



Investigation of the adsorption performance of polystyrenic resin and GAC for the removal of BTEX compounds from industrial wastewater

**Submitted in fulfilment of the requirements of the degree of
Master of Engineering - Chemical in Faculty of Engineering and
the Built Environment**

Thobeka Pearl Makhathini

June 2015

Supervisor : S Rathilal

DEDICATION

I dedicate my dissertation work to my family. A special feeling of gratitude to my loving husband, Siyabonga, whose words of encouragement is still ringing in my ears. My children Nqobile and Ndalo have been on my side throughout and are very special. All of you have been my best cheerleaders.

I also dedicate this dissertation to my friends and church family who have supported me through the process. I will always appreciate their spiritual and academic support. I also appreciate Dr Bakare for many hours of proof reading.

DECLARATIONS

I, **THOBEKA PEARL MAKHATHINI** declare that

- (i) This research reported in this thesis expect where otherwise indicated is own original work.
- (ii) This thesis has not been submitted for any degree or examination at any other University or academic institution.
- (iii) This thesis does not contain other persons' data, pictures graphs or other information, unless specifically acknowledged as being sourced from other persons.
- (iv) This thesis does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other sources have been quoted, then:
 - (a) Their words have been re-written but general information attributed to them has been referenced;
 - (b) Where their exact words have been used, their writing has been placed inside quotation marks, and referenced.
- (v) Where I reproduced a publication of which I am an author, co-author or editor, I have indicated in detail which part of the publication was actually written by myself alone and have fully referenced such publications.
- (vi) This thesis does not contain text, graphics or tables copies and pasted from the internet, unless specifically acknowledged, and the source being detailed in the thesis and in the References sections.

Signed:

NAME OF SUPERVISOR (1):

DR SUDESH RATHILAL

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Dr Rathilal for the continuous support of my MEng Degree study and research. His guidance helped me in the time of research and writing of this thesis.

Besides my supervisor, I would like to thank my post graduate peers: Miss Precious, Khaya Shabangu, Sihle Mtsweni, Cyprian Muruti and Portia Lubisi, for their encouragement, insightful comments and hard questions.

My sincere thanks also go to Nomaxhosa for trusting me enough to let me work in the Chemistry Laboratory where I was doing the sample analysis. I am grateful to Dr Ndinisa who was my first supervisor for enlightening me with the first glance of research.

ABSTRACT

Industrial wastewater containing organic compounds and/or substances is an increasing problem due to its increasing toxic threat to humans and the environment. The removal of organic compounds has become an imperative issue due to stringent measures that are introduced by the Department of Environmental Affairs in South Africa to enforce regulations concerning wastes that emanate from petrochemical industries. Thus, wastewater containing these compounds must be well understood so as to devise adequate treatment processes.

In this study, the adsorptive capacity of PAD 910 polystyrenic resin originating from China and granular activated carbon (GAC) 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 experiments were conducted at the mixing strength of 180 rpm, in order to comfortably assume negligible external diffusion. The equilibrium isotherms for the adsorption of the adsorbates on the PAD 910 polystyrenic resin were analyzed by the Langmuir, Freundlich and linearized Dubinin-Radushkevich models at a pH of 5.86. The Langmuir model fitted the data adequately; this result was supported by the work done by Site (2001) which concluded that the Langmuir 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 and GAC has 66.2 mg/g. 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.

BTEX adsorption was a two-stage process: a short, fast initial period then followed by a longer, slow period corresponding to the intra-particle diffusion of BTEX molecules in macropores and micropores. The adsorption capacity was determined by total surface area accessible to BTEX and the availability of active surface chemical groups. The dependence of adsorption capacity on the surface of the two adsorbents and temperature was observed, suggesting the chemical nature of the BTEX adsorption. The interaction between BTEX/activated carbon was however weak and energetically similar to that of hydrogen

bonds. Generally, BTEX adsorption was an exothermic process that combined physisorption and chemisorption. The PAD 910 polystyrenic resin had a greater specific surface area (SSA) of $1040 \text{ m}^2/\text{g}$ which yielded in higher capacity compared to GAC which had a low SSA of $930 \text{ m}^2/\text{g}$. The normalized adsorption capacity was found to be higher for PAD 910 polystyrenic resin than GAC (0.66 and 0.27 mg/m^2 respectively) which suggests that the resin has a good potential of the adsorbent for removing BTEX compound compared to GAC.

Fixed bed columns were used to evaluate the dynamic adsorption behaviour of BTEX/PAD 910 polystyrenic resin through a dynamic column approach. The performance of small-scale fixed bed columns, each containing PAD 910 polystyrenic resin and the other containing GAC were evaluated using 14.47 mg/L of BTEX concentration. The columns with 32 mm diameter, studied bed depths of 40 , 80 and 120 mm and flow rate of 6 ml/min were used in order to obtain experimental breakthrough curves. The bed depth service time (BDST) model was used to analyze the experimental data and design parameters like adsorption capacity, adsorption rate and service time at 20% and 60% breakthrough. BDST was also used to predict the service times of columns operated under different influent concentrations and flow rates to produce theoretical values that were compared to the experimental values.

Adsorption model by Dubinin and colleagues (Dubinin, 1960), based on the theory of volume filling micropores was used to fit the measured adsorption isotherms. Agreement between the modelled and experimental results for GAC and PAD 910 polystyrenic resin using Dubinin-Radushkevich equation generally improved with increasing the surface area and produced reasonable fits of the adsorption isotherms for both GAC and PAD 910 polystyrenic resin.

Granular activated carbon had a lesser performance compared to the PAD 910 polystyrenic resin, in terms of kinetic studies, and this finding was attributed to the pore structure which made accessibility of BTEX molecules more difficult in this study. The results indicate that PAD 910 polystyrenic resin show potential as an adsorbent for removing low concentrations of BTEX from wastewater. It is suggested that necessary treatment of GAC might improve the performance of this adsorbent by creating more mesopore volume and fraction which is essential to enhance adsorption rate. A substantial different SSA could be achieved through high porosity development in GAC by using templating method with a higher potassium hydroxide mixture ratio.

TABLE OF CONTENTS

DEDICATION.....	(i)
DECLARATION.....	(ii)
ACKNOWLEDGEMENTS.....	(iii)
ABSTRACT.....	(iv)
TABLE OF CONTENTS.....	(vi)
LIST OF FIGURES.....	(ix)
LIST OF TABLES.....	(xi)
LIST OF APPENDICES.....	(xiii)
LIST OF ABBREVIATIONS.....	(xiv)
1 INTRODUCTION	1
1.1 Background and Motivation	1
1.2 Justification	3
1.3 Problem Statement	4
1.4 Research Objectives	6
1.5 Thesis Outline	6
2 REVIEW OF LITERATURE.....	8
2.1 Introduction.....	8
2.1.1 Water pollution and environmental degradation.....	8
2.1.2 Water scarcity	9
2.2 Volatile Aromatic Fractions (BTEX).....	10
2.3 Existing Technologies.....	14
2.3.1 Chemical oxidation	14
2.3.2 Biological treatment process.....	14
2.3.3 Air stripping	15
2.3.4 Organic removal using membrane technology	15
2.3.5 Adsorption process.....	16
2.3.6 Available alternate approach for adsorption	22

2.4	Exposure Limits	24
2.4.1	In aquatic organisms	25
2.5	Adsorption Kinetics	25
2.5.1	Empirical models (Global Rate Models)	25
2.5.2	Mechanistic models	27
2.6	Adsorption Isotherms.....	30
2.6.1	Classification of adsorption isotherms.....	31
2.6.2	Isotherm models.....	32
2.7	Gap Analysis	36
3	MATERIALS AND METHODS.....	38
3.1	Materials.....	38
3.1.1	Adsorbate material	38
3.1.2	Adsorbent(s).....	39
3.2	Equipment for Characterization and Analytical Analysis	40
3.3	Experimental Methods	41
3.3.1	Adsorption kinetics study	41
3.3.2	Batch studies	41
3.3.3	GC-MS analysis	42
3.3.4	Dynamic column studies.....	43
3.4	Chemistry Analysis	45
3.4.1	Surface Chemistry Analysis.....	45
3.4.2	Porous Structure Analysis.....	45
3.4.3	Surface Morphology Analysis	45
3.5	Adsorption Data Quality and Repeatability	46
4	RESULTS AND DISCUSSION.....	47
4.1	Physical and chemical characterization of the adsorbent	47
4.1.1	Porous Structure Analysis.....	47
4.1.2	Morphology.....	48
4.1.3	Fourier transform infrared spectroscopy (FTIR) analysis	49
4.1.4	Chemical properties	50
4.1.5	Physical properties	50
4.2	Adsorption Study	51
4.2.1	Effect of residence time	51
4.2.2	Effect of mixing strength	53
4.2.3	Effect of internal diffusion.....	56
4.2.4	Effect of initial concentration	63
4.2.5	Effect of adsorbate	65

4.3	Adsorption Isotherm Study	69
4.3.1	Effect of internal diffusion.....	69
4.3.2	Effect of adsorbate	72
4.3.3	Effect of temperature	74
4.3.4	Thermodynamic analysis of BTEX adsorption.....	75
4.4	Adsorption Dynamic Column Studies	77
4.4.1	Effect of bed depth on breakthrough	79
4.4.2	Data evaluation	79
4.4.3	Design adsorption column for different concentrations.....	81
4.4.4	Design of adsorption column for different flow rate	82
4.4.5	Comparison	83
5	CONCLUSIONS AND RECOMMENDATIONS	84
5.1	Conclusions	84
5.2	Recommendations	87
6	REFERENCES	89

LIST OF APPENDICES

APPENDIX A:	Equipment.....	96
APPENDIX B:	Adsorption Porous Structure Measurement.....	98
APPENDIX C:	BTEX Calibration Curve.....	99
APPENDIX D:	Adsorption Data.....	103
APPENDIX E:	Column Dynamic Data.....	109
APPENDIX F:	Design Example.....	113
APPENDIX G:	ANOVA Results.....	115
APPENDIX H:	Acceptance Trade Effluent.....	116
APPENDIX I:	Material Safety Data Sheet.....	119

LIST OF FIGURES

Figure 1.1 Location of the companies discharging industrial effluent to SWWTP (Source: Ethekwini Municipality Annual Report 2007)	4
Figure 1.2 Possible contributors to the Badulla line (Source: Ethekwini Municipality Annual Report 2007)	5
Figure 2.1: Input of the food division to the production of organic water contaminants (WWAP, 2012)	8
Figure 2.2 Regions of where the surface water originates in South Africa (Driver <i>et al.</i> 2004)	10
Figure 2.3: Molecular structure of adsorbates (a) benzene; (b) toluene; (c) ethylbenzene; (d) m-xylene; (e) p-xylene and (f) o-xylene (Burrows <i>et al.</i> 2009).....	12
Figure 2.4: A schematic representation of the structure of activated carbon. (Adapted from (Stoeckli 1990))	18
Figure 2.5: A structure of a hydrophobic, macro-recticular resin bead. (Adapted from Cabal <i>et al.</i> (2009))	19
Figure 2.6: Adsorption approach for the solution to wastewater treatment.....	22
Figure 2.7: Schematic diagram of a heterogeneous adsorption process (Noll, Gounaris and Hou 1994)	28
Figure 2.8: IUPAC Types of Adsorption Isotherms (IUPAC 1985)	31
Figure 3.1: Adsorption Kinetic Experimental Protocol	41
Figure 3.2: Schematic Diagram of Experimental Setup for Column Studies	44
Figure 4.1: N ₂ Adsorption Isotherm at 77K of Granular Activated Carbon	47
Figure 4.2: SEM Images of (a) GAC and (b) PAD 910 polystyrenic resin	48
Figure 4.3: FTIR Spectra for a) Granular Activated Carbon; b) PAD 910 Polystyrenic Resin	49
Figure 4.4: Effect of residence time on the amount of BTEX compounds removed from aqueous solution with (a) GAC and (b) PAD 910 polystyrenic resin.....	52
Figure 4.5: Effect of mixing strength on adsorption of a mixture of BTEX for 4 hrs (0.25 g of (a) resin and (b) activated carbon; initial concentration: Benzene ~ 3.69ppm; toluene ~ 6.6ppm; Ethylbenzene ~ 0.34ppm; m-p-Xylene ~ 2.56ppm; o-Xylene ~ 1.18ppm)	54
Figure 4.6: Effect of mixing strength on adsorption of Toluene onto 0.25g (a) resin and (b) activated carbon. (Initial concentration ~ 6.6ppm)	55
Figure 4.7: Long Term BTEX adsorption on two types of adsorbent (0.25g of PAD 910 polystyrenic resin and GAC in 25ml of simulated waste water)	56
Figure 4.8: Validation of Kinetic Model Choice a) pseudo-first order; b) pseudo-second order	58

Figure 4.9: Short Term BTEX adsorption on two adsorbents (0.25g of PAD 910 polystyrenic resin and GAC in 25 ml of simulated waste water).	59
Figure 4.10: HDPM Regression of BTEX adsorption onto PAD 910 polystyrenic resin and granular activated carbon.	61
Figure 4.11: Weber-Morris plot of BTEX adsorption onto PAD 910 polystyrenic resin and granular activated carbon	61
Figure 4.12: Effect of Initial BTEX concentration on adsorption onto PAD 910 polystyrenic resin.	63
Figure 4.13: Plot of BTEX sorbed capacity versus time showing initial concentration effect	64
Figure 4.14: Adsorption of BTEX compounds over a short period (0.25g of PAD 910 polystyrenic resin, 25 ml simulated wastewater with 3.69 ppm Benzene, 6.66 ppm Toluene, 0.34 ppm Ethylbenzene, 2.56 ppm m-;p-Xylene and 1.18 ppm o-Xylene)	66
Figure 4.15: Adsorption of BTEX compounds over a long period (0.25g of GAC, 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)	66
Figure 4.16: BTEX adsorption isotherm on GAC and PAD 910 polystyrenic resin at 25 ⁰ C (0.25 g adsorbent in 25 ml simulated wastewater of initial concentration range: 7 – 15 ppm)	70
Figure 4.17: Benzene, Toluene, Ethylbenzene and Xylene Adsorption isotherm on PAD 910 polystyrenic resin at 25 ⁰ C (0.25 g in 25 ml simulated wastewater of initial concentration range: 0.1 – 7 ppm)	72
Figure 4.18: BTEX Adsorption Isotherm on PAD 910 polystyrenic resin at different temperature (0.25 g adsorbent in 25 ml simulated wastewater on initial concentration range: 0.34 – 15 ppm)	74
Figure 4.19: Breakthrough curves for benzene BTEX onto GAC	77
Figure 4.20: Breakthrough curves for BTEX onto PAD 910 polystyrenic resin	77
Figure 4.21: BDST plot for BTEX adsorption onto GAC, determined from a theoretical approach	78
Figure 4.22: BDST plot for BTEX adsorption onto PAD 910 polystyrenic resin determined from a theoretical approach.	78
Figure 4.23: Comparison of BDST model predictions based on $C_0 = 14.47$ mg/l with calculated BDST for BTEX adsorption with $C_0 = 30$ mg/l	82

LIST OF TABLES

Table 2.1: Physico-chemical properties of BTEX compounds.....	12
Table 2.2: Differences between physisorption and chemisorption (Everett 1971).....	23
Table 2.3: Exposure limits allowable values for BTEX organic compounds. Adapted from OSHAAct (85) of 1993.....	25
Table 3.1: Trade effluent monitored average results to sea outfall.....	38
Table 3.2: Materials and reagents used.....	39
Table 3.3: Instruments employed in adsorption experiments	40
Table 3.4: Adsorption data quality.....	46
Table 4.1: Removal rate of BTEX after 6 hrs of agitation.....	51
Table 4.2: Global rate parameters for short term BTEX adsorption onto PAD 910 resin.....	56
Table 4.3: Global rate parameters for long term BTEX adsorption onto GAC.....	57
Table 4.4: Global parameters for short term BTEX adsorption.....	60
Table 4.5: Diffusion parameters for PAD 910 polystyrenic resin and GAC.....	62
Table 4.6: Rate parameters for initial BTEX concentration effect on the adsorption process	63
Table 4.7: Diffusion parameters for the effect of initial concentration on BTEX adsorption .	65
Table 4.8: Rate Parameters for adsorption of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene for short period	67
Table 4.9: Rate parameters of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene for long period.....	67
Table 4.10: Diffusion parameters for the adsorption of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene.....	68
Table 4.11: BTEX adsorption isotherm parameters for Two Different Adsorbents GAC and Resin	71
Table 4.12: Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene adsorption isotherm parameters.....	73
Table 4.13: BTEX adsorption isotherm parameters at different temperatures	75
Table 4.14: Thermodynamics properties of the adsorption of BTEX onto PAD 910 polystyrenic resin.....	76
Table 4.15: % Adsorbate removal at a breakthrough contact time of 4 hrs.....	80
Table 4.16: Comparison of theoretical and experimental adsorption capacity at 20% breakthrough of initial adsorbate concentration	80
Table 4.17: Comparison of theoretical and experimental adsorption capacity at 60% breakthrough of initial adsorbate concentration	80
Table 4.18: 20% breakthrough time for experimental data based on 14.47 mg/l with calculated data for adsorbates adsorption with 30 mg/l.....	82
Table 4.19: 20% breakthrough time for theoretical data based on 6 ml/min with calculated data for adsorbates adsorption with 3 ml/min.....	83

LIST OF ABBREVIATIONS

BTEX	Benzene, Toluene, Ethyl-benzene, m-;p-;o-Xylene
GAC	Granular Activated Carbon
EPA	Environmental Protection Agency
WWAP	World Water Assessment Programme
WAO	Wet-Air-Oxidation
OPEC	Organization of Petroleum Exporting Countries
MBR	Membrane Bio-Reactor
ABS	Acrylonitrile-Butadiene-Styrene
BOD	Biological-Oxygen-Demand
NF	Nano-Filtration
MF	Micro-Filtration
UF	Ultra-Filtration
RO	Reverse-Osmosis
NOM	Natural Organic Matter
TOC	Total Organic Compounds
VOC	Volatile Organic Compounds
TLV	Threshold Limit Value
OEL	Occupational Exposure Limit
CL	Control Limit
WHO	World Health Organization
SSA	Specific Surface Area

1 INTRODUCTION

1.1 Background and Motivation

The amount of water across the earth is unevenly distributed, however it is constant hence it cannot be increased or decreased. South Africa as a country receives a rainwater of 492 mm while the other part of the world receives a mean annual rainfall of 985 mm. It is almost half of the world's standard, hence South Africa is classified as a water-stressed region (Smakhtin et al., 2001).

