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Efficient Fenton like degradation of Methylene blue in aqueous solution by using Fe_3O_4 nanoparticles as catalyst

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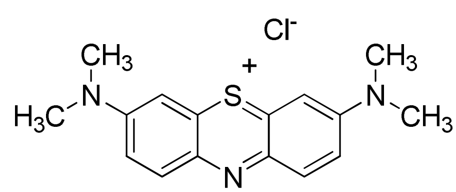
ABSTRACT

Fe_3O_4 nanoparticles were prepared hydrothermally and characterized by X-Ray diffraction spectroscopy (XRD), and scanning electron microscopy (SEM). It was found that these nanoparticles can act as an efficient catalyst in the degradation of Methylene blue dye in aqueous solution in a Fenton like system in presence of 30% perhydrol. Uv-Vis spectroscopy was used to determine the concentration of dye during optimization of different affecting factors such as pH, catalyst loading, and amount of the oxidant. Based on these results, 0.6 g/L of the catalyst and 0.32 mmol/L of the oxidant at pH=4.8 were selected as the optimum conditions and this resulted in a considerable degradation in less than 20 minutes. The catalyst was also found to be recyclable with no considerable decrease in its efficiency in successive runs.

Keywords: Fenton, Degradation, Methylene Blue, Fe_3O_4 nanoparticles

1. INTRODUCTION

Wastewater of many industries such as textile, food, printing etc, contains various ingredients especially dye molecules such as Methylene blue, and has become a major concern for environment and ecosystem due to high toxicity and resistance against biodegradation. Methylene blue (Scheme 1) is one of thiazole dyes which have been used for a long time in textile, food, paper, plastic and leather industries.



Scheme 1. Structure of Methylene blue

Advanced oxidation technologies have emerged as a versatile route for removal of pollutants in wastewater [1,2]. Former methods for removal of dye molecules from wastewater include absorption, reverse osmosis, ion exchange, ultrasonication and nanaofiltration. Fenton processes have attracted attention due to their high impact in degradation of wastewater contaminants, since it breaks down the organic molecules to simpler inorganic fragments. Traditional Fenton processes, however, have dis-advantages such as need for pretreatment of the samples, and recyclability [3]. In a heterogenous Fenton like process, on the other hand, a solid catalyst performs the major role in formation of highly active hydroxyl radicals which are key intermediates in the process and have a high oxidation potential to attack most of the organic molecules with no selectivity [4-6]. While homogeneous Fenton processes would result in pollution and raise the costs, heterogenization with a solid recoverable catalyst would be an interesting alternative [7,8], but due to heterogeneity, less activity is a major concern. This could be overcome by changing the size to nano which offers higher surface areas.

2. EXPERIMENTAL

2.1. Materials

Fe_3O_4 nanoparticles were prepared with a slight modification to a previously reported method [9] by using a five-necked reactor as follows: A stock solution of $FeCl_3.6H_2O$ (10.4 g), $FeCl_2.4H_2O$ (4.0 g) and HCl (1.7 mL, 12 mol L^{-1}) in 50 mL of deionized water which was degassed with nitrogen gas for 20 min before use, added dropwise (by using a dropping funnel connected to one neck) into 500 mL of degassed NaOH solution (1.5 molL^{-1}) at 80 °C during 30 min. Central neck was connected to a home-made condenser allowing circulation of cold water to prevent vaporization of solution. A glassware stirrer rotating at 1000 rpm, was passed through the condenser and central neck. Third neck was used to sparge nitrogen gas during the synthesis. The other necks were used for temperature monitoring and sampling. After completion, the obtained dark brown Fe_3O_4 nanoparticles were separated from the reaction medium by a magnetic field (1.4 T strength), and washed with 500 mL deionized water four times.

2.2 Typical procedure for degradation of Methylene blue in presence of Fe_3O_4 nanoparticles

To a solution of Methylene blue in distilled water (100 mL, 10 mg/L) at pH of 4.8, 60 mg of Fe_3O_4 nanoparticles were added and the suspension stirred by using a mechanical stirrer at 1000 rpm. 2.0 mL of commercial hydrogen peroxide 30% solution (Perhydrole 30%) was then injected into the reaction mixture. The reaction mixture was sampled at various time intervals and the absorbance of the clear solution (obtained by applying an external magnetic field) was measured at 664 nm.

2.3 Instrumentation

Uv-vis spectra were recorded on a Perkin Elmer LAMBDA 25 recording spectrophotometer. X-ray powder diffraction (XRD) measurements were performed on a Philips diffractometer with mono chromatized Cu kα radiation at 40 kV and 20 mA (Ni filter, $2\theta=10°$ to $70°$, 0.05° step size, 1 s count time). Morphology of the synthesized samples was characterized with a scanning electron microscope (SEM) from Philips Company (XL30 ESEM).by the dissolution of metal salts in deionized water.

