

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

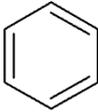
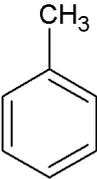
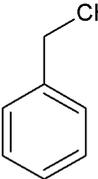
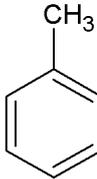
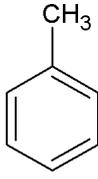
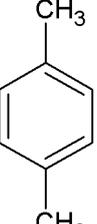
2.1 Origin of BTEX

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 $\mu\text{g/L}$ 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	Xylene		
				<i>o</i> -	<i>m</i> -	<i>p</i> -
Formula	C ₆ H ₆	C ₆ H ₅ CH ₃	C ₆ H ₅ --C ₂ H ₅	C ₆ H ₄ --(CH ₃) ₂		
Structure						
Molecular weight (g/mol)	78.12	92.10	106		106.2	
Appearance				Colorless liquid		
Odor (smell)				Aromatic		
Boiling point ^a (°C)	80	111	136	144	139	138
Melting point (°C)	6	-95	-95	-25	-48	13
Specific gravity ^b	0.88	0.86	0.865	0.88	0.86	0.86
Solubility in water ^c (ppm)	1780	535	158	175	135	198
Solubility in seawater (ppm)	1398	389	114	133	108	114
Vapor density ^d	2.7	3.1	3.7		3.7	
Vapor pressure ^e (mmHg)	75	22	7	7	9	9
Log K _{ow}	2.13	2.69	3.15	3.15	3.20	3.10
Evaporation rate ^f	5.1	2.24	<1.0		0.7	
Flash point (°C)	-11.1 (cc)	4.0 (cc)	15.0 (cc)	32.0 (cc)	28.9	27.2
Auto ignition temperature (°C)	498	480	432	465	530	530

^aBoiling point at atmospheric pressure; ^bSpecific gravity of water = 1; ^cSolubility in water at 20 °C; ^dVapor density of air at compound boiling point = 1; ^eVapor pressure at 20 °C; ^fEvaporation rate of butyl acetate = 1; Log K_{ow} = log octanol-water partition coefficient (hydrophobicity); cc = closed cup.

reservoir and pipe leakage caused by imperfections of the tank and piping system are also other sources that contribute to BTEX contaminations in the water body. It is alluded in the previous study that up to 4.5% of the underground gasoline tanks in the United States were detected leaks [12]. Underground gasoline tanks which served 15 years and above are experiencing a higher chance to crack and leak as alluded by Cheng et al. (2016). Moreover, the mistake happens and improper practices during petroleum transportation also are the possible causes of the BTEX contaminations in the water body [13].

Table 2 Composition of BTEX detected in produced water.

