




Article

# Magnetic Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> Nanocomposites for Effective Mercury Removal from Water

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**Abstract:** In this study, magnetic Fe<sub>3</sub>O<sub>4</sub> particles and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites were prepared by a facile and green method, fully characterized and used for the removal of Hg<sup>2+</sup> from water. Characterizations showed that the Fe<sub>3</sub>O<sub>4</sub> particles are quasi-spherical with an average diameter of 217 nm and metallic silver nanoparticles formed on the surface with a size of 23–41 nm. The initial Hg<sup>2+</sup> removal rate was very fast followed by a slow increase and the maximum solid phase loading was 71.3 mg/g for the Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> and 28 mg/g for the bare Fe<sub>3</sub>O<sub>4</sub>. The removal mechanism is complex, involving Hg<sup>2+</sup> adsorption and reduction, Fe<sup>2+</sup> and Ag<sup>0</sup> oxidation accompanied with reactions of Cl<sup>-</sup> with Hg<sup>+</sup> and Ag<sup>+</sup>. The facile and green synthesis process, the fast kinetics and high removal capacity and the possibility of magnetic separation make Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites attractive materials for the removal of Hg<sup>2+</sup> from water.

**Keywords:** nanocomposites; magnetite; silver; mercury; amalgamation

## 1. Introduction

Mercury and its compounds are considered to be extremely hazardous pollutants. Contamination of the environment with mercury has become a global problem and mercury polluted areas have been identified worldwide [1]. In most cases, the release of Hg<sup>0</sup> or Hg<sup>2+</sup> into the environment occurs due to industrial emissions, transportation, waste treatment or technological accidents [2]. Therefore, the development of efficient methods for the removal of mercury from water is imperative. Several removal and immobilization methods are available, such as membrane separation, reduction, precipitation, physical and chemical adsorption, ion exchange and bioremediation [3,4]. Of these methods, adsorption exhibits several advantages in terms of process design, operation and cost and it is the most studied one [4]. A number of materials have been used as adsorbents for the removal of Hg<sup>2+</sup> from water, including activated carbons [5], zeolites [6,7], resins and other polymers [8–11] and silver-modified materials [7,12,13].

Silver is an important metal that can form various amalgam compounds with mercury such as AgHg, Ag<sub>2</sub>Hg<sub>3</sub>, Ag<sub>3</sub>Hg<sub>4</sub>, Ag<sub>4</sub>Hg<sub>5</sub> and Ag<sub>10</sub>Hg<sub>13</sub> [14]. The amalgamation reaction can be greatly enhanced by utilizing Ag in the form of nanocomposites. Such nanocomposites based on silica,

magnetite, titanium oxide and alumina have been studied for the removal of heavy metals and mercury from water [15–19]. Among them, magnetite-based nanocomposites are being broadly studied for use in water purification owing to their low cost, simple application, and absence of toxicity towards the environment [20,21]. Furthermore, magnetite nanoparticles are easily separable from the aqueous solution when a magnetic field is applied and can be reused several times [22]. Heavy metals can be bound to the surface of magnetite by complexation, precipitation and adsorption mechanisms. Various types of magnetic nanomaterials are being investigated for the extraction of hazardous pollutants from water. In particular, magnetite-based nanocomposites show high efficiency in the removal and recovery of copper, zinc, nickel and mercury ions from industrial wastewater [23,24].

