

Adsorption characteristics and separation of Cr(III) and Cr(VI) on hydrous titanium(IV) oxide

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Abstract

A hydrous titanium(IV) oxide was prepared to study the adsorption characteristics and the separation of chromium species. Batch sorption studies have been carried out to determine the effect of pH on the sorption of Cr(III) and Cr(VI) on hydrous TiO₂. An excellent separation efficiency of Cr(III) and Cr(VI) was obtained at pH 2. The adsorption percentage of Cr(VI) was above 99%, whereas that of the Cr(III) was less than 1% at this pH. The adsorption isotherm of Cr(VI) on hydrous TiO₂ at pH 2 was in good agreement with the Langmuir isotherm. The maximum adsorption capacity of Cr(VI) on TiO₂ was 5 mg g⁻¹. The rate of adsorption of Cr(VI) by hydrous TiO₂ with average particle diameter 250 and 500 μm has been studied under particle diffusion controlled conditions. The diffusion coefficients of Cr(VI) for both hydrous TiO₂ having average particle diameter of 250 and 500 μm was calculated at pH 2 as 3.84 × 10⁻¹⁰ m² s⁻¹ and 8.86 × 10⁻¹⁰ m² s⁻¹, respectively. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

The importance of chemical speciation of inorganic chromium in environmental samples has been recognised owing to accurate assessment of pollution levels. Chromium exist in two stable oxidation states, Cr(III) and Cr(VI). The Cr(III) state is considered one of the essential elements for living organisms, whereas Cr(VI) state is toxic. Chromium is introduced into natural bodies of water from industries like electroplating, leather tanning, cement industries, steel industries and photography. Cr(VI) can also enter the drinking water distribution system from the corrosion inhibitor used in water pipes. So the determination and elimination of Cr(VI) from water is of great concern. The most common techniques (AAS, ICP–AES, etc.) can only yield information on the total concentrations of chromium. The determination of total chromium cannot be utilized to determine environmental impact. Therefore, the separation and preconcentration of chromium species are required. Traditional methods for separation and preconcentration of

chromium species are mainly based on solid–liquid extraction [1], solvent extraction [2], coprecipitation [3] and chromatography [4]. All these methods have the disadvantage of introducing additional laborious and time-consuming sample manipulation steps. Among the various treatment techniques, sorption is the most commonly used. Extensive studies on the sorption and ion-exchange properties of hydrous oxides have been carried out from the point of view of analytical separation, adsorbents for the recovery of trace metals present in natural waters, matrices for radioactive nuclear wastes, etc. Ion-exchange and sorption properties of hydrous oxides arise from the pH dependent protonation and deprotonation reactions of surface hydroxyl groups, when in contact with solution [5]. Many authors have studied the sorption behaviour of metal ions on the hydrous metal oxides, reproducibly prepared and fully characterized [6–9]. However, work on hydrous oxides devoted to the kinetic studies is generally little. The kinetics is important properties for understanding the ion-exchange mechanism. A measurement of the rate of adsorption provides fundamental data which are useful for elucidating ion-exchange kinetics. Ion-exchange is generally a surface phenomenon and is expected to be affected by surface properties. By the modification of the preparation procedure it is possible to

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prepare different types of hydrous oxides with considerably different surface properties.

Titanium dioxide is an ideal model adsorbent for studies of the relationship between the surface charging and adsorption. Its solubility is negligible, and its point of zero charge (PZC) in the middle of the pH scale makes it possible to study adsorption on positively and negatively charged surface of titanium dioxide over a broad range of pH and ionic strength. Hydrous titanium dioxide has been intensively studied owing to its high chemical stability, insolubility in acid and alkaline solutions and reasonable rate of adsorption and desorption when used in column operation.

In the present study a hydrous titanium(IV) oxide was prepared and characterized. The structure, adsorption characteristics and the potential use of hydrous titanium(IV) oxide for separation of chromium species were investigated.

2. Experimental

2.1. Reagents

Titanium(IV) chloride and sodium hydroxide were purchased from BDH Chemicals Ltd. and Merck (AnalaR grade), respectively and were used to prepare hydrous titanium dioxide.

