ХИМИЯ

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THE STUDY OF ADSORPTION PROPERTIES OF MAGNETIC SPINELS. 1. INFLUENCE OF SYNTHESIS CONDITIONS ON ADSORPTION OF CONGO RED*

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Several varieties of the synthesis of fine spinel $Mn_{0.7}Zn_{0.3}Fe_2O_4$ samples: at different temperatures, in different media and with attempts to modify the surface in liquid phase, were carried out by a chemical co-precipitation. The study of the samples by X-ray analysis, FTIR spectroscopy, scanning electron microscopy (SEM) and microprobe elemental analysis, as well as the determination of the specific surface of the samples (BET) showed that all the samples have a spinel structure and composition $Mn_{0.7}Zn_{0.3}Fe_2O_4$ and large enough (for a given type of sorbent) specific surface area (from 128 to 250 m^2/g). All the samples had magnetic properties. Analysis of the sorption properties of these samples on the adsorption of the dye Congo red (CR), the concentration of which was determined using a spectrophotometer, SF 2000, showed that the samples which have been synthesized at 85°C; in a solution of 40% ethyl alcohol; or modified with polyvinyl alcohol have better adsorption properties. Refs 17. Figs 6. Tables 1.

Keywords: magnetic spinel, co-precipitation, surface modification, adsorption.

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ИССЛЕДОВАНИЕ АДСОРБЦИОННЫХ СВОЙСТВ МАГНИТНЫХ ШПИНЕЛЕЙ. 1. ВЛИЯНИЕ УСЛОВИЙ СИНТЕЗА НА АДСОРБЦИЮ КОНГО КРАСНОГО

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Методом химического соосаждения проведен ряд вариантов синтеза образцов мелкодисперсной шпинели $Mn_{0,7}Zn_{0,3}Fe_2O_4$ — при разных температурах, в различных средах и с попытками поверхностного модифицирования из жидкой фазы. Исследование полученных образцов методами рентгенофазового анализа, ИК-фурье-спектроскопии, сканирующей электронной микроскопии (СЭМ) и микрозондовым элементным анализом, а также определение удельной поверхности образцов (БЭТ) показало, что все полученные образцы обладают структурой шпинели состава $Mn_{0,7}Zn_{0,3}Fe_2O_4$ и достаточно большой (для данного типа сорбентов)

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удельной поверхностью (от 128 до 250 м^2/г). Анализ сорбционных свойств полученных образцов по адсорбции красителя Конго красного (КК), концентрация которого определялась на спектрофотометре СФ 2000, показал, что лучшие адсорбционные свойства имеют образцы: синтезированные при 85°С; в растворе 40% этилового спирта; модифицированные поливиниловым спиртом. Библиогр. 17 назв. Ил. 6. Табл. 1.

Ключевые слова: магнитная шпинель, соосаждение, модификация поверхности, адсорбция.

Introduction. Modern production is impossible without creating a complex of industrial wastewater. Lack of cleaning can lead to a sharp increase in territory contamination with toxic salts, heavy metals, harmful organic compounds, etc. The successful implementation of clean-up is not possible without the use of the latest scientific developments in this field.

Among the methods employed to actively address these problems, sorption purification is one of the most effective. It can remove a wide variety of pollution to virtually any residual concentrations, regardless of their chemical stability.

In recent years, increasing attention is paid to the use of magnetic materials [1–4] as a good sorbents, in particular of ferromagnetic spinels which can be prepared by various methods [5]. Due to the wide range of applications of magnetic materials in modern industry and science, the number of scientific minds facing to the problems of preparation of compounds having magnetic properties is increasing every year [6–10]. As a consequence, over the past decade there was a significant leap in the development of methods for the synthesis of magnetic materials, which sometimes allow you to control not only the magnetic properties of the synthesized objects, but also their size and shape on the nanoscale.

