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REMOVAL OF PYRIDINE FROM WASTEWATER USING MICROWAVE RADIATION

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Abstract

Pyridine contaminated wastewater presents a great threat on water resources safety. In this study, microwave (MW) radiation was developed for the removal of pyridine from wastewater. The effects of pH, radiation time, post irradiation and initial pyridine concentration on the removal were investigated. The initial pH and radiation time showed significant effects on the removal of pyridine. The largest removal was obtained at pH 9 with initial pyridine-concentration of 20 ppm (MW radiation time 5 min). Wastewater containing high concentration of Pyridine was treated by MW radiation. Up to 97.5% removal. It could be proposed that MW radiation was an effective method for the removal of Pyridine from wastewater.

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1. Introduction

Pyridine and its derivatives are volatile, toxic, and flammable with a pungent and unpleasant odor. Exposure to pyridine has harmful effects on the liver, kidneys, immune systems and reproductive functions, and has potential carcinogenicity [1–7]. Industrial wastewaters containing pyridine and its derivatives show toxicity to aquatic life and create nuisance because of their malodorous and unpleasant smell [6,7,9].

The pyridine concentration in the wastewaters emanating from the plants manufacturing pyridine and its derivatives is generally in the range of 20–300 mg.dm⁻³. During emergency spills, the concentration can be as high as 600–1000 mg.dm⁻³. At a pyridine concentration of 0.82 mg.dm⁻³ in wastewaters, unpleasant pyridine odor is easily detectable [10]. Although no pyridine concentration limit has been prescribed in the industrial wastewaters for their safe discharge into sewers or on land, it is recommended that the pyridine concentration in wastewater should not exceed 1 mg.dm⁻³. This is to minimize its toxicity and to control the odor.

Wastewater that contains pyridine at low concentration is treated in multiple-effect evaporators and incinerators. However, the process is energy intensive and in case of failure of the incinerator, the wastewater is generally discharged with wastewater [11]. Adsorption has been used for the removal of pyridine and its derivatives from wastewater. Adsorbents like: Rundle oil shale [11], montmorillonite and kaolinites [12], -Al₂O₃ and iron powders [13], Zeolite [14], sepiolite [15], granular activated carbon (GAC) [6], activated carbons from coconut fibers and shells [16–18], ion-exchange and porous resins [19] and bagasse fly ash (BFA) [7–9]. Mohan et al. [16–18] have been reported detailed to remove pyridine.

Researchers have attempted the use of MW radiation in environmental remediation. It has been applied to remove dyes from wastewaters [15], and to remediate organics-contaminated soils [16, 17]. In some cases, can be used to remediate soils from and heavy metals [18]. After extensive search, no reports on the removal of pyridine from wastewater by MW radiation have been determined. Applying MW radiation for waste destruction is attracting due to its molecular-level heating which leads to homogeneous and quick thermal reactions [9]. The aim of this work is to use MW radiation to remove pyridine from pyridine-bearing wastewater and to optimize the operating conditions. The mechanism of pyridine removal from wastewater is presented in this work as well.

2 Experimental

2.1 Chemicals

Pyridine (99%, analytical reagent) was used to prepare a synthetic wastewater. Deionized water was used for the preparation of solutions. All reagents were above analytical grade.

2.2. Procedures and equipments

The schematic diagram of the applied experimental apparatus to remove pyridine is shown in Fig. 1. A modified domestic microwave oven (800W, 2450 MHz, Hot plait Co., Korea) with different power setting was used as MW source. A 100-ml glass column reactor was placed in the oven. The reactor was filled with 50 ml of wastewater and radiated by MW under different conditions. The initial pH of the solution was adjusted by NaOH (2.5 M) and HCl (2.5 M). A thermometer was used for the measurement of temperature at the end of radiation. The top of the column was connected to a condensing system to control wastewater volume. The generated contaminant vapor passed through two bottles containing H₂O solution. Each experiment was performed in duplicate to insure the accuracy of data.