Chromium nitrate and potassium dichromate (AnalaR grade) were purchased from Merck and were used to prepare Cr(III) and Cr(VI) stock solutions (1000 mg/L, in 2% HNO₃), respectively.

Na₂⁵¹CrO₄ was purchased from Amersham plc, Hp 79 NA UK (specific activities ranged from 3.70 MBq to 37 MBq μg⁻¹ chromium).

Ultrapur water (Resistivity 18.2 MΩ cm, TOC Level 1–5 ppb) prepared with Millipore model water purification system including Elix and Mili-Q was used in the experiments.

2.2. Preparation of the sorbent

The appropriate amount of TiCl₄ was slowly added to distilled water in an ice-water bath to prepare 1 M TiCl₄ solutions. When TiCl₄ dissolved in distilled water, the heat of the exothermic reaction explosively generated formation of orthotitanic acid. 5 mL of HCl (35%) per 100 mL of distilled water was added to prevent the formation of orthotitanic acid.

Hydrous titanium(IV) oxide was prepared by drop-wise addition of 1 M NaOH, with stirring at about 298 K to

250 mL of a solution of 1 M TiCl₄ to make pH 4. The precipitate was filtered after 2 h and washed to remove chlorine ion from the cake until the pH of washings become about 5. After being dried at room temperature, the white precipitate was powdered and sieved into different particle sizes. The ~500 μm average particle size fraction (–600 μm + 425 μm) were used in all experiments. In the kinetic experiments the ~250 μm average particle size fraction (–300 μm + 250 μm) were also used.

2.3. Identification and characterization

Hydrous titanium(IV) oxide was characterized by DTA/TGA analysis using a Shimadzu thermal analyser, by Fourier transform infrared spectroscopy (FTIR) using the potassium bromide (KBr) pellet technique and a Shimadzu FTIR spectrometer and by X-ray diffraction analysis using a Perkin-Elmer model diffractometer.

The specific surface area was measured by the BET method using a high speed surface area analyzer (Micro-metrics 2200 model).

The equivalent diameter of hydrous titanium dioxide particles was calculated from images obtained through optic microscope and video camera, using the image analysis instruments Optomax V and Vids III.

2.4. Effect of pH on the adsorption of Cr(III) and Cr(VI) on TiO₂

To investigate the effect of pH on the adsorption of Cr(III) and Cr(VI) on TiO₂, 10 mL of 10 ppm standard solutions of Cr(III) and Cr(VI) with different pH values were prepared and following the addition of 0.5 g of TiO₂ the samples were shaken for 2 h at 298 K ± 1. The supernate solutions were filtered through a filter paper (Whatman 41) and the concentrations of chromium were determined by Optima 2000DV model Perkin-Elmer ICP-OES. The operating conditions and the analytical wavelength are summarized in Table 1. The adsorption percentage of chromium on TiO₂ were calculated.

2.5. Isotherm studies

The investigation of adsorption isotherm were conducted by batch process. The 25 mL of chromium species standard solutions at different concentrations were prepared and the different pH values of these solutions were adjusted with 1 M NaOH and 1 M HNO₃. Hydrous TiO₂, 0.5 g, were added to

Table 1
Instrumental parameters of ICP–OES for chromium analysis

Gas flow (L/min)			RF power (watt)	Pump (mL/min)	Wavelength (nm)	Sample read delay (s)	Replicate
Plazma	Auxiliary	Nebulizer					
18	0.2	0.59	1400	1.5	267.716	30	2

each sample. The samples were shaken for 2 h in a shaker at $298\text{ K} \pm 1$. The supernates were filtered through a filter paper (Whatman 41) and the concentrations of chromium species were determined by Optima 2000DV model Perkin-Elmer ICP–OES. The quantity of adsorbed chromium on hydrous titanium dioxide was calculated as the difference between initial and final concentration at equilibrium (Eq. (1)). The analysis of the relationship between hydrous titanium dioxide adsorption capacity and chromium concentration was performed using the equation of Langmuir (Eq. (2)):

$$q = (C_i - C) \frac{V}{W} \tag{1}$$

$$\frac{C}{q} = \frac{1}{q_s b} + \frac{C}{q_s} \tag{2}$$

where q is the quantity of chromium ion adsorbed per unit of mass of hydrous titanium dioxide; q_s , the adsorption capacity of hydrous titanium dioxide; b , the constant related to adsorption intensity; C , the chromium concentration at equilibrium; C_i , the initial concentration of chromium; V , the volume of solution and; W , the mass of the sorbent.