An advantage of the magnetic adsorbents consists in the fact that their location can be determined by a magnetic field which allows easy removal of the spent magnetic sorbent from dispersion medium using a magnetic probe, traps etc. Adsorbents with magnetic properties might be applied to the contact cleaning of substances, which greatly simplifies and facilitates the adsorption process and the step of separating the spent adsorbent from the solution. Another advantage is the relatively low cost and high mechanical strength. Magnetic sorbents can be widely used for sewage treatment, oil recovery from water and in medicine [11–14]. It should be noted that the ferrite phase (mostly magnetite) is usually used in magnetic sorbents only as a carrier of the magnetic properties, while other substances, e. g., polymeric, organic coatings which are applied to the magnetic matrix, are used for adsorption [15, 16]. Although modern methods of synthesis of ferrites allow obtaining a high degree of dispersion of the samples, the possibility to use them as stand-alone sorbents still not widely considered. Actually adsorption properties of fine magnetic powders are studied not enough.

The objective of this work was to study the influence of the conditions of synthesis and surface modification of magnetic spinels on their adsorption properties.

Experimental part.

Objects of research. The study of the adsorption processes was conducted on magnetic spinels $Mn_{0.7}Zn_{0.3}Fe_2O_4$ synthesized and modified on the following methods.

Synthesis of the basic sample. Next coprecipitation reaction is the basis for obtaining the spinel structure $Mn_{0.7}Zn_{0.3}Fe_2O_4$:

$$2FeCl_3{\cdot}6H_2O + 0.7MnCl_2{\cdot}4H_2O + 0.3Zn(NO_3)_2{\cdot}6H_2O + 8NaOH \rightarrow$$
$$\rightarrow Mn_{0.7}Zn_{0.3}Fe_2O_4 + 7.4NaCl + 0.6NaNO_3 + 20.6H_2O.$$

Alkali solution with 50% excess was poured in a thin stream into 30% (by weight) salt solutions (in a stoichiometric ratio). The resulting slurry, with constant stirring, was heated in a water bath at a temperature of 80–90°C for about an hour up to browning of the precipitate. The resulting precipitate was washed with distilled water to neutral pH, then filtered on a Buchner funnel and dried at a temperature of 90°C. The dried sample was ground using an agate mortar (hereinafter, the sample obtained by this procedure, will be designated — "basic").

Qualifications of the starting reactives. Manganese chloride $MnCl_2{\cdot}4H_2O$ (reagent grade), sodium hydroxide NaOH (reagent grade), iron(III) chloride $2FeCl_3{\cdot}6H_2O$ (reagent grade), zinc nitrate $Zn(NO_3)_2{\cdot}6H_2O$ (reagent grade); double distilled water.

Synthesis of spinel at different physical conditions. The adsorption properties of the adsorbent to a large extent depend on the state of its surface, which may be associated with the synthesis conditions. Different synthesis conditions such as the temperature of synthesis, composition of the medium, the effect of an external magnetic field or ultrasound may have a different impact on the degree of formation of the crystal structure of the synthesized object, the state of its surface layer and consequently the processes that occur on the surface of the object. In this regard, the study of the influence of these parameters on the sorption characteristics of the synthesized spinel is important.

Synthesis at different temperatures. Prepared solutions of salts were heated in a thermostat at temperatures of 55, 75 and 85°C respectively. The samples were synthesized at these temperatures (hereinafter were designated — "55°C", "75°C" and "85°C" respectively).

Synthesis by sonication. Synthesis of this sample was performed like the basic sample in a water bath at 80°C under continuous sonication up to complete the formation of spinel (40–45 min) (hereinafter designated — "ultrasound").

Synthesis in a 40% solution of C_2H_5OH. To check the influence of the medium of spinel synthesis, experiment was carried out in 40% C_2H_5OH solution (alkali and salts were dissolved in this solution). This sample will be identified — "40% ethanol".

Modification by $Zn(NO_3)_2$. Modification of the surface layer of spinel was conducted by adding $Zn(NO_3)_2$ in an amount of 15% of the theoretical weight of the sample, at the end of coprecipitation (hereinafter the sample will be designated — "Zn").

Modification by polyvinyl alcohol (PVA). PVA surface modification was performed by adding 10 ml of a 5% PVA solution at the end of coprecipitation (hereinafter the sample will be designated — "PVA").

Methods of analysis of the synthesized samples.

