



RESEARCH ARTICLE

Synthesis of Fe₃O₄/humic acid/silver nanoparticles and their application in Cu and Cd adsorption

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ABSTRACT

Nanoparticle technology developed rapidly due to the multifunctional utilization of nanoparticles in many disciplines such as medicine, drug delivery, environmental chemistry, food chemistry and analytical chemistry. In concept of this study, magnetic nanoparticles with a core-shell structure were synthesized and applied to the adsorption of copper and cadmium. The synthesis procedure consists of two steps. In the first step a core-shell structure was formed with Fe₃O₄ and humic acid. In the second step, the coating of synthesized core/shell structure with silver occurs. The characterization of synthesized nanoparticles was performed with the aid of Scanning Electron Microscope (SEM) images combined with an elemental distribution image (EDX mapping), Zeta Potential, and Dynamic Light Scattering (DLS) analyses. Adsorption isotherms of copper and cadmium on Fe₃O₄/HA/Ag multi-component structure were studied. The optimum adsorption conditions in aqueous solutions were fixed at pH 9 and at 300 K. As a result, the Fe₃O₄/HA/Ag multi-component structure showed excellent adsorption capacity for both copper and cadmium ions with removal percentages of 92% and 97% after the calculations were performed using the absorbance values measured by Flame Atomic Absorption Spectrometer (FAAS) respectively. Langmuir isotherm, which describes the monolayer adsorption was found to be the most adequate to fit the overall procedure.

Keywords: Nanocomposites, magnetic nanoparticles, humic acid, metal removal, Langmuir isotherm

1. INTRODUCTION

There are two different types of pollutants in industrial waters as organic and inorganic pollutants. Inorganic pollutants mostly consist of heavy metal ions that result from industrial metal coating processes [1, 2]. Toxic heavy metal pollution is a global problem and new environmental regulations are required to control the release of heavy metal ion concentrations to the environment. Earlier, various types of materials and techniques were used for the removal of toxic ions, such as ultra-filtration, ion exchange chromatography, or precipitation [3 - 5]. However, adsorption on a magnetic surface is an easy technique to enrich or clean aqueous solutions when they have very low ion concentrations [6]. During magnetic separation a coated or modified surface first adsorbs the analyte and then an external magnetic field removes the particle with the analyte from the solution. The removed particles can be re-used after cleaning to repeat the adsorption process [7 - 9]. In this method, magnetic nano-sized particles form a

core/shell structure. Magnetic separation with these particles is a very fast, and eminently selective method. It is also very popular in environmental applications, mining, food & steel industries and biotechnology due to their practical industrial utilization. The magnetic property of nanoparticles depends on the surface coating, size and composition of the particles. Moreover, coating the synthesized nanoparticles with polymers or surfactants prevent the oxidation and agglomeration providing long-time stability within composites [10, 11].

In soil, the end product of microbiological decomposition of animals and plants are humic acids. These are large natural acidic organic polymers that are able to interact with cations and herbicides in soil. Cation binding mostly occurs because of carboxyl (COOH), carbonyl (C=O), hydroxyl (OH) or hydrophobic aliphatic and aromatic groups [12]. Some studies show the efficiency of calcium humate for the removal of some metals from wastewater such as iron, mercury, cadmium, and copper [13, 14]. Further studies show that humus based filters or humate can

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remove hydrogen sulfide, mercaptan, and sulfur dioxide [15]. Moreover, HA has high affinity for magnetic nanoparticles and a Fe₃O₄/HA, core/shell, structure is able to remove heavy metal ions with a 93% yield [16 - 18]. Although there are many studies using core/shell structures in the literature, to our knowledge there are few that focus on multiple component systems [19]. Humic acid which itself is a biodegradable substance can easily be used as an ecology friendly material. The aim of this study is to coat magnetite nanoparticles with humic acid and silver, forming a multicomponent nanostructure for the removal of heavy metal and bacterial pollution in water. In this part of the study only the synthesis of multicomponent nanoparticles and their synthetic heavy metal applications is reported. The combination of Fe₃O₄, HA and Ag for the synthesis of magnetic nanoparticles occurs for the first time in concept of this study bringing novelty in literature.

