

DETERMINING THE INFLUENCE OF THE MEDIUM REACTION AND THE TECHNIQUE OF MAGNETITE MODIFICATION ON THE EFFECTIVENESS OF HEAVY METALS SORPTION

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Розробка надійних, екологічно безпечних і економічно вигідних методів очищення води від важких металів є першочерговим завданням для охорони навколишнього середовища. Досліджено ефективність сорбційного очищення та доочищення природних вод від іонів важких металів при використанні модифікованого магнетиту. Як сорбент використовували зразки магнетиту отримані при співвідношенні концентрацій іонів заліза (II) і заліза (III) 1:2; 1:1 і 2:1, та зразки модифіковані сульфідом натрію. Експериментальними дослідженнями показано, що сорбційна ємність магнетиту по іонах важких металів зростає при збільшенні співвідношення $[Fe^{2+}]/[Fe^{3+}]$ від 1:2 до 2:1. Досліджено вплив рН середовища на ефективність сорбції іонів важких металів на магнетиті. Показано, що сорбційна ємність магнетиту по іонам міді, цинку, нікелю та кадмію зростає при збільшенні рН середовища від 6,0 до 8,6, що обумовлено частковим гідролізом іонів важких металів. Підвищення сорбційної ємності магнетиту відбувається при модифікуванні його гуанідіном, тіосемікарбазідом і сульфідом натрію, що дозволяє зменшити залишкові концентрації важких металів до $мкг/дм^3$. Використання модифікованого сульфідом натрію магнетиту, отриманого при $K=2$, дозволяє повністю з води вилучити іони кадмію, а концентрацію міді знизити до $1,2 мкг/дм^3$. Це підтверджує доцільність використання даних сорбентів для доочищення чи глибокого очищення води від іонів важких металів. Показано, що магнетит доцільно використовувати для вилучення із води іонів важких металів при наявності іонів жорсткості, які не впливають на селективність даного сорбенту по іонах важких металів. Таким чином, на основі отриманих результатів сорбційного очищення води від іонів важких металів при використанні магнетиту, запропоновано принципову технологічну схему очищення стічних вод атомних електростанцій при скиді у водойми

Ключові слова: магнетит, важкі метали, сорбційна ємність, модифікування, гуанідін, тіосемікарбазід, сульфід натрію

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1. Introduction

As a result of prolonged growth of anthropogenic loading, the environment gets polluted. At present, it is impossible to imagine human existence without permanent water supply, and the issue of contamination of water sources is becoming increasingly urgent. Some regions of the planet suffer from a catastrophic shortage of water; moreover, they face another problem – a low quality of water resources. It is felt particularly acute in industrial densely populated regions, where mine water discharges significantly contribute to this issue. The content of organic substances, petroleum products and heavy metals exceeds the established norms. Heavy metals arrive in natural sources with drains of galvanic, instru-

ment-making, chemical productions, mining and concentrating plants, thermal power plants and mine waters. Many enterprises have galvanic shops or areas of application of galvanic coating. Galvanic productions are among the largest water consumers and, accordingly, discharge huge amounts of waste – both liquid (galvanic drains) and solid (galvanic sludge). In paper [1], it is indicated that most often found heavy metals include copper, cadmium, and zinc. At the discharge of untreated or insufficiently treated galvanic drains into rivers, lakes and other surface water bodies, which contain a significant amount of heavy metals in its composition, the environment suffers huge damage. This leads to disruption of functioning of active sludge at municipal wastewater treatment plants, loss of natural ability of water bodies to

self-purification. High level of contamination of water sites with mineralized waters and toxic substances requires the development of effective measures to reduce this impact. In this regard, the problem of rational nature use and the transition to the use of environmentally friendly energy-efficient technologies is acute.

