Investigation of BTEX compounds adsorption onto polystyrenic resin

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ABSTRACT

In this study, the adsorptive capacity of polystyrenic resin was evaluated for the removal of benzene, toluene, ethylbenzene and isomers of xylene (BTEX) from an aqueous solution. Batch studies were performed to evaluate the effects of various experimental parameters such as mixing strength, contact time, internal diffusion, adsorbates and initial concentration on the removal of the BTEX compounds. The equilibrium isotherms for the adsorption of the adsorbates on the PAD 910 polystyrenic resin were analyzed by the Langmuir and linearized Dubinin—Radushkevich models at pH of 5.86. The Langmuir model fitted the data adequately; is concluded that the latter is the most practical model in representing the adsorption of aromatic compounds. The Langmuir model indicated that resin has the highest adsorption capacity of 79.44 mg/g. At temperature of 25 °C, 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. The pseudo-second order rate model fitted better to the adsorption kinetics. The thermodynamic analysis resulted in a negative equilibrium enthalpy change suggesting an exothermic process.

1. Introduction

The mass of organic wastes produced in our society and the disposal cost has persistently increased over the years and this creates a challenge to process, civil and environmental engineers to develop better cost effective and environmentally secured treatment and discarding methods. The dangers of these organic compounds make their reduction and elimination necessary. Organic elements are commodities and raw materials of industries like petrochemical, oil refinery, explosives, dye, pigment and pesticides industries (Edgehill and Lu Max, 1998). The unacceptable discharge of organic compounds in water banks for a long period of time can cause worsening of water environments, while its consumption by human beings and animals causes liver function failure, kidney damage, central nervous coordination injury, diarrhea and secretion of murky urine (Sarkar and Acharya, 2006). Currently, an approval of trade effluent for release into South African local municipality sewage clearance system does not specify the limits for the BTEX compounds. It is anticipated that, in the upcoming times, stringent regulations in South Africa will be compulsory on the concentrations of these compounds in wastewater before discharge. BTEX compounds have already been selected by the US Environmental Protection Agency as main concern chemicals that need to be condensed to low levels of concentration before discharge (Lin and Huang, 1999). Treatment of BTEX in wastewater becomes a fundamental part of wastewater treatment for oil and chemical industries.

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An alternative for the removal of BTEX from a solution is by adsorption, of which the recovery of such compounds for likely recycling to the manufacturing process is permitted. The adsorption process is one of the prominent treatment options for the reduction of BTEX pollutants from aqueous media since it is possible to recover the adsorbent and adsorbate (Aivalioti et al., 2012). The adsorption of BTEX compounds can be achieved by macro reticular resin (Cornel and Sontheimer, 1986; Crook et al., 1978) and activated carbon (Furuya et al., 1997; Noll et al., 1994). Other adsorbents may include carbon nano tube, diatomite (Aivalioti et al., 2010, 2012) and organo-clay. All of the studies mentioned above investigate removal at higher concentration. None have been recorded on the low range concentration (less than 1 ppm) adsorption of BTEX using a polystyrenic resin. Hence, it was decided to embark on this investigation.

The main objective of this study was to evaluate the ability of untreated polystyrenic PAD 910 resin in the batch process to remove BTEX compounds from aqueous solution. In this work, the influence of mixing strength, contact time, internal diffusion, temperature, adsorbates and initial concentration on the removal of the BTEX compounds were investigated. The Langmuir and linearized Dubinin—Radushkevich models were used to examine fitness with the equilibrium data. The kinetic models and intra-particle diffusion models were also applied to evaluate the nature of the sorption process.

1.1. Isotherm models

The adsorption isotherms are defined by many mathematical formations often based on empirical fittings while simplifying the physical properties and processes involved in the adsorption. The major models that have mostly been used in fitting equilibrium adsorption isotherm of hydrocarbons in the literature are highlighted in this section.

1.1.1. Langmuir isotherm model
This is the simple and most commonly used model. It is a semi-empirical isotherm originating from a proposed kinetic mechanism (Langmuir, 1916). This is normally based upon four assumptions that are summed up in a homogeneous sorbent: (a) Localized adsorption; molecules are adsorbed at a set number of localized sites; (b) There is no interaction in between adsorbed molecules; (c) Monolayer adsorption: one adsorbate molecule can be held per site and (d) Equivalence of energetic sites.

The model is derived from rational considerations, hence is defined as:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \frac{1}{C_e} \tag{1}$$

where: q_e is the mass of adsorbate adsorbed per unit mass of adsorbent (mg adsorbate/g activated carbon); K_L is the Langmuir constant; C_e is the equilibrium concentration of adsorbate in solution after adsorption (mg/L) and q_{max} is the maximum amount of adsorption equivalent to complete monolayer coverage on the surface (mg/g).

1.1.2. The Dubinin—Radushkevich isotherm model (D—R model)
The D—R model is often utilized to give insight into the adsorption mechanism by finding the apparent free energy of the adsorption process. The model is given by Dubinin (1960):

$$q_e = q_D \exp(-\beta \varepsilon^2) \tag{2}$$

$$\text{Where:} \quad \varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{3}$$

In the above equations, q_e and q_D are the equilibrium adsorption capacity and the maximum adsorption capacity under optimized conditions in the D—R isotherm model in mg/g respectively; C_e is the equilibrium concentration in mg/L; β is a constant related to energy in mol^2/kJ^2 and ε is the Polanyi potential. The linearized form of Eq. (2) is used in obtaining the parameter β from which the mean free energy in kJ/mol is obtained by Hasany and Chaudhary (1996).

2. Materials and methods

2.1. Adsorbate material

The aqueous solution used in this research was synthetically prepared with a composition which is similar to that discharged by the local petrochemical companies to the mixing point before it is pumped to sea. The samples were collected randomly for six months so as to determine the reference average concentrations for a long time period. All samples were taken at different times of the day, which included steady and unsteady state operating conditions. Dilution of required quantities of benzene, toluene, ethyl-benzene and o-, m-, p-xylene were prepared to make a stock solution in the required volume of distilled water to find solutions of adsorbate for different initial concentrations (C_o) within the range of 0.35—14.47 ppm. Ten samples of different initial concentration were prepared within the given range.