2. MATERIALS AND METHOD

2.1 Instrumentation

Varian Flame Atomic Absorption Spectrometer (FAAS) was used to measure the absorbance values of standard metal solutions and synthetic mixture solutions to observe the adsorption characteristics of synthesized composite particles. For an equal and homogeneous sorption process, an Edmund Bühler 7.400 Tubingen shaker was used. The Shaker period was adjusted to 300min⁻¹. A JOEL JSM-7600F Scanning Electron Microscope and FEI Quanta 250 FEG was used for the SEM analysis. Zeta potential analyses were made using ZetaPals Zeta potential Analyzer BIC (Brookhaven Inst. Corp.). A Chiltelrn Hotplate Magnetic Stirrer was used to achieve homogeneous heating during the co-precipitation process of nanoparticles. A regular magnet was used to collect particles from the sample solution. For successful coating at all stages of synthesis BANDELIN RK100H ultrasonic bath was used.

2.2 Chemicals and reagents

All reagents and standards were of analytical grade and were used without any further purification. All dilutions have been carried out with milliQ pure deionized water. The chemical reagents used in this procedure were Fluka ferrous chloride hexa hydrate (98% pure), Merck Ammonium iron(II)sulfate hexa hydrate, Aldrich Humic acid sodium salt, Merck Ammonia (%25), Merck Tin(II)chloride, Merck Hydrochloric acid, Fluka Silver nitrate, Fluka Sodium Hydroxide, Merck Copper(II) and Cadmium(II) standard solutions.

2.3 Synthesis Procedure of Magnetite Nanoparticles

Particles were prepared using co-precipitation process. A stoichiometric mixture of FeCl₃.6H₂O and

NH₄FeSO₄.6H₂O (molar ratio 1.5:1) was heated to 90°C for 45 minutes on Chiltelrn hot plate magnetic stirrer. For this purpose, 6.1 g FeCl₃.6H₂O and 4.2 g NH₄FeSO₄.6H₂O were weighed and dissolved in 100 mL pure water separately. Once the heating is over 10.0 mL of 1.0 mg L⁻¹ humic acid sodium salt solution was mixed along with iron(III) chloride and iron(II) chloride solutions and 10.0 mL 25% ammonia solution was appended immediately to precipitate HA coated magnetite nanoparticles. For a complete reduction and coating, heating was carried out in 90°C for an hour. Particles were washed with milliQ pure water twice and sonicated for 30 minutes. A simple magnet easily worked for the collection of particles from the bottom of the beaker, and a Pasteur pipette was used to collect supernatant from the surface. Very small particles with a very weak magnetic property were observed in supernatant liquid. These particles were discarded with the supernatant liquid.

After several trials, a redox reaction between Sn²⁺ ions and silver ions was found useful to coat the particles with silver [20]. Therefore, the coating of Fe₃O₄/HA particles with silver resulted in two steps and ultrasonication was used at the end of each. It is known that Sn²⁺ ions can reduce Ag⁺ to Ag⁰ and can be adsorbed on the HA surface through negatively charged groups. A 0.063 M acidic Tin(II) chloride solution was mixed with Fe₃O₄/HA particles and the mixture was sonicated for 30 minutes. Hence, Sn²⁺ ions were adsorbed on the surface of core/shell structure. After sonication, the mixture was cleaned with milliQ water twice. The second part of silver coating process consisted of the electrochemical plating of silver on the core/shell structure. The suspension was mixed with freshly made 0.13 M Tollen's reagent (ammonium silver nitrate), sonicated for 30 minutes and washed twice with milliQ water. At the end Fe₃O₄/HA/Ag magnetic particles were separated from the suspension by using a magnet and then dried at 60°C in air. Fig 1 below shows the schematic illustration of the formation of Fe₃O₄/HA/Ag multi-component structure.

2.4 Characterization of Synthesized Particles

The characterization of synthesized Fe₃O₄/HA/Ag composite structure was made using SEM and Zeta potential analysis. For each selected area on SEM, an EDX mapping analyses were made for surface elemental analysis. Sample preparation was carried out mechanically on dried samples. These samples were Fe₃O₄, Fe₃O₄/HA as the intermediates, and Fe₃O₄/HA/Ag as the final product.

