Green synthesis of magnetic nanoparticles using leaf extracts of *Aloe vera* and *Kalanchoe daigremontiana* to remove divalent mercury from natural waters

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Abstract. In this study, magnetic nanoparticles of magnetite were prepared by an eco-friendly method using aqueous leaf extracts of *Aloe vera* and *Kalanchoe daigremontiana*. These vegetal extracts have suitable characteristics such as high availability, low cost, and serve as good colloidal stabilizers. Synthetized products were characterized by Transmission Electron Microscopy (TEM), Room Temperature Mossbauer Spectroscopy (RT-MS), and their potential use as adsorbents for Hg (II) removal in natural waters was evaluated by Atomic Absorption Spectroscopy (AAS). Size distribution and morphology of the products obtained by TEM show spherical nanoparticles composites, with sizes between 3 and 10 nm for both extracts. Mossbauer spectra are consistent with superparamagnetic particles for both samples. Moreover, particles from both extracts showed mercury removal efficiencies above 75%.

1. Introduction

Owing to the growing anthropic affectation of natural systems, the development of novel and more effective systems for removal of pollutants has drawn the attention of researchers [1]. Nanostructured adsorbents are studied as promising materials due to their large surface area, high reactivity, and catalytic properties, which make them suitable in natural and waste waters for the remediation of pollutants such as heavy metals, dyes, persistent organic pollutants, among others [2-4]. Within these materials, magnetic iron oxide-based nanoparticles or magnetic composites are of particular interest considering their magnetic properties, which allows the removal of the adsorbent from the reaction media when applying an external magnetic field, and particles can be reused after a pollutant desorption process [5-8].

Conventionally, synthesis of micro and nanometric materials for their use as environmental adsorbents has been performed by chemical processes that frequently use toxic precursors and non-biodegradable stabilizers [9-11]. Moreover, these chemical routes are usually expensive, and their use in large-scale processes could be limited. Conventional chemical processes have started to be replaced by green methods, using renewable materials and biosynthetic routes with low environmental impact,
thus, obtaining biodegradable products [12, 13]. In the synthesis of magnetic materials, the use of natural extracts as stabilizing agents of particles has been recently studied, finding better dispersions and increases in adsorption capacities of pollutants. The use of a large variety of natural extracts in the one-pot synthesis of magnetic ferrites has been reported [14-16].

This study shows the synthesis of magnetic iron oxide-based nanoparticles by a chemical co-precipitation method using Aloe vera and Kalanchoe daigremontiana extracts as stabilizing agents. Synthesized products were characterized by structural and magnetic techniques. The absorption capacity of Hg (II) by synthesized products was evaluated by atomic absorption spectroscopy.

2. Materials and Methods

2.1 Preparation of particles
Ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous chloride tetrahydrate (FeCl₂·4H₂O), sodium hydroxide (NaOH) and mercuric chloride (HgCl₂) were supplied by Merck KGaA. Analytical grade reagents were used without further purification. Lyophilizates of Aloe vera mucilage and Kalanchoe daigremontiana leaves were used to prepare the vegetable extracts. Milli-Q water was used in the particle synthesis and preparation of extracts.

2.2 Preparation of Aloe vera and Kalanchoe daigremontiana extracts
In a 250 mL Erlenmeyer-flask, 3.0 g of lyophilized vegetal material was mixed with 100.0 mL of milli-Q water until complete hydration of the material. Then the mixture was heated at 90 C during 60 minutes in an ultrasonic bath. The extract was filtered by gravity and using a membrane filter of 0.45 µ. Supernatant was used in the synthesis of particles.

2.3 Synthesis of magnetic iron oxide nanoparticles using vegetable extracts

Magnetic particles were obtained by a chemical co-precipitation method using a colloidal stabilizer [16]. Prior to the synthesis, solutions were deaerated with N₂(g). Afterward, 40 mL of a solution containing 0.2-mol of FeCl₃·6H₂O and 0.1-mol of FeCl₂·4H₂O was added dropwise in 50 mL of vegetable extract. The reaction solution was maintained in pH range of 11.5 - 12.0 by adding a 0.5M NaOH solution during 60 minutes in constant agitation. During synthesis, solutions were constantly bubbled with N₂(g). Synthesized products were washed by dialysis until reaching a conductivity similar to the distilled water used for washing.

2.4 Characterization
Synthesized particles were characterized by TEM and RT-MS techniques, and Magnetization measurements (MH). TEM images were obtained using a Tecnai F20 Super-Twin TMP field-emission gun equipment, with a resolution of 0.1 nm at 200 kV and 1.0 of maximum magnification TEM MX camera GATAN US 1000XP-P. Samples for TEM measurements were suspended in ethanol and dispersed ultrasonically. A transmission Mössbauer spectrometer (Wissel MR 260) of 512 channels with a ⁵⁷Co/Rh source was used. The Mössbauer spectra were adjusted using the Recoil software. Magnetization measurements were performed with a vibrating sample magnetometer developed in the Laboratory of Instrumentation and Spectroscopy of EAFIT University in Medellín, whose magnetic field ranges from 0-5.5 kOe and whose resolution in magnetic moment is 1.3×10⁻⁵ emu. An atomic absorption spectrophotometer Thermo Scientific™ CE3000 fitted with a Thermo Scientific VP100 was used to measure the remainder mercury.

