Uptake of CrO_4^{2-} Ions by Fe-Treated Tri-Calcium Phosphate

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Abstract. CrO_4^{2-} ion adsorption on Fe-treated tri-calcium phosphate was studied by batch experiments as a function of contact time, initial concentration of metal ion and temperature. Adsorption results showed that at pH 5.5 and $1.0x10^{-4}$ M chromium concentration the adsorption capacity of Fe-treated tri-calcium phosphate for CrO_4^{2-} ions was 7.10×10^{-3} mmol/g. Chromium adsorption data on Fe-treated tri-calcium phosphate at various initial concentration fitted the Freundlich isotherm. By temperature studies the thermodynamic parameters ΔH^0, ΔG^0 and ΔS^0 were estimated and the obtained results showed that the adsorption reaction was endothermic and spontaneous.
Keywords: Fe-treated tri-calcium phosphate, chromate ions, adsorption, isotherm, thermodynamics parameters.

Resumen. Por medio de experimentos estáticos se estudió la adsorción de iones CrO_4^{2-} en fosfato tricálcico tratado con Fe, como una función del tiempo de contacto, concentración inicial y temperatura. Los resultados mostraron que a un pH de 5.5 y una concentración $1.0x10^{-4}$ M de cromo la capacidad de adsorción del fosfato tricálcico tratado con Fe para los iones cromato fue de 7.1×10^{-3} mmol/g. Los datos de adsorción del cromo en el adsorbente modificado con Fe, como una función de su concentración, se ajustaron a la isoterma de Freundlich. A través de estudios de temperatura se determinaron los parámetros termodinámicos ΔH^0, ΔG^0 y ΔS^0 y los resultados obtenidos mostraron que el proceso de adsorción de los iones cromato es endotérmico y espontáneo.
Palabras clave: Fosfato tricálcico, Fe, cromatos, adsorción, isoterma, parámetros termodinámicos.

Introduction

Chromium ionic species pollute inland surface waters through discharges from leather tanning, paints and pigments, electroplating and metal finishing industries, among others. Chromium is one of the most toxic metals and can be found in aqueous systems in both trivalent Cr(III) and hexavalent Cr(VI) form. Hexavalent chromium compounds are significantly more toxic than trivalent ones even at low concentrations, and they have a potential carcinogenic effect. Before the discharge of effluents contaminated with chromium to aqueous systems, the content of this toxic element should be reduced to the allowable limit of 0.1 mg /L.

Various methods are available to remove chromium from wastewater and well established methods are reverse osmosis, ion exchange, electro-dialysis, coagulation, solvent extraction, adsorption and some others. In the case of adsorption process, many materials such as activated carbon [1-3], calcium alignate beads [4,5], biological wastes [6-8], Fe-modified pozzolane [9], tri-calcium phosphate [10], hydrotalcite [11] and others materials have been used for the removal of Cr(VI). Granados et al [10] studied the ball milling effect on tri-basic calcium phosphate (TCP) and its chromium (VI) ion sorption properties and they found that chromium (VI) sorption on milled TCP samples increased, unexpectedly, as the specific area became smaller. The presence of Fe originated from the steel balls of the high energy mill in the milled samples explained the increasing in Cr(VI) sorption. Fe is deposited in very small amounts on TCP nanometric particles surface causing a slight increase in the adsorption of Cr(VI) ions through interactions of these ions with the hydroxyl groups attached to Fe atoms. Hence, probably

the increase in the amount of Fe deposited in calcium phosphate may enhance the uptake of chromate ions. On the basis of this idea, tri-calcium phosphate has been treated in the present work with a heated $FeCl_3$ aqueous solution and the obtained Fe-treated phosphate surveyed as adsorbent of chromate ions. Thus, the aim of this work is to study the chromium ions removal from aqueous solutions through their adsorption on Fe-treated tri-calcium phosphate as a function of contact time, initial pH, chromium concentration and temperature, by batch experiments. Temperature studies were also carried out to determine thermodynamic parameters of the Cr(VI) adsorption process.

