Batch Adsorptive Removal of Btex From Aqueous Solution: A Review

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ABSTRACT

This study performs a review of the adsorptive removal of volatile organic compounds such as benzene, toluene, ethylbenzene and xylene (BTEX) from various industrial wastewaters. The literature has been reviewed in accordance with a variety of adsorbents that have been applied in BTEX removal based on previous studies. The wide range of adsorbents includes carbonaceous materials, silica materials, clay materials, zeolite and zeolite-like materials, polymeric materials and biomass. The summary of adsorption capacities, isotherm, kinetics and thermodynamics of these adsorbents are presented in extensive tables.

Keywords: BTEX, adsorption, biomass adsorbent, kinetics, isotherm

1. INTRODUCTION

Benzene, toluene, ethylbenzene and the three isomers of (ortho-, meta- and para-) xylenes (BTEX) can be found in various household products such as glue, paints and insecticide. They exist in either liquid or gaseous form. These compounds are among the most greatly needed chemicals in the world as they are widely used as important solvents in fine chemical and petrochemical industries such as paint, insecticide and glue production industries. They are also employed in equipment cleansing and organic (e.g.: rubber and resin) synthesis [1]. Toluene is reported as the most dominant among BTEX found in gasoline [2]. The summary of general BTEX properties is shown in Table 1. Xylene has the largest molecular weight followed by ethylbenzene, toluene and lastly benzene. The specific gravity of BTEX compounds varies from 0.86-0.88. BTEX compounds are thus partially soluble in the freshwater and solubility of these compounds decreases with the increasing of molecular weights and ring number [3]. The values log \( K_{ow} \) (log octanol-water partition coefficient) of BTEX compounds presented in Table 1 show that BTEX are moderately hydrophobic [4].

2. BTEX CONTAMINATION IN WATER AND WASTEWATERS

2.1 Origin of BTEX

Produced water from the oil and gas production field is the main source of BTEX. Produced water is generated associating with the oil and gas production activities, where produced water is generated at up to 8 times of the crude oil produced every single day [5]. Approximately 3000-5000 L produced water is generated yearly in the United States, where only 65% of this produced water is recycled and used for pressure maintenance in the activities, and the rest of it is discharged [6]. BTEX are the most abundant hydrocarbon detected in produced waters. Simpson and Bowman (2009) reported that up to 578 mg/L of total BTEX has been detected in produced water [7]. Dórea and co-workers (2007) reported that total BTEX of 97 to 1397 µg/L has been measured in produced water in the State of Sergipe, which is the fourth largest production in the world. In particular, BTEX compositions detected in the produced water of Indonesia and Gulf of Mexico are tabulated in Table 2, where the concentration of each BTEX component is found respectively higher in Mexico produced water [8].

BTEX compounds are some of the most commonly detected contaminants found in water bodies. The primary source of BTEX contaminants found in water bodies is the likelihood of accidental leakage or spillage [9]. Chang and Lin (2006) had reported that there are more oil leakage and spillage accidents occur in these recent years. In addition, there are approximately 74% of the accidents occurred in petroleum refineries, oil terminals or underground gasoline storage tanks [10]. Furthermore, underground gasoline
Table 1 Summary of the general properties of BTEX compounds [11].

| Properties/Compounds | Benzene | Toluene | Ethylbenzene | o-Xylene | m-Xylene | p-Xylene |
|----------------------|---------|---------|--------------|----------|----------|----------|
| Formula              | C₆H₆    | C₆H₅CH₃| C₆H₅–C₆H₅   | C₆H₅–(CH₃)₂|
| Structure            | ![Structure](Structure.png) | ![Structure](Structure.png) | ![Structure](Structure.png) | ![Structure](Structure.png) |
| Molecular weight (g/mol) | 78.12   | 92.10   | 106          | 106.2    |
| Appearance           | Colorless liquid | Aromatic | Aromatic | Aromatic |
| Odor (smell)         |        |         |             |          |
| Boiling point⁴(°C)   | 80      | 111     | 136          | 144      |
| Melting point (°C)   | 6       | -95     | -95          | -25      |
| Specific gravity⁵    | 0.88    | 0.86    | 0.865        | 0.88     |
| Solubility in water⁶ (ppm) | 1780    | 535     | 158          | 175      |
| Solubility in seawater (ppm) | 1398    | 389     | 114          | 133      |
| Vapor density⁷       | 2.7     | 3.1     | 3.7          | 3.7      |
| Vapor pressure⁸ (mmHg) | 75      | 22      | 7            | 7        |
| Log Kow              | 2.13    | 2.69    | 3.15         | 3.15     |
| Evaporation rate⁹    | 5.1     | 2.24    | <1.0         | 0.7      |
| Flash point (°C)     | -11.1 (cc) | 4.0 (cc) | 15.0 (cc)   | 32.0 (cc) |
| Auto ignition temperature (°C) | 498    | 480     | 432          | 465      |
|                     | 530     |

*Boiling point at atmospheric pressure; ⁴Specific gravity of water = 1; ⁵Solubility in water at 20 °C; ⁶Vapor density of air at compound boiling point = 1; ⁷Vapor pressure at 20 °C; ⁸Evaporation rate of butyl acetate = 1; Log Kow = log octanol-water partition coefficient (hydrophobicity); cc = closed cup.

Table 2 Composition of BTEX detected in produced water.

| Constituent   | Amount detected in produced water (µg/L) |
|---------------|-----------------------------------------|
| Benzene       | Indonesian: 84 - 2300; Gulf of Mexico: 440 - 2800 |
| Toluene       | 89-800; 340-1700 |
| Ethylbenzene  | 26 – 56; 26 - 100 |
| Xylene        | 13 - 480; 160 - 720 |

Petrochemicals and fine chemical industries such as textile dyeing industries also contribute BTEX contaminations in their effluent streams [11]. It is indicated that BTEX generally made up more than 75% of total VOC detected from the textile dyeing wastewater stream since the 1980s. It is also revealed that BTEX compounds are detected in various household products including pesticides, insecticides, cleansing agents, personal care and pharmaceuticals. The municipal solid wastes which contain the remarkably high concentration of BTEX are usually disposed in landfills. BTEX components may migrate by flowing air from one point to another due to their high volatilities and low molecular weights. Therefore, hazardous BTEX compounds can easily be carried to the water bodies through landfills leaching [14].