$\text{Fe}_3\text{O}_4@\text{SiO}_2$  magnetic nanoparticles modified by grafting poly(1-vinylimidazole) oligomer were used to remove  $\text{Hg}^{2+}$  from water reaching a maximum capacity of 346 mg/g [21].  $\text{Fe}_3\text{O}_4$  nanoparticles coated with silica shells functionalized with dithiocarbamate groups were used for mercury removal from seawater and quantification of mercury in natural waters [25,26]. Nanocomposites based on  $\text{Fe}_3\text{O}_4$  nanoparticles, chitosan nanoparticles and polythiophene were used for  $\text{Hg}^{2+}$  removal from aqueous solutions reaching a loading of about 50 mg/g [27]. Thiol-functionalized  $\text{Fe}_3\text{O}_4$  nanoparticles have shown a high removal capacity for  $\text{Hg}^{2+}$  reaching 345 mg/g [28].  $\text{Fe}_3\text{O}_4$  nanoparticles coated with amino organic ligands and yam peel biomass reached a loading of about 60 mg/g [29]. Dithiothreitol functionalized  $\text{Fe}_3\text{O}_4$  nanoparticles showed a capacity of 6.3 mg/g and activated carbon doped with  $\text{Fe}_3\text{O}_4$  nanoparticles reached a capacity of 38.3 mg/g [30]. Dithiocarbamate surface functionalized  $\text{Fe}_3\text{O}_4$  particles reached a loading of 122–246 mg/g [31]. Zeolite-magnetite composites were used to remove  $\text{Hg}^{2+}$  from water reaching a maximum loading of 26.2 mg/g [32].  $\text{Fe}_3\text{O}_4$  particles have been also used as core covered with a silica shell [33,34].

As the literature review demonstrates the direct surface interactions of mercury ions with bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites have not been studied so far. An exception is the work of Dong et al. [35] who used  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  particles but for the removal of  $\text{Hg}^0$  from flue gas. On the synthesis part, great attention is paid to the development of green processes with minimal use of toxic substances [36]. Plant extracts utilization as reducing and stabilizing agents have drawn considerable attention for the synthesis of metallic nanoparticles as it is considered an eco-friendly method [37,38]. Furthermore, the synthesis process should be low-cost and easily scalable for mass production. Such a green synthesis of Ag nanoparticles on magnetic iron oxide modified by a herbal tea extract has been studied for antibacterial activity and 4-nitrophenol reduction [37]. In this study, we synthesized magnetic  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites by a facile method using green tea extract. The nanocomposite was then used as a magnetically separable adsorbent for efficient mercury removal from water. The mechanism of mercury removal is discussed in detail and verified by advanced characterization methods.

## 2. Materials and Methods

### 2.1. Chemicals

High purity iron (III) chloride hexahydrate ( $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ , 99%), anhydrous sodium acetate ( $\text{CH}_3\text{COONa}$ , 99.0%), anhydrous ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ , 99.8%), silver nitrate ( $\text{AgNO}_3$ ,  $\geq 99\%$ ), mercury (II) chloride ( $\text{HgCl}_2$ , 99.8%) were used as received. Green tea was purchased at the local market.

### 2.2. Synthesis of $\text{Fe}_3\text{O}_4$

Magnetite particles were synthesized according to previously published protocols [39,40]. In a typical synthesis process,  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (2.16 g) and  $\text{CH}_3\text{COONa}$  (6 g) were dissolved in 15 mL ethylene glycol. The prepared mixture solution was then transferred to a Teflon-lined stainless-steel autoclave and then heated at 200 °C for 8 h, with heating rate of 10 °C per 1 min. The black product was washed by magnet decantation several times with water/ethanol and then dried at 40 °C. 2.3. Synthesis of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$ .

Green tea extract (GTE) was prepared by boiling 0.2 g of dried green tea leaves in 20 mL of water for 5 min. The GTE was then filtered using a Whatman filter paper N1 to obtain an aqueous extract of green tea. To prepare the Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites, 100 mg of magnetite spheres were dispersed in 10 mL of water and dispersed for 20 min. To the above solution, 500 µL of GTE was added and the solution was stirred at room temperature for 24 h. Finally, AgNO<sub>3</sub> (20 mg) was added to the solution and kept under stirring for 24 h. The as-prepared composite was separated by the magnet, washed with water/ethanol and then dried at 30 °C.

