Fe_3O_4/Tea waste nanocomposite as heterogeneous photo-Fenton reagent for the degradation of Methyl Orange

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Abstract
Magnetite nanoparticles (Fe_3O_4) loaded on tea waste (TW) as a low-cost heterogeneous catalyst (MTW) for photo-Fenton reaction was successfully synthesized by co-precipitation method. The photocatalytic degradation of methyl orange (MO) as an azo dye in the presence of MTW was investigated under UVC irradiation. The effect of several factors such as initial pH of the dye solution, H_2O_2 concentration, MTW dosage, and initial concentration of MO were studied on the degradation efficiency. The obtained results indicated that, the degradation efficiency increased by decreasing the initial pH of the MO solution and the initial concentration of MO. The optimum H_2O_2 concentration was achieved 50 mg/L with heterogeneous photo-Fenton process in maximum of 50 min reaction time. The Maximum 100% degradation of MO (10 mg/ L) was achieved in MTW/UVC/H_2O_2 process after 220 min irradiation , in the presence of MTW (1 g/L), and H_2O_2 (0.5 mM).

Keywords: Photo-Fenton, Tea waste, Fe_3O_4, Methyl orange.

1. Introduction
Water pollution is one of the major problems of the world. Textile processing is one of the most important industries in the world and it uses a variety of chemicals such as different types of dyes. The wastewater of this industry is usually extremely colored, and the discharge of it into natural water bodies can cause damage to human and other organisms' health [1, 2]. Azo dyes like methyl orange (MO) are the largest group of the synthetic dyes which has at least one azo functional group (-N=N-) in their structure [3]. Among the different methods which are available for wastewaters treatment, advanced oxidation processes (AOPs) are more effective because they are capable of oxidizing a large number of organic pollutants [4]. One of the most important parts of AOPs is Photo-Fenton reaction based on ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) under artificial or solar irradiation that causes the generation of highly reactive radicals (especially hydroxyl radicals ($^{\bullet}OH$)) which can non-selectively oxidize a wide range of organic compounds [5]. The iron sludge formed during the process is the major drawback of the homogeneous photo-Fenton reaction. The best way to overcome the disadvantage is using heterogeneous catalysts which have long-term stability in addition to good photo-catalytic performance [6]. In recent years, supporting catalysts with natural biomaterials such as hydroxyapatite, eggshell, clamshell has been developed since they are low cost and environmentally friendly materials [7].

In this study, tea waste-based Fe_3O_4 nanocomposite (MTW) was synthesized by co-precipitation method and applied as heterogeneous catalyst for the degradation of MO during the photo-Fenton reaction under UVC irradiation. The effect of different factors, such as initial concentration of MO, H_2O_2 concentration in the solution, pH of the solution, and MTW catalyst dosage were studied.

2. Experimental

2.1. Materials

Tea waste (TW) was provided from a tea factory in Guilan province, Iran. The analytical grade chemicals used in this study were $FeSO_4.7H_2O$, $FeCl_3.6H_2O$, ammonia solution (25%), hydrochloric acid (37%), sodium hydroxide, hydrogen peroxide (20%), and Methyl orange ($C_{14}H_{14}N_3NaO_3S$) which all were supplied by Merck, Germany. All chemicals were used without further purification.

2.2. Synthesis of Fe_3O_4 /TW (MTW)

The collected TW was washed several times with distilled water till the wash water has no color and dried in an air oven at 60℃ for 24 h. The dried TW then was crushed into a standard mesh size 35–140 (105–500 μm) and stored in glass bottles for use. To obtain Fe_3O_4/TW nanocomposite (MTW) by co-precipitation method, 2.1 g $FeSO_4.7H_2O$ and 3.2 g $FeCl_3.6H_2O$ (Fe^{3+}/Fe^{2+} molar ratio was 2:1) were dissolved into 80 mL distilled water under inert condition with vigorous stirring. While the temperature of the solution reached to 80℃, 10 mL of ammonia solution (25%) was added. To ensure the good growth of nanoparticles 10 g of the stored TW was added into the solution and the reaction was carried out for 30 min under stirring at 80℃.

