

**ACTIVATED RICE HUSK-BASED ADSORBENTS  
FOR CHLOROPHENOL REMOVAL AND THEIR  
BIOREGENERATION**

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**UNIVERSITI SAINS MALAYSIA**

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FOR CHLOROPHENOL REMOVAL AND THEIR  
BIOREGENERATION**

**by**

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## LIST OF ABBREVIATIONS

2,4-DCP	2,4-Dichlorophenol
4-CP	4-Chlorophenol
ARH	Activated Rice Husk (Acid + Methanol + 300 °C)
BET	Brunauer, Emmett and Teller
COD	Chemical Oxygen Demand
FTIR	Fourier Transform Infrared Spectroscopy
KRH	Activated Rice Husk (KOH + N <sub>2</sub> 800 °C)
MLSS	Mixed Liquor Suspended Solid
MRH	Activated Rice Husk (Ethylenediamine + 300 °C)
PAC	Powdered Activated Carbon
PZC	Point of Zero Charge
RH	Raw Rice Husk
SBR	Sequencing Batch Reactor
SEM	Scanning Electron Microscope
UV-Vis	UV-Visible

## LIST OF SYMBOLS

$C_0$	Initial concentration of the adsorbate (mg/L),
$C_e$	Equilibrium concentration of the adsorbate (mg/L)
$m$	Weight of adsorbent (g)
$V$	Volume of adsorbate (L)
$q_e$	Amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g)
$q_m$	Monolayer maximum adsorption capacity (mg/g)
$K_L$	Affinity of the binding sites (L/mg)
$R_L$	Dimensionless equilibrium parameter
$K_F$	Freundlich adsorption capacity [(mg/g)(1/mg) <sup>1/n</sup> ]
$n$	affinity of interaction between adsorbate and the adsorbent
$K_{RP}$	Redlich Peterson isotherm constant (L/g)
$\alpha$	A constant (L/mg)
$\mu$	An exponent which lies between 0 and 1
$A$	Equilibrium binding constant (L/mg)
$b$	A constant related to the heat of adsorption (J/mol)
$T$	Absolute temperature in Kelvin (K)
$R$	Gas constant (8.314 J/mol K)
$X_m$	Maximum adsorption capacity of adsorbent for D-R isotherm (mg/g)
$\beta$	A constant related to the adsorption energy
$\varepsilon$	Polanyi sorption potential
$E$	Sorption energy (J mol <sup>-1</sup> )



$q_t$	Amounts of adsorbates adsorbed at time $t$ (mg/g)
$k_1$	Pseudo-first-order rate constant (1/min)
$k_2$	Pseudo-second-order rate constant (g/mg min)
$h$	Initial adsorption rate (mg/ g min)
$k_{id}$	Intraparticle diffusion rate constant at stage $i$ (mg/g min <sup>1/2</sup> )
$C_i$	Thickness of the boundary layer at stage $i$ (mg/g)
$\Delta G^o$	Gibbs free energy change (J/mol)
$\Delta H^o$	Enthalpy change (J/mol)
$\Delta S^o$	Entropy change (J/mol K)
$C_L$	Initial loading concentration (mg/L)
$M_a$	Amount of adsorbed adsorbate (mg/g)
$M_d$	Amount of desorbed adsorbate (mg/g)
$Q_i$	Initial amounts of adsorbates adsorbed (mg/g)
$Q_{reload}$	Amounts of adsorbates adsorbed during reloading (mg/g)
$Q_{sat}$	Saturated amounts of adsorbates adsorbed (mg/g)
$Q_{il}$	Initial amounts of adsorbates adsorbed in the first cycle (mg/g)

# **PENJERAP BERASASKAN SEKAM PADI TERAKTIF BAGI PENYINGKIRAN KLOOROFENOL DAN BIOREGENERASINYA**

## **ABSTRAK**

Objektif kajian ini ialah untuk menghasilkan penjerap yang berasaskan sekam padi teraktif dengan agen pengaktifan yang berbeza, iaitu kalium hidroksida (KRH), asid nitrik dan metanol (ARH), dan etilenadamina (MRH) dan membandingkan kapasiti penjerapan dan kecekapan bioregenerasinya untuk menyingkirkan 4-klorofenol (4-CP) dan 2,4-diklorofenol (2,4-DCP) daripada larutan akueus dengan serbuk karbon teraktif (PAC) yang tersedia secara komersil.

Daripada kajian penjerapan keseimbangan 4-CP dan 2,4-DCP, tren kapasiti penjerapan maksimum,  $q_m$ , antara penjerap mengikut KRH > PAC > ARH > MRH dan bertepatan dengan tren luas permukaan BET. Data penjerapan keseimbangan bagi KRH dan PAC boleh dihuraikan dengan baik oleh model Langmuir ( $R^2 > 0.98$ ) manakala model Freundlich adalah sesuai untuk menghuraikan data penjerapan keseimbangan bagi MRH dan ARH ( $R^2 > 0.99$ ). Pemerhatian ini boleh disahkan oleh nilai pemalar keheterogenan,  $\mu$ , yang diperoleh daripada model Redlich-Peterson. Boleh disimpulkan bahawa permukaan penjerap MRH dan ARH adalah heterogen, manakala yang bagi KRH dan PAC adalah homogen. Bagi model isoterma Dubinin-Radushkevich dan Temkin yang bersandarkan pada suhu, model Dubinin-Radushkevich berpadanan baik dengan data penjerapan eksperimen jika dibandingkan dengan model Temkin.

