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Effect of Silica on the Ultrasonic/Persulfate Process for Degradation of Acid Black 1 in Aqueous Solutions

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Abstract

Azo dyes are the greatest classes of synthetic dyes, which are widely used in the textile industries. This study aimed at examining Acid Black 1 (AB1) removal from aqueous solution thermal activated persulfate using silica (SiO_2). The effects of operational parameters such as initial pH, initial concentration of AB1, SiO_2 dosage, and persulfate concentration were investigated and the chemical oxygen demand content was considered as a response. The results indicated that the removal efficiency had a direct relationship with concentration of SiO_2 and persulfate up to their optimum values, and was inversely correlated with the alkaline pH and elevated concentrations of AB1. Moreover, the removal efficiency was increased significantly by increasing the silica concentration from 25 mg/L to 100 mg/L. Ultimately, AB1 was completely removed after 45 minutes.

Keywords: Ultrasonic, Persulfate, Silica, Acid Black 1, Azo Dyes

1. Introduction

Overpopulation and the consequent increase of industrial activities generate high concentrations of pollutants leading to aquatic environment contamination (1). Rapid growth and developing of the textile industry result in the generation of high concentration of synthetic dyes, leading to contamination of the aquatic environment, which has become one of the main pollutants in water resources (2). In addition, contaminants generated from industrial effluents cause a main environmental problem. Various dyes have been used in various industry such as leather manufacturing, cosmetic, publishing and printing, food, paper, plastics and pigment industry (3). It was estimated over 7×10^5 tones of colors are made universally every year and about 10% to 15% of the colors are discharged into the environment without any purification process (4). In addition, 70% of the total production of dyes are azo dyes, which are difficult compounds to decompose due to the azo bond (N = N) and the aromatic rings, their toxicity, mutagenic, and aesthetic problems in the nature (5). Acid black1 is one of the azo dyes. Although toxic effects and environmental impact of the azo dyes are dependent on the number, type and position of substituent groups on aromatic compounds, these compounds have been poisoned for various organisms, including humans, animals, and plants. Hence, the removal of azo compounds is regarded as one of the greatest global concern (6, 7). There are several processes for treating colored wastewaters such as advanced oxidation, chemical oxidation, adsorption, biological filtration, and a combination of these procedures (3). The advanced oxidation process (AOP) is the most important process in the treatment of the colored wastewaters. High cost, long retention time, and generation of toxic by-products are drawbacks to the widespread use of some of these elimination processes. Nowadays, AOPs have been attracting much attention due to their ease of use, high efficiency and being economical (8-10). In recent years, the use of sulfate radicals has been considered as an effective AOP method to remove organic contaminants. Like hydroxyl radical (E = 2.8 V), sulfate radical (E = 2.6V) has a high oxidation potential. Additionally, sulfate radical has more chances to oxidize organic compounds at acidic pH compared to hydroxyl radical; also, it has a longer half-life (1). Persulfate (PS) as a source of sulfate radical possesses high stability at room temperature and aquatic environments. Persulfate can be activated by heat, UV light, and the transition metal elements (Men+) according to Equations below:

$$S_2O_8^{2-} + \frac{heat}{UV} \rightarrow 2SO_4^{-\bullet} \quad (1)$$

$$S_2O_8^{2-} + \left(Men^{+}\right) \rightarrow SO_4^{-\bullet} + \left(Me^{n+1}\right) + SO_4^{2-} \quad (2)$$

Among the advanced oxidation processes, ultrasonic is considered one of the most modern methods (11). Despite the advantages of these waves in the water treatment, the results of previous studies showed that the application of this wave alone is not sufficient for treating colored water.

Due to its low performance and requiring additional time and energy, this method cannot be used in large scales. To overcome these problems, a sonochemical process is used in combination with other processes such as the silica (SiO_2), US/O_3, and US /H_2O_2, which cause an increase in the performance and decrease in energy consumption (12, 13). There are three reaction sites in the mechanism of sonochemical reaction: a) cavity interior, b) the gas-liquid phase, and c) bulk liquid. Intranet of cavitation bubbles of water molecules occurs in the pyrolysis process and the hydroxyl radicals and hydrogen atoms are formed in the gas phase. Each of the pollutants reacts with hydroxyl radicals or heat and decomposed. In the common area of the gas-liquid, the similar reaction occurs but not in the liquid phase. The extra reaction is combining of hydroxyl radical to form H_2O_2. In the liquid phase, essentially all the contaminants react with the hydroxyl radical or H_2O_2 (14). The presence of SiO_2 during the cavitation process of US improved the decomposition rate of organic molecules, which provides extra cores for cavitation that is increased in the number of collisions (9). Nano particles smaller than cavitation bubbles can easily enter the area between the bubbles and water as a carrier and transmitter and polluting contact with the bubbles, particularly it is more necessary for nonvolatile hydrophilic contaminants (9).

