Effective functional materials for treatment of water from organic compounds

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The paper substantiates and experimentally confirms the possibility of obtaining copper-zinc ferritic materials from a sulfate copper-zinc electrolyte by co-precipitation in four modifications at a ratio of the initial molar concentrations of the components: $\sum Me^{2+} : Fe^{2+} = 1 : 2.5$. The main stages of obtaining copper-zinc ferritic materials are determined. The possibility of using the synthesized ferrite materials for water purification from organic dyes has been experimentally confirmed. The features and efficiency of using the synthesized ferrites as sorption materials are evaluated. The mechanism of purification of aqueous solutions from organic dyes by ferrite materials has been studied. It has been established that the adsorption process during purification of aqueous solutions from organic dyes by ferrite materials is described by first-order kinetic equations. The adsorption rate of methylene blue and methyl violet is 6 times higher than that of Congo red. Using CurveExpert Professional curve fitting and data analysis, non-linear $C_{02}-n$ dependences were analyzed. A scheme of the method to optimize the process of wastewater treatment from organic dyes by means of copper-zinc ferrite is proposed.

Keywords: copper-zinc ferrites, composite materials, mineral composition, organic dyes, treatment, cleaning process kinetics, sorption and photocatalytic properties.

Ефективні функціональні матеріали для очищення вод від органічних сполук.
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У роботі обґрунтовано та експериментально підтверджено можливість отримання мідно-цинкових феритних матеріалів із сульфатного мідно-цинкового електроліту методом співосадження у чотирьох модифікаціях при співвідношенні вихідних молярних концентрацій компонентів: $\sum Me^{2+} : Fe^{2+} = 1 : 2,5$. Визначено основні стадії одержання мідно-цинкових феритних матеріалів. Експериментально підтверджено можливість використання синтезованих феритних матеріалів для очищення вод від органічних барвників. Оцінено особливості та ефективність застосування синтезованих феритів як сорбційних матеріалів. Вивчено механізм очищення водних розчинів від органічних барвників феритними матеріалами. Встановлено, що адсорбція процесу очищення водних розчинів органічних барвників функціональними матеріалами описується кінетичними рівняннями першого порядку. Швидкість адсорбції метиленового синього і метилвіолету вище, ніж Конго червоного у 6 разів. За допомогою апроксимації кривих та аналізу даних CurveExpert Professional проаналізовано нелінійні моделі $C_{02}-n$. Запропоновано схему способу оптимізації процесу очищення стічних вод від органічних барвників за допомогою мідно-цинкового фериту.

1. Introduction

Modern scientific and technological progress is associated with a constant increase in water consumption by industrial enterprises. Chemical, construction, petrochemical and other industries consume large volumes of fresh water. At the end of the technological cycle, wastewater from enterprises contains various pollutants, including petroleum products, dyes, surfactants, heavy metal ions, etc. The entry of untreated or insufficiently treated wastewater

into water bodies causes economic damage and negatively affects the environment [1, 2]. The development of new highly effective wastewater purification technologies is still relevant. Treatment of industrial wastes and cyclic use of technical water is the basis of the technology of reusing water resources in many countries of the world.

The variety of industrial wastewater treatment methods presented in the scientific literature [3–5] shows the high efficiency of sorption methods of water treatment. Research in the field of obtaining sorption materials based on secondary resources is applicable, as it allows saving raw materials [6, 7]. One of the actively developing areas of chemical technology is the synthesis of ferrite composite materials (FC) and the study of their properties as sorbents [3, 8]. The ferrite method is a modification of the oxidizing reagent method of wastewater treatment from various pollutants using iron-containing reagents. In comparison with traditional reagent methods of industrial wastewater treatment [9], the possibilities for treating industrial wastewater using ferrites are significantly expanding. Magnetic nanocomposite sorbents synthesized by the authors [10] showed high efficiency in the utilization of anionic surfactants and polyphosphates from wastewater. Works [11–14] consider the sorption effect of ferrites when purifying water from organic dyes, as well as their use in treatment facilities in the oil industry. There is also an ecological aspect to using ferrites as sorbents. In [15, 16], the process of purifying copper-containing wastewater from impurities with the subsequent formation of ferrite compounds was investigated. The purifying effect of ferritization was more than 99.9 %. The presented results make it possible to assess the features and effectiveness of the application of ferrite materials. It has been shown [3] that the basis for the development of this method is the study of the physicochemical properties of the precipitate formed during ferritization. Research on the creation of sorption materials based on secondary resources is relevant, since waste recycling reduces the resource intensity of production, cheap sorbents with unique properties are synthesized, and environmental problems of water treatment processes are solved.

