CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2024,
Vol. 18, No. 4, pp. 474–484

Chemistry

INVESTIGATION OF THE ADSORPTION PROPERTIES OF A NEW COMPOSITE CATALYST FOR THE FENTON SYSTEM

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https://doi.org/10.23939/chcht18.04.474

Abstract. The influence of the structure of the SiO_2 layer on the adsorption properties of magnetosensitive $CoFe_2O_4/SiO_2/CuO$ nanocomposites created as catalysts for the Fenton system was studied. For this, the formation of the SiO_2 layer was carried out by the sol-gel method using surfactants of synthetic and natural origin. To determine the process parameters, a previously proposed mathematical model of the dye adsorption process from an aqueous solution was used. The presented model considers dye adsorption from an aqueous solution as a pseudo chemical reaction of displacement of the solvent molecules from adsorption sites on the adsorbent surface by the adsorbate molecules. It has been established that the process of formation of the SiO_2 layer is influenced by surfactants (sodium dodecyl sulfate or rhamnolipids), and the adsorption properties of the prepared $CoFe_2O_4/SiO_2/CuO$ composites depend on the structure of the stabilizing SiO_2 layer. The kinetic parameters of the methylene blue (MB) adsorption process from aqueous solutions at concentrations of $(2 - 5)\cdot 10^{-5}$ mol/L were determined. The obtained results are perfectly fitted by the proposed pseudo-first-order equation. The calculated value of the activation energy of MB adsorption on the $CoFe_2O_4/SiO_2(RL)/CuO$ catalyst indicates the physical adsorption of the dye. The results of using the investigated composites in the Fenton system as catalysts for the oxidation process of the organic dye MB are shown.

Keywords: Fenton system, core-shell catalyst, methylene blue adsorption, kinetics, activation energy.

1. Introduction

In recent decades large amounts of wastewater have caused a great burden on the planet's water resources. As the conducted studies have shown, more than 700 new pollutants are present in the water environment of Europe, and their list is constantly growing.[1] Synthetic organic pollutants, including pharmaceuticals, personal hygiene products, pesticides, and dyes, which are widely used in various sectors of the economy and everyday life, pose a great threat to the ecosystem. The harmful effect of organic substances, in particular, dyes that enter water bodies, increases due to the cumulative effect (progressive increase in the content of harmful compounds in each subsequent link of the trophic chain).[2]

Effective methods of wastewater treatment from such pollutants are advanced oxidation processes (AOP), based on the formation of highly active radicals (in particular, hydroxyl) for catalytic oxidation of organic substances to carbon dioxide.[3,4] Generation of hydroxyl radicals from hydrogen peroxide (H_2O_2) is an environmentally friendly process with "green" by-products H_2O and O_2. This process can be carried out at atmospheric pressure and low temperatures (below 100°C). Traditional AOPs include the Fenton process, in which soluble ferrum salts are used as catalysts for $OH^{\bullet}$ radical formation.

However, the use of homogeneous catalysts has some drawbacks, among which are a narrow pH range (2.8 - 3.5), the formation of a large amount of sludge, and the impossibility of their reuse.[5] To solve these problems, it is advisable to apply heterogeneous oxidation processes using transition metal-based catalysts. In such heterogeneous catalytic systems, the catalytically active sites are transition metal atoms located on the surface of the catalyst. The access of reagents to the active sites is not limited, at the same time the use of transition metals simplifies the separation of the catalyst at the end of the process.[6] The development of effective catalysts is a key issue for obtaining the desired results in organic pollutant degradation processes.

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One of the methods of improving the heterogeneous catalyst efficiency is to increase the surface area in contact with the reagent. An increase in the surface area of the particles can be achieved by reducing their size, but difficulties arise in removing the catalyst from the reaction medium for reuse. The creation of catalytic systems that possess magnetic properties can help to solve this problem.

High adsorption capacity is an important characteristic of any catalyst. For many heterogeneous catalytic processes, the limiting stage is the transport of reactants from the bulk solution or gas phase to the adsorbent surface. Adsorption of reagents on the surface of the catalyst leads to an increase in their concentration around the catalytic sites, thus the efficiency of the catalyst increases. The use of highly porous materials, in particular, SiO_2,[7,8] as carriers for catalytic sites, makes it possible to significantly increase the adsorption efficiency of the catalyst and, accordingly, the efficiency of the Fenton process as a whole.

Taking into account the main requirements for the Fenton system catalysts in the processes of wastewater treatment from organic pollutants, we designed novel nanostructured magnetosensitive catalysts of the "core-shell" type based on CuO. These catalysts have a magnetosensitive core from cobalt ferrite ($CoFe_2O_4$), covered with a protective layer of porous SiO_2, on the surface of which clusters of copper oxides (CuO) are immobilized, which play the role of catalytic sites.

In the technology of synthesis of nanostructured catalysts of the "core-shell" type, a layer of SiO_2 is used to stabilize a magnetic core and as a support for immobilization of the catalytic sites. The porosity of the SiO_2 layer determines to some extent the adsorption properties of the catalyst, which is an important indicator of its activity. Considering the above, the aim of the work was to study the adsorption properties of the $CoFe_2O_4/SiO_2/CuO$ catalyst samples synthesized by us, which differed only in the stage of SiO_2 deposition on the surface of cobalt ferrite $CoFe_2O_4$ using surfactants of synthetic and natural origin and without surfactants. The research was carried out on the example of MB adsorption from an aqueous solution with the determination of the kinetic parameters of the process.

2. Experimental

2.1. Materials

2.1.1. Synthesis of the Adsorbent

The synthesis of the nanostructured magnetosensitive $CoFe_2O_4/SiO_2/CuO$ catalysts was carried out using a multi-stage technology,[9] according to which a layer of SiO_2 was deposited on the magnetic core of $CoFe_2O_4$ formed previously, and then catalytically active CuO sites were immobilized on the SiO_2 layer. The SiO_2 layer has two important functions: it stabilizes the magnetosensitive core and also serves as a support for CuO catalytic site formation. To increase the porosity of the SiO_2 layer, the sol-gel synthesis was carried out in the presence of synthetic (sodium dodecyl sulfate) and natural (rhamnolipid) surfactants.

Sodium dodecyl sulfate $C_{12}H_{25}SO_4Na$ (NaDS) ("Systema Optimum", Ukraine) and rhamnolipid (RL) (*Pseudomonas* sp. PS-17) (Department of Physical Chemistry of Fossil Fuels of the Institute of Physical–Organic Chemistry and Coal Chemistry named after L. M. Lytvynenko of the National Academy of Sciences of Ukraine) were used for research.

