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Chromium removal using poly(4-vinylpyridinium)-modified treated clay salts

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ABSTRACT

New composite materials, able to remove hexavalent chromium [Cr(VI)] ions from aqueous solutions, were obtained by reacting poly(4-vinylpyridine) (P4VP) with treated clay [TC]. Two composite samples [TCP4VP-5-0.5] and [TCP4VP-5-1.5], were prepared by varying initial amounts of P4VP and TC and characterized. The retention of Cr(VI) was investigated by batch equilibrium procedure. The good efficiency in removing chromium ions from acidic solutions was demonstrated by adsorption kinetics. Freundlich and Langmuir isotherm models were used to determine adsorption capacity of the TC and of the modified composites [TCP4VP-5-0.5] and [TCP4VP-5-1.5], at 25˚C and at pH = 1. The specific role of P4VP salt in new composite materials was evaluated by comparing the kinetics of the TC and [TCP4VP-5-0.5] and [TCP4VP-5-1.5] composites. The obtained results showed clearly that the pyridinium positive charges on the polymer were efficient in hexavalent chromium removal from aqueous solutions. The thermodynamics of the rate processes showed the adsorption of chromium ions to be endothermic, accompanied by decreases in Gibbs free energy. The results showed these composites as potential adsorbent for the chromium ions from aqueous solutions.

Keywords: Treated clay; Poly(4-vinylpyridine)-modified treated clay; Adsorption; Cr(VI); Kinetics; Isotherm

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1. Introduction

The environment contains several heavy metals in natural manner that are necessary for our organism as micronutrients; however, they are also an important source of water contamination because they can accumulate in the trophic chain and cause serious problems to the ecosystems and public health [1]. Chromium is one of these heavy metals which is used in many industrial processes, such as plating, alloying, tanning of animal hides, and as water corrosion inhibitor [2]. Chromium exists in trivalent (Cr(III)) and hexavalent (Cr(VI)) oxydation states in the environment. Every oxidation state has different chemical, biological, and environmental characteristics.

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 most studied chemical equilibria involving Cr(VI) are:

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$$H_2CrO_4 \underset{pH<1}{\overset{pH>1}{\rightleftharpoons}} HCrO_4^- + H^+ \tag{1}$$

$$HCrO_4^- \underset{pH<6.9}{\overset{pH>6.9}{\rightleftharpoons}} CrO_4^{2-} + 2H^+ \tag{2}$$

$$2HCrO_4^- \rightleftharpoons CrO_7^{2-} + H_2O \tag{3}$$

Cr(VI) is toxic to both plants and animal. As a strong oxidizing agent and a potential carcinogen, it can have teratogenic and mutagenic effects. Concentrations as low as 0.5 ppm in solution and 5 ppm in soil can be toxic to plants [3]. Cr(VI) is approximately 100 times more toxic [4] and 1,000 times more mutagenic than Cr(III) [5].

In order to meet the Cr(VI) limits on liquid industrial waste release established by the authorities, the industries treat their effluents to reduce the concentration of Cr(VI) using different methods including: reduction followed by chemical precipitation, ion exchange, electrochemical precipitation, reduction, adsorption, solvent extraction, membrane separation, concentration, evaporation, reverse osmosis and biosorption and emulsion per traction technology. Adsorption is the most powerful separation and purification method. Its advantages include high efficiency, easy handling, and high selectivity, lower operating costs, easy regeneration of adsorbent, and minimized production of chemical or biological sludge [6].

During recent years, a number of different types of adsorbents such as activated carbon, liquid–liquid extraction have also been shown to work for the treatment of chromium containing effluents and waters. A number of different types of adsorbents, such as activated carbon [7–12], bioadsorbents [13–18], wine processing [19] and distillery [20] sludge, residual lignin [21], and amine modified coconut [22] were shown to remove chromium from wastewater. However, many of the available adsorbents have low chromium removal capacity and slow process kinetics. Thus, there is a need to develop innovative low-cost adsorbents with affinity towards metal ions for the removal of chromium from aqueous solution within a short time.

During recent years, many modified polymers and copolymers were used for the removal of chromium ions from aqueous solutions. *N*-alkyle quaternized poly(4-vinylpyridine) (P4VP) was used to remove hexavalent chromium ions at $pH = 8$ [23]. About 97.3% of hexavalent chromium ions was retained using initial concentration of 10^{-4} mol/L. Quaternized cross-linked P4VP were also used to remove hexavalent chromium ions from aqueous solutions. About 32 mg/g of hexavalent chromium ions was retained using initial concentration of 116 mg/L [24].

Clay minerals, due to their large surface area and high cation exchange capacity [25], have been studied for potential applications as environmental remediation agents [26], and in removal of heavy metals and organic compounds [27,28]. However, clays possess a net negative structural charge that leads to little or no affinity for anionic species such as that of Cr(VI). In order to adsorb anions, the modified surface must possess positively charged exchange sites. This goal is reached by the adsorption of cationic surfactants on clay minerals. Our previous work focused on retention of hexavalent chromium using Algerian clay modified by poly(4-vinylpyridinium) salts [29].