Results and Discussion

Adsorbent characterization

X-ray diffraction (XRD) patterns

The obtained X-ray diffraction pattern of tri-calcium phosphate showed (Figure 1a) sharp and well defined peaks which correspond to the hydroxylapatite structure (JCPDS file 055-0898). On the other hand, the X-ray diffraction pattern of the Fe-treated tri-calcium phosphate showed (Figure 1b) an amorphous structure since sharp and defined lines were not observed at all. The Fe-treated tri-calcium phosphate amorphous structure indicates that the hydroxylapatite structure of tri-calcium phosphate was destroyed with the $FeCl_3$ treatment applied to the original material. For comparison purposes, the XRD pattern of $FePO_4$ (Fluka) was also obtained and displayed an amorphous structure also.
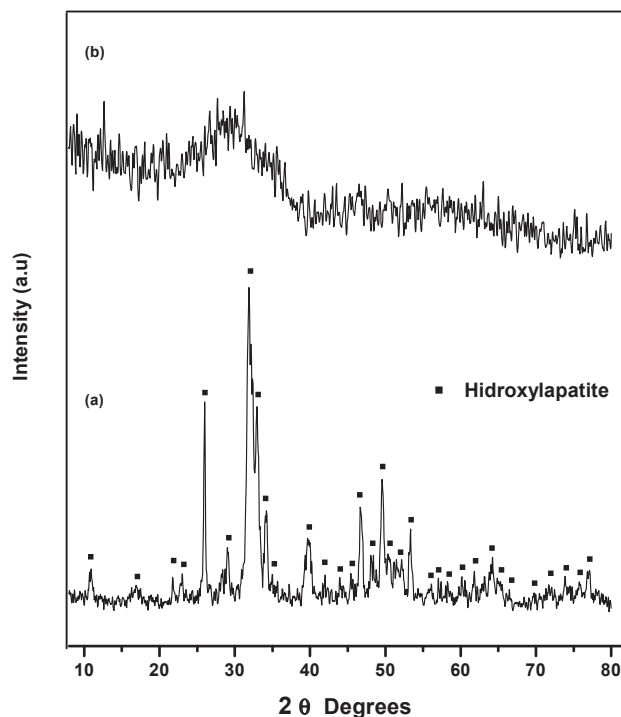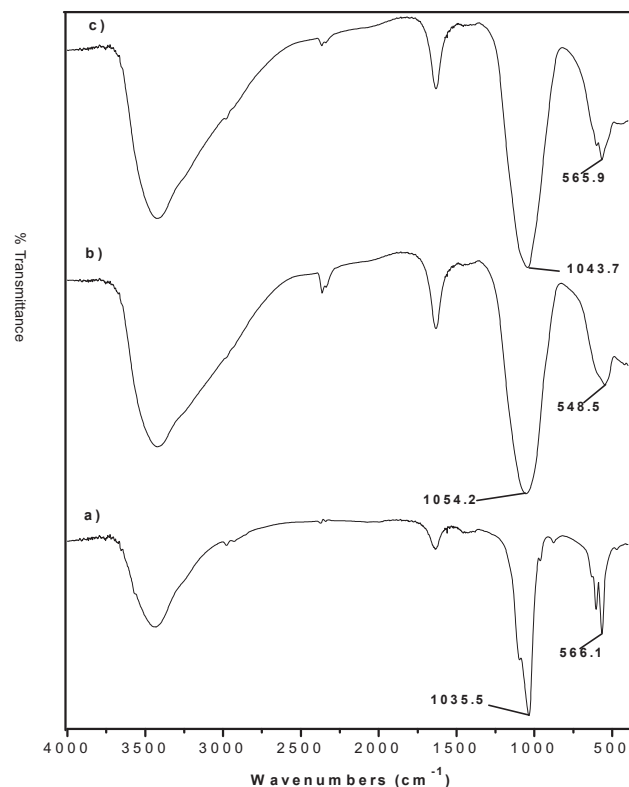
Fig. 1. X-ray diffraction pattern of (a) tri-calcium phosphate with hydroxylapatite structure and (b) Fe-treated tri-calcium phosphate.

