

**IRON OXIDES NANOPARTICLES FOR HEAVY METALS REMOVING
FROM INDUSTRIAL WATERS**

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Abstract

In the environment, the iron oxides may be useful for depollution process by means of a wide range of redox reactions. Hexavalent chromium (CrVI) is a toxic form of chromium, whereas the trivalent form is not. Reduction of CrVI to CrIII is, thus, a detoxifying process and takes place in soils and sediments under anoxic conditions. Hexavalent Cr reacts with magnetite to form CrIII. The reaction yields to a surficial transformation of magnetite into maghemite. Substitution of a large range of cations can be easily induced in magnetite and maghemite because tetrahedral as well as octahedral positions are available. Dissolution curves indicated that Co, Ni and Zn were randomly distributed within the structure and replaced octahedral Fe. In contrast, Cu, Mn and Cd appear to be concentrated near the surface of the crystals. Trace amounts of chromate ions adsorbed on magnetite are reduced to Cr (III) at the surface of Fe ions. A solid state reaction in which the surface layers of magnetite are converted into maghemite appears to be involved: as more chromate is adsorbed, further reduction is halted.

Key words: magnetite nanoparticles,

1. INTRODUCTION

Isomorphous substitution of iron oxides is important for several reasons. In the electronics industry, trace amounts (dopants) of elements such as Nb and Ge are incorporated in hematite to improve its semiconductor properties. Dopants are also added to assist the reduction of iron ores. In nature, iron oxides can act as sinks for potentially toxic heavy metals. Investigation of the phenomenon of isomorphous substitution has also helped to establish a better understanding of the geochemical and environmental pathways followed by Al and various trace elements.

Various properties of Fe oxides change regularly with increasing substitution. Among these are the positions of the visible and infrared absorption bands, magnetic properties, dehydroxylation temperature, rate of acid and reductive dissolution and crystal size and aspect ratio. It is, however, often difficult to assign changes in a single property unequivocally to substitution because several properties may be modified simultaneously. Multiple correlations, although usually highly significant, vary between different sample sets and, thus, do not allow the separate effects of the two parameters to be quantified.

Substitution of a large range of cations can be readily induced in magnetite and maghemite because tetrahedral as well as octahedral positions are available. Dissolution curves indicated that Co, Ni and Zn were randomly distributed within the structure and replaced octahedral Fe. In contrast, Cu, Mn and

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Cd appear to be concentrated near the surface of the crystals. After conversion of these magnetites to maghemite, an outer zone free from trace elements was formed around the crystal indicating that oxidized Fe had migrated outwards and formed a new maghemite layer leaving the trace elements in the core [1]. When the magnetite was converted to hematite, the divalent trace elements were ejected (because of their valency and size) and concentrated in the surface layers of the oxide, whereas Cr and Mn, which are compatible with the corundum structure, remained in the hematite.

Substituted magnetites prepared at pH 12 from ferrihydrite usually contain more than 0.1 mol mol⁻¹ Mn, Cu, Co or Ni [2, 3]. The products ranged from magnetites with low levels of substitution up to the fully substituted MFe₂O₄ (ferrites). For Co-substituted magnetites there appears to be a continuous variation in surface area and interfacial properties with increasing substitution.

Adsorption of chromate (Cr^{VI}) has been widely investigated because chromate is a toxic waste product of many industrial processes adsorption of the chromate ion (CrO₄⁻²) is at a maximum between pH 3 to 6 on all Fe oxides studied and falls off rapidly at higher pH. Adsorption is very high (0.1 μmol Cr per mol⁻¹ Fe) on ferrihydrite at pH 5.5. Chromate has been considered to be intermediate in binding capacity on Fe oxides between strongly and weakly adsorbing anions. Earlier workers considered adsorption to involve an outer sphere complex, but later studies involving FTIR, EXAFS and electrophoresis, support an inner sphere mechanism [4, 5]. Trace amounts of chromate ions adsorbed on magnetite are reduced to Cr (III) by the surface Fe ions. A solid state reaction in which the surface layers of magnetite are converted into maghemite appears to be involved: as more chromate is adsorbed, further reduction is halted.