Fresh solutions were prepared on a daily basis with the initial concentration of the adsorbate calculated before the start of each experiment. The pH value for the aqueous solution containing the mixture of benzene, toluene, ethyl-benzene and o-, m-, p-xylene (0.35—14.47 ppm) was measured and found to be between 5.86 and 5.99 before the adsorption tests were conducted. All pH measurements were done with a pH/conductivity meter (Orion Star A215), where an average of two results was recorded. Every flask was closed with a cap and overturned several times to blend the materials carefully and then allowed to stabilize for 15 min in the pyrex conical flask until experiments were run.

2.2. Adsorbent

PuroSorb PAD 910 polystyrenic adsorbent is a synthetic polymer that is highly cross linked and also has a highly porous structure as part of the polymer matrix. This adsorbent in many cases may replace carbon which is a common generic adsorbent with an advantage of being regenerated. The graded resin utilized in this investigation was sourced from Purolite Co. Ltd. in China. The pH of the PAD 910 polystyrenic was measured after 2.5 g of resin was mixed with 10 ml of distilled water and shaken at 25 °C for 6 h. The procedure was replicated from Battelle (1992). The mixture was filtered and the pH was measured as 6.85. The resin was stored in a cool dry place (approximately 22 °C) in the Laboratory until experiments were carried out.

2.3. Adsorption kinetic study

Dilutions of the stock solution were prepared in distilled water (simulated waste water) in a series of 250 ml bottles. From 100 mg to 400 mg of PAD 910 resin were dosed into the series of sample bottles containing 50 ml of the simulated wastewater and the bottles were placed in an incubator at 25 °C (±1°). The samples were placed in an orbital shaker (Stuart — SSL1) running at 150 rpm, having determined this was the mixing strength at which external diffusion was minimized negligibly. The simulated wastewater was prepared from stock BTEX solutions and then stored in the refrigerator at 4 °C to prevent any possible evaporation since the BTEX compounds are highly volatile.

2.4. Batch studies

Batch studies were performed to obtain the equilibrium data for the adsorbate and the adsorbent (PAD 910 polystyrenic resin). The adsorbates were the mixture of 99.9% benzene, 99.7% toluene, 99.9% ethylbenzene and 99.8% of each isomer of xylene from Merck Chemical Ltd, SA. The batch technique was used because of its straight forwardness to obtain equilibrium data. The initial solute concentration was recorded before adding the sample to the polystyrenic resin. Adsorption experiments for short time kinetics and isotherms were repeated twice and the duplicate adsorption data is reported, while the repeatability of the different instruments used in analyzing the four BTEX compounds are reported in terms of % relative standard deviation (RSD). Fig. 1 protocol that was followed to carry out the adsorption kinetic experiments.

For every adsorption data point, a 50 ml aliquot of the adsorbate mixture had an initial concentration of benzene, toluene, ethylbenzene, m-;p-xylene, o-xylene of 3.70 mg/l, 6.66 mg/l, 0.34 mg/l, 2.57 mg/l and 1.20 mg/l respectively. The adsorbent-to-simulated waste water ratio on a mass/volume basis was varied from 1 to 5 (Chern and Chien, 2002); when it was introduced into a series of 100 ml Pyrex conical flasks at a temperature of 25 °C. The conical flasks were positioned and shaken in a shaker where equilibrium was attained since no further adsorption occurred after 6 h of residence time and at a steady stirring speed of 150 revolutions per minute. The

samples were enclosed using aluminum foil during the experiment and the supernatant solution filtered after different time intervals of agitation through Whatman microfiber filters. The concentration of the filtrate left was then determined using GC/MS and recorded, as shown in Fig. 1. The adsorbent capacity for BTEX adsorption was calculated using Eq. (4) and the removal percentage used Eq. (5a):

$$Q_t = \frac{(C_o - C_e)V}{M} \tag{4}$$

$$\%R = \frac{100\,(C_o - C_e)}{C_o} \tag{5a}$$

where C_o is the initial sorbate concentration (mg/l), C_e the equilibrium sorbate concentration (mg/l), M is the mass of the adsorbent (g) and V is the volume of solution (l).

3. Results and discussion

3.1. Adsorbent physical properties

Particle size distribution analysis was manually done. Initially, a resin sample of 400 g was analyzed. This sample was passed through different sieves and an amount of fine and course particles were measured in the US Standard mesh size number 30—45. The nominal particle size was found to be 0.45 mm. Density of the adsorbent is particularly important for adsorption. The Brunauer—Emmett—Teller (BET) surface area of PAD 910 polystyrenic resin was measured and found to be 480 m²/g, which was close to the manufacture's specification of 510 m²/g. The porous structural properties of the samples were analyzed by obtaining the nitrogen adsorption and desorption isotherms at 77 K using the Autosorb 1 specific surface area analyzer. The average pore diameter was given as 18 Å for PAD 910 polystyrenic resin by the manufacturer. These results showed that this adsorbent is reasonably good for adsorption.