Rhamnolipids synthesized by the strain *Pseudomonas* sp. PS-17 (the microorganism collection of the Department of PhChFF InPOCC NAS of Ukraine). Cultivation of the strain *Pseudomonas* sp. PS-17 was carried out using the liquid nutrient medium (g/L): $NaNO_3$ – 4.0; $K_2HPO_4 \times 3H_2O$ – 2.0; KH_2PO_4 – 1.2; $MgSO_4 \times 7H_2O$ – 0.5; sodium citrate – 4.0, distilled water – to 1L. Glycerol was used as a carbon and energy source (4% weight). 1-day culture of the strain *Pseudomonas* sp. PS-17 grown on the same medium (primary inoculum was added in a quantity of 5% of the medium volume) was used as an inoculum.[10] Microorganisms were cultivated in 750 mL Erlenmeyer flasks with 150 mL medium on the rotary shaker (220 rpm) at 28 - 30 °C for 5 days.

The biomass was separated via centrifugation of cultural broth at 6000 rpm for 20 minutes. The biocomplex of rhamnolipids was precipitated from the culture fluid supernatant (CLS)[11] by acidification to pH 3 - 4 with cooling (4°C) and dried. The RLs were isolated from rhamnolipid biocomplex by extraction with ethanol, their composition was determined by thin layer chromatography (TLC) (Merck Silica gel 60, Germany), chloroform – methanol - water 65 : 2 : 4, visualization – by 5% phosphomolybdic acid.[12]

2.1.2. Preparation of the Adsorbate

Methylene blue (MB) dye of cationic structure ("Sfera Sim", Ukraine), $C_{16}H_{18}N_3SCl$; MW 319.9 g/mol (Fig. 1). In an aqueous solution, methylene blue forms complexes with solvent molecules [$C_{16}H_{18}N_3SCl + 3H_2O$], which have a molecular weight of 373.9 g/mol. The solution was prepared by dissolving an appropriate amount of dye in distilled water.

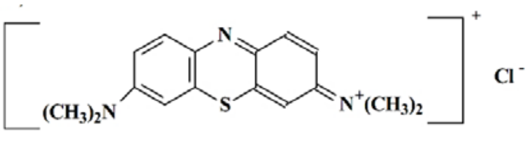


Fig. 1. Structural formula of methylene blue

2.2. Methods

2.2.1. Characterization of Particles

The structure of the $CoFe_2O_4/SiO_2/CuO$ catalyst was investigated using X-ray diffraction (XRD). The samples of composites were analyzed at room temperature on a DRON-3M X-ray diffractometer in CuK_α radiation (λ = 1,5418 Å) in 2θ range (20-100°) (by step of 0.05°). The electronic database of powder diffractometry (PDF-files) was used to identify the phases. Standard maps JCPDS 1-1121 and JCPDS 5-661 were used for comparison. The surface morphology of the particles and the elemental composition of the samples were obtained using a REMMA 102-02 scanning electron microscope with an X-ray microanalyzer (ESD) system.

2.2.2. Experimental Protocol

10 mg of the catalyst as a sorbent was added to 5 mL of MB solution of a defined initial concentration. The mixture was constantly stirred at room temperature until equilibrium was established. The samples of solution were withdrawn at specified time intervals after magnetic separation of the catalyst. The dye concentration in the solution was determined at a wavelength of 620 nm on Spekol 11 spectrophotometer. The aqueous solutions with the initial MB concentrations of $2 \cdot 10^{-5}$ – $5 \cdot 10^{-5}$ mol/L were used for research.

The adsorption efficiency was calculated using the following equation:

$$A_{ef} = \frac{C_0 - C_e}{C_0} \cdot 100\%. \quad (1)$$

The amount of the dye adsorbed on the studied sorbent was determined by the formula:

$$q_e = \frac{(C_0 - C_e) M_{MB}}{m} \cdot V, \quad (2)$$

where q_e is the amount of the dye (mg per g of sorbent), mg/g; C_0 and C_e are the initial and equilibrium MB concentration in the solution, mol/L; M_{MB} is a molar mass of the dye, mol/L; V is the solution volume, L; m is the sorbent mass, g.

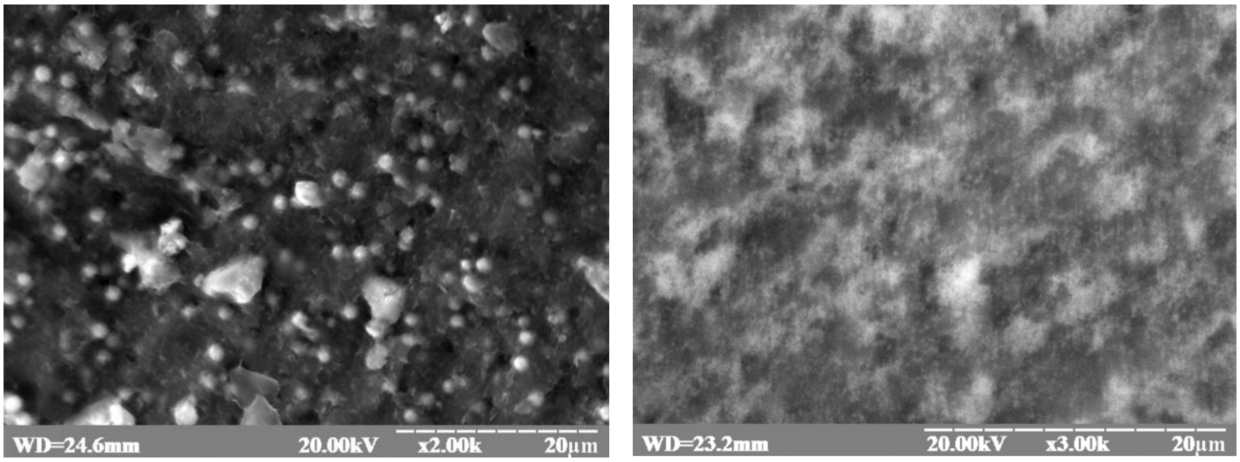
3. Results and Discussion

3.1. Characteristics of Catalyst Particles

Fig. 2 shows SEM images of $CoFe_2O_4/SiO_2/CuO$ and $CoFe_2O_4/SiO_2$(RL)/CuO catalysts.