3. RESULTS AND DISCUSSION

SEM image of Fe_3O_4 nanoparticles (Figure 1) showed agglomeration of many ultrafine particles of about 40-50 nm.

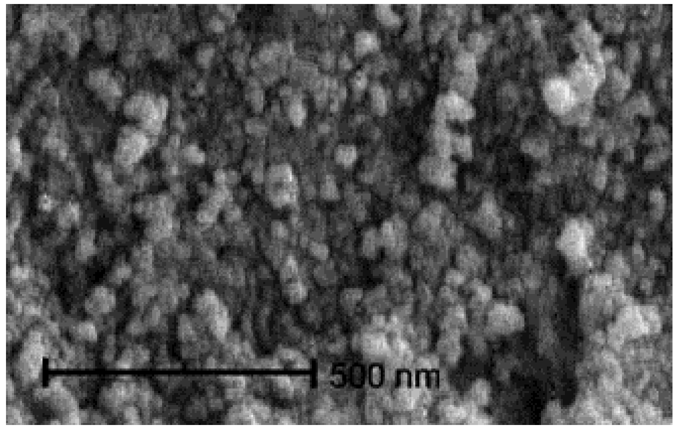


Figure 1. SEM image of the Fe_3O_4 nanoparticles

X-ray diffraction pattern (XRD) of the nanoparticles (Figure 2), showed characteristic diffraction peaks of the cubic crystal system of magnetite and matched well with the library patterns (JCPDS No. 19-629).

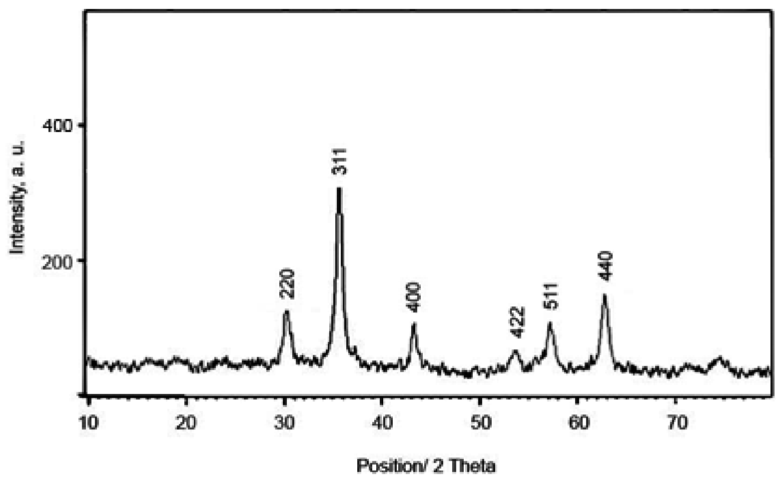


Figure 2. XRD pattern of the Fe_3O_4 nanoparticles

After characterization, application of the obtained nanoparticles was evaluated in the aqueous phase degradation of Methylene blue dye molecules (10 mg/L) by using commercial 30% perhydrol solution. In order to find the optimum conditions, various parameters were examined and Uv-Vis spectrometry was used to monitor the changes. It was found that pH of the solution had an impact on the efficiency of degradation and the best results were obtained at the range of $3<pH<5$ (Figure 3).

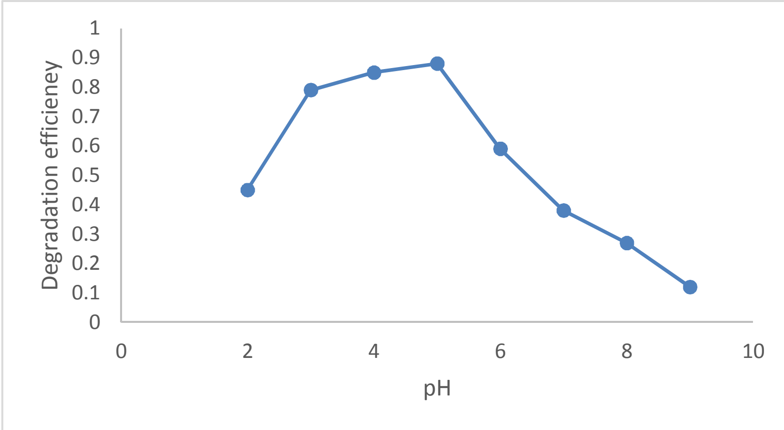


Figure 3. Effect of pH on the degradation efficiency of MB

Examining the amount of the oxidant showed that an increase in the hydrogen peroxide from 0.0 to 0.32 mmol/L results in a sharp increase of degradation and afterward no considerable promotion was observed (Figure 4).

