Modelling competitive BTEX compounds removal from industrial wastewater in packed-bed columns using polystyrenic resin

T. P. Makhathini and S. Rathilal

ABSTRACT

The competitive simultaneous removal of petrochemical hydrocarbons including benzene, toluene, ethylbenzene and isomers of xylene (BTEX) from an aqueous solution by polystyrenic resin (PAD 910) was investigated at dynamic conditions in a packed bed column. The column was operated under conditions of bed length \( Z = 30 - 90 \text{ cm} \), flow rate \( Q = 18.5 - 53.5 \text{ cm/min} \), bed diameter \( D = 2.5 - 5 \text{ cm} \) and initial concentration of \( C_0 = 5 - 14.5 \text{ mg/l} \) to investigate the adsorption characteristics of BTEX at an influent pH of 6.85. There was evidence of improved column performance with increasing operating height and decreased flow rate. Breakthrough curves of fixed-bed adsorption process were developed by the constant-pattern approach using a constant driving force model in the liquid phase. A fairly good fit to the experimental data was obtained using the constant-pattern approach and a Langmuir isotherm model obtained from previous work. In addition, a prediction of volumetric mass transfer coefficient correlation in the liquid phase was suggested. Desorption from polystyrenic resin adsorbed with BTEX was investigated by using two different organic solvents as desorbates.

Key words | breakthrough curves, BTEX, packed-bed adsorption, polystyrenic resin

INTRODUCTION

Industrial wastewater containing organic compounds and/or substances is an escalating problem due to its increasing toxic threat to humans and the environment (Gavrilescu et al. 2015). These organic compounds present in industrial waste may lead to groundwater contamination (Simantiraki & Gidaros 2015). Disposal of these organic pollutants at high concentrations has hazardous effects on surface water and groundwater quality (Costa et al. 2012). The World Health Organization (WHO) has established permissible limits in potential potable water contaminated by benzene, toluene, ethylbenzene and isomers of xylene (BTEX) as up to 0.01 mg/L (benzene), 0.7 mg/L (toluene), 0.3 mg/L (ethyl-benzene) and 0.5 mg/L (isomers of xylene) (WHO 2004). Therefore, removal of BTEX from wastewater is necessary. Other treatment techniques such as chemical oxidation, air stripping, biological treatment, condensation, membrane separation and adsorption have been used successfully for the removal of BTEX from wastewater (McCaff 2004; Aivalioti et al. 2012). Adsorption is one of the best treatment alternatives for the removal of these pollutants from wastewater because it is possible to recover both the adsorbent and adsorbate (Pan et al. 2005). Furthermore, the adsorption process of these pollutants has proven to be highly efficient, even for low concentrations (Can et al. 2010).

Various studies have reported on technologies that can achieve the highest removal of organic pollutants from industrial wastewater (Tomaszewska & Mozia 2002; Fu & Wang 2011). It is acknowledged that many adsorption processes
used to remove organic pollutants showed high efficiency at high concentrations (Can et al. 2010). The present study is focussed on the further treatment of treated wastewater from a local petrochemical company which is currently being pumped to sea. The analysis of this effluent was done over a period of six months and results are shown in Table 1. Hence the study focuses on low concentrations which are less than 20 mg/l, with an intention to remove more organic compounds so as to recover this wastewater for reuse as process water. One of the areas where South Africa can potentially save water is through the application of improved water treatment and recycling methods. The South African Department of Water and Environmental Affairs has developed environmental policies which are becoming stricter with regards to wastewater discharge. Hence South African industries are continually searching to set-up processes to achieve lower concentrations of pollutants in wastewater.

