

# Photocatalytic Oxidation of Dyes in the Presence of Pillar Materials Under the Influence of Solar and UV Radiation

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**ABSTRACT:** The adsorption and catalytic activities of pillar materials in the oxidation reactions of cationic and anionic dyes were studied. The dependence of the conversion of methylene blue (MB) and Congo red (CR) during non-catalytic oxidation with dissolved oxygen in a dye solution with dissolved oxygen proceeds only by 2–3% at an initial dye concentration of 4 mg/l for 120 min. When hydrogen peroxide is introduced into the system, the shape of the dye optical density curve slightly changes. At the same time, the degree of conversion of methylene blue increases only by 2–3%, while there are no noticeable changes for the system with Congo red.

**KEYWORDS:** Montmorillonite clay, intercalation, chromium, aluminium, methylene blue, congo red, hydrogen peroxide, adsorption, catalytic activity.

## I. INTRODUCTION

At the moment, the issue of neutralizing natural and waste water from harmful organic substances is considered relevant. organic dyes, phenol and its derivatives, surfactants, etc. These polluted effluents are formed during the production of drugs, polymeric materials, surfactants, herbicides and pesticides, dyes, etc. media is catalytic oxidation, which can significantly reduce other costs in the form of reducing the amount of reagents, temperature and pressure [1–3].

Ozone, hydrogen peroxide (HP), chlorine are effective oxidizers in wastewater treatment. The main advantage of hydrogen peroxide over other oxidizing agents is its environmental friendliness, because after application, there is no possible secondary pollution of various waters.  $H_2O_2$  is an environmentally friendly and cost-effective oxidizing agent for wastewater treatment from sulfur compounds, cyanide compounds and organic pollutants [4–6].

Modern industrial practice for the removal of some toxic organic substances from wastewater uses a mostly homogeneous oxidizing system of Fenton and Ruff ( $Fe^{2+}/Fe^{3+}-H_2O_2$ ), despite a number of significant drawbacks. The disadvantages are associated with the impossibility of reusing the catalysts of this process and re-contamination of wastewater with ions of these catalysts [5–7].

## II. SIGNIFICANCE OF THE SYSTEM

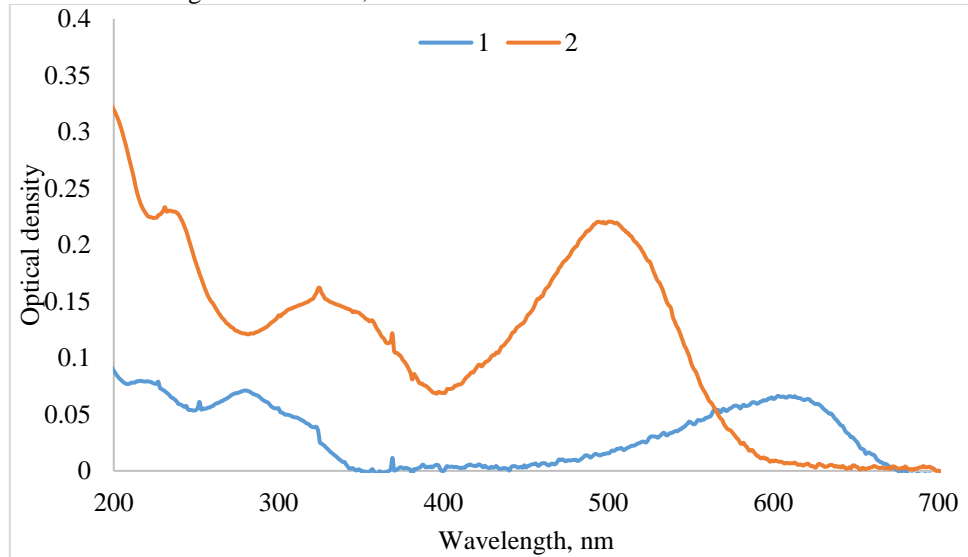
The adsorption and catalytic activities of pillar materials in the oxidation reactions of cationic and anionic dyes were studied. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

## III. METHODOLOGY

The technique of photocatalysis by UV irradiation is given in [8]. The photocatalytic activity of pillar bentonites was studied under laboratory conditions by a spectrophotometric method in the range of 190–1000 nm using solutions of MB and CR [1, 9].

