Original Article

Removal of Acid Red 18 dye from Aqueous Solutions Using Nanoscale Zero-Valent Iron

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Abstract

Background and Purpose: 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 was to evaluate the performance nanoscale zero-valent iron (NZVI) in the removal of dye acid red 18 (AR18) from aqueous solutions.

Materials and Methods: This study was conducted at the laboratory scale. In this study, the removal efficiency of AR18 from a synthetic solution by NZVI was investigated. As well as the effect of solution pH, dye concentration, the concentration of NZVI and contact time in decolorization efficiency was investigated.

Results: The results show that in pH = 3, contact time of 80 minutes, dye concentration of 25 mg/l and concentration of NZVI of 2 g/l, the removal efficiency was about 94%.

Conclusion: According to the results of experiments, NZVI has high efficiency in removal of AR18 from aqueous solution.

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Key words: Acid Red 18 (AR18), Dye Removal, Nanoscale Zero-Valent Iron

1. Introduction

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% of annual worldwide production of colorants (700 thousand tons) are the azo type. Colors and organic materials with complex structures are often toxic, carcinogenic, mutagenic, non-biodegradation and resistant in environment and if they release it without any treatment may endanger the environment and human health (2-5). 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 the 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 (6-8). 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 chemical oxygen demand from wastewater (7-11). Among the methods, the use of nanoparticles (e.g., Al^0, Sn^0, Zn^0, Fe^0, Dendrimers) for the treatment of contaminated water, a process is developing and acceptable (12-15). Today the versatility of zero-valent iron nanoparticles for use in environmental engineering has proven and nanoscale zero-valent iron (NZVI) in recent years has been widely used to reduce hazardous and toxic organic pollutants. 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 into cycle by a magnetic are the characteristics of this nanoparticle (16,17). Also a wide variety of contaminants, including chlorinated organic compounds, poly-chlorinated biphenyls, heavy metal ions, oxyanion, dimethyl phthalate and 2,4-dichlorophenoxyacetic acid can be treated with the NZVI (18-20). Colors are chemical materials that may be unsustainable by this process and recently they have been used for the removal of several azo dyes (16,21-24). The main objective of this study is to evaluate the efficacy of NZVI in the remove of the AR18 dye from aqueous solutions.

2. Materials and Methods

This is a fundamental-practical study which is carried out in the laboratory scale and in a batch process. The variations in this study include contact time (5, 10, 30, 80, 140, and 210 minutes), initial concentration NZVI (0.5, 2, 3, 4) g/l, pH (3, 5, 7, 9) and initial concentration of AR18 dye (25, 50, 75, 100) mg/l. Mettler toledo pH meter was used for measuring of pH. NaOH and HCL 1 N 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 transmission electron microscope TEM (model XL30, Philips Electronics Company, Eindhoven, Netherlands). AR18 dye was purchased from Rang Alvan Sabet Company in Iran. The chemical formula of AR18 dye is, $C_{20}H_{11}N_2Na_3O_{10}S_3$. Chemical structure of AR18 is shown in figure 2 (25,26). To perform the experiments, 250 ml of dye with different concentrations were added to 500 ml of glass beakers and the amount of pH was adjusted to the desired range. Then, different concentrations of NZVI were added into 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 AR18 solutions at 506 nm wavelength were determined by using spectrophotometer (CECIL 7250) ultraviolet (UV)/visible (27,28). Then, by knowing adsorption amount and using calibration curve, the remained concentration of dye was determined. The calibration curve of the spectrophotometer is shown in figure 3. For example, at pH = 3 and initial dye concentration of 50 mg/l, different doses of NZVI were added and at specified contact times the sampling process were done and the remained dye concentration were determined.

