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Removal of methylene blue from aqueous solution: A comparison between adsorption by iron oxide nanospheres and ultrasonic degradation

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Abstract
Methylene blue as one of the pollutant compounds was removed from water by two different methods including adsorption by magnetic iron oxide nanospheres and degradation by ultrasonic radiation. The prepared iron oxide nanospheres were characterized by XRD and SEM methods. The effect of hydrogen peroxide on the removal efficiency of both methods was studied. The effect of contact time and initial dye concentration on the removal efficiency were studied too. Finally, the performance of dye removal by adsorption and ultrasonic degradation methods were compared.

Keywords: Methylene blue, Adsorption, Iron oxide, Nanospheres, Ultrasonic, Degradiation.

Introduction
Environmental pollution is one of the main problems for human and human life in recent years. By the increase of industrial activities, environmental pollution increased too. Different kinds of pollutants release from industries to the environment which one of the toxic compounds is dye molecules. Dye molecules release to the environment by the textile, cosmetic and dye industries. Waste waters including dye molecules have high BOD and COD and also prevent the light transmission. So it is necessary to purify the water from dye molecules. There are different methods for removal of pollutants from waste water including: adsorption [1-6] membrane separation [7], electrochemical [8], photocatalytic decomposition [9] and ultrasonic irradiation [10]. The purpose of the present work is to investigate the capability of iron oxide nonospheres as adsorbent for removal of methylene blue from aqueous solution and also the performance of ultrasonic radiation for destruction of methylene blue. The effect of hydrogen peroxide on the performance of both methods was investigated too. The iron oxide nanoparticles were selected as adsorbent because they can be easily separated from solution by external magnet.

Materials and Method
$FeCl_3$ (99%), methylene blue, H_2O_2 (98%) were purchased from Merck Co. The iron oxide nanosphere was prepared based on previous reported method [4,5,10]. The prepared iron oxide nanospheres were characterized by X-ray diffraction (XRD) (ADP2000 ITALSTRUCTURE) and scanning electron microscope (SEM) (Hitachi, Japan- S4160) Methods. An ultrasonic bath was used as the source of ultrasound radiation. Uv/visible spectrophotometer (PG-T80 Instrument Ltd.) was used for determination of methylene blue concentration at 664nm. The effect of different variables such as contact time, initial concentration and presence of H_2O_2 on the adsorption by iron oxide nanospheres or destruction by ultrasound were investigated too.

Results and Discussions
Fig.1 represents the SEM image of the prepared iron oxide. Based on the SEM image the iron oxide are spherical with different diameter ranging from 50 to 170 nm.
The XRD pattern of the prepared iron oxide nanosphoeres is presented in Fig. 2. There are two characteristic peaks at $2\theta=37.6^0$ and 43.9^0 of (110) and (202) planes of α-Fe_3O_4 [5] and also five characteristic peaks at $2\theta=30.1^0$, 35.8^0, 43.1^0, 57.3^0 and 63.0^0 of (220), (311), (400), (511) and (440) planes of Fe_3O_4, respectively [5]. Therefore based on the XRD pattern it is clear that the prepared iron oxide nanospheres are a combination of α-Fe_3O_4 and Fe_3O_4.

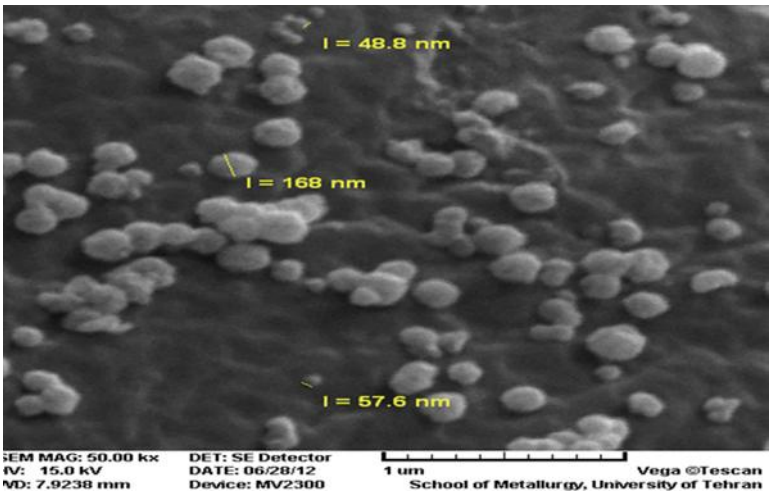


Figure 1: The SEM image of the prepared iron oxide.

