SYNTHESIS AND CHARACTERIZATION OF SURFACE MODIFIED BANANA TRUNK AS ADSORBENT FOR BENZENE REMOVAL FROM AQUEOUS SOLUTION

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SYNTHESIS AND CHARACTERIZATION OF SURFACE MODIFIED BANANA TRUNK AS ADSORBENT FOR BENZENE REMOVAL FROM AQUEOUS SOLUTION

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A thesis submitted in fulfilment of the requirements for the award of the degree of Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering
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To my beloved family
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ABSTRACT

Petroleum monoaromatics especially benzene contamination in water and wastewater is the major concern in the industry today. Various removal techniques have been studied. The adsorptive removal process is considered as one of the most cost-efficient and feasible methods because it does not require a large amount of energy and additional chemical. In adsorption technology, several problems such as adsorbent cost, adsorption selectivity and adsorbent reusability are the main concerns. Therefore, the potential conversion and modification of agrowaste adsorbent into an effective adsorbent alternative to removing benzene constituent from the wastewater were studied. The banana trunk (BT) was selected as an agrowaste model in the present study. The raw BT (Raw-BT) was first mercerized and this mercerized BT (M-BT) was then reacted with different surfactants, namely cetyltrimethylammonium bromide, CTAB (M-CTAB-BT), 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol, Triton X-100 (M-TX100-BT) and sodium dodecyl sulfate, SDS (M-SDS-BT). Surface etherification was also conducted by using 3-chloro-2-hydroxypropyl trimethylammonium chloride, CTA with the mass ratio of 1 and this etherified BT (M-1CTA-BT) was then coated with SDS (M-1CTA-SDS-BT). All the adsorbents were characterized by using a Fourier transform infrared spectrometer, a field emission scanning electron microscope, an x-ray photoelectron spectroscopy analyzer and nitrogen adsorption/desorption analysis. The experimental batch adsorption studies showed that the adsorption capacity increased in the following order: Raw-BT < M-BT < M-CTAB-BT < M-TX100-BT < M-1CTA-SDS-BT. The Langmuir maximum benzene adsorption capacity, $q_{L,max}$ achieved by the M-1CTA-SDS-BT was $468.187 \times 10^{-3}$ mmol/g. The fundamental adsorption equilibrium and kinetic studies revealed that the benzene adsorption data were fitted well into the Langmuir isotherm and pseudo-second order kinetic models which suggested that the adsorption process was governed by a physical phenomenon. The film diffusion was considered as the rate-limiting step for the overall benzene adsorption process. The adsorbents were chemically stable within the pH range. It was revealed the benzene adsorption was an endothermic and non-spontaneous process. The regeneration study using 50 % ethanol-water as the desorbing agent, demonstrated that the modified adsorbents could withstand five adsorption/desorption cycles without a drastic reduction of adsorption uptake (8.5 - 13.0 %). The BT could potentially be employed as an adsorbent precursor for benzene adsorptive removal from aqueous solution.
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</tr>
<tr>
<td>$C_e$</td>
<td>Equilibrium adsorbate concentration (mmol/L)</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>Molecule diffusivity</td>
</tr>
<tr>
<td>$D_{eff}$</td>
<td>Effective diffusion coefficient (m$^2$/min)</td>
</tr>
<tr>
<td>$D_{film}$</td>
<td>Film diffusion coefficient (m$^2$/min)</td>
</tr>
<tr>
<td>$D_p$</td>
<td>Pore diffusion (m$^2$/min)</td>
</tr>
<tr>
<td>$D_s$</td>
<td>Surface diffusion (m$^2$/min)</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Polanyi potential</td>
</tr>
<tr>
<td>$K$</td>
<td>Thermodynamic constant at equilibrium</td>
</tr>
<tr>
<td>$k_1$</td>
<td>PFO equilibrium rate constant (min$^{-1}$)</td>
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<tr>
<td>$k_2$</td>
<td>PSO equilibrium rate constant (min$^{-1}$)</td>
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<tr>
<td>$K_F$</td>
<td>Freundlich constant (L$^n$mmol$^{n-1}$/g)</td>
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<td>$k_{id}$</td>
<td>Intraparticle diffusion constant</td>
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<tr>
<td>$k_L$</td>
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<td>$K_L$</td>
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<tr>
<td>$M_B$</td>
<td>Water molecular weight (18.0 g/mol)</td>
</tr>
<tr>
<td>$n$</td>
<td>Adsorption intensity</td>
</tr>
<tr>
<td>$pH_i$</td>
<td>Initial adsorbate pH</td>
</tr>
</tbody>
</table>
q - Adsorption capacity (mmol/g)
q_e - Equilibrium adsorption capacity (mmol/g)
q_{max} - Maximum adsorption capacity (mmol/g)
q_t - Adsorption capacity at time t (mmol/g)
\Gamma_e - Retained CTAB loading capacity on the adsorbent (mmol/g)
R - Universal gas constant (8.314 J K^{-1}mol^{-1})
R^2 - Linear coefficient of determination
S/L - Adsorbent dosage (solid to liquid ratio, mg/mL)
S_{eff} - Slope of the Boyd plot
T - Temperature (°C)
t - Time (min)
V - Adsorbate volume (L)
V_A - Liquid molar volume (m^3/mol)
W - Adsorbent Weight (g)
\alpha - Initial Adsorption Rate (mmol/g·min)
\beta - Desorption constant (g:mmol)
\delta - Nernst film thickness
\Delta q_e - Normalized standard deviation for adsorption capacity (%)
\Delta \Gamma_e - Normalized standard deviation for CTAB loading capacity (%)
\phi - Adsorbent to CTA ratio
\chi^2 - Pearson's chi-squared
\Gamma_e - CTAB loading capacity (mmol/g)
**LIST OF ABBREVIATIONS**