Penjerapan 4-CP dan 2,4-DCP didapati mengikut kinetik pseudo-tertib-kedua. Mekanisme proses penjerapan ditentukan daripada model resapan intra zarah. Peringkat kedua proses resapan intra zarah dipengaruhi oleh muatan penjerapan

penjerap. Dua langkah resapan intra zarah boleh diperhatikan bagi ARH dan MRH yang mempunyai kapasiti penjerapan rendah dengan kadar difusi tinggi diperhatikan pada langkah permulaan. Sebaliknya, bagi KRH dan PAC, hanya satu langkah difusi sahaja diperhatikan. Daripada kajian termodinamik, proses penjerapan bagi semua penjerap didapati berlaku secara spontan dengan kerawakan yang meningkat dan adalah eksotermik secara semula jadi.

Potensi regenerasi penjerap berasaskan sekam padi teraktif adalah didapati lebih tinggi daripada yang bagi PAC. Daripada kajian penyahjerapan dan bioregenerasi, kecekapan bioregenerasi bagi semua penjerap yang terjerap dengan klorofenol didapati lebih tinggi daripada kecekapan penyahjerapan. Keputusan bagi kajian kebolegunaan semula menunjukkan bahawa KRH dan PAC mengekalkan kehilangan kapasiti penuh yang lebih tinggi berbanding dengan MRH dan ARH dengan penggunaan berbilang kitaran. Namun demikian, KRH boleh dimuat dan diregenerasikan dengan jumlah klorofenol yang tinggi berbanding MRH, ARH dan PAC.

# ACTIVATED RICE HUSK-BASED ADSORBENTS FOR CHLOROPHENOL REMOVAL AND THEIR BIOREGENERATION

## ABSTRACT

The objectives of this study are to develop rice husk-based adsorbents activated with different activating agents, namely potassium hydroxide (KRH), nitric acid and methanol (ARH), and ethylenediamine (MRH), and compare their adsorption capacities and bioregeneration efficiencies to remove 4-chlorophenol (4-CP) and 2,4-dichlorophenol (2,4-DCP) from the aqueous solutions with the commercially available powdered activated carbon (PAC).

From the adsorption equilibrium studies of 4-CP and 2,4-DCP, the trend of maximum adsorption capacity,  $q_m$ , among the adsorbents followed  $KRH > PAC > ARH > MRH$  and in agreement with the trend of BET surface areas. The equilibrium adsorption data of KRH and PAC were best described by the Langmuir model ( $R^2 > 0.98$ ) while the Freundlich model was suitable to describe the equilibrium adsorption data for MRH and ARH ( $R^2 > 0.99$ ). These observations were confirmed by the values of heterogeneity constant,  $\mu$ , obtained from the Redlich-Peterson model. It could be concluded that the adsorbent surfaces of MRH and ARH were heterogeneous, while those of the KRH and PAC were homogenous. For the temperature-dependent Temkin and Dubinin-Radushkevich isotherm models, the Dubinin-Radushkevich model was better fitted to the experimental data than the Temkin model.

The adsorption of 4-CP and 2,4-DCP was found to follow the pseudo-second-order kinetics. The mechanism of the adsorption process was determined from the intraparticle diffusion model. The second stage of intraparticle diffusion process was

affected by the adsorption capacity of the adsorbent. Two steps of intraparticle diffusion could be observed for ARH and MRH of lower adsorption capacities, with higher diffusion rate observed at the initial step. In contrast, for KRH and PAC, only a single diffusion step was observed. From the thermodynamic studies, the adsorption process for all the adsorbents was found to occur spontaneously with increased randomness and was exothermic in nature.

The regeneration potential of the activated rice husk-based adsorbents was found to be higher than that of PAC. From the desorption and bioregeneration studies, the bioregeneration efficiencies of all the chlorophenol-loaded adsorbents were found to be higher than the desorption efficiencies. The results of the reusability study show that the KRH and PAC sustained higher total capacity losses as compared to those of the MRH and ARH with multi-cycles of use. However, KRH can be loaded and regenerated with higher amount of chlorophenol compared to that of MRH, ARH and PAC.

## CHAPTER 1

### INTRODUCTION

#### 1.0 Background

Chlorophenols are a group of phenols that contain one or more chlorine atoms in the *para*, *meta* or *ortho* positions. The main pollution sources containing chlorophenols are the wastewaters from pesticide, paint, solvent, pharmaceuticals, wood, paper and pulp industries as well as water disinfecting process (Hameed et al., 2008a). Discharge of wastewater or effluent containing these phenolic compounds into receiving waters poses serious risk to aquatic organisms and human beings besides imparting unpleasant odor and taste. Thus, it is essential to remove these compounds from wastewater before discharge. Various methods that have been employed to remove chlorophenols include biological degradation (Carucci et al., 2010), electrochemical oxidation (Chen et al., 2010), photodegradation (Gomez et al., 2010), wet oxidation (Chaliha and Bhattacharyya, 2008) and adsorption (Lorenc-Grabowska et al., 2010; Sze and McKay, 2010). Among these methods, the adsorption process is recognised as an efficient and simple technique that is most widely used (Foo and Hameed, 2009).

#### 1.1 Adsorption Process

Adsorption is a process of attracting and retaining the molecules of a substance on the surface of a liquid or a solid resulting into a higher concentration of the molecules on the surface. The substance thus adsorbed on the surface is called the adsorbate and the substance on which it is adsorbed is known as adsorbent. The adsorption method has the advantage over other techniques in chlorophenol removal effectiveness, cost and equipment handling and hence is the most frequently used.

## **1.2 Adsorbents**

Commercial activated carbon is the preferred adsorbent due to its microporous structure. However, attempts have been made in studying the feasibility of using agricultural by-product as the alternative adsorbent (Ahmaruzzaman, 2008). If successful, it would solve partially the disposal problem and provide an efficient and low cost material for the adsorption to remove the pollutants.

