Original Article

The Effect of Nitrate as a Radical Scavenger for the Removal of Humic Acid from Aqueous Solutions by Electron Beam Irradiation

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Abstract

Introduction: Humic acids have adverse effects on the water quality, then should be removed from water resources. The aim of this study was to evaluate the effect of nitrate as a radical scavenger for removal of humic acid from aqueous solutions by electron beam irradiation.

Materials and Methods: In this study, after preparation of stock humic acid solution in alkaline condition, different concentrations of humic acid (10, 25 and 50 mg/l) were prepared. Different concentrations of nitrate (25, 50 and 100 mg/l) added to humic acid samples and then absorption of samples was measured at 254 nm by using UV-Vis spectrophotometer before and after the electron beam irradiation. This study has done at pH= 8 and at different electron beam adsorbed dose of 1, 3, 6, 9 and 15 kGy.

The results: The results of this study showed that the increasing of absorbed dose from 1 to 15 kGy, the removal efficiency of humic acid also increased. By increasing of nitrate concentration from 25 to 100 mg/l, the removal efficiency of humic acid has decreased from 43.8% to 36.6% and nitrate acts as a radical scavenger. By increasing of humic acid concentration from 10 to 50mg/l, removal efficiency decreased at all adsorbed doses. Kinetic analysis of our results showed that the results well fitted with the second - order reaction.

Conclusion: We can conclude from this study that electron beam irradiation could be a useful process for the treatment of natural organic matter (humic acid) from surface waters.

Keywords: Humic Substances; Nitrates; Radiation

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Introduction

Many of the world's water resources, particularly surface water sources, contain plenty of natural organic matters (NOMs) [1, 2]. NOMs are a group of organic macromolecules that cause problems in water treatment processes, including the formation of disinfection by-products (DBPs) such as trihalomethanes (THMs), which are mutagenic and carcinogenic compounds. Approximately 50 percent of natural organic materials in water are humic substances (HSs) [3]. In general, HSs divided into humic acid, fulvic acid and humin [2]. Humic acids (HAs) are classified a part of HSs that is not soluble in water under acidic conditions (pH <2), but dissolve in higher pH [4.5]. Because of the adverse effects, HSs should be removed from the water before disinfection in water treatment plants [1].

In recent years, several methods, including electro-microfiltration (EMF) [6], adsorption on activated carbon [7, 8], ion exchange [9], enhanced coagulation [10], membrane separation [11] and advanced oxidation processes (AOPs) have been done for removing NOMs from water resources [4]. But among these methods, the advanced oxidation processes just appeared more appropriate for treatment of water resources that contain organic matter [2]. This method caused oxidizing of NOM into harmless end products such as carbon dioxide and water [4]. AOP is defined as the advanced oxidation processes for water treatment that produces enough quantities of hydroxyl radicals (OHs) to cause water purification. Hydroxyl radical that formed during advanced oxidation treatment [12] is a powerful and non-selective chemical oxidant that rapidly reacts with organic compounds [2, 13]. Radical scavengers such as nitrate (NO_3^-) can react with hydroxyl radicals and then the removal efficiency of organic pollutants decreased by reducing of efficiency of AOPs [14].

Electron- beam irradiation is one of the AOPs for water purification that is more efficient than other methods. Irradiation is very effective for reducing of toxic organic compounds and biological contaminants in controlled conditions [15].

The advantages of electron-beam irradiation are that no chemical disinfectant is needed, no toxic by-products are produced and a short contact time is required [16]. Irradiation process decreases the risk of secondary contamination [17].

The aim of this study was to evaluate the effect of nitrate as a radical scavenger in the presence of electron beam irradiation for removal of humic acid from aqueous solutions. The variables in this study include initial Humic acid concentrations, initial concentrations of nitrate, pH and the amount of absorbed dose.

