Abstract

Introduction: Natural organic matters (NOMs) existing in water resources led to various problems such as formation of disinfectant by-products (DBPs). Humic matters like humic acid (HA) are component of NOMs that should be removed from water. Advanced oxidation process (AOPs) is one of the NOMs removal methods. The aim of this study was to survey the degradation of humic acid by electron beam irradiation/Mn II ion from aqueous solutions.

Materials and Methods: This experimental study was performed in laboratory batch study. In this study, effect of pH (4 to 10), different doses of electron beam radiation (1 to 15 kGy), initial concentration of manganese ions (0.1 to 0.4 mg/l) and the initial concentration of humic acid (10 to 50 mg/l) in degradation of humic acid were investigated. Electron irradiation was performed using an electron accelerator model TT200 (IBM company, Belgium). Residual concentrations of humic acid in the samples were determined by spectrophotometer UV/Visible (Optima SP-3000 Plus model, Japan) at wavelength of 254 nm.

Results: According to results, pH changes had no effect on removal efficiency of humic acid. Results showed that increase of absorbed dose led to increase of removal efficiency. With increase of Mn II ion concentration to 0.2 mg/l, removal efficiency was increased but in higher concentrations, removal efficiency decreased. So that in concentration of 0.2 mg/l and 0.4 mg/l of Mn II ions, removal efficiencies were equal to 65.83% and 50.26%, respectively. Survey on the experimental data showed that degradation of humic acid by e-beam irradiation in presence of Mn II ions follows second-order kinetic.

Conclusion: The results of this research showed that electron beam irradiation coupled Mn II ions is an effective method for removal of humic acid from aqueous solutions.

Keywords: Humic Substances, Water Purification, Organic Chemistry Processes

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Introduction

Natural organic matters (NOMs) are a mixture of organic compounds that occurs universally in ground and surface waters [1]. The NOMs existing in natural waters include both hydrophobic and hydrophilic components, where the largest fraction is generally hydrophobic acids, which makes up approximately 50% of the total organic carbon (TOC) in water. These hydrophobic acids can be described, on the basis of their solubility in water and as a function of pH, into humic acids (HA), fulvic acids (FA) and humin [2, 3, 4]. Humic acid is comprised of high-molecular-weight organic substances that are soluble in alkaline condition and insoluble in acidic condition [2, 5]. Humic acid is one of the most humic compounds produced by degradation of animal and plant residues and consists 60-90% of natural organic matters [6].

NOMs are responsible for the majority of the demand for coagulants and disinfectants, fouling of membranes as well as that have potential to act as substrate for bacterial growths and contribute to corrosion in distribution systems. NOMs also contribute to annoying color, taste and odor problems, formation of DBPs that are carcinogenic and act as a carrier for metals [3, 4, 7]. Various combinations of oxidants, radiation and catalyst have been investigated, such as UV/H₂O₂, O₃/H₂O₂, UV/TiO₂, UV/O₃, UV/Fenton reagents, ionizing radiation and electron beam [3, 11, 12]. The electron beam (E-beam), one of the advanced oxidation processes (AOPs), has been widely studied for degradation of environmental pollutants in water and wastewater [1, 3, 13]. Most studies in the AOPs including E-beam processes have focused on the highly reactive hydroxyl radicals (OH). Hence, the formation of OH radicals is important for determining the efficiency of E-beam reactions [1, 13, 14]. Ionizing radiation produces both oxidizing and reducing species simultaneously in approximately the same concentration. The treatment of water and wastewater by electron beam irradiation can decrease the concentration of organic pollutants, provided that the E-beam absorbed dose is sufficient [15].

To improve the efficiency of pollutant removal or decrease the applied radiation dose, the results of some researches proposed adding a catalyst or reactive oxidant before treatment with electron beam [15]. Ma and Graham (2000) reported that in presence of a small amount of Mn²⁺ the oxidation of atrazine by ozone was greatly enhanced [11]. Mn²⁺ also has been shown to be effective for catalytic degradation of oxalic acid [16].

The aim of the present study was to investigate the effect of Mn²⁺ ion on degradation of humic acid by electron beam irradiation.
Materials and Methods

Solution preparation: Humic acid (HA) was provided by Aldrich Company (USA). Other used chemicals were of analytical grade and purchased from Merck. Stock humic acid solution (100 mg/L) was prepared by dissolving the humic acid powder in deionizer distilled water under alkaline condition by 0.1 N NaOH solution (pH=10) \[^5\]. The different initial concentrations of humic acid (10, 25 and 50 mg/l) were prepared by diluting the stock solution. Hydrated manganese sulfate (MnSO\(_4\).4H\(_2\)O) from Merck Company was used as an oxidant (0.1, 0.2 and 0.4 mg/l).

Electron accelerator: All irradiation experiments were conducted using electron beam from Rhodotron accelerator, which belonged to IBA Company, Belgium (model TT200). The electron energy was 10MeV. The Samples were placed in polystyrene containers with a volume of 100 ml. The experiments were carried out at absorbed doses of 1–15 kGy.

