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DEGRADATION OF LEUCOMALACHITE GREEN ON AQUEOUS SOLUTION USING ELECTRON BEAM IRRADIATION

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Abstract: Leucomalachite green (LMG) was eliminated using the Electron beam process on an aqueous solution. The study examines the impact of some factors, i.e. initial pH, absorbed dose, LMG concentration and Hydrogen peroxide (H_2O_2) concentration on the treatment process. The maximum degradation efficiency of malachite green (98.2%) was reached at pH 6, absorbed dose of 4 kGy, LMG concentration of 4 mg/L and H_2O_2 concentration of 8 mM. This environmentally friendly electron beam could be applied to degrade of LMG or other organic compounds on an aqueous solution.

***Keywords*:** leucomalachite green; parasiticide; electron beam; hydrogen peroxide.

Introduction

In Vietnam, aquaculture production is one of the important and biggest sector. In 2015, aquaculture production was valued at 4.26 billion USD, accounting for 6.1 percent of the national Gross Domestic Product

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(GDP), up from 2.2 percent a decade ago.[1] Over the same period, capture fisheries' share of GDP fell from 5.0 percent to 3.6 percent. The rapid growth of the sector has been a major source of agricultural diversification over the past decade. It is a direct result of adapting operating practices together with a focus on the production of exportable species at increased levels of intensification. However, the use of drugs or pharmaceuticals for treating diseases in this sector could cause a lot of environmental issues. One of the typical drug utilized in this purpose is malachite green and its reduced form, leucomalachite green (LMG), which is highly soluble in water and has long been used in the aquaculture industry as a fungicide, parasiticide, and disinfectant.[2] LMG is also used extensively for dyeing silk, wool, jute, leather, ceramics, and cotton and as a cytochemical staining agent.[3] LMG presently is not permitted as a food colouring agent or for use in food fish in the United States (Figure 1); however, it is still used elsewhere in the aquaculture and seafood industries, despite the lack of approval from regulatory authorities and some researcher clasified LMG as a recalcitrant compound.[4]

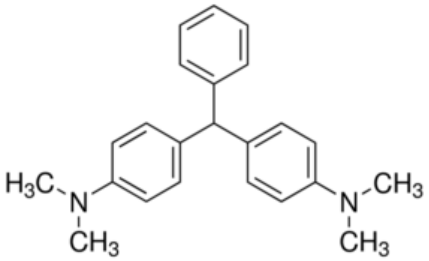

Figure 1. Structure of leucomalachite green.

A variety of techniques, including adsorption, sedimentation, coagulation, electrocoagulation, biological methods, and advanced oxidation processes[5-8] were used to treat this pollutant. However, these traditional technologies require expensive or large areas of land, which are

being challenged by urbanization, lack of space and shortcomings. Biological methods, for example, take a long time and can not degrade the recalcitrant compounds.[9] Besides, recalcitrant compounds are harmful to some microorganisms.[10] Furthermore, the absorbent cannot be reused in general.[8,11] Chemical flocculation even causes pollution due to the production of colloids in wastewater.[12] Common chemical oxidation processes such as chlorine use are slow and need dangerous reactive materials to transport and store.[13] Another problem is that these methods are not effective enough because of the chemical complexity of the wastewater[9] Advanced oxidation and oxidation (AOPs) methods such as ozonation, photocatalysis, and Fenton, which are release hydroxyl radical ($OH^{\bullet}$) are very expensive and uneconomical.[14] Therefore, there should be ways to treat wastewater that consumes appropriate amounts of chemicals and energy, more efficient outputs that meet effluent standards.

Currently, researchers have identified a series of electron beam (EB) -a kind of AOP method- for radioactive disinfection applications. This method can be used to disinfect medical instruments, glassware, as well as to disinfect bottles in the food industry[15] Additionally; some studies indicate that EB is capable of treating domestic wastewater from organic pollutants, petroleum waste,[16] urban wastewater disinfection,[17] increasing the biodegradability of textile wastewater,[18] slaughterhouse wastewater wastewater.[19,20] Estimating the cost of handling EB compared to conventional methods shows that EB is more expensive than chlorine and less expensive than activated sludge.[17]

Although numerous researches have been conducted on the influence of EB on the degradation of recalcitrant organic compounds,[18-20] much less is known about EB degradation on LMG and how H_2O_2 affects

the EB process. Therefore, this approach aims to assess the impacts of EB on the degradation of LMG by factors such as initial LMG concentration, initial pH, the concentration of H_2O_2 and absorbed dose.