The DLS experiments were conducted at a 90° angle using 35 mW solid state laser detectors operating at 658 nm. The change in the particle size in response to pH was also determined by DLS measurements, adjusting the pH with 0.1M HCl and 0.1M NaOH in 10⁻² M KNO₃ aqueous solution.

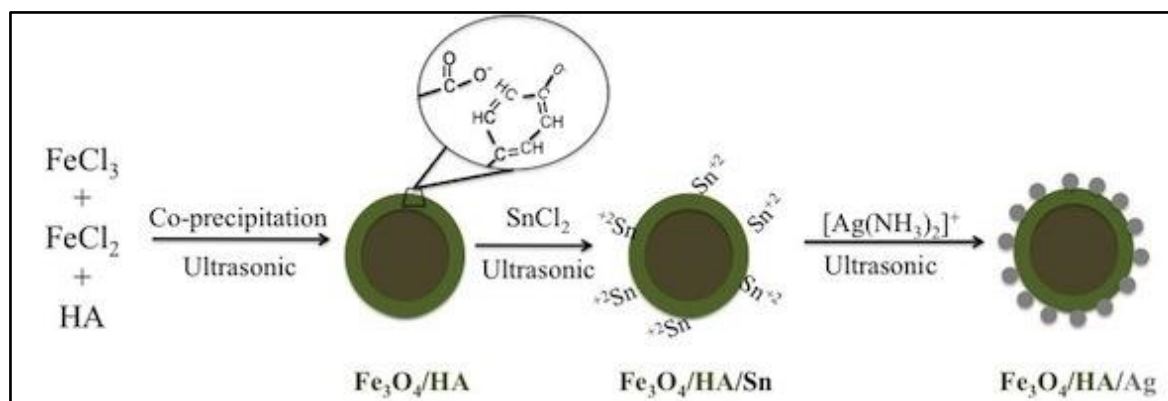


Fig 1. Schematic illustration of the formation of $\text{Fe}_3\text{O}_4/\text{HA}/\text{Ag}$ multi-component structure

A diluted aqueous solution of particles was prepared for the zeta measurements, which were carried out in triplicate, as were the DLS measurements. The first sample was diluted (portions were 1/50 and 1/100) with 10 mL KNO_3 in sonicator for 5 minutes. The second and third samples diluted in 10 mL KNO_3 and sonicated for 5 minutes. Only then, zeta potentials were measured.

2.5 Procedure of Heavy Metal Adsorption

The adsorption of copper and cadmium was investigated by batch adsorption method using FAAS. The initial concentrations of copper and cadmium were prepared in the concentration range of 1.0-3.0 mg L^{-1} for copper and 0.5- 2.0 mg L^{-1} for cadmium, respectively. Particles were collected with a magnet after the adsorption process has reached to the equilibrium. Adsorption parameters as pH value, sorption time, and particle mass on heavy metal removal were optimized in separate sets of experiments. pH value adjustments were made using 0.01 M NaOH and 0.001 M HCl solutions and values were varied to 3.0, 5.0, 7.0, and 9.0. In order to obtain the optimum pH value, the particle mass was set constant at 0.01 g with a 10 min. of contact time. On these conditions, the optimum metal removal was obtained at pH 9.0. All adsorption experiments were performed at pH 9.0 except those in which the effects of particle mass and contact time was investigated. Finally, three different trials were made with these optimized values and a mixture of cadmium and copper solutions were prepared to understand the selectivity of magnetic nanoparticle between two metal ions.

The adsorbed heavy metal amount (q_e) per unit absorbent mass was calculated as follows;

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where C_0 is the initial heavy metal concentration, C_e is the concentration of heavy metal at equilibrium (mg L^{-1}), m is the magnetite mass (mg) and V is the solution volume (L). Calculations were made using these data and adsorption curves of copper and cadmium on magnetic nanoparticles were obtained.

