Voltammetric Study of the Affinity of Divalent Heavy Metals for Guanine Functionalized Iron Oxide Nanoparticles

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INTRODUCTION

Heavy metals are non-biodegradable, ubiquitously distributed and can lead to great risk on human health and the environment. The toxicity mechanism of heavy metal ions is through impaired antioxidant mechanism, enzyme inhibition and oxidative stress. Consequently, the on-site monitoring and removal of heavy metals is of great importance.

Recently nucleobases and their derivatives have proved to be of interest in the therapeutic, biological and chemical fields, including heavy metals complexation. However, their use for on-site heavy metal sensing and removal is still being developed. On the other hand, nanoparticles (NPs), and specifically magnetic nanoparticles, are gaining wide recognition in almost all fields due to their unique magnetic properties as well as their low toxicity and biocompatibility.

Amongst the different methods developed for heavy metal adsorption and determination, electrochemical techniques have shown superior performance compared with conventional methods. They offer simplicity, rapid analysis, possibility of in-field application, along with excellent sensitivity and selectivity.

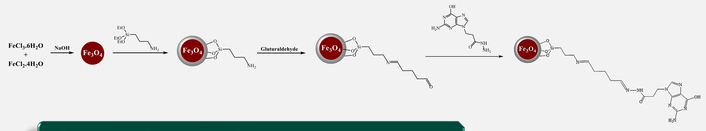
OBJECTIVES

- Synthesize magnetic beads.
- Functionalize the beads with a nucleobase derivative: guanine hydrazide (GH).
- Evaluate the electrochemical interaction of some divalent ions (Cd^{2+}, Cu^{2+},Pb^{2+}) with the beads.

METHODS

Magnetic beads synthesis

The iron oxide nanoparticles were synthesized using a modified Massart's method by mixing ferrous and ferric chloride in basic medium. The nanoparticles were then coated with (3-aminopropyl)triethoxysilane (APTES) followed by functionalization with guanine hydrazide using glutaraldehyde as a crosslinker.



Electrochemical measurements

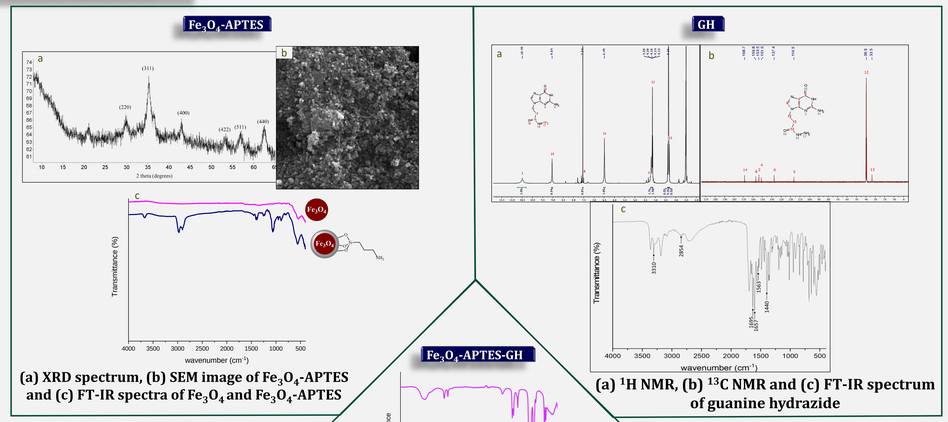
All electrochemical measurements were performed using a PalmSens4 in a citrate buffered medium pH 4. A conventional three electrode system was employed:

- Working electrode: boron doped diamond modified with the magnetic beads
- Counter electrode: Platinum
- Reference electrode: Ag/AgCl

Square Wave Voltammetry
- frequency 50 Hz
- amplitude 50 mV
- step potential 10 mV
- time of equilibration 2 min

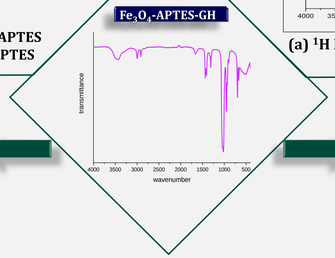
RESULTS

Characterization



(a) XRD spectrum, (b) SEM image of Fe_3O_4-APTES and (c) FT-IR spectra of Fe_3O_4 and Fe_3O_4-APTES

