Humic Acid Degradation via Solar Photo-Fenton Process in Aqueous Environment

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ABSTRACT

Control of mutagenic and carcinogenic disinfection by-products, particularly Trihalomethanes (THMs) and Halo Acetic Acids (HAAs) in water treatment process is critical, due to their adverse effects on human health. Generally, reducing the toxicity of these by-products hinges on prior removal of the precursor materials, such as Humic Acid (HA) in drinking water. This study was conducted to investigate the role of some parameters that could affect the removal of HA, including HA (5 and 10 ppm) and H_2O_2 (20, 40, 60, and 80 ppm) initial concentrations, Iron (II), sulfate heptahydrate dosage (4, 8, 12, and 16 ppm), pH (2, 3, 4 and 5), Oxidation time (5, 10, 15 and 30 min), and Sunlight levels (322±13 kWm^{-2}). To accelerate the process of HA removal, the Solar Photo-Fenton (SPF) process was employed by direct irradiation of converged sunlight in a Parabolic Trough Collectors (PTC), with $3m^2$ effective area. HA levels were measured via quantifying Dissolved Organic Carbon (DOC) concentrations by means of a TOC Analyzer method. The results showed that the SPF process is under control of the Fe & H_2O_2 ratio, the Fe^{2+} dosage and especially the pH quantity. In optimal condition, (pH: 4, oxidation time: 30min, initial HA levels: 50 ppm, H_2O_2 concentrations: 20 ppm Fe+2 levels: 4 ppm), the study found more than 98% DOC removal. In conclusion, the SPF, as an economically effective technique, could be applied for the removal of HA in aqueous environments.

Key words: Humic Acid, DOC, Sunlight, Solar Photo-Fenton Process, Hydrogen Peroxide

INTRODUCTION

The presence of Natural Organic Matter (NOM) in drinking water causes a major concern due to their yellowish to brown colour, unpleasant odour and taste [1-2], and accelerating bacteria regrowth in water distribution systems [3].

Moreover, high chemical activity of humic substances for bonding with various pollutants, particularly heavy metals, results in contaminating ground and surface water [4]. On the other hand, NOM could react with the most common disinfectants, chlorine, and form mutagenic/carcinogenic disinfection by-products (DBPs), specifically THMs and HAAs in water treatment processes [5]. NOM may also react with ozone and produce harmful DBPs such as aldehydes, ketoacids and carboxylic acids [6]. Organic matter can generally be divided into two categories: humic and non-humic substances [7]. Humic acids (HA) are one of the major components of humic substances which may account for up to 90% of the NOM [8]. Humic substances are in the range of 20 to 30000 $g\mu^{-1}L^{-1}$ with negative charge at pH values more than 2 in natural water resources. In addition, more than 60% of dissolved organic carbon related to the humic materials and Humic Acid forms more than 50% of organic carbon in the structure of humic substances in the water bodies [10].

Based on World Health Organization, (WHO) guidelines, the levels of DBPs in drinking water should not exceed $100\mu gL^{-1}$ [9]. The USEPA recommends 80 and $60\mu gL^{-1}$ as maximum levels of THMs and HAAs in drinking water, respectively [11]. In view of that, the removal of HA from raw water running into treatment facilities is very critical since could pose significant health and environmental effects. This could be achieved through a variety of techniques and processes such as coagulation, precipitation, filtration, ion-exchange, adsorption, or biological treatment [12].

