Optimizing the Factors of Color Concentration, pH and the Amount of Nanoparticles in Removal of R198 Reactive Dye under UV Rays by Zinc Oxide Nanoparticles Extracted from Leaching Residue of Zinc Melting Factory

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Abstract

In this study, zinc oxide nanoparticles were obtained from purified solution from the zinc melting residue factory in Bafgh. The obtained nanoparticles by various devices were studied and analyzed. The formation, purity and optical properties of zinc oxide nanoparticles were investigated by the infrared spectrometer (FTIR) test. Ultimately, these nanostructures were used to investigate their photocatalytic properties in the removal of reactive color R198 under UV rays, which has been widely used color in the textile industry and is harmful for the environment. In the bleaching process of reactive color R198, three effective parameters which include the color concentration, pH and amount of nanoparticle were optimized. The results of X-Ray Diffraction patterns (XRD) represent the crystallinity and hexagonal structure of the samples. According to the Transmitted Electron Microscope (TEM) images, the sample have clear spherical shapes and distinct hexagonal dimensions in the range of 40-120nm. Under optimal conditions with color concentration of 30 ml, pH = 7 and the amount of nanoparticle 0.12gm at 120 minutes the bleaching process under ultra-violet rays about 99% of the color was degraded or destroyed.

Keywords: Zinc Oxide Nanoparticles, Photocatalytic Properties, Reactive Color, UV Rays.

1. Introduction

Textile and dyeing industries are important industries in every country, and they are considered as the origin of many other industries. These industries use a large amount of water [1] and are among the largest water consuming industries. As a matter of fact, the rate of water consumption in these industries is between 25 to 250 cubic meters per ton of product [2]. Studies has shown that annually about 40 million tons of textiles are produced in the world, and the residue produced by the industries is about 4 to 8 million cubic meters [3].

The most characteristic feature of the textile industries residue is its color [4]. More than 100,000 types of colors are commercially available and more than 7x10⁵ tons of colored materials are produced annually [5, 6]. The colors are classified into anions (acidic and reactive colors), cations (alkaline colors) and non-ion [7-10]. It is estimated that annually, about half million tons of Azo and two hundred thousand tons of reactive colors are produced worldwide. Also, the Azobenzene dyes and reactive colors constitute 60-70% and 20-25% of the usage in the industries, respectively [11]. Red color RB198 is a highly reactive chemical color in the textile industry.

Red198, with a molecular weight of 984.183 grams per mole and the chemical formula of C₂₇H₁₈ClN₇Na₄O₁₆S₅, is an anion soluble in water, referred to by the trademark R198 [12]. Reactive colors, which are soluble in water, are one of the most important group of colors used in the textile industries, due to high brightness, low energy consumption and simple application method [13]. The discharged wastewater (or residue) from textile industry has low BOD and high COD [8]. Wastewater containing colors such as R198 is hazardous to the ecosystem and health. These materials, with their low light penetration, may affect the light activity of aquatic plants and increase the suspended matter and water turbidity. In addition, colors are cancerous to humans. Therefore, it is necessary to investigate a proper purification method, according to existing standards [14]. Removing colors from sewage is more important than the colorless organic matter, because the presence of a small amount of color (less than 1 ppm) is visible [15].

