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CATALYTICAL REMOVAL OF COOMASSIE BRILANT BLUE R-250 DYE BY Fe_3O_4 MAGNETITE NANOPARTICLES

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Abstract. In this article, the synthesis and stabilization of Fe_3O_4 magnetite nanoparticles in the presence of surfactant of polyethylene glycol (PEG) was carried out and the optimal conditions of obtaining magnetic nanoparticles were determined. The structure of Fe_3O_4 magnetic nanoparticles was studied by X-ray roentgen diffraction analysis (XRD) and scanning-electron microscopy (SEM). During the XRD analysis, it was determined that the synthesized particles are suitable for magnetite particles with a cubic spinal crystal structure. From the SEM analyses, it was determined that the shaped Fe3O4 nanoparticles are monodisperse and homogeneous, and have a size of 5-8 nm. EDS analysis showed that the synthesized nanoparticles are pure magnetite nanoparticles. In this study, the catalytic oxidation of Cooumassie Brilliant Blue R-250 (CBB R-250) dye with hydrogen peroxide in the presence of Fe3O4 magnetite nanoparticles was carried out in different conditions and analyzed. It was determined that the maximum removal of the CBB R-250 dye is observed at pH = 11 and during the period of 5 hours.

Keywords: *ecology, dye, environment, nanoparticles, catalyst, magnet.*

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1. Introduction

In the dye industry, harmful particles with different aggregate states are discharged into the environment. They remain in the environment for a long time and fall into the ecosystem being subjected to various transformations under the influence of environmental factors. This also leads to the emergence of various undesirable problems in organisms. Given the increased demand for dye substances in modern times, one can imagine how dangerous emissions in large quantities into the atmosphere could become in the future. Therefore, it is necessary to develop more advanced methods in order to neutralize solid, liquid and gaseous compounds discharged into the environment from the dye industry and to ensure the economic efficiency of this process (Wang *et al*., 2014).

It is known that synthetic dyes are widely used as colorants in the textile, food, plastic, and biomedical industries. It is estimated that about 10–14% of the total dye used in the dyeing process may be found in wastewater. These pollutants not only add color to water but they also cause extensive toxicity to aquatic and other forms of life. Coomassie Brilant Blue R-250 (CBB R-250) dye is one of the most widely utilized synthetic dyes in the textile industry recently. Various treatment methods such as reverse osmosis, ion exchange, precipitation, adsorption, ultrasonic decomposition, chemical oxidation, nano-filtration and other methods are used for the removal of RB and other dyes from water (Altikatoglu & Celebi, 2014; Jiang, 2011). However, these methods do not completely treat the wastewater from dye contamination.

Thus, advanced oxidation processes are considered one of the most effective methods for removal of persistent organic pollutants. Photocatalysis, sonochemistry and Fenton reactions are widely used to obtain reaction-capable particles. The main disadvantage of sonochemical processes to treat wastewater from dyes is that this method is expensive. Classical Fenton reaction (Fe (II)+H_2O_2) is another method of obtaining hydroxyl radicals in the solution. Although the system has great efficacy, it creates the need to use low pH (pH < 3.0) to prevent iron deposit. Also Fe^{2+}/ Fe^{3+} high quantity can not be recycled by creating a large amount of iron slurry in traditional Fenton systems. Recent studies have shown that various organic contaminants in water or soil can be oxidized by means of hydrogen peroxide in the presence of iron oxide particles. For example, studies have shown that hetite particles (-FeOOH) are able to effectively decompose n-chlorbutane by splitting H_2O_2 into hydroxyl radicals.

Recently, application of magnetic nanoparticles for purification of dye-contaminated wastewater has attracted considerable interest. This is mainly due to the fact that magnetic nanoparticles have a large particular surface area, high thermal resistance, high mechanical strength and low toxicity. These particles are also characterized by easy extraction methods, easy optimization of its size and morphology, as well as easy separation in an external magnetic field. Magnetite (Fe_3O_4) nanoparticle is considered to be one of the promising catalysts because of its low-cost, natural abundance and environmentally friendly properties. Fe_3O_4 can be used for the effective oxidation of organic dye contaminants by accelerating the degradation rate of hydrogen peroxide (Hung *et* al., 2016; Magsino *et al*., 2020).

