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Study of Hg²⁺ adsorption on nanoscale magnetite-based samples

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Abstract

Nanoscale magnetite (Fe_3O_4) and nanocomposite (NC) (Fe_3O_4/DMSA (meso-2,3-dimercaptosuccinic acid)) were synthesized, and their composition and acid-base properties were studied by infrared spectroscopy and potentiometric titration. The changes of solution concentrations before and after adsorption of Hg^{2+} were determined by UV-Vis spectroscopy with disubstituted dithizone (λ = 490 nm). The dependence of the adsorption activity on the pH and the isoelectric point (pI) of the surface is established. Experimental kinetic dependences and sorption isotherms were analyzed for compliance with theoretical models that take into account the processes of chemical interaction in the sorbent - sorbate system. It is established that the kinetic dependences of the sorption of Hg^{2+} ions can well describe by the kinetic model of the pseudo-second order, the sorption isotherms fit by the Freundlich model. The obtained results can be useful in the creation of magnetically controlled sorption materials for the extraction of Hg^{2+} ions from aqueous solutions.

Keywords: magnetite, nanocomposite, modification, kinetics, adsorption, Hg^{2+} ions.

I. Introduction

A lot of promising sorption materials for detoxification of aquatic and biological media from heavy metal ions (Kusyak (2015), Melnyk (2018)), as well as for the most hazardous Hg^{2+} ions, were created by chemical design of nanostructures based on single-domain magnetite. Due to the formation of strong complexes with mercury ions, the surface of such materials is mainly functionalized with thiol groups. The use of 3-mercaptopropyltrimethoxysilane (MPTMS) (Lin (2017) as a modifier allows obtaining stable nanocomposites (NCs) at different pH values with high sorption capacity. In addition, the source of functional SH-groups on the surface of the composites may be DMSA, which is known as a chelating agent. The physicochemical properties of such NCs are characterized in the work of Usov (2009), toxic effects evaluated by Zhang (2016). The purpose of this work is to compare the adsorption properties of non-functionalized nanosized Fe_3O_4 and Fe_3O_4/DMSA to Hg^{2+} ions under the same conditions from aqueous solutions.

II. Experimental Set-up and Procedure

Synthesis of nanosized Fe_3O_4: nanodisperse magnetite in the single-domain state was synthesized by the Elmore reaction: $Fe^{2+} + 2Fe^{3+} + 8NH_4OH \rightarrow Fe_3O_4 + 4H_2O + 8NH_4^+$.

Synthesis of Fe_3O_4/DMSA: surface modification of Fe_3O_4 NPs was performed by DMSA as in Usov (2009).

Investigation of acid-base surface characteristics of Fe_3O_4 NPs and Fe_3O_4/DMSA NC: the pH values of the pI were determined by the potentiometric titration techniques.

Hg^{2+} *adsorption study:*

The dependence of the adsorption activity of composites on pH was carried out in the pH range 3 – 7.7; kinetic dependences (C_{Hg}^{2+} = 36 mg l⁻¹, pH = 3, contact time - 15 - 180 min), and sorption processes (C_{Hg}^{2+} = 1 - 40 mg l⁻¹, pH = 3) were studied.

Experimental data were used to calculate the capacity of sorbent A (mg g⁻¹) and the degree of extraction R (%) by the formulas:

$A = (C_0 - C_{eq})\cdot V/m;$

$R = ((C_0 - C_{eq})/ C_0)\cdot 100\ \%$

where C_0 – is the concentration of the initial solution (mg l⁻¹); C_{eq} – is the equilibrium concentration of the solution after adsorption (mg l⁻¹); V – is the volume of the solution (ml); m – is the mass of the adsorbent (g).

III. Analysis

The study of synthesized samples and adsorption processes was carried out by a set of physicochemical methods: the specific surface area ($S_{sp.}$) of the samples was determined from isotherms of low-temperature adsorption-desorption of nitrogen measured on a sorptometer KELVIN 1042 Sorptometer "COSTECH Instruments"; composition study of synthesized and modified samples was performed by IR-spectroscopy on"Perkin Elmer", 1720X equipment; potentiometric measurements were done on I-160M; determination of the concentration of Hg^{2+} ions before and after contact with the adsorbents was performed on ULAB 102UV (λ = 490 nm, disubstituted dithisonate Hg^{2+} in CCl_4).

