

**BIOREGENERATION OF GRANULAR  
ACTIVATED CARBON LOADED WITH PHENOL  
AND *p*-NITROPHENOL: EFFECTS OF PHYSICO-  
CHEMICAL AND BIOLOGICAL FACTORS**

**CHAN POH YING**

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CHEMICAL AND BIOLOGICAL FACTORS**

**by**

**CHAN POH YING**

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## LIST OF ABBREVIATIONS

AC	Activated carbon
AO7	Acid Orange 7
AS-PAC	Activated sludge-powdered activated carbon
ATU	Allylthiourea
BAC	Biological-activated-carbon
BET	Brunauer, Emmett and Teller
BOD	Biochemical oxygen demand
BOD <sub>resp</sub>	Respiromeric oxygen uptake
COD	Chemical oxygen demand
FTIR	Fourier Transform Infrared
GAC	Granular activated carbon
MAMS	Mono-amine modified silica
MLSS	Mixed liquor suspended solids
NISS	Non-ionogenic surfactants
ONP	<i>o</i> -Nitrophenol
PAC	Powdered activated carbon
PACT	Powdered activated carbon assisted activated sludge treatment
PNP	<i>p</i> -Nitrophenol
SBR	Sequencing batch reactor
SEM	Scanning electron microscopy
SOCs	Synthetic organic chemicals
UV-Vis	Ultraviolet-visible

## LIST OF SYMBOLS

A	Volumes of ferrous ammonium sulfate (FAS) used for blank (mL)
B	Volumes of ferrous ammonium sulfate (FAS) used for sample (mL)
C	Weight of dried suspended solids + filter medium (g)
$C_{des}$	Amount of substrate desorbed (mg/L) from substrate-loaded GAC in the bulk solution at equilibrium
$C_e$	Amount of unadsorbed substrate in the bulk solution at equilibrium (mg/L)
$C_e'$	Residual substrate concentration in the bulk liquid at time t (mg/L)
$C_o$	Substrate concentration in the solution (mg/L) initially
$C_t$	Residual substrate concentration in the bulk liquid at time t (mg/L)
D	Weight of filter medium (g)
$F_p$	Fraction of the pore that is filled at equilibrium
$k$	First-order biodegradation rate constant ( $h^{-1}$ )
$k_a$	Second-order adsorption rate constant for abiotic system ( $L\ mg^{-1}\ h^{-1}$ )
$k_d$	First-order desorption rate constant for abiotic system ( $h^{-1}$ )
$k_d'$	First-order desorption rate constant for biotic system using first-order biodegradation model ( $h^{-1}$ )
$k_d''$	First-order desorption rate constant for biotic system using Haldane biodegradation model ( $h^{-1}$ )
$k_{ir}$	First-order irreversible adsorption rate constant ( $h^{-1}$ )
$k_{ir}'$	First-order irreversible adsorption rate constant for biotic system using first-order biodegradation model ( $h^{-1}$ )
$k_{ir}''$	First-order irreversible adsorption rate constant for biotic system using Haldane biodegradation model ( $h^{-1}$ )
$k_{max}$	Haldane maximum specific substrate removal rate ( $mg\ mg\ MLSS^{-1}\ h^{-1}$ )
$k_1$	First-order bioregeneration rate constant (1/h)

$K_F$	Freundlich constant denoting the adsorbent capacity (mg/g)(L/g) <sup>1/n</sup>
$K_i$	Haldane substrate inhibition coefficient (mg/L)
$K_L$	Langmuir constant related to the affinity of the binding sites (L/mg)
$K_S$	Haldane saturation constant (mg/L)
$m$	Weight of adsorbent per unit volume (g/L)
$M$	Concentration of FAS (mg/L)
$M(O_2)$	Molecular weight of oxygen (32000 mg/mol)
$n$	Freundlich constant denoting the adsorption intensity
$\Delta p(O_2)$	Difference of the partial pressure of oxygen (hPa)
$q_{bio-oxidized}$	Amount of substrate bio-oxidized (mg/g)
$q_e$	Amount of phenol or PNP adsorbed on the GAC at equilibrium (mg/g)
$q_e'$	Amount of adsorbed substrate at time t (mg/L)
$q_{if}$	Final amount of substrate adsorbed on the irreversible sites which cannot be regenerated (mg/g)
$q_{ir}$	Amount of substrate adsorbed on the irreversible sites per unit weight at time t (mg/g)
$q_m$	Maximum adsorption capacity (mg/g)
$q_o$	Amount adsorbed per unit weight of adsorbent initially/during preloading (mg/g)
$q_r$	Amount of substrate adsorbed on the reversible sites per unit weight at time t (mg/g)
$q_{reload}$	Amount of substrate adsorbed onto the bioregenerated GAC (mg/g)
$q_{sat}$	Saturated amount of phenol adsorbed onto GAC (mg/g)
$q_t$	Amount adsorbed per unit weight of adsorbent at time t (mg/g)
$R$	Gas constant (83.144 L.mbar/mol.K)
$R_L$	Separation factor or equilibrium parameter

$t$	Time (h)
$T_m$	Measuring temperature (298 K)
$T_o$	Reference temperature (273 K)
$V$	Solution volume (L)
$V_p$	Specific pore volume of the adsorbent ( $\text{cm}^3/\text{g}$ )
$V_{tot}$	Reaction vessel volume (510 mL)
$V_1$	Sample volume (mL)
$W$	Weight of adsorbent (g)
$X$	Biomass concentration (mg/L)
$\alpha$	Bunsen adsorption coefficient
$\rho$	Density of the solute ( $\text{g}/\text{cm}^3$ )

# **BIOREGENERASI BUTIRAN KARBON TERAKTIF YANG TERJERAP DENGAN FENOL DAN *p*-NITROFENOL: KESAN FAKTOR FIZIKOKIMIA DAN BIOLOGI**