Furthermore, HA degradation with ozone [13], heterogeneous photo-catalysis, electrochemical and photo-electro-catalytic techniques [14] are the other methods. Recent studies reported that Solar Photo-Fenton process (SPF), a combination of H_2O_2 and Fe^{2+} in the presence of sunlight, can significantly accelerate decomposition of many persistent organic compounds [15]. The rapid decomposition of organic matter in this process is partially due to photolysis of water, Hydrogen peroxide and regeneration of Fe^{+2} from Fe^{+3}. However, all photochemical reactions may produce further hydroxyl radicals (Eqs. 1- 4) [16, 17]. The absorption of sunlight by chromospheres leads to the breakdown of aromatic structures or conjugated bonds and gradual decomposition, which is called photo-degradation [18].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + OH^\bullet \quad (2)$$

$$H_2O_2 + h\nu \rightarrow 2OH^\bullet \quad \lambda \leq 400\ nm \quad (3)$$

$$H_2O + h\nu \rightarrow H^\bullet \quad (4)$$

The SPF process is believed to have many advantages that make it suitable for purifying contaminated water. It oxidizes a range of organic compounds significantly faster than other traditional methods such as ozonation. Reaction degrees increase considerably in the presence of sunlight which leads to produce additional hydroxyl radicals. High efficiency and low cost are the other advantages of this technique; a number of low-priced oxidants such as iron, sunlight and hydroxyl radicals can initiate a large number of useful reactions [5, 18, and 19].

Thus, the SPF process can be an effective approach for decomposition of various organic pollutants in water treatment. This study was conducted as, to our knowledge, there was little and insufficient information about the degradation of HA using the SPF process. The key parameters controlling the SPF process, pH, initial Fe^{2+} concentration, H_2O_2 levels and the oxidation time, were investigated in this study.

MATERIALS AND METHODS

All chemicals being used in the present work were purchased from Merck Company, as an approved trademark. Commercial hydrogen peroxide (H_2O_2), Iron (II) sulfate Heptahydrate ($FeSO_4$, $7H_2O$), sodium bisulfite ($NaHSO_3$), Sodium hydroxide (NaOH) and Perchloric acid ($HClO_4$) were used as received. All other chemicals and solvents were of the purest grade commercially available and were used without further purification. Experiments were performed in a Polyethylene terephthalate (PET) bottle [20]; the volume (V) of the solution of each batch reactor was 1000ml. Working solutions (HA in levels of 50 and 100 ppm) were prepared by dilution of the stock solution (1000 ppm) in de-ionized water. PET bottles containing HA solutions were placed in Parabolic Trough Collectors (PTC) to collect and concentrate the solar radiation. As shown in Fig. 1, the depth, width, length, focal length of PTCs were 16, 100, 30 and 39cm, respectively, with effective area of $3m^2$.