Procedure and analysis: The solutions pH was adjusted with NaOH and H\(_2\)PO\(_4\) (0.1 N). The pH value was measured by pH meter (model Mi-151). After irradiation, the humic acid solutions contained of manganese was filtered through 0.45\(\mu\)m acetate cellulose filter (model sartorius\[^6\]). Then, Residual concentrations of humic acid in the samples determined by spectrophotometer UV/Visible (model SP-3000 Plus) at wavelength of 254 nm. The removal efficiency of humic acid was calculated using the following relationship:

\[
\% \text{Removal Efficiency} = \frac{C_0 - C}{C_0} \times 100 \tag{1}
\]

Where \(C_0\) and \(C\) (mg/L) are the initial and after irradiation concentration of humic acid, respectively \[^7\].

Kinetic study: For kinetic studies, the humic acid solutions with known concentration (25 mg/l) with and without manganese ion in optimum pH were taken under irradiation in different absorbed doses of 1, 3, 6, 9 and 15 kGy. The first-order and second-order kinetics were also investigated. The kinetics equations were represented by Eq.2 and Eq.3, respectively \[^18, 19\].

\[
\begin{align*}
\ln \frac{C}{C_0} &= -kD \tag{2} \\
\frac{1}{C} - \frac{1}{C_0} &= kD \tag{3}
\end{align*}
\]

Where \(C\) and \(C_0\) are the residual and initial concentration of humic acid in mg/l, respectively. \(D\) is the absorbed dose in kGy and \(k\) is the first-order and second-order rate constant in kGy\(^{-1}\) and mg\(^{-1}\)kGy\(^{-1}\), respectively.

Results

Effect of Ph: Figure 1 shows the effect of different pH value on humic acid degradation by electron beam irradiation. According to these results, increasing the initial pH from 4 to 10 had no effect on the decomposition efficiency of humic acid. At pH 7, a reduction of removal efficiency (59.88%) was observed; while at higher and lower pH, removal efficiency was increased. At pH 6, 8 and 10, the degradation values of humic acid were 71.43%, 66.29% and 78.33%, respectively.
Effect of absorbed Dose: The effect of absorbed doses (1, 3, 6, 9 and 15 kGy) on degradation of humic acid were done in initial humic acid concentration 25 mg/l with and without addition Mn$^{II}$ ion at pH=8. Obtained results are shown in Figure 2. According to the results, degradation of humic acid increased as absorbed dose increased. By increasing irradiation absorbed dose from 1 to 15 kGy, the removal efficiency of humic acid in presence of Mn$^{II}$ ion was increased from 55% to 90.71%. The removal efficiencies of humic acid in absence of Mn$^{II}$ ion were equal to 29.58% and 78.61%, respectively.
Effect of initial Mn$^{II}$ ion concentration: The effect of three different concentrations of Mn$^{II}$ ion (0.1, 0.2 and 0.4 mg/l) on the degradation of humic acid were studied. Examinations of this stage were done in initial humic acid concentration 25 mg/l, pH 8 and dose 3 kGy. The Results (Figure 3) showed that increasing the concentration of Mn$^{II}$ ion to 0.2 mg/l led to increase of humic acid removal efficiency and then addition of Mn$^{II}$ ion higher concentrations led to decrease of removal efficiency. So that in initial Mn$^{II}$ ion concentrations 0.1, 0.2 and 0.4 mg/l, the removal efficiency was 58.7%, 65.83% and 50.26%, respectively.

![Figure 3: Effect of Mn$^{II}$ initial concentration on degradation of humic acid by electron beam process (pH: 8, absorbed dose: 3 kGy, initial humic acid concentration: 25 mg/l)](image)

Effect of initial humic acid concentration: At a Mn$^{II}$ ion concentrations of 0 and 0.2 mg/l, the initial humic acid concentrations (10, 25 and 50 mg/l) in dose 3 kGy and pH 8, were investigated.

The results showed that by increase of the initial humic acid concentration, the removal efficiency of humic acid was decreased (Table1). The removal efficiency at concentrations of 10, 25 and 50 mg/l in presence of manganese ion were 85.98%, 65.83% and 59.26%. But in absence of manganese ion with same condition were 62%, 49.61% and 35.48%.

<table>
<thead>
<tr>
<th>Initial humic acid concentration (mg/l)</th>
<th>Electron beam process</th>
<th>Electron beam/ Mn$^{II}$ process</th>
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<tbody>
<tr>
<td>10</td>
<td>62</td>
<td>85.98</td>
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<tr>
<td>25</td>
<td>49.61</td>
<td>65.83</td>
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<tr>
<td>50</td>
<td>35.48</td>
<td>59.26</td>
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Table 1: Effect of initial humic acid concentration (pH: 8, absorbed dose: 3 kGy, initial concentration Mn$^{II}$ ion: 0.2 mg/l)
Kinetic study of humic acid degradation by E-beam irradiation: Kinetic experiments were performed in presence and absence of manganese ions and electron beam irradiation. The results showed the degradation of humic acid followed by second-order reaction kinetic. R² values in second-order kinetic were obtained 0.983 and 0.957 for electron beam and electron beam/Mn⁡II that confirm better degradation of humic acid by second-order reaction. Also the values of reaction rate constants were 0.009 and 0.025 mg⁻¹kGy⁻¹.