## **ABSTRAK**

Bioregenerasi ditakrifkan sebagai suatu proses yang mana permukaan bahan penjerap tersebut diperbaharui oleh mikroorganisma hidup untuk penjerapan selanjutnya. Kesan kepekatan biojisim teraklimasi, dosej penjerap, jenis butiran karbon teraktif (GAC) dan kepekatan aklisasi biojisim terhadap kecekapan dan kadar bioregenerasi GAC yang termuat dengan fenol dan *p*-nitrofenol (PNP) dikaji dengan menentukan jumlah substrat terjerap dan kepekatan substrat baki mengikut masa di bawah pendekatan penjerapan dan biodegradasi secara berturutan. Min kecekapan bioregenerasi bagi GAC termuat fenol dan PNP masing-masing didapati bernilai  $78 \pm 2 \%$  dan  $77 \pm 1 \%$ . Keputusan kajian menunjukkan bahawa peningkatan kepekatan biojisim teraklimasi dan dosej penjerap tidak mempengaruhi kecekapan bioregenerasi bagi GAC termuat dengan fenol dan PNP. Tambahan pula, kecekapan bioregenerasi bagi GAC 830 dan GAC 1240+ yang termuat dengan fenol tidak menunjukkan sebarang perbezaan ketara tetapi kecekapan bioregenerasi bagi GAC 1240+ yang termuat dengan PNP didapati lebih besar berbanding dengan GAC 830 yang termuat dengan PNP. Ini menunjukkan bahawa peningkatan kecekapan bioregenerasi bagi GAC terpakai melalui pengaktifan kimia lanjut bergantung kepada jenis bahan terjerap. Bagi bioregenerasi GAC yang termuat dengan fenol dengan menggunakan biojisim yang teraklimasi kepada 350 dan 600 mg/L fenol, kecekapan bioregenerasi didapati hampir sama bagi dosej GAC yang sama. Dua model kinetik yang menggabungkan kinetik biodegradasi tertib-pertama (Model I) dan Haldane (Model II), serta kinetik penyahjerapan tertib-pertama telah dibangunkan untuk menerangkan bioregenerasi mengikut masa di bawah pendekatan penjerapan dan

biodegradasi secara berturutan. Keputusan menunjukkan bahawa Model II memberi penyesuaian yang lebih baik daripada Model I secara relatif. Pemalar kadar penyahjerapan bagi GAC termuat dengan fenol dan PNP meningkat dengan peningkatan kepekatan awal teraklimasi biojisim dan penurunan dosej GAC, tetapi ia tidak bergantung kepada jenis GAC dan kepekatan aklimasi biojisim yang digunakan dalam kajian. Di bawah keadaan biotik, nilai bagi pemalar kadar penyahjerapannya pada kepekatan biojisim yang lebih tinggi adalah lebih besar daripada pemalar kadar di bawah keadaan abiotik menunjukkan bahawa kesan bagi penyahjerapan didorong secara biologi adalah lebih ketara pada kepekatan biojisim yang tinggi. Secara keseluruhannya, pemalar kadar penyahjerapan tertib-pertama didapati lebih kecil daripada pemalar kadar biodegradasi tertib-pertama dan ini menunjukkan bahawa proses penyahjerapan merupakan langkah penentuan kadar dalam bioregenerasi bagi GAC termuat dengan fenol dan PNP.

# BIOREGENERATION OF GRANULAR ACTIVATED CARBON LOADED WITH PHENOL AND *p*-NITROPHENOL: EFFECTS OF PHYSICO-CHEMICAL AND BIOLOGICAL FACTORS

## ABSTRACT

Bioregeneration is defined as a process during which the adsorbent surface is renewed by living microorganisms for further adsorption. The effects of acclimated biomass concentration, adsorbent dosage, type of granular activated carbon (GAC) and biomass acclimation concentration on the efficiency and rate of bioregeneration of GAC loaded with phenol and *p*-nitrophenol (PNP) were investigated by determining the time courses of adsorbed substrate amount and residual substrate concentration during bioregeneration under the sequential adsorption and biodegradation approach. The mean bioregeneration efficiencies of phenol- and PNP-loaded GAC were found to be  $78 \pm 2$  % and  $77 \pm 1$  %, respectively. The results revealed that increasing the acclimated biomass concentration and adsorbent dosage did not have an observable effect on the bioregeneration efficiencies of phenol- and PNP-loaded GAC. Additionally, bioregeneration efficiencies of phenol-loaded GAC 830 and GAC 1240+ did not show any observable difference but the bioregeneration efficiency of PNP-loaded GAC 1240+ was greater than that of PNP-loaded GAC 830. This indicates that the improvement of bioregeneration efficiency of spent GAC through further chemical activation was dependent on the type of adsorbate. As for the bioregeneration of phenol-loaded GAC using biomasses acclimated to 350 and 600 mg/L, the bioregeneration efficiencies were found to be almost similar at the same GAC dosage. Two kinetic models incorporating the first-order (Model I) and Haldane (Model II) biodegradation kinetics, as well as first-order desorption kinetics were developed to describe the time courses of bioregeneration under sequential adsorption and biodegradation approach. The results showed that Model II gave a

relatively better fit than Model I in all cases. The desorption rate constant for phenol- and PNP-loaded GAC increased with increasing initial biomass concentration and decreasing GAC dosage, but was not dependent on the types of GAC and biomass acclimation concentration employed in the study. Under biotic conditions, the values of desorption rate constant were greater than those under abiotic conditions at higher initial biomass concentration indicating that the effect of biologically induced desorption was more distinct at higher initial biomass concentrations. Overall, the first-order desorption rate constant was observed to be much smaller than first-order biodegradation rate constant demonstrating that the desorption process was the rate-determining step in the bioregeneration of phenol- and PNP-loaded GAC.



# CHAPTER 1

## INTRODUCTION

### 1.1 Background

Over the decades, the development of science and technology has improved tremendously the quality of life but it has also brought negative consequences, especially to the environment. In recent years, environmental issues such as air pollution, acid rain, noise pollution, water pollution, etc. are of growing concern in both developed and developing countries. Today, many countries are facing clean water crisis. Although 70 % of the earth is covered by water, only 3 % of all water is fresh and drinkable. Of that 3 %, 75 % is frozen and only 1 % of the grand total of the earth's surface water is readily available for consumption (Gleick, 1993). Hence, protection and enhancement of the quality of fresh and clean water supply are of paramount importance. In order to control and prevent pollution from getting worse, environmental legislation has been enacted in most countries. In Malaysia, the Environmental Quality Act was promulgated in 1974 and the Department of Environment is empowered to enforce the Act.