In the present paper, a new adsorbent based on P4VP-modified treated clay salt was prepared and used for its sorption properties of Cr(VI).

Since, composite materials from the [TC] contain more poly(4-vinylpyridinium) copolymer than those from the drilling clay, we have proposed in this work to expect their retention efficiency toward chromate anions. Indeed, for the same rate (clay/polymer), the adsorption percentage increases considerably from 4.8% in the drilling clay [29] to 8.8% in the treated clay. One then expects greater retention percentage of chromate ions in solution. This supposition is confirmed in this work.

Several adsorption parameters, such as initial chromium concentration, pH, isotherm, and kinetic were investigated. In addition, the equilibrium parameters of Cr(VI) at $pH = 1$ were investigated at 35, 40, 50, and 60°C.

2. Experimental

2.1. Materials

The treated clay obtained by the industrial treatment of the drilling clay by a concentrated sulfuric acid solution was supplied by a local company known as ENOF.

- The drilling clay is the result of the industrial sodium carbonate treatment of natural clay issued from the fields of Hammam–Boughrara–Maghnia–Algeria.

The different chemical elements of the treated clay were transformed into oxides and analyzed by X-ray fluorescence at the ENOF central laboratory. Results are given in Table 1, which confirm that treated clay consists essentially of montmorillonite, since the ratio SiO_2/Al_2O_3 is equal to 4.52 and belongs to the family of the phyllosilicates [30]. In addition, as common aspects, these clays give stable suspensions in water

Table 1
Chemical composition of the treated clay

Species	% (w/w)
SiO_2	65.4
Al_2O_3	14.46
Fe_2O_3	1.19
Na_2O	2.15
CaO	2.03
K_2O	0.08
MgO	1.93
TiO_2	0.11
LOI	12.1

and have flat plates or needle-like structures. Granulometry of the treated clay was performed locally in the Civil Engineering Department (Tlemcen University) using a sedimentation technique with a 0.1% sodium hexametaphosphate solution; 95% of treated clay grains have a diameter less than 100 µm. The cation exchange capacity was 48.2 meq/100 g of treated clay and the surface area was 185 m^2/g with an average pore size of 7 nm.

P4VP was supplied by Aldrich. Its average molecular weight, close to 64,000 g/mol, was determined by capillary viscosity using the empirical Mark-Houwink power law [31].

All the solvents were supplied by Aldrich (analytical grade) and used without further purification.

Potassium dichromate was purchased from BIOLAB, recrystallized five times in ethylether, and dried at 70°C for two days.

2.2. Physicochemical investigation techniques

2.2.1. Thermogravimetric analysis

Thermogravimetry experiments were carried out on a TA-Instruments 2950 analyzer. Measurements were performed under air atmosphere. The same conditions were used for all the tests, with a heating rate of 10°C/min in the temperature range between 20 and 800°C.

2.2.2. UV-visible spectrophotometry

A Shimadzu-UV-240A UV–vis. Spectrophotometer was used to monitor the kinetics of Cr(VI) adsorption on treated clay and polymer-modified treated clays. All measurements were carried out in a 1-cm quartz cell.

2.2.3. Infrared analysis

The IR spectra were recorded on an FTIR Perkin–Elmer-2000 spectrophotometer with samples in the form of KBr pellets.

2.2.4. Preparation of polymer-modified treated clay

Five g of treated clay were dispersed in 50 mL of distilled methanol, and then introduced into a 100 mL flask under nitrogen. A known amount of P4VP was dissolved in 7 mL of methanol previously degassed with nitrogen was added dropwise. The mixture was stirred during 24 h and then precipitated twice in ethylether, filtered, and dried at 75°C during 24 h.

The modified treated clays are named as [TCP4VP-5-0.5] (5 g of treated clay and 0.5 g of P4VP) and [TCP4VP-5-1.5] (5 g of treated clay and 1.5 g of P4VP) (see Table 2). These samples were characterized by FTIR and TGA.

2.3. Adsorption of Cr(VI) by natural and polymer-modified treated clay

2.3.1. Adsorption equilibria

For removal studies, all experiments were performed thrice and results were reproducible with an error range inferior to 3% and the average value was considered for data analysis. Twenty mL of potassium bichromate ($K_2Cr_2O_4$) solutions was initially prepared with Cr(VI) ion concentrations ranging between 35 and 370 mg/L. The pH of these solutions was carefully adjusted in the range between 1 and 11 by addition of aliquots of 0.1 M solutions of hydrochloric acid (HCl) or sodium hydroxide (NaOH) using a B375 Microanal pH meter and a glass/Ag/AgCl electrode. The ionic strength of the solutions was fixed at 0.1 M and adjusted at this value by adding 0.1 M NaCl solutions. Then, 0.1 g of air-dried

Table 2
Weight percentage of coated P4VP on TC clay (5 g) in relation to initial P4VP (initial P4VP in 57 mL of methanol, contact time: 24 h)

Sample	Initial amount of P4VP (g)	Weight loss % from 20–200°C (water)	Weight loss % from 300–800°C (P4VP)
P4VP			92.5
TC		0.5	3.9
[TCP4VP-5-0.5]	0.5	7.2	7.3
[TCP4VP-5-1.5]	1.5	5.9	8.8

treated clay or polymer-modified treated clays was introduced in these $K_2Cr_2O_4$ solutions. The mixtures were equilibrated by stirring in a water bath for 3 h. The temperature was varied between 25 and 60°C. The mixtures were then centrifuged at 10,000 rpm for 10 min. The amount of Cr(VI) present in the supernatant from bichromate determination was analyzed using 1,5diphenylcarbohydrazide spectrophotometric method at $\lambda = 540$ nm.