Materials & Methods

Batch experiments were performed on this survey in laboratory scale. In this study, Humic acid powder purchased from Sigma-Aldrich Co, USA. Phosphoric acid and sodium hydroxide used in this study, for pH adjustment was from Merck Co, Germany. A radical scavenger solution that used in this study, was prepared from sodium nitrate ($NaNO_3$), Merck Co, Germany. All material that used in this study are pure analytical. Electron-beam irradiation has done using an electron accelerator, TT 200 model manufactured by IBM, Belgium. Absorption of the samples was measured by UV-Vis spectrophotometer, SP-3000 Puls Model, Japan, and pH were adjusted by pH meter HACH, model HQ40d, USA.

Firstly, to prepare synthetic sample, the humic acid powder was dissolved in distilled water in alkalin condition by sodium hydroxide 0.1 N. After preparation of stock solution, different concentrations of humic acid (10, 25 and 50 mg/l) were prepared. Then, different concentrations of nitrate (25, 50 and 100 mg/l) added to various concentrations of humic acid. Prepared samples were transferred to petridishs which the sample volume was 40 ml with 1 cm sample thickness, then it were irradiated by energetic electron beams.

At the beginning, a study was done with a fixed dose of 3 kGy and different pH of 4, 6, 7, 8 and 10, and finally the optimal pH was selected as 8 because most of the water resources have pH closed in 8 and also significant differences between the values of efficiency at different pH was not observed. The other experiments for determining the effect of nitrate and humic acid concentration and EB absorbed dose were carried out in pH=8. Initial absorption of the samples was measured at 254 nm by using UV-Vis spectrophotometer before and after the irradiation. The removal efficiency of humic acid is calculated using the following relation:

$$R\,(\%) = \frac{Abs_0 - Abs}{Abs_0} \times 100 \qquad (1)$$

Where Abs_0 and ABS are initial and final absorbances of HA, respectively [18, 19]. Excel was used for analyzing data and drawing graphs.

Results

Effect of different pH

In this study the effect of pH was studied for removal efficiency of humic acid by electron beam irradiation. In the first, a study was done with a fixed dose of 3 kGy and different pH of 4, 6, 7, 8 and 10. The pH was adjusted by adding of NaOH or H_2PO_4. Figure 1 shows the effect of different pH on the removal efficiency of 25 mg/l HA and 50 mg/l nitrate concentration with an irradiated dose of 3 kGy. As shown in Figure 1, pH has no effect on the removal efficiency of initial HA concentration of 25 mg/l. The optimum pH achieved 8. The removal efficiency of humic acid was from 45.37% (pH=10) to 49.51% (pH=4) and by adding nitrate was from 23.34% (pH=6) to 32.86% (pH=4). In this study, the removal efficiency of humic acid was just depends on the initial concentration of nitrate and the amount of absorbed dose.

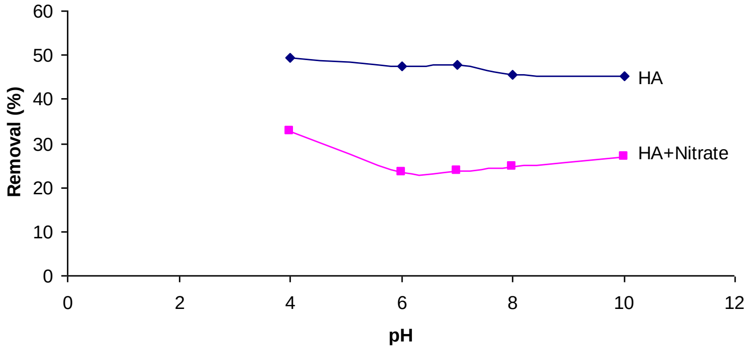

Figure 1. Effect of pH on the removal of humic acid (HA=25 mg/l and Nitrate= 50 mg/l and irradiation dose= 3 kGy).

Effect of nitrate concentrations

Regarding to the effect of different concentrations of nitrate as a radical scavenger on the removal efficiency of 25 mg/l humic acid by 3 kGy irradiation dose. We observed that by increasing the nitrate concentration from 0 to 100 mg/l, the removal efficiency of humic acid has decreased from 51% to 15%, respectively (Figure 2). Nitrate ions react with OH radicals as a radical scavenger and caused to decrease the removal efficiency of humic acid [14].

