviciute, A. Zemaitaitis, Adsorption of hexavalent chromium on cationic starches with different degree of crosslinking, J. Appl. Polym. Sci. 107 (2008) 3469–3475.
[13] J. Bajpai, R. Shrivastava, A.K. Bajpai, Dynamic and equilibrium studies on adsorption of Cr(VI) ions onto binary bio-polymeric beads of crosslinked alginate and gelatine, Colloids Surfaces A: Physicochem. Eng. Asp. 236 (2004) 81–90.
[14] S. Qian, G. Huang, J. Jiang, F. He, Y. Wang, Studies of adsorption behaviour of crosslinked chitosan for Cr(VI), Se(VI), J. Appl. Polym. Sci. 77 (2000) 3216–3219.
[15] S.P. Ramnani, S. Sabharwal, Adsorption of Cr(VI) onto radiation crosllinked chitosan and its possible application for the treatment of wastewater containing Cr(VI), React. Funct. Polym. 66 (2006) 902–910.
[16] M.Y. Arica, G. Bayramoglu, Chromium biosorption from aqueous solutions using free and immobilized biomass of Lentimus sajor-caju: preparation and kinetic characterization, Colloids Surf. A 253 (2005) 203–211.
[17] D. Park, Y.S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of Aspergillus niger, Water Res. 39 (2005) 533–540.
[18] Y.S. Li, C.C. Liu, C.S. Chiou, Adsorption of Cr(III) from wastewater by wine processing waste sludge, J. Colloid Interface Sci. 273 (2004) 95–101.
[19] K. Selcaraj, S. Manonmani, S. Pattabhi, Removal of hexavalent chromium using distillery sludge, Bioresour. Technol. 89 (2004) 207–211.
[20] S. Chand, V.K. Agarwal, C. Pavankumar, Removal of hexavalent chromium from wastewater by adsorption, Ind. J. Environ. Health 36 (3) (1994) 151–158.

[21] M.R. Unnitah, V.P. Vinod, T.S. Anirudhan, Synthesis, characterization and application as a chromium (VI) adsorbent of mine-modified polyacrylamide-grafted coconut Coir Pith, Ind. Eng. Chem. Res. 43 (2004) 2247–2255.
[22] C. Raji, T.S. Anirudhan, Batch Cr(VI) removal by polyacrylamide grafted sawdust: kinetics and thermodynamics, Water Res. 32 (12) (1998) 3772–3780.
[23] S. Deng, R. Bai, Removal of trivalent and hexavalent chromium with aminated polyacrylonitrile fibers: performance and mechanisms, Water Res. 38 (2004) 2423–2431.
[24] M. Yigitoglu, M. Arslan, Adsorption of hexavalent chromium from aqueous solutions using 4-vinyl pyridine grafted poly(ethylene terephtalate) fibers, Polym. Bull. 55 (2005) 259–268.
[25] E. Salazar, M.I. Ortiz, A.M. Urtiaga, J.A. Arabien, Kinetics of the separation-concentration of chromium(VI) with emulsion liquid membranes, Ind. Eng. Chem. Res. 31 (1992) 1523–1529.
[26] B. Saha, M. Iglesias, I.W. Cumming, M. Streat, Sorption of trace heavy metals by thiol containing chelatin resins, Solvent Extr. Ion Exch. 18 (2000) 133–141.
[27] T. Vincent, GuibalF E., Cr(VI) extraction using Aliquat 336 in a hollow fiber module made of chitosan, Ind. Eng. Chem. Res. 40 (2001) 1406–1411.
[28] A.K. Sengupta (Ed.), Ion Exchange Technology—Advances in Pollution Control, Technomic, Lancaster, PA, 1995, p. 115.
[29] A.K. Sengupta, D. Clifford, Chromate ion exchange mechanism for cooling water, Ind. Eng. Chem. Fundam. 25 (1986) 249–259.
[30] A.K. Sengupta, D. Clifford, Important process variables in chromate ion exchange, Eng. Sci. Technol. 20 (1986) 149–155.
[31] S. Mustafa, H. Bashir, N. Rehana, A. Naeem, Selectivity reversal and dimerization of chromate in the exchanger Amberlite IRA-400, React. Funct. Polym. 34 (1997) 135–144.
[32] I. Untea, E. Tudorache, V. Neagu, Cr(VI)-containing wastewater treatment by means of ion exchange on weak- and strong-base anion exchangers, J. Appl. Polym. Sci. 86 (2002) 2093–2098.