Numerous methods and technologies designed to treat industrial wastewaters and domestic sewage before being discharged to the environment have been adopted. Among them, adsorption using various adsorbents is the most frequently used technique in reducing the amount of contaminants present in the wastewaters (Hsieh and Teng, 2000a, 2000b; Dutta et al., 2001; Jain and Suhas, 2002; Gupta et al., 2004; Ahmaruzzaman and Sharma, 2005; Zhang et al., 2006; Lin and Juang, 2009). However, adsorption is only a process in which contaminants are removed from liquid phase and are adsorbed onto the surface of adsorbent. As the adsorbent

becomes saturated with pollutants, it loses its adsorption capacity and needs to be either disposed of or regenerated. The disposal option will cause secondary environmental pollution and is a waste of resource. Thus, greater attention has been paid to regeneration of exhausted adsorbents for their reuse.

Activated carbon is regarded as one of the most widely used adsorbents in wastewater treatment due to their outstanding adsorption capacities towards target pollutants (Pan et al., 2003; Dąbrowski et al., 2005). In recent years, various methods to regenerate the spent activated carbon, namely chemical, thermal and biological regenerations have been developed. Among these methods, biological regeneration has emerged as the most popular technology as it reduces the negative impact of the generation of hazardous secondary waste. As a result, many studies on the regeneration of spent activated carbons loaded with various types of organic pollutants via biological regeneration approach have been conducted (Chudyk and Snoeyink, 1984; de Jonge et al., 1996a; Orshansky and Narkis, 1997; Li et al., 1998; Walker and Weatherley, 1998; Ha and Vinitnantharat, 2000; Ha et al., 2001; Sirotkin et al., 2001; Vinitnantharat et al., 2001; Martin et al., 2004; Lee and Lim, 2005; Putz et al., 2005; Aktaş and Çeçen, 2006a, 2007a, 2010; Ng et al., 2009, 2010; Nath et al., 2011; Oh et al., 2011; Al-Amrani et al., 2012a).

## **1.2 Phenolic compounds**

Phenolic compounds are a common group of toxic environmental contaminants as they are widely present in the effluents of many industrial processes, including oil production, coal conversion, paper production, coal gasification sites, petrochemical units and others (Aleksieva et al., 2002; Dąbrowski et al., 2005; Lin and Juang, 2009). The presence of phenolic compounds even at low concentrations

have resulted in noxious effects on health and ecology (Guerra, 2001). They are known to be extremely toxic to aquatic organisms even at parts per million level. For instance, phenol at relatively low levels of e.g. 5-25 mg/L is lethal to fish (Kibret et al., 2000; Chung et al., 2003). Acute exposure of *p*-nitrophenol (PNP) may cause liver and kidney damages, anemia, skin and eye irritation, and systemic poisoning (Yi et al., 2006; Michalowicz and Duda, 2007). Besides, when water containing phenols is chlorinated, it gives an unpleasant smell and odour even at a few ppb concentrations (Davì and Gnudi., 1999).

### **1.2.1 Phenol**

Phenol is an aromatic compound consisting of a hydroxyl group bonded to a benzene ring. It is a colourless, crystalline substance with sweet tar like odour and is soluble in water and organic solvents. Phenol was one of the first compounds written into The List of Priority Pollutants by the US Environmental Protection Agency (US EPA). Naturally, phenol is found in decaying dead organic matter and in coal. Phenol was first extracted from coal tar in 1834 by a German chemist, Runge. Due to phenol's commercial importance, various methods have been developed for its production. Phenol is manufactured by extraction from coal tar as it is obtained by transformation of cumene (1-methylethylbenzene) present in plants used for tar production. Other methods involved reaction between chlorobenzene and sodium hydroxide, toluene oxidation and oxidation between benzene and nitrous oxide. Phenol is an important precursor in polycarbonate plastics and epoxy resin production, nylon and polyamide plastics manufacturing processes and surfactants and detergent production. It is also used in medical antiseptics, production of aspirin and other pharmaceuticals.

### **1.2.2 *p*-Nitrophenol (PNP)**

*p*-Nitrophenol, also called 4-nitrophenol or 4-hydroxynitrobenzene, is an aromatic organic compound that has a nitro group located at the para position of hydroxyl group on the benzene ring. PNP is a colorless to light yellow solid with very little odor and is moderately soluble in cold water (10 g/L at 15 °C). PNP is a man-made organic compound which is not found in any natural source. PNP is of considerable industrial importance because of its widespread use in the manufacturing of drugs (e.g. acetaminophen), pesticides (e.g. methyl and ethyl parathion), and is also in leather tanning, dyestuff production and for military purposes (Spain and Gibson, 1991).

### **1.3 Adsorption**

Adsorption is a process in which a substance from one phase, typically an aqueous solution, concentrates at the surface of a solid. Generally, adsorption process occurs via two kinds of interactions, namely physisorption and chemisorption. Physisorption involves weak van der Waals forces between the adsorbed substance and the solid surface whereas chemisorption involves the formation of a strong chemical bonding between the substance and the solid surface resulting in irreversible adsorption. Adsorption is one of the most widely used techniques due to its versatility in removing diverse pollutants and its flexibility in using with biochemical or chemical techniques. Activated carbon adsorption has been quoted by the US Environmental Protection Agency as one of the best available environmental control technologies (Moreno-Castilla, 2004). Despite its effectiveness, fast adsorption kinetics and simplicity of design, the usage of commercial activated carbon has been restricted due to the use of expensive starting material. Besides, the

production of the vast amount of solid waste (secondary by-products), which requires additional treatment and disposal, and also the difficulties of regeneration, has gained researchers' attention to develop methods for minimizing the generation of secondary solid waste and extending the service life of activated carbon. Adsorption in conjunction with biological treatment is more preferable due to relatively low operational costs and the possibility of complete mineralization.

### **1.3.1 Activated carbon as adsorbent**

Activated carbon is a versatile adsorbent due to its high surface area, microporous structure, and a high degree of surface reactivity. Its porous structure is formed by pores of different sizes and have been classified by IUPAC into three major groups based on different adsorption mechanisms at pores with specified width range: (i) micropores with pore width less than 2 nm, (ii) mesopores with pore width between 2 to 50 nm and (iii) macropores with pore width larger than 50 nm. Activated carbon is usually used in the form of granular and powder-like activated carbon. Generally, it is an adsorbent derived from natural precursors such as wood, bituminous coal, lignite, or other carbon-containing material. In practice, carbonaceous materials with low inorganic matter content, ease of activation, availability and low cost, low degradation upon storing are suitable for the preparation of activated carbon (Dąbrowski et al., 2005).