Constituent	Amount detected in produced water (µg/L)	
	Indonesian	Gulf of Mexico
Benzene	84 - 2300	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 disposal 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-headedness, 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 adverse 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	US EPA	
	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	<ul style="list-style-type: none"> - Large specific surface area. - Adequate pore size distribution. - High presence of active sites. - Available in various configurations and sizes. 	<ul style="list-style-type: none"> - High purchasing cost. - High reactivation/regeneration cost. - 10 -15% loss of adsorbent during the regeneration process. - Can be prematurely exhausted. 	[24–26]
Cellulose	<ul style="list-style-type: none"> - Low-cost. - Renewable. - Most abundant. - More hydroxyl groups that can be modified. 	<ul style="list-style-type: none"> - Properties of native cellulose not constant (depends on the origin and preliminary treatment). - Low presence of active sites. - Pricier than agro-industrial by-products and agrowastes. 	[24,27]
Diatomite	<ul style="list-style-type: none"> - Abundant. - High permeability. - High porosity and surface area. - Small particle size. - Low density and thermal conductivity. 	<ul style="list-style-type: none"> - The total oxide content in diatomite varies and is dependent on the source of the earth. - The laden diatomite is difficult to recycle and thus more sewage sludge is created due to its fine powder form. 	[25,28,29]
Silica aerogel	<ul style="list-style-type: none"> - Large surface area. - High porosity. - Low density (much lighter than water). - Low conductivity. 	<ul style="list-style-type: none"> - It is naturally hydrophilic, less efficient to adsorb slightly hydrophobic BTEX compounds. 	[30]
Smectite (natural clay)	<ul style="list-style-type: none"> - High cation exchange capacity (CEC). - Can be easily modified by cationic surfactants. 	<ul style="list-style-type: none"> - 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)	<ul style="list-style-type: none"> - High surface area. - Low-cost. - Environmental-friendly. - High adsorption tendency. 	<ul style="list-style-type: none"> - Hydrophilic nature. 	[32]
Zeolite	<ul style="list-style-type: none"> - Clay-alike surface chemistry. - Has structures with external and internal surface areas (like a cage). - Does not show shrink-swell characteristic. - Exhibits hydraulic behavior. 	<ul style="list-style-type: none"> - It is naturally hydrophilic. - Has a negative-charged surface. - Has less affinity towards anionic and non-ionic organic compounds. 	[31,33]
Fungal biomass	<ul style="list-style-type: none"> - Economic - Cheap and abundant carbon source - Contains useful functional groups such as amino, carboxyl, hydroxyl and sulfate on the cell surfaces. 	<ul style="list-style-type: none"> - Required chemical and/or physical modification to enhance the adsorption affinity. 	[34]
Agricultural by-product	<ul style="list-style-type: none"> - Abundant and low-cost 	<ul style="list-style-type: none"> - Low adsorption affinity - 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 : $2.21 \times 10^{-3(E)}$	[35]
		Toluene : $4.25 \times 10^{-3(E)}$	Condition: ($T = 25 \pm 1$; $C_0 = 0.1$; $S/L = 7.69$)
		Ethylbenzene : $3.68 \times 10^{-3(E)}$	
		<i>m-, p-Xylene</i> : $11.43 \times 10^{-3(E)}$	
		<i>o-Xylene</i> : $9.72 \times 10^{-3(E)}$	
Peat	Unmodified	Benzene : $6.65 \times 10^{-3(E)}$	
		Toluene : $8.99 \times 10^{-3(E)}$	
		Ethylbenzene : $7.11 \times 10^{-3(E)}$	
		<i>m-, p-Xylene</i> : $9.07 \times 10^{-3(E)}$	
		<i>o-Xylene</i> : $6.45 \times 10^{-3(E)}$	
Durian shell	Biomass activated carbon	Toluene : $57.14^{(L, Gas)}$	[37] Condition: ($T = 25.5$; $C_0 = 230-920$; $S/G = 0.5/5$)
Chitin	As-purchased	Ethylbenzene : $20.12^{(L)}$	[39]
Chitosan	As-purchased	Ethylbenzene : $31.35^{(L)}$	Condition: ($T = 22 \pm 1$; $C_0 = 5-200$)
Banana trunk	Mercerized and Triton X-100 coated	Benzene : $17.67^{(L)}$	[42] Condition: ($pH = 7$; $T = 30$, $C_0 = \sim 40-780$, $S/L = 1$)
		CTAB coated	Benzene : $29.87^{(L)}$
	Mercerized and CTAB coated	Benzene : $41.84^{(L)}$	Condition: ($pH = 7$; $T = 30$, $C_0 = \sim 8 - 300$, $S/L = 0.5$)
		Cationized and SDS coated	Benzene : $36.57^{(L)}$

(E): Experimental data; (L): Langmuir data; (Gas): gas adsorption; T: temperature ($^{\circ}C$); C_0 : 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 sub-sections:

(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].

$$-V \frac{dC_A}{dt} = mSk_L(C_{Ab} - C_{Ai}) \quad (1)$$

where C_{Ab} and C_{Ai} 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 (m^2/g), m is the adsorbent mass (g), V is the aqueous volume and k_L is expressed as the external mass transfer coefficient (m/min). Equation 1 becomes Equation 2 when time (t) approaches 0, $C_{Ai} \rightarrow 0$ and $C_{Ab} \rightarrow C_{A0}$, where C_{A0} is the initial concentration

(mmol/L). The slope of C_A/C_{A0} versus t is plotted and k_L is calculated.

$$\left[\frac{d(C_A/C_{A0})}{dt} \right]_{t=0} = -mSk_L/V \quad (2)$$

(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.

$$q_t/q_e = 6 \sqrt{\frac{D_{film}}{\pi a^2}} \cdot t^{0.5} \quad (3)$$

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_t versus t was plotted. The B_t value for the adsorption at different time stages (q_t/q_e) is obtained using Equations (4) and (5).