3.2. Adsorbent characterization

Surface morphological images obtained by scanning electron microscopy (SEM) for some of the samples used in this study are shown in Fig. 2.
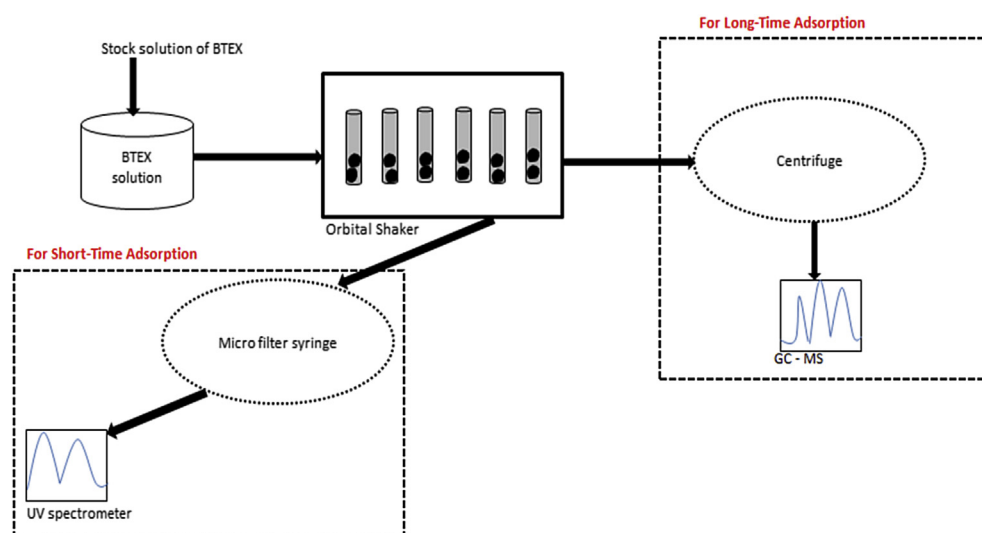

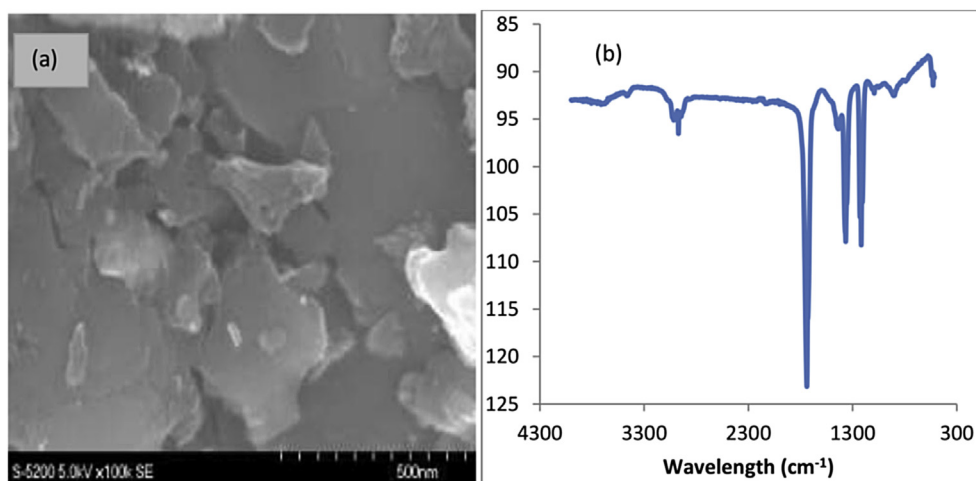**Fig. 1 — Adsorption kinetic experimental protocol.**

Fig. 2 – (a) SEM Image and (b) FTIR spectra of PAD 910 polystyrenic resin.

The image in Fig. 2(a), gives evidence to the porous nature of the resin. However there was essentially little porosity seen in the commercial PAD 910 polystyrenic resin. The porous structure of the sample of PAD 910 resin appears to be honeycomb (or spongy) like, and it is in agreement with the pores size distribution (Byrd, 1998; Gou and Rockstraw, 2007; Jiang et al., 2008). The FTIR spectra in Fig. 2(b) displayed a peak between 2800 and 3200 cm^{-1}. The peaks ascribed to the stretching vibration of groups such as −OH associated with the aromatic and carboxylic functional groups (Chern and Chien, 2002). The band around 1150 cm^{-1} is attributed to the stretching vibration of C−O associated with the lactonic group (Laleh et al., 2011). The band between 1600 and 1800 cm^{-1} is ascribed to the oscillation of C=O associated with carbonyl and carboxylic groups (Byrd, 1998; Gou and Rockstraw, 2007; Jiang et al., 2008).

3.3. Effect of mixing strength

The mixing strength is a major factor in the adsorption process. This is due to the fact that external mass transfer of aromatic hydrocarbon molecules from the bulk liquid to the surface of the adsorbent is dependent on the dynamics of the system whereby the process occur due to the boundary layer effect at the solid−liquid interface (Site, 2001). The boundary layer distorts surrounding non-viscous flow, which will then limit the adsorption process (Allen-King et al., 2002).

Fig. 3 shows the removal percentage against the varying mixing strengths. It demonstrates that an increase in the mixing strength increases the % removal of the BTEX compounds. This is attributed to the increased turbulence, which then reduces the boundary layer effect.

Given these results, subsequent experiments were conducted at a mixing strength of 120 rpm, 150 rpm and 180 rpm, in order to comfortably assume negligible external diffusion limitations. Fig. 4 shows data obtained to verify the validity of this assumption in a non competitive kinetic experiment over the time regime to be studied. The trend shows that at the mixing strength of 150 and 180 rpm, the same result of C_t/C_o is obtained hence it can be confirmed that adsorption is not dependant on the mixing strength beyond 120 rpm. Hence subsequent experiments were carried out at a fixed mixing strength of 150 rpm.

