

ХИМИЯ

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*E. V. Gribanova, O. A. Vasutin, M. I. Larionov, A. E. Kuchek***THE STUDY OF ADSORPTION PROPERTIES OF MAGNETIC SPINELS.
2. INFLUENCE OF SYNTHESIS CONDITIONS ON ADSORPTION
OF HEAVY METAL IONS***

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Analysis of sorption properties of the fine spinel $Mn_{0.7}Zn_{0.3}Fe_2O_4$, obtained by co-precipitation method (“basic” sample) and also: at different temperatures; in different media (“40% ethanol”) and surface modification in the liquid phase (“PVA” and “Zn”), — was performed by adsorption of Cu^{2+} and Pb^{2+} ions. The concentration of these ions was determined by atomic emission spectroscopy with inductively coupled plasma on Perkin Elmer Optima 7300 DV. The experiments have shown that the best adsorption of Cu^{2+} and Pb^{2+} ions was detected on the spinel modified by $Zn(NO_3)_2$ (“Zn” sample). It has been found that the isomorphic substitution makes a significant contribution to the adsorption of ions. The isomorphic substitution was the determining factor of adsorption in the case of samples with modified surface. The results obtained also allow concluding that the magnetic spinels obtained by co-precipitation are as themselves the good enough adsorbents. Refs 5. Figs 5. Tables 2.

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

*E. V. Грибанова, О. А. Васютин, М. И. Ларионов, А. Э. Кучек***ИССЛЕДОВАНИЕ АДсорбЦИОННЫХ СВОЙСТВ
МАГНИТНЫХ ШПИНЕЛЕЙ. 2. ВЛИЯНИЕ УСЛОВИЙ
СИНТЕЗА НА АДсорбЦИЮ ИОНОВ ТЯЖЁЛЫХ МЕТАЛЛОВ**

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Анализ сорбционных свойств мелкодисперсной шпинели $Mn_{0.7}Zn_{0.3}Fe_2O_4$, полученной методом соосаждения при разных температурах, в различных средах и при поверхностном модифицировании из жидкой фазы, был проведён по адсорбции ионов Cu^{2+} и Pb^{2+} . Концентрация этих ионов определялась методом атомно-эмиссионной спектроскопии с индуктивно-связанной плазмой на приборе Perkin Elmer Optima 7300 DV. опыты показали, что лучше всего адсорбция ионов Cu^{2+} и Pb^{2+} прошла на шпинели, модифицированной $Zn(NO_3)_2$. Обнаружено, что значительный вклад в адсорбцию ионов вносит изоморфное замещение. В случае образцов с модифицированной поверхностью изоморфное замещение было определяющим фактором при адсорбции. Результаты также позволяют сделать вывод, что магнит-

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ные шпинели, полученные путём соосаждения, являются сами по себе достаточно хорошими адсорбентами. Библиогр. 5 назв. Ил. 5. Табл. 2.

Ключевые слова: магнитная шпинель, соосаждение, модификация поверхности, адсорбция, ионы тяжёлых металлов.

Introduction. One of the serious environmental problems is the content of heavy metal ions in industrial wastes [1–4]. This sort of contamination includes, for example, copper and lead ions. Therefore, in addition to the experiments on adsorption of Congo red (CR) on the surface of the samples of magnetic spinel $Mn_{0.7}Zn_{0.3}Fe_2O_4$ [5] which was obtained by simple co-precipitation method (“basic” sample) and also by co-precipitation: at different temperatures; in different media (“40% ethanol”) and surface modification in the liquid phase (“PVA” and “Zn”), a series of experiments on the adsorption of ions of copper and lead was also conducted.

Research methods. Samples of studied spinel weighing 0.1 g were placed in volumetric flasks of 50 ml. Different volumes of 0.1M solution of $Cu(NO_3)_2$ (0.1M $Pb(NO_3)_2$ at studying the adsorption of Pb^{2+} ions), and water were poured into the flask to obtain solutions of different concentrations.

Concentration of metal ions after adsorption C_{ads} was determined by atomic emission spectroscopy with inductively coupled plasma on Perkin Elmer Optima 7300 DV. There was also an attempt to determine the concentration of ions using ion-selective electrodes. However, a number of significant shortcomings were detected in this method, which had an impact on the findings. Therefore, later this method was abandoned.

