

Research note

## Degradation of Azo Dye Reactive Black 5 and Acid Orange 7 by Fenton-Like Mechanism

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### Abstract

Colored wastewater is one of the most important sources of environmental pollution and because of their visibility and bearing toxic chemicals, it is very important to be treated before released into the environment. In recent years, several methods have been used for treatment of dyestuff effluents. In this work, removal of two azo dyes, Acid Orange 7 and Reactive Black 5 as an indicator of synthetic dyes by Fenton-like reaction were studied. In this process,  $\text{OH}^\bullet$  radicals will be generated by using  $\text{Fe}^0$  and UV light, so it can occur without the addition of hydrogen peroxide. Various parameters such as pH, amount of iron powder, initial dye concentration, UV light and contact time were studied in terms of their effect on the reaction progress. It is observed that high removal of dyes for UV system was obtained at pH=11, while in the  $\text{Fe}^0$  and  $\text{Fe}^0/\text{UV}$  system, high removal occurred at pH=3. Removal of dye was increased by increasing the iron mass and contact time. High removal of dye was at the time equivalent of 120 min and reached equilibrium. Initial dye concentration has different effects for Acid Orange 7 and Reactive Black 5 removal. Increasing the initial dye concentration of Acid Orange 7 has increased dye removal in the  $\text{Fe}^0/\text{UV}$  and  $\text{Fe}^0$  system, while it was decreased in the UV system. For RB5 removal, it was decreased in the  $\text{Fe}^0/\text{UV}$  and  $\text{Fe}^0$  system by increasing the initial dye concentration, while it increased in UV system.

**Keywords:** Fenton-Like, Azo Dye Removal, Zero Valent Iron, UV

### 1. Introduction

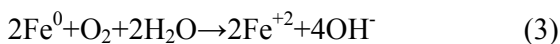
Industrial effluents are one of the most important sources of pollution in the environment. The dye effluents from textile industries are significant sources in environmental pollution [1]. Synthetic dyes

have been used in many industries such as textile, paper printing, food, pharmaceutical, leather and cosmetics [2]. Traditionally, synthetic dyes are classified into acid, reactive, direct, basic, vat, disperse, metal complex, mordant and sulphur dyes. Acid

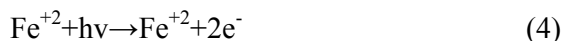
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and reactive dyes are mostly used [3]. Azo dyes, one of the greatest groups of synthetic dyes, have one or more azo bounds (-N=N-) and because of their solubility, low expense, stability and color variety, are widely used in many applications [4-6]. Removal of azo dyes from colored effluents due to their complex composition, toxicity, poor degradability and high solubility, have attracted great interest in the last few years [7]. Conventional methods such as chemical precipitation and biological treatment cannot effectively remove of dyes from effluents, so finding an effective technique is necessary.

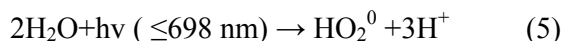
In recent years, zero-valent iron (ZVI), because of its availability, low toxicity, low cost and effectiveness has been successfully used as a reagent for removal of pollutants from the environment [8]. Many researchers used ZVI for removal of pollutants such as phenol [9], nitro aromatic compound [10], nitrates [11], EDTA [12], and herbicide [13]. In aquatic solution, zero-valent iron with an  $E_H^0 = 0.440$  V, serve as a reducing agent [14]. In aquatic solution metallic iron, according to the following reaction converted to  $Fe^{+2}$ :



In this reaction, as seen above, two free electrons are generated and work as reducing agents. In addition, irradiation of UV light, oxides  $Fe^0$  to  $Fe^{+2}$  so generate two free electrons as in the following reaction [15]:



On the other hand,  $OH_2^0$  radicals will be produced in the presence of UV light at aquatic solution as in the following:



This reaction starts the following reactions:



