RADIATION INDUCED TREATMENT OF ORGANIC POLLUTANTS

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Abstract

In this period of the research, aerobic and anaerobic digestion, characterization of alkaloids present and radiolysis products formed after irradiation, under different conditions of ambient and additives, optimization of dose to achieve desired end characteristics for discharge of waste water were aimed. In this regard, unirradiated and irradiated wastewaters were subjected to aerobic and anaerobic digestions. Substrate removal efficiencies of unirradiated and irradiated wastewater with various initial COD values were determined with SBR aerobic digestion treatment method. On the other hand Fenton's advanced oxidation treatment method was also applied for pre-treatment. BMP tests of anaerobic digestion were also completed. LC/MS studies were carried out on unirradiated and irradiated alkaloid standard solutions of morphine, codeine, thebaine, papaverine, and noscapine to determine the degradation mechanisms and byproducts. Dose optimization studies were completed and found to be a lower dose of 5 kGy rather than 40 kGy for ambient irradiation conditions.

1. Objective of the research

The main objective of the research was to investigate the aerobic/anaerobic biological treatability of opium alkaloid industry wastewaters in conjunction with irradiation as a means of pre-treatment and the tasks carried out during frame time of the research are:

- Aerobic and anaerobic digestion studies of the radiation treated waste water.
- Characterization of specific organic pollutants present and radiolysis products formed after irradiation.
- Irradiation of alkaloid industry waste water under different conditions of ambient and additives and study the effect on effluent characteristics
- Optimization of absorbed dose to achieve desired end characteristics for discharge of waste water.

2. Introduction

Opium alkaloid industry produces mainly morphine to be used in medical field. Licensed opium poppy cultivation for medical purposes currently takes place in 12 countries around the world. The four main producers are India, Australia, Turkey and France. Opium Alkaloid Plant in Afyon, Bolvadin produces around 30% of global morphine production. Consequently, alkaloid industry is important for Turkey from financial and prestigious point of view. Effluent generated from alkaloid extraction and processing is on average 480 m^3/day. The average hourly flow rate of the wastewater is about 27.5 m^3/h. The effluent is discharged to Eber Lake through Akarçay River.

The wastewater generated by the opium alkaloid industry is heavily polluted with very high COD and BOD_5 content, and have intense dark brown color. Color causing substances in wastewater are almost totally dissolved and resistant to biodegradation. The pollutant

constituents in alkaloid wastewater mainly consist of morphine, codein, thebain, papaverine, noscapine, protopine, laudonosine, wax-like substances and cellulose.

3. Materials and metods

Each sample was irradiated at ambient atmosphere and temperature with a source of gamma irradiation ^{60}Co at a dose rate of 0,67 kGy/h.

3.1. Aerobic biotechnology

The bacterial seed sludge used in the preliminary batch treatability studies was taken from an aerobic membrane bioreactor (MBR) treating domestic wastewater of ODTUKENT area at Middle East Technical University (METU) campus. Inoculum used in all the later studies, including batch and sequencing batch reactors, was obtained from the return line of the activated sludge unit of the Ankara Central Wastewater Treatment Plant. Prior to use, activated sludge was aerated one day and washed two times with tap water.

3.1.1 Unirradiated Wastewater

Aerobic biological treatability of opium alkaloid wastewater was investigated in batch reactors. Various pre-designated initial concentrations of wastewater (COD between 2,500 and 26,000 mg/L) were added into reactors inoculated with unacclimated culture. It is obvious from the results obtained that the wastewater is not inhibitory to bacteria even at the highest concentrations studied, i.e. there is no substrate inhibition. Results show also that almost all of the COD biodegradation occurs within the first 5 days for batch run 1, and occurs around 10 days for batch run 2. In experiments with high initial organic loads, namely 7,000, 18,000 and 26,000 mg/L, a slight increase in COD values is observed in the first day of experiment. Unacclimated biomass removed 83 – 90 % of the organic carbon, depending on the initial COD values. Overall, these results suggest that the opium alkaloid wastewater has a good biodegradability and therefore it is suitable for aerobic biological treatment.