The Department of Water and Environmental Affairs states that, the demand for water will exceed supply in South Africa by 2025. South Africa is financially strained since it is one of the fastest developing countries and as a result it cannot afford to build new water transfer schemes (Ashton and Haasbroek, 2002). The other factor for this increasing demand of water in South Africa is the increase in human population with its increasing needs for survival hence the requirement of water becomes greater.

One of the areas where South Africa can be able to save water is through treatment and recycling methods. The Department of Water and Environmental Affairs have developed environmental policies which are becoming stricter with regards to wastewater discharge. Hence South African industries are continually searching to set-up standards of lower concentrations of the pollutants in wastewater. Industries are steadily adjusting their processes with new measures in order to produce less and eliminate more noxious elements that are present in the discharge. In addition to this factor, South Africa is a semi-arid country with marked high rates of potential evapo-transpiration (Livia, 2010).

The mass of organic wastes produced in our society and the disposal cost has persistently increased, 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 (Srivastava et al., 2006). 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, diarrhoea and secretion of murky urine (Sarkar and Acharya, 2006).

The production stages of the oil industry are partially accountable for generating large mass of waste water to be discharged to the environment. Effluent generated in the oil industries contains different compositions of organic, inorganic, salts and metal substances. The dissolved phenols, toluene, benzene, ethyl-benzene and isomers of xylene (BTEX) are the most profuse hydrocarbons of which they are the more vital contaminants due to their high toxicity (Coughlin and Ezra, 1968).

Currently, an approval of trade effluent for release into the Ethekwini Municipality sewage clearance system does not specify the limits for the BTEX compounds as illustrated in Appendix G2. It is anticipated that, in the upcoming times, stringent regulations in South Africa will be compulsory on the concentrations of these compounds in the 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.

Conventionally, activated sludge treatment has been the commonly and generally used method. Micro-organisms in an activated sludge system, can deal with chemical wastewater containing relatively low BTEX concentrations which are normally less than 100 mg/L since there is low biodegradability properties on these compounds (Chang et al., 1993, Bielefeldt and Stensel, 1999). In cases where concentrations are exceeding this volume, physical or chemical treatment methods may offer better alternatives.

In some instances, hydrocarbons are not easily degraded by the micro-organisms which are present in predictable activated sludge processes. Hence micro-organisms suitable to degrade hydrocarbons are formulated so as to add them into traditional activated sludge processes (Cardinal and Stenstrom, 1991). According to Judd (2006), the application of membrane bioreactors (MBR) to familiar wastewater methods has steadily increased and the increase is in interest to relate this promising technology to industrial wastewater which is also growing rapidly. It seems apparent that the utilisation of the MBR has some advantages like high removal efficiency and high biomass concentration (Scholz and Fuchs, 2000, Cheng et al., 2005).

Incineration is one of the chemical alternatives. As much as it is practical to use incineration with waste solvents, it is measured as too expensive for other practical applications. For the past three decades, wet-air-oxidation (WAO) process has emerged as the alternative potential.

The WAO technique is competent enough to oxidize high concentrations of organic elements in the aqueous solution under high pressure and high temperature. The study done by Lin and Wu (1996) found the oxidation decomposition process to be fast and capable, however maintaining high temperatures can be highly costly.

Another 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 mediums 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, Aivalioti et al., 2012) and organo-clay.

1.2 Justification

Various techniques have been investigated for adsorption of inorganic and organic waste by activated carbon over the recent years. Several research studies had been reported on the characterization of activated carbon and adsorption of organic waste using granular activated carbon. None have been recorded on the low range concentration adsorption of BTEX using activated carbon and PAD 910 polystyrenic resin for the purpose of process modelling in South Africa.

This research work seeks to assist the Ethekwini Municipality in setting the waste water quality standards which includes BTEX compounds limit into the waterworks which are currently not reflected on the Ethekwini Municipality acceptance trade of effluent (see Appendix G2). The set quality limits may ultimately be used as baseline in improving compliance with the current and future permit conditions by decreasing the BTEX concentration in the effluent. The research findings are predicted to have an overall positive impact on the effluent quality discharge to the Southern Wastewater Treatment Works (SWWTW). This will be due to the reduction of the toxicity of effluent as compared with the *status quo*; therefore the SWWTW will not cause adverse impacts to the marine life. The research will result in further environmental benefits in terms of reducing the frequency and the volume of potential releases to the natural environment.

1.3 Problem Statement

Local petrochemical refineries and factories in Jacobs are pumping effluent through a pipeline called Badulla line. The influent to SWWTW from the Badulla line is not treated but is collected in a catch-point sump then pumped to sea. Approximately 15 000m³ of un-reclaimed wastewater is discarded to sea each day through this water works. The SWWTW is located in the Merebank Area which lies approximately 10 km south of the Durban Metropolitan City. The Merebank area is characterized by a range of industrial activities including Engen Refinery, Mondi Paper Mill, Sapref, NCS Resins and Sasol Wax. Other industries in the adjacent area include FFS Refiners, Feltex, Hosaf and PQ Cooperation. To the north of Merebank are numerous residential areas which include: Austerville, Wentworth, Bluff, Treasure Beach and Island View. Figure 1.1 shows the location of some of the companies and residential area around SWWTW. Figure 1.2 shows the possible contributors to the Badulla line, which are mostly refineries and oil companies.



Figure 1.1 Location of the companies discharging industrial effluent to SWWTP (Source: Ethekekwini Municipality Annual Report 2007)



Figure 1.2 Possible contributors to the Badulla line (Source: Ethekewini Municipality Annual Report 2007)

Mainly activated carbon in wastewater containment technology has been common due to the effectiveness it offers, however, due to less literature of BTEX adsorption kinetics and equilibrium data, many of the containment technologies have been designed based on limited equilibrium data (Valderrama et al., 2007). Published literature on BTEX adsorption focus on higher concentrations which are above 20 ppm, hence less data is available for lesser concentrations. In previous work, Battelle (1992) studied the feasibility of using potassium hydrate activated oil sands petroleum coke for competitive adsorption of aromatic hydrocarbons from the aqueous phase, and recommended the influence of the carbon porosity, surface functionality and specific area on the adsorption process.

1.4 Research Objectives

This research objective(s) are to:

- a. Examine the success or effectiveness of the PAD 910 polystyrenic resin in comparison to activated carbon in the adsorption of BTEX from an aqueous phase;
- b. Determine the underlying factors that influence the rate of adsorption of BTEX from the aqueous phase onto both polystyrenic resin and activated carbon, and explain the role of such factors in the process;
- c. Examine the influence of the factors identified in an equilibrium study of the adsorption of BTEX onto selected adsorbents.
- d. Determine the breakthrough point for a dynamic column operated under different bed depths and flow rates in order to evaluate its performance.
- e. Determine the applicability of Freundlich, Langmuir and the Bed Depth Service Time (BDST) approach to estimate design parameters characterizing the performance of batch and dynamic column tests.
- f. Propose a process mechanism in favour of the adsorption of BTEX from aqueous phase onto selected adsorbents.

1.5 Thesis Outline

The research and findings of this investigative study are covered in the following four Chapters:

Chapter two is the literature review which presents the holistic overview of the world water status. The literature review of the existing different technologies for treating organic waste water and the application of liquid phase adsorption processes as a suitable handling method for the elimination of organic compounds is presented in this chapter. The utilization of other adsorbents was also discussed and presented in this chapter with detailed focus on the properties of the resin and the activated carbon in the field of adsorption.

Detailed experimental methods conducted for the adsorption of organic elements are discussed in chapter three. Characterization results obtained are presented and the approaches of both batch and dynamic column studies to adsorption are also discussed. The uses, toxicity and physiochemical properties of the adsorbates (benzene, toluene, ethyl-benzene and xylene) are discussed thoroughly in this chapter.

Chapter four discusses the results obtained from the adsorption of organic compounds onto GAC and resin. Batch tests were used to obtain equilibrium time necessary for the adsorbents to reach equilibrium and dynamic test were used to determine the equation which can be used to estimate the size of bed column required for waste removal.

2 REVIEW OF LITERATURE

2.1 Introduction

This chapter provides a broad overview about current water status in the world, in the continent of Africa and more importantly in South Africa.

2.1.1 Water pollution and environmental degradation

According to World Water Development Report (2012), about 90% of wastewater in developing regions like South Africa flow as untreated water into river streams and highly coastal regions. This practice threatens wellness, food protection and right of entry to safe water for consumption. A lot of industries (some known to be greatly polluting like, chemical and leather industries) are moving from elevated revenue countries to up-and-coming market economies (WWAP, 2012).

The World Water Assessment Programme further states that in just beginning countries, 70% of manufacturing waste is discarded untreated into water streams where they heavily contaminate the area. WWAP (2012) also emphasised the fact that, part of the world's wetlands have vanished since 1900. Figure 2.1 shows that, the input of the food divisions to the creation of organic contaminants is of high concern in small revenue countries (54%) in comparison to high income countries (40%).

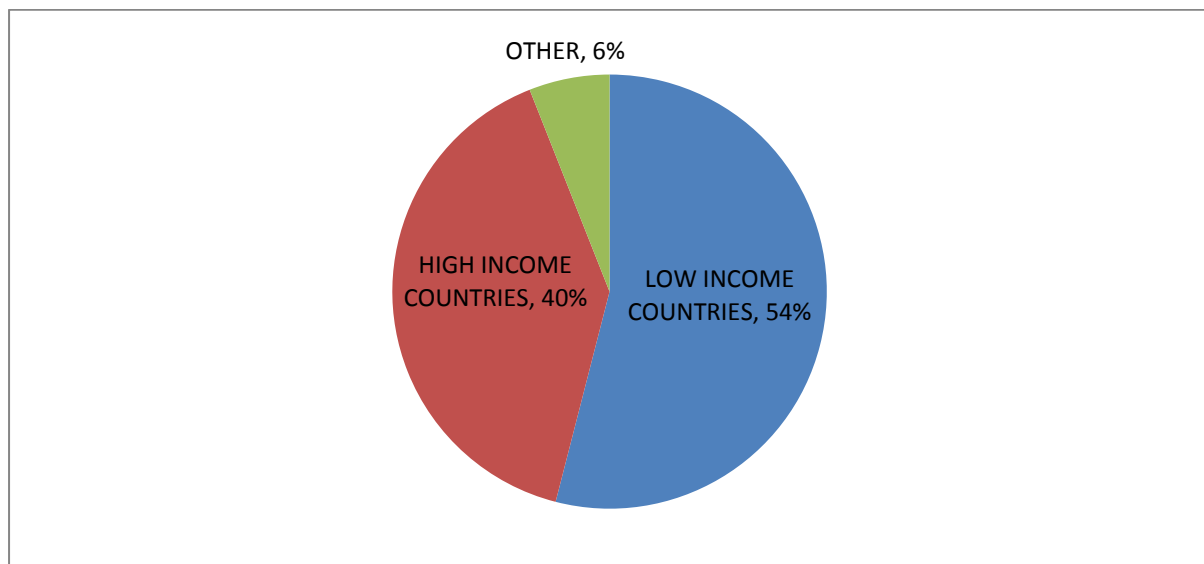


Figure 2.1: Input of the food division to the production of organic water contaminants (WWAP, 2012)

2.1.2 Water scarcity

In the last century, there has been a global growth which has further doubled the rate of population increment. In many regions of the world, the challenge is to reach the limit at which water services can be sustainably delivered. Population growth and monetary development are currently exerting extraordinary pressure on renewable water resources (WWAP, 2012).

According to Ashton (2002), water is acknowledged as the main primary and essential of all natural resources throughout the world. Therefore, it is clear that neither public and profitable development nor ecological variety can continue without water. Ashton (2002) further states that the South African region is a persistently water strained country which range between 500 m³ and 1000 m³ of water accessible per each citizen in a year. Surface water is profoundly dedicated for consumption and the water that is sourced from nearby countries and restricted ground water resources are not expected to offer large volumes (Scholes, 2001).

The necessity for clean water is additionally highlighted by the reality that, water insufficiency and shortage in the emerging country like South Africa is directly related to the dominance of poor quality, lack of food and sickness (Falkenmark, 1994, Ashton and Haasbroek, 2002). Previously, water resource management which confirmed the growing water demand through a multifaceted structure of engineering provided plane solutions which are inclusive of water basin transfer and pumping schemes in massive distance (Smakhtin et al., 2001).

Ashton (2002) made a comparison that; allocation of water resources in African continent are enormously unpredictable and water provisions are inequitably allocated in geological coverage compared to the rest of the world. Most regions of the African continent focused to sequence of long-lasting and severe droughts and in most cases; these droughts are broken by evenly flood situations (Costa et al., 2012).

In most African countries, population have grown noticeably over the last hundred years; this trend is likely to carry on although at a lesser rate, regardless of the mortality caused by the HIV/AIDS epidemic that is also far-reaching across many parts of Africa as a whole (Whiteside and Sunter, 2000, Ashton and Ramasar, 2002).

The growing shortage of water has made it an elevated service which is tradable. This shortage follows the ecological network commodity that influence water delivery which also turn out to be expensive (Turpie et al., 2008). Figure 2.2 shows that for the most part of South Africa as a region, surface water originates from elevated height grassland areas dominated by the Drakensburg Mountains and the Cape Mountains (Driver et al., 2004).

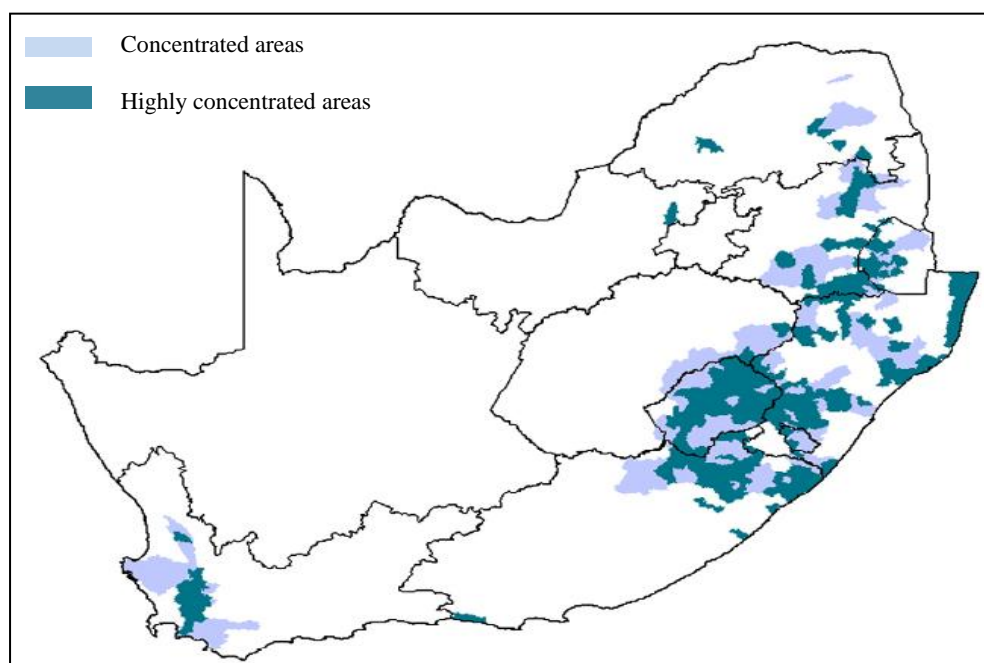


Figure 2.2 Regions of where the surface water originates in South Africa (Driver et al., 2004)

2.2 Volatile Aromatic Fractions (BTEX)

In reference to what Organization of Petroleum Exporting Countries (OPEC, 2011) stated; requirement for energy has elevated from 5.5×10^6 barrels of oil per day in year 1960 to 2.27×10^6 barrels of oil per day in year 2008. Energy requirement will maintain an upward trend as economies enlarge, the world population increases and living conditions enhances (Costa et al., 2012). It is noted that there are apparent environmental concerns correlated to the management of fresh mineral deposits around the world, knowing the universal background of growing petroleum demand and production.

The chemical composition of refinery waste water is subjective to the character of the geographical formation. Produced water can have a variety of dangerous compounds of

normal foundation, for example volatile aromatic fractions of the oil (inclusive of BTEX), polycyclic aromatic hydrocarbons (PAH's), high salt concentration, phenols, alkylated phenols, organic acids, as well as metals and radionuclide's (Dorea et al., 2007).

Compounds which include aromatics such as mono aromatic hydrocarbons, for example BTEX, are in the midst of the most important contaminants of produced waste water (Costa et al., 2012). If humans are exposed to these compounds, this might lead to health problems such as mucous membranes, irritation of eyes and nervous system failure, cancer and reduced bone marrow diseases (Laleh et al., 2011). From all BTEX compounds, benzene proved to be the one which is more toxic and is categorized by the World Health Organization as a strong carcinogen, sitting at the sixth place in the record of hazardous substances (Mathur et al., 2007).