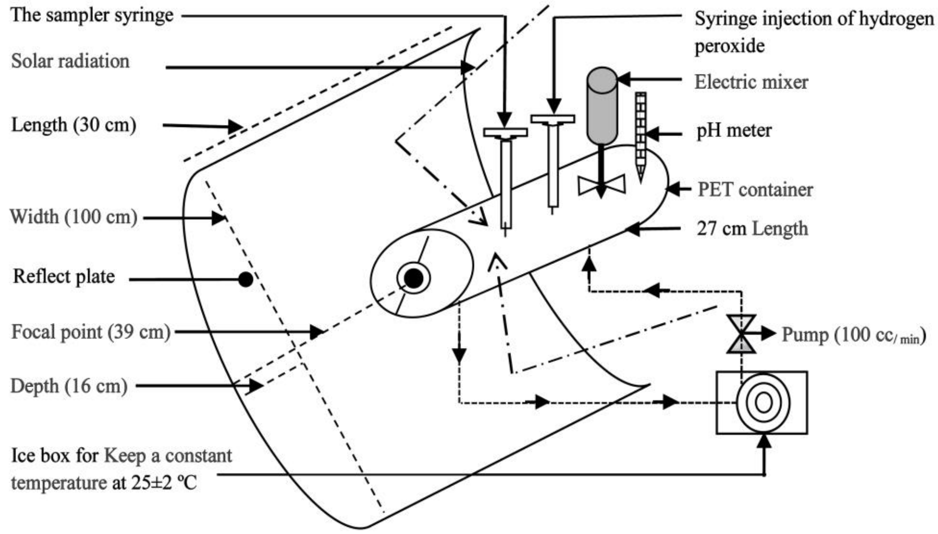

Fig. 1: Schematic of Parabolic Trough Collectors (PTC), built and used

The number of samples was calculated according to each experimental design while each collector could place up to 4 bottles. Experiments were conducted in sunny days of June, between 12 and 12:30 noon, to maximize sunlight capture. The power of sunlight was measured by a solar metre, Model TES 1333 R. Approximately, 26±3 kWm^{-2} of radiations was related to UV, as an effective light. (The solar energy that reaches the Earth surface is a wide range of electromagnetic waves which their wavelengths are greater than the UVc). Each solar collector was positioned as a non-tracking static system inclined longitude +29°29′ latitude 61°51′, and the bottles were aligned in 22.82±0.15 degrees of solar radiation divergence. The removal of HA were examined at various concentrations of Fe^{2+} and H_2O_2, and different pH and oxidation times. As Table 1 shows, pH was adjusted at initial values of 2, 3, 4 and 5 using $HClO_4$ and NaOH solutions. The concentrations of ferrous sulfate were 4, 8, 12, and 16 ppm; and it was 20, 40, 60, and 80 ppm for Hydrogen Peroxide. The examined oxidation times were 5, 10, 15 and 30 minutes. To deactivate the potential effects of ${}^{\bullet}OH$ radicals, 0.24 g of $Na_2S_2O_3$ was added to samples instantly after irradiation [21].

To stabilize pH and temperature during experiments, all samples were prepared in a buffer solution of Ammoniac and kept at 25±1ºC, using icebox. Moreover, the working solutions were homogenized by using electric mixer at 50 RPM [23, 24]. Before adding H_2O_2, all sample bottles were covered by an aluminum foil sheet. To serve as a control, some HA solutions were stored in the dark at room temperature.

Table 1: Experimental condition

Parameter	Value
pH	2, 3, 4, 5
Time (min.)	5, 10, 15, 30
Temperature (°C)	25±2
Fe^{+2} (ppm)	4, 8, 12, 16
HA (ppm)	50, 100
H_2O_2 (ppm)	20, 40, 60, 80

One of the conventional methods for measuring organic compounds such as Humic Acid in aquatic environments is weighing the levels of organic carbon via the Chemical Oxygen Demand (COD) technique. However, measuring Total Organic Carbon (TOC) is another method which, in this study, was employed to define the HA concentrations. Since the samples must be carefully prepared for injecting into the TOC Analyzer, all samples were initially filtered through Wattman (0.45µm) filter. To validate the outputs, measuring TOC was repeated for each sample. As a final point, the results were computed and presented as dissolved organic carbon (DOC) levels. In general, DOC forms 50 - 70% of TOC. Based on Eq. 5, the cut of HA in samples was calculated via quantifying DOC concentrations in TOC Analyzer [22].

Eq.5: $$\text{HA Removal } (\%) = \frac{DOC_{Control} - DOC_{Sample}}{DOC_{Control}}$$

RESULTS AND DISCUSSION

The effects of pH

pH influences, directly and indirectly, the oxidation of organic substances such as HA. The quantity of photo-regenerated Fe^{2+} is strongly changed by the pH-dependent hydrolytic speciation of Fe^{3+}; pH controls the generation of ${}^{\bullet}OH$ radicals, and thus affect the oxidation. Furthermore, with pH rise, the oxidation potential of ${}^{\bullet}OH$ radicals decrease [23]. At initial pH, above 7.0, HA resists degrading due to the precipitation of Fe^{3+} complex, usually to $Fe(OH)_3$ form; therefore, the catalytic reaction of Fe^{2+} ions drops with the oxidants [24].Moreover, the declining of oxidation yield with pH rise (above 5.0) can be explained by the degeneration of hydrogen peroxide amount, as well as by the deactivation of the ferrous catalyst, due to the formation of ferric hydroxide complexes, leading to a reduction of $\bullet OH$ radicals [25]. From this, pH effect was only examined in the range of 2 to 5.