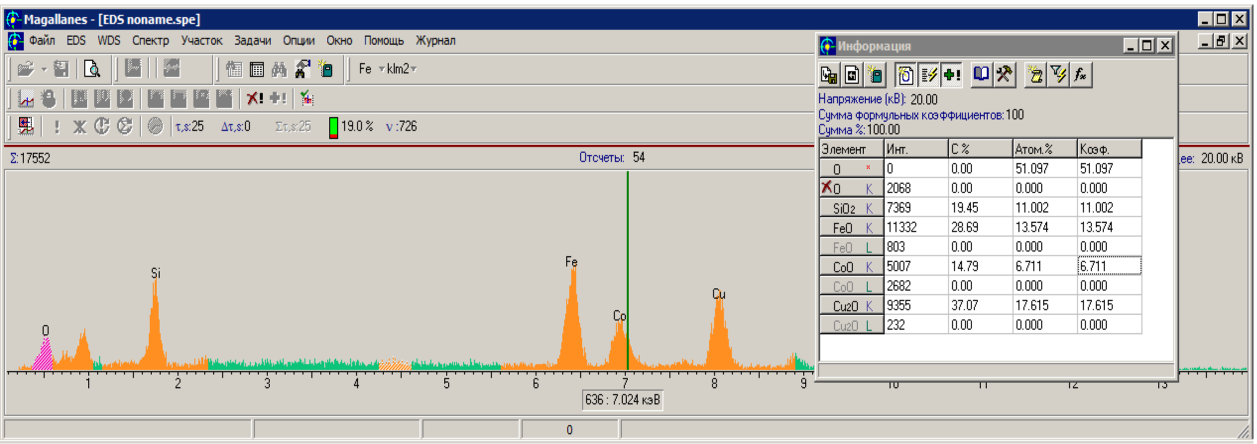
The microphotographs show an uneven porous surface on which the CuO catalytic sites are located. As can be seen, the introduction of surface-active substances at the stage of SiO_2 immobilization leads to a change in the surface morphology of the composite. The SiO_2 surface becomes developed, and the number of CuO crystallization centers increases significantly. The EDS spectra of the synthesized $CoFe_2O_4/SiO_2/CuO$ catalyst (Fig. 3) show that the sample consists of 5 elements (Co, Fe, Si, Cu, and O), and their percentage content corresponds to the stoichiometric composition of the composite.

The peaks in the obtained X-ray pattern of the $CoFe_2O_4/SiO_2/CuO$ multilayer catalyst (Fig. 4) indicate the presence of only two crystal structures: the spinel structure of cobalt ferrite and the monoclinic structure of copper oxide. The absence of the peaks attributed to Si in the X-ray pattern indicates the amorphous state of SiO_2 in the composite.



a) b)

Fig. 2. FESEM images of $CoFe_2O_4/SiO_2/CuO$ (a) and $CoFe_2O_4/SiO_2$(RL)/CuO (b) particles obtained using a REMMA 102-02 scanning electron microscope



Напряжение (кВ): 20.00
Сумма формульных коэффициентов: 100
Сумма %: 100.00

Элемент		Инт.	C %	Атом.%	Коэф.
O	*	0	0.00	51.097	51.097
O	K	2068	0.00	0.000	0.000
SiO2	K	7369	19.45	11.002	11.002
FeO	K	11332	28.69	13.574	13.574
FeO	L	803	0.00	0.000	0.000
CoO	K	5007	14.79	6.711	6.711
CoO	L	2682	0.00	0.000	0.000
Cu2O	K	9355	37.07	17.615	17.615
Cu2O	L	232	0.00	0.000	0.000

Fig. 3. EDS spectra of $CoFe_2O_4/SiO_2/CuO$ particles

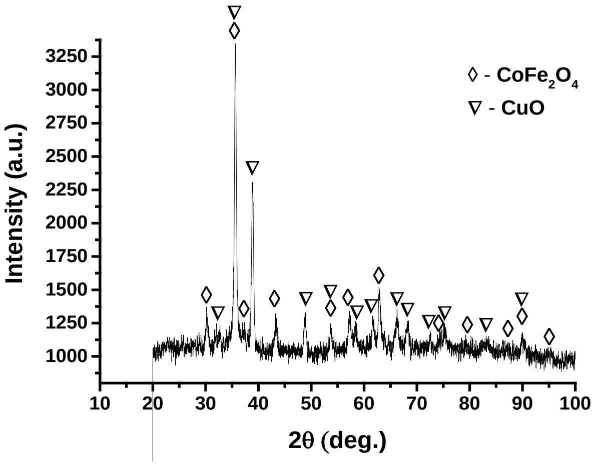


Fig. 4. X-ray pattern of the $CoFe_2O_4/SiO_2/CuO$ sample

According to the obtained results, it can be stated that the structure of the catalyst consists of three layers: the inner layer – the magnetic core of cobalt ferrite of the spinel structure, the shell of amorphous porous SiO_2, and the outer layer – catalytic sites of monoclinic copper oxide located on SiO_2.

3.2. Adsorption of MB

The study of adsorption properties was carried out for three samples that differ in the porosity of the SiO_2 stabilizing layer: $CoFe_2O_4/SiO_2/CuO$ (0), $CoFe_2O_4/SiO_2$ NaDS)/CuO (NaDS) and $CoFe_2O_4/SiO_2$(RL)/CuO (RL). A different structure of SiO_2 layers was achieved during immobilization in the presence of surface-active substances of synthetic (sodium dodecyl sulfate) (NaDS) and natural (rhamnolipid) (RL) origin. The zero sample (0) is without a surfactant. The effect of the initial dye concentration on MB adsorption on the studied composites was investigated in the concentration range of $2 \cdot 10^{-5}$ - $5 \cdot 10^{-5}$ mol/L.

Figs. 5–7 present kinetic curves of MB adsorption on three samples of composites at different initial concentrations of the dye in solution.

The obtained adsorption isotherms are classical Langmuir isotherms, which have a sharply curved initial section. This indicates a high rate of filling of adsorption sites with MB molecules, which is almost independent of the initial dye concentration in the solution. The saturation of adsorption sites with dye molecules occurs quickly, but the optimal contact time is different for each sample and decreases from 40 to 60 min for the (0) sample up to 15 - 20 min for the (RL) sample (Figs. 5–7). It evidences an increase in the number of adsorption sites on the catalyst surface when using surfactants in the process of the SiO_2 layer formation.