Normal process engineering practice considers adsorption isotherms which can be used for preliminary screening of adsorbents before running a continuous column. Batch experiments were performed in a previous study and the results of the measure of effectiveness of the adsorbent (PAD 910 polystyrenic resin) are provided in the literature (Makhathini & Rathilal 2011). From this previous publication, using the Langmuir and linearized Dubinin-Radushkevich models at pH of 6.85 it was demonstrated that the data fitted the Langmuir model adequately with a highest adsorption capacity of 79.44 mg/g. Furthermore, the resin was found to adsorb 98% of benzene, 88% of toluene, 59% of ethylbenzene, 84% m-, p-xylene and 90% o-xylene at an initial concentration of 14.47 mg/l (Makhathini & Rathilal 2011). These findings using batch experiments provide information about the effectiveness of the BTEX-adsorbent system. However, as stated in Laleh et al. (2011), the data determined under batch conditions are generally not applicable to most treatment processes operated under continuous conditions. This could be due to contact time not being long enough to reach equilibrium. Hence, this study focuses on the continuous fixed-bed adsorption column.

A continuous packed-bed does not operate on equilibrium conditions and the hydrodynamic conditions at the cross section of the column affect the flow behaviour downstream (Srivastava et al. 2008). Hence, the breakthrough characteristics of the adsorbent bed play a dominant role in the evaluation of the effectiveness of an adsorbent during continuous column operation (Vinod & Anirudhan 2003). Even though numerous studies have reported on column behaviour concerning the removal of several adsorbates from aqueous solution, only a few have reported on the dynamics of BTEX adsorption in a packed bed column using polystyrenic resin. Furthermore, there is an existing concern of effective regeneration procedures in terms of process economics, including optimization of regeneration efficiency (Zhang et al. 2015). Hence cost-effective regeneration of spent adsorbent is crucial in this adsorption study.

In order to properly design and operate fixed-bed adsorption processes, the adsorption isotherms and the fixed-bed dynamics in the form of pollutant breakthrough curves must be known (Chern & Chien 2002). To predict the breakthrough curve of a fixed bed with a mass transfer model, many parameters that are determined by independent batch kinetic study are needed (Wolborska 1989). Hence Wolborska & Pustelnik (1996) developed a simplified method using one parameter to predict the breakthrough times of fixed bed processes. Although this method caters for low concentrations, it is important that a model is refined enough to

### Table 1 | Trade effluent monitored average results to sea outfall

<table>
<thead>
<tr>
<th>Date analysed Units</th>
<th>Apr-14 μg/litre</th>
<th>May-14 μg/litre</th>
<th>Jun-14 μg/litre</th>
<th>Jul-14 μg/litre</th>
<th>Aug-14 μg/litre</th>
<th>Sep-14 μg/litre</th>
<th>Average μg/litre</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>3,700</td>
<td>8,425</td>
<td>1,400</td>
<td>5,124</td>
<td>6,100</td>
<td>3,900</td>
<td>4,775</td>
</tr>
<tr>
<td>Toluene</td>
<td>2,452</td>
<td>1,400</td>
<td>900</td>
<td>6,052</td>
<td>6,152</td>
<td>3,981</td>
<td>3,490</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>180</td>
<td>140</td>
<td>19</td>
<td>360</td>
<td>&lt;10</td>
<td>420</td>
<td>224</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>3,300</td>
<td>6,700</td>
<td>7,210</td>
<td>2,487</td>
<td>2,745</td>
<td>1,500</td>
<td>3,990</td>
</tr>
<tr>
<td>o-xylene</td>
<td>1,600</td>
<td>3,900</td>
<td>3,400</td>
<td>1,800</td>
<td>2,100</td>
<td>840</td>
<td>2,273</td>
</tr>
<tr>
<td>Total BTEX</td>
<td>11,232</td>
<td>20,565</td>
<td>12,929</td>
<td>15,823</td>
<td>17,097</td>
<td>10,641</td>
<td>14,751</td>
</tr>
</tbody>
</table>
describe the main parameters for a much wider range, yet is simple enough for easy analysis. Therefore, this study applies the constant-wave propagation theory to predict the breakthrough curves of resin beds for simultaneous removal of BTEX compounds. The effectiveness of a regeneration procedure was investigated, where the amount of water treated per cycle was compared with regeneration waste produced.

This study aims at providing useful information for understanding the features of both adsorption and desorption processes, thus assisting in the design of water treatment processes based on microporous materials: in particular, the impact of bed depth, flow rate, concentration, temperature and regeneration technique.