Fig. 2. FT-IR spectra of (a) tri-calcium phosphate (hydroxylapatite), (b) $FePO_4$ and (c) Fe-treated tri-calcium phosphate.
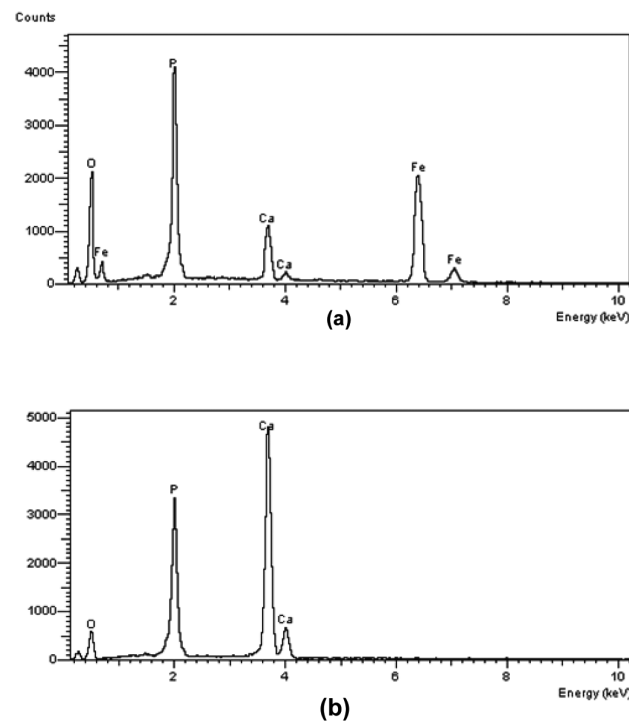
Infrared spectra

As a tetrahedral molecule, tri-calcium phosphate molecule presents four normal modes of vibrations but only the frequencies v_3 and v_4 are infrared active [12]. Figure 2a shows the IR spectrum of the hydroxylapatite sample. It is seen that n_3 and v_4 frequencies appear strongly at 1036 cm^{-1} and 566 cm^{-1}, respectively. The infrared spectrum (Figure 2b) of $FePO_4$ also displays two bands at 1054 cm^{-1} (v_3) and 549 cm^{-1} (v_4) and for the Fe-treated tri-calcium phosphate the two infrared active bands (Figure 2c) appear at 1044 cm^{-1} (v_3) and 566 cm^{-1} (v_4). These results show that the chemical treatment given to hydroxylapatite with the heated 0.1 N $FeCl_3$ solution did not exert any chemical change in the phosphate group; however, some fraction of the original tri-calcium phosphate must have changed to amorphous $FePO_4$ as the resemblance of $FePO_4$ and Fe-treated hydroxylapatite IR spectra suggests.

Energy dispersive X-ray spectroscopy (EDS) analysis

Figures 3a and 3b show EDS spectra of Fe-treated tri-calcium phosphate and hydroxylapatite, respectively. As can be seen in the EDS spectra of hydroxylapatite sample, the presence of phosphorous, oxygen and calcium were detected, while for the Fe-treated tri-calcium phosphate besides O, P and Ca, iron was also detected. For hydroxylapatite the corresponding

Fig. 3. EDS spectra of (a) Fe-treated tri-calcium phosphate and (b) hydroxylapatite.

semiquantitative analysis displayed the following element % composition: O = 41.07 ± 1.6, P = 17.67 ± 0.2, and Ca = 41.26 ± 1; and for the Fe-treated tri-calcium phosphate the determined element % composition was as following: O = 39.48 ± 1.97, P = 19.16 ± 0.24, Ca = 6.52 ± 0.28 and Fe = 34.85 ± 1.9. These results indicate that with the $FeCl_3$ treatment calcium was displaced in high proportion by Fe in the original tri-calcium phosphate to form $FePO_4$ and only a small amount of the material remained as the original tri-calcium phosphate. In resume, the results of the characterization analyses indicate that the material obtained after the $FeCl_3$ treatment given to the tri-calcium phosphate (with a hydroxyapatite crystalline structure) is a mixture of amorphous $FePO_4$ and tri-calcium phosphate where some iron must have been adsorbed on the surface of their grains. Thus and hereafter, this Fe-modified mixture will be referred in this paper as Fe-mPO_4.