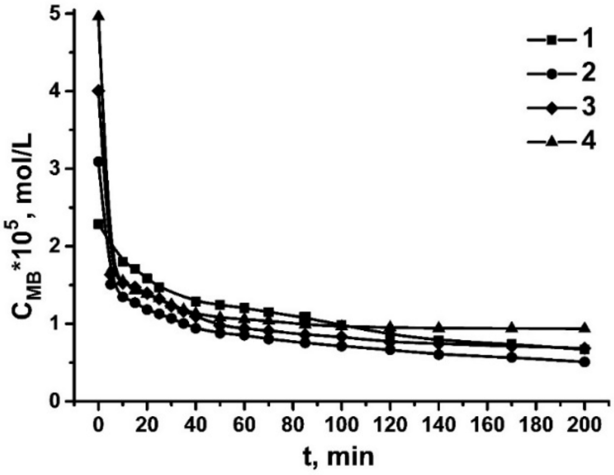


Fig. 5. Kinetic curves of MB adsorption onto the $CoFe_2O_4/SiO_2/CuO$ catalyst at different initial concentrations of the dye C_0, mol/L: 1 – $2 \cdot 10^{-5}$; 2 – $3 \cdot 10^{-5}$; 3 – $4 \cdot 10^{-5}$; 4 – $5 \cdot 10^{-5}$

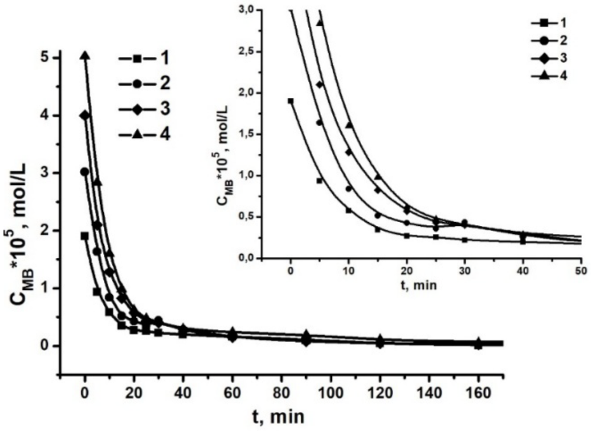


Fig. 6. Kinetic curves of MB adsorption onto the $CoFe_2O_4/SiO_2$(NaDS)/CuO catalyst at different initial concentrations of the dye C_0, mol/L: 1 – $2\cdot10^{-5}$; 2 – $3\cdot10^{-5}$; 3 – $4\cdot10^{-5}$; 4 – $5\cdot10^{-5}$

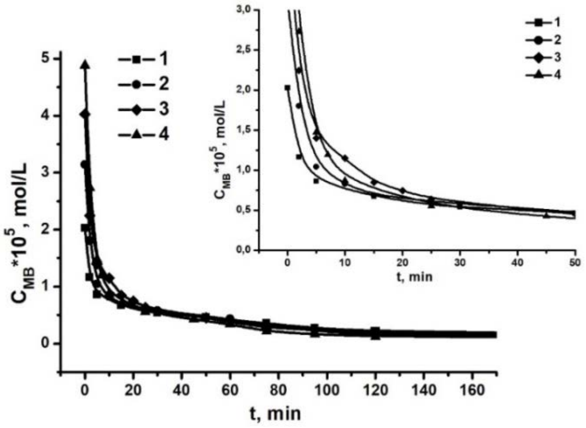
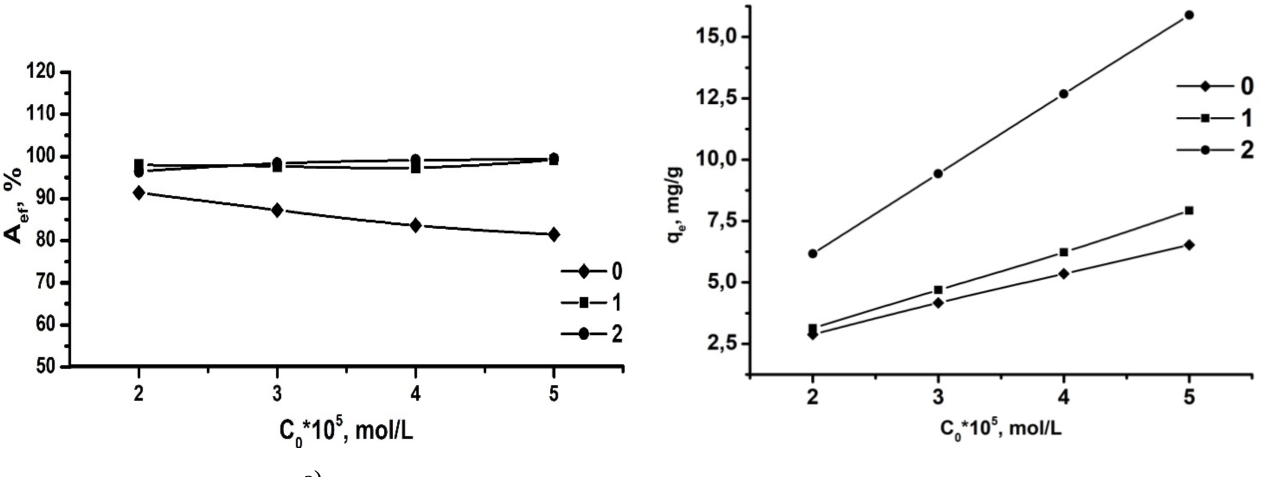


Fig. 7. Kinetic curves of MB adsorption onto the $CoFe_2O_4/SiO_2$(RL)/CuO catalyst at different initial concentrations of the dye C_0, mol/L: 1 – $2\cdot10^{-5}$; 2 – $3\cdot10^{-5}$; 3 – $4\cdot10^{-5}$;
4 – $5\cdot10^{-5}$



a) b)

Fig. 8. The dependence of the adsorption efficiency (a) and adsorption value (b) on the surface of $CoFe_2O_4/SiO_2$/CuO (0), $CoFe_2O_4/SiO_2$(NaDS)/CuO (1), $CoFe_2O_4/SiO_2$(RL)/CuO (2) catalysts on the dye concentration in solution

The calculations of the main parameters of the adsorption process showed the effectiveness of the synthesized composites (Fig. 8). As can be seen from the results, the dependence of the parameters of the adsorption process on the dye concentration in the solution is related to the structure of the SiO_2 layer. Thus, for the (0) sample, with an increase in the initial concentration of the dye in the solution, a decrease in the efficiency of MB adsorption and a simultaneous increase in the amount of the adsorbed dye are observed. Probably, this is due to a small number of adsorption sites on the surface of the composite, at the saturation of which the equilibrium of the dye adsorption-desorption process occurs. For the (NaDS) and (RL) samples with a more developed surface and a greater number of adsorption sites, the efficiency and the amount of the adsorbed dye increase with increasing the dye concentration. At the same time, the degree of the dye removal by the catalysts reaches 99%, which indicates their high adsorption capacity.