### **1.2.1 Commercial Activated Carbon**

The adsorption by activated carbon has gained wide acceptance as it can remove, not only selective organic compounds up to the satisfactory limits but also a broad spectrum of other inorganic and organic compounds generally discharged from any industries (Kennedy et al., 2007a). Commercially available activated carbons in both granular and powdered forms are the most widely used adsorbents because of their excellent adsorption capability for chlorophenol (Kumar et al., 2007; Fierro et al., 2008; Lorenc-Grabowska et al., 2010; Sze and McKay, 2010;). Most of the commercial activated carbon show microporous nature and have the BET surface area in the range of 500 – 1300 m<sup>2</sup>/g. The BET values of the commercial activated carbon depend on their activation method. Generally, the chemically activated commercial activated carbon gives higher BET value compared to the physically/thermally activated commercial activated carbon (Aktas and Cecen, 2006a). However, the high cost in the production and regeneration of activated carbon has led many researchers to search for alternative adsorbents from agricultural waste/by-products.

## **1.2.2 Agricultural by-product as an Adsorbent**

In the case of the removal of phenolic compounds, various agro-based adsorbents have been derived from different kinds of precursor, such as rice husk (Akhtar et al., 2006; Kennedy et al., 2007a; Srihari and Das, 2008; Liou and Wu, 2009), rice husk ash (Foo and Hameed, 2009), rice straw (Wang et al., 2007), palm pith (Sathishkumar et al., 2007), oil palm shell (Hamad et al., 2010), oil palm empty fruit bunch (Shaarani and Hameed, 2010), date pith (El-Naas et al., 2010), cocoa shell (Ahmad et al., 2011), pinewood (Tseng et al., 2005; Liu and Zhang, 2011), fir wood (Wu et al., 2005a), coconut shell (Radhika and Palanivelu, 2006; Hameed et al., 2008a; Singh et al., 2008; Kurniawan et al., 2010), sawdust (Jadhav and Vanjara, 2004; Hameed et al., 2007; Ofamaja, 2011), pistachio shell (Wu et al., 2005b; Tseng et al., 2010), etc.

### **1.2.2.1 Rice Husk**

Rice husk is an abundantly available agricultural by-product from rice milling industries in Malaysia. The major components of rice husk which may be responsible for adsorption are carbon and silica. Silica is composed of  $\text{SiO}_4 \cdot 4\text{H}_2\text{O}$  in which each oxygen atom is shared between two adjacent tetrahedrons (Akhtar et al., 2006). Li et al. (2011) reported that carbon content in rice husk was utilized to produce carbon-based adsorbent, whereas silica content in rice husk was used to form silica-based adsorbent. Akhtar et al. (2006) developed thermally and chemically treated rice husk to remove dichlorophenol. Kennedy et al. (2007b) developed rice husk activated with phosphoric acid at 900 °C to remove phenol from aqueous solution. Utilization and transformation of rice husk into carbon-based adsorbent with good adsorption properties would solve disposal problem and management of this waste by-product,



while producing value added-products from rice husks for wastewater treatment in the activated carbon market.

### **1.3 Activation Methods**

The precursors are usually subjected to physical activation and/or chemical activation to prepare the porous structure with increased adsorption capacity.

#### **1.3.1 Physical Activation**

Physical activation involves the carbonization of a precursor using a gaseous activating agent such as steam or carbon dioxide at different activation temperature. Carbon dioxide produces an opening, followed later by widening of narrow microporosity, whereas steam widens the microporosity from the early stages of the activation process, even in the case in which the removal rate of carbon atoms from the char is the same for the two activating agents (Williams and Nugranad, 2000; Tsai et al., 2007; Chen et al., 2011; Liu et al., 2011). Wu et al. (1999, 2005a,b) successfully prepared meso- and micropore carbon from plum kernel, fir wood and pistachio shells by steam activation. Juang et al. (2000, 2001) prepared activated carbon from bagasse and plum kernels by steam activation. Activated carbons were prepared by Hsieh and Teng (2000) with bituminous coal char by CO<sub>2</sub> gasifying.

#### **1.3.2 Chemical Activation**

Chemical activation involves mixing the precursor with a chemical activating agent such as phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), zinc chloride (ZnCl<sub>2</sub>) or alkali hydroxides (NaOH and KOH) and then heating in an inert gas (Kennedy et al., 2005; Yalçın and Sevinç, 2000; Guo et al., 2002). A comparison of chemical activation with physical activation shows that chemical activation provides a lower reaction temperature, and

its global yield tends to be greater (Liou and Wu, 2009). Rahman et al. (2005) derived rice husk-based activated carbon with  $H_3PO_4$  and NaOH by chemically activation. Liou and Wu (2009) showed that  $ZnCl_2$  activation produces higher surface area and adsorption capacity compared to  $H_3PO_4$ .

### **1.3.3 Combination of Activation Methods**

Recently, preparation of the rice husk-based activated carbon by precarbonization of rice husk and chemical activation had gained researchers' interest (Guo et al., 2003). Qi et al. (2004) developed micro- and mesoporous rice husk-based active carbons by precarbonized rice husk in the presence of nitrogen and KOH or NaOH activation. Kennedy et al. (2007a,b) reported that porous carbon was prepared from rice husk by using phosphoric acid activation through precarbonization. Foo and Hameed (2011) reported the preparation of activated carbon by microwave induced KOH and  $K_2CO_3$  chemical activation. Besides activation method, Liou and Wu (2009) showed that the base-leaching process of rice husk before chemical activation and the acid-washing procedure after the chemical activation improved the surface area and pore volume of the sample.

## **1.4 Factors Affecting the Adsorption**

The adsorption capacity of adsorbents depends on three major factors: (i) the physical nature of the adsorbent, (ii) the nature of the adsorbate, and (iii) the solution conditions (Dąbrowski et al., 2005).

