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Radiation induced destruction of thebaine, papaverine and noscapine in methanol

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HIGHLIGHTS

- Oxygenated and methoxy group containing by-products were observed in the mass spectra.
- The addition of methanol radiolysis products to alkaloid structure was suggested.
- Intermediate products were decomposed at doses above 50 kGy.
- The destruction efficiency and degradation *G*-value of alkaloids were calculated.

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ABSTRACT

The presence of methanol decreases the efficiency of radiation-induced decomposition of alkaloids in wastewater. Intermediate products were observed before the complete degradation of irradiated alkaloids. In order to identify the structure of the by-products and the formation pathway, thebaine, papaverine and noscapine solutions were prepared in pure methanol and irradiated using a ^{60}Co gamma cell at absorbed doses of 0, 1, 3, 5, 7, 10, 30, 50 and 80 kGy. The dose-dependent alkaloid degradation and by-product formation were monitored by ESI mass spectrometer. Molecular structures of the by-products and reaction pathways were proposed. Oxygenated and methoxy group containing organic compounds was observed in the mass spectra of irradiated alkaloids. At initial dose values oxygenated by-products were formed due to the presence of dissolved oxygen in solutions. After the consumption of dissolved oxygen with radicals, the main mechanism was addition of solvent radicals to alkaloid structure. However, it was determined that alkaloids and by-products were completely degraded at doses higher than 50 kGy. The *G*-value and degradation efficiency of alkaloids were also evaluated.

1. Introduction

Opium poppy contains several important alkaloids such as morphine, codeine, thebaine, papaverine and noscapine. These alkaloids and their derivatives are effective for the treatment of severe pain; therefore, poppy plant is cultivated in many countries and used for legitimate medical purposes. Opium Alkaloid Plant (Afyon, Turkey) effluent containing alkaloids and solvents is being discharged to Eber Lake. Pollution in Eber Lake has become intimidating to bird and fish species which use the lake as their habitat and even to people living in district. Previous treatment studies on both biological (Kunukcu et al., 2004; Sevimli et al., 2000, 1999) and physicochemical (Koyuncu, 2003; Aydin et al., 2002) treatment of alkaloid wastewater could not present a remedy to the problem. Radiation technology is regarded to be a promising alternative for the treatment of opiate rich wastewater (Bural et al., 2010; Özdemir, 2006). In our studies on treatment of wastewater, effluent samples from the alkaloid factory are irradiated at ambient atmosphere and subjected to an anaerobic treatment in a laboratory-scale Upflow Anaerobic Sludge Blanket (UASB) reactor. Irradiation leads to the increase of the number of low-molecular weight substrates that become available for the anaerobic digestion (AD).

With regard to gamma irradiation of polluted water, it is well known that OH radicals are very reactive species and quite effective for removal of contaminants. However, one of the processes in Opium Alkaloid Plant involves methanol extraction, so the factory generates effluent rich in methanol. Methanol is known as an effective scavenger for the hydroxyl radicals. Trojanowicz et al. (1997) observed a significant decrease in degradation efficiency of chlorophenols due to the presence of even very small amount of

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methanol in aqueous samples. Takriti et al. (2004) investigated the effect of scavengers on radiation-induced degradation of benzene and its chlorinated derivatives in aqueous solutions. They reported that the addition of scavengers such as methanol and ethanol required larger doses to decompose the pollutants when compared to those solutions with no additives. Beside the radical scavenging effect of methanol, another adverse effect was observed in our wastewater treatment studies. As it is well known, radiolysis of methanol yields $CH_3O\bullet/\bullet CH_2OH$ and H• radicals (Spotheim-Maurizot et al., 2008; Woods and Pikaev, 1994; Getoff et al., 1993), which may lead to addition of organic molecules and formation of oxygen-bearing compounds (Nakagawa, 2010; Butt and Qureshi, 2008). The formation of new molecular species during irradiation causes an important problem. These by-products should also be destroyed; therefore, much higher doses are required to achieve decomposition of all molecules in the wastewater. In order to identify the structure of by-products and determine the dose value for the destruction of these compounds, alkaloid solutions were prepared separately using methanol and subjected to gamma irradiation from a ^{60}Co source. In our previous work (Kantoğlu and Ergun, 2015), new compounds with a molecular weight greater than morphine and codeine were observed after the radiolysis of methanolic solution of these alkaloids. Main reaction mechanisms for the formation of these by-products were oxidation and hydrogen and/or methoxy radical addition to the radicalic sites or double bonds. The present study was carried out with the purpose of determining the effect of methanol on thebaine, papaverine and noscapine structure (Fig. 1) during gamma irradiation. Electrospray ionization mass spectrometry (ESI-MS) was used to detect the by-products. The dose value for the degradation of alkaloids and by-products was found.

