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Treatment of petroleum refinery wastewater containing furfural by electron beam irradiation

Naser Dalali[a,*], Masoud Kazeraninejad[a], Azam Akhavan[b]

[a]*Phase Separation & FIA-Laboratory, Faculty of Science, Department of Chemistry, University of Zanjan, Zanjan, Iran, Tel. +98 24 33052579; email: Nasser_zn@yahoo.com (N. Dalali), Tel. +98 24 33052343; email: m_kazerani@znu.ac.ir (M. Kazeraninejad),*
[b]*Radiation Applications Research School, Nuclear Science and Technology Research Institute, Tehran, Iran, Tel. +98 21 82064176; email: azakhavan@aeoi.org.ir*

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ABSTRACT

In this study, the degradation of furfural ($C_5H_4O_2$) by electron beam (EB) irradiation in aqueous solutions and petroleum refinery wastewaters has been investigated. The influence of experimental parameters such as pH, initial furfural concentration, irradiation dose, and salt concentration on the efficiency of the technique was studied. A maximum degradation of furfural (>99%) was achieved with an irradiation dose of 6 kGy for model solutions of 100 mg L^{-1} with pH value of 3; however, salt concentration variation had no significant effect on the efficiency of furfural degradation. The capability of proposed method was compared with that of two other methods of advanced oxidation such as UV/H_2O_2 and UV/H_2O_2/Fe^{2+} for degradation of furfural. The comparative results revealed the highest efficiency for EB radiation; this method was applied to two wastewater samples with satisfactory results.

Keywords: Electron beam irradiation; Furfural; Degradation; Petroleum refinery wastewater

1. Introduction

Water pollution is one of the most important environmental problems worldwide. Industrial effluents are an important source of water pollution. The release of complex chemicals from petrochemical industries, oil refineries, and oil processing and chemical plants into the environment has been considered as a major source of air and water pollution.

Furfural (furan-2-carbaldehyde) is a toxic and hazardous substance for human and environment. It is an aromatic aldehyde, with the cyclic structure shown in Fig. 1. Furfural and its derivatives such as furfuryl alcohol, alone or in combination with phenol, acetone, or urea are mainly used in the production of resins. Furfural is converted to furfuryl alcohol by enteric bacteria, which can also be formed by hydrolysis of furfuryl alcohol esters [1]. Furfural and the corresponding alcohol are rapidly taken from the gastric tract at doses of 0.1–200 mg kg^{-1} body weight and virtually totally excreted mainly in urine within 24 h [2,3].

The second major application of furfural is concerned with the production of solvents such as furan and tetrafuran frequently used as selective solvent in the production, treatment, and refining

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*Corresponding author.

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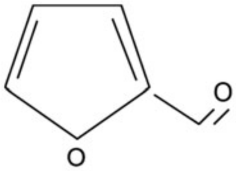


Fig. 1. Chemical structure of furfural.

lubricants from petroleum products. It is used as an excellent organic solvent in oil extraction unit of oil refineries and in petrochemical refining to extract dienes and aromatics from other hydrocarbons. The application of furfural as an extractant is based on a phenomenon called "intermolecular conjugation". This means that when molecules with conjugated double bonds such as furfural come in contact with other molecules containing double bonds, they form an enlarged conjugated double bond system, and this enlargement liberates energy analogous to intramolecular bond formation [4]. Consequently, furfural hooks onto molecules containing double bonds but ignores molecules without such bonds. It is also an intermediate in the production of the solvents [5]. The content of this pollutant in the industrial wastewater is usually higher than the standard limit (less than 5 mg L^{-1}) [6].

This substance is harmful in contact with skin and is toxic when inhaled or swallowed; it also shows some limited carcinogenic effects. It can be easily absorbed through the skin and must not be released in sewer and water bodies. In the case of long-term exposure, it leads to liver enlargement, feeling of weakness, skin rash or inflammation, tremor, and nose bleeding [7]. The discharge of untreated furfural wastewater can cause severe environmental pollution. The furfural wastewater treatment commonly adopts biological and chemical methods. Presence of furfural increases the toxicity of wastewater and makes biological treatment very difficult. Removal of this substance will require modifications or alternatives for the existing systems [8].