### **1.4.1 Physical Nature of the Adsorbent**

The physical nature of the adsorbent includes pore structure, ash content, functional groups, surface charge, precursor material and preparation method. It is

known that adsorbents have highly heterogeneous surfaces. The heterogeneity of adsorbent surface stems from two sources known as geometrical and chemical ones. Geometrical heterogeneity is the result of the differences in size and shape of pores, cracks, pits, and steps. Chemical heterogeneity is associated with different functional groups, mainly oxygen groups. The porous structure of the adsorbent is a function of the precursor used in the preparation, the activation method used and the extent of activation. The selection of precursor is based mainly on (i) low inorganic matter content, (ii) ease of activation, (iii) availability and low cost, and (iv) low degradation upon storing.

Commonly, adsorbent prepared from physical activation achieved higher adsorption capacity, but the adsorbent yield from chemical activation is higher than that from physical activation (Dąbrowski et al., 2005). Other possible advantages of chemical activation are simplicity, lower activation temperature and good development of porous structure. Pore structures, in terms of surface area, pore volume and pore size distribution, are important properties of the adsorbent and they determine the performance of the adsorbent during adsorption. Kennedy et al. (2007b) reported that the micropore volume was observed to be a near constant with the rise in activation temperature higher from 700 to 900 °C, but there was a considerable linear increase in the mesopore volume. Kennedy et al. (2007a) showed that the presence of considerable mesopores volume which behaved as an entrance for the movement of cresol molecules from the bulk phase to the inner micropores without any hindrance, led to acceleration of the diffusion into micropore surface and increase of the equilibrium coverage of micropore surface. Liou and Wu (2009) reported that the base-leaching process of rice husk before chemical activation which can remove ash content and the acid-washing procedure after the chemical activation

which can remove metallic impurities, improved the surface area and pore volume of the sample. In order to produce high surface area of porous carbon, Guo et al. (2002) reported that the cellulose and lignin should be removed from rice husk by precarbonized, and silica should be removed by alkali hydroxide. In contrast, Akhtar et al. (2006) showed that chlorophenol has strong affinity for silica surfaces.

Depending on the nature of the precursor and activation condition, different pore sizes that cover the micro-, meso- and macropore ranges can be obtained. However, the adsorptive properties of adsorbent are determined by its chemical composition. The presence of oxygen and hydrogen in the surface groups affects strongly the adsorptive properties of the adsorbent. These surface groups may be for the original precursor, or introduced during the activation process or after preparation via post-treatment. Oxygen, for instance, may be present in various forms, such as carboxyl, carbonyl, phenolic hydroxyl and lactonic ones, and are acidic. The existence of pyrone, chromene and quinone structures was postulated to account from the basic nature of the carbon surface. Owing to the amphoteric character of the carbon surface, i.e., due to the presence of acidic and/or basic functional groups, the surface properties of adsorbent may be influenced by the pH value of the coexisting liquid bulk phase. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). For typical amphoteric adsorbents, the surface is positively charged at  $\text{pH} < \text{pH}_{\text{PZC}}$  and negatively charged at  $\text{pH} > \text{pH}_{\text{PZC}}$ . Kennedy et al. (2007a) reported that the adsorption capacity for m-cresol was higher at  $\text{pH} < \text{pH}_{\text{PZC}}$ . Hameed et al. (2008a) found that the adsorption capacity for trichlorophenol decreased at  $\text{pH} > \text{pH}_{\text{PZC}}$ . They suggested that the adsorption of phenolic compounds decreased due to the electrostatic repulsion between the negative surface charge of adsorbent and the phenol species.

### 1.4.2 Nature of the Adsorbate

The nature of the adsorbate includes its solubility,  $pK_a$ , functional groups present, polarity, molecular weight and size. It is commonly assumed that for  $pH < pK_a$ , the adsorption of molecular chlorophenol does not depend on the surface charge of adsorbent. However, for  $pH > pK_a$ , chlorophenol is dissociated and adsorption of its ionic form depends on the surface charge. Hamdaoui and Naffrechoux (2007) reported that the uptake of phenols increased in the order of phenol < 2-chlorophenol < 4-chlorophenol < dichlorophenol < trichlorophenol, which correlates well with the respective increase in molecular weight, cross-sectional area, hydrophobicity and the decrease in solubility and  $pK_a$ . In addition, the magnitude of adsorption increases with the degree of chlorination.

The molecular size also has some implications on the adsorption. The molecule with a suitable size would adsorb more favourably since it has more contact sites with the carbon surface. Liu et al. (2010) found that the adsorption capacity of dinitrophenol was only slightly higher than that of 4-nitrophenol. This is because the molecular size of dinitrophenol is relatively large and it might cause steric effect. The steric effects are possibly caused by the following reasons: (i) some extremely low-size pores might be inaccessible for dinitrophenol molecules, (ii) the interior part of the pores might not be reached due to the blockage of the adsorbed molecules and (iii) the molecules could not be so compact in pores due to the introduction of the nitro group.

### 1.4.3 The Solution Conditions

The solution conditions include temperature, pH, ionic strength, adsorbate concentration and oxygen availability. The pH of the solution is one of the main

factors that affects the adsorption process because it controls the electrostatic interactions between the adsorbent and the adsorbate. The pH of the solution usually influences the adsorption to a large extent as it affects the properties of both the adsorbent and adsorbate. When  $\text{pH} > \text{pK}_a$  and  $\text{pH}_{\text{PZC}}$ , the chlorophenol is dissociated and the surface of adsorbent is negatively charged, leading to the existence of electrostatic repulsion force between the chlorophenol and adsorbent (Liu et al., 2010).