Activated carbon can be manufactured either through physical (thermal) or chemical activation. During physical or thermal activation, the raw material is carbonized in an inert atmosphere, and the resulting char is reacted at high temperature (above 800 °C) with steam, carbon dioxide or their mixture (Rodriguez-Reinoso et al., 1995). Chemical activation involves co-carbonization of a raw

material with a chemical such as zinc chloride, phosphoric acid, and potassium hydroxide/carbonate at approximately 500 °C followed by washing to remove the activating chemical. It is usually conducted on wood or peat which acts as the raw material. Physically activated carbons have aromatic-like carbon skeleton with some functional groups involving heterogeneous oxygen atoms at their edges. On the other hand, chemically-activated carbons comprise a partly aromatic and aliphatic structure or a highly cross-linked polymer produced from an almost infinite number of different monomers and contains a relatively large amount of heteroatoms (Jung et al., 2001). According to Haghseresht et al. (2002), the adsorption capacity of activated carbon for aromatic compounds is dependent on a few factors: (i) the physical nature of the adsorbent – pore structure, ash content and functional groups, (ii) the nature of the adsorbate, its  $pK_a$ , functional groups present, polarity, molecular weight and size and (iii) the solution conditions such as pH, ionic strength, and the adsorbate concentration.

Hsieh and Teng (2000a) explored the influence of the mesopore volume and adsorbate size on the adsorption capacities of activated carbons in aqueous solutions. Adsorption capacity of carbons with similar surface areas and micropore volumes increases with the increasing mesopore volume of the carbons. The mesopores facilitate the adsorption of the larger adsorbates in the inner and narrow micropores, which contain adsorptive sites with higher adsorption energies.

Jung et al. (2001) investigated the adsorption of phenol and chlorophenols on four commercial granular activated carbons (GAC) by batch experiment to correlate with the structure of activated carbons. The batch adsorption data were found to be well fitted to the Freundlich equation. The correlation between the characterization and Freundlich parameters indicated that the adsorption behavior of phenol and

chlorophenols on activated carbons was affected by the dispersion force between the  $\pi$ -electrons of double bonds in activated carbon and those in phenol molecules. However, the adsorption behavior was not affected by physical properties such as surface area and pore diameter of activated carbons. The electron-withdrawing chloro substituent decreased the  $\pi$ -electron density in aromatic ring and hence increased the affinity to the  $\pi$ -electrons of double bonds in activated carbons.

The effects of surface chemistry on the adsorption of aromatic compound onto three untreated activated carbons from dilute aqueous solutions were studied (Haghseresht et al., 2002). Results by surface characterization methods showed that the dominant adsorption forces in the hydrophilic activated carbon were observed to be dipolar interactions when the solutes were in their molecular form, whereas dispersion forces, such as  $\pi - \pi$  interactions were most likely dominant in the hydrophobic activated carbon. Nevertheless, when the solutes were in their ionic form, adsorption occurs in all cases via dispersion forces.

The type of modification method for activated carbon was also found to have an effect on the adsorption and desorption processes. Coelho et al. (2006) observed a relatively lower adsorption capacity of acid treated activated carbon for the herbicide molinate compared with thermally activated carbon. The presence of larger amount of oxygen surface groups on acid treated activated carbon caused a decrease in the surface hydrophobicity of activated carbon, resulting in weaker attraction between molinate (apolar molecule) and hydrophobic carbon surface. Conversely, molinate desorption occurred at a slightly lower extent for thermally activated carbon attributed to its high affinity towards molinate.

## **1.4 Regeneration of spent adsorbents**

In the past, when activated carbon lost its adsorption capacities, it was often disposed of in landfill. However, stringent environmental regulations have made this no longer a viable option. Attempts have been made to regenerate the spent activated carbon by thermal (Salvador and Jiménez, 1996; Álvarez et al., 2004), chemical (Garcia et al., 2002; Guo et al., 2011) and biological regeneration methods (Ng et al., 2009; Oh et al., 2011; Al-Amrani et al., 2012a).

### **1.4.1 Thermal regeneration**

The most widely employed regeneration method is the thermal regeneration processes due to their high efficiency. Thermal regeneration processes are performed typically between 800 and 1000 °C under mildly oxidizing atmospheric conditions (usually carbon dioxide and steam) (San Miguel et al., 2001; Cong and Wu, 2007). During the heating stage, the spent carbon passes through the following procedures: drying (water evaporation), thermal desorption (desorption of volatile compounds, 100-260 °C), pyrolysis and carbonization (pyrolysis and carbonization of non-volatile compounds, 200-650 °C) and gasification of pyrolytic residue at high temperature (650-850 °C) in the presence of small amounts of oxidant (water vapour, oxygen, etc). These processes are carried out in multiple hearth furnaces, rotary kilns and fluidized bed furnaces (Salvador and Jiménez, 1996). The major drawbacks to this method include: (i) 5-15 % carbon loss due to particle attrition and entrainment in the moving gas streams (Álvarez et al., 2004; Nath et al., 2011), (ii) high energy consumption in order to maintain regeneration temperature around 850 °C (Yun et al., 2000), (iii) changes in the activated carbon properties which may alter the adsorption properties,



(iv) generation of substantial amount of carbon dioxide and (v) release of reactive, oxidized and partially oxidized state of adsorbate into the atmosphere.

Thermal and ozone regenerations of granular activated carbon (GAC) used in the removal of phenol from aqueous solution was performed by Álvarez et al. (2004). The findings of the work showed that exhausted carbons failed to recover their adsorption characteristics when thermal regeneration was carried out under inert conditions. However, thermal regeneration in the presence of carbon dioxide was effective at about 15 % of carbon burn off. Ozone as an oxidizing gas in thermal regeneration was also investigated and it was found that the regeneration performance was much dependent on the ozone dose and the nature of GAC. Optimum ozone dose managed to regenerate the spent GAC without incurring carbon surface chemical alterations, whereas excessive ozone dose produced various surface oxygen groups that decreased regeneration efficiency.

