Density functional theory studies of the adsorption of Cr (VI) on Fe-(hydr) oxide: Gibbs free energies and pH effect

N Y Acelas* and E Flórez
Grupo de Materiales con Impacto, Mat&mpac, Facultad de Ciencias Básicas, Universidad de Medellín, Carrera 87 No. 30-65, Medellín, Colombia

*E-mail: nyacelas@udem.edu.co

Abstract. Adsorption of chromium (VI) on iron oxides is a potential removal method from industrial wastewater. Cr (VI) is a toxic specie for human health due to its easy mobility in the environment. Currently, US EPA drinking water standards establish a maximum Cr level of 100 μg/L. Since the adsorption process occurs in the solid/liquid interface, pH is one of the main factors that affect this process and it is a very important parameter to study. Understanding the adsorption process and the molecular geometries of complexes, is essential to predict the environmental transport of Cr (VI) and to develop appropriate models for the remediation of Cr (VI). Therefore, in this work, we describe the adsorption of Cr (VI) onto Fe-hydr (oxides) through computational methods. A complete characterization of the adsorbed surface complexes was performed, and three different pH conditions were simulated (acidic, intermediate and basic). It was found that, the thermodynamic favourability of the different adsorbed complexes was directly related to the pH. Bidentate complex (BB) was the most thermodynamically favourable complex with an adsorption energy of -143.3 kJ/mol under acidic pH conditions.

1. Introduction

Chromium (VI) has high mobility and is easily leaching in soil and groundwater, is toxic to ecosystems and its disposal near rivers and lakes alters the food chain. It is very dangerous for human health [1, 2], and in high concentrations is carcinogenic, mutagenic and teratogenic. Currently, US EPA drinking water standards establish a maximum Cr level of 100 μg/L[3].

The presence of chromium (VI) in the environment is due to its extensive use in a variety of industrial processes, such as catalysis, preservation of wood, dyeing of leather, among others [4, 5]. Chromium (VI) exists in nature as the chromate anion [HCrO4-] and its transport in the environment is controlled by adsorption on mineral surfaces [6]. Adsorption is a very attractive method due to its low cost and easy to implement [7, 8]. Aluminium and iron hydr (oxide) [9, 10] are minerals which present high reactivity for the adsorption of oxyanions [11-13]. Therefore, the adsorption of chromium on iron oxides is a potential removal method from industrial wastewater [14-16].

This mineral has high surface area, reactive functional groups and the presence of a partially filled 3d shell in trivalent iron, with its high chemical bonding affinity, and highly anisotropic character. The adsorption process can be driven by ligand exchange (Lewis acid-base interaction), where the chromate
anion donates pairs of electrons to form inner sphere complexes by bonding with the metal center of the Fe-(hydr) oxide; or by electrostatic interaction through the formation of external sphere complexes.

Chromate adsorption on iron oxides is significantly affected by pH, hydration, and surface charge [1]. Among these parameters, pH is one of the most important to regulate the adsorption–desorption process between the hydrated metal oxide surface and the aqueous solution. Previous studies [14] have indicated that the adsorption of chromate on ferrihydrite at pH 5 showed almost twice the sorption density of adsorption than higher pH values. At pH < 6, Johnston and Chrysochoou (2012) [17] revealed monodentate and bidentate inner-sphere surface complexation. Many IR vibrational spectra of chromate on several minerals (such as, ferrihydrite, hematite and boehmite) have shown abundant coordination information [1, 4, 14].

Understanding the adsorption process and the molecular geometries of complexes, is essential to predict the environmental transport of Cr (VI) and to develop appropriate models for the remediation of Cr (VI). In this work, density functional theory (DFT) was used to investigate the thermodynamic favorability of the formation of chromate species on hydrated iron oxides under different pH conditions.