2.3. MO degradation Procedures

Each reaction was carried out in the beaker filled with 50 mL MO aqueous solution with a desired initial concentration. The pH of the solution was set by adding the diluted NaOH or HCl solutions followed by the addition of the certain dosage of MTW. At the beginning, the mixture was stirred for 15 min in dark for adsorption/desorption equilibrium. Then, the photo-Fenton reaction was started when predetermined amount of H_2O_2 added to the solution and the UVC light (Philips 15 W λ_{max} =254 nm) turned on. The solution was sampled every 20 min, centrifuged and analyzed by using of a UV-visible spectrophotometer (Cary 50 bio UV-visible). The degradation efficiency of MO was determined as follows:

$$R(\%) = \frac{C_0 - C_t}{C_0} \times 100 \qquad (1)$$

Where C_0 (mg/L) and C_t (mg/L) represent the initial concentration and the time-dependent concentration of the dye solution, respectively.

3. Results and discussion

3.1. Study of degradation efficiency in different conditions

We carried out decolourisation of MO in different conditions such as H_2O_2/MTW/UVC (photo-Fenton process), H_2O_2/MTW/dark (Fenton process), H_2O_2/dark, H_2O_2/UVC, MTW/UVC and the direct photolysis of the dye solution (UVC) to compare the degradation efficiency of MO.

Fig. 1 shows the comparison of the degradation efficiency among the above processes. According to the obtained results, 1.37% degradation of MO in H_2O_2/dark process and 80.53% in the presence of H_2O_2/UVC was achieved at 220 min. The reason of this phenomenon can be explained by the following reaction [8]:

$$H_2O_2 + UVC \rightarrow 2HO^{\bullet} \quad (2)$$

The dye degradation% for H_2O_2/MTW/dark (Fenton process) and H_2O_2/MTW/UVC (photo-Fenton process) were obtained 34.97% and 99.98%, respectively within 220 min. The $HO^{\bullet}$ radicals in Fenton process were generated as below [9]:

$$Fe^{2+} \text{ on the surface of MTW} + H_2O_2 \rightarrow Fe^{3+} \text{ on the surface of MTW} + HO^{\bullet} + OH^{-} \quad (3)$$

In photo-Fenton process in addition to the above reactions, hydroxyl radical can be produced during the following reaction [9]:

$$Fe^{3+} \text{ on the surface of MTW} + H_2O + UVC \rightarrow {}^{\bullet}OH + Fe^{2+} \text{ on the surface of MTW} + H^{+} \quad (4)$$

As an important result, it can be claimed that the more effective process to degradation of MO is the photo-Fenton reaction in the presence of H_2O_2/MTW/UVC. In other words, MTW due to containing sufficient amounts of iron ions exhibited a good photocatalitic performance in the presence of H_2O_2 under UVC irradiation.

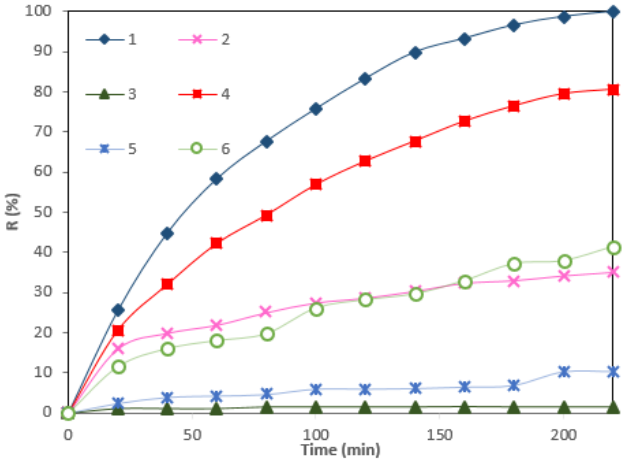

Fig. 1. Degradation efficiency comparison among different processes. (1) H_2O_2/MTW/UVC (photo-Fenton process), (2) H_2O_2/MTW/dark (Fenton process), (3) H_2O_2/dark, (4) H_2O_2/UVC, (5) UVC, (6) MTW/UVC. [MO] = 10 mg/l; [H_2O_2] = 0.5 mM; MTW = 1 g/l; pH = 3.