In view of the above reaction,  $H_2O_2$  would be produced without the addition of this compound, so a Fenton-like reaction is generated. Metallic iron reaction depends on the pH of the solution. In acidic pH, the surface of iron was maintained refresh, so the following reaction would be faster than the other pH range [16]. It is clear from the above reaction that production of hydrogen ions and gases can help to enhance the reaction rate. In the present study, we investigate degradation of two azo dyes, Reactive Black 5 and Acid Orange 7. The following are the aims of our study:

- Effect of UV light on removal efficiency
- Effect of  $Fe^0$  on dye removal
- Effect of UV/ $Fe^0$  on removal of dyes
- Comparison of two system on removal of two azo dyes

## 2. Materials and Methods

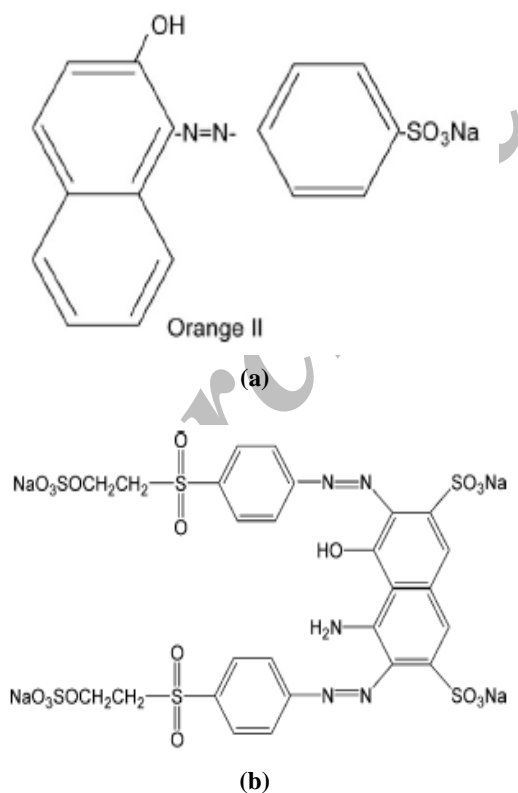
### 2.1. Chemicals

All chemicals used in our work were in GR grade. Iron powder with effective size 150

$\mu\text{m}$  was purchased from Merck (Germany) and used without any purification. A UV lamp with 40 W intensity and 0.8 m in length obtained from Nojan Teb (Iran) was used as a source of UV light at a distance of 10 cm from the surface of the dye solution. The light intensity was measured by a Radiometer at 300 to 400 nm (Hagner ECI-UV-A). 1 N NaOH and  $\text{H}_2\text{SO}_4$  solution was used for pH control. All experiments were conducted in batch system.

## 2. 2. Dyes

Reactive Black 5 (RB5) and Acid Orange 7 (AO7) as indicators of azo dyes were obtained from Merck and used without any treatment. The structures of the dyes are shown in Fig. 1



**Figure 1.** chemical structure of Acid Orange 7 (a) and Reactive Black 5 (b)

## 2. 3. Experimental Procedure

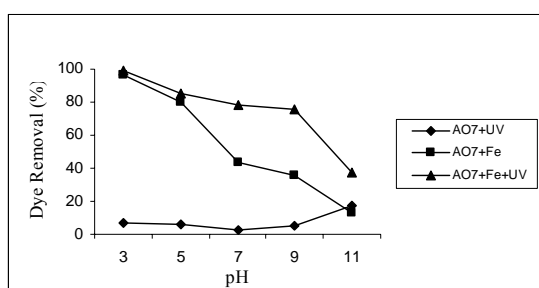
A stock solution of dyes was prepared in a 1000 ml flask, and a practical solution was prepared from the stock solution in an appropriate concentration. For the experiments, 150 ml of dye solution was added to a 250 ml beaker and after addition of a given amount of iron powder and UV light irradiation, the samples were stirred mechanically (Hanna-Hi 190M, Singapore) at a speed of 100 rpm. At a predetermined time interval, the sample was taken and after filtration (Wathman) and centrifuging, the final concentration of dyes was determined by using UV/VIS spectrophotometer (model 1700, Shimadzu Japan) at a maximum absorbance wavelength of 599 and 487 nm for RB5 and AO7; respectively.