### 2.3. Mercury Removal Efficiency

The Hg<sup>2+</sup> removal efficiency of Fe<sub>3</sub>O<sub>4</sub> particles and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites was studied in HgCl<sub>2</sub> solutions. A stock solution of Hg<sup>2+</sup> (100 and 200 ppm) was prepared by dissolving HgCl<sub>2</sub> in deionized water. The Hg<sup>2+</sup> solution volume was 20 mL and the solids mass 50 mg. All adsorption experiments were performed without any stirring at room temperature (23 ± 2 °C) without pH adjustment. The mercury concentration in the solutions was measured by a mercury analyzer (Lumex RA-915M) until no concentration changes were observed, i.e., until equilibrium was attained. All experiments were performed in duplicate and the average standard deviation was 2%.

### 2.4. Characterization

The crystalline phase and the structure of the synthesized Fe<sub>3</sub>O<sub>4</sub> particles and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites before and after mercury adsorption were performed using an X-ray diffractometer (XRD) (RigakuSmartLab, Tokyo, Japan). The surface of the materials was studied by Scanning Electron Microscopy (SEM) using a Zeiss Auriga Crossbeam 540. Chemical analysis was carried out using an Energy-Dispersive X-ray spectrometer (Aztec, Oxford Instruments, Abingdon, UK). The nanoscale analysis was done with a high-resolution JEOL JEM-1400 Plus transmission electron microscope (TEM), operating at 120 kV.

### 2.5. Calculations

The kinetics of mercury removal from water was studied in order to obtain information about the adsorption mechanism of the pure Fe<sub>3</sub>O<sub>4</sub> particles and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites. The percentage of mercury removal (R) was calculated using as follows:

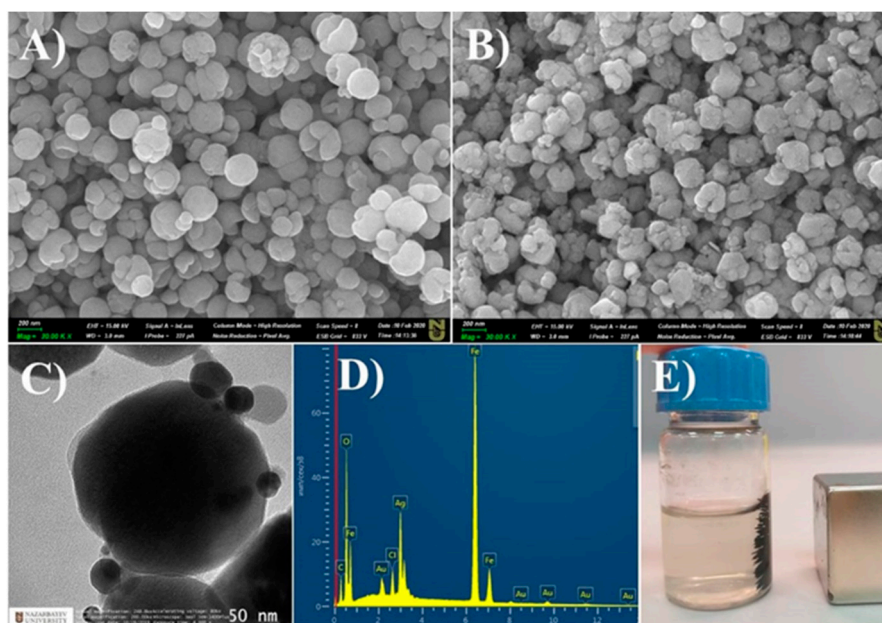
$$R (\%) = ((C_i - C_f)/C_i) \times 100 \quad (1)$$

$$q (\text{mg/g}) = (C_i - C_f) \times V/m \quad (2)$$

where C<sub>i</sub> and C<sub>f</sub> (mg/L) are the initial and final concentrations of Hg<sup>2+</sup>, V (L) is the volume of the solution and m (g) is mass of the adsorbent.

