Properties of magnetic iron oxides used as materials for wastewater treatment

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Abstract. The paper describes the properties of some nanopowders obtained by coprecipitation and used as adsorbent for wastewater treatment. The Fe₃O₄ and γ-Fe₂O₃ nanopowders were obtained using iron salts and NaOH as precipitation agents. D-sorbitol was used to prevent the agglomeration between the nanoparticles. The particle size and distribution were detected using a transmission electron microscopy (TEM) and a scanning electron microscope (SEM) equipped with dispersive analyze system in X radiation energy (EDS). The structure of the iron oxide nanoparticles was characterized by X-ray powder diffraction. Thus, the nanoparticles were characterized and compare in terms of particle size and chemical composition and used for adsorption studies in order to removal hexavalent chromium from waste waters.

1. Introduction
The recent advanced researches regarding the use of nanoscale materials in different applications have made possible the separation and detection of various analytes from complex environmental and biological matrices [1]. For environmental application, the attention has been focused on the synthesis and functionalization of magnetic nanoparticles with diameter < 50 nm. These nanomaterials have the potential to remove heavy metals and organic compounds. Magnetic nanomaterials are adsorbents with high chemical specificity, being capable to retain the pollutant from the contaminated water system.

It is important to mention that the variations regarding shape, core size and surface functionality can decide the magnetic properties of the nanomaterials. In these conditions, the synthesis method plays a critical role for the final product used as adsorbent. The industrial waste waters consists of different heavy metals, with a great environmental and public health impact, because their toxicity and persistence in the environment. Chromium and its compounds are presented in wastewaters from iron and steel, metal finishing, leather industries or nuclear power plants [2].

There are many types of nanomaterials but magnetic iron oxide nanoparticles are an efficient adsorbent, which couples magnetic separation with ionic exchange capacity for removal of heavy metals pollutants [3].

In this paper the synthesis and characterization of two magnetic iron oxide nanoparticles (Fe₃O₄ and γ-Fe₂O₃) and batch adsorption studies are described. The batch experiments were made for adsorption of hexavalent chromium from aqueous solutions. The chromium is a common contaminant,
being detected in soil and waters. Also, chromium species with trivalent and hexavalent oxidation state are usually presented in industrial processes such as electroplating, leather tanning or metallurgical applications. The hexavalent form is highly mobile and soluble in environments and has been widely known to be toxic, carcinogenic, and mutagenic. Therefore, remediation technologies have been developed to reduce Cr(VI) in subsurface to Cr(III) which is immobile, insoluble and less toxic. [4]

2. Materials and methods

The iron oxide nanoparticles were synthesized, characterized and evaluated in order to be used as adsorbents for hexavalent chromium. The magnetite (Fe₃O₄) nanoparticles were synthesized by coprecipitation method and transformed by air oxidation at 200°C into maghemite (γ-Fe₂O₃).

2.1. Synthesis of iron oxide nanoparticles

In the literature, various methods are known for preparation of iron oxide nanoparticles, the first coprecipitation method being described by Massart [5] achieved by the addition of NaOH or NH₄OH to an aqueous mixture of FeCl₂ and FeCl₃ as it is indicated by reaction:

\[ \text{FeCl}_2 + 2\text{FeCl}_3 + 8\text{NaOH} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} + 8\text{NaCl} \]

Some of the most used methods applied for synthesis of iron oxide nanoparticles are presented in the table 1.

| Synthesis method                  | Reagents                  | Characteristics of the synthesis               | Reference                        |
|-----------------------------------|---------------------------|-----------------------------------------------|----------------------------------|
| Coprecipitation                   | FeCl₂, FeCl₃, NaOH or NH₄OH | fast method; without unprotected shell is possible the agglomeration; low costs. | Massart (1981), Qu et al. (1999) |
| Hydrothermal / solvothermal method| Iron salts, surfactants   | narrow size distribution and a good shape control; long time of the reaction. | Wang et al. (2006), Liang et al. (2009) |
| Microemulsion                    | Oil/water/surfactant      | control of particle size; it is necessary a large quantity of solvent. | Hayashi et al. (2002) |