Advanced oxidation processes (AOPs) are defined as the processes that generate hydroxyl radicals in sufficient quantity to be able to oxidize majority of the refractory and complex chemicals present in the aqueous effluents. There are different methods of AOPs for treatment of furfural such as ozonation [9], UV photolysis [10], photo catalysis [11], and Fenton reactions [12]. The one of AOPs is also radiation process, where irradiation with beam of accelerated electrons is employed. Radiation process is the most efficient source of strongly oxidizing hydroxyl radicals $OH^{\bullet}$ in aqueous solutions in comparison to other AOPs. Electron beam (EB) irradiation is a promising technology for the removal of toxic organic compounds from the industrial effluents [13]. The EB technology is used to destroy organic compounds in liquid wastes. This technology irradiates water (H_2O) with a beam of high-energy electrons, causing the formation of three primary transient reactive species: aqueous electrons (e^-_{aq}), hydrogen radicals ($H^{\bullet}$), and hydroxyl radicals ($OH^{\bullet}$). Since both strong reducing (e^-_{aq} and $H^{\bullet}$) and oxidizing species ($OH^{\bullet}$) are formed in approximately equal concentrations, multiple mechanisms or chemical pathways for organic compound destruction are provided by the technology. As high-energy electrons impact flowing water, they slow down, lose energy, and react with water to produce the three reactive species responsible for organic substance destruction, as well as hydrogen (H_2), hydrogen peroxide (H_2O_2), and hydronium ions (H_3O^+) [14,15], given by (Eq. (1)):

$$\begin{aligned} H_2O + E - \text{beam} \rightarrow\ & e^-_{aq}(2.6) + H^{\bullet}(0.55) + OH^{\bullet}(2.7) \\ & + H_2(0.45) + H_2O_2(0.71) \\ & + H_3O^+(2.7) \end{aligned} \tag{1}$$

Eq. (1) indicates the estimated relative concentrations of the reaction products, 10^{-7} seconds after the EB impacts the water. The actual concentrations of reactive species produced depend on the EB dose. In addition, (Eq. (1)) indicates that $OH^{\bullet}$ and e^-_{aq} account for about 90% of the three primary reactive species formed by the EB; therefore, the chemistry of these two species is of primary interest for the EB technology.

The degree to which electrons transfer their energy to water is expressed in G values. The organic compounds removal after irradiation is described as the destruction of G value and defined as the number of molecules decomposed per 100 eV of the absorbed dose that was calculated using (Eq. (2)) [16]:

$$G = \Delta RDN_A/D(6.24 \times 10^{15}) = \text{mol}\,J^{-1} \tag{2}$$

where ΔRD is the change in organic solute concentration (mol L^{-1}) at a given dose, D is the absorbed dose (kGy), 6.24×10^{15} kGy in 100 eV L^{-1} is conversion constant, and N_A is Avogadro's number.

This paper presents the furfural degradation in aqueous model solutions and wastewater samples by EB irradiation. The efficiency of the method was investigated by spectrophotometry using aniline [17].

2. Material and methods

2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade (AR) or highest purity available, obtained from Merck (Darmstadt, Germany) and Sigma–Aldrich (St. Louis, MO, USA), and aqueous solutions were prepared in doubly distilled water. The stock solution of furfural was prepared by dissolving appropriate amount of it in doubly distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution. The pH of the solutions was adjusted by means of HCl and/or NaOH solutions (0.1 mol L^{-1}). COD digestion reagent consisting of potassium dichromate (TNT 825) was provided by HACH (Germany). Petroleum refinery wastewaters were obtained from two refineries located in center and south of Iran.

2.2. Apparatus

EB irradiation was performed with a Rhodotron TT200 accelerator (Beljium). FWT-60 film dosimeter was used to measure the absorbed dose. A digitally calibrated pH meter Metrohm, model 827 (Herisau, Switzerland) and a conductivity meter WTW, model LF 90 (Germany) were used to measure/adjust the pH and the conductivity of waste samples. The analytical determination of furfural was carried out using UV–Vis spectrophotometer PerkinElmer, Lambda25 (Waltham, MA, USA). Chemical oxygen demand (COD) of the wastewater samples before and after EB irradiation was determined (after sample digestion using a reactor, HACH model DRB200) by UV–Vis spectrophotometer, HACH model DR5000 (Germany).