The purpose of the work was to study and justify the effectiveness of the synthesized copper-zinc ferrite materials for purifying water from organic compounds.

2. Experimental

The choice of model solutions is justified by the qualitative and quantitative composition of wastewater from enterprises using α-brass processing. The process of ferritization of sulfate copper-zinc electrolyte includes the following stages:

− mixing a model solution with a water-soluble salt of Fe(II);

− formation of metal hydroxides;

− oxidation of Fe(II) ions and formation of ferrites;

− separation of the obtained ferrites from the liquid phase and their washing;

− determination of the composition of the obtained ferrites.

The sequence of the stages ensures the production of copper and zinc ferrites in a short time interval with complete precipitation of heavy metal ions from the copper-zinc electrolyte.

The precipitated compounds were identified by XRD phase analysis on a powder diffractometer "Siemens D–500" in copper radiation with a graphite monochromator. Full profile diffraction patterns were recorded in the angle range $5 < 2\theta < 80°$ with a step of $0.02°$ and an accumulation time of 40 seconds. The initial search for phases was performed by PDF-1 card index [17], after which X-ray diffraction calculations were performed according to the Rietveld method using the FullProf program [18].

Elemental composition and morphological features of the precipitates were studied by electron-probe microanalysis (ERMA) on a JSM-6390 LV scanning electron microscope with an INCA X-ray microanalysis system. Deviations in determining the mass fractions of elements were 1.5–8.5 %.

The sorption activity of FC was studied using the organic dyes methyl violet (MV), methylene blue (MB) and Congo red (CR). MV has a stable color in the range of pH≥7. The quantitative characteristics of the sorption process were calculated according to formulas (1) and (2): E is the efficiency of the FC sorption process and a is the specific activity of ferrite composites FC (the mass of transformed and absorbed substance per unit mass of FC)

$$E = \frac{(C_0 - C_x)100}{C_0} \text{ , \%;} \qquad (1)$$

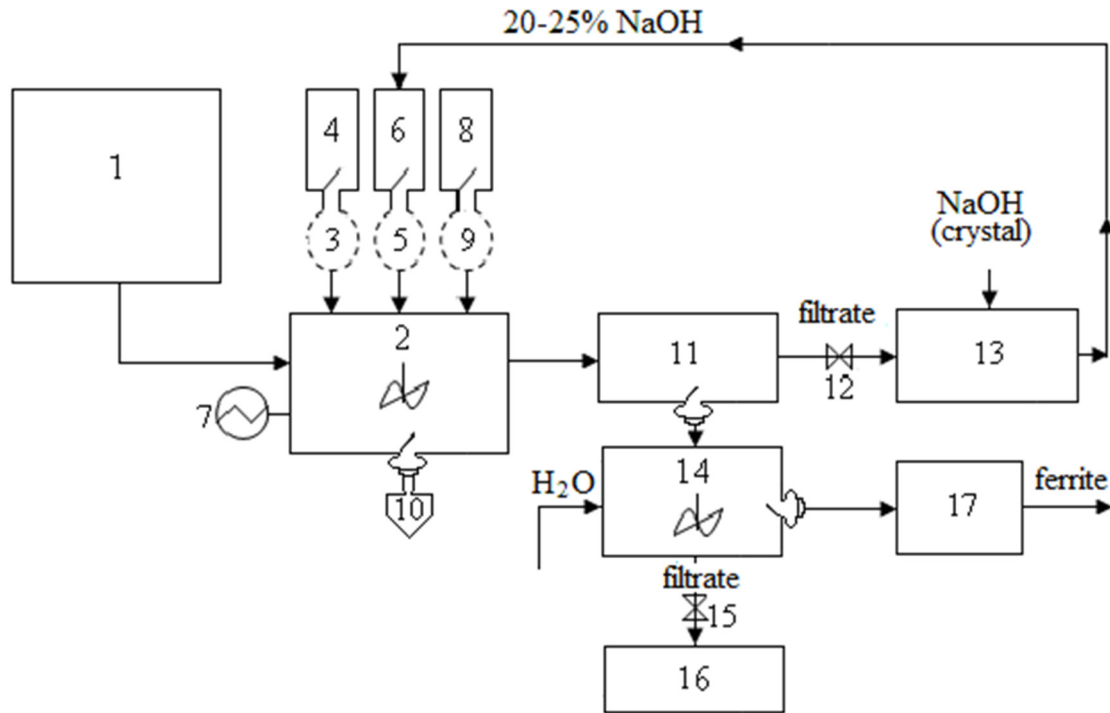$$a = \frac{(C_0 - C_x)V}{m} \text{ , mg/g.} \qquad (2)$$

