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The use of ferrite composites for waste water purification from organic dyes

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The photocatalytic and sorption properties of the Cu–Zn-ferrite composites (FCs) were studied spectrophotometrically during the purification of solutions from methylviolet MV, methylene blue MB, and Congo red CR. It is shown that the first-order reaction is observed throughout the entire time interval of the purification process when the mechanism is changed from the predominant photocatalysis to adsorption within 3–5 h. The purification efficiency (E) and activity of individual FCs vary depending on the type of dye and the ferrite composition. The specific activity of FC is high when purified from all dyes at a mass ratio of "FC-to-dye" $n \geq 500$. Optimal n varies within 700–1370. Anionic character of CR reduces the purification efficiency E in comparison with MV and MB. The reuse of FCs with a reduced E is advisable in the case of prolonged contact of FC with colored solutions in sedimentation tanks. The mathematical model of the cleaning process was created using the MATLAB application package (Toolbox subsystem). Optimization of the total cleaning processes was carried out by deriving third-order regression equations "E196n–time" with an extended range of optimal values of the process parameters.

Keywords: ferritic composite, organic dyes, photocatalysis, sorption, efficiency, mathematical model.

Використання феритних композитів для очищення стічних вод від органічних барвників. *В.В.Даценко, Е.Б.Хоботова, В.М.Колодяжний, Д.О.Лісін*

Фотокаталітичні та сорбційні властивості Cu–Zn-феритних композитів (ФК) досліджували спектрофотометрично при очищенні розчинів від метилвіолету МВ, метиленового синього МС та Конго червоного КЧ. Показано, що реакція першого порядку спостерігається на всьому часовому інтервалі процесу очищення при зміні механізму з переважного фотокаталізу на адсорбційний протягом 3–5 годин. Ефективність очищення (ІЕ) та активність окремих ФК варіюються залежно від типу барвника та складу фериту. Питома активність ФК висока при очищенні від усіх барвників при масовому співвідношенні "ФК:барвник" $n \geq 500$. Оптимальне n варіює в межах 700–1370. Аніонний характер КЧ знижує ефективність очищення проти МВ і МС. Повторне використання ФК із зниженою величиною E доцільно при тривалому контакті ФК із забарвленими розчинами у відстійниках. Математична модель процесу очищення створювалася за допомогою пакету прикладних програм MATLAB (підсистема Toolbox). Оптимізація сумарних процесів очищення проводилася шляхом виведення рівнянь регресії третього порядку "E–n–час" з розширеним діапазоном оптимальних значень параметрів процесу.

1. Introduction

Creation of low-waste cycles is the urgent task of chemical technology. This applies to technological processes with the formation of colored wastewater. Recently, the use of oxide and ferritic materials has been intensified for adsorption purification [1–5] and photocatalytic degradation of dyes up to photo-mineralization [1, 6–11]. The main task is to achieve high efficiency of photocatalytic processes using nanomaterials. For example, as was shown for TiO_2 [12], additions of the *p*-type semiconductor CdO [13] and Cu(II) affect the band gap of the base material, expanding the light-absorbing ability of TiO_2 into the visible region [14, 15]. The activity of photocatalysts depends on the type of anions in the solution. Sulfate ions have a double effect: they cause colloidal instability and reduce the surface contact between the dye and the photocatalyst [16]. On the other hand, they enhance the photodegradation of dyes under UV irradiation [17], and increase the ionic strength of the solution, which leads to an increase in photocatalytic efficiency [18].

Optimization of the photocatalyst dose for efficient removal of dyes is topical. The dose depends on the morphology of the photocatalyst particles, the radiation intensity, the type of dye and the degree of its adsorption. The adsorption of dyes on the TiO_2 surface extends the absorption spectrum from UV to the visible range [19]. However, with an increase in the catalyst dose, the adsorption of dyes increases greatly, the layers of dye molecules screen the surface and reduce the intensity of photocatalysis. As the catalyst mass increases, the rate of photo-processes first increases and then decreases [20].