## 3. Results and Discussion

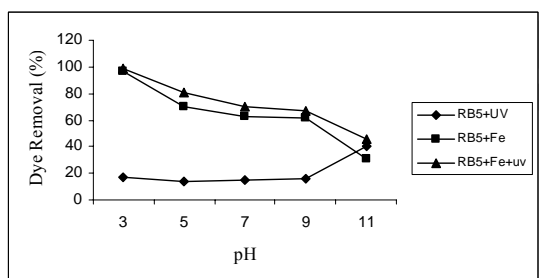
### 3. 1. Effect of pH

Parameter of pH was investigated in the range of 3, 5, 7, 9 and 11. Fig. 2 shows the effect of pH solution on dye removal. In view of this figure, it is clear that the pH of the solution has a significant effect on dye removal. In the UV system, high removal occurred at pH=11, while in the Fe and Fe/UV system it was high at pH=3. The main mechanism in the Fe system is the oxidation-reduction process, while the production of  $\text{OH}^\bullet$  radical is dominant in the Fe/UV system, so the latter can be as an advanced oxidation process (AOPs). For this reason dye removal was high in the Fe/UV system rather than the others. As mentioned above, in acidic pH the surface of iron over time would be refreshed so production of free electron can be faster than other pH. Also, in advanced oxidation process the production of

$\text{OH}^\bullet$  radicals in acidic pH is much faster, so dye removal is much higher than others. In the UV system, the main mechanism for pollutant removal is production of  $\text{OH}^\bullet$  radicals, and because of the turbidity of the dye solution the UV light could not percolate to the depth of the solution, so removal of dye was low. The same result was observed for removal of nitrate [11], phenol [9], and Reactive Blue 4 [17] in the presence of metallic iron.



(a)



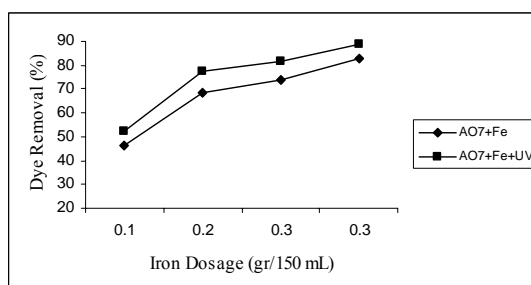
(b)

**Figure 2.** Effect of pH on Dye Removal, (a) AO7, (b) R5 (Dye Solution=50 mg/L, Contact Time=120 min, Iron Dosage=0.3 gr/150 mL)

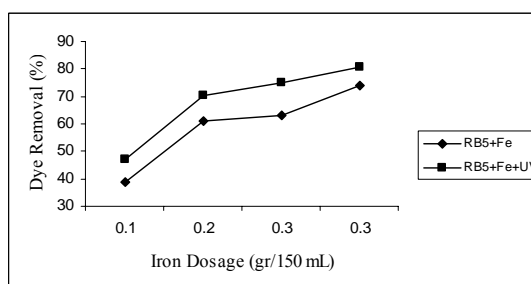
### 3. 2. Iron Powder Mass

The effect of iron powder dosage was investigated by adding different weights of iron powder (0.1, 0.2, 0.3 and 0.4 gr) into 150 ml of dye solution; respectively. The results showed that by increasing the ZVI mass, dye removal was increased (Fig. 3). As the iron mass increased, the surface of the present iron and subsequently the production of free radical would be increased, so

