

# Peptides Conjugated-Magnetite Nanoparticles for Heavy-Metal Detoxification

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## Introduction

Environmental pollution has increased proportionally with economic growth, generating a loss in the quality of air, water and soil because industrialization and mining directly or indirectly discharge large amounts of toxic metals, such as cadmium and lead, threatening the environment. Therefore, it is recognized as one of the most important problems of the 21st century [1]. Heavy metals are considered strong environmental contaminants, their toxicity being a problem of growing importance from ecological, evolutionary, nutritional, and environmental perspectives [2]. This is because, once emitted, they are neither chemically nor biologically degradable, affecting the quality of the different ecosystems with repercussions on the entire food web and generating problems for human health [3]. Nanotechnology has gained attention in recent decades due to the unique physical properties of nanoscale materials. In the case of magnetite nanoparticles, due to their large surface area, it is possible to modify their surface with specific molecules, such as peptides, to increase the heavy metal affinity [4]. As mentioned before, metals, especially non-essential ones, have toxic effects on living beings. As a consequence of exposure to these metals, cells have developed a series of detoxification mechanisms, such as bioprecipitation, bioadsorption and bioaccumulation, among others. In the latter case, the cells, when in contact with metals such as Cd and Pb, synthesize molecules with the ability to chelate them; among these molecules are metallothioneins, phytochelatin and glutathione [4]. Nanotechnology has gained attention in recent decades due to the unique physical properties of nanoscale materials, such as magnetite, known for its magnetic properties and its large surface area, which allows its surface to be modified with functional groups that can form specific molecules like heavy metals [5]. Functionalized magnetite nanoparticles (MNPs) to remove heavy metals in water are becoming very important for the recovery of aquatic ecosystems, since they are excellent sorbents of these metallic contaminants, and their superparamagnetic properties prevent their agglomeration and allow them to be quickly removed along with the contaminants from the solutions by magnetism [6]. Solutions are currently being sought hand in hand with nanotechnology to reduce the concentrations of heavy metals in different aquatic ecosystems. According to that, this research aims to test the capacity of peptide nanoconjugates for the removal of cadmium and lead in aqueous solutions.

## Results and Discussion

Two peptide nanoconjugates were synthesized. First, the synthesis of magnetite nanoparticles (Fe<sub>3</sub>O<sub>4</sub> MNPs) was carried out by co-precipitation of Fe(II) and Fe(III) in ammonia solution. Then these nanoparticles were directly functionalized with glutathione (MNPs@GSH). On the other hand, modified MNPs on their surface with (3-aminopropyl) triethoxysilane (APTES) were used to be then functionalized with previously protected and activated phytochelatin 2 (MNPs@APTES-PC2).

As a first step, the adsorption of cadmium and lead on MNPs@APTES-PC2 at pH 6 and different initial concentrations of Cd(II) and Pb(II) (1, 10, 30, 50 and 100 ppm) was evaluated. The concentrations of both metals were measured by atomic absorption spectroscopy (Table 1). The nanoconjugate MNPs@APTES-PC2 had a lead removal of 95% at 1 ppm from aqueous solution, followed by 57.9% removal at 10 ppm. As seen, as the Pb concentration increased, the percent removal decreased.

Table 1. Percentages of Cd and Pb removal by MNPs@APTES-PC2.

<i>Metal</i>	<i>Initial Concentration (ppm)</i>	<i>% Removal</i>
Cd	1	0.1
	10	2
	30	18.2
	50	13.3
	100	7.2
Pb	1	95
	10	57.9
	30	24.8
	50	17.5
	100	12.1

The highest percent of Cd removal was 18.2% at 30 ppm, followed by 13.2% at 50 ppm. Also in this case, its removal decreased with increasing concentrations, implying that this nanoconjugate has a sufficient number of adsorption sites to adsorb metal ions. However, at higher concentrations, the adsorption sites of the nanoadsorbents would become saturated due to the increasing ratio between the number of metal ions and the number of adsorption sites [7].

Table 2. Adsorption isotherm parameters for the removal of Cd(II) and Pb(II) from aqueous solution with MNPs@APTES-PC2.

