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Sorption Concentration of Ions of Copper (II) and Lead (II) By Magnetic Sorbent.

Damir A. Kharlyamov*, Ilnar A. Nasyrov, Radif R. Zinnatov, Gennady V. Mavrin and Mikhail P. Sokolov.

Kazan Federal University, Russia, 423810, Naberezhnye Chelny, Prospect Mira, 68/19.

ANNOTATION

By a chemical method, using a method offered by Massart, where as the use of initial solutions of chlorous and chloric iron magnetite is produced, possessing sorbate properties in relation to the ions of lead(II) and copper(II). Influence of different factors (pH, temperature, time) on the degree of sorption is investigated. A specific surface area of magnetite is measured by the method of Bruner-Emmet-Teller on the analyzer of NOVA 1000e. Structural parameters and phase composition of standards are investigationed by X-ray fluorescence energy-dispersive spectrometer of brand «BRA-18». The best values of acidity of environment are determined for flowing of sorption process on magnetite. Conducted measurements of ζ -potential before and after the sorption indicate the change of charge of double electric layer at the surface of magnetic iron metal-lics, that is related to adsorption of the positively charged cations of the solution. Influence of the interfering ions is indicated, influence of phosphates and sulfates is set on the sorption of IST. The isotherms of sorption of IST are got on magnetic iron. The offered method is tested on the standards of the melted water of snow-cover in the affected of casting production zone.

Keywords: heavy metals, sorption, concentration, magnetite.

**Corresponding author*

INTRODUCTION

Analysis of the maintenance of small concentrations of ions of heavy metals (IHM) in the objects of environment is an actual analytical task. However insignificant concentrations of analysable matters, the presence of interfering ions and difficult composition complicates and sometimes does impossible the receipt of reliable results. Usually procedure of analysis includes the selection of test, sample preparation, measuring and treatment of results. However, a researcher on the stage of measuring of analytical signal can run into the row of problems related to the sensitiveness of the applied method. One of perspective ways of solution is the application of method of concentration on the stage of preparation of the test sample for the analysis. The use of concentration allows to shorten the volume of the test, decreasing the influence of test samples and increasing the sensitiveness of analysis [1].

For a concentration use the great number of different methods: freezing, evaporation, besieging, sorption extraction and other [2]. At the analysis of small maintenances of elements most effective is a sorption method allowing to conduct the concentration of microcomponents from the large volumes of solutions on relatively small mass of sorbent [3]. Main dignity of sorption method consists in that he practically does not bring in new, extraneous ions and matters in the cleared solution. It allows to use him for the regeneration of row of technological solutions, and also for cleaning of muddy waters.

Last years the special attention is spared microfine powder-like sorbents. Because of their high specific surface of sprinkle of snow with ultra-fine particles possess maximal sorbing properties and are perspective materials for deleting from water of chemical admixtures [4]. However friendly to the sorption small size of particles, to a great extent hampers the processes of separation of sorbents from water solution by the generally accepted methods of filtration and defending. The described problem can be decided, if as a sorbent to apply particles, possessing magnetic properties which after adsorption of pollutants can be dissociated from solution through magnetic separation.

The example of sorbent, possessing magnetic properties, is magnetite. In works of foreign authors sorption activity of particles of magnetite is demonstrated relatively IHM, phenol, nitrates [5, 6, 7, 8]. Also a few methods of water treatment are now known from different contaminations with the use of magnetite, speaker in a role of sorbent, or being an element, built in different filter elements [9]. Magnetite is applied as an active layer of running filters, or as a sorbent with the further removal of bound particles by facilities of magnetic separation [10]. The use of magnetite is known as a sorbent for deleting of oil and oil-containing organic pollutants and butters from sewages, and also for effective raw water treatment from bacteria [11, 12].

By virtue of prevalence of magnetite in nature, great number of simple methods of his receipt, and also sorption ability, within the framework of the presented work his application is offered for the concentration of IHM in the sample preparation.