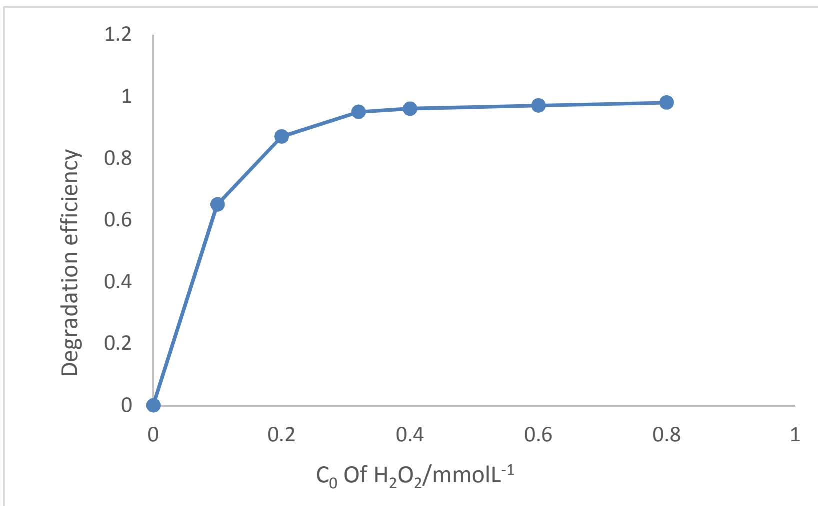


Figure 4. Effect of the amount of the oxidant on degradation of Methylene blue

It was also found that trend of degradation depends on the amount of Fe_3O_4 nanoparticles and rising of the catalyst loading to 0.6 g/L improves the degradation, while afterward the trend of degradation seems to be independent of the catalyst loading. This is shown in Figure 5.

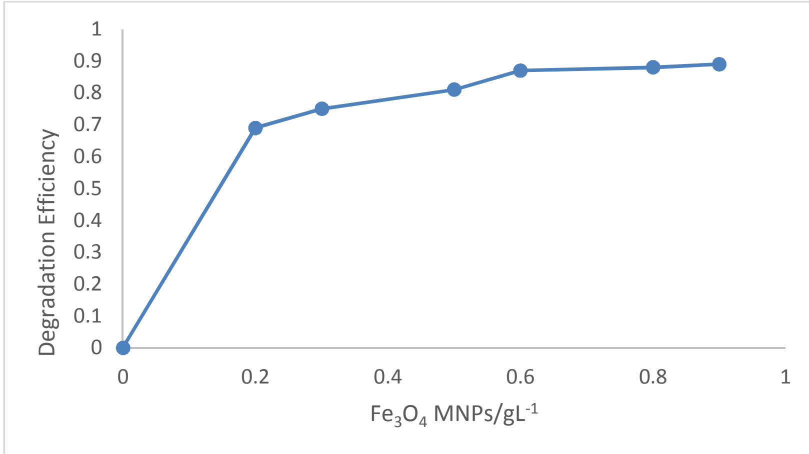


Figure 5. Effect of the catalyst loading on degradation of Methylene blue

Control experiments also showed that nearly no degradation was occurred when only hydrogen peroxide or Fe_3O_4 nanoparticles were present. Based on these results, 0.6 g/L of the catalyst and 0.32 mmol/L of the oxidant at pH=4.8 were selected as the optimum conditions and this resulted in a considerable degradation in less than 20 minutes (Figure 6).

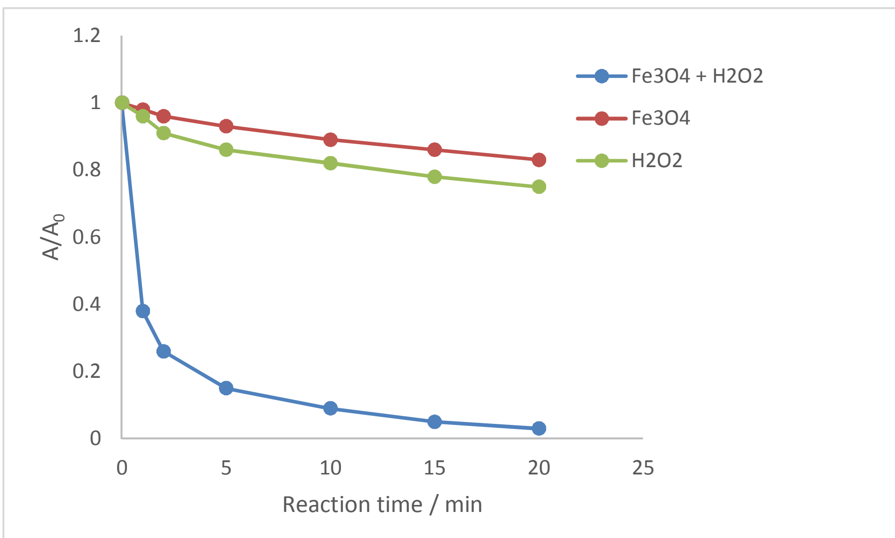


Figure 6. Trend of degradation of Methylene blue in presence of the catalyst, Oxidant and optimum conditions