2.3.2. Determination of the amount of adsorbed chromium

The amount of adsorbed Cr(VI) at various equilibrium times (q_t, mg/g) was calculated using following relationship:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{4}$$

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).

3. Results and discussion

3.1. Study of the adsorption of P4VP on treated clay

Thermogravimetric analysis allows the quantification of the amount of P4VP coated onto treated clay. Thermograms of treated clay show an initial weight loss between 20 and 200°C is observed due to the residual water. There is also decomposition between 380 and 650°C associated with dehydroxylation of the alumino-silicate.

Pure P4VP decomposes in a narrow range of temperature beyond 330°C and up to 414°C. The percentage (g/g) of adsorbed P4VP onto treated clay was simply estimated as the difference between the weight loss of polymer-modified treated clay between 300 and 800°C and that obtained for treated clay. The results clearly show that the quantity of adsorbed P4VP increases with the initial amount of P4VP in the equilibrium solution; 8.8% represents a maximum amount of adsorbed P4VP which corresponds to the initial amount of 1.5 g of polymer used with 5 g of treated clay.

FTIR was used to confirm the adsorption of P4VP on treated clay. Fig. 1(a) and (b) gives, respectively, the FTIR spectra of pure P4VP and treated clay.

For treated clay, only a broad absorption band appears between 1,600 and 1,800 cm^{-1}, with a maximum at 1,650 cm^{-1}. It corresponds to adsorbed water.

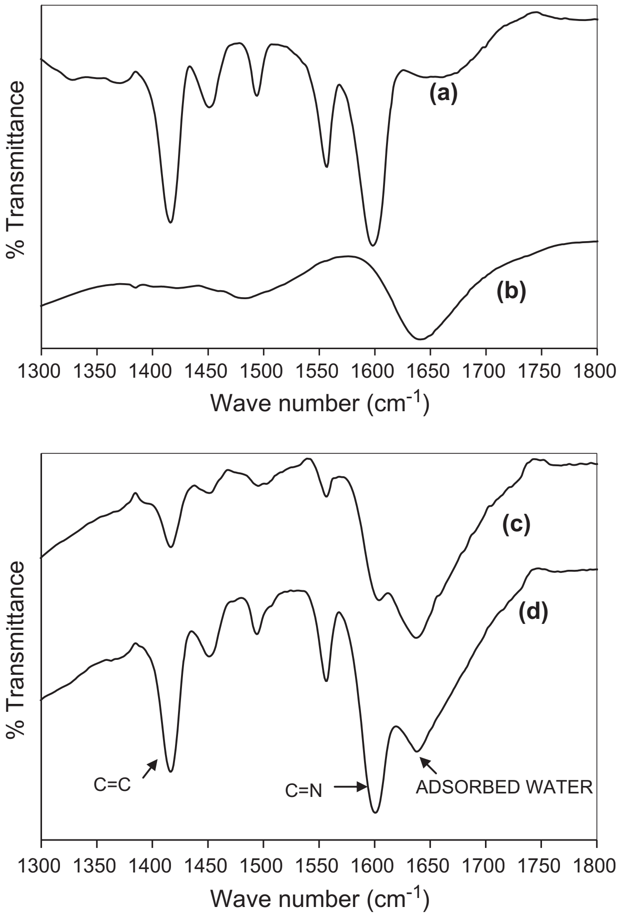


Fig. 1. FTIR spectra of (a) P4VP, (b) TC, (c) [TCP4VP-5-0.5], and (d) [TCP4VP-5-1.5].

For pure P4VP, the spectrum is characterized by two main bands: at 1,600 cm^{-1} (C=N stretching vibration in the aromatic ring) and at 1,420 cm^{-1} (C=C stretching vibration in the aromatic ring). In the FTIR spectra of [TCP4VP-5-0.5] and [TCP4VP-5-1.5] (Fig. 1(c) and (d)), both characteristic bands of the polymer and unmodified treated clay are represented.

The presence of P4VP on treated clay is clearly attested by two narrow bands at 1,600 and 1,420 cm^{-1}.

3.2. Study of chromium ion adsorption on treated clay and composites

3.2.1. Effect of contact time

Adsorption experiments were carried out for 3 h to find the optimal contact time. Adsorption kinetics of Cr (VI) at pH = 1 and at 25°C. Fig. 2 shows that equilibrium was attained after 30 min. There is no significant change in equilibrium concentration after 30 min up to 3 h.