For moderate times,

$$\frac{q_t}{q_e} < 0.85; B_t = \left(\sqrt{\pi} - \sqrt{\pi - \left[\frac{\pi^2 (q_t/q_e)}{3} \right]} \right)^2 \quad (4)$$

For large times,

$$\frac{q_t}{q_e} < 0.85; B_t = -0.4997 - \ln \left[1 - \left(\frac{q_t}{q_e} \right) \right] \quad (5)$$

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.

$$S_{eff} = \frac{\pi^2 D_{eff}}{a^2} \quad (6)$$

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

$$q_e = k_{id} t^{0.5} \quad (7)$$

where k_{id} is the intraparticle diffusion constant (mmol/g.min^{0.5}). 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.

$$q_t = q_e(1 - e^{-k_1 t}) \quad (8)$$

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_e^2} + \frac{t}{q_e}\right)} \quad (9)$$

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 ($\log K_{ow}$). 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.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (10)$$

Freundlich model is a simple expression for multi-layer adsorption which has a parameter for surface heterogeneity. The equation for Freundlich model 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.

$$q_e = K_F C_e^{1/n} \quad (11)$$

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.

$$q_e = \frac{RT}{b_T} (a C_e) \quad (12)$$

D-R isotherm 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.

$$q_e = q_{max} \exp(-\beta E^2) \quad (13)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (14)$$

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	0.26	[32] Condition: (T = 25; pH = 7; C ₀ = 150; S/L= 5)
			T	0.24	
			E	0.20	
			X	0.15	
Raw diatomite	240 h	PSO	B	3.33	[25] Condition: (T = 20±1; C ₀ = ~250; S/L= 100)
			T	1.83	
			E	0.91	
			<i>p</i> -X	0.92	
			<i>o</i> -X	0.52	
Thermal-treated diatomite (750 °C)	240 h	PSO	B	18.10	
			T	7.24	
			E	4.73	
			<i>p</i> -X	2.19	
			<i>o</i> -X	2.66	
Raw diatomite	24 h	PSO	B	14.14	[59] Condition: (T = 20; S/L= 50)
			T	22.80	
			E	20.49	
			<i>m</i> -, <i>p</i> -X	27.45	
			<i>o</i> -X	22.08	
Thermal-treated diatomite (550 °C)	6-24 h	PSO	B	20.28	
			T	29.31	
			E	30.28	
			<i>m</i> -, <i>p</i> -X	32.27	
			<i>o</i> -X	31.19	
Acid-treated diatomite	6 h	PSO	B	22.70	
			T	30.60	
			E	30.73	
			<i>m</i> -, <i>p</i> -X	33.85	
			<i>o</i> -X	32.16	
Raw lignite	3 h	PSO	B	8.83	[18] Condition: (T = 20)
			T	14.12	
			E	22.64	
			<i>m</i> -, <i>p</i> -X	26.37	
			<i>o</i> -X	21.66	
Thermal-treated diatomite (750 °C)	3 h	PSO	B	1.79	
			T	3.47	
			E	3.02	
			<i>m</i> -, <i>p</i> -X	4.43	
			<i>o</i> -X	2.35	
6mM CPB-natural zeolite particle	72 h	PSO	B	1.94	[49] Condition: (pH = 6.8; C ₀ = 9; S/L: 5)
			T	1.64	
			E	1.47	
			X	1.42	
6mM CPB-granulated zeolite nanoparticles	72 h	PSO	B	1.94	
			T	4.46	
			E	7.27	
			X	4.88	
Surfactant modified synthetic zeolite	24 h	PSO	B	0.01	[60] Condition: (T = 20; C ₀ = 50; S/L= 30)
			T	0.02	
			E	0.02	
			X	0.01	