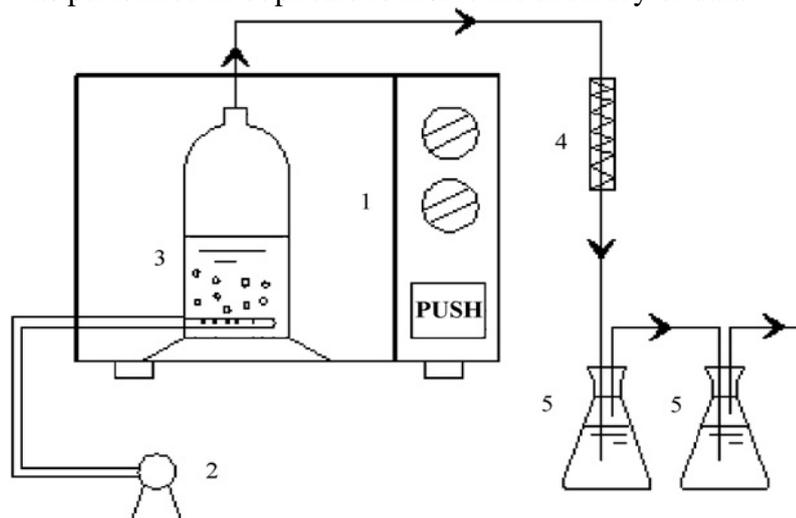


Fig1. Schematic diagram of the microwave reactor system. (1)MW oven, (2) air compressor, (3) glass reactor, (4) condenser, (5) absorption vessel.

2.3. Analysis

In the MW treatment process, the volume of wastewater slightly decreased due to evaporation of water. When the wastewater was cooled to room temperature at the end of experiment, deionized water was added into the reactor to keep the same initial volume of the wastewater. Pyridine concentration was determined by measuring its absorbance 254 nm using UV-visible spectrophotometer. HPLC was used to confirm the determined concentration values. GC/MS technique was also applied to find out if some products were present after irradiating pyridine-wastewater by MW-radiation. For all fresh samples, pH values were adjusted with a pH meter.

1. Results and discussion

Optimization of operation parameters

In order to achieve the maximal removal of pyridine from wastewater by MW radiation, the operation conditions were first optimized. Four factors were considered to evaluate; initial pH, MW radiation time, post irradiation and initial pyridine concentration.

3.1.1. Effect of pH

Fig. 2(a) illustrates the removal of pyridine at different pH initial values. The optimal pH was found to be 9 which resulted in 97.5% pyridine removal after 5 minutes where pH 5 and 7 shows only 80% and 50% removal. No significant increase of pyridine removal was observed when solution pH was further increased. However, at acidic medium (pH<5) the removal efficiency decreased considerably. It is suggested at higher acidity values, formation of ammonium salt predominate which is more stable in solution.