X-ray analysis. Radiographic study of the synthesized products was carried out on powder samples by Debye on a DRON company Shimadzu using CuK_α radiation, tube voltage 30 kV, current 30 mA, scanning speed 1°/min, at angles from 20 to 70° 2θ.

XRD of powder pattern "basic" and sample "Zn" showed that in the first case, the powder is a pure spinel $Mn_{0.7}Zn_{0.3}Fe_2O_4$, and in the second, in addition to $Mn_{0.7}Zn_{0.3}Fe_2O_4$, there is also a small amount of phase ZnO. XRD analysis confirmed that all the other samples represent spinel composition $Mn_{0.7}Zn_{0.3}Fe_2O_4$ as well (Fig. 1).

Specific surface. Specific surface area was determined for the obtained samples by thermal desorption of argon (BET) (see table).

Sample	S, m^2/g	Δ, %
Basic	200	5
55°C	225	5
75°C	195	5
85°C	195	5
Ultrasound	250	2
40% ethanol	210	2
Zn	128	5
PVA	225	5

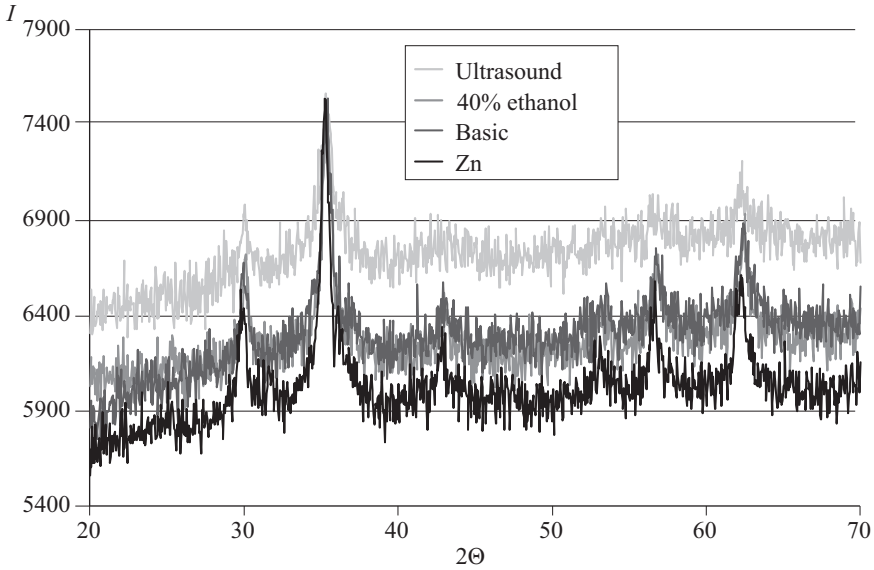

Fig. 1. Radiographs of the synthesized samples

FTIR spectroscopy. Direct absorption of light when it passes through a layer of substance underlies obtain IR spectra. Middle region (400–4000 cm^{-1}) from the extensive range infrared radiation is used. Transmission spectra in the wave number range 400 to 4000 cm^{-1} were recorded on a FTIR spectrometer brand Shimadzu IR Prestige 21 in KBr tablets.

Comparison of the IR spectra of the sample with the surface-modified PVA, and the basic samples showed that the band positions are identical. This means that the IR-spectrum does not allow identifying the presence of molecules of PVA on the surface of the spinel. This may be due to a low content of PVA on the surface of the sample, and the presence of water adsorption. Therefore, we cannot say that the surface of the sample does not contain PVA. Moreover, the results of adsorption of Congo red, and Pb^{2+} and Cu^{2+} ions (below) implicitly indicate the opposite.

Scanning electron microscopy (SEM) and microprobe elemental analysis. Synthesized powder products were examined by these methods to determine the chemical composition of individual particles. After obtaining micrographs of spinel samples (Fig. 2) some particles were selected for microprobe elemental analysis.

