Removal of Malachite Green Dye from Aqueous Solution Using MnFe$_2$O$_4$/Al$_2$O$_3$ Nanophotocatalyst by UV/H$_2$O$_2$ Process

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A-R-T-I-C-L-EI-N-F-O

A-B-S-T-R-A-C-T

Background & Aims of the Study: Malachite Green (MG) is the most commonly used substance for dying cotton, food & pharmacy industries, paper, leather and silk. On inhalation it can cause difficult breathing, while on the direct contact it may cause permanent injury of the eyes of human and animals, burning sensations, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia; also it can causes cancer in livers. The aim of this study is the removal of Malachite Green (MG) dye from aqueous solutions, using MnFe$_2$O$_4$/Al$_2$O$_3$ nanophotocatalyst by UV/H$_2$O$_2$ process which was used as a low cost method.

Materials & Methods: In this research, photocatalytic decomposition of malachite green in water was done by nanocatalyst MnFe$_2$O$_4$/Al$_2$O$_3$ in discontinuous photoreactor under UV light and the injection of H$_2$O$_2$. In order to identify and analyze the provided catalyst, SEM image and XRD diffraction pattern were used. The effect of operational factors in the photocatalytic decomposition of the desired pollutant such as pH, the initial thickness of the dye, the thickness of H$_2$O$_2$ and the quantity of the catalyst were investigated.

Results: The finding showed that the right conditions for the elimination of the pollutant included pH equals 4, the initial thickness of the dye being 10 ppm, the thickness of H$_2$O$_2$ being 250ppm, the amount of catalyst being 50mg, the Correlation Coefficient being 0.998 and the dye removal was 94 percent at the end of the experiment. the reaction of Malachite green decomposition was in terms of kinetics investigated through integral method as well; also it showed the kinetic reaction is the first type and the constant speed rate is K=0.047 min^{-1}.

Conclusions: According to the results, because of the complexity of dye structure, biological system was not able to remove the dye as efficient as hybrid system of advanced oxidation processes UV/H$_2$O$_2$ with nanophotocatalyst as an efficient way to remove the Malachite green dye from water solution is obtained that increases the decomposability of organic materials. This way has proved to be able to decompose the hard compounds that are resistant to decomposition.

Background

Textile industries is known as one of the most basic industries in any country and usually the main characteristic of these industries sewage is its being colored which is because of the use of colored materials in these industries.

colored wastewaters are produced by various industries such as textile, dyeing, pharmacy, food industries, the production of cosmetics, paper and leather (1-2). Many of these industries don't respect the limits of wastewater disposal in the resources which are receiving them and actually about 15 percent of the whole dyes produced by them ends in the wastewater causing serious consequences for the ecological system of the waters which are receiving the wastewater. Most of the dyes used in these industries are the synthetic type. Synthetic dyes are generally divided into different groups include acidic, reactive, direct, basic dyes, organic and mineral materials (3-5). The contamination caused by these industries in accordance with the amount of dye which is exists in wastewaters can reduce the light penetration in recipient waters (6). The Chief environmental concern about the sewage of these industries is due to the large amount of COD and the intense dye contains. Most dyes when coming into contact with the light, water or chemical actions and reactions resist fading color.

Malachite green is the most common dye combination which is exist in wastewaters with triphenylmethane chemical structure, used to fight against external parasites, fungus and bacteria in the industry of breeding fish crustaceans widely.