With reference to Finlayson-Pitts and Pitts (1997), ozone is principally created by photolysis of nitrogen oxide and then dissociate in the presence of sunlight to form an electronically charged atom which reacts with water vapour to produce a hydroxyl (OH^\cdot) radical. Then OH^\cdot radical oxidises the organic compounds which will then change nitrogen oxide to nitrogen dioxide, then the cycle resumes (Hart and Schuetz, 1966). A high concentration of ozone in the troposphere is related with damage to vegetation and harmful health impact (Atasoy et al., 2004, Zunckel et al., 2004). Hence VOCs must be monitored, regulated and controlled.

The VOCs are significant because of their impact on the environment and human health however, BTEX compounds are viewed as the largely harmful compared to other compounds from their group in the petrochemical industry (Graham et al., 2001). BTEX compounds are vital members of the family of organo-pollutants which are components of aviation fuel and gasoline which are greatly used in industrial processes (Cavalcanti et al., 2012). According to Yadav and Reddy (1993), BTEX compounds are neurotoxic and carcinogenic hence are categorized as main concern pollutants by the Environmental Protection Agency (EPA). It has been proven that they can be degraded by anaerobic and aerobic bacteria. Table 2.2 presents BTEX kinetic and thermodynamics properties.

Table 2.1: Physico-chemical properties of BTEX compounds.

Compounds	Chemical Formula	Molecular Weight (g/mol)	Ha (atm.m ³ /gmol)	Vapour Pressure ^b	Boiling pt. ^c (K)	Molar volume ^d (m ³ /mol)
Benzene	C ₆ H ₆	78.11	5.50×10^{-3}	0.125	353.2	0.096
Toluene	C ₇ H ₈	92.14	6.68×10^{-3}	0.037	383.8	0.118
Ethylbenzene	C ₈ H ₁₀	106.17	6.44×10^{-3}	0.013	409.3	0.141
o-Xylene	C ₈ H ₁₀	106.17	5.27×10^{-3}	0.009	417.6	0.144

^aValues were obtained from (Atasoy et al., 2004) at 298K, ^bvalues calculated from Antoine's equation (Antoine's constants found in (Sinnot, 1999)), ^cvalues obtained at 1 atm from (Sinnot, 1999), ^dvalues at normal boiling point obtained from (Lee et al., 2004)

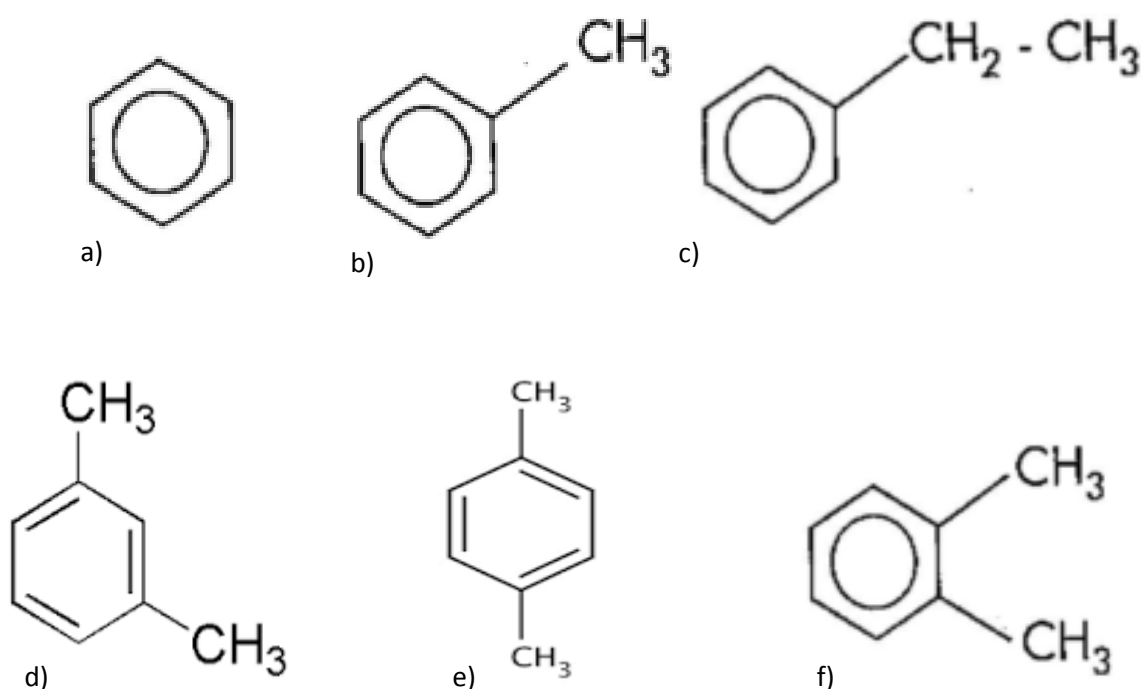


Figure 2.3: Molecular structure of adsorbates (a) benzene; (b) toluene; (c) ethylbenzene; (d) m-xylene; (e) p-xylene and (f) o-xylene (Burrows et al., 2009).

2.2.1.1 Benzene

Benzene is said to be a colourless, clear liquid with a sweet aromatic odour (Aivalioti et al., 2010). Hart and Schuetz (1966) states that benzene can be treated as the parent compound of

all other aromatic substances. The coal tar is said to be a significant resource of benzene and huge amounts are formed during petroleum refining by aromatization of alkenes (Hart and Schuetz, 1966). Benzene escapes when fossil fuels are burnt and also when gasoline evaporates (Lee et al., 2004). According to Yadav and Reddy (1993), exposure to benzene over a period of two weeks has sensitive health effects such as dizziness, headaches, skin irritation and eye infections. Over a longer period than a year, these effects can become chronic and these chronic illnesses may include reproductive problems in women, aplitic anaemia leukemia and cancer.

2.2.1.2 Toluene

Toluene is a colourless, clear liquid with a sweet aromatic odour which is almost similar to benzene odour. It originates from crude-oil fuels and it also escapes during the process of making gasoline. It is a highly flammable liquid, it can decompose at high temperatures to form toxic gases since its vapour is heavier than air. Yoon and Park (2002) states that, toluene is dangerous to the kidneys, liver and central nervous system when it comes into contact with the body by inhalation or by skin contact.

2.2.1.3 Ethyl-benzene

Ethyl-benzene is a colourless liquid with a smell which is similar to gasoline and has a molecular formula of C_8H_{10} . Ethyl-benzene is used in automotive fuels and aviation in the manufacture of the precursor to styrene and cellulose acetate. It may be released into the atmosphere from fugitive emissions from its use in gasoline and other industrial fuels. Ethyl-benzene is also documented to have chronic health effects and also to have acute effects but not enough information is available in this regard. EPA does not classify this compound as a carcinogen in humans (Weber, 1972).

2.2.1.4 Xylene

Xylene is classified as the most complicated compound amongst the other three. It has three dissimilar isomers, meta-, ortho-, and para-xylene. All these three forms will formulate a compound which is called xylene. Xylene occurs naturally in coal and oil refineries, and mainly used in solvents in the rubber, printing and leather industries. EPA does not classify Xylene as a carcinogenic to humans (Weber, 1972). Xylene is like toluene, it may be toxic to the kidneys, liver and central nervous system when they enter the body by inhalation or by skin contact (Yoon and Park, 2002).

2.3 Existing Technologies

2.3.1 Chemical oxidation

Chemical oxidation treatment of organic compounds is a process performed on waste water either to plan a detailed noxious waste for elimination or to accurately choose to change the toxicity of a contaminant by varying its chemical structure. This kind of process needs the utilization of influential chemical oxidizers in order to eliminate and demolish organic contaminants within contaminated waste water (Weber, 1972). Among the various oxidizing agents used in treating wastewater are ozone, potassium permanganate, chlorine dioxide, chlorine and hydrogen peroxide (Weber, 1972, Lagrega et al., 1994). Recently, the combination of ultraviolet light ozone and hydrogen peroxide was applied in various advanced oxidation technologies in treating recalcitrant organic compounds (Kurniawan et al., 2006).

Ozone is applied as a tertiary waste water treatment method for removing resistant organic compounds after the bulk removal of the compound has been accomplished by less expensive processes. The ozone oxidation process occurs also by the production of the hydroxyl radicals because of ozone breakdown and succeeding attack by the radicals on the contaminant or straight electrophilic attack of the ozone fragment of the contaminant (Kurniawan et al., 2006). Utilization of ozone as an oxidant does not formulate any contaminants at a secondary level in the environment in reference to the carcinogenic halogenated hydrocarbons and/or chlorinated by-products obtained during the application of chlorine as oxidants (Fettig et al., 1996).

Hydrogen peroxide alone is not efficient enough in degrading organic compounds because of its sluggish reaction rates with organic compounds and also its self disintegration. However, its ability to remove organic compounds depends on a transitional relationship to produce hydroxyl radicals, OH^\cdot and HO_2^\cdot (Neyens and Baeyens, 2003), and these hydroxyl radicals are responsible for the elimination of organic compounds from aqueous solution (Pera-Titus et al., 2004).

2.3.2 Biological treatment process

Biological treatment processes can be achieved by the transformation or degradation of organic wastewater by specific microorganisms, including aerobic and anaerobic bacteria and fungi (Lagrega et al., 1994). Biological processes such as advanced oxidation process, trickling filters and aerobic digestion are by far the most feasible and cost effective processes

for removing inorganic and organic elements from wastewater (Kornaros and Lyberatos, 2006). Convectional treatment method is utilized in the United States of America which includes coagulation, reverse osmosis, chemical oxidation, sono-chemical treatment, filtration and an electrochemical method (Lagrega et al., 1994).

A trickling filter is a genetic process developed for treating mixed effluent wastewater and it is operated aerobically in a continuous and/or sequential set reactor function approach. The process begins in a dynamic column or reaction tank consisting of bacterial supporting expansion substance (silica gravel), waste water and the filter. Kornaros and Lyberatos (2006) established that convectional genetic treatment methods for treating organic compounds are not the largely successful means of eliminating contaminants produced from organic amalgamation operations. This is due to the formation of the unacceptable population of microbial, elevated intractable occurrence and higher concentration of poisonous organic compounds (Kornaros and Lyberatos, 2006).

2.3.3 Air stripping

Stripping of air is a phase change process which is used in removing volatile organic compounds from contaminated wastewater by providing contact between the wastewater and gas (air), where the air stream acts as a means of transferring the pollutant into the atmosphere (Lagrega et al., 1994). The transferred pollutant also causes air pollution thereby increasing the operation complexity and the cost of cleaning the air in a stripper unit. This process is not practicable when the concentration of the pollutant has a low Henry's law constant (Haas and Vamos, 1995) less than 100 atmospheres. The management of acrylonitrile – butadiene – styrene (ABS) resin waste water was carried out using air stripping methods based on economical and environmental considerations (Crook et al., 1978). Chang et al. (2006) utilized the combination of air stripping and biodegradation for the elimination of BOD from waste water using a pilot – scale submerged membrane bioreactor.

2.3.4 Organic removal using membrane technology

Membrane filtration processes can be generally defined as a separation route that uses semi-permeable membrane to split the inlet flow into two portions: permeate that contains the substance that transient through the membranes, and retentate material being left after (Mallevalle et al., 1996). Specifically, membrane filtration can be better explained and grouped in relation to the range variety of the permeating group, the mechanism of negative

response, the driving force engaged, and the chemical configuration and geometry of construction (Suzuki and Motoyuki, 1990). Most importantly, the types of membrane filtration methods are pressure-driven processes including reverse osmosis (RO), nano filtration (NF), ultra filtration (UF) and microfiltration (MF).

According to Zhou and Smith (2002) the distinction in the size of the membrane pores and dissimilar membrane processes proved vast inconsistency in eliminating organic compounds. Generally, microfiltration and ultra filtration are not efficient in eliminating dissolved organic compounds in surface water management, where a usual efficiency of less than 15% is shown. However the elimination efficiency can be enhanced to a degree by utilizing coagulation as a pre-treatment. Zhou and Smith (2002) further states that the maximum removal was experimentally demonstrated at a coagulation pH range of 5 to 7, equivalent to the highest adsorption of natural organic matter (NOM) on the coagulation flocculants.

In comparison, NF and RO processes were successful in reducing many compounds including NOM elements. It was recommended that NF might be preferable to GAC adsorption for total organic carbon (TOC) and dibutyl phthalate (DBP) antecedent elimination from water origins with TOC concentrations above 8.1 mg/L (Noll et al., 1994).

Membrane and filtration processes are also utilized to eliminate various dissolved organic elements from industrial and municipal waste water (Mallevialle et al., 1996, Brindle and Stephenson, 1996). Recommended applications consider the division of organic dye-stuffs from textile processing waste streams, decolourization of pulp mill waste streams, oil concentration from oil-field salty water and fuel producers and land fill leachate management (Weber and Benjamin, 1980). For cost-effective reasons, these applications are partial to cases where waste water and/or contaminants can be improved.

2.3.5 Adsorption process

Adsorption is a process of accumulating substances that are in a solution onto a suitable interface or boundary. Adsorption, as noted by Metcalf and Eddy (2004) is an accumulation of mass transfer operation in that a component in the liquid state is transferred and moved to the solid state. An adsorbate is the substance that is being eliminated from the liquid phase at the suitable boundary. An adsorbent is the gas, liquid or solid part onto which the adsorbate accumulates. Metcalf and Eddy (2004) state that the adsorption as a process has not been utilized lengthily in waste water management but require a superior excellence of treated

waste water streams which might lead to a rigorous assessment and utilization of the adsorption process on activated carbon as an adsorbent.

There are different forms of adsorbents which comprise of polymeric, synthetic, activated carbon and silica-based adsorbents. However it is highlighted that silica-based and synthetic polymeric adsorbents are not frequently used for waste water adsorption due to expenditure being high. However, activated carbon is widely used in sophisticated waste water management applications; the focus of this project is on activated carbon and a synthetic polymeric as an adsorbent resin.

2.3.5.1 Activated carbon

Activated carbon is a granulated carbon-material that is transformed to activated carbon by thermal decomposition in a furnace using a controlled atmosphere and heat (Metcalf and Eddy, 2004). This product has an extremely large surface area per unit volume and a network of sub microscopic pores where adsorption is concerned (Lei et al., 2006).

This adsorbent is a black carbonaceous, porous and solid material. GAC is distinguished from fundamental carbon by the lack of oxidized surface (Mattson and Mark, 1971). Carbon (which is activated) can be prepared from a great number of sources for example as cellulose residues, peat, coconut, coal, and wood (Lambiotte, 1942). It is important to note that a carbon source can be transformed into an activation and carbonization state. Usually, the process is separated into activation and carbonation. For the duration of carbonization, mainly the non-carbon elements are eliminated in the gaseous type by the pyrolytic disintegration of the supply material. A porous structure is generally developed for the period of activation by means of an activation agent that reacts with the carbon. Such agents may contain bases and synthetic acid substances in a stream of activating gases such as nitrogen (N_2), carbon dioxide (CO_2) or steam (H_2O).

Activated carbon as an adsorbent has larger surface areas and larger pore volume, which makes this adsorbent more suitable for a wide variety of applications. The adsorbent can also be used as a decolourizing driving force, an odour or taste eliminating material or as a refinement agent in processing of food (Lee et al., 2002). Another use of this type of adsorbent is in water purification, as well as the making of drinking water and management of waste and ground water (Podoll et al., 1989). Treatment of water accounts for approximately fifty percent of the total utilization of activated carbon in the United States of America (Baker et al., 1992). The other uses include its utilization as an adsorbent for

pollution control in an array of filters (Ashford, 1994). This adsorbent is also used as a major adsorbent in filters and canisters since it adsorbs a wide spectrum of organic compounds, it is less expensive and it can be reused if the adsorbed matters are cleaned out. This process is called regeneration, it is likely to be achieved by heating (Battelle, 1992).

Granular activated carbon is formed in a range of final products; cylindrical extrudates, granules, spherical beads, and fibres (Suzuki and Motoyuki, 1990). The model that is slit-shaped in Fig. 2.3 represents the micro structure of a typical activated carbon (Stoeckli, 1990)

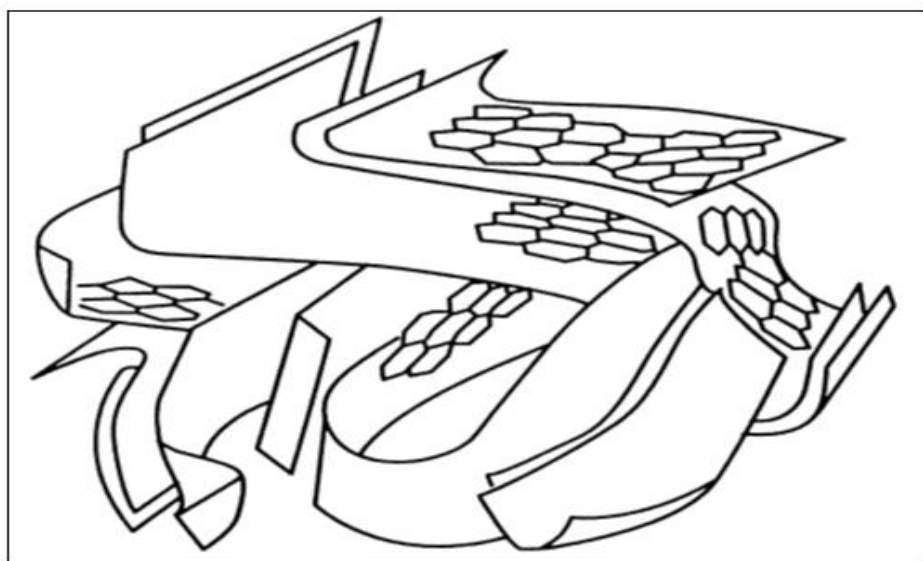


Figure 2.4: A schematic representation of the structure of activated carbon. (Adapted from (Stoeckli, 1990)).