2. Literature review and problem statement

For the mining industry the method, developed in [2], provides a cost-effective treatment process for dumping in water bodies with the subsequent disposal of sediment. It was shown, that reagent purification is a very promising method of water demineralization, but the selection of reagents should be directed to making the process easier and simpler and avoiding re-contamination. The processes of treatment of water with low pollutant concentrations were not considered in the paper. The results of the studies of extraction of heavy metals based on the reagent deposition methods are cited in [3]. Residual concentrations are as follows: Cu^{2+} 0.09 mg/dm³, Ni^{2+} 0.009 mg/dm³, Sn^{4+} <0.005 mg/dm³. The impact of the type and concentration of complexing compounds on the effectiveness of reagent removal of heavy metals was studied in paper [4]. It was possible to decrease the residual concentration of pollutants to the values by Cu^{2+} 0.02 mg/dm³, Sn^{4+} <0.01 mg/dm³, Ni^{2+} <0.005 mg/dm³ at pH of 9.39 and Cu^{2+} 0.07 mg/dm³, Sn^{4+} <0.01 mg/dm³, Ni^{2+} 0.006 mg/dm³ at pH of 7.79. The methods of disposal of sediments formed in the process of the reagent water purification were not determined. In paper [5], nano-filtration and inverse osmotic membranes were used for water purification from the ions of copper, aluminum, iron and manganese, the rate of extraction of cations exceeds 95 %. However, the problem of the influence of high concentration of hardness ions on the productivity and selectivity of the membrane remains unresolved. The methods for stabilizing treatment of mineralized and mine waters before feeding to nano-filtration [6] and reverse osmotic membranes [7] were developed. It results in the increase in performance by 8–17 %, selectivity exceeded 90 %. However, the issue of the influence of hardness ions and pH on the effectiveness of catching heavy metals remains unresolved. The authors of paper [8] proposed to use the electro-coagulation method for wastewater purification from heavy metals. In paper [9], it was established that at the original concentration Zn^{2+} 50–2,000 mg/dm³, the extraction process passes most effectively at pH 4.0–6.5, current density of 4.2 mA/cm². However, this process is quite effective only for low concentrations of heavy metals or it requires pre-treatment of the solution. However, there are no data on deep water purification from the ions of heavy metals. Water is quite effectively purified from chromium when using ion exchange resins Amberlite IRN77 and Purolite C160, the sorption capacity of which is 25.63 mg/g, 15.44 mg/g, respectively [10]. For copper ions, they use C106 and IRC-748, the sorption capacity of which is 267.2 mg/g and 120 mg/g, respectively [11]. However, only the results of water treatment when using the ion exchange methods, there are no data on recycling the formed regenerative solutions. Biological methods of treatment are cost-effective, environmentally expedient and do not lead to the secondary contamination of water. Paper [12] showed that at the original concentrations of Cr^{3+} +50, 100, 150, 200 mg/dm³, the purification process lasts for 5, 12, 96, and

168 hours. Reduction of process duration is essential. The authors of the paper showed the negative influence of hardness ions on the efficiency of biological water purification from heavy metals. The methods of extraction of heavy metal ions from water in the presence of hardness ions, for example, at the discharge of water from nuclear power plants into surface water bodies were not determined. A promising method for extracting heavy metals from aqueous solutions can be sorption, which involves the use of low-cost effective sorbents [13]. It should be noted that the authors used sorbents in the untreated form, due to which they are characterized by low absorption properties. The feasibility and prospects for using ecologically friendly biosorption materials were determined in work [14]. However, there are no data on the disposal of used-up sorbents. Thus, having explored papers [2–14], it is possible to conclude that the problem of development of highly effective economic methods of deep-water purification from ions of heavy metals in the presence of hardness ions remains unresolved. To solve these problems, it is advisable to use the modified sorbents based on magnetite, which make it possible to remove ions of heavy metals from water with a high degree of purification. In addition, the effectiveness of water purification is also quite high in the presence of hardness ions. Used-up sorbents are fed to the metallurgical production for recycling. This makes it possible us to talk about the prospects of conducting research into sorption extraction of heavy metals ions in order to create ecologically safe water treatment technologies.

3. The aim and objectives of the study

The aim of this study is to modify sorbents based on magnetite and the methods of their application to enhance the effectiveness of processes of water purification from the ions of heavy metals to the levels that are lower than BAC.