The aim of the work was to study the efficiency of purifying the solutions from dyes depending on the type of dye, the composition of the Cu–Zn-ferrite composite (FC) and its repeated use; create a mathematical model of the purification process.

2. Experimental

FCs based on copper and zinc ferrites were obtained by coprecipitation from copper-zinc solutions, which are waste products of galvanic production. A similar approach to processing waste was used by the authors earlier in the production of technically useful galvanic sludge [21]. The synthesis of FC was carried out by heating with pH 10–10.5 in two versions: 1) with addition of $FeSO_4 \cdot 7H_2O$ and further introduction of oxidizing agents O_2 (FC-O was obtained), H_2O_2 (FC-PH), $K_2S_2O_8$ (FC-PDS) [22–24]; 2) by the introduction of $Fe_2(SO_4)_3$, Na_2SO_3 with simultaneous oxygen saturation (FC-FS). FC samples were washed from soluble impurities. The mineral and elemental composition of FC was calculated taking into account the free phases of CuO, Cu_2O and Fe_2O_3: FC-O — $Zn_{0.875}Cu_{0.1}Fe_{4.42}O_4$ [23], FC-PH — $Zn_{0.98}Cu_{0.37}Fe_{3.66}O_4$ [23], FC-PDS — $Zn_{1.66}Cu_{0.448}Fe_{3.77}O_4$ [22], FC-FS — $Zn_{2.28}Cu_{1.6}Fe_{7.23}O_4$ [24].

Photocatalytic and sorption properties of FCs were studied during the purification of aqueous solutions from dyes: methyl violet MV, methylene blue MB (cationic dyes), and Congo red CR (anionic dye). Dye concentrations were determined spectrophotometrically on a SPEKOL 11 spectrophotometer at wavelengths of $\lambda = 620$ nm (MV, MB) and $\lambda = 500$ nm (CR). Purification of aqueous solutions from dyes was carried out in a static mode for 1–96 hours. The change in the rate of the dye conversion process in time "*C*–time" was determined at various mass ratios n = "FC:dye" (mg : mg); as well, the dependence of the efficiency E of the process of purifying the solution from the dyes and the mass of the converted dye per unit of FC mass a (FC specific activity) were established. The quantitative indicators of the process are calculated using the following formulas:

$$E = \frac{(C_0 - C_x)100}{C_0}, \%; \quad a = \frac{(C_0 - C_x)V}{m}, {}^{mg}/_{g}, \quad (1)$$

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

Sorption and photocatalytic properties of FC. The obtained FCs have a number of characteristics that make it possible to exhibit photocatalytic and sorption activity: nanocrystallinity, the corresponding mineral composition with the presence of ferrite phases of the general formula $Zn_xCu_yFe_zO_4$ including the semiconductors ZnO, Fe_2O_3 and CuO. The band gap of ferrite phases can change significantly with a change in the content of transition metals Cu and Zn [13], as shown in [6] for Zn. The band gap is also affected by the average

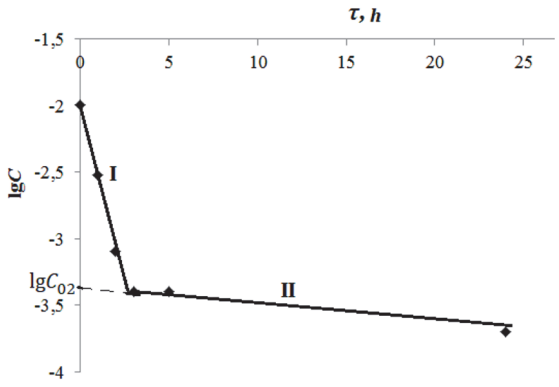

Fig. 1. Dependence of $\lg C_{MV}$ on time when using FC-PH with n = 1000.

crystallite size, deformation and the lattice parameter, phase purity, and concentration of charge carriers. The presence of SO_4^{2-} ions in the solution leads to their adsorption on the FC surface. The interaction of SO_4^{2-} with the holes in the valence band produces a very strong oxidizing agent SO_4^{-} with a long half-life and high selectivity for the oxidation of organic pollutants in a wide pH range [18, 25]. Apparently, FC exhibit photocatalytic activity already during the first hours of contact with dye solutions. The change in the dye concentration with time, presented in semilogarithmic coordinates (Fig. 1), indicates that, if the first order of the reaction is observed, the mechanism of the process changes after 3–5 h for all values of n. Section I corresponds to a rapid decrease in the concentration of the dye during photocatalytic transformations, section II shows the course of adsorption. The value of the oxygen concentration C_{02} determines the maximum amount of dye that can be adsorbed by FC at a given n.

