UNIVERSITI PUTRA MALAYSIA

ADSORPTION STUDIES OF PHENOLS IN AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM SEVERAL PART OF OIL PALM TREE

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By
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LIST OF ABBREVIATIONS

EPA	Environmental Protection Agency
WHO	World Health Organization
PORIM	Palm Oil Research Institute of Malaysia
SIRIM	Standard Instrumentation Research Institute of Malaysia
UTM	Universiti Teknologi Malaysia
15-CP	Chips of Oil Palm Trunk with 15% $ZnCl_2$ Impregnation
15-PP	Powder of Oil Palm Trunk with 15% $ZnCl_2$ Impregnation
10-CP	Chips of Oil Palm Trunk with 10% $ZnCl_2$ Impregnation
FZ-CP	Chips of Oil Palm Trunk with 0% $ZnCl_2$ Impregnation
KI 5060	Commercial Activated Carbon
15-CP(co_2)	Chips of Oil Palm Trunk with 15% $ZnCl_2$ Impregnation and CO_2 Activation
15-EFB	Empty Fruit Bunch with 15% $ZnCl_2$ Impregnation and CO_2 Activation
15-OPS	Oil Palm Shell 15% $ZnCl_2$ Impregnation and CO_2 Activation
SEM	Scanning Electron Microscope
FTIR	Fourier Transform Infrared Analysis
BET	Brunauer, Emmett and Teller
UV/VIS	Ultra Violet/ Visible
$ZnCl_2$	Zinc Chloride

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science.

ADSORPTION STUDIES OF PHENOLS IN AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM SEVERAL PARTS OF OIL PALM TREE

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August 1999

Chairman: **Associate Professor Zulkarnain Zainal, Ph.D.**

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The activated carbon used in the adsorption of phenols were prepared from oil palm trunk, shell and empty fruit bunches. A commercial activated carbon obtained from a local manufacturer (KI 5060) was used as comparison.

The study was carried out to investigate several factors affecting the extent of phenol adsorption. The study was divided into two parts. The first part was the characterization of the activated carbon including surface area and porosity analysis, determination of iodine number, ash content, trace elements, infrared analysis and the morphology of activated carbon. The second part dealt with the adsorption of phenol and its derivatives onto the activated carbon. The study included investigation of the effects of initial concentration, types of activated carbon particles (chips or powder), surface area, pH solution, and types of substituent groups on adsorption.

The higher uptake was achieved in higher concentrations of phenol, but the percentage removal gave the opposite result. The higher uptake was also obtained with higher surface area (15-CP) than low surface area due to more vacant area that need to be occupied. The adsorption of phenol was constant with low pH solutions and decreased with high pH solutions. Oil palm trunk gave better adsorption than oil palm shell or empty fruit bunches.

The substituent group of benzene rings of phenol play an important role in adsorption. The electron withdrawal group (NO_2 and Cl) enhanced the adsorption; whereas the electron-donating group (CH_3) gave the opposite reaction. The adsorption data were tested for Freundlich and Langmuir isotherms. In addition, the Brunner, Emmet and Teller (BET) isotherm was also tested. Phenol and o-nitrophenol followed all adsorption isotherm (Langmuir, Freundlich and BET), but o-chlorophenol, m-chlorophenol, p-chlorophenol, m-cresol and p-cresol were only valid for Freundlich and BET isotherm.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
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KAJIAN JERAPAN FENOL DI DALAM LARUTAN AKUES MENGGUNAKAN KARBON TERAKTIF YANG DISEDIAKAN DARIPADA BEBERAPA BAHAGIAN POKOK KELAPA SAWIT

Oleh

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Karbon teraktif yang digunakan dalam kajian jerapan terhadap fenol disediakan daripada batang kelapa sawit, tempurung dan tandan. Karbon teraktif komersial keluaran tempatan (KI 5060) digunakan sebagai perbandingan.

Kajian jerapan dilakukan untuk mengetahui beberapa faktor yang mempengaruhi tahap jerapan. Kajian ini dibahagikan kepada dua bahagian. Bahagian pertama melibatkan pencirian karbon teraktif melibatkan analisis luas permukaan dan keliangan, penentuan nombor iodin, kandungan abu, pengesanan unsur, analisis inframerah dan analisis bentuk permukaan karbon aktif. Bahagian kedua merupakan kajian proses jerapan fenol dan terbitannya ke atas karbon teraktif. Kajian ini termasuk kesan kepekatan awal, jenis partikel karbon teraktif (serbuk atau kepingan), luas permukaan, pH larutan, jenis kumpulan pengganti terhadap jerapan dibuat kajian.