3.4. Effect of internal diffusion

With the initial concentration of BTEX aqueous solution of 14.47 ppm, a long term kinetic study was conducted with PAD 910 polystyrenic resin. Fig. 5 shows the evolution of the BTEX concentration with time. The equilibrium concentration of
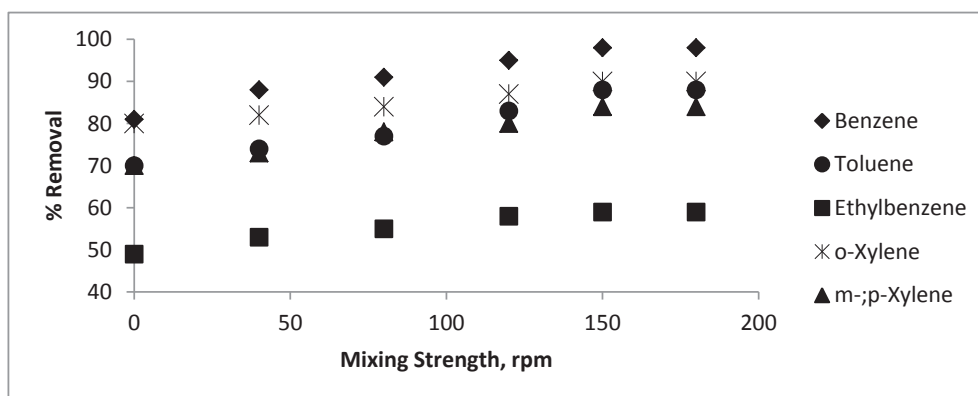

Fig. 3 – Effect of mixing strength on adsorption of a mixture of BTEX for 6 h (0.25 g of resin, 25 ml simulated waste water with 3.69 ppm Benzene, 6.66 ppm Toluene, 0.34 ppm Ethylbenzene, 2.56 ppm Ethylbenzene, 2.56 ppm m-;p-Xylene and 1.18 ppm o-Xylene).
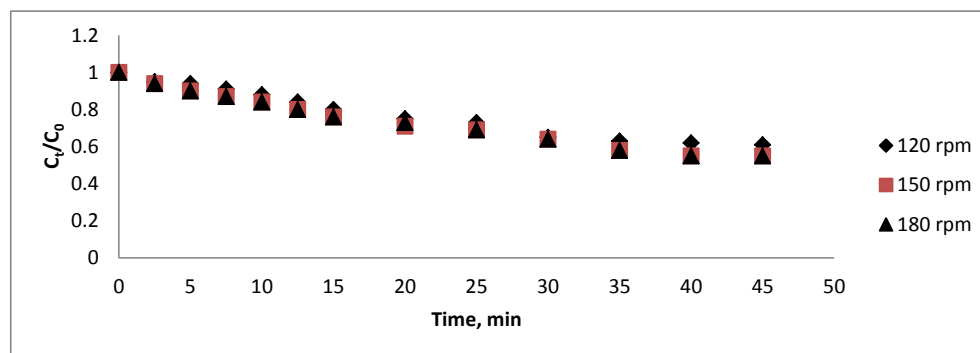
Fig. 4 — Effect of mixing strength on adsorption of Toluene onto 0.25 g resin. Initial concentration ~6.6 ppm.
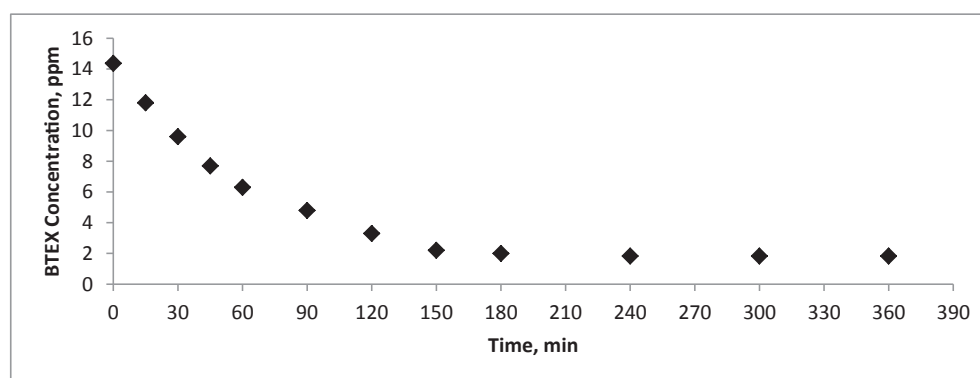

Fig. 5 — Long Term BTEX adsorption on 0.25 g of PAD 910 polystyrenic resin in simulated waste water.

2 ppm was achieved for the adsorbent after 3 h. The global kinetic parameters were obtained and are given in Table 1.

Short term adsorption is based on the initial phase of adsorption which is 45 min and the long term adsorption is the final phase of the adsorption which occurred at 6 h.

Obviously, the Elovich model does not fit the experimental data adequately as shown by the low correlation coefficients hence it was not considered in subsequent analyses. The choice between the pseudo-first order and pseudo-second order was however relatively more subtle given the very high correlation coefficients. The pseudo-second order model as shown in Fig. 6(b) has been identified as the best performing model for this study based on the following reasons.

A plot of the predicted residual concentration at different sampling times versus the experimental residual concentrations for all adsorption kinetics experiments is presented models in Fig. 5. It is observed that the pseudo-second order model represents the experimental values better for the whole concentration range.

The Pseudo-first order model also seemed to represent the experimental data fairly well. Another validity criterion commonly used in the literature for pseudo-first order is the plot of $\ln(q_e - q_t)$ versus t, which yields a linear relationship in which the intercept should give a value close to $\ln q_e$ (Ho and McKay, 1998; Hall et al., 2009). Performing this validity test did not exactly yield values of q_e that were close to those obtained for the pseudo-first order model in all cases. In addition, one way ANOVA was used to validate the effect of pseudo first and second order models on the experimental data. There was a significant effect of $p = 0.027 < 0.05$ level for all conditions. In addition, a post hoc comparison was done which indicated that the mean score for BTEX concentration had a significant difference for Fig. 6(a) while there is no significant difference in Fig. 6(b).