The most vital property of activated carbon is the property that confirms its usage which is the pore structure (Lambiotte, 1942). Total number of pores, their size and shape establish the adsorption capacity and also the active adsorption rate of the activated carbon (Crittenden et al., 2000). The complex network of pores of activated carbon, its specific surface area and surface chemistry are some critical properties to the efficiency of the adsorption process (Kurniawan et al., 2006). IUPAC (1985) categorized the network of pores into three: macropores ($d_0 > 50$ nm), meso-pores ($2 \leq d_0 \leq 50$ nm) and micro-pores ($d_0 < 2$ nm), where d_0 is the pore width for slit pores or pore diameter for pores that are cylindrical.

A pore structure is dependent robustly on the nature of the raw material and activation process (Lozano-Castello et al., 2001). However, according to Bansal et al. (1998) by varying activation process parameters such as activating agent, oxidant flow rate, and temperature,

the adsorbent with different adsorptive properties can be formed from the identical initial material.

2.3.5.2 Adsorbent resin (PAD 910)

PuroSorb PAD 910 is one of a range of polymeric adsorbents. The range includes many products which offer variations in their chemical, physical structure (pore volume, surface area) and particle size range (Ahmaruzzaman and Sharma, 2005). This resin has the largest pores within the current range and is macroporous, non-ionic, polymeric adsorbent designed to remove hydrophobic organic compounds from aqueous solutions and polar solvents. Its special properties are derived from having a cross-linked polystyrenic structure incorporating pores, which can be as large as 1200 angstroms (USEPA, 2010). Figure 2.4 shows a structure of a hydrophobic bead resin bead and enlarged microspheres of the bead.

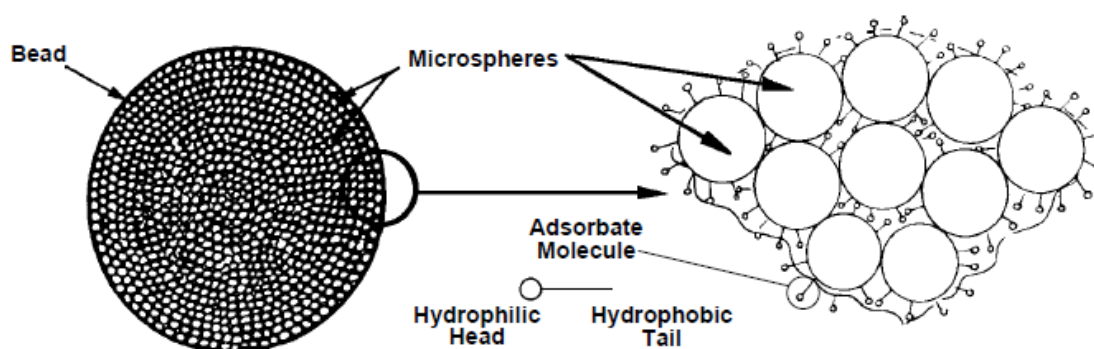


Figure 2.5: A structure of a hydrophobic, macro-recticular resin bead. (Adapted from Cabal et al. (2009))

Resin with oil affinity is vital to the coalescence process and probably inclined to several factors (Yang et al., 2007). The surface electrostatic hydrophobic characteristics of the resin are two major factors that considerably manipulate the oil-resin similarity and the oil elimination success in coalescence processes. The hydrophobic characteristic of a material that has a solid surface can be related with the link between liquid and solid interface (Battelle, 1992). There are available methods for measuring contact angle of particles based on sessile drops, bubbles on compressed discs and liquid penetration into particle beds (Yang et al., 2007). Determination of contact angle of the packing medium directly because of its non uniform grading, surface roughness and shapes is always difficult. It is noted that the

resin coalescence is comparable to a porous particle bed. The Washburn equilibrium capillary pressure test (Chang et al., 2009) can be engaged to assess the hydrophobic characteristic of the modified and base resin with regards to water/oil wet capability.

2.3.5.3 Carbon regeneration and reactivation

Cost-effective application of activated carbon is mostly due to an efficient effort of regenerating then reactivating the carbon after its adsorptive capacity has been exhausted (Mohan et al., 2001). Regeneration is the relative term used to illustrate all the processes that are used to improve the adsorptive competence of the used carbon, excluding reactivation, including: (i) chemicals to oxidize the material that has been adsorbed, (ii) steam is needed to drive the material that has been adsorbed, (iii) solvents and (iv) biological conversion processes (Vijayaraghavan et al., 2006).

Typically some of the adsorptive capacity of the carbon (about 4 to 10 percent) is also lost in the regeneration process, depending on the compounds being adsorbed and the regeneration method used (Crittenden et al., 2000). In some applications, the capacity of the carbon following regeneration remains essentially the same for years. A major setback for the utilization of activated carbon is the fact that a systematic method for its regeneration is not defined well. Battelle (1992) further details the regeneration methods in his study.

Reactivation of granular carbon includes fundamentally the equivalent process used to generate the activated carbon from fresh virgin material. Used carbon is reactivated by introducing it into a furnace and then by oxidizing organic material that has been adsorbed, then eliminating it from the surface of the carbon (Sahu, 2009). The following sequence of events occurs in the reactivation of spent activated carbon: (i) carbon is heated to drive off the absorbed organic material, (ii) in the process of driving off the absorbed material some new compounds are formed that remain on the surface of the carbon, and (iii) the final step in the reactivation process is to burn the newly formulated compounds which were formed during the burning off the material that was adsorbed already (Cavalcanti et al., 2012).

With effective process control, the adsorptive capacity of reactivated carbon will be essentially the same as that of the virgin carbon (Crittenden et al., 2000). For planning purposes, it is often assumed that a loss of 2 to 5 percent will occur during the reactivation process (Gou and Rockstraw, 2007). Thus, it is imperative to highlight that most other losses of carbon occur through attrition due to mishandling. In general, a 4 to 8 percent loss of

carbon is understood; which might be caused by handling. Stock of new carbon must be available so as to make up for the losses (Hall et al., 2009).

No matter how well the adsorbent polymer removes the species, the ability to readily generate will probably be the determining factor to choose one adsorbent over another (Allen-King et al., 2002). Hence, it is vital that a consideration of the way in which a compound is disassociated from the adsorbent is made. Steam and water (60°C) are possibilities for elution and regeneration, however because the products that are being separated are sensitive to temperature, this might not be an ideal way. In this case a solvent might be considered. A solvent might enable the interaction of the compound with the polymer adsorbent thereby giving selective desorption (Aivalioti et al., 2012).

According to Pera-Titus et al. (2004), another possibility might be to change the pH, possibly changing the strength of the charge and eluting the species that is being captured (Lei et al., 2006). The physical and chemical strength of PAD 910 polystyrenic adsorbents will provide unique techniques and options, no matter what process is chosen to elute and regenerate the adsorbent (Balan et al., 2009).

2.3.5.4 Factors affecting adsorption

Primarily, the factors that have the potential to influence an adsorption process are: (a) Adsorption condition: this could be the pH of the solution, the temperature under which the experiments are carried under, the mixing strength and the initial concentration of the aqueous solution. The pH of the solution is more relevant in the case of adsorbates that are electrolytic in nature, as this will determine the electrostatic force of attraction (or repulsion) that take place during the adsorption process. Likewise, for aqueous phase adsorption process, mass transport is less temperature sensitive since there is limited random molecular motion. As a result, the effect of temperature was only investigated for the long time regime of equilibrium process to better understand the thermodynamics of the process. (b) Adsorbent properties: this could be the physical properties of the adsorbent such as the porosity or chemical properties like surface functionality. These factors were presented in section 4.1. (c) Adsorbate properties: the adsorbate's affinity and capacity onto the sorbent could be affected by such sorbate properties as the size, polarity and hydrophobicity.

A projected solution path to the proposed system is shown in Figure 2.6 to represent an outline of adsorption theory, problem related to adsorption and mechanism associated with sorption process.

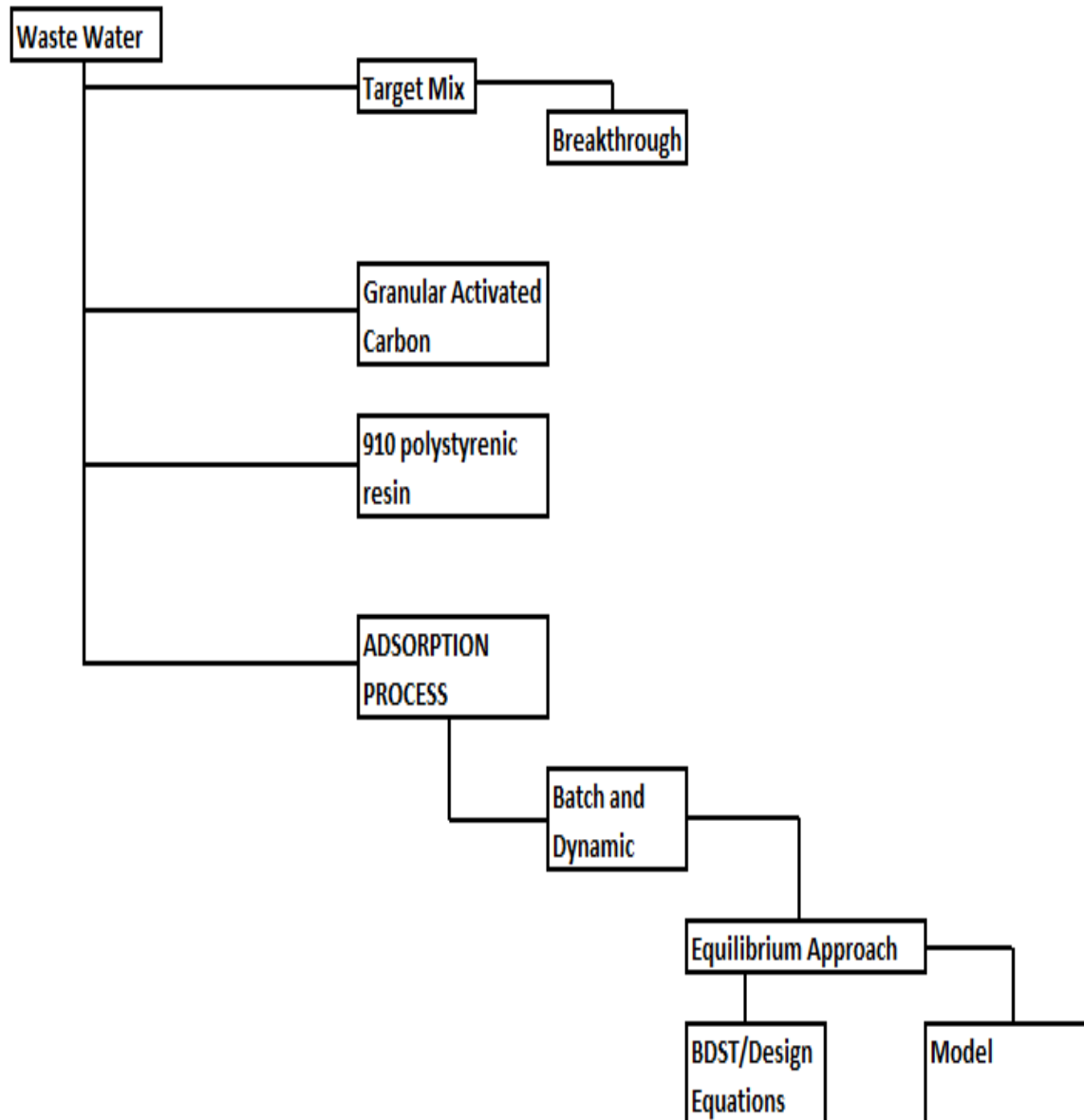


Figure 2.6: Adsorption approach for the solution to wastewater treatment

2.3.6 Available alternate approach for adsorption

The alternative approach to these existing technologies for the removal or management of organic waste accumulated by our society is the stabilization of organic waste using a liquid-phase adsorption process (Kurniawan et al., 2006). Liquid-phase adsorption demonstrates high efficiency for the elimination of organic compounds as well as heavy metals from the waste effluents because of its ease and the accessibility of a variety of adsorbents (Akgerman and Zardkoohi, 1999, Ahmaruzzaman and Sharma, 2005). The impact of surface features of activated carbon on adsorption of BTEX compounds was investigated by Daifullah and Girgis (2002). The study concluded that air oxidized activated carbon at a temperature of

352⁰C demonstrated a significant decrease in porosity over and above enhancement of capacity for BTEX compounds per unit area and an increase in acidity (Turpie et al., 2008).

Adsorption further compares to the sticking together of ions, atoms, molecules of gas or bio-molecules, liquid or dissolved solids (adsorbate) onto a surface (adsorbent). Adsorption occurs either as physical adsorption (also called physisorption) or chemical adsorption (also called chemisorption) (Costa et al., 2012).

2.3.6.1 *Physical versus chemical adsorption*

The categorization of an adsorption process is initiated on the force of attraction between the adsorbent surface and the adsorbate. According to IUPAC's recognised definition, 'chemisorption is adsorption where the forces concerned are called valence forces of the identical type with the one operating in the development of chemical compounds while physisorption is adsorption where the forces concerned are called intermolecular forces (van der Waals forces) of the identical type as the one liable for the deficiency of the condensation of vapours and the real gases and which no significant changes in the electronic orbital patterns of the species are involved' (Everett, 1971). Table 2.2 contrast the physical and chemical adsorption approach which can be used independently of each other.

Table 2.2: Differences between physisorption and chemisorption (Everett, 1971)

Physisorption	Chemisorption
1. Occurs in any solid/fluid system	Categorized by chemical specificity
2. Confirmation for the electronic states of adsorbent and adsorbate is minimal	Changes in the electronic condition may be measurable by an appropriate physical means (e.g. U.V., infrared or electrical conductivity)
3. Adsorbed species are chemically matching with those in the fluid phase, hence reversible	Chemical nature of the adsorbate(s) may be altered, hence might be irreversible.

4. The energy of interaction between the molecules of adsorbate and the adsorbent is usually low	Energy of chemisorption is of the similar order as the energy change in a chemical reaction. (high heat of adsorption).
5. There is no involvement of activation energy	Elementary step in chemisorptions likely to involve an activation energy
6. Establishment of equilibrium between the fluid phase and the adsorbate	Activation energy for adsorption is huge, accurate equilibrium may be obtained slowly
7. Under appropriate conditions, molecules can be adsorbed in surplus of those in straight contact with the surface (multilayer adsorption)	Adsorbates normally inhabit certain adsorption sites on the surface and only one layer of chemisorbed molecules is formed (monolayer adsorption)

2.4 Exposure Limits

The South African Occupational Health and Safety Act, No. 85 of 1993 had set exposure limits for diverse chemicals including toluene, benzene, and xylene ethylbenzene in the industry. The occupational exposure limit – control limit (OEL-CL) like threshold limit value (TLV) is said to be the highest concentration of an airborne substance averaged over a particular period to which workers may be exposed to by inhalation or skin contact. The occupational exposure limit – recommended limit (OEL-RL) is defined as the concentration of an airborne substance averaged over a reference period. In reference to present knowledge, currently no evidence has been brought forward to prove that it can harm the workers.

The effect of harmful chemicals on human health due to contact is dissimilar, depending on the nature of the substance and exposure time frame. Hence, there are diverse characteristics of TLVs. The extended period of exposure limit (eight-hour time as a weighted average) is planned to control and confine the overall intake by inhalation not more than one shift cycle. The little period exposure limit (over fifteen minutes) may also be applied to substances for which effects may be seen after brief contact which has occurred once or on numerous occasions. Table 2.3 shows the exposure limit for each organic compound as stipulated by OHSAct (85) of 1993. Benzene is the only compound with an extended period control limit.

Table 2.3: Exposure limits allowable values for BTEX organic compounds. Adapted from OSHAAct (85) of 1993

Exposure Limit	Toluene mg/m ³	Ethylbenzene mg/m ³	Xylene mg/m ³	Benzene mg/m ³
OEL-RL (shorter period)	560	545	650	-
OEL-RL (extended period)	188	435	435	-
OEL-CL (extended period)	-	-	-	16

2.4.1 In aquatic organisms

Toxicity tests of BTEX compounds have also been carried out on aquatic organisms. Normally water concentrations above 1 mg/L are obligated to generate acute toxic effects in organisms such as daphnids, fish and algae. The low concentrations of these chemicals in water, their low to moderate toxicity and rapid volatilization result in the total risk to the marine environment regarded as low. However, it can be noted, that higher concentrations of these chemicals can occur in water at polluted sites (USEPA, 2010).

2.5 Adsorption Kinetics

Several attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid-solid phase sorption systems. Existing kinetic models in the literature are easily grouped into two: empirical models and mechanistic models.

2.5.1 Empirical models (Global Rate Models)

The sorption process of organic compounds, for example aromatic rings onto ordinary sorbents has been concluded on a molecular level as a complex process by models which

involve complicated mathematical computations (Valderrama et al., 2007). Hence, attempts at simplification have been considered on a macroscopic scale for practicality and ease of understanding the process of sorption and probable rate controlling sequence such as chemical reaction and mass transport rate processes. Looking at the macroscopic view point, three global kinetic rate models are often used in the literature, which are: pseudo-first-order kinetics, pseudo-second-order kinetics and the Elovich model.