Jerapan yang tinggi diperolehi bagi kepekatan fenol yang tinggi. Jerapan yang tinggi juga duperolehi bagi luas permukaan yang tinggi (15-CP) kerana kewujudan lebih banyak tapak aktif yang boleh diduduki. Jerapan fenol tidak berubah pada pH larutan yang rendah dan berkurangan pada pH larutan yang tinggi manakala, batang kelapa sawit memberikan jerapan yang lebih baik berbanding dengan tempurung kelapa sawit dan tandannya.

Jenis kumpulan pengganti pada gelang benzena memainkan peranan penting di dalam jerapan. Kumpulan penarik elektron (NO_2 dan Cl) meningkatkan tahap jerapan, manakala kumpulan penderma elektron (CH_3) memberi kesan yang sebaliknya. Data jerapan telah diuji untuk isoterma Freundlich dan Langmuir. Isoterma Brunner, Emmet and Teller (BET) turut diuji. Fenol dan o-nitrofenol mamatuhi semua isoterma (Langmuir, Freundlich dan BET), tetapi o-klorofenol, m-klorofenol, p-klorofenol, m-kresol dan p-kresol hanya mematuhi isoterma Freundlich dan BET sahaja.

CHAPTER I

INTRODUCTION

Modernization and development of industries results in the appearance of organic compounds in water. These compounds are released in industrial effluent such as from oil palm refineries, pulp and paper mills, chemical spills, pharmaceuticals, and agricultural pesticides. Phenol and its derivatives are common organic compounds found in industrial effluent and water streams.

Gupta *et al.*, 1997 reported that more than 700 specific organic chemicals have been identified in drinking water. Phenolic compound was considered to constitute the 11th of the 126 organic chemicals, which were designated as priority pollutants by the Environmental Protection Agency (EPA), in USA (Caturla *et al.,* 1988).

Adsorption of organic compounds in aqueous solution by activated carbon is the most common technology in water and wastewater treatment (Halhouli *et al.*, 1995 and Hitomi *et al.*, 1993). Activated carbon is being used because of its high adsorption capacity due to high surface area and porosity. The adsorption of organic compounds such as phenol into activated carbon was first done by Honig in 1926. Since then, many studies have been done on the removal of organic compounds from aqueous solution. The work by

Rodriguez and associates in 1981 was considered successful for the adsorption of phenolic compound from industrial effluent in the range of 80 – 4000 mg/l. This is reported in Sing *et al.*, 1996.

Many of studies have been carried out on activated carbon from agricultural by-products as adsorbents for removing organic compounds. Rivera-Utrilla and associates (1991) discovered that activated carbon from agricultural by-products (almond shells) are better adsorbents than spanish lignite in removing chlorophenol. Johns *et al.* 1998, found that activated carbon from nutshell is very effective for the adsorption of 1,4-dioxane in aqueous solution.

Sources of Organic Compounds

The release of organic compounds into the environment has been widely found in manufacturing of phenolic (phenol formaldehyde) resin, caprolactam, bisphenol A, alkyl phenol and adipic acids. These organic compounds are released either directly or indirectly.

In addition, organic compounds especially phenolic compounds can occur naturally in water. During water chlorination, p-hydroxylbenzoic acid which exists in water will react with chlorine and be converted into trichlorophenol (Larson and Rockwell, 1987).

The Department of Chemistry, Ministry of Science and Technology Malaysia (1996) has reported that major sources of river pollution are suspended solids and organic pollution. Palm oil mills, feed mills, food and beverage industries and sewage were named as major contributors to water pollution.

Toxicity of Phenols

Phenols are the most frequently occurring contaminants in industrial waste. They are not only carcinogenic, but give bad taste and odour even at low concentrations (Mostaffa *et al.*, 1990). Phenol is skin active. Once absorbed, it will attack the liver and kidney. Chronic symptoms are weight loss, weakness, kidney trouble and enlarged liver. Acute poisoning will cause abdominal pain, dark urine, weakness, cyanosis and tumors. Treatment for phenolic poisoning involves treating the convulsions with sedatives and attempting to stave off liver and kidney damage. Chronic exposure will result in sensitisation of the skin and chronic liver and kidney disease (Buzzi, 1993).