| Table 1 — Global rate parameters for short term BTEX adsorption onto polystyrenic resin.					
Model	Benzene	Toluene	Ethylbenzene	m-;p-Xylene	o-Xylene
Pseudo 1st order					
k_1 (min^{-1})	0.10	0.22	0.11	0.16	0.06
q_{e1} (mg/g)	0.13	0.25	0.19	0.19	0.14
r^2	0.966	0.992	0.961	0.956	0.987
Pseudo 2nd order					
k_2 (g mg^{-1} min^{-1})	0.98	0.5	0.13	0.25	0.41
q_{e2} (mg/g)	1.14	2.5	0.08	0.22	0.19
r^2	0.993	0.995	0.983	0.990	0.994
Elovich					
b (g mg^{-1})	3.86	10.25	1.22	62.44	84.33
a (mg g^{-1} min^{-1})	3.45×10^{14}	2.09×10^{32}	3.23×10^4	∞	∞
r^2	0.442	0.624	0.852	0.421	0.392
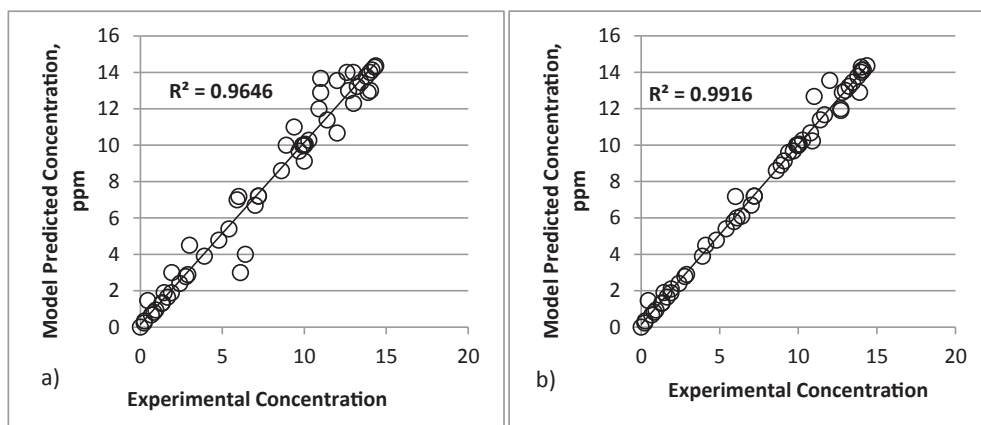
Fig. 6 – Validation of kinetic model choice a) pseudo-first order; b) pseudo-second order.
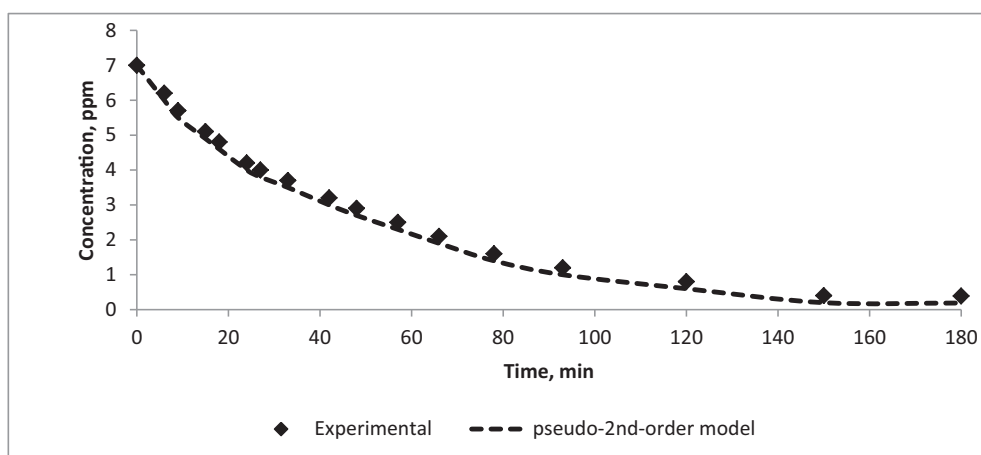

Fig. 7 – Short Term BTEX adsorption on 0.25 g of PAD 910 polystyrenic resin.

It was also confirmed that the adsorption process was extremely fast within the first 45 min in both cases, which was followed by a slower transport stage. This suggested a shift of the BTEX molecule transport regime from macropore/meso-pore to the micropore channel of the resin. A shorter time regime experiment method was then designed to capture the process better and also for analysis of the diffusion process. An aqueous system of initial BTEX concentration was reduced by 50% to 7 ppm and then was adsorbed using PAD 910 poly-styrenic resin and the concentration–time dependence plots are shown in Fig. 7.

When assuming that C_e tends to zero, the linear Eq. (5b) was obtained from which the rate parameter in terms of the residual concentration, k'_2 could be obtained.

The rate parameters are reported in Table 2.

$$\frac{1}{C_t} = k'_2 t + \frac{1}{C_0} \qquad (5b)$$

3.5. Effect of initial concentration

The effect of initial BTEX concentration on the adsorption process was investigated using three different batches of 25 ml BTEX simulated wastewater each treated with 0.25 g of PAD 910 polystyrenic resin. The quantity-time dependence plot is shown in Fig. 8.

Rate parameters obtained from the experimental data are highlighted in Table 3, while Fig. 8 shows the typical sorption data curves for the effect of initial BTEX concentration on the quantity of BTEX adsorbed per time.

