Comparison of the adsorption capacity of methylene blue nanostructured composites based on $CoMnO_2$ and CuO

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Abstract* – *The adsorption kinetics of methylene blue dye from aqueous solutions of various concentrations on the surface of nanostructured magnetosensitive catalysts based on CoMnO2 and CuO have been studied. The kinetic parameters of the process have been investigated. The adsorption process is presented as a quasi-chemical process of displacement of solvent molecules by dye molecules from the adsorption layer. The equilibrium state is described by the Langmuir equation. The limiting adsorption of methylene blue was determined.

Keywords – "core-shell" type catalyst, methylene blue, Fenton system, kinetics, adsorption.

Introduction

One of the effective methods of wastewater treatment from organic pollutants is their catalytic oxidation by the Fenton process. The use of heterogeneous catalytic systems in the Fenton process, on the one hand, does not limit the access of reagents to the active centers, because the transition metal atoms are on the surface of the catalyst. On the other hand – simplifies the process of removing the catalyst at the end of the process.

The composition of the nanostructured catalysts of the "core-shell" type developed by us based on transition metals includes a magnetically sensitive core of cobalt ferrite ($CoFe_2O_4$) and a protective layer of porous SiO_2. On the SiO_2 surface, there are clusters of cobalt and manganese oxides ($CoMnO_2$) and copper oxide (CuO), which play the role of catalytic centers. The presence of a layer of highly porous SiO_2 due to its adsorption properties should lead to an increase in the concentration of reagents around the catalytic centers, which can increase the efficiency of the Fenton process.

This work presents the results of the study of the adsorption capacity of the synthesized catalysts $CoFe_2O_4/SiO_2/CoMnO_2$ and $CoFe_2O_4/SiO_2/CuO$ by the example of the adsorption of methylene blue (MB) dye from an aqueous solution.

Results and discussion

The kinetics and equilibrium state of adsorption of methylene blue by the composite were investigated using a spectrophotometer Spekol 11 under the following conditions: up to 5 ml of a model solution with a defined initial concentration of MB ($2\cdot10^{-5}$ – $5\cdot10^{-5}$ mol/L) was added 10 mg of catalyst as sorbent.

The obtained kinetic adsorption curves are Langmuir isotherms, which made it possible to calculate the main parameters of the MB adsorption process on the catalyst surface (Fig. 1). The optimal contact time, during which the saturation of adsorption centers with dye molecules occurs, is 50-60 minutes. The difference in the behavior of composites is primarily associated with the composition of the catalytic layer. The nature of the dependence of the adsorption efficiency for different adsorbate concentrations is similar for both samples, however, the adsorption efficiency is higher for the catalyst based on CuO. This indicates its greater affinity for the selected dye. The adsorption kinetics parameters for this composite correspond to the proposed model of the pseudo-first order (Table 1). The adsorption process is presented as a pseudochemical equilibrium reaction of the displacement of solvent molecules by molecules of adsorbate from adsorption centers on the adsorbent surface [1].