Temperature has an important effect on the adsorption process as it can increase or decrease the amount of adsorption (Kennedy et al., 2007a). If the adsorption capacity decreases as the temperature increases, this indicates that the adsorption process is exothermic. If the adsorption capacity increases as the temperature increases, this indicates that the adsorption process is endothermic. Adsorption of adsorbate onto the adsorbent increases with an increase of adsorbate concentrations. This could be explained by the greater concentration gradient in the bulk solution phase and the solid phase (Hameed et al., 2008b; Sze and McKay, 2010). Leng and Pinto (1997) showed that the presence of dissolved oxygen in the adsorbate solution increased the adsorption capacity of phenol onto the activated carbon by forming oxidative polymerization complex between the adsorbate and adsorbent.

### **1.5 Interaction between Adsorbent and Adsorbate**

Three important mechanisms have been proposed to interpret the adsorption behaviour between adsorbent and adsorbate, namely: the electron donor-acceptor complex, the  $\pi$ - $\pi$  dispersion interactions and the solvent effects (Moreno-Castilla, 2004).

### 1.5.1 The Electron Donor-acceptor Complex

The electron donor-acceptor complex mechanism assumes that the aromatic rings of the adsorbate act as the electron acceptors and the basic sites on the carbon surface serve as the donors. Moreno-Castilla et al. (1995) found that the adsorption capacity of phenols was related to the electron-withdrawing or electron-donating properties of the substituent of the phenol compound. The existing of the electron-withdrawing groups in benzene ring, such as nitro and chloro, favors the formation of the electron donor-acceptor complexes between this rings and basic groups on the surface of carbon. In contrast, the electron-donating groups, such as amine and methyl, deactivate the formation of electron donor-acceptor complexes.

### 1.5.2 The $\pi$ - $\pi$ Dispersion Interactions

The  $\pi$ - $\pi$  dispersion interactions derive from the interactions between the  $\pi$  electrons in the aromatic rings of the phenols and  $\pi$  electrons in the graphitic planes (carbon layers), which might comprise charge-transfer, dispersive force and polar electrostatic components. The introduction of substituent groups would alter the  $\pi$ - $\pi$  interactions between phenols and activated carbon. It is proposed that electron-withdrawing groups, such as nitro and chloro, enhance the  $\pi$ - $\pi$  interactions by reducing the electron density of  $\pi$  electrons, thus diminishing the repulsive electrostatic interactions between the aromatic rings (Liu et al., 2010). Hamdaoui and Naffrechoux (2007) reported that the adsorption of phenolic compounds on activated carbon may imply dispersion forces between  $\pi$ -electrons in phenols and  $\pi$ -electrons in activated carbon. They also showed that as chloro group is an electron withdrawing group, the electron density in aromatic ring decreases as the number of chloro group increases.

### **1.5.3 The Solvent Effects**

The solvent effects should be taken into consideration in the adsorption studies. Water molecules can be adsorbed on the surface oxygen groups by hydrogen bonding, which is unfavourable for the adsorption of phenols as some active sites are occupied (Mahajan et al., 1980). The solvent effects are closely related to temperature since temperature influences not only the adsorption of water but also the hydration degree of the phenolic molecules (Dąbrowski et al., 2005). Liu et al. (2010) reported that increased adsorption capacities and negative entropy changes were observed for phenol and 2-chlorophenol with the increase of temperature. Therefore the solvent effects are significant for the adsorption. In the adsorption process, increase of temperature would diminish the solvent effects.

## **1.6 Adsorption Equilibrium Models**

Adsorption isotherm is basically important to describe the interaction between the adsorbate and the adsorbent, and it is critical in optimizing the use of adsorbent (Juang et al., 2001). Adsorption equilibrium is the most important information in understanding an adsorption process. The adsorption equilibria of pure components are the essential information for the understanding of how much those components can be accommodated by a solid adsorbent (Hamdaoui and Naffrechoux, 2007).

### **1.6.1 Langmuir Isotherm Model**

The Langmuir model was developed based on several assumptions. This model assumes monolayer adsorption on a set of distinct localized adsorption sites and that all the adsorption sites are alike and the energies of the monolayer adsorption onto adsorbent surface are uniform. It also assumes that there are no



interactions or steric hindrance between the adsorbates and no transmigration of adsorbate on the surface of adsorbent (Langmuir, 1916). The well-known Langmuir expression of the model is given by:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (\text{non-linear form}) \quad (1.1)$$

The linear form of Langmuir adsorption isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (1.2)$$

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1.3)$$

where  $C_0$  (mg/L) is the initial concentration of the adsorbate,  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $m$  (g) is the weight of adsorbent,  $V$  (L) is the volume of adsorbate,  $q_e$  is the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g),  $q_m$  is monolayer maximum adsorption capacity (mg/g) and  $K_L$  is a constant related to the affinity of the binding sites (L/mg). For Langmuir isotherm model, the essential characteristics can be expressed in terms of a dimensionless equilibrium parameter ( $R_L$ ):

$$R_L = \frac{1}{1 + K_L C_0} \quad (1.4)$$

where  $C_0$  is the initial concentration of adsorbate (mg/L). The value of  $R_L$  indicates the type of the isotherm to be unfavorable, linear, or favorable. The adsorption is considered as irreversible when  $R_L = 0$ , favorable when  $0 < R_L < 1$ , linear when  $R_L = 1$  and unfavorable when  $R_L > 1$ .

### 1.6.2 Freundlich Isotherm Model

The Freundlich isotherm model is the most widely used empirical expression that accounts for the surface heterogeneity, exponential distribution of active sites of sorbent and their energies towards adsorbate (Freundlich, 1906). Although it does not take the solids finite capacity for sorption at high concentration of the solute into account, it can describe the experimental data well on a phenomenological basis. The Freundlich model is given by:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (\text{non-linear form}) \quad (1.5)$$

The linearized form of Freundlich isotherm is given in the following form:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (1.6)$$

where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $q_e$  is the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g),  $K_F$  is related to the adsorption capacity [(mg/g)(1/mg)<sup>1/n</sup>] and  $n$  is the affinity of interaction between adsorbate and the adsorbent. A favorable adsorption tends to have  $n$  value between 1 and 10. Larger value of  $n$  implies stronger interaction between adsorbent and adsorbate.

