

About the possibility of sorption concentration of heavy metals using magnetite

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Abstract. This paper addresses the possibility of using magnetite nanoparticles for sorption concentration of heavy metals ions in the analysis of their trace amounts. On the example of copper, lead and nickel ions, optimum conditions for concentrating have been determined, pH, temperature and contact time effect on the adsorption process have been studied in the static mode, and magnetite sorption capacity has been calculated on the basis of experimental data.

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Introduction

Determination of trace amounts of heavy metals in the environment is an important analytical task. However, complex composition, minor concentrations of the substances being analyzed, presence of interfering ions makes it difficult and sometimes impossible to obtain reliable results. The analytical cycle usually includes sampling, preparation for identification, identification itself and processing results. However, at the phase of measuring analytical signal, the researcher may encounter a number of problems associated with sensitivity of the method used. One of the promising ways to solve this problem is the use of the method of concentrating at the stage of sample preparation for analysis. Use of concentrating makes it possible to reduce sample volume, considerably reduce or eliminate the influence of background macro-components and increase analysis sensitivity [1].

Various methods are used for concentrating: extraction, sorption, precipitation, evaporation, freezing, etc. [2]. In analysis of trace amounts of elements, the most efficient is the sorption method which involves concentrating microcomponents from large volumes of solutions onto a relatively small mass of sorbent [3]. The main advantage of the sorption method is the fact that it virtually does not introduce new substances and extraneous ions to the solution cleaned. Therefore, this method may be used for regeneration of a number of technological solutions, as well as for cleaning polluted natural waters.

In recent years, particular attention has been paid to fine powder sorbents. Due to their high specific surface, powders with nanosized particles have maximum sorption properties and are a promising material for removing chemical impurities from water [4]. However, the small particle size that is favorable for sorption greatly impedes separation sorbents from aqueous solution using conventional

methods of filtering and settling. This problem can be solved if small magnetic particles powder is used as a sorbent that can, after impurities sorption, be separated from the solution under the influence of a gradient magnetic field.

Magnetite is an example of magnetic sorbent. Works [5, 6, 7, 8] show sorption activity of magnetite particles with regard to heavy metals, arsenic, phenol, nitrates. Also, at present, there are several methods of water purification from various contaminants using magnetite that acts as a sorbent itself, or is an element embedded into various sorbents [9]. Magnetite is used as the active layer in flow filters, or as a sorbent with subsequent removal of the bound particles by means of magnetic separation [10]. Magnetite as a sorbent is used for removing oil and oil-containing organic pollutants and oils from sewerage water, as well for effective raw water purification from bacteria [11, 12].

Due to magnetite abundance in the nature, many simple ways to obtain it, and its sorption capacity, it is advisable to study the possibility using it for concentrating heavy metals, particularly ions of copper, nickel and lead.

Main part

For obtaining magnetite particles, the method proposed by R. Massart [13] was used, where iron dichloride and ferric chloride at the ration of 1 to 2 were used as initial solutions for obtaining synthetic magnetite. Sedimentation was performed under optimal temperatures of 25 - 30 °C [14] with sesquialteral excess of the precipitant, ammonia water. The resulting precipitate was separated using a permanent magnet, flushed repeatedly with deionized water until pH of the solution that reached 7-8, and then dried at 80 °C. During synthesis of nanoparticles, special attention was paid to high quality and purity of the product. Reactants of "chemical purity" and "ultra high purity" grades were used in the work.

In order to determine the density of the resulting powder, pycnometer method was used, the results obtained (5.1 g/cm^3) correspond to magnetite density reference data. The specific surface of magnetite area was measured by Bruner-Emmett-Teller (BET) method and amounted to $75 \text{ m}^2/\text{g}$.

In order to select the optimum concentration conditions, research of magnetite sorption properties in the static mode was made, the effect of pH, temperature and contact time on adsorption of heavy metals was determined, as well as sorption capacity (CE) of magnetite.

The best values of acidity for the sorption process were determined experimentally. 0.1 g of dry magnetite were added to 20 ml of the solution with 2 μg of the element, the necessary acidity value was determined, and the mixture had been stirred in a stirrer for 2 hours at room temperature ($20 \pm 2 \text{ }^\circ\text{C}$). The filtrate was then separated from the sorbent using a permanent magnet. In the filtrate, content of unabsorbed element was determined by atomic-absorption spectroscopy (AAS), and the container with the sorbent was filled with concentrated nitric acid, and samples were decomposed in determination of acid-soluble forms of elements according to [15]. Quantitative determination of the adsorbed element was also performed using the AAS method.

The degree of extraction of the element was calculated by the formula:

$$R = \frac{q_k}{q_p} \cdot 100\%, \quad (1)$$

Where q_k is the absolute content of metal in concentrate; and q_p is the absolute metal content in the sample. Basing on the obtained data, graphs were made for dependence of the degree of extraction on pH of the environment (Fig. 1). Value R for each point was taken as an average of three independent replicate tests. As we can see from Figure 1, the maximum sorption of copper was observed in the pH range between 6 and 8; that of lead - in pH range between 5 and 6; and that of nickel - in pH range between 7 and 8.

The process of heavy metals sorption by magnetite is strongly influenced by such factors as time and temperature. Elements sorption rate is of great practical importance, since it greatly influences the time spent at the step of concentrating. Dependence of the degree of elements extraction on the time of stirring elements solutions (t , min) with sorbents was studied at optimum pH (Fig. 1), time was measured in the range between 5 and 120 minutes. Sorbent weight was 0.1 g, and weight of the element was 2 μg . For studying the effect of temperature on the extent of extraction, it was changed in the range between 20 and $60 \pm 2 \text{ }^\circ\text{C}$.