The colorful water is not only unpleasant aesthetically, but also reduces the penetration of light into the water, resulting in decrease in the yield of photosynthesis of aquatic plants [15-18]. Generally, because of complex molecular structures of colors, they are relatively resistant to biodegradability [19].
The purification of wastewater containing color is very difficult; because the colors are tough organic molecules resistant to aerobic decomposition and stable to light, heat and oxidizing agents [20]. Various methods have been mentioned for removing the colors from water and sewage, including biological processes, combination of biochemical and chemical processes, chemical oxidation, absorption, coagulation, membrane processes, and each has its own advantages and disadvantages [21]. Biological purification systems, due to the high toxicity of dyes for the microorganisms present in the process, and most of which resistant against biological degradation, have a low efficiency in color removal. Ultrasonic and reverse osmosis methods are not economical, because of high operating costs, while other methods are limited due to the operating costs [22]. In addition, in the purification method, the pollutant is transmitted from one phase to another, and the mineralization of toxic pollutants is not done thoroughly [23]. The advanced oxidation processes have been considered, based on photocatalytic reactions and due to their efficiency ability for mineralization of pollutants and the fact that they do not create a waste problem [24]. The photocatalytic process is one of the advanced oxidation processes, which has shown the capability for eliminating various toxic and degradable compounds. When semi-conductive photocatalyst materials are exposed to certain light, they start or accelerate chemical reactions (such as decomposition of organic molecules). Metal nanoparticles and metal oxide are the most commonly used nanostructured nano-catalyst. Nanometric catalyst particles, with respect to the ratio of surface to volume, in comparison with larger particles or bulk materials, have shown significant reaction [25]. Semiconductors with nano structure, such as nanoparticles of zinc oxide, nanocomposites, nanotubes and nano-titanium dioxide membranes are widely used as catalysts for the decomposition and mineralization of organic dyes [23,24,26-34]. Zinc oxide, as a semiconductor, can be considered an ideal photocatalyst, which is both economical and environmentally friendly. The dispersion and cross-section of zinc oxide, which depends on its synthesis method, is an important factor for determining its photocatalytic activity; it has gained attention because of high optical sensitivity, non-toxic nature, high stability, polar property, wide energy gap (3.37 EV) and high efficiency in electron production [34, 35]. Literature studies suggest that zinc oxide nanoparticles can act as catalyst in the presence of ultraviolet radiation. Photocatalytic processes are based on the production of active hydroxyl radicals, which results in the complete mineralization of organic molecules [28, 32, 36]. When zinc oxide semiconductor is exposed to UV rays, it results in the formation of a pair of electron-cavities, due to light stimulation. The formed cavities have the potential of high oxidation that can directly oxidize the organic pollutants or react with water molecules and hydroxide ions and produce reactive hydroxyl radicals [37]. Electrons in the conduction band can produce hydroxyl radicals, or react with electron-receptor factors such as oxygen, and produce reactive peroxide radicals (superoxide anions) that can be part of the mineralization process [23].

Zinc oxide are one of the main materials used in technology, due to their optical and electrical properties, the ability to absorb a wide range of electromagnetic waves, photocatalytic capability when exposed to radiation, high electron yield and movement, separation of light electrons and the presence of pores within technology [38, 39]. In this research, zinc oxide nanoparticles, obtained from the purified solution of the residual waste of zinc melting factory in Baftgh, were used for bleaching operations. The main aim of this research was to bleach R198 reactive dye solutions under UV rays and study the effect of three parameters of color concentration, pH and the amount of nanoparticles on coloring.

2. Materials and Methods
2.1. Implemented Materials

The raw materials used in this study include sodium carbonate, standard German Merck and purified zinc solution obtained from Baftgh zinc melting factory. The dye material used was red reactive color RB model Red198, with the trademark R198, a molecular mass of 988.215 grams per mole and the chemical formula of C_{27}H_{18}CIN_{7}Na_{4}O_{16}S_{5}, obtained from the Gohar Chap Textile Company, whose chemical structure is shown in Fig. 1..

![Chemical structure of Reactive Red 198.](image)

2.2. Equipment

All measurements were done on a laboratory scale. Volumetric flask, filter paper, burette, thermometer, pH meter, magnetic stirrer, high mechanical agitator, oven dryer, glass watch, crucible and high temperature furnace were used for making nano zinc oxide.
The resulting nanoparticles were approved by the FTIR device of Tensor 27 Bruker model. The measurement of the dimensions of the nanoparticles was done by Transmitted Electron Microscopy (TEM; JEOL 2010), and the measurement of the shape of nanoparticles was done by Scanning Electron Microscope (SEM; Philips XL30). Characterization of the formed nanoparticles was conducted by XRD (GNR Model APD 2000 Pro).

The average size of nanoparticles of zinc oxide was calculated by Sherer equation, using the XPERET software. In order to measure the amount of color absorbance in these experiments, a spectrophotometer device was used with the UV-Visible Cary100 model created by the Australian Varian Inc.