(a) ^1H NMR, (b) ^{13}C NMR and (c) FT-IR spectrum of guanine hydrazide

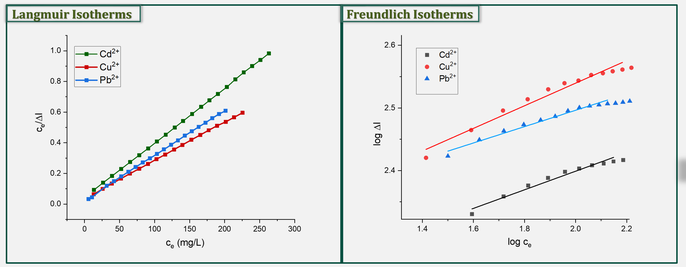


Crosslinking between APTES and GH was confirmed

- peak at 1663 cm^{-1} corresponding at C=C
- shift in the peak corresponding to N-H stretching from 3672 cm^{-1} to 3440 cm^{-1} is consistent with N-H stretching of an amide group along with an increased peak intensity
- $-CH_2$ stretching peaks also increased in intensity due to the increased number of CH_2 groups from the hydrazide function

Adsorption studies

The adsorption capacity of the guanine functionalized iron oxide nanoparticles for three heavy metal ions (copper, cadmium and lead) was investigated using Langmuir and Freundlich isotherms. Each experiment was done in triplicates. The adsorption isotherms of the heavy metals were built using the variation of the peak maximum (ΔI) of the electrochemical signal, which is proportional to the adsorbed concentration of the heavy metals at the modified electrode surface, and the concentration of heavy metals at equilibrium (c_e).

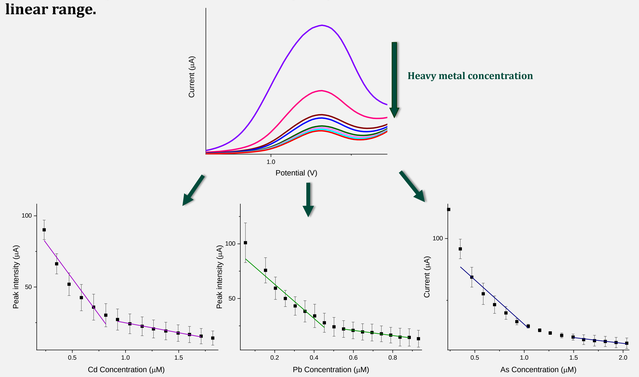


Isotherm	Langmuir				Freundlich		
Constants	Q_0 ($mg.g^{-1}$)	b ($L.mg^{-1}$)	R_L	r^2	n	k_F ($mg.g^{-1}$)	r^2
Cd^{2+}	280.1	0.087	0.0394	0.9999	6.4168	122.7	0.9677
Cu^{2+}	400	0.0707	0.0341	0.9998	5.125	142.5	0.9758
Pb^{2+}	343.6	0.1046	0.0271	0.9999	7.3986	168.7	0.9796

- Adsorption is favorable for all the studied heavy metals
- Adsorption capacity of the functionalized nanoparticles towards the studied heavy metal ions decreases in the following order: $Cu^{2+} > Pb^{2+} > Cd^{2+}$
- Adsorption is of a typical monomolecular layer form
- Adsorption is localized, all active sites have similar energies and no interaction between the adsorbed molecules exists

Analytical performance

The analytical performance of the synthesized beads was assessed electrochemically using square wave voltammetry. Upon increasing the concentration of each heavy metal, the signal corresponding to guanine hydrazide at 1.1 V decreased. For each heavy metal, 2 distinct linear ranges were observed. The sensitivity and limit of detection (LOD) were determined based on the first linear range.



Linear ranges of (a) cadmium, (b) lead and (c) copper at the GH-APTES-Fe_3O4 NP electrode

Heavy metal	Sensitivity (µA/µM)	Linear range (µM)	LOD (µM)
Cu^{2+}	171.6	0.209 – 1.03	0.069
Cd^{2+}	101.4	0.483 – 4.97	0.077
Pb^{2+}	156	0.232 – 0.809	0.0161

CONCLUSIONS

- The magnetic beads were successfully synthesized and functionalized.
- The Langmuir isotherm was a better model for the adsorption.
- Adsorption isotherms showed that the adsorption capacity of the nanoparticles decreased with increasing ionic radii and electronegativity of the heavy metals.
- The signals generated by square wave voltammetry exhibited two distinct linear response ranges along with sensitivities towards the heavy metals following the same order as the adsorption capacity.

PERSPECTIVES

- Evaluate the adsorption behavior and assess the electrochemical performance using different nucleobase derivatives and with other heavy metals.