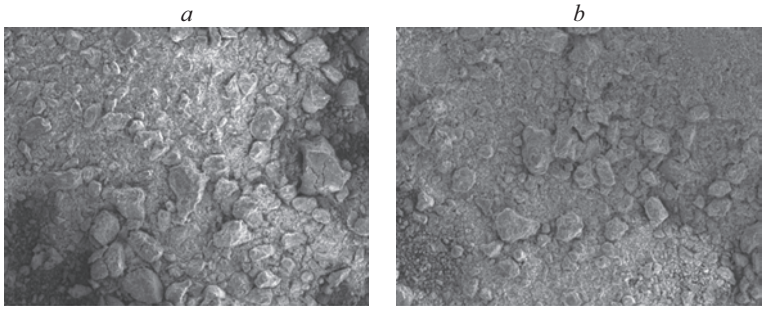

Fig. 2. Micrograph of starting spinel sample (*a*); of Zn modified spinel samples (*b*)

It was found that the particles of the basic sample consist of 9.8% Mn, 4.3% Zn, 28.6% Fe, 57.3% O (in atomic percentages), which corresponds to the spinel structure. Sample particles with a surface layer, modified by Zn, consist of 2.3% Mn, 12.2% Zn, 28.6% Fe, 57.1% O. High content of zinc atoms in the surface layer of the spinel can be explained by the fact that addition of excess zinc nitrate at the end of co-precipitation process led to the formation of the surface layer of spinel with a ratio zinc and manganese atoms different from the bulk.

Investigation of the adsorption properties of the synthesized samples. Study of the influence of the synthesis conditions on the sorption characteristics of the spinel was one of the goals of this work. Anionic dye Congo red (CR) $[C_{10}H_5(NH_2)(SO_3NaN{:}NC_6H_4)]_2$ was chosen as the subject of organic nature for the study of adsorption. Adsorption of dyes is used in industry for various purposes. For example, it is widely used for the sensitization of photographic emulsions, coloring of anodized aluminum surfaces, in determining the specific surface area and porosity of the commercial powdery materials. Thus, purification of industrial waste water from various dyes may also be relevant.

Adsorption of Congo red (CR) on the surface of the spinel. CR aqueous solution of 0.001M concentration was prepared by dissolving a sample of a dye.

To measure the adsorption a sample of 0.1 g of the spinel was placed in a 50 ml of CR solution (concentrations of 60, 100, 200, 300, and 400 μM/l). The time of adsorption was 7 days. Measurement of the optical density (D) of solution after adsorption was performed on SF 2000 (cuvette with the optical layer thickness of 10 mm) at a wavelength $\lambda = 500$ nm. Distilled water as the comparison solution was used. Concentration of CR in solution after adsorption C_{ads} was calculated using calibration curve equation. Adsorption value Γ was calculated by the formula: $\Gamma = (C_0 - C_{\text{ads}}) \cdot V/m$, where V — volume of the solution; m — adsorbent weight.

To study the effect of temperature of the synthesis at the adsorption properties of spinel, adsorption of CR was carried on samples synthesized at 55, 75 and 85°C. The results of these experiments are shown in Fig. 3.

It can be seen that the best adsorption took place at the sample synthesized at 85°C. Adsorption activity of the sample synthesized at a temperature of 75°C was also somewhat higher than that of the basic sample (synthesized by the standard procedure described above). Worse proved himself a sample obtained at 55°C.

It is known that the surface properties of the same chemical compound in the crystalline and amorphous state can vary considerably among themselves [17]. The results of this study suggest that the synthesis temperature affects the degree of formation of spinel crystalline

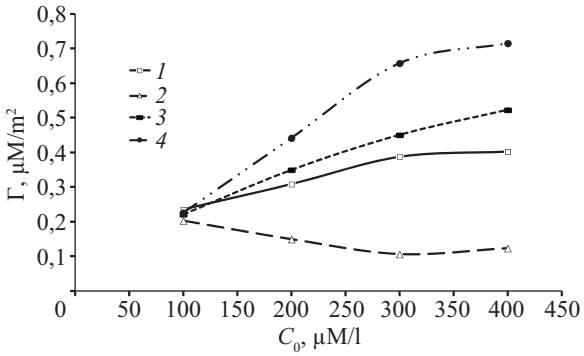

Fig. 3. Adsorption of CR on spinel, obtained at different synthesis temperatures:
1 — basic; *2* — 55°C; *3* — 75°C; *4* — 85°C

lattice (different color of the sample prepared at 55°C, also testifies to this) which in turn affects formation of surface adsorption sites and, consequently the adsorption activity. Specific surface area of all samples has similar values. This suggests that the synthesis temperature, in this case, is not affected. So far as studies have shown that a change in the conditions of synthesis and surface modification of spinel samples can affect both their adsorption activity, and their specific surface area, the results of experiments in some cases will be presented for both Γ units μM/m^2 (adsorption activity of the sample) and Γ units μM/g (its sorption capacity).