k_2 : PSO rate constants ((g/mg h); h: initial adsorption rate constant (g/mg h); PEG: poly ethylene glycol; CPB: *n*-cetylpyridinium bromide, T: temperature (°C); C₀: 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_F/K_L	n_F/q_{max}	Reference/Condition
CNT (NaOCl)	Langmuir	B	0.04	247.87	[61]
	K_L (L/mg)	T	0.04	279.81	Condition:
	q_{max} (mg/g)	E	0.05	342.67	(pH = 7; T = 25; C_0 = 20-
		X	0.05	413.77	200; S/L= 0.6)
	Freundlich	B	26.10	2.42	
	K_F (mg/g)·(L/mg) ^{1/n}	T	36.93	2.32	
		E	44.56	2.31	
		X	59.63	2.38	
P-SWCNT	Langmuir	o-X	0.28	59.53	[56].
	K_L (L/mg)	p-X	1.37	85.47	Condition:
	q_{max} (mg/g)				(pH = 5.4; T = 25; C_0 = 7-107; S/L= 0.36)
O-SWCNT	Langmuir	B	1.16	1.26	[57]
	K_L (L/mmol)	T	1.91	0.83	Condition:
	q_{max} (mmol/g)				(pH = 3-11; T = 25; C_0 = 15-180; S/L= 0.18)
P-SWCNT	Langmuir	B	1.81	1.21	
	K_L (L/mmol)	T	1.61	1.46	
	q_{max} (mmol/g)				
F-400	Langmuir	B	0.08	183.29	[45]
	K_L (L/mg)	T	0.08	194.11	Condition:
	q_{max} (mg/g)				(pH = 7; T = 30; C_0 = 35-442; S/L= 1.5)
Thermal-treated F-400 (800 °C)	Langmuir	B	0.07	240.07	
	K_L (L/mg)	T	0.09	254.74	
	q_{max} (mg/g)				
Thermal-treated ACF (800 °C)	Freundlich	B	66.00	2.22	[62]
	K_F (mg/g)·(mg/L)	E	237.00	6.25	Condition:
		p-X	185.00	2.70	(pH = 7; T = 20; C_0 = ~100; S/L= 12.5)
Raw diatomite	Freundlich	B	3.68×10^{-5}	2.47	[25]
	K_F (mg/kg·(mg/L) ⁿ)	T	1.92×10^{-3}	1.33	Condition:
		E	0.04	0.55	(T = 20±1; C_0 = 250; t: 240; S/L= 10.1)
		p-X	0.06	0.48	
		o-X	0.05	0.46	
Thermal-treated diatomite (550 °C)	Freundlich	B	1.55×10^{-13}	8.13	
	K_F (mg/kg·(mg/L) ⁿ)	T	6.61×10^{-12}	7.29	
		E	7.41×10^{-11}	6.07	
		p-X	2.74×10^{-10}	5.71	
		o-X	6.02×10^{-13}	7.43	
Thermal-treated diatomite (750 °C)	Freundlich	B	1.35×10^{-7}	4.45	
	K_F (mg/kg·(mg/L) ⁿ)	T	9.82×10^{-9}	5.50	
		E	1.95×10^{-6}	3.63	
		p-X	3.18×10^{-6}	3.47	
		o-X	1.02×10^{-9}	5.46	
Raw diatomite	Freundlich	B	6.80×10^5	7.75	[59]
	K_F	T	2.30×10^6	7.72	Condition:
	(mmol/g·(L/mmol) ^{1/n})	E	7.67×10^3	4.65	(T = 20; t: 6-24; S/L= 50)
		m-, p-X	26.98	3.85	
		o-X	303.10	3.92	
Thermal-treated diatomite (550 °C)	Freundlich	B	1442.00	5.30	
	K_F	T	753.20	4.43	
	(mmol/g·(L/mmol) ^{1/n})	E	520.60	3.85	