#### **1.4.2 Chemical regeneration**

In chemical regeneration process, the nature of the adsorbed adsorbent is changed by means of redox or acid-base reactions. It is either conducted by the desorption of adsorbed adsorbate using suitable organic solvents (Grant and King, 1990), inorganic chemicals (e.g. sodium hydroxide) (Leng and Pinto, 1996; Garcia et al., 2002) or by decomposition of adsorbed adsorbate using oxidizing agents (e.g. hydrogen peroxide, potassium dichromate, ozone) under subcritical or supercritical conditions (Ryu et al., 2000). In the first two cases, the regeneration process is simple and inexpensive as it involves desorption and extraction of adsorbates. However, it has a few drawbacks including (i) low regeneration efficiency below 70 % (Berenguer et al., 2010), (ii) incomplete regeneration due to pore blockage by the

solvent (Schweiger and LeVan, 1993) and (iii) expensive purification step for recovering solvent free of pollutants. For the last approach, the use of oxidizing agents able to destroy the adsorbed adsorbate and regenerate the spent activated carbon would also modify and/or destroy the genuine structure and surface chemistry properties of activated carbon (Álvarez et al., 2004).

An investigation of the mechanisms of chemical regeneration of activated carbon loaded with four different aromatic adsorbates, namely, phenol, aniline, benzoic acid and nitrobenzene was carried out by Leng and Pinto (1996). The results showed that the regeneration of activated carbon was dependent primarily on the solubility of the adsorbate in the regenerant solution and surface characteristics of the adsorbent.

Berenguer et al. (2010) studied and compared the regeneration of phenol-saturated activated carbon (AC) by chemical, thermal, and electrochemical methods. The results showed that very low porosity recoveries (less than 38 %) were achieved by chemical regeneration, regardless of sodium hydroxide concentration, and the optimal regeneration efficiencies were 20 % lower than those obtained by the thermal and electrochemical regenerations. Thermal and electrochemical regeneration, on the other hand, produced similar regeneration efficiencies, 80-86 % and 80-85 %, respectively, but electrochemical regeneration showed slightly higher porosity recoveries than those obtained by thermal regeneration.

Guo et al. (2011) used four solvents, namely *n*-pentane, methylene dichloride, ethyl ether and dodecylbenzenesulphonic acid sodium to regenerate spent activated carbon. The results indicated that *n*-pentane could remove refractory organic compounds adsorbed on the surface of activated carbon and enabled multiple regenerations of spent activated carbon.

### **1.4.3 Biological regeneration (Bioregeneration)**

It is necessary to devise an effective, economical and ecologically safe regeneration technique to enhance and improve the capability of activated carbon for long term operation. In this context, biological regeneration of spent activated carbon seems to be a better alternative to physical and chemical regenerations. Bioregeneration is defined as the restoration of the adsorptive capacity of the adsorbents through microbial action (Sublette et al., 1982; de Jonge et al., 1996a). The feasibility of bioregeneration process in prolonging the service life of adsorbents has been reported by many researchers (Orshansky and Narkis, 1997; Sirotkin et al., 2001; Klimenko et al., 2004; Lee and Lim, 2005; Aktaş and Çeçen, 2006a, 2007a, 2009; Ng et al., 2009, 2010; Oh et al., 2011; Al-Amrani et al., 2012a, 2012b, 2013). According to Klimenko et al. (2004), an effective bioregeneration has to satisfy the following microbiological and technological preconditions: (i) presence of microbiological agents capable of utilizing the adsorbate as the sole carbon source, (ii) presence of mineral components (nitrogen, phosphorus, sulfur, etc.) needed for a normal metabolism of the adsorbate, (iii) creation of the optimum conditions for important activities of microorganisms (temperature, pH, dissolved oxygen concentration, etc.) and (iv) optimization of the proportion between the concentrations of the microorganisms and the adsorbate, etc.

Bioregeneration can be conducted in two ways, namely sequential adsorption and biodegradation processes, and simultaneous adsorption and biodegradation processes. The major benefit of bioregeneration is the flexibility of time and locations for the occurrence of adsorption and biodegradation steps in the treatment process.

#### **1.4.3.1 Simultaneous adsorption and biodegradation processes**

The most usual procedure of bioregeneration is through biological-activated-carbon (BAC) or powdered activated carbon assisted activated sludge treatment (PACT) systems, where adsorption of the organic compounds is accompanied by biodegradation, thus regeneration of the exhausted activated carbon at the same time (Sirotkin et al., 2001; Klimentko et al., 2002; Lee and Lim, 2005).

Orshansky and Narkis (1997) compared the removal of phenol and aniline from aqueous solutions by biological treatment alone, by adsorption on powdered activated carbon (PAC) alone and by simultaneous adsorption and biodegradation. The simultaneous adsorption and biodegradation proved to enhance the removal of phenol and aniline than by biotreatment alone. The presence of PAC in the biological treatment of phenol improved the degradation of microbial but the opposite result was shown in the case of aniline. Aniline was strongly adsorbed on the PAC surface and was not available for biodegradation due to higher adsorption energy of aniline than of phenol.

The simultaneous occurrence of biodegradation and adsorption of non-ionogenic surfactants (NISS) in the biological-activated carbon (BAC)-process showed a synergistic effect in the bioregeneration of activated carbon (Sirotkin et al., 2001). The desorption from micropores occurred because of the reverse concentration gradient, attributed to the microbial degradation of wastewater contaminants in the liquid phase. The desorption from mesopores was also supported by the microorganism exoenzymes activity. The substantial losses of adsorptive capacity during bioregeneration can be related to the difficulty of desorption of the adsorbed substrate and microbial degradation products and also to the filling of mesopores with decay products of microbial cells.

The performance of activated sludge-powdered activated carbon (AS-PAC) bench scale continuous reactors operating with commercial and sludge-based adsorbents was monitored by Martin et al. (2004) and the extent of bioregeneration of the two adsorbents was evaluated. No differences were found between the two reactors in spite the higher adsorption capacity of the commercial activated carbon for phenol. It was found that the extent of bioregeneration of powdered activated carbon in the AS-PAC reactor may be impaired by the pore blockage attributed to the bacterial growth. The effect was more significant when bioregeneration took place for the commercial activated carbon with a narrower pore size distribution.