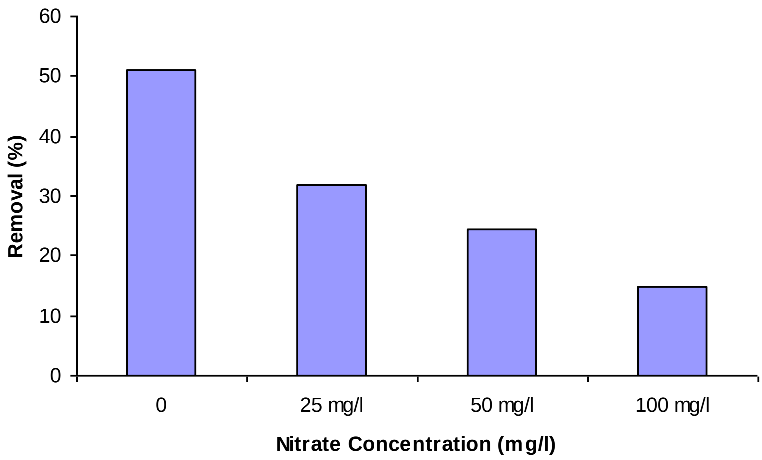

Figure 2. Effect of nitrate concentrations on the removal efficiency (HA=25 mg/l and pH=8, irradiation dose= 3 kGy).

Effect of irradiation dose

The effect of different irradiation dose (1, 3, 6, 9 and 15 kGy) on the removal efficiency of 25 mg/l HA and different concentration of nitrate (25, 50 and 100 mg/l) was studied.This study showed that by increasing of irradiation dose from 1 to 15 kGy, the removal efficiency of humic acid with or without nitrate ion has also increased. As the radical species increase in higher radiation dose rates, producing of OH radical also increase [12], so that with increasing of irradiated dose from 1 to 15 kGy, more OH radical produce while in the presence of nitrate, removal efficiency was decreased because it reacts with the OH radical, resulting in a decrease in the effective radical concentrations (OH radical) for the reaction to HA [12]. As shown in Figure 3, by increasing of nitrate concentration from 25 to 100 mg/l, the efficiency of humic acid removal has decreased.

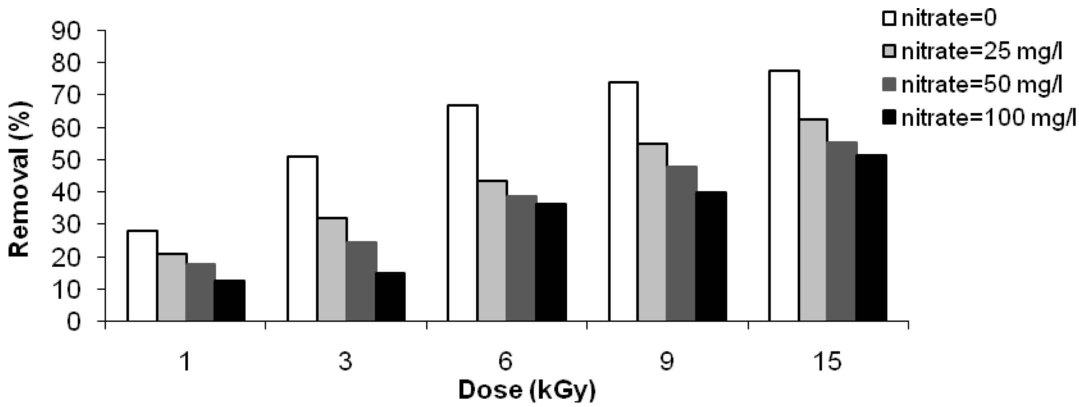

Figure 3. Effect of irradiation dose (1, 3, 6, 9 and 15 kGy) on the removal efficiency (HA=25 mg/l and Nitrate= 25, 50 and 100 mg/l, pH= 8)

Effect of humic acid concentrations

As shown in Figure 4, by increasing of initial concentration of humic acid from 10 to 50 mg/l, removal efficiency is decreased in all irradiated doses. So that in 1 kGy, by increasing of humic acid concentration from 10 to 50 mg/l, the removal efficiency is reduced from 23% to 13.3%, respectively. While in 15 kGy dose, efficiency decreases from 61.3% in 10 mg/l concentration to 46.8% in 50 mg/l concentration, respectively.