Due to the advantages and specific characteristics of advanced oxidation processes for the removal of organic compounds, in particular dye compounds and due to lack of adequate information on various oxidants such as PS activated with SiO_2 and synergistic effects of each of the components involved in oxidation processes, this study aimed at examining the effect of SiO_2 on the thermal activated PS process in acid black 1 (AB1) removal. Moreover, the effect of operational parameters on the process efficiency was examined.

2. Methods

2.1. Reagents and Instruments

All chemicals, including sodium hydroxide, sulfuric acid, potassium PS and AB1 with molecular formula $C_{22}H_{14}N_6Na_2O_9S_2$ (Figure 1) were purchased from Merck Millipore. The pH was measured using a pH meter and the ultrasound wave was generated using a digital ultrasound machine (LUC-405 model, HACH Co).

2.2. Procedure

This experimental study was conducted using a batch reactor at the water and wastewater laboratory of Hamadan University of Medical Sciences. The bench scale reactor is made of a 1250 mL Plexiglas beaker. Sonication of

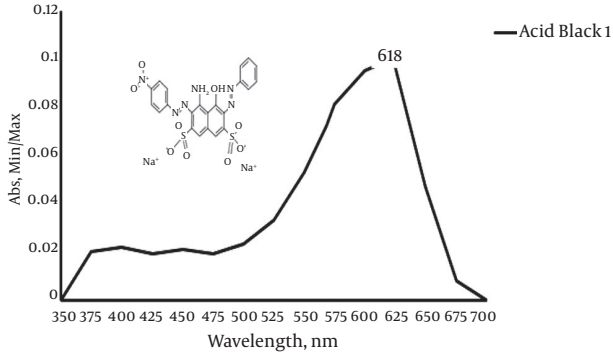

Figure 1. Molecular Structure and Absorption Spectrum of the Acid Black 1

the reaction media was performed by a digital ultrasonic with a frequency of 40 kHz and power of 350 W. Distillated water was used to prepare solutions. A known amount of AB1 solution and sodium PS ($Na_2S_2O_8$) were poured into the reactor. Adjusting of the solution pH was performed using sulfuric acid (1N) and NaOH (1N). The effect of parameters on the process, including the initial dye concentration 200 to 400 mg/L, pH of the dye solution (3 to 9), concentrations of SiO_2, (25 - 100 mg/L) and S_2O8_2- (1-10 mM/L) was studied in different stages. Sampling was conducted at 0 to 20 min and then the samples were centrifuged (6000 RPM for 10 minutes) and absorption amounts of the remaining AB1 were measured through direct photometry by using UV-V, which is a spectrophotometer at the wavelength of 618 nm (15).

3. Results and Discussion

3.1. Effect of pH

The effect of solution pH (3 - 11) on dye degradation was studied and the results have been shown in Figure 2. This step of experiments was performed using the dye initial concentration of 200 mg/L, and the PS concentration of 2.5 mM. The results showed that the solution pH in the dye degradation process was meaningful. After 20 minutes of reaction, the maximum dye decolonization obtained 83.89% at pH 3. With increasing pH from 3 to 11, the decolonization efficiency dramatically decreased, so that decolonization efficiency at pH 11, at pH 7 and pH 9, the removal efficiencies of dye were 76.25% and 61.39%, respectively. In other words, the dye removal efficiency decreases linearly with increasing pH. Another study showed that the effect of initial pH depends on the type of pollutant and the process (16). This trend is explained by the fact that in the acidic pH, dye is faced with a maximum molecular ionization results in an increased electrostatic force be-

tween the anionic and cationic species. In addition, in the alkaline pH, the hydroxide ion forms water-soluble compounds, and a delay appears in absorption of the color (4). Also, at acidic pH, the hydroxyl radicals are generated more than at the alkaline pH, and they are also more stable than at the alkaline pH. So, AOPs at acidic conditions have a better efficiency (5). Results of the Rao et al. study showed that the optimum conditions for theremoval of carbamazepine occurred in pH 3 in the process of S_2O8^{2-}/Fe^{2+} (4).