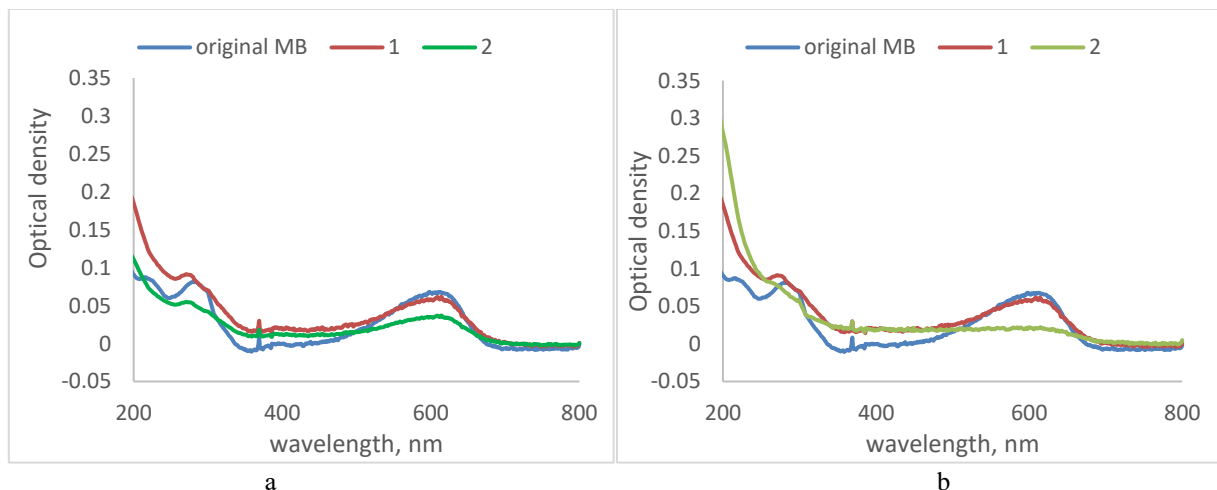
**IV. EXPERIMENTAL RESULTS**

The absorption spectrum of the CR solution (Fig. 1) in the visible part of the spectrum contains absorption peaks in the wavelength region of 501 nm, due to  $n \rightarrow \pi^*$  transitions of the electrons of the azo group [9], as well as in the UV part in the wavelength region of 320 and 228 nm, related to  $\pi \rightarrow \pi^*$  transitions in aromatic rings [1]. These peaks for the system with MG are observed in the region of 610-620; 310 and 210 nm

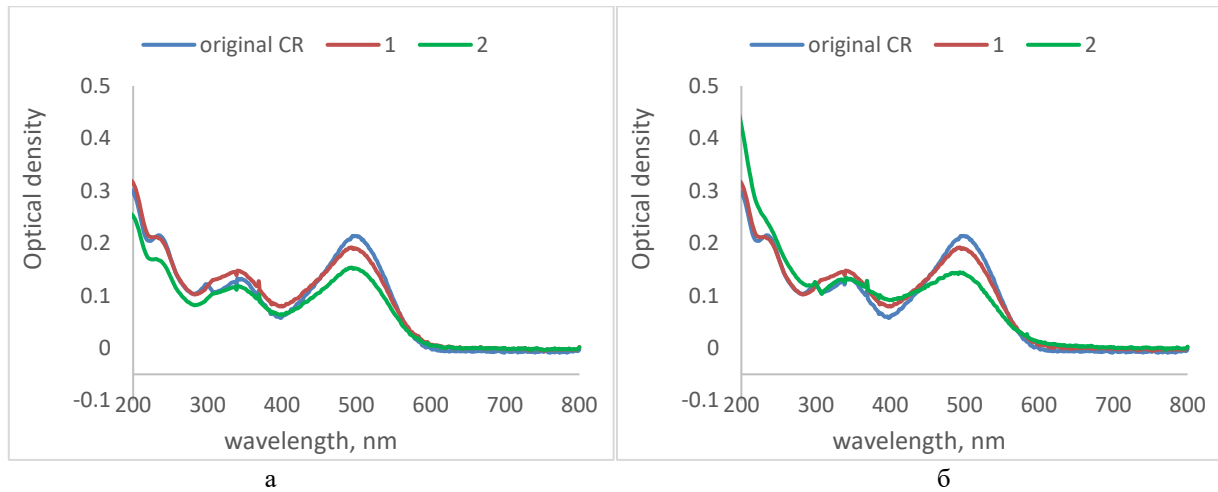


**Fig. 1. Electron absorption spectrum of the solution: 1) MB; 2) CR. The concentration of the dye in the solution is 10 mg/L.**

The dependence of the conversion of MB and CR during noncatalytic oxidation with dissolved oxygen in a dye solution proceeds only by 2–3% at an initial dye concentration of 4 mg/L for 120 min (Figs. 2 and 3).