Corresponding changes in the absorbance spectrum of Methylene blue solution in the visible range is also illustrated in Figure 7. One can note that the maxima at 667 nm preserved its position during continuous decrease of intensity.

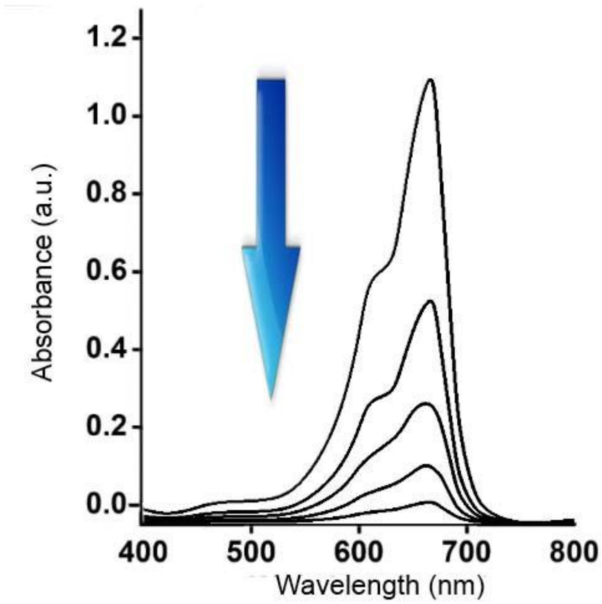


Figure 7. Degradation trend of Methylene blue in the visible range of spectrum

One of the major concerns in the wastewater treatment technologies is minimization of the waste. Our study on the recyclability of the catalyst showed that Fe_3O_4 nanoparticles could be recycled easily by using an external magnet and the recycled catalyst preserved its activity for successive runs. Figure 8 shows that after 5 runs, no considerable decrease in the efficiency of the catalyst was occurred.

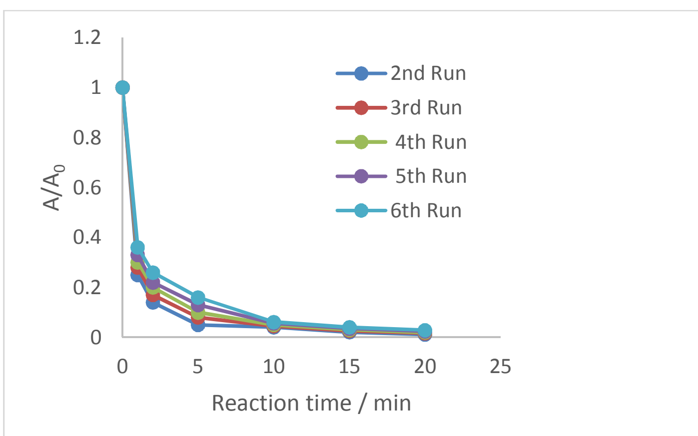


Figure 8. Degradation of Methylene blue in presence of the recycled catalyst during 5 cycles

Mechanistically, the following sequences may rationalize the overall process, with the final products being water and oxygen which are definitely clean.

I. $Fe^{III} + H_2O_2 \leftrightarrow Fe^{III} \ldots H_2O_2 \rightarrow Fe^{II} + {}^{\cdot}O_2H$

II. $Fe^{II} + H_2O_2 \leftrightarrow Fe^{II} \ldots H_2O_2 \rightarrow OH^{-} + Fe^{III} + {}^{\cdot}OH$

III. $MB + {}^{\cdot}OH \rightarrow CO_2 + H_2O$

IV. $MB + {}^{\cdot}O_2H \rightarrow CO_2 + H_2O$

In order to approve the above mechanism, it was assumed that if the reaction involved radical species, then a radical scavenger would be able to quench the reaction. In the presence of 2-propanol as a well-known radical scavenger, indeed, the degradation process interrupted, which confirms the involvement of radical species.

4. CONCLUSION

Our study showed that Fe_3O_4 nanoparticles can be used as an efficient Fenton like catalyst in degradation of Methylene blue dye as a model system. The catalyst was found to be recyclable with no considerable loss in activity. Further manipulation of this protocol is currently under way in our laboratory.

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