HETEROGENEOUS CATALYTIC OZONATION USING MAGNETICALLY RECOVERABLE COPPER FERRITE FOR THE TREATMENT OF SURFACTANT CONTAINING LAUNDRY WASTEWATER

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FACULTY OF SCIENCE AND NATURAL RESOURCES
UNIVERSITI MALAYSIA SABAH
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ABSTRACT

Laundry detergent wastewater is a potential renewable resource that can be recycled and reused in order to mitigate water scarcity. The negative impacts of surfactant from laundry detergent wastewater on the environment, increased usage of detergent due to intense population growth, and the ineffectiveness of conventional treatment technologies, have resulted in the eutrophication of lakes and rivers. The catalytic ozonation process as one of the most effective advanced oxidation processes (AOPs) has shown tremendous potential in the treatment and reclamation of laundry wastewater as an alternative water source. In this research, a magnetically recoverable copper ferrite was prepared by the modified sol-gel method for the treatment of laundry detergent wastewater using the catalytic ozonation process. The catalyst was characterized by X-ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET), X-ray photoelectron spectroscopy (XPS), field-emission scanning electron microscope (FESEM), magnetization measurements (VSM), and Fourier transform infrared (FT-IR) spectroscopy. The effects of important parameters such as catalyst dosages (0.1 to 1.5g/L), solution pH (3, 7 and 10), initial surfactant concentrations (2.5, 5.0 and 10 ppm), and ozone dosages (0.88, 3.68 and 4.88mg/min) on the efficiency of catalytic ozonation were investigated. The best conditions for surfactant removal (98.4%) were obtained at an initial surfactant concentration of 10ppm, reaction time of 30 minutes, a catalyst dosage of 0.2g/L, an initial solution pH of 7 and an ozone dosage of 3.68mg/min. At this condition, further chemical oxygen demand (COD) removal testing was determined to be 79.5%, compared to that of the ozonation process at 26.7%. The biochemical oxygen demand (BOD) removal percentages for ozonation and catalytic ozonation were 33.3% and 93.3%, respectively. The experimental data fits well with the pseudo-first-order kinetics model. The repetitive use of the catalyst showed that even after three consecutive runs, the catalytic activity had not decreased much. The utilisation of copper ferrite in catalytic ozonation encounters certain restrictions, such as the leaching of metal ions and the agglomeration of the catalyst. The quality of the treated wastewater complies with the standard approved by the Environmental Quality Acts Standard 2009. The potential reaction mechanism of catalytic ozonation utilising copper ferrite involves the integration of molecular ozone oxidation, as well as heterogeneous and homogeneous catalytic ozonation processes. Furthermore, the economical evaluation by means of the calculation of electric energy per order of pollutant removal (EE/O) indicated that the catalytic ozonation process required less electrical energy (60.31 $kWhm^{-3}order^{-1}$) compared to ozonation process (381.68 $kWhm^{-3}order^{-1}$). Overall, catalytic ozonation with copper ferrite is a feasible method for laundry detergent wastewater treatment.

ABSTRAK

PENGOZONAN PEMANGKIN HETEROGEN MENGGUNAKAN KUPRUM FERIT BOLEH PULIH SECARA MAGNETIK UNTUK RAWATAN AIR SISA PENCUCI PAKAIAN YANG MENGANDUNGI SURFAKTAN