For the sample synthesized under ultrasonic treatment (Fig. 4, *a*), the adsorption activity was almost the same as for the basic sample. However, its specific surface increased significantly (250 m^2/g and 200 m^2/g, respectively). For this case (for the sample synthesized under sonication) an increase in specific surface leads to the increase of the sorption capacity of the sample (Fig. 4, *b*). It should be noted that in this case the time of formation of the spinel was somewhat more lasting than for the basic sample. Synthesized particles were smaller than these of the basic sample (settling time in the magnetic field was more than a day, instead of 2–3 hours), but particles were aggregated or escalated during washing, and that resulted in a not so large increase of specific surface area, as one could imagine. However, such a specific surface area (250 m^2/g) for spinel $Mn_{0.7}Zn_{0.3}Fe_2O_4$ is by far the highest of the samples synthesized by us. Thus, the use of ultrasound can be considered a promising method for obtaining samples of fine spinel.

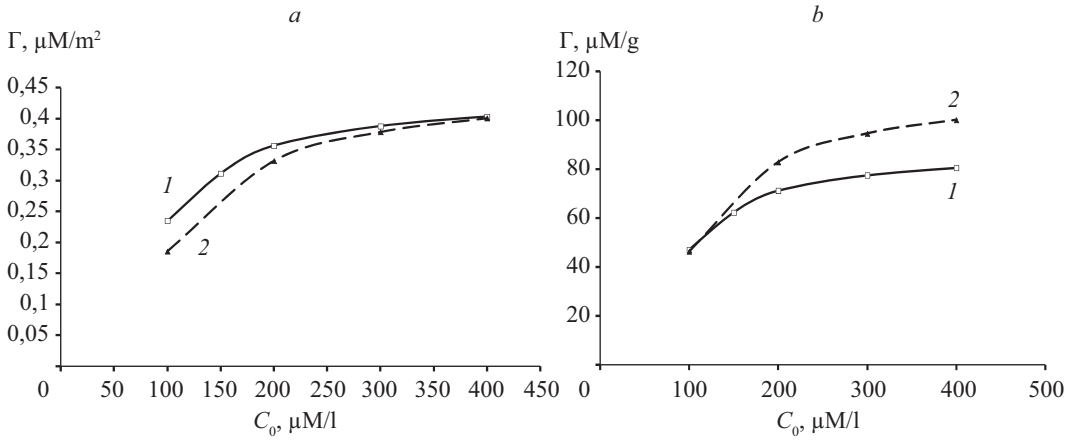

Fig. 4. Adsorption of CR on basic sample and sample synthesized using ultrasound per m^2 (*a*); per gram of sorbent (*b*):
1 — basic; *2* — ultrasound

To study the effect of the medium on the adsorption properties of synthesized samples, experiments were carried out at spinel synthesized in an aqueous solution (40%) of ethyl alcohol. The CR adsorption results revealed that the adsorption on the sample synthesized in a 40% ethanol held better than on the basic sample. These findings suggest a marked influence of the medium in which synthesis of the spinel is carried out on its adsorptive properties.

Results of experiments on the effect of surface modification of sorbents on their sorption properties are shown in Fig. 5.