### 1.6.3 Redlich-Peterson Model

The Redlich-Peterson model is a combination of the Langmuir and Freundlich isotherm models. This model approaches the Freundlich isotherm model at high concentration and is in accord with the low concentration limit of the Langmuir isotherm model (Chen et al., 2011). The Redlich-Peterson equation is given by:

$$q_e = \frac{K_{RP} C_e}{1 + \alpha C_e^\mu} \quad (1.7)$$

where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $q_e$  is the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g),  $K_{RP}$  is the Redlich Peterson isotherm constant (L/g),  $\alpha$  is a constant (L/mg) and  $\mu$  is an exponent which lies between 0 and 1.

Equation (1.7) reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when  $\mu$  is equal to 1.

#### 1.6.4 Temkin Model

The Temkin isotherm considers a factor that explicitly takes into account adsorbing species-adsorbate interactions (Temkin, 1941). This model assumes that: (a) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate-adsorbate repulsions, (b) the adsorption is a uniform distribution of maximum binding energy, and (c) the fall in the heat of adsorption is linear rather than logarithmic. This model is expressed as:

$$q_e = B \ln AC_e \quad (1.8)$$

$$b = \frac{RT}{B} \quad (1.9)$$

where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $q_e$  is the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g),  $A$  is the equilibrium binding constant (L/mg),  $b$  is a constant related to the heat of adsorption (J/mol),  $T$  is the absolute temperature in Kelvin and  $R$  is the gas constant.

### 1.6.5 Dubinin-Radushkevich Model

The Dubinin-Radushkevich model does not assume a homogenous surface or constant sorption potential. This model is often used to estimate the characteristic porosity and the apparent free energy of adsorption (Akhtar et al., 2006). One of the best features of the Dubinin-Radushkevich equation lies on the fact that it is temperature-dependent. If the adsorption data at different temperatures are plotted as the logarithm of the amount of adsorbed adsorbate per unit weight of adsorbent versus the square of potential energy, all the suitable data shall in general lie on the same curve, called as the characteristic curve (Febrianto et al., 2009). This curve can later be utilized as an initial “tool” to measure the applicability of Dubinin-Radushkevich equation in expressing the adsorption equilibria data. This isotherm is represented as:

$$q_e = X_m e^{-\beta \varepsilon^2} \quad (1.10)$$

The linear form of Dubinin-Radushkevich isotherm is represented as:

$$\ln q_e = \ln X_m - \beta \varepsilon^2 \quad (1.11)$$

where  $q_e$  is the amount of adsorbed adsorbate per unit weight of adsorbent at equilibrium (mg/g),  $X_m$  is the maximum adsorption capacity of adsorbent (mg/g),  $\beta$  is a constant related to the adsorption energy, and  $\varepsilon$  is the Polanyi sorption potential which is equal to:

$$\varepsilon = RT \ln \left( 1 + \frac{I}{C_e} \right) \quad (1.12)$$

where  $C_e$  (mg/L) is the equilibrium concentration of the adsorbate,  $T$  is the absolute temperature in Kelvin and  $R$  is the gas constant. The Polanyi sorption theory

postulates fixed volume of sorption sites close to the sorbent surface and the existence of sorption potential over these sites. Polanyi sorption potential,  $\varepsilon$ , is the work required to remove a molecule to infinity from its location in the adsorption space, independent of the temperature. This model assumes the heterogeneity of sorption energies within its space. The value of sorption energy,  $E$  ( $\text{J mol}^{-1}$ ), can be correlated to  $\beta$  using the following relationship:

$$E = \frac{I}{\sqrt{2\beta}} \quad (1.13)$$

## 1.7 Adsorption Kinetic Models

Adsorption kinetics describes the reaction pathways and the time needed to reach the equilibrium. Adsorption kinetics show large dependence on the physical and chemical characteristics of the adsorbent material which also influence the adsorption mechanism that can either be film or pore diffusion or a combination of both, depending on the system hydrodynamics (El-Naas et al., 2010). The adsorption kinetics is commonly described by the pseudo-first-order and pseudo-second-order models.

### 1.7.1 Pseudo-First-Order Model

The pseudo-first-order equation of Lagergren is given by (Lagergren, 1898):

$$\frac{dq}{dt} = k_1(q_e - q) \quad (1.14)$$

Integration of equation (1.14) with the boundary conditions:  $t = 0, q = 0$ , and  $t = t, q = q_t$ , gives

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1.15)$$

where  $q_t$  and  $q_e$  are the amounts of adsorbates adsorbed at time  $t$  and at equilibrium (mg/g), respectively, and  $k_1$  is the pseudo-first-order rate constant for the adsorption process (1/min).

### 1.7.2 Pseudo-Second-Order Model

The pseudo-second-order chemisorption kinetic rate equation is expressed as (Ho, 2006):

$$\frac{dq}{dt} = k_2(q_e - q)^2 \quad (1.16)$$

Integration of equation (1.16) with the boundary conditions:  $t = 0, q = 0$ , and  $t = t, q = q_t$ , gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (1.17)$$

Equation (1.17) can be rewritten as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (1.18)$$

where  $q_t$  and  $q_e$  are amounts of adsorbates adsorbed at time  $t$  and at equilibrium (mg/g), respectively, and  $k_2$  is the pseudo-second-order rate constant for the adsorption process (g/mg min).

The pseudo-second-order rate constant,  $k_2$ , is used to calculate the initial adsorption rate as given by:

$$h = k_2 q_e^2 \quad (1.19)$$

where  $h$  is the initial adsorption rate (mg/ g min).