3.2. Effects of pH

The pH of the dye solution is the most important factor in photo-Fenton process because of controlling the number of hydroxyl radicals in addition to the concentration of the availabe ferrous ion (Fe^{2+}) on the solid surface of heterogeneous photo-Fenton process. According to Eq. (3), the generation of $HO^{\bullet}$ radicals is effected by the pH of the solution. The $HO^{\bullet}$ free radicals can be effectively produced especially under acidic condition. The effect of pH on the degradation of MO by photo-Fenton process is shown in Fig. 2. The experiments were carried

out at three different initial pH of 3, 5.5, and 7. The results indicated that by increasing of pH from 3 to 7 the degradation% was decreased from 95.01% to 59.15% at 220 min.This is attributed to the fact that, there are more H^+ at pH=3 condition and these ions can cause the production of more $HO^\bullet$ radicals (as a major agent of degradation at photocatalytic reactions) to degrade MO. On the other hand, in higher pH values H_2O_2 is dissociated to form HO_2^- as shown below [10]:

$$H_2O_2 \rightarrow HO_2^- + H^+ \quad (5)$$

Excess amounts of H_2O_2 which are not dissociated, react with HO_2^- and instead of $HO^\bullet$ free radicals, lead to water and oxygen as the following reaction [10]:

$$H_2O_2 + HO_2^- \rightarrow H_2O + O_2 + OH^- \quad (6)$$

Therefore, by decreasing the number of $HO^\bullet$ radicals the degradation efficiency will be decreased.

3.3. Effects of H_2O_2 concentration

H_2O_2 is normally used as an effective oxidant in AOPs. Fig.3 shows the effluent of different initial H_2O_2 concentration on the degradation efficiency of MO during the photo-Fenton process. It was observed that by increasing H_2O_2 concentration from 0.5 mM to 50 mM, the degradation efficiency was increased from 62.58% to 99.98%, respectively within 80 min. Because higher concentration of H_2O_2 can produce more $^\bullet OH$ radicals. However, by further increase of H_2O_2 dosage up to 100 mM, the degradation performance was reduced due to scavenging $^\bullet OH$ radicals by excess amounts of H_2O_2 according to following reactions [8]:

$$H_2O_2 + {}^\bullet OH \rightarrow H_2O + HO_2^\bullet \quad (7)$$

$$HO_2^\bullet + {}^\bullet OH \rightarrow H_2O + O_2 \quad (8)$$

Other experiments would be carried out in the presence of 0.5mM initial H_2O_2 concentration.

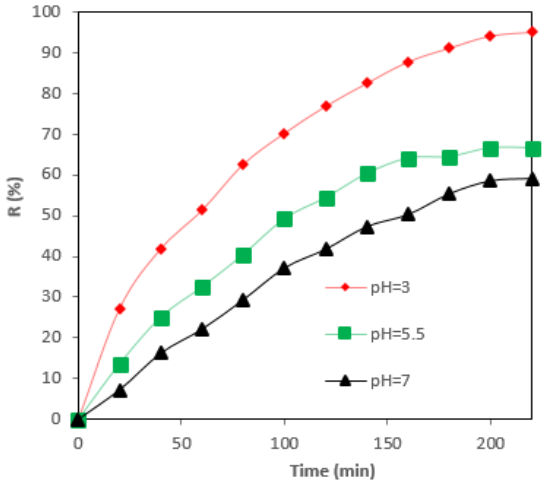

Fig. 2. Effects of pH on the degradation of MO. [MO] =10 mg/L; [H_2O_2] =0.5 Mm;

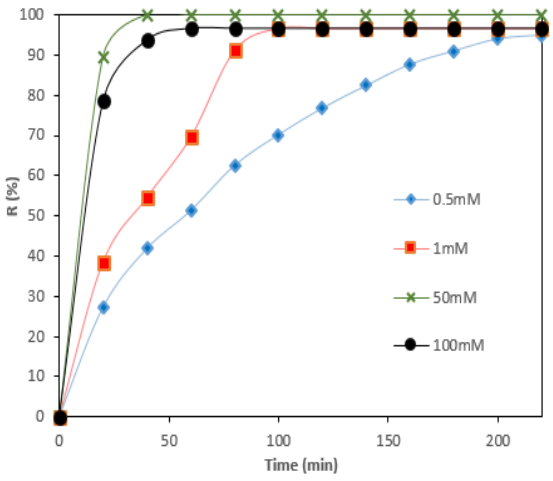

Fig. 3. Effects of H_2O_2 dosage on the degradation of MO. [MO] = 10 mg/L; pH = 3;

3.4. Effects of MTW dosage

In heterogeneous photo-Fenton process, H_2O_2 reacts with ferrous ion (Fe^{2+}) or ferric ion (Fe^{3+}) at the surface of the solid catalyst. According to Fig. 4 by increasing of MTW dosage from 0.1 g/L to 1 g/L the degradation efficiency was increased from 86.71% to 98.7%, respectively, within 220 min of the reaction. This is attributed to the fact that the more amounts of iron ions

on the catalyst and increasing the generation of hydroxyl free radicals. However, as MTW dosage increase above 1 g/L, the degradation efficiency decreased. This is because the high amounts of MTW can make the solution more viscous and decrease the mass transfer rate in the system. On the other hand, the opacity and screening effect of excess MTW act as a shield, and hinder the penetration of UVC irradiation, and consequently cause reduction of the catalytic activity of MTW. Therefore, the optimal dosage of MTW was determined as 1 g/L.

