RESEARCH ARTICLE

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Application of H_2O_2 and H_2O_2/Fe^0 in removal of Acid Red 18 dye from aqueous solutions

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Background & Aims of the Study: Organic dyes with a complex structure are often toxic, carcinogenic, mutagenic, non-biodegradation and stable in the environment and if released to the environment without treatment can endanger the environment and human health. The aim of this study was to evaluate the performance of H_2O_2 and H_2O_2/Fe^0 Iron in removal of dye Acid Red 18 from aqueous solutions.

Materials & Methods: This study was conducted at the laboratory scale. In this study, the removal efficiency of Acid Red 18 from a synthetic solution by H_2O_2 and H_2O_2/Fe^0 was investigated. As well as Effect of solution pH, dye concentration, Concentration of Nanoscale Zero-Valent Iron, H_2O_2 and contact time in decolorization efficiency was investigated.

Results: Results show that in pH=3, Contact time of 80 minutes, dye concentration of 50 mg/l and Concentration of Nanoscale Zero-Valent Iron of 2 g/l and H_2O_2 concentration equal to 200 mmol/l, the removal efficiency was about 98%.

Conclusions: According to the results of experiments, H_2O_2/Fe^0 has high efficiency in removal of Acid Red 18 from aqueous solution.

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Background

One of the most environmental polluting industries is industrial wastewaters. Textile and dyeing industries are very important for the development of countries. Furthermore, other industries such as cosmetics, paper and pharmaceutical also produce colored wastewater [1]. In dyeing processes, about 15% of the generated colors release to the sewage and then in this way painted wastewaters formed [2]. Different color-causing substances were used in industries and azo group dyes are the most common colors. One of the largest groups of synthetic colors which belongs to azo dyes contains one or more azo bond -N = N-. It is estimated that about 50 percent of annual worldwide production of colorants (700 thousand tons) are azo type. Colors and organic materials with complex structures are often toxic, carcinogenic, mutagenic, non-biodegradation and resistant in environment and if they release to it without any treatment may endanger the environment and human health [2, 3, 4, 5]. Colored wastewater discharging from industries into water streams can cause Eutrophication and interference in ecology and cause chemical changes in water streams. Also, dye molecules in wastewater are completely visible in water, even in very low concentrations, because of their strong bonds. Therefore, colors are one of the most obvious water contamination indicators. In previous decades, dye wastewaters treatment were highly regarded by Environmental engineers and has motivated some studies in recent decades done in the development of new processes for the removal of color and organic load from colored wastewater [6, 7, 8]. Diverse methods for wastewater treatment has been studied by many researchers including different physical chemical methods such as ultra-filtration, reverse osmosis, ion exchange and adsorption on different materials, such as activated carbon, coal, wood chips and Silica gel in order to remove dye and COD from wastewater. But since these methods can only transfer the pollutants from the aqueous phase to the solid phase and they aren't destructive or eliminating processes, they were not considered as universal techniques. Hence, in recent years, advanced oxidation processes based on the production of free radicals, which rely on the power of oxidation, especially OH have been fairly accepted scientifically [9]. In the process of Nanoscale Zero-Valent Iron and H_2O_2 than conventional Fenton process, hydroxyl radical production occurs in two stages. Thus, the efficiency increases. On the other hand, in Fenton process by ferrous ions formation, the efficiency of the process reduces and stops, While if Nanoscale Zero-Valent Iron is used, at first Ferro ions and then ferrous ions formed. So actually the efficiency of process would be more than the efficiency of conventional Fenton process [10]. The most important reactions in organic material removing by the hydrogen peroxide process in the presence of Nanoscale Zero-Valent Iron are as the following:

$$Fe^0 + H_2O_2 \rightarrow Fe^{+2} + OH^- + OH^0$$
$$Fe^{2+} + H_2O_2 \rightarrow Fe^{+3} + OH^- + OH^0$$
$$OH + \text{Acid Red 18} \rightarrow \text{oxidized dye} + H_2O$$

Nanoscale Zero-Valent Iron (NZVI) is used as a regenerative for activation of hydrogen peroxide. Because Nanoscale Zero-Valent Iron ions release Fe (II) into solution under acidic conditions, these dissolved ions are the first step for oxidation of pollutants (such as dyes) in H_2O_2/Fe^0 process. While the oxidation of dye occurs, Fe^{+2} ions consumed and the pollutants oxidation depend on the solubility of Fe^{+2} in solutions [11].