2.6. Kinetics

The rate of sorption may be determined by the spherical diffusion model under the conditions in which the shapes of particle are assumed as being ideal spheres with the same radius and the rate determining step of sorption is controlled by intraparticle diffusion. In the present study, the kinetics of extraction of chromium by hydrous titanium dioxide was studied under vigorous stirring conditions to eliminate bulk diffusion and to minimize the film diffusion contribution to the rate. Thus, it is presumed that the concentration gradient of the chromium ion between the sorbent–film interface and the center of the sorbent particle is the driving force for the diffusion.

A typical equation relating the rate of adsorption to the diffusion of ion in a spherical particle is given by,

$$\frac{\partial C}{\partial t} = D \left[\frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \frac{\partial C}{\partial r} \right] \tag{3}$$

where, D is the intraparticle diffusion coefficient ($\text{m}^2 \text{s}^{-1}$), C is the concentration of the ion diffusing into the sorbent ($\mu\text{eq dm}^{-3}$), and r is the radial distance from the center of the particle (μm).

The solution of Eq. (3) is given by Boyd et al. [10] which is reproduced in Eq. (4). This expression relates the fractional attainment of equilibrium, $F_t = Q_t/Q_e$, as a function of time, where Q_t and Q_e are the total amount of the metal ion adsorbed at time t and at equilibrium (infinite time), respectively.

$$F_t = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{(-n^2 Bt)} \tag{4}$$



Photo 1. Image of TiO₂ particles.

$$B = \frac{\pi^2 D}{r_0^2} \tag{5}$$

where, D is the diffusion constant of the ion in the sorbent and r_0 is the radius of the particle. When $F_t < 0.85$, Bt values can be calculated with fairly good approximation [11] from the measured values of F_t by using the Eq. (6),

$$Bt = 2\pi - \frac{\pi^2}{3} F_t - 2\pi \left(1 - \frac{\pi}{3} F_t \right)^{1/2} \tag{6}$$

The magnitude of Bt obtained is plotted against t to give a straight line passing through the origin with a slope giving a magnitude of diffusion coefficient D , according to Eq. (5).

Two different fractions of titanium dioxide particles classified as 250 and 500 μm average particle sizes were taken for the kinetic studies. For the determination of the dimension and sphericity of each group of titanium dioxide particles, images obtained through optic microscope and video camera were analyzed using the image analysis instruments Optomax V and Vids III (Photo 1). To determine the sphericity, the amount of particles for each group were chosen randomly; the maximum and minimum diameters were measured; the mean values and sphericity were calculated. Equivalent diameters were calculated from the Eq. (7),

$$\text{Eq } \phi = [(\phi \text{ max})^2 (\phi \text{ min})]^{1/3} \tag{7}$$

The calculated values were given in Table 2.

Sorption kinetics of Cr(VI) on TiO₂ (with average particle sizes of 250 and 500 μm) were studied at $298\text{ K} \pm 1$ by using an apparatus equipped with a cage type mixer (Photo 1). In each experiment 1 g of sorbent was placed in the cage and immersed in 200 mL solution including 5 mg Cr(VI) at pH 2. To calculate the diffusion coefficients, 74 MBq ⁵¹Cr/g

Table 2
The dimension and sphericity of TiO₂ particles

	Mean value			
	ϕ Max (μm)	ϕ Min (μm)	Eq ϕ (μm)	Sphericity
Group I	265	240	256	1.104
Group II	520	470	502	1.106

stable Cr were added to each solution and the initial activities were measured by scintillation. The solutions were stirred vigorously during equilibration. Aliquots, 0.02 mL, were directly withdrawn from aqueous phase at a fixed interval of time and the emission rate of 320.08 keV. The γ -rays of ^{51}Cr were measured using a well-type NaI(Tl) detector and Packard-Cobra Auto Gamma Counter. The adsorption percentage was calculated from the activity of Cr-51 present in the aqueous phase.