2.3. Production of Zinc Oxide Nanoparticles from Purified Zinc Solution

In order to prepare zinc oxide nanoparticles, first the purified zinc solution obtained from the residue of zinc melting factory in Bafgh was prepared. The concentration of this solution was 110 g/l with the solution concentration of 0.1 molar. The pH of the diluted solution was 6.27, hence 96% of sulfuric acid was added to reach a pH of 1 to 2.

Then, 400 ml of the above solution was heated at 54° C on a heater, while the heater was on, underneath a mechanical stirrer with 1000 rpm was placed, while stirring the solution, sodium carbonate of 0.5 molar was added in drops through the burette (to prevent the aggregate dimension of the nanoparticles).

Later, at pH 3.6, the solution was precipitated. The solution was passed through a filter paper, and when it settled down, it was washed twice with distilled water. Afterwards, the filter paper was placed on a watch glass and dried in the oven for 24 hours at 70° C (Fig. 2.). Finally, the produced material was heated at 830° C for 3 hours in a furnace and the sample obtained was identified and analyzed using XRD, FTIR, SEM and TEM methods.

2.4. Reactive Color R198 Degradation by Photocatalytic Method under UV Rays

At the beginning of the bleaching experiments, an initial 'A' solution of the desired color was made. First, a solution with a concentration of 0.7487 g/l from R198 color was created.

From this initial solution ‘A’, samples with specific color concentrations were prepared for bleaching experiments.

The design of the bleaching experiment of R198 was carried out according to the usual experimental design. Since the nature of the reactions changed at different levels of the parameter, it was not possible to use statistical methods for the experiments.

As a result, conventional design methods were used. For this purpose, three series of experiments were designed based on the pH of variables, the color concentration variable of R198 and the amount of nanoparticles of different minerals at 30 to 120 minutes in four levels (Table 1.).

Optimization of factor levels was performed by examining one parameter as a variable and the rest of parameters as constant.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
<th>Level 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min)</td>
<td>30</td>
<td>60</td>
<td>90</td>
<td>120</td>
</tr>
<tr>
<td>Color Concentration R198 (ml from mother color solution)</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>95</td>
</tr>
<tr>
<td>pH</td>
<td>3</td>
<td>5</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Amount of Mineral Nanoparticles (gr)</td>
<td>0.060</td>
<td>0.080</td>
<td>0.100</td>
<td>0.120</td>
</tr>
</tbody>
</table>

In this investigation, each parameter was examined at different time intervals. For the purpose of optimizing a parameter, in the next experiment, the constant parameter value was considered as the optimum value.

3. Results and Discussion

3.1. Specifications of Zinc Oxide Nanoparticles Produced from Purified Zinc Solution

The raw material used to prepare the nanoparticles should be of high purity, so that the solution produced is pure and shows even properties.

Thus, the purified solution was taken from the zinc melting factory of Bafgh. The FTIR test result for the synthesized sample of zinc oxide nanoparticles is shown in Fig. 2.. The FTIR spectrum in Fig. 2. shows, a band of 3500 that relates to the tensile vibration of hydroxyl (OH) group of water molecules that are connected by hydrogen bond to the surface of zinc oxide nanoparticles. Three peaks of absorption are seen at 1107, 1174 and 1221 (in the range of 1000).

![Fig. 2. FTIR Diagram of Synthesized Zinc Oxide Nanoparticles.](image-url)
At this limit, with respect to the goal to investigate the possibility of forming a metal bond with the organic structure of zinc oxide nanoparticle, the emergence of a strong peak in the range below 1000 indicates the formation of nanoparticles of mineral zinc oxide in the formation of bonding to remove the color pollutants. The observed peak in the 459 wave number is known as the tensile vibration of ZnO. The appearance of this peak with high intensity indicates the structural formation of a nanoparticle of zinc oxide. The results of XRD test for the synthesized sample of zinc oxide nanoparticle is shown in Fig. 3. As shown in Fig. 3., the initial material, when heated for an hour at 825° C, easily decomposed into ZnO crystalline phase. The results show that the products are pure phase. The average size of zinc oxide nanoparticles was calculated by Sherrer equation, using Xpert software of about 85 nm.

