

**IMMOBILIZED BIOMASS IN POLYMERIC GELS  
FOR THE BIOREGENERATION OF GRANULAR  
ACTIVATED CARBON LOADED WITH ISOMERIC  
CRESOL COMPOUNDS**

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ACTIVATED CARBON LOADED WITH ISOMERIC  
CRESOL COMPOUNDS**

**by**

**KEW SOOK LING**

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## LIST OF ABBREVIATIONS

AO7	Acid orange 7
AR14	Acid red 14
AY9	Acid yellow 9
BAC	Biological activated carbon
BE	Bioregeneration efficiency
BET	Brunauer-Emmett-Teller
BJH	Barrett-Joyner-Halenda
3-CB	3-Chlorobenzoic acid
COD	Chemical oxygen demand
COP	Critical oxidation potential
4-CP	4-Chlorophenol
<i>m</i> -Cresol	<i>meta</i> -Cresol
<i>o</i> -Cresol	<i>ortho</i> -Cresol
<i>p</i> -Cresol	<i>para</i> -Cresol
CWAO	Catalytic wet air oxidation
2,4-DCP	2,4-dichlorophenol
DO	Dissolved oxygen
EDX	Energy dispersive X-ray
FAS	Ferrous ammonium sulfate
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
HDI	Hexamethylene diisocyanate
MAMS	Mono-amine modified silica
MLSS	Mixed liquor suspended solid
PAC	Powdered activated carbon
PACT	Powdered activated carbon treatment
PEG	Polyethylene glycol
PNP	<i>p</i> -Nitrophenol
PRH	Pyrolysed rice husk
PU	Polyurethane
PVA	Polyvinyl alcohol
SBR	Sequencing batch reactor
SEM	Scanning Electron Microscope
SMPs	Soluble microbial products
SRT	Solid retention time
UV-Vis	Ultraviolet-visible

## LIST OF SYMBOLS

$A_0$	Initial amount of adsorbed substrates on virgin activated carbon
$A_{reg}$	Amount of adsorbed substrates remained on regenerated activated carbon
$C$	Amounts of residual substrate concentration in the bulk solution (mg/L)
$C_e$	Residual adsorbate concentration at equilibrium (mg/L)
$C_2$	Concentration of substrate after reloading the adsorbent (mg/L)
$C_{2e}$	Equilibrium concentration of the substrate after reloading (mg/L)
$C_i$	Amounts of initial substrate concentration in the bulk solution (mg/L)
$C_{ro}$	Initial concentration of cresol in reloading (mg/L)
$C_{re}$	Equilibrium concentration after reloading (mg/L)
$C_t$	Residual substrate concentration in the bulk solution at time $t$ (mg/L)
$k$	Biodegradation rate constant ((1/h)
$k_a$	Adsorption rate constant for biotic system (L/mg h)
$k_d$	Desorption rate constant for biotic system (1/h)
$K_i$	Substrate inhibition coefficient (mg/L)
$k_{ir}$	Irreversible adsorption rate constant for biotic system (1/h)
$K_L$	Langmuir constant related to the affinity of adsorption (L/mg)
$k'_a$	Adsorption rate constant for abiotic system (L/mg h)
$k'_d$	Desorption rate constant for abiotic system (1/h)
$k'_{ir}$	Irreversible adsorption rate constant for abiotic system (1/h)
$k_{max}$	Maximum specific removal rate (mg/mg MLSS h)
$K_s$	Saturation constant (mg/L)
$1/\eta_{ads}$	Adsorption intensity
$1/\eta_{des}$	Desorption intensity
$m$	GAC dosage (g/L)
$N$	Number of measurements
$q_e$	Amount of adsorbed adsorbate at equilibrium (mg/g)
$Q_{if}$	Experimentally determined maximum amount of substrate irreversibly adsorbed onto the adsorbent (mg/g)
$Q_m$	Langmuir maximum monolayer adsorption capacity of the adsorbent (mg/g)
$Q_o$	Initial adsorption capacity of the adsorbent (mg/g)
$Q_r$	Amount of substrate adsorbed at the reversible sites at time $t$ (mg/g)
$Q_t$	Amount of adsorbed substrate at time $t$ (mg/g)
$Q_v$	Amount of cresol required to saturate the fresh GAC in reloading (mg/g)

$Q_{\alpha}$	Amount of irreversibly adsorbed substrate on GAC determined at the end of bioregeneration (mg/g)
$R^2$	Coefficient of determination
$S_m$	Maximum substrate concentration above which growth was completely inhibited (mM)
$v$	Total volume of sample (L)
$V_{max}$	Maximum consumption rate constant ( $\mu\text{M mg}^{-1} \text{ protein h}^{-1}$ )
$w$	Weight of adsorbent (g)
$X$	Biomass concentration (mg MLSS/L)
$Y_{i,cal}$	Calculated data
$Y_{i,exp}$	Experimental data