The synthesis method, for this paper, was coprecipitation and all chemicals were analytical grade purchased from Merck. The used reagents were chloride of ferrous ion (Fe²⁺) and ferric ion (Fe³⁺) with NaOH solution. D-sorbitol was used to prevent the agglomeration between the nanoparticles. The molar ratio was 1:2:8 for FeCl₂: FeCl₃: NaOH [7]. The experiments were carried out in a laboratory installation consists of: a four necked rounded flask equipped with a mechanical stirrer, a dropping funnel, a thermometer and a refrigerator. The iron solutions were strongly stirred in water, after adding NaOH solution. After mixing of the solutions, the color of the solution changes into black indicating the nucleation of Fe₃O₄ nanoparticles [8]. The precipitate was separated by magnetic decantation and washed several times with distilled water and ethanol. The magnetite nanoparticles were dried into
oven at 60°C. In order to obtain maghemite (γ-Fe₂O₃), a part from obtained magnetite nanoparticles was heated at 200°C, for 3 hours and finally, red-brown maghemite nanoparticles were collected.

2.2. Characterization of the iron oxide nanoparticles
The particle size and distribution were detected by high resolution transmission electron microscopy (HRTEM). The samples were prepared in ethanol and ultrasonicated and placed onto carbon grids in order to be analyzed at a TECNAI F30 G² transmission electron microscope. The crystalline structure was verified by X-rays diffraction (XRD) at room temperature. The Panalytical X'PERT MPD X-ray diffractometer was equipped with a copper anode generating high-intensity Cu Kα radiation (λ = 1.54065 Å) with the 2θ range from 10° to 90°. Also, the scanning electron microscopy (SEM) measurements were performed, after batch adsorption studies in order to detect the chromium presence onto iron oxides surface. A QUANTA INSPECT F microscope was used equipped with field emission gun (FEG) with 1.2 nm resolution and spectrometer with energy dispersive spectra (EDS) with 133 ev resolution at MnK.

2.3. Adsorption studies of the hexavalent chromium onto iron oxide nanoparticles surface
The adsorption studies were made by adding of 0.1 g γ-Fe₂O₃ into about 100 mL solution of hexavalent chromium at different concentrations: 10, 20, 40, 100 mg/L Cr⁶⁺. In this paper, the results for 40 and 100 mg/L are presented, the others results being already presented in another paper [6].

The optimum pH was 2.5. The maghemite (γ-Fe₂O₃) was analyzed after adsorption of the hexavalent chromium onto the surface in order to identify the presence of the chromium by SEM and EDS techniques.

3. Results

3.1. Structural and morphological investigations
The XRD investigations showed the presence of magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃). Unfortunately, the data diffraction patterns indicate that the two phases are very similar as it can be seen in Figure 1. The difference between magnetite and maghemite appears with position and intensities of peaks. Also, characteristic peaks of impurities were not detected in XRD investigations. The final samples were not a mixture of the two nano-phases.

![Figure 1](image)

**Figure 1.** XRD patterns obtained for magnetite nanoparticles (a) and maghemite nanoparticles (b).

All the detected diffraction peaks were indexed. The analyzed samples showed very broad diffraction lines, in accordance with their small particle size and high specific surface area. The figure 2(a) indicates the small dimension for synthesized magnetite, with diameters smaller than 20 nm. Combined with XRD patterns, the data indicates the inverse cubic spinel structure of Fe₃O₄.
The morphology of the Fe$_3$O$_4$ samples was investigated by transmission electron microscopy through bright field (TEMBF). The image is presented in Figure 2(a). Spherical particles with a reduced size and a good dispersion can be observed in this figure. Selected area electron diffraction (SAED) image from Figure 2(b) confirms the presence of Fe$_3$O$_4$ in analyzed sample.

The image is associated with the surface area presented in Figure 2(a).

**Figure 2.** (a) TEMBF image for Fe$_3$O$_4$; (b) SAED image associated to the sample from figure (a).

The magnetite (Fe$_3$O$_4$) was oxidized in air at 200ºC for 3 hours and the obtained product was γ-Fe$_2$O$_3$. The product was a red-brown precipitate and TEMBF and SAED images are shown in the Figure 3 (a) and (b) respectively.