The SEM image of the synthesized samples of zinc oxide nanoparticles is shown in Fig. 4. As shown in Fig. 4, some nanoparticles agglomerated together and precipitated during the heating process and demonstrated the morphology of zinc oxide particle as spherical nanosized.

As can be seen, the average size of the particle is between 40 and 120 nm, which is consistent with the results of XRD analysis.

3.2. Optimization of the Factors of Color Concentration, pH and the Amount of Nanoparticle in R198 Color Degradation

3.2.1. Optimization of Color Concentration in Bleaching R198

In Fig. 6.(a), the color degradation test results related to 30 to 120 minutes for a sample with concentrations of 50, 70, 95 and 30 ml color for the R198 specimen with nanoparticle value of 0.1 gram and pH = 7 are shown. In addition, for a sample of 95 ml, the color concentration was continued for up to 150 minutes (Fig. 6.(b)). The absorbance amount proportional to the test time of the above samples with different color concentrations at different times, obtained from the spectrophotometer device, is shown in Fig. 7. As it can be seen, at 30 minutes, the rate of sample color at 30 ml concentration was higher than others, and after that, the sample were concentrated with a concentration of 50, 70 and 95 ml. At 60 minutes, the specimen with color concentration of 30 ml was completely decolored, and the sample at color concentration of 50 ml was close to being complete colorless. Samples with a concentration of 70 and 95 ml diminished relative to the time interval of 30 minutes. At 90 minutes, samples of 30 and 50 ml of color concentration were colorless, the sample with a color concentration of 70 ml was almost completely colorless and the specimen with a concentration of 70 ml gave a better result than the rest. The sample with 95 ml color concentration at 60 minutes, became less colored. At 120 minutes, all three samples with color concentration of 30, 50 and 70 ml were colorless and the sample with color concentration of 95 ml was less colored than it was at 90 minutes. The specimen with color concentration of 95 ml at 120 minutes, in comparison with the rest of the samples with color concentrations of 30, 50 and 70 ml, did not lose its color. Therefore, the test for the sample with color concentration of 95 ml was continued for 150 minutes.
At 150 minutes, it was observed that the sample with 95 ml concentration became completely colorless. Based on the results, it was found that the sample with color concentration of 30 ml yields the best result. It grew completely colorless at 60 minutes, after which the sample with concentration of 50 ml turned pale. At 90 minutes, the sample with color concentration of 70 ml was almost colorless, and finally, the sample with 95 ml concentration became colorless at 150 minutes. From this test, it was concluded that the bleaching of R198 up to 60 minutes has an inverse relationship with color concentration. The lesser the color concentration is, the faster the bleaching will be, but from 90 to 120 minutes, the sample with concentration of 70 ml is superior than the rest.

3.2.2. pH Optimization in Bleaching R198 Dye

In Fig. 8, the test results relating to the R198 color sample with color concentration of 70 ml and 0.1 gram amount of nanoparticle for 30 to 120 minutes at different pH values are shown. Fig. 9, shows, the absorbance time for the samples with different pH values at different times, obtained from the spectrophotometer device. As can be seen, at 30 minutes, the colorless amount of the samples is at maximum with the pH value of 7 and 10. At 60 minutes, the samples with a pH of 7 and 10 exhibited roughly the same degree of colorlessness, and at 30 minutes there is more decrease. The sample with pH of 5 was colorless relative to 30 minutes, and the sample with pH of 3 remained almost unchanged. At 90 minutes, the sample with pH of 7, was close to the state of complete colorlessness and its colorlessness was less than that of the sample with pH of 10. At 60 minute the sample with pH of 10 became less intense. The samples with pH of 3 and 5, each were colorless for the duration of 60 minutes. At 120 minutes, the two samples with pH of 7 and 10 were colorless and the two samples with pH of 3 and 5 became less than 90 minutes. Based on the results, the sample with pH of 7 gave the best result and colorlessness within 90 minutes. At 30 and 60 minutes, the performance of the two samples with pH of 7 and 10 were similar to each other, and at 90 minutes it was determined that whose pH is better.
This test result shows, that bleaching R198 color with different pH values was optimal at pH 7, and then at pH of 10, the performance was better. This is not a linear relationship, since after these two pH values, the better performance belonged to pH of 5.