3.5. Effects of initial concentration of MO

The dye concentration plays an important role in photo-Fenton process. The results of this part are shown in Fig. 5. It is clear that, by increasing initial concentration of MO, photocatalytic degradation efficiency decreased. Increase of MO concentration from 5 mg/l to 20 mg/l, decreased the decolourisation rate from 90.08% to 67.59% after 120 min. In the presence of constant amounts of hydrogen peroxide and MTW, constant amounts of hydroxyl free radicals are generated. On the other hand, in higher concentration of the dye solution due to increasing the number of dye molecules, there are not sufficient $^{\bullet}OH$ radicals to remove all of the dye molecules, so the degradation efficiency decreases. The another reason is that the colored solution by high concentration prevents from entering the photons of the UVC light into the solution and subsequently decreasing the decolourisation efficiency.

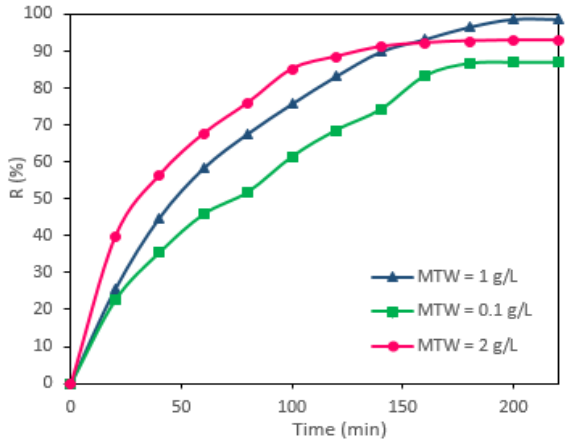

Fig.4. Effects of MTW dosage on the degradation of MO. [MO] = 10 mg/L, pH = 3, [H_2O_2] = 0.5 mM.

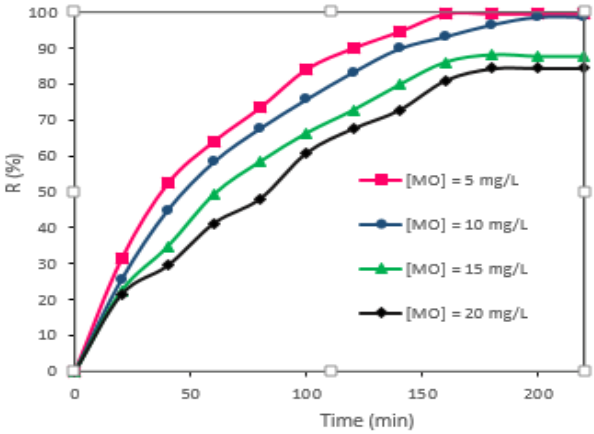

Fig. 5. Effects of initial concentration of MO on the degradation efficiency. pH=3; [H_2O_2] = 0.5 mM; MTW = 1 g/L.

4. Conclusion

In the present study, in order to reduce the sludge of ferric hydroxide forming in the homogeneous photo-Fenton reaction, a low cost biomaterial (tea waste) was supported by magnetite iron oxide (Fe_3O_4). The magnetite tea waste (MTW) was used as a heterogeneous catalyst for the degradation of MO during the photo-Fenton process. The effects of initial pH of the dye solution, the amount of catalyst, hydrogen peroxide dosage, and initial concentration of dye on the degradation efficiency have been studied. The results indicated that, more than 98% degradation efficiency of MO (10 mg/ L) was achieved after 220 min irradiation , in the presence of MTW (1 g/L), H_2O_2 (0.5 mM). Also, for investigating the effect of the heterogeneous catalyst, several different processes in addition to photo-Fenton

process were studied. The results showed that, the degradation efficiency of these processes are as follows: [H_2O_2/MTW/UVC (hetrophotocatalyst photo-Fenton process)] > [H_2O_2/UVC] > [H_2O_2/MTW/dark (Fenton process) ≅ MTW/UVC] > [UVC] > [H_2O_2/dark].

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