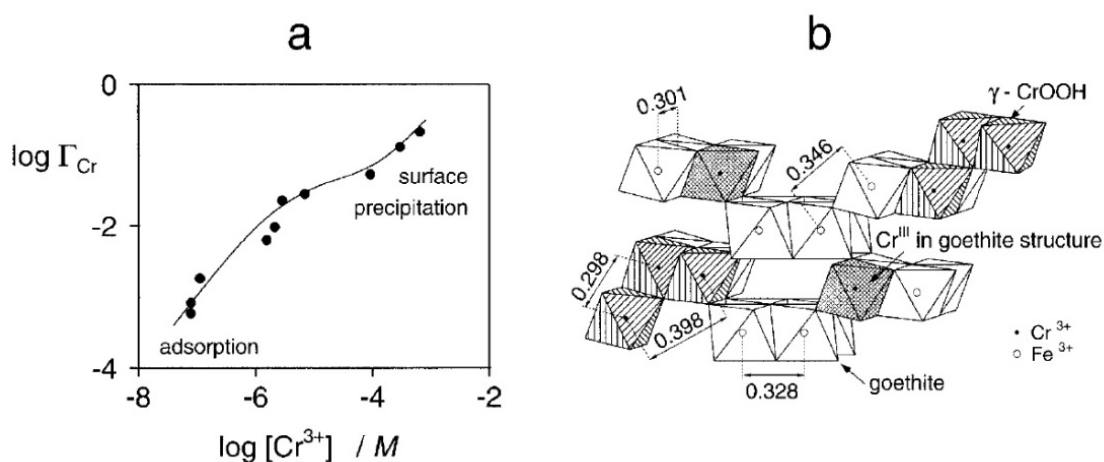


Fig. 1 a) Retention of Cr(III) by goethite; Γ_{Cr} (unitless) vs. Cr(III) equilibrium concentration showing the transition from adsorption to surface precipitation, b) Structural model of incorporated and adsorbed Cr(III) by goethite.

Chromium adsorbs as the cation (Cr³⁺) over the pH range 2.5-4 on ferrihydrite and goethite: it is less toxic in the trivalent than in the hexavalent state. Adsorption of low levels (10⁻⁵ M) of chromium follows a Langmuir isotherm and can be modeled with a single, inner sphere complex. At higher concentrations of Cr, there was a transition from adsorption to surface precipitation (Figure 1) [5]. There is controversy about the structure of the surface precipitate. EXAFS suggested that the adsorbed species are grouped in multinuclear clusters which have the lepidocrocite structure; whereas scanning force microscopy appeared to show that the precipitate is distributed as a coating over the entire goethite surface.

2. EXPERIMENTAL

1.1. Materials

The magnetite nanoparticles were obtained as presented in a previous paper as sample 2 [6]. The obtained nanoparticles were kept in the suspension and the solution of K_2CrO_7 is added over in the suspension. After 1 hour the nanoparticles were separated and dried in the autoclave at 60 °C for 10 hours.

1.2. Apparatus

Fourier transformed IR spectroscopy (FT-IR) standard spectra were collected using a Perkin Elmer Spectrum GX spectrometer. Scans in the range of 400–4000 were accumulated for each spectrum at a spectral resolution of 4 cm^{-1} . It was possible to use the drift accessory with the powdered pure substance, thereby allowing for a better and easier analysis.

The samples were examined using a Mettler 4000 TA, TG 50 thermal analyzer system at a rate of 10°C min^{-1} in a static air atmosphere; and a Perkin-Elmer thermoanalyzer TG S-2 and DTA 1700 at a rate of 10°C min^{-1} . Also, a TG (Du Pont TGA) thermobalance is connected to a PC running Du Pont data processing software. About 15 mg of gently ground stones were subjected to analysis in a Pt plate in a temperature range 35–1000 °C (10°C min^{-1}). It is to be made sure after opening the furnace that both the sample pan and the reference pan are empty and new and no other application is running. After taring the instrument, sample was put inside the pan and furnace was closed. The experimental details like the sample name, procedure, ramp field and the temperature rate were fed into the software. Liquid nitrogen's flow rate was set around 3 l/h.

Atomic force microscopy (AFM) investigations were carried out with an Agilent 5500 SPM system, described by PicoSPM controlled by a MAC Mode module and interfaced with a PicoScan controller from Agilent Technologies, Tempe, AZ, USA (formally Molecular Imaging). A multipurpose large scanner and Point Probe Plus Silicon SPM Sensor cantilevers (PPP-FM cantilevers), n^+ -silicon material and none coating, of about 227 μm length, 1.8 N m^{-1} spring constants, with the tips oscillated near their resonant frequencies (NANOSENSORS) in air, of about 64 kHz were used for all measurements. All AFM measurements (256 samples/line $\times$ 256 lines) were done by scanning the surface at a rate of 0.8–1.2 lines per second and were done at room temperature in tapping mode. The original images for the samples, the 3D topographical images and section analysis over the magnetite particles were performed using the PicoView SPM Software, version 1.6.2, Molecular Imaging.

Height image data obtained by the AFM is three-dimensional. The usual method for displaying the data is by using a color mapping for height, for example black for low features and white for high features. The images were processed by first order flattening in order to remove the background slope and the contrast and brightness were adjusted.

