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COOMASSIE BRILLIANT BLUE DYE REMOVAL IN AQUEOUS SOLUTION BY HYDROGEN PEROXIDE IN THE PRESENCE OF IRON OXIDE NANOPARTICLES

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Abstract. In this work, was investigated of catalytic oxidative degradation of the Coomassie Brilliant Blue synthetic dye (CBB R-250) by hydrogen peroxide H_2O_2 in the presence of Fe_3O_4 magnetite nanoparticles. It was found that in the presence of Fe_3O_4 magnetic nanoparticles, the dye degradation rate significantly increases, which is explained by the strong interaction of Fe_3O_4 nanoparticles with hydrogen peroxide with the formation of highly reactive hydroxyl radicals followed by an increase in the rate of oxidative degradation. Also in the article, it was found that the degradation of the CBB R-250 dye is highly dependent on conditions of process, such as pH of the medium and degradation time. The relatively low rate of oxidative degradation CBB R-250 dye at high pH is explained by the formation of Fe^{3+} complexes, which leads to a decrease in the concentration of Fe^{2+} ions, which are responsible for the formation of free radicals.

Keywords: *Magnetite, dye, hydrogen peroxide, nanoparticles, catalytic.*

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1. Introduction

The problem of clean water is nationwide and affects the interests of all industries and the entire population of the country, so the fight against pollution of the aquatic environment is of great importance. A significant contribution to the pollution of natural water bodies is made by textile and light industry enterprises. The main components of almost all technological processes of such enterprises are complex organic compounds - synthetic dyes. Industrial waters containing organic dyes are subject to discoloration by physicochemical, oxidative or biological methods.

Advanced oxidative processes (AOPs) are undoubtedly a promising direction for resource conservation, minimizing environmental damage and reducing water consumption. These include, in particular, the processes of joint use of ozone, UV irradiation or metal ions of variable valence and hydrogen peroxide (Fenton's reactions). The main feature of such methods is that they are based on two successive stages: the generation of active particles and their interaction with pollutants dissolved

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in water. Recently, scientists around the world have paid great attention to Fenton processes for the oxidation of various organic compounds. Ferric sulfate and chloride are often used in such systems in combination with hydrogen peroxide, which leads to high environmental and economic costs. There are a number of works devoted to the study of the Fenton process using heterogeneous iron-containing catalysts, which leads to a decrease in the amount of precipitate formed. The authors of these works found that heterogeneous oxidation of organic dyes leads to complete discoloration of solutions in a short period of time with minimal costs. Thus, the search for new methods of purification of textile wastewater using cheap catalysts for oxidative degradation is an urgent task (Shaban *et al*., 2017; Jiang *et al*., 2011; Pham *et al*., 2020; Ngo *et al*., 2020; Chu *et al*., 2019; Yan *et al*., 2014; Mehrdad & Hashemzadeh, 2010).

Recently, interest in utilizing magnetic nanoparticles in the cleaning of wastewater contaminated with dyes has increased considerably. Magnetite nanoparticles (Fe_3O_4) are considered one of the good catalysts due to their low cost, abundance in nature, easy separation in an external magnetic field, simple extraction and environmental characteristics. Fe_3O_4 can be applied to effectively decolorized organic dyes from waste water by improving the decomposition of hydrogen peroxide (Giraldo *et al*., 2013; Dalali *et al*., 2011, Liang *et al*., 2013; Jiaqi *et al*., 2019; Gupta & Gupta, 2005; Godoi *et al*., 2014).

Wan et al. (2023) in their work synthesized nanocomposites based on poly (acrylamide-co-acrylic acid), KH570 magnetic nanoparticles and polyvinyl pyrrolidone (PVP). They discovered that the nanocomposites can absorb methylene blue by approaching absorption equilibrium at 90 min. Dye absorption using hydrogel magnetic nanocomposites is observed at pH=8 and methylene blue adsorption capacity was 255.4 mg/g, 326.3 mg/g and 418.5 mg/g in the condition of initial dye concentrations of 700 mg/L, 900 mg/L and 1100 mg/L, respectively.