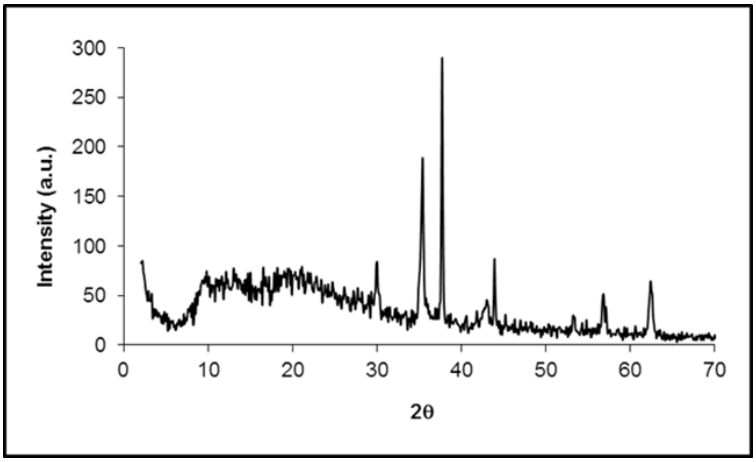


Figure 2: The XRD pattern of the prepared iron oxide.

The adsorption experiments were performed at two different concentrations of methylene blue. The amount of methylene blue adsorbed per unit mass of iron oxide at any time (q_t) and also the removal percentage of dye are presented in Fig.3. It is clear that the removal percentage increases by time. But half of the removal takes place within 10 min. Fig.3 shows that by increasing of dye initial concentration, the q_t increases but the removal percentage decreases.

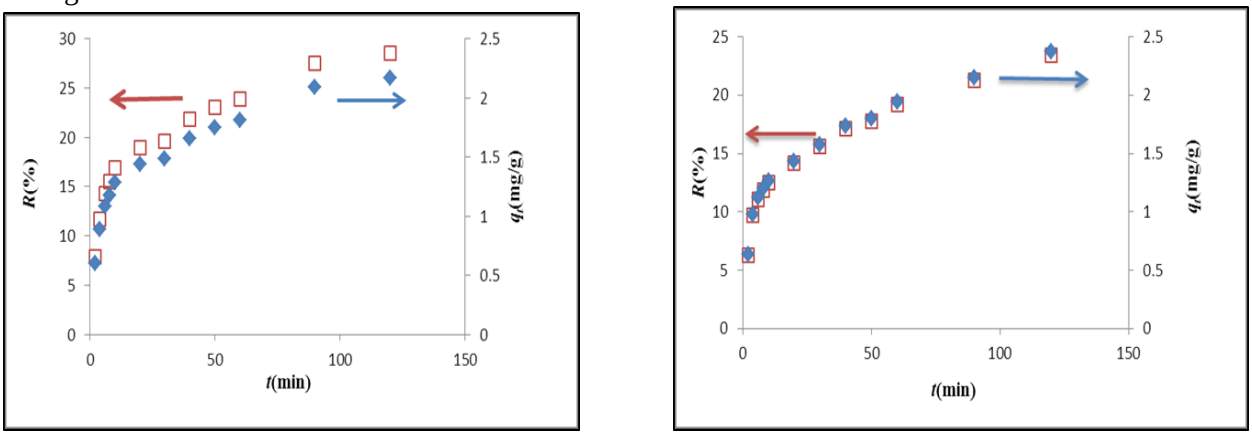
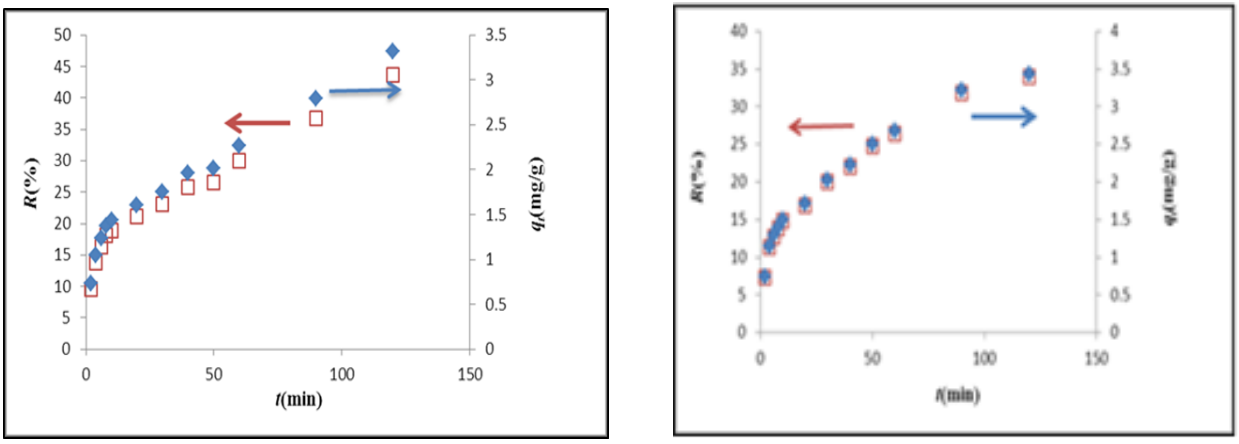


Figure 3: Removal percentage and amount of ad-species, as a function of adsorption time in the absence of H_2O_2 at different dye concentrations. (a) 2.5 mg/l and (b) 3.4 mg/l.