In this study, the catalytic oxidation of Coomassie Brillant Blue R-250 (CBB R-250) dye with hydrogen peroxide in the presence of Fe_3O_4 magnetic nanoparticles was carried out and analyzed in various conditions.

2. Experimental

2.1. Materials:

Iron sulphate heptahydrate ($FeSO_4 \times 7H_2O$, 98% chemically pure, PLC 141362), ferric chloride hexahydrate ($FeCl_3 \times 6H_2O$, 98% chemically pure, PLC 141358), ammonium hydroxide (25% PLC 141129), polyethylene glycol-6000 (PEG-6000, PLC 163325), Coomassie Brilliant blue R-250 (PLC 1711949 A), hydrogen peroxide (H_2O_2).

The molecular weight of Coomassie Brilliant Blue R-250 (CBB R-250) dye used as a dye in the experiments is 825.97 g/mol and its chemical structure is shown in Fig. 1.

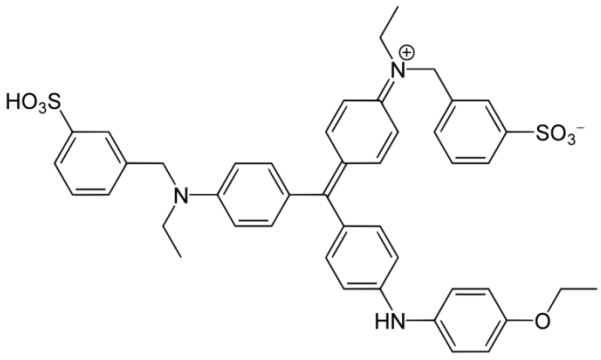

Fig.1. Chemical structure of the dye Coomassie Brilliant Blue R-250.

2.2. Synthesis of magnetite Fe_3O_4 nanoparticles

Fe_3O_4 magnetite nanoparticles were synthesized by the precipitation of Fe^{3+} and Fe^{2+} ions together with ammonium solution (NH_4OH) in the molar ratio of 3:2. Salts of $FeSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ (molar ratio Fe^{3+}:Fe^{2+}=3:2) are dissolved in 100 ml of distilled water. A 0.5% solution of cetyltrimethylammonium bromide surfactant is also prepared separately. 50 ml $FeCl_3 \times 6H_2O$, 50 ml $FeSO_4 \times 7H_2O$ solution and 20 ml setiltrimethylammonium bromide solution are added to 250 ml measuring cup, the mixture is intensively mixed in magnetic mixer at 80^0C temperature. Then 100 ml of 25% ammonium solution is quickly added to the saline solution and the reaction solution is adjusted to pH=11. The solution immediately turns black, which indicates the formation of Fe_3O_4. The mixture is stirred vigorously for another 1 hour. The resulting black precipitate is separated by the method of decantation and washed several times by distilled water. The decanter is separated from the main mass by a centrifuge and then washed again in water. To prevent agglomeration of particles, the precipitated particles are poured into a Petri dish and dried after decantation and washing, not by centrifugation (Ang & Iskandar, 2007; Bee *et* al., 1995; Ghandoor & Zidan, 2012; Eivari & Rahdar, 2013).

The use of ammonia creates the conditions for a gentle co-precipitation of oxides, which leads to the reaction forming a highly dispersed magnetite containing Fe_3O_4 or Fe_2O_3. Compared to other magnetites, FeO has better magnetite characteristics. The resulting NH4Cl ammonium salts are easily decomposed by releasing ammonia in the form of gas when heated. Cl- ions and soluble salts were removed by washing them several times by distilled water. As a result, the number of ions of different names decreases, causing coagulation of magnetite particles in the solution or preventing their peptization in the carrier fluid, as well as reducing the durability of nanoparticles obtained later.

2.3. The methodology of the study

Experiments were conducted in laboratory conditions, in the range of ΔpH=1÷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 Commasia Brillant blue R-250 is stirred in 100 ml distilled water until it has completely dissolved. Then 10 mg (0.01 gram) of catalyst Fe_3O_4, 0.5 ml of dye solution, 0.1 ml of hydrogen peroxide are added to each flask, i.e. 11 flasks (pH 1-11) 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÷24 hours.