The bioregeneration of powdered activated carbon in the treatment of alkyl-substituted phenolic compounds in simultaneous adsorption and biodegradation processes was quantitatively determined by Lee and Lim (2005). The bioregeneration efficiency of loaded PAC decreased in the order of phenol > *p*-methylphenol > *p*-ethylphenol > *p*-isopropylphenol. This showed that the alkyl phenols were less strongly desorbed than phenol itself and desorption efficiency decreased with the lengthening of the hydrophobic alkyl chain.

Ng et al. (2009) succeeded in quantifying the bioregeneration of powdered activated carbon (PAC) loaded with phenol and *p*-nitrophenol (PNP) by two approaches, namely, simultaneous and sequential adsorption and biodegradation processes. The results showed that the mean bioregeneration efficiencies of phenol- and PNP-loaded PAC, respectively, obtained using the two approaches were in good agreement.

The bioregeneration of GAC in simultaneous adsorption and biodegradation of chlorophenols was assessed quantitatively by Oh et al. (2011). It was observed that the highest bioregeneration efficiency was achieved when the biomass acclimated

concentration was higher than the initial adsorbate concentration. For bioregeneration process in which the chlorophenol concentration was to be higher than the biomass acclimated concentration, excess adsorbent had to be used to improve the extent of bioregeneration.

#### **1.4.3.2 Sequential adsorption and biodegradation processes**

Sequential adsorption and biodegradation process is another approach of bioregeneration, which involves two stages of treatment. Initially, the adsorbate is removed from the bulk liquid and concentrated by adsorption onto activated carbon. Then, the loaded activated carbon is bioregenerated using acclimated biomass during which the desorbed compound is biodegraded by specific microorganisms.

The potential of using the three types of bacteria, namely, *Ps. Putida*, *Arthrobacter* and *Moraxella* to biodegrade PNP and consequently bioregenerate the coal char saturated with PNP was investigated (Li et al., 1998). Of these bacteria, *Moraxella* has been shown to be the most effective for biodegrading PNP even at high concentrations. The removal rate of PNP from the coal char by desorption and biodegradation was found to be much faster than by desorption alone.

The feasibility of bioregeneration of azo-dye-loaded GAC and non-activated bone char by a consortium of bacteria was studied by Walker and Weatherley (1998). It was found that no desorption occurred for azo-dye-loaded GAC resulting in negligible bioregeneration. However, azo-dye-loaded bone char was found to be successfully regenerated with the extent of regeneration corresponding well with the amount of dye desorbed in abiotic systems.

In the study by Ha et al. (2001), the phenol- and 2,4-dichlorophenol-loaded GAC were incubated for 14 days with and without inoculated acclimated

microorganisms. The results showed that the presence of microorganisms induced desorption of both phenol and 2,4-dichlorophenol, thus resulting in the bioregeneration efficiencies of 76 % and 57 %, respectively.

Coelho et al. (2006) studied the effect of the textural and surface chemistry properties of the activated carbon in a combined treatment system for herbicide molinate removal. The process involved molinate adsorption as an initial step followed by the bioregeneration of the activated carbon through the employment of a defined bacterial mixed culture. It was noticed that the reduction of the adsorbate concentration in bulk solution due to biological metabolism promotes successive desorption of molinate. The researchers also found that the adsorption and partial bioregeneration of molinate was favoured with activated carbons with larger pores, consisting mainly of meso- and macropores.

The bioregeneration of mono-amine modified silica (MAMS) and GAC loaded with Acid Orange 7 (AO7) in batch system was carried out by Al-Amrani et al. (2012a). It was found that the regeneration efficiency of AO7-loaded MAMS, at 77-98 %, was very much higher than that of AO7-loaded GAC of 0-15 %. The deterioration of the adsorption capacity of MAMS for AO7 with increasing regeneration cycles suggested both chemical and microbial fouling of the adsorption sites.

## **1.5 Mechanism of bioregeneration process**

The real mechanism of activated carbon bioregeneration is still a subject of much debate. The existing hypotheses accounting for the regenerative effects only complement one another (Sirotkin et al., 2001). There are two main hypotheses, namely exoenzymatic reaction and concentration gradient.

### 1.5.1 Exoenzymatic reaction

Perrotti and Rodman (1974) suggested that the degradation of adsorbed substances during bioregeneration was due to exoenzymes (extracellular enzymes) of microorganisms. According to the proposed mechanism, although the large size of microorganisms makes them difficult to colonize the micropores of the carbon, enzymes excreted by microorganism could easily diffuse into the micropores and interact with adsorbed substrate and promote its hydrolytic decay. Owing to a weaker adsorbability of the decay products, they are desorbed and become accessible for further degradation by microorganisms.

However, some of the researchers disagreed with this theory. Xiaojian et al. (1991) indicated that exoenzymatic reactions could hardly occur within the tiny micropores of carbon due to the larger size of the enzyme molecules to the micropores' size. According to them, the pore diameter should be at least three times greater than the enzyme size to allow the enzyme to approach, orientate and induce a fit. Considering a monomeric enzyme (molecular weight between 13000 and 35000 g/mol) with an average molecular diameter above 3-4 nm, they concluded that the enzymatic reaction would possibly occur in pore diameter greater than 10 nm, which excludes micropores (diameter,  $d < 2$  nm) and some of mesopores ( $2 \text{ nm} \leq d \leq 50$  nm). They suggested that BAC process is just a simple combination of biodegradation and carbon adsorption, without mutual enhancement.

According to Martin et al. (2002), some of the low-molecular-weight aromatic compounds, such as phenol, are mainly adsorbed in pore with diameter less than 0.7 nm, thus exoenzymatic reactions were predicted to be restricted in such cases. Some researchers claimed that the presence of adsorbed molecules inside micropores limited the space available for enzyme penetrations (Klimenko et al.,



2002; Aktaş and Çeçen, 2006b). Nevertheless, other researchers corroborated the idea that inaccessibility of micropores for exoenzymes does not contradict the probable exoenzyme activity in meso- and macropores (Sirotkin et al., 2001; Klimenko et al., 2004).