Fig. 1. Scheme of the method of obtaining ferrites using spent copper-zinc sulfate solutions: 1 – spent copper-zinc sulfate electrolyte; 2 – tank for mixing with water-soluble salt $FeSO_4 \cdot 7H_2O$; 3, 5, 9 – dispenser; 4 – tank with salt $FeSO_4 \cdot 7H_2O$; 6 – container with NaOH ; 7 – temperature controller; 8 – tank with oxidizer; 10 – sampler; 11 – settler-distributor; 12, 15 – pump; 13 – tank for adjusting the concentration of the NaOH solution; 14 – tank for washing the received ferrite; 16 – tank with washed ferrite

where: C_0 is the initial concentration of the dye in the solution, 10 mg/L; C_x is the concentration of the dye at a certain point in time, mg/L; V is the volume of the solution, L; m is the mass of ferrite, g.

3. Results and discussion

Ferritic copper-zinc composites were obtained by the method of coprecipitation of copper, zinc and iron(II) ions introduced in $FeSO_4 \cdot 7H_2O$ salt, with the ratio of initial molar concentrations: $\sum Me^{2+} : Fe^{2+} = 1 : 2.5$. The process was carried out with stirring and heating. After dissolving Fe(II) sulfate, a 20–25 % solution of sodium hydroxide was added to the mixture to pH10. Mixed hydroxides of heavy metals were formed in an alkaline medium. at a temperature of 60–65 °C

$$xCu^{2+} + yZn^{2+} + zFe^{2+} + nOH^- \rightarrow Cu_xZn_yFe_z(OH)_n\downarrow. \quad (3)$$
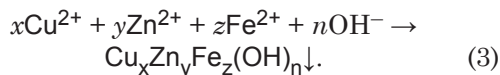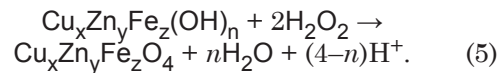
Modifications of co-precipitation differed in the method of supplying the oxidant – molecular oxygen:

– in the form of gaseous oxygen (with the production of composite FC-O materials) [19]

$$Cu_xZn_yFe_z(OH)_n + (2{-}0{,}25n)O_2 \rightarrow Cu_xZn_yFe_zO_4 + 0{,}5nH_2O. \quad (4)$$
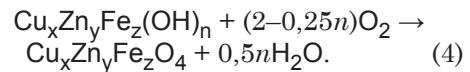
– 35% hydrogen peroxide solution (FC-HP) [20]

$$Cu_xZn_yFe_z(OH)_n + 2H_2O_2 \rightarrow Cu_xZn_yFe_zO_4 + nH_2O + (4{-}n)H^+. \quad (5)$$

– solid salt of potassium peroxodisulfate $K_2S_2O_8$ (FC-PDS) [21]

$$Cu_xZn_yFe_z(OH)_n + S_2O_8^{2-} \rightarrow Cu_xZn_yFe_zO_4 + 2SO_4^{2-} + (8{-}n)H^+ + (n{-}4)H_2O. \quad (6)$$
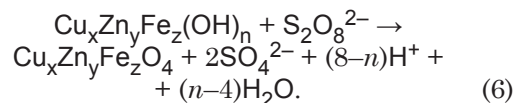
In the fourth modification of co-precipitation, the salt $Fe_2(SO_4)_3$ was added to the solution of copper and zinc salts in the ratio $\sum(Cu^{2+} + Zn^{2+}) : Fe^{3+} = 1 : 1$ [22]. In an alkaline medium, with the injection of oxygen and the introduction of sodium sulfite, $\gamma\text{-}Fe_2O_3$ was formed, which serves as the basis for the formation of Cu-Zn-ferrite (FC-FS)