[33] F. Gode, E. Pehlivan, Removal of Cr(VI) from aqueous solution by two Lewatit-anion exchange resins, J. Hazard. Mater. B119 (2005) 175–182.
[34] T.S. Anirudhan, S. Jalajamony, P.S. Suchithra, Improved performance of a cellulose-based anion exchanger with tertiary amine functionality for the adsorption of chromium (VI) from aqueous solutions, Colloid Surf. A: Physicochem. Eng. Asp. 335 (2009) 107–113.
[35] Taihong Shi, Zhuochao Wang, Yang Liu, Shigua Jia, Du Changming, Removal of hexavalent chromium from aqueous solution by D301, D314 and D354 anion exchange resins, J. Hazaed. Mater. 161 (2009) 900–906.
[36] E.J.T. Pehlivan, S. Cetin, Sorption of Cr(VI) ions on two Lewatit-anion exchange resins and their quantitative determination using UV–visible spectrophotometer, J. Hazard. Mater. 163 (9) (2009) 448–453.
[37] L. Rafati, a.H. Mahvi, A.R. Asgari, S.S. Hosseini, Removal of chromium (VI) from aqueous solutions using Lewatit FO36 nano ion exchange resin, Int. J. Environ. Sci. Technol. 7 (1) (2010) 147–156.
[38] N. Shen, X. Lin, H.B. Cao, F. Guo, Y. Zhang, Removal of vanadium (V) and chromium (VI) from high concentration sodium phosphate solution with ion exchange resins, Chin. J. Process. Eng. 9 (5) (2009) 871–876.
[39] S.P. Kumar, K. Kirthika, K.S. Kumar, Removal of hexavalent chromium ions from aqueous solutions by an anion exchange resin, Adv. Sci. Technol. 26 (9) (2008) 693–703.
[40] O. Mojdeh, M.K. Aroua, W.A. Wan Daud, S. Baroutian, Removal of hexavalent chromium-contaminated water and wastewater: a review, Water Air Soil Pollut. 200 (2009) 59–77.
[41] F. Gode, E. Pehlivan, Removal of chromium from aqueous solutions using Lewatit S100; the effect of pH, time, metal concentration and temperature, J. Hazard. Mater. B136 (2006) 330–337.
[42] D. Zhao, A.K. SenGupta, L. Stewart, Selective removal of Cr(VI) oxyanions with a new anion exchanger, Ind. Eng. Chem. Res. 37 (11) (1998) 4383–4387.
[43] V. Neagu, I. Untea, E. Tudorache, C. Luca, Retention of chromate ion by conventional and N-ethylpyridinium strongly basic anion exchange resins, React. Funct. Polym. 57 (2003) 119–124.
[44] V. Neagu, I. Untea, E. Tudorache, C. Orbeci, Sorption equilibrium of Cr(VI) ions by strong base anion exchangers with pyridine structures, J. Appl. Polym. Sci. 93 (2004) 1957–1963.
[45] I. Untea, C. Orbeci, E. Tudorache, V. Neagu, Cr(VI) retention capacity and selectivity of some strong and weak base anion exchangers, Environ. Eng. Manag. J. 3 (3) (2004) 221–230.
[46] Violeta Neagu, Removal of Cr(VI) onto functionalized pyridine copolymer with amide groups, J. Hazard. Mater. 171 (2009) 410–416.
[47] G. Mckay, Adsorption of dyestuffs from aqueous solutions with activated carbon. I. Equilibrium and batch × studies, J. Chem. Technol. Biotechnol. 32 (1982) 759–772.
[48] M. Chanda, G.L. Rempel, Selective chromate recovery with quaternized poly (4-vinylpyridine), React. Polym. 21 (1993) 77–88.
[49] S. Lagergren, Der, Sogenannten adsorption geloster Stoffe Kungliga Svenska Vetenska psalka de Miens, Handlingar 24 (1898) 1–7.
[50] W. Rudzinski, W. Plazinski, Kinetics of solute adsorption at solid/solution interfaces: a theoretical development of the empirical pseudo-first and pseudo second order kinetic rate equations, based on applying the statistical rate theory of interfacial transport, J. Phys. Chem. 110B (2006) 16514–16521.
[51] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, Water Res. 34 (2000) 735–741.
[52] S. Azizian, Kinetic models of sorption: a theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–53.
[53] L.L. Hyung-Jun Park, Tavlarides, Adsorption of chromium(VI) from aqueous solutions using an imidazole, functionalized adsorbent, Ind. Eng. Chem. Res. 47 (2008) 3401–3409.