3. RESULTS & DISCUSSION

3.1 Characterization of $\text{Fe}_3\text{O}_4/\text{HA}/\text{Ag}$ Particles

A JOEL JSM-7600F and FEI Quanta 250 FEG SEM were used for the characterization. EDX mapping was performed for the surface elemental analysis. On the SEM images, the bright particles represent silver, the gray parts represent humic acid coated magnetite particles and the black parts represent empty spaces. Fig 2 and Fig 3 below show the SEM images of the intermediates and final products respectively. The most suitable closest image was obtained with $\times 50,000$ magnifications. The dispersion of silver particles was not uniform on the surface but EDX mapping proved the existence of silver shown in Fig 4. On EDX mapping, there was no sign of tin (II) which shows the efficiency of ultrasonication and repeated particle cleaning after each step.

The Zeta potential was used to prove negative charge of double layer and DLS analysis was used to procure the mean diameter size of particles. Since HA has negatively charged large groups on the surface, it was easy to predict that zeta potential of the particles had a negative value. Results showed that this value was -23.09 mV. According to Zeta potential data, synthesized multi-component structure can be accepted to have incipient stability. The DLS analysis showed that in the given conditions the mean diameter of the particles was as 291.0 nm. This results from large structure of humic acid and aggregation of particles during DLS measurement.

3.2 Optimization of Adsorption Parameters

3.2.1 Effect of pH

In the pH study, adsorption of ions investigated at varying pH values of 3.0, 5.0, 7.0 and 9.0. The particle mass was fixed 0.01 g with a contact time of 10 minutes. Adsorption percentages were calculated to compare the results and as it is seen on Fig 5-a, the maximum adsorption percentage was recorded at pH value 9.0 for the removal of copper and cadmium with 89.92% and 94.26% removal percentages, respectively.

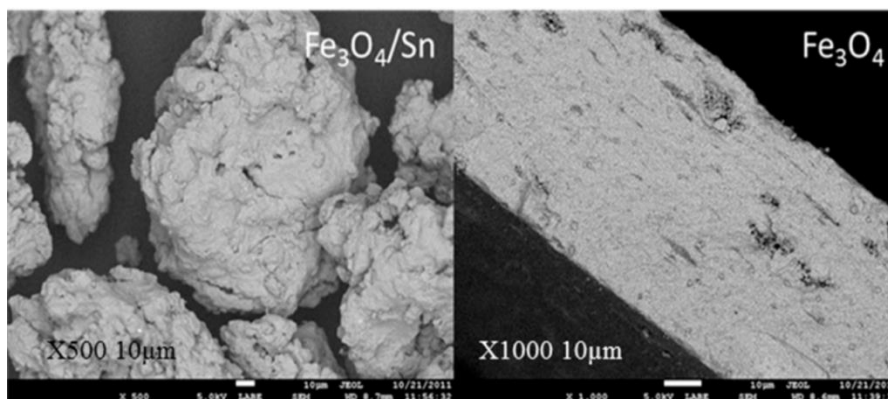


Fig 2. SEM images of intermediates a) in Fe₃O₄/HA nanoparticles after the dispersion of Sn⁺² solution ×500

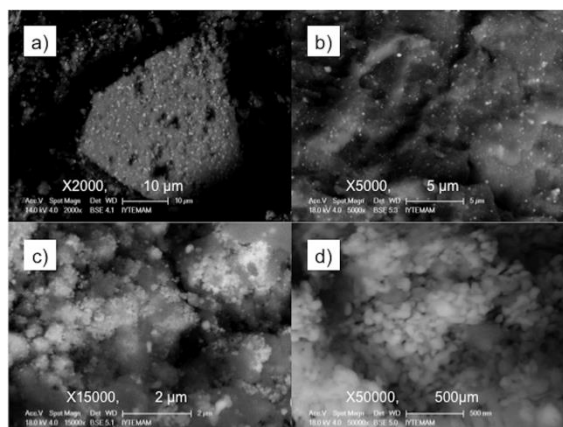


Fig 3. SEM images of the prepared Fe₃O₄/HA/Ag particles at different magnification ranges a) ×2.000 b) ×5.000 c) ×15.000 d) ×50.000