MATERIALS AND RESEARCH METHODS

For the receipt of magnetite a chemical method used a method, offered Massartom, where as initial solutions at the receipt of magnetite applied chlorous and chloric iron in correlation 1 by 2 [13]. Was the got sediment separated through a permanent magnet, washed repeatedly with deionized water, until pH solution will not be attained by 7, and then dried out at a temperature 80 °C before constancy of mass. Structural parameters and phase composition of standards are the study was carried by X-ray fluorescence energy-dispersive spectrometer of brand «BRA-18». According to X-ray analysis the main component of synthesized powder is magnetite - Fe_3O_4 . Middle size of particles of Fe_3O_4 , collected in by the associates size of 0,2-0,5 mkm, 20-30 nm made at the calculation of areas of coherent dispersion.

The specific area of surface of magnetite was measured the method of Bruner-Emmett-Teller on the analyzer of NOVA 1000e and 75 m^2/g made.

To determine the particle size and ζ -potential method was used electrophoretic light scattering analyzer implemented in Nano Brook Omny. On results measurings is the got sorbent by recommendation of suspension on dispersion is polydisperse, ζ -potential at neutral pH is -8,0 mV, that corresponds literary information [14].

In order to select the optimal conditions of concentration, conducted studies of the sorption properties of magnetite in a static mode, determines the effect of pH, temperature, contact time, the presence of interfering ions in the sorption process, as well as the value of the specific adsorption of magnetite. The analysis of IHM was carried out the method of atomic-absorbing spectroscopy (AAS) on a spectrometer KBAHT.Z-ЭТА.

RESULTS

The values of pH, at which the most complete extraction of ions of copper(II) and lead(II) is produced by magnetic iron, are determined experimentally on dependence of degree of sorption on acidity of environment. Results of experiments provided the maximal degree of sorption (R, %) of lead with magnetic iron, with happens in the interval of pH 4–12, the results is 96–99% and copper in the interval of pH 6–12, the result is 95–97%.

The study of dependence of degree of sorption from time of interfusion was conducted at optimum pH, time was changed in an interval from 5 to 120 minutes. It is set that duration of sorption makes 10 minutes for a copper, 5 minutes for lead. At the increase of temperature to 60°S time of sorption of ions of Cu²⁺ and Pb²⁺ grows short insignificantly. Further researches conducted at a temperature 20±0,5 °Ñ during optimum time for every sorbent.

Influence of interfering ions is defined, influence of phosphates and sulfates is set on the sorption of IHM (Figure 1). So at the increase of concentration of phosphates to 5 mg/dm³, the degree of sorption on lead goes down up to 25%, copper more than on 30%. Increase of concentration of sulfates to 100 mg/dm³ reduces the efficiency of sorption on the average up to 15 %. For the removal of influence of interfering matters application of ion-selective resins is offered (anionite EDE-10P).