2.3. Sampling

Samples of wastewater from petroleum refinery at the center (sample 1) and south (sample 2) of Iran were collected from the unit pound (B) during two consecutive visits in June and December 2014 and transported to the laboratory and processed on the same day. The samples were collected again in a second visit to check the consistency of parameters measured and to verify the stability of the treatment process. The samples were filtered with the filter paper to remove any suspended materials before performing treatment.

2.4. Experimental method

The samples were irradiated with 10 MeV EB accelerator. The irradiation was performed in a batch system using plexi-glass vessels (5 cm diameter and 1 cm height) with dose range of 1–10 (±3.5%) kGy; the current of EB was varied from 1 to 10 mA, and the absorbed radiation dose was measured using film dosimeter. The energy dispersion and resolution of beam current at 10 MeV were ±300 keV and ±50 μA, respectively.

After irradiation, 5 mL of furfural solutions mixed with 15 mL of ethyl alcohol (90%). Then 0.5 mL of aniline and five drops of hydrochloric acid were added while the solution was mixed on the stirrer. Absorbance was measured at 520 nm by spectrophotometer immediately after mixing.

The efficiency of furfural removal was calculated by (Eq. (3)):

$$\%\,\text{Removal} = \frac{(A_0 - A_f)}{A_0} \times 100 \tag{3}$$

where A_0 and A_f are the absorbance of furfural solutions before and after treatment, respectively.

3. Results and discussions

3.1. Effect of radiation dose

Furfural after reaction with aniline had a strong absorption band in visible region at 520 nm. The UV–vis absorption spectra of aqueous solutions containing 100 mg L^{-1} furfural irradiated with doses of 0, 1, 3, 6, and 10 kGy are shown in Fig. 2. It implies that the characteristic peak value of furfural decreased rapidly with increasing the absorbed dose from 0 to 10 kGy.

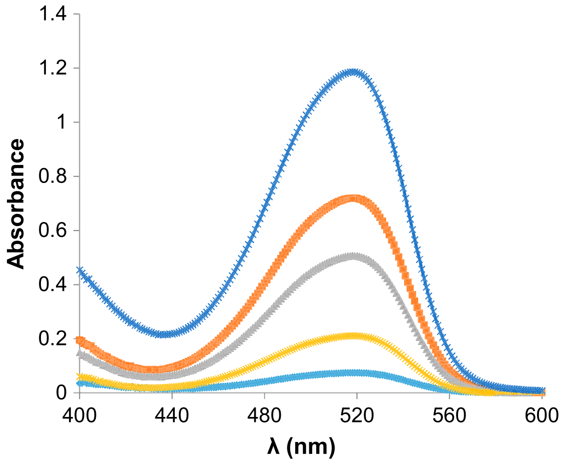


Fig. 2. Absorption spectra of furfural aqueous solution (100 mg L^{-1}) irradiated with different doses in ascending order from top to bottom (0–10 kGy).

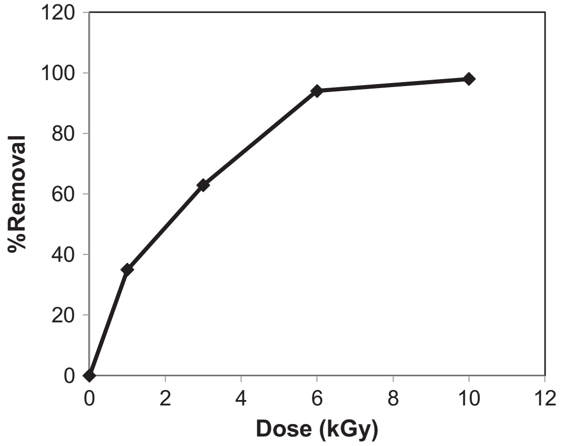


Fig. 3. Effect of radiation dose on the removal of furfural; conditions: initial furfural concentration = 100 mg L^{-1}, pH 7.