Ghosh et al. (2015) synthesized Fe_3O_4 nanoparticles using Vasaka (*Justicia adhatoda*) leaf extract (JA-MIONs) for a fast removal approach in MB dye and TCH antibiotics. Adsorption kinetics and isotherms show that it follows the pseudo-first-order kinetic and the Freundlich isotherm, with maximum adsorption capacities of 76.92 mg/g for MB and 200 mg/g for TCH at 298 K. The reusability of the JA-MIONs eventually exhibited a decline in the adsorption percentage of MB and TCH after five and four times respectively. After the desorption-adsorption cycles, this adsorbent continued to exhibit significant adsorption capacity.

Unal et al. (2019) in the work investigated the catalytic activity of the Fe_3O_4 nanoparticles modified by borosilicate glass for the removal of basic red 18 (BR18) and acid red 8 (AR88) azo dyes by adsorption and Fenton oxidation reaction. Have established that, Fe_3O_4 nanoparticles modified by borosilicate glass enhanced maximum 77% and 82% color removal efficiencies for adsorption and Fenton oxidation of BR18 dye. Maximum 86% and 100% color removal efficiencies were obtained for adsorption and Fenton oxidation of AR88 dye.

Hassani et al. (2018) were studied a catalytically degradation of basic violet 10 (BV10) dye via sono-Fenton reactions in the presence Fe_3O_4 nanoparticles. It was determined that the ball-milled Fe_3O_4 of 6 h showed the highest catalytic activity in dye removal as compared with that for ball-milled Fe_3O_4 of 4 h (66.12% after 120 min) and 2 h (48% after 120 min).

The aim of the work was the decolorization and degradation of aqueous solutions of Coomassie Brilliant Blue synthetic dye (CBB R-250) in the presence of colloidal magnetite nanoparticles in combination with hydrogen peroxide.

2. Experimental Part

2.1. Synthesis of Fe_3O_4 magnetite nanoparticles

Magnetic Fe_3O_4 nanoparticles were prepared by co-precipitation of Fe^{3+} and Fe^{2+} taken in a molar ratio of 3:2 in the presence of ammonium solution (NH_4OH) as the precipitating agent under nitrogen atmosphere in presence of surfactant of PEG-6000 (Di Palma *et al*., 2018; Ramazanov *et al*., 2018; 2019). The resulting black precipitate was washed with distilled water by decantation to pH=7. The mixture was centrifuged in an ultracentrifuge and the precipitate was separated from the main mass and then redispersed in water. Magnetite nanoparticles dispersed in water were subjected to ultrasonic treatment using an ultrasonicator (VSX 500) in order to prevent aggregates and agglomerates formed as a result of a chemical reaction. In this case, the ultrasound power was 500 W, the ultrasound frequency was 20 kHz and the sonication time was 10 minutes. The ultrasonified powders were transferred to a Petri dish and dried for 24 hours in air.

2.2. Characterization

X-Ray diffractograms were measured at room temperature on a Rigaku Mini Flex 600 diffractometer. All experiments were conducted using X-ray Cu K-α at 15 mA and 30 kV. The analysis of the morphology of nanoparticles was carried out in the scanning electron microscope (Jeol JSM-7600F) with 15 kV energy and 4,5 mm working distance in SEI mode. The energy-dispersion spectrum (EDS) was conducted on the X-Max 50 (Oxford Instruments) device. UV-spectra of samples were conducted at room temperature in the range of 200-700 nm wavelength on the Specord 250 Plus device.

2.3. Degradation experiments

Experiments were conducted in laboratory conditions, in the range of ΔpH=2÷11, at room temperature and on the surface of Fe_3O_4 magnetic nanoparticles catalyst. Hydrogen peroxide was taken as an oxidizer and the kinetics of its degradation process on the catalyst surface was studied. 0.1 gram of Coomassie Brilliant Blue R-250 is stirred in 100 ml distilled water until it has completely dissolved. Then 0,1 ml of the colloidal solution of Fe_3O_4, 0.5 ml of dye solution, 0.1 ml of hydrogen peroxide are added to each flask, i.e. 10 flasks (pH 2-11) and the amount of CBB P-250 dye which decomposes in different time intervals is determined. The quantitative analysis of the fissionable CBB R-250 dye substance is studied on a spectrophotometer, weighing its spectra in the interval of $\Delta\tau = 0 \div 24$ hours.