Also it is used in dyeing industries to dye material such as silk whole, hemp, leather and paper. Malachite green can control the infections caused by bacteria, fungus, protozoa, trematode, nematode, cestode in aquaculture, but its very toxic and can causes cancer in mammals livers (7). In addition, the studies have shown that malachite green causes muscular glycogenesis, placental protein synthesis, severe damage to gills and decay changes in fish. Malachite green, along with its reduced form which is leucomalachite green that is extremely toxic effects in edible tissues of fish for a long time. Therefore, using too much malachite green due to its destructive

effects on the environment, threatening mammals and human health is a great significance and paying close attention to solve this problem is vital; because the current biological system cannot purify the wastewaters (8-10). Many of the chemicals exist in the wastewaters can't be killed by using the common ways of water purification, hence, they have more extreme limits when being disposed in the environment (11). So far, many chemical and physical processes have been used to purify the wastewaters that are chemical precipitation, absorption, electro coagulation, ion exchange resins and membrane coagulation and separation. One of the common problems related to these ways is that they don't remove pollutants and it is just movement of the contamination from one phase to another phase or they produce solid waste, as a result, a new and different kind of contamination appears, which requires extra purification (12). The new approach to the wastewaters is to reuse them after purification in contrast to disposing them in the environment but the expenses of chemical materials, supplying water and energy are increasing continuously. The numeral ratio of BOD_5/COD shows that how much biological organic materials are capable to being decomposed, but the ratio is usually less than 0.25-0.1 about dyes; this shows that wasters contain large amounts of organic materials which cannot be biologically decomposed. So, decomposing the organic materials that are in the wastewater of dyeing industries which are resistant to being biologically decomposed, will be possible through the ways that increase the power of decompose the organic materials biologically (13-15).

In the process of advanced oxidation, because of the cast of the ultraviolet ray on hydrogen peroxide, active hydroxyl radical is produced, which is because of having considerable oxidation power (E_0=2.8ev), can cause a break in many of the polluting molecules (14-16-17). Among advanced oxidation ways such as $O_3/UV/H_2O_2$, UV/O_3, UV/H_2O_2,

hemogenization process UV/H_2O_2, due to the fairly low expense, easy utilization and a little chemical materials has been used as a clean alternative to remove the pollutants which are resistant to biological decomposition in industrial wastewaters purification (18-21).
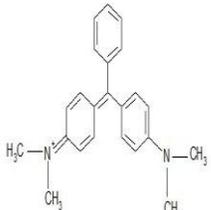
Aims of the study:

The aim of this study is to removal of malachite green dye from aqueous solution.

Materials & Methods

Materials:

In this study, in Markazi province, Iran, were assess over 5 month period (Feb-Jul 2015). In this research the malachite green ($C_{23}H_{25}ClN_2$) dye manufactured by Kimia Co, Iran, was used without purification. characteristics of malachite green are presented in table 1.

Table1) Characteristics of malachite green

Dye	Chemical Structure	Molecular formula	λmax (nm)	Mw (g/M)
Malac hite Green		$C_{23}H_{25}ClN_2$	625	364.91

All chemicals used in this study, include Manganese(II) nitrate ($Mn(NO_3)_2 \cdot 4H_2O$), Iron(III) nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), Maustic Soda (NaOH), Ethyl alcohol (C_2H_5OH), Alumina powder, Hydrogen peroxide(H_2O_2), were obtained from the Merck company, Germany.

Devices which were used in this study, included XRD (Siemens D500 model), SEM (Jeol JSM 5800 model), UV-Vi (Agilent 8453 model-USA). The pH values were measured with a Metrohm pH-meter (Model: Sartorius PT-10P model - Germany) supplied with a glass-combined electrode. A Hettich centrifuge (Model Universal320R, Germany) was used for centrifugation.

Methods:

Photoreactor:

With regards to Figure 1, a cubic wooden box was used to place different parts of the desired system. A magnetic mixer was placed at the bottom of the box in order to mix the contents inside of the reactor and Pyrex container was put on the mixer as a reactor.

The solutions contaminated by dyes are poured into this reactor, then the process of removing the pollutant by nanophotocatalyst was done.

the UV light, put above the reactor which was used to supply the ultraviolet beam need for the process was a low pressure lamp mercury kind 15 watts mode by Philips company, having 2.5cm diameter and 45 cm length.