3.1.2. The effect of Irradiation on Biological Treatability

In order to see the effect of irradiation on the biodegradability of opium alkaloid wastewater, BOD and COD measurements were performed on wastewater irradiated at doses 40 kGy and 140 kGy. Unirradiated and irradiated wastewater samples with various initial COD concentrations were fed to reactors. Substrate removal efficiencies that were achieved with irradiated wastewaters were slightly lower than the case with unirradiated wastewater (Table 1).

Apart from this, another set of batch experiments was conducted with wastewaters, both raw and irradiated (COD around 35,000 mg/L). In order to simulate the conditions in conventional activated sludge systems, reactors were inoculated with higher amount of seed sludge, which was around 3,000 mg/L. COD removal efficiencies obtained were as high as 89, 88 and 84 % for unirradiated, 40 kGy and 140 kGy irradiated samples fed into reactors, respectively.

TABLE **1.** SUBSTRATE REMOVAL EFFICIENCIES FOR UNIRRADIATED AND IRRADIATED WASTEWATERS WITH VARIOUS INITIAL COD CONCENTRATIONS.

Initial COD	**Substrate Removal %**		
(mg/L)	**Unirradiated**	**40 kGy**	**140 kGy**
3,000	82	80	78
5,000	84	81	79
10,000	87	84	82
20,000	94	87	82
30,000	91	87	-

The COD removal efficiency in reactor fed with 40 kGy irradiated wastewater was only slightly better than the case with raw wastewater. Hourly COD degradation profile for the reactor fed with 40 kGy irradiated wastewater is shown for one cycle in Figure 1. Profile suggests that almost all COD removal (corresponding to 99 % of the total COD removal) occurred in approximately 5 hours as similar to the case with raw wastewater. Other than that, the application of higher radiation dose, namely 140 kGy, seems to have resulted in lowered COD removal efficiency.

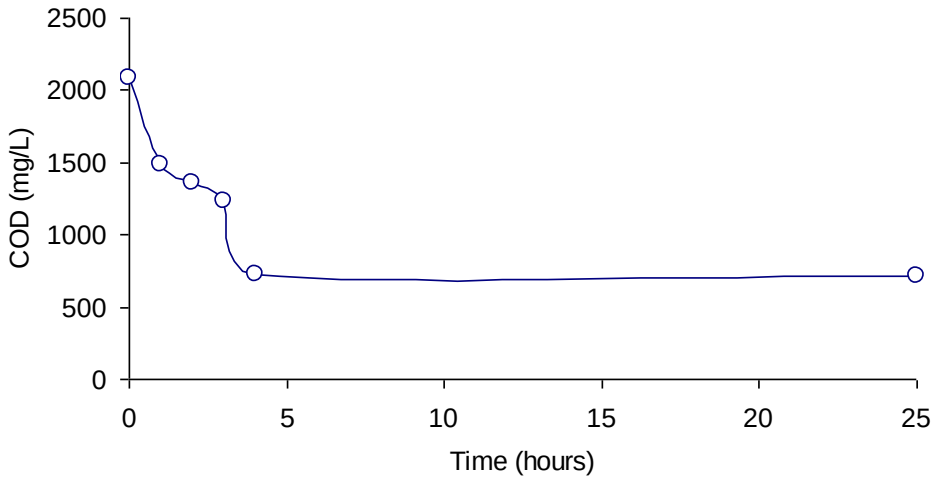


Fig. 1. Degradation of COD over time in SBR reactor fed with 40 kGy irradiated wastewater.

3.1.3. Fenton's Oxidation as a Pre-treatment

In this part, results obtained from the Fenton's oxidation, which was applied as a pre-treatment alternative process, are presented. Firstly, a preliminary study was conducted in order to assess the required initial doses of Fenton's reagents to initiate the research. A set of experiments was conducted in order to examine the effect of hydrogen peroxide dosage at different reagent ratios. First, hydrogen peroxide concentration was kept constant at 30 g/L and $FeSO_4 7H_2O$ dose was varied so as to provide H_2O_2 / Fe^{+2} mass ratios between 0.5 and 5. Experiment was repeated for 10 and 20 g/L hydrogen peroxide doses respectively providing the same H_2O_2 / Fe^{+2} ratios. Higher hydrogen peroxide concentrations resulted in better COD