3.3. Kinetics of MB Adsorption

Adsorption kinetics deals mainly with the rate of reaction between an adsorbent and an adsorbate and the factors affecting a reaction. In the Langmuir theory, adsorption is considered as a pseudo chemical equilibrium reaction between an adsorbate molecule and a free adsorption site on the adsorbent surface with the formation of a complex. However, at adsorption from the solution, one must take into account the presence of solvent molecules on the catalyst surface, so this process should be considered as the adsorption of both adsorbate and solvent molecules. Under such conditions, the adsorption process can be described as a pseudo chemical equilibrium reaction of displacement of solvent molecules from adsorption sites on the adsorbent surface by adsorbate molecules:

$$\mathrm{d}C/\mathrm{d}t = kC(1-\Theta), \qquad (3)$$

where *k* is the reaction rate constant; *C* is the current concentration of the dye in solution (mol/L); Θ is the fraction of adsorption sites occupied by MB molecules, which can be expressed by the equation:

$$\Theta = \frac{V(C_0 - C)}{q_0 S}, \qquad (4)$$

where $V(C_0 - C)$ is the number of the adsorbed substance moles; *V* is the solution volume, L; C_0 is the initial concentration of the dye in solution, mol/L; q_0S is a number of adsorption sites determined by the adsorption capacity (q_0, mol/m^2) and the surface (S, m^2) of the adsorbent.

Taking into account that for a separate experiment V, q_0 and S are determined values, we introduce the constant into Eq. (4)

$$\Theta = A(C_0 - C), \qquad (5)$$

where $A = \frac{V}{q_0 S} = \mathrm{const}$ for the given process, L/mol.

Substituting Eq. (5) into Eq. (4) we get after transformation:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = kC(a + C), \qquad (6)$$

where $a = \frac{1}{A} - C_0 = \mathrm{const}$ for the given value of C_0, mol/L.

After integration and subsequent transformations, the equation of heterogeneous adsorption from solution takes the form:

$$\ln\frac{C}{a+C} + \ln\frac{a+C_0}{C_0} = a \cdot k \cdot t. \qquad (7)$$

After selection of the coefficient *a* in Eq. (7) for each initial MB concentration, we obtain linear dependences $\ln\frac{C}{a+C} = f(t)$, according to which the main kinetic parameters of the process were determined for three composites (Figs. 9–10, Tables 1–3).

The straight lines obtained for three samples have high correlation coefficients (R^2), which indicates a good correspondence of the proposed equation for fitting the isotherms of MB adsorption on the surface of $CoFe_2O_4/SiO_2/CuO$. The parameters of adsorption kinetics for all composites correspond to the proposed pseudo-first-order model, according to which the reaction rate is proportional to the residual concentration of the dye in solution and the number of adsorption sites occupied by the solvent, provided that the adsorption is controlled by the diffusion stage.[13]

Thus, obtaining the SiO_2 layer in the presence of surfactants (especially RL) makes it possible to obtain a surface with a larger number of adsorption sites, which increases the adsorption rate by 1.5 - 2 times.

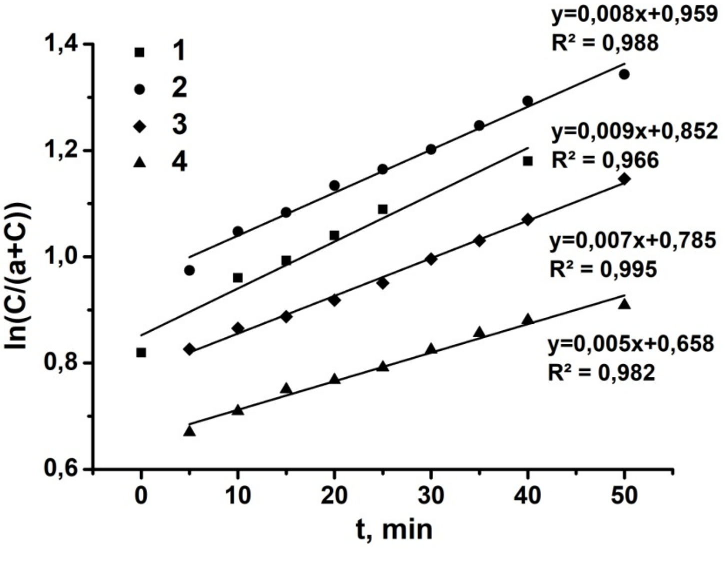
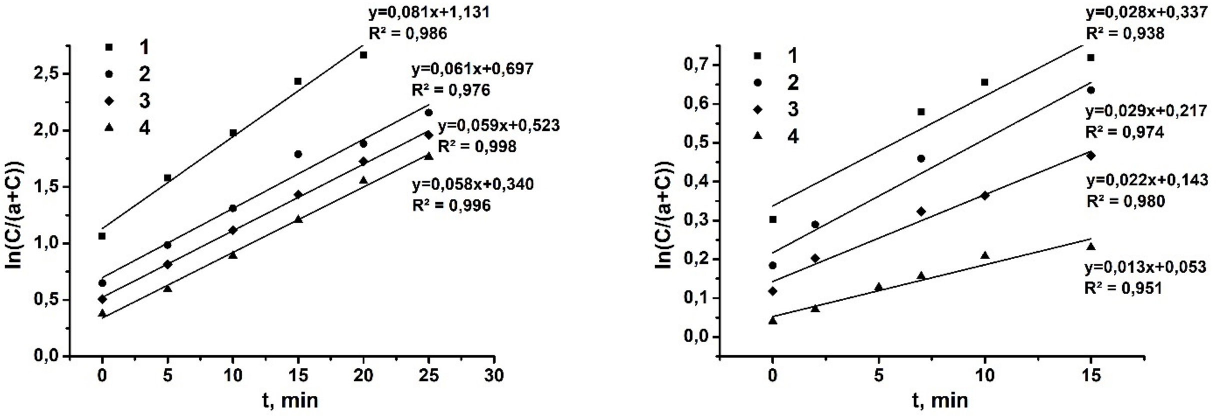


Fig. 9. Isotherms of MB adsorption on the surface of the sample (0) at different initial concentrations of the dye C_0, mol/L: $1 - 2\cdot10^{-5}$; $2 - 3\cdot10^{-5}$; $3 - 4\cdot10^{-5}$; $4 - 5\cdot10^{-5}$



a) b)

Fig. 10. Adsorption isotherms of MB on the surface of samples (NaDS) (a) and (RL) (b) at different initial concentrations of the dye C_0, mol/L: 1 – $2\cdot10^{-5}$; 2 – $3\cdot10^{-5}$; 3 – $4\cdot10^{-5}$; 4 – $5\cdot10^{-5}$