3. Results and discussion

The characteristics of the sorbent were: apparent density, 2.22 g mL^{-1} and; specific surface area, $185\text{ m}^2\text{ g}^{-1}$. From the XRD patterns it was observed that TiO_2 has an amorphous structure.

Fig. 1(a) and Fig. 2(a) show FTIR spectra of the heat treated titanium dioxide xerogels, (500°C for 3 h, in air) before and after chromium adsorption process, respectively. The broad band between 3700 and 3300 cm^{-1} centered around 3471 cm^{-1} , indicating the presence of $-\text{OH}$ groups on the surface of titanium dioxide, the $\delta_{\text{H}_2\text{O}}$ band around 1643 cm^{-1} demonstrating the presence of molecularly adsorbed water in dried gel, appear in both spectra. No characteristic peaks corresponding to chemisorbed $\text{CrO}_4^{=}$ ions were observed. Differences between two spectra begin at the low frequency region, where the influence of chromium can be seen. The peaks of pure and chromium adsorbed titanium dioxide in this region were given in Fig. 1(b) and Fig. 2(b), respectively. The components at 447.45 cm^{-1} , 478.31 cm^{-1} and 489.89 cm^{-1} seen in pure TiO_2 show an increased intensity in chromium adsorbed TiO_2 . On the contrary the component at 428.17 cm^{-1} show a decreased intensity

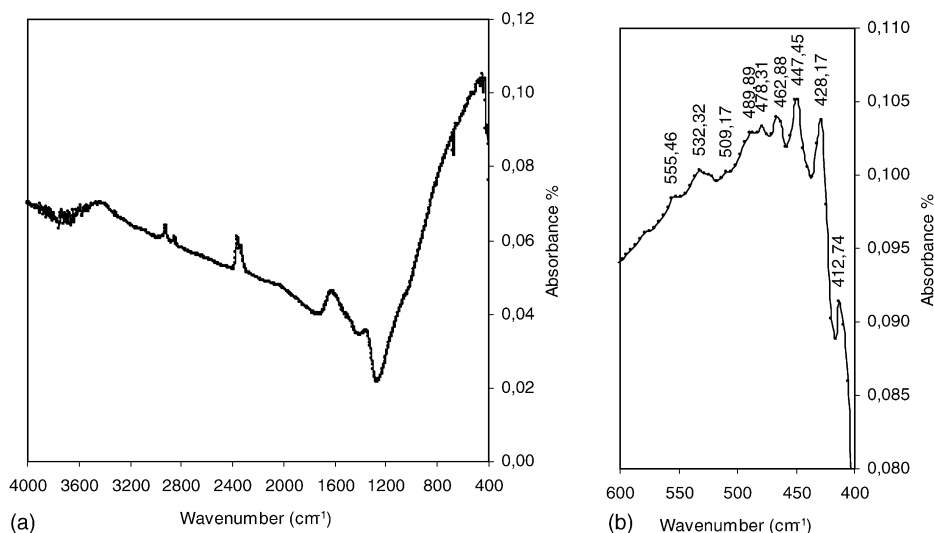


Fig. 1. The FTIR spectrum of hydrous titanium dioxide: (a) $400\text{--}4000\text{ cm}^{-1}$ region; (b) $400\text{--}600\text{ cm}^{-1}$ region.