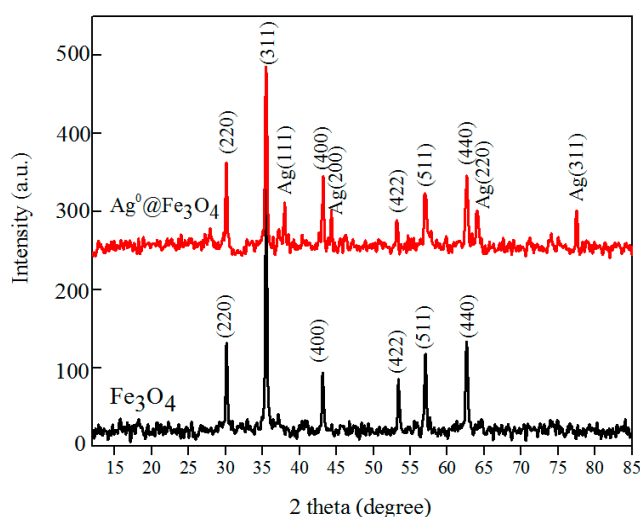
## 3. Results and Discussion

SEM analysis was used to investigate the morphology of as-prepared bare Fe<sub>3</sub>O<sub>4</sub> particles and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites. Figure 1A shows that the bare Fe<sub>3</sub>O<sub>4</sub> particles were quasi-spherical and had a mean diameter of 217 ± 76 nm. Figure 1B shows that the surface of the Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites became rougher because of Ag nanoparticle (23–41 nm) deposition on the surface of the Fe<sub>3</sub>O<sub>4</sub> particles. The TEM image (Figure 1C) and EDX analysis (Figure 1D) confirmed that Fe<sub>3</sub>O<sub>4</sub> particles were decorated with Ag nanoparticles. In particular, main elements such as Fe, O and Ag were clearly detectable in the EDX spectrum of Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites. Figure 1E shows that Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposites were magnetic and could be conveniently extracted by the use of a permanent magnet.



**Figure 1.** SEM images of (A) bare Fe<sub>3</sub>O<sub>4</sub> and (B) Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> particles. TEM image (C) of an individual Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> particle, (D) EDX spectrum and (E) digital image of Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> particles in a water solution attracted by a permanent magnet.

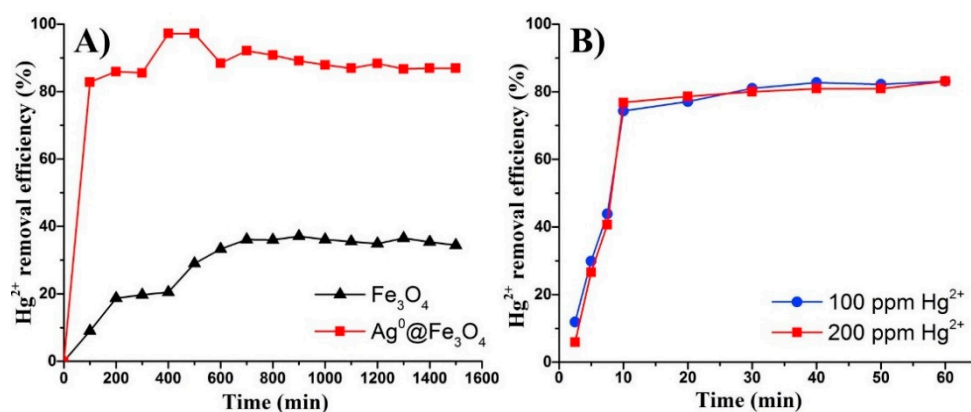
XRD analysis of the bare Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> confirmed the successful deposition of Ag nanoparticles on the surface of Fe<sub>3</sub>O<sub>4</sub> particles. Figure 2 shows that diffraction peaks at 30.1°, 35.5°, 43.1°, 53.7°, 57.3° and 62.6° could be indexed to the (220), (311), (400), (422), (511) and (440) planes of the face-centered cubic structure of the Fe<sub>3</sub>O<sub>4</sub> (JCPDS # 19-629) and the four peaks located at 38.2°, 44.3°, 64.2° and 73.9° corresponded to the characteristic (111), (200), (220) and (311) reflection planes of the face-centered cubic Ag (JCPDS # 04-0783). It should be noted that the strong diffraction peaks indicated the formation of particles with good crystallinity and purity since no other peaks were detected.