Table 3 shows that the initial concentration influences the rate parameters, which demonstrates that the adsorption process is controlled by the diffusive mass transport of BTEX compounds onto the adsorption remaining "active sites". The dependence is inconsistent with the diffusive mass transport theory with a negative dependence of the rate constant with the concentration trend. However, the unit of the second

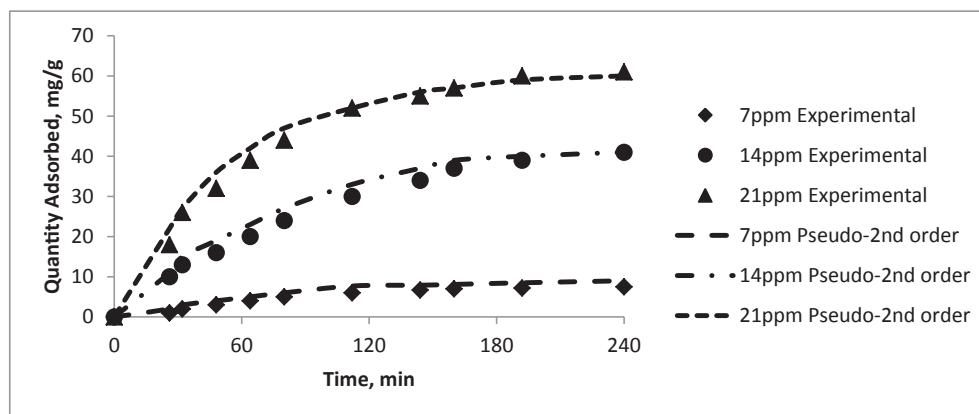| Table 2 – Global parameters for short term BTEX adsorption.					
Model	Benzene	Toluene	Ethylbenzene	m-;p-Xylene	o-Xylene
Pseudo 2nd order (Resin)					
k'_2 (L mg^{-1} min^{-1})	0.03	0.52	0.17	0.16	0.22
r^2	0.923	0.992	0.962	0.976	0.994

Fig. 8 – Plot of BTEX sorbed capacity versus time showing initial concentration effect.

Table 3 – Rate parameters for initial BTEX concentration effect on the adsorption process.

Pseudo-2nd order model	7 ppm	14 ppm	21 ppm
k_2' (L mg^{-1} min^{-1})	0.39	0.044	0.021
h_0 (mg g^{-1} min^{-1})	1.8	5.6	14.3
r^2	0.99	0.94	0.92

order rate constant demonstrate that it has an inverse relation to the BTEX concentration in the aqueous phase. It may be concluded that the rate constant is positively influenced by the concentration of BTEX in the aqueous phase. This positive dependence of the rate on the BTEX concentration is attributed to the greater concentration driving force for the transport process. A simple inspection of Fig. 8 shows that the initial concentration influenced the contact time required to reach equilibrium. Exaggerated results for residual concentration and rate of adsorption at 7 ppm are observed, this result could be attributed to the fact that less quantity is adsorbed at lower concentration which is logical because there is less amount of BTEX available in the aqueous system.

In terms of the initial concentration and the initial rate of adsorption (h_0) as time tends to zero, the rate law of the adsorption process could be written as

$$h_0 = kC_0^n \tag{6}$$

A non linear regression of h_0 against the initial concentrations was used to determine the order (n) of the process as

1.23. This may be the reason behind both the pseudo-1st order and the pseudo-2nd order models predicted data giving a relatively high coefficient of regression with respect to the experimental data in all cases.

4. Study of the adsorption equilibrium

4.1. Effect of internal diffusion

The adsorption isotherm of BTEX at 25 °C onto PAD 910 polystyrenic resin was studied and the experimental data with the Langmuir model fitted plot is shown in (see Fig. 9).

The isotherm parameters from the Langmuir and D–R models are highlighted in Table 4. From the maximum adsorption capacity parameter q_m obtained from the Langmuir model, it is evident that there is a direct correlation between this parameter and the specific surface area (SSA) of the adsorbent. This is due to the adsorption capacity being reached as the number of 'active sites' available for the monolayer adsorption (as assumed by Langmuir) is saturated. The amount of the adsorption 'active sites' is expectedly proportional to the specific surface area. However, on normalizing the maximum adsorption capacity by the SSA, the influence of the pore size distribution is demonstrated.

4.2. Effect of adsorbate

Fig. 10 shows the adsorption isotherm data obtained from a comparative competitive study of the equilibrium adsorption
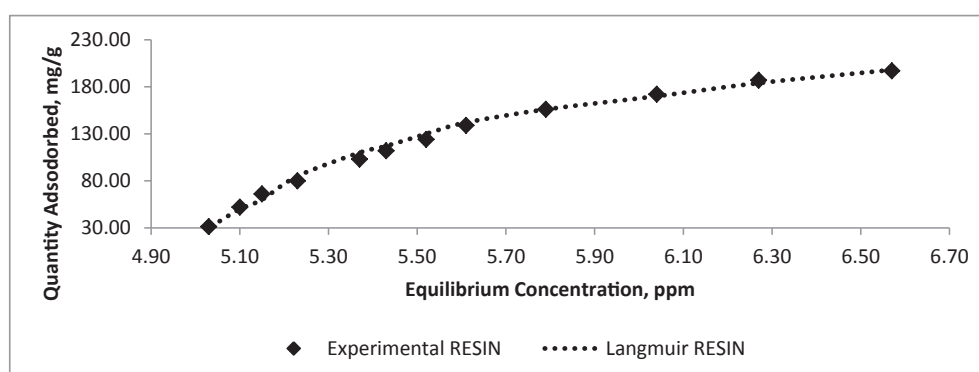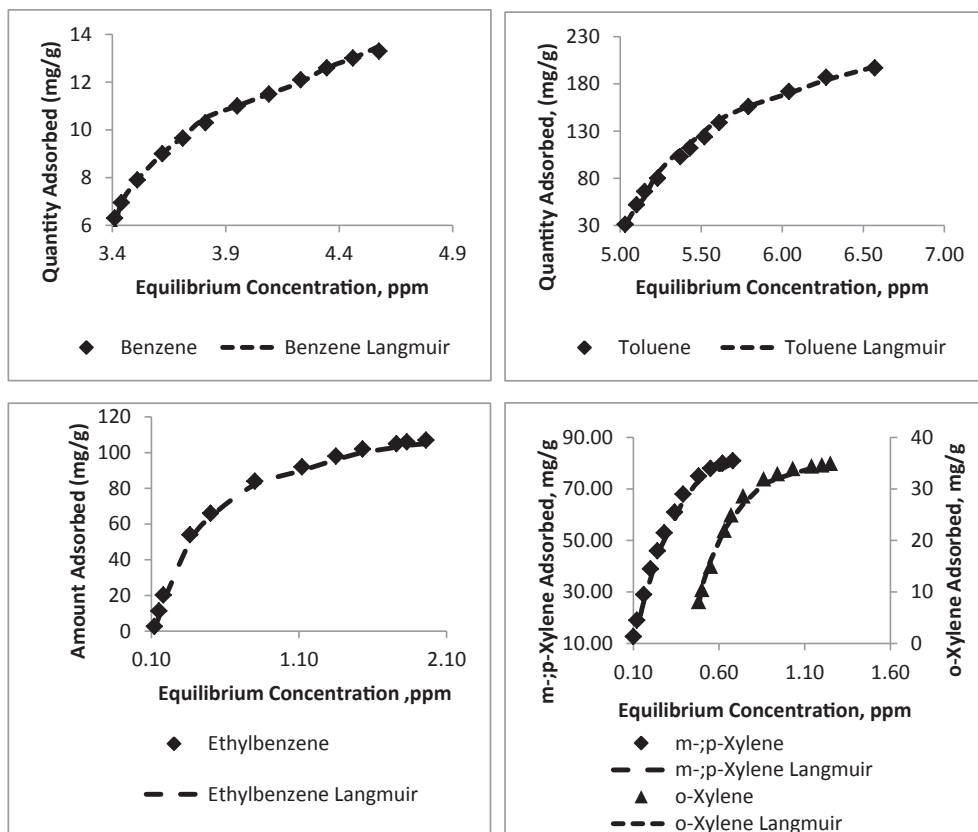