A similar phenomenon was observed during chromium removal by some modified polyvinylpyridine polymers [23]. A reaction time of 10 minutes was sufficient for chromium removal at pH = 8 from initial Cr(VI) 5.2 mg/L by N-alkyl quaternized P4VP [23]. The rate of hexavalent chromium ions adsorption (13–116 mg/L) by quaternized cross-linked P4VP remains almost constant up to 1 h [24].

A reaction time of 50–350 h was observed for chromium removal at pH = 2 from initial Cr(VI) 25–200 mg/L by the fungal biomass *Aspergillusniger* at a dose of 10 g/L [18]. Another HNO_3 pre-treated seaweed biomass *Ecklonia* required 9 h for complete removal of total chromium from initial concentration of 200 mg/L [32]. In terms of total chromium removal kinetics, polymer-modified treated clays showed fairly good results. It is further observed that the removal curve is smooth and continuous indicating the possibility of the formation of monolayer coverage of Cr(VI)ions at the interface of the polymer/treated clay. All the following results correspond to an equilibrium time of 3 h.

The data in Fig. 2 were treated according to pseudo-first and pseudo-second-order kinetic models.

(1) Pseudo-first-order model [33]:

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \qquad (5)$$

where k_1 is the pseudo-first-order rate constant (min^{-1}) of adsorption and q_e and q_t (mg/g) are the amounts of adsorbed Cr(VI) at equilibrium and time t, respectively.

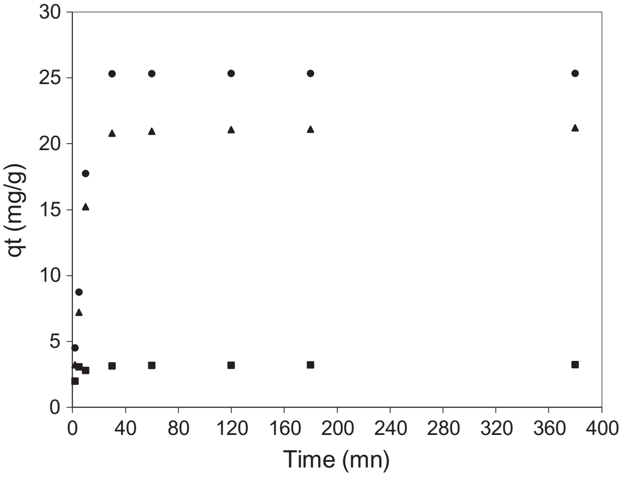


Fig. 2. Kinetics of Cr(VI) adsorption on (■) TC, (▲) [TCP4VP-5-0.5], and (●) [TCP4VP-5-1.5] at pH = 1 of the metal solution (*V* solution, *m* adsorbent) (20 mL, 0.1 g), initial metal ion concentration 350 mg/L, *T* = 298 K).

(2) Pseudo-second-order model [34]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \qquad (6)$$

where k_2 is the pseudo-second-order rate constant of adsorption (g $\text{mg}^{-1}\text{min}^{-1}$). The kinetic parameters in both the two models are determined from the linear plots of log $(q_e - q_t)$ vs. t for pseudo-first-order or (t/q_t) vs. t for pseudo-second-order. The validity of each model is checked by the fitness of the straight line (R^2) as well as the experimental and calculated values of q_e.

Accordingly, and as shown in Table 3, pseudo-second-order model (Eq. (6)) is more valid for adsorption process than the pseudo-first-order one (Eq. (5)) (the values of q_e of pseudo-second-order model are more comparable with the experimental ones).

3.2.2. Effect of pH

The pH parameter varied between 1 and 11. In the case where hexavalent chromium generates trivalent ions form at low pH = 1, this later will be strongly retained by the treated clay support in viewing its anionic character.

The pH effect is well explained by the chromium ions nature, since when pH decreases, the P4VP copolymer takes its cationic form and the interaction between anionics bichromates and the copolymer becomes strong leading to an increasing in retention rate. In the other hand, trivalent chromium Cr(III) will move easily in the interlayer space of the clay where will be strongly retained by the mineral negative charges.

The Cr(VI) removal at a fixed Cr(VI) concentration of 350 mg/L as a function of equilibrium pH is shown in Fig. 3. Behaviors of both pure treated clay and modified polymer composites can be compared. Two important observations can be made:

- first, in the whole range of pH, the removal of chromium ions by pure treated clay appears very small compared to those observed with polymer-modified clays;
- second, adsorption is the highest at lowest pH values (Fig. 2). Adsorption decreases, becoming almost negligible at pH 9 for both treated clay and modified treated clays.