removals due to generation of greater amount of ·OH radicals. At all fixed dosages of peroxide (10, 20 and 30 g/L) COD removal performances increased with increasing iron dosages. For H_2O_2 dosage of 30 g/L such increase was not as significant in comparison to other oxidant doses. H_2O_2/Fe^{+2} mass ratio of 0.5 provided the best COD removal efficiencies at all H_2O_2 dosages studied. However, it should be noted that, the use of greater amounts of iron should be avoided as the removal of settled iron hydroxide sludge would require an additional treatment step resulting in higher cost[1]. Therefore, in the following experiments optimum concentration of Fe^{+2} was sought keeping the hydrogen peroxide concentration constant at 30 g/L, where better removal efficiencies were obtained, especially at lower iron dosages. The results are shown Figure 2. As it is seen in Figure 2, 6 g/L Fe^{+2} concentration was the optimal dosage resulting in approximately 44 % COD removal efficiency. However, for 480 m^3/day flow rate of Afyon alkaloid factory, this treatment would require very high amounts of both chemicals which would be neither economical nor feasible.

3.2. Anaerobic biotechnology

Mixed anaerobic cultures, which were used in Biochemical Methane Potential (BMP) assays were obtained from anaerobic sludge digesters of the Greater Municipality of Ankara Tatlar Domestic Wastewater Treatment Plant. The digesters have a retention time of 14 to 20 days and pH measured in the digester ranges from 7 to 7.5.

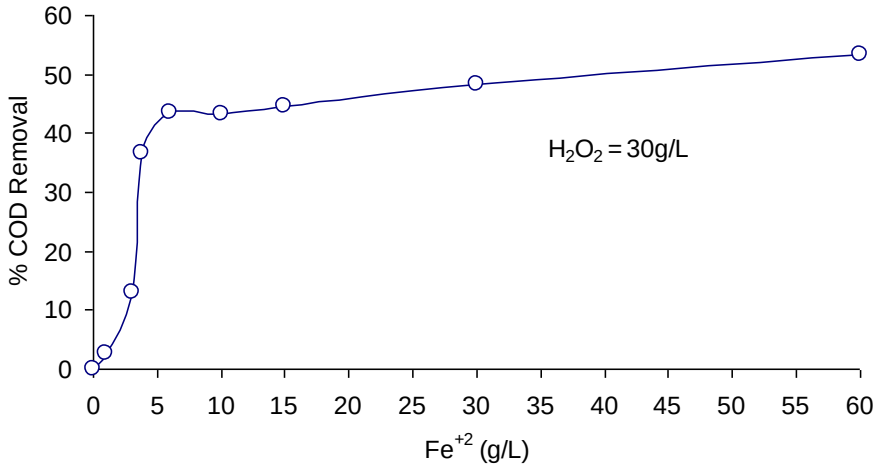


Fig. 2. Effect of Fe^{+2} dosage on COD removal efficiency at constant H_2O_2 = 30 g/L.

3.2.1 BMP assay for treatability of opium alkaloid wastewater

Treatability of opium alkaloid wastewater was investigated by means of BMP assay for initial COD concentrations of 2400, 6000 and 9600 mg/L with and without basal medium. The cumulative gas production for these three concentrations and control reactors were given in Figure 3. It can be seen from Figure 3 that no significant gas production was observed for both seed control reactors with and without basal medium (BM) throughout the experimental period of 48 days. This result pointed out that basal medium and seed cultures did not have a significant contribution to the cumulative gas production, although gas produced in the control reactor with BM was slightly higher than gas produced in the control reactor without BM. The difference was due to presence of basal medium. Gas produced in other reactors was emanated from biodegradation of alkaloid wastewater and net cumulative

gas production (NCGP) for these reactors were calculated by subtracting seed control gas.