3. Results and discussion
Figures 1(a) and 1(b) show TEM micrographs of the two synthesized samples. From the micrographs, it can be seen that both samples are composed of particles with diameters less than 10 nm embedded in the vegetable extract. For both extracts, stabilized particles display a regular size distribution.
Figure 1. TEM micrographs of magnetic iron oxide nanoparticles synthesized using leaf extract of (a) Aloe Vera and (b) Kalanchoe daigremontiana.

Figure 2 shows the Mössbauer spectra at room temperature of synthesized products using (a) Aloe Vera and (b) Kalanchoe daigremontiana extracts. In both cases, spectra were adjusted with a doublet and the hyperfine parameters are reported in Table 1. These adjustments show that particles from both syntheses have diameters below the critical superparamagnetic diameter. The superparamagnetic character of products from the two syntheses shows that both extracts act as good particle stabilizers during their formation, and thus controlling their growth.

Figure 2. Room temperature Mössbauer spectrum of magnetic iron oxide Nanoparticles synthesized using extract of (a) Aloe Vera and (b) Kalanchoe daigremontiana.

Table 1. Mössbauer parameters of magnetic iron oxide nanoparticles synthesized using extract of (a) Aloe Vera and (b) Kalanchoe daigremontiana.

| Sub-spectrum         | Aloe vera       | Kalanchoe daigremontiana |
|----------------------|-----------------|---------------------------|
|                      | Doublet         | Doublet                   |
| δ (mm/s)             | 0.47 ± 0.02     | 0.47 ± 0.02               |
| Δ (mm/s)             | 0.76 ± 0.02     | 0.70 ± 0.02               |
| Γ (mm/s)             | 0.24 ± 0.02     | 0.24 ± 0.02               |

δ: isomer shift relative to αFe. Δ: quadrupolar splitting. Γ: linewidth
Magnetic measurements of magnetization vs. applied magnetic field at 300 K of synthesized products are shown in Figure 3. For both products, Aloe Vera (a) and Kalanchoe daigremontiana (b) extracts a positive slope is observed, and particles did not reach saturation in the range of the applied magnetic field (0-5 kOe). Both hysteresis curves show a paramagnetic behavior, which agrees with the TEM and RT-MS measurements presented previously.

![Figure 3](image)

**Figure 3.** Magnetization curves of the samples obtained in presence of (a) Aloe vera extract; (b) Kalanchoe daigremontiana extract.

### 4. Mercury adsorption tests

The adsorption capacity of synthesized products was evaluated in solutions by a divalent mercury test. Three Hg$^{2+}$ concentrations (5, 10 and 15 ppm) were taken to measure the adsorption in each case using three dilutions of a nanoparticle suspension (40, 60 and 80% v/v). Remaining mercury content in supernatant samples was determined by hydride generation atomic absorption spectroscopy. Figure 4 shows the percentage of mercury removal vs. mercury concentrations using Aloe vera (a) and Kalanchoe daigremontiana (b) extracts.

![Figure 4](image)

**Figure 4.** Mercury removal percentage at different concentration of Hg$^{2+}$ and three different suspension dilutions

The adsorption capacity of particles stabilized with Aloe vera was similar for the three extract dilutions. Furthermore, the maximum percentage of mercury removal (higher than 75%) was found using the 5 ppm Hg$^{2+}$ solution. Solutions with higher mercury concentration were found having a lower percentage of adsorption, which could be related to a saturation of the adsorbent.
Synthesis using *Kalanchoe daigremontiana* (figure 4 (b)) had a greater cation adsorption capacity with 80% (v/v) dilution, corresponding to an 86% of mercury removal. As the dilution increases, the percentage of mercury removal decreases, for all Hg\(^{2+}\) concentrations evaluated. These results could indicate a direct relationship between the concentration of adsorbent particles and their adsorption capacity. As the Hg\(^{2+}\) concentration increases, the percentage of removal decreases, indicating a possible saturation of the adsorbent for Hg\(^{2+}\) concentrations above 10 ppm.

**Conclusions**

Magnetic iron oxide-based nanoparticles were synthesized using vegetal extracts from *Aloe vera* mucilage and *Kalanchoe daigremontiana* leaves. TEM images showed that particles from both syntheses are embedded in the extract, indicating this vegetal extracts had remarkable potential as stabilizing agents of magnetic particles. Both products have diameters less than 10 nm. Mössbauer spectroscopy and magnetization measurements for both syntheses confirm the obtaining of superparamagnetic particles, with sizes smaller than their critical diameter. These results are in agreement with TEM images. The synthesized particles were used to recover divalent mercury from a test solution and an adsorption capacity greater than 70% was found for both syntheses. This work allow us to conclude that our green synthesis method is a good option to obtain magnetic nanoparticles with potential use as adsorbents of heavy metals in natural waters.

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