2.4. Research methods

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. Samples were measured in the angle range of 20-70°.

UV-spectra were conducted at room temperature in the range of 200-700 nm wavelength on the Specord 250 Plus device.

The analysis of the morphology of nanoparticles was carried out in the scanning electron microscope (Jeol JSM-7600F) with 15 keV energy and 4,5 mm working distance in SEI mode. The energy-dispersion spectrum was conducted on the X-Max 50 (Oxford Instruments) device.

3. Results and discussions

In Fig. 2, the XRD diffractogram of Fe_3O_4 magnetite nanoparticles is given. As can be seen from the Fig.2., at 2θ angle 30.36^0 (220), 35.68^0 (311), 43.3^0 (400), 57.36^0 (511) and 62.95º (440) hkl indices correspond to magnetite particles with a cubic spinel crystal structure corresponding to the database DB (00-001-1111) (Ang & Iskandar, 2007; Bee *et* al., 1995; Ghandoor & Zidan, 2012; Eivari & Rahdar, 2013; Jiang *et al*., 2003).

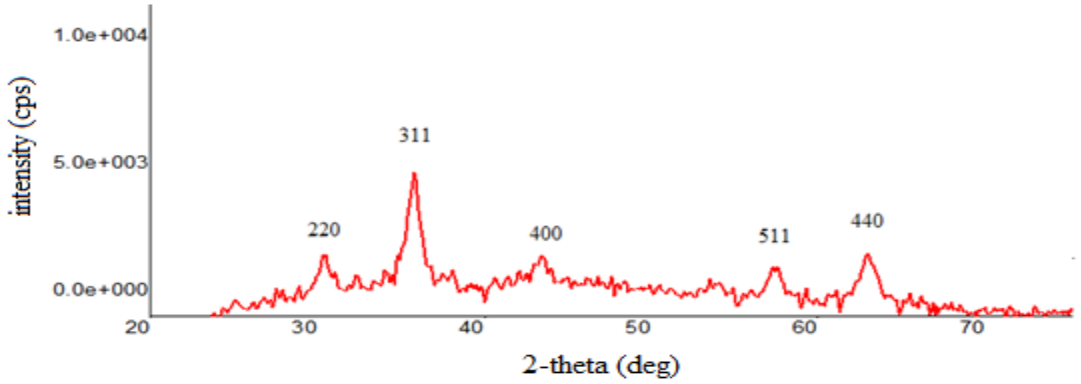

Fig. 2. XRD of Fe_3O_4 magnetite nanoparticles

Fig. 3 shows SEM image of Fe_3O_4 magnetic nanoparticles (a) and energy-dispersive spectrum (EDS) (b). SEM image of the nanoparticles is obtained at a magnification of 300.000. As can be seen from the SEM image, the size of nanoparticles synthesized and stabilized in the presence of a surface-active substance polyethylene glycol by chemical co-precipitation are 5-8 nm. It also appears from SEM analyses that formalized nanoparticles are monodisperse 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.

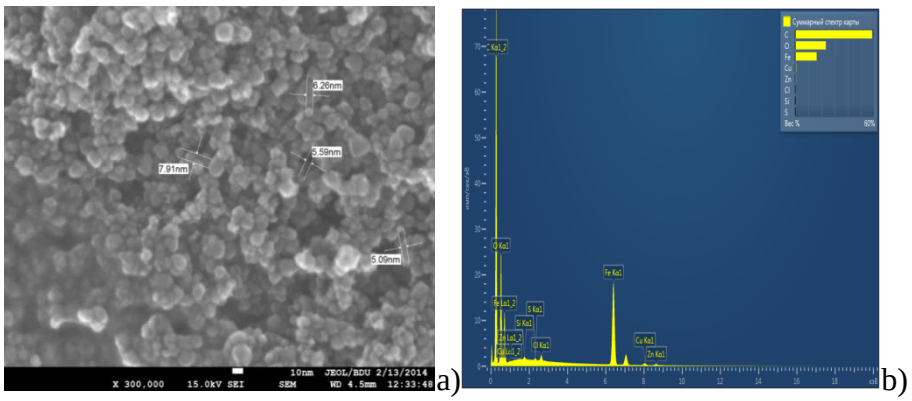

Fig. 3. SEM image of Fe_3O_4 magnetite nanoparticles (a) and energy-dispersive pectrum (EDS) (b)

Since the pH of the environment is one of the most important factors affecting the catalytic degradation of dye substances, all studies were conducted in comparative form both in the form of control and inspection experiments, the results obtained were shown in graphs.