On the other hand, the EDS analysis of a $FePO_4$ sample as obtained from Fluka showed the following element % composition: O = 36.62 ± 0.31, Na = 3.1 ± 0.19, Al = 0.54 ± 0.20, P = 20.35 ± 0.22, S = 1.21 ± 0.005 and Fe = 37.62 ± 0.48. These results indicate that the $FePO_4$ sample is not a pure compound.

Effect of contact time

The Cr(VI) adsorption on Fe-mPO_4 was carried out by batch experiments at an initial pH of 5.5, using a 1×10^{-4} M K_2CrO_4 solution at 293 K. The results shown in Figure 4 indicate that the Cr(VI) adsorption on Fe-mPO_4 reached complete equilibrium within 5 hours of shaking time. Granados et al. reported [9, 13] that the adsorption of Cr(VI) on Fe-modified pozzolane and boehmite reached the equilibrium in 2 h and 1 hours, respectively. At equilibrium, the retention of Cr(VI) on the adsorbent was found to be 7.10×10^{-3} mmol/g at the surveyed pH 5.5. On the other hand, for the milled tri-calcium phosphate the corresponding value reported by Granados-Correa et al [10] was 7.5×10^{-5} mmol/g. The higher equilibrium retention of chromate ions on Fe-mPO_4 proves that the increase in the amount of Fe deposited in calcium phosphate enhances the uptake of chromate ions. Figure 4 also shows the chromate ions adsorption rate on $FePO_4$, which also has an amorphous structure and was utilized as obtained from Fluka. As can be seen, the chromate ions adsorption rate on this adsorbent was slower than that on Fe-mPO_4 since the complete equilibrium was reached within approximately 17 h, and the maximum retention was lower: 6.15×10^{-3} mmol/g. These results indicate that Fe-mPO_4 is more efficient than $FePO_4$ to adsorb chromate ions. As the EDS analysis revealed, $FePO_4$ is not a pure sample and the presence of the impurities (probably sulfide ions) makes $FePO_4$ less efficient to adsorb CrO_4^{2-} ions. For comparison purposes also, the adsorption of chromate ions on Fe-modified pozzolane [9] at the same pH value (5.5) was lower (3.23×10^{-3} mmol/g). On the other hand, at pH 4.0 the equilibrium in the CrO_4^{2-} ion distribution was also reached in 5 h. For pH 7.5, 9 and 11, the distribution equilibrium of chromate ions was attained in about 6, 8 and 12 h, respectively.
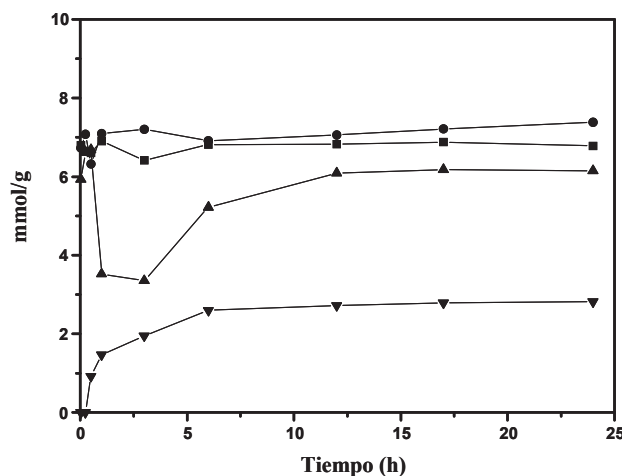

