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ABSTRACT
Although dyes are widely used in textile industries, they are carcinogenic, teratogenic and mutagenic. Industries discharge their wastewater containing a variety of colors into water resources and make harmful effect on the environment. The present study aims to Evaluate removal of reactive red 198 by nanoparticle zero valent iron (NZVI) in the presence of hydrogen peroxide from aqueous solution. The effective parameters on the removal of dye such as the hydrogen peroxide concentration of NZVI, contact time, pH and dye concentration were investigated and optimized. According to the results, the combination of NZVI with hydrogen peroxide is more effective than single hydrogen peroxide. At pH = 4, contact time= 40 min, 200 M of hydrogen peroxide, dye concentration= 75 mg/L and concentration of NZVI 2g/L, color removal was achieved 91% approximately. Based on the results of experiments, using hydrogen peroxide- NZVI has high efficiency in removal of azo dye type.

Keywords: Dye removal, Hydrogen peroxide, Reactive Red 198, Zero valent-iron nanoparticles

INTRODUCTION
Textile industry is known as an important industry and indicates the rate of development in countries around the world. In addition, industries which produce chromatic wastewater include intiction industry, cosmetic industry, paper and pharmaceutical [1-8]. In intiction industries, about 15 percent of total color enter into the sewage system and color wastewater becomes produced [9]. There are several chromogenic materials which are used in industry and most common colors are azo group. Azo dyes contain a large synthetic group which have one or more azo bands (-N = N-). In order to decolor colored wastewater, various methods have been studied by many researchers, including physio-chemical methods such as ultrafiltration, reverse osmosis, ion exchange and surface adsorption to activated carbon, charcoal, wood chips and silica gel for color removal from effluent, which are relatively successful in applicability of COD [10, 11]. Since they just transfer aqueous pollution to the solid phase, they are not degraded and removed and they are not considered as comprehensive techniques as well. Thus, in recent years, advanced oxidation process, which is based on the production of free and active radicals, especially OH, is widely used by researchers and that is because of high oxidation power [12, 13]. In the process of zero-valent iron nanoparticles and
hydrogen peroxide in contrast with conventional Fenton process, hydroxyl radical production occurs in two stages. So, process efficiency is increased. On the other hand, after ferrous ion formed in Fenton processing, the efficiency of the process is reduced and stopped [14]. The most important reactions in the removal of organic material by hydrogen peroxide in the presence of zero-valent iron nanoparticles, are included as follows:

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\begin{align*}
\text{Fe}^0 + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{OH}^* \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^* \\
\text{OH}^* + \text{Reactive Red 198} & \rightarrow \text{H}_2\text{O} + \text{oxidized color}
\end{align*}
\]

A wide variety of polluters including chlorinated organic compounds, polychlorinated biphenyls, heavy metal ions, oxy-anions and dimethyl phthalate could be decolored with Nanoparticles Zero Valant Iron (NZVI) [15, 16]. Furthermore, inactivation of microorganisms in drinking water, wastewater, surface water and other resources are some applications of NZVI [17]. Colors are kinds of chemicals that may be unstable by this process and recently some azo colors are used for investigating on degradation [18, 19]. So, according to the introduction, due to the high efficiency of this process for removal of various polluters like chromatic materials, the main purpose of this study is to evaluate the efficiency of hydrogen peroxide with the presence of zero-valent iron nanoparticles for removal of Reactive Red 198 solutions in water.

**EXPERIMENTAL**

**Materials and methods**

All the sodium borohydride and ferric chloride (96%w/w) were supplied from Merck and High Media Co. respectively. Synthesis of Nano-particles zero-valent iron Nanoparticles were synthesized by adding the solution of sodium borohydride 0.16 M to the solution of hydrated ferric chloride 0.1 M at ambient temperature. In order to produce the Ferric chloride solution, deionized water that neutralized with N$_2$ gas is used. In order to produce a solution of sodium borohydride, Sodium hydroxide 0.1 M is applied. After preparation, a solution of sodium borohydride is added to ferric chloride solution drop by drop and in vacuum conditions and
intense mixing. This phase takes about 30 min. During the process, the beaker was closed so that the synthesis takes place in a vacuum condition. Sodium borohydride reacted with ferric chloride according to first reaction and finally it leads to Fe\textsuperscript{0} revival.

\begin{equation}
2\text{FeCl}_3\cdot6\text{H}_2\text{O}_2 + 6\text{NaBH}_4 \rightarrow 2\text{Fe}^0 + 6\text{B(OH)}_3 + 21\text{H}_2 + 6\text{NaCl}
\end{equation}

After reaction, iron nanoparticles were deposited in black particles. Reaction was conducted under hood because as a result of chemical reactions, hydrogen gas is produced. In addition, it is necessary to mix reaction vessel with a blast-resistant hopper to reduce possibility of ignition. SEM electron microscopy is used to determine characteristics of iron nanoparticles.