Air sisa pencuci pakaian ialah sumber air berpotensi yang boleh dikitar semula serta digunakan semula untuk mengatasi masalah kekurangan air. Kesan negatif detergen daripada air sisa pencuci pakaian terhadap alam sekitar, peningkatan penggunaan detergen akibat pertumbuhan populasi yang pesat, dan ketidakberkesanan teknologi rawatan konvensional, telah mengakibatkan eutrofikasi tasik dan sungai. Proses pengozonan dengan pemangkin sebagai salah satu prosess oxidasi lanjutan yang berkesan telah menunjukkan potensi yang besar dalam rawatan dan pemulihan air sisa pencuci pakaian sebagai sumber air alternatif. Dalam kajian ini, kuprum ferit yang boleh dipulihkan secara magnetik telah disintesis dengan kaedah sol-gel untuk rawatan air sisa pencuci pakaian menggunakan proses pengozonan dengan pemangkin. Pemangkin itu dicirikan dengan difraksi serbuk sinar-X (XRD), Brunauer-Emmett-Teller (BET), spektroskopi fotoelektron sinar-X (XPS), mikroskop elektron imbasan elektron (FESEM), pengukuran sifat kemagnetan (VSM), dan inframerah transformasi Fourier (FT-IR). Kesan parameter-parameter yang penting seperti dos pemangkin (0.1 hingga 1.5g/L), pH larutan (3, 7 dan 10), kepekatan detergen awal (2.5, 5.0 dan 10ppm), dan dos ozon (0.88, 3.68 dan 4.88mg/min) tentang kecekapan proses pengozonan dengan pemangkin telah dikaji. Pestasi terbaik untuk penyingkiran detergen (98.4%) diperolehi pada kepekatan detergen awal 10ppm, masa tindak balas 30 minit, dos mangkin 0.2g/L, nilai pH awal 7 dan dos ozon 3.68mg/min. Dalam keadaan ini, ujian penyingkiran permintaan oksigen kimia (COD) selanjutnya menunjukkan penurunan sebanyak 87.5%, berbanding dengan proses pengozonan tanpa pemangkin yang mempunyai penurunan sebanyak 26.7%. Ujian penyingkiran permintaan oksigen kimia (BOD_5) menunjukkan penurunan sebanyak 33.3% bagi proses ozon dan 93.3% bagi proses pengozonan dengan pemangkin. Data eksperimen kajian ini berpadanan dengan model kinetik pseudo-tertib pertama. Penggunaan pemangkin secara berulang kali menunjukkan bahawa walaupun selepas tiga penggunaan secara berturutan, aktiviti pemangkinan tidak banyak berkurangan. Ada beberapa isu yang mengehadkan penggunaan kuprum *ferit dalam pengozonan dengan pemangkin, termasuk keterlarutlesapan logam dan penggumpalan pemangkin. Kualiti air sisa terawat mematuhi piawaian yang diluluskan oleh Piawaian Akta Kualiti Alam Sekeliling 2009. Mekanisme tindak balas bagi proses pengozonan dengan ferit kuprum ialah gabungan pengoksidaan ozon molekul, pengozonan pemangkin secara proses heterogen dan homogen. Tambahan pula, penilaian ekonomi melalui pengiraan tenaga elektrik bagi penyingkiran bahan pencemar (EE/O) menunjukkan bahawa proses pengozonan dengan pemangkin (60.31 $kWhm^{-3}order^{-1}$) menggunakan tenaga elektrik yang rendah berbanding dengan penggunaan tenaga elektrik oleh proses pengozonan tanpa pemangkin (381.68 $kWhm^{-3}order^{-1}$). Secara keseluruhannya, pengozonan dengan pemangkin, iaitu kuprum ferit ialah kaedah yang boleh digunakan untuk rawatan air sisa pencuci pakaian.*