To achieve the aim, the following tasks were set:

- to explore the processes of sorption of heavy metal ions and to determine the influence of pH of the medium on sorption capacity of magnetite-based sorbents, obtained at different ratios of concentrations of Fe^{2+} and Fe^{3+} in magnetite;
- to determine the influence of sodium sulfide, guanidine and thiosemicarbazide on sorption capacity of magnetite-based sorbents by heavy metals ions and to establish the minimum concentrations of heavy metals ions, which can be achieved with the use of magnetic sorbents.

4. Materials and methods for water purification from ions of heavy metals when using modified sorbents

4. 1. Studied materials used in the experiment

When the mixtures of salts of iron (II) and iron (III) were treated with 10 % alkaline solution in the range of 1:2; 1:1, 2:1, the sorbents with magnetic properties were obtained. In order to modify magnetite, we used guanidine, thiosemicarbazide in concentration of 1 % and sodium sulfide in concentration of 1 and 2 %. Solutions of ions of copper, zinc, cadmium, nickel and lead at the concentration from 1–10 mg/dm³ to 1,000 mg/dm³ were used as working solutions. Sorption was conducted under static conditions, 1,300 mg/dm³ of magnetite were added to the sample of the solution of the volume of 100–200 cm³ and residual concentrations were determined. During the studies, the concentra-

tion of iron in solutions was controlled, at pH of more than 6.0, their dissociation and dissolution in water were not observed.

4.2. Technique for determining the effectiveness of water treatment

The residual concentrations of heavy metal ions in water were determined by the method of Chronopotentiometry (analyzer M-CA 1000-5); residual values of pH of the medium were determined as well. All operations of the electrochemical cycle in the device were programmed and executed automatically, except for the introduction of the standard and the change of a sample. Sorption capacity (*a*) and purification degree (*Z*) were calculated from formulas:

$$a = \frac{V_p \cdot (C_o - C_e)}{M_c}, \text{ mg/g,}$$

$$Z = \left(1 - \frac{C_e}{C_o}\right) \cdot 100, \%$$

where *V_p* is the volume of the solution, dm³; *C_o* and *C_e* are the initial and equilibrium concentration of metal, mg/dm³; *M_c* is the sorbent weight, g.

5. Results of studies of water purification from ions of heavy metals

5.1. Determining the influence of pH on the sorption capacity of magnetite

The sorption capacity of magnetite for copper ions increases at the ratio of $K=[Fe^{2+}]/[Fe^{3+}]$ in the series 1:2; 1:1 and 2:1, at $K=1:1$ by 10 % higher than at $K=1:2$ (Fig. 1). In the study of the influence of pH on sorption capacity, it was found that at the increase in pH of the solution from 5.7 to 6.5 and further to 7.9 and 8.52, there is a significant increase in sorbent capacity. It is obvious that at these pH values, there is partial hydrolysis of copper ions with the inclusion of copper hydroxide into crystalline lattice of magnetite. That is why in this case, the mechanism of activated adsorption, which is irreversible and is characterized by large values of sorption capacity at insignificant values of equilibrium concentration of metal, is implemented. The equilibrium concentration of copper of pH=7.9 did not exceed 3.04 mg/dm³, and at 8.52 was below 0.2 mg/dm³, at this, boundary sorption achieved the value of 1135 mg/g. It is clear that magnetite crystals in this case were the centers of crystallization of copper hydroxide or oxide, formed due to hydrolysis of copper ions.

To extract the ions of lead, zinc and cadmium, the sorbent, synthesized at the ratio of the concentrations of $Fe^{2+}:Fe^{3+}$ (*K*) of 1:2, was used (Fig. 2).