Adsorption of Cu^{2+} ions. Fig. 1 shows the results of a study of adsorption of Cu^{2+} ions for various samples of spinel. As in the case of CR adsorption [5, Fig. 6, b] the smallest capacity for the sorption of copper ions (Fig. 1, b) was found for the basic sample. All other samples showed sorption capacity in some degree higher. Particularly high adsorption of copper ions was shown by the sample of spinel “Zn”. The curves of copper ion adsorption obtained for the other samples, are parallel to each other and reach a plateau at a concentration of Cu^{2+} about 1 mM/l, which evidently indicates surface saturation of spinel by Cu^{2+} ions at a given concentration. The data in Fig. 1, a show that the adsorption activity curves for these samples are substantially identical, i. e. their adsorption properties are the same. An exception is the sample “Zn”, which shows extremely high adsorption properties that force to assume in this case the presence of some additional mechanism of adsorption.

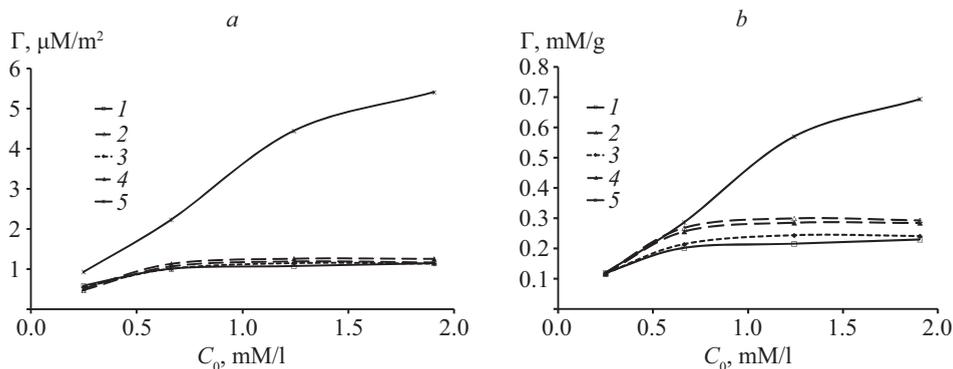


Fig. 1. Adsorption of Cu^{2+} ions per m^2 (a); per gram of sorbent (b):
1 — “basic”; 2 — “ultrasound”; 3 — “40% ethanol”; 4 — “PVA”; 5 — “Zn”

Since the theory of adsorption of ions of electrolytes is now difficult to call quite developed, experiments were conducted that would take into account not only the change in concentration of the ion, which adsorption is being studied, but those ions that can appear in the solution because of the processes occurring on the surface of this sorbent (e. g., ion exchange of various nature, etc.). The study of the content of Mn^{2+} , Zn^{2+} , Fe^{3+} , Cu^{2+} ions in solution after the adsorption was carried out by atomic emission spectroscopy, inductively coupled plasma. The evaluation results were obtained using the following equation: $\Gamma = (C_0 - C_{\text{ads}})V(0,001/m)S_{\text{sp}}$, where C_0 and C_{ads} are ion concentration before and after adsorption; V — the flask volume; m — the sorbent weight; S_{sp} — specific surface. In the case of Cu^{2+} ions Γ is a positive value and represents the adsorption per unit of the surface area (m^2) of the sorbent. For other ions the value of Γ is negative and represents the content of the separated ions as a result of the interaction of the adsorbent with a solution (per m^2 of sorbent). The results are shown in Fig. 2 (this Figure does not contain data on the content of Fe^{3+} ions because of their number was either negligible or they were not detected at all).

From Fig. 2 it is easy to see that for the “basic” sample, the sample synthesized in 40% ethanol solution and a sample, synthesized under the effect of ultrasound, the total quantity of the desorbed ions Mn^{2+} and Zn^{2+} is considerably less than the amount of adsorbed ions Cu^{2+} . Samples “PVA” and “Zn” extracted into solution much more Mn^{2+} and Zn^{2+} ions, but still less than the amount of adsorbed ions Cu^{2+} . It must be emphasized here that the sample “Zn” adsorbed 4–5 times more Cu^{2+} ions than all other samples. This fact suggests that the adsorption of Cu^{2+} ions on this sample may also occur due to isomorphic substitution. The similarity of the curves of adsorption of Cu^{2+} ions (all samples) with the curves of extraction of Mn^{2+} and Zn^{2+} ions into the solution and also the fact that these curves are reaching the plateau at the same concentrations can evidence in favor of this assumption. It should also be noted that in the case of sample “PVA”, and both samples “ultrasound” and “40% ethanol” preferably Mn^{2+} ions are released, the sample “Zn” is extracting Zn^{2+} ions.