Experimental

Synthetic solutions

A stock 100 mg/L LMG's solution was prepared by dissolving 100,00 mg standard LMG (Sigma-Aldrich) in 1000 mL sterilized deionized water. Working LMG solutions from 1.0 to 8.0 mg/L were obtained by serial dilutions of the stock solutions with deionized water. The liquid chromatography (LC, Agilent Technologies, Palo Alto, CA, USA) tandem mass spectrometry (MS/MS, 4000 QTRAP, Applied Biosystems, USA) to monitor transitions m/z 331 → 239 for quantitating LMG . All solvents and other chemicals supplied were analytical grades. The chemical and solutions were protected from light and stored at 4ºC.

Irradiation procedures

The EB irradiation experiments could be found in our previous study[18]. Briefly, 1000 mL of LMG solutions with or without H_2O_2 containing on the plastic box (thickness 2.5 cm) were irradiated with doses from 1.0 to 10 kGy by electron accelerator UERL – 10 – $15S_2$ (10 MeV, 15 kW) in Vietnam Atomic Energy Institute, Vietnam. The absorbed doses were measured using dichromate dosimetry (ASTM International, 2004).[21] Hydrogen peroxide concentration was varied from 1.0 to 4.0 mM, while the initial pH of the samples was adjusted from 3 to 11.

Analysis method

LMG concentrations of samples were analyzed by LC-tandem MS equipped with a turbo spray electrospray (ESI) interface, monitoring transitions m/z 331 → 239 for quantitating LMG. The initial pH values of the solution were measured using an Inolab 740 pH meter. Results were expressed as the mean of triplicate determinations and all statistical analyses were conducted using Microsoft excel software release 2010 (Microsoft Corp., USA).

Results and Discussion

Effect of absorbed dose

In the EB process, absorbed dose determines the $OH^{\bullet}$ production rate that could increment the LMG removal capacity.[22]

$$H_2O \rightarrow [2.8]OH^{\bullet} + [2.7]e^{-}_{aq} + [0.6]H^{\bullet} + [0.72]H_2O_2 + [2.7]H_3O^{+} + [0.48]H_2 \quad (1)$$

In order to evaluate the effect of absorbed dose on LMG removal, the experiment was carried out using various absorbed doses from 0 to 10 kGy at pH 6 and 4 mg/L of LMG without adding H_2O_2.

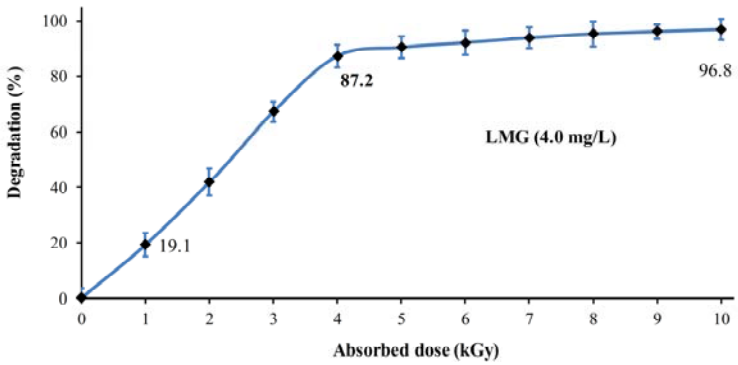

Figure 2. The effect of absorbed dose on the removal efficiencies of leucomalachite green (pH= 6).