Table 1. Kinetic parameters of MB adsorption on the surface of the (0) composite

№	$C_0\times10^5$, mol/L	$k\times10^{-3}$, min^{-1}	$\ln\frac{a+C_0}{C_0}$	$a\times10^5$, mol/L	$A\times10^{-4}$, L/mol	R^2
1	2	3.0	0.85	2.90	2.0	0.966
2	3	3.3	0.81	2.50	1.8	0.988
3	4	3.4	0.71	2.10	1.6	0.995
4	5	3.4	0.54	1.60	1.5	0.982

Table 2. Kinetic parameters of MB adsorption on the surface of the (NaDS) composite

№	$C_0\times10^5$, mol/L	$k\times10^{-3}$, min^{-1}	$\ln\frac{a+C_0}{C_0}$	$a\times10^5$, mol/L	$A\times10^{-4}$, L/mol	R^2
1	2	2.26	1.13	3.60	1.79	0.986
2	3	2.24	0.70	2.75	1.74	0.976
3	4	2.23	0.56	2.64	1.51	0.998
4	5	2.52	0.32	2.30	1.37	0.996

Table 3. Kinetic parameters of MB adsorption on the surface of the (RL) composite

№	$C_0\times10^5$, mol/L	$k\times10^{-3}$, min^{-1}	$\ln\frac{a+C_0}{C_0}$	$a\times10^5$, mol/L	$A\times10^{-4}$, L/mol	R^2
1	2	4.04	0.300	0.70	3.70	0.938
2	3	4.87	0.184	0.60	2.78	0.974
3	4	4.48	0.118	0.50	2.22	0.980
4	5	6.65	0.040	0.20	1.92	0.951

3.4. The Langmuir Equation for the Equilibrium State of Adsorption

Experimental data of the equilibrium state of the process were analyzed using the Langmuir model, which predicts monolayer adsorption on a surface containing a limited number of adsorption sites having the same adsorption activation energy without adsorbate movement in the surface plane.[14]

We consider the equilibrium adsorption from the solution as pseudo chemical reactions between adsorbent active sites (Z) and solvent molecules (A_1) with the formation of (ZA_1) complexes on the one hand and between adsorbent active sites (Z) and the solute (A_2) with the formation of (ZA_2) complexes on the other hand:

$$\mathrm{Z} + \mathrm{A}_1 = \mathrm{ZA}_1, \mathrm{Z} + \mathrm{A}_2 = \mathrm{ZA}_2.$$

Since all active sites of the adsorbent immersed in the solution are occupied with molecules of either a solvent or a solute

$$\eta_{ZA_1} + \eta_{ZA_2} = 1, \tag{8}$$

where η_{ZA_1} and η_{ZA_2} are fractions of adsorbent-solvent and adsorbent-solute complexes formed.

The equilibrium constants of complex formation reactions are defined as:

$$K_1 = \frac{\eta_{ZA_1}}{\eta_Z[A_1]}, \tag{9}$$

$$K_2 = \frac{\eta_{ZA_2}}{\eta_Z[A_2]}, \tag{10}$$

where η_Z is a number of free sites; $[A_1]$ and $[A_2]$ are solvent and solute concentrations in solution, respectively.

Then from Eq. (8):

$$\frac{K_1[A_1]}{\eta_{ZA_1}} = \frac{K_2[A_2]}{\eta_{ZA_2}}. \tag{11}$$

If we express η_{ZA_1} in terms of η_{ZA_2} and η_{ZA_2} in terms of η_{ZA_1} and substitute in Eq. (8), we get:

$$\eta_{ZA_1} = \frac{K_1[A_1]}{K_1[A_1]+K_2[A_2]}, \tag{12}$$

$$\eta_{ZA_2} = \frac{K_2[A_2]}{K_2[A_2]+K_1[A_1]}. \tag{13}$$

The equilibrium condition of a process is the adsorption-desorption of solvent and solute molecules:

$$\eta_{ZA_1} + [A_2] = \eta_{ZA_2} + [A_1]. \tag{14}$$

Thus, if a solute interacts more actively with adsorbent sites, $\eta_{ZA_1} + [A_2] > \eta_{ZA_2} + [A_1]$, it displaces solvent molecules from the sites and takes their place (the dye adsorption process). Provided that the activity of a solute is less than the activity of a solvent $\eta_{ZA_1} + [A_2] < \eta_{ZA_2} + [A_1]$, its molecules gradually displace solute molecules from adsorbent active sites (the dye desorption process).

The equilibrium constant of this reaction has the form:

$$K_e = \frac{\eta_{ZA_2}[A_1]}{\eta_{ZA_1}[A_2]}. \tag{15}$$

If we express η_{ZA_2} in terms of η_{ZA_1}, after substituting into Eq. (8), we get:

$$\eta_{ZA_2} = \frac{K_e\frac{[A_2]}{[A_1]}}{1+K_e\frac{[A_2]}{[A_1]}}. \tag{16}$$

Thus, the amount of the adsorbed solute depends both on its concentration $[A_2]$ in the solution and on the solvent concentration $[A_1]$. If the solute concentration is small, i.e. $[A_1] \gg [A_2]$, we can suggest $[A_1] = \mathrm{const}$. Then:

$$\eta_{ZA_2} = \frac{K_{ef}[A_2]}{1+K_{ef}[A_2]}, \tag{17}$$

where $K_{ef} = \frac{K_e}{[A_1]}$.

Thus, the Langmuir equation for the equilibrium state can be written as:

$$q_{ef} = \frac{K_{ef}C}{1+K_{ef}C}, \tag{18}$$

where K_{ef} is an effective equilibrium constant of displacement adsorption; $C = [A_2]$ is a solute concentration, mol/L.

In a linear form, the Langmuir equation can be written:

$$\frac{1}{q_{ef}} = 1 + \frac{1}{K_{ef}C}. \tag{19}$$

The analysis of the data of the equilibrium state of the adsorption process according to the proposed model showed that this equation satisfactorily described the adsorption process for three studied composites.