It should also be noted that in the case of the sample b), c) and d) (see Fig. 2) the amount of extracted Mn^{2+} ions is more than Zn^{2+} ions, but in the case of the basic sample these values are equal. If we consider the stoichiometry of spinel ($\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Fe}_2\text{O}_4$) it is quite logical that the amount of extracted Mn^{2+} ions should be more than Zn^{2+} one. The equality of these values in the case of the “basic” sample and significant difference between these values for the “PVA” sample remains unclear. Regarding the sample “PVA”, these data suggest that this sample is not promising for the treatment of waste waters from heavy metal ions.

Oversize values of extracted Zn^{2+} ions for the sample e) may be caused as follows: the addition of excess zinc nitrate at the end of co-precipitation [5] probably led to the fact that zinc ion occupied excessive seats in the surface layer of crystal lattice of the spinel versus initial stoichiometry. First of all absorption of Cu^{2+} -ions, much bigger in comparison with other samples, is a consequence of it. And therefore when carrying out researches on adsorption, due to isomorphic replacement the quantity of ions of Zn^{2+} , allocated at this sample in solution, is more in comparison with other samples.

Adsorption of Pb^{2+} ions. Similar experiments were carried out for adsorption of Pb^{2+} ions at the same molar concentrations. The results obtained are shown in Fig. 3. As in the case of adsorption of Cu^{2+} ions, the largest Pb^{2+} ions adsorption was observed for the sample with the surface, modified by $\text{Zn}(\text{NO}_3)_2$. The dependence of the adsorption activity on the concentration (Fig. 3, a) shows that in this case the difference between all curves, except for the sample “Zn”, is significantly reduced.