In addition to being a strong reduction in powder form of NZVI, inexpensive, easy to use, non-toxic, quick reaction and high efficiency for pollutants decomposition and returning NZVI in to cycle by a magnetic are the characteristics of this nano particle [12, 13]. Also a wide variety of contaminants including chlorinated organic compounds, poly-chlorinated biphenyls, heavy metal ions, oxy anion, dimethyl phthalate and 2, 4-dichlorophenoxyacetic acid can be treated with the NZVI [13, 14, 15]. Colors are chemical materials that may be unsustainable by this process and recently they have been used for the removal of several azo dyes [12, 16, 17, 18].

Aims of the study: The main objective of this study is to evaluate the efficacy of Nanoscale Zero-Valent Iron in the presence of hydrogen peroxide (Fe^0/H_2O_2) in order to remove the Acid Red 18 dye from aqueous solutions.

Materials & Methods

This is a fundamental- practical study which is done in the laboratory-scale and in a batch process. The variations in this study include contact time (5, 10, 30, 80, 140, 210) min, initial concentration Nanoscale Zero-Valent Iron (0.5, 2, 3, 4) g/l and pH (3, 5, 7, 9), hydrogen peroxide (24, 90, 140, 200, 300) mmol/l, initial concentration of Acid Red 18 dye (25, 50, 75, 100) mg/l. Mettler Toledo pH meter was used for measuring of pH. NaCl and HCL 1N were used for adjusting the pH. In this study, NZVI with an effective size of 50-35 nm, surface-to-mass ratio equal to 8-14 m^2/g and American product (USNANO) was purchased from Nanosany Company. Figure 1 shows NZVI image which is taken by electron microscope (TEM)[1]. Acid Red 18 dye was purchased from Rang Alvan Sabet Company in Iran. Chemical structure of Acid Red 18 is shown in Figure 2. Acid Red 18 dye specifications are shown in Table 1 [19]. To perform the experiments, 250 ml of dye with different concentrations were added to 500 ml glass beakers and the amount of pH was adjusted to the desired range. Then different concentrations of Nanoscale Zero-Valent Iron-hydrogen peroxide and hydrogen peroxide were added in to 250 ml of dye with different initial concentrations and after mixing by Jar Test at 250 rpm, Samples were taken at specified intervals. Maximum absorption of Acid Red 18 solutions at 506 nm wavelength were determined by using spectrophotometer (CECIL 7250) UV/VIS [21, 20]. Then, by knowing adsorption amount and using calibration curve, the remained concentration of dye was determined. The Calibration curve of spectrophotometer is shown in Figure 2. For example, at pH =3 and initial dye concentration of 50 mg/l, different doses of zero iron nanoparticles-Hydrogen peroxide and hydrogen peroxide were added and at specified contact times the sampling process were done and the remained dye concentration were determined.

Results

The results of the experiments are shown in Figures 4 to 8. In these figures the effects of contact time, initial dye concentration, pH, NZVI and hydrogen peroxide concentration on color removal efficiency in each stage is shown.

The results show that by increasing the concentration of NZVI, hydrogen peroxide and contact time increase the removal efficiency. By the decrease of initial concentration and the amount of pH to a certain value the removal efficiency also increases.