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<tr>
<td>ACF</td>
<td>Activated carbon fiber</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet Teller</td>
</tr>
<tr>
<td>BT</td>
<td>Banana trunk</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, toluene, ethylbenzene and xylene</td>
</tr>
<tr>
<td>CAE</td>
<td>Constant analyzer energy</td>
</tr>
<tr>
<td>CNT</td>
<td>Carbon nanotubes</td>
</tr>
<tr>
<td>CPB</td>
<td>Cetyl pridinium bromide</td>
</tr>
<tr>
<td>CTA</td>
<td>(3-chloro-2-hydroxypropyl) trimethylammonium chloride</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>D-R</td>
<td>Dubinin-Raduchkevich</td>
</tr>
<tr>
<td>FESEM</td>
<td>Field emission scanning electron microscope</td>
</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infra-red</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography (GC)</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>KBr</td>
<td>Potassium bromide</td>
</tr>
<tr>
<td>NAD</td>
<td>Nitrogen adsorption/desorption</td>
</tr>
<tr>
<td>NPD</td>
<td>Naphthalene, phenanthrene and dibenzothiophene</td>
</tr>
<tr>
<td>OPEFB</td>
<td>Oil palm empty fruit bunch</td>
</tr>
<tr>
<td>PEG</td>
<td>Poly ethylene glycol</td>
</tr>
<tr>
<td>PFO</td>
<td>Pseudo-first order</td>
</tr>
<tr>
<td>Pluronic 123</td>
<td>Poly(ethylene glycol)-<em>block</em>-poly(propylene glycol)-<em>block</em> poly(ethylene glycol)</td>
</tr>
<tr>
<td>PSO</td>
<td>Pseudo-second order</td>
</tr>
<tr>
<td>O-SWCNT</td>
<td>Oxydized single-walled carbon nanotubes</td>
</tr>
<tr>
<td>P-SWCNT</td>
<td>Purified single-walled carbon nanotubes</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulfate</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>SPME</td>
<td>Solid phase micro-extraction</td>
</tr>
<tr>
<td>TOC</td>
<td>Total organic carbon</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra-violet</td>
</tr>
<tr>
<td>Vis</td>
<td>Visible</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent decades, many industries such as fossil fuels production, oil and gas refinery, plastic and synthetic rubber manufacturing have been growing extensively every year in order to fulfill the global application and demand (Vidal et al., 2012). As a consequence, water pollution caused by the petroleum production, transportation, processing and application activities has been the major concern all over the world (Tiburtius et al., 2005; Falkova et al., 2016; Li et al., 2016). Petroleum monoaromatic compounds such as benzene, toluene, ethylbenzene and xylene (BTEX) are commonly detected in almost any gasoline and petrol spill in water bodies (Aivalioti et al., 2010). According to a report by the Ohio Department of Health, 18% of gasoline is made up by BTEX components, by which 11% of them is benzene component (Ohio Department of Health, 2014). Benzene can enter water bodies by the cracked pipelines, underground fuel tank leakages as well as improper effluent discharge (Sharmasarkar et al., 2000; Seifi et al., 2011a).