Fig. 2 shows the effects of pH values on the degradation of HA. A maximum degradation of 99% was obtained at pH= 4. To account for this trend, it should be noted that at this pH, Fe^{3+} hydroxyl complexes are highly soluble and $Fe(OH)^{2+}$, which has the highest photo reactivity, is the predominant form of the Fe^{3+} hydroxyl complexes [1]. The low HA degradation observed at pH 2-3 could be due to the formation of Fe^{3+} oxalate [25]; however, the lowest degradation was obtained at pH= 5. At this pH, the formation of scales on the tube redound to reduce the transmission of the radiation and also photo reduction of Fe^{3+} complexes to Fe^{2+} [1]. Similar results have been reported in other studies on Humic Acid oxidation by the Fenton process [26, 27].

The effects of H_2O_2

The levels of hydrogen peroxide is very important in the degradation of organic pollutant such as Humic Acid in water and wastewater. It is a source of $^{\bullet}OH$ radical generation in the Fenton's reaction [28]. Fig. 3 indicates the effects of hydrogen peroxide concentration from 20 to 80 ppm on the Humic Acid degradation at an initial levels of 5 ppm and 4 ppm of ferrous ion at pH= 4.

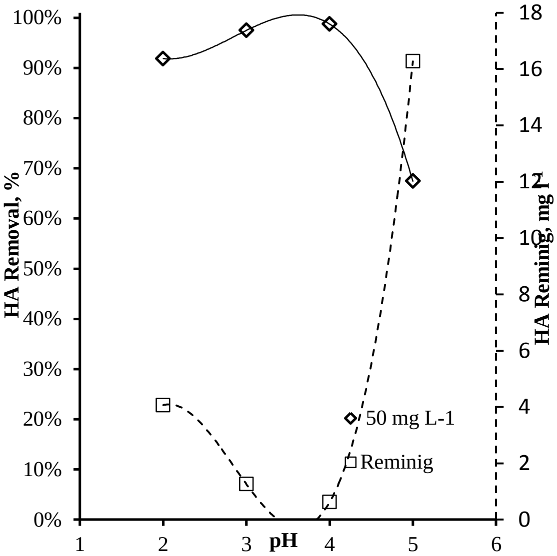

Fig. 2: The effects of pH on the removal of Humic Acid by photo-Fenton process (4 ppm Fe^{+2}, 20 ppm H_2O_2 & 30 min. reaction time)

Normally, the higher hydrogen peroxide concentrations, the faster and higher Humic Acid degradation, owing to the improvement of $^{\bullet}OH$ radical's formation for an increasing amount of H_2O_2, according to the following equation:

Eq. 6: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$

However, increasing H_2O_2 levels led to declining of degradation yields (Fig.3). To account for this, it should be noted that at high H_2O_2concentrations acts as a consumer of the $^{\bullet}OH$ radicals to produce perhydroxyl radicals ($^{\bullet}OOH$) that according to Eq. 7, which had much lower oxidation capability than $^{\bullet}OH$ [1, 22, 29].

Eq. 7: ${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + {}^{\bullet}OOH$

The range of H_2O_2 concentrations investigated revealed that there was most likely a significant contribution to the production of $^{\bullet}OOH$ radicals from the reaction of $^{\bullet}OH$ radicals with H_2O_2, leading to the decrease of degradation yields of Humic Acid [31].

The effects of reaction time

Decomposition of Humic Acid is very depending on molecular weight of its structure, as Components with high molecular weight decompose easily and faster than low molecular weight elements [23]. A number of studies reported that the increase of oxidation time increases the efficiency of processing in some degrees; however, in a particular point, this trend decelerates [23, 25]. On the other hand, some studies claimed that the presence of carbonate and bicarbonate released from Humic Acid decomposition is responsible for such low removal efficiency [25].