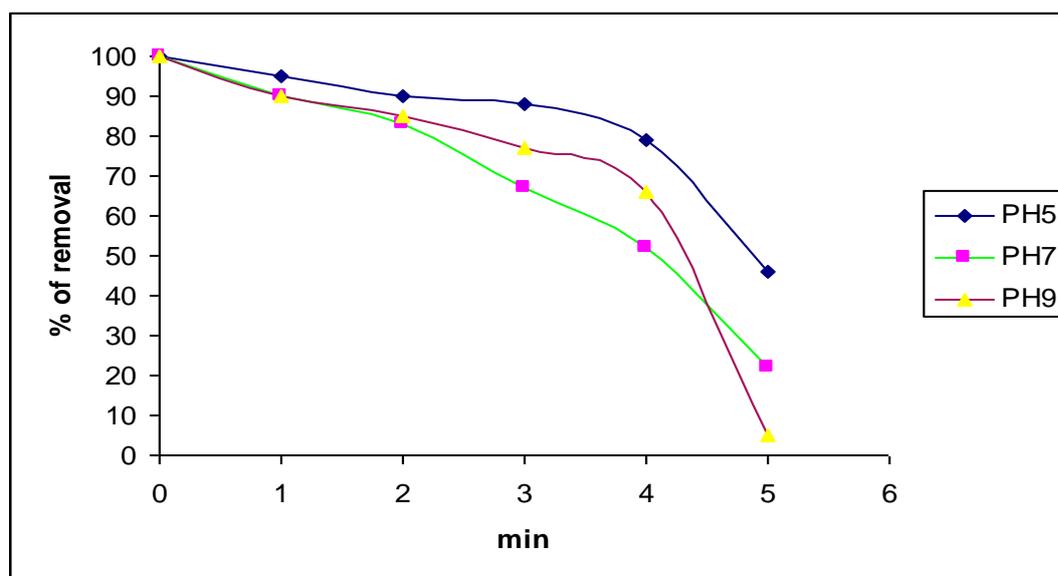


Fig.2. Influence of pH (20 mg/L pyridine, 750W MW power, 10 min radiation time)

3.1.2. Effect of MW radiation time

Fig.3 demonstrates that the removal of pyridine increased with radiation time until attaining removal value of 97.5% after about 5 minutes. With longer MW radiation time, more heat could be generated and this should be avoided. Thus, the solution temperature was measured during irradiation to guarantee safe operating temperature. As shown in the figure, temperature did not exceed 53°C. Consequently, it is believed that remediation is not solely due to heat effect; however it is due to more vigorous and rapid molecular motion induced by MW radiation. As a recommendation, almost all the pyridine in solution could be removed within 10 min of MW radiation and longer radiation time would result in an excessive cost. through an auxiliary experiment, 10 minutes of irradiation did not cause boiling of solution. Regarding the mechanism of MW radiation, it has been generally assumed that energy absorption involves degradation by heat thermal effect should be considered [11,19]. Some other research claimed the non thermal effect in conclusion thermal and non thermal effect is responsible for pyridine removal [20].

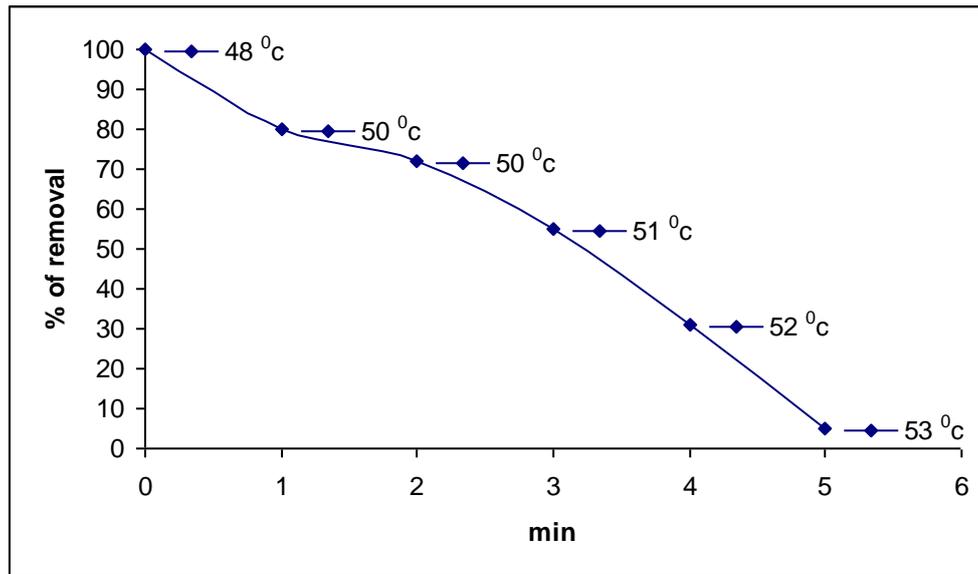


Fig.3. Influence of radiation time (20 mg/l pyridine, , pH = 9, 750W MW power level 1, 5 min radiation time)

3.1.4. Effect of initial pyridine concentration

Figure (4) shows the removal of pyridine at different initial concentrations (10-30 ppm). It could be seen that pyridine could be largely removed by MW radiation, even at the highest initial concentrations. For higher range of concentration (300-1000 ppm), table 1 summarizes the removal of pyridine for this range which also indicates effective degradation of pyridine. When the initial concentration increased from 300 to 1000 ppm, a slight decrease of removal efficiency was observed. However, the removal efficiencies were still above 94%. Accordingly, it is suggested that the effect of the initial concentration on the removal is limited.