![Kinetic results of humic acid degradation by electron beam radiation (pH: 8, initial humic acid concentration: 25 mg/l, initial concentration MnII ion: 0.2 mg/l)](image)

Figure 4: Kinetic results of humic acid degradation by electron beam radiation (pH: 8, initial humic acid concentration: 25 mg/l, initial concentration MnII ion: 0.2 mg/l)

Discussion

Based on obtained results from this study, change of pH in electron beam process relative to electron beam/Mn⁡II had further effect on removal efficiency; however, no significant differences (p-value> 0.05) were observed in removal efficiency value especially in electron beam process. So, as regards pH amount in natural water resources is about 8, the initial pH 8 was considered as the basis of experiments in research in the next stages.

The results of our study indicated that by increase of absorbed dose from 1 to 15 kGy, the removal efficiency would be also increased. These indicate that the concentration of the transient reactive species such as OH, H, and eaq⁻ increases rapidly as dose increases [15]. In Yu et al. (2007) study on radiolytic decomposition of cephalosporin, the increase of absorbed dose lead to decomposition of cephalosporin increase [20]. Kwon et al. (2012)
and Zhang et al. (2007) reported the same results. They investigated the degradation of iopromide and hexachlorobenzene by electron beam irradiation, respectively [19, 21]. By increasing the initial manganese ion concentration to 0.2 mg/l, the removal efficiency increased but by addition of manganese ions over 0.2 mg/l, the removal efficiency was inhibited. As MnII is a reducing agent, it can not only accelerate the degradation of humic acid but also may react with some oxidative intermediates, and therefore the concentration of MnII may have different influence on the degradation of humic acid. This phenomenon may suggest that an above-optimal concentration of MnII may scavenge the generated hydroxyl radicals, so causing a reduction in the degradation of humic acid. As seen in Figure 3, only a very little quantity of MnII (0.2 mg/l) is required to reach to a considerable reduction in humic acid concentration. Ma et al. studied the degradation of atrazine by manganese-catalysed ozonation. The greatest removal of atrazine was appeared at the lowest MnII concentrations (0.3 and 0.6 mg/l). Excessive MnII didn’t have any synergistic effect on the degradation of atrazine; rather it had a slightly negative effect [11].

Our results showed that the increase of humic acid concentration in electron beam and electron beam/MnII led to decrease of removal efficiency. In fact, the competition from the recombination of the active species decreased when the concentration of the humic acid increased. Criquet et al. study on electron beam irradiation of citric acid from aqueous solutions containing persulfate also showed that the citric acid degradation was high for the smallest initial concentration of persulfate [18]. The results of the present study showed that in presence of MnII in E-beam process, the removal efficiency increased. For development of pollution removal efficiency or reduction of irradiation dose usage, it is suggested to add a reactive catalyst or oxidant before treatment with electron beam [7]. So far, the effects of oxidants such as ozone, hydrogen peroxide, persulfate and manganese were investigated in removing the organic pollutants [14, 18, 19, and 22]. In the present study, manganese oxidant was studied for removing the humic acid from aqueous solutions.

The experimental data were analyzed by using the most commonly used first-order and second-order reaction models. The removal of compounds by electron beam irradiation can usually be expressed by first-order equation [18]. In Yu et al. study on radiolytic decomposition of cephalosporin and Criquet et al. study on electron beam irradiation of citric acid and acetic aqueous solutions, the results were followed first-order kinetic [18,20,23]. The results of the present study showed that degradation of humic acid followed second-order kinetic with correlation coefficient (R²) values (0.983, 0.957) higher than first-order kinetic (0.973, 0.896) for electron beam/Mn and electron beam, respectively. In 2012, Kwon et al.
studied the degradation of iopromide (IPM) by using electron beam irradiation. The results of their study showed that experimental data fitted by second-order kinetic ($R^2 = 0.98$). They stated that the IPM is very sensitive to reactive species such as $\text{OH}^\cdot$ and $e_{aq}^-$ generated by the e-beam process [19].

**Conclusion**

Nowadays, nearly all of communities have problems to safe water supply. So, new methods like AOPs developed. Humic acid contains substances that causes water quality gets worse; it should be removed from water resources.

Our results showed that water containing humic acid was degraded by electron beam/Mn$^{ll}$ ion, effectively. The results of this research can be used by water and wastewater Companies. The electron beam irradiation coupled Mn$^{ll}$ ions have significant effect on organic compounds removal.

**References**