Efficiency of purifying solutions from dyes when using FC. The quantitative assessment of the process of purifying solutions from dyes was carried out according to the values of a and E after 96 h (Fig. 2). The results (Fig. 2, curves 1, 3, 5, 7) show that all FCs are characterized by a high a in the processes of purification of solutions from dyes. The specific activity of FC in terms of dye conversion is different (Fig. 2a–c). The value of a from FC-PH (curve 1) and FC-O (curve 3) is greater than from FC-PDS (curve 5) and FC-FS (curve 7). Ferrite composites are characterized by high values of a when removed from all dyes at $n \geq 500$. The "$a - n$" dependences are characterized by two sections with different slope angles. With an increase in the weight of the FC sample in the first section (interval

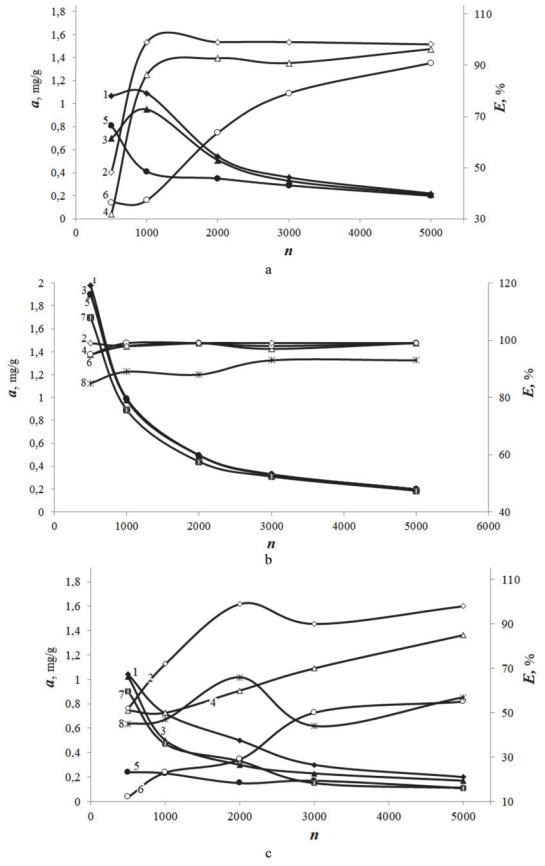

Fig. 2. Dependence of the specific gravity of the converted dye by ferrite composites a (curves 1, 3, 5, 7) and the efficiency of the process of purification of solutions E (curves 2, 4, 6, 8) on the dyes MB (a), MV (b), and CR (c) in the presence of FC-PH (curves 1, 2), FC-O (curves 3, 4), FC-PDS (curves 5, 6) and FC-FS (curves 7, 8) depending on n.

n = 500–1000), a sharp decrease in a occurs during purification from SM, MB, and CR using FC-PDS and FC-O. At n = 1000–2000, the decrease in a is smoother and ends with the stabilization of the process.

In the purification of MB and MW solutions with different n, for FC-PDS and FC-FS the values of E and a exceed these values for the case of purification of the solution from CR (Fig. 2a–c, curves 5, 7). When purifying the solution from MB using FC-PDS, this excess is 1.8–3.4 times; upon purification from MV, it is 1.8–7.9 for FC-PDS and 1.8–1.9 for FC-FS.