MATERIALS AND METHODS

 Adsorbate

The adsorbate sample (BTEX) was synthetically prepared using analytical reagent grade chemicals supplied by Merck SA. Various concentrations ($C_0$) were prepared within the range 0.35–14.47 ppm. This range was determined from results of samples that were collected randomly for six months in the discharge line of a local petrochemical company. The concentration of the aqueous solution was determined by a Perkin Elmer Gas Chromatograph–Mass Spectrometer (GC-MS) Clarus 580.

 Adsorbent

The PAD 910 polystyrenic resin adsorbent was purchased from Purolite Co. Ltd in China. A procedure from Battelle (1992) was replicated to determine the pH of the resin, where 2.5 g was mixed with 10 ml of distilled water and shaken at 25°C for 6 h. Then the mixture was filtered and the pH was found to be 6.85. The resin was kept in a cool dry place until experiments were carried out. The characteristics of the resin are given in Table 2.

 GC-MS analysis

The GC-MS was equipped with a capillary column (Elite 5MS, 30 m $\times$ 0.30 $\mu m$ internal diameter, 0.25 $\mu m$ thickness film) and a spectrometric detector (mass). A split/split-less type injector was used and its temperature was set at 180°C. The temperature of the column was kept at 50°C for 1 minute, increased to 180°C at a rate of 6°C/min and held at this temperature for 10 minutes, then ramped to 200°C at 10°C/min and kept there for 2 minutes. The temperature of the transfer line was 180°C. Helium gas was used as a carrier gas at a flow rate of 1.0 ml/min. The increase of the sensitivity and selectivity of the GC-MS was done by the selective ion monitoring (SIM) mode which was employed after the full scan mode was used for selecting ions. The volume for injection was 0.6 $\mu L$. This method was developed on a trial and error basis which is based on the analyte’s boiling point. The compounds p-xylene and m-xylene could not be differentiated by this method; hence they were considered as a single pseudo-compound.

Tuning and calibration of the GC-MS was done using heptacosane, where m/z for heptacosane was found as 69, 219, 502, and 614 mol/kg. The calibration was declared successful every time since all of the molar masses were confirmed. In addition, the verification of the calibration was done by using individual pure standards of benzene, ethylbenzene, toluene and isomers of xylene; the results were confirmed by comparison with the NIST Library.

 Column studies

An adsorbent’s effectiveness depends on the good flow of influent through the adsorption bed when running simple isotherms. Each Perspex column used in this phase of the work was of length 50, 60, 90 cm and internal diameter

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Characteristics of the adsorbent and column</th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>Average resin pore diameter</td>
<td>18Å</td>
</tr>
<tr>
<td>Void fraction$^a$</td>
<td>0.82</td>
</tr>
<tr>
<td>Nominal particle size (mm)</td>
<td>0.45</td>
</tr>
<tr>
<td>BET surface area (m$^2$/g)</td>
<td>510</td>
</tr>
<tr>
<td>Column diameter (cm)</td>
<td>2.5–5</td>
</tr>
<tr>
<td>Column height (cm)</td>
<td>30–90</td>
</tr>
<tr>
<td>Void fraction in the column$^a$</td>
<td>0.34</td>
</tr>
<tr>
<td>Bulk density of the bed (kg·m$^{-3}$)</td>
<td>319</td>
</tr>
</tbody>
</table>

$^a$Void fraction calculated from Pushnov (2006).
2.5, 3.0, 5.0 cm, respectively. All columns were operated under downflow conditions, regulated by a constant speed pump. This condition also ensured that the adsorption bed remained stable and steady during the entire operation period. Hence, there was maximum contact between the PAD 910 polystyrenic resin and the feed of organic (BTEX) compounds. The BTEX aqueous solution with known concentrations was fed at the top of the column. The effluent samples were collected at intervals and analysed using a GC-MS.

Walker & Weatherley (1997) stated that to determine the bed length (z) and the operating lifespan and regeneration of the bed, there should be a prediction of the column breakthrough. There are factors that affect the column breakthrough, such as operating variables and characteristics of the adsorbate and the adsorbent (Srivastava et al. 2008). This study focused on the models described below that can be used for the prediction of the breakthrough time.