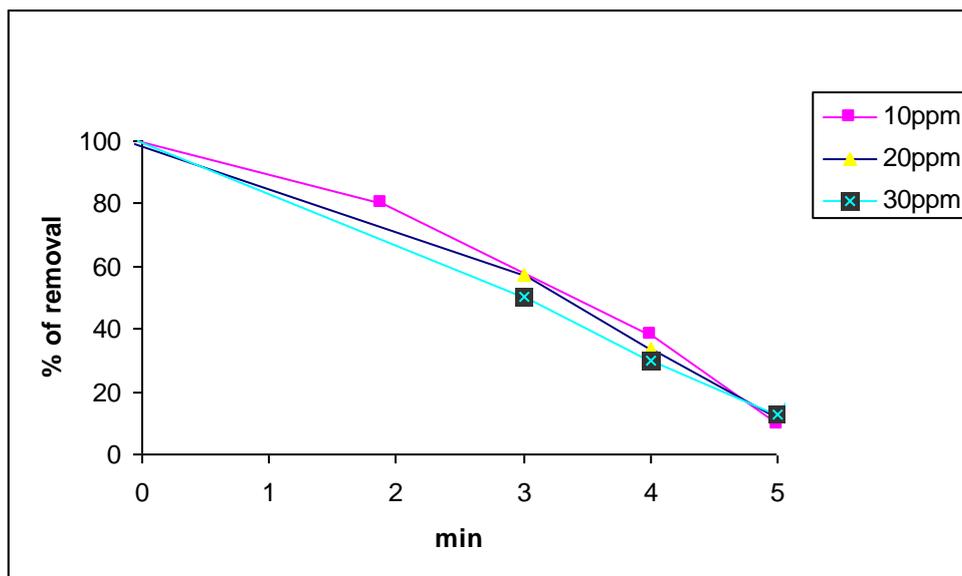


Fig.4. Influence of initial concentration (10, 20, 30 mg/l pyridine, 750W MW power level 1, 5 min radiation time).

Table 1 Removal of pyridine at different high initial concentrations.

Concentration (ppm)	300	500	800	1000
% of removal	95.2	95	94.12	94.01
% of S.D	4.8	5	5.88	5.99

3.1.5 The effect of post irradiation

The effect of post-irradiation was studied in which the sample was radiated for 1 minute and then concentration was determined every 1 hr for a total period of 5 hours. Fig 5 shows that the removal efficiency increased during this period without irradiation. This result is of great interest and may suggest presence of some radiolytic products that is responsible for this post degradation. this phenomenon may suggest that non thermal effects are responsible for the enhancement of pyridine degradation. This idea needs more investigation which is considered to be performed in the near future through a separate work.

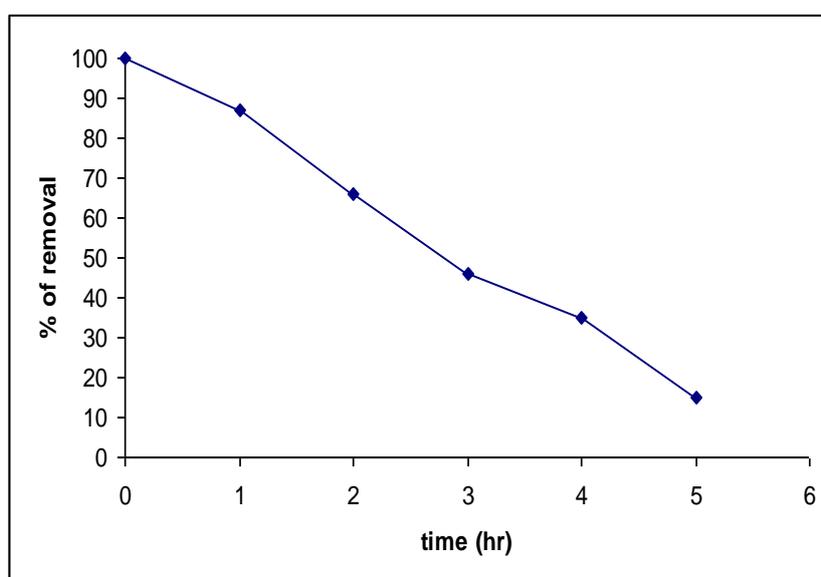


Fig.5. Influence of post irradiation (20 mg/L pyridine, 750W MW power level 1, 1 min radiation time).