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Å - Bond length in Angstorm

F_2 - Fluorine

$^{\cdot}OH$ - Hydroxyl Radical

O_3 - Ozone

H_2O_2 - Hydrogen Peroxide

$^{\cdot}HO_2$ - Hydroperoxide Radical

$^{\cdot}HO_3$ - Hydrogen Trioxide Radical

$^{\cdot}O_3^-$ - Ozonide Anion

MnO_4^- - Permanganate

CO_2 - Chlorine Dioxide

$HClO$ - Hypochlorus Acid

Cl_2 - Chlorine Gas

Br_2 - Bromine Gas

I_2 - Iodine Gas

O_2 - Oxygen Gas

OH^- - Hydroxide Ion

NO_2^- - Nitrite Ion

Cl^- - Chloride Ion

$^{\cdot}O_2^-$ - Superoxide Anion

HO_2^- - Hydroperoxide Ion

pK_a - Acid Dissociation Constant

$^{\cdot}HO_4$ - Hydrogen Tetraoxide Radical

$^{\cdot}R$ - Organic Radicals

$^{\cdot}ROO$ - Organic Peroxyl Radicals

HCO_3^- - Bicarbonate

CO_3^{2-} - Carbonate

$H_2PO_4^-$ - Dihydrogen Phosphate Ion

EEO - Electric Energy Consumption Per Order

pH_{PZC} - Point Of Zero Charge

H_c - Coercivity

M_s - Magnetisation

M_r - Retentivity

v - Volume of Gas

A - Absorbance

$\in$ - Molar Absorbance Coefficient

L - Path Length

c - Concentration

P_0 - Pressure

LIST OF ABBREVIATIONS

EC - Electrical Conductivity
TDS - Total Dissolved Solid
TSS - Total Suspended Solid
TH - Total Hardness
TA - Total Alkalinity
TOC - Total Organic Carbon
BOD_5 - Biochemical Oxygen Demand
COD - Chemical Oxygen Demand
NTU - Nephelometric Turbidity
LAS - Linear Alkylbenzene Sulfonates
AOPs - Advanced Oxidation Processes
UV - Ultraviolet Irradiation
SDS - Sodium Dodecyl Sulfate
SDBS - Sodium Dodecylbenzene Sulfonates
O - Ozonation
CO - Catalytic Ozonation
SWOT - Strengths, Weaknesses, Opportunities, and Threats
PAC - Powdered Activated Carbon
AC - Activated Carbon
XRD X-Ray Diffraction Technique
FESEM Field Emmision Scanning Electron Microscopes
BET Brunauer-Emmett-Teller
EDX Energy Dispersive X-Ray Spectroscopy
TGA Thermogravimetric Analysis
XPS X-Ray Photoelectron Spectrocopy
KPMS - Potassium Hydrogen Monopersulfate

PMS - Peroxymonosulfate

DMAC - N,N-dimethylacetamide

DZN - Diazinon

2,4-D - 2,4-dichlorophenoxyacetic acid

MOF - Metal Organic Frameworks

KI - Potassium Iodide

TBA - Tert-butanol

IUPAC - International Union of Pure and Applied Chemistry

MBAS - Methylene Blue Active Substances Reagent

ABS - Absorbance

FT-IR - Fourier-Transform Infrared Spectroscopy

JCPDS - Joint Committee on Powder Diffraction Standards

NaOH - Sodium Hydroxide

HCl - Hydrochloric Acid

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CHAPTER 1

INTRODUCTION

1.1 Introduction

All living things, including humans, livestock, marine life, and natural ecosystems, are dependent on clean water resources. The available freshwater reserves on earth are insufficient to satisfy the growing water demands of increasing various human activities including agriculture, industrial, and domestic activities (Date *et al.*, 2022; Mannina *et al.*, 2022). The problem of water shortage has been exacerbated by environmental pollution, the increasing water contamination resulting from human activities, industrial waste, and climate change. There are currently an estimated 1.5 billion people living in water-scarce regions, and this figure is expected to increase to 4 billion by 2050 (Furlong *et al.*, 2019). The global water demand is expected to rise from 3,500 km^3 per year in 2000 to approximately 5,500 km^3 per year in 2050 (Willet *et al.*, 2019).

Exploration of clean water resources is a crucial and long-term effort to ensure the future sustainable growth of society. Recovering, reusing, and reclaiming water should be stressed for water conservation (Date *et al.*, 2022). Alternative water sources, such as treated laundry wastewater is a potential renewable resource that can alleviate water shortage issues and be used for agricultural, industrial, and urban applications (Gisi *et al.*, 2017; Joseph *et al.*, 2021). There are large amount of laundry detergent wastewater discharge produced by domestic, industrial, and institutional sectors that were reported (Braga & Varesche, 2014; Joseph *et al.*, 2021; Yaseen *et al.*, 2019). Japan and Malaysia were reported to have the greatest volume of laundry wastewater discharge, which ranges from 60 to 80 m^3/household/year as shown in Figure 1.1 (Ho *et al.*, 2021).