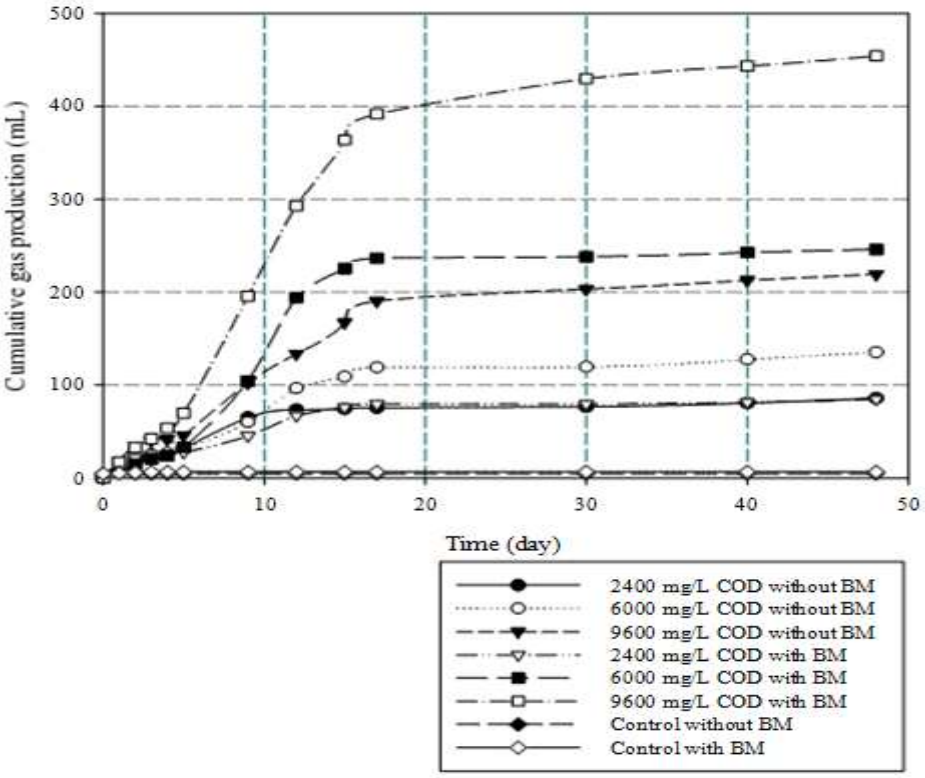


Fig. 3. BMP experiment result for opium alkaloid wastewater (2400, 6000 and 9600 mg COD/L) with and without basal medium.

3.3. LC/MS studies of standard solutions of opiates

Irradiated and unirradiated opiate standards solutions were analyzed by high performance liquid chromatography (HPLC:Waters 2695 separation module) coupled with mass spectrometry (Waters Micromass ZQ) using a reverse phase column (INERTSIL ODS 3.3 µm, 15cm×3.2mm i.d.) from Hichrom. The initial HPLC conditions were 5% methanol and 0.5% acetic acid in water, at flow rate of 0.3 mL/min. The column was then developed to 100% methanol over 40 min. The positive mode of electron spray was employed for ionization of the analytes. Parameters were: capillary voltage 4.25 kV, cone voltage, 70 V; source temperature, 150°C; desolvatation temperature, 450°C; cone gas flow, 250 L/h; desolvatation gas flow, 500 L/h. Nitrogen was used as desolvation and nebulization gas.

3.3.1. Characterization of Organic Pollutants and Radiolysis Products

Five opiate standards were disolved in methanol and the solutions were irradiated with γ-ray at different doses. Then both unirradiated and irradiated standard solutions were analyzed with LC/MS in order to examine degradation mechanism and the radiolysis byproducts. Obtained mass spectrum of morphine standard solutions irradiated at 0, 10, 30 and 50 kGy and their fragment ions are given in Figure 4 and Scheme 1, respectively.