### **1.5.2 Concentration gradient**

The second bioregeneration hypothesis postulates that desorption precedes biodegradation of substrate due to a concentration gradient between the adsorbent and bulk liquid. According to this hypothesis, a concentration gradient was established when the substrate concentration on the carbon surface rises more than the equilibrium adsorption concentration through the decrease of substrate concentration in the bulk liquid by microorganism biodegradation activity. As a result, desorption of adsorbed substrate takes place due to a concentration gradient between the adsorbent and bulk liquid (Schultz and Keinath, 1984; de Jonge et al., 1996a; Kim et al., 1997). The desorbed substrate is then further biodegraded by microorganisms in the bulk liquid. Hence, bioregeneration process continues until all the reversibly adsorbed substrates are biodegraded. Klimenko et al. (2002) also suggested the difference in the Gibbs free energy between the molecules in solution ( $-\Delta G_{\text{ads}}^{\circ}$ ) and the modified adsorbed molecules inside the porous structure ( $-\Delta G_{\text{mod}}^{\circ}$ ) is the driving force for bioregeneration.

## **1.6 Factors affecting bioregeneration**

An effective bioregeneration is dependent on various factors, which includes biodegradability of target substrate, reversibility of adsorption, substrate's physical and biological properties, carbon particle size and porosity, carbon activation process,

physical surface properties of carbon, desorption kinetics, substrate-carbon contact time, concentration gradient and carbon saturation, biomass concentration, dissolved oxygen concentration, microorganism type, substrate and biomass associated products of biodegradation and presence of multiple substrates (Aktaş and Çeçen, 2007b; Nath et al., 2011). Some of the factors are discussed in detail in the following sections.

### **1.6.1 Biodegradability of target substrate**

The ready biodegradability of target substrate is one of the key factors that leads to bioregeneration. In the case of poorly biodegradable compounds or compounds which are resistant to biodegradation in conventional biological treatment systems, acclimated microorganisms or peculiar microorganisms are needed to promote the occurrence of biodegradation (Janeczko and Oleszkiewicz, 1993; Topalova et al., 1999; Aktaş and Çeçen, 2007b). Janeczko and Oleszkiewicz (1993) studied the removal of *o*-nitrophenol (ONP) and oxygen consumption patterns in batch respirometers using acclimated and un-acclimated activated sludge. It was found that acclimated activated sludge performed immediate and complete biodegradation of ONP, unlike un-acclimated activated sludge which demonstrated a 170 to 230 h lag before initiation of rapid and complete biodegradation of ONP. Continuous-flow GAC bioregeneration experiments were carried out using mixtures of a biodegradable (benzene or toluene) and a non-biodegradable (perchloroethylene or carbon tetrachloride) synthetic organic chemicals (SOCs) (Putz et al., 2005). In the mixture of toluene and perchloroethylene, the decreased toluene concentration in the aqueous phase stimulated the desorption and biodegradation of adsorbed toluene and eventually resulting in a decrease in perchloroethylene concentration in the effluent

as well. It was explained by the increased availability of adsorption sites on the GAC and also the decreased competition for these sites by toluene. A similar trend was also shown by the mixture containing benzene and carbon tetrachloride. These results concluded that the bioregeneration of biodegradable SOCs increased the removal efficiency for non-biodegradable SOCs.

Bioregeneration of 2-chlorophenol-loaded activated carbon using acclimated and non-acclimated activated sludges was studied by Aktaş and Çeçen (2007a). Lower desorbability and biodegradability of very persistent 2-chlorophenol led to less bioregenerability. However, Aktaş and Çeçen (2006b) reported activated carbons loaded with less persistent phenol were successfully bioregenerated. These reported studies implied that the degree of biodegradability of targeted substrate affects the bioregeneration process.

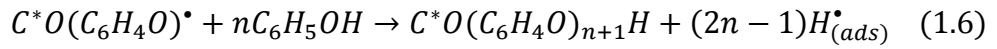
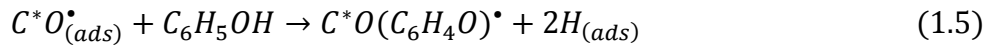
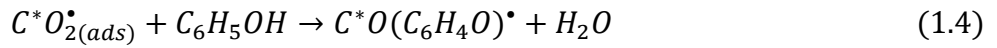
### **1.6.2 Reversibility of adsorption**

Since desorption is recognized as a prerequisite step for bioregeneration, any condition that affects desorption of the adsorbed substrate would ultimately affect the bioregeneration efficiency. Bioregeneration is controlled by the desirability or reversibility of adsorption (de Jonge et al., 1996a; Schultz and Keinath, 1984). There are two mechanisms leading to irreversible adsorption. The first mechanism involves high adsorption energy of adsorbate to functional groups on the active sites of carbon surface resulting in covalent bonding (Yonge et al., 1985; de Jonge et al., 1996b). According to Yonge et al. (1985), reversible adsorption was attributed to the forming of van der Waals forces and/or weaker charge-transfer complexes that occurred at adsorption site on the activated carbon surface whereas the irreversible adsorption was explained by the chemisorption (high energy) bond that formed between

adsorbates and activated carbon surface. Aniline was found to be more resistant towards biodegradation as compared to phenol (Orshansky and Narkis, 1997). The percentage of the non-biooxidized phenol remained adsorbed on PAC was in the range of 4-9 % compared to 15-32 % for aniline. The higher adsorption energy of aniline as determined from the adsorption isotherms indicated aniline was adsorbed strongly to the PAC surface and not available for biodegradation as compared to phenol. Klimenko et al. (2002) reported that the higher the change in the Gibbs free energy of adsorption of an adsorbate with GAC surface, the lower the bioregeneration efficiency was. The higher energy of adsorptive binding of adsorbed adsorbate with the adsorbent surface resulting in lower reversible adsorption.