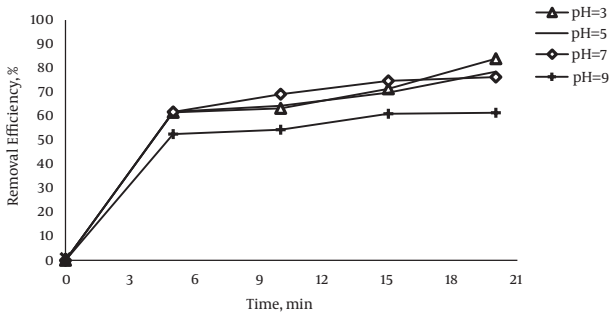

Figure 2. Effect of pH on Removal of AB1 in the Presence of US/PS (AB1 Concentration 200 mg/L, the US Frequency 40 KHz and Persulfate 2.5 mM)

3.2. Effect of Persulfate Concentration

To optimize the PS concentration, the effect of different concentrations of PS (1 - 10 mM) was investigated under the optimal conditions: pH 3, and dye concentration 200 mg/L, which were obtained from the previous steps. The results of this study indicated that the PS removal efficiency increased linearly with increasing the PS concentration. So, at 20 minutes, with increasing the concentrations of PS from 1 to 7.5 mM, the removal efficiency of dye was increased from 76.81% to 88.20%, respectively. By increasing the PS concentration as much as 7.5 mM, an opposite trend was indicated in the removal of AB1, which is followed by a decline in the process efficiency (Figure 3). Sulfate radical is a powerful electro-oxidant that decomposes many organic compounds, especially aromatic compounds (17). Persulfate anion is one of the two electron-oxidation agents, which can compete with ozone and hydrogen peroxide because it can generate sulfate radicals with a high-redox potential (18). When the PS ion concentration is increased, sulfate and hydroxide radicals are able to attack aromatic compounds; therefore, the process efficiency is increased (2). In this situation, increasing concentration of oxidizing agent to a certain extent will increase the reaction rate, and by increasing PS concentration as much as 7.5 mM, an opposite trend was observed in the removal of organic matter. On the other hand, excessive addition of oxidizing agent concentration to more than the optimal level leads to $SO_4^{\bullet-}$, which can also be scavenged by $S_2O_8^{2-}$ and consequently reduces the process efficiency based on the Equations below (2).

$$SO_{4(aq)}^{\bullet-} + SO_{4(aq)}^{\bullet-} \rightarrow S_2O_{8(aq)}^{2-} \quad (3)$$

$$SO_{4(aq)}^{\bullet-} + S_2O_8^{2-}{}_{(aq)} \rightarrow SO_{4(aq)}^{2-} + S_2O_{8(aq)}^{\bullet-} \quad (4)$$

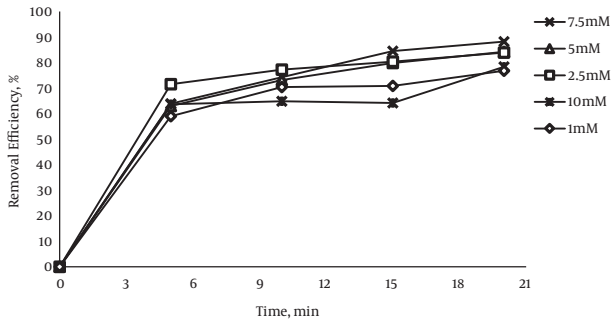

Figure 3. The Effect of Persulfate Concentration on Removal of AB1 in the Presence of US/PS (AB1 Concentration 200 mg/L, the Frequency of US 40 kHz, Reaction Time 20 min, Persulfate 1 - 10 mM, and pH 3)

Comparisons of the results of similar studies were listed in Table 1.

3.3. Effect of Acid Black 1 Concentration

The effect of AB1 initial concentration in the US/PS processes was examined in the range of 200 - 400 mg/L, as previous stages, desired parameters were variable and other parameters were stable (Figure 4). The shows shows with increasing of the AB1 concentrations from 200, and 300, to 400 mg/L, the removal efficiencies decrease from 88.20%, and 73.3% to 61%, respectively after 20 minutes. In estimating the influence of dye concentration on removal efficiency, the concentrations of the pollutants are one of the important parameters (26). The results showed that when the dye concentration is increased, a removal rate is reduced. It is clear that increasing the initial concentration of pollutants needs more oxidant. So, in the constant amount of the oxidant, the efficiency of the process would be decreased. The intermediate compounds generated during the reaction would be increased in high initial concentrations, which consume hydroxyl and sulfate radicals. This may lead to competition between pollutant molecules and intermediate in reacting with hydroxyl and sulfate radicals. Thus, the decomposition rate drops in high initial concentrations (2).