Fig. 4. Cr(VI) adsorption on Fe-mPO_4 as a function of shaking time.
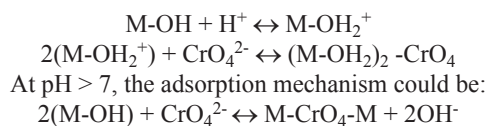
Effect of initial pH

The influence of initial pH on the chromium ions adsorption was studied by using a 1×10^{-4} M CrO_4^{2-} ions solution. All the experiments were carried out without addition of any buffer to avoid the presence of any external electrolyte, which may influence the adsorption process. The initial pH of the Cr(VI) solutions was adjusted in the range from 4 to 11 by using HNO_3 and a concentrated NaOH aqueous solution. The obtained results are shown in Table 1. The chromate ion adsorption as a function of initial pH showed a maximum value at an initial pH 5.5 and then decreased as the initial pH was increased. At pH 5.5 Cr(VI) ions exist as the anions $HCrO_4^-$ and CrO_4^{2-} [14] which are adsorbed on the positively charged surface of the Fe-mPO_4, where $-Fe-OH_2^+$ groups are formed in the utilized acid conditions. Although CrO_4^{2-} ion is not the main chemical species [14] at pH 5.5, its adsorption is highly efficient because of it bears a double electrical charge, which can explain the high chromium retention (7.10×10^{-3} mmol/g) found at that initial pH value. At pH 4.0 only $HCrO_4^-$ ions are present in solution but its adsorption on Fe-mPO_4 is less efficient than that for CrO_4^{2-} ions since $HCrO_4^-$ ions bear

Table 1. mmol of CrO_4^{2-} ions adsorbed on 1 g of Fe-mPO_4 as a function of pH. Concentration of K_2CrO_4 aqueous solutions: 1×10^{-4} M.

pH	mmol/g
4.0	6.8×10^{-3}
5.5	7.10×10^{-3}
7.5	6.16×10^{-3}
9.0	5.11×10^{-3}
11.0	3.66×10^{-3}

only one negative electrical charge and thus, a lower chromium retention was obtained. In alkaline media the chromate ion adsorption was even lower due to a competition between CrO_4^{2-} and OH^- ions for the exchanging hydroxyl groups attached to Fe atoms. At initial pH values of 9 and 11, CrO_4^{2-} ion is the only chemical species of Cr(VI) present in solution.

According to the above statements, a possible mechanism of the CrO_4^{2-} ion adsorption on Fe-mPO$_4$ at pH < 7.0 could be:

$$M\text{-}OH + H^+ \leftrightarrow M\text{-}OH_2^+$$
$$2(M\text{-}OH_2^+) + CrO_4^{2-} \leftrightarrow (M\text{-}OH_2)_2 \text{-}CrO_4$$
At pH > 7, the adsorption mechanism could be:
$$2(M\text{-}OH) + CrO_4^{2-} \leftrightarrow M\text{-}CrO_4\text{-}M + 2OH^-$$

where M represents the Fe$^-$ phosphate group.

Desorption studies

Regenerability of Cr(VI)-loaded Fe-mPO$_4$ is a key factor for improving process economics. Water with acidic and alkaline pH values were used to investigate the Cr(VI) desorption. It was found that Fe-mPO$_4$ samples were dissolved at pH values 1 and 2. When distilled water with pH 5 was used less than 0.1 % of chromate ions were desorbed from the loaded Fe-mPO$_4$. Water with lower pH values slightly increased the percentage of CrO_4^{2-} detected in solution. Desorption experiments with alkaline water showed that best results were obtained with pH 10: about 72.8 % of CrO_4^{2-} were desorbed into the alkaline water. This last result suggests that Cr(VI)-loaded Fe-mPO$_4$ can be regenerated with alkaline water and probably be used again to adsorb chromate ions from aqueous solutions.