removal efficiency can be increased. Another point that can be denoted from this figure is that the increasing of iron mass is effective for dye removal up to a point. For example, by increasing the iron dosage from 0.1 gram/150 ml to 0.2 gram/150 ml, 45% and 53% of dye removal was obtained in the  $\text{Fe}^0$  and  $\text{Fe}^0/\text{UV}$  system for AO7, respectively. In addition, by increasing the iron dosage from 0.2 gram/150 ml to 0.4 gram/150 ml, only 20% and 32% of dye removal was observed for AO7 in the  $\text{Fe}^0$  and  $\text{Fe}^0/\text{UV}$  system for AO7, respectively. The reason for this unusual precept denoted that dye removal in the iron dosage between 0.2 gram/150 ml to 0.4 gram/150 ml reaches nearly to the equilibrium point, so increases of iron dosage upon 0.4 gram/150 ml would be a waste action [17]. As an example, the reduction of Acid Orange 7 in the presence of metallic iron is shown on Fig. 4.



(a)



(b)

**Figure 3.** Effect ZVI mass on dye removal, (a) AO7, (b) RB5, (pH=7, Dye Solution=50 mg/L, Contact Time=120 min)

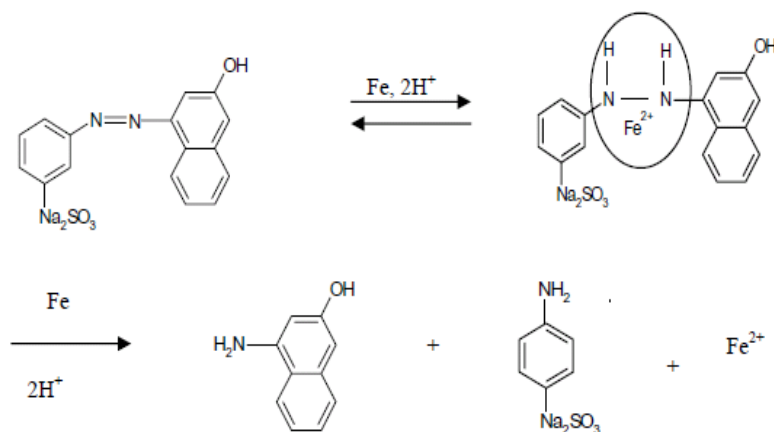


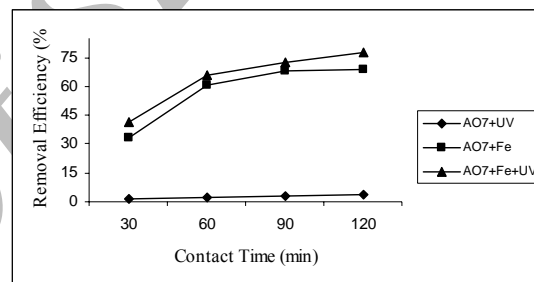
Figure 4. removal mechanism of Acid Orange 7 by metallic iron

### 3. 3. Contact Time

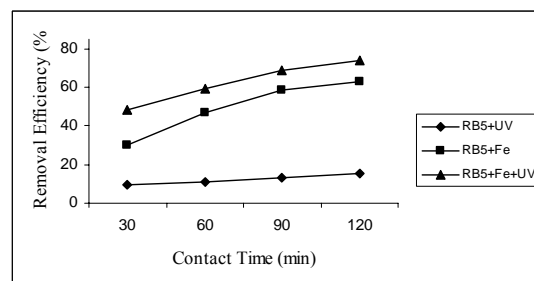
The removal of dye was investigated at time intervals of 30, 60, 90 and 120 min from initial time. Results showed that by lapse of time, dye removal was increased and reached equilibrium at 120 min. Fig. 5 shows the effect of contact time on dye removal. Contact time is an important parameter in environmental engineering. For the removal of pollutant it is critical to obtain a contact time that is economical and enough to remove pollutants in a conscionable condition [15]. In this work dye removal to equilibrium point at 120 min for both dyes is shown in Fig. 5. This point (120 min) is sensible as well as economical and effective in environmental engineering. Similar results have been observed by Demetrios et al. [18], Haining et al. [19].