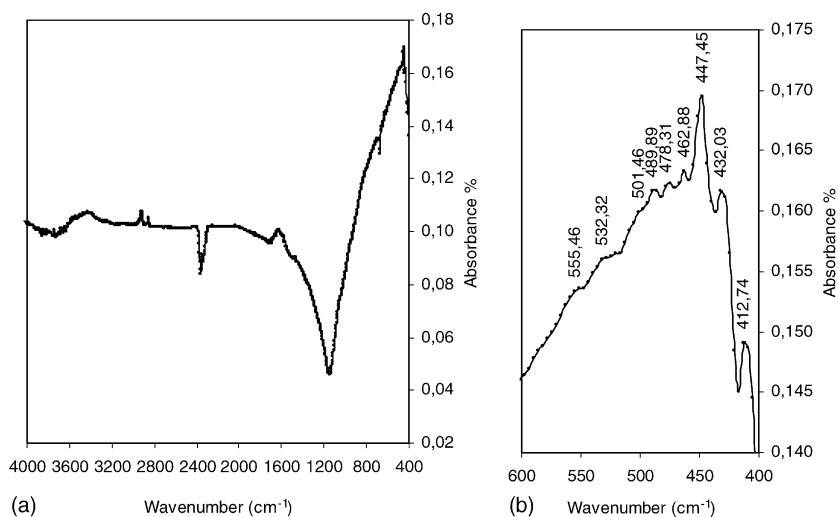


Fig. 2. The FTIR spectrum of chromium adsorbed hydrous titanium dioxide: (a) $400\text{--}4000\text{ cm}^{-1}$ region; (b) $400\text{--}600\text{ cm}^{-1}$ region.

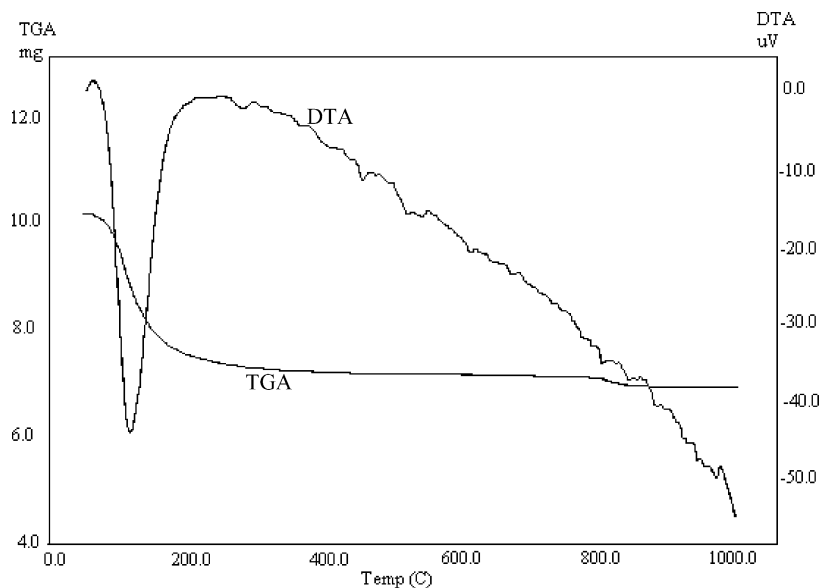


Fig. 3. TGA-DTA curves of hydrous titanium dioxide.

and the peak is shifted to 432.03 cm^{-1} . The broad peak at 532.32 cm^{-1} seen in Fig. 1(b) disappeared in Fig. 2(b).

It is generally admitted that titanium dioxide strongly retain adsorbed undissociated water due to the strong Lewis acidity of the coordinatively unsaturated Ti^{4+} surface sites [12]. In addition, a charge separation can occur in these coordinated water molecules because of the surface ionicity [13]. This charge separation strengthens the formation of hydrogen bonds between the coordinated water molecules, thus stabilizing their link onto the surface.

TGA and DTA curves are shown in Fig. 3. The TGA curve indicates that decrease of weight, caused by vaporization of water, continued until about 700 K. Then above 700 K, the curve was flat. The DTA curve shows a single peak at 373 K, which corresponds to endothermic reaction due to vaporization of water. The value of n in $\text{TiO}_2 \cdot n\text{ H}_2\text{O}$, calculated from the thermal analysis data was 1.79. The number of bound water n , can be varied over wide limits depending on the method of preparation. It is well known that the amount of free water aids to ion transport in the adsorbent.