Magnetite has sufficiently large selectivity for lead ions, at pH=6.9, its sorption capacity was 550 mg/g. Probably, at this pH value, lead can partially be hydrolyzed. Zinc and cadmium at these pH values are in the ionic form, so their extraction mainly occurs due to physical adsorption. At the same time, boundary capacity for zinc ions reached 92 mg/g, and for cadmium ions – 205 mg/g. If calculated in the molar ratio, capacity for zinc was 2.82 mg-equiv./dm³, and for cadmium, it was 3.66 mg-equiv./dm³. However, equilibrium concentrations of zinc and cadmium exceeded 7 mg-equiv./dm³, and equilibrium concentration of lead in the first sample

was at the level of 0.8 mg/dm³. If we talk about additional purification or deep purification of water from ions of heavy metals, it involves quite high residual concentrations. At the increase in pH up to 8.69, capacity of magnetite for zinc ions increases up to 550 mg/g and equilibrium concentrations were more than 4 mg/dm³, which is unsatisfactory result (Fig. 2).

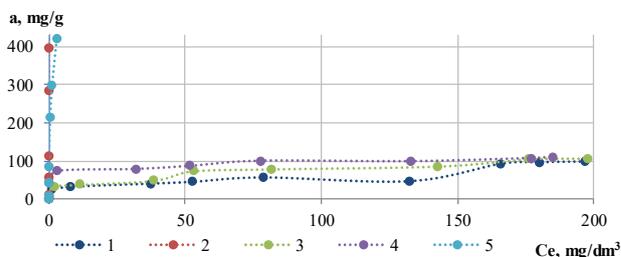


Fig. 1. Isotherms of copper absorption on magnetite: 1, 2 – $K=1/2$; 3, 4, 5 – $K=1$; 1, 3 – pH=5.7; 4 – pH=6.5; 5 – pH=7.9; 2 – pH=8.5.
1: $y=0,394x+19,39$; $R^2=0,867$;
2: $y=37989x^2-3465x+14,25$; $R^2=0,746$;
3: $y=-0,002x^2+0,969x+17,32$; $R^2=0,919$;
4: $y=-0,004x^2+1,207x+32,22$; $R^2=0,752$;
5: $y=-53,73x^2+289,1x+34,10$; $R^2=0,967$

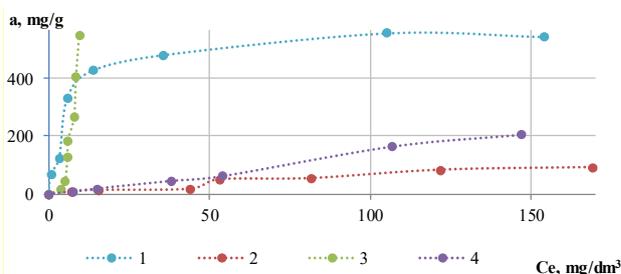


Fig. 2. Isotherms of absorption of heavy metal ions on magnetite $K=1/2$: 1 – Pb^{2+} ; 2, 3 – Zn^{2+} ; 3 – Cd^{2+} ;
1, 2, 4 – pH=6.9; 3 – pH=8.69.
1: $y=-5E-05x^4+0,016x^3-1,588x^2+50,88x+14,66$;
 $R^2=0,976$;
2: $y=0,571x+4,829$; $R^2=0,934$;
3: $y=9,731x^2-36,48x+2,330$; $R^2=0,973$;
4: $y=1,458x-5,323$; $R^2=0,989$

5.2. An increase in the effectiveness of extraction of heavy metals when using modified magnetite

To enhance the effectiveness of water purification from ions of heavy metals, modified magnetite was used. Magnetite obtained at the ratio of $K=2$, has capacity for copper by 4.4 times higher in comparison with magnetite, obtained at $K=1:2$ (Fig. 3). In this case, modification of magnetite by thiosemicarbazide leads to an increase in its sorption capacity by copper by 1.5–2.0 times. At magnetite modification by sodium sulfide, its sorption capacity for copper at $K=1:2$ increases from 85 to 332 mg/g, and at $K=2$ from 375 to 550 mg/h. Sorption was performed at pH 6.0–6.7. At $K=2$, in comparison with the case when $K=1:2$, there occurs an increase in sorption capacity of magnetite. This is due to the fact that in the first case, in the received sorbent, much of its mass is in the amorphous state, which increases the sorption surface area and adsorption volume. Magnetite at $K=1:2$ consists mainly of crystals. When introducing guanidine, thiosemicarbazide or sodium sulfide into the reactive

mass during the magnetite synthesis, the molecules of these compounds or sulfide anions are included in the magnetite structure. It is obvious that guanidine fragments containing groupings of type >C=N or thiosemicarbazide, containing groups >C=S, are able to form complex bonds with d-metals and consequently increase their sorption on magnetite. Sulfide anion is capable of forming insoluble compounds with many d-metals, which is why it is the most effective modifying reagent.