For measurement pH with pH meter model Mettler Toledo and to pH adjustment we use Sodium hydroxide (1.5 mol L\textsuperscript{-1}) 0.1 N and hydrochloric acid (37%w/w) 0.1 N. Reactive Red 198 is a color-molecular-weight anionic equivalent of 968.21 g/mole and absorption peak $\lambda_{\text{max}}=530$ nm. Reactive Red 198 ($\text{C}_{27}\text{H}_{18}\text{Cl}\text{N}_7\text{Na}_4\text{O}_{15}\text{S}_5$) which is used in this study is of laboratory type and manufactured by Merck, Germany. Chemical formula of this compound is shown in Fig 1 [20].

**Removal of Reactive Red 198 Tests**

In this research, studied variables include: exposure time (5, 10, 20, 40, 80 min), initial concentration of nanoparticles (0.5, 1, 2, 3, 4 g/L), pH (4, 6, 8, 10), hydrogen peroxide (25, 100, 150, 200, 300 Mmol) and initial concentration of...
reactive red 198 (25, 50, 75, 100 mg/L).
To perform experiments, different concentrations of color was added to volume of 250 ml to 500 ml beakers and pH of color was adjusted in desired range. Then, different concentrations of nanoparticles and hydrogen peroxide were added in 250 ml of color with different initial concentrations and after mixing by jar with around 250 rpm at certain intervals, sampling were done. Remaining concentration was determined by rate of absorbance and using a calibration curve.

RESULTS
Characterizations of Nanoparticles
In Fig 2. image of synthesized nanoparticles is shown. results of SEM particle, shows size range of particles in nano limitation (diameters of <100 nm). XRD pattern of dry NZVI particles was shown in Fig. 3. X-ray diffraction (XRD) analysis (Siemens, D5000 with Cu Kα radiation) was used to determine the presence of zero-valent iron nanoparticles in the studied absorbent structure. XRD pattern of Fe⁰ is visible in Fig. 3. The peak at the 2θ=44.7° indicated the presence of NZVI in the synthesized absorbent structure.

Results of Reactive Red 198 removal
Results are shown in Figs. 4 to 8. In these graphs effect of contact time, initial dye concentration, pH, concentration of nanoparticles and hydrogen peroxide concentration on color removal efficiency is shown. Results show that increasing...
concentrations of nanoparticles, hydrogen peroxide, contact time, initial dye concentration and pH reduction to a specified level, increases removal efficiency. Optimum experimental results show that exposure time of 40 min, pH=4, dye concentration of 75 mg/L, concentration of nanoparticles 2 g/L and hydrogen peroxide concentration 200 Mmol, hydrogen peroxide dye removal in process with nanoparticles and hydrogen peroxide about 91 and 34% respectively and by increasing pH to 10, color removal rate of about 27 and 10% reduced. Effects of pH on color removal efficiency are clearly shown in Fig. 4. So that by lowering pH of 10 to 4, removal process, hydrogen peroxide and hydrogen peroxide-iron nanoparticles has increased from 27 to 91 and 10 to 34%, respectively. Fig. 5 shows that with increasing contact time, color removal rate is increased so that by increasing time from 5 to 80 min, removal process, hydrogen peroxide and hydrogen peroxide-iron nanoparticles increased from 50 to 97 and 8 to 29%, respectively. Fig. 6 shows that with increasing concentrations of color, its removal rate is reduced so that by increasing the dye concentration of 25 to 100 mg/L, the removal process, hydrogen peroxide and hydrogen peroxide-iron nanoparticles reduced 99 to 80 and 38 to 26%, respectively. Fig. 7 shows clearly different levels of color removal efficiency of NZVI. With increasing NZVI from 0.5 to 4 g/L at pH 4 and 200 Mmol for hydrogen peroxide, in the process of hydrogen peroxide-iron nanoparticles, color removal rate is increased about 25 to 98%. In Fig. 8 The effect of hydrogen peroxide was investigated in doses of 25 to 300 Mmol, in pH=4 and it was found that the removal efficiency for the highest and lowest amounts of H₂O₂ was about 8 to 37%. The impact of increased efficiency of hydrogen peroxide color removal clearly has shown in Fig. 8. Efficiency of color removal increases by increasing amount of hydrogen peroxide in presence of NZVI. So that by increasing amount of hydrogen peroxide at a pH of 4 from about 25 to 300 Mmol, color removal rate increases 80 to 99 percent.