3. Results and Discussion

Figure 1 shows the XRD pattern of synthesized and stabilized of Fe_3O_4 NPs. XRD analysis confirms the crystal structure and phase purity of Fe_3O_4 NPs. The diffraction peaks appeared at $2\theta = 30.26^0$, 35.5^0, 43.12^0, 53.74^0, 57.10^0 and 62.92^0 corresponding to planes (220), (311), (400), (422), (511) and (440), respectively, consistent with

standard magnetite with cubic spinel structure according database № 00-001-1111. Figure 2 (a) and (b) shows the SEM and EDS image of the Fe_3O_4 magnetic nanoparticles (Ramazanov *et al*., 2018). As can be seen from the SEM image, the size of nanoparticles synthesized and stabilized in the presence of polyethylene glycol surfactant is 5-12 nm. SEM analysis also have shown that the formed nanoparticles are monodispersed and homogeneous. As can be seen from the EDS spectrum, the element composition of Fe_3O_4 nanoparticles consists mainly of Fe, O, C and there is no additional mixture, which indicates that the synthesized nanoparticles belong to magnetite nanoparticles.

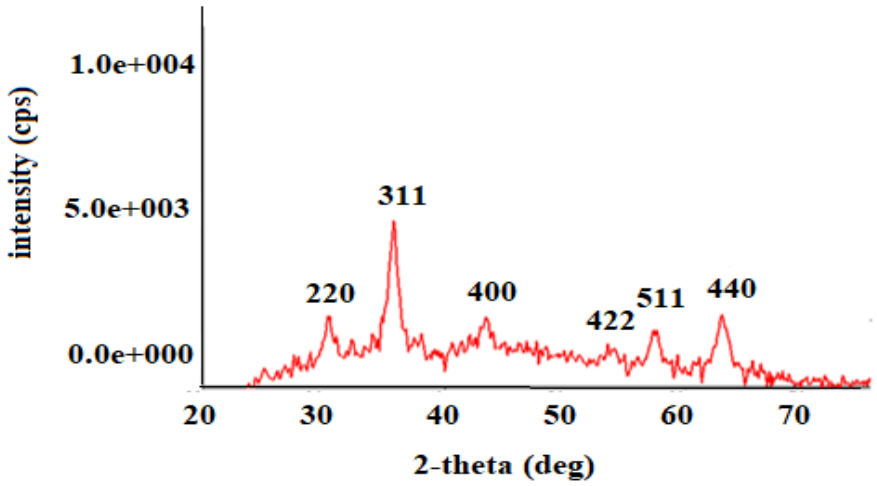

Figure 1. XRD pattern of Fe_3O_4 nanoparticles

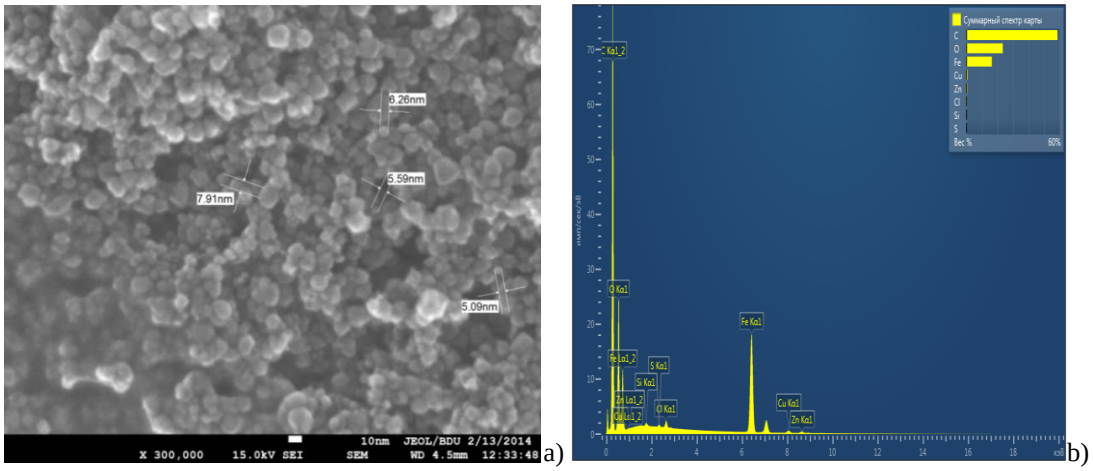

Figure 2. SEM image (a) and EDS spectrum (b) of Fe_3O_4 nanoparticles

Figure 3 shows the UV optical absorption spectra of CBBR-250 in the presence of H_2O_2/Fe_3O_4 as a function of the pH of the medium. As seen from Figure 3 the rate of degradation of CBB was highly pH-dependent and the maximum rate of degradation was observed at pH 3 in the presence and the absence of NPs. At high concentrations of H^+ ions (pH < 3), peroxide gets solvated to form stable oxonium ions, which enhanced the activity of H_2O_2 and restricted the generation of hydroxyl radicals. Moreover, the