Another mechanism for irreversible adsorption was attributed to the oxidative polymerization of phenolic compounds in the presence of oxygen (oxic conditions) (Grant and King, 1990; Vidic and Suidan, 1991; Vidic et al., 1993; de Jonge et al., 1996b; Vinitnantharat et al., 2001). The adsorption capacity of GAC for phenolic compounds was greatly affected under oxic conditions (Vidic et al., 1990; Vidic and Suidan, 1991; Vidic et al., 1993). Generally, the oxidative polymerization of phenols was initiated by the formation of phenoxy radicals from the phenol molecule or phenolate ions followed by direct coupling with other phenoxy radicals at room temperature with activated carbon surface acting as a catalyst (Vidic et al., 1993). The authors revealed that the oxic adsorption capacity for 2-methylphenol was 3-fold the adsorption capacity that was obtained in the absence of molecular oxygen (anoxic condition). A similar trend was also observed for the adsorption of phenol, 2-chlorophenol, and 3-ethylphenol. This was attributed to the oxidative polymerization of adsorbate on the carbon surface under oxic conditions (Vidic et al., 1993). Adsorbate polymerization on the carbon surface showed significant irreversible

adsorption hence resulting in lower bioregeneration efficiency. Apparently, molecule oxygen played an important role in the mechanism of irreversible adsorption of phenols on activated carbon. The mechanism of phenol polymerization proposed by Terzyk (2003) was shown as below:



where  $n$  is in the range from 1 to 7 (Grant and King, 1990),  $C^*$  is the carbon surface and  $\bullet$  is the free radical . Equations (1.1)-(1.7) show that the occurrence of phenol polymerization was governed by the presence of free radicals on the carbon surface. de Jonge et al. (1996b) discovered that the adsorption capacity of PAC for *o*-cresol increased in the presence of oxygen due to oxidative polymerization but the adsorption of non-phenolic compounds, 3-chlorobenzoic acid was totally unaffected by the availability of molecular oxygen. It was deduced that non-phenolic compound was less susceptible to oxidative polymerization. On the other hand, the type of substituent groups of the adsorbate affects the occurrence of oxidation. Saturated groups such as methyl and ethyl groups increase the susceptibility to oxidation whereas unsaturated groups such as carboxyl and nitro groups decrease the probability of oxidation occurring (Vidic et al., 1993).

A few studies (de Jonge et al., 1996a, 1996b; Aktaş and Çeçen, 2006a, 2006b) demonstrated that oxidative polymerization of phenolic compounds was also

influenced by the carbon activation process. In those studies, the chemically activated carbon exhibited a higher reversibility of adsorption and higher bioregeneration efficiency than the thermally activated carbon. Oxidative polymerization of phenolic compounds was a reasonable explanation for a lower extent of bioregeneration of the thermally activated carbon. Thermally activated carbon was prepared during the exclusion of free oxygen leading to a more reactive surface towards oxygen and eventually changed the surface chemistry of activated carbon. Conversely, chemical activated carbon had a surface with fully oxidized active sites and surface remain unaffected upon interaction with oxygen.

### **1.7 Quantification of bioregeneration**

There are various studies reporting quantitative measurements of bioregeneration to date. The extent of bioregeneration can be quantified using direct and indirect measurements. Direct measurement involves direct determination of the amount of adsorbate adsorbed on the activated carbon through reloading of the bioregenerated activated carbon (Klimenko et al., 2004; Aktaş and Çeçen, 2006a, 2009, 2010; Oh et al., 2011, 2013; Al-Amrani et al., 2012a) and solvent extraction (Ha et al., 2000). Indirect measurement involves quantification of biodegradation products such as carbon dioxide (de Jonge et al., 1996a), radiochemical  $^{14}\text{C}$ -labelled adsorbates (Schultz and Keinath, 1984; Speitel and Digiano, 1987b; Putz et al., 2005), chloride ion from chlorinated adsorbates (Nakano et al., 2000; Caldeira et al., 1999) and oxygen uptake measurement using respirometry (Orshansky and Narkis, 1997; Ivancev-Tumbas et al., 1998; Lee and Lim, 2005; Ng et al., 2009). The results of extent of bioregeneration from various studies as shown in Table 1.1 show that bioregeneration efficiency of chemically activated carbons generally was always

Table 1.1: The results of bioregeneration efficiency from various studies in batch system.

Adsorbate	Quantification method	Activated carbon	Major carbon features	Reactor type	Bioregeneration efficiency (%)	Reference
Phenol	Direct measurement	PAC Norit SA4	Thermally activated	Batch	58.1	Aktaş and Çeçen (2006a)
		PAC Norit CA1	Chemically activated		93.6	
		GAC Norit PKDA	Thermally activated		66.6	
		GAC Norit CAgran	Chemically activated		84.8	
Phenol and 2-chlorophenol	Direct measurement	PAC Norit SA4	Thermally activated	Batch	23.7-27.0 for phenol and 28.9-39.4 for 2-chlorophenol	Aktaş and Çeçen (2009)
		PAC Norit CA1	Chemically activated		55.4-65.2 for phenol and 66.3-66.6 for 2-chlorophenol	
		GAC Norit PKDA	Thermally activated		50.6 for phenol and 38.6 for 2-chlorophenol	
		GAC Norit CAgran	Chemically activated		81.5 for phenol and 52.1 for 2-chlorophenol	
Phenol and 2-nitrophenol	Direct measurement	PAC Norit SA4	Thermally activated	Batch	19.5-32.6 for phenol and 64.9-84.9 for 2-nitrophenol	Aktaş and Çeçen (2010)
		PAC Norit CA1	Chemically activated		82.3-90.0 for phenol and 64.7-89.8 for 2-nitrophenol	

found to be higher than that of thermally activated carbon for same aromatic compound. The explanation for the phenomenon was given in the previous section.

The majority of the studies on the quantification of bioregeneration were conducted under sequential adsorption and biodegradation approach due to the difficulty in determining the extent of bioregeneration in the simultaneous adsorption and biodegradation processes. Quantification of bioregeneration using oxygen uptake measurement in simultaneous adsorption and biodegradation could hardly be ascertained unless there is prior establishment of adsorption equilibrium before biodegradation. For any other systems which failed to fulfill this condition, oxygen uptake measurement appears to be an inappropriate method as it is difficult to determine the initial substrate loading of the adsorbent. Oxygen uptake measurement only provides bioregeneration efficiency of adsorbent after completion of bioregeneration. However, it cannot be used to track the change of the amount of substrate adsorbed onto the adsorbent during bioregeneration process. Direct determination of the time courses of the substrate amount adsorbed onto adsorbent overcomes the inadequacy of the oxygen uptake measurements. In this study, direct measurement of the substrate loading was adopted to ascertain the extent of bioregeneration of phenol- and PNP-loaded GAC under sequential adsorption and biodegradation approach.

## **1.8 Kinetic models of bioregeneration**

### **1.8.1 Background**

To date, several mathematical models have been proposed to describe bioregeneration in the sequential adsorption and biodegradation processes for batch systems. Most of the reported studies assumed that bioregeneration is a single-step