The light spectrum intensity on the basis of the radiative wavelength of this light is shown in Figure 2. In order to sample the contents inside the reactor a sampling syringe was used.
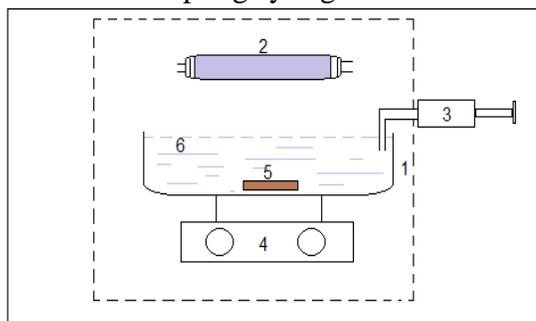
Figure 1) Schematic view of experimental setup.
1- Wooden box, 2- UV lamp, 3- Sampling syringe, 4- Magnetic stirrer, 5- Magnet, 6- The reactor contains aquatic solution of MG
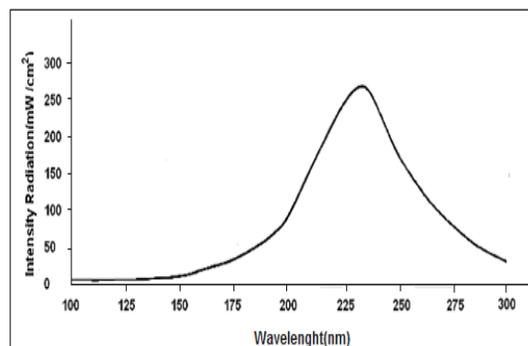
Figure 2) Spectrum intensity on the basis of the wavelength of the UV light used

Providing catalyst MnFe₂O₄

In order to provide the catalyst $MnFe_2O_4$, first, 25.65gr of $Mn(NO_3)_2.4H_2O$ and 40.40 gr of $Fe(NO_3)_3.9H_2O$ were dissolved in distilled water separately. Then the $Mn(NO_3)_2.4H_2O$ was added to $Fe(NO_3)_3.9H_2O$ slowly and it was heated so much to reach the boiling point.

After that, several thick drops of NaOH were added to the solution until to achieve 9.5 to 10.5. After the solution got cool, the sediment was separated from the solution through filtration; then it was washed, using distilled water until its pH got neutral. In order to make the sediment free from distilled water, the sediment was washed with ethanol and dried at 100°C for two hours. At the end, dried sediment was put in a furnace for 3 hours at 950°C to 1000°C and then it was sifted with the standard (100mesh).

Making MnFe₂O₄/Al₂O₃

In order to make $MnFe_2O_4/Al_2O_3$, the catalyst $MnFe_2O_4$ which was produced in the previous stage needed to be stabilized on the alumina base. For this purpose, first, the catalyst $MnFe_2O_4$ was mixed with alumina powder at the ratio of 1 to 3 (the original amount of the catalyst is three times), then the same amount of the ethanol was added to that till it had doughy form. The produced dough was kneaded enough to completely mix the base with the catalyst. The dough was dried first in the air and then in the oven. After wards, it was put inside furnace at 500°C. Theproduction, after coming out of the furnace, was ground and sieved with the standard (100 mesh).

Results

Optimizing the factors affecting the process of photocatalytic decomposition

In this study, Removal of Malachite Green dye from aqueous solution, using $MnFe_2O_4/Al_2O_3$ nanophotocatalyst by UV/H_2O_2 process. Before the beginning of the photocatalytic process, the factor which was   decomposing affect on pollutant must be identified and optimized. Therefore in every experiment, an optimized amounts of catalyst, the concentration of the pollutant, the concentration of H_2O_2 and pH were determined. As a matter of fact, 1000 ml of the original dye, containing desired pH, was poured into the reactor and a certain amount of the desired catalyst was added to them; then, while mixing the solution inside the reactor with the magnetic mixer, hydrogen peroxide was added. The UV light turned on and a sampling syringe was used for seven times in each sample in which 5ml was taken as the sample. The samples were investigated by spectrophotometer device and the concentration of the dyes in the samples was determined through calibration equation. Also the effective factors on photocatalytic decomposition were investigated. The information related to the optimizational operation of the effective factors have been shown in table 2. As seen in this table, four parameters affecting the pollutant decomposition were investigated. In every experiment, three parameters were stable and the other one was variable. The effect of the variable parameter on removing the pollutant can be investigated in this way.