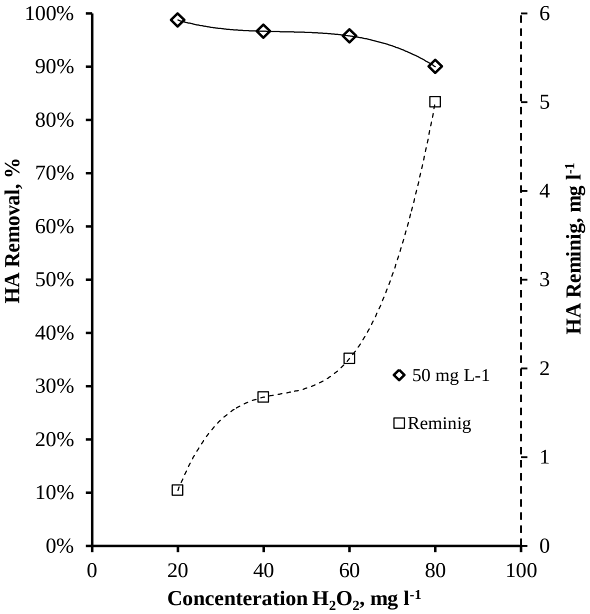

Fig. 3: The effects of H_2O_2 on the removal of Humic Acid by photo- Fenton process (4 ppm Fe^{+2}, pH = 4 & 30 min. reaction time)

Iran has high potential for using solar energy; though, this essential issue has been reflected in a few studies [32, 33]. Solar energy in Iran is available for approximately 2800 hours per year, ranging from 2.8 $kWhm^{-2}$ in the north to 5.4 kWh m-2 in the southern areas [33]. It is logical that with the increase of daylight and exposure time, removal of Humic Acid slightly improves, as a study reported similar and consistent findings [29].

Fig. 4 shows the effects of the irradiation and/or reaction time on the Humic Acid degradation during the photo-Fenton process. The results show that the reaction time has a slight effect on the removal efficiency since nearly 90 percent of removal was obtained after 5 minutes. Whereas, the total removal was observed in 30 minutes which was considered as the optimal reaction time.

The effects of the Fe^{+2}

The levels of catalysts are one of the main parameters controlling the photo-Fenton process. The production of $^{\bullet}OH$ radicals from H_2O_2 are catalyzed by Fe^{2+}, thus, the process depends on the concentrations of the catalyst [34].

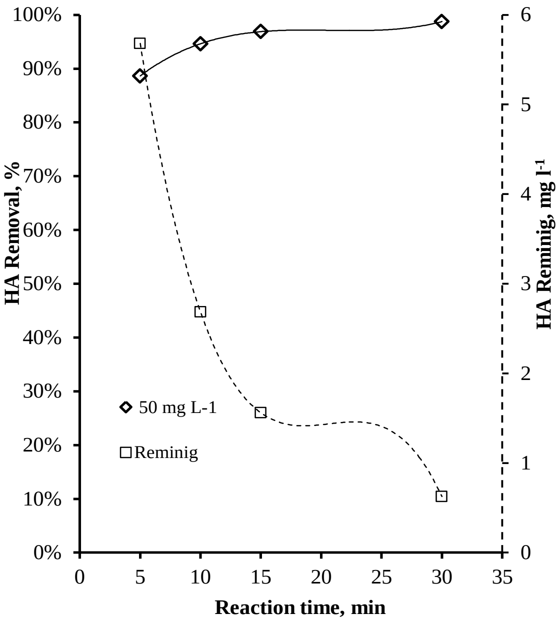

Fig. 4: The effects of reaction time on the removal of Humic Acid by photo- Fenton process (4 ppm Fe^{+2}, 20 ppm H_2O_2 & pH = 4)

An increase of Fe^{2+} dosage is believed to accelerate the generation of $^{\bullet}OH$ radicals, and hence, that should enhance the oxidation yield of Humic acid. As saw in Fig. 5, the higher Humic Acid degradation yield was obtained for 4 ppm Fe^{2+} dosage. It drops with the higher levels of Fe^{2+}. This decrease is more likely attributed to the scavenging effects of ferrous ion on radicals in high dosages, according to reactions 8 and 9. It leads to less available radicals for Humic Acid oxidation, and consequently, to decline to degradation yields [31, 35].