The influence of the reaction conditions on the kinetics of the transformation of Fe_3O_4 nanoparticles of CBB R-250 dye on the catalyst surface was investigated comparatively. Fig. 4-6 shows the degradation kinetics of CBB R-250 dye in the presence of Fe_3O_4 at different value of pH.

According to the obtained spectra, depending on the reaction medium in the presence of Fe_3O_4 nanoparticles catalyst, the maximum degradation was 35-65% at pH =11 (Dalali *et al*., 2011; Bokare *et al*., 2008; Foster *et al*., 2019).

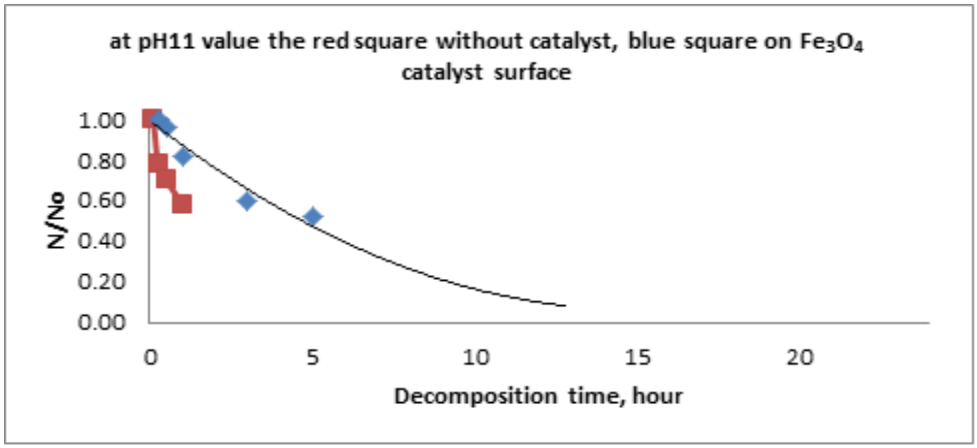

Fig. 6. Kinetics of Fe_3O_4 CBB R-250 dye degradation at pH = 11 value (the red square without catalyst, blue square on Fe_3O_4 catalyst surface)

The processes of decomposition of CBB R-250 dye on the surface of Fe_3O_4 nanocatalytic at different time intervals of the reaction medium have been comparatively studied. It was found that CBB R-250 dye undergoes maximum disintegration within 5 hours (Lianga *et al*., 2013; Santhosh *et al*., 2018; Ishaq *et al*., 2021; Joshi *et al*., 2019).

4. Conclusion

In this article, the synthesis and stabilization of Fe_3O_4 magnetite nanoparticles in the presence of surfactant of polyethylene glycol (PEG) was carried out and the optimal conditions of obtaining magnetic nanoparticles were determined. The structure of Fe_3O_4 magnetic nanoparticles was studied by X-ray roentgen diffraction analysis (XRD) and scanning-electron microscopy (SEM). During the XRD analysis, it was determined that the synthesized particles are suitable for magnetite particles with a cubic spinal crystal structure. From the SEM analyses, it was determined that the shaped Fe_3O_4 nanoparticles are monodisperse and homogeneous, and have a size of 5-8 nm. EDS analysis showed that the synthesized nanoparticles are pure magnetite nanoparticles. In this study, the catalytic oxidation of Cooumassie Brilliant Blue R-250 (CBB R-250) dye with hydrogen peroxide in the presence of Fe_3O_4 magnetite nanoparticles was carried out in different conditions and analyzed. It was determined that the maximum removal of the CBB R-250 dye is observed at pH=11 and during the period of 5 hours.

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