A similar type of behavior was also reported for the adsorption of anionic species on metal oxides/oxyhydroxides [35,36]. The pH effect on the removal capacity of treated clay and polymer-modified treated clays may be attributed to the combined effect of pH

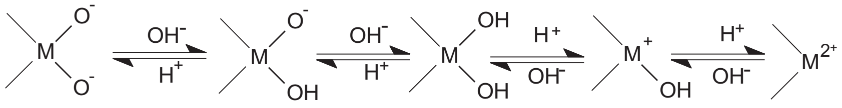
Table 3
Parameters of the pseudo-first-order and pseudo-second-order models for the adsorption of Cr(VI) on TC, [TCP4VP-5-0.5] and [TCP4VP-5-1.5]

Sample	q_e, exp (mg/g)	Pseudo-first-order			Pseudo-second-order		
		k_1 (min^{-1})	q_e, calc (mg/g)	R^2	k_2 (g mg^{-1}min^{-1})	q_e, calc (mg/g)	R^2
TC	3.25	0.018	1.99	0.825	0.247	3.25	0.999
[TCP4VP-5-0.5]	20.83	0.029	12.27	0.933	0.008	21.64	0.999
[TCP4VP-5-1.5]	25.35	0.052	14.5	0.909	0.008	25.83	0.999

on the nature of treated clay surface, adsorbed Cr(VI) species, and the cationic or/and neutral character of polymer.

To explain the observed behavior of Cr(VI) removal with varying pH, it is necessary to examine various mechanisms, such as electrostatic attraction/repulsion, chemical interaction, and ion exchange which are responsible for adsorption on sorbent surfaces.

For TC, the aluminum, calcium, magnesium, iron, and silicium oxides are present in varying amounts in treated clay (see Table 1). The hydroxylated oxide surfaces develop a charge on the clay surface in aqueous solution through amphoteric dissociation [37].



where *M* stands for Al, Ca, Mg, Si, etc. the surface is expected to be positively charged at low pH and consequently will favor the adsorption of anionic form as $HCrO_4^-$ [38]. This is in agreement with previous results [39], which show that amphoteric oxides favor the adsorption of anions at low pH. Similar interpretation was presented by Fritzen et al. who studied the distribution of Cr(VI) species across different clays [40].

For the polymer-modified clays, the maximum in chromate ions removal amounts was observed at lowest pH values. P4VP exhibits a weak alkaline character. In an acidic medium, the pyridine group exists in the protonated ammonium (–NH$^+$) form and electrostatic attraction between the protonated ammonium ion and negatively charged $HCrO_4^-$ ion is expected for Cr(VI) removal from aqueous solution. With an increase in pH, the pyridinium character disappears and the polymer is less and less protonated and finds again its neutrality. These observations are similar with those of Albino Kumar et al. [41] who used aniline formaldehyde condensate coated silica gel for Cr(VI) removal.

Another phenomenon is the fact that below pH = 9 there may be a competition between OH^- and chromate ions (CrO_4^-), the former being the dominant species at higher pH values. The net positive surface potential of adsorbent decreases, resulting in weakening in electrostatic attractions between negatively charged adsorbed ions and the adsorbent which ultimately leads to the lowering of the adsorption capacity. Similar results were also observed with activated red mud used for Cr(VI) removal [42].

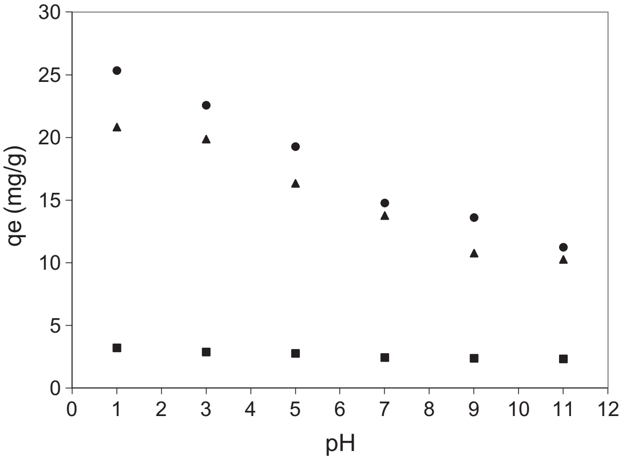


Fig. 3. Effect of pH on the adsorption of Cr(VI) by (■) TC, (▲) [TCP4VP-5-0.5] and (●) [TCP4VP-5-1.5], shaking time (3 h) (*V* solution, *m* adsorbent) (20 mL, 0.1 g), initial metal ion concentration 350 mg/L, *T* = 298 K).

3.2.3. Effect of initial Cr(VI) ion concentration on adsorption

The concentrations of both the metal ions and the adsorbent are very two important factors to reach an effective adsorption. In order to demonstrate the effect of the Cr(VI) ion concentration on the adsorption, experiments were carried out at different initial Cr(VI) ion concentrations ranging from 35 to 370 mg/L (Fig. 4). At low initial Cr(VI) concentrations, the available sorption sites were easily occupied by $HCrO_4^-$ anions resulting in higher removal efficiencies. However, as the initial concentration of $HCrO_4^-$ anion increased, most of the available sorption sites became occupied leading to a decrease in the removal efficiency.