2.5.1.1 Pseudo-first-order

Lagergren was the first author to represent the pseudo-first order equation for the sorption of malonic acid and oxalic acid onto charcoal (Lagergren and Svenska, 1898). The model is commonly articulated as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2-1)$$

Where q_e and q_t are the sorption capacities at equilibrium and at a particular time t , correspondingly in mg/g and k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). Then after integrating and applying the boundary $q_t = 0$ at $t = 0$ and q_t at $t = t$, equation (2-1) yields:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2-2)$$

The rate constant is attained by a linear regression examination of the $\log(q_e - q_t) = f(t)$ function in equation 2-2 above. Ho and McKay (1998) made an observation that most literature shows that, the pseudo-first-order equation of Lagergren (Lagergren and Svenska, 1898) less fits the entire range of contact time, and is basically applicable over the first 20 – 30 minutes of the sorption process.

2.5.1.2 Pseudo-second-order

Chang et al. (2004b) and Vinod and Anirudhan (2003) are some examples of researchers who have used the pseudo-second-order equation originated from the sorption equilibrium capacity. The equation is represented as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2-3)$$

Integrating equation (2-3) with the boundary conditions gives:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2-4)$$

Where k_2 is the pseudo-second-order rate constant ($\text{g.mg}^{-1}.\text{min}^{-1}$) and together with the q_e is obtainable by a linear regression analysis of the $t/q_t = f(t)$. Ho and McKay (1998) introduced two new parameters which are: initial adsorption rate $h_0 = k_2 q_e^2$ which defines the rate of adsorption as time approaches to zero; and adsorption half life $t_{1/2} = \frac{1}{k_2 q_e}$ which defines the time necessary for adsorption to reach 50% of the equilibrium capacity. Intra-particle diffusion model based on the theory proposed by Weber and Morris (1963) was tested to identify the diffusion mechanism. According to this theory, $q_t = k_p t^{1/2}$. Hence, equation 2-4 can also be presented as:

$$t^{1/2} = \frac{tk_p}{1/h_0 + t/q_e} \quad (2-5)$$

2.5.1.3 The Elovich model

The Elovich model is based on adsorption capacity as established by the work of Zeldowitsch (1934). It is presented as:

$$\frac{dq_t}{dt} = a \exp(-bq_t) \quad (2-6)$$

where q_t is the sorption capacity at particular a time, t in mg/g , a and b are defined as the Elovich parameters related to the desorption constant (g.mg^{-1}) and the initial sorption rate ($\text{mg.g}^{-1}.\text{min}^{-1}$) during any one experimental run, respectively.

On integrating equation (2-6), applying the earlier stated boundary conditions, Chien and Clayton (1980) further simplified the Elovich equation by assuming $a, b, t \geq 1$, thus arriving at:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln(t) \quad (2-7)$$

a and b are obtained by the linear regression analysis of the function $q_t = f(t)$.

2.5.2 Mechanistic models

According to Yu and Zhang (2006); from a molecular perspective, the adsorption of aromatic hydrocarbon molecules and also any adsorbate from an aqueous phase system onto activated carbon has generally been described to proceed in three successive steps, namely:

- Transport of molecules from the bulk of the solution to the exterior surface of porous carbon particles through a boundary layer (external diffusion or liquid film);
- Diffusion process of the aromatic hydrocarbons from side to side of the interior pores of the carbon (internal diffusion or intra particle); and
- The adsorption of aromatic hydrocarbons molecules onto the active sites on the interior surface.

All these steps are schematically represented in Figure 2.7.

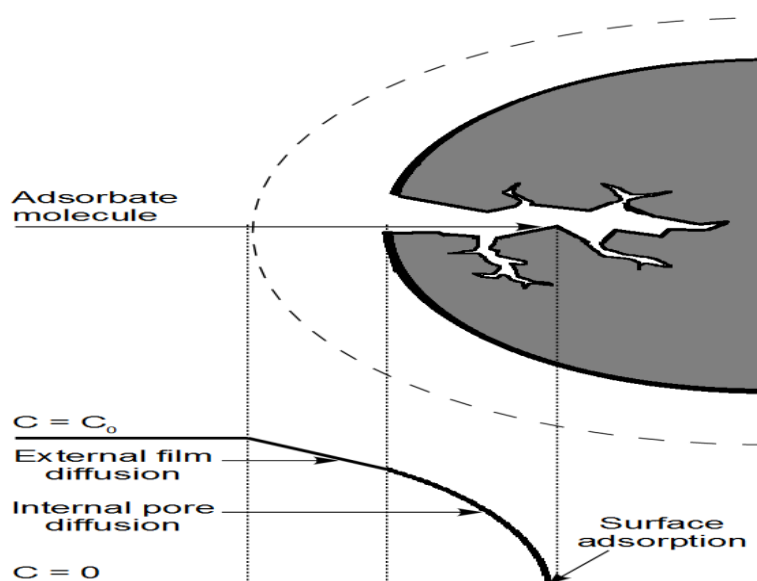


Figure 2.7: Schematic diagram of a heterogeneous adsorption process (Noll et al., 1994)

All three steps could potentially have an effect on adsorption kinetics, mean while the third step also controls the intensity and the specific adsorption capacity. Generally, one of three steps offers a greatest resistance and is thus referred to as the rate limiting action of the whole sorption process. It is however noted that, unless chemical modifications occur during the sorption process, the third stage is presumed to be too quick to contribute significantly to the entire sorption rate (Valderrama et al., 2008). It is then normally understood that sluggish sorption kinetics emanates from the rate-limiting diffusive mass transfer (Ball and Roberts, 1991, Wu and Gschwend, 1988).

2.5.2.1 Film diffusion model

The work published by Mohan et al. (2001) highlighted the conditions under which the film diffusion controls the rate of adsorption. They are under-listed as:

- i. Low adsorbate concentrations;
- ii. Poor mixing;
- iii. Small adsorbent particle size;

Importantly it is noted that even in the absence of these conditions the film diffusion still controls the initial stage of any adsorption process, since the last two steps take some time to set in. The equation proposed to govern a film diffusion controlled adsorption process is given by:

$$\ln\left(\frac{C}{C_0}\right) = -k_s \frac{S_s}{V} t \quad (2-8)$$

where: k_s is defined as the diffusion coefficient in m/s; S_s is the external adsorbent surface area in m²; t is time in seconds and V is the solution volume, in m³.

2.5.2.2 Intra-particle diffusion models

Numerous models have been used to explain the intra-particle diffusion of adsorbates into the porous structure of activated carbons. The research work by Valderrama et al. (2008) fitted their hydrocarbons adsorption experimental data to the homogeneous particle diffusion model (HPDM) which is a kinetic model based on solute extraction as discussed by Helfferich (1962) whilst another classical model employed by many researchers is the Weber-Morris intra-particle diffusion model (Weber and Morris, 1963).

a) The homogeneous particle diffusion model (HPDM)

This model applies the diffusion of adsorbates onto a homogeneous adsorbent surface, assuming unlimited dilution, diffusion rate and spherical particle geometry controls the adsorption process. In a similar work Valderrama et al. (2008) gave a solution of the algebraic equations and simultaneous set of differential equations from this model as:

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{z=1}^{\infty} \frac{1}{z^2} \exp\left[\frac{-z^2 \pi^2 D_e t}{r^2}\right] \quad (2-9)$$

The fraction $\frac{q_t}{q_e}$ is referred to as the fractional accomplishment of equilibrium at time t , denoted by $X(t)$. A simplification of equation (2-9) by the Vermeulen's approximation where the whole range fits $0 < X(t) < 1$ for sorption on spherical particles, gave the expression:

$$-\ln(1 - X^2(t)) = 2Kt, \quad \text{where } K = \frac{\pi^2 D_e}{r^2} \quad (2-10)$$

Parameters in equation (2-9) and (2-10) are defined as follows: t (time in seconds); r (average particle radius in m); D_e (effective diffusion coefficient in solid phase in m.s^{-1}). Linear regression analysis of the left hand side of equation (2-10) versus time yields the mass transfer parameter K from which D_e could be obtained.

b) Weber-Morris intra-particle diffusion model

Weber and Morris (1963) proved that if intra-particle diffusion is the limiting step, uptake would vary according to:

$$q_t = k_i \sqrt{t} + C \quad (2-11)$$

where: q_t is amount adsorbed (mg/g); k_i is intra-particle diffusion rate constant ($\text{mg.g}^{-1}.\text{min}^{-1/2}$), t is time in seconds; C is constant related to resistance offered by the boundary layer. The simplicity of this model has made it widely used in the literature (Graham et al., 2001, Cabal et al., 2009, Valderrama et al., 2008, Ho and McKay, 1998).

2.6 Adsorption Isotherms

The quantity of adsorbate that can be accumulated in an adsorbent is a function of the characteristics of the temperature and concentration of adsorbate. The characteristics of the adsorbate that are imperative include: hydrocarbon saturation, molecular structure, solubility, polarity and molecular weight. Normally, the quantity of material adsorbed is formed as a function of concentration under a constant temperature and the resulting function is called an adsorption isotherm (Metcalf and Eddy, 2004). Adsorption isotherms are formulated by exposing a given quantity of adsorbate in a constant volume of liquid to a changing quantity of an adsorbent.

Typically, more than six containers are used and the minimum time allowed for the samples to equilibrate where powdered activated carbon is used is seven days. If granular activated carbon is used, it is usually powdered to minimize adsorption times. The amount of adsorbate remaining in solution is measured at the end of the test period. The adsorbent phase concentration after equilibrium is calculated using Eq. (2-12). The adsorbent phase

concentration information calculated using Eq. (2-12) is used to formulate adsorption isotherms as shown herewith:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2-12)$$

Where: q_e is an adsorbent concentration after equilibrium (mg adsorbate/g adsorbent); C_0 is the initial concentration of adsorbate (mg/L); V is the volume of the liquid (L); C_e is the final equilibrium concentration of adsorbate after absorption has occurred (mg/L); m is a mass of adsorbent (g).

In the environmental application of sorbents, the predominant scientific basis for selection has been said to be the equilibrium isotherm, while diffusion rate is normally second in the order of importance (Yang, 2003). This is confirmed by the fact that when the diffusion rate is extremely fast a primary concern would be the capacity of the sorbent for the target compound within the functional temperature, concentration and pressure conditions as equilibrium is reached.

2.6.1 Classification of adsorption isotherms

According to IUPAC (1985) adsorption isotherms are categorized into six types and this helps better understand the origin of the adsorption process: micropore filling, monolayer, capillary condensation or multilayer adsorption. The categories are as given in the Fig. 2.8 below:

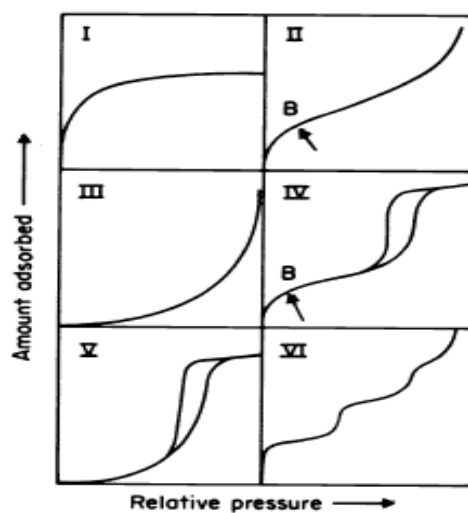


Figure 2.8: IUPAC Types of Adsorption Isotherms (IUPAC, 1985)

The Type I isotherms are defined by microporous solids in which the pore size is not very much greater than the molecular diameter of the sorbate molecule. As such, the restricted uptake is controlled by the accessible micropore volume with the saturation limit corresponding to the complete filling of the micropores. The Type II isotherm is defined with non-porous or macro porous adsorbent representing open monolayer-multilayer adsorption processes. At point B, the initial of the most linear middle section of the isotherm is often taken to demonstrate the stage at which the monolayer contact is complete and multilayer adsorption resumes.

Type III isotherm is u-shaped to the relative pressure axis over the overall range and hence it does not display a Point B (inflection point). They are uncommon and the adsorbate-adsorbate interactions assumes a vital role in this kind of system. Characteristic feature of the Type IV isotherm is the hysteresis loop connected with capillary condensation happening in mesopores. At the initial stage of the isotherm, the adsorption is credited to monolayer-multilayer adsorption since it follows the same trend as the equivalent part of a Type II isotherm. The Type IV isotherms are known by several mesoporous industrial adsorbents.

Type V isotherm is unusual and is associated to the Type II isotherm in that the adsorbant-adsorbate relation is weak, but is obtained with certain porous adsorbents. Then Type VI isotherm exhibits a stepwise multilayer adsorption on a uniform non-porous surface, where the sharpness of the order depends on the temperature and the system. The step-height demonstrates the monolayer capacity for each adsorbed layer and the remainder stay constant for two or three adsorbed layers.

2.6.2 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.

2.6.2.1 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.
- d) Equivalence of energetic sites.

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

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L q_{max}} \frac{1}{C_e} \quad (2-13)$$

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).

If all assumptions for the Langmuir model hold for any adsorption process, then the adsorption process will be defined by the Langmuir model. However, according to El-Dib (1975) the good fitting of the model to experimental results does not necessarily mean that the underlying assumptions have been characterized by the sorbent. Weber and Benjamin (1980) confirmed that it is unlikely to have the assumption of all sites being energetically equivalent even when the model fits experimental results very well. Therefore, this deviation limits the interpretation of the values a and b , although the value of a would not represent a practical limiting adsorption capacity for the sorbent under investigation.

2.6.2.2 Freundlich isotherm model

Contrary to monolayer and localized adsorption assumptions of the Langmuir model, Freundlich (1926) derived an empirical model with an exponential allocation of site energies and immobile adsorption. Ahn et al. (2005) suggested that there are multiple sets of sites on the surface of the adsorbent which is heterogeneous. The model is expressed as follows:

$$\frac{x}{m} = K_f C_e^{1/n} \quad (2-14)$$

Where: K_f is the Freundlich capacity factor (mg adsorbate/g activated carbon)(L water/ mg adsorbate)^{1/n}; C_e is the equilibrium concentration of adsorbate in solution after adsorption, mg/L and $1/n$ is the Freundlich intensity parameter (mg adsorbate/g activated carbon) x/m = mass of adsorbate adsorbed per unit mass of adsorbent (mg/g).

The Freundlich equation however does not give a limit of adsorption capacity (due to the $1/n$ th power of concentration), making the quantity adsorbed go to infinity when

concentration goes higher. This limits its application to concentrations below saturation where adsorption phenomena would no more be significant (Suzuki and Motoyuki, 1990). Over the past few years, the Freundlich isotherm has been criticized for its restriction of lacking a primary thermodynamic basis, when not approaching the Henry's law at diminishing concentrations (Ho et al., 2002).

2.6.2.3 Polanyi-Dubinin-Manes (PDM) isotherm model

According to Long et al. (2008), a major limitation of the Langmuir and Freundlich models have been the fact that even though they give good fits, they have not been able to mechanistically capture aqueous phase adsorption processes well nor can they forecast the adsorption equilibrium capacity of adsorbent from basic adsorbate properties. Then the adsorption promising theory further developed by Dubinin (1960) and Manes and Hofer (1969) referred to as PDM has been successfully applied to aqueous phase adsorption processes (Li et al., 2005, Allen-King et al., 2002).

The model provides a theoretical framework for the prediction of adsorption equilibrium capacities of adsorbents based on usually available adsorbate/adsorbent properties. This theory assumes a preset space adjacent to the adsorbent surface where sorption surface occurs, i.e. adsorption is also a process of micro-pore filling rather than surface adsorption process. In a given sorbate in this space, there is an existence of adsorption potential (ε) that depends on the immediacy to the surface and the origin of the sorbent, i.e. every point equidistant from the surface will have the same ε , which is defined as the energy necessary to move a molecule from its location in the adsorption space to a point outside the attractive force field of the sorbent surface.

Then the model is of the type:

$$\log Q_e = \log Q^0 + a(\varepsilon V_s)^b \quad (2-15)$$

Where: $\varepsilon = RT \ln \left(\frac{C_e}{C_s} \right) \quad (2-16)$

where Q_e is the equilibrium sorbed concentration (mol of adsorbate/g of sorbent); Q^0 is the adsorption capacity (mol/g); a and b are fitting parameters; ε is the effective adsorption potential (kJ.mol⁻¹); V_s is the molar volume of solute (ml.mol⁻¹); R is universal gas constant (8.314 x 10⁻³ kJ(molK)⁻¹); T is an absolute temperature (K); C_e is the equilibrium solution phase concentration (mol/L) and C_s is the aqueous water solubility (mol/L).

2.6.2.4 The Dubinin-Radushkevish 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):

$$q_e = q_D \exp(-\beta \varepsilon^2) \quad (2-17)$$

Where:
$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (2-18)$$

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 equation 2-17 is used in obtaining the parameter β from which the mean free energy in kJ/mol is obtained by (Hasany and Chaudhary, 1996):

$$E = \frac{1}{\sqrt{2\beta}} \quad (2-19)$$

2.6.2.5 Flory-Huggins isotherm model

The Flory-Huggins isotherm model (Horsfall and Spiff, 2005), which is occasionally used for deriving the amount of surface coverage description of adsorbate onto adsorbent, can convey the spontaneous nature and the viability of an adsorption process. Retrospectively, Θ is the amount of surface coverage, where K_{FH} and n_{FH} indicates model exponent and the equilibrium constant. This model equilibrium constant, K_{FH} which is utilized for the calculation of impulsiveness for free Gibbs energy, which is then correlated to the equation by Vijayaraghavan et al. (2006):

$$\Delta G^0 = -RT \ln(K_{FH}) \quad (2-20)$$

2.6.2.6 Hill isotherm model

The Hill equation which originates from the non ideal competitive adsorption (NICA) (Koopal et al., 1994) model, was postulated to define the fastening of dissimilar species onto homogeneous substrates (Hill, 1910). The Hill model is based on an assumption that the

adsorption is a mutual occurrence, where the binding ability at one site on the macromolecule may persuade dissimilar binding sites on the same macromolecule (Ringot et al., 2007).