3.2. Analysis of pyridine degradation by HPLC and GC/MS

As being volatile to semi-volatile material, pyridine can be determined by gas chromatography using mass spectrometric (MS) detection. High-performance liquid chromatography (HPLC) has also been used to measure pyridine and its metabolites in urine (Shaker et al. 1982). This method has the advantage of compatibility with the liquid matrix samples. . In order to identify the degradation of pyridine different samples were analyzed by HPLC (direct injection) view of the results degradation for pyridine disappearance is suggested in fig 6 (a)the pyridine retention time was 4.435 min without microwave radiation in which pyridine in alkaline medium in (b) the concentration decrease up to 80% with 3min MW radiation time. With the same retention time

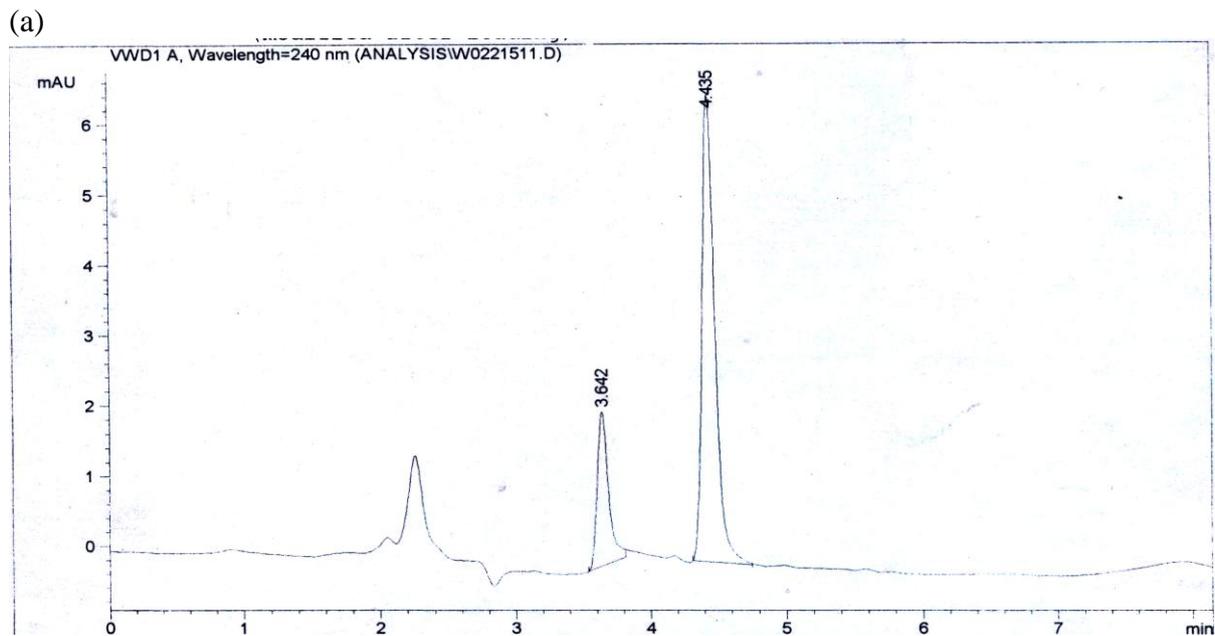


Fig.6.(a) HPLC analysis (20 mg/L pyridine, 750W MW power level 1,PH9, 0 min radiation time)