Benzene is generally used as either a raw material or a solvent in various chemical and petrochemical related industries (Hindarso et al., 2001; Torabian et al., 2010; Asenjo et al., 2011). It is also one of the volatile organic compounds (VOC) which is colorless and flammable (Bennett and Peters, 1988; Fawell et al., 2003). Many studies have reported that it is highly toxic and carcinogenic to humans (Wibowo et al., 2007; Aivalioti et al., 2012a). It is revealed that a long-term exposure to its compounds at high concentration can cause cancers of the blood forming organs
such as aplastic anemia and leukemia (Weisel, 2010). The stringent regulations have been enforced on its concentration in water bodies due to its toxicity which is harmful to the aquatic environment and human health (Carvalho et al., 2012). According to the World Health Organization (WHO) drinking water guidelines, the maximum permissible its concentration is 0.01 ppm (Gorchev and Ozolins, 2011).

Due to the acute toxicity of the hazardous benzene in water and wastewater, it is utmost crucial to remove it from the waters and wastewaters. Consequently, a wide variety of removal technologies involves chemical, physical and/or biological methods have been investigated. In particular, the most common technologies are chemical or thermal oxidation, bioremediation, volatilization, condensation, membrane separation, and adsorption are developed (Lin and Huang, 1999; Ranck et al., 2005; Farhadian and Ducheze, 2008; Fakhru’l-Razi et al., 2009; Aivalioti et al., 2012b; Ali et al., 2012; Carvalho et al., 2012). Among all the conventional removal methods, the adsorption process is suggested to be the most cost-efficient and feasible method because it does not require a large amount of energy and additional chemicals. Besides that, adsorptive removal offers advantages including simple design and operation as well as cheap operating costs (Zytner, 1994; Lin and Huang, 1999; Wibowo et al., 2007; Liang and Chen, 2010; Moura et al., 2011; Yakout and Daifullah, 2013; Ray and Shipley, 2015; Mohammed et al., 2015).

In adsorption technology, activated carbon has been most commonly used as an adsorbent for removing a wide variety of pollutants, such as aromatic organic compounds, heavy metals and dyes, from aqueous solution (Wibowo et al., 2007; Karnib et al., 2014; Sulaymon and Abood, 2014). This is because activated carbon possesses high specific surface area and chemical stability (Hindarso et al., 2001; Su et al., 2010a; Asenjo et al., 2011; Serrano et al., 2011). However, activated carbon is very expensive and not locally available in most of the countries (Daifullah and Girgis, 2003; Seifi et al., 2011c). Besides activated carbon, other materials such as carbon nanotubes (Lu et al., 2008; Su et al., 2010b; Yu et al., 2012), macro-reticular resins (Lin and Huang, 1999), clays (Jaynes and Vance, 1999; Sharmasarkar et al., 2000; Vianna et al., 2005; Nourmoradi et al., 2012), zeolites (Ghiaci et al., 2004; Seifi et al., 2011b), carbon-silica aerogel composites (Dou et al., 2011), diatomite (Aivalioti et al.,
2010, 2012a), and membranes (Ohshima et al., 2005; Mukherjee and De, 2016; Uragami et al., 2016) have been employed as adsorbents for the adsorption of benzene and other VOCs.

1.2 Problem Statement

The simple design and operation as well as the capability of adsorbent regeneration, have made the adsorption process as one of the most cost-effective pollutant removal alternatives (Delval et al., 2006; Johari et al., 2013). The active carbon is one of the most effective and conventional adsorbent employed in this process as it can adsorb organic pollutants at a wider spectrum. However, the high affinity toward the adsorbed pollutant molecules causes the difficulty in activated carbon regeneration (Koyuncu et al., 2011). Nowadays, the synthetic adsorbents which are bio-converted from the agricultural wastes (i.e. agrowastes), especially plant fibers, seeds, husks, piths and leaves, have been developed in recent years. This is because agrowastes are cheap, locally available, renewable, natural and biodegradable (Shin and Rowell, 2005; Saman et al., 2014). The applications of raw/unmodified agrowastes such as rice bran, angico saw-dust and peat as agrowaste-based adsorbents for BTEX removal were reported (Adachi et al., 2001; Akhtar et al., 2005; Costa et al., 2012). However, the use of unmodified agrowaste adsorbent has been proven to have low adsorption affinity and selectivity (Ibrahim et al., 2010a; Johari et al., 2016). It is reported that raw agrowastes contain a large number hydroxyl (-OH) groups which has made the agrowastes to be readily functionalized with various chemical functional groups (Kumar et al., 2014). The adsorbent functionalization or modification is conducted to improve their adsorption affinity towards specific pollutants (Tiemann et al., 1999; Delval et al., 2005; Fu and Wang, 2011).