Table 2) The amounts related to the parameters

pH	Concentration H_2O_2 (ppm)	Amount of catalyst (mg)	Initial concentration of dye (ppm)
4,6,7,9,10	50	50	10
4	50,100,150, 200 ,250	50	10
4	250	10,20,50,100, 150,200, 250	10
4	250	50	10,20,30,40,50

which affect the phtocatalystic decomposition of MG in order to optimization of parameters

The UV-Vis spectrums of the pollutant of Malachite Green

In order to investigate the possibility of the photocatalytic decomposability of malachite green, as a result of the cast of ultraviolet beam in the reactor, after five minutes periods of casting, the polluting solutions to be

decomposed were taken as samples and their absorptive spectrum were logged. Four UV-Vis spectrum related to the pollutant of malachite green, before and after the costing are shown in figure 3. The strongest spectrum was related to the before casting and the other three spectrums are after 5, 10, 15 minutes casting respectively which has caused more decomposition of the pollutant, as a result, the severity of the spectrum reduced. Actually, due to the cast of ultraviolet beam on the reactor, the molecular structure of the dye molecules were broken and caused to reduction in the severity of the absorption.
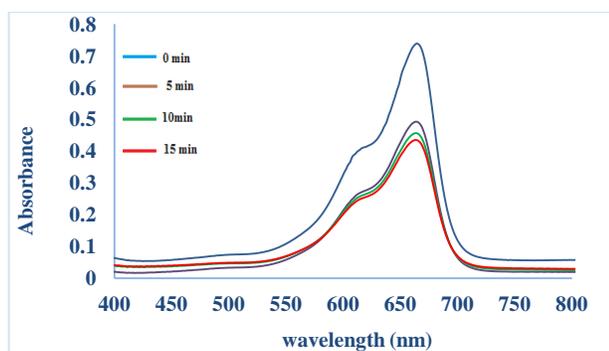

Figure 3) The UV-Vis spectrums related to MG dye before and after casting UV beam

The analysis of the stabilized catalyst

Three XRD patterns related to the lone catalyst ($MnFe_2O_4$), the lone alumina base (Al_2O_3) and the stabilized catalyst on the alumina base are shown in figure 4. By investigation of these three patterns and comparing them, it can be clearly understood that the placement of the catalyst on the alumina base has been done very well in a way that after the placement of the catalyst $MnFe_2O_4$ on the base Al_2O_3 no change happened to the structure of the catalyst or the base and this claim is clearly provable and under standable because of the XRD pattern related to $MnFe_2O_4/Al_2O_3$ and the peaks emerged in it which is a mixture of the catalyst and basic peaks.
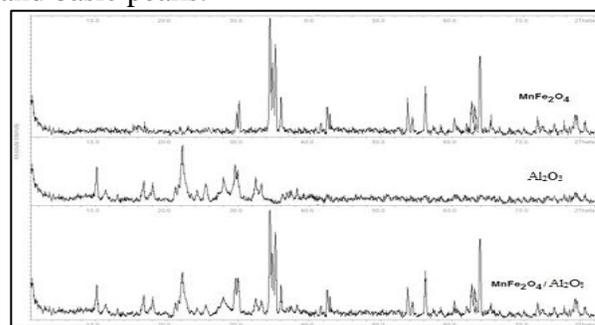