2.6.2.7 Temkin isotherm model

This model is an early model which describes the adsorption of hydrogen onto platinum electrodes contained by the acidic solutions. According to Temkin and Pyzhev (1940) the isotherm has a factor that clearly takes into account the adsorbate-adsorbent relations. By eliminating the particularly large and low values of concentration, the model will assume that the heat of adsorption (which is a function of temperature) of all molecules in the layer would linearly decrease instead of having a logarithmic coverage (Aharoni and Ungarish, 1977).

The equation illustrates that the derivation is categorized by a constant allocation of binding energies for up to some maximum binding energy level. The Temkin equation is regarded as an excellent model for predicting the gas phase equilibrium, for example, when the medium is in a tightly packed structure with identical orientation. On the contrary multifaceted adsorption systems inclusive of the liquid-phase adsorption isotherms are normally not suitable to be presented (Kim et al., 2004).

2.6.2.8 Sips isotherm model

Sips (1948) derived the model which is a joint form of the Langmuir and Freundlich terms deduced for predicting the heterogeneous adsorption systems (Gunay et al., 2007) and showing the disadvantages of the increasing adsorbate concentration related to the Freundlich isotherm model. Low adsorbate concentrations reduces the Freundlich isotherm model while at elevated values of concentration, it assumes a monolayer adsorption capacity feature of the Langmuir isotherm. Generally, the equation parameters are controlled mainly by the functioning conditions such as the adjustment of concentration, pH and temperature (Perez-Marin et al., 2007).

2.7 Gap Analysis

Several adsorbents have been proposed in the literature for the removal of BTEX organic compounds from an aqueous solution. The cheaper carbonaceous materials have been used successfully for removal of toxic ions and organic constituents from wastewater. GAC have been investigated and utilized for many applications including removal of BTEX compounds, but there is not enough literature and data for the removal of low concentration BTEX

organic compounds from wastewater. The 910 polystyrenic resins have been recently developed and have characteristics of an absorbent that can remove organic compounds. There is no published literature and data where this specific type of resin has been used and compared with GAC. Various authors had also previously investigated the influence of variables such as adsorbent dosage, contact time and initial concentration on the adsorption of BTEX compounds and therefore it is important to consider these parameters for the removal of organic compounds using the 910 polystyrenic resin and GAC.

From the research conducted by Yadav and Reddy (1993), the adsorption capacity of the activated carbon and dried seeds for the removal of BTEX was shown to be a function of initial concentration of the solution and the adsorbent particle size. Consequently, the effect of various parameters such as adsorbent porous structure and BTEX concentration were investigated for the removal of low concentration BTEX compounds in a solution by Banerjee et al. (1997). These authors show that BTEX adsorption increases with decreasing particle size. The same result was also observed by Sarkar and Acharya (2006), where the decrease in particle size of fly ash leads to an increase in its surface area. The removal of BTEX was also found to increase with increasing concentration and this was due to the increase in concentration gradient between the solute and the solid phase, and the high degree of interaction between BTEX and the adsorbents (Yadav and Reddy, 1993). All these parameters are investigated in this study so as to make a comparison between GAC and 910 polystyrenic resin effectiveness and also generate data for this resin which has limited literature.

3 MATERIALS AND METHODS

3.1 Materials

The material used for this project includes:

- Adsorbates : Benzene, Toluene, Ethyl-benzene and m-, o-, p-Xylene
- Solvent: Distilled water
- Adsorbent: Activated carbon and polymeric resin

3.1.1 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 the catch point of the Southern Wastewater Treatment Works influent from the surrounding companies. All samples were taken at different times of the day, which included steady and unsteady state operating conditions. Samples were analysed by the GC/MS and they were done in duplicates. The values presented in Table 3.1 are the averages of many measurements that were conducted each month. 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_0) within the range of 0.5 ppm – 14.47 ppm. Ten samples of different initial concentration were prepared within the given range.

Table 3.1: Trade effluent monitored average results to sea outfall

Date Analyzed	Apr 2013	May 2013	Jun 2013	Jul 2013	Aug 2013	Sept 2013	Average
Units	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre
Benzene	4 800	9200	16 000	15 000	6100	3900	9167
Toluene	2 900	14 000	29 000	16 000	8900	40 000	14466
Ethylbenzene	180	140	19	360	<10	420	188
m,p-Xylene	3300	7700	8000	3200	3900	1500	4600
o-Xylene	1600	3900	3400	1800	2100	840	13640
Total BTEX	12780	34940	56419	36360	21000	46660	46061

Table 3.2: Materials and reagents used

Material	Specification	Supplier
Benzene	99.9% purity	Merck, SA
Toluene	99.7% purity	Merck, SA
Ethylbenzene	99.9% purity	Merck, SA
m-; Xylene	99.8% purity	Merck, SA
o-; Xylene	99.8% purity	Merck, SA
p-; Xylene	99.8% purity	Merck, SA
Methanol	99.9% purity	Merck, SA
Acetone	99.8% purity	Merck, SA

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 (0.5 ppm to 10ppm) 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). Every flask was closed with a cap and overturned several times to blend the materials carefully and then allowed to stabilize for 15 minutes in the pyrex conical flask until isotherm experimental runs for both batch and column studies were performed.

3.1.2 Adsorbent(s)

3.1.2.1 Granular activated carbon

The activated carbon utilized in this research was an average grade granular activated carbon (GAC) obtained from Merck Chemical Ltd, South Africa. The pH of the sample was measured after 2.5 g of GAC was mixed with 10 ml of distilled water and shaken at 25⁰C for 6 hrs and the slurry was filtered then pH was measured as 6.64. The GAC pH measuring method was replicated from Lei et al. (2006). The adsorbent pH was measured to ensure all experiments were carried out at natural pH values. The physical-chemical characteristic of the adsorbent was determined using the (standard procedure) in Appendix B and the samples were stored inside a desiccator until experiments were performed.

3.1.2.2 PAD 910 resin

PuroSorb PAD 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 in situ. The graded resin utilized in this investigation was sourced from Purolite Co. Ltd, 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 25⁰C for 6 hrs. 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 in the Laboratory until experiments were performed as per the Material Safety Data Sheet provided in Appendix H.

3.2 Equipment for Characterization and Analytical Analysis

The instruments used in the adsorption experiments are listed in Table 3-3.

Table 3.3: Instruments employed in adsorption experiments

Instrument	Model	Manufacturer
GC	Clarus 580	Perkin Elmer
MS	Clarus SQ 8 S	Perkin Elmer
1μL Syringe	SGE	Analytical Science
Weighing balance	AS 220/C/2	Radwag
Oven	5018U	Labcon
Platform Orbital Shaker	SSL1	Stuart
pH/conductivity meter	A215	Orion Star
Centrifuge	IEC HN-S	Tech Laboratories
Centrifuge tube	50ml, conical bottom	Tech Laboratories
N₂ (gas)	99.99% purity	Afrox
Electron Microscope	S-5200	Hitachi

3.3 Experimental Methods

3.3.1 Adsorption kinetics 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 porous activated carbon were dosed into the series of sample bottles containing 50ml of the simulated wastewater and the bottles were placed in an oven used as an incubator at 25°C ($\pm 1^{\circ}$) and the orbital shaker placed inside the oven was running at 180rpm, having determined this was the mixing strength at which external diffusion was minimized negligibly. Same procedure was employed for the PAD 910 polystyrenic resin. 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.

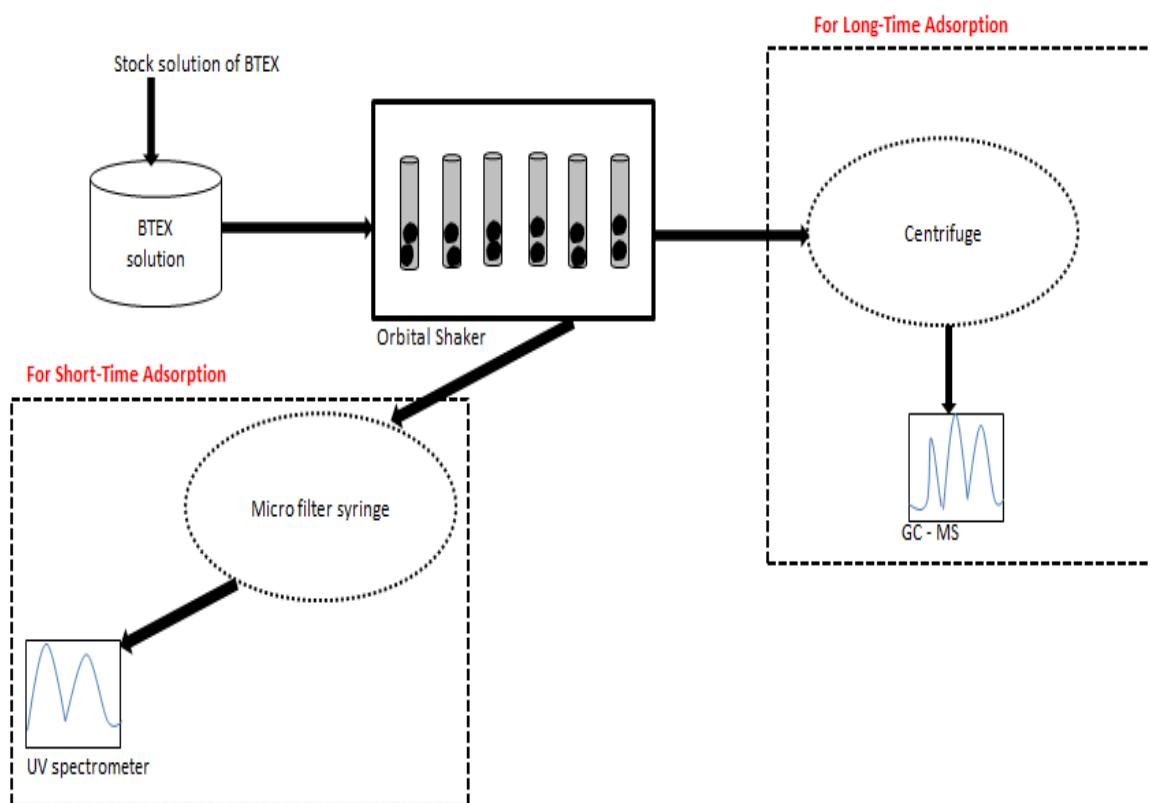


Figure 3.1: Adsorption Kinetic Experimental Protocol

3.3.2 Batch studies

This study was performed to obtain the equilibrium data for the adsorbate and the adsorbents (granular activated carbon and PAD 910 polystyrenic resin). The adsorbates were the mixture

of benzene, toluene, ethylbenzene and isomers of xylene. The batch technique was used because of its straightforwardness to obtain equilibrium data. The initial solute concentration was recorded before adding the sample to the GAC and the polystyrenic resin.

In every adsorption data point, a 50 ml aliquot of the adsorbate mixture that have an initial benzene, toluene, ethylbenzene, m-;p-xylene, o-xylene were 3.70 mg/l; 6.66 mg/l; 0.34 mg/l; 2.57 mg/l and 1.20 mg/l in that order. The adsorbents quantity was varied at a ratio of 1:5 (Chern and Chien, 2002) when it was introduced into a series of 100 ml Pyrex conical flasks at a temperature of 25⁰C and pH of 6.64. The conical flasks were positioned and shaken in a shaker to attain equilibrium after 6 hrs of contact time and at a steady stirring speed of 180 revolutions per minute. The samples were enclosed using aluminium foil the whole time of the experiment and the supernatant solution filtered after specific time intervals of agitation through microfiber filters. The microfilter that was used to filter the samples was checked if it had a removal impact on the BTEX compounds and the results were insignificant. The concentration of the filtrate left was then determined and recorded.

Data gathered from the adsorption isotherm experiments was used in determining the adsorption capacity of the granular activated carbon and PAD 910 polystyrenic resin. The equilibrium adsorption uptake and percentage removal of BTEX from the aqueous solution q_e (mg of adsorbate/g of adsorbent) was calculated using the subsequent correlation:

$$\text{Amount adsorbed, } q_e = \frac{(C_o - C_e)V}{w} \quad (3-1)$$

$$\% \text{ removal, } q_e = \frac{100 (C_o - C_e)}{C_o} \quad (3-2)$$

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

3.3.3 GC-MS analysis

The GC-MS was equipped of with a capillary column (Elite - 5MS, 30 m X 0.30 μ m internal diameter, 0.25 μ m thickness - film) and a spectrometric detector (mass). A split/split-less type injector was used and its temperature was set at 180⁰C. The temperature of the column was kept at 50⁰C for 1 minute, increased to 180⁰C at a rate of 6⁰C/min and held at this temperature for 10 minutes, then ramped to 200⁰C at 10⁰C/min and kept there for 2 minutes.

The temperature of the transfer line was 180⁰C. 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 used after the full scan mode was used for selecting ions. The volume for injection was 0.6 μ L . This method was developed on a trial an error basis which is based on chemical properties of the analytes boiling point. The compounds p-xylene and m-xylene could not be differentiated by this method; hence they were solved as a single compound.

Tuning and calibration of this instrument was done using heptacosa where m/z heptacosa was found as following; 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 NIST Library.

3.3.4 Dynamic column studies

In dynamic column adsorption, the waste water continuously entered and left the column. This was done so that the GAC and PAD 910 resin meet fresh solution all the time. Hence, adsorption takes place due to the changes in the concentration of the organic waste as the mass transfer zone moves through the bed. However, this condition does not exist in a batch isotherm study procedure. The dynamic column study provides the necessary information for the scale-up data useful for industrial system design and it minimizes adsorbent usage by maximizing its utilization.

An adsorbent 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 300 mm and internal diameter of 33 mm. Both columns were operated under down flow conditions, which allowed the influent to be gravity fed. This condition also ensured that the adsorption bed remained stable and steady during the entire operation period. Hence, there was a maximum contact between the GAC, PAD 910 resin and the feed of organic (BTEX) compounds.

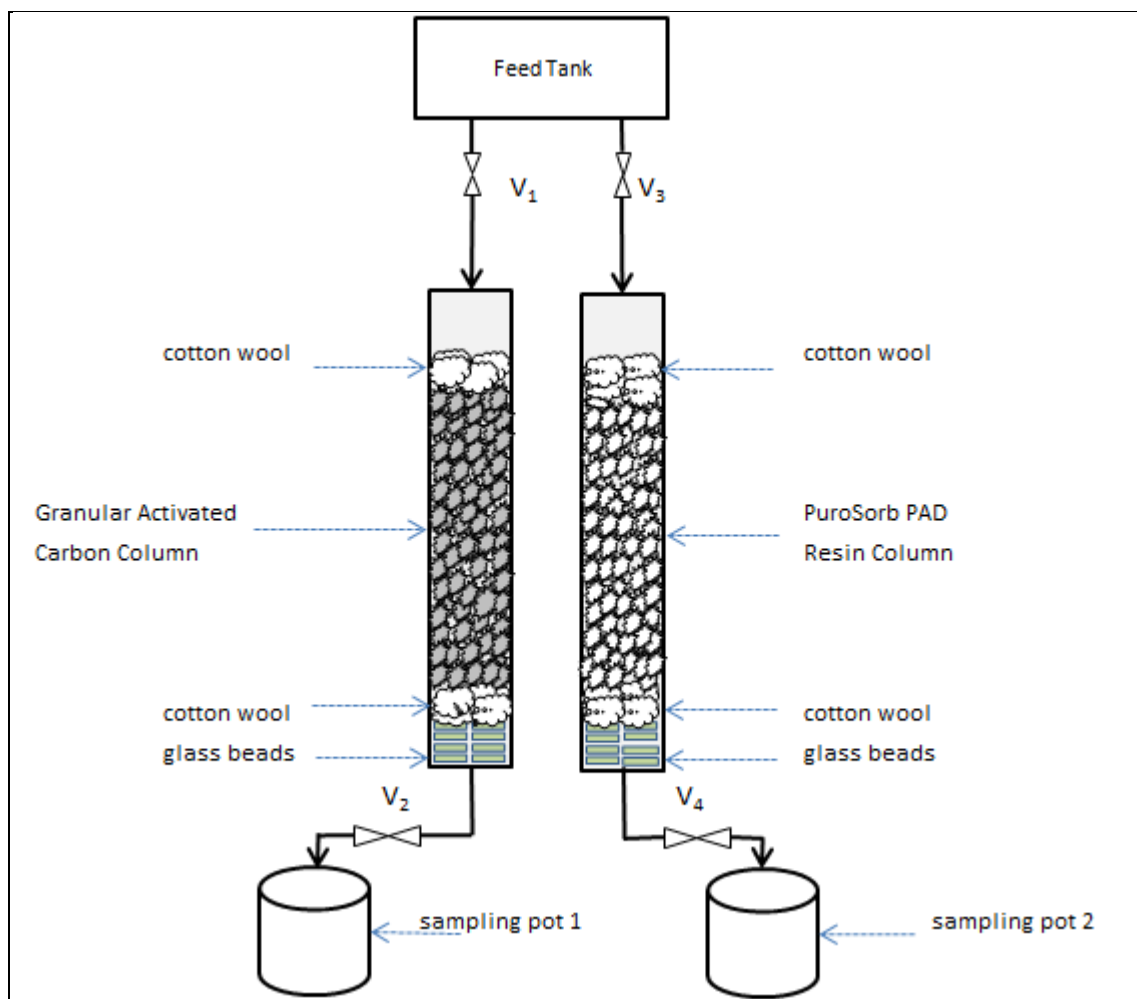


Figure 3.2: Schematic Diagram of Experimental Setup for Column Studies

The set-up for the continuous flow studies is shown in Figure 3.2 where both columns were packed with 30 mm glass beads between supporting layers at different bed depths. GAC and PAD 910 resin masses of 17, 35 and 55 g respectively were added to yield different bed heights of 40, 80 and 120 mm respectively while the process was performed at a flow rate of 3 ml/min and 14.47 mg/l initial BTEX solute concentration. Wire mesh filter was used as the supporting layers to keep the glass beads in position and to support the GAC and Pad 910 resin. A cotton layer was packed on top of the glass beads to ensure the stability of the bed.