2.2 Toxicity and Occurrence

Benzene is highly toxic, and it has been classified by US EPA as a carcinogenic component. Exposure to low levels of benzene compound can cause headaches, dizziness, drowsiness, nausea, rapid heartbeats, unconsciousness, tremors and confusion. High levels of benzene exposure can
cause irregular heartbeats, vomiting, coma and seizures. Chronic exposure to volatile benzene by no matter by inhalation or ingestion can harm the human immune system and can possibly contribute to severe health impacts such as cancer, leukemia, anemia (decrease in blood platelet) and death [15]. Toluene is neurotoxic which can get into the human body by inhalation and skin contact. Inhaling high levels of toluene can cause dizziness, fatigue, sleepiness, light-headness, unconsciousness and death. On the other hand, breathing in high levels of toluene can cause lung, liver and kidney problems. Long term exposure to toluene may cause damage to the human nervous system and lead to mental disability in humans such as depression, memory loss, difficulties in concentrating, personality changes and muscle weakness [16]. On the other hand, exposure to a high concentration of ethylbenzene through inhalation can contribute to sore throat, dizziness, burning feeling in the eyes and chest tightening. Chronic exposure to ethylbenzene can cause liver and central nervous system problems in humans. Apart from that, exposure to a high concentration of xylene compound can lead to dizziness, headache, confusion, changes in balance and coordination. In contrast, severe exposure to xylene can cause skin, eyes, nose and throat irritations, breathing difficulties, lung, liver and kidney problems, stomach-ache and memory losses [17]. BTEX compounds may reach the soil, lakes, groundwater reservoirs or water supply providing for domestic and industrial purposes easily due to their physical properties [18]. Volatile BTEX compounds can easily evaporate into the atmosphere and then cause greenhouse gases effect and ozone layer depletion to the mother earth. Furthermore, BTEX compounds can cause adherence effects to human health and the environment even at relatively low concentrations [19]. Due to the severe impacts contributed by BTEX contaminations in the water bodies, World Health Organization (WHO) also governs the maximum permissible BTEX contents in drinking water [20]. Table 3 displays the maximum concentrations of BTEX contents by the WHO which shows the maximum allowable concentration of benzene contaminated in drinking water indicating the least value among BTEX compounds and it is followed by ethylbenzene, xylene and finally toluene. This is mainly because benzene compound contributes to the most severe environmental impact. Apart from that, United States Environmental Protection Agency (US EPA) has also regulated a guideline for BTEX contents in drinking water. Table 3 shows the summary of primary drinking water regulations formulated by WHO and US EPA which also shows benzene compound must be controlled at the lowest drinking water maximum contaminant level because benzene compound is carcinogenic to human health followed by ethylbenzene, toluene and xylene compounds.

### 3. BTEX ADSORPTION

The toxicological properties of BTEX compounds and their persistence in the freshwater sources can be worrisome, especially in vulnerable regions where the citizens are facing water scarcity [11]. Adsorption technology is the best alternative separation process for water treatment other than conventional technologies such as incineration, oxidation and bioremediation. It is one of the most economically attractive and effective techniques to remove organic contaminants, with the possibility to recycle BTEX [21].

#### Table 3 Maximum allowable BTEX contents in drinking water.

| Constituent | WHO Concentration (ppm) | MCL (ppm) | MCLG (ppm) |
|-------------|-------------------------|-----------|-----------|
| Benzene     | 0.01                    | 5.00×10⁻³ | 0.00      |
| Toluene     | 0.70                    | 1.00      | 1.00      |
| Ethylbenzene| 0.30                    | 0.70      | 0.70      |
| Xylene      | 0.50                    | 10.00     | 10.00     |

*MCLG: Maximum Contaminant Level Goal
*MCL: Maximum Contaminant Level

#### 3.1 Conventional Adsorbents

A suitable adsorbent plays the utmost important role in this context to perform good adsorption. There are several significant criteria to select an appropriate substrate for adsorption on purpose. The selection criteria include: (i) good adsorption capacity and efficiency, (ii) variety of adsorption capability, (iii) high adsorption rate, selectivity and surface area, (iv) strong mechanical structure (v) ability to be regenerated, (vi) economical effective and (vii) ability to tolerate in different adsorption conditions [22]. A summary of adsorbent types which have been employed in BTEX adsorption from aqueous solution is made in Table 4. There are a few adsorbent categories listed in the table such as clay, zeolite, silica, carbonaceous and polymeric materials. Each type of adsorbent material possesses its own characteristics and specialties in the adsorption process. Generally, carbonaceous, silica and clay materials mostly perform good adsorption due to the high specific surface areas. However, activated carbon is not economically attractive, as it is expensive and hard to be regenerated [23]. On the other hand, natural clays are naturally hydrophilic which are not suitable to adsorb hydrophobic compounds unless they are modified. Yet, biomass materials are cheap and abundantly abundant especially biomass materials. The hydroxyl groups presented in biomass material make it easier to be modified.

#### 3.2 Biomass as Adsorbents

Various low-cost adsorbent precursors are introduced in adsorption technology. One of the most common and renewable precursors is biomass. Biomass is biological material derived from living organisms (flora and fauna). There are many recent studies reporting on biomass conversion into potential adsorbent and employed in BTEX adsorptive removal, as shown in Table 5.
Table 4: Summary of conventional adsorbents for BTEX adsorption removal.