excess of H^+ ions acts as hydroxyl radical scavenger and with the increase in H^+ ions, the concentration of HO^* radicals decreases, thus, decreasing the rate of reaction. The observed lower rate of reaction at higher pH may be related to the formation of the Fe^{3+}-complexes, which decreases the dissolved Fe^{2+} ions that were available to generate free radicals. Also the interaction of Fe_3O_4 NPs with H_2O_2 generates hydroxyl and peroxyl radicals, which are able to undergo the oxidative degradation of CBB R-250 synthetic dye (Ishaq *et al*., 2021; Ansari *et al*., 2020).

Ali et al. (2024) in the paper studied degradation of the azo dye by iron oxide nanoparticles from wastewater. Has been established that in the presence of Fe_3O_4 nanoparticles achieve a maximum degradation of azo dye (99.99% efficiency) at the 3 g/L of adsorbent concentration, 5 mg/L azo dye dose, pH 2 and 180 rpm in 120 min at 23°C.

Ghoohestani et al. (2024) in their work achieved the fast and cheap preparation of iron oxide (Fe_3O_4) nanoparticles using *Cordia myxa* leaf extracts for efficient degradation of methylene blue (MB). Have determined that the maximum adsorption capacity is 17.79 mg/g and after 1 hour incubation is observed at pH 7.5. From the pH_{PZC} of 7.1 of the obtained adsorbent, the electrostatic attraction between methylene blue dye and iron oxide nanoparticles plays an essential role in the adsorption process.

Ahmed et al. (2023) in study determined that iron oxide (Fe_3O_4) nanoparticles can be obtained using moringa residues extract, onion, tea and potato as the reducing agent. The optimum conditions for the adsorption process were achieved at a contact time of 45 min and a dose of 0.4 g of nanoparticles. Due to the good absorbance ability of onion and moringa in the removal of pollutants from wastewater it can be applicate as an efficient adsorbent in the treatment of water and wastewater.