The observed decrease in absorbance is attributed to degradation of furfural because the hydroxyl radical, hydrated electron, and hydrogen atoms attack the double bonds in the molecule and destroy the conjugated system. By increasing intensity of the radiation source, the concentration of these species increases.

The relationship between degradation efficiency and absorbed dose was investigated. Fig. 3 shows the effect of irradiation dose (1–10 kGy) on the degradation of 100 mg L^{-1} furfural in aqueous solution with a pH value of 7. The degradation percentage increased with increasing irradiation dose up to 6 kGy, beyond which there was no considerable change (35, 62.9, 94, and 98% with 1, 3, 6, and 10 kGy, respectively). Since there was no much difference in degradation efficiency between 6 and 10 kGy, 6 kGy was the selected dose in order to avoid the energy over consumption in further studies.

3.2. Effect of pH

Another important parameter in the EB irradiation is the sample pH. To examine the effect of pH, the sample was adjusted at different pH values using NaOH or HCl solutions. Fig. 4 shows the effect of various pH values on percentage removal of furfural applying 6 kGy dose. The percentage removal decreased with increasing pH from 3 to 11. The data showed that the percentage removal of furfural at pH 3 was >99% and decreased gradually with increasing pH up to 9 (91%). At pH values > 9, an intense decline in the percentage removal was observed. The lowering of removal efficiency in this pH range is attributed to reduction of hydroxyl radical concentration. In alkaline medium, the oxidizing species hydroperoxy anion (HO_2^-) is also formed (HO_2^- anion is the conjugated base of H_2O_2). This HO_2^- anion reacts with $OH^{\cdot}$ radical and residual H_2O_2, decreasing the hydoxyl radicals and consequently the rate of reaction [18]. This phenomenon occurs probably due to greater relative scavenging of the $OH^{\cdot}$ at alkaline pH than lower pHs. Therefore, pH 3 was chosen as the optimum value for removal of furfural.

3.3. Effect of initial furfural concentration

The initial concentration of furfural solution was varied from 50 to 400 mg L^{-1}. After adjusting the pH of the solutions at 3, the samples were irradiated with

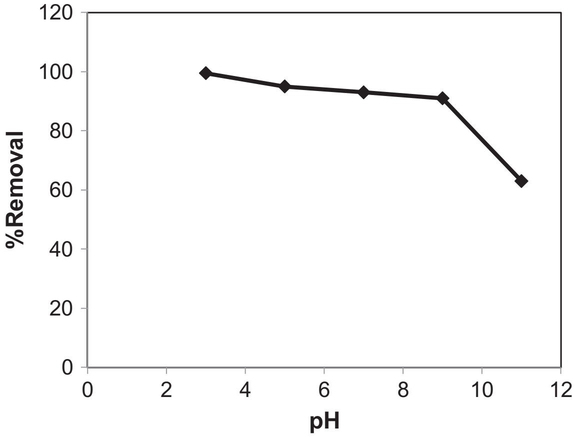


Fig. 4. Effect of solution pH on the removal of furfural; conditions: initial furfural concentration 100 mg L^{-1}, radiation dose = 6 kGy.

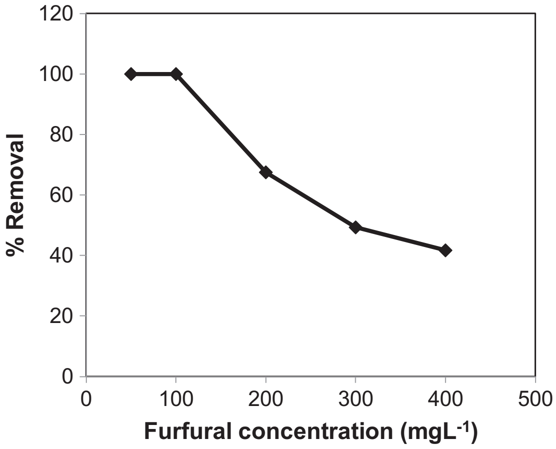


Fig. 5. Effect of initial furfural concentration on its removal; conditions: pH 3, radiation dose = 6 kGy.