Effect of chromium concentration

Adsorption Isotherms

The experiments to study the effect of chromate ion concentration on its adsorption on Fe-mPO$_4$ were carried out at 293 K and for 24 h of shaking time and the adsorption data were examined with the Freundlich and Langmuir adsorption isotherms [15]. The chromate adsorption data on Fe-mPO$_4$ fitted well the Freundlich isotherm but did not fit the Langmuir isotherm since in this case a straight line was not obtained when C_e/a_e was plotted versus C_e, where a_e is the amount of chromate ions adsorbed at equilibrium and C_e is the residual chromium concentration at equilibrium. In Figure 5 the logarithm of a_e has been plotted versus the logarithm of C_e. The obtained straight line is described by Freundlich equation:

$$\text{Log } a_e = 1/n \log C_e + \text{Log } K_F$$

where K_F and $1/n$ ($0 < 1/n < 1$) are the Freundlich constants corresponding to the adsorption capacity and intensity of adsorption, respectively. These constants can be estimated by the intercept and the slope (less than 1) of the straight line, respectively. The values of K_F and $1/n$, computed by using
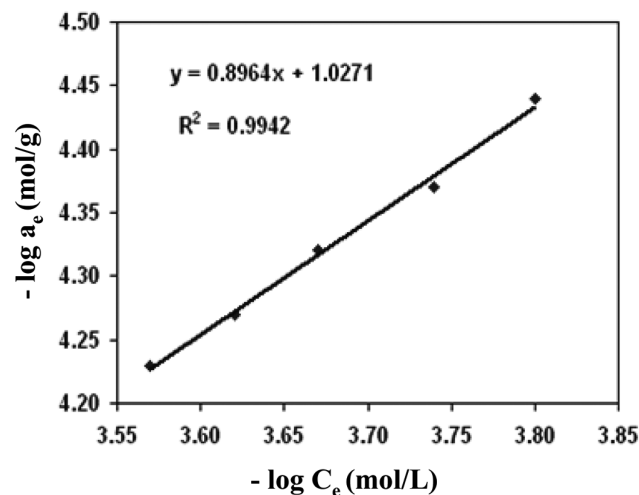

Fig. 5. Freundlich adsorption isotherm for chromate ions on Fe-mPO$_4$.

the least square technique, were 1.52×10^{-3} mol/g and 0.89, respectively, and the correlation coefficient was found to be 0.9942. The value of $1/n$ (less than one) found in this work confirms that the Freundlich isotherm is valid for the Cr(VI) adsorption data on Fe-mPO$_4$. The value $1/n$, less than unity, is attributed to a heterogeneous surface structure of the adsorbent and also indicate an exponential distribution of energy sites [16]. On the other hand, as the $1/n$ value increases, the adsorption capacity of the adsorbent, for the given adsorbate, also increases.

Temperature effect

To search the temperature effect on chromium adsorption batch experiments were carried out at 293, 303, 313, 323 and 333 K with an initial Cr(VI) ion concentration of 1×10^{-4} M at pH 5.5, a contact time of 24 h and an adsorbent amount of 0.1 g. The amount of Cr(VI) adsorbed at equilibrium at various temperatures are displayed in Table 2 and as seen the adsorption of chromate ions increases with increasing temperature

Table 2. Temperature effect on the amount of Cr(VI) ions adsorbed on Fe-mPO$_4$ (mmol/g), at equilibrium. Initial concentration of chromium solution: 1×10^{-4} mol/L, pH 5.5.

Temperature (K)	Amount of CrO_4^{2-} ions adsobed	
	(mmol/g) $\times 10^{-3}$	Adsorpios (5)
293	7.02	70.21
303	7.10	71.02
313	7.22	72.29
333	7.56	75.58

from 293 to 333 K. The augmentation in chromium adsorption with temperature is induced by the enhanced mobility of Cr(VI) ionic species present in aqueous solution and the possible acceleration of some adsorption steps which are originally slow; or even more by the creation of some new active sites on the Fe-mPO$_4$ surface.