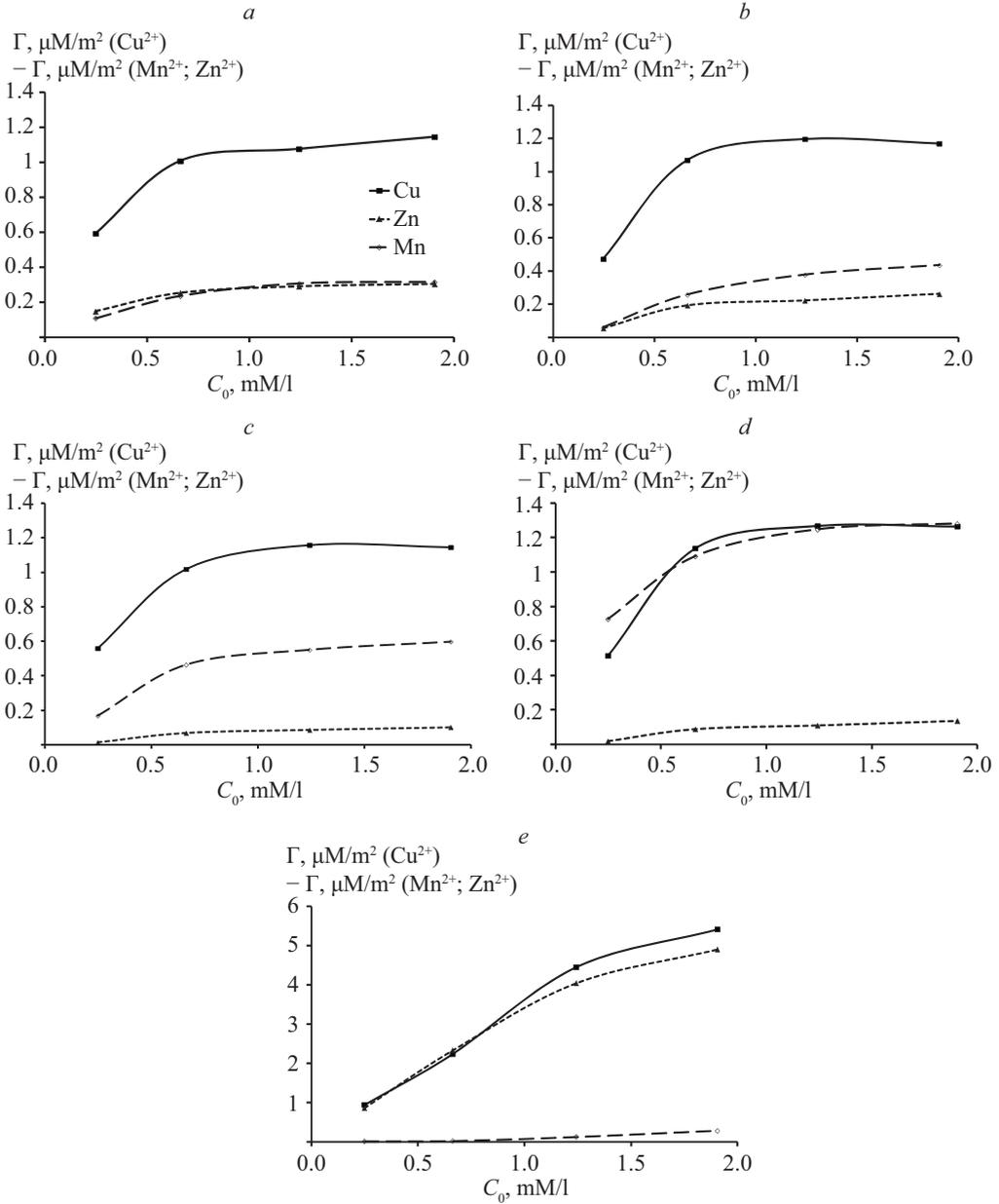


Fig. 2. Desorption of Mn^{2+} and Zn^{2+} -ions in the process of adsorption of Cu^{2+} on the spinel surface:

a — “basic”; b — “ultrasound”; c — “40% ethanol”; d — “PVA”; e — “Zn”

In the process of adsorption of Pb^{2+} ions from solution, the desorption of Zn^{2+} and Mn^{2+} ions was also evaluated (Fig. 4).

In general, the foregoing description of the mechanism of Cu^{2+} ions adsorption describes well the adsorption of Pb^{2+} ions. Also similar in nature are curves showing the extraction of Mn^{2+} and Zn^{2+} ions into solution: increased desorption of Mn^{2+} ions from the samples

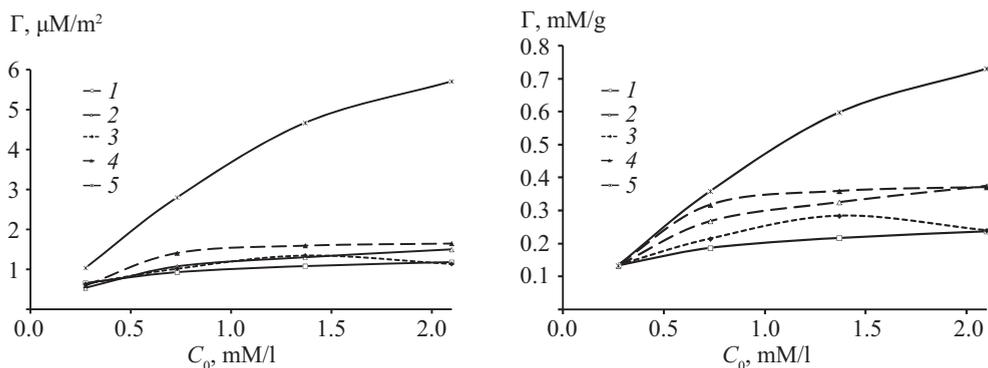


Fig. 3. Adsorption of Pb^{2+} ions per m^2 (a); per gram of sorbent (b):
 1 — “basic”; 2 — “ultrasound”; 3 — “40% ethanol”; 4 — “PVA”; 5 — “Zn”