6 kGy dose. The percentage removal of furfural vs. various concentrations is shown in Fig. 5. As seen, the highest percentage removals were obtained for 50 and 100 mg L^{-1} solutions. The EB technology generates strong reducing (e^-_{aq} and $H^{\cdot}$) and oxidizing species ($OH^{\cdot}$) simultaneously and in approximately equal concentrations. However, the number of this species was insufficient for degradation at higher furfural concentrations. Hence, 100 mg L^{-1} concentration of furfural was selected for the following experiments.

3.4. Effect of sodium chloride concentration

Concerning the fact that some petroleum wastewater has high salinity, salt effect was investigated on performance of EB irradiation. The furfural solution with concentration of 100 mg L^{-1} was prepared and adjusted to pH 3. Knipping et al. [19] offered that halide ions might act as scavengers that attract reactive species such as hydroxyl radicals in aqueous phase, but in this investigation, there was no significant effect observed. Likely in high dose due to hydroxyl radical production increase, salt concentration was ineffective. Fig. 6 shows the effect of salt concentration on degradation of furfural.

3.5. Comparison of AOPs

The degradation of furfural in aqueous solution by photo-oxidation technology using UV/H_2O_2 and UV/H_2O_2/Fe^{2+} processes was performed and compared with EB irradiation method. Radiation with a wavelength lower than 400 nm is able to photolize H_2O_2 molecule. The mechanism accepted for the photolysis of hydrogen peroxide is the cleavage of the molecule into hydroxyl radicals with a quantum yield of two $OH^{\cdot}$ radicals formed per quantum of radiation absorbed [20] according to the following reaction:

$$H_2O_2 \xrightarrow{hv} 2OH^{\cdot} \tag{4}$$

The photo reactor was charged with 1 L of an aqueous solution of furfural, with an initial concentration of 100 mg L^{-1}. The first set of experiments was carried out with hydrogen peroxide at 100 mM concentration used with a 125-W medium pressure mercury lamp as a UV source for evaluation of photo-degradation behavior of furfural in the UV/H_2O_2 system. Removal percentage of furfural under photo-peroxide system was 91.5% after 110 min. At second set of experiments, the decomposition of furfural was explored by means of the very reactive and oxidizing hydroxyl radicals, which are simultaneously generated by the Fenton's reagent, a mixture of hydrogen peroxide and ferrous ions. Fenton reagent was prepared by mixing 10 mL of H_2O_2 (30%) and 20 mL of $FeSO_4$ (57 mM). The mixture was added to 1 L of aqueous solution containing furfural in the reactor. After 110 min, removal percentage of furfural under Fenton's reagent was about 90%. Both experiments were performed at pH 3. Fig. 7 shows the percentage reduction of furfural vs. time for UV/H_2O_2 and UV/H_2O_2/Fe^{2+} processes.

In contrast to both aforementioned techniques, the removal percentage of furfural by EB irradiation at optimum conditions was >99%. Moreover the time required for performance of this method is very short.

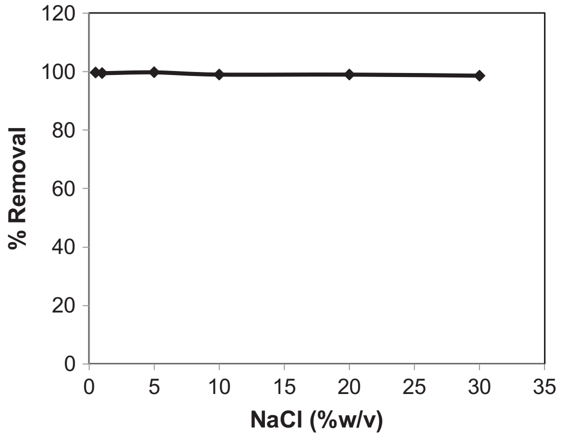


Fig. 6. Effect of salt concentration on the percentage removal of furfural; conditions: initial furfural concentration = 100 mg L^{-1}, pH 3, radiation dose = 6 kGy.

