



Fabrication of glycine-functionalized maghemite nanoparticles for magnetic removal of copper from wastewater



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HIGHLIGHTS

- Glycine-functionalized magnetic nanoadsorbents are proposed for copper removal.
- Nanoadsorbents present highly efficient removal of copper ions from wastewater.
- Nanoadsorbents are magnetically separable and reusable for removal of copper.
- Synthesis utilizes a cost-effective and environmentally friendly procedure.
- Removal can be extended to other heavy metal ions from wastewater.

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ABSTRACT

Maghemite nanoparticles (MNPs) were functionalized with glycine, by a cost-effective and environmentally friendly procedure, as an alternative route to typical amine-functionalized polymeric coatings, for highly efficient removal of copper ions from water. MNPs were synthesized by co-precipitation method and adsorption of glycine was investigated as a function of ligand concentration and pH. The efficiency of these functionalized nanoparticles for removal of Cu²⁺ from water has been explored and showed that adsorption is highly dependent of pH and that it occurs either by forming chelate complexes and/or by electrostatic interaction. The adsorption process, which reaches equilibrium in few minutes and fits a pseudo second-order model, follows the Langmuir adsorption model with a very high maximum adsorption capacity for Cu²⁺ of 625 mg/g. Furthermore, these nanoadsorbents can be used as highly efficient separable and reusable materials for removal of toxic metal ions.

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1. Introduction

Contamination of water with toxic metal ions is becoming a severe environmental and public health problem. Thus, rising demands for clean and safe water in extremely low levels of heavy metal ions make it greatly important to develop improved technologies for heavy metal ions removal. The conventional methods commonly used for the removal of metals from liquid effluents, such as precipitation and flocculation, have several disadvantageous features such as expensive equipment requirement, continuous replenishment of chemicals, time consuming and easy to produce secondary pollution. Alternative methods, as adsorption, present several advantages on the other tech-

niques for water reuse in terms of the initial cost, simplicity of design, ease of operation, low quantity of residues generated, easy recovery of metals and the possibility to reuse the adsorbent [1]. Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles (NPs), nanofiltration or other products resulting from the development of nanotechnology [2]. Particularly, nanostructured materials have been investigated due to its high superficial adsorbent area and capability of functionalization with different molecules. Moreover its unique physical and physico-chemical properties (structural, electrical, optical, magnetic, etc.) can provide unprecedented opportunities for the adsorption of heavy metals ions in highly efficient and cost-effective approaches. Advantageously, the manipulability of magnetic nanoparticles by an external magnetic field gradient opens up many applications involving the environmental area [3,4]. However, bare magnetic nanoparticles present non-specific adsorbent surface, easily

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aggregating in aqueous systems so that, for effective application, the stabilization of the nanograins by surface modification is desirable. The performance of these nanosystems depends on the nature of the magnetic core and the coatings, which must be of a non-toxic and adsorptive material. By far, magnetite is the most commonly magnetic core employed in these applications, nevertheless it easily oxidizes to maghemite – a more stable magnetic oxide – in aqueous media. Most of these coatings which have been utilized for separating and removing metal contaminants of water are based on biocompatible polymeric matrixes or long chain molecules [5,6]. Nevertheless, in spite of bringing specificity to the nanograins, the non-magnetic coating decreases the saturation magnetization and increases the particle volume. It is important to consider that smallest particles present highest adsorption capabilities and high magnetizations optimize the magnetic separation. To avoid these constraints, an alternative to polymer coatings is the chemical modification of the magnetic nanoparticle surface by small functional molecules.

In this way, glycine was chosen as it is a short molecule with carboxylate groups, easily adsorbed onto the iron oxide surface, and $-NH_2$ groups at surface that could interact with the bio-environment. In fact, the potential of amine-functionalized magnetic nanoparticles was already evidenced for magnetic removal of organic contaminants [7] and heavy metals in water treatment [8–13]. Nevertheless, in these works, authors use polymers or long chains to functionalize magnetite nanoparticles before application on metal removal.

To our knowledge, the papers that study the incorporation of amino acids in the elaboration of magnetic colloids deal normally with the synthesis of magnetite cores followed by its functionalization with different amino acids [14–19] or even synthesizing magnetite nanoparticles in the presence of amino acids, in one step [20]. Specifically for glycine, Viota et al. [21] discuss the electrokinetic characterization of magnetite nanoparticles functionalized with different amino acids, including glycine and Barick and Hassan [22] show a single-step approach for the synthesis of glycine-passivated Fe_3O_4 nanoparticles, both for biomedical applications. Thus, the innovation of this work is, mainly, the use of glycine-functionalized magnetic nanoparticles for the highly efficient magnetic removal of Cu^{2+} from wastewater. This indicates a cost-effective and environmentally friendly procedure since it involves a safe route of synthesis for magnetic nanograins and the use of the low-cost and low-toxicity molecules of glycine.