## **1.8 Adsorption Mechanism**

The pseudo-first- and pseudo-second-order adsorption kinetic models only show the adsorption rate but do not explain the mechanism of adsorption. Adsorption is a multi-step process involving the transport of the adsorbate from the aqueous phase to the surface of the adsorbent followed by diffusion into the adsorbent's interior pores. The slowest step of the transport steps would determine the overall rate of adsorption. The adsorption process of the adsorbate from the bulk liquid phase onto the adsorbent surface is presumed to involve three stages: (1) mass transfer of the adsorbate across the external boundary layer (film diffusion); (2) intraparticle diffusion within the pores of the adsorbent (particle diffusion); (3) adsorption at a site on the surface (Liu et al., 2010).

Sarkar et al. (2003) reported that either film diffusion or particle diffusion should govern the overall process and determine the rate limiting step. The overall rate is governed by the particle diffusion if the external transport is greater than that of the internal transport. If the external transport is less than the internal transport, the overall rate is governed by the film diffusion. It is observed that external transport is usually the rate-limiting step for a system having (a) poor mixing, (b) dilute adsorbate concentration, (c) small particle size of adsorbent, and (d) high affinity of adsorbate for adsorbent. In contrast, intraparticle step limits the overall transfer for a system having (a) good mixing, (b) high adsorbate concentration, (c) larger particle size of adsorbent, and (d) low affinity of adsorbate for adsorbent.

### **1.8.1 Intraparticle Diffusion Model**

The intraparticle diffusion model proposed by Weber and Morris (1962) is applied to study the adsorption process, which is written as:

$$q_t = k_{id}t^{\frac{1}{2}} + C_i \quad (1.20)$$

where  $q_t$  is the amount of adsorbate adsorbed at time  $t$  (mg/g),  $k_{id}$  is the intraparticle diffusion rate constant at stage  $i$  (mg/g min<sup>1/2</sup>), and  $C_i$  is the thickness of the boundary layer at stage  $i$  (mg/g).

## 1.9 Adsorption Thermodynamics

The effect of temperature on adsorption is evaluated with the thermodynamic parameters. The thermodynamic quantity of Gibbs free energy change,  $\Delta G^\circ$  (J/mol), indicates the spontaneity and feasibility of the adsorption process. The  $\Delta G^\circ$  value can be calculated using the following equation:

$$\Delta G^\circ = -RT \ln K \quad (1.21)$$

where  $K$  is the thermodynamic equilibrium constant,  $R$  is the gas constant (8.314 J/mol K) and  $T$  is the absolute temperature in Kelvin. Liu (2009) has shown that for neutral adsorbates or adsorbates with weak charges as in the case of organic compounds, the thermodynamic equilibrium constant of adsorption could be approximated by the Langmuir equilibrium constant,  $K_L$ .

For the enthalpy change,  $\Delta H^\circ$  (J/mol) and the entropy change,  $\Delta S^\circ$  (J/mol K), their relationship is shown as follows:

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (1.22)$$

where  $K_L$  is the Langmuir equilibrium constant.



## **1.10 Regeneration of Adsorbent**

Most of the recent studies focus on the development of high adsorption capacity adsorbents without considering the regeneration potential of the adsorbents. The regeneration potential of the adsorbent must be highlighted and it is another important goal in the development of adsorbent. After adsorption, the adsorbent becomes exhausted. The exhausted adsorbent would create another environmental problem and the disposal of loaded adsorbent is an important issue. The service life of the adsorbent can be extended through the regeneration of the loaded adsorbent. Studies had been carried out to investigate the regeneration of chlorophenols-loaded adsorbents chemically (Wang et al., 2011), thermally (Álvarez et al., 2004; Sabio et al., 2004; Zhang et al., 2009) and biologically (Aktaş and Çeçen, 2009; Ng et al., 2009; Oh et al., 2011). Other alternative regeneration methods included microwave assisted regeneration (Yuen and Hameed, 2009) and electrochemical regeneration (Weng and Hsu, 2008; Narbaitz and McEwen, 2012).

### **1.10.1 Regeneration Methods**

The thermal regeneration process uses gradual heating to desorb and volatilize certain contaminants and to convert others to char, followed by pyrolysis of the char and finishes with an oxidation step (Narbaitz and McEwen, 2012). The disadvantages of the thermal regeneration include high cost in terms of energy consumption, time consuming, and 5 – 15 % of carbon loss by attrition, burn-off and washout.

Chemical regeneration can be carried out by desorption of adsorbates using specific solvents or by decomposition of adsorbed species using oxidizing chemical agents (Álvarez et al., 2004). Akhtar et al. (2006) showed that the desorption

efficiencies of 2,4-dichlorophenol from rice husk were 99 and 90 %, by using methanol and NaOH, respectively. Sathishkumar et al. (2009) reported that desorption of 2,4-dichlorophenol with NaOH solution resulted in 77.8 and 69.5 % recoveries of the adsorbate from 10 and 20 mg/L 2,4-dichlorophenol-loaded carbons. El-Naas et al. (2010) showed that chemical regeneration with ethanol showed better regeneration efficiency in repeated cycles compared to thermal regeneration with steam and hot water. They also reported that thermal regeneration affects the characteristics of adsorbent after repeated cycles, leading to a drop in the regeneration efficiency. Wang et al. (2011) recommended ethanol and NaOH as the effective reagents for the regeneration of the spent activated carbons in their study. However, the extraction with solvent requires further purification of the solvent and it is only recommended when a valuable product is recovered (Álvarez et al., 2004).