**BIOJISIM TERPEGUN DALAM GEL POLIMERIK UNTUK BIOREGENERASI  
BUTIRAN KARBON TERAKTIF YANG SARAT DENGAN SEBATIAN  
ISOMER KRESOL**

**ABSTRAK**

Kaedah penjerapan menggunakan karbon teraktif sebagai bahan penjerap telah digunakan secara meluas bagi penyingkiran sebatian fenolik dari air buangan. Oleh sebab kapasiti penjerapan bahan penjerap akan berkurangan dengan aplikasi yang berpanjangan, penjanaan semula bahan penjerap yang digunakan adalah pilihan yang baik untuk mengurangkan sisa dan memulihara sumber. Dalam bioregenerasi, penggunaan biojisim terpegun akan mengatasi beberapa masalah yang berkaitan dengan penggunaan biojisim terampai dalam proses bioregenerasi termasuklah berlakunya pengotoran mikrob pada permukaan bahan penjerap dan kesukaran pengasingan bahan penjerap yang dijana semula daripada biojisim. Kajian ini mengkaji kesan faktor operasi yang berbeza dan penggunaan polivinil alkohol (PVA) dan poliuretana (PU) sebagai matriks pemegun terhadap bioregenerasi butiran karbon teraktif (GAC) sarat kresol menggunakan biojisim terpegun.

Keputusan menunjukkan bahawa kecekapan bioregenerasi untuk GAC sarat kresol dipengaruhi oleh struktur kimia isomer kresol, kepekatan awal kresol, dos GAC, masa sentuhan bagi GAC dan ketumpatan biomass kering. Kecekapan bioregenerasi untuk GAC yang sarat dengan *m*-kresol pada 1 g/L didapati adalah  $76 \pm 1\%$ ,  $64 \pm 1\%$  dan  $72 \pm 1\%$  masing-masing menggunakan biojisim terampai, PVA- dan PU-biojisim terpegun. Ini menunjukkan bahawa kekangan resapan bagi gel manik terpegun

merendahkan kadar biodegradasi bagi kresol mengakibatkan darjah pempolimeran oksidatif yang lebih disebabkan oleh masa sentuhan yang lebih panjang antara permukaan GAC dan larutan kresol. Kecekapan bioregenerasi untuk GAC dengan menggunakan manik PU-biojisim terpegun adalah lebih tinggi daripada yang menggunakan manik PVA-biojisim terpegun disebabkan oleh tahap keliangannya yang lebih tinggi. Kelebihan menggunakan PU-biojisim terpegun dilihat dalam pengurangan kesan pempolimeran oksidatif disebabkan oleh pemendekkan masa sentuhan antara GAC dan larutan kresol yang mengakibatkan peningkatan dalam kecekapan bioregenerasi untuk GAC sarat kresol. Kesan kedudukan metil pada gelang aromatik terhadap kecekapan bioregenerasi untuk GAC diperhatikan dalam kedua-dua sistem biojisim terampai dan terpegun.

Dua model kinetik telah dibangunkan untuk menerangkan bioregenerasi untuk GAC sarat kresol dengan menggunakan biojisim terampai dan terpegun melalui pendekatan penjerapan dan biodegradasi berturutan. Data eksperimen perjalanan masa bagi jumlah substrat terjerap pada GAC dan kepekatan baki substrat dalam larutan pukat dapat dipadankan dengan baik kepada model yang dibangunkan ( $R^2 = 0.800$ ). Persamaan kadar diselesaikan dengan menggunakan kaedah berangka untuk kedua-dua sistem abiotik dan biotik untuk mendapatkan pemalar kadar penjerapan ( $k'_a$  dan  $k_a$ ), penyahjerapan ( $k'_d$  dan  $k_d$ ), biodegradasi ( $k$ ) dan penjerapan tak berbalik ( $k'_{ir}$  dan  $k_{ir}$ ). Didapati bahawa pemalar kadar untuk penyahjerapan adalah lebih rendah berbanding pemalar kadar biodegradasi dalam sistem biotik yang menunjukkan bahawa proses penyahjerapan adalah langkah penentuan kadar dalam bioregenerasi. Oleh itu, pemalar kadar penyahjerapan boleh digunakan untuk mencirikan kadar bioregenerasi.

**IMMOBILIZED BIOMASS IN POLYMERIC GELS FOR THE  
BIOREGENERATION OF GRANULAR ACTIVATED CARBON LOADED  
WITH ISOMERIC CRESOL COMPOUNDS**

**ABSTRACT**

Adsorption method using activated carbon as the adsorbent has been widely used for the removal of phenolic compounds from wastewater. As the adsorption capacity of the adsorbent will diminish with prolonged application, regeneration of the spent adsorbent is a good option to reduce wastes and conserve resources. In bioregeneration, the use of immobilized biomass would overcome several problems associated with the use of suspended biomass in bioregeneration process including the occurrence of microbial fouling on the surface of adsorbent and separation difficulty between the regenerated adsorbent and biomass. This study investigates the effects of different operational factors and the use of polyvinyl alcohol (PVA) and polyurethane (PU) as immobilizing matrices on the bioregeneration of cresol-loaded granular activated carbon (GAC) using immobilized biomass.