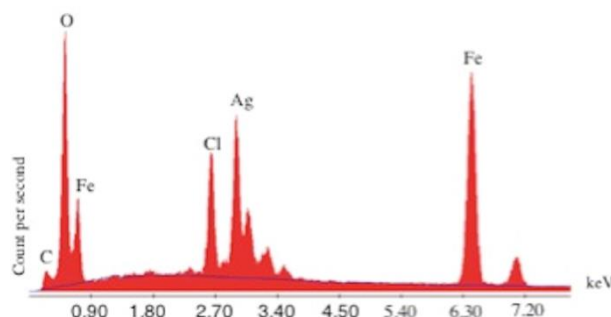


Fig 4. EDX mapping of the surface labeled as b on Fig 2

According to the studies reported in the literature, many different pH values were maintained due to the maximum adsorption of copper and cadmium. When compared to the other studies where pH value was kept at 9.0 removal percentage obtained in our study was found to be the highest.

3.2.2 Effect of Contact Time

During the investigation of contact time, adsorption process was performed using 0.01 g particles at a pH value of 9.0. The absorbance values were measured at time intervals of 5, 10, 20, 25, and 30 minutes and adsorption percentages were calculated. Adsorption of copper and cadmium was found to be 90.25% and 94.37% respectively. Although there were small fluctuations between 20 and 30 minutes contact time for copper and cadmium, the highest removal

percentage was accepted at 20 minutes for both metals. Fig 5-c found below, represents the removal percentages of cadmium and copper ions in the given conditions. This data related with the physical character of adsorption also gives clue about the favorability of increased surface area of the sorbent.

3.2.3 Adsorption Isotherms

For the design and analysis of adsorption process, adsorption isotherms should be well understood. Langmuir isotherm stands as the simplest theoretical model for the monolayer. By modeling single coating layer on adsorption surface it supposes that the adsorption takes place at a specific adsorption surface and as it gets further from the adsorption surface the attraction between molecules decrease [21].

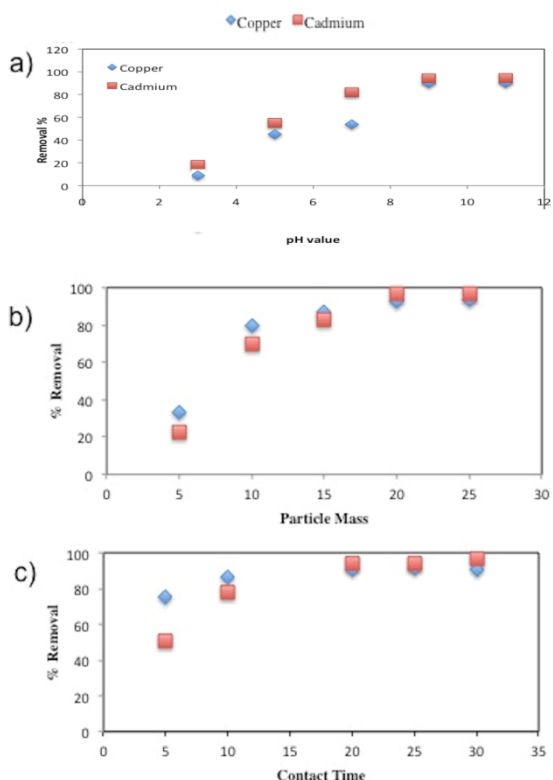


Fig 5. Influence of a) pH, b) particle mass and c) contact time on the removal of copper and cadmium by prepared Fe₃O₄/HA/Ag particles to aqueous solution containing Cd and Cu and 2 mg L⁻¹ respectively

The following formulas related to Langmuir isotherm are given below;

$$q_e = V_m k C_e / (1 + k C_e) \tag{2}$$

where q_e is the amount of adsorbed heavy metal per unit magnetite mass (mg g⁻¹), V_m is the monolayer capacity, k is the equilibrium constant and C_e is the equilibrium concentration of the solution (mg L⁻¹).