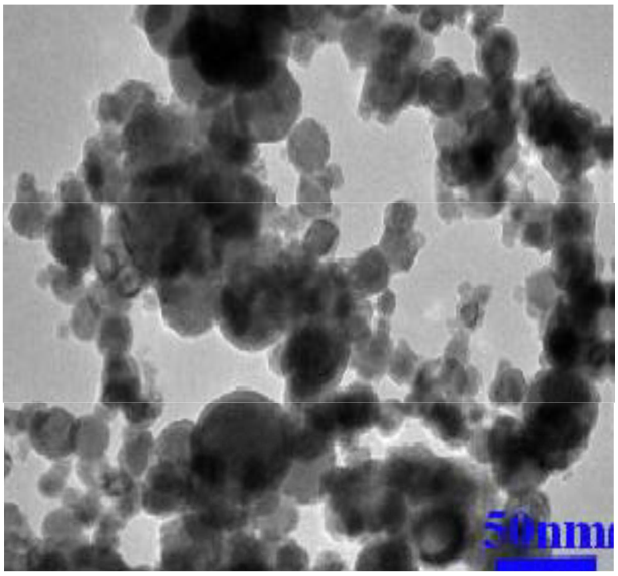

Figure 1. Nanoscale zero-valent iron (NZVI) image with transmission electron microscopy

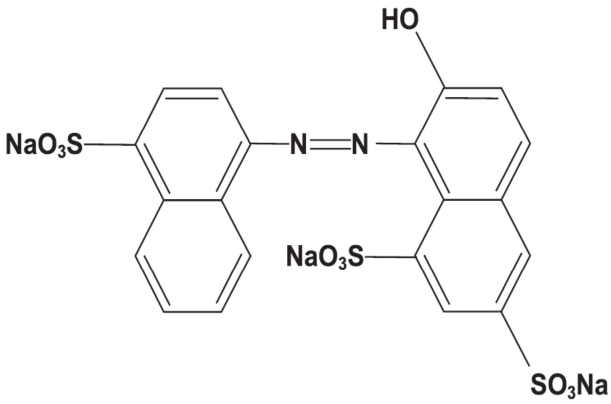

Figure 2. Chemical structure of acid red 18 (AR18)

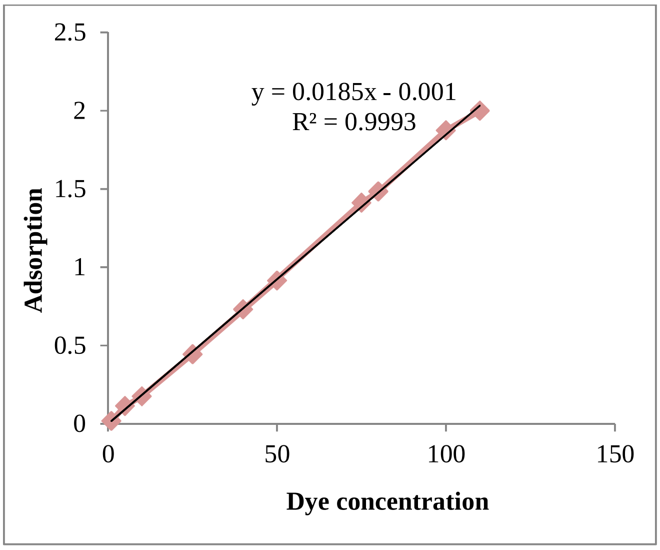

Figure 3. Calibration curve for measuring acid red 18 (AR18) concentration

3. Results

The results of the experiments are shown in figures 4-7. In these figures 4-7 the effects of contact time, initial dye concentration, pH and NZVI concentration on color removal efficiency in each stage is shown. The results show that by increasing the concentration of NZVI and contact time increase the removal efficiency. By the decrease of initial dye concentration and the amount of pH to a certain value the removal efficiency also increases.

Test results show that at contact time of 80 minutes, pH = 3 and concentration of NZVI = 2 g/l, the dye removal efficiency was 94% and by increasing the pH to 9, the removal efficiency of the processes were decreased to 28%.