One of the optimal process conditions is $n \geq 500$ (Fig. 2). In this case, when purifying solutions from MV with FC-PH and FC-O composites, the purification efficiency of is 99–100 % with the highest value of a = 1.9 mg/g. When water is purified from MB with FC-PH, E = 98–99 % (n = 100–5000);

Table 1. Optimal ranges of mass ratios n

	n	n = ±10 %	n	n = ±10 %	n	n = ±10 %
FC-O	770	693–840	710	639–781	700	630–770
FC-PH	800	720–880	720	648–792	740	666–814
FC-PDS	1370	1233–1507	700	630–770	1000	900–1100
FC-FS	–	–	780	702–858	780	702–858

with FC-O, E = 90–96 % (n = 1000–5000); with FC-PDS, E = 90 % (n = 5000). The efficiency of purifying the solution from CR when using FC-PH and FC-O, respectively, is 98–99 % (n = 2000–5000) and 85 % (n = 5000); while with FC-PDS and FC-FS, relatively low values of purification were observed: 55 % (n = 5000) and 66% (n = 2000), respectively.

The synthesized FCs are most effective in the purification of solutions from MB and MV dyes (Fig. 2a, b); FCs are less efficient in the removal of CR (Fig. 2c). In the latter case, the decrease in E can be explained by the fact that CR is an anionic dye, while MB and MV are cationic. The electrostatic repulsion of the CR anion from the negatively charged surface of ferrites with a large number of OH-groups inhibits the conversion of CR into possible photocatalytic processes and adsorption.

The mass of FC significantly affects the efficiency of purifying solution from dyes. With a lack of FC, a high E cannot be achieved due to insufficient removal of the dye from the solution in any physicochemical processes. An excess of FC does not bring significant benefits in terms of increasing E with a simultaneous overconsumption of ferritic material. In this regard, it is important to determine the optimal value of n, at which a high degree of purification of solutions from the dye and a large mass of the convertible dye per unit mass of FC is achieved. In Fig. 2 the points of intersection of the curves "E – n" and "a – n" correspond to this. Table 1 shows the optimal intervals of n when purifying solutions from dyes. The values of n indicated in Table 1 can be recommended for the practical use of composite materials based on copper-zinc ferrite as reagents for cleaning solutions from organic dyes.

Reuse of FC in the process of colored water purification. A comparison was made of the purification efficiency E of an aqueous solution of MV in time (Fig. 3) before (curves 1–4) and after reuse (curves 1′–4′) of FC samples. With repeated use of FC, the

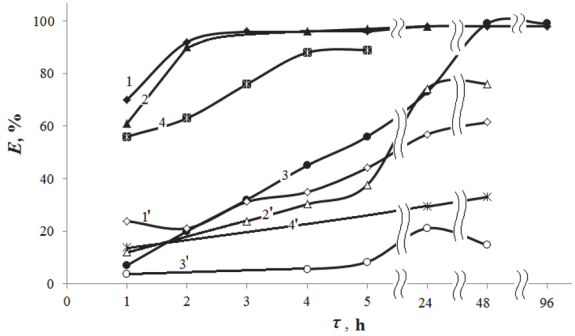

Fig. 3. Dependence of the efficiency of purification of the MV solution on time at n = 1000 for the initial (curves 1–4) and reuse (curves 1′–4′) FC: 1, 1′ — FC-PH; 2, 2′ — FC-O; 3, 3′ — FC-PDS; 4, 4′ — FC-FS.

efficiency E (curves 1′–4′) decreases in comparison with similar indicators for the initial use (curves 1–4). The course of the curves "E–τ" (Fig. 3) for different FCs during initial use (curves 1–4) has an S-shaped character with a plateau. The maxima of a and E values: a = 0.98 mg/g, E = 98 % for FC-PH (curve 1) and for FC-O (curve 2) were noted after 2 hours; a = 0.99 mg/g, E = 99 % for FC-PDS after 48 hours (curve 3); a = 0.89 mg/g, E = 89 % for FC-FS after 5 hours of exposure (curve 4).