The pH value of the solution is an important factor that controls the sorption of Cr(III) and Cr(VI). Fig. 4 shows the effect of pH on the adsorption efficiency of Cr(III) and Cr(VI) on hydrous titanium dioxide. The adsorption of Cr(VI) decreases with an increase in pH values, while the adsorption of Cr(III) shows an opposite trend. The maximum adsorption percentage of Cr(VI) (>99%) were observed at pH 2. The adsorption percentage of Cr(III) at this pH was minimum (<1%). The variation in adsorption can be explained by taking into account the isoelectric point of titanium dioxide and the existing forms of chromium species at different pH values. Surface acidity of titanium dioxide is a very important factor that influences the adsorption of chromium species. Titanium dioxide has an isoelectric

point at pH 6.2 [14]. In acidic solutions, at pH values lower than the isoelectric point, the surface of titanium dioxide is electropositive, and it attracts Cr(VI) anions. When the pH is higher than the isoelectric point, the surface of titanium dioxide becomes electronegative and it attracts Cr(III) cations. Different species of Cr(VI) coexist at acidic pH (HCrO_4^- , CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$) [15]. Under strong acidic conditions, Cr(III) mainly exist as Cr^{3+} . With an increase in pH value, it might convert to $\text{Cr}(\text{OH})_2^{2+}$, $\text{Cr}(\text{OH})_2^+$, $\text{Cr}(\text{OH})_3^0$, $\text{Cr}(\text{OH})_4^-$, $\text{Cr}_2(\text{OH})_2^{4+}$ and $\text{Cr}_3(\text{OH})_4^{5+}$ [16].

Fig. 5 shows the relationship between the quantity of chromium(VI) adsorbed per unit mass of TiO_2 and the

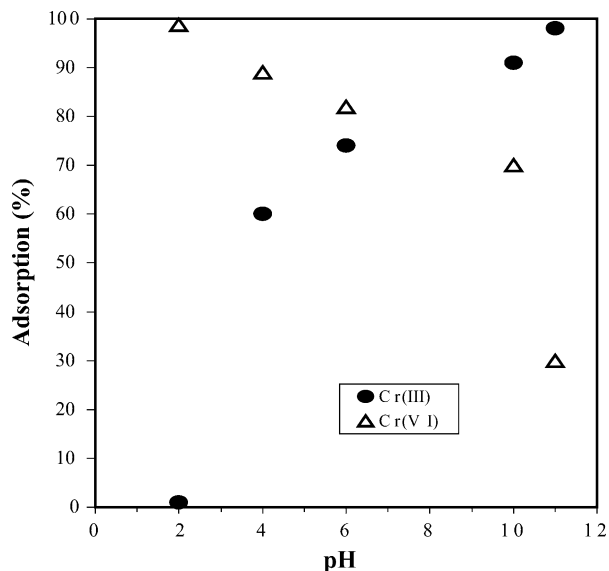


Fig. 4. Effect of pH on the adsorption of Cr(III) and Cr(VI) on TiO_2 . Initial concentration of chromium = 10 mg/L ; adsorbent dosage = 0.5 g/10 mL ; equilibration time = 2 h.

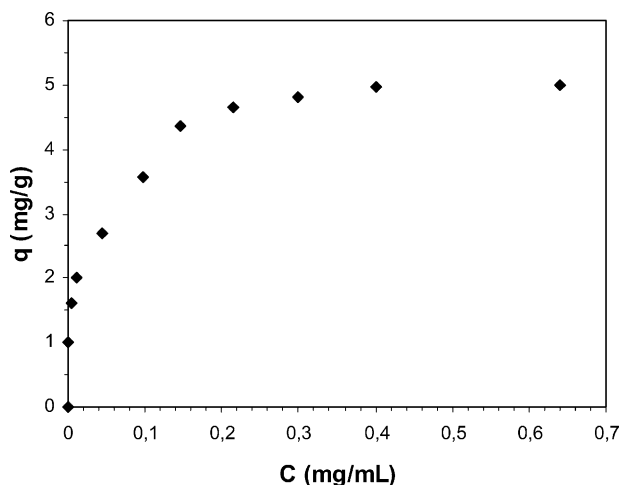
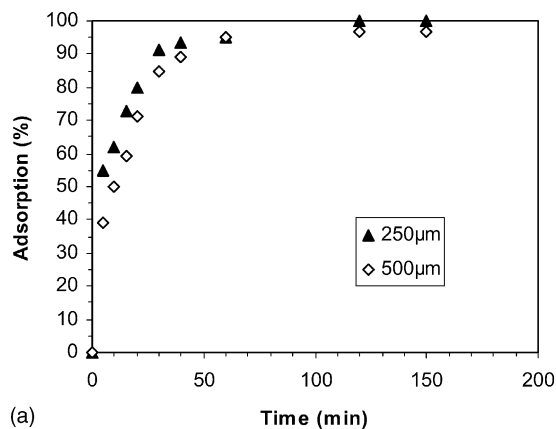