Figure 4) The XRD patterns of the provided catalyst

The SEM images related to the lone catalyst $MnFe_2O_4$, lone catalyst Al_2O_3 and the catalyst placed on the base $MnFe_2O_4/ Al_2O_3$ are shown in figure 5.
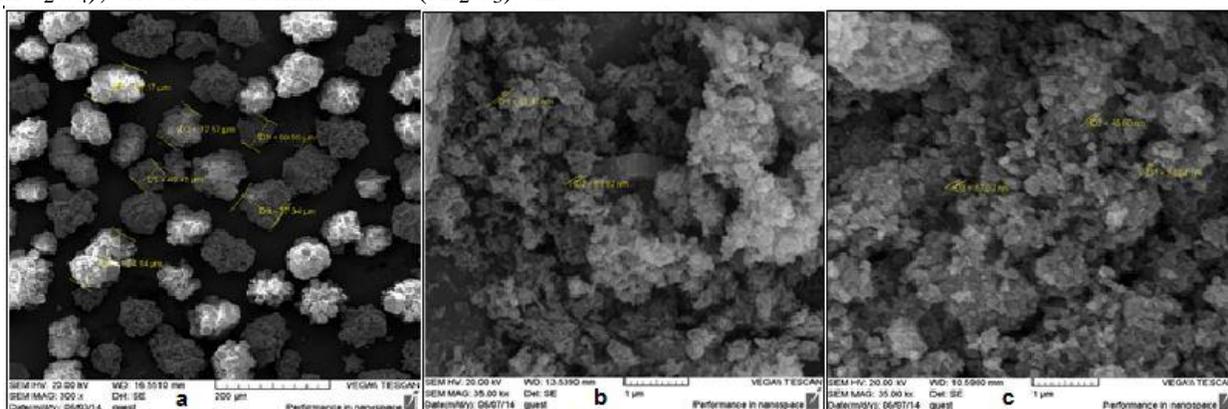

Figure 5) the SEM images related to: Al_2O_3 (a) , $MnFe_2O_4$ (b) , $MnFe_2O_4/ Al_2O_3$ (c)

pH effect

with regards to table1,for investigation of the pH effect on photocatalytic decomposition of the malachite green dye, the other three effective parameters were kept stable and just pH parameter was variable in a way that the experiments were done after 40 minutes in solutions, having different pH (4,6,7,8,9 and

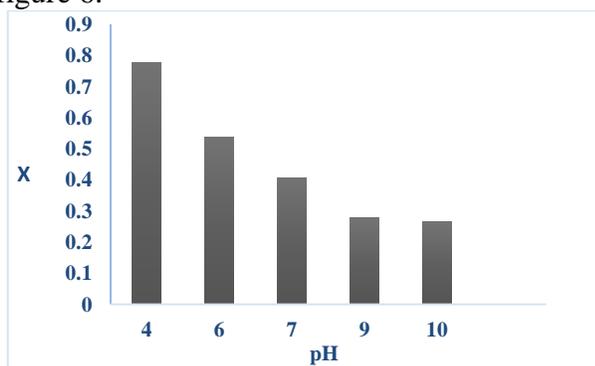10). The results of the pH effect are shown in figure 6.

Figure 6) Effect of pH on the photocatalytic degradation of MG.
T: 293 K, Time: 40 min, Amount of catalyst: 50 mg, Initial concentration of dye: 10 ppm, Concentration of H_2O_2: 250 ppm.

The effect of the initial amount of the catalyst

The diagram which is related to the effect of the amount of the catalyst used on decomposition process is shown In figure 7.
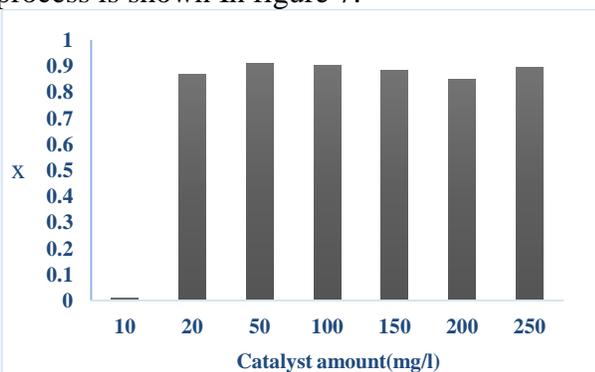

Figure 7) The effect of catalyst on the photocatalytic degradation of MG.
T: 293 K, Time: 40 min, Initial concentration of dye: 10 ppm, pH: 4, Concentration of H_2O_2: 250 ppm.