| Adsorbent                  | Advantage                                                                 | Drawback                                                                                      | Reference          |
|----------------------------|---------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------|--------------------|
| Natural activated carbon   | - Large specific surface area.                                            | - High purchasing cost.                                                                       | [24–26]            |
|                            | - Adequate pore size distribution.                                       | - High reactivation/regeneration cost.                                                        |
|                            | - High presence of active sites.                                         | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            | - Available in various configurations and sizes.                         | - Can be prematurely exhausted.                                                               |
|                            |                                                                          | - High reactivation/regeneration cost.                                                        |
|                            |                                                                          | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            |                                                                          | - Can be prematurely exhausted.                                                               |
|                            |                                                                          | - Available in various configurations and sizes.                                              |
|                            |                                                                          | - High reactivation/regeneration cost.                                                        |
|                            |                                                                          | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            |                                                                          | - Can be prematurely exhausted.                                                               |
|                            |                                                                          | - Pricier than agro-industrial by-products and agrowastes.                                   |
|                            |                                                                          | - Properties of native cellulose not constant (depends on the origin and preliminary treatment). |
|                            |                                                                          | - Low presence of active sites.                                                              |
| Cellulose                  | - Low-cost.                                                              | - High reactivation/regeneration cost.                                                        |
|                            | - Renewable.                                                            | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            | - Most abundant.                                                       | - Can be prematurely exhausted.                                                               |
|                            | - More hydroxyl groups that can be modified.                            | - Available in various configurations and sizes.                                              |
| Diatomite                  | - Abundant.                                                             | - The total oxide content in diatomite varies and is dependent on the source of the earth.   | [25,28,29]         |
|                            | - High permeability.                                                    | - The laden diatomite is difficult to recycle and thus more sewage sludge is created due to its fine powder form. |
|                            | - High porosity and surface area.                                       | - Available in various configurations and sizes.                                              |
|                            | - Small particle size.                                                  | - High reactivation/regeneration cost.                                                        |
|                            | - Low density and thermal conductivity.                                  | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            |                                                                          | - Can be prematurely exhausted.                                                               |
|                            |                                                                          | - High reactivation/regeneration cost.                                                        |
|                            |                                                                          | - 10-15% loss of adsorbent during the regeneration process.                                  |
|                            |                                                                          | - Can be prematurely exhausted.                                                               |
|                            |                                                                          | - Pricier than agro-industrial by-products and agrowastes.                                   |
|                            |                                                                          | - Properties of native cellulose not constant (depends on the origin and preliminary treatment). |
|                            |                                                                          | - Low presence of active sites.                                                              |
| Silica aerogel             | - Large surface area.                                                   | - It is naturally hydrophilic, less efficient to adsorb slightly hydrophobic BTEX compounds. |
|                            | - High porosity.                                                       | - It is naturally hydrophilic, less efficient to adsorb slightly hydrophobic BTEX compounds. |
|                            | - Low density (much lighter than water).                                | - It is naturally hydrophilic, less efficient to adsorb slightly hydrophobic BTEX compounds. |
|                            | - Low conductivity.                                                    | - It is naturally hydrophilic, less efficient to adsorb slightly hydrophobic BTEX compounds. |
| Smectite (natural clay)    | - High cation exchange capacity (CEC).                                  | - It is hard to distinguish between internal and external surface adsorption of surfactant molecules, due to the two-dimensional plate-like structure. | [31]              |
|                            | - Can be easily modified by cationic surfactants.                       | - It is hard to distinguish between internal and external surface adsorption of surfactant molecules, due to the two-dimensional plate-like structure. | [31]              |
| Montmorillonite (natural clay) | - High surface area.                                                   | - Hydrophilic nature.                                                                        | [32]              |
|                            | - Low-cost.                                                            | - Hydrophilic nature.                                                                        | [32]              |
|                            | - Environmental-friendly.                                               | - Hydrophilic nature.                                                                        | [32]              |
|                            | - High adsorption tendency.                                             | - Hydrophilic nature.                                                                        | [32]              |
| Zeolite                    | - Clay-like surface chemistry.                                          | - It is naturally hydrophilic.                                                               | [31,33]           |
|                            | - Has structures with external and internal surface areas (like a cage). | - It is naturally hydrophilic.                                                               | [31,33]           |
|                            | - Does not show shrink-swell characteristic.                            | - Has a negative-charged surface.                                                            | [31,33]           |
|                            | - Exhibits hydraulic behavior.                                          | - Has less affinity towards anionic and non-ionic organic compounds.                         | [31,33]           |
| Fungal biomass             | - Economic                                                              | - Required chemical and/or physical modification to enhance the adsorption affinity.         | [34]              |
|                            | - Cheap and abundant carbon source                                      | - Required chemical and/or physical modification to enhance the adsorption affinity.         | [34]              |
|                            | - Contains useful functional groups such as amino, carboxyl, hydroxyl and sulfate on the cell surfaces. | - Required chemical and/or physical modification to enhance the adsorption affinity.         | [34]              |
| Agricultural by-product    | - Abundant and low-cost                                                 | - Low adsorption affinity                                                                   | [35]              |
|                            |                                                                          | - Modification is needed                                                                    | [35]              |

The adsorbents synthesized from lignocellulosic agricultural materials consist of a large number of carboxyl, amine and hydroxyl groups [36]. Due to the presence of these functional groups in lignocellulosic materials, they are easier to be modified. A case to this point, Tham et al. (2011) has carried out a toluene gas adsorption onto durian shell activated carbon [37]. The utilization of agricultural waste as an adsorbent precursor helps in preventing fouling and nuisance caused in municipal landfills [38]. Apart from agricultural waste, chitin and chitosan represent another type of biomass. According to Mohamed et al. (2011), chitin is a type of natural polymer (mucopolysaccharide) that can be found in insects, crabs, shrimps and the family of crustaceans [39]. Chitosan is the derivative of chitin which formed by chemical treatment. Furthermore, chitin and chitosan are environmental-friendly, abundant (the
second most abundant natural polymer after cellulose) and biodegradable. Thus, chitin and chitosan are potential low-cost adsorbent due to their physical and chemical characteristics. Recently, Costa et al. (2012) have conducted BTEX adsorption onto angico sawdust and peat from produced water [40]. The adsorption capacities are displayed in Table 5. As it can be clearly seen, peat adsorbent has better adsorption uptake toward benzene and toluene. Meanwhile, angico sawdust adsorbent has a higher adsorption capacity toward ethylbenzene and xylene (meta-, para- and ortho-). It can be noted that chitosan has relatively better ethylbenzene adsorption performance in comparison with chitin [39]. In the previous study, the chemical modified banana trunk gives relatively promising adsorption performance as shown in Table 5. However, the modification method is subjected to the targeted pollutants as the modification methods are usually employed to control the surface functional groups [41].

Table 5 Comparison of BTEX adsorption uptake, q (mg/g) for biomass materials.

| Precursor       | Modification                  | Adsorption capacity (mg/g) | Reference/Condition                                           |
|-----------------|--------------------------------|----------------------------|---------------------------------------------------------------|
| Angico sawdust  | Unmodified                     | Benzene: 2.21×10^{3(E)}    | [35]                                                          |
|                 |                                | Toluene: 4.25×10^{3(E)}    |                                                               |
|                 |                                | Ethylbenzene: 3.68×10^{3(E)}|                                                               |
|                 |                                | m-, p-Xylene: 11.43×10^{3(E)}|                                                               |
|                 |                                | o-Xylene: 9.72×10^{3(E)}   |                                                               |
| Peat            | Unmodified                     | Benzene: 6.65×10^{3(E)}    |                                                               |
|                 |                                | Toluene: 8.99×10^{3(E)}    |                                                               |
|                 |                                | Ethylbenzene: 7.11×10^{3(E)}|                                                               |
|                 |                                | m-, p-Xylene: 9.07×10^{3(E)}|                                                               |
|                 |                                | o-Xylene: 6.45×10^{3(E)}   |                                                               |
| Durian shell    | Biomass activated carbon       | Toluene: 57.14^{3(E)}      | [37]                                                          |
|                 |                                |                            | Condition: (T = 25.5; C₀ = 230-920; S/L= 0.5/5)               |
| Chitin          | As-purchased                   | Ethylbenzene: 20.12^{3(E)} | [39]                                                          |
|                 |                                |                            | Condition: (T = 22 ± 1; C₀ = 5-200)                           |
| Chitosan        | As-purchased                   | Ethylbenzene: 31.35^{3(E)} |                                                               |
|                 |                                |                            | Condition: (T = 22 ± 1; C₀ = 5-200)                           |
| Banana trunk    | Mercerized and Triton X-100 coated | Benzene: 17.67^{3(E)}    | [42]                                                          |
|                 |                                |                            | Condition: (pH = 7; T = 30, C₀ = ~40-780, S/L = 1)            |
|                 | CTAB coated                    | Benzene: 29.87^{3(E)}      | [43]                                                          |
|                 |                                |                            | Condition: (pH = 7; T = 30, C₀ = ~8 - 300, S/L = 0.5)         |
|                 | Cationized and SDS coated      | Benzene: 36.57^{3(E)}      | [44]                                                          |
|                 |                                |                            | Condition: (pH = 7; T = 30, C₀ = ~8 - 300, S/L = 0.5)         |