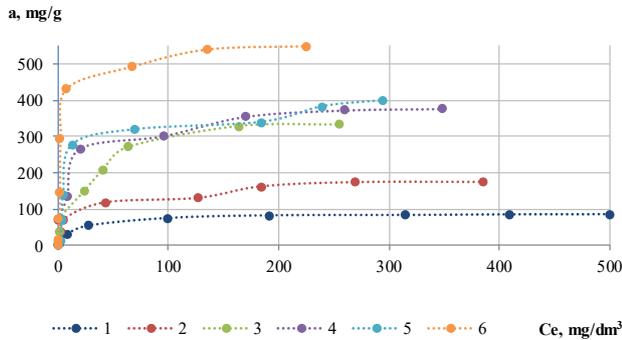


Fig. 3. Isotherms of adsorption of copper ions on magnetite: 1, 2, 3 – $K=1/2$; 4, 5, 6 – $K=2$; 1, 4 – non-modified; 2, 5 – modified by thiosemicarbazide; 3, 6 – modified by sodium sulfite.
 1: $y=3E-06x^3-0,003x^2+0,877x+14,11$; $R^2=0,911$;
 2: $y=-0,001x^2+0,896x+48,40$; $R^2=0,851$;
 3: $y=-0,010x^2+3,864x+38,42$; $R^2=0,939$;
 4: $y=-0,005x^2+2,648x+78,26$; $R^2=0,83$;
 5: $y=8E-05x^3-0,041x^2+6,593x+63,02$; $R^2=0,842$;
 6: $y=-0,018x^2+5,912x+146,6$; $R^2=0,694$

Magnetite modified by sodium sulfide ($K=2$) has a very high sorption capacity for ions of nickel and cadmium. For ions of zinc, the boundary sorption capacity reaches 300 mg/g (Fig. 4). A lower capacity of magnetite for zinc ions is due to the fact that during the sorption, pH of the solution decreased from 6.8 to 4.95, whereas in the case of nickel ions, pH changes within 7.15–5.39, and for ions of cadmium, pH changes within 6.70–6.34 (Fig. 5).

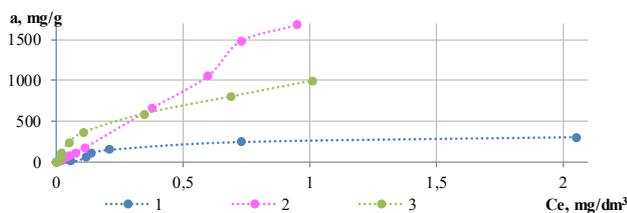


Fig. 4. Isotherms of adsorption on magnetite ($K=2$) modified by 2% solution of sodium sulfite: 1 – Zn^{2+} ; 2 – Cd^{2+} ; 3 – Ni^{2+}
 1: $y=-152,0x^2+449,1x+15,31$; $R^2=0,932$;
 2: $y=1860x-22,67$; $R^2=0,992$;
 3: $y=-928,3x^2+1836x+47,94$; $R^2=0,964$

It should be noted that in all cases, the degree of water purification from ions of heavy metals exceeded 99%. The equilibrium concentrations in the case of zinc ions changed from 0.06 to 2.05 mg/dm³, for cadmium ions, they increased from 0.016 to 0.950 mg/dm³ and for nickel ions from 0.008 to 1.010 mg/dm³.