Figure 2 shows the behaviour of LMG removal efficiencies under the impact of the variation of the absorbed dose. The results indicate that the removal efficiencies of LMG sharp rise from 19.1% at 1.0 dose to 87.2% at 4.0 dose and then marginal increase to 96.8% at 10.0 dose, respectively which means that the final LMG in the treated water decreased from 4.4 to 0.57 and finally 0.14 mg/L, respectively, These results may be due to the $OH^{\bullet}$ initial rate imcrement and finally attain saturation as reaching equilibrium in LMG solution.[22,23] Which finding ties well with previous studies of Guo and Shen.[24] Therefore, the suitable irradiation dose of 4 kGy was chosen for the next experiment.

Effect of the LMG's concentration

LMG's concentration can play a critical role in the EB process. To investigate the effect of the LMG's concentration on the removal efficiency by EB technique, LMG's concentration is varied from 1 to 8 mg/L, with a fixed absorbed dose (4 kGy) and initial pH (6) without adding H_2O_2.

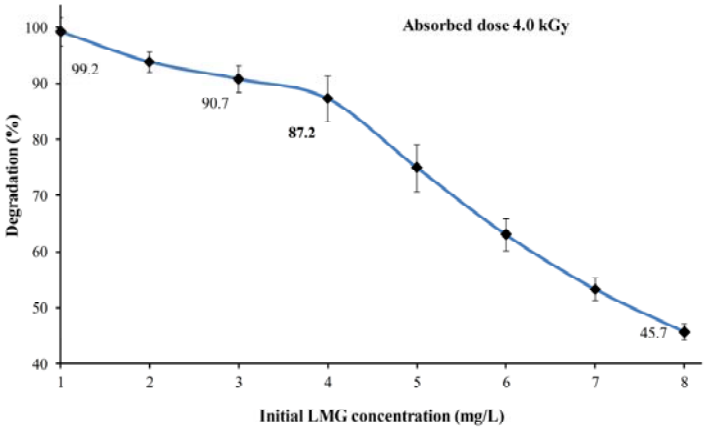

Figure 3. The effect of LMG's concentration on the removal efficiencies with absorbed dose 4kGy at pH= 6.

The results in Figure 3 show that the LMG degradation rate increased much faster for lower initial LMG concentration-response from 4.0 to 1.0 mg/L. However, beyond 4.0 mg/L, the degradation efficiency was sharply reduced from 87.2 (4 mg/L) to 45.7% (8 mg/L). The reason may be due to high concentrations of LMG increased intermediate products which compete with LMG to react with hydroxyl radicals and can also become limiting reagents. Consequently, LMG of 4 mg/L was used in further experiments.

Effect of initial pH

The effects of initial pH on the removal of LMG by EB were studied within the range from 4 to 10. LMG concentrations and absorbed dose were fixed at 4.0 mg/L and 4.0 kGy, respectively, for all the batch experiments, no H_2O_2 were added.

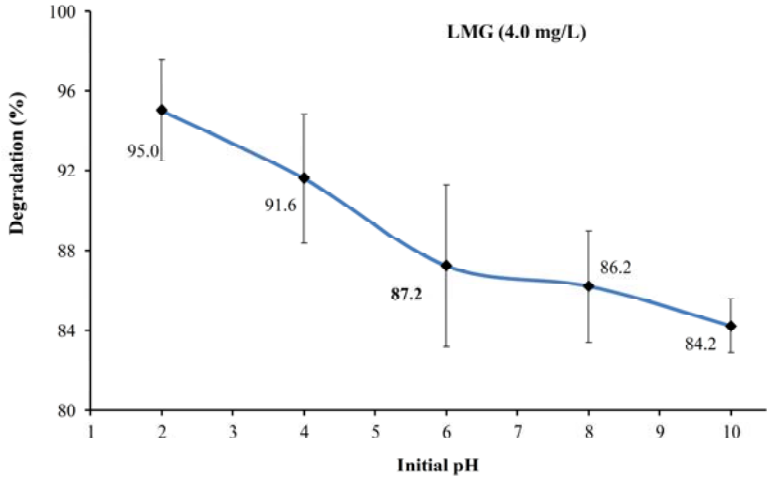

Figure 4. The effect of initial pH on the removal efficiencies with absorbed dose 4 kGy and LMG 4.0 mg/L.