Fig. 9 – BTEX adsorption isotherm on PAD 910 polystyrenic resin at 25 °C (0.25 g adsorbent in 25 ml simulated wastewater of initial concentration of 15 ppm).

Table 4 — BTEX adsorption isotherm parameters for PAD 910 resin.

Adsorbent	Langmuir				Linear D—R			
	K_L (L/mg)	q_m (mg/g)	SSA (m^2/mg)	R^2	$\beta \times 10^8$ (mol^2/J^2)	q_D (mg/g)	E (kJ/mol)	R^2
Resin	0.79	78.9	0.66	0.95	1.77	63.23	5.21	0.98

Fig. 10 — Benzene, Toluene, Ethylbenzene and Xylene Adsorption isotherm on PAD 910 polystyrenic resin at 25 °C (0.25 g in 25 ml simulated wastewater of initial concentration of 7 ppm).

of benzene, toluene, ethylbenzene and isomers of xylene with the adsorption conditions, while the parameters are tabulated in Table 5.

As demonstrated in Table 5, the equilibrium capacity of the PAD 910 polystyrenic resin used was greater for toluene. Compared to the other compounds, toluene has a smallest size which makes it easier for its molecules to diffuse into more micropores for the adsorption process to take place. This further gives proof to the argument that there is a form of molecular sieving in the adsorption process with some portion of the micropores being inaccesssible to some aromatic molecules. In a competitive study Valderrama et al. (2007) also observed a similar trend of the form of molecular sieving towards larger aromatic hydrocarbons.

4.3. Effect of temperature

The effect of adsorption of BTEX at different temperatures was investigated using PAD 910 polystyrenic resin and the experimental data is provided in Fig. 11 while the parameters obtained from the isotherm models are given in Table 6. Evidently there is an increase in the adsorption equilibrium capacity as the temperature increased. The increasing sorption capacity is further indicative of the chemisorption process. For any chemical process, the positive influence of temperature has been well documented, as explained by the Arrhenius equations. Furthermore, according to Rodriguez and Linares (1989), water molecules attached to carbon surface oxygen groups through hydrogen bonding and may

Table 5 — Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene adsorption isotherm parameters.

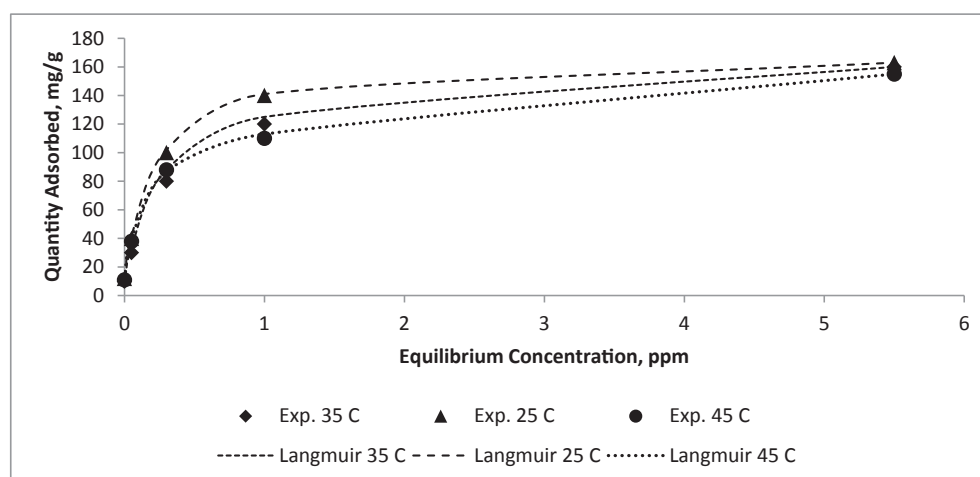| Adsorbate	Langmuir				Linear D—R			
	K_L (L/mg)	q_m (mg/g)	q_m (mmol/g)	R^2	$\beta \times 10^8$ (mol^2/J^2)	q_D (mg/g)	E (kJ/mol)	R^2
Benzene	17.23	9.89	0.078	0.94	0.93	10.56	7.13	0.96
Toluene	6.45	13.67	0.45	0.98	2.78	9.88	4.45	0.93
Ethylbenzene	3.67	12.9	0.11	0.99	5.78	14.45	3.98	0.94
m-;p-Xylene	21.78	11.45	0.67	0.91	3.12	11.56	4.99	0.99
o-Xylene	19.45	10.45	0.56	0.97	2.23	8.55	5.87	0.92

Fig. 11 — BTEX adsorption isotherm on PAD 910 polystyrenic resin at different temperatures (0.25 g adsorbent in 25 ml simulated wastewater with initial concentration of 15 ppm).

cause steric hindrance to the adsorption of aromatic compounds by the adsorbents. This steric hindrance could be reduced at an elevated temperature and hence an observed increased adsorption equilibrium capacity.