In spite of the saturation magnetization of maghemite ($\gamma-Fe_2O_3$) being slightly lower than the one of magnetite (Fe_3O_4), maghemite was chosen in this work since the difference of magnetization is largely counterbalanced by the gain of chemical stability. In fact, magnetite nanoparticles can dissolve in acidic medium: this dissolution is faster as the particles size is smaller, and as the concentration of acid is higher [23]. In order to avoid this dissolution, magnetite can be deliberately oxidized to maghemite [24].

In the present work, a series of experiments of glycine adsorption on MNP from aqueous solutions at different initial concentrations and pHs were performed. To elucidate the interaction between glycine and maghemite during adsorption, several techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), magnetization measurements, dynamic light scattering (DLS), Fourier transform infrared (FTIR), and thermogravimetric analysis (TGA) were employed. Thus, the applicability of amine-functionalized NPs in the removal of Cu^{2+} was evaluated in the view of pH, time and adsorbate/adsorbent concentrations. The adsorption kinetics and adsorption isotherms were investigated by using the conventional models of adsorption. The synthesis method proposed here has some clear advantages including low-cost, simplicity, high quality, ease of scale-up and good reproducibility. Moreover, results indicate that copper adsorption

Table 1

Percentual of adsorbed glycine and surface coverage by ligand.

Mass ratio glycine:MNP		Surface coverage	
$R_{G:M}$ (%)	$R'_{G:M}$ (%)	(Molecules/nm ²)	θ
2	1.96	0.90	0.27
5	3.16	1.44	0.43
10	8.55	3.91	1.17
25	9.59	4.38	1.32
50	9.77	4.47	1.34
75	9.91	4.53	1.36

$R_{G:M}$ is the mass percentage of glycine used in functionalization, $R'_{G:M}$ is the mass percentage of glycine adsorbed on NPs and θ is the surface coverage in area by the molecules on the NPs.

capacity was larger than many other reports on the adsorption of metal ions by magnetic materials.

2. Experimental

2.1. Synthesis of maghemite nanoparticles (MNP)

For the synthesis of $\gamma-Fe_2O_3$ nanoparticles, an adaptation of the method described in reference [25] was used: 50 mmol of NH_4OH was added to an aqueous solution containing 1.5 mmol of Fe^{2+} and 3.0 mmol of Fe^{3+} at room temperature. The resulting mixture was heated to reflux at boiling temperature under vigorous stirring. After 6 h precipitate was collected and washed with water several times after successive centrifugations.

2.2. Functionalization with glycine (Gly@MNP)

The typical approach employed for the functionalization of nanoparticles was used, as follows: 500 mg of MNP sample and an aliquot of 0.5 mol/L glycine, sufficient to give the mass ratios ($R_{G:M}$) between glycine and maghemite that are specified in Table 1, were introduced in a test tube. Thus, the pH was adjusted to the desired value and the volume completed to 2000 μ L. After 60 min of mixing in a vortex agitator, solid was separated from supernatant by magnetic decantation or by centrifugation, washed once with water and dried under vacuum at room temperature.

2.3. Procedure of Cu^{2+} adsorption and kinetics

For adsorption investigation, in a typical experiment, 7.5 mg of the as-prepared Gly@MNP ($R_{G:M} = 10\%$) was added into a 50 mL of 5 mg/L Cu^{2+} solution. The mixture was adjusted to pH 6.5 with HCl and NaOH and stirred for 120 min. Thereafter, magnetic adsorbent with adsorbed copper ions were separated from the mixture with a permanent hand-held magnets (NdFeB ~ 0.3 T). The residual Cu^{2+} in the solution and nanoparticles was determined with ICP-OES [26]. In order to obtain the adsorption isotherms, solutions with varying initial concentration of copper were treated with the same procedure as above at room temperature. Control samples with only distilled water were utilized and monitored for the duration of all experiments.

2.4. Nanoparticles characterization

XRD was performed on powder samples with a Bruker D8-Focus Discover diffractometer using radiation of 1.541 Å (40 kV and 30 mA). TEM images were obtained on a JEOL 1100 microscope operating at an accelerating voltage of 80 kV. The room-temperature nanoparticle magnetization curves were obtained using an ADE vibrating sample magnetometer model EV7. Hysteresis loops were performed under applied magnetic fields varying from -18 to 18 kOe at 300 K. A dynamic light scattering analyzer

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