**Figure 3.** (a) TEMBF image for γ-Fe$_2$O$_3$; (b) SAED image associated to the sample from figure (a).

Table 2 shows the most intense powder diffraction peaks of the Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ samples. The d-spacing values (nm) calculated from the electron diffraction patterns inserted in Figure 2 and Figure 3 and the standard atomic spacing for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ along with respective $hkl$ indexes from the JCPDS card (19-629) and (39-1346) respectively.
Table 2 The d-spacing values (nm) calculated from the electron diffraction patterns inserted in Figures 2 and 3 and the standard atomic spacing for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ along with respective hkl indexes.

| Ring | Calculated d spacing | JPCDS data for Fe$_3$O$_4$ | hkl | Calculated d spacing | JPCDS data for γ-Fe$_2$O$_3$ | hkl |
|------|----------------------|-----------------------------|-----|----------------------|-------------------------------|-----|
| 1    | 0.486                | 0.483                       | 111 | 0.482                | 0.482                         | 111 |
| 2    | 0.297                | 0.296                       | 220 | 0.295                | 0.295                         | 220 |
| 3    | 0.253                | 0.252                       | 311 | 0.252                | 0.252                         | 311 |
| 4    | 0.210                | 0.209                       | 400 | 0.208                | 0.208                         | 400 |
| 5    | 0.193                | 0.192                       | 331 |                     |                               |     |
| 6    | 0.171                | 0.170                       | 422 | 0.171                | 0.170                         | 422 |
| 7    | 0.162                | 0.162                       | 333 |                     |                               |     |
| 8    | 0.161                | 0.161                       | 511 | 0.161                | 0.161                         | 511 |
| 9    | 0.147                | 0.148                       | 440 | 0.149                | 0.148                         | 440 |

3.2. Adsorption studies for hexavalent chromium

0.1 g/L γ-Fe$_2$O$_3$ nanoparticles were mixed with 50 mL of Cr (VI) solution, the solution concentrations being 40 and 100 mg/L. The pHs of solutions were 2.54 and 6.46 for each concentration. The rate of removal for hexavalent chromium decreases gradually with an increase of pH from 2.54 at 6.46. The contact time was between 0 and 120 minutes. First samples were analyzed after 10 minutes and the last after 120 minutes. About 90% from hexavalent chromium was removed, after first minute of the reaction.

The effect of pH on adsorption of 40 mg/L Cr (VI) can be seen in the Figure 4.

Figure 4. The time effect of the adsorption of Cr (VI) at different pH values.

It is known from the literature [9] that the surface charge is neutral at the zero point of charge (pHpzc). The pHpzc value is 6.3 for maghemite. Below this value, the adsorbent surface is positively charged and the anions are adsorbed by electrostatic attraction. Above this value of pHpzc, the adsorbent surface is negative charged and the cations are adsorbed on the maghemite. From the
Figure 4 it is observed that the optimum pH value is 2.5 this value being an expected results, in these conditions. With the increase in pH, the uptake of Cr (VI) ions decreased, because in the aqueous phase, the surface of the metal oxides is covered with hydroxyl groups that vary at different pH values.

Hexavalent chromium in wastewaters is presented in forms as chromates (CrO$_4^{2-}$), dichromate (Cr$_2$O$_7^{2-}$) and bichromate (HCrO$_4^-$), in these conditions, the OH$^-$ groups from mixture will compete with chromium species for adsorptions sites.

Also, if the adsorption surface is negatively charged, the electrostatic repulsions increase between negatively charged Cr (VI) species and negatively charged nanoparticles, leading to the removal of some adsorbed species such as bichromate (HCrO$_4^-$) or chromate (CrO$_4^{2-}$) [2].

The results regarding adsorption efficiency, at pH 2.5, for initial concentrations of 40 and 100 mg/L Cr(VI) are presented in Figure 5.

![Figure 5](image)

**Figure 5.** The adsorption efficiency for different concentrations of Cr (VI) onto maghemite nanoparticles.

It can be seen the rapid adsorption of chromium on maghemite nanoparticles, initially quite high, followed by a much slower removal rate this leading to an equilibrium state. Also, it is obviously that the removal of 40 mg/L Cr (VI) solution is more efficiently than the 100 mg/L Cr (VI) solution, but for the two concentrations the removal is very efficiently.

The Langmuir isotherm was chosen for estimating the maximum adsorption capacity corresponding to adsorbent surface saturation and the linear equation is expressed as (1):

$$\frac{C_e}{q_e} = \frac{1}{\theta \cdot b} \cdot C_e + \frac{1}{\theta \cdot b}$$  \hspace{1cm} (1)

where:
- $C_e$ – equilibrium concentration, mg/L;
- $q_e$ – adsorbed amount at equilibrium, mg/g;
- $\theta$ and $b$ – constants related with adsorption capacity and apparent heat change.