The thermal treatment or carbonization is one of the most common methods used in synthesizing adsorbents (Singh et al., 2003; Demirbas, 2009; Zhou et al., 2015). It was reported that agrowastes such as peach stone, olive stone, date pit, coconut shell, almond shell, and Moringa oleifera pods have been employed to produce agrowaste-
based activated carbon for BTEX removal from aqueous solution (Daifullah and Girgis, 2003; Akhtar et al., 2007; Mohammed et al., 2015). A strong binding between the benzene molecules and carbon surface has made it difficult for regeneration and thus increased the material and operating cost (Koyuncu et al., 2011; Zhang et al., 2012b). The alkaline treatment or mercerization process is revealed to create more carboxyl groups and thus produce more potential binding sites on the adsorbent surfaces (Hashim et al., 2012). The mercerization process also resulted in the irregular adsorbent surface as well as increased the adsorbent pore size and surface area by degrading the surface lignin. This leads to better binding effects between the adsorbate and the adsorbent surfaces (Ibrahim et al., 2010a; Koay et al., 2014).

Other chemical modifications such as esterification, acetylation, sulfonation, graft polymerization, impregnation and etherification are also conducted to enhance the adsorption performance towards target adsorbates (Chakraborty et al., 2005; Shin and Rowell, 2005; Alila and Boufi, 2009; Carvalho et al., 2012; Foo and Hameed, 2012b; Song et al., 2013; Teli and Valia, 2013). It was reported that adsorption uptake of BTEX removal relies on the surface hydrophobicity of the adsorbent employed (Seifi et al., 2011b). The surface modification by surfactants (i.e. cationic, anionic and non-ionic) is one of the well-known methods to increase the adsorbents surface hydrophobicity. Agrowastes (e.g. barley and wheat straw, peanut husk, coconut coir pith as well as yeast) functionalized by various cationic surfactants with different molecular weights (e.g. cetylpyridinium bromide (CPB), cetylpyridinium chloride (CPC), cetyltrimethylammonium bromide (CTAB) and hexadecyltrimethylammonium (HDTMA)) prepared using simple impregnation technique are successfully employed in the adsorption of a wide variety of pollutants including oil, dyes and metal ions from waters and wastewaters (Bingol et al., 2004; Namasivayam and Sureshkumar, 2008; Ibrahim et al., 2009, 2010a; Oei et al., 2009; Zhang et al., 2014; Zhao et al., 2014).

The utilization of agrowastes modified with surfactant for removal of benzene or BTEX has so far not been reported. However, inorganic adsorbents such as clay and zeolite modified with cationic surfactants including, benzyldimethyltetradecylammonium (BDTDA), benzyldimethylammonium (BTMA),
CPB and HDTMA (Koh and Dixon, 2001; Ghiaci et al., 2004; Vianna et al., 2005) have also been employed in volatile organic compounds (VOC) adsorption successfully. It was revealed that the BDTDA modified clay can achieve up to 70% benzene adsorption uptake of those shown by activated carbon (Koh and Dixon, 2001). Polyethylene glycol (PEG, a type of non-ionic surfactant) was used to modify montmorillonite which showed promising results for the BTEX adsorpive removal process (Nourmoradi et al., 2012). It was suggested that adsorbents modified with non-ionic surfactants may achieve higher BTEX adsorption uptake than that achieved with the adsorbents modified with cationic surfactants. Adsorbents such as bentonite, sawdust, alumina and montmorillonite modified with anionic surfactants (e.g. sodium dodecyl sulfate (SDS) and sodium stearate) were reported for total organic carbon (TOC) and dyes adsorption from aqueous state (Adak et al., 2005; Chen et al., 2010; Ansari et al., 2012; El-dars et al., 2015).