3.2.3. Optimization of the Amount of Nanoparticle in Bleaching R198

The adsorption rate related to 30, 60 and 70 minutes, with different amounts of mineral nanoparticles for the R198 color with a color concentration of 50 ml and pH of 7 (optimal pH), obtained from the spectrophotometer device is shown in Fig. 10. And Fig. 11. Since the performance of the sample with pH=7 and 0.1g of nanoparticles was investigated, only three nanoparticle amounts of 0.06, 0.08 and 0.12 g were investigated. As observed, according to the experiments of series 1 and 2 for the sample with a color concentration of 50 ml and pH=7 and nanoparticle amount of 0.1g, at 30 minutes, the sample with value of 0.12g of nanoparticles had better performance than the samples with the amount of 0.06, 0.08 and 0.1g nanoparticles. It was shown that the performance of the sample with a value of 0.1g nanoparticles was weaker than the rest. In fact, 0.12 grams of nanoparticles was better than the rest, and after that, 0.08 grams and 0.06 grams had better performances, and finally, 0.1 grams nanoparticles showed weaker performance. According to the experiments of series 1 and 2, the sample with color concentration of 50 ml, pH=7 and 0.1gram amount of nanoparticles at 60 minutes as well as the sample with 0.12g amount of nanoparticles performed better than the samples with 0.06, 0.08 and 0.1 grams of nanoparticles. It is clear that at this time (i.e. 60 minutes), the sample with 0.12g nanoparticles was completely colorless. The sample with 0.1 grams of nanoparticles was near the state of colorlessness, and next in rank, it was the sample with 0.08 grams of nanoparticles that performed better, and finally, the sample with 0.06 grams of nanoparticle.

At 70 minutes, it was found that the samples with 0.08 grams and 0.12 grams of nanoparticles were completely colorless, and the sample with 0.06 grams of nanoparticles was almost colorless. Based on the results, it was found that the sample with 0.12 grams nanoparticle yields the best result and is completely colorless at 60 minutes, after which, it was the sample with 0.1 gram nanoparticles that became completely colorless. Meanwhile, the sample at 30 minutes had a weaker performance compared to the rest.

At 30 minutes, better performance in terms of colorlessness, belonged first to the sample with 0.12 grams nanoparticles, followed by sample of 0.08 grams, followed by two samples with the value of 0.06 grams and finally, the sample with 0.1 gram of nanoparticle.

At 60 minutes, the preferences of the sample in terms of colorlessness differ from the time of 30 minutes. From this test, it was concluded that bleaching R198 dye with different amounts of nanoparticles from 60 minutes onwards has a linear and direct relationship, and no matter how much more the amount of nanoparticles is, the bleaching is faster and stronger.

![Fig. 10. Test results of Series 5 from 30 to 70 minutes.](image)

![Fig. 11. The Effect of the Amount of Nanoparticles on Bleaching R198 Dye from 30 to 70 Minutes.](image)

4. Conclusions

This research was carried out with the aim of bleaching R198 dye from Gohar Chap Factory with zinc oxide nanoparticles extracted from leaching residues of the zinc factory in the city of Bafgh. In this regard, a purified zinc solution with a concentration of 110 g/l of waste was prepared from the zinc melting factory in Bafgh, and it was used for the production of nanoparticles. The test obtained results are as follows:

1. Material thermal decomposition (deposited sediment after drying in an oven) was performed at 830°C for three hours and zinc oxide was produced with dimensions of 40 to 120 nm.
2. X-Ray Diffraction patterns (XRD) results showed that the obtained structure is hexagonal.
3. Transmission Electron Microscopy (TEM) studies showed that the resulting nanoparticles have a spherical shape.
4. The optimum pH, nanoparticle and color concentration in the study of each effect on
bleaching R198 dye at 120 minutes were 7 gm, 12 gm, and 70 ml, respectively.

5. Color removal efficiency was measured in a test of studying the effect of amount of nanoparticles at 70 minutes, the effect of pH and the influence of R198 color concentration at 120 minutes, and the obtained results were 98.91%, 99% and 99%, respectively.

References