(E): Experimental data; (L): Langmuir data; (Gas): gas adsorption; T: temperature (°C); C₀: initial concentration (mg/L); S/L: solid to liquid ratio (mg/mL).

3.3 Adsorption Parameters

Adsorption from aqueous solution (liquid phase) can be affected by various factors including initial concentration and pH of adsorbate, reaction contact time and temperature as well as adsorbent dosage and particle size toward adsorption uptake and performance are investigated [45]. According to the previous studies, adsorption uptake/capacity increases with the increment of adsorbate initial concentration. This is because driving force (e.g. van der Waal’s force) to the active site of adsorbent increases when the initial concentration of adsorbate increases [46]. Park et al. (2010) had reported that the increment of adsorbate initial concentration increases the quantity of adsorbate per unit weight of adsorbent and thus increases the adsorption capacity [47]. However, adsorption efficiency (removal percentage) reduces with the increment of adsorbate initial concentration. It is reported that changes in adsorbate pH do not influence BTEX adsorption significantly since ion exchange does not take part in this process [48]. Reaction time will also influence the BTEX adsorption uptake, where the longer the contact time allowed between adsorbent and adsorbate, the higher the adsorption capacity. Based on the previous studies, the adsorption rate is conclusively rapid at the beginning of reaction due to the
abundant vacant active sites on the adsorbent surface. Then, the adsorption rate will possibly slow down within some duration and finally achieve equilibrium. In the equilibrium stage, there is no more adsorption taking place because all the adsorbent active sites are fully occupied. However, the equilibrium contact time of each adsorption may differ and dependence on the numerous factors such as type of adsorbent and adsorbate, adsorbate concentration, reaction temperature, adsorbent dosage and etc [25,46,49]. Furthermore, the reaction temperature can also influence the amount of BTEX adsorbed onto the adsorbents. Chin et al. (2010) and Nourmoradi et al. (2012) have conducted a study to study the effect of temperature toward BTEX adsorption onto single-walled carbon nanotubes and PEG-montmorillonite respectively. These studies are carried out in the temperature within 10 to 40 °C. BTEX adsorption cannot be done at a higher temperature because BTEX compounds are highly volatile (low boiling point). At high temperatures, BTEX compounds may evaporate. According to the study that has been done earlier, adsorption capacity increases with the reaction temperature due to increasing of kinetic energy and surface activity [47].

3.4 Adsorption Mechanism

3.4.1 Kinetics

Kinetics study describes the adsorption response with the respect to different time intervals. The adsorption rate regulates the adsorbate residence time at the solid-liquid interface. Adsorption kinetics provide significant adsorption mechanism insights [50]. It is crucial in designing a real good adsorption system. The adsorption kinetics generally comprises both physical and chemical phenomena. The physical phenomenon can be described by three consecutive rate-controlling steps: (i) external mass transfer from bulk solution to the adsorbent surface; (ii) film diffusion across the liquid film from the adsorbent surfaces and (iii) intraparticle diffusion (i.e. surface diffusion, pore diffusion or a combination of both diffusions). These adsorption steps were described in the following subsections:

(i) External mass transfer

The external mass transfer is referred to the mass flux of adsorbate from the bulk solution towards the adsorbent surface. According to the principle of mass balance, the mass flux of the adsorbate must equate to the rate of mass decay rate and can be mathematically presented in Equation 1 [51].

\[
\frac{dC_A}{dt} = mSk_i(C_{Ab} - C_A)
\]

where \(C_{Ab}\) and \(C_A\) are the adsorbate concentration in the bulk aqueous solution and at the interface of the adsorbent boundary layer, respectively. \(S\) is the adsorbent external surface area per unit mass (m²/g), \(m\) is the adsorbent mass (g), \(V\) is the aqueous volume and \(k_i\) is expressed as the external mass transfer coefficient (m/min). Equation 1 becomes Equation 2 when time (t) approaches 0. \(C_A \rightarrow 0\) and \(C_{Ab} \rightarrow C_{A0}\), where \(C_{A0}\) is the initial concentration (mmol/L). The slope of \(C_{A0}/C_A\) versus t is plotted and \(k_i\) is calculated.

\[
\left[ \frac{d(C_{A0}/C_A)}{dt} \right]_{t=0} = -mSk_iV
\]

(ii) Film diffusion

The film diffusion is the transport of adsorbate molecules across the liquid stagnant film surrounding the adsorbent particles, where the transfer rate is inversely proportional to the film thickness. At the very early stage of the adsorption process where t is very small, the film diffusion coefficient (\(D_{film}\)) can be expressed mathematically by Equation 3.

\[
q_t/q_e = 6 \left( \frac{D_{film}}{\pi a^2} \right) t^{0.5}
\]

where \(q_t\) and \(q_e\) are respectively the adsorption capacity at any time t and equilibrium t (mmol/g) and \(a\) is the radius of the adsorbent particle. \(D_{film}\) can be estimated from the linear plot of \(q_t/q_e\) versus \(t^{0.5}\) at the small t.

(iii) Intraparticle diffusion

The intraparticle diffusion is the incorporating effect of both pore and internal surface diffusions, where the pore diffusion is the adsorbate transport within the adsorbent pores and the surface diffusion is the movement of the adsorbate molecules from one site to another site on the adsorbent surface. The intraparticle diffusion coefficient, \(D_{eff}\) can be obtained from the Boyd plot slope where \(B_i\) versus t was plotted. The \(B_i\) value for the adsorption at different time stages (\(q_t/q_e\)) is obtained using Equations (4) and (5).