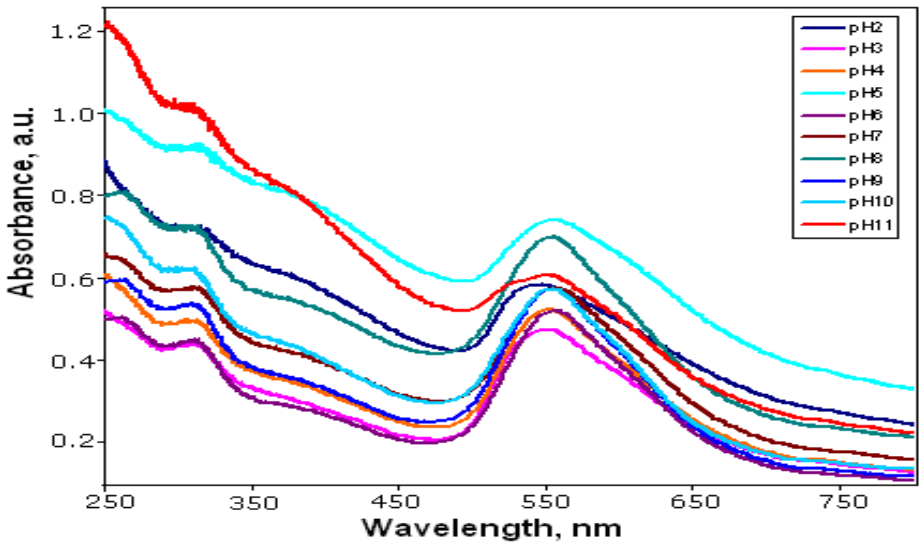

Figure 3. UV-visible spectra of Coomassie Brilliant Blue Dye (CBB R-250) in the presence of H_2O_2/Fe_3O_4 at various pH

The effects of time on the degradation of the CBB R-250 were studied. It has been established that at the maximum degradation of the CBB R-250 dye is observed during 2 hours (Figure 4).

Thabet et al. (2023) applied Fe_3O_4 nanoparticles as an efficient catalyst in the adsorption/oxidation process for the degradation and absorption of reactive textile dye

wastewater. The optimal conditions of process were at pH 2.5, 828 mg/L concentration of Fe_3O_4 nanoparticles and H_2O_2. It was established that the 100% removal of dye was observed within 30 minutes. Harja et al. (2022) in the work used composites based on Fe_3O_4 nanoparticles and fly ash for the removal of Congo red dye from wastewater. The experimental results shows that the composite has a maximum adsorption capacity of 153 mg/g and a fast adsorption rate (a contact time of approximately 20 min).

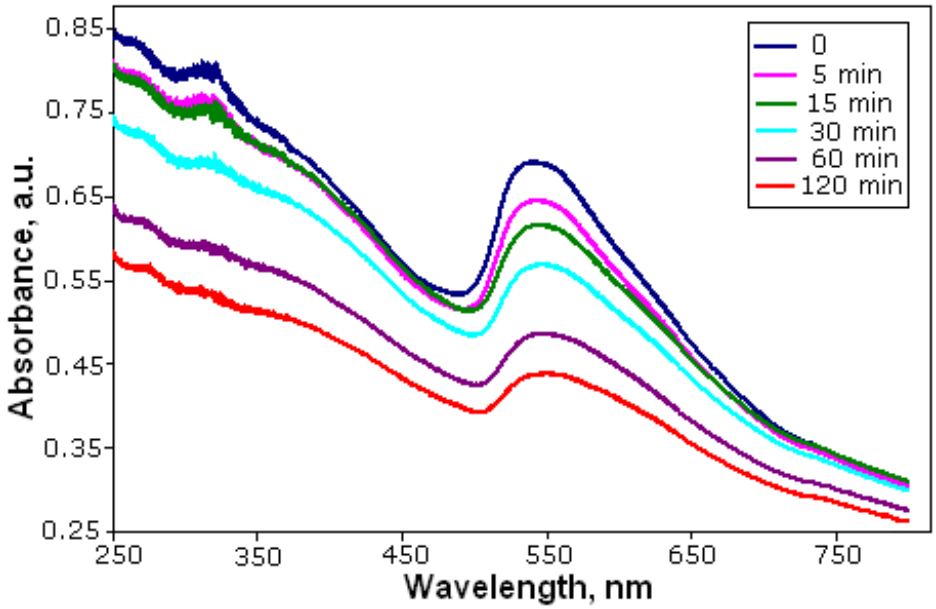

Figure 4. UV-visible spectra of CBB R-250 in the presence of H_2O_2/Fe_3O_4 at different time