However, the adsorption coefficient decreased as temperature increased. This may be indicative of decreased adsorption intensity associated with an exothermic process. Site (2001) in his review paper, concluded that due to the dependence of both sorption coefficients and solubility with temperature, the measured effect of temperature on sorption isotherm is a result of combined sorption and solubility contributions. Unfortunately, there was no data available for the solubility of some BTEX compounds at the elevated temperatures of 35 °C and 45 °C, which could have been used to normalize the equilibrium capacities.

4.4. Thermodynamic analysis of BTEX adsorption

The mean free energy of adsorption, E, in kJ/mol, was obtained in the form of the D—R model and reported for all cases. According to Balan et al. (2009) values of the mean free energy that are smaller than 8 kJ/mol are characteristic of a physisorption mechanism while values between 8 and 16 kJ/mol indicate an ion exchange mechanism. In all cases, values of mean free adsorption energy were less than 8 kJ/mol, suggesting the process involved physisorption. This seemed contrary to the chemisorption mechanism suggested by the kinetic study and the observed temperature effect, hence a thermodynamic study to investigate the adsorption enthalphy was explored. The thermodynamic property associated with the change in Gibbs free energy (ΔG^0) was derived for all the systems studied according to the equation:

$$\Delta G^0 = -R \times T \times \ln K_l \qquad (7)$$

where, R, is the ideal gas constant, 8.134 J/mol K; T is the absolute temperature in K; K_L is the equilibrium coefficient of

the aromatic adsorption on adsorbents, which is equivalent to the equilibrium adsorption coefficient constant in the Langmuir model where it is applicable (converted to L/mol). The values obtained ranged from −20.3 kJ/mol to 36.6 kJ/mol, indicating the likely spontaneity of the adsorption process as expected. Similarly, the (ΔG^0) is also equivalent to:

$$\Delta G^0 = \Delta H^0 - T \times \Delta S^0 \qquad (8)$$

By which the other thermodynamic properties, entropy in J/mol, ΔS^0 and enthalpy, in kJ/mol, ΔH^0 could be calculated from combining both equations to yield:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R*T} \qquad (9)$$

Table 7, highlights the thermodynamics properties obtained by linear regression of K_L values obtained from the temperature study (see Table 7).

The positive value (although small) of entropy changes suggests an increase in randomness at the water/carbon interface during the BTEX molecules adsorption on the adsorbents. This is likely due to desorption on smaller molecules into the aqueous system as the adsorption process proceeded. The negative value of the enthalpy change indicates the exothermic nature of the adsorption process. This is consistent with conclusions made by Site (2001), that adsorption processes are generally believed to be exothermic, although the influence of temperature on the process may however vary depending on the variations that occur in the solubility of the sorbate with increasing temperature.

The relatively small equilibrium enthalpy of adsorption is within the range for hydrogen bonded processes (about −7 kJ/mol) as reported by Site (2001). In addition, as discussed earlier, hydrogen bonding is an intermediate between physisorption and chemisorption, with an average enthalpy of between 4 kJ/mol and 40 kJ/mol. This explains why the process

Temp. °C	Langmuir			Linear D—R			
	K_L (L/mg)	q_m (mg/g)	R^2	$\beta \times 10^8$ (mol²/J²)	q_D (mg/g)	E (kJ/mol)	R^2
25	0.66	198	0.97	4.27	43.96	3.43	0.97
35	0.59	211	0.98	3.29	62.49	3.77	0.96
45	0.53	218	0.98	2.93	55.21	4.09	0.9

Table 6 — BTEX adsorption isotherm parameters at different temperatures.

Table 7 – Thermodynamics properties of the adsorption of BTEX onto PAD 910 polystyrenic resin.

Temperature, K	K_L L/mol	$-\Delta G^0$ kJ/mol	$-\Delta H^0$ kJ/mol	ΔS^0 J/mol	R^2
298	6.98×10^4	20.3	4.67	69.34	0.88
308	6.54×10^4	26.12	4.17	62.19	0.84
318	5.77×10^4	36.6	–	–	–

has often been described as an interplay of both physisorption ($E < 7$ kJ/mol) and chemisorption process (i.e pseudo-second order fitting and positive correlation with temperature).

5.   Conclusions

It was shown that the PAD polystyrenic resin can be successfully utilized as an adsorbent for the removal of benzene, toluene, ethylbenzene and isomers of xylene from wastewater. The equilibrium adsorption data is better fitted by the Langmuir adsorption model rather than the D–R adsorption model for these adsorbates. Due to the lower adsorption capacity of the PAD 910 polystyrenic resin, the adsorbent requirements for this resin will be high. This will lead to larger adsorbent bed volumes required for treatment when the PAD 910 polystyrenic resin adsorbent is used. For larger volumes of adsorbent to be accommodated to treat the influent with the PAD 910 polystyrenic resin, it means larger equipment is required. The mean free energy parameter, E from D–R model was however from 3.45 to 4.12 kJ/mol, indicative of a rather weak interaction between BTEX hydrocarbons and the carbon surface. The thermodynamic analysis resulted in a negative equilibrium enthalpy change, ΔH^0 suggesting an exothermic process. The positive entropy change ΔS^0 shows a random increase which is likely due to desorption of smaller molecules as BTEX molecules were adsorbed onto the carbon surface. In addition, the positive temperature effect is consistent with the chemisorptions process. A method for maximum regeneration of adsorbents is an important aspect of this work and should be included in further studies.

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