Adsorption of hexavalent chromium on dunite
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ABSTRACT

The paper presents and discusses the effect of various physicochemical parameters (e.g. pH, ionic strength, Cr(VI) initial concentration, amount of the adsorbent, temperature and contact time between metal ion and adsorbent) on the adsorption efficiency of Cr(VI) on dunite in aqueous solutions under atmospheric conditions. Evaluation of the experimental data shows that dunite presents increased affinity for Cr(VI) over a wide pH range and Cr(VI) concentration, and the experimental data are well fitted by the $K_d$ adsorption model. The relative adsorption is pH dependent and decreases slightly (about 10%) with increasing pH, because of changes in the surface charge of the solid. The effect of the ionic strength is significant (particularly at low pH), indicating the predominance of outer-sphere complexes. Moreover, adsorption experiments at various temperatures, two different pH values (pH 3 and pH 8) and three different ionic strengths (0.0, 0.1 and 1.0 M NaClO$_4$), indicate an endothermic but spontaneous entropy-driven processes.

Key words | adsorption, dunite, hexavalent chromium, $K_d$

INTRODUCTION

Pollution of the environment with hexavalent chromium (Cr(VI)) and associated toxicity to microorganisms, plants, animals, and humans is of major concern (Mathur et al. 1977; Holdway 1988; Palmer & Wittbrodt 1991). Indeed, chromium in environmentally significant concentrations is found near to tanneries and processing facilities and usually involves large volumes of wastewater. Removal of Cr(VI) from such large volumes of wastewaters require a cost effective remediation technology. Conventional wastewater treatment technologies usually rely on mineral adsorbents (Davis & Leckie 1979; Zachara et al. 1987; Bhutani et al. 1992). On the other hand, chemical behavior and migration of Cr(VI) species in the geosphere is strongly governed by adsorption/desorption phenomena on the underlying rock formations (Davis & Leckie 1979). Hence, studies regarding Cr(VI) adsorption on natural minerals and the evaluation of the corresponding thermodynamic data is of fundamental importance with respect to the treatment of Cr(VI) contaminated waters and environmental impact assessments related to Cr(VI) disposal and migration in the geosphere (Richard & Bourg 1991).

Extensive studies on chromium behavior in soils show that adsorption and desorption processes play a significant role in controlling the concentration of Cr species and their mobility in natural environment. On the other hand, investigations on chromate adsorption onto solids such as metal oxides, clays, minerals and biomass by-products (Davis & Leckie 1979; Zachara et al. 1987; Richard & Bourg 1991; Bhutani et al. 1992; Weng et al. 1996) show that the adsorption of chromate on these solids occurs generally at low pH. Apparently, chromate adsorption on a solid surface occurs primarily via electrostatic interactions between the negatively charged chromate species ($HCrO_4^-$, $pK_a1 = 0.8$ and $CrO_4^{2-}$, $pK_{a2} = 6.5$) and the positive charged surface (pH < pzc). Zachara et al. (1987) and Davis & Leckie (1979) suggest that Cr(VI)-anion adsorption onto amorphous iron oxy hydroxide and kaolinite can be described by outer-sphere complexation.

The objective of this study was to investigate the chemical interaction between Cr(VI) and dunite particles in aqueous systems. Dunite is an igneous, plutonic rock, of ultramafic composition, with coarse-grained or phaneritic texture. The mineral assemblage is typically greater than 90% olivine with minor pyroxene and chromite. Dunite is the olivine rich end member of the peridotite group of mantle-derived rocks (Department of Geological Survey 2002). In this study, parameters, such as pH, ionic strength, initial chromate concentration, amount of dunite, temperature and contact
time between metal ion and adsorbent, that may affect the adsorption processes were investigated.

MATERIALS AND METHODS

A periodically mixed batch technique was selected for the adsorption experiments. All experiments were performed at room temperature (22 ± 3°C) under atmospheric conditions in aqueous solutions, two pH values (3 and 8) and three different ionic strengths (0.0 M, 0.1 M and 1.0 M NaClO₄). The ionic strength (0.1 M and 1.0 M) in the test solutions was adjusted by addition of sodium perchlorate (NaClO₄, Merck Co) in de-ionized water. It is necessary to note that I = 0.0 M indicates no background electrolyte (e.g. NaClO₄) was added in the suspension to maintain the ionic strength. NaClO₄ was selected as background electrolyte because of the low chemically affinity of this species regarding surface complexation. However, because acid or base was added to the suspension to adjust pH values during the experiments, a zero-ionic strength experiment was impossible. pH adjustment in the test solution was performed upon addition of standard acid (0.01 M HClO₄ and 0.1 M HClO₄) and base (0.01 M NaOH and 0.1 M NaOH) solutions and was controlled during the experiments. The pH during the experiments remained almost constant and the use of buffers was negligible. All experiments were performed in polypropylene tubes because preliminary experiments have shown that metal ion sorption onto the tube walls was negligible. For comparison, parallel measurements were made for solutions of similar composition without dunite (reference solutions). The experiments were performed in duplicate and the mean values have been used for data evaluation. Generally the difference between the two corresponding results was below 1%.