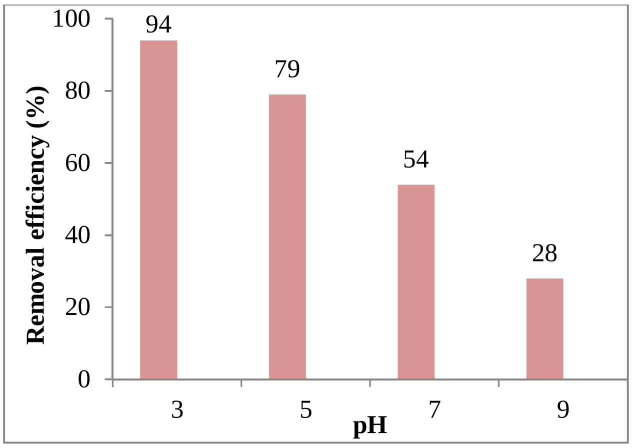

Figure 4. Effect of pH on the efficiency of the process (dye concentration = 25 mg/l, contact time = 80 minutes, nanoscale zero-valent iron concentration = 2 g/l)

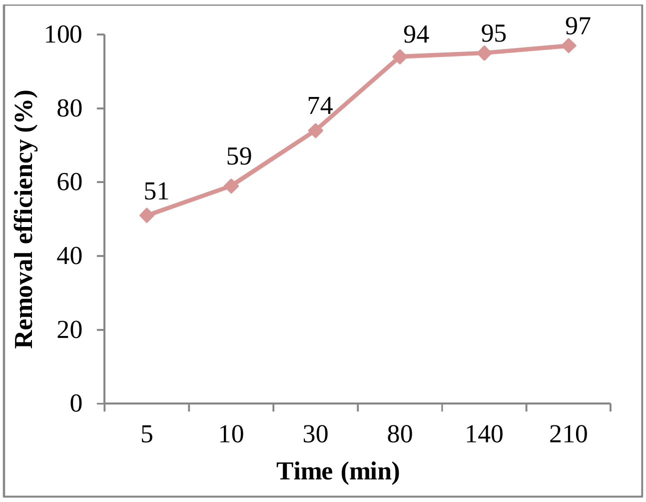

Figure 5. Effect of contact time on the efficiency of the process (dye concentration: 25 mg/l, pH = 3, nanoscale zero-valent iron concentration: 2 g/l)

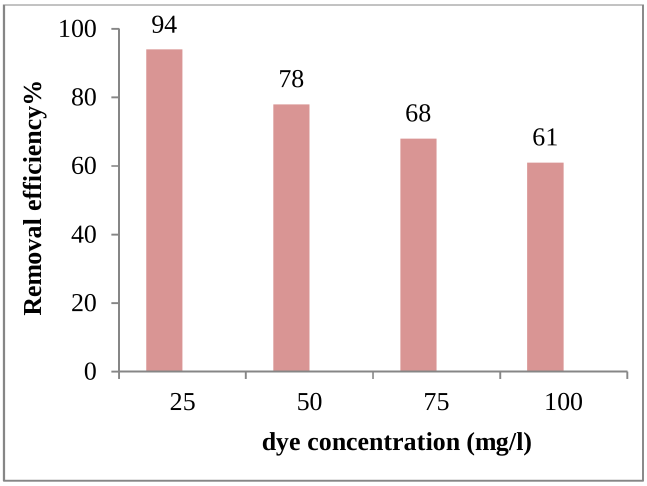

Figure 6. Effect of initial dye concentration on the efficiency of the process (time = 80 minutes, pH = 3, nanoscale zero-valent iron concentration = 2 g/l)

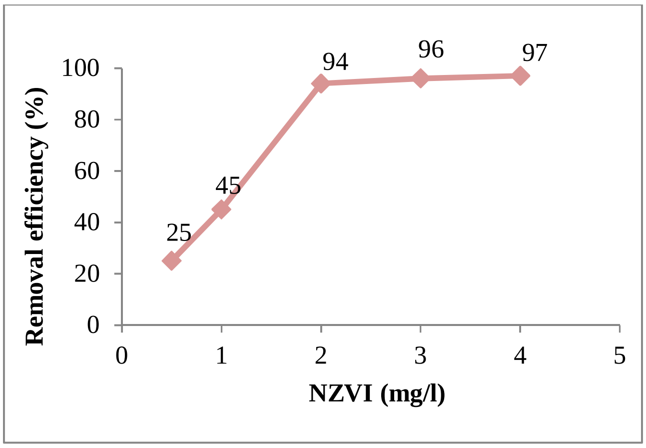

Figure 7. Effect of nanoscale zero-valent iron on the efficiency of the process (time = 80 minutes, pH = 3, initial dye concentration = 25 mg/l)