### 3. 4. Initial Dye Concentration

Dye solution of 25, 50, 75 and 100 mg/L was used for the study of initial dye concentration on removal efficiency. It is observed that initial dye concentration has a significant effect on dye removal (Fig. 6). The results



(a)



(b)

Figure 5. Effect of contact time on dye removal, (a) AO7, (b) RB5, (pH=7, Dye Solution=50 mg/L, Iron Mass=0.3 gr/150 mL)

showed that by increases in the initial dye concentration, the removal efficiency for AO7 at the  $Fe^0$  and  $Fe^0/UV$  system was increased, while for the UV system it was decreased. In addition, by increasing the initial dye concentration for RB5 in the  $Fe^0$

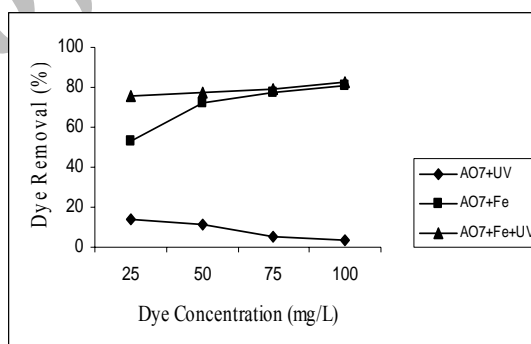
and  $Fe^0/UV$  system, dye removal was decreased, while in the UV system it increased. The reason for the effect of the initial dye concentration can be explained by the chemical structure of dyes. It is possible that the chemical structure of the dye is too complex, so by increasing the initial dye concentration the removal efficiency can be decreased. On the other hand, if the chemical structure of a dye is simple, it is possible that increasing the initial dye concentration would have a positive effect on removal efficiency. As shown in Fig. 1, the chemical structure of Acid Orange 7 is simple and it has one azo bond, so in the case that other parameters are steady, the increases of the initial dye concentration show the positive effect on removal efficiency. This is true on the removal of Reactive Black 5. It has a complex structure and also two azo bonds, so at stable condition of other parameters the increases of the initial dye concentration shows the dye removal decreased. Many researchers such as Mariana et al. [20] and Jianxim et al. [21] reported the same results.

#### 4. Conclusions

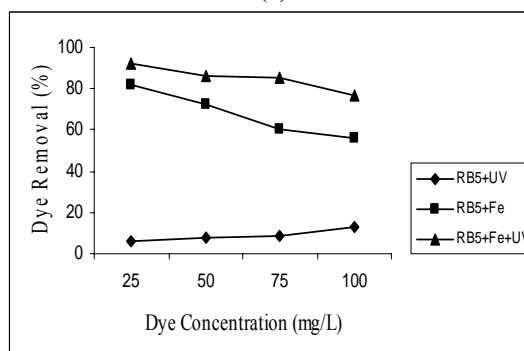
This work was conducted by Fenton-like reaction for the effective removal of azo dyes AO7 and RB5 from aquatic solution. The following are the main results:

- High removal for AO7 and RB5 in the UV system was obtained at pH=11.
- Removal capacity was increased by increasing the iron powder mass.
- Removal efficiency was high in  $Fe^0/UV$  and  $Fe^0$  at pH=3 and iron powder mass=0.4/150 ml

- Increasing the initial dye concentration has had different effects, so removal of AO7 in  $Fe^0/UV$  and  $Fe^0$  was increased by increasing the initial dye concentration, while in the UV system it was decreased.
- Removal of RB5 in the  $Fe^0/UV$  and  $Fe^0$  system was decreased by increasing the initial dye concentration, while in the UV system it was decreased by increasing the initial dye concentration.
- Removal of dyes in the  $Fe^0/UV$  and  $Fe^0$  and UV system increased by increasing the contact time, and in the  $Fe^0$  system it reached equilibrium at 120 min.



(a)



(b)

**Figure 6.** Effect of initial dye concentration on dye removal, (a) AO7, (b) RB5, (pH=7, Contact Time=2 (h), Iron Mass=0.3 gr/150 mL)

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