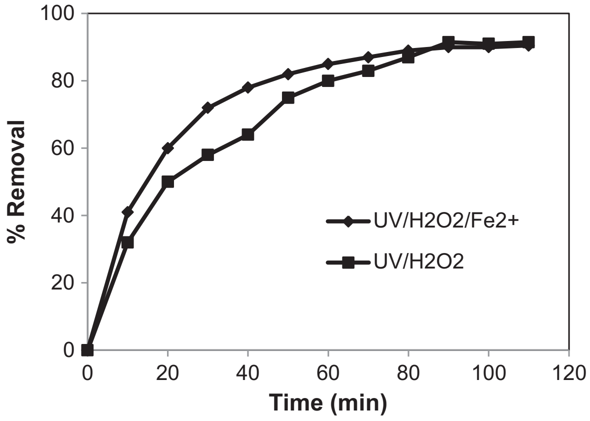


Fig. 7. Removal percentage of furfural by photo-oxidation methods; conditions: initial furfural concentration = 100 mg L^{-1}, pH 3, UV lamp electrical power = 125 W.

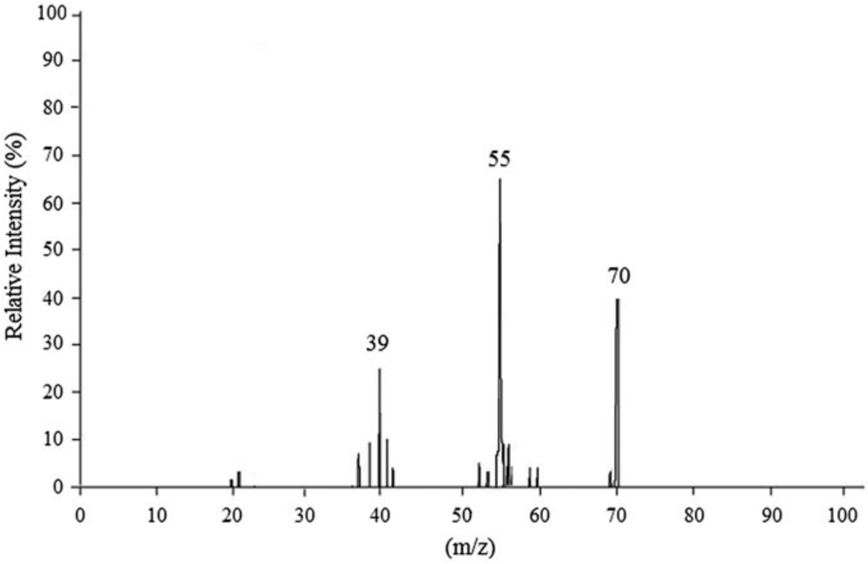
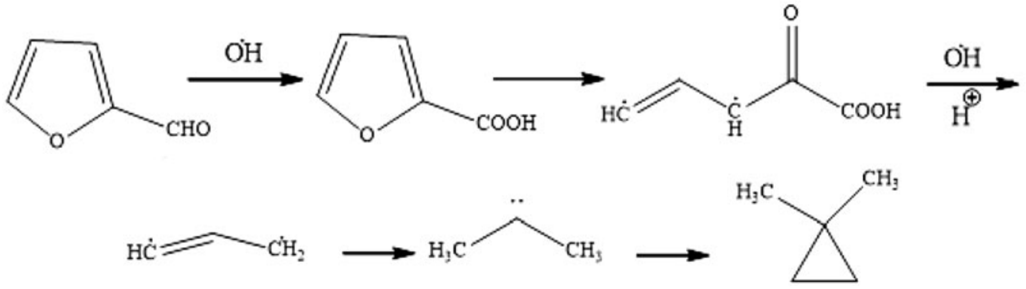


Fig. 8. GC–MS chromatogram of the model solution; conditions: same as that of Fig. 6.