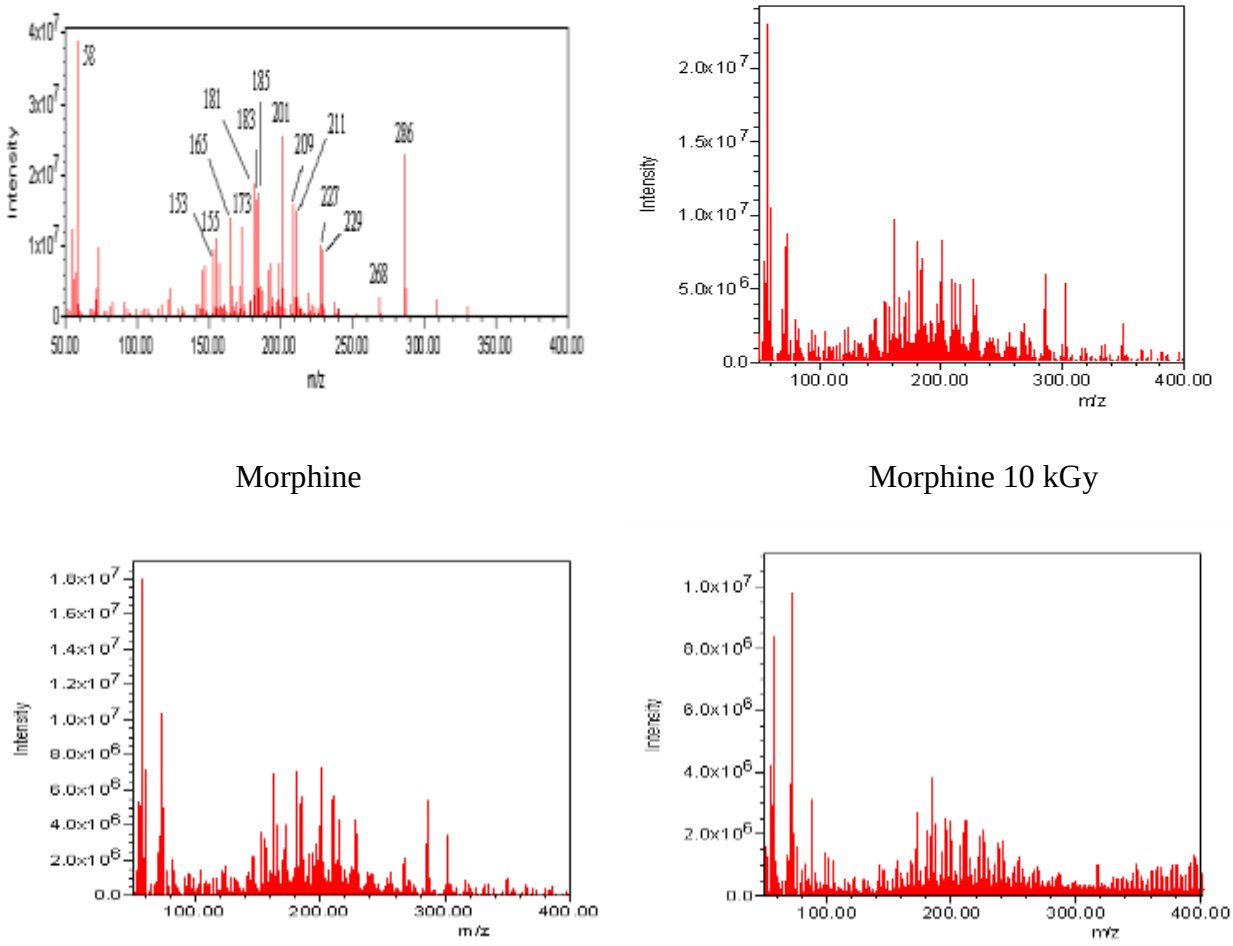
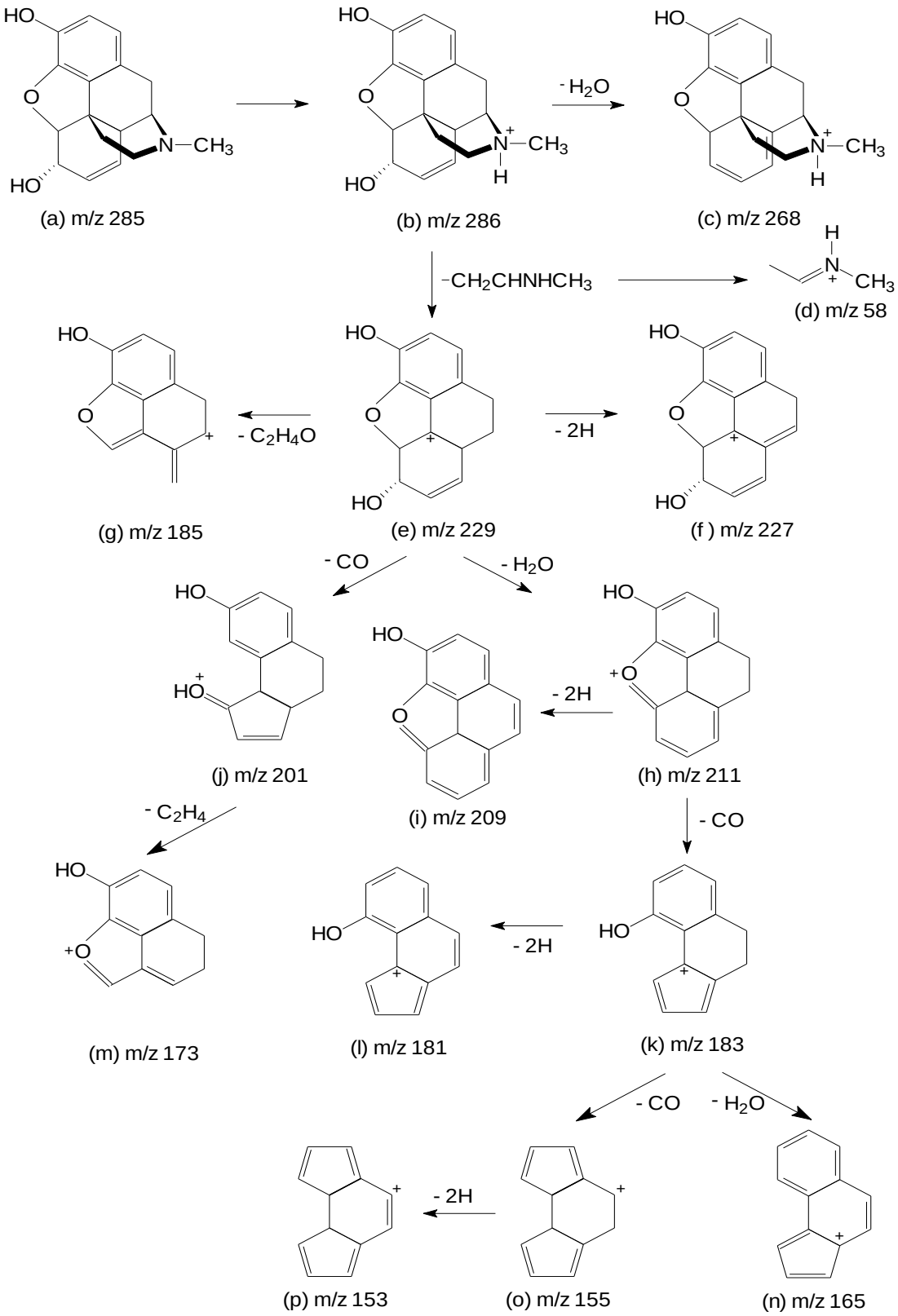