**Mass transfer model**

An aqueous solution was fed at the top of the column packed with resin particles, for which the equation for predicting the column dynamics is (Chern & Chien 2002):

\[
\varepsilon \frac{\partial C}{\partial t} + u_0 e \frac{\partial C}{\partial z} + \rho \frac{\partial q}{\partial t} = 0
\]  

(1)

where \( \varepsilon \) is the bed void fraction, \( t \) is the contact time, \( u_0 \) is the interstitial flow rate, \( z \) is the distance from the inlet of the bed, \( \rho \) is the bed density, \( C \) and \( q \) are the adsorbate concentration in the liquid and solid phases, respectively. Equation (1) is the unsteady-state mass balance for the adsorbate.

The adsorption rate can be described by the linear driving force model in terms of the overall liquid-phase mass transfer coefficient (Sherwood et al. 1975):

\[
\rho \frac{\partial q}{\partial t} = \varepsilon K_L a (C - C^o)
\]  

(2)

where \( K_L \) is the overall liquid-phase mass-transfer coefficient, \( a \) is the contact area per unit volume of the bed, \( K_L a \) can be described as the volumetric coefficient in the liquid-phase, and \( C^o \) is the liquid-phase concentration in equilibrium. According to the constant wave theory of Chern & Chien (2002), the waves move at a constant velocity \( u_c \). Then the liquid-phase concentration can be expressed as a unique function of the adjusted time \( \tau \), defined as:

\[
\tau = t - \frac{z}{u_c}
\]  

(3)

Substituting Equation (3) into Equation (1), leads to:

\[
\left(1 - \frac{u_0}{u_c}\right) \frac{dC}{d\tau} + \frac{\rho q}{\varepsilon} \frac{dq}{d\tau} = 0
\]  

(4)

Integrating Equation (4), gives:

\[
\left(1 - \frac{u_0}{u_c}\right) C + \frac{\rho q}{\varepsilon} = 0
\]  

(5)

Since the boundary condition \( q = q_F \) at \( C = C_F \) is satisfied all the time, then you may substitute and have this valid equation:

\[
\left(1 - \frac{u_0}{u_c}\right) C_F + \frac{\rho q_F}{\varepsilon} = 0
\]  

(6)

Then, the adsorption rate becomes a basis for deriving the breakthrough curves of fixed-bed adsorption. Combining Equations (2) and (6):

\[
\frac{\rho q_F}{C_F} \frac{dC}{d\tau} = \varepsilon K_L a \left[C - f\left(\frac{q_F C}{C_F}\right)\right]
\]  

(7)

This can be rearranged and integrated with the following boundary condition \( C = C_{F/2} \) at \( \tau = \tau_{1/2} \):

\[
\int_{C}^{C_{F/2}} \frac{1}{C - f(q_F C/C_F)} dC = \int_{\tau_{1/2}}^{\tau} \varepsilon K_L a \frac{C_F}{\rho q_F} d\tau
\]  

(8)

where \( \tau_{1/2} \) is the adjusted time when the effluent adsorbate concentration reaches half of the feed concentration. Assuming \( K_L a \) is constant, \( \tau - \tau_{1/2} = (t - (z/u_c)) - (t_{1/2} - (z/u_c)) = t - t_{1/2} \)
from Equation (3), and the breakthrough curves at \( z = L \) can be calculated by the following equation:

\[
t = t_{1/2} + \frac{\rho q_F}{e K_L a C_F} \int_{C_{r/2}}^C \frac{1}{C - g(C/C_F)} dC
\]  

(9)

\[\text{Bed depth service time model}\]

According to Bohart & Adams (1920), this model is based on the assumption that the rate of adsorption is controlled by the surface reaction between the adsorbate and the residual capacity of the adsorbent. Equation (10) uses the initial part of the breakthrough curve, linking \( C/C_0 \) to time \( t \), for a continuous flow for the column:

\[
\ln \left( \frac{C_0}{C} - 1 \right) = \ln \left[ \exp \left( \frac{k N_0 Z}{U} - 1 \right) - k C_0 t \right]
\]  

(10)

where \( C_0 \) is the initial concentration of the adsorbate (mg/dm³), \( C \) is the desired concentration of the adsorbate at time \( t \) (mg/dm³), \( k \) is the adsorption rate constant of the column [dm³/(min·mg)], \( Z \) is the length of the bed (cm), \( N_0 \) is the adsorptive capacity of the adsorbent bed (mg/dm³) and \( U \) is the linear flow velocity of the fresh feed to the bed (cm/min).