Acoustic AC Mode (AAC mode, tapping mode) is an oscillating technique that is less sensitive than MAC Mode, but gentler and less destructive than contact mode. AAC mode excites the cantilever by vibrating the piezo where the cantilever holder is attached. The AAC mode option includes an AAC mode controller and an AAC mode scanner module. The piezo causes the probe tip to oscillate, typically at or near one of its resonance frequencies, such that it taps gently on the surface. The tip is then raster-scanned over the region of interest while the amplitude of oscillation is monitored to produce images. Through this method, lateral forces on the tip are virtually eliminated, enabling higher resolution imaging than is possible with Contact Mode.

The solutions of magnetite samples for AFM imaging were freshly prepared before each experiment by suspending of the appropriate quantity of each sample in absolute ethanol purchased from Sigma-Aldrich. In order to improve the stability of the particles onto the freshly cleaved mica surface, the magnetite and magnetite-chromium samples have been dried in air before being observed by AFM.

The AFM results in tapping mode showed that both samples adsorb freely at the mica surface and the adsorption is fast.

3.RESULTS AND DISCUSSION

FTIR was used to understand structure, bonding and reactivity of magnetite and chromium sorbed on its surface. The adsorbate will influence the symmetry and thus the vibrational spectrum of the surface atoms to which it is bound upon sorption.

Figure 2 shows FTIR spectra of chromium oxide which gives characteristic peaks at 510 cm^{-1} and 477 cm^{-1} . The spectrum was recorded to observe later if any of the chromium treated magnetite showed any of these peaks which might be indicative of the presence of the chromium ions in the magnetite structure. This observation although becomes challenging as the region beyond 500 cm^{-1} is spectroscopically rich or a busy region with magnetite peaks overlapping. There was a shift of the Fe-O stretching band (570 cm^{-1}) observed in some of the samples to higher wave numbers. Magnetite processed with chromium showed a shift to 582 cm^{-1} . Upon interaction of the sorbent with 150 and 175 ppm of chromium, the stretching band shifted to 478 cm^{-1} . Some of the samples indicate splitting of the Fe-O stretching band. There is peak broadening observed in the Fe-O stretching band for all the treated samples. There are no new peaks observed. No 557 cm^{-1} peak corresponding to maghemite transformation is seen. Absence of any new peaks suggests that physisorption is occurring which involves weaker interactions, is less site-specific and with no electron transfer between the sorbate and the sorbent.

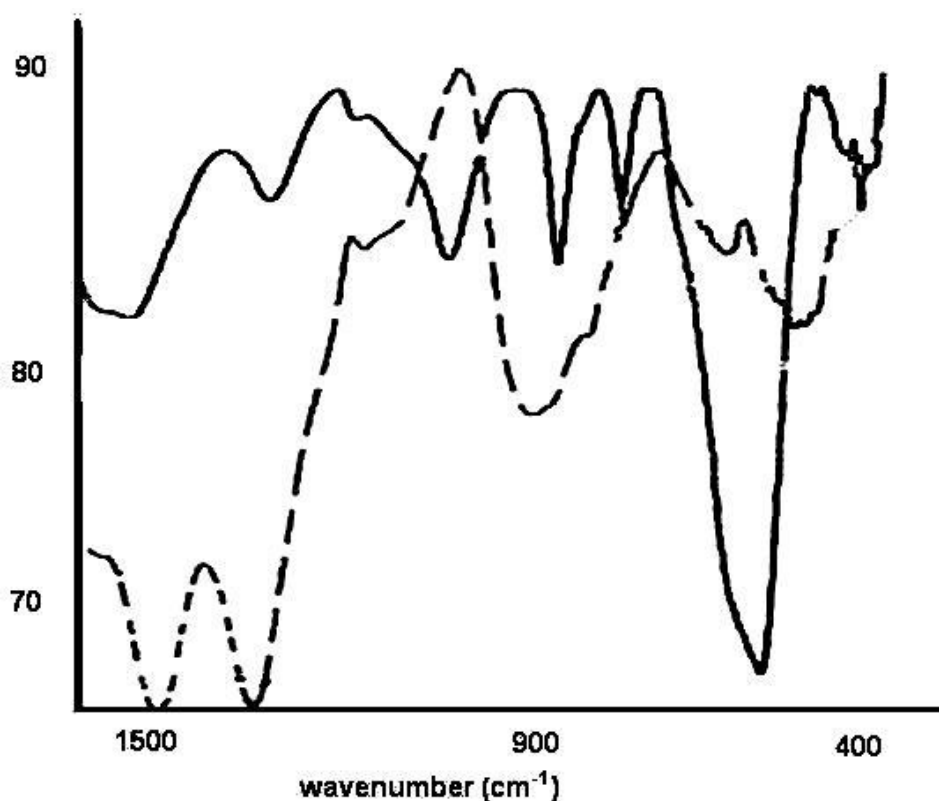


Figure 2. FTIR spectra of obtained magnetite and magnetite-chromium compound after the uptake

From FTIR results chromium's presence in the magnetite structure or physical sorption of chromium on the sorbent is occurring due to the shifts observed and the broadening of the peaks from the unloaded magnetite spectrum in the same treated conditions.