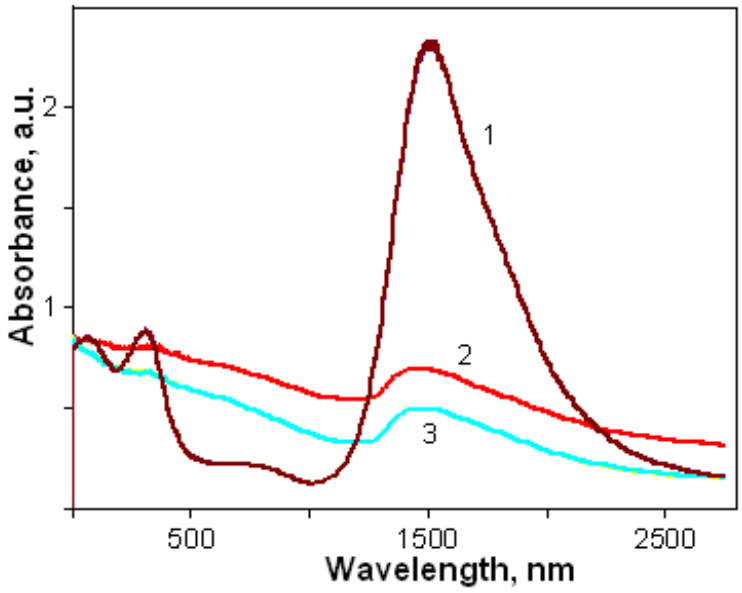

Figure 5. UV-visible spectra of CBB R-250 dye (1), in the presence of H_2O_2 (2) and in the presence of H_2O_2/Fe_3O_4

Figure 5 shows the comparative optical absorption spectra of a CBB dye (1), a CBB dye in the presence of H_2O_2 (2) and a CBB dye in the presence of H_2O_2/Fe_3O_4 (3).

As can be seen from Figure 5, the rate of oxidative degradation of CBB dye in the presence of magnetite nanoparticles increases significantly. The observed enhancement in the rate of the CBB degradation in presence of Fe_3O_4 can be described through the production of highly reactive hydroxyl radicals due to the interaction between the Fe_3O_4 NPs and H_2O_2 followed by the formation of peroxyl radicals and the subsequent oxidation of CBB by these radicals.

The observed enhancement in the rate of the CBB degradation in presence of Fe_3O_4 can be described through the production of highly reactive hydroxyl radicals due to the interaction between the Fe_3O_4 NPs and H_2O_2 followed by the formation of peroxyl radicals and the subsequent oxidation of CBB by these radicals, as described by the following reactions:

1) $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^* + OH^-$ The possible reactions of free radicals are:

2) $Fe^{2+} + HO^* \rightarrow Fe^{3+} + OH^-$

3) $H_2O_2 + HO^* \rightarrow H_2O + HO_2^*$

4) $HO_2^* + HO^* \rightarrow H_2O + O_2$,

5) $HO^* + HO^* \rightarrow H_2O_2$,

6) $HO^* + CBB \rightarrow$ Products,

7) $HO_2^* + CBB \rightarrow$ Products.

4. Conclusions

In this work, was investigated of catalytic oxidative degradation of the Coomassie Brilliant Blue synthetic dye (CBB R-250) by hydrogen peroxide H_2O_2 in the presence of Fe_3O_4 magnetite nanoparticles. It was found that in the presence of Fe_3O_4 magnetic nanoparticles, the dye degradation rate significantly increases, which is explained by the strong interaction of Fe_3O_4 nanoparticles with hydrogen peroxide with the formation of highly reactive hydroxyl radicals followed by an increase in the rate of oxidative degradation. Also in the article, it was found that the degradation of the CBB R-250 dye is highly dependent on conditions of process, such as pH of the medium and degradation time. The relatively low rate of oxidative degradation CBB R-250 dye at high pH is explained by the formation of Fe^{3+} complexes, which leads to a decrease in the concentration of Fe^{2+} ions, which are responsible for the formation of free radicals. The results obtained in this paper allow us to conclude that magnetite nanoparticles in the presence of hydrogen peroxide can be effectively used in the purification of Coomassie Brilliant Blue dye from wastewater.

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