The results showed that the bioregeneration efficiencies of cresol-loaded GAC were affected by the chemical structure of cresol isomers, initial cresol loading concentration, GAC dosage, contact time of GAC and dry biomass density. The bioregeneration efficiencies of *m*-cresol-loaded GAC at 1 g/L at  $76 \pm 1\%$ ,  $64 \pm 1\%$  and  $72 \pm 1\%$  using suspended, PVA- and PU-immobilized biomasses, respectively, were found to be lower using immobilized biomass compared to those using suspended biomass. This indicated that the diffusion constraint of the immobilized gel beads

lowered the biodegradation rate of cresols resulting in greater degree of oxidative polymerization due to longer contact period between the GAC surface and cresol solution. The bioregeneration efficiencies of GAC using PU-immobilized biomass were higher than those using PVA-immobilized biomass due to higher porosity of PU immobilized gel beads. The advantage of using PU-immobilized biomass was seen in the reduction of the oxidative polymerization effect due to shortening of the contact period between GAC and cresol solutions resulting in the enhancement in the bioregeneration efficiencies of cresol-loaded GAC. The effect of the position of the methyl substituent in the aromatic ring on the bioregeneration efficiencies of GAC was observed in both the suspended and immobilized systems.

Two kinetic models were developed to describe the bioregeneration of cresol-loaded GAC using suspended and immobilized biomasses under sequential adsorption and biodegradation approach. The experimental data of the time courses of the amount of adsorbed substrate on GAC and the residual substrate concentration in the bulk solution were mostly well fitted ( $R^2 = 0.800$ ) to the developed models. The rate equations were solved numerically for both abiotic and biotic systems to obtain the rate constants of adsorption ( $k'_a$  and  $k_a$ ), desorption ( $k'_d$  and  $k_d$ ), biodegradation ( $k$ ) and irreversible adsorption ( $k'_{ir}$  and  $k_{ir}$ ). The rate constant of desorption was found to be lower than that of biodegradation in biotic system indicating that the desorption process was the rate-determining step in bioregeneration. Therefore the desorption rate constant could be used to characterize the rate of bioregeneration.

## CHAPTER 1

### INTRODUCTION

#### 1.1 Background

Water pollution by phenolic compounds is a prominent environmental issue over decades. The outbreak of water pollution threatens human health and natural ecosystem. For this reason, the presence of phenolic compounds in wastewaters has been a subject of great concern. Phenolic compounds are the persistent pollutants and recognized as the main target compounds in wastewater treatment systems. Phenolic compounds are considered as priority pollutants by United States Environment Protection Agency. Due to their extensive use, phenolic compounds are widespread pollutants present in the environment. Large amounts of phenolic compounds are generated in many industries such as petroleum processing plant, oil refineries, coke oven, and pharmaceutical (Lobo et al., 2013). Furthermore, phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides and insecticides (Dąbrowski et al., 2005). Wastewater containing phenolic compounds gives rise to a serious discharge problem due to their poor biodegradability, high toxicity and long term ecological damage (Bayramoglu et al., 2013). In view of this, the removal of phenolic compounds from wastewaters is of great concern. Many treatment techniques such as adsorption (Dąbrowski et al., 2005), microbial degradation (Basheer et al., 2012), chemical oxidation (Comninellis and Pulgarin, 1993; Rubalcaba et al., 2007) and solvent extraction (Rao et al., 2009) have been employed for the removal of phenolic compounds.

## 1.2 Phenolic compounds

Phenolic compounds are classified as priority pollutants in wastewater. There are many classifications of phenolic compounds. Among them, methyl-, chloro- and nitro-substituted phenols are the most common phenol derivatives compounds. Substituent can be categorized into three groups, namely *ortho*-, *meta*- and *para*-substituted phenols.

### 1.2.1 Cresols

Cresols are the methylated derivatives of phenol, which have a methyl group substituted onto the aromatic ring of phenol. There are three cresol isomers, namely *ortho*-cresol (*o*-cresol), *meta*-cresol (*m*-cresol) and *para*-cresol (*p*-cresol). Substituted phenolic compounds are considered to be one of the major pollutants in wastewater (Kennedy et al., 2007). Cresols are toxic organic compounds and widely used in the manufacture of pesticides, biocides, antioxidants and other chemicals which are commonly found in many industrial wastewaters. These compounds have strong odor emission, suspected carcinogenicity, are persistent in the environment and have potential toxicity toward humans and animals (Basheer et al., 2012; Chu et al., 2013). Therefore, a proper treatment is essential for the treatment of cresols before discharging into water bodies. Three cresol isomers were selected in this study. The physical and chemical properties of cresols are presented in Table 1.1.