<i>Isotherm</i>	<i>Parameters</i>	<i>Metal</i>	
		<i>Cd(II)</i>	<i>Pb(II)</i>
Langmuir	<i>K</i>	-0.015	0.128
	<i>b</i>	-39387	30.864
	$R^2$	0.278	0.957
Freundlich	<i>Kd</i>	0.004	6.988
	1/n	2.130	0.332
	$R^2$	0.939	0.979

To determine the capacity and the adsorption process of the MNPs@APTES-PC2 nanoconjugate, Langmuir and Freundlich isothermal models for Cd(II) and Pb(II) were performed. From the linearized fit it was observed that for the adsorption of both metals the model that better fitted the experimental data was the Freundlich model, being the correlation coefficient  $R^2$  0.939 for Cd(II) and 0.979 for Pb(II) (Table 2). It should be noted that the Freundlich isotherm indicates a heterogeneous nature of the surface, which lacks a plateau, indicating a multilayer adsorption, with different adsorption energies and with non-identical adsorption sites that are not always available [8].

For the nanoconjugate MNPs@GSH, the adsorption experiments with both metals were carried out at pH 6 and at different concentrations (10, 30, 50 and 100 ppm) (Table 3). In the removal assays, it was found that the highest percent removal was for Cd with 27.84% at 50 ppm. The percent removal of Pb with this nanoconjugate was much lower, being 8.20% at a concentration of 10 ppm, again percentage removal of Pb(II) decreased with concentration, exhibiting the same pattern of removal obtained with MNPs@APTES-PC2.

Table 3. Percentages of Cd and Pb removal by MNPs@GSH.

<i>Metal</i>	<i>Initial Concentration (ppm)</i>	<i>% Removal</i>
Cd	10	0.5
	30	0.4
	50	27.8
	100	16.3
Pb	10	8.2
	30	3.47
	50	4.08
	100	1.43

Taking into account the above results, the highest percent removal was for Cd. This agrees with data reported by Jacquart et al. [8], where the complexes with Cd(II) had greater affinity than with Pb(II), and are driven by the enthalpy change that occurs with the thiol groups of GSH and this metal [8]. In GSH-Cd(II) and GSH-Pb(II) complexes, only one thiol group could bind to the metal ion compared to PC2, which can bind up to two ions [9]. In the case of MNPs@GSH, it is not possible to determine which is the adsorption site, since with the functionalization carried out in this study, the GSH was able to bind to the magnetite either by the -NH<sub>2</sub> group or by the -SH group, as reported by Maleki et al. al., (2020). In the case of the adsorption of MNPs@GSH with the Cd(II) ion, it can be seen that the adsorption capacity of this nanoconjugate increases at the concentration of 50 ppm and this can be attributed to the increase in the driving force for the mass transfer between the aqueous and the solid phase when increasing the concentration of Cd(II) [9,10].

Table 4. Adsorption isotherm parameters for the removal of Cd(II) and Pb(II) from aqueous solution by MNPs@GSH.

<i>Isotherm</i>	<i>Parameters</i>	<i>Metal removed</i>	
		<i>Cd(II)</i>	<i>Pb(II)</i>
Langmuir	<i>K</i>	-0.012	0.157
	<i>b</i>	-0.865	40
	<i>R</i> <sup>2</sup>	0.435	0.917
Freundlich	<i>Kd</i>	0.000	1.100
	1/n	2.892	0.299
	<i>R</i> <sup>2</sup>	0.674	0.569

In the case of Cd(II) neither the Langmuir nor the Freundlich isothermal models (Table 4) fitted the data with this nanoconjugate, while in the case of Pb(II) removal from aqueous solution, the model that better fitted the experimental data was the Langmuir isotherm, where the correlation coefficient  $R^2$  was greater than 0.90; the parameters resulting from these modeling are shown in Table 2. It should be noted that the Langmuir model indicates that all active adsorption centers are equivalent and that the ability of a molecule to bind to the surface is independent of whether or not there are positions next busy. Furthermore, adsorption is restricted to a monolayer and there are no lateral interactions between the adsorbate molecules [11].

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