The effect of the initial concentration of the pollutant

In this section, the initial concentration of the pollutant was variable and the other parameters were stable. Results can be observed in Figure 8.
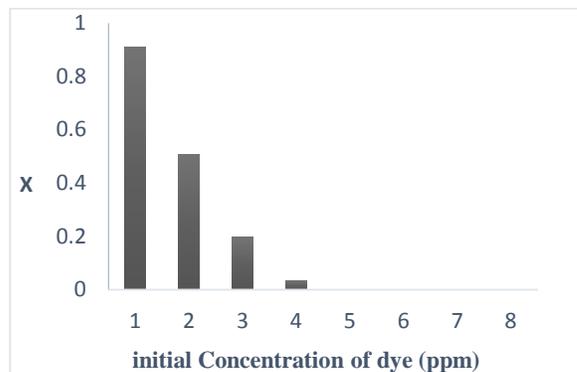

Figure 8) Effect of initial concentration of dye on the photocatalytic degradation of MG.
T: 293 K, Time: 40 min, amount of catalyst: 50 mg, pH: 4, Concentration of H_2O_2: 250 ppm.

H_2O_2 concentration effect

The results of the effect of the concentration of H_2O_2 on the decomposition process of the pollutant is shown in figure 9.
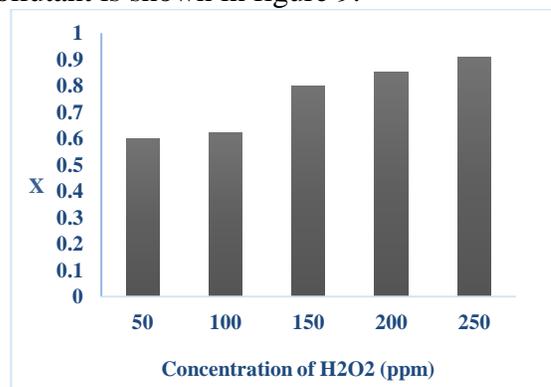

Figure 9) Theeffect of H_2O_2 concentration on the photocatalytic degradation of MG.
**T: 293 K, Time: 40 min, Amount of catalyst: 50 mg, pH: 4, Initial concentration of dye: 10 ppm**

Kinetic reaction of photocatalytic decomposition of malachite green

One of the ways to get the speed equation of a chemical reaction is the integral way. Based on this way, first the reaction degree is guessed and then draw a diagram which is related to the reaction degree; the correctness of the guess is investigated. If the diagram based on the guess degree is linear it means that the guess is correct and the reaction degree is determined. After the determination of the reaction degree, calculations are performed for the stable determination of the speed and at the end, the

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speed equation is obtained. In this study, based on the findings of previous researches which are about the photocatalytic processes, the kinetic reaction of the photocatalytic decomposition of malachite green was assumed to be the first degree.

So, assuming the chemical reaction:

$$A \longrightarrow B$$
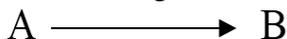
the speed relationship is shown at below(assumed to be the first degree):

$$-r_A = \frac{-dC_A}{dt} = kC_A^1$$

Where in:

r_A = Rate

k = Rate constant

C_A = the final concentration of A

C_{A0} = the initial concentration of A

Through calculating the integral of speed relationship:

$$\int_{C_{A0}}^{C_A} \frac{-dC_A}{C_A^1} = k \int_0^t dt$$

It well be obtained that:
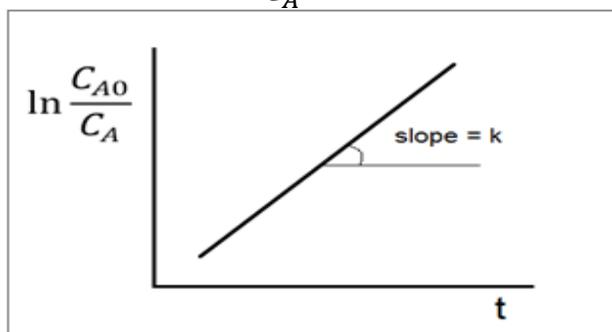
$$\ln \frac{C_{A0}}{C_A} = kt$$