Table 1. Comparison of the Similar Studies

Reference	Pollutant	Process	Comparison of the similar studies
(19)	Atrazine	UV/H_2O_2/Fe^{2+} UV/$S_2O^{2-}_8$/Fe^{2+} UV/HSO^-_5/Fe^{2+}	In this comparative study, the optimal pH for the oxidation of atrazine was 3.
(4)	Carbamazepine	$S_2O8^-_2$/Fe^{2+}	The highest removal was obtained at pH 3.
(20)	Reactive black 5	US/H_2O_2/Fe^0	In this study, the zero-valent iron was used for activation of H_2O_2, and pH optimum was 3.
(21)	Acid orange7	Electro/Fe_3O_4/PDS	In this study, the optimal pH for the maximum of sulfate radicals was 3 and the total organic carbon removal efficiency was 30% after 90 min.
(22)	Phenol	Sono-electro-Fenton	The phenol removal in the EPS and EF processes were 95.18% and 93.99%, respectively; the operating condition of pH was 3, the initial concentration of phenol was 100 mg /L, and concentration of persulfate was 0. 4 mM.
(23)	Acid humic	US/PS	In this study, the optimal pH was achieved at 3 and by increasing the concentration of 10 mM to 100 PS, the removal efficiency increased.
(24)	Antibiotic	US/Fe^0/PS	With the ratio of PS 0.1 to 1, Fe^0 removal efficiency was increased, as well as maximum performance was at pH 3.
(25)	Acid red B	Sono-Fenton	Maximum efficiency was related to the US / Fe^{2+}/H_2O_2, Fe^{2+}/H_2O_2, US/H_2O_2 and separate US.
(21)	Acid orange7	US/Fe^0/PS	The use of separate operation in the US, PS and Fe^0 removal efficiency processes was not observed, but at the same time, the US/Fe^0/PS removed 90% of the color in 20 min.

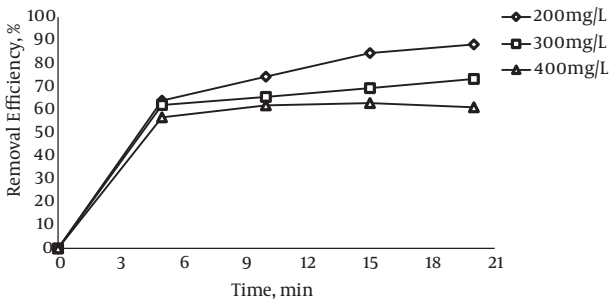

Figure 4. The Effect of Different Concentrations of Dye on Performance in Optimal Conditions (Reaction Time 20 min, Persulfate Concentration 7.5 mM, the Frequency of US 40 kHz, and pH 3)

3.4. Effect of Silica Concentration

To optimize the SiO_2 concentration, the effect of different concentrations of SiO_2 in the range 25 - 100 mg /L was investigated (an initial dye concentration: 200 mg/L, PS concentration: 7.5 mM, and pH: 3) (Figure 5). With increasing of the SiO_2 concentration from 25 to 100 mg/L, the removal efficiency increases from 80.36% to 100%. The collapse of cavities in the ultrasonic process results in the broken silica particles leading to an increase in the surface area and the formation of reactive sites (27). This phenomenon provides proper mixing motivation for increasing dye removal efficiency. It was found that the decomposition rate increased with increasing the amount of SiO_2 removal efficiency (after 20 minutes of ultrasonic radiation). The results showed that when the SiO_2 concentration escalates, it is converted into hydroxyl radicals that are combined together, which is followed by a decline in the process efficiency. The reason is that with increasing the amount of these particles, hydroxyl oxidizing agents are consequently increased and thus the dye removal efficiency increased (27, 28).