IV. Results and discussions

The synthesized Fe_3O_4 NPs in the original ensemble are characterized by sizes 3–23 nm and a single-domain state. A slight increase in the values of the specific surface area ($S_{sp.\ (Fe3O4)}$ = 105 m²/g, $S_{sp.\ (Fe3O4/DMSA)}$ = 140 m²/g) indicates the functionalization of magnetite and an increase in dispersion.

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The IR spectrum of Fe_3O_4/DMSA is characterized by the presence of three main groups of absorption bands S-S, C=O and S-H bonds at 550, 1400, 1630 and 2505 - 2510 cm^{-1}, respectively, that confirm the presence of the products of the modification on the NC surface. Also due to the modification, there were changes with the pI and its value moved to a more acidic pH range pI (Fe_3O_4) = 6.8, pI (Fe_3O_4/DMSA) = 3.5.

It was found that the highest sorption R (%) for the studied samples occurred at pH=3, which is consistent with the acid-base properties of the surface and literature data on the existence of neutral and anionic forms of Hg^{2+} at higher pH values in solution.

Experimental kinetic curves were analyzed using models that take into account the contribution of the chemical reaction to the sorption process. The high correlation coefficient (r^2 = 0.993) and similar values of experimental and calculated adsorption indicate the correctness of using the pseudo-second order model. Langmuir and Freundlich models were used to quantify equilibrium processes. The values of r^2 during linearization indicate the correctness of the use of the Freundlich model for the calculation of sorption parameters (Fig. 1, Tab. 1).
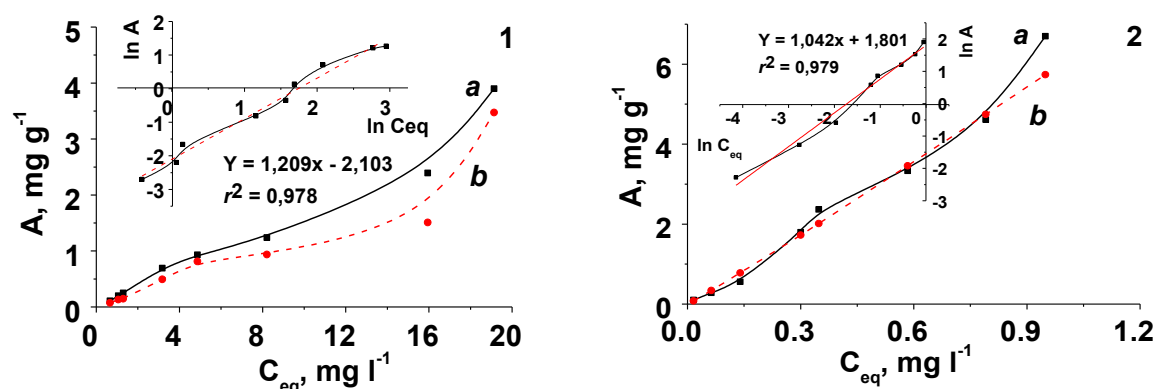

Fig. 1 Isoterms of Hg^{2+} adsorption on Fe_3O_4 NPs (1) and Fe_3O_4/DMSA NC (2) obtained from adsorption experiment (a); calculated from the parameters of the Freindlich equation (b); on inserts - linearized form of Freindlich isotherm

Tab. 1: Values of sorption parameters calculated using the Freundlich model

Sample	A mg g^{-1}	Freundlich model			
		A_{cal} mg g^{-1}	K_F	n	r^2
Fe_3O_4	3.54	4.32	0.122	0.827	0.978
Fe_3O_4/ DMSA	6.69	5.73	6.05	0.959	0.979

V. Conclusions

The processes of Hg^{2+} adsorption (pH dependence, kinetics, concentration changes) were studied. on the surface of Fe_3O_4 NPs and Fe_3O_4/DMSA NC have been studied. It has been shown that the adsorption and the degree of extraction of Hg^{2+} ions increase on DMSA modified surface from 55% to 99%. The highest correlation coefficients were obtained for the pseudo-second order kinetic model from mathematical analysis of the kinetic adsorption curves of Hg^{2+} ions. The fitting of experimental isotherms to the Freundlich model of adsorption isotherms confirms the heterogeneous nature of the surfaces of the synthesized materials.

Synthesized Fe_3O_4/DMSA NC can be used to extract Hg^{2+} ions from aqueous solutions at low pH values.

Acknowledgements

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