Figure 10) Speed diagram for first degree reactions

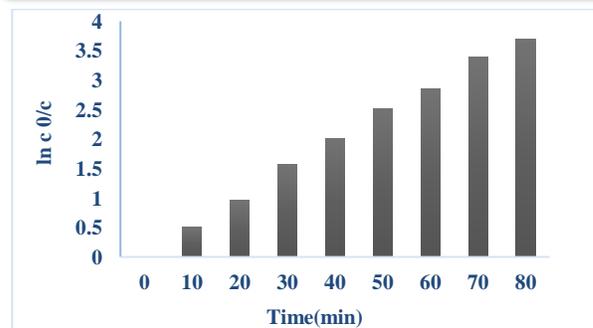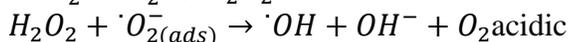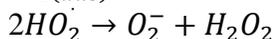The diagram ln $C_0/$ C for the decomposition of the malachite green was drawn as shown in Figure 10.
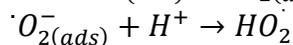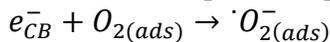

Figure 11) The diagram ln C_0/C on the basic of the time related to the reaction of MG decomposition T: 293 K, Time: 40 min, Amount of catalyst: 50 mg, pH: 4, Initial concentration of dye: 10 ppm.

Discussion

Oxidation processes are not affordable due to the high consumption of materials and energy to achieve the complete oxidation of organic compounds. Biological processes could not remove the hard biodegradable organic pollutants alone and their usage is not justified because of their low efficiency. In a study on the dyestuff Malachite green by Xeo Dang Li et al (2010) and Yan et al (2010), the significant results were not obtained (22-23). In the present study, the combination of two processes UV/H_2O_2 and nanophotocatalyst $MnFe_2O_4/Al_2O_3$ was used and the results showed that the proposed method is an effective one for the removal of dyestuff in the water and wastewater. The dyestuff removal is affected by the presence of H_2O_2, pH, initial concentration of pollutant and the catalyst. According to Figure 5, the size of $MnFe_2O_4$ particles are too big to penetrate into the holes and become stable there. This is because of the size of the particles which are bigger than the size of the holes of the alumina. Also the SEM images make it clear that the morphology of the alumina surface has changed after the placement of $MnFe_2O_4$. These findings prove that the changes in the surface morphology of the catalyst, the surface of the alumina and its holes openings are filled by the catalyst $MnFe_2O_4$.

Considering the results, it can be concluded that in acidic environments, the rate of transformation (the rate of the pollutant decomposition MG) is increased which can be related to doing the reactions below in acidic environments (Figure 6).

Therefore the optimized pH is considered 4.

$$e_{CB}^- + O_{2(ads)} \rightarrow \dot{O}_{2(ads)}^-$$
$$\dot{O}_{2(ads)}^- + H^+ \rightarrow H\dot{O}_2$$
$$2H\dot{O}_2 \rightarrow O_2^- + H_2O_2$$
$$H_2O_2 + \dot{O}_{2(ads)}^- \rightarrow \dot{O}H + OH^- + O_2 \text{ acidic}$$

increases the reaction rate and thus increases the efficiency of dye removal. A hydroxyl radical oxidant is active and dominant in acidic conditions, but under alkaline conditions because hydrogen peroxide is converted to HO_2 ($H2O2+OH\bullet\leftrightarrow HO_2 \bullet + H_2O$) which reacts with molecules of H_2O_2 and produce water and oxygen instead of the active oxide it should be stated that the dye removal efficiency is reduced in alkaline conditions . Figure 7 shows that, with increasing the quantity of the catalyst from 10 to 20 mg, increases the transformation rate tremendously, but increasing the quantity of the catalyst (up to 250 mg), reduces the transformation rate. Hence, the optimized quantity for the catalyst is 50 mg.