The surfactant-modified agrowastes was investigated as low-cost adsorbents for benzene removal from aqueous solution. The banana trunk (BT) was selected as a model agrowastes in the present study since banana is one of the most cultivated fruits in the tropical region (Hameed et al., 2008). It is generally left unmanaged/decomposing in the plantation estates or disposed at a landfill after fruit harvesting (Sathasivam and Mas Haris, 2010). It is reported that it contains up to 33% (dry basis) of holocellulose (hemicellulose and cellulose). It also contains a lot of pectin and polyphenols in its extract (Medeiros et al., 2000; Bilba et al., 2007). The high content of holocellulose has made it a potential adsorbent precursor because it is easy to be functionalized to treat the desired pollutant species. It was reported that it was used as adsorbents in adsorptive removal of heavy metal ions such as cobalt (Co(II)), cadmium (Cd(II)), copper (Cu(II)), iron (Fe(II)) and Zinc (Zn (II)), oil and methylene blue (Shibi and Anirudhan, 2005; Hameed et al., 2008; Sathasivam and Mas Haris, 2010; Teli and Valia, 2013). Thus, in the present study, the BT adsorbents were synthesized by surface modification followed by surfactant functionalization to enhance benzene adsorption from aqueous solution.
1.3 Research Objectives

(a) To synthesize low-cost agrowaste based adsorbents by surface mercerization; surfactants modification; and surface etherification.

(b) To characterize synthesized agrowaste based adsorbents.

(c) To investigate the adsorption performance of the synthesized adsorbents towards benzene removal from aqueous solution.

1.4 Research Scopes

The banana trunk (BT) was selected agrowaste based adsorbent precursor. The raw agrowaste adsorbent was firstly modified by surface mercerization. The mercerized adsorbent was coated with various surfactants (i.e. cationic, anionic and non-ionic), namely cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic 123) and 4-(1,1,3,3-tetramethylbutyl)phenyl-polyethylene glycol (Triton X-100). The surface etherification of adsorbent was also conducted by introducing the quaternary ammonium groups, namely (3-chloro-2-hydroxypropyl) trimethylammonium chloride solution (CTA) to enhance its surface reactivity towards surfactant coating.

The raw/unmodified and modified adsorbents surface morphologies were characterized by a field emission scanning microscope (FESEM). The existing functional groups on the adsorbent surfaces were determined with the Fourier transform infrared (FTIR) spectrometer and X-ray photoelectron spectrometer (XPS). The Brunauer-Emmet Teller surface area and pore diameters of the adsorbents were also investigated by nitrogen adsorption/desorption analyzer.
The adsorption performance of the surface modified adsorbent towards benzene removal from the aqueous solution was evaluated. The effects of adsorption parameters namely initial pH, initial benzene concentration, adsorbent dosage, temperature and contact time toward benzene adsorption capacity were studied. The isotherm adsorption data were analyzed by using the existing isotherm models namely Langmuir, Freundlich, Temkin and Dubinin-Raduchkevich (D-R) isotherm models, while pseudo-first-order (PFO), pseudo-second-order (PSO), Elovich and Weber and Morris models were applied to investigate the benzene adsorption kinetics. The analysis of the adsorption results led to the proposed adsorption mechanism. The adsorbent regeneration was also investigated.

1.5 Thesis Outline

This research thesis contains seven chapters. Chapter 1 describes briefly of the research background, problem statement, objective and scopes of the study. Chapter 2 presents a critical review on the benzene as pollutants in water, pollutants removal technologies, potential adsorbent precursors, adsorbent modifications as well as technical aspects of adsorption systems. The materials and procedures for adsorbent synthesis and characterization as well as benzene adsorption experiments are discussed in Chapter 3. The research findings are discussed in Chapters 4. The research conclusions and recommendations for future works are presented in Chapter 5.

1.6 Summary

Benzene pollutant existing in the water and wastewater must be removed since it is extremely hazardous and carcinogenic. Flora and fauna as well as humans’ health can be seriously affected by its contamination in water. Adsorption is one of the simplest technologies to remove benzene pollutant from aqueous solution using low-cost adsorbents synthesized from agricultural wastes such as the banana trunk. The banana trunk (BT) is cheap and environmentally friendly. In addition, it contains a
large amount of holocellulose which can be easily functionalized. The benzene adsorption by the synthesized adsorbents was evaluated at various experimental conditions followed by the theoretical thermodynamic and kinetic analyses of the experimental adsorption data.
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