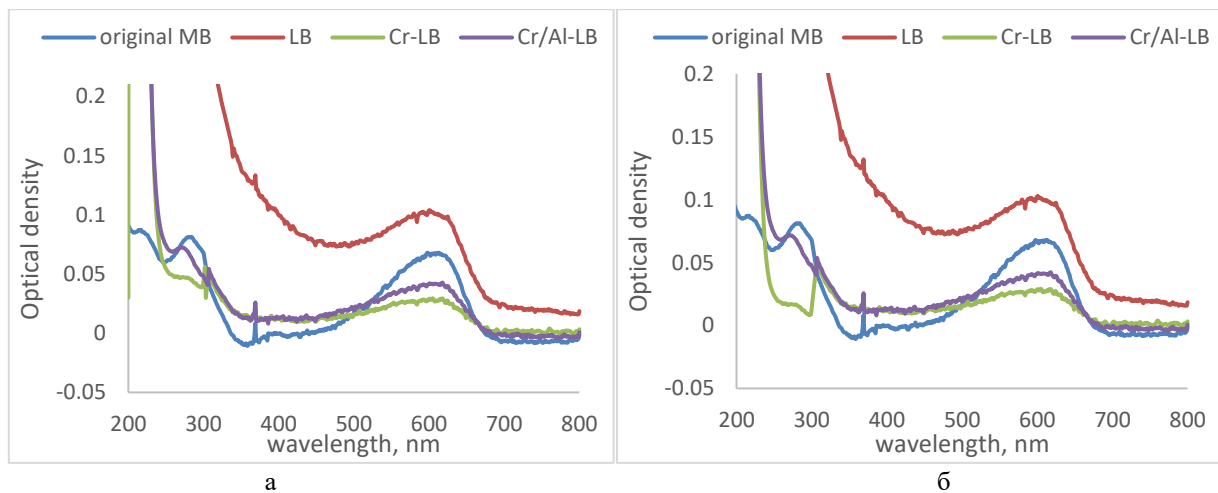


**Fig. 2. Dependence of the optical density of aqueous solutions of MB on the duration of the irradiation process: a) sunlight; b) UV; 1) without HP; 2) with HP.**



**Fig. 3. Dependence of the optical density of aqueous solutions of CR on the duration of the irradiation process: a) sunlight; b) UV; 1) without PV; 2) with PV.**

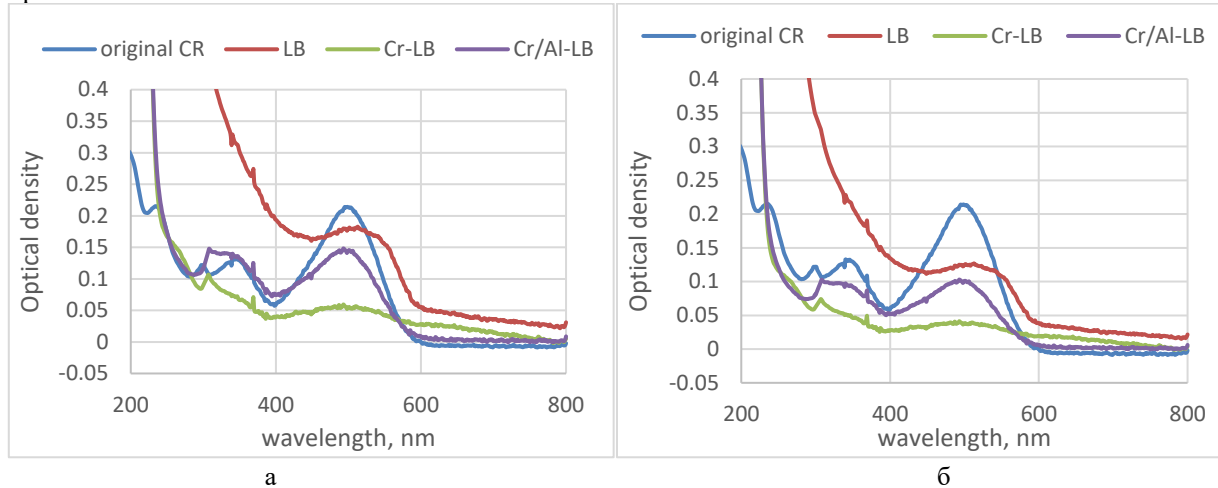
When hydrogen peroxide is introduced into the system, the shape of the dye optical density curve slightly changes. In this case, the degree of conversion of MB increases only by 2–3%, while there are no noticeable changes for the system with CR. The data obtained indicate the stability of CR molecules to the action of this oxidizing agent and the absence of dye oxidation under the influence of solar radiation.