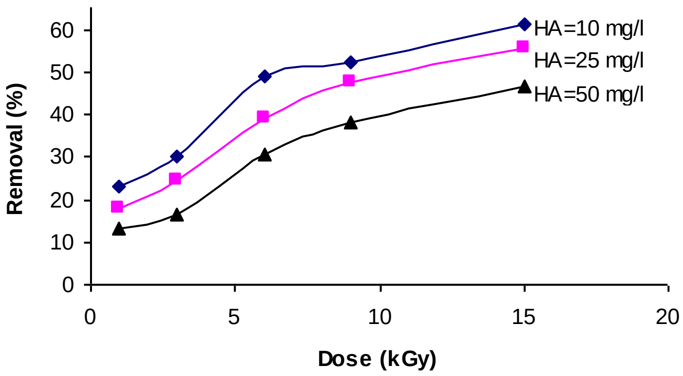

Figure 4. Effect of different concentrations of HA (10, 25 and 50 mg/l) on the removal efficiency of HA= 50 mg/l nitrate at different dose.

Kinetic study

Kinetic analyses of this study were performed using pseudo first and second order reactions but they fitted well with the second -order reaction. In most irradiation decomposition studies, the concentration of the targeted organic compound decreases with increasing of absorbed doses, which can be represented by equation 2 [20]:

$$C=C_0e^{-kD} \quad (2)$$

Where C is the concentration of humic acid after irradiation, C_0 the initial concentration of humic acid, k the dose constant and D the absorbed dose. The exponential equation 2 is analogous to a pseudo first-order.

The dose constraint is considerably dependent on the experimental conditions, such as the initial humic acid concentration, the molecular structure of the humic acid and the addition of a radical scavenger (nitrate) to the aqueous solution [18, 20].

All the experimental data fitted the pseudo first-order reaction model by equation 3:

$$-\ln (C/C_0) = kD \quad (3)$$

Equation 3, a modified version of equation 2, was used to calculate the dose constant from a linear least squares fit of the experimental study data [20]. Kinetic studies in other studies also during the radiation follow a pseudo-first-order reaction [21, 22].

The first-order kinetic is common for most of the electron beam irradiation for contaminating removal. The second-order kinetic equation was represented in equation 4:

$$\frac{1}{C}-\frac{1}{C0}=kD \quad (4)$$

Where C is the residual concentration of humic acid, C_0 is the initial concentration of humic acid, D is the absorbed dose in kGy, and k is the second-order rate constant in mg^{-1} kGy^{-1} [23]. In this study, humic acid seems to be also removed by first-order kinetic (R^2 = 0.956), but the second-order kinetic (R^2 = 0.971) was better fitted in overall removal tendency, which reveals a rapid removal followed by a rather retarded degradation profile (Figure 5).

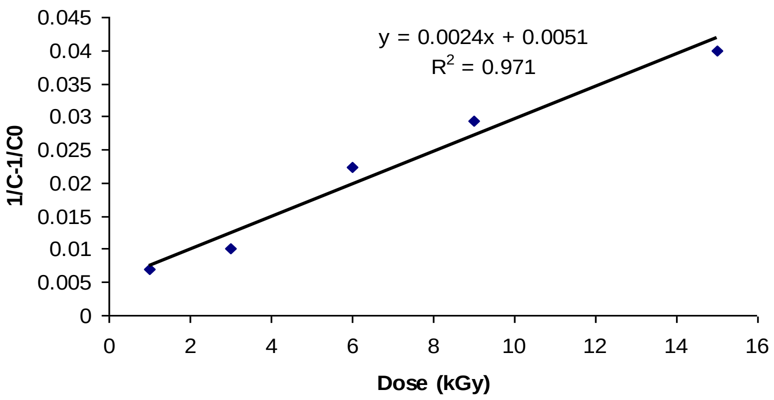

Figure 5. Kinetic results (pseudo-second-order) for the irradiated decomposition of 25 mg/l HA.

Discussion

In this survey, the effect of pH on electron beam irradiation showed that the pH had no effect on the removal efficiency of humic acid.