Fig.4 shows the adsorption data with the same conditions of the data in Fig.3 but in the presence of H_2O_2. These data shows that the presence of hydrogen peroxide caused an increase in the removal percentage. This may be attributed to the destruction methylene blue by the OH radicals from H_2O_2 and the easier adsorption of fragmented dye molecule.



(a) **(b)**

Figure 4: Removal percentage and amount of ad-species, as a function of adsorption time in the presence of H_2O_2 at different dye concentrations. (a) 2.5 mg/l and (b) 3.4 mg/l.

The adsorption kinetic data were fitted with different kinetic models including pseudo-first order [11], pseudo–second order [11] and Elovich [12] equations.

$$q_t = q_e(1-\exp(-k_1 t)) \quad (1)$$

$$q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \quad (2)$$

$$q_t = \frac{1}{a} Ln(1+abt) \quad (3)$$

where q_t and q_e are the adsorbed amounts per unit mass of adsorbent at any time and at equilibrium, respectively. k_1 and k_2 are the pseudo-first and pseudo second order rate coefficients, respectively. a and b are Elovich constants. The best fitting were obtained with Elovich equation and the results of fitting are listed in Table1.

Table 1: Obtained constants of Elovich equation at different conditions.

C_0 (mg/l)	b	a	R^2
1.7 (In the absence of H_2O_2)	2.573	1.01	0.9813
2.5 (In the absence of H_2O_2)	2.741	2	0.9825
3.4 (In the absence of H_2O_2)	2.208	0.203	0.9799
1.7 (In the presence of H_2O_2)	1.846	0.108	0.9565
2.5 (In the presence of H_2O_2)	0.350	0.028	0.9657
3.4 (In the presence of H_2O_2)	0.714	0.063	0.9856

In the second sets of experiments the removal of methylene blue from aqueous solution by ultrasonic irradiation was investigated. The results of experiments are presented in Fig.5.

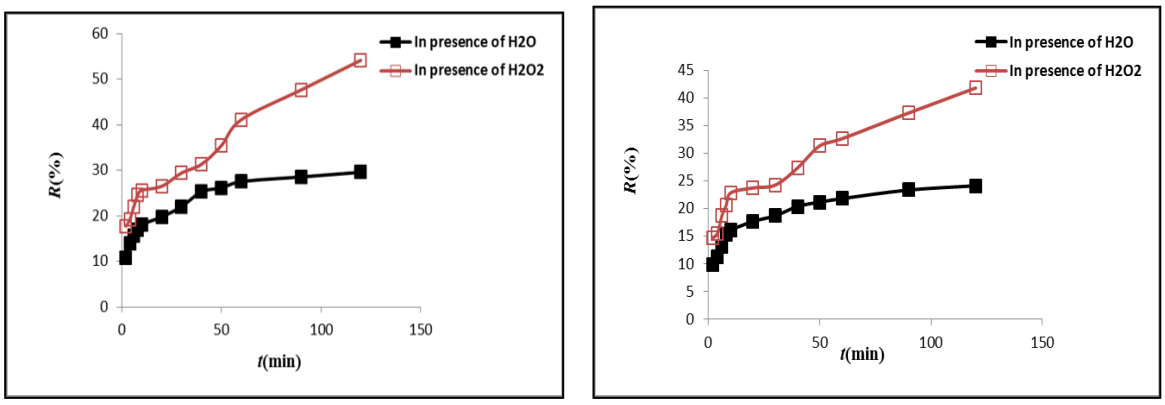


Figure 5: Removal percentage, as a function of ultrasonic radiation time in the presence and absence of H_2O_2 at different dye concentrations. (a) 2.5 mg/l and (b) 3.4 mg/l.

The experiments were performed at two different initial concentrations of methylene blue and also in the absence and presence of H_2O_2. The presented results in Fig.5 indicate that the methylene blue can be destructed by ultrasonic radiation. By increase of radiation time the removal percentage increases too. Also the presence of H_2O_2 caused an increase in the removal efficiency. In this case both hydroxyl radicals and ultrasonic radiation destruct the dye molecule and therefore the removal efficiency increased in the presence of H_2O_2. In this case, also the removal percentage decreases by increase of dye concentration. The rate of dye removal by ultrasonic radiation is slightly higher than adsorption process.

Conclusion

The results of the presented work show that the methylene blue can be removed from aqueous solution by adsorption with iron oxide nanospheres and also ultrasonic radiation. The presence of hydrogen peroxide improves the removal efficiency in both methods. The rate of dye removal by ultrasonic radiation is slightly higher than adsorption. But the adsorption by iron oxide nanospheres has some advantages including, ease of operation and lower energy consumption. Also it should be noted that the iron oxide nanospheres can be separated from solution easily and by use of an external magnet.

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