$$2Fe^{3+} + 1.5O_2 + 6\bar{e} = \gamma\text{-}Fe_2O_3. \quad (7)$$
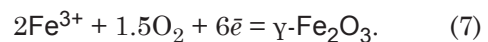
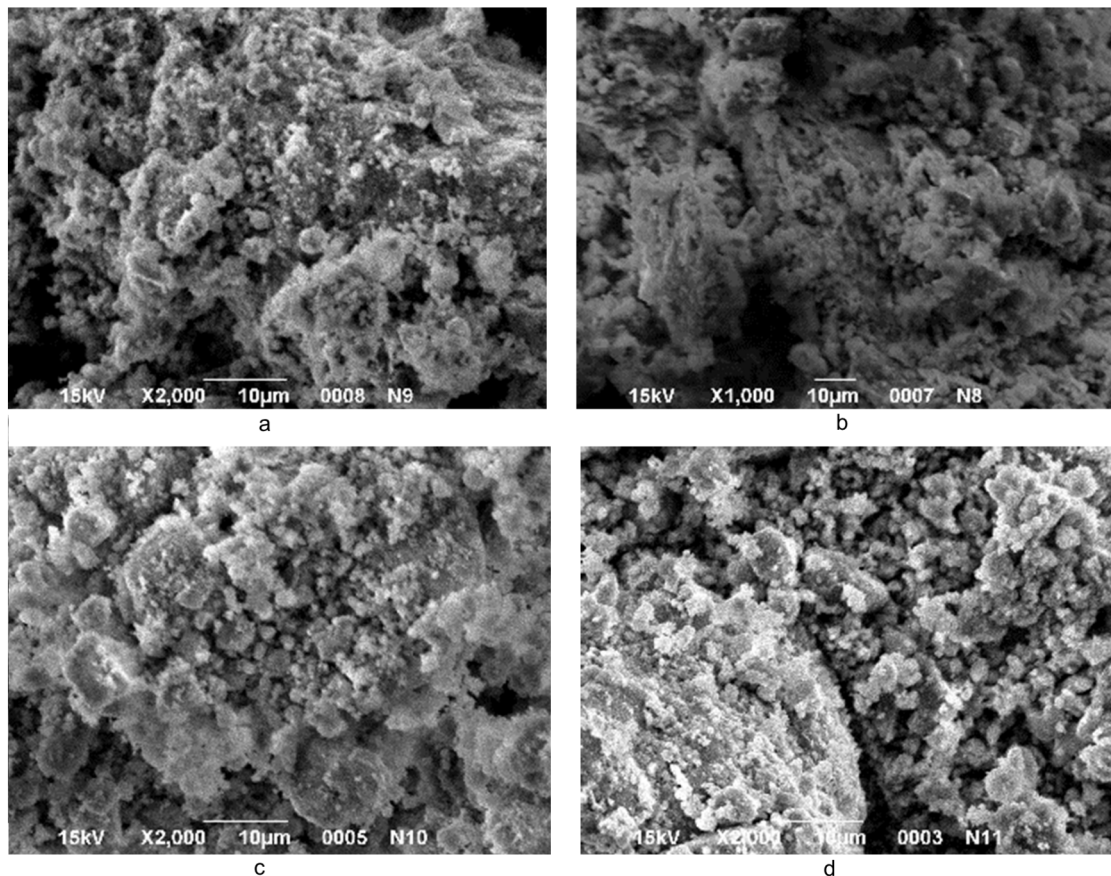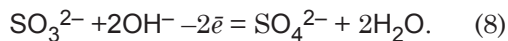In this case, the oxygen reducing reagent is salt Na_2SO_3, which was introduced in the ratio $Fe^{3+} : Na_2SO_3 = 1 : 0.5$

Fig. 2. Microphotographs of the surface of FC particles (magnification 1000–2000): a – FC-O, b – FC-HP, c – FC-PDS, d – FC-FS

$$SO_3^{2-} + 2OH^- - 2\bar{e} = SO_4^{2-} + 2H_2O. \quad (8)$$

After synthesis, Cu-Zn ferrites were washed with water to remove impurities and dried. The process of obtaining ferrites using spent copper-zinc sulfate solutions is presented in Fig. 1.