The rock material (dunite) used in this study originated from a mountainous area (Troodos massif) of Cyprus. Prior application the material was sieved and the particle fraction of 80 mesh was selected for the adsorption experiments and was used without any further purification or other pre-treatment. The BET surface area of the adsorbent (granulated material) was measured by N₂-adsorption (Micromeritics Co, ASAP 2000) and has been shown that dunite has small internal surface (6 m²/g), indicating that adsorption of Cr(VI) occurs on its external surface. Chemical characterisation and properties of dunite used in this study is given elsewhere (Demetriou et al. 2010).

The preparation of stock solutions was carried out by dissolution of K₂CrO₄ (MW = 194.19 g/mol; BDH Co). Immediately, after the addition of 100 mL of the test solutions to the adsorbent, the bottles were shaken and left to reach equilibrium. During the equilibration period the bottles with the test solutions were shaken regularly. Following one day equilibration, the solutions were first centrifuged at 5000 rpm (Lab centrifuge, Memmert Co), then passed through a 0.45-µm Millex filter (Type GV) and the concentration of Cr(VI) in solution was determined spectrophotometrically by means of DCP (1,5-diphenylcarbazide; Merck Co) (Bartlett & James 1979).

To investigate the effect of various parameters (e.g. pH, initial Cr(VI) concentration, amount of adsorbent etc.) on Cr(VI) adsorption, six different classes of experiments were conducted. In these experiments the parameter under investigation was varied while other experimental parameters were kept constant. The effect of pH was studied in an adsorption system (0.05 g adsorbent and 100 mL of the test solution: [Cr(VI)]₀ = 5 × 10⁻³ mol L⁻¹ in which pH was varied between 2 and 10 by addition of HClO₄ or NaOH. For studying the effect of initial Cr(VI) concentration, the latter was varied between 7 × 10⁻³ mol L⁻¹ and 5 × 10⁻⁵ mol L⁻¹, at a prefixed amount of adsorbent (adsorbent dosage = 0.05 g per 100 mL). The effect of the amount of dunite was investigated by adding different amounts of adsorbent (between 0.001 and 0.1 g) into a polyethylene screw capped bottle, containing 100 mL test solutions of constant Cr(VI) concentration (5 × 10⁻⁵ mol L⁻¹).

The effect of temperature was studied between 25 and 70°C and measurements were carried out after an equilibration time of three days. The amount of adsorbent (0.05 g), initial Cr(VI) concentration (5 × 10⁻³ mol L⁻¹) and pH in the test solutions (100 mL) were kept constant. For kinetic studies certain amount of dunite (0.05 g) was mixed with Cr(VI) solution (5 × 10⁻⁵ mol L⁻¹). Samples withdrawn at time intervals were centrifuged, then filtered and the Cr(VI) concentration was determined by photometry.

RESULTS AND DISCUSSION

pH effect

The pH of an aqueous solution is an important parameter, which governs the adsorption of metal ions on mineral surfaces. Variation in pH affects speciation and stability of soluble species as well as surface properties (e.g. the charge of functional groups responsible for surface sorption). Figure 1 shows the effect of pH (in the range between 2 and 10) on the adsorption efficiency of Cr(VI) on dunite.
At low pH ($2<\text{pH}<5$) the relative adsorption reaches its maximum value because the surface of the adsorbent is positively charged and attracts the negatively charged $\text{HCrO}_4^-$ ions, which are the predominant Cr(VI) species at the respective pH range. Increasing pH above 4.5 results in a prompt decrease of the adsorption efficiency due to the gradual deprotonation of the surface as well as the presence of the $\text{CrO}_4^{2-}$ which formation is favoured at increased pH ($pK_a = 6.5$). For pH $>5$ the relative adsorption decreases and reaches a plateau for pH $>7$, because $\text{CrO}_4^{2-}$ is the predominant species in solution and the number of positively charged sites of solid, which correspond basically to $=\text{Mg-OH}_2^+$ moieties, remains almost constant in the respective pH range ($8<\text{pH}<10$). Nevertheless, even above pH 8 the relative adsorption of Cr(VI) on dunite is high (about 90%), indicating that dunite can be used as an effective adsorbent for the Cr(VI) removal from (waste)waters with pH ranging from 2 to 10. Furthermore, the fact that almost 90% of the chromate adsorbed remains unaffected by pH changes indicates also the presence of outer-sphere complexes. The adsorption of chromate on the dunite surface can be ascribed to inner-sphere and to a lesser extent to outer-sphere complex formation and could be formulated for inner-sphere complexes as follows:

$$\text{HCrO}_4^- + \equiv \text{S} - \text{OH}_2^+ \leftrightarrow \equiv \text{S} - \text{O} - \text{CrO}_3\text{H} + \text{H}_2\text{O} \quad \text{at pH 3}$$

and

$$\text{CrO}_4^{2-} + \equiv \text{S} - \text{OH}_2^+ \leftrightarrow \equiv \text{S} - \text{O} - \text{CrO}_3^{-} + \text{H}_2\text{O} \quad \text{at pH 8}$$

whereas for outer-sphere complexes the corresponding reaction equations could be formulated as:

$$\text{HCrO}_4^- + \equiv \text{S} - \text{OH}_2^+ \leftrightarrow \equiv \text{S} - \text{OH}_2^+ \cdots \text{HCrO}_4^- \quad \text{at pH 3}$$

**Effect of the initial Cr(VI) concentration**

Figure 2 illustrates the effect of initial Cr(VI) concentration on adsorption of Cr(VI) on dunite (adsorption isotherms) at various ionic strengths and two different pH values (e.g. pH 3 and pH 8). The experimental data indicate that the amount of Cr(VI) uptake is increased as a function of the Cr(VI) concentration in solution. The adsorption data (Figure 2), irrespective of the ionic strength, follow the linear adsorption isotherm ($K_d$ model), indicating that the adsorption of Cr(VI) on dunite is far from saturation and suggesting that dunite could be a useful adsorbent regarding the removal of Cr(VI) from aqueous solutions.

The value of $K_d$ is almost similar for suspensions of different pH (pH 3 and pH 8) and ionic strength (0.0, 0.1 and 1.0 M NaClO$_4$) with a median value of $18.5 \pm 0.14 \text{ g l}^{-1}$. In agreement with the pH measurements, the negligible effect of ionic strength on the chromate adsorption indicates also on inner-sphere complex formation.

**Effect of the amount of adsorbent**

Figure 3 shows the relative adsorption (%) of Cr(VI) onto dunite as a function of mass$_{\text{adsorbent}}$ at various ionic strengths and two different pH values (e.g. pH 3 and pH 8). According to the data in Figure 3 increasing ionic strength results in decreasing adsorption efficiency, particularly in suspensions of pH 8, indicating on the increased stabilisation of outer-sphere complexes at this pH region. The effect of ionic strength on the stability of outer-sphere complexes is ascribed to the electrostatic character of the surface species. This is in agreement with previous studies on the adsorption of Cr(VI) on amorphous iron oxy hydroxide (Zachara et al. 1987) and kaolinite (Davis & Leckie 1979), which describe the adsorption by the formation of outer-sphere complexes. Furthermore, according to the data in Figure 3, at saturation the plateau of the relative adsorption never reaches the value of 100%, which indicates also the presence of outer-sphere complexes.
The positive charge on the dunite surface at increased pH values (e.g. pH 8) is attributed to the MgO content of the dunite (Demetriou et al. 2010). The point of zero charge of magnesia in the alkaline pH region (pzcmgO~12), which suggest that the surface of magnesia is positively charged up to pH 12 (Konstantinou et al. 2007).

Generally, the above reactions and based on the adsorption isotherms shown in Figure 2 can be described by the simplest adsorption isotherm, which is the linear distribution coefficient or linear $K_d$:

$$K_d = \frac{[Cr(VI)]_{ads}}{[Cr(VI)]_{aq}}$$

where $[Cr(VI)]_{aq}$ is the concentration of Cr(VI) in solution in (mol l$^{-1}$) and $[Cr(VI)]_{ads}$ is the amount Cr(VI) adsorbed on the solid phase in (mol kg$^{-1}$). According to the $K_d$ model the amount of surface sites available for Cr(VI) complexation is relatively high and remains almost constant despite the preceding adsorption. Moreover, the linear distribution coefficient involves no variables other than the concentration of the species of interest make it computationally simple and hence widely used in hydrologic transport models. The numerical value of a distribution coefficient is a function of the properties of the solid substrate and the composition of the solution.

### Temperature effect

The temperature dependence of Cr(VI) adsorption on dunite was investigated to evaluate the apparent thermodynamic parameters ($\Delta G^0$, $\Delta H^0$ and $\Delta S^0$) of the adsorption based on
following equations:

\[
\Delta G^0 = -R \cdot T \cdot \ln K_d
\]

and

\[
\ln K_d = \frac{\Delta S^0}{2.303R} - \frac{\Delta H^0}{2.303R \cdot T}
\]

where \( T \) is temperature in Kelvin, \( R \) is the gas constant and \( K \) is the equilibrium constant of the adsorption reaction. The corresponding experimental data were obtained from experiments performed at various temperatures, three different ionic strengths and two pH values (e.g. pH 3 and pH 8). The graphical presentation of the van't Hoff plot is shown in Figure 4 and the thermodynamic data evaluated are summarized in Table 1 and 2.