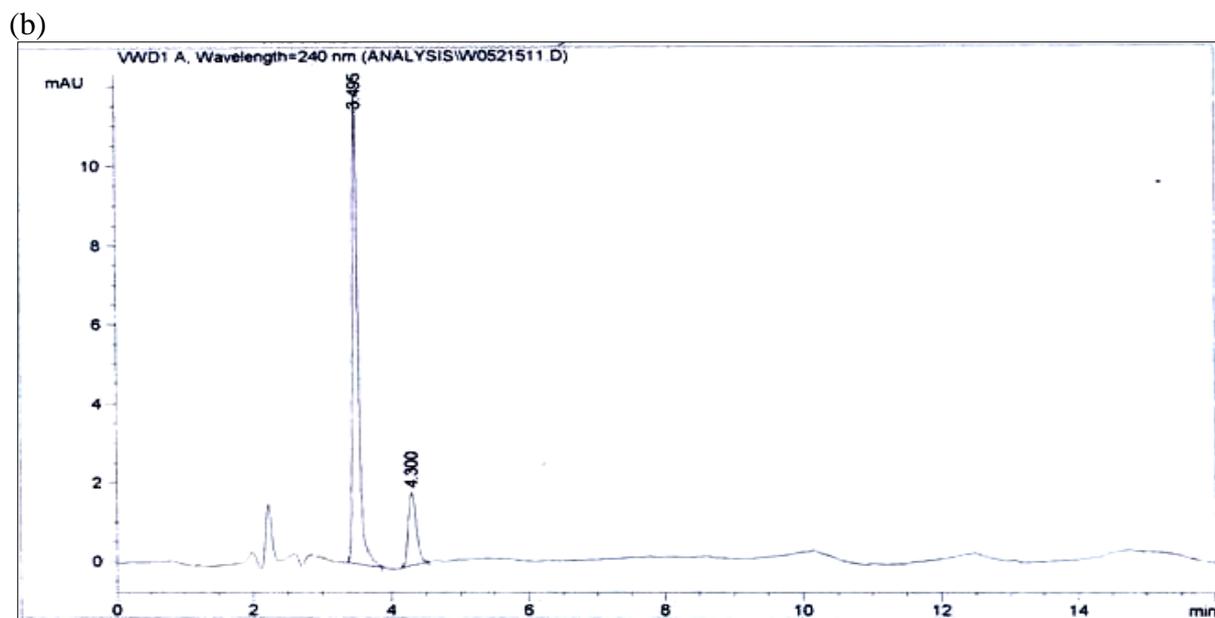


Fig.6.(b) HPLC analysis (20 mg/L pyridine, 750W MW power level 1,PH9, 3 min radiation time)

Through the analysis with GC/MS the abundance of pyridine without MW radiation is shown in fig7 (a) that showed high intensity of pyridine concentration after radiated to 5 min the concentration of pyridine decreased up to 98% as showed if fig7(b)

(a)