After processing the brass, the spent copper-zinc sulfate electrolyte from tank 1 is sent to the first stage of purification into reactor 2 for heating and mixing with the water-soluble salt $FeSO_4 \cdot 7H_2O$, supplied through dispenser 3 from tank 4. After the dissolution of iron(II) sulfate the stage of precipitation of heavy metal hydroxides follows, NaOH solution is supplied to reactor 2 through dispenser 5 from container 6. Mixing in reactor 2 is carried out at a temperature of 60–70 ºC, maintained by thermostat 7. Oxidation of Fe(II) ions occurs with an oxidizing reagent, which is fed into reactor 2 from tank 8 through dispenser 9. At the same time, the temperature increases to 85–100 ºC and is maintained by temperature regulator 7. To control and adjust the pH of the mixture, samples are taken from reactor 2 using sampler 10.

The mixture enters the settler-distributor 11, in which, after settling, the solid precipitate is separated. The filtrate containing sodium hydroxide is pumped through pump 12 into tank 13, where the concentration of the resulting NaOH solution is adjusted to the values required by the technological regulations and returned to the technological process in tank 6. The precipitate is sent to tank 14 for the purpose of washing away soluble impurities. After settling and decanting the precipitate, the filtrate is pumped by pump 15 into tank 16. The purity of obtained ferrite precipitate is controlled using X-ray phase analysis 17.

Mineralogical and elemental composition of FC. Composition of copper-zinc ferrites is calculated from mineral and elemental composition of ferrite composites. According to the X-ray phase analysis, the samples of the composite materials contain ferrite phases in the form of spinel with the general formula $Fe_xZn_yCu_zO_4$, as well as impurities Na_2SO_4, $NaHSO_4$, $KNaSO_4$, $K_3Na(SO_4)_3$, CuO, Cu_2O, Fe_2O_3. The CuO phase is contained in FC-O (9 %), FC-HP (4 %) and FC-PDS (7 %) samples. The presence
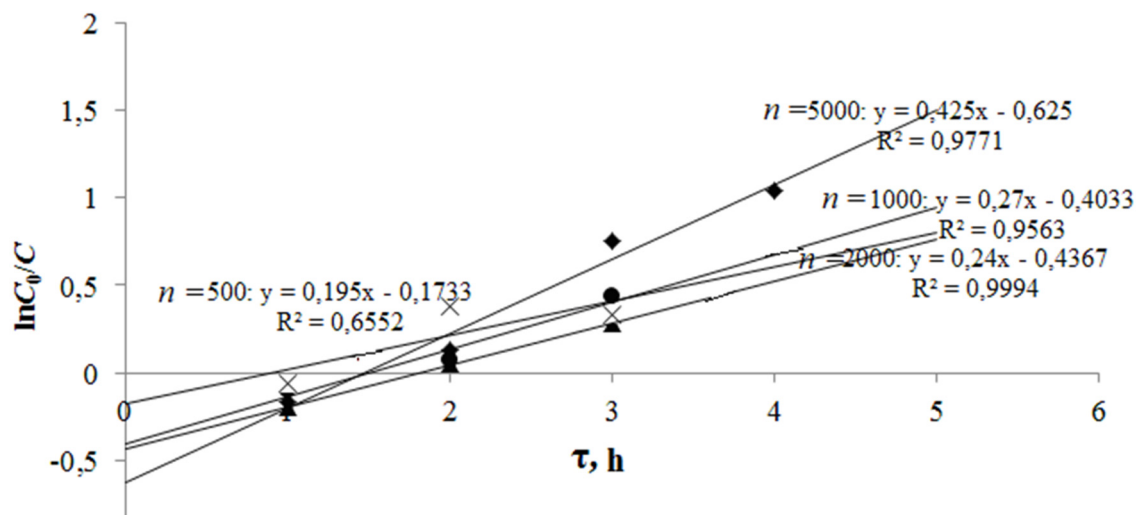
Fig. 3. Purification of MB solutions over time at different mass ratios n

of maghemite γ-Fe_2O_3, found in FC-HP (10.5 %), FC-PDS (36 %) and FC-FS (37 %), indicates some instability of the ferrite phase, since Fe_2O_3 was absent before water washing. Fe_2O_3. The multicomponent nature of FC and the presence of insoluble CuO, ZnO, and Fe_2O_3 oxides are not critical for the use of FCs as sorbents, since these oxide phases exhibit sorption properties.