Effluent concentrations were monitored as a function of time for each column and the break point for breakthrough curves generated for each bed depth were selected at 20% and 60% of the influent concentration remaining to determine the BDST equation which can be used to evaluate any desired effluent quality.

3.4 Chemistry Analysis

3.4.1 Surface Chemistry Analysis

The surface chemistry of the carbon was studied using Fourier Transform Infrared (FTIR) spectroscopy. All the surface functional groups on the adsorbent samples were qualitatively detected by FTIR spectroscopy using the spectrum spectrophotometer. Adsorbent samples were dried at 90⁰C for up to 24 hrs prior to analysis (Vinod and Anirudhan, 2003). Spectra of PAD 910 polystyrenic resin and activated carbon were obtained in a frequency band range from 3500 to 500 cm⁻¹ using powdered KBr as reference in KBr/Carbon pellet (200:1 mass ration formed in die).

3.4.2 Porous Structure Analysis

The porous structural properties of the samples were analyzed by obtaining the nitrogen adsorption and desorption isotherms at 77K using the Autosorb 1 specific surface area analyzer. The samples were degassed at about 250⁰C for up to 3 hours prior to each measurement. The isotherm volume data, calculated by subtracting the free volume space of sample tube from the total volume of gas dozed to the sample is measured at the sample pressure relative to the saturation vapour pressure of the adsorbate (N₂ gas).

The volume of N₂ adsorbed plotted against the relative pressure (the adsorption isotherm curve) was used to determine the porous structural properties of the samples using different models as described in Appendix B. Total pore volume, V_t in cc/g, was calculated based on the adsorption isotherm relative pressure around 0.97 ~ 0.99. Micropore volume, V_m in cc/g, and mesopore surface area, S_{mes} in m²/g were calculated by t-plot method. The average pore radius, r_{ave} was also calculated as described in Appendix B.

3.4.3 Surface Morphology Analysis

Surface topographical information was obtained by a surface morphological study in the field electron Hitachi S-5200 Scanning Electron Microscope. Grounded carbon samples were placed on a sample stub with aid of a graphite conductive adhesive paste before being firmly loaded on a cylindrical rod which serves as the sample holder. The rod was thereafter placed in the analysis chamber of the SEM which remains under vacuum all through the analysis. Various secondary electron detectors attract the scattered electrons and the signals were used to form images of the specimen

3.5 Adsorption Data Quality and Repeatability

Adsorption experiments for short time kinetics and isotherms were repeated and the duplicate adsorption data are reported in Appendix D, while the repeatability of the different instruments used in analyzing the five BTEX compounds are reported in terms of % relative standard deviation (RSD) in Table 3.4.

Table 3.4: Adsorption data quality

Instrument	Condition	Benzene	Toluene	Ethyl-benzene	m;p-Xylene	o-Xylene
		%R.S.D. (C_i , n)*	%R.S.D. (C_i , n)*	%R.S.D. (C_i , n)*	%R.S.D. (C_i , n)*	%R.S.D. (C_i , n)*
GC-MS	GC only	4.11 (3.69, 2)	4.92 (6.6, 2)	2.52 (0.34, 2)	3.56 (2.56, 2)	1.96 (1.18, 2)
		4.28 (7.38, 2)	2.78 (13.2, 2)	1.32 (0.68, 2)	2.34 (5.12, 2)	1.11 (2.36, 2)

* C_i =initial BTEX concentration in ppm; n = number of repetitions

In probability theory, Table 3-4 indicate that there was a low variability in the data set since the GC-MS analysis has less than 5% standard error for all compounds. This is an acceptable result for the %RSD, hence the reported results can be confirmed as reliable.

4 RESULTS AND DISCUSSION

4.1 Physical and chemical characterization of the adsorbent

4.1.1 Porous Structure Analysis

The N₂ adsorption isotherms of the carbon is shown in Figure 4.1

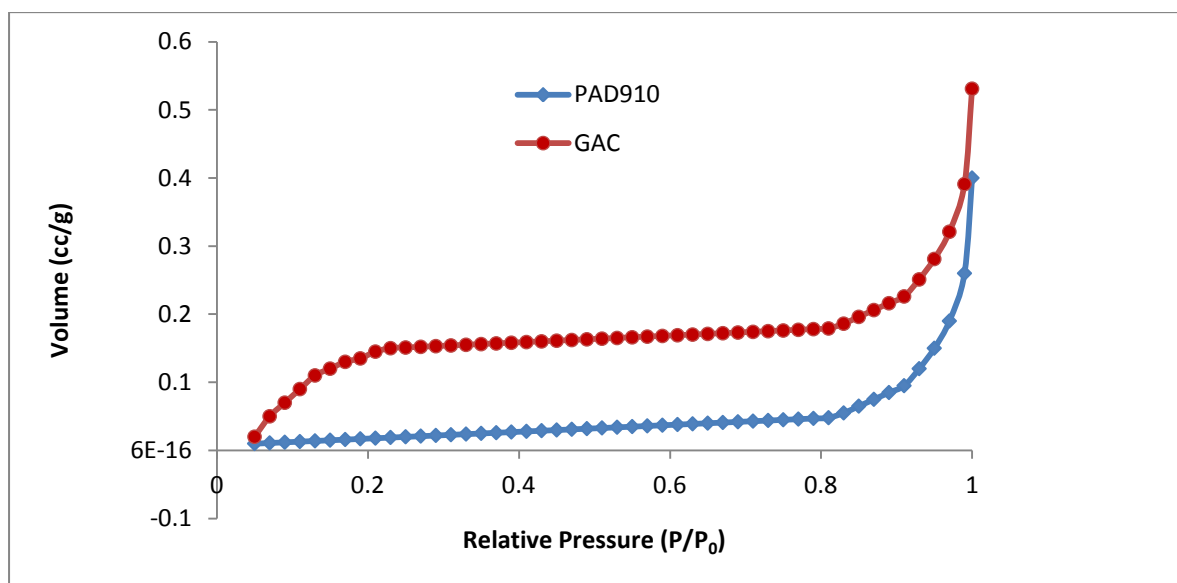


Figure 4.1: N₂ Adsorption Isotherm at 77K of Granular Activated Carbon

As expected the untreated resin samples have little porous structure while the granular activated carbon have moderately high SSA and developed porous structure. Since micropores are the major contributor to the specific surface area, there was thus explainable lower SSA for the PAD 910 polystyrenic resin compared to GAC.

Surface oxidation of activated carbons could positively or negatively affect the porous structure of an activated carbon (Edgehill and Lu Max, 1998). Positively, new micropores could be formed as a result of reaction of oxygen with the reactive carbon skeleton leading to an increased SSA. On the other hand, a negative effect by enlargement of micropores to mesopores and macropores leading to a reduction of SSA could also occur. According to Bansal et al. (1998) either effect of surface oxidation occurring is dependent on the initial surface area and pore size distribution. This suggests that the GAC used in this study could be further treated by humidified oxygen set-up which will oxidize the surface of the activated carbon.

4.1.2 Morphology

Surface morphological images obtained by SEM for some of the samples used in this study are shown in Figure 4.2. The significance in porous structure of GAC than the PAD 910 polystyrenic resin informed the morphology study.

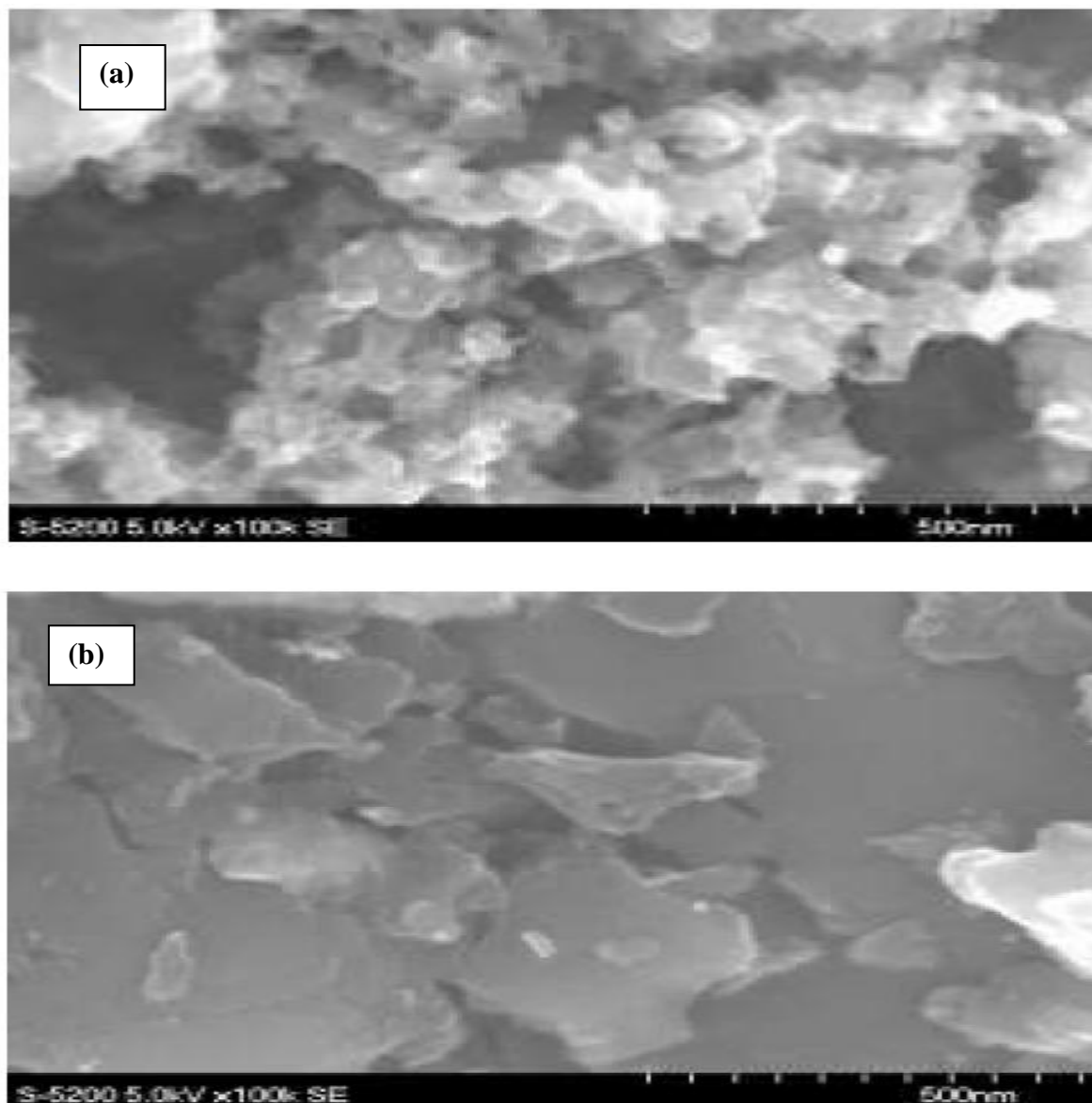


Figure 4.2: SEM Images of (a) GAC and (b) PAD 910 polystyrenic resin

The images give further evidence to the more porous nature of the resin, while 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.

4.1.3 Fourier transform infrared spectroscopy (FTIR) analysis

Surface functionality groups were qualitatively identified by Perkin Elmer FTIR Spectroscopy to study the effect of surface functional groups on the adsorption process.

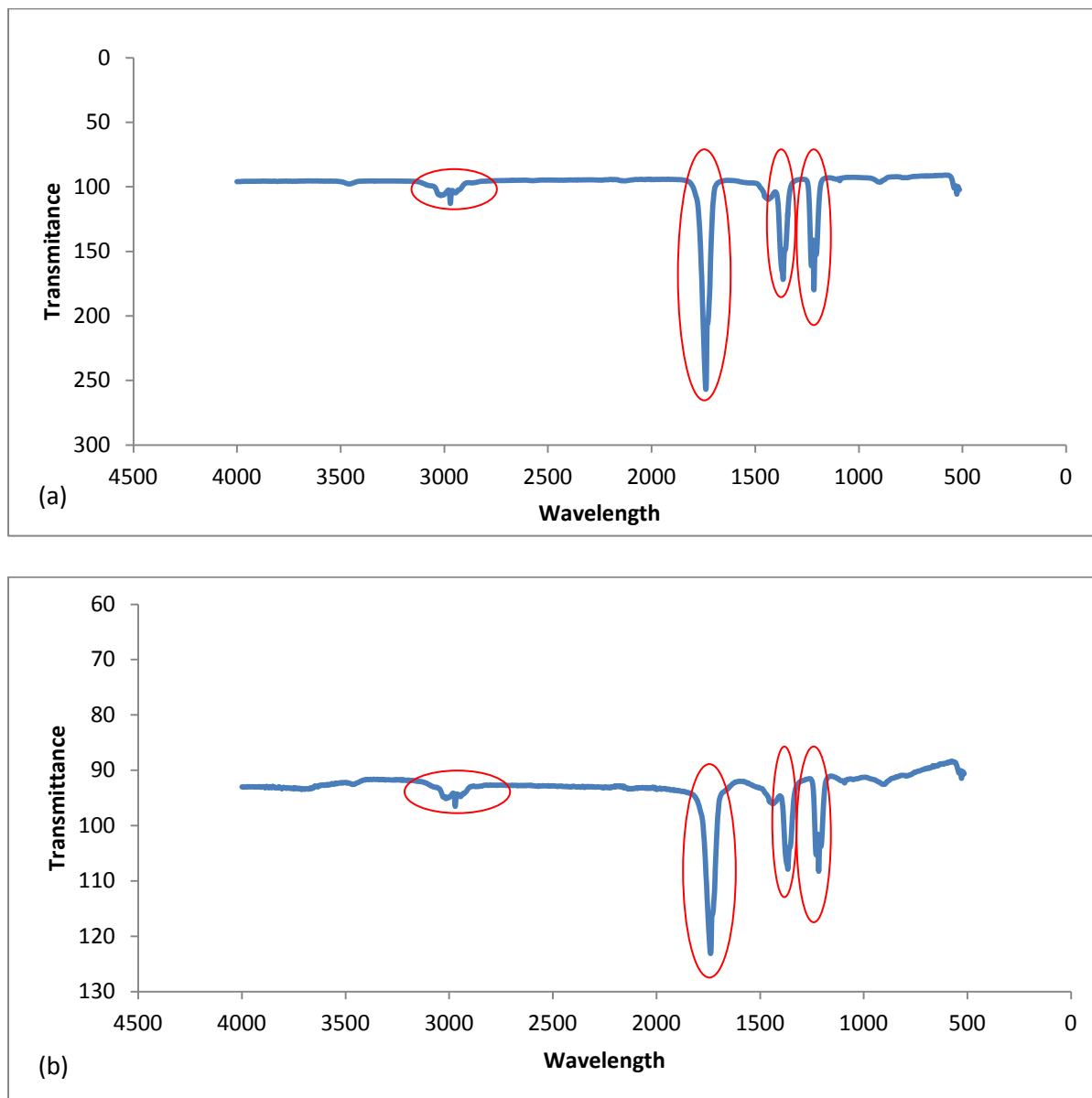


Figure 4.3: FTIR Spectra for a) Granular Activated Carbon; b) PAD 910 Polystyrenic Resin

The FTIR spectra of both granular activated carbon and PAD 910 polystyrenic resin displayed a wide peak between $3330 \sim 3500 \text{ cm}^{-1}$. The IR Spectrum was plotted for the adsorbents as shown in Fig. 4.1. 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 peak around $2800 \sim 3100 \text{ cm}^{-1}$ for GAC is attributed to stretching vibrations from

aliphatic C-H groups, which was not observed in the commercial PAD 910 polystyrenic resin. The vibration band between $2000 \sim 2350 \text{ cm}^{-1}$ is ascribed to the alkyne group. The band between $1600 \sim 1800 \text{ cm}^{-1}$ is ascribed to the oscillation of C=O associated with carbonyl and carboxylic groups, and this appears to be the major difference between GAC and PAD 910 polystyrenic resin. 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 multiple peaks between $510 \sim 1000 \text{ cm}^{-1}$ are ascribed to the bending vibration of C-H on aromatic rings (Byrd, 1998, Gou and Rockstraw, 2007, Jiang et al., 2008).

4.1.4 Chemical properties

According to Sahu (2009), granular activated carbon pH may manipulate the removal efficiency. Distinctly acidic activated carbon may react with the material to be removed and may hamper the surface properties of the activated carbon. For this study, the experiments were carried out with the GAC pH being 6.64 and PAD 910 polystyrenic resin pH being 6.85. Ash content of the carbon is the residue that remains when carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminium, iron, magnesium and calcium. Ash in activated carbon is not required and considered to be an impurity. The GAC ash content is 5.1% which resembles a good adsorbent, as published by Dwivedi et al. (2007).