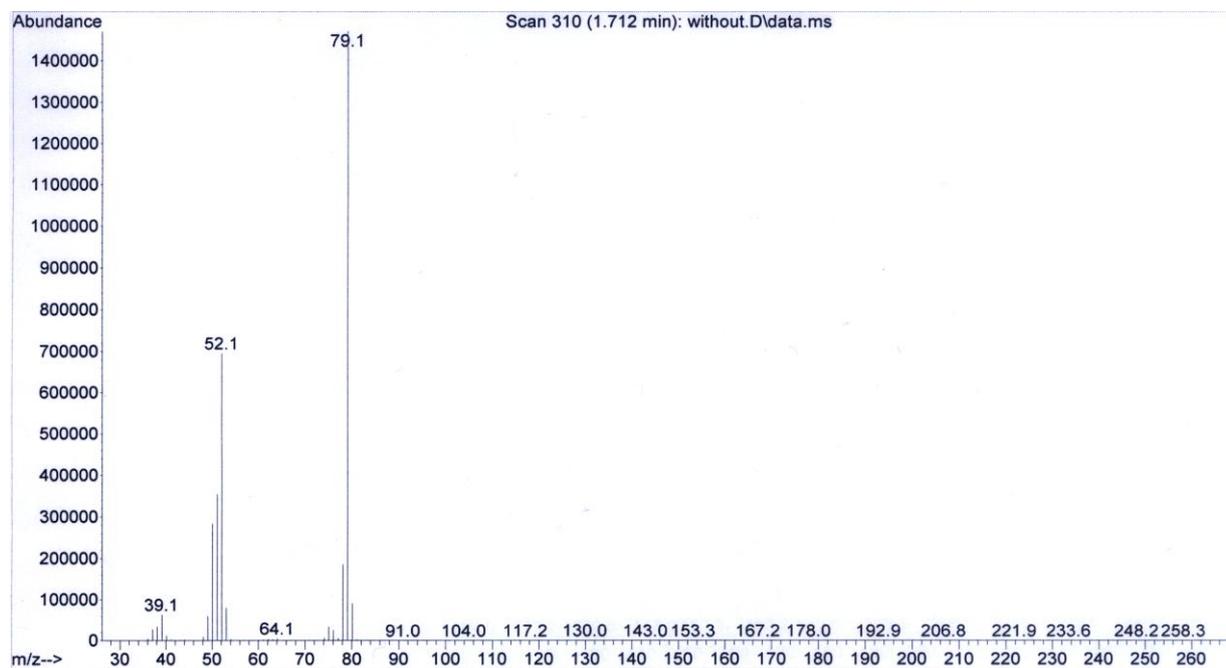


Fig.7.(a) GC/MS analysis (20 mg/L pyridine, 750W MW power level 1,PH9, 0 min radiation time)

(b)

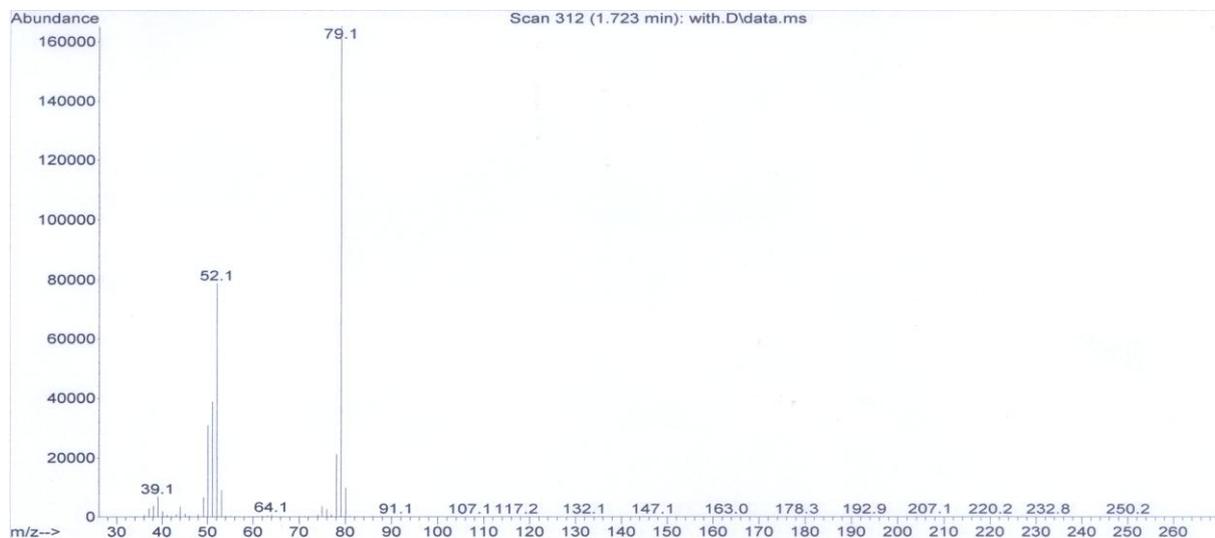


Fig.7.(b) GC/MS analysis (20 mg/L pyridine, 750W MW power level 1,PH9, 0 min radiation time)

4. Conclusions

(1) MW radiation had been proved to be an effective technique for the removal of pyridine in waste water. Large removal of pyridine was achieved by MW radiation in a short time. PH and MW radiation time showed heavy influence on pyridine removal, while and initial pyridine concentration presented minute effect. Higher pH and longer MW radiation time resulted in larger removal efficiencies.

(2) MW radiation can be considered as an alternative approach for the removal of pyridine from wastewater. 10min MW radiation could reduce pyridine concentration from 20 mg/l to 0.5 mg/l at pH 11, when the MW power was 750W, the volume of the wastewater was 100mL.

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