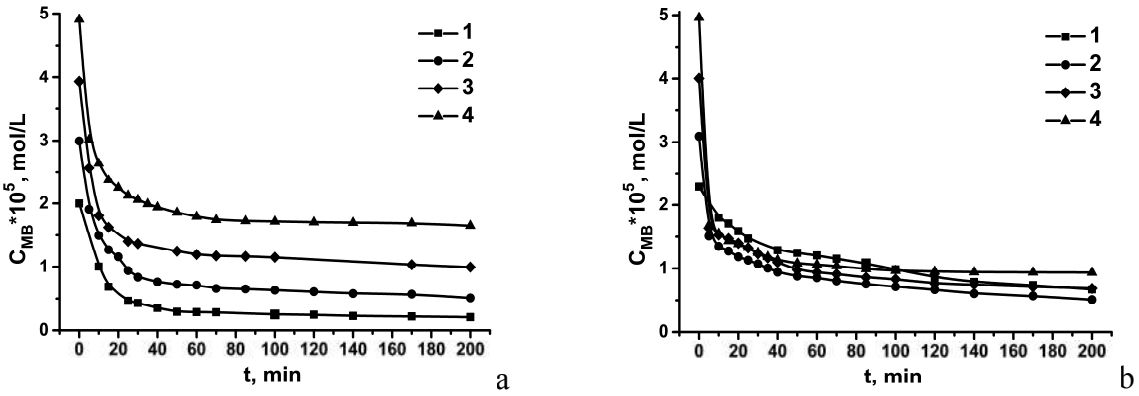

Fig. 1. Kinetic curves of the adsorption of methylene blue on the surface of the catalyst $CoFe_2O_4/SiO_2/CoMnO_2$ (a) and $CoFe_2O_4/SiO_2/CuO$ (b) at different initial concentrations of the dye C_{MB}, mol/L: 1 – $2\cdot10^{-5}$; 2 – $3\cdot10^{-5}$; 3 – $4\cdot10^{-5}$; 4 – $5\cdot10^{-5}$.

Table 1. Kinetic parameters of MB adsorption on the surface of catalysts

No	$C_0\times10^5$, mol/L	$CoFe_2O_4/SiO_2/CoMnO_2$					$CoFe_2O_4/SiO_2/CuO$				
		$k\times10^{-3}$, min^{-1}	$\ln\frac{a+C_0}{C_0}$	$a\times10^5$, mol/L	$A\times10^{-4}$, L/mol	R^2	$k\times10^{-3}$, min^{-1}	$\ln\frac{a+C_0}{C_0}$	$a\times10^5$, mol/L	$A\times10^{-4}$, L/mol	R^2
1	2	1,09	1,12	3,80	1,7	0,98	3,0	0,85	2,9	2,0	0,96
2	3	1,08	0,59	2,50	1,8	0,98	3,3	0,81	2,5	1,8	0,99
3	4	1,05	0,36	1,55	1,8	0,96	3,4	0,71	2,1	1,6	0,99
4	5	1,03	0,13	0,60	1,8	0,93	3,4	0,54	1,6	1,5	0,98

The equilibrium data were analyzed using the Langmuir model. It provides for the adsorption of a monolayer on the surface, which contains a finite number of adsorption centers with homogeneous energies without adsorbate movement in the surface plane [1].

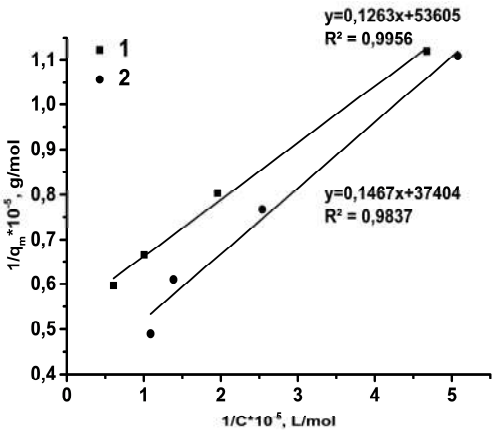

Fig. 2. Linearized Langmuir adsorption isotherms: $CoFe_2O_4/SiO_2/CoMnO_2$ (1) and $CoFe_2O_4/SiO_2/CuO$ (2)

The plots constructed from the experimental data for both samples (Fig. 2) demonstrated that the adsorption isotherms of methylene blue on the catalyst surface within a certain concentration range are well described by the proposed equation (R^2 = 0,99).

Carrying out investigations showed that with 30 minutes of adsorption before adding the oxidizing agent to the reactor, the completeness of the dye destruction increases by 13%.

Conclusion

It has been determined that the adsorption of a dye from an aqueous solution can be represented as a pseudochemical reaction of the displacement of solvent molecules by adsorbate molecules from adsorption centers on the adsorbent surface. The results are described by the proposed pseudo-first order equation. The investigated adsorption properties of catalysts have a positive effect on the process of oxidative destruction of MB.

[1] Makido, O.Yu., Medvedevskikh, Yu.G., Khovanets′, G.I. (2020). Investigation into the adsorption of methylene blue on the surface of a «core–shell» type catalyst for the Fenton system. Voprosy khimii i khimicheskoi tekhnologii, 6 (133), pp. 91-98. http://dx.doi.org/10.32434/0321-4095-2020-133-6-91-98