4.1.5 Physical properties

Particle size distribution analysis was manually done. Initially, the GAC sample of 400 g was analyzed. This sample was passed through different sieves and an amount of fine and coarse particles were measured in the US Standard mesh size number 30 – 45. The nominal particle size was found to be 0.55 mm. The same procedure was repeated for PAD 910 polystyrenic resin and the nominal particle size was found to be 0.45 mm. Density of the adsorbent is particularly important for adsorption. Average bulk density for GAC was calculated by the water displacement method. In this method, the volume of water displaced was observed by a particular amount of carbon. The average bulk density was found to be 0.5102 g/cm^3 . The BET surface area of PAD 910 polystyrenic resin was measured and found to be $580 \text{ m}^2/\text{g}$, which was close to the manufacture's specification. The surface area for GAC was found to be $770 \text{ m}^2/\text{g}$. The average pore diameter was found to be 18 \AA for GAC and 20 \AA for PAD 910 polystyrenic resin as stipulated by the manufacturer. These results showed that both these adsorbents are reasonably good for adsorption.

4.2 Adsorption Study

The factors that have the potential of affecting the adsorption process are adsorption condition, adsorbent properties and adsorbate properties as discussed in section 2.4.5.

4.2.1 Effect of residence time

Kinetic experiments were conducted to investigate the rate constants of adsorption for BTEX compounds onto activated carbon and PAD 910 polystyrenic resin. The amounts of adsorbates removed by the GAC and PAD 910 polystyrenic resin were also evaluated in these studies. All completed analysis was done in duplicate to ensure repeatability and elimination of error hence the mean values are reported as final results in this study. Equilibrium concentration values were generated by using BTEX calibration curves that are presented in Appendix C.

Table 4.1 presents the results for the effect of residence time on the removal of benzene, toluene, ethylbenzene, m-;p-Xylene and o-Xylene from an aqueous solution at an initial concentration of 3.69, 6.6, 0.34, 2.56 and 1.18 mg/L respectively. It is evident that the amount of all adsorbates adsorbed onto the PAD 910 polystyrenic resin and GAC increases with time. Table 4.1 summarizes the results on the plot in Figure 4.2.

Table 4.1: Removal rate of BTEX after 6 hrs of agitation

Adsorbent	Benzene	Toluene	Ethylbenzene	m-;p-Xylene	o-Xylene
GAC	98%	88%	59%	84%	90%
Resin	97%	88%	50%	83%	89%

This is due to the large number of vacant spaces existing on the surface of the GAC and the PAD 910 polystyrenic resin that are available for adsorption during the initial agitation stage. Figure 4.4 confirms that the profile for the adsorbates is a single, smooth and continuous curve when adsorption assumed to stop after 360 minutes. The profile further demonstrates that after a lapse of 45 minutes, there is a repulsive force that exists between the adsorbates in the bulk phase and the adsorbent due to the non-availability of more vacant spaces for adsorption onto GAC and PAD 910 polystyrenic resin.

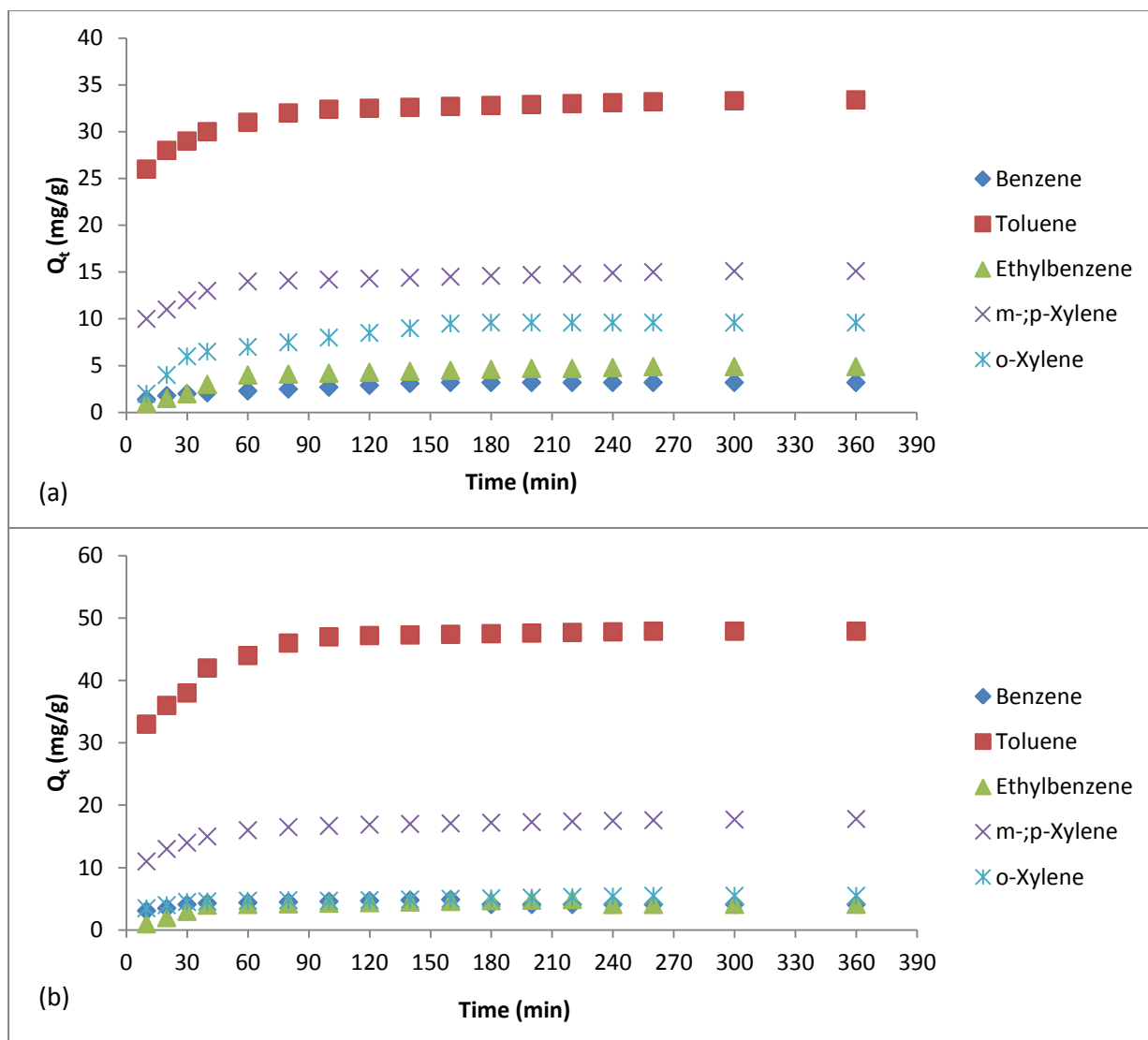


Figure 4.4: Effect of residence time on the amount of BTEX compounds removed from aqueous solution with (a) GAC and (b) PAD 910 polystyrenic resin.

The adsorption capacity (Q_t) generally increases with the increase in residence time and the adsorption equilibrium reached values as high as 4.11 mg/g; 47.9 mg/g; 4.13 mg/g; 17.8 mg/g and 5.5 mg/g for benzene, toluene, ethylbenzene, m;p-Xylene and o-Xylene respectively for polystyrenic resin after 6 hrs of agitation. Agitation after 6 hrs using GAC produced adsorption equilibrium values of 3.2 mg/g; 33.4 mg/g; 4.9 mg/g; 15.1 mg/g and 9.6 mg/g for benzene, toluene, ethylbenzene, m;p-Xylene and o-Xylene respectively. Further increases in adsorption capacity after 6 hrs of contact time will depend on the creation of fresh internal surfaces (Giles et al., 1974). The work done by Allen (1987) stated that further interaction of the adsorbate and the adsorbent cannot continue indefinitely without irreparable damage to the adsorbent.

Toluene was found to adsorb more than the other compounds due to its lower solubility in the aqueous solution. The result was confirmed by Cooney (1999) when he stated that, the more non-polar an organic compound, the lesser its affinity for the solvent and the higher its adsorption affinity by the adsorbent. The adsorption capacity for ethylbenzene was found to be slightly higher than o-Xylene and this shows that solubility is not all important in this system because if solubility was to be the controlling factor then, ethylbenzene should have had a higher adsorption affinity for GAC and PAD 910 polystyrenic resin than Xylene because of its lower solubility in water than Xylene.

4.2.2 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 in which the process occurs 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).

Figure 4.5 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.

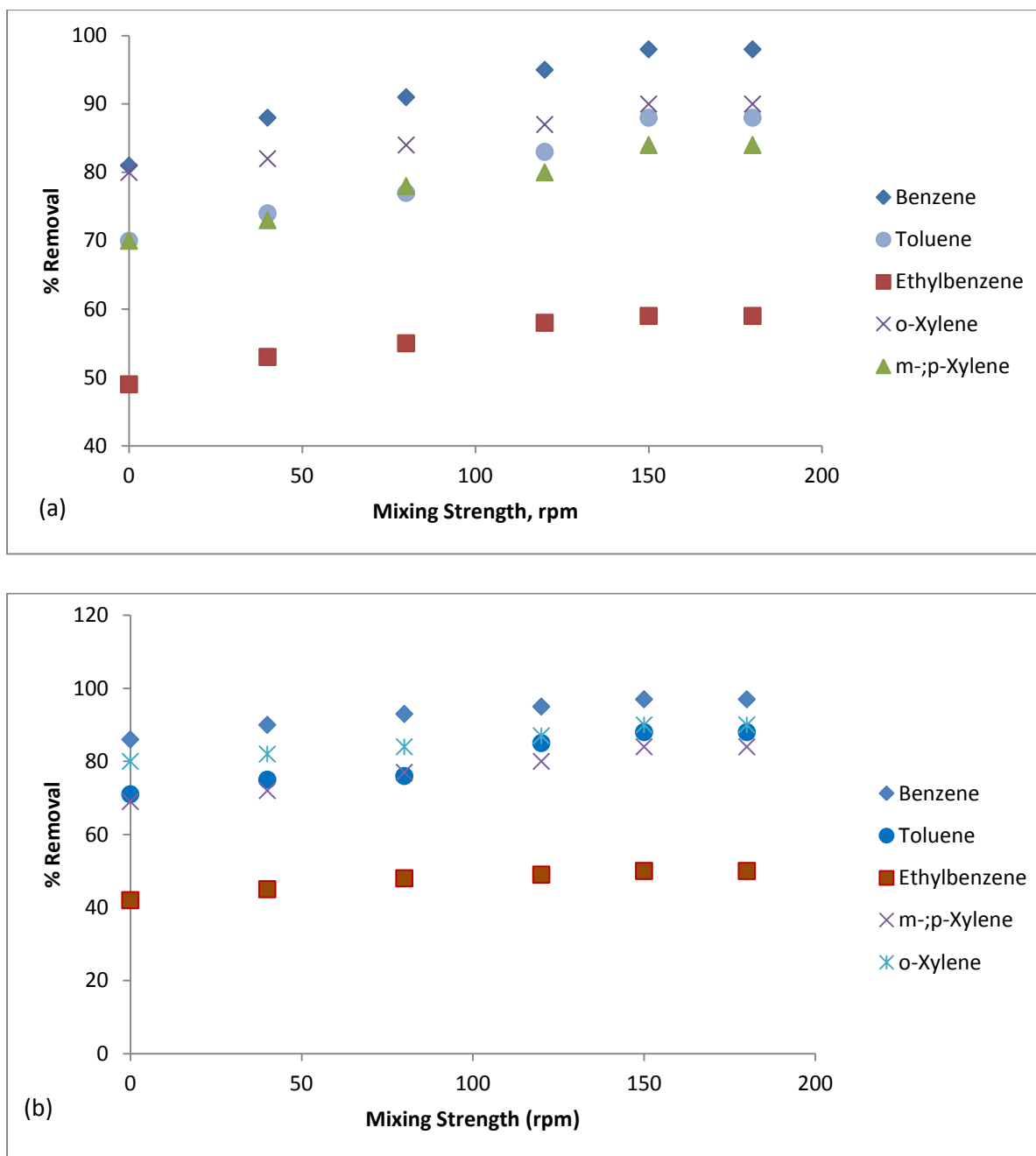


Figure 4.5: Effect of mixing strength on adsorption of a mixture of BTEX for 4 hrs (0.25 g of (a) resin and (b) activated carbon; initial concentration: Benzene ~ 3.69ppm; toluene ~ 6.6ppm; Ethylbenzene ~ 0.34ppm; m-p-Xylene ~ 2.56ppm; o-Xylene ~ 1.18ppm)

As shown above, the adsorption efficiency increased with mixing strength up to a certain point (in this case its 120 rpm), beyond which adsorption is independent of mixing strength. This confirms the importance of external diffusion on the molecules below 120 rpm mixing strength. It is also shown that, with no mixing, there was still a high removal efficiency (about 42% being the lowest efficiency for ethylbenzene) onto GAC indicating that the

adsorption process, though could be influenced by external diffusion, is strongly dependant on internal diffusion of molecules from sorbent surface to the pores.

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. Figure 4.6 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.

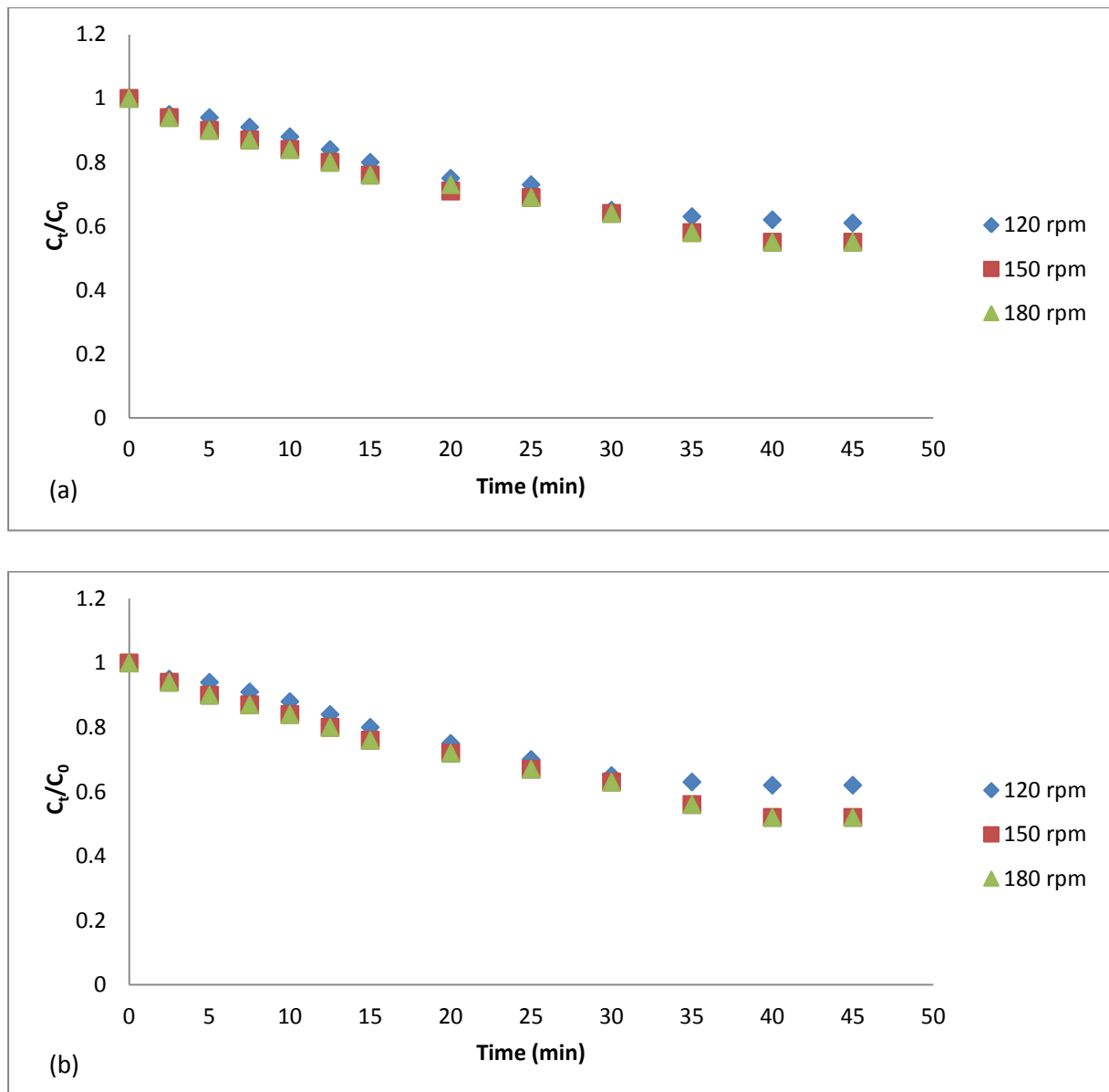


Figure 4.6: Effect of mixing strength on adsorption of Toluene onto 0.25g (a) resin and (b) activated carbon. (Initial concentration ~ 6.6ppm)

4.2.3 Effect of internal diffusion

With the initial concentration of BTEX aqueous solution of 14.47 ppm, a long term kinetic study was conducted with two adsorbents: PAD 910 polystyrenic resin and granular activated carbon. Figure 4.7 shows the evolution of the BTEX concentration with time. The equilibrium concentration of 2 ppm was achieved for both adsorbents after 3 hrs. The global kinetic parameters were obtained as described in section 2.6.1 and are given in Table 4.2 and Table 4.3.