K_F : 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); 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_F/K_L	n_F/q_{max}	Reference/Condition
Thermal-treated diatomite (550 °C)	Freundlich	m-, p-X	0.33	2.06	[59]
	K_F (mmol/g·(L/mmol) ^{1/n})	o-X	40.30	3.12	Condition: (T = 20; t: 6-24; S/L= 50)
Acid-treated diatomite	Freundlich	B	22.13	0.30	[59]
	K_F (mmol/g(L/mmol) ^{1/n})	T	21.06	0.33	Condition:
		E	24.84	0.39	(T = 20; t: 6-24; S/L= 50)
		m-, p-X	1.62	0.4	
		o-X	15.54	0.37	
Raw lignite	Freundlich	B	2.80×10 ⁴	0.20	[18]
	K_F (mmol/g(L/mmol) ^{1/n})	T	140.00	0.37	Condition:
		E	4.50	0.67	(T = 20; t: 3; S/L= 12.5)
		m-, p-X	3.60	0.63	
		o-X	19.00	0.53	
Thermal-treated lignite (750 °C)	Freundlich	B	0.22	0.91	
	K_F (mmol/g(L/mmol) ^{1/n})	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]
	K_F (L/g)	T	0.04	1.38	Condition:
		E	0.03	1.57	(pH = 7; t = 24; S/L= 5)
		X	0.02	1.39	
Tire crumb rubber	Freundlich	T	239.00	1.02	[63]
	K_F (μg/g)	X	723.00	0.90	Condition:
Carbon black	Freundlich	T	621.00	0.64	(pH = 6; C ₀ = 0.05 - 60;
	K_F (μg/g)	X	1327.00	0.62	S/L= 5)
Polymer	Freundlich	T	355.00	0.95	
	K_F (μg/g)	X	991.00	0.95	
Surfactant treated cellulose fibre	Langmuir	B	2750.00	210.00	[24]
	K_L (L/mol) q_{max} (μmol/g)				Condition: (pH = 6.5-7; T = 25; C ₀ = 0-200; S/L= 10)
Octyl grafted cellulose fiber	Langmuir	B	8600.00	210.00	
	K_L (L/mol) q_{max} (μmol/g)				
JLPALM	Langmuir	B	3.00	501.78	[27]
	K_L (L/mol) q_{max} (μmol/g)				Condition: (T = 25 ± 1; C ₀ = 390-1500; S/L= 0.5)
20 mM CPB-Clinoptilote	Langmuir	B	0.01	23.07	[31]
	K_L (L/g) q_{max} (mg/g)				Condition: (T = 20; C ₀ = 6-100; S/L= 4)
20 mM CPB-ZSM 5-31Zeolite	Langmuir	B	0.01	14.95	
	K_L (L/g) q_{max} (mg/g)	T	0.01	16.44	
As-synthesized MCM-41	Langmuir	B	0.01	112.90	
	K_L (L/g) q_{max} (mg/g)	T	0.01	145.20	
Polystyrenic resin	Langmuir	B	17.23	9.89	[64]
	K_L (L/mg)	T	6.45	13.67	Condition:
	q_{max} (mg/g)	E	3.67	12.90	(C ₀ = 0.34 - 6.66; t: 6; S/L= 1 - 5)
		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 palmitic anhydride; CPB: *n*-cetylpyridinium bromide; 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/K_L	n_F/q_{max}	Reference/Condition
Zeolite	Langmuir	B	0.71	0.04	[54]
	K_L (L/mg)	T	1.07	0.05	Condition:
	q_{max} (mg/g)	p-X	1.47	0.13	($C_0 = 1.3$ -20; t: 24;
		o-X	1.21	0.15	S/L= 50)
As purchased synthetic zeolite	Langmuir	B	4.50×10^{-3}	14.36	[60]
	K_L (L/mg)	T	7.20×10^{-3}	10.44	Condition:
	q_{max} (mg/g)	E	0.01	6.20	(T = 20; $C_0 = 10$ - 130;
		X	0.01	7.80	t: 24; S/L= 30)
Surfactant-modified synthetic zeolite	Langmuir	B	0.01	9.50	
	K_L (L/mg)	T	0.02	8.55	
	q_{max} (mg/g)	E	0.03	7.77	
		X	0.03	7.27	

K_L : Langmuir constant; n : intensity of adsorption; q_{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 (ΔH), entropy (ΔS) and Gibbs free energy (ΔG) [57,65]. These parameters can be obtained from Equation (15) to Equation (18).

$$\Delta G = -RT \ln K' \tag{15}$$

$$K = \frac{q_e}{c_e} \tag{16}$$

$$\Delta G = \Delta H - T\Delta S \tag{17}$$

$$\ln K' = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{18}$$

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	ΔG (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)	Reference/Condition	
PEG-montmorillonite	B	283K	-0.34	33.01	117.81	[32] Condition: (pH = 7; S/L= 5)
		293K	-1.52			
		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] Condition: (S/L= 0.2)
		303K	-5.08			
		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	308K	26.12	4.17	62.19	Condition:
	wastewater	318K	36.60	-	-	($C_0 = 15$; S/L= 1)

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).

Table 8 (Continued) Thermodynamic parameter for BTEX adsorption.

Adsorbent	Adsorbate	ΔG (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol·K)	Reference/Condition
Citric acid-modified ostrich bone waste	B	288K	-19.80	0.02	0.07
		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		
	<i>p</i> -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)

It can be concluded from Table 8, all the values of ΔG 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, ΔG increases with the increasing temperature for all adsorbate tested. It is reported that the low ΔG in between -20 kJ/mol to 0 kJ/mol reflects physisorption where chemisorption is suggested by ΔG in the range of -400 kJ/mol to -80 kJ/mol. Likewise, ΔH in the order of 25 kJ/mol suggests physisorption, while ΔH in the order of 200 kJ/mol represents chemisorption [69]. Chin *et al.* (2010) have noted that negative and small magnitude of ΔH indicates exothermic physisorption. Nourmoradi *et al.* (2012) noted positive ΔH that indicates that BTEX adsorption onto PEG-montmorillonite is endothermic physisorption. Furthermore, the positive ΔS indicates that the adsorbate molecules are more scattered after the adsorption process as the hydration layers of the aqueous solution may be disturbed.

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.

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