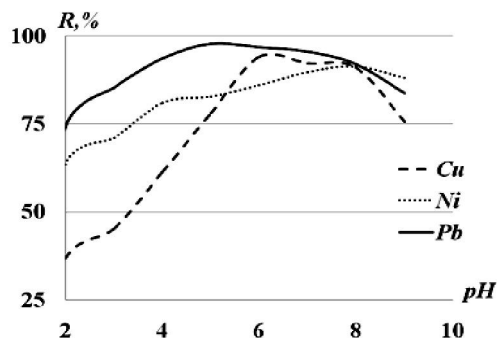


Fig.1. Influence of environment acidity on magnetite sorption of copper, nickel and lead

At the end of each experiment, the extraction rate was calculated, and the obtained data was used to build charts of dependence: "Extraction rate - time" (Figure 2).

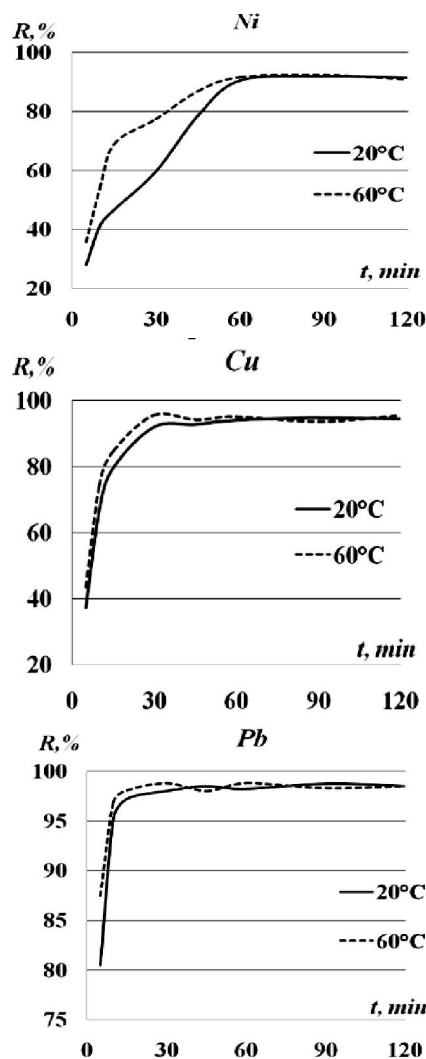


Fig. 2. Influence of stirring time and temperature on magnetite sorption of copper, nickel and lead

It was established that duration of sorption is 10 to 30 minutes for copper, 40 to 60 minutes for nickel, and 10 to 15 minutes for lead. If the temperature is increased to 60 °C, time of sorption is slightly reduced (by 5 to 10 minutes). Further studies were performed at 20 ± 2 °C during the optimum time for each sorbent.

Sorption capacity of magnetite was determined under optimal conditions for elements sorption defined in the process of studying influence of pH and temperature.

For the studied "sorbent-element" system, a series of solutions was prepared with equal sorbent content and varying increasing content of the element. After that, the amount of adsorbed element in each experiment was determined, as described above, and a chart was built in coordinates: "degree of extraction - weight of the element introduced". By plotting this relationship, the maximum weight of the element (x , mg) was found, which was the sorption limit for a given weight of sorbent (m , g). The CE value was calculated using the formula:

$$CE = \frac{x}{m}, mg / g, (2)$$

The results of defining CE value obtained by reaction of various amounts of metal ions with a constant weight of magnetite are shown in Fig. 3. As it can be seen from Figure 3 that the sorption capacity of magnetite that ensures at least 90% recovery rate was as follows: for copper - 1.5 mg/g, for nickel - 0.5 mg/g, and for lead - 1.8 mg/g

CE values can later be used for calculating the required weight of sorbent used for concentrating elements during the stage of sample preparation.

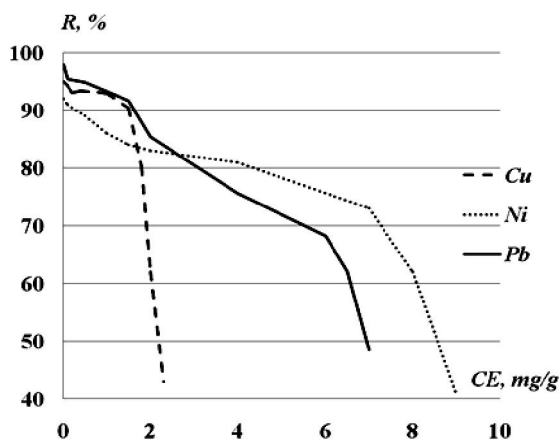


Fig. 3. Determination of magnetite sorption capacity for copper, lead and nickel

Conclusion

The nanoparticles obtained by settling of magnetite with specific surface with the area of 75 m²/g can be used for sorption concentration of heavy metals ions. Best values for environment acidity for the process of sorption on magnetite was observed in the pH range between 6 and 8 for copper; pH range between 5 and 6 for lead, and pH range between 7 and 8 for nickel. Duration of sorption at optimal acidity of the environment was 30 minutes for copper, 60 minutes for nickel, and 15 minutes for lead. If the temperature is increased to 60 °C, the time of sorption is reduced by not more than 5 to 10 minutes. Sorption capacity of magnetite was: 1.5 mg/g for copper, 0.5 and 1.8 mg/g for nickel and lead respectively. Thus, the proposed method makes it possible to further consider magnetite as an effective and low-cost sorbent for heavy metals ions in analysis of their trace amounts, e.g., in natural waters.

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