DISCUSSION
Results of this study show that acidic pH is effective in achieving maximum color removal. This is a major problem that requires to acidification environment. At lower pH than 3 to formation of Fe(OH)²⁺ development with hydrogen peroxide reacts slowly, reduces amount of hydroxyl radicals, resulting in reduced process efficiency. In alkaline pH Fe²⁺ is also converted to Fe³⁺ and in Fe(OH)₃ state removed from catalytic cycle [21]. In this study, pH of 4 is optimized condition and it’s clear in Fig. 4 that maximum efficiency is achieved in pH=4 and color removal efficiency has decreased with increasing pH. It has been demonstrated in previous studies that solution pH can affect on absorbent surface charges, degree of ionization various contaminants, separating functional groups on active sites attractive and effective dye molecule structures [22, 23] In fact, under acidic pH, linked sites absorbing hydrogen ions works closely with each other as ligands interface (bridge) between absorber and dye molecule.
In these conditions, lower pH values, provides favorite conditions for reactive dyes removal [24, 25]. Gulnaz et al removal of reactive dye by Potamogeton Crispus 198 indicates that decrease pH from 5 to 1, increase color removal efficiency that is compatible with results of present study [20]. As shown in Fig. 8 is color removal efficiency increases by increasing amount of hydrogen peroxide at pH=4. This is because of increasing concentration of hydrogen peroxide, which due to acidification of environment and amplify generates ions Fe²⁺ and increased production of hydroxyl radicals, and result increasing efficiency of dye removal [26]. Contact time is one of most important parameters for practical applications in adsorption process. Based on results of this study (Fig. 5), removal percent of Reactive Red 198 by adsorbent increased rapidly during early stages of adsorption and then at a slower speed and appropriate time, spend time to reach a state of equilibrium during a period of about 80 min. In other hand, as shown in Fig. 5, dye uptake was very rapid during first 5 min, and then absorbs speed decreased rapidly over time and eventually balance is reached after 80 min, maximum reduction in contact time of 80 min was 97 percent [27]. Generally, rate of removal (adsorbent) is rapid at first, but gradually decreased with time until equilibrium is reached. It is due to fact that at beginning and in early stages of absorption, a large number of empty surface sites are available for absorption, but with spending of time, empty remain site surface, are difficult to absorb pollutants. Which could be due to deterrent forces between molecules adsorb on surface of solid and liquid mass [28]. Similar results have been reported by Gulnaz [20]. In another study, mozia et al have used hybrid membrane system to analyze Acid Red 18 for decomposition in photocatalytic process. In this study, color is completely removed in 5 hours had less efficiency compared to presented study [29]. Initial dye concentration, provides a significant driving force to overcome overall resistance substantially phases of mass transfer between liquid and solid colors. With increasing concentrations of color, its removal rate decreases that this could be due to NZVI surface occupation by dye molecules, ions Fe²⁺ less access to NZVI dye molecules and less access to hydrogen peroxide. This topic is similar to other studies [30]. Adsorbent concentration, an important parameter that effects on absorption and hence determining absorption capacity for a given initial concentration of color is for Reactive Red 198, is important. As is shown in Fig. 7, Removal of Reactive Red 198, is applied by adsorbent dosage and by increasing adsorbent dose increases up to a certain value highly. This result can be explained by fact that absorption site, remained saturated during adsorption, while Increasing number of sites available dose increases adsorbents. In another study, mozia et al use photocatalytic process to analyze Acid Red 18. In this study, initial concentration of adsorbrates, catalysts dose and reaction temperature were investigated [31]. This process compared to processes of this research is a quite complex process. According that this process iron nanoparticles in presence of hydrogen peroxide, is more accessible, environmentally safer, easy operation with high efficiency rather than other advanced oxidation processes [18]. Widespread use of this method is result of these advantages. Therefore, this process is useful for removal of azo dyes.

CONCLUSION
According to results of research, nanoparticles of hydrogen peroxide has advantages such as high removal efficiency and short reaction time and could be considered as an appropriate option for removal of azo dyes in aqueous environment. But hydrogen peroxide has less efficiency for removal of azo dyes in aqueous environments. The results confirm, Azo dyes can be removed by this process. When NZVI were used with Fenton process, amount of removing will be increased. 5 factors effects were studied like pH, contact time, initial dye concentration, adsorbent concentration and initial Hydrogen peroxide concentration. Optimized parameters for this process are pH=4, contact time= 40 min, initial dye concentration= 75 mg/L, adsorbent concentration= 2 g/L and initial Hydrogen peroxide concentration= 200 Mmol.

CONFLICT OF INTEREST
The authors declare that there are no conflicts of interest regarding the publication of this manuscript.

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