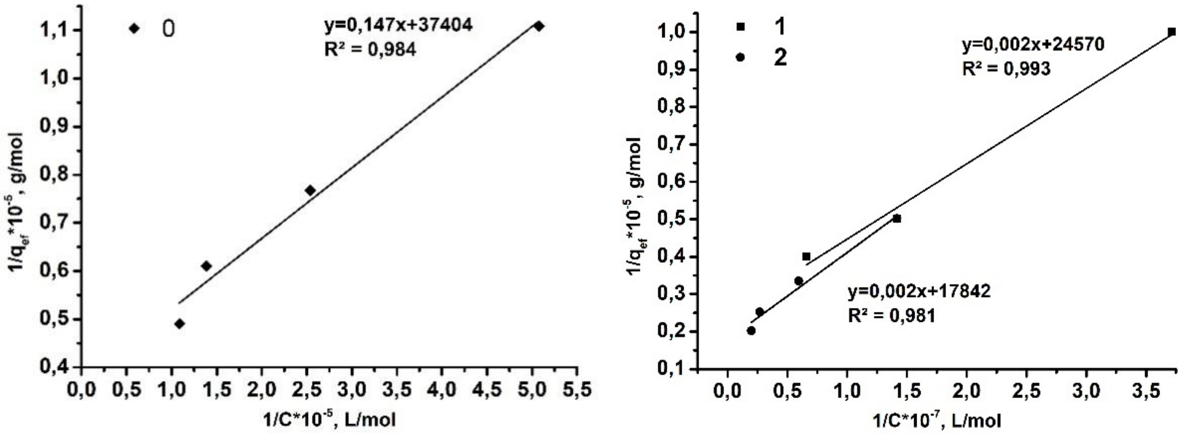
Plots of experimental data for three cases give straight lines (Fig. 11) with high correlation coefficients (R^2). Thus, the isotherms of MB adsorption on the surface of the composites are perfectly described by the proposed equation within the defined concentration range. The intercept on the y-axis is equal to the reciprocal of q_0, *i.e.*, q_0 = 8.5 mg/g for the (0) composite, q_0 = 12.4 mg/g for the (NaDS) composite and q_0 = 17.4 mg/g for the (RL) composite, which is close to the obtained experimental results (Fig. 7). The obtained results showed that the affinity of the adsorbent to sorbents depends on the structure of the porous SiO_2 layer, which is affected by the presence of surfactants during deposition.

Based on the obtained data, the specific surface area of the catalyst (*SSA*) was calculated. The calculation was carried out according to the equation:

$$SSA = \frac{q_m N_A S_M}{M_{MB} \cdot 10^{21}}, \tag{20}$$

where q_m is the maximum adsorption of MB monolayer, mg/g; N_A is Avogadro's number; S_M is the area occupied by one MB molecule, nm; M_{MB} is MB molar mass. Since the MB molecule has the shape of an elongated ellipse and the size of the site varies from 0.69 to 2.7 nm depending on the orientation to the surface,[14] the value of 1.06 nm was taken for calculations.

The specific surface area of the (0) catalyst obtained without the use of surfactants is 17.1 m^2/g when using surfactants: for the (NaDS) catalyst – 24.8 m^2/g, for the (RL) catalyst – 34.9 m^2/g. The obtained results confirm the effect of surfactants on the structure of SiO_2 and, accordingly, on the number of active sites on the surface of the composite.



a) b)

Fig. 11. Linearized Langmuir isotherms of MB adsorption on the surface of the (0) (a), (NaDS) (1b) and (RL) (2b) catalysts

3.5. The Activation Energy of the Adsorption Process

To determine the activation energy of MB adsorption on the surface of the $CoFe_2O_4/SiO_2$(RL)/CuO catalyst, studies were carried out in the temperature range of 293-333 K (Fig. 12). The research was carried out for a model MB solution with the concentration of $5 \cdot 10^{-5}$ mol/L, to which 5 mg of the composite was added as a sorbent.

The dependence of the reaction rate on temperature can be expressed using the Arrhenius equation in a differential form:

$$\frac{d\ln k}{dT} = \frac{E_a}{R{\cdot}T^2}, \qquad (21)$$

in integral form:

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R} \cdot \left(\frac{T_2 - T_1}{T_2 {\cdot} T_1}\right) \qquad (22)$$

$$\ln k = -\frac{E_a}{R{\cdot}T} + const \qquad (23)$$

$$k = k_0 \cdot e^{-E_a/R \cdot T}, \qquad (24)$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 (K); R is the universal gas constant (8.314 J/(mol·K); E_a is the activation energy (J/mol).

The calculation of the main kinetic parameters of the MB adsorption process was carried out according to the equations proposed above (Fig. 13, Table 4). The high values of the correlation coefficients for the obtained straight lines indicate that the adsorption kinetics is well described by the pseudo first-order model considered above.

Based on the determined adsorption rate constants, the activation energy of adsorption at the temperature range of 293 – 333 K was calculated:

$$E_a = \frac{R \cdot T_1 \cdot T_2}{T_2 - T_1}\ln\frac{k_2}{k_1} = \frac{8{,}314 \cdot 293 \cdot 333}{333 - 293}\ln\frac{9333}{7160} = 5375{,}8\,J.$$

This value of the activation energy indicates the physical nature of methylene blue adsorption on the surface of the $CoFe_2O_4/SiO_2$(RL)/CuO catalyst. The rate of adsorption is practically independent of the process temperature.

Table 4. Kinetic parameters of MB adsorption on the surface of the $CoFe_2O_4/SiO_2$(RL)/CuO composite at different temperatures

№	*T*, K	$k \times 10^{-3}$, min^{-1}	$\ln\frac{a + C_0}{C_0}$	$a \times 10^5$, mol/L	$A \times 10^{-4}$, L/mol	R^2
1	293	7.16	0.098	0.50	1.82	0.997
2	303	7.81	0.052	0.26	1.90	0.997
3	313	8.73	0.030	0.15	1.94	0.996
4	323	7.58	0.019	0.10	1.96	0.991
5	333	9.33	0.006	0.03	1.99	0.971

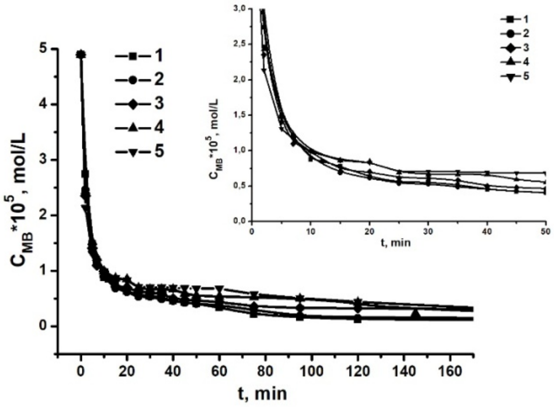


Fig. 12. Kinetic curves of MB adsorption on $CoFe_2O_4/SiO_2$(RL)/CuO: 1 – 293 K; 2 – 303 K; 3 – 313 K; 4 – 323 K; 5 – 333 K