2. Computational details and models

Previous studies conducted in our research group [7, 12] have shown that using a cluster consisting of two iron atoms in octahedral coordination with 10 oxygen atoms is a very good model to simulated Ferric hydroxide. To simulate the pH effect, charges on each Fe-(hydr)oxide were varied by adjusting the radio of OH/H2O functional groups ranging from +2 to 0 (i.e., changing the number of H+ in the model). For example, those clusters with 6 (-H2O) and 4 (-OH) as functional groups have a +2 charge, which represents acidic pH conditions, complexes with 5 (-H2O) and 5 (-OH) have a +1 charge corresponding to neutral pH and complexes with 4 (-H2O) and 4 (-OH) have a 0 charge, which is basic pH. The application of DFT and cluster models to predict the thermodynamical properties of oxyanion surface complexes has been described in detail previously [4, 7, 18] . All solvated species, such as, [HCrO4(H2O)6]13-, [OH(H2O)2]7-, [(OH)2(H2O)6]2-, [OH(H2O)6]13-, (H2O)6, (H2O)7, and (H2O)8 involved in the adsorption processes were obtained by the use of the ASCEC algorithm [19], a stochastic-like search strategy. These candidate structures were subsequently optimized using traditional gradient-based minimization procedures. ASCEC is a simulated annealing optimization procedure, which uses a modification of the Metropolis acceptance test. Only the potential−energy surfaces for the solvated anions were stochastically searched. Geometry optimization was performed at the DFT level of theory using the PBE0 functional and the DFT2TZVP basis set on O and H atoms. The LANL2DZ relativistic electron core potential (RECP) was used for Fe and Cr. Harmonic vibrational frequencies for the optimized structures were calculated at the same level of theory to verify that they correspond to true minima in the respective potential energy surface (i.e., no imaginary frequencies). Long-range solvation was accounted for using the integral exchange formalism of the polarizable continuum model (IEFPCM). It was used the dielectric constant of bulk water (ε = 78.4). And to account for the explicit solvation a total of six water molecules were added during the optimization process for each structure. Gibbs adsorption energies of inner and outer-sphere complexes were estimated as follows (Equation 1). All calculations were carried out with the Gaussian 09 program [20].

\[ \Delta G_{ads} = \bar{G}_{complex} - \bar{G}_{HCrO_4^3} + \bar{G}_{cluster} \]  Eq (1)

It has been reported before that 5N + 1 multiplicities are energetically preferred in systems containing N Fe atoms [18]. Figure 1 shows all the possible spin states up to 13 for the [Fe5(OH)6(H2O)4]CrO4(H2O)3+]11 (Bidentate Binuclear Complex) under acidic pH conditions. It can be observed that the lowest-energy structure is the one corresponding to a total spin multiplicity of 11.
3. Results and discussion

3.1. Adsorption complexes

In this paper two adsorption modes of chromate are illustrated: ligand exchange to form the inner sphere complexes and electrostatic interaction to form the outer sphere complexes. Formation of inner sphere complexes, Mononuclear Monodentate (MM) and Bidentate Binuclear (BB) can be explained by the Lewis acid-base interaction between the Chromate anion and the iron of the Fe-(hydr) oxide. For MM, there is an exchange between one of the functional groups of the oxide surface (OH⁻ o –H₂O) with the anion, to form a chemical bond, while during the formation of BB, there is an exchange of two surface functional groups of the oxide with two oxygen atoms of the anion (Figure 2). Similar mechanisms have been proposed by various authors for the adsorption of Cr (VI) on iron oxides [1, 4, 17, 21-23].

Figure 1. Relative stability of the BB complex, [Fe₂(OH)₄(H₂O)₄·HCrO₄(H₂O)₆]⁺¹ under acidic conditions. All calculations using the PBE0 functional in conjunction with the DEF2TZVP basis set for O and H atoms and the LANL2DZ relativistic electron core potential for Fe and Cr.

3.2. Adsorption complexes

In this paper two adsorption modes of chromate are illustrated: ligand exchange to form the inner sphere complexes and electrostatic interaction to form the outer sphere complexes. Formation of inner sphere complexes, Mononuclear Monodentate (MM) and Bidentate Binuclear (BB) can be explained by the Lewis acid-base interaction between the Chromate anion and the iron of the Fe-(hydr) oxide. For MM, there is an exchange between one of the functional groups of the oxide surface (OH⁻ o –H₂O) with the anion, to form a chemical bond, while during the formation of BB, there is an exchange of two surface functional groups of the oxide with two oxygen atoms of the anion (Figure 2). Similar mechanisms have been proposed by various authors for the adsorption of Cr (VI) on iron oxides [1, 4, 17, 21-23].
Figure 2. DFT-calculated structures of inner and outer sphere adsorption products of chromate on Fe-(hydr)oxide under acidic pH conditions.