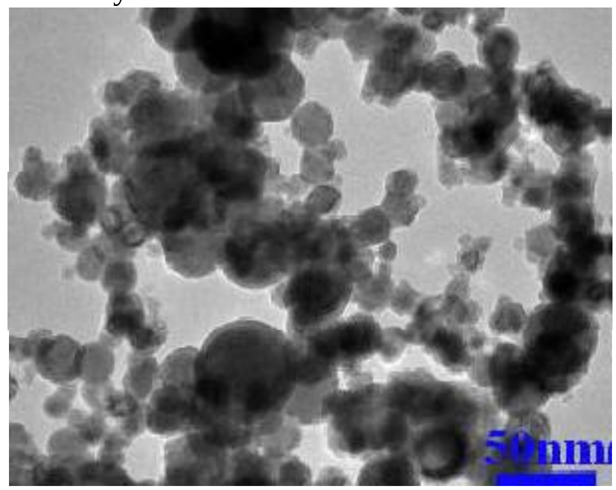

Figure1: zero valent iron nanoparticles image with transmission electron microscopy (TEM)

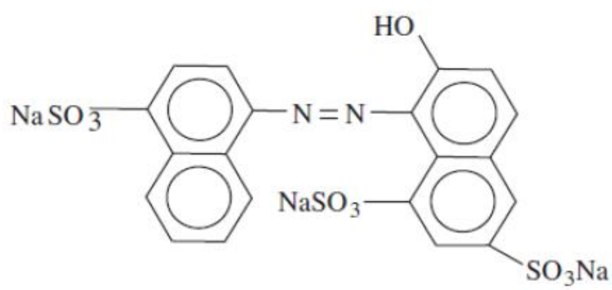

Figure 2: chemical structure of Acid Red 18

Transmission Electron Microscope[1]

Table 1) Characteristics of Acid Red 18

molecular weight	Number of azo bond	maximum wavelength (nm)	Chemical formula	Brand
604.5	Mono azo	506	$C_{20}H_{11}N_2Na_3O_{10}S_3$	Acid Red 18

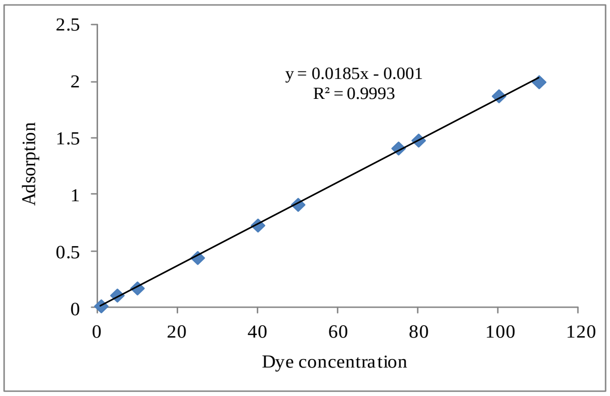

Figure 3: Calibration curve for measuring Acid Red 18 concentration

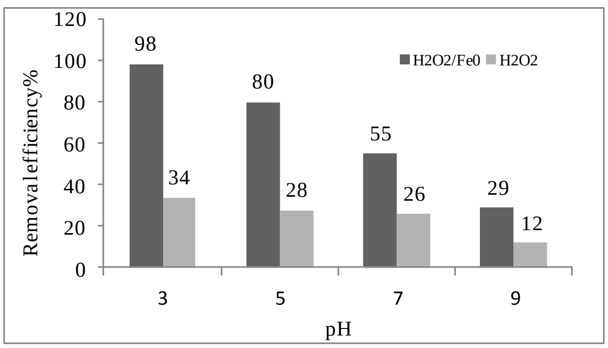

Figure 4: Effect of pH on the efficiency of the process (dye concentration = 50 mg/l, contact time = 80 min, Fe nanoparticles concentration = 2g, hydrogen peroxide concentration = 200 mmol/l).