Hutchins (1973) linearized Equation (1) to give

\[
t = \frac{N_0}{C_0 U} Z - \frac{1}{k C_0} \ln \left( \frac{C_0}{C} - 1 \right)
\]  

(11)

which describes the point at which the depth of the column is sufficient to prevent the effluent solute concentration exceeding \( C \) at \( t = 0 \). The parameters of the bed depth service time (BDST) model for any given flow can be scaled to predict the slope of the model for differing flow rate (Hasfalina et al. 2012).

\[\text{Adapted BDST model}\]

According to Pember et al. (2016), a modified BDST model can be further developed assuming the bed capacity did not change with the column height. In addition, the model assumes that the equilibrium isotherm is irreversible and that any mass transfer resistance is negligible. When substituting \( N_0 \) for \( N_t \) in Equation (11), then using Equation (12), a changing bed capacity can be defined (Ko et al. 2003), assuming a square root time dependence on the bed depth.

\[
N_t = N_0 \left( 1 - \exp \left( -a \sqrt{t} \right) \right)
\]  

(12)

The new variable, \( a \), is a rate parameter which is dependent on mass transfer resistance. Modifying Equation (11), by substituting Equation (12) on it, results in Equation (13), which is a modified BDST model:

\[
t = \frac{N_0}{C_0 U} Z - \frac{1}{k C_0} \ln \left( \frac{C_0}{C} - 1 \right)
\]  

(13)

\[\text{RESULTS AND DISCUSSION}\]

The goal of this research is to study hydraulic parameters, such as preferential flow, which were not part of the batch mode experiments presented in previous work by Makhathini & Rathilal (2017). The main, if not the only, aim of the continuous mode experiments, is to simulate the field conditions where the aqueous solution flows through the column and the effluent concentration begins to increase with time until it reaches a breakthrough concentration (Plassard et al. 2000). The breakthrough curves in Figure 1 present the ratio of effluent and influent concentration with the volume of BTEX solution passed through the column. The results are consistent with Simantiraki & Gidarakos (2015) even though these authors used a different
adsorbent (zeolite), where isomers of xylenes have sharper curves compared with toluene, benzene and ethylbenzene. The findings indicate that their removal is less efficient with polystyrenic resin and the material is exhausted much faster. According to Monazam et al. (2013), the column’s efficiency to reach saturation can be adjusted by the steepness of the breakthrough curve. Therefore, the breakthrough curves in Figure 1 indicate that the polystyrenic resin is a fairly good adsorbent for BTEX as shown by the ratio $C/C_0$, and the column needs some time to be exhausted.

**Breakthrough dynamics**

Combination of Equation (9) with the Langmuir model capacity equation yields:

$$t = t_{1/2} + \frac{\rho q_m}{\varepsilon K_L C_0} \left[ \ln 2x + \frac{1}{1 + bC_0} \ln \frac{1}{2(1 - x)} \right]$$

(14)

where $x$ is the normalized effluent concentration ($x = C/C_0$). Equation (14) is justified by the linear plot as shown in Figure 2, which demonstrates its applicability. The values of $t_{1/2}$ and $K_La$ were determined from the intercept and slope of the linear fit to the plot of $\ln 2x + [1/(1 + bC_0)] \ln [1/(2 - 2x)]$ versus time. The experimental and predicted breakthrough curves calculated by Equation (14) are shown in Figure 3. The results show that the developed mass-transfer model can predict BTEX adsorption from simulated wastewater onto polystyrenic resin satisfactorily. Larger values of $K_La$ and $t_{1/2}$ for benzene (401 h$^{-1}$), toluene (331 h$^{-1}$), ethylbenzene (298 h$^{-1}$) and m-, p-xylene (158 h$^{-1}$) may be related to their different adsorption capacity and hydrophobicity.