Eq. (2) can be linearized as follows:

$$C_e/q_e = 1/kV_m + C_e/V_m \tag{3}$$

The results obtained from the empirical studies were applied to Langmuir isotherm.

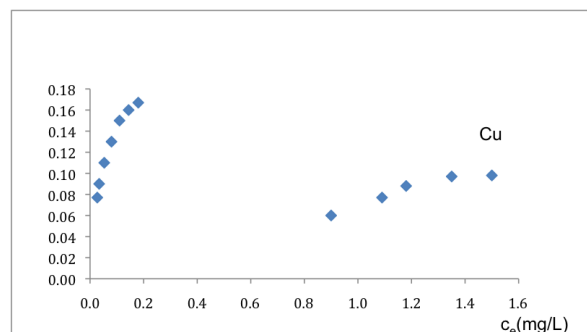


Fig 6. Adsorption isotherm of Cu and Cd on magnetic nanoparticle fits of Langmuir Model

The dependence of C_e/q_e from C_e was obtained by using empirical results. The linear form of Langmuir equation for copper and cadmium adsorption on magnetites are calculated with the aid of adsorption graph shown in Fig 7 and found as;

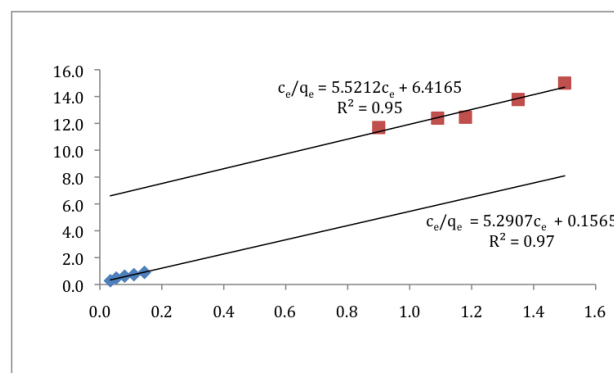


Fig 7. Linearized adsorption isotherm of Cu and Cd fits of Langmuir Model at 300 K

$$C_e/q_e = 5.2907C_e + 0.1565, R^2 = 0.97 \text{ for Cd} \tag{4}$$

$$C_e/q_e = 5.5212C_e + 6.4165, R^2 = 0.95 \text{ for Cu} \tag{5}$$

As it can be seen from Table 1, the Langmuir model can represent the actual adsorption data. Adsorption (q_e) reaches a plateau region (possibly corresponding to monolayer coverage) with respect to equilibrium concentration of the aqueous phase (C_e) beyond a limiting concentration, which is a characteristic property of the Langmuir isotherm.

Table 1. Parameters of Langmuir Isotherm

Name of metal adsorbed	Isotherm Equation	Slope	K_L	R^2
Cu	$C_e/q_e = 5.5212C_e + 6.4165$	5.5212	92.54	$R^2 = 0.9$
Cd	$C_e/q_e = 5.2907C_e + 0.1565$	5.2907	0.87	$R^2 = 0.97$

4. CONCLUSIONS

The Fe₃O₄/HA/Ag multi-component structure was synthesized using co-precipitation and electroplating methods. In order to build a multi-component system with three components, a redox reaction between Tin (II) chloride and Tollen's reagent is required otherwise it is not possible to coat the particles with silver. Hence, there are two intermediates obtained during the process. Ultrasonication and cleaning of the suspension after each step is very important because it allows a homogeneous core/shell structure to form. The SEM images supported with EDX mapping showed the existence of silver and humic acid in the structure and the mean diameter of synthesized particles were found as 291 nm in DLS analysis when their zeta potential was -23.09 mV. Between 92% and 98%, of the heavy metal ions were removed from the solution at optimum conditions. The optimum conditions were a pH value of 9.0, a 20 mg particle mass and 20 minutes of sorption time. The adsorption characteristics of magnetic nanoparticles were defined by Langmuir isotherm giving an adsorption capacity of 33.63 mg g⁻¹ for Cd and 0.87 mg g⁻¹ for Cu.

As an addition to this study, the antibacterial property of the synthesized particles, which were derived from the silver component, were observed but will be reported at a later date.

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