Data of temperatures dependence of chromate ion adsorption on Fe-mPO$_4$ were utilized to evaluate the changes in standard enthalpy (ΔH^0), standard entropy (ΔS^0) and Gibbs free energy (ΔG^0) with aid of the following equations:

$$\log K_d =(-\Delta H^0/2.303R)(1/T) + \Delta S^0/2.303R$$
$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

where K_d is the distribution coefficient, described elsewhere [17], T is the absolute temperature in degrees Kelvin and the gas constant R = 8.31434 kJ/mol K. In Figure 6 values of log K_d have been plotted *vs.* $1/T$. By utilizing the van´t Hoff equation in its linearized form:

$$\log K_d = (\Delta H^0/2.303R)(1/T) + \text{constant}$$

and the slope of the straight line in Figure 6, as computed by using the least square technique, a simple calculation with $-\Delta H^0/2.303R$ and the numerical value of the slope (-0.1989), the change in enthalpy of the chromate ion adsorption was found to be 3.81 kJ/mol. This small value suggests that the chromium adsorption on Fe-mPO$_4$ is favored since a small change in enthalpy is required for dehydration of the metal ion to be adsorbed on the Fe-modified tri-calcium phosphate. The positive value also indicates the endothermic nature of chromium adsorption on Fe-mPO$_4$ [18]. On the other hand, the values of change in entropy (ΔS^0) and Gibbs free energy (ΔG^0) of the uptake process were also calculated and they found to be 56.86 kJ/mol K and −16.7 kJ/mol, respectively. As seen the value of ΔS^0 is positive which indicates that the degree of freedom of

ions increases with adsorption. In relation to Gibbs free energy, the negative value of the calculated change ΔG^0 discloses that the chromium adsorption process is spontaneous.

The results above described show that Fe-mPO$_4$ can remove chromate ions from aqueous solution with a high efficiency, under the surveyed experimental conditions. This novel modified material can be obtained easily in the laboratory and its uptake capacity is higher than those of iron phosphate and Fe-modified pozzolane [9], although lower than those of activated carbon [2] and organic resins [19]. Further benefits of Fe-mPO$_4$ include its great thermal stability, very low solubility in a wide pH range (3 - 14) and high chemical resistance.

Conclusions

When the tri-calcium phosphate (with hydroxyapatite crystalline structure) was treated with a heated FeCl$_3$ solution the obtained material was a mixture of FePO$_4$ and Ca$_3$(PO$_4$)$_2$ (both with an amorphous structure) with some iron adsorbed on the surface of their grains. The adsorption in the equilibrium was found to be a function of the initial pH of chromium solution, Cr(VI) concentration and temperature. Adsorption data of CrO$_4^{2-}$ ions obeyed the Freundlich isotherm. The positive values of ΔH^0 and ΔS^0 indicate that the chromium adsorption on Fe-mPO$_4$ is an endothermic process and that the randomness of the system is increased, respectively. The negative value of ΔG^0 indicates an spontaneous adsorption process of CrO$_4^{2-}$ ions. The results of this research showed the high efficiency of Fe-treated tri-calcium phosphate to remove CrO$_4^{2-}$ from aqueous solutions.