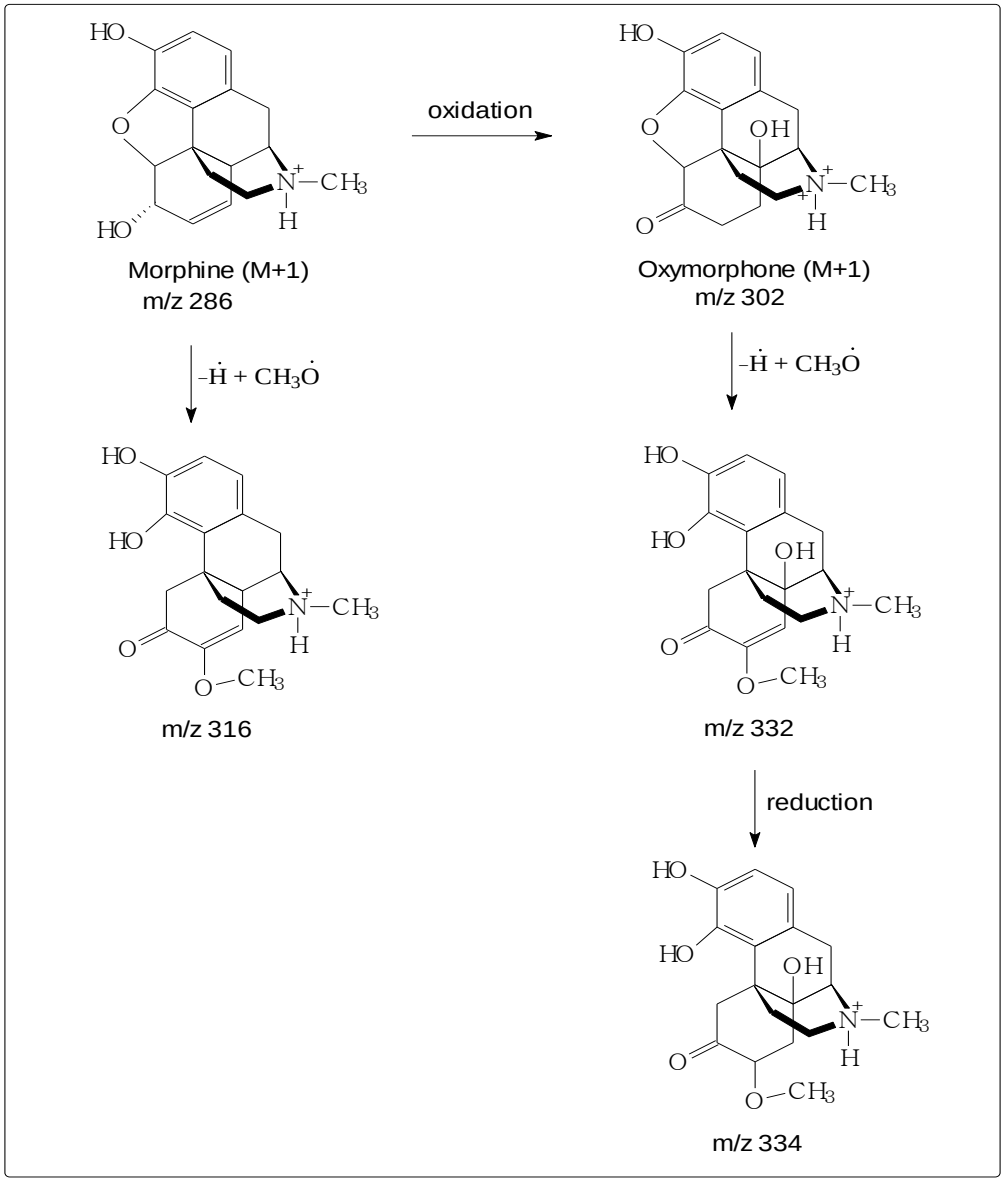
Fig. 4. Mass spectra of morphine solutions.

