

**REMOVAL OF ENDOSULFAN FROM
WATER USING ADVANCED OXIDATION
TECHNIQUES**



BY

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**NATIONAL CENTRE OF EXCELLENCE IN
PHYSICAL CHEMISTRY
UNIVERSITY OF PESHAWAR, PAKISTAN
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**It is recommended that the dissertation prepared by
NOOR SAMAD SHAH
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DEDICATION

My thesis is dedicated to the most respectable personality and ideal man of the world, Prophet Mohammed (PBUH). I dedicate my effort of writing dissertation to my sweet and loving mother whose spiritual and immortal love has always helped me to keep my determination steady. It is also dedicated to my respectable teacher, Prof. Dr. Hasan Mahmood Khan whose proper guidance enabled me to complete this effort successfully.

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Abstract

This study investigated the removal of endosulfan, an organochlorine insecticide and an emerging water pollutant, from water using gamma rays and UV-C radiation based advanced oxidation and reduction processes (AORPs).

For gamma rays induced degradation, starting from an initial endosulfan concentration of 1.0 μM , 96% removal of endosulfan was achieved at an absorbed dose of 1020 Gy. The removal of endosulfan by gamma irradiation was mainly due to the reaction of hydrated electrons (e^-_{aq}) and removal was inhibited in the presence of e^-_{aq} scavengers, such as nitrous oxide gas (N_2O), H_2O_2 , H^+ , nitrate, and Fe^{3+} ions. In addition, removal of endosulfan was inhibited to lower extent in the presence of tert-butanol (*t*-BuOH) and isopropanol (*i*-PrOH), and humic acid (HA) showing the minor contribution of hydroxyl radical in the degradation of endosulfan. The radiation yield (G-value) decreased with an increase in absorbed dose. A decrease in observed dose constant and increase in radiation yield (G-value) was observed with increasing initial concentrations of the target contaminant. At an absorbed dose of 300 Gy, destruction of endosulfan increased from 62% to 83% with decreasing dose rate from 296 to 97 Gy/h. The radiolytic degradation of endosulfan I was comparatively higher than endosulfan II at the same absorbed dose. The efficiency of gamma irradiation was also studied for the dechlorination of endosulfan and degradation of by-products of endosulfan, i.e., endosulfan sulfate. It was found that gamma irradiation based AORPs are also highly efficient for the removal of endosulfan sulfate from a water environment. It was concluded that radiolytic degradation of endosulfan sulfate also occurs due to the reaction of e^-_{aq} and was inhibited in the presence of e^-_{aq} scavengers, such as N_2O gas, H_2O_2 , nitrate, and Fe^{3+} ions. The degradation of endosulfan sulfate was more

efficient at neutral pH, followed by alkaline pH while least at the acidic pH. The degradation of endosulfan sulfate followed *pseudo-first-order* kinetics and the observed *pseudo-first-order* degradation rate constants decreased with increasing initial concentrations of endosulfan sulfate. The G-value decreased with increasing absorbed gamma ray dose while it increased with increasing initial concentrations of the target contaminant.

Degradation pathways of endosulfan and endosulfan sulfate were proposed based on identified degradation by-products and pattern of degradation. The degradation by-products included endosulfan ether, endosulfan lactone, acetate, chloride and sulfate ions.

In case of UV-C based advanced oxidation processes (AORPs), i.e., UV/S₂O₈²⁻, UV/HSO₅⁻, and UV/H₂O₂, significant removal, 91%, 86%, and 64% for endosulfan and 97.5%, 90%, and 70% for endosulfan sulfate was achieved, respectively, at a UV fluence of 480 mJ/cm². The degradation of endosulfan and endosulfan sulfate by the AOPs was found to be due to reactions of hydroxyl and/or sulfate radicals. The efficiency of the radicals was however, inhibited in the presence of radical scavengers, such as alcohols (*t*-BuOH and *i*-PrOH) and natural organic matter (NOM) and some inorganic anions, such as nitrite and bicarbonate. The observed *pseudo-first-order* rate constant decreased while the degradation rate increased with increasing initial concentration of the target contaminant. The efficiency of AOPs was further evaluated for the degradation of the by-products of endosulfan and endosulfan sulfate i.e., endosulfan ether. Results of this study suggest that UV-C based AOPs are promising methods for the degradation of endosulfan and its by-products from a contaminated water environment.