The World Health Organisation (WHO) has set water quality standards as shown in Table 1 for domestic use (Nik Abllah, 1990). The table shows that the highest phenol allowed in water is 0.002 mg/l.

Table 1: Water Quality Standard (WHO) (Nik Abllah, 1990)

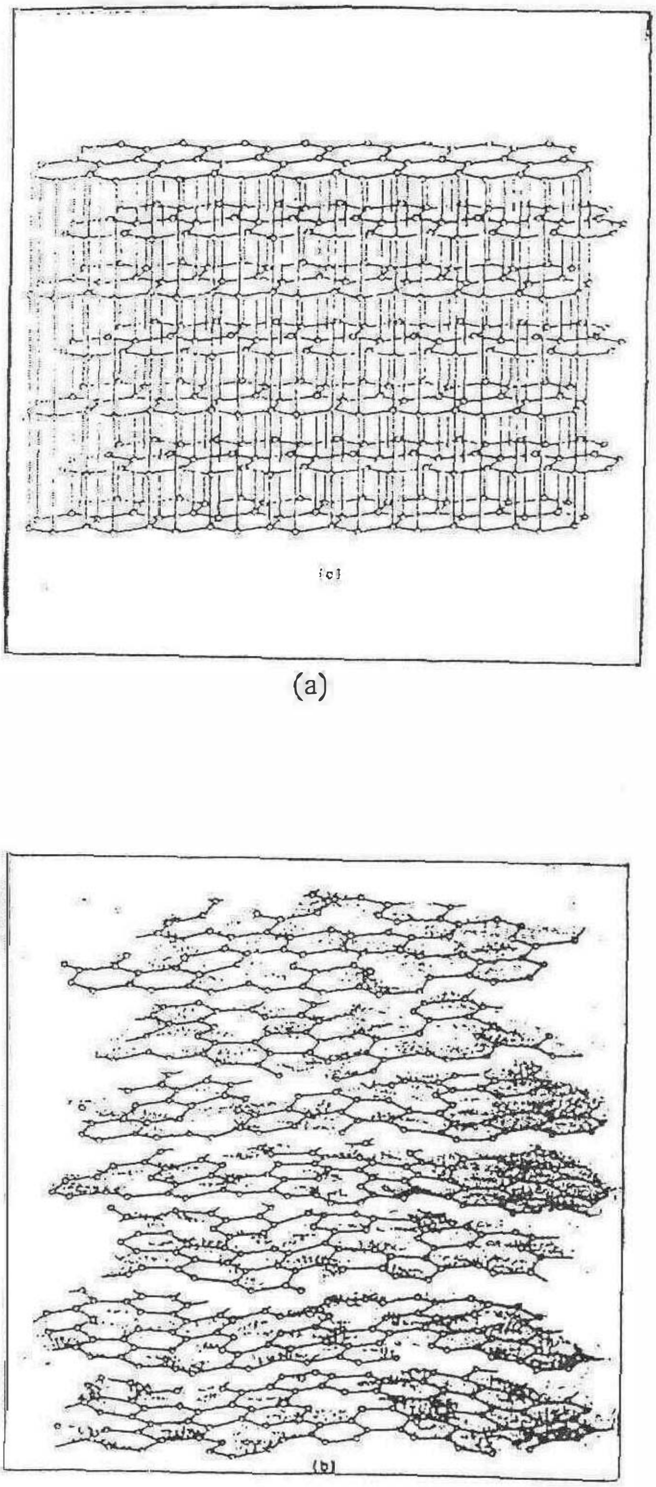
Compound	Highest Concentration needed	Maximum Concentration allowed
Total Solid (mg/l)	500	1500
Colour (Cobalt Scale)	5	50
Turbidity (Jackson)	5	25
Ferum (mg/l)	0.3	1
Arsenic (mg/l)	0.05	0.05
Manganese (mg/l)	0.1	0.5
Cyanide (mg/l)	0.2	0.2
Copper (mg/l)	1	1.5
Zinc (mg/l)	5	15
Lead (mg/l)	0.05	0.05
Calcium (mg/l)	75	200
Magnesium (mg/l)	50	150
Sulphate (mg/l)	200	400
Chloride (mg/l)	200	600
Phenol (mg/l)	0.001	0.002
Alkyl Benzyl Sulphonate (mg/l)	0.5	1
Chloroform (mg/l)	0.2	0.5
Hardness (mg/l)	200	300

Therefore some precaution has to be taken in handling the chemical either in the laboratory or in industry. The industrial effluent must be well treated before disposed of into rivers or streams.