High-resolution imaging using atomic force microscope (AFM) has been applied to observe the differences between height of the magnetite particles and height of the magnetite-chromium compound particles. The topography of the surfaces was investigated by AFM in tapping mode in a range of scan lengths from 100 μm to 300 nm.

By using atomic force microscopy, it could be observed the average of magnetite particles size which is about 10 nm, and the height of the magnetite-chromium compound particles, which is between 25-45 nm.

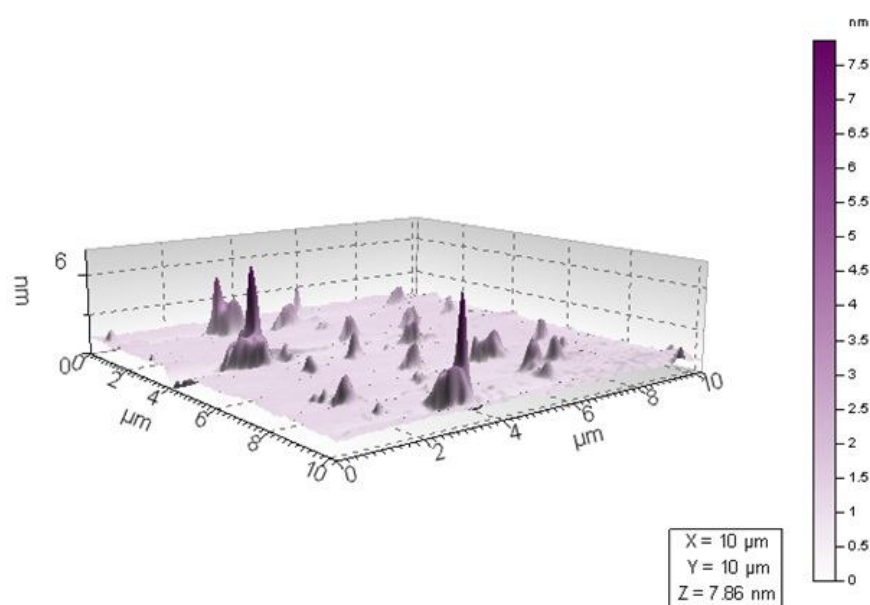


fig 3 AFM images 3D of magnetite sample

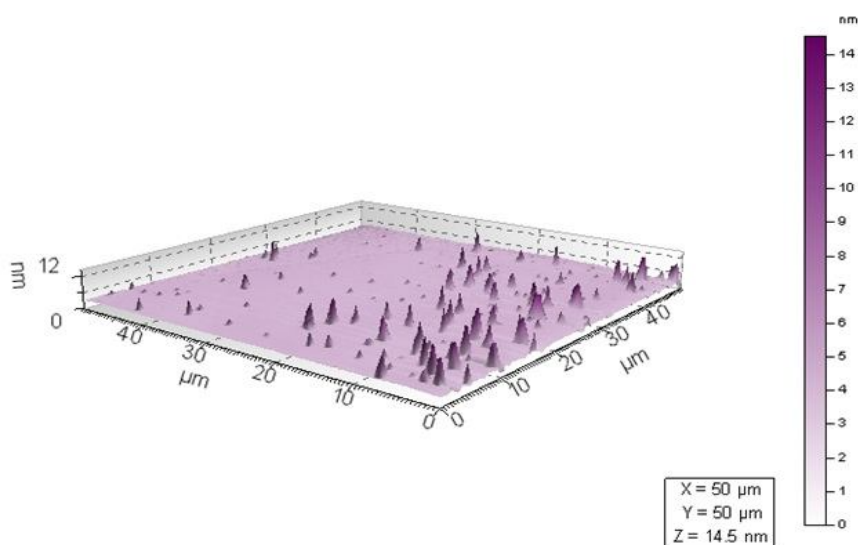


Figure4. AFM images 3D of magnetite sample

4. CONCLUSION

Magnetite can immobilize chromium as evident from the present study by forming a solid solution with it and forming outer sphere complexes in cation exchange sites. Also presence of chromium in magnetite structure would retard its transformation to higher state oxides. The present methodology of adsorption study has been successful in evaluating chromium's sorption behavior on magnetite.

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