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COMBINED PHYSICOCHEMICAL AND BIOLOGICAL  
TREATMENT OF REFINERY WASTEWATER

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REFINERY WASTEWATER

by

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UNIVERSITI TEKNOLOGI PETRONAS

COMBINED PHYSICOCHEMICAL AND BIOLOGICAL TREATMENT OF  
REFINERY WASTEWATER

by

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DECLARATION OF THESIS

Title of thesis

COMBINED PHYSICOCHEMICAL AND BIOLOGICAL  
TREATMENT OF REFINERY WASTEWATER

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## ABSTRACT

Petroleum refining industries are producing wastewater that contains hydrocarbons, phenol and dissolved minerals. These compounds result in environmental and health effects. In this study, actual petroleum refinery wastewater was treated using the Fenton process to improve its biodegradability for post treatment by a laboratory-scale Sequencing Batch Reactor (SBR). Response Surface Methodology (RSM) was applied for optimization and data analysis of the Fenton process. The maximum biodegradability was achieved at the reaction time of 60 minutes and at a constant  $\text{H}_2\text{O}_2/\text{COD}$  molar ratio of 2 and  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  molar ratio of 5 to give 0.44  $\text{BOD}_5/\text{COD}$  with 79 and 77% COD and BOD removal efficiency, respectively. The results is considered acceptable and satisfied based on ANOVA analysis ( $P$ : <0.0001,  $R^2$ :0.95,  $Adj. R^2$ :0.91,  $AP$ : 16.479 and  $CV$ : 6.09). Preliminary performance of the SBR indicated wastewater load (food) to microorganisms ratio (F/M) of 0.1 was the most suitable ratio as the lowest COD concentration was achieved in the effluent. SBR was run in 3 cycles/d and consisted of fill (2 minutes), react (6 hours), settle (1 hour 50 minutes), and idle and draw (8 minutes). Experiment was completed within 49 days as the SBR reached steady state condition with constant removal efficiency of COD and gradual increase of microorganism population (MLVSS). The study indicates good performance of SBR with removal efficiency of 70, 76, 96, 96, 97, 90, 100 and 93% for COD, TSS,  $\text{BOD}_5$ , oil and grease, colour, ammonia nitrogen, phenol and sulphide, respectively. SBR effluent met the Standard B of discharge limits established by the Department of Environment (DOE), Malaysia.

## ABSTRACT

Industri penapisan petroleum menghasilkan air sisa yang mengandungi hidrokarbon, fenol dan mineral larut. Sebatian ini memberi kesan kepada alam sekitar dan kesihatan manusia. Dalam kajian ini, air sisa penapisan petroleum sebenar telah dirawat menggunakan proses Fenton bagi meningkatkan biodegradasi untuk rawatan pasca oleh reaktor berskala makmal-Sequencing Batch Reactor (SBR). Response Surface Methodology (RSM) telah digunakan untuk mengenalpasti kadar optimum dan analisis data bagi proses Fenton. Kadar biodegradasi maksimum telah dicapai dalam masa 60 minit pada nisbah molar  $H_2O_2$ /COD 2 dan  $H_2O_2/Fe^{2+}$  5 dan menunjukkan keputusan 0.44  $BOD_5/COD$  dengan 79 dan 77% kadar penyingkiran COD dan BOD. Keputusan ini diterima berdasarkan analisis ANOVA ( $P$ : <0.0001,  $R^2$ :0.95,  $Adj. R^2$ : 0.91,  $AP$ : 16.479 and  $CV$ : 6.09). Kajian awal SBR mengenalpasti 0.1 adalah nisbah makanan/mikroorganisma (F/M) yang paling sesuai dengan kadar COD terendah dalam efluen. SBR telah dijalankan dalam 3 kitaran/hari dan terdiri dari fasa pengisian air sisa (2 minit), reaksi (6 jam), pemendapan (1 jam 50 minit), penurasan air terawat dan stabilisasi (8 minit). Eksperimen SBR telah diselesaikan dalam tempoh 49 hari dan mencapai keadaan 'steady state' berdasarkan efisiensi kadar penyingkiran COD secara berterusan dan peningkatan populasi mikroorganisma (MLVSS) secara beransur-ansur. Kajian menunjukkan prestasi SBR adalah baik dengan penyingkiran sebanyak 70, 76, 96, 96, 97, 90, 100 dan 93% bagi pepejal terampai, COD,  $BOD_5$ , minyak dan gris, warna, nitrogen ammonia, fenol dan sulfit. Efluen SBR mematuhi piawaian Standard B yang ditetapkan oleh Jabatan Alam Sekitar (JAS), Malaysia.

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## LIST OF ABBREVIATIONS

### Abbreviation

PP (M) SB	PETRONAS Penapisan (Melaka) Sdn. Bhd.
ETS	Effluent Treating System
PRW	Petroleum Refinery Wastewater
SBR	Sequencing Batch Reactor
F/M	Food to Microorganism ratio
AOPs	Advanced Oxidation Processes
RSM	Response Surface Methodology
CCD	Central Composite Design
ANOVA	Analysis of Variance
<i>P</i>	Probability of Error
<i>AP</i>	Adequate Precision
<i>CV</i>	Coefficient of Variance
COD	Chemical Oxygen Demand
BOD <sub>5</sub>	Biochemical Oxygen Demand, 5 days
MLSS	Mixed Liquor Suspended Solid
MLVSS	Mixed Liquor Volatile Suspended Solid
SVI	Sludge Volume Index
DO	Dissolved Oxygen

TSS	Total Suspended Solid
TKN	Total Kjeldahl Nitrogen
TOC	Total Organic Carbon

#### Nomenclatures

$\text{H}_2\text{O}_2$	Hydrogen Peroxide
$\text{Fe}^{2+}$	Ferrous Iron
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Ferrous Sulphate Heptahydrate
$\text{H}_2\text{SO}_4$	Sulphuric Acid
NaOH	Sodium Hydroxide