**Fig. 4. Dependence of the optical density of an aqueous solution of MG (C=4 mg/l) in the presence of pillar materials on the duration of the irradiation process: a) sunlight; b) UV.**

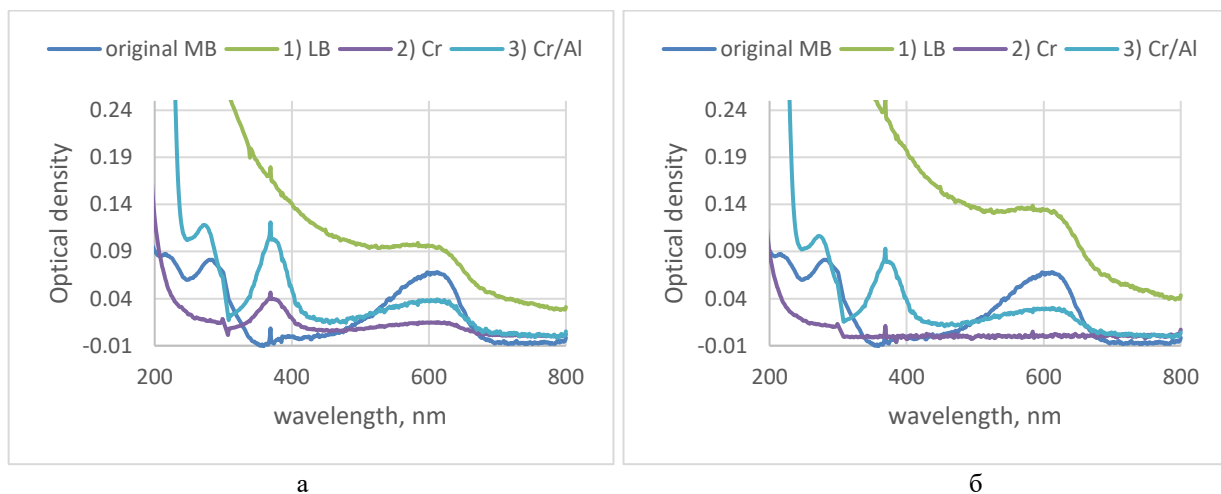
When Cr-, Cr/Al-LB is introduced into an aqueous solution, MB noticeably changes the location of characteristic peaks; there is a decrease in the intensity of the bands at 610 nm. Complete discoloration of the solution of this dye occurs during storage, which occurs due to the destruction of the chromophore azo group. In this case, after a 2-hour interaction, complete disappearance (100%) of the absorption bands at 240 nm for the system with Cr-LB is observed, which may indicate the destruction of the aromatic systems of anthracene or its adsorption on the surface of pillar materials. However, under such conditions of oxidative degradation for the system with Cr/Al, the characteristic values of the conversion yield are about 60%, while for the system with LB, the decrease in characteristic peaks is only 18–21%, which is probably due not to the oxidation of MB, but only to adsorption. dye on LB. Similar changes are observed in CR solutions (Fig. 5).

The catalytic activity of the studied materials when added to the HP system correlates with the % content of Cr in their composition and increases in the series LB<Cr/Al-LB<Cr-LB.