For moderate times,

\[
\frac{q_t}{q_e} < 0.85; \quad B_i = \left( \sqrt{\pi} - \sqrt{\pi - \frac{q_t}{q_e}} \right)^2
\]

For large times,

\[
\frac{q_t}{q_e} < 0.85; \quad B_i = -0.4997 - ln\left[ 1 - \left( \frac{q_t}{q_e} \right) \right]
\]

The linear Boyd plot gradient (\(S_{eff}\)) is employed to determine \(D_{eff}\) by applying Equation (6), where \(q_t\) and \(q_e\) are the adsorption capacity at any time t and equilibrium (mmol/g) while “a” is the particle radius of the adsorbent.

\[
S_{eff} = \frac{\pi a^2 D_{eff}}{q_e}
\]

To determine the rate-limiting step for the physical phenomenon, the Weber-Morris equation as shown in Equation (7),

\[
q_t = k_{ad} t^{0.5}
\]

where \(k_{ad}\) is the intraparticle diffusion constant (mmol/g.min⁰.⁵). It is stated that the intraparticle diffusion is the only rate-limiting step if the linear plot. The chemical phenomenon is represented by the surface interactions between adsorbent active sites and pollutant molecules [52]. There are two well-known chemical-based
kinetic models that are normally employed in BTEX adsorption, namely pseudo-first order (PFO) and pseudo-second order (PSO) models. The equation of PFO kinetic model is shown in Equation (8), where \( q_e \) is the amount of component adsorbed at equilibrium, \( q_t \) is the amount of component adsorbed at the time \( t \) and \( k_1 \) is PFO constant [53]. PSO kinetic equation is displayed in Equation (9), where \( k_2 \) is PSO constant.

\[
q_t = q_e (1 - e^{-k_1t}) \\
q_t = \frac{q_e}{1 + \frac{t}{k_2}}
\]

(8)  

(9)

Table 6 is constructed to summarize the best kinetic model fitting of the various adsorbents. It can be concluded that all the adsorption cases shown are well defined by PSO kinetic model. Equilibrium time for each adsorption process may vary from one another and it is dependent on the type of adsorbent employed. Many recent studies have concluded that BTEX adsorption onto various potential adsorbents favors the adsorption rate order of B\( > T\)E\( > X \). This is most probably because of the decrement of water solubility as well as the increment of molecular weight and hydrophobicity (log \( K_w \)). The bulky of xylene chemical structure might make it easier to be adsorbed by the adsorbent [25,46,54]. It is reported that less hydrophobic and more soluble component such as benzene has less tendency toward adsorbent [18]. Based on the studies conducted by Aivalioti et al. in 2010 and 2012, it can be clearly concluded that diatomite treated at 550 °C has obviously increased the BTEX adsorption kinetic rate from various aqueous solution. On the other hand, adsorbent modified by cationic surfactant exhibits BTEX adsorption favorable selectivity in the order of B\( > T\)E\( > X \). This result is also justified in the study conducted by Torabian et al. (2010). This is most probably because of the hydrophobic properties of surfactants including polar head groups and unique formula structure [44].

### 3.4.2 Isotherms

Adsorption isotherm study is critical in optimizing and improving the use of adsorbents as the isotherm curve provides the qualitative information on the natural interaction of adsorbate and adsorbent surface. Generally, there are few well-known isotherm models, include Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R), which have been developed by the previous researchers to analyze the relationship between adsorbents and adsorbate molecules. Table 7 shows isotherm models and isotherm parameters for the adsorption of BTEX onto several adsorbents. Generally, the Langmuir and Freundlich models are the two isotherm models that could describe the isotherm data. Langmuir model estimates the maximum adsorption capacity, \( q_{max} \) of the adsorbent. In addition, Langmuir model is a simple expression of monolayer adsorption [55]. The Langmuir isotherm is shown by Equation (10), where \( q_e \) is the equilibrium adsorption capacity, \( q_{max} \) is the maximum adsorption capacity, \( K_L \) is Langmuir constant and \( C_e \) is the equilibrium adsorbate concentration [47]. As it can be observed from Table 7, most of the adsorptions onto carbonaceous adsorbents, such as carbon nanotubes and activated carbon F-400, are well described by Langmuir model [45,48,56,57]. BTEX adsorption onto zeolite material (clinoptilolite and ZSM 5-31 zeolite), MCM-41, fiber and starch-based adsorbents also found to fit well by Langmuir model [27,31,58]. Based on the studies conducted by Ghiaci et al. (2004) and Aloulou et al. (2006), benzene and toluene adsorptions onto adsorbent modified by cationic surfactant such as n-cetylpyridinium bromide (CPB) follow Langmuir model.

\[
q_e = \frac{q_{max}K_FC_e}{1 + K_FC_e}
\]

(10)

Freundlich model is a simple expression for multi-layer adsorption which has a parameter for surface heterogeneity. The equation for Freundlich isotherm is displayed in Equation (11), where \( K_F \) is Freundlich constant denoting adsorption capacity and \( n \) is adsorption intensity. Moreover, a higher value of \( K_F \) indicates higher adsorption capacity in this context. In the meanwhile, the higher the value of \( n \) is the stronger the interaction adsorption bonding between adsorbent and adsorbate molecule. Thus, it can be concluded that BTEX adsorptions onto diatomite, lignite, activated carbon (ACF), montmorillonite and some polymeric materials (tire crumb rubber and carbon black) are well explained by Freundlich isotherm model. Among all these adsorbents, carbonaceous materials include ACF and lignite (pre-treated at 750 °C) has a relatively high value of \( n \) (more than 1.5). This means the interactions between BTEX molecules and the carbonaceous adsorbent surfaces are relatively stronger than silica and clay materials.

\[
q_e = K_FC_e^{1/n}
\]

(11)

Temkin isotherm model is a simple expression in describing gas adsorption, as expressed in Equation 12. This model expresses the significance of adsorbate interaction on the adsorption isotherm, where the heat of adsorption, \( b_T \) decreases when the adsorbent surface coverage increases. Temkin model does not have saturation limitation which it is not applicable over a wide range of concentration.

\[
q_e = \frac{K_T}{b_T} (aC_e)
\]

(12)

D-R isothermal model is a temperature-dependent model as shown in Equation 13, that possesses volatile thermodynamic principle at very low loading. The mean free energy, \( E \) (kJ/mol) analysis (Equation 14) can be employed to determine whether the chemical interaction is physisorption or chemisorption. It is stated that physisorption can be reflected when \( E \) smaller than 8 kJ/mol, where chemisorption can be determined when \( E \) is greater than 16 kJ/mol. Moreover, the chemical ion exchange can occur if \( E \) falls between (8-16) kJ/mol.

\[
q_e = q_{max}exp(-\frac{E}{RT})
\]

(13)

\[
E = \sqrt[\frac{1}{2}]{\frac{RT}{\beta}}
\]

(14)
Table 6  Best fitted kinetic model and parameter for BTEX adsorption.