The fundamental characteristics of Langmuir equation can be interpreted in terms of a dimensionless constant separation factor ($R_L$), defined as (2):

$$R_L = \frac{1}{1 + bC_0}.$$  \hspace{1cm} (2)

where: $C_0$ is initial concentration, mg/L and $b$ was defined above.

The value $R_L$ indicates the types of Langmuir isotherm of irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$).
The adsorbed amount at equilibrium was 19.16 mg Cr (VI) adsorbed /g adsorbent after 10 minutes and it remained almost the same after 120 minutes. Calculation of the data was presented in another work [6]. This value indicates a good adsorption capacity in comparison with others common adsorbent such as activated carbon or diatomite, according to the results from literature, namely: 11.5 mg/g for diatomite and 15.47 mg/g for activated carbon, respectively [9]. The adsorption data were fitted well with Langmuir monolayer adsorption isotherm, considering a homogenous surface of adsorbent, without interaction between adsorbate molecules. The linearized Langmuir isotherm for hexavalent chromium removal is shown in Figure 6.

![Figure 6: Linearized Langmuir isotherm for Cr (VI) adsorption on the maghemite nanoparticles.](image)

The $R_L$ factor can be calculated, from obtained data, according to the equation (2), thus $R_L$ is 0.0462 for an initial concentration of hexavalent chromium of 40 mg/L. This result indicates that the uptake of Cr (VI) by maghemite is favorable.

The values of Langmuir constants and correlation factor are shown in Table 3.

| pH values | Langmuir constants | $R^2$ | $R_L$ |
|-----------|---------------------|-------|-------|
|           | $q_e$ (mg/L) | $b$ (L/mg) |       |       |
| 2.54      | 19.16             | 0.51   | 0.9874| 0.0462|
| 6.46      | 17.85             | 0.12   | 0.9352| 0.1701|

These values indicate a favorable Langmuir isotherm according to $R_L$ factor (0.0462) and a good adsorption capacity at 19.16 mg/g for pH 2.54. These values are available for an initial concentration at 40 mg/L Cr (VI). Also, for a better correlation factor ($R^2$), more data are necessary regarding the time contact and the rotation speed between chromium solution and maghemite. In this experiment, the solution was manually mixed with maghemite nanoparticles. The magnetic separation can be seen in the Figure 7.
Figure 7. Magnetic separation of the maghemite from Cr (VI) solutions.

The hexavalent chromium was analyzed by molecular absorption spectrometry (diphenylcarbazide method) and the total chromium was analyzed with flame atomic absorption spectrometry. The results are shown in table 4.

Table 4. Chromium concentration analyzed before and after adsorption process at pH 2.54.

| Before adsorption | After adsorption |
|-------------------|------------------|
| $Co$ Cr (VI), mg/L | $Ce$ Cr (VI), mg/L | $Ce$ Cr tot, mg/L |
| 40                | 1.675            | 1.671             |
| 100               | 4.300            | 4.310             |

Dissolved hexavalent chromium form a colored compound with diphenylcarbazide detectable at wavelength of 530 nm. The detection method was molecular absorption spectrometry. Total chromium (trivalent and hexavalent) was detected by atomic absorption spectrometry. Small differences indicate that there is no chemical redox reaction during the adsorption process. Also, the adsorption of the hexavalent chromium onto maghemite surface can be seen by EDAX analysis from Figure 8.

Figure 8. EDAX spectra for Cr (VI) adsorbed onto maghemite.
The hexavalent chromium adsorbed onto maghemite was analyzed by atomic absorption spectrometry, after mineralization. The results obtained as average were about 0.098 mg Cr(VI) for 1 g $\gamma$-Fe$_2$O$_3$.

4. Conclusions
The nanoparticles used as adsorbent for Cr (VI) were synthesized by coprecipitation method, having 10 nm diameters. These nanoparticles were characterized by XRD, TEM and SEM methods. The adsorption studies indicated a good correlation between chromium concentration and maghemite quantity at pH 2.54 and adsorption data were fitted well with Langmuir isotherm. The hexavalent chromium was analyzed before and after adsorption onto maghemite by atomic absorption spectrometry and molecular absorption spectrometry and also an EDAX analysis was provided for identification of chromium onto maghemite surface during adsorption process. The obtained data showed that the electrostatic attraction was responsible for the hexavalent chromium removal.

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