**Figure 2.** XRD patterns of bare Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> particles.

Figure 3A shows the adsorption kinetics results. It was found that Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> removed more than 80% of the mercury within the first hour followed by a slow approach to an equilibrium point with a maximum solid phase loading of 71.3 mg/g. On the other hand, the bare Fe<sub>3</sub>O<sub>4</sub> removed less than 10% of mercury after the first hour and less than 40% at equilibrium, reaching a solid phase loading of

about 28 mg/g. Qualitatively similar trends were observed for the removal of  $\text{Hg}^0$  from flue gas by using bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  [35]. Some studies argue that magnetite either does not remove  $\text{Hg}^{2+}$  or removes only up to 1.14 mg/g [21,41]. As mentioned in the introduction, there are no studies on the removal of  $\text{Hg}^{2+}$  from water by the use of this material and for comparison representative published studies are presented in Table 1. As is evident, capacity depends on the materials and conditions used. An important advantage of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  is the ease of separation of the solid phase after the adsorption process.



**Figure 3.**  $\text{Hg}^{2+}$  removal efficiency using bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  at 100 ppm (A) and the comparison between 100 and 200 ppm for  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  (B).

**Table 1.** Published studies on the removal of mercury from aqueous solutions.

Material	Capacity (mg/g)	Reference
Dithiothreitol functionalized $\text{Fe}_3\text{O}_4$ nanoparticles	6.3	[30]
$\text{SiO}_2\text{-Ag}^0$ nanocomposites	7.8–8.3	[19]
Synthetic zeolites	20.5–22.3	[42]
Zeolite-magnetite composites	26.2	[32]
Activated carbon doped with $\text{Fe}_3\text{O}_4$ nanoparticles	38.3	[30]
Nanocomposites based on $\text{Fe}_3\text{O}_4$ nanoparticles, chitosan nanoparticles and polythiophene	50	[27]
$\text{Fe}_3\text{O}_4$ nanoparticles coated with amino organic ligands and yam peel biomass	60	[29]
Dithiocarbamate surface functionalized $\text{Fe}_3\text{O}_4$ particles	122–246	[31]
Mesoporous silica-ammonium (4-chloro-2-mercaptophenyl) carbamodithioate	164	[43]
Thiol-functionalized $\text{Fe}_3\text{O}_4$ nanoparticles	345	[28]
$\text{Fe}_3\text{O}_4\text{@SiO}_2$ magnetic nanoparticles modified by grafting poly(1-vinylimidazole)	346	[21]
Cryogels	240–742	[11]

Additional experiments for short time demonstrated that reaction on the surface of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  particles was rapid and the majority of mercury ions are removed within the first 10 min (Figure 3B). Almost the same trend was observed for two different concentrations of  $\text{Hg}^{2+}$ .

The interaction of  $\text{Hg}^{2+}$  with bare  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  was further investigated using SEM, EDX and XRD. Figure 4A shows the SEM analysis of the bare  $\text{Fe}_3\text{O}_4$  after contact with  $\text{Hg}^{2+}$  for 12 h. It was clear that the  $\text{Fe}_3\text{O}_4$  particles still retained the quasi-spherical shape. An EDX survey (Figure 4B) revealed that a small quantity of Hg and Cl were adsorbed on the surface of  $\text{Fe}_3\text{O}_4$  particles. Analysis of the  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  after contact with  $\text{Hg}^{2+}$  for 12 h was also performed for comparison. Figure 5A shows that the morphology of the  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  particles was not changed significantly. However, EDX analysis revealed that the quantity of adsorbed Hg and Cl significantly increased. The detected amount of Hg

(wt.%) became five times higher, while the detected amount of Cl (wt.%) became eight times higher. These results demonstrated that the addition of Ag<sup>0</sup> was beneficial in terms of Hg<sup>2+</sup> removal.