As reported in a previous study, the Langmuir and linearized Dubinin-Radushkevich models fitted the experimental data well (Makhathini & Rathilal 2017). This is due to the low adsorbate concentration ranges (5–15 mg/L), since the adsorption sites of the polystyrenic resin seem to be uniform and the occurrence of multiple-layer adsorption is less likely. Previous study on batch adsorption identified that data performed well with pseudo-second order model, which is confirmed with the s-shape of the breakthrough curves in Figure 3.

**Effect of flow rate and feed concentration**

Figure 4 shows the breakthrough curves at different feed flow rates. The influence of the feed flow rate on the half breakthrough time $t_{1/2}$ and $K_La$ is shown in Figures 5 and 6, indicating a strong linear dependence. The term $t_{1/2}$ decreases and $K_La$ increases with increasing feed flow rate, which is consistent with the conclusion that $K_La$ varied linearly with the feed flow rate (Lin & Huang 1999). Figure 7 shows the breakthrough curves at different feed concentrations. The $t_{1/2}$ values decrease with increasing $C_0$, whilst $K_La$ increases slightly with increasing $C_0$. As seen in these figures, this is confirmed by the breakthrough curve which is much steeper at higher $C_0$. It is likely that the driving force of mass-transfer in the liquid-film is enhanced when $C_0$ is increased. Aleghafouri et al. (2015) observed a similar trend while studying adsorption of BTEX compounds from aqueous solution of diethanolamine using activated carbon.

As seen in Figure 7, the constant-pattern wave approach with constant liquid-phase driving force fits the
experimental breakthrough curves well, except for xylene which has the highest boiling point compared with toluene, ethylbenzene and benzene. Here, the solid-phase mass-transfer may dominate the overall adsorption rate. It has been demonstrated that for rate control in the mobile phase, the wave front has a sharp tail; for rate control in the stationary phase, the wave tail has a sharp front (Helfferich & Carr 1993). Therefore, the results suggest that there is a dominance of solid-phase mass-transfer resistance over the adsorption rate, since the solid-phase becomes saturated, thus resulting in higher mass transfer resistance (Chern & Chien 2002).
The distribution of solute adsorbed in the polystyrenic resin may be determined by the intraparticle diffusion rate of the solute into the matrix, which depends on the concentration gradient of the solute and the resin porosity (Pan et al. 2005). In this case, there is evidence of an increase in \( C_0 \), which may be linked to the higher initial flux resulting in the solute penetrating into the interior matrix of the resin (Li et al. 2010). Also the adsorption sites within the micropore of the resin could be adequately occupied, which led to higher adsorption capacity at larger \( C_0 \) values.

In Figure 7, it is demonstrated that as the input concentration increased, the zone velocity increased. It is also seen that the shape of the breakthrough curve is somewhat steeper at a higher input concentration of 14.5 mg/l than at a lower input concentration of 5 mg/l. This may result from larger intraparticle diffusivity because the adsorption zone is reduced by higher diffusion flux (Lee et al. 2010).

**Effect of bed height and temperature**

The value of \( t_{1/2} \) is relatively proportional to the bed height at different flow rates (\( Q \)), as demonstrated in Figure 8. However, there is no clear evidence of the effect of bed height on the \( K_L a \) value. A similar trend was observed by Lin & Huang (1999) on sorption of BTEX onto macro reticular resin and Aleghafoori et al. (2015) on sorption of BTEX onto activated carbon.