Microscopic studies showed that the FC-O, FC-HP, FC-PDS, FC-FS samples have a developed surface with a large number of pores of different shapes and sizes (Fig. 2).

The complex morphology of the FC surface can facilitate layer-by-layer penetration and retention of adsorbed metal ions, molecules of organic compounds, petroleum products, and other hydrocarbon products. This means that, according to the characteristics of the surface layer, all studied FCs are good sorbents.

The mechanism of purification of aqueous solutions from organic dyes using FC. To increase the efficiency and completeness of treatment, an experimental database on the kinetics of the process has been created on the mechanism of purification of aqueous solutions from organic dyes (OD) – MB, MV and CR using a ferritic composite material $Zn_{0.875}Cu_{0.1}Fe_{4.42}O_4$ at various mass ratios n = "FC: OD". To determine the order of the reaction, a graphical method was used: experimental data on changes in the concentration of dyes over time were presented in such coordinates that the dependence was linear. The first order of the purification process is confirmed by the linearity of the graphs in coordinates $\ln C_0/C = f(t)$; for example, Fig. 3 shows the treat-

ment of MB solutions over time using FC with various mass ratios n.

Previously, a change in the kinetics of the purification process with time was found [9]. The presence of two linear sections with different angles of inclination on the "$\lg C$ – time" dependences indicates a change in the mechanism of the process. At the initial stage of treatment, a significant role is played by mass transfer along the phase boundary and the predominance of photocatalytic transformations of OD on the surface of ferrites. The dye concentration sharply decreases within 5 hours. The subsequent gradual decrease in the concentration of OD in the time interval of 5–24 hours indicates the occurrence of adsorption.

The results of processing the kinetic curves of solution purification according to the mechanism of photocatalysis and adsorption in chemical kinetics models are presented in Tables 1 and 2. The rate of dye removal depends on the value of n; this is explained by a change in the surface area of phase separation with a change in the mass of ferrite. Tables 1 and 2 present the averaged values k_{av1} and k_{av2}, on the basis of which the half-transformation periods τ_{av1} and τ_{av2} were calculated using the relation:

$$\tau = \frac{0,693}{k}$$

The kinetic equations presented in Tables 1 and 2 make it possible to calculate the dye concentration and the rate of solution purification at various time intervals.

The highest photocatalytic activity of ferrite was registered towards the MV dye. The value of τ_{av1} for the MB dye is ~1.5 times less than

Table 1 – Rate constants and kinetic equations for the processes of purifying solutions from organic dyes using ferrite with the predominance of photocatalytic transformations

n, mg/g	k, h^{-1}
MB	
500	0.195
1000	0.27
2000	0.24
3000	–
5000	0.425
$k_{average1}$, h^{-1}	0.2825
$\tau_{average1}$, h^{-1}	2.4531
Kinetic equation	$C_1 = C_{01} \cdot e^{-0.28t}$
MV	
500	0.413
1000	0.606
2000	0.507
3000	0.318
5000	0.309
$k_{average1}$, h^{-1}	0.4306
$\tau_{average1}$, h^{-1}	1.6094
Kinetic equation	$C_1 = C_{01} \cdot e^{-0.43t}$
CR	
500	0.055
1000	0.111
2000	0.163
3000	0.109
5000	0.2
$k_{average1}$, h^{-1}	0.1276
$\tau_{average1}$, h^{-1}	5.431
Kinetic equation	$C_1 = C_{01} \cdot e^{-0.13t}$