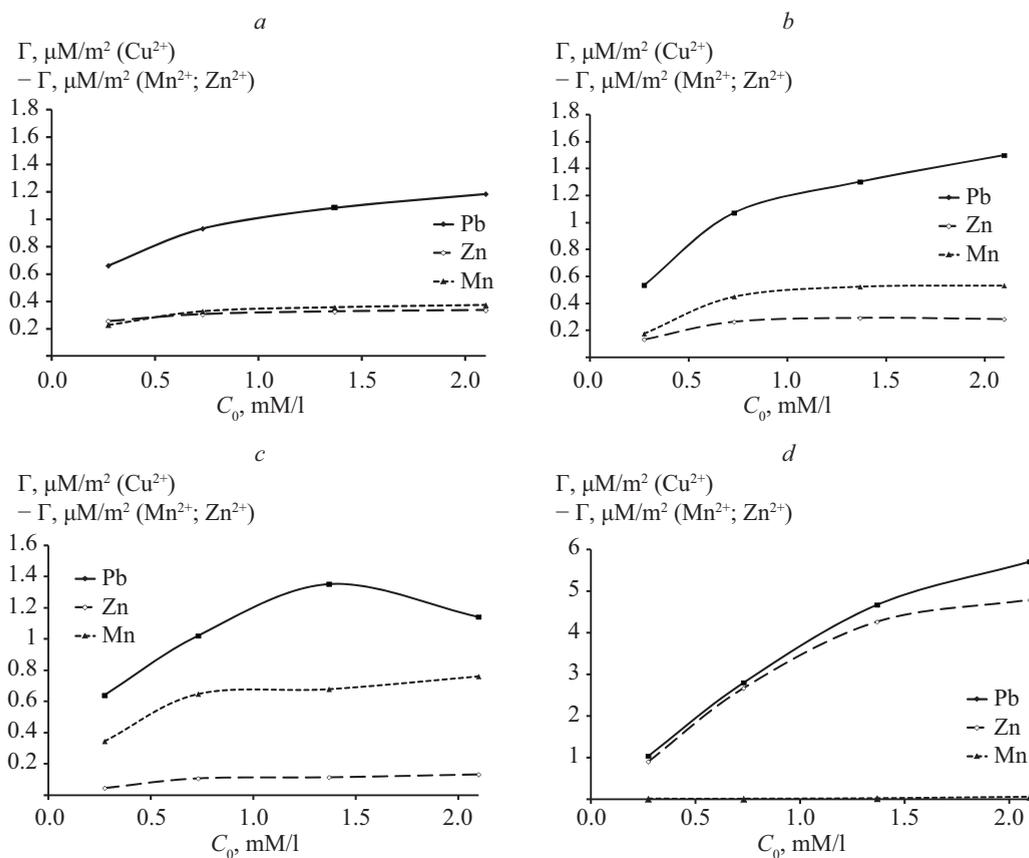


Fig. 4. Desorption of Mn^{2+} and Zn^{2+} ions in the process of adsorption of Pb^{2+} on spinel surface:
 a — “basic”; b — “ultrasound”; c — “40% ethanol”; d — “Zn”

treated with ultrasound and synthesized in 40% ethyl alcohol, extremely high values of desorption Zn^{2+} from the sample with reformulated surface layer (“Zn”). Very high values of desorption of Mn^{2+} ions in a sample treated with PVA was found in this case too. This

high degree of similarity between the curves of adsorption of Cu^{2+} ions and Pb^{2+} speaks about the similarity of the mechanisms of their interaction with the surface.

Analyzing the full range of data on the results of adsorption obtained on synthesized samples, we can come to the next set of general conclusions. Comparing the results of the adsorption of organic and inorganic sorbates, it becomes apparent that their adsorption mechanisms are several different from each other in nature.

In the case of CR it can be seen that not only increase of specific surface of the sorbent, but also the conditions of synthesis of the sorbent and a method of modifying its surface, influencing the adsorption activity, can change the sorption capacity. This fact is interesting because CR is often used to determine the specific surface of the sorbent.