Methanol solutions of five opiate standards were irradiated with γ-rays at 10, 20, 30, 40 and 50 kGy and their mass spectra were obtainedwith LC/MS. Concerning the LC/MS analyses of the irradiated sample solutions, following things were found. The intensity of the protonated parent species (m/z 286 for morphine, m/z 300 for codeine, m/z 312 for thebaine, m/z 340 for papaverine and m/z 414 for noscapine) and the fragment ions are decreased with increasing doses. However, after the initial irradiation doses several degradation products are observed for mophine, codeine and thebaine. It is suggested that these products are formed by the addition of the methoxy radical ($CH_3O\cdot$) to the parent molecules[2].

Besides this, oxidation and reduction reactions occur, due to these reactions degradation products which has higher m/z values than the parent species were seen in the spectra. At higher dose values these molecules could not be observed. It is said that the percentage degradation of opiates is higher (less degradation products are formed) in the case of higher dose values. Obtained mass spectrum of irradiated morphine solution and degradation products are given in Scheme 2.



Scheme 1. Fragmentation of protonated morphine, m/z 286 (structure b)



Scheme 2. Mass fragments of irradiated morphine solution.

As it was seen from the mass spectra and degradation mechanisms at low dose values of gamma rays irradiation, an addition reaction of a solvent radical ($CH_3O\cdot$) was the dominant process. The radical adduct abstracts hydrogen from solvent molecule to reproduce a solvent radical. However, at the higher dose values degradation products could not be observed. Therefore, degradation efficiency of opiates is increased by applying higher dose values (≥50 kGy).

References

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