Table 2 – Rate constants and kinetic equations for the processes of purifying solutions from organic dyes using ferrite with the predominance of adsorption

n, mg/g	k, h^{-1}
MB	
1000	0.06616
2000	0.048
3000	–
5000	0.0445
$k_{average2}$, h^{-1}	0.0529
$\tau_{average2}$, h^{-1}	13.1002
Kinetic equation	$C_2 = C_{02} \cdot e^{-0.0529t}$
MV	
50	0.0026
100	0.0198
500	0.0519
1000	0.0285
2000	0.0085
3000	0.0559
5000	0.1207
$k_{average2}$, h^{-1}	0.0476
$\tau_{average2}$, h^{-1}	14.5588
Kinetic equation	$C_2 = C_{02} \cdot e^{-0.0476t}$
Dependence of C_{02} on n	$C_{02} = C_{01} \cdot 0.8456 \cdot e^{-0.00259n}$
CR	
500	0.0047
1000	0.0016
2000	0.008
3000	0.0196
5000	0.0042
$k_{average2}$, h^{-1}	0.0076
$\tau_{average2}$, h^{-1}	91.1842
Kinetic equation	$C_2 = C_{02} \cdot e^{-0.0076t}$
Dependence of C_{02} on n	$C_{02} = C_{01} 0.671\, e^{126.4/n}$

that for MV, and 3.4 times for CR, which is due to the anionic nature of the CR dye and the repulsion of its anion from negatively charged ferrite surface.

A comparative analysis of the data in Tables 1 and 2 shows that the kinetic characteristics of photocatalytic processes involving ferrite are an order of magnitude higher than those for dye adsorption ($k_{av1} > k_{av2}$). The decrease in the rate of photocatalytic transformations of dyes with time is associated with a change in the ferrite surface due to its shielding by the OD layer during adsorption. As a result, photogenerated active particles cannot migrate away from the centers of their formation, which leads to a sharp decrease in the rate of photoprocesses.

Adsorption during the purification of aqueous solutions from organic dyes using FC is described by first-order kinetic equations. The adsorption rate is low and practically the same for all dyes: $k_{av2} = 0.008$–0.07 h^{-1}. In
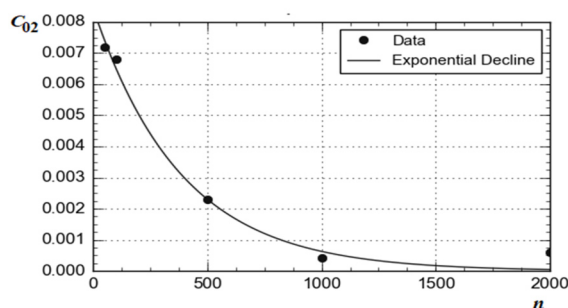

Fig. 4. Nonlinear C_{O2}–n dependence

this case, the time τ_{av2} for adsorption is much longer than τ_{av1} for photocatalysis. The adsorption rate of MB and MV is 6 times higher than that of CR.
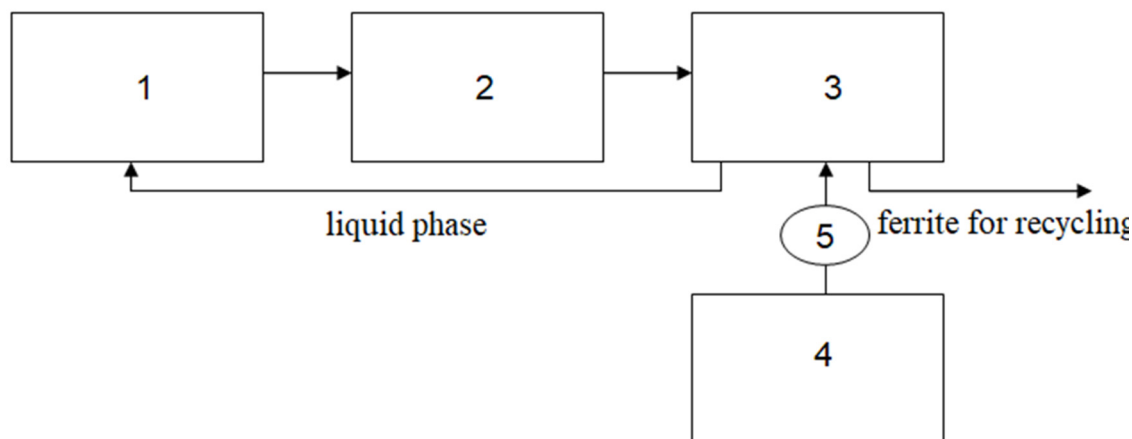
Fig. 5. Scheme of the method for optimizing the process of purifying wastewater with copper-zinc FC from OD: 1 – OD aqueous solution; 2 – analysis of the OD solution to replenish the experimental database; 3 – tank for purification; 4 – tank with synthesized copper-zinc FC; 5 – dispenser