Guo et al (2009) in study of radiation removals of low-concentration halomethanes in drinking water have reported that removals of four halomethanes at absorbed dose of 3.0 kGy, increased with increasing pH values. In their study, results showed that the decreased removal percentage at low pH and the increased removal percentage at high pH of four halomethanes further demonstrate the importance of e^-_{aq} in their degradation during gamma radiation [22]. But in our study the removal efficiency of humic acid was just depends on the initial concentration of HA and nitrate and also the amount of absorbed dose.

The results of study by Roshani and Karpel Vel Leitner showed that persulfate has an intensification effect and removal efficiency of humic acid was increased to a fixed radiation dose of 15 Gy [3]. In our study, nitrate acted as a radical scavenger and caused to removal efficiency of humic acid decreased. Other studies that have done on the removal of humic acid by advanced oxidation processes with other radical scavengers have also been reported that all of radical scavengers reduce the removal efficiency of humic acid, because they can react with OH radicals that produce during advanced oxidation processes and decreased the effect of these processes. Wang et al (2000) found that carbonate and bicarbonate ions act as a radical scavenger as they avoid to decompose the humic acid in UV/H_2O_2 process [24]. Gehringer and Eschweiler (2002) have studied the electron beam dosimetry in aqueous flow systems. In their study, common scavengers have been oxygen as well as nitrate usually contained in water as natural solutes and the water contains enough additional scavengers to scavenge more than 99% of the solvated electrons [25]. In our study also nitrate was as a radical scavenger that reduced the removal efficiency of humic acid from aqueous solution.

Paul et al (2011) in a study on decoloration and degradation of Reactive Red-120 dye by electron beam irradiation in aqueous solution concluded that irradiation process for treatment of textile wastewater is very effective [26]. Our results also showed that this process is an effective method for removal of contaminated water sources that by humic acids in the environment.

Pa'lfi et al (2007) have studied the degradation of humic acid and its derivative in aqueous solution by ionising radiation, it can be concluded that these compounds can be destroyed effectively by OH radicals that form during water radiolysis. OH radicals are produced during the irradiation process by electron beam [27] and in this study, humic acid was degraded in the presence of them. Chung et al in degradation of Naturally Contaminated Polycyclic Aromatic Hydrocarbons in Municipal Sewage Sludge by electron beam irradiation showed that in 5 kGy, the removal efficiency of PAHs was about 90% [28]. Mahvi et al (2009) in study of reduction of humic substances in water by application of ultrasound waves and ultraviolet irradiation concluded that in lower concentrations of humic substances, removal efficiency was more appropriate [2]. In our study, in lower concentrations of humic acid (10 mg/l), removal efficiency was more appropriate than in higher concentrations (50 mg/l).

Most of the studies that have done on the removal of different pollutants by electron beam irradiation processes showed that they fitted to pseudo-first-order kinetics. Momani (2007) has done degradation of cyanobacteria anatoxin-a by advanced oxidation processes and the oxidation reaction was fitted to pseudo-first-order kinetic [29]. In radiation removals of low-concentration halomethanes in drinking water have done by Guo et al (2009), halomethanes removal during the radiation followed a pseudo-first-order kinetics model [22]. Miao et al (2008) in kinetic study of humic acid ozonation in aqueous media reported that kinetic was a pseudo first-order model [30]. Kinetic analyses of our study were performed using pseudo first- and second-order reactions but fitted well with second-order reaction. Kwon et al (2012) in removal of iopromide and degradation characteristics in electron beam irradiation process reported that the second-order kinetic was fitted in the removal tendency of iopromide [23].

Conclusion

The results of our study showed that the treatment with electron beam irradiation was very effective in the removal of humic acid from aqueous solutions. OH radicals are mainly responsible for the decomposition of humic acid. Nitrate ion is a very strong radical scavenger that reacts with OH radicals and decreased the removal efficiency of humic acid. Kinetic analyses of this study were performed using pseudo first- and second-order reactions that they fitted well with second-order reaction. In conclusion, electron beam irradiation could be useful process for the treatment of water resources contaminated by humic acid.

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