2. Experimental

Thebaine, papaverine and noscapine standards were supplied by Lipomed. Sample solutions were prepared in methanol (CHROMASOLV®, for HPLC, ≥ 99.9%, Sigma-Aldrich) at the concentration of 5 mg/L. For each absorbed dose (0, 1, 3, 5, 7, 10, 30, 50 and 80 kGy), 2 ml of sample together with its duplicate was prepared in a glass vial.

It is commonly perceived that oxygen acts as an inhibitory and toxic agent in AD. However, this conventional perception is refuted, moreover, it is reported that limited quantities of oxygen can even lead to improved AD reactor performance under certain operating conditions (Botheju and Bakke, 2011). In our lab-scale studies, therefore, irradiation is carried out under neither hypoxic nor oxygenated conditions, so the source of the oxygen load in the wastewater is the dissolved oxygen. In this regard, in both previous (Kantoğlu and Ergun, 2015) and present studies in order to simulate this irradiation environment and identify the potential degradation products that can be formed under this conditions, sample containing vials were sealed properly to avoid oxygen diffusion through the overall sample. Gamma irradiation was carried out in a ^{60}Co source at a dose rate of 2 kGy/h.

The analyses of irradiated and non-irradiated sample solutions were performed on a mass spectrometer with electrospray ionization (ESI) source and quadrupole mass analyzer (Waters Micromass ZQ 2000). Samples were directly infused into the ESI source using a microsyringe with a flow rate of 10.0 μL/min. The major conditions were as follows: scan range, *m*/*z* 50–500; capillary voltage, 3.5 kV; cone voltage, 20 V; source temperature, 150 °C; desolvation temperature, 400 °C. All mass spectra were acquired in the positive mode. The data were collected and analyzed using Masslynx V 4.1 software.

3. Results and discussion

The irradiated and non-irradiated samples were analyzed using ESI mass spectrometer. In our studies, in-source dissociation was eliminated by applying low cone voltage (20 V). Under these conditions, mass spectra containing only the protonated molecular ions of the alkaloids and by-products were obtained.

It was observed that radiolysis products of methanol initiated some characteristic reactions such as hydrogen abstraction from the substrate and addition of the radicals to electron deficient-sites or double bonds of the compounds. In addition, oxygenated products were identified at initial dose values. Detailed results and dose-dependent structural changes were given in the next sections.

3.1. Thebaine

In the ESI mass spectrum of non-irradiated thebaine solution only protonated molecular ion of this molecule (*m*/*z* 312) was observed (Fig. 2a). At doses between 1 and 5 kGy, the main radiation-induced by-product was oxygenated thebaine (*m*/*z* 328). As mentioned above, this by-product was formed due to the attachment of dissolved oxygen (Eq. (1)). Thebaine is chemically similar to both morphine and codeine. According to the studies of Zayed et al. (2006), having low bond order and high bond strain, C5-O22 is the less stable bond in codeine-like structures. Tandem MS results reported in our previous work were in agreement with this report. Therefore, proposed mechanism for the oxidation of thebaine was radiation-induced cleavage of less stable bond (C5-O22) and addition of oxygen to the radical site which was generated at C7 due to allylic rearrangement of the C6-C7 double bond. As a result, observed peak at *m*/*z* 328 was proposed as oxygenated thebaine, which has salutaridine-like structure.

Methoxy and hydrogen adducts were detected in lower amounts than oxygenated by-product of thebaine at doses

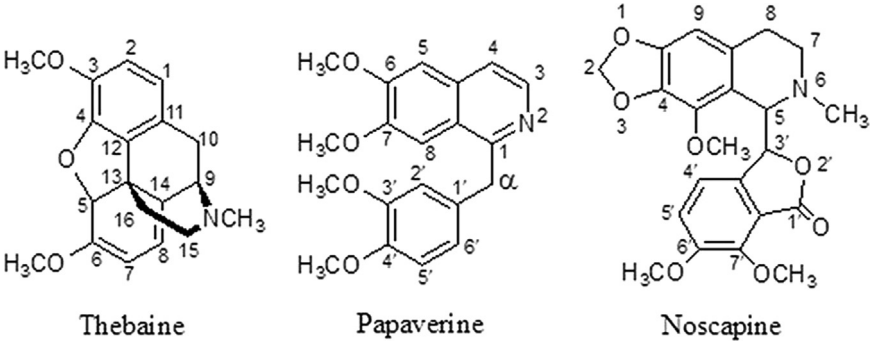

Fig. 1. Chemical structures of thebaine, papaverine and noscapine.