3.6. Proposed mechanism for degradation of furfural

Based on the results, the mechanism for the degradation of furfural is proposed as follows:



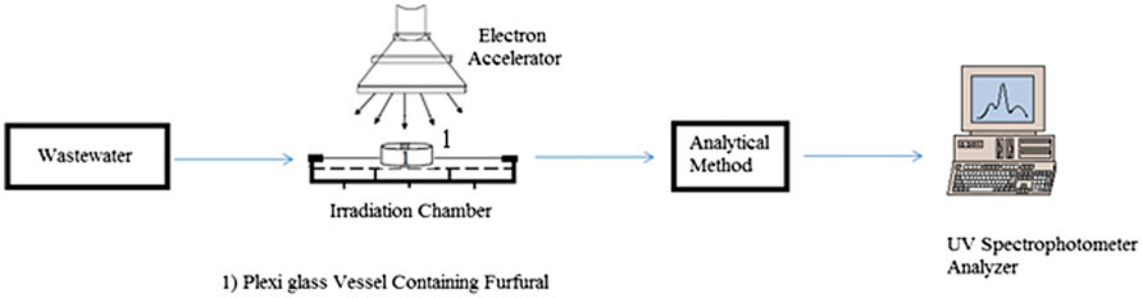
The OH$^{\cdot}$ radical generated by irradiation of water (Eq. (1)) reacts with furfural to produce 1,1 dimethyl cyclopropane which is nonhazardous, as the main product. This is proposed on the basis of GC-MS chromatogram obtained for model solutions after irradiation by 6 kGy dose (Fig. 8).

3.7. Treatment of petroleum refinery wastewater

Furfural is being used as an extraction solvent or as a base for synthesizing its derived solvent in oil refining industry in Iran; hence petroleum refinery wastewater containing certain amounts of furfural. Therefore, it should be treated before discharge. The aforementioned sample (1) (Section 2.3) was used in order to examine the applicability of the proposed method.

First, the samples were filtered with filter paper then pH was adjusted at optimum value and spilled in Pyrex glass vessels. Afterward, irradiation was carried out using 6 kGy dose (Scheme 1). Table 1 shows the physical characteristics of sample (1) before and after treatment with 6 kGy (±3.5%) dose.

The parameter of COD has been used to monitor the general status of effluent and quality of treated sample. In order to measure the COD, 100 mL of the sample was homogenized for 30 s in a blender. 2.00 mL of the sample was added to the COD digestion reagent vials containing a strong oxidizing agent, potassium dichromate. The oxidizable organic



Scheme 1. Diagram representing the irradiation process.

Table 1
Physical characteristics of sample (1) before and after EB irradiation treatment

Parameter analysis	Before treatment	After treatment
pH	6.3	5.6
COD (mg L^{-1})	502	350
Conductivity (mS/cm)	1.63	2.34
Furfural content (mg L^{-1})	10	0.1

compounds react, reducing the dichromate ion ($Cr_2O_7^{2-}$) to green chromic ion (Cr^{3+}). For blank preparation, 2.00 mL of deionized water was added to the vial. Capped tightly, the vials were gently inserted several times to mix and then inserted into the reactor (preheated to 150°C) for 2 h; the reactor was then turned off, and the vials were left to cool to 120°C or less. The vials were then placed into a rack to cool to room temperature, then the blank and sample vials were inserted into the 16-mm cell holder of spectrophotometer, respectively, and mg L^{-1} COD was measured. The data (Table 1) show that although EB irradiation reduces the furfural content 100 times (10–0.1 mg L^{-1}), but it alone cannot reduce COD effectively. The reason for this low efficiency is the formation of other organic species in effect of radiation [21].

4. Conclusions

Based on the results of the experiments, it can be concluded that degradation of furfural by means of EB irradiation is a promising method with high performance. A high efficiency of degradation (>99%) was achieved under the optimum conditions i.e. pH, initial furfural, and radiation dose as 3, 100 mg L^{-1} and 6 kGy, respectively. Also the dose required for the degradation of furfural in the real sample was 6 kGy because it's concentration in effluent is about 10 mg L^{-1}. The percentage of COD reduction in petroleum refinery wastewater was about 30–34%, which shows that furfural was not mineralized but only the ring structure rupturing of furfural occurs and converts to other organic compounds.

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