Depending on the initial concentration of dye C_{O1}, the concentration C_{O2} will also change; thus the maximum amount of dye that ferrite can adsorb at a given value of n is determined. The C_{O2} value is determined at the point of intersection of the extrapolated segment II with the OY axis (Fig. 4). From the obtained experimental data, the C_{O2}–n dependences were derived. CurveExpert Professional cross-platform solution for curve fitting and data analysis was used for non-linear model fitting. The resulting nonlinear C_{O2}–n dependences are exponential in nature. They are described by the following equations: $C_{02} = C_{01} \cdot 0.8456 \cdot e^{-0.00259n}$ for the case of MV dye (in Fig. 4, the curve is obtained with a standard error $3.99 \cdot 10^{-4}$ and a correlation coefficient 0.995) and $C_{02} = C_{01} 0.671 \, e^{126.4/n}$ for the case of CR dye.

Determination of the optimal contact time of FC with OD solutions. The optimal contact time of FC with solutions of organic dyes was calculated. When purifying a solution from MV with an efficiency of 85%, then $C_{MV} = 0.15 \, C_{0MV}$. Assuming that the decrease in dye concentration is associated with photocatalytic transformations (Fig. 4), to calculate the process time we use the equation $C_{1MV} = C_{01MV} \cdot e^{-0.43t}$. This time actually corresponds to the first part of the broken curve. Thus, the experimental database makes it possible to determine with great accuracy an important process parameter – the time of contact of the FC and the OD solution without additional analyses and with the timely release of the settling tanks for new portions of wastewater.

A method for optimizing the process of wastewater purifying from OD with cop-per-zinc ferrite is schematically shown in Fig. 5. From the technological cycle (1) wastewater containing organic dyes is supplied to research (2) to replenish the experimental database. Then the wastewater is supplied to the tank (3) for treatment. The pre-synthesized copper-zinc ferrite is supplied from the tank (4) using a dispenser (5) to the tank (3). After the purification is completed, water is supplied into the technological cycle (1). The spent ferrite material is sent for recycling.

This method reduces the time of the technological process, taking into account the change in time of its mechanism, allows varying the process parameters: the concentration of dyes or the mass of ferrites, provides optimization of the process and the possibility of achieving a certain efficiency of wastewater treatment using an experimental database of kinetic data, rapid release of sedimentation tanks, an increase in volumes of treated wastewater.

4. Conclusions

The possibility of obtaining copper-zinc ferrite materials from sulfate copper-zinc electrolyte by co-precipitation in the form of four modifications at a ratio of initial molar concentrations of components $\sum Me^{2+} : Fe^{2+} = 1 : 2.5$ was substantiated and experimentally confirmed.

The main stages of production of copper-zinc ferritic materials were determined: mixing of the spent sulphate copper-zinc solution with water-soluble ferrous salt; formation of metal hydroxides; oxidation of Fe(II) ions and formation of ferrites; separating the obtained ferrites from the eluate and washing them; determination of the composition of the obtained ferrites.

The presence of ferrite phases in the form of a spinel with the general formula $Fe_xZn_yCu_zO_4$ and the complex developed morphology of the FC surface can characterize their sorption properties from the standpoint of choosing an effective sorbent.

It has been established that the adsorption process during purifying aqueous solutions from organic dyes of FC is described by first-order kinetic equations. The adsorption rate is low and practically the same for all dyes. The adsorption rate of MB and MV is 6 times higher than that of CR.

Using curve approximation and data analysis with the CurveExpert Professional program in a nonlinear model, it was found that the resulting nonlinear C_{02}–n dependences are exponential in nature. The proposed equations for the nonlinear C_{02}–n dependences made it possible to determine with great accuracy the time of contact between the FC and OD solution; this allows eliminating additional analyzes and timely empty settling tanks for new portions of wastewater.

A scheme of the optimized process of purifying wastewater from OD using copper-zinc ferrite is proposed.

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