The type and the amount of functional groups on the iron oxide surfaces is determinable by the pH value. These functional groups interact with the chromate anion and to form the adsorption complexes. Thus, under acidic pH conditions there will only be the functional groups -H$_2$O to be exchanged, at basic pH conditions the exchange of ligands will be given with the functional group -OH$^-$ and at intermediate pH conditions both functional groups (-H$_2$O and -OH$^-$) can be exchanged. This last condition generates the possibility to form two types of monodentate complexes, MM$_1$ and MM$_2$, which are formed by the exchange of the functional group -H$_2$O and -OH$^-$, respectively. For inner sphere complexes, BB and MM, optimized under acidic pH conditions (Figure 2), Cr-Fe distances of 3.26, and 3.48 Å, respectively were found. These values are in good agreement with EXAFS values previously reported for chromate adsorption on goethite [24]. The outer sphere complexes (H-bonded), are formed by the electrostatic interaction of the surface functional groups of oxide and the anion. In this type of complex there is no ligand exchange. Many authors consider this mode of adsorption as a reactive intermediate of the complexation by internal sphere [3], for this reason, the formation of internal sphere configurations show a decrease in the Gibbs free energy. The complex formed at acidic pH conditions presents Cr-Fe distance of 4.861 Å. (Figure 2)

3.3. Gibbs free energies of adsorption

To estimate the adsorption Gibbs free energy of Cr (VI) on Fe-(hydr)oxide, a series of balanced equations were used under different pH conditions. Figure 4 represents a stoichiometric adsorption reaction as inner sphere complex of chromate on Fe-(hydr)oxide under acidic pH conditions. By applying equation 1, it is possible to obtain the adsorption Gibbs free energy, which is useful to predict the thermodynamic favorability of each complexes at different pH conditions (Figure 4).

Figure 3. Adsorption of chromate as bidentate complex on Fe-(hydr)oxide under acidic pH conditions. Red, blue, purple, and gray denote O, Fe, Cr and H atoms, respectively.
Figure 4. Gibb's free energies of Chromate adsorption on Fe-(hydr)oxide at different pH conditions. MM\(_1\): Monodentate mononuclear complex exchanged to one \(-\text{H}_2\text{O}\) surface functional group and MM\(_2\): Monodentate mononuclear complex exchanged to one \(-\text{OH}\) surface functional group.

Figure 4 shows the Gibb's energies of the different adsorption modes under the three simulated pH conditions. It can be observed that there is a strong dependence between the thermodynamic favorability of the adsorption and the pH. Acid pH conditions favor both the adsorption modes of inner and outer sphere complexes.

According to this, the most favourable inner sphere species is BB with an energy of -143.3 kJ/mol, followed by the MM\(_1\) with an energy of -105.2kJ/mol and finally the H-bonded complex with an energy of -65.5kJ/mol. Intermediate pH conditions favor the BB and MM\(_1\) adsorptions mode with a Gibbs energy of -90.5kJ/mol and -53.2kJ/mol, respectively. Basic pH conditions do not favor the adsorption process. This can be explained by the variation in the surface charge on iron oxide with the increase in pH: by increasing the pH, the surface of the oxide becomes more negative, which generates electrostatic repulsion with the Cr (VI) anion. Our results are in good agreement with various theoretical and experimental studies. For example, Dzombak and Morell [25] have described through experimental methods the effect of pH on Cr (VI) adsorption on ferrihydrite. They found that below pH 7 the adsorption depends on the pH and that at a pH of 3, a maximum adsorption capacity of 290 mg / kg was found. Other authors [26] show that chromate exhibits strong affinity with goethite surface and, that almost 100% is adsorbed under acidic pH conditions, with a decrease observed with the increase in pH.

Respect to the most favorable adsorption modes, various spectroscopic analyzes have been carried out, such as, extended X-ray fine structure (EXAFS) spectroscopy, which have shown evidence of the formation of inner sphere complexes during the adsorption process of Cr(VI) on ferric oxide surfaces [17, 24]. Besides, Johnston and Chrysochoou [17] using in situ attenuated total reflectance Fourier transform infrared spectroscopy (ATR–FTIR) found MM and BB complexes for the adsorption of Cr(VI) on ferrihydrite. Our results are in agreement with previous studies and specifically with those reported by Xie et al [26], who found that BB complex is the dominant species at low pH.

According to the thermodynamic results it is possible to conclude that the adsorption behavior of Cr (VI) on Fe-(hydr)oxide is well described using a combination of inner and outer sphere complexes, which is in agreement with several studies reported in the literature [1, 4, 17, 22, 24, 26].

4. Conclusion

In this work we presented the characterization of the potential energy surface for the adsorption of Cr (VI) on Fe-(hydr)oxide in aqueous medium. It was found that, as the pH value decreased, the thermodynamic favorability increased, which indicated that pH is a very important factor to regulate the adsorption process between Fe-(hydr)oxide and Cr(VI). Our results indicated that the adsorption process
is favorable under acid pH conditions and that the inner sphere BB complex is preferred (-143.3kJ / mol).

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