The effect of pH value on the AR18 decolorization was examined at initial pH values of 3, 5, 7, and 9 (Figure 4). As figure 4 illustrates, initial pH value of the solution significantly influenced color removal. The removal efficiency of AR18 was much higher at initial pH values of 3 and 5 compared to values of 7 and 9. With initial pH concentration of 3, 94% removal efficiency was achieved after 80 minutes of treatment. However, with pH concentration of 9, 28% removal efficiency was achieved after 80 minutes. The color removal percentage was 94.0, 78, 68, and 61% at initial dye concentrations of 25, 50, 75, and 100 mg/l, respectively (Figure 6). Figure 7 shows dye removal efficiency in different concentrations of NZVI. By increasing NZVI from 0.5 to 4.0 g/l at pH concentration of 3, the removal efficiency increased from 25% to 97%.

4. Discussion

The real dye wastewater has an extensive range of initial pH values, and the solution pH is an important operating parameter affecting AR18 removal efficiency in NZVI process. The surface of NZVI generates Fe^{2+} in solutions in acidic conditions, which is presented as Eq. (1). (29, 30).

$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2$ (1)

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. This occurs because NZVI is easily dissolved in acidic solutions, and hence, produces Fe^{2+} ions. In increased pH values, Fe^{2+} ions originating from the NZVI can form ferrous hydroxide precipitates on the surface of NZVI, occupying the reactive sites, and hence, hindering the reaction process (30). Therefore, optimized pH value for conducting the NZVI process experiments is found to be 3.0. Barbusinski and Majewski (25) were reached to 99.9% removal efficiency in a study with AR18 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 a significant effect on the dye removal. They also found that in the pH range of 2.5-3.5, dye removal happen with high speed and if the amount of pH descends to 2 or increase from 3.5 to 4.0, a rapid decline will occur in removal efficiency.

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 26.0% to 99.2%. pH = 3 and NZVI equal to 2 g/l were the optimum values for acid yellow 28 removal (16).

A study by Shu et al. (17) on the removal of dye solution of acid black 24 through the integration of NZVI and UV/H_2O_2, they concluded that when pH = 3, the concentration of NZVI is 0.33 g/l, concentration of hydrogen peroxide is 93 mmol/l and in the contact time of 60 minutes, had the highest efficiency so that more than 99% of the existed dye in the solution was removed.

Mozia et al. (28) have used hybrid membrane system using photocatalytic decomposition process for AR18 decomposition. The dye was completely decomposed during 5 hours but in nano iron particles process as shown in figure 5 at 80 minutes contact time, thus, the removal efficiency was 94% and it was better than Mozia et al. (29), 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 nanoparticle iron process decrease from 94% to 61%. 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 (16,17).

Figure 7 shows that by increasing NZVI concentration, the removal efficiency increases. This is due to the fact that a higher dosage of NZVI provides substantially more surface active sites to accelerate the initial reaction. This results in more iron ions colliding with azo dye molecules, and thus, removing color (30).

In another study, Mozia et al. (29) used the photocatalytic process for decomposition of AR18. In this study, the initial adsorbent concentration, dosage, and reaction temperature were studied. This process compared to the process which was used in our research is quite complex. This process (iron nanoparticles) compared to other processes is used more because of its accessibility, safety for the environment, ease of operation, and high efficiency (16,22). This process is useful for the removal of azo dyes.

According to the results, the iron nanoparticle 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.

Conflict of Interests

The Authors have no conflict of interest.

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