| Adsorbent                                | Time  | Model | Adsorbate | $k_2$   | Reference/ Conditions |
|------------------------------------------|-------|-------|-----------|---------|-----------------------|
| PEG-montmorillonite                      | 24 h  | PSO   | B T E X   | 0.26    | [32]                  |
|                                          |       |       |           |         | Condition:            |
|                                          |       |       |           |         | (T = 25; pH = 7; $C_0$ = 150; S/L= 5) |
| Raw diatomite                           | 240 h | PSO   | B T E X   | 3.33    | [25]                  |
|                                          |       |       |           |         | Condition:            |
|                                          |       |       |           |         | (T = 20±1; $C_0$ = ~250; S/L= 100) |
| Thermal-treated diatomite (750 °C)      | 240 h | PSO   | B T E X   | 18.10   |                       |
|                                          |       |       |           |         |                       |
| Raw diatomite                           | 24 h  | PSO   | B T E X   | 14.14   | [59]                  |
|                                          |       |       |           |         | Condition:            |
|                                          |       |       |           |         | (T = 20; S/L= 50)     |
| Raw diatomite                           | 6-24 h| PSO   | B T E X   | 20.28   |                       |
| Thermal-treated diatomite (550 °C)      |       |       |           |         |                       |
| Acid-treated diatomite                  | 6 h   | PSO   | B T E X   | 22.70   |                       |
|                                          |       |       |           |         |                       |
| Raw lignite                             | 3 h   | PSO   | B T E X   | 8.83    | [18]                  |
|                                          |       |       |           |         | Condition:            |
|                                          |       |       |           |         | (T = 20)              |
| Thermal-treated diatomite (750 °C)      | 3 h   | PSO   | B T E X   | 1.79    |                       |
| 6mM CPB-natural zeolite particle        | 72 h  | PSO   | B T E X   | 1.94    | [49]                  |
|                                          |       |       |           |         | Condition:            |
|                                          |       |       |           |         | (pH = 6.8; $C_0$ = 9; S/L: 5) |
| 6mM CPB-granulated zeolite nanoparticles| 72 h  | PSO   | B T E X   | 1.94    |                       |
| Surfactant modified synthetic zeolite   | 24 h  | PSO   | B T E X   | 0.01    | [60]                  |

$k_2$: PSO rate constants ((g/mg h); h: initial adsorption rate constant (g/mg h); PEG: poly ethylene glycol; CPB: n-cetypyridinium bromide, T: temperature (°C); $C_0$: initial concentration (mg/L); S/L: solid to liquid ratio (mg/mL).
Table 7  Best fitted isotherm model and parameter for BTEX adsorption.

| Adsorbent     | Model   | Adsorbate | $K_L$/$K_T$ | $n$/$q_{max}$ | Reference/Condition |
|---------------|---------|-----------|-------------|---------------|---------------------|
| CNT (NaOCl)  | Langmuir| B         | 0.04        | 247.87        | [61] Condition:     |
|               |         | T         | 0.04        | 279.81        | (pH = 7; T = 25; C₀ = 200-200; S/L= 0.6) |
|               | Freundlich| B         | 26.10       | 2.42          |                     |
|               |         | T         | 36.93       | 2.32          |                     |
|               |         | E         | 44.56       | 2.31          |                     |
|               |         | X         | 59.63       | 2.38          |                     |
| P-SWCNT       | Langmuir| α-X       | 0.28        | 59.53         | [56] Condition:     |
|               |         | p-X       | 1.37        | 85.47         | (pH = 5.4; T = 25; C₀ = 7-107; S/L= 0.36) |
| O-SWCNT       | Langmuir| B         | 1.16        | 1.26          | [57] Condition:     |
|               |         | T         | 1.91        | 0.83          | (pH = 3-11; T = 25; C₀ = 15-180; S/L= 0.18) |
| P-SWCNT       | Langmuir| B         | 1.81        | 1.21          |                     |
|               |         | T         | 1.61        | 1.46          |                     |
| F-400         | Langmuir| B         | 0.08        | 183.29        | [45] Condition:     |
|               |         | T         | 0.08        | 194.11        | (pH = 7; T = 20; C₀ = 35-442; S/L= 1.5) |
| Thermal-treated F-400 (800 °C) | Langmuir| B         | 0.07        | 240.07        |                     |
|               |         | T         | 0.09        | 254.74        |                     |
| Thermal-treated ACF (800 °C) | Freundlich| B         | 66.00       | 2.22          | [62] Condition:     |
|               |         | E         | 237.00      | 6.25          | (pH = 7; T = 20; C₀ = ~100; S/L= 12.5) |
|               |         | p-X       | 185.00      | 2.70          | (pH = 7; T = 20; C₀ = ~100; S/L= 12.5) |
| Raw diatomite | Freundlich| B         | 3.68×10⁻⁵  | 2.47          | [25] Condition:     |
|               |         | E         | 1.92×10⁻³  | 1.33          | (T = 20±1; C₀ = 200; t: 240; S/L= 10.1) |
|               |         | p-X       | 0.04        | 0.55          |                     |
|               |         | α-X       | 0.05        | 0.46          |                     |
| Thermal-treated diatomite (550 °C) | Freundlich| B         | 1.55×10⁻³  | 8.13          |                     |
|               |         | E         | 6.61×10⁻¹² | 7.29          |                     |
|               |         | p-X       | 7.41×10⁻¹¹ | 6.07          |                     |
|               |         | α-X       | 2.74×10⁻¹⁰ | 5.71          |                     |
| Thermal-treated diatomite (750 °C) | Freundlich| B         | 1.35×10⁻⁷  | 4.45          |                     |
|               |         | E         | 9.82×10⁻⁴  | 5.50          |                     |
|               |         | p-X       | 1.95×10⁻⁶  | 3.63          |                     |
|               |         | α-X       | 3.18×10⁻⁶  | 3.47          |                     |
| Raw diatomite | Freundlich| B         | 6.80×10⁰   | 7.75          | [59] Condition:     |
|               |         | E         | 2.30×10⁴   | 7.72          | (T = 20; t: 6-24; S/L= 50) |
|               |         | m-, p-X   | 7.67×10³   | 4.65          |                     |
|               |         | α-X       | 26.98      | 3.85          |                     |
|               |         | 303.10    | 3.92        |                     |
| Thermal-treated diatomite (550 °C) | Freundlich| B         | 1442.00     | 5.30          |                     |
|               |         | T         | 753.20      | 4.43          |                     |
|               |         | E         | 520.60      | 3.85          |                     |

$K_r$: Freundlich constant; $K_L$: Langmuir constant; $n$: intensity of adsorption; $q_{max}$: maximum adsorption capacity; P-SWCNT: Purified single-walled carbon nanotubes; O-SWCNT: oxidized single-walled carbon nanotubes; ACF: activated carbon fibre; F-400: granular F-400 activated carbon, T: temperature (°C); C₀: initial concentration (mg/L); t: contact time (h); S/L: solid to liquid ratio (mg/mL).
Table 7 (Continued) Best fitted isotherm model and parameter for BTEX adsorption.