This figure, which shows classical adsorption isotherms, confirms that polymer-modified treated clays have a much higher chromium anion adsorption capacity than pure treated clay. It is clear that polyvinylpyridinium ions are responsible for 90% removal of chromium anions. In fact, when considering the amount of metal adsorbed per unit weight of adsorbent (q_e), the adsorption efficiency increases with polymer content in different composites. We note also that the anion quantities adsorbed on modified treated clays ([TCP4VP-5-0.5] and [TCP4VP-5-1.5]) are not proportional to the amount of adsorbed polymer. [TCP4VP-5-0.5] [73 mg/g, (P4VP/treated clay)] retains 20.83 mg of Cr(VI), but the [TCP4VP-5-1.5] (88 mg/g, P4VP/treated clay) adsorbs only 25.35 mg/g of polymer-modified treated clay. It is evident that several main factors govern the adsorption phenomenon:

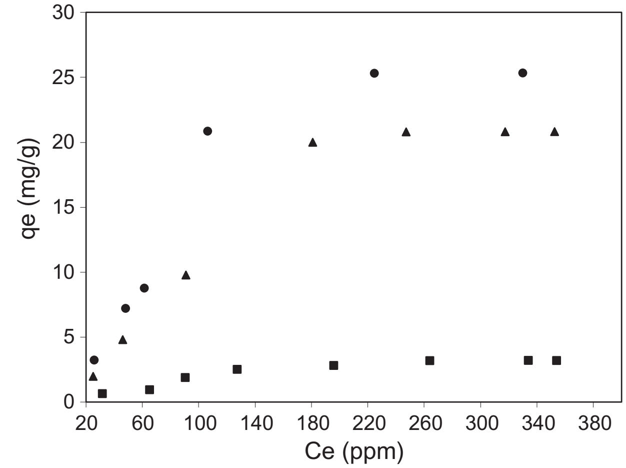


Fig. 4. Isotherm plots (q_e vs. C_e) for adsorption of Cr(VI) on (■) TC, (▲) [TCP4VP-5-0.5] and (●) [TCP4VP-5-1.5] at pH = 1 of the metal solution, shaking time (3 h), (*V* solution, *m* adsorbent) (20 mL, 0.1 g); initial metal ion concentration 35, 70, 100, 140, 210, 280, 350, 370 mg/L; *T* = 298 K).

(1) Number of ammonium groups,
(2) accessibility of these groups to the metal ion,
(3) partial solubility of the P4VP/Cr(VI) complexes which tend to perturb the measurements of the total amount of adsorbed Cr(VI).

From the isotherm plateaus, 25.3 and 20.83 mg of Cr(VI) were find to be fixed per g of modified treated clay for [TCP4VP-5-1.5] and [TCP4VP-5-0.5], respectively.

Since the number of monomers/moles per g of clay is 6.94×10^{-4} for [TCP4VP-5-0.5] and 8.37×10^{-4} for [TCP4VP-5-1.5], this means that there is 0.58 mol of $HCrO_4^-$ fixed per one pyridinium ion mole for both composites ([TCP4VP-5-0.5] and [TCP4VP-5-1.5]). If one of $HCrO_4^-$ was considered to neutralize one pyridinium positive charge, the maximum capacity is not reached and all the positive polymer sites are not occupied by of $HCrO_4^-$ anions. This result shows that pyridine sites are partially present under pyridinium form and there is neutral form of nitrogen remaining in copolymer.

The equilibrium data have been correlated with the Langmuir isotherm, according to:

$$q_e = \frac{1}{q_m \times b \times C_e} + b \times C_e \tag{7}$$

where C_e is the equilibrium concentration in mg/L, q_m (mg/g) and b (L/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. We used the linearized form of this expression:

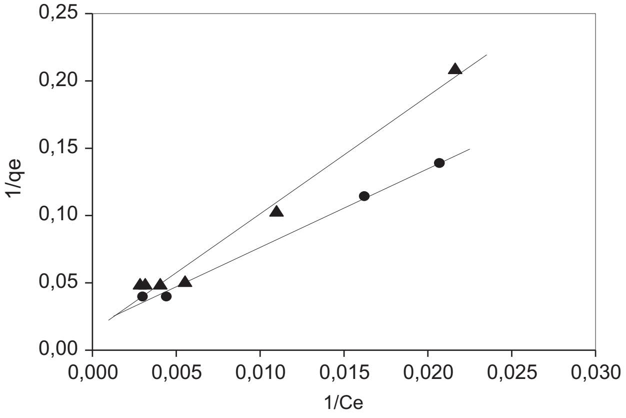


Fig. 5. Langmuir isotherm for adsorption of Cr(VI) on (▲) [TCP4VP-5-0.5] and (●) [TCP4VP-5-1.5] at pH = 1 of the metal solution, shaking time (3 h), (*V* solution, *m* adsorbent) (20 mL, 0.1 g).

Table 4
Freundlich and Langmuir coefficients for adsorption of Cr(VI) on [TCP4VP-5-0.5] and [TCP4VP 5-1.5] at pH = 1 metal solution, shaking time, 3 h (*V* solution, *m* adsorbent) (20 mL, 0.1 g)

Sample	Freundlich coefficients			Langmuir coefficients		
	n	*k*	*r*	q_m (mg/g)	*b* (L/mg)	*r*
[TCP4VP-5-0.5]	0.89	0.14	0.971	72.46	1.57×10^{-3}	0.991
[TCP4VP 5-1.5]	0.91	0.18	0.992	55.86	3.06×10^{-3}	0.997

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m \times b}\frac{1}{c_e} \tag{8}$$

The values of Langmuir constants q_m and b were obtained from the intercept and slope of the plot between $(1/q_e)$ vs. $(1/C_e)$ presented in Fig. 5. The computed constants are shown in Table 4.