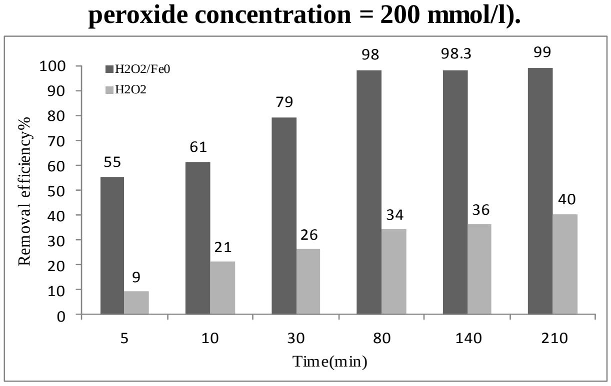

Figure 5: Effect of contact time on the efficiency of the process (dye concentration = 50 mg/l, pH = 3, concentration of iron nanoparticle = 2 g/l, hydrogen peroxide concentration = 200 mmol/l).

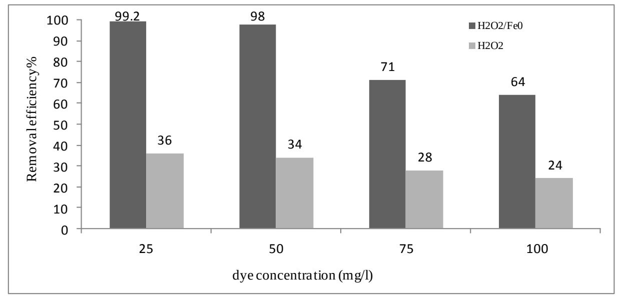

Figure 6: Effect of initial dye concentration on the efficiency of the process (time = 80 min, pH = 3, concentration of iron nanoparticles = 2 g/l, hydrogen peroxide concentration =200 mmol/l).

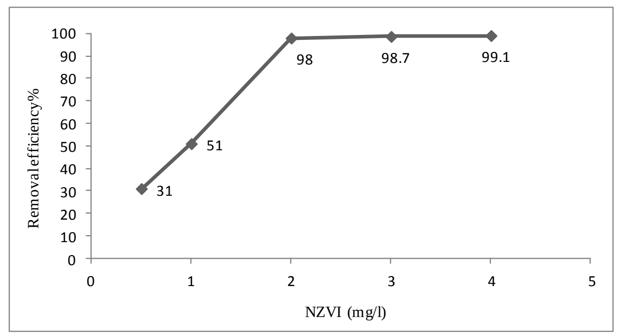

Figure 7: Effect of NZVI on the efficiency of the process (time = 80 min, pH =3, initial dye concentration = 50mg/l, hydrogen peroxide concentration =200 mmol/l).

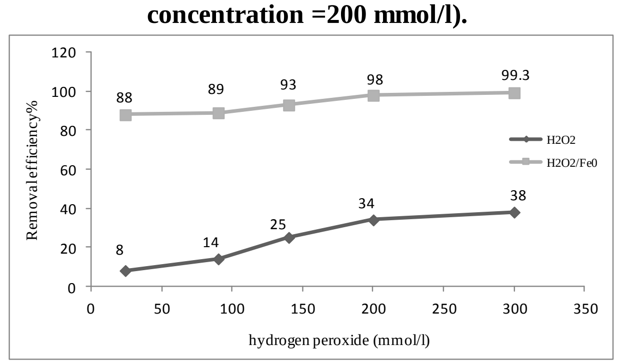

Figure 8: Effect of initial hydrogen peroxide concentration on the efficiency of the process (time = 80 minutes, pH = 3, initial dye concentration = 50 mg/l, the concentration of iron nanoparticles = 2 g/l).

Figure 7 shows dye removal efficiency in different concentrations of NZVI. By increasing

NZVI from 0.5 to 4 g/l at pH 3 and hydrogen peroxide equal to 200 mmol/l, in hydrogen peroxide-NZVI process the removal efficiency increase from 31 to 99.1%. The effect of hydrogen peroxide a lonely in values of 24 to 300 mmol/l, at pH 3 were studied and observed that the removal efficiency for maximum and minimum amount of H_2O_2 were 8 to 38% respectively. The effect of hydrogen peroxide in increasing the dye removal efficiency is shown in figure 8. The removal efficiency enhance with increase in hydrogen peroxide amount in presence of NZVI. Thus by increasing hydrogen peroxide amount from 24 to 300 mmol/l at pH 3, the dye removal efficiency enhance from 88 to 99.3% (Fig. 8).