The effect of the temperature on experimental and predicted breakthrough curves is shown in Figure 9. In general, adsorption processes are exothermic, hence the amount of adsorption decreases with increasing solution temperature (Chern & Chien 2002).
and $K_{L}a$ decrease with increasing temperature since the adsorption of BTEX onto polystyrenic resin is physical and its adsorption capacity decreases with increasing temperature (Özcan & Özcan 2004). Numerous correlations have been developed to express the Sherwood number as a function of the Reynolds number and Schmidt number, where its prediction of the liquid-film mass transfer coefficient in the adsorption column is satisfactory (Wang et al. 2005):

$$Sherwood \text{ no.} = \left( 2 + 0.644Re^{1/2}Sc^{1/3} \right) \left[ 1 + 1.5(1 - e) \right]$$

(15)

where:

$$Sherwood \text{ no.} = \frac{d_p k_L}{D} \quad Re = \frac{ued_p \rho_L}{\mu} \quad Sc = \frac{\mu}{D \rho_L}$$

Determining $k_L$ from Equation (15) and calculating the mass transfer area per unit bed volume by $a = 6(1 - e)/d_p$, the volumetric mass-transfer coefficients based on the liquid film were found to be slightly higher than the experimental breakthrough curves. It was found that the correlation produced an estimate of $k_{L}a = 198 \text{ h}^{-1}$ for run 3 in the column, while the experimental data yielded $k_{L}a = 96 \text{ h}^{-1}$. These results suggest that the solid-phase mass-transfer
resistance does exist and may have an impact on the breakthrough curve.

The present study proposes the following correlation to relate the overall volumetric liquid-phase mass-transfer coefficient as a function of wastewater:

\[ K_{La} = k_1 + k_2 Q^{1/2} \]  

(16)

In a case where this correlation is adequate, a \( K_{La} \) versus \( Q^{1/2} \) plot should follow a straight line. In Figure 10, the trend demonstrated a linear plot with a good fit of \( R^2 = 0.9949 \). Equation (16) suggests that the overall liquid-phase volumetric mass-transfer coefficient of a fixed bed is independent of the bed depth but increases linearly with increasing wastewater flow rate. The linear fluid velocities were found to be too low compared with Lin & Huang (1999). It is suggested that in the future, experiments using a wider range of wastewater should be collected to validate Equation (16) further.

**Application of the adapted BDST model**

Figure 11 demonstrates the modified Bohart-Adams model developed by Pember et al. (2016) plot for the removal of BTEX on a continuous fixed bed of polystyrenic resin at 10%, 25% and 50% breakthrough for different flow rate values. The modified BDST model produced considerable improvement when compared with the original BDST model, where critical bed depth was enhanced by higher flow rates and concentrations. The adsorption capacity \( (N_0) \) determined from the slope of 50% plot from Equation (13) was 75.66 mg/l. The value of the rate constant \( (k) \) characterises the rate of transfer from the liquid phase to the solid phase. The \( k \) value for the combined BTEX adsorption was 0.7124 which is large; therefore a shorter bed that will avoid breakthrough is required.

Theoretically, the plot of \( t_{0.5} \) with \( Z \) must result in a straight line passing through the origin. Application of Equation (12) to the experimental data gives a linear relationship for \( t_{0.1}, t_{0.25} \) and \( t_{0.5} \) with \( Z \), as shown in Figure 11. The adsorption rate constant and adsorption capacity of the column were found to be 72.45 mg/l and \( 0.145 \times 10^{-4} \) l/mg-min, respectively. Then, the \( N_0 \) value used to predict a 10% breakthrough plot shows a deviation of 9.78% from the value predicted from the 50% breakthrough plot. There was no difference in the values of bed capacity and critical bed depth when fitted to modified BDST model by Pember et al. (2016).

**Column regeneration**

The solvent regeneration of polymeric adsorbents is particularly effective when the components adsorbed are very soluble in the solvent and the solvating force is much greater than the physical adsorption force holding the adsorbate onto the resin (Lee et al. 2003). More often, they penetrate the gel phase of polymeric matrix. This results in the solvent displacement of the component adsorbed in the resin. In this study, methanol and isopropyl alcohol were used as regenerants to desorb BTEX compounds from the polystyrenic resin. Desorption breakthrough curves of BTEX in the polystyrenic resin column used to check the effect of methanol and isopropyl alcohol are shown in Figure 12. In comparing isopropyl alcohol and methanol as regenerants, there was an indication of overshoot in the desorption curve which occurred more quickly with isopropyl alcohol than with methanol. The high regeneration efficiency of isopropyl alcohol results from the contribution of solubility and affinity of BTEX to polystyrenic resin. In the case where isopropyl alcohol is not interfering with the process of removing BTEX compounds dissolved in water, a higher concentration of isopropyl alcohol is proposed to perform the regeneration step more effectively. However, the optimal condition depends on the economic considerations.
and being cautious of higher concentration of organic solvents, which poses a fire risk in the plant. The proposed dynamic model describes desorption breakthrough curves satisfactorily without adjustment of the model parameters determined in the previous section. As shown in Figure 12, high BTEX concentration was obtained in isopropyl alcohol within the first 1–2 hours and most desorbed BTEX was extracted by isopropyl alcohol.