The Freundlich adsorption isotherm was also applied for Cr(VI) adsorption on treated clay and polymer-modified treated clays:

$$q_e = k \times C_e^n \tag{9}$$

with its linearized form:

$$\ln q_e = \ln k + n \ln C_e \tag{10}$$

The constant k represents the adsorption capacity, while n is indicative of the intensity of reaction. The values of n and k were calculated from the slope and intercept of the plot between ln q_e and ln C_e (Fig. 6). The calculated constants are reported in Table 4.

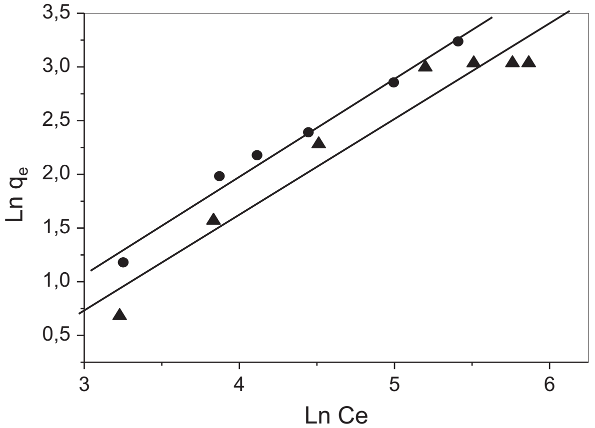


Fig. 6. Freundlich isotherm for adsorption of Cr(VI) on (▲) [TCP4VP-5-0.5] and (●) [TCP4VP-5-1.5] at pH = 1 of the metal solution, shaking time (3 h), (*V* solution, *m* adsorbent) (20 mL, 0.1 g).

The experimental sorption isotherms of treated clay and polymer-modified treated clays are presented in Fig. 4. The linearized forms of Langmuir and Freundlich adsorption isotherms were used to evaluate the sorption data (Figs. 5 and 6), respectively.

The linear plot of $1/q_e$ vs. $1/C_e$ shows that the adsorption seems to follow the Langmuir model (Fig. 5) for all the adsorbents. Using the Langmuir isotherm, the equilibrium data yielded the ultimate adsorption capacity value as 72.46 and 55.86 mg/g for ([TCP4VP-5-0.5] and [TCP4VP-5-1.5]), respectively. One finds again the higher capacity observed for [TCP4VP-5-0.5] than for [TCP4VP 5-1.5].

In Table 5, we show the results of adsorption capacity using other adsorbents.

The adsorption capacity for chromium is considerably better than capacity obtained using other adsorbents under the same operating conditions, and in good range adsorption capacity compared to the value of 40 and 44.68 mg/g obtained with smectite and acid-treated oil palm shell charcoal, respectively [45,46]. Our polymer-modified treated clays are less efficient compared to the value of 94.34 mg/g

Table 5
Adsorption capacity using other adsorbents comparing to our study

Adsorbent	q_e (mg/g)	References
Montmorillonite	0.78	[40]
Kaolinite	1.3	[40]
Hexadecyltrimethylammonium-modified clay	18.2	[43]
Distillery sludge	5.7	[44]
Smectite	40	[45]
Acid treated oil palm shell charcoal	44.68	[46]
Cationic surfactant-modified yeast	94.34	[47]
[TCP4VP-5-0.5]	20.83	Present work
[TCP4VP 5-1.5]	25.35	Present work

Table 6
Adsorption capacity of hexavalent chromium ions on [Bf0.3] and [TCP4VP-5-1.5]

Composite	[Bf0.3]	[TCP4VP-5-1.5]
q_e (mg/g)	20.16 [29]	25.35

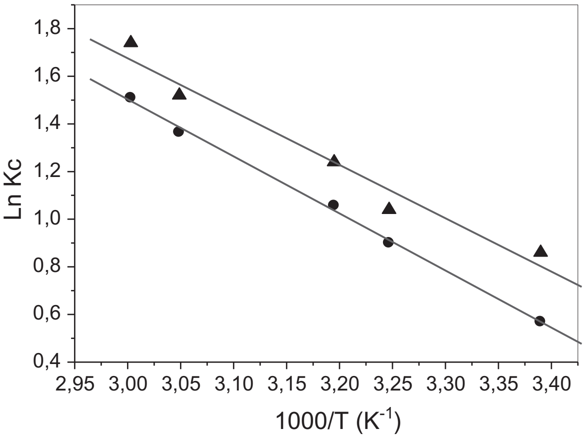


Fig. 7. Van't Hoff plot for the adsorption of Cr(VI) onto (▲) [TCP4VP-5-0.5] and (●) [TCP4VP-5-1.5] at pH = 1 of the metal solution, shaking time (3 h), (*V* solution, *m* adsorbent) (20 mL, 0.1 g), initial metal ion concentration 350 mg/L.

obtained with cationic surfactant-modified yeast [47]. Nevertheless, the differences of ultimate adsorption capacity between [TCP4VP-5-0.5] and [TCP4VP 5-1.5] allow thinking that efficiency of our system may be improved by optimizing the amount of P4VP adsorbed.