Discussion

The results indicate that acidic pH is effective in achieving maximum dye removal. One of the main problems of this approach is requiring an acidic environment. At pH lower than 2.5 the formation of $Fe(OH)^{+2}$ which slowly reacts with hydrogen peroxide cause reduction in hydroxyl radicals and thus the efficiency of the process decreases. At alkaline pH, Fe^{+2} converted into Fe^{+3} and removed from the catalytic cycle in the form of $Fe(OH)_3$ [20, 21]. Test results show that at contact time of 80 min, pH = 3, concentration of NZVI = 2g/l and hydrogen peroxide concentration = 200 mmol/l, the dye removal efficiency in hydrogen peroxide with NZVI process was 98% and in hydrogen peroxide process was equal to 34% and by increasing the pH to 9, the removal efficiency of the processes were decreased to 29 and 12 % respectively. Barbusinski et al were reached to 99.9% removal efficiency in a study with Acid Red 18 dye removal by Fenton's reagent in the presence of iron powder. They found that the optimum amount of hydrogen peroxide and Fe were 60 and 50 mg/dl respectively and it was mentioned that pH reduction and contact time increase has significant effect on the dye removal. They also found that in the pH range of 2.5 to 3.5, dye removal happen with high speed and if the amount of pH descend to 2 or increase from 3.5 to 4, a rapid decline will occur in removal efficiency. They mentioned that hydrogen peroxide reaction in the presence of iron powder has an important advantage than Fenton. Thus, by increasing the amount of iron powder in combination process of iron and in the presence of hydrogen peroxide, at the end, pH level increases. Thus to neutralize wastewater, less substance will be needed [11]. In other study which was done about removing Acid Yellow 28 founded that increase in NZVI concentration and acidic pH are significant in achieving the maximum efficiency; So that the dye removal efficiency were increased from 26 to 99.2 % [12]. pH = 3 and NZVI equal to 2 g/l were the optimum values for Acid Yellow 28 removal [12]. This is why increasing in hydrogen peroxide concentration cause to the formation of acidic environment and so the production of Fe^{+2} intensifies. After that, hydroxyl radical production will increase, thus the dye removal efficiency enhances [22]. Mozia et al have used hybrid membrane system using photocatalytic decomposition process for Acid Red 18 decomposition [23]. In their study the dye was completely decomposed during 5 hours but in hydrogen peroxide-nano iron particles process as shown in figure 5 at 80 min contact time, thus, the removal efficiency was 98% and it was better than Mozia et al results. Figure 6 shows that by increasing dye concentration, the removal efficiency decreases as the concentration increases from 25 to 100 mg/l, the removal efficiency of hydrogen peroxide-nanoparticle iron and hydrogen peroxide process decrease from 99.2 to 64 % and 36 to 24 % respectively. This could be due to the NZVI's surface occupation by molecules of dye and Inaccessibility of Fe^{+2} ions to dye molecules. This is similar to other studies [12, 22]. In another study, Mozia et al used photocatalytic process for decomposition of

Acid Red 18. In this study, the initial adsorbent concentration, dosage and reaction temperature were studied [24]. This process compared to the process which was used in our research is quite complex. This process (iron nanoparticles in the presence of hydrogen peroxide) compared to other advance oxidation processes is used more because of its accessibility, safety for environment, ease of operation and high efficiency [12]. This process is useful for the removal of azo dyes.

Conclusion

According to the results, the iron nano particle-hydrogen peroxide has many advantages such as high removal efficiency and short reaction time and it could be used as a proper option for removing azo dyes from aqueous environments. While, hydrogen peroxide singly has less efficiency in removing azo dyes from aqueous solutions

Footnotes

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Conflict of Interest:

The authors declare no conflict of interest.

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