With the repeated use of FC in an aqueous solution of MV, the course of the "E–τ" curves is smooth over the entire time interval (curves 1′–4′). For all FC, a gradual E increase in time is observed. These indicators reach the maximum values after 24 hours of FC exposure in solutions with a dye: E = 76 % for FC-O (curve 2′) and E = 21 % for FC-PDS (curve 3′); after 48 hours of exposure: E = 61 % for FC-PH (curve 1′) and E = 33 % for FC-FS (curve 4′). In comparison with the initial use, the repeated use of FC reduces the efficiency of purification of an aqueous solution of MV by a factor of 2–4 and increases the time of reaching the maximum E by a factor of 10–24 (with the exception of FC-PDS).

A possible explanation for the decrease in the efficiency of the FC action can be the

Table 2. Regression equations "E–n–τ"

Dye	FC	Regression equation	N
MV	FC-O	$E = 7.815 + 1.736\tau + 0.06714n - 0.01424\tau^2 - 0.0002691\tau n - 2.591\cdot10^{-5}n^2 + 1.863\cdot10^{-6}\tau^2 n + 5.263\cdot10^{-9}\tau n^2 + 2.906\cdot10^{-9}n^3$	1
	FC-PH	$E = 10.4 + 1.787\tau + 0.06014n - 0.0156\tau^2 - 0.000473\tau n - 2.169\cdot10^{-5}n^2 + 3.75\cdot10^{-6}\tau^2 n + 1.599\cdot10^{-8}\tau n^2 + 2.322\cdot10^{-9}n^3$	2
	FC-PDS	$E = 20.8 + 5.612\tau + 0.0613n - 0.3177\tau^2 + 0.002477\tau n - 2.69\cdot10^{-5}n^2 - 1.526\cdot10^{-5}\tau^2 n - 2.625\cdot10^{-7}\tau n^2 + 3.13\cdot10^{-9}n^3$	3
	FC-FS	$E = 14.56 + 3.928\tau + 0.04291n - 0.2224\tau^2 + 0.001734\tau n - 1.883\cdot10^{-5}n^2 - 1.068\cdot10^{-5}\tau^2 n - 1.838\cdot10^{-7}\tau n^2 + 2.191\cdot10^{-9}n^3$	4
MB	FC-O	$E = 22.67 + 2\tau - 0.02173n - 0.02081\tau^2 + 0.0002241\tau n + 1.007\cdot10^{-5}n^2 + 1.545\cdot10^{-6}\tau^2 n - 5.869\cdot10^{-8}\tau n^2 - 1.112\cdot10^{-9}n^3$	5
	FC-PH	$E = 16.94 + 0.49\tau + 0.0187n - 0.0043\tau^2 + 0.000478\tau n - 4.893n^2 - 2.922\cdot10^{-6}\tau^2 n - 3.096\cdot10^{-8}\tau n^2 + 3.91\cdot10^{-10}n^3$	6
	FC-PDS	$E = 56.74 - 0.6798\tau - 0.05555n + 0.00455\ \tau^2 + 0.0008003\tau n + 2.039\cdot10^{-5}n^2 - 2.968\cdot10^{-6}\tau^2 n - 7.182\cdot10^{-8}\tau n^2 - 2\cdot10^{-9}n^3$	7
CR	FC-O	$E = 4.352 + 0.5597\tau + 0.01044n - 0.002677\tau^2 + 0.0003149\tau n - 4.928\cdot10^{-6}n^2 - 2.892\cdot10^{-6}\tau^2 n + 3.241\cdot10^{-9}\tau n^2 + 6.54\cdot10^{-10}n^3$	8
	FC-PH	$E = 1.147 + 0.3985\tau + 0.01329n - 0.002499\tau^2 + 0.0006791\tau n - 5.232\cdot10^{-6}n^2 - 4.371\cdot10^{-6}\tau^2 n - 4.265\cdot10^{-8}\tau n^2 + 6.911\cdot10^{-10}n^3$	9
	FC-PDS	$E = 7.297 + 1.08\tau - 0.001011n - 0.01227\tau^2 - 3.127\cdot10^{-5}\tau n - 1.655\cdot10^{-6}n2 + 3.215\cdot10^{-6}\tau^2 n - 2.814\cdot10^{-8}\tau n^2 + 3.153\cdot10^{-10}n^3$	10
	FC-FS	$E = 26.14 + 0.9425\tau + 0.00983n - 0.01108\tau^2 + 0.0001192\tau n - 7.532\cdot10^{-6}n^2 + 1.477\cdot10^{-7}\tau^2 n - 2.14\cdot10^{-9}\tau n^2 + 9.911\cdot10^{-10}n^3$	11