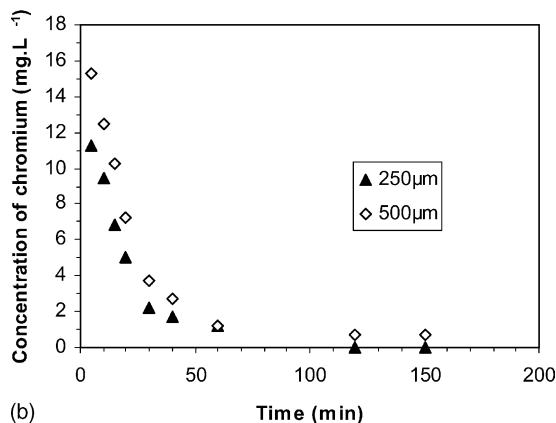
Fig. 5. Adsorption isotherm of Cr(VI) on TiO₂ at pH 2.

equilibrium concentrations at pH 2. Based on the value of correlation coefficient (R^2) for Langmuir ($R^2 > 0.99$), it can be seen that the behaviour of chromium adsorption on TiO₂ was described as an isotherm of Langmuir type (Fig. 6). The Langmuir values of q_s was calculated as 5 mg g^{-1} by the slope of the isotherm and b was calculated as 0.047 L mg^{-1} through the ordinate at the origin of the isotherm line. Hydrous titanium dioxide, adsorbing chromium species indicated that TiO₂ has the most different affinity for Cr(III) and Cr(VI) at pH 2.

Adsorption percentages of Cr(VI) for both hydrous TiO₂ with an average particle diameter of 250 and 500 μm , calculated from the decreasing activity of Cr-51 (relative uncertainty <5%) in solution as a function of time is shown in Fig. 7. By construction of Bt-t lines (Fig. 8), the slopes were calculated as 0.0606 and 0.035, respectively. The correlation coefficients were high ($R^2 > 0.99$ for 250 μm and $R^2 > 0.97$ for 500 μm). The good agreement of our data points confirms the applicability of the particle diffusion mechanism to



(a)



(b)

Fig. 7. Kinetics of adsorption of Cr(VI) on TiO₂ at pH 2 as a function of time: (a) as an adsorption percent (%); (b) as a concentration of chromium in solution.

the system. Using the slope values, the diffusion coefficients of Cr(VI) at pH 2 were calculated as $3.84 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $8.86 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for both hydrous TiO₂ having average particle diameter of 250 and 500 μm , respectively.

For the ICP-OES measurements, the calibration curve was linear in the concentration range of 100–1200 $\mu\text{g/L}$