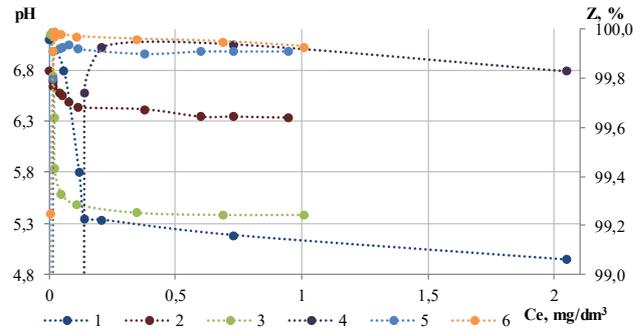


Fig. 5. Dependence of characteristics of the solution at sorption on magnetite ($K=2:1$), modified by 2% solution of sodium sulfite: 1, 2, 3 – pH; 4, 5, 6 – extraction degree; 1, 4 – Zn^{2+} ; 2, 5 – Cd^{2+} ; 3, 6 – Ni^{2+} .
 1: $y=-6,570x^3+19,52x^2-13,51x+7,209$; $R^2=0,937$;
 2: $y=-2,737x^3+4,709x^2-2,407x+6,706$; $R^2=0,877$;
 3: $y=-14,26x^3+25,04x^2-12,13x+6,742$; $R^2=0,674$

6. Discussion of results of studying the impact of magnetite modification on the effectiveness of water purification from ions of heavy metals

When dumping water into the fishing reservoir or during preparation of drinking water, there exist high requirements for the quality of water purification from ions of heavy metals. That is why the minimum concentrations which can be achieved with the use of magnetite-based sorbent were determined. When using magnetite, modified by sodium sulfide, it was possible to decrease the copper concentration to 5.44 $\mu\text{g}/\text{dm}^3$ at $K=1:2$ (Fig. 3). When using magnetite modified by sodium sulfite, obtained at $K=2$, it was possible to completely purify water from cadmium ions, and copper concentration was reduced to 1.2 $\mu\text{g}/\text{dm}^3$ (Fig. 4). The data obtained prove the appropriateness of the use of these sorbents during additional purification of water from ions of heavy metals.

Moreover, at pH of the solutions at the level of 7.9–8.5 (Fig. 1), capacity of magnetite by copper ions exceeds 400 mg/g, and at pH 6.9–8.7, capacity of magnetite for lead ions exceeds 400 mg/g and for zinc ions – 500 mg/g at low equilibrium metal concentrations (Fig. 2). The effectiveness of water purification from ions of heavy metals exceeds 99% (Fig. 5). If we consider that magnetite selectivity for ions of heavy metals is not affected by hardness ions, it is quite advisable to use this sorbent to extract heavy metal ions from water when there are hardness ions. Water consumption during water discharge from reservoirs of nuclear power plants can reach 10 m³/s, at the level of water hardness of 4–5 mg-equiv./dm³, it is not realistic to de-salt this amount of wastewater. The need for their extraction is caused by strict regulations on water discharge in the fishing reservoirs. The content of copper and zinc ions in wastewater in this case should be no more than 5–7 $\mu\text{g}/\text{dm}^3$. The low-waste technology of water demineralization involves complex recycling of formed sediments [15]. That is why, based on the obtained results, we proposed a fundamental technological circuit for treatment of wastewater of NPP during their discharge in fishing reservoir, shown in Fig. 6.

In this case, magnetite suspension is fed in the calculation of 50 mg/dm³, lime in the calculation for achieving

pH at the level of 8.0–8.5. The magnetite dose was chosen based on the magnetite capacity of 1 mg per 1 g of the sorbent. The clarifier with a suspended layer of sediment (5) is characterized by high productivity. In this case, a suspended magnetite layer that is accumulated in the clarifier plays the role of the sorption filter. The excess of magnetite is accumulated in the sediment accumulation zone and enters the sludge storage. Magnetite residue is extracted from water by the magnetic filter (8). After washing the filter, together with the sediment from the clarifier, it is dehydrated on the filter press. The resulting sediment enters the metallurgical production for recycling. The filtrate and purified water are discharged into the water body. The residue of heavy metals ions in the purified water is not more than 3–5 $\mu\text{g}/\text{dm}^3$.