screening adsorption of dyes. Initially, a monomolecular adsorption layer of the dye is formed on the FC surface, then a polymolecular one. The adsorption process slows down, and desorption of the dye from the FC surface begins. Therefore, with repeated use of FCs, the effectiveness of their action decreases.

The obtained results on the decrease in the efficiency of purification of colored waters using ferrite composites are not an obstacle when the time factor is not critical; it is also possible to use FC in settling tanks or other wastewater tanks for a longer time.

Mathematical modeling of the processes of purifying colored waters by using FC. For the mathematical description of the total effect of all processes occurring during the purification of water from the MV, MB and CR dyes with the help of FC, the software package MATLAB and its Toolbox subsystem (mathematical package) were used — a set of specialized mathematical functions that were used to optimize systems. The least squares method was used to construct the third-order regression equations for the "E–n–τ" dependencies (Table 2) with an extended range of optimal values of n and τ. Equation coefficients were obtained with 95 % probability. The regression equations make it possible to calculate the efficiency of purification from all dyes by using all synthesized FCs at any moment of time at a fixed "FC-to-dye" mass ratio.

Figure 4 is a graphical representation of one of the dependencies.

4. Conclusions

The purification of aqueous solutions from MV, MB, and CR organic dyes is due to the simultaneous occurrence of photocatalytic processes and adsorption of dyes on the surface of Cu–Zn-FC.

The efficiency of purifying the solutions from dyes and the specific activity of individual FCs vary depending on the type of the dye and the composition of ferrite. FCs are more efficient in the purification of solutions from MV and MB than from CR. The optimal mass ratio "FC-to-dye" varies within the range of 700–1370.

Ferrite composites lose their efficiency when reused, the cleaning process slows down, but their use is advisable in cases where the time factor is not critical, and

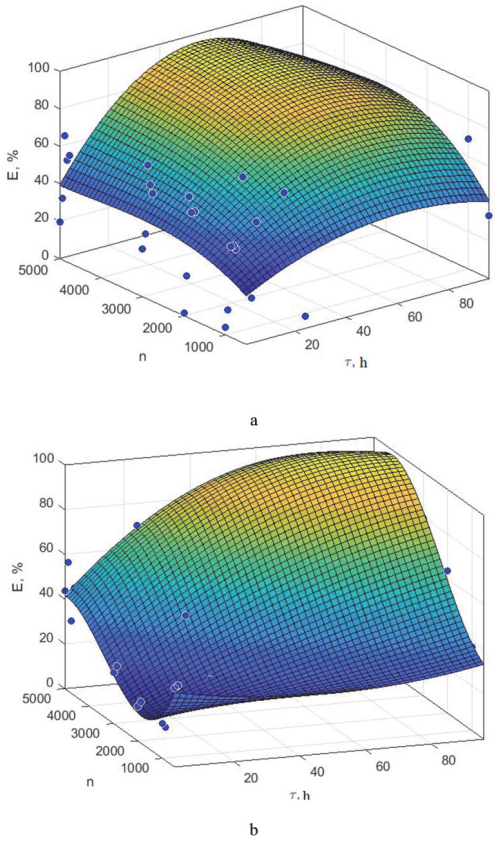

Fig. 4. Graphic representation of the dependencies "E–n–τ" (Table 2): a — 6; b — 7.

there is a possibility of a longer exposure of colored wastewater in contact with ferrite in sedimentation tanks.

With the help of mathematical modeling, the regression equations for the dependence of efficiency of the purification process on time and mass ratio "FC-to-dye" were derived, which make it possible to determine the optimal process conditions.

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