It is noted that the maximum adsorption capacity of BTEX on the polystyrenic resin decreased in the order the column experiments were run. The results suggested that desorption procedure may not have been sufficient to completely restore the adsorption sites. Figure 13 shows desorption curves for each column as BTEX was
recovered from the polystyrenic resin beds with 0.25 M of isopropyl alcohol contact at 18.5 cm/min. Regeneration of the third column occurred after 50 ml of alcohol was passed through the resin bed, and for the other columns recovery occurred after 50 and 100 ml of regenerant solution passed through.

Furthermore, the reusability of polystyrenic resin was studied by measuring the adsorption capacities of BTEX compounds and their desorption properties. As demonstrated in Figure 14, it is difficult to desorb BTEX due to the affinity between BTEX molecules and the hydrophobic cavities of the adsorbent (Yang et al. 2016). This study used isopropyl alcohol and methanol as desorption agents for BTEX because they are good solvents for BTEX.

Figure 14 demonstrates that the adsorption capacity of BTEX was changed by small amounts for four complete cycles after reuse. These results demonstrate that the polystyrenic resin can be efficiently recycled and reused. As seen in Figure 14, the adsorption capacity of the regenerated adsorbent was 24.2% for benzene, 21.6% for toluene, 19.5% for ethylbenzene and 18.4% for m-xylene while the adsorption capacity of the original polystyrenic resin was 62.1% for benzene, 60.5% for toluene, 55.3% for ethylbenzene and 52.3% for m- and p-xylene. The adsorption capacity of regenerated polystyrenic resin compared with the original resin was in the relative order of B > T > E > X. This may be related to boiling point of these compounds: benzene 80.1°C, toluene 110.7°C, ethylbenzene 136.2°C and xylene 138°C (Su et al. 2010).

![Figure 14](https://iwaponline.com/jwrd/article-pdf/8/3/372/240901/jwrd0080372.pdf)

**CONCLUSIONS**

The results of the continuous flow system for the adsorption of BTEX compounds from aqueous solution show a reasonable removal efficiency. Although the required adsorption capacities give an estimate of the polystyrenic resin required, the actual adsorption capacity will vary according to the various adsorption parameters. The selectivity of the resin follows the order of m-, p-xylene, ethylbenzene, toluene and benzene. Sarkar & Acharya (2006) concluded from their research that if the pH of the wastewater is higher than the pKₐ value of the adsorbates, then there will be less adsorption due to dissociation of the adsorbate molecules. Therefore, the engineering applications would also have to be carried out under different conditions and the pH of the influent will also be adjusted. Moreover, the polystyrenic requirements should be seen as a function of the desired influent and effluent concentration. Therefore, pilot scale experiments using the same operating conditions need to be carried out with the same wastewater stream prior to design scale up. It is recommended that more work needs to be done on how to improve the adsorption capability of polystyrenic resin by subjecting it to physical and chemical treatment in order to increase its specific surface area and to promote the development of micropores within the resin, as these treatments have been demonstrated to enhance adsorption capacity. Hence, further work on desorption studies is required for the analysis of desorption mechanisms and the determination of diffusivity in terms of the water–alcohol mixing ratio. Adsorption of BTEX compounds onto polystyrenic resin is promising because of its easy regeneration.

**REFERENCES**


First received 15 August 2017; accepted in revised form 11 October 2017. Available online 1 December 2017