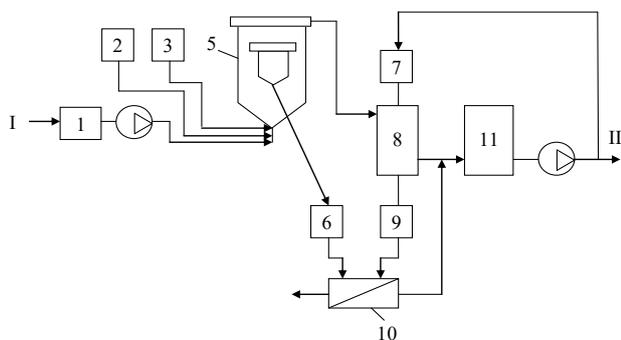


Fig. 6. Fundamental technological circuit of NPP wastewater purification from ions of heavy metals: 1 – suction chamber; 2, 3 – consumption tanks of lime and magnetite, respectively; 4, 12 – pumps; 5 – clarifier with a suspended sediment layer; 6, 9 – sludge storage; 7 – wash water tank; 8 – magnetic filter; 10 – tape filter-press; 11 – purified water reservoir; I – water intake from reservoir; II – water discharge into river

The main disadvantage of this method is the use of finely dispersed magnetite, which involves the mandatory use of clarifiers with a suspended layer of sediment and other equipment for its extraction in the water treatment processes. In addition, practical application of the method is limited to the need for dehydration and recycling moist sediments extracted from water. Another serious drawback of the direction is the withdrawal of used magnetite from the technological process and the need of synthesis of a fresh reagent.

The prospect of the development of this water treatment method is the application of the sorption layer of magnetite on the surface of the strongly acidic cation that

can be realized by the method of sorption of $\text{Fe}^{2+}/\text{Fe}^{3+}$ at the ratio of 2:1 followed by hydrolysis of iron salts during treatment with solution of alkali. The resulting sorbent will increase the process effectiveness by purifying water under dynamic conditions. Given the high capacity of the sorbent by ions of heavy metals and its regeneration simplicity, it will be possible to implement low-waste technology of water purification from heavy metals in the presence of hardness ions during its use.

7. Conclusions

1. It is established that sorption capacity of magnetite-based sorbents for ions of copper, zinc, nickel and cadmium depends on pH of the medium. The effectiveness of extraction of heavy metals increases at the increase in pH from 6.0 to 8.6. It was shown, that sorption capacity of magnetite-based sorbents for heavy metals ions depends on the ratio of concentrations of Fe^{2+} and $\text{Fe}^{3+}(K)$ ions in the reactive mixture. At the increase in K from 1/2 to 2, sorption capacity of sorbent increases for ions of copper by 4.4 times, cadmium – by 1.4 times, zinc – by 2.7 times, nickel – by 3.2.

2. The effectiveness of heavy metal ions on the magnetite modified by guanidine, thiosemicarbazide and sodium sulfide was studied. It was established that the highest degree of extraction of heavy metals was on magnetite, modified by sodium sulfide. It was found that when using modified magnetite-based sorbents, it is possible to decrease the concentration of heavy metals to microgram/ dm^3 . The fundamental technological circuit for the NPP wastewater purification from ions of heavy metals was proposed. Its features are the use of modified magnetite, which acts as a sorbent of heavy metals ions. The sorption of heavy metals ions, as shown in the studies, is implemented by stirring water suspensions. This process is implemented in the technology by the application of a clarifier with a suspended layer of sediment, which performs the functions of a mixer, a sorption filter, and a tank. The magnetite residues are removed from water on a magnetic filter (in laboratory research – on a mechanical filter). Used-up magnetite is dehydrated by the known technologies and arrives at metallurgical enterprises for recycling. Due to this, the circuit provides the possibility of purification of large volumes of water from ions of heavy metals in the presence of hardness ions to the norms on waste water discharge into fishing reservoirs. The developed technology for water purification from heavy metals is environmentally safe and energy efficient.

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