Eq. 8: $Fe^{2+} + {}^{\bullet}HOO \rightarrow Fe^{3+} + HO^{-}$

Eq. 9: $Fe^{2+} + {}^{\bullet}OH \rightarrow OH^{-} + Fe^{3+}$

Fe^{2+} plays a significant role in initiating the decomposition of H_2O_2 to generate the very reactive $^{\bullet}OH$ radicals in Fenton reactions. When the initial Ferrous ion concentration increases, the catalytic effect also accordingly increases to some extent, but afterward, further iron salt does not affect the DOC removal in the Fenton process [1, 36].These results clearly indicated that there must be an optimum ferrous ion concentration in the Fenton reaction. Consistent results were found in similar researches dealing with the Fenton's oxidation [34, 35].

The effects of the initial levels of Humic Acid

Two initial concentrations, 50 and 100 ppm, for Humic Acid were examined; meanwhile, the levels of H_2O_2 and Fe^{2+} were 20 and 4 ppm, respectively. As shown in Fig. 6, at the highest initial concentration, 100 ppm, the lower removal efficiencies were obtained. It could be probably due to non-availability of sufficient amount of hydroxyl radicals [37]. In addition, the presence of Humic Acid may affect H_2O_2 oxidation process due to absorption of UV light by Humic acid. In a study in China, for initial levels of 3, 5 and 8 ppm Humic acids, the authors observed a slightly lower efficiency for 8 ppm samples [38].

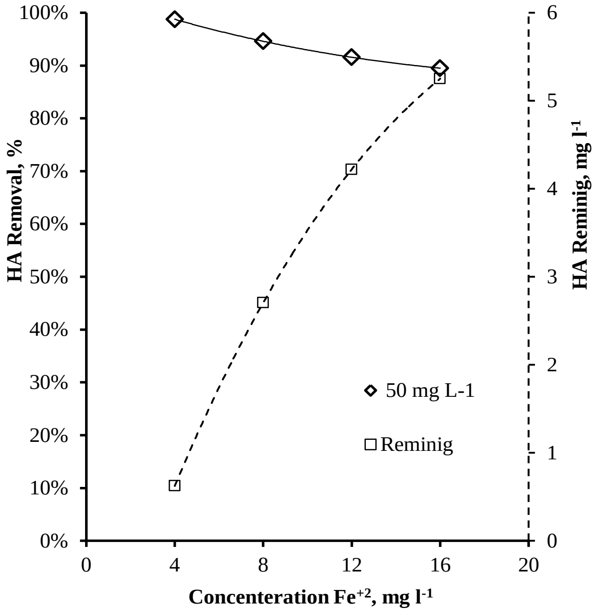

Fig. 5:.The effects of Fe^{+2} on the removal of Humic Acid by photo-Fenton process (4 ppm Fe^{+2}, 20 ppm H_2O_2, pH = 4 & 30 min. reaction time)

Table 2 presents the summary of findings of this study and compares the optimum conditions of similar studies, which investigate other techniques, with the optimum conditions of present work.

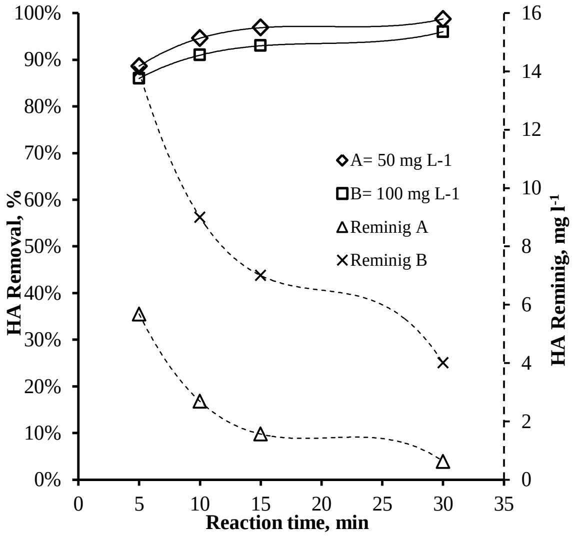

Fig. 6: The effects of initial concentrations on the removal of Humic Acid by photo-Fenton process (20 ppm H_2O_2, pH = 4 & 30 min. reaction time)