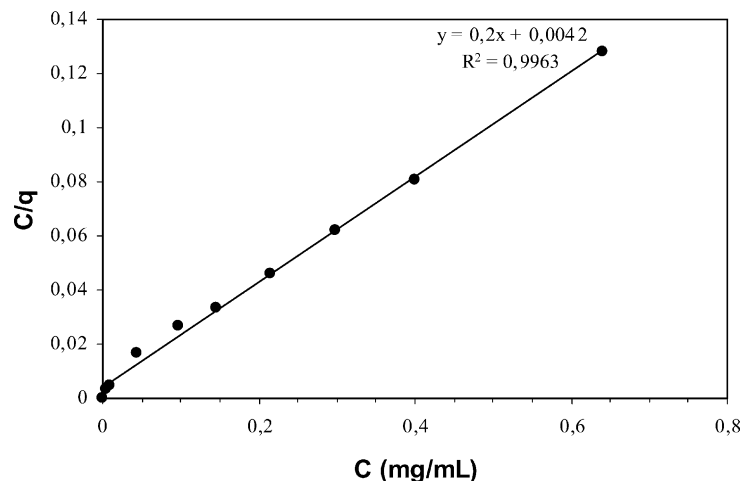


Fig. 6. Langmuir isotherm for chromium(VI) adsorption on TiO₂ at pH 2.

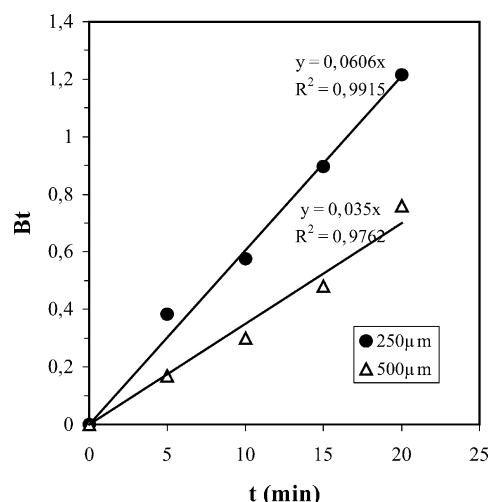


Fig. 8. Variation of Bt with time.

chromium at pH 2. The calibration equation of $Y = 2162X - 54,736$; ($r^2 = 0.9990$) for Cr(VI) and $Y = 2142X - 27,609$; ($r^2 = 0.9993$) for Cr(III) were obtained, where Y , X and r^2 were the counts/s, the concentration in $\mu\text{g/L}$ and the correlation coefficient, respectively. No significant influence of the pH adjustment on chromium calibration was found. The relative standard deviation ($n = 11$) at $100 \mu\text{g/L}$ Cr(VI) and Cr(III) were 2.1 and 1.9%, respectively. The detection limits, corresponding to the three times of the standard deviation of the blank solution, were $0.35 \mu\text{g/L}$ and $0.22 \mu\text{g/L}$ for Cr(VI) and Cr(III), respectively.

4. Conclusion

- Hydrous TiO_2 which the specifications are mentioned above, has selective affinity for Cr(III) and Cr(VI) and an excellent separation efficiency was obtained at pH 2.
- The adsorption isotherm of Cr(VI) had a part of irreversible adsorption at pH 2. This means that if the concentration of Cr(VI) was in range of irreversible adsorption, Cr(VI) could be adsorbed completely by TiO_2 . This result was very significant for the separation and individual determination of Cr(III) and Cr(VI) in aqueous solution to accurate assessment of pollution levels.
- The maximum adsorption capacity of Cr(VI) on TiO_2 was 5 mg g^{-1} .
- The diffusion coefficients of Cr(VI) at pH 2 were calculated as $3.84 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and $8.86 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for hydrous TiO_2 having average particle diameter of 250 and $500 \mu\text{m}$, respectively. The rate of the reaction is controlled by the particle diffusion and is much faster in the particles of $500 \mu\text{m}$ than in the particles of $250 \mu\text{m}$.
- Ultrapur water (Resistivity $18.2 \text{ M}\Omega \text{ cm}$, TOC level 1–5 ppb) used in the experiments was prepared with Millipore model water purification system (including Elix and Mili-Q). When the method is applied for fresh

water containing organic material (TOC/DOC) at high concentrations, Cr(VI) is reduced to Cr(III) and dissolved carbon may complex Cr(III) which may influence the sorption efficiency. The method is valid for the concentration range tested with ppb levels of humic substances (TOC/DOC). For natural water containing humic substances (TOC/DOC) and low concentrations of Cr-species, the method must be revalidated.

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