With respect to the results of the adsorption of Cu^{2+} and Pb^{2+} ions, we also observe that the efficiency of the sorbents depends upon their specific surface area, except for sample “Zn”. Effect of the specific surface area upon the sorption capacity is particularly evident in the analysis of Cu^{2+} adsorption curves (as can be seen from Fig. 1, *a*, all curves practically coincide). Adsorption curves for Pb^{2+} (Fig. 3, *a*), differ somewhat among them, but also have a similar trend. Apart from the specific surface area a significant contribution to the adsorption introduces apparently another factor, which has already been mentioned above — an isomorphic substitution. As already mentioned, the closest form of Cu^{2+} and Pb^{2+} ion adsorption curves and the curves of desorption of Mn^{2+} and Zn^{2+} ions (Fig. 2, *d*, *e*, Fig. 4, *e*) is evidence in favor of this factor for the samples “PVA” and “Zn” respectively. The similarity of behavior of these curves and attainment of a plateau in the case of the remaining samples is evidence as well. There is also a couple of circumstantial evidence in favor of the assumption of surface exchange processes. First, evaluation of the content of OH-groups on the surface of the spinel samples at $\text{pH} = 6$ (based on electrometric titration) gives a value of $0.6 \cdot 10^{18}$ per m^2 . The adsorption results show that these samples can adsorb up to $0.7 \cdot 10^{18}$ – $0.9 \cdot 10^{18}$ Cu^{2+} and Pb^{2+} -ions, respectively. Given that these ions are bivalent; this result suggests that more complicated surface ion exchange probably occurs during adsorption. It may be a surface process of isomorphic substitution. The next evidence of isomorphic substitution process is the results of the blank experiment, shown in Fig. 5. In this experiment the samples of studied sorbents were placed in distilled water (flask 50 ml) and were kept there for about 7 days.

As it is seen from Fig. 5, there is no appreciable extraction of Mn^{2+} and Zn^{2+} ions in most cases. The exception is a sample “PVA” and a sample “Zn” (but even in this case, the release of these ions was negligible in comparison with the data obtained in the adsorption process, Fig. 2 and Fig. 4). The existence of two different factors, affecting the adsorption of

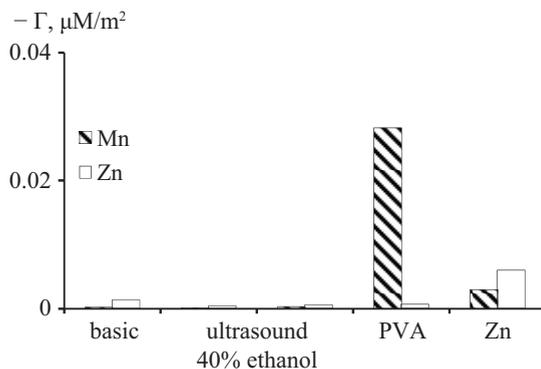


Fig. 5. The release of Zn^{2+} and Mn^{2+} ions in water in the blank experiment

Cu²⁺ and Pb²⁺ ions, may explain some differences in their adsorption, which was mentioned above. In other words, the contribution of both factors may be different for various ions.

Summing the final evaluation of the effectiveness of the synthesized samples we can draw the following conclusions. The samples “ultrasound” and “40% ethanol” are the most effective in practical application. These samples have the highest sorption capacity with a minimum release of ions Zn²⁺ and Mn²⁺. Thus these samples are effective, if the task is general wastewater cleaning, i. e. with a minimum residual concentration of any extraneous substance in the water. But if you need urgent removal of toxic heavy metal ions, the most effective sample may be “Zn”, which absorbs 4–5 times more toxic metal ions, replacing them with a fewer amount of Zn²⁺ ions.

It is also interesting to know whether there is a difference between the mechanisms of adsorption of Cu²⁺ and Pb²⁺ ions. The comparison of adsorption of Cu²⁺ and Pb²⁺ ions on the sample “basic” showed that the adsorption of both ions passed virtually identically, which may indicate that Cu²⁺ and Pb²⁺ ions were adsorbed on the same surface active sites.

Since the problem of industrial wastewater containing ions of heavy metals is a serious environmental problem, there are a lot of papers on this problem, including the case when the magnetic materials were used. As we discussed in [5], the magnetic component of adsorption mixtures is mainly used for easy retrieval of spent sorbent at the end of the process. For adsorption the universally accepted sorbents, such as activated carbon, silica gel, various aluminosilicates are preferably used. It is interesting to compare some of the published data with our results. As for the evaluation of the results of their research in different papers different parameters were used, we did some calculations according to these authors’ data to make such a comparison. Adsorption is more often calculated in units of mg adsorbed ion per gram of sorbent. But in [4] the K_d value was used as a parameter:

$$K_d = \frac{C_0 - C_f}{C_f} \frac{V}{m}.$$

Wherein C_0 and C_f — concentration before and after adsorption in mM/l; V — the volume of a sample in ml; m — sorbent mass in grams (g).

This is very interesting work, whose main objective was to achieve a high degree of purification of river water from heavy metal ions using sorbents obtained by grafting organic acceptor of heavy metals ions on the magnetite. They studied the removal of ions from the water with the original content of the studied ion 0.5 ppm. A good result in some cases has been achieved by using very small batches of adsorbent. For comparison, the table shows the best result of adsorption of lead ions which was obtained in [4]. The relevant data and calculations are shown in Tables 1 and 2.