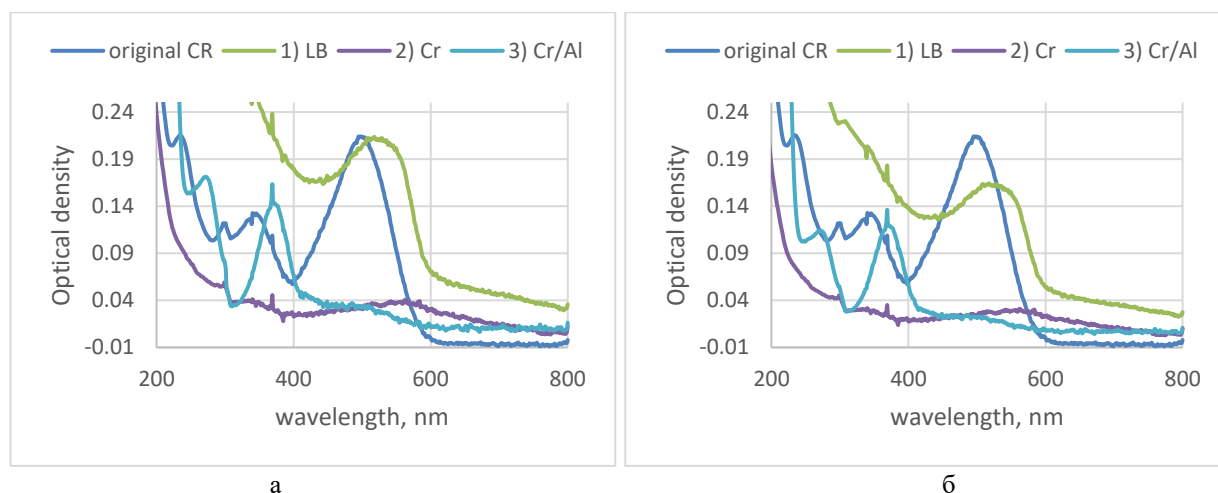


**Fig. 5. Dependence of the optical density of an aqueous solution of CR in the presence of pillar materials on the duration of the irradiation process: a) sunlight; b) UV.**

In the reaction system with HP, there is a clear catalytic activity of pillar materials and a noticeable decrease in the concentration of both dyes.



**Fig. 6. Dependence of the optical density of an aqueous solution of MB in the presence of pillar materials and HP on the duration of the irradiation process: a) sunlight; b) UV. 1) LB; 2) Cr-LB; 3) Cr/Al-LB.**



**Fig. 7. Dependence of the optical density of an aqueous solution of CR in the presence of pillar materials and HP on the duration of the irradiation process: a) sunlight; b) UV. 1) LB; 2) Cr-LB; 3) Cr/Al-LB.**

As it turned out, the intercalated mononuclear chromium polyoxocation is distinguished by catalytic activity in reactions with hydrogen peroxide. The presence of aluminum ions has a significant effect on the activity of the pillar material, because the catalytically active component is reduced, but increases its stability. So, to remove the aromatic substance (100%), the required duration of the process is reduced to 20–30 min at a consumption of Cr-LB 1 g/l and PV 7 mol/mol MB. At the same time, for chromium pillar montmorillonite, the duration of the aromatic cycle transformation processes for various dyes (MB and CR) do not differ significantly from each other, which shows the possibility of using them in various oxidative processes that are associated with the surface acidity of catalysts. At the same time, in the system with LB, the introduction of an oxidizing agent into the solution does not cause any changes in the spectra, i.e., the absorption bands for dye solutions obtained both without HP and with HP are identical, which indicates the absence of catalytic activity in the initial montmorillonite.

As shown by the results of adsorption processes, the pH of systems strongly affects the surface properties of pillar materials and the structures of the dyes themselves. The results of studying the degradation kinetics of MB and CR at different pH values show their dependence on the rate of dye oxidation and the final result of the process. It turned out that the lower the pH value, the greater the rate of degradation reaction and the maximum values are achieved at pH=2–3. At the same time, the decrease in pH, i.e. an increase in acidity contributes to the leaching of  $\text{Cr}^{3+}$  ions from the catalyst surface into the solution. Therefore, it is necessary to control the pH of the catalytic oxidation system.

The study of the effect of the content of catalysts on the MB conversion showed that an increase in the amount of Cr-LB over 1 g/l practically does not affect the result of the oxidation of the HP dye, while for Cr/Al-LB an increase from 1 to 2,5 g/l somewhat times increases the speed, which is reflected in the outputs of the process. For a system with CR, an increase in the content of both catalysts from 1 to 3–3,5 g/l contributes to an increase in the rate of the conversion process and the yield of the process, and a further increase in the concentration of catalysts does not affect the change in CR molecules (on the duration of the process of 100% removal).

## V. CONCLUSION AND FUTURE WORK

The dependence of MB and CR conversion during noncatalytic oxidation with dissolved oxygen in a dye solution with dissolved oxygen proceeds only by 2–3% at an initial dye concentration of 4 mg/l for 120 min. When hydrogen peroxide is introduced into the system, the shape of the dye optical density curve slightly changes. In this case, the degree of conversion of MB increases only by 2–3%, while there are no noticeable changes for the system with CR.

The catalytic activity of the studied materials when added to the HP system correlates with the % content of Cr in their composition and increases in the series  $\text{LB} < \text{Cr/Al-LB} < \text{Cr-LB}$

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ISSN: 2350-0328

**International Journal of Advanced Research in Science,  
Engineering and Technology**

**Vol. 9, Issue 5 , May 2022**

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