Figure 8 shows that, with decreasing in the initial concentration of the pollutant, increases the transformation rate; because increasing the concentration of dye causes the absorption of UV light by dye molecules increases, thus, the whole dye molecules in the solution don't receive enough photon containing an appropriate energy. Therefore, the transformation rate decreases by increasing the concentration of the dye. So the initial optimized concentration of the pollutant is considered 10 ppm.

Considering the diagram figure 10, it is understood that by increasing the concentration of H_2O_2, the transformation rate accelerates. The reason is that by increasing the amount of H_2O_2, producing of the hydroxyl radical which is a powerful oxidizer increases, hence, the decomposition rate of the pollutant increases as

well. So, the optimized concentration for H_2O_2 was considered 250 ppm. by reducing the amount of H_2O_2 than the optimum value, constant of speed and removal efficiency have been reduced.The reason of this phenomenon can be stated as follows: At lower concentration, Hydrogen peroxide removes the hydroxyl radical and there is a competition between the hydrogen peroxide and the dyestuff; so the removal efficiency has been decreased. It is noteworthy that H_2O_2 could not remove the dye alone because H_2O_2 could not produce hydroxyl radicals lonely; And considering to Figure 8, with increasing amounts of pollutants than optimal, the dye removal efficiency has been reduced. The reason for this phenomenon can be attributed to the penetration of UV. As stated, H_2O_2 could not remove the dyestuff alone.

With regards to figure 10, if the diagram ln C_{A0}/C_A is drawn based on the time, the slope of the diagram will be equal with K. If, for the desired diagram, this diagram ends in a direct line it means that the reaction degree is of the first degree. The diagram ln C_0/C for the decomposition of malachite green was drawn as shown in figure 10. Considering the obtained diagram itis determined that the liner diagram and thus the assumption are both correct and the reaction degree is 1.

The slope of the diagram which is 0.047 equals with K or the very stable speed (K=0.047 min^{-1}) which can be understood from the direct line equation shown in figure 11. So, speed relationship for malachite green dye decomposition is:

$$-r_A = \frac{-dC_A}{dt} = 0.047 \, C_A^1$$

Conclusion

Malachite Green (MG) is the most commonly used substance for dying cotton, food & pharmacy industries, paper, leather and silk. On inhalation, it can cause difficult breathing,

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while on the direct contact, it may cause permanent injury of the eyes of human and animals, burning sensations, nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia; also can causes cancer in mammals livers. In this research the photocatalytic decomposition of malachite green as a polluting dye in water solution was investigated by nanophotocatalyst $MnFe_2O_4$ which was stabilized on alumina base ($MnFe_2O_4/Al_2O_3$). First, the effective factors were optimized. The Results showed that the optimization conditions to decompose the pollutant are included pH=4, the amount of the catalyst being 50 mg, the correlation coefficient being 0.998 and the dye removal was 94 percent at the end of the experiment. the initial concentration (of the pollutant) being 10 ppm and the concentration of H_2O_2 being 250 ppm.

At the end, the kinetics of the desired reaction were investigated by an integral way. The results showed that the desired reaction of the first degree with the stable speed was K=$0.047 min^{-1}$.

On the whole, the findings revealed that the utilized way in producing the catalyst $MnFe_2O_4/Al_2O_3$ was an efficient way to decompose polluting dyes which are malachite green types.

Footnotes

Conflict of Interest:
The authors declared no conflict of interest.

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