The values for \( \Delta H^0 \) and \( \Delta S^0 \) were obtained from the slope and the intercept of \( \ln K_d \) vs \( 1/T \) upon linear regression analysis of the experimental data. The positive value of \( \Delta H \) shows that the adsorption of Cr(VI) is endothermic. However, adsorption of Cr(VI) on dunite is a spontaneous, entropy-driven process. The exothermic character of the adsorption reaction is ascribed a) to the relatively small value of \( \Delta H \), which is associated with the fact that overall a surface oxygen bond is broken and reformed and b) to the increased entropy due to water molecule release upon surface complexation of the chromate anions. This effect is less pronounced when outer-sphere complexes are formed, particularly at pH 8. This explains also the significant differences and the lower values for \( \Delta H \) and \( \Delta S \) evaluated for the adsorption reaction at pH 8 in comparison to pH 3.

The existence of both types of surface complexes of chromate anions on the dunite surface can be ascribed to the mixed oxide character of dunite, which is consists of different metal oxides such as silicon, iron, aluminium and magnesium oxides (Demetriou et al. 2010). On the other hand the complex composition of dunite is most probably responsible for the high affinity of the material for chromate over a wide pH range in comparison to other materials studied (Davis & Leckie 1979; Zachara et al. 1987; Bhutani et al. 1992). Despite the fact that chromate sorption on hydroxy-oxides, sediments and soils has been examined extensively, the information on the precise mechanism of surface complexation is still in debate. There are studies supporting inner-sphere complex formation (Zachara et al. 1988; Hsia et al. 1993; Weerasooriya & Tobschall 2000) and other investigations with data that support outer-sphere complex of Cr(VI) onto Fe and Al hydrous oxides as well as in soil surfaces (Davis & Leckie 1979; Zachara et al. 1987; Hu et al. 2007).

Effect of contact time

Figure 5 shows the relative amount of adsorbed Cr(VI) as a function of time under atmospheric conditions, pH 3 at three...

| Table 1 | Thermodynamic parameters for the Cr(VI) adsorption on dunite at pH 3 |
|---------|------------------|-------|-------|-------|-------|-------|
| \( \Delta H^0 \) (kJ/mol) | \( \Delta S^0 \) (J/K.mol) | 298 K  | 303 K  | 313 K  | 323 K  | 333 K  | 343 K  |
| 56.7 ± 0.07 | 225.0 ± 1.02 | -10.4 | -11.5 | -13.7 | -16.0 | -18.2 | -20.5 |
different ionic strengths. According to Figure 5 the adsorption of Cr(VI) on dunite occurs in one step, indicating that adsorption of Cr(VI) on dunite takes place on the external surface of the adsorbent. It is a relatively fast step, which is completed within 1000 minutes and almost 98% of the total Cr(VI) is adsorbed. Also the data obtained from these experiments show clearly the effect of the ionic strength pointing out also the presence of outer-sphere complexes.

The kinetics of Cr(VI) adsorption on dunite regarding the first step follows the first order rate expression given by Lagergren (1898). The apparent $k_{\text{ad}}$ value has been calculated based on the Lagergren Equation (6) for experimental data obtained at 25°C and pH 3 and is found to be about $5 \times 10^{-3}$ min$^{-1}$.

$$\log(q_e - q) = \log(q_e) - k_{\text{ad}}t/2.303$$

(6)

where $q$ represents the amount of component bound to the solid matrix at a given time (mol kg$^{-1}$), $q_e$ is the amount bound to the solid matrix at equilibrium (mol kg$^{-1}$) and $k_{\text{ad}}$ is the kinetic adsorption constant (min$^{-1}$).

**CONCLUSIONS**

The results obtained from this study lead to the following conclusions:

(a) dunite exhibits excellent properties regarding Cr(VI) adsorption and could be used as an effective adsorbent in a wide pH range (2 < pH < 10),

(b) the values of the relative adsorption vary between 90% (at pH > 7) and 98 (at pH < 3),

(c) the experimental data can be fitted by the linear adsorption isotherm ($K_d$),

(d) above 90% the relative adsorption depends on the ionic strength, indicating also on the formation of outer-sphere complexes and

(e) the adsorption of Cr(VI) on dunite is an endothermic, entropy-driven process and follows a first order rate expression.

**REFERENCES**


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