It is seen that the surface-modified samples showed a better adsorption than the basic sample. Most large sorption capacity was observed for the spinel, which surface has been

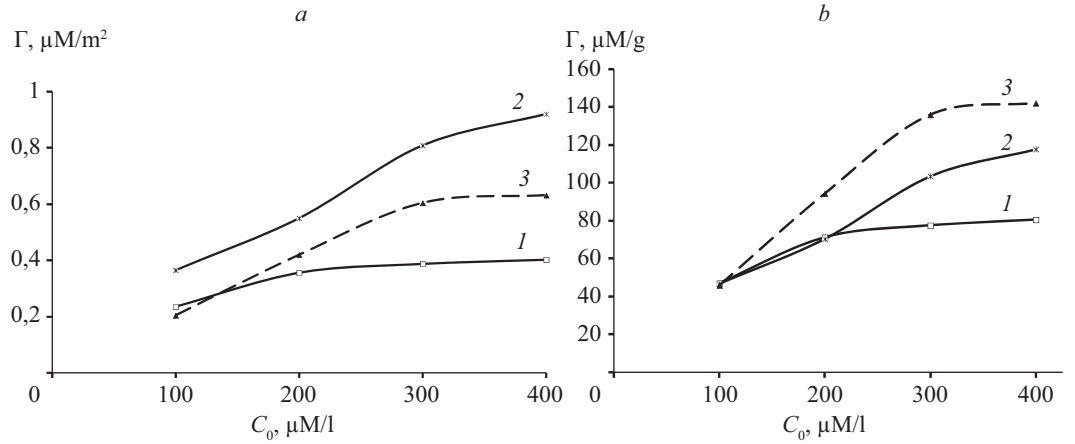

Fig. 5. Adsorption of CR on samples with modified surface per m^2 (*a*); per gram of sorbent (*b*):
1 — basic; *2* — Zn; *3* — PVA

PVA modified (Fig. 5, *b*) due to the significantly higher specific surface area. However, the greatest adsorption activity was found for the specimen "Zn" (Fig. 5, *a*).

Fig. 6 shows the results of CR adsorption on samples, which showed itself most promising. At low concentrations of CR (up to 100 μmol/l) the sorption capacity of all samples is almost the same (Fig. 6, *b*). Spinel modified by PVA shows the best result in this case. At CR concentrations up to 300 μmol/l adsorption on the sample synthesized at 85°C and on the sample synthesized in a 40% ethanol solution was almost identical.

When considering the adsorption activity of the obtained samples (Fig. 6, *a*) it can be seen that the best result the sample "Zn" shows. The samples "PVA", "40% alcohol" and "85°C" gave similar values of the adsorption activity (Fig. 6, *a*). The minimum values of adsorption activity were obtained for the basic sample and the sample "ultrasound". Thus, it can be concluded that the choice of sorbent from the data presented above of the adsorption activity at low concentrations of CR (100 μmol/l) is not essential, but at higher concentrations it is preferable to use samples "PVA" and "40% ethanol".

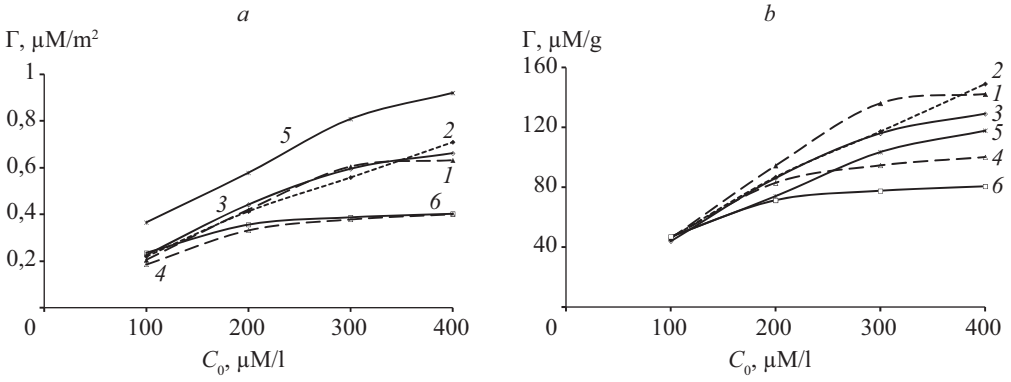

Fig. 6. Comparative CR adsorption on the samples with the best adsorption characteristics per m^2 (*a*); per gram of sorbent (*b*):
1 — PVA; *2* — 40% ethanol; *3* — 85°C; *4* — ultrasound; *5* — Zn; *6* — basic

Studies on the adsorption of ions of copper and lead on the synthesized samples of magnetic spinels were also held. The results obtained will be given in the following report.

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