Table 2: Comparison of results of some published researches on HA removal by different processes

Process	Favorable Conditions	Measured Parameter	Removal efficiency (%)	Ref.
O3	50 mg L^{-1} HA, pH 11, O_3 21 mg min^{-1}, t 60 min, flow rate of 3 L min^{-1}	COD	43	[39]
O3/UV	UVC 9W, 50 mg L^{-1} HA, pH 11, O_3 21 mg min^{-1}, t 60 min		83	
Fenton	pH 3, 8×10^{-4} M, H_2O_2/Fe^{2+} 10:1, t 60 min		50	
Fenton/UV	pH 3, 8×10^{-4} M, H_2O_2/Fe^{2+} 10:1, t 60 min, UVC 9 W		87	
Fe^0/air	pH 3, 50 mg L^{-1} HA, Fe^0 of 20 g L^{-1}, t 9 min, flow rate of 5 L min^{-1}		90	
UV/Fe^0/air	UVC 9W, pH 3, 50 mg L^{-1} HA, Fe^0 of 20 g L^{-1}, pH^0 of 3, t 9 min		91	
Electrocoagulation	20 mg L^{-1} HA, t 75 min, 50 V, 3000 µS cm^{-1}, pH 5	TOC	92.69	[7]
photo-Fenton	10.5 mg L^{-1} HA, t 120 min, 0.1 mM Fe^{+2}, 30 °C, 0.5 mM H_2O_2, pH 4	DOC	90	[22]
Fenton	1000 mg L^{-1} HA,120 min, 40 mM Fe^{+2}, 160 mM H_2O_2, pH 4, 30 °C	UV_{254}	93.3	[40]
Adsorption	20 mg L^{-1}, Adsorbent 1 g L^{-1}, pH 4, 40 °C, 60 min	UV_{254}	92	[41]
Coagulation	50 mg L^{-1} HA, coagulant 30 mg L^{-1}, pH 7, t 30 min, room temp	DOC	91.6	[42]
filtration	40 mg L^{-1} HA, porosity (ultrafiltration)	UV_{254}	95.05	[43]
Present study	50 mg L^{-1} HA, t 30 min, 4 mg L^{-1} Fe^{+2}, 20 mg L^{-1} H_2O_2, pH 4, 25°C	DOC	98	-

CONCLUSION

Solar radiation is a natural cost-free and environmentally friendly energy source which is available largely for the most parts of Iran. Utilizing such infinite energy has almost no adverse effects on human health or environment. This study provided reasonable evidence that photo-Fenton technique could be considered as one of the most efficient means for HA removal which, in comparison, reduce the harmful health effects and prevent formation of disinfection by-products. However, the study found some information on optimum conditions of process; it could not describe quantitatively the multi-factorial outputs, as well the other parameters that are possibly associated with the process. Such investigations are left to further experiments and interpretation in future studies. Altogether, the availability of solar energy in many countries in the region, especially in Iran, along with practical findings of this study suggest a new approach towards the removal of organic pollutants from water and wastewater; however, as previously mentioned, it needs more researches.

ETHICAL ISSUES

Ethical issues entirely have been considered by the authors. And desperately tried to avoid plagiarism.

CONFLICT OF INTERST:

Authors declare that there is no conflict of interests.

AUTHORS' CONTRIBUTIONS

Sajjadi was statistical consultant and text editor of the study. Biglari was designer, performer and leader of the study. Afsharnia and Azrah were advisor of experiment, sampling and analyzing. Javan was conducted the study.

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