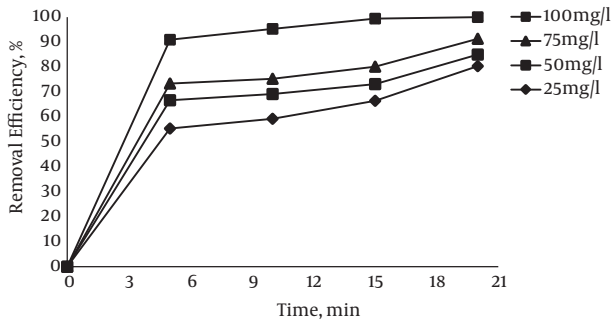

Figure 5. The effect of SiO_2 under optimum conditions (AB1: 200 mg/L, persulfate 7.5 mM and pH = 3)

3.5. Chemical Oxygen Demand Removal

The effect of various times on the removal efficiency of chemical oxygen demand (COD) has been shown in Figure 6. These indicated indicated a decreasing trend in the CODt/COD0 ratio. Initial COD in optimum condition at a concentration of dye 200 mg/L, a PS concentration of 7.5 mM and pH 3 was 250 mg/L. The result of the COD reduction at the end of a 120 min was achieved 90%.

As shown in Figure 6, the molecular structure of AB1 has three peak wavelengths of 318, 493 and 618 nm, respectively. Among them, the peak wavelength at a 618 nm is pertain to the position azo group (-N = N-), which is determinative of the type of dye and color combination. The peaks of wavelengths 493 nm and 318 nm are also the aromatic rings in the structure of dyes. In The oxidation processes, azo dyes are breakdown rapidly and the solution is colorless, but more time will be needed to remove the aromatic rings. Therefore, in the studies of oxidation dyes, the index of organic compounds was considered by scientists (11, 28). In this study, the peak of the azo bond has declined more quickly than that of the aromatic ring in this process.

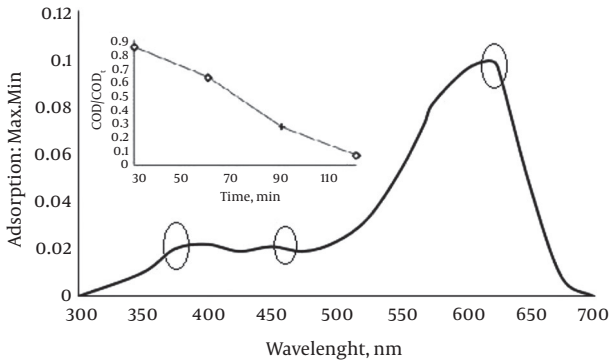

Figure 6. Chemical Oxygen Demand Removal Efficiency in Optimized Conditions

3.6. Synergistic Effect of Process Components

To determine the impact of components in the US/PS/SiO_2 processes, six samples were prepared and tested separately (Figure 7). In the first sample, in the US/PS/SiO_2 processes, which occurred in optimal conditions, a removal efficiency of 100% was experienced after 20 minutes. In the second sample, no ultrasonic and silica/PS was applied and the efficiency rate was 35.36%. In the third sample, the US/PS processes were carried out and the rate of removal efficiency was 66.83% after 20 minutes. In the fourth sample, the PS was carried out without the US. In sample five, the US process was carried out without the PS. In sample six, only the SiO_2 process was performed and the removal efficiency was 4.74%.

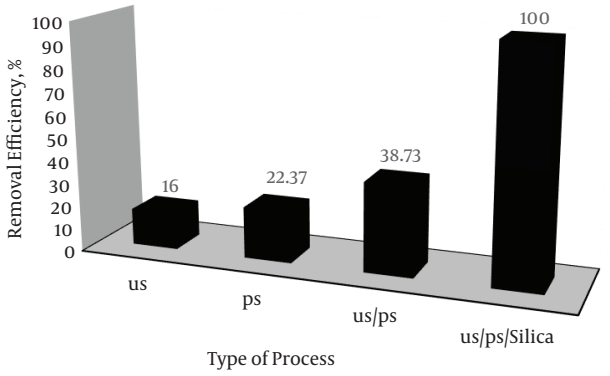

Figure 7. Comparison of Efficiency of the Study and the Synergistic Effect of the Compounds Used in Removal of Acid Black 1

3.7. Conclusions

The present study showed that the dye removal efficiency has a direct relationship with an increase in contact time and had an inverse relationship with dye initial concentration. Among the effective parameters, the concentration of PS is more important because increased concentrations of this compound can optimize, and boost the performance, but in higher concentrations may reduce the efficiency. The dye removal efficiency was maximized and the dye was removed completely when 100 mg/L SiO_2 was added and also when ultrasonic was used in combination with a chemical oxidation.

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