

UNIVERSITI TEKNOLOGI MARA

**MECHANISMS AND KINETICS OF
ENHANCED OXIDATIVE
DEGRADATION OF
TETRACHLOROETHENE BY IRON
BEARING SOIL MINERALS AND
GLUTATHIONE IN HYPORHEIC
ZONE**

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Thesis submitted in fulfillment
of the requirements for the degree of
Doctor of Philosophy of Civil Engineering
(Environmental Engineering)

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AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

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ABSTRACT

The feasibility study on the physical and chemical characterization of hyporheic zone at the Klang River Basin was conducted to evaluate the controlling factors to the oxidative degradation of PCE as natural attenuation process in the hyporheic zone. The presence of iron-bearing soil minerals (IBSMs) (magnetite (Fe_3O_4), hematite (Fe_2O_3)), electrolytes (Fe , NO_3^- and SO_4^{2-}) and natural organic matter were detected in the hyporheic zone as important environmental factors that significantly influenced the mechanisms and kinetics of oxidative degradation of PCE. The oxidative degradation of PCE was initiated by nano-IBSMs (nano- Fe_3O_4 and nano- Fe_2O_3) via Fenton-like reaction. However, PCE was incompletely degraded due to the instability of $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox in the nano-IBSMs suspension. The oxidative degradation of PCE was enhanced through the coupling of redox reactions between nano-IBSMs and glutathione (GSH). The potential role of GSH as a reductant could sustain the redox of Fe^{3+} to Fe^{2+} and promote the generation of reactive oxygen species ($\text{OH}\cdot$ and $\text{O}_2^{\cdot-}$) for the enhanced oxidative degradation of PCE by nano-IBSMs. The oxidative degradation kinetic rate constant of PCE in the nano- Fe_3O_4 -GSH suspension was 11.7 times faster ($0.035 \pm 0.001 \text{ hr}^{-1}$) than that in the nano- Fe_3O_4 suspension ($0.003 \pm 0.08 \text{ hr}^{-1}$). Contrarily, PCE was oxidatively degraded 600 times faster ($0.014 \pm 0.003 \text{ hr}^{-1}$) in the nano- Fe_2O_3 -GSH than that in the nano- Fe_2O_3 ($0.00023 \pm 0.00008 \text{ hr}^{-1}$). The oxidative degradation of PCE was predominantly controlled by the concentration of $\text{OH}\cdot$ than the $\text{O}_2^{\cdot-}$ in the nano-IBSMs-GSH suspension. The comparison of enhanced oxidative degradation of PCE between nano- Fe_3O_4 -GSH and nano- Fe_2O_3 -GSH revealed that the oxidative degradation kinetics of PCE by the nano- Fe_3O_4 -GSH was 2.5 times faster ($0.035 \pm 0.001 \text{ hr}^{-1}$) than the nano- Fe_2O_3 -GSH ($0.014 \pm 0.003 \text{ hr}^{-1}$), indicating nano- Fe_3O_4 was more reactive as iron catalyst than nano- Fe_2O_3 . The enhanced oxidative degradation of PCE by nano-IBSMs-GSH were conducted at different environmental conditions to evaluate the kinetics of the oxidative degradation. The enhanced oxidative degradation kinetics of PCE significantly increased by the increased of concentration of nano-IBSMs and GSH in alkaline condition. Interestingly, a remarkable enhancement of the oxidative degradation of PCE by the nano-IBSMs-GSH in the presence of NO_3^- and SO_4^{2-} due to the generation of $\text{NO}_3\cdot$ and $\text{SO}_4^{\cdot-}$ radicals. However, the presence of HA and increased concentration of PCE significantly decreased the kinetics of the oxidative degradation of PCE. PCE was completely transformed to oxalic acid as a major by-product via hydroxylation and oxidation reactions.

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