Structure of Activated Carbon

Activated carbon is known as an efficient adsorbent for organic substances. It is used in sugar refineries, food industries, air purification and water treatments and in pharmaceuticals. Activated carbon contains a large volume of very fine pores called micropores which substantially influence its adsorption properties.

Activated carbon has a similar structure to turbostratic carbon, having microcrystallite, which is only a few layers in thickness and less than 100 Å in width. This is shown in Figure 1. It consists of rigid interlinked clusters of microcrystallite. Each of them has 5-15 layers of graphite planes. Each carbon atoms with a particular plane is joined to three adjacent carbon atoms by sigma bonds with the fourth electron participating in a π bond. The microcrystallite is interconnected by the interaction of functional groups terminating the graphite planes. This resulting channel is considered to be composed of macropores whereas micropores are fissured within and parallel to the graphite planes. The intraparticle surfaces of activated carbon consist of basal planes.



(a)

(b)

Figure 1: Schematic diagram comparing (a) a three-dimensional graphite lattice with (b) a turbostratic structure (Mattson and Mark, 1971).

The cumulative basal planes surface area which are predominantly located within intra-activated carbon are mainly microporous, but they also contain meso- and macropores, which are very important in facilitating access of the adsorbate molecules to the interior of the carbon particle and in many of the adsorption applications in the liquid phase (Ahmadpour and Do, 1995).

Manufacturing of Activated Carbon

Activated carbon can be prepared from various sources of carbonaceous substances including bones, coal, wood dust, peat, nutshell, oil palm trunk, oil palm shell, coconut shell, wood charcoal, etc. The manufacture of activated carbon includes two important stages: the carbonization of the precursor and the activation of the resulting char.

According to Bansal *et al.* (1988), during carbonization, most of the noncarbon elements are eliminated. The residual carbon form itself into a sheet consisting of a condensed aromatic ring system, often bent, the mutual arrangement of which is irregular, leaving free interstices that may be filled or blocked by disorganized carbon resulting from the deposition and decomposition of tars.

The activation process involves three primary variables: the nature of the precursor, the composition of the activation process, and the time and temperature of the activation process. In this process charcoal is heated to a sufficiently high temperature to cause an extensive burn-off degradation of noncarbon impurities, leaving a highly porous product with a large surface area (Mattson *et al.* 1971).

The development of porosity in activated carbon is very important for the adsorption of liquid and gases. This porosity can be developed with activating gases such as carbon dioxide. Activation generates narrow microporosity, the diameters of pores remain constant and the tensile strength decreases during the whole burn off. Steam activation produces a wider pore size distribution the diameter of fibers and the tensile strength decrease with burn off (Alcantz-Monge *et al.*, 1994).

(i) Chemical Activation

There are two types of activation: chemical and physical activation. Chemical activation is carried out by adding chemical agents such as $ZnCl_2$, K_2CrO_5, H_2SO_4 or H_2PO_4 with lignocellulosic precursor thus restricting the formation of tars. The resulting precursor then is kneaded carbonized and washed to produce the final activated carbon (Rodriguez *et al.* 1992).

Ropandi *et al.* (1995) and Hussien *et al.* (1995) converted oil palm trunk into activated carbon. They found that the surface area of activated carbon obtained through chemical activation with $ZnCl_2$ can be increased up to 1892 m^2/g. Besides that, there was an indication that $ZnCl_2$ could modify some of the original micropores to mesopores. Oil palm trunk was proposed as suitable raw material for the preparation of activated carbon.

The amount of the $ZnCl_2$ incorporated in the precursor governs the porosity of the activated carbon; thus, making this activation method a flexible way for the preparation of activated carbon with different pore size distributions (Rodriguez *et al.*, 1992).

(ii) Physical Activation

The physical activation does not include the addition of a chemical agent. The raw material containing carbon, hydrogen and oxygen is carbonized at a temperature 500-900 °C and reacted with carbon dioxide, steam and air or a mixture of these until a degree of activation has been achieved (Smisek and Cerny, 1970). The resulting activated carbon from physical activation does not have a large of a surface area as that resulting from chemical activation.