As can be seen in **Figure 4**, degradation efficiency slightly decrements with an increment of initial pH from 1 (95.0%) to 11 (84.2%). This results probably due to the dominant formation of $OH^{\bullet}$ which could interact with

LMG at lower pH value. The findings are consistent with the study of Dessouki, et al. [25] for the degradation of pesticides. Although the removal efficiency is predominant at lower pH, however, insignificantly effects on degradation efficiency are recorded within the assayed pH values (around 10%). Moreover, the natural pH value of 4 mg/L of LMG is approximately 6.0 (87.2%), which means there is no cost for addition adjusting pH chemicals (NaOH or HCl), which lead the EB process is more economical. Therefore, pH 6 was selected for the next experiment.

Effect of hydrogen peroxide concentration

A lot of previous studies indicate that H_2O_2 could enhance $OH^{\bullet}$ generation and then improve the organic removal in some kind of wastewater[17,18] as shown in Equations 2 and 3.

$$e^-_{aq} + H_2O_2 \rightarrow OH^{\bullet} + OH^- \quad (2)$$

$$H^{\bullet} + H_2O_2 \rightarrow OH^{\bullet} + H_2O \quad (3)$$

The effect of H_2O_2 was studied by changing the H_2O_2 concentrations from 1.0 to 6.0 mM while keeping initial pH, absorbed dose and LMG concentration constant.

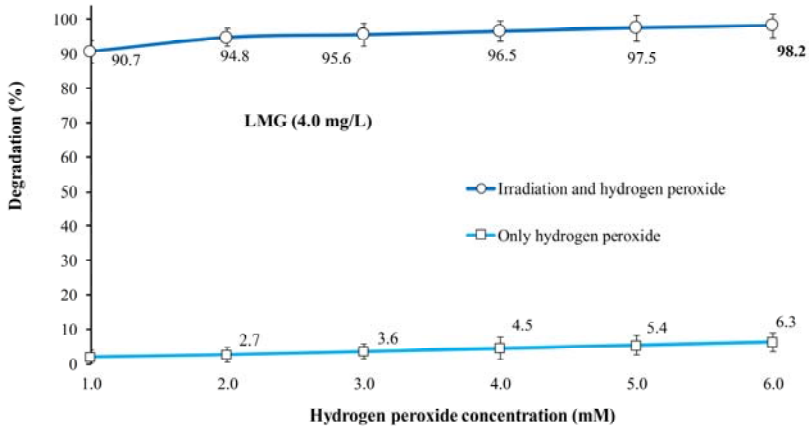

Figure 5. The effect H_2O_2 on the removal efficiencies with absorbed dose 4 kGy and LMG 4.0 mg/L at pH 6.

The results presented in Figure 5, it was observed that degradation slightly increases with H_2O_2 alone (6.3% at 6 mM) while EB coupled H_2O_2 significantly increase removal efficiency from 87.2 (EB alone) to 90.2% (EB/1 mM H_2O_2) and 98.2% (EB/6 mM H_2O_2). The combined effect of H_2O_2 and EB was much higher than the effect of either component or even of the sum of the individual effect. The results again demonstrate that H_2O_2 is able to activate EB and produce more $OH^{\bullet}$ in water, the findings are directly in line with previous reports.[17,18]

Conclusions

This present work investigates the efficiency of electron beam coupled with H_2O_2 performed to the treatment of leucomalachite green in aqueous solution. The experiment was carried out at different leucomalachite green concentration, absorbed dose, H_2O_2 concentration and initial pH values. EB techniques for degradation of LMG could be favoured at lower initial pH, higher absorbed dose and higher H_2O_2 concentration. At the optimum values of the variables (4 kGy absorbed dose, 4 mg/L of LMG, pH 6 and 6 mM of H_2O_2), almost LMG had been eliminated (98.2%). However, beyond the optimum value, the further increase in absorbed dose and H_2O_2 concentration could lead to the degradation of LMG declining. The results show that electron beam radiation is a promising method for the degradation of organic pollutants in aqueous solutions.

Acknowledgments

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