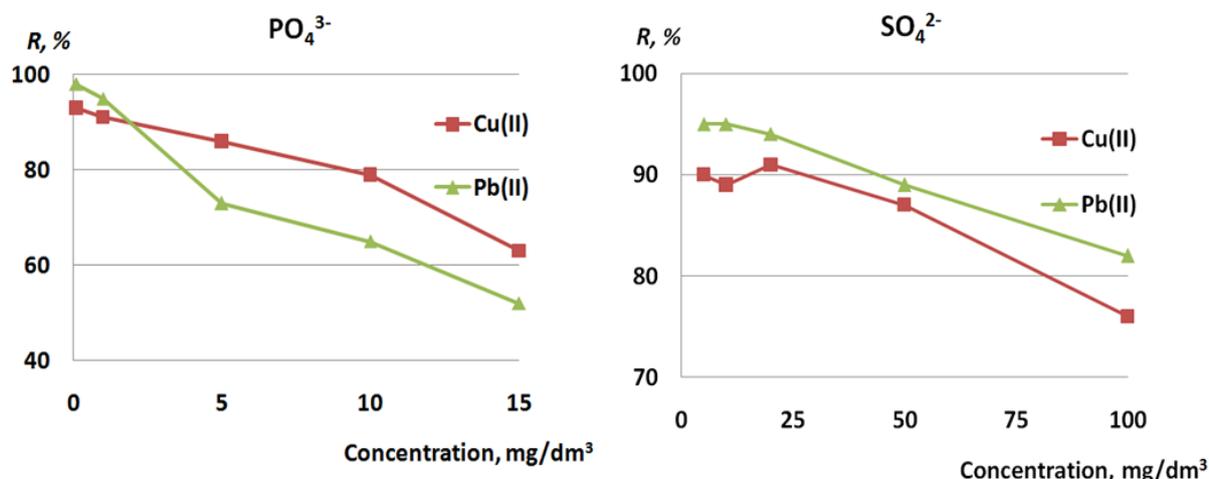


Figure 1: Influence of interfering ions on the degree of sorption IHM

A desorption is one of the important stages during the process of analysing through a concentration and enables the repeated use of sorbent. For the regeneration of sorbent 0,1 M HNO₃ was used . it is noted, that on a 6th cycle of application of sorbent efficiency of sorption on lead and copper is reduced by more than on 10%, that probably is related to oxidization of magnetic iron.

The isotherms of sorption of IHM are got on magnetic iron (Figure 2). Information of the analysis of isotherms ground to assert that at the point of satiation of their projection on a y-axis specify on the size of sorption capacity of sorbent in relation to IHM. Maximal specific adsorption for the ions of Cu²⁺ is 130 mgs/gr, Pb²⁺ are 24 mgs/gr.

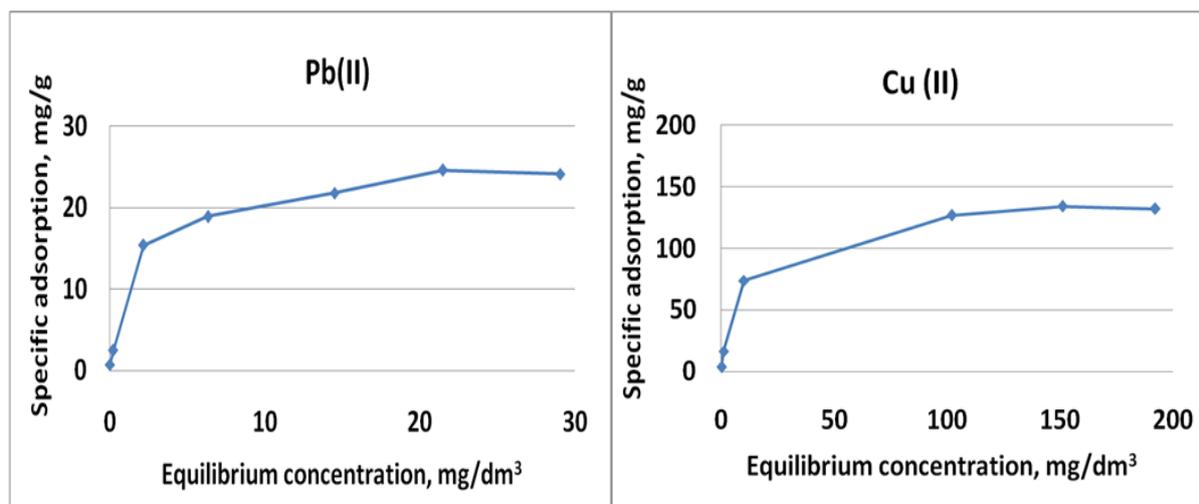


Figure 2: The isotherms of sorption of IHM

RESULTS AND DISCUSSION

On the basis of the collected results the method of preliminary sorption concentration of copper and lead is offered with subsequent quantitative determination including the followings stages:

- Sample preparation of the tested standards;
- Concentration and selection of IHM at optimum terms through magnetic iron;
- Desorption by washing of sorbent solution with a less volume aquafortis;
- Determination of ions of IHM in concentrates.

The possibility of individual concentration and determination of copper and lead is approved by standardized test solutions. The validity of results is tested by the method of «entered-found» (table 2).

Relative standard (S_r) deviation at determination of copper, lead in model solutions after a preliminary concentration did 0,04-0,06 make on magnetite, limit of discovery - 0,1 mkg/dm³.