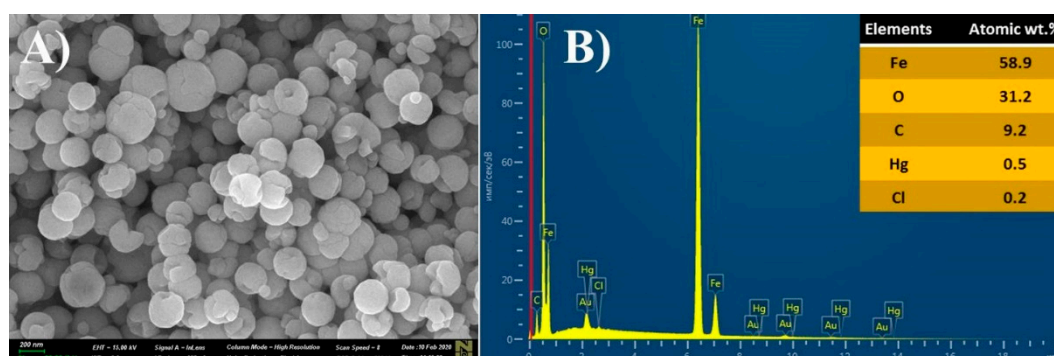


Figure 4. SEM image (A) and EDX survey (B) of bare Fe<sub>3</sub>O<sub>4</sub> after contact with Hg<sup>2+</sup> for 12 h.

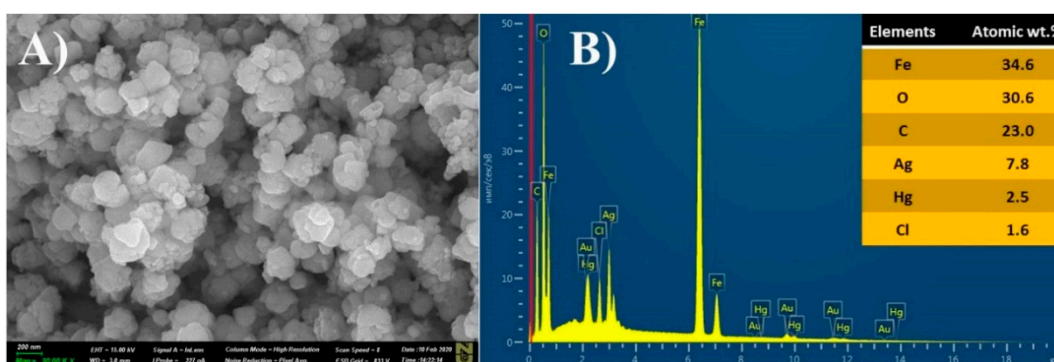


Figure 5. SEM image (A) and EDX survey (B) of Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> after contact with Hg<sup>2+</sup> for 12 h.

An XRD analysis was performed to elucidate the adsorption pathways on the surface of bare Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> (Figure 6). Upon contact of Fe<sub>3</sub>O<sub>4</sub> particles with Hg<sup>2+</sup>, new peaks at 24° and 32° appeared due to the formation of HgO [44] and a peak at 44° appeared due to the formation of Hg<sub>2</sub>Cl<sub>2</sub> [45]. The reaction mechanism between mercury and magnetite is still not well understood. However, a recent report suggested that Hg<sup>2+</sup> could be adsorbed on the surface of magnetite from a HgCl<sub>2</sub> solution and then reduced to volatile Hg<sup>0</sup> by Fe<sup>2+</sup> [46]. The formation of volatile Hg<sup>0</sup> is difficult to confirm but if it happens it obviously gives no trace on the XRD. Another study on magnetite found that in the absence of chloride ions, Hg<sup>2+</sup> is reduced to Hg<sup>0</sup>, while in the presence of chloride ions it is reduced to Hg<sup>+</sup> resulting in Hg<sub>2</sub>Cl<sub>2</sub> [47], which is in agreement with the results of the present study. The interaction of Fe species with Hg<sup>2+</sup> and the redox reactions resulting in Hg<sub>2</sub>Cl<sub>2</sub>, Hg<sup>0</sup> and HgO are discussed in other studies as well [41]. The possible reactions are the following:



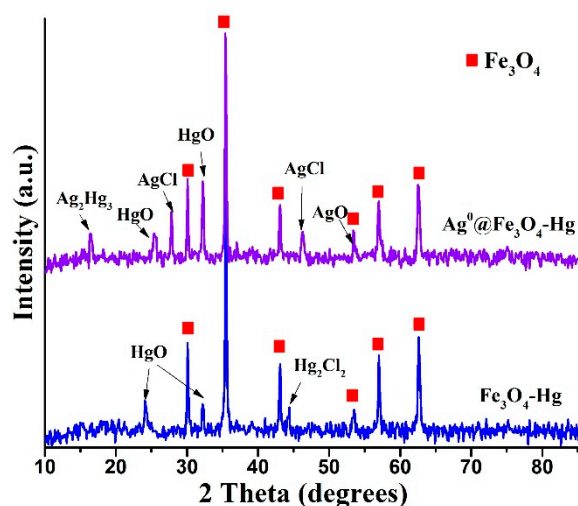


Figure 6. XRD patterns of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  after 12 h contact with  $\text{HgCl}_2$  solution.

In the case of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites, the appearance of a new peak at around  $17^\circ$  probably indicated the formation of an Hg-Ag amalgam (moschellandbergite phase,  $\text{Ag}_2\text{Hg}_3$ ) [48]. The absence of literature on the removal of  $\text{Hg}^{2+}$  from aqueous solutions by the use of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites is difficult to support this conclusion. However, there are papers presenting the removal of Hg from a gas phase by the use of  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites [35] where the formation of Hg-Ag amalgams is offered as the best explanation for the efficiency of the nanocomposite in comparison to the bare magnetite. Additional peaks at around  $27^\circ$  and  $46^\circ$  were indexed to the AgCl [49] structure, which appeared due to the reaction between the  $\text{Ag}^+$  and  $\text{Cl}^-$ . Furthermore, a peak at  $53^\circ$  appeared due to the formation of monoclinic AgO [50]. The formation of  $\text{Ag}_2\text{Hg}_3$  and  $\text{Hg}_2\text{Cl}_2$  and the effect of  $\text{Hg}^{2+}$  speciation on the reaction mechanisms are discussed in more detail on different  $\text{Ag}^0$  nanocomposites elsewhere [19,42]. Thus, in addition to reactions (3)–(6), in the presence of  $\text{Ag}^0$  the following reactions can occur:



The results suggest that the interactions on the surface of  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  are complex and there is a competition between several reactions, which govern the removal rate of  $\text{Hg}^{2+}$  from water. As it is clear, XPS analysis should be conducted in order to further investigate the possible redox reactions.

#### 4. Conclusions

$\text{Fe}_3\text{O}_4$  particles and  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites were successfully synthesized, characterized and used for the removal of  $\text{Hg}^{2+}$  from water. The results showed that micron-sized magnetite particles are formed on which  $\text{Ag}^0$  nanoparticles are anchored. The mercury removal experiments showed that  $\text{Fe}_3\text{O}_4\text{-Ag}^0$  nanocomposites are more effective than  $\text{Fe}_3\text{O}_4$  particles. XRD analysis revealed the formation of several compounds on the surface of the materials, including HgO,  $\text{Hg}_2\text{Cl}_2$ , AgCl, AgO and possibly  $\text{Ag}_2\text{Hg}_3$ . The formation of these compounds is a strong indication of surface redox reactions between  $\text{Fe}^{2+}$ ,  $\text{O}_2$ ,  $\text{Ag}^0$  and  $\text{Hg}^{2+}$ . Thus, several reactions can occur at the same time and further characterizations, such as XPS, are needed in order to draw safe conclusions. The facile synthesis,

the fast removal and the magnetic properties render the Fe<sub>3</sub>O<sub>4</sub>-Ag<sup>0</sup> nanocomposite a promising material for Hg<sup>2+</sup> removal from water.

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