Table 1

The data on lead ions adsorption

N	Sorbent	m , g	V , mL	C_0 , mM/L	C_f , mM/L	K_d	Γ , mg/g	Ref.
1	magnetic clinoptilolite	0.5	1000	0.193	0.053	5270	58	[1]
2	pure zeolite	2	1000	4.66	2.24	540	251	[2]
3	magnetically modified zeolite	2	1000	4.66	3.47	171	123	[2]
4	bare Fe ₃ O ₄	0.0001	10	0.0024	0.0014	78 000	20.7	[4]

N	Sorbent	m , g	V , mL	C_0 , mM/L	C_f , mM/L	K_d	Γ , mg/g	Ref.
5	Fe ₃ O ₄ + MBA*	0.0001	10	0.0024	0.00013	1800 000	47.0	[4]
6	spinel** "basic"	0.1	50	0.2736	0.0067	19 718	27.4	our
				2.098	1.6231	146	49.1	data
7	spinel "ultrasound"	0.1	50	0.2736	0.0033	40 185	27.7	our
				2.098	1.3465	278	77.6	data
8	spinel "Zn"	0.1	50	0.2736	0.0058	22 886	27.6	our
				2.098	0.6264	1166	151.4	data

* — mercaptobutyric acid;

** — Mn_{0.7}Zn_{0.3}Fe₂O₄.

Table 2

The data on copper ions adsorption

Sorbent	m , g	V , mL	C_0 , mM/L	C_f , mM/L	K_d	Γ , mg/g	Ref.
magnetic clinoptilolite	2	1000	0.315			14	[1]
bare Fe ₃ O ₄	0.0001	10	0.008	0.0075	7400	3.2	[4]
Fe ₃ O ₄ + MBA*	0.0001	10	0.008	0.0015	440 000	41.3	[4]
spinel** "basic"	0.1	50	0.2484	0.0095	12 469	7.5	our
			1.9047	1.4470	158	14.6	data
spinel "ultrasound"	0.1	50	0.2484	0.0104	11 403	7.5	our
			1.9047	1.3159	222	18.6	data
spinel "Zn"	0.1	50	0.2484	0.0089	13 496	7.6	our
			1.9047	0.5176	1339	44.0	data

* — mercaptobutyric acid;

** — Mn_{0.7}Zn_{0.3}Fe₂O₄.

It's rather difficult to compare the data in the table, because different concentration of adsorbed component (C_0) and not the same ratio of the mass of the sorbent to the solution volume (V/m) were used in different studies. Nevertheless, we can draw the following conclusions. The most important parameters are the value of the sorbent adsorption (Γ) and the residual concentration (C_f). From listed in Tables 1 and 2, the only one sample (N 5) showed quite a good result for Γ and C_f for lead ions, apparently, due to the donor-acceptor interaction of ions Pb²⁺ with mercaptobutyric acid (MBA), which was grafted onto Fe₃O₄. It should be noted that the adsorption was investigated for dilute solutions (0.5 ppm) [4]. In the case of more concentrated solutions, on the order of 2–4 mM/l the high adsorption was observed for the samples N 2, 3 [2] and N 6, 7 and 8 (our data), but the value of C_f was too large to the cleaning process can be stopped. Good results for the residual concentration C_f our samples (N 6, 7 and 8) have shown for the initial concentration of 0,274 mM/l.

The data in Table 2 for the adsorption of copper ions show that adsorbents of [1, 4] can adsorb Cu²⁺ significantly worse than Pb²⁺, i. e. there is a specificity of used sorbents for lead ion. Our study (spinel samples N 6–8) revealed that Cu²⁺ and Pb²⁺ ions sorption is practically identical, i. e. no specificity.

Comparison spent for the data in Table 1 leads to the following basic conclusions. Industrial wastewater is better to clean in several stages. For this type can be used sorbents N 2, 3, 6, 7, 8, and probably N 4, presented in the Table 1. If it is required to achieve the MPC a more efficient (and much more expensive) adsorbent such as №5 must be used.

Our results also allow us to conclude that the magnetic spinels obtained by co-precipitation, are as themselves good enough adsorbents.

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