| Adsorbent                              | Best fitting model | Adsorbate | K_F | m/q_{max} | Reference/Condition |
|----------------------------------------|--------------------|-----------|-----|-----------|---------------------|
| Thermal-treated diatomite (550 °C)     | Freundlich         | m-, p-X   | 0.33| 2.06      | [59]                |
|                                        |                    | o-X       | 40.30| 3.12      |                     |
|                                        | K_F                |           | (mmol/g·(L/mmol)^{1/n}) | |                     |
| Acid-treated diatomite                 | Freundlich         | B         | 22.13| 0.30      | [59]                |
|                                        |                    | T         | 21.06| 0.33      |                     |
|                                        |                    | E         | 24.84| 0.39      |                     |
|                                        |                    | m-, p-X   | 1.62 | 0.4       |                     |
|                                        |                    | o-X       | 15.54| 0.37      |                     |
| Raw lignite                           | Freundlich         | B         | 2.80×10^4| 0.20     | [18]                |
|                                        |                    | T         | 140.00| 0.37      |                     |
|                                        |                    | E         | 4.50 | 0.67      |                     |
|                                        |                    | m-, p-X   | 3.60 | 0.63      |                     |
|                                        |                    | o-X       | 19.00| 0.53      |                     |
| Thermal-treated lignite (750 °C)       | Freundlich         | B         | 0.22 | 0.91      |                     |
|                                        |                    | T         | 0.15 | 3.23      |                     |
|                                        |                    | E         | 0.38 | 1.89      |                     |
|                                        |                    | m-, p-X   | 0.40 | 2.63      |                     |
|                                        |                    | o-X       | 0.24 | 2.63      |                     |
| PEG-montmorillonite                    | Freundlich         | B         | 0.02 | 1.31      | [32]                |
|                                        |                    | T         | 0.04 | 1.38      |                     |
|                                        |                    | E         | 0.03 | 1.57      |                     |
|                                        |                    | X         | 0.02 | 1.39      |                     |
| Tire crumb rubber                      | Freundlich         | T         | 239.00| 1.02     | [63]                |
|                                        |                    | X         | 723.00| 0.90      |                     |
| Carbon black                           | Freundlich         | T         | 621.00| 0.64     | (pH = 6; C_0 = 0.05 - 60; S/L = 5) |
|                                        |                    | X         | 1327.00| 0.62     |                     |
| Polymer                                | Freundlich         | T         | 355.00| 0.95     |                     |
|                                        |                    | X         | 991.00| 0.95     |                     |
| Surfactant treated cellulose fibre     | Langmuir           | B         | 2750.00| 210.00  | [24]                |
| Octyl grafted cellulose fiber          | Langmuir           | B         | 8600.00| 210.00  |                     |
| JLPALM                                 | Langmuir           | B         | 3.00 | 501.78    | [27]                |
|                                        |                    | B         | 0.01 | 23.07     |                     |
|                                        |                    | T         | 0.01 | 14.95     |                     |
|                                        |                    | E         | 0.01 | 16.44     |                     |
|                                        |                    | m-, p-X   | 0.01 | 112.90    |                     |
|                                        |                    | o-X       | 0.01 | 145.20    |                     |
| 20 mM CPB- Clinoptilite                | Langmuir           | B         | 17.23 | 9.89      | [64]                |
|                                        |                    | T         | 6.45 | 13.67     |                     |
|                                        |                    | E         | 3.67 | 12.90     |                     |
|                                        |                    | m-, p-X   | 21.78| 11.45     |                     |
|                                        |                    | o-X       | 19.45| 10.45     |                     |

K_F: Freundlich constant denoting adsorption capacity; K_L: Langmuir constant; n: intensity of adsorption; q_{max}: maximum adsorption capacity; PEG: poly-ethylene glycol; JLPALM: jute fibre esterified with palmatic anhydride; CPB: n-cetypyridinium bromide; T: temperature (°C); C_0: initial concentration (mg/L); t: contact time (h); S/L: solid to liquid ratio (mg/mL).
Table 7 (Continued) Best fitted isotherm model and parameter for BTEX adsorption.

| Adsorbent         | Best fitting model | Adsorbate | $K_r/K_L$ | $n/q_{\text{max}}$ Reference/Condition |
|-------------------|--------------------|-----------|-----------|----------------------------------------|
| Zeolite           | Langmuir           | B         | 0.71      | 0.04 [54]                               |
|                   | $K_r$(L/mg)        | T         | 1.07      | 0.05 Condition:                         |
|                   | $q_{\text{max}}$(mg/g) | p-X | 1.47      | 0.13 (C$_0$ = 1.3 - 20; t: 24; S/L= 50) |
|                   |                    | o-X       | 1.21      | 0.15                                    |
| As purchased      | Langmuir           | B         | 4.50×10$^{-3}$ | 14.36 [60]                          |
| synthetic zeolite | $K_r$(L/mg)        | T         | 7.20×10$^{-3}$ | 10.44 (T = 20; C$_0$ = 10 - 130; t: 24; S/L= 30) |
|                   | $q_{\text{max}}$(mg/g) | E | 0.01      | 6.20                                    |
|                   |                    | X         | 0.01      | 7.80                                    |
| Surfactant-       | Langmuir           | B         | 0         | 9.50                                    |
| modified          |                    | T         | 0.02      | 8.55                                    |
| synthetic zeolite | $q_{\text{max}}$(mg/g) | E | 0.03      | 7.77                                    |
|                   |                    | X         | 0.03      | 7.27                                    |

$K_r$: Langmuir constant; $n$: intensity of adsorption; $q_{\text{max}}$: maximum adsorption capacity; T: temperature (°C); C$_0$: initial concentration (mg/L); t: contact time (h); S/L: solid to liquid ratio (mg/mL).

3.5 Thermodynamics Analysis

Thermodynamic analysis parameters involved enthalpy ($\Delta H$), entropy ($\Delta S$) and Gibbs free energy ($\Delta G$) [57,65]. These parameters can be obtained from Equation (15) to Equation (18).

\[
\Delta G = \Delta H - T \Delta S
\]  
(17)

\[
\ln K' = \frac{\Delta S}{R} - \frac{\Delta H}{RT}
\]  
(18)

where R is the ideal gas constant (8.314 J/mol.K), T is the temperature in unit Kelvin (K), K’ is the thermodynamic constant, which must be dimensionless by multiplying with the solution density [66]. The thermodynamic parameters obtained from the previous studies are tabulated in Table 8.