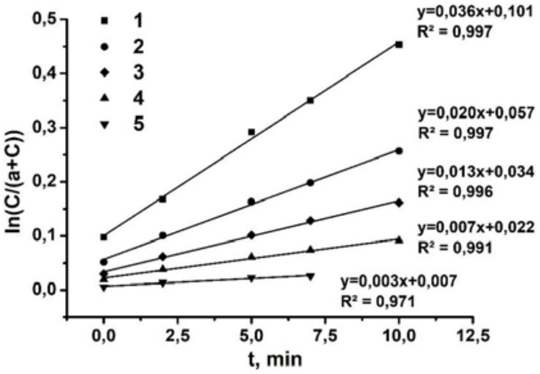


Fig. 13. MB adsorption isotherms on the surface of the $CoFe_2O_4/SiO_2$(RL)/CuO composite at different temperatures: 1 – 293 K; 2 – 303 K; 3 – 313 K; 4 – 323 K; 5 – 333 K

3.6. Catalytic Properties of Composites in the Fenton System

The synthesized CuO-based composites were used as catalysts in the Fenton system. The research was carried out on a model solution of the methylene blue dye. Hydrogen peroxide was used as an oxidizing agent. The results showed (Fig. 14) that for samples with a developed SiO_2 structure (the (NaDS) sample (curve 1) and the (RL) sample (curve 2)), the degree of oxidation of the MB dye reaches 90% and 95%, respectively, in 120 minutes of the process. At the same time, for the (0) sample (curve 0) – only 44%. It can be concluded that the catalytic properties of $CoFe_2O_4/SiO_2/CuO$ composites depend proportionally on their adsorption properties. The use of surfactants of natural origin (rhamnolipids) makes it possible to obtain a developed surface of the SiO_2 layer, which improves not only the adsorption but also the catalytic properties of this composite.

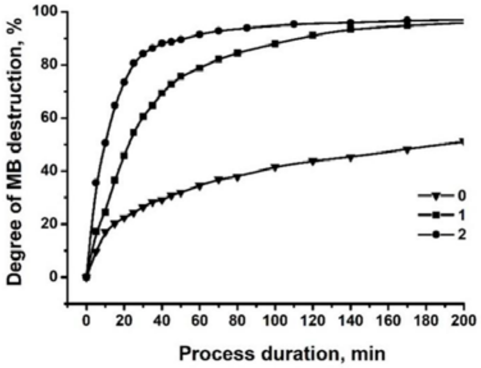


Fig. 14. Kinetic curves of the oxidation of MB dye with a concentration of $5{\cdot}10^{-5}$ mol/L in the solution in Fenton system on the surface of the $CoFe_2O_4/SiO_2$/CuO (0), $CoFe_2O_4/SiO_2$(NaDS)/CuO (1), $CoFe_2O_4/SiO_2$(RL)/CuO (2) composites

At the same time, these results indicate the effectiveness of the $CoFe_2O_4/SiO_2$(RL)/CuO catalyst in the Fenton system, which makes it promising for use in the processes of oxidation of organic compounds, in particular, in the processes of wastewater treatment of various origins.

4. Conclusions

Using the example of methylene blue dye adsorption from aqueous solutions with different initial concentrations, the adsorption capacity of the synthesized magnetosensitive $CoFe_2O_4/SiO_2$/CuO nanocomposites was investigated. It was determined that the dye adsorption from an aqueous solution can be represented as a pseudo chemical reaction of displacement of solvent molecules from adsorption sites on the adsorbent surface by adsorbate molecules. The obtained results are well described by the proposed pseudo-first order equation. The equilibrium state of MB adsorption from the solution is described by the Langmuir equation, in which the effective adsorption constant is the ratio of equilibrium constants of the Langmuir interaction of the dye and the solvent with the active site of the adsorbent. The maximum amount of the adsorbed MB and the adsorption constant characterizing the affinity of the dye to the catalyst surface were determined. The specific area of the catalyst was calculated, if the area occupied by the dye molecule is known.

The obtained activation energy value for the $CoFe_2O_4/SiO_2$(RL)/CuO catalyst indicates the physical nature of methylene blue adsorption on the surface.

It was also investigated that the adsorption capacity of the studied composites is influenced by the presence of surfactants during the deposition of the SiO_2 layer using the sol-gel method. When the SiO_2 layer is formed in the presence of surfactant, the number of active sites increases, which improves the adsorption and catalytic properties of the composite. A higher adsorption capacity was found for the nanocomposite with the SiO_2 layer immobilized in the presence of the natural surfactant (rhamnolipid). This sample also showed the best catalytic properties in the Fenton system.

The $CoFe_2O_4/SiO_2$(RL)/CuO composites obtained by the proposed technology are promising for use in Fenton-like oxidation processes of organic compounds, such as wastewater treatment processes of various origins.

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Received: March 03, 2024 / Revised: May 17, 2024 / Accepted: June 08, 2024

ДОСЛІДЖЕННЯ АДСОРБЦІЙНИХ ВЛАСТИВОСТЕЙ НОВОГО КОМПОЗИТНОГО КАТАЛІЗАТОРА ДЛЯ СИСТЕМИ ФЕНТОНА

Анотація. *Досліджено вплив структури шару* SiO_2 *на адсорбційні властивості магніточутливих нанокомпозитів* $CoFe_2O_4/SiO_2$*/CuO, створених як каталізатори для системи Фентона. Для цього формування шару* SiO_2 *проводили золь-гель методом з використанням ПАР синтетичного та природного походження. Для визначення параметрів процесу була використана раніше запропонована математична модель процесу адсорбції барвника з водного розчину. Представлена модель розглядає адсорбцію барвника з водного розчину як псевдохімічну реакцію витіснення молекулами адсорбату молекул розчинника з адсорбційних центрів на поверхні адсорбенту. Встановлено, що на процес формування шару* SiO_2 *мають вплив ПАР (додецилсульфат натрію або рамноліпіди), а адсорбційні властивості отриманих композитів* $CoFe_2O_4/SiO_2$*/CuO залежать від структури стабілізуючого шару* SiO_2*. Були визначені кінетичні параметри процесу адсорбції метиленового синього (МС) для концентрацій 2 -* $5 \cdot 10^{-5}$ *моль/л. Отримані результати добре описуються запропонованим рівнянням псевдопершого порядку. Розраховане значення енергії активації для каталізатора* $CoFe_2O_4/SiO_2$*(RL)/CuO свідчить про фізичну адсорбцію МС. Показано результати використання досліджуваних композитів у системі Фентона як каталізаторів процесу окиснення органічного барвника МС.*

Ключові слова: *система Фентона, каталізатор типу «ядро-оболонка», адсорбція метиленового синього, кінетика, енергія активації.*