Experimental

Obtention of Fe-treated tri-calcium phosphate

10 g of tri-calcium phosphate (Bio-rad Laboratories) were put in contact with 250 mL of 0.1 N FeCl$_3$ aqueous solution in a 500 ml glass beaker and then the suspension was heated up to boiling. The boiling was kept for 1 h and afterwards the red-brown suspension was cooled to room temperature and then the clear supernatant was eliminated by decantation. These operations were repeated 5 times before the supernatant becomes yellow. To eliminate the chloride ions, the solid was suspended in distilled water and poured in centrifuge tubes and then centrifuged for 30 min. The supernatant was discarded. This operation was repeated five or six times until chloride ions were not detected with AgNO$_3$ in the discarded liquid. The centrifuge tubes that contained a red-brown solid were put into a boiling water bath to dry the solid. Once recovered in a ceramic dish, the Fe-treated tri-calcium phosphate was heated at 423 K for 5 h, and the obtained red-brown solid was then used as the adsorbent for chromate ions.
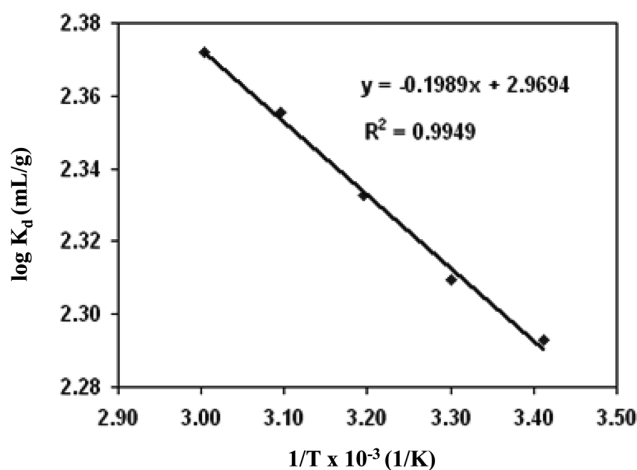

Fig. 6. Variation of log K$_d$ with $1/T$ for adsorption of chromate ions on Fe-mPO$_4$.

Adsorbent Characterization

Tri-calcium phosphate and Fe-treated tri-calcium phosphate were characterized by X-ray diffraction using a Siemens D500 diffractometer coupled to a copper anode X-ray tube, the wavelength K_α was selected with a diffracted beam mono-chromator. The X-ray tube was operated at 35 kV and 20 mA. Diffraction patterns were obtained in scanning mode with a 0.02º (2θ) step size. The compounds were identified comparing the experimental diffraction patterns with the JCPDS cards in the conventional way. Transmission infrared spectra of tri-calcium phosphate, Fe-treated tri-calcium phosphate and FePO$_4$ were obtained with a Nicolet Fourier Transform Infrared Spectrometer model Magna 550. These three compounds were also analyzed by EDS technique.

Adsorption Experiments

Batch type experiments were carried out at 293 K to determine the kinetic removal of CrO$_4^{2-}$ ions by shaking in closed vials 100 mg of the adsorbent Fe-treated tri-calcium phosphate and 10 mL aliquots of 1.0 x 10^{-4} mol/L CrO$_4^{2-}$ ion solution with a pH 5.5, for different time intervals (5 min to 24 h) to attain the equilibrium distribution. Later, the samples were centrifuged to recover the liquid phase. All of the experiments were performed in duplicate, by running two independent closed vials, simultaneously. The adsorption capacity of Fe-treated tri-calcium phosphate for CrO$_4^{2-}$ ions was determined from the difference between the initial and final concentrations of CrO$_4^{2-}$ ions in the aqueous solutions before and after adsorption, by using a Shimadzu ultraviolet-visible 265 spectrophotometer analyzer at λ = 370 nm. The amount of CrO$_4^{2-}$ ions adsorbed per unit mass of the adsorbent and the percent adsorption of CrO$_4^{2-}$ ions were calculated by the following equations:

$$q = ((C_0 - C_e)V)/m$$
$$\%Ads = ((C_0 - C_f)100)/C_0$$

where q is the amount of CrO$_4^{2-}$ ions adsorbed on Fe-treated tri-calcium phosphate (mmol/ g), C_0 and C_e are the initial and equilibrium concentration of chromate ions (mol/L), C_f is the final concentration (mol/L), V is the volume of solution (L) and m is amount of adsorbent (g). For the chromate concentration studies, solutions with the desired concentrations of CrO$_4^{2-}$ ions were prepared by successive dilutions of a stock solution of 9.0 × 10^{-4} mol/L K$_2$CrO$_4$ in distilled water.

Desorption experiments were carried out at 20 ºC in the same manner as the equilibrium sorption experiments, by employing 0.100 g of Fe-mPO$_4$ loaded with known amounts of Cr(VI).

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