Table 8 Thermodynamic parameter for BTEX adsorption.

| Adsorbent                | Adsorbate | $\Delta G$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$(kJ/mol·K) | Reference/Condition |
|--------------------------|-----------|---------------------|---------------------------|---------------------------|---------------------|
| PEG-montmorillonite      | B         | 283K -0.34          | 33.01                     | 117.81                    | [32]                |
|                          | 293K -1.52          |                     |                           |                           | Condition: (pH = 7; S/L= 5) |
|                          | 303K -2.70          |                     |                           |                           |                     |
|                          | 313K -3.88          |                     |                           |                           |                     |
|                          | T         | 283K -0.69          | 31.09                     | 112.24                    |                     |
|                          | 293K -1.81          |                     |                           |                           |                     |
|                          | 303K -2.93          |                     |                           |                           |                     |
|                          | 313K -4.05          |                     |                           |                           |                     |
|                          | E         | 283K -0.98          | 28.49                     | 104.09                    |                     |
|                          | 293K -2.02          |                     |                           |                           |                     |
|                          | 303K -3.06          |                     |                           |                           |                     |
|                          | 313K -4.10          |                     |                           |                           |                     |
|                          | X         | 283K -1.15          | 28.61                     | 105.09                    |                     |
|                          | 293K -2.20          |                     |                           |                           |                     |
|                          | 303K -3.25          |                     |                           |                           |                     |
|                          | 313K -4.30          |                     |                           |                           |                     |
| P-SWCNT                  | B         | 293K -4.98          | -1.36                     | 12.34                     | [57]                |
|                          | 303K -5.08          |                     |                           |                           | Condition: (S/L= 0.2) |
|                          | 313K -5.23          |                     |                           |                           |                     |
|                          | T         | 293K -5.20          | -1.02                     | 14.13                     |                     |
|                          | 303K -5.31          |                     |                           |                           |                     |
|                          | 313K -5.44          |                     |                           |                           |                     |
| Polystyrenic resin       | BTEX      | 298K 20.30          | 4.67                      | 69.34                     | [64]                |
| simulated wastewater     | 308K 26.12          | 4.17                 | 62.19                     |                           | Condition: (C$_0$ = 15; S/L= 1) |
| simulated wastewater     | 318K 36.60          | -                     | -                         |                           |                     |

PEG: poly ethylene glycol; P-SWCNT: Purified single-walled carbon nanotubes, C$_0$: initial concentration (mg/L); S/L: solid to liquid ratio (mg/mL).
It can be concluded from Table 8, all the values of $\Delta G$ for all the adsorption conducted are negative and small. This means that the adsorption process is thermodynamically spontaneous and feasible [68]. In addition to that, $\Delta G$ increases with the increasing temperature for all adsorbate tested. It is reported that the low $\Delta G$ in between -20 kJ/mol to 0 kJ/mol reflects physisorption where chemisorption is suggested by $\Delta G$ in the range of -400 kJ/mol to -80 kJ/mol. Likewise, $\Delta H$ in the order of 25 kJ/mol suggests physisorption, while $\Delta H$ in the order of 200 kJ/mol represents chemisorption [69]. Chin et al. (2010) have noted that negative and small magnitude of $\Delta H$ indicates exothermic physisorption. Nourmoradi et al. (2012) noted positive $\Delta H$ that indicates that BTEX adsorption onto PEG-montmorillonite is endothermic physisorption. Furthermore, the positive $\Delta S$ indicates that the adsorbate molecules are more scattered after the adsorption process as the hydration layers of the aqueous solution may be disturbed.

| Adsorbent                  | Adsorbate | $\Delta G$ (kJ/mol) | $\Delta H^\circ$ (kJ/mol) | $\Delta S^\circ$ (kJ/mol-K) | Reference/Condition |
|---------------------------|-----------|---------------------|---------------------------|-----------------------------|---------------------|
| Citric acid-modified ostrich bone waste | B         | 288K                | -19.80                    | 0.02                        | 0.07                | [67]                |
|                           |           | 298K                | -20.49                    |                             |                     |
|                           |           | 312K                | -21.46                    |                             |                     |
|                           |           | 353K                | -24.28                    |                             |                     |
|                           | T         | 288K                | -13.73                    | 0.01                        | 0.05                |                     |
|                           |           | 298K                | -14.21                    |                             |                     |
|                           |           | 312K                | -14.87                    |                             |                     |
|                           |           | 353K                | -16.83                    |                             |                     |
|                           | E         | 288K                | -38.70                    | 0.04                        | 0.13                |                     |
|                           |           | 298K                | -40.05                    |                             |                     |
|                           |           | 312K                | -41.93                    |                             |                     |
|                           |           | 353K                | -47.45                    |                             |                     |
|                           | $p$-X     | 288K                | -45.12                    | 0.04                        | 0.16                |                     |
|                           |           | 298K                | -46.68                    |                             |                     |
|                           |           | 312K                | -48.88                    |                             |                     |
|                           |           | 353K                | -55.31                    |                             |                     |

$C_0$: initial concentration (mg/L); $t$: contact time (h); S/L: solid to liquid ratio (mg/mL)

4. CONCLUSION

The presence of volatile organic compounds (BTEX) in water and wastewater is the utmost concern for human health and environmental conservation. Adsorption is one of the easy and convenient alternative methods to remove these compounds from aqueous solutions. Carbonaceous materials have been long known to be a very promising adsorbent employed in adsorption technology due to their high specific surface area and porosity. However, it is expensive and hard to be regenerated. Hence, there are numerous adsorbent materials including biomass have been employed as alternative adsorbent precursors. Modifications (physical, chemical or/and thermal) are basically conducted onto biomass adsorbent to enhance the adsorption performance. The modification of biomass leads to higher adsorption uptake and is subjected to the subject of interest to completely employ the advantages of biomass. Different BTEX adsorption uptake onto these adsorbents is displayed in the extensive table accordingly. BTEX adsorption can be obviously influenced by adsorbate initial concentration and reaction temperature. Adsorption mechanism begins with adsorbate transportation by the external mass transfer process, film and intraparticle diffusions, which is noted as a physical phenomenon; and tightly followed by adsorbate-adsorbent interaction, which is noted as a chemical phenomenon. Adsorption kinetics and isotherm analysis can be conducted to reliably predict the adsorption mechanism. The future perspective is to produce effective adsorbents that are economically feasible and environmentally friendly from locally abundant biomass. However, more extensive mechanism studies are needed to facilitate the adsorption process.

ACKNOWLEDGMENT

The financial supports by the Ministry of Higher Education (MOHE) Fundamental Research Grant Scheme (FRGS Vote 4F0977) form MOHE and UTM Post-Doctoral Fellowship Scheme (PDRU 04E09) are gratefully acknowledged.

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