The offered method is tested on the standards of the melted water of snow-cover in the affected of galvanic production zone for determination of ions of Cu²⁺ (table 3).

The analysis of results of the research of standards of natural water rotined that maintenance in them of copper below than levels of PDK (1 mkg/ dm³) and the limit of determining the applied method, that requires application of methods of concentration. For a concentration points in which entered for a 10 mcg of ions of Cu²⁺ were arbitrarily chosen. As a result of desorption the values of maintenance of ions of Cu²⁺ are got in the melted water of snow-cover with a high producibility ($S_r=0,04-0,06$).

Table 2: Validity of determination of ions of Pb²⁺ and Cu²⁺ in standard test solutions by a method AAS ($V_0=1 \text{ dm}^3$, $V_1=0,01 \text{ dm}^3$, $m_c =1 \text{ gr}$, $n=5$, $P=0,95$)

Entered (C_0), mkg/dm ³	Found (C_1), mkg/dm ³	Coefficient of efficiency of concentration (κ)	S_r
Pb ²⁺			
0,5	0,47±0,03	0,94	0,06
Cu ²⁺			
0,5	0,48±0,02	0,92	0,04

Table 3 - Results of sorption-atomic-absorption determination of ions of copper in natural water (n=5, P=0,95)

Sample	Entered (C_0), mkg/dm ³	Found (C_1), mkg/dm ³	Standard deviation S_r
№1	0	0,9±0,05	0,06
	10	11,0±0,44	0,04
	20	21,2± 1,06	0,05
№2	0	0,5± 0,3	0,06
	10	10,7±0,54	0,05
	20	21,0± 0,84	0,04
№3	0	0,6± 0,04	0,06
	10	10,8±0,43	0,04
	20	20,7±1,04	0,05

FINDINGS

The method of the chemical besieging is get particles, possessing magnetic properties. By the basic component of the synthesized powder is magnetic iron of Fe₃O₄. Middle size of particles of Fe₃O₄, collected in by the associaty size of 0,2-0,5 mkm, 20-30 nm made, the specific area of surface of magnetic iron on the method of BET made 75 m²/g. By electrophoretic light scattering measured ζ-potential of the magnetite particles at neutral pH, which was - 8.5 mV. Conducted measurings of ζ -potential before and after a sorption testifies to the change of charge of double electric layer on-the-spot particles of magnetite, that is related to adsorption of the positively charged cations from solution.

The best values of acidity of environment for flowing of process of sorption with magnetic iron are observed in the interval of pH 6–12 for Cu, pH 4–12 for Pb. Duration of sorption at optimum acidity of environment makes 15 minutes for Cu, 10 minutes for Pb.

The isotherms of sorption IHM, maximal specific adsorption for the ions of Cu²⁺ is 130 mgs/gr, Pb²⁺ are 24 mgs/gr.

A complete desorption is for Pb and Cu at application of 0,1 M HNO₃.

On standardized test solution possibility of individual concentration and determination of Cu and Pb is approved. The test validity is checked by “entered-found” method. Limit of search is 0,1 mkg/dm³ for the ions of Cu²⁺ and Pb²⁺ is 0,1 mkg/dm³.

The offered method is tested on the standards of the melted water of snow-cover in the affected of casting production zone for determination of ions of Cu²⁺.

On the basis of the results for the analysis of microquantity of ions of Cu²⁺ and Pb²⁺ the method of preliminary sorption concentration is offered with the use of magnetic iron. The developed chart foresees the use of different methods of eventual quantitative determination.

CONCLUSION

Experimental researches of the sorption of heavy metals found that magnetic iron effectively concentrates the ions of lead and copper from water solutions. Influences of pH, temperatures, time of contact and interfering ions on the processes of adsorption are studied, the isotherms of adsorption are got and eluants are neat for the desorption of the probed elements.

As a result a new method of sorbate concentration of copper and lead on magnetic iron with subsequent quantitative determination was developed and approved on model solutions and natural water. The developed chart foresees the use of different methods of eventual quantitative determination. The offered method is not intensive in implementation and characterized by a sufficient precision.



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