Biological regeneration is the renewing of activated carbon by microbial activities. Ha et al. (2000, 2001) reported bioregeneration for their phenol- and 2,4-dichlorophenol-loaded activated carbon. Lee and Lim (2005) used bioregeneration approach to renew their activated carbon loaded with alkyl-substituted phenolic compounds. Bioregeneration approaches had been carried out for regenerating phenol-, 2-chlorophenol- and 2-nitrophenol-loaded activated carbons (Aktaş and Çeçen, 2006b, 2007a, 2010), phenol- and 4-nitrophenol-loaded activated carbons (Ng et al., 2009) and 4-chlorophenol- and 2,4-dichlorophenol-loaded activated carbons (Oh et al., 2011).

Electrochemical regeneration and microwave-assisted regeneration are other alternatives of regeneration methods. Higher regeneration efficiencies were achieved for date seeds activated carbon (above 96 % after ten cycles) compared to activated carbon by using the microwave-assisted technology (Al-Mutairi, 2010). Zhang et al.

(2009) found that the regeneration of activated carbon with microwave heating was better to retain the original porous framework of samples compared to the conventional furnace thermal heating. Narbaitz et al. (2012) reported that the electrochemical regeneration could be the alternative method to replace the thermal regeneration. They reported that the carbon replacement and energy costs are less for electrochemical regeneration.

### **1.10.2 Factors Affecting the Regeneration**

Desorption is a prerequisite step for regeneration. Thus any condition that affects desorption of the adsorbed solute eventually affects the extent of regeneration. The reversibility of the adsorption will affect the efficiency of desorption from the adsorbent.

Reversible adsorption is attributed to adsorption as a result of the van der Waals forces and/or weaker charge-transfer complexes that occur at adsorption sites (Aktaş and Çeçen, 2007b). On the other hand, two mechanisms can explain the irreversible adsorption. One of the mechanisms is the high energy bonding of adsorbate molecules to specific functional groups on the active sites of carbon surface resulting in covalent bonding (Ha and Vinitnantharat, 2000; Jonge et al., 1996a). Depending on the type of surface functional group and sorbate, a sufficiently strong bond can be formed thus resisting desorption. The second mechanism is the oxidative polymerization of phenolic compounds onto activated carbon due to the presence of oxygen (Jonge et al., 1996a). Jonge et al. (1996a) demonstrated that the adsorption of a phenolic compound, o-cresol, increased in the presence of molecular oxygen due to oxidative polymerization, whereas the adsorption of a non-phenolic compound, 3-chlorobenzoic acid, was not affected by the presence of oxygen.

In general, oxidative coupling of phenolic compounds, except nitrophenols, was found to decrease the reversibility of adsorption (Aktaş and Çeçen, 2010). Oxidative coupling of phenolic compounds is also dependent on carbon activation process. In several studies, a higher degree of irreversible adsorption was observed for thermally activated carbon (Jonge et al., 1996a, 1996b; Aktaş and Çeçen, 2006a, 2009). This was explained by the affinity of thermally activated carbons towards oxygen and changes in surface chemistry upon contact with oxygen. Contrary to this, chemically activated carbons have a surface with fully oxidized active sites so that interaction with oxygen does not affect the surface, whereas thermal activation of the carbons is originally carried out in the absence of oxygen leading to a more reactive surface. Jonge et al. (1996a) suggested that functional groups influence the probability of the adsorbate being oxidized. In general, unsaturated groups (e.g. carboxyl and nitro groups) decrease the susceptibility to oxidation, whereas saturated groups (e.g. methyl groups) increase the probability of oxidation.

Klimenko et al. (2002) reported that the higher the change in the Gibbs free energy of adsorption of an adsorbate, the lower the regeneration was observed. This could be attributed to the high energy of adsorptive binding with the sorbent surface that results in a lower reversible adsorption. The extent and nature of substitution on phenols affects the occurrence of regeneration. Lee and Lim (2005) reported that carbons loaded with alkyl-substituted phenols exhibited less regeneration with an increase in the length of the alkyl chain. Thus phenol-loaded carbon regenerated more efficiently compared to *p*-methylphenol-, *p*-ethylphenol and *p*-isopropylphenol-loaded carbons. Ha and Vinitnantharat (2000) also reported that the extent of carbon regeneration was higher with phenol compared to 2,4-dichlorophenol. Aktaş and Çeçen (2007a) found that lower desorbability of 2-chlorophenol resulted in much

less regenerability compared to phenol. The regeneration of *p*-nitrophenol is the only exception for phenolic compounds, as its regeneration was found to be higher than that of phenol (Ng et al., 2009). This finding may be due to irreversible adsorption of phenol caused by the oxidative coupling whereas oxidative coupling does not occur with nitrophenols.

### **1.11 Bioregeneration**

Bioregeneration of an adsorbent takes place as a result of the interaction among microorganisms and molecules of the adsorbed matter. Bioregeneration is defined as the renewal of the adsorptive capacity of adsorbent by microorganisms for further adsorption. Bioregeneration of adsorbent increases the service-life of adsorbents. It is traditionally believed that bioregeneration occurs as a result of the concentration gradient between the adsorbent and the bulk liquid. Therefore, bioregeneration can only occur for compounds that readily desorb (Aktaş and Çeçen, 2007b). With respect to water pollution control, ideally, adsorption should be irreversible for nonbiodegradable compounds. Otherwise desorption would lead to an undesired leakage of compounds to the receiving waters. However, for the readily biodegradable compounds, desorption will lead to bioregeneration and a renewal of the adsorptive capacity of activated carbon. Irreversible adsorption of biodegradable compounds will unnecessarily deteriorate the adsorptive potential and shorten the service life of activated carbon.

Effective bioregeneration processes depend on numerous factors including reversibility of adsorption (refer Section 1.10.2), the presence of microbial organisms capable of metabolizing the adsorbate, the settings of optimal microbial growth conditions including nutrients (nitrogen, phosphorus, sulfur, etc.), temperature,