If we compare the amount of hexavalent chromium ions adsorbed on the composites in this work with those of our previous work [29] and for the same rate (clay/polymer), it is evident that the nature of the used clay for preparation of composites is very important. Indeed, the acid treatment of the clay will increase it specific surface area and deport most of the cations outside of clay structure. The sulfate ions from sulfuric acid deviate interlayer distance to leave space for polymer adsorption. However, the acid treatment increases the amount of protons which encourages better adsorption effect of hexavalent chromium ions by electrostatic attraction.

Around 5 mg/g of retained chromium ions is the difference between the two composites [Bf0.3] prepared in our earlier work [29] and [TCP4VP-5-1.5] for the same rate (clay/polymer) and under the same conditions of initial chromium concentration, pH, and the temperature (see Table 6).

3.2.4. Thermodynamic parameters

The influence of temperature on the Cr(VI) adsorption behavior onto polymer-modified treated clays ([TCP4VP-5-0.5] and [TCP4VP-5-1.5]) was also studied using 350 mg/L of Cr(VI) under the optimized conditions of shaking time (3 h), pH = 1 at 35, 40, 50, 55, and 60°C. The enthalpy change (ΔH) and entropy change (ΔS) were calculated by using the Van't Hoff equation in the form [48]:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

$$K_c = \frac{C_e}{C_0 - C_e} \tag{12}$$

where K_c is the equilibrium constant equivalent to the fractional attainment of metal ion adsorbed onto polymer-modified treated clay, C_0 and C_e are, respectively the initial and equilibrium concentrations of Cr(VI), T is the temperature (K) and R the gas constant equal to 8.3143 J mol^{-1}K^{-1}. Values of ΔH and ΔS were calculated from the slope and intercept of ln K_c (1000/T) plot (Fig. 7). The values of the thermodynamic parameters for the Cr(VI) adsorption are given in Table 7.

The positive value of ΔH shows that adsorption of Cr(VI) ions on polymer-modified treated clays is an endothermic process. The ΔG values become more negative with increasing temperature, demonstrating the spontaneity of the process. The ΔS value is positive; it is probably attributed to the fixation of the

Table 7
Thermodynamic data for adsorption of Cr(VI) on polymer-modified treated clays ([TCP4VP-5-0.5] and [TCP4VP-5-1.5]) at pH = 1 metal solution, shaking time (3 h) (*V* solution, *m* adsorbent) (20 mL, 0.1 g), initial metal ion concentration 350 mg/L

Sample	ΔH (kJ/mole)	ΔS (J/mole/K)	ΔG (kJ/mole)			
			308 K	313 K	323 K	333 K
[TCP4VP-5-0.5]	18.61	69.78	−2.88	−3.23	−3.93	−4.63
[TCP4VP-5-1.5]	19.92	72.26	−2.33	−2.70	−3.42	−4.14

Cr(VI) ions onto the active sites of the randomly distributed polymer species. This behavior was observed for the adsorption of some metal ions on various other materias [49–51].

Thermodynamic data on metal adsorption on clays are scarce. Echeverria et al. [51] have reported for Ni (II) adsorption onto illite Δ*H*, Δ*S*, and Δ*G* values of 16.8 kJ/mol, 58 J/(mol K), and −1.04 kJ/mol, respectively. Lin and Juang [52] investigated the adsorption of Cu(II) and Zn(II) onto montmorillonite modified with sodiumdodecylsulfate. The values of Δ*H*, Δ*S*, and Δ*G* were reported as 7.05 kJ/mol, 9.09 J/(K mol), and −9.66 kJ/mol, respectively, for Cu(II) and7.39 kJ/mol, 6.39 J/(K mol), and −9.17 kJ/mol, respectively, for Zn(II) at 298 K. These values are not so different from values obtained in this work.

4. Conclusions

This experimental work demonstrates that the system treated clay/poly(4-vinylpyridinium) is efficient for the adsorption of Cr(VI) ions.

Adsorption of hexavalent chromium ions on the treated clay was not significant and its modification using P4VP lead to the inorganic–organic composites with retention properties. The retention of hexavalent chromium in aqueous solution is significantly better at low pH, for this, all experiments were performed at pH = 1.

The Cr(VI) retention occurs at very low pH when P4VP is positively charged and can efficiently interact by electrostatic attraction with such anions. The positive charges of P4VP are associated and neutralized and may form P4VP/Cr(VI) complex.

The use of the composites based on treated clay and P4VP for hexavalent chromium ions adsorption gives better rates than those obtained with composites prepared using drilling clay because of higher capacity P4VP adsorption in the case of treated clay.

It is clear that the final result depends on the various interactions: treated clay/P4VP, treated clay/Cr (VI), P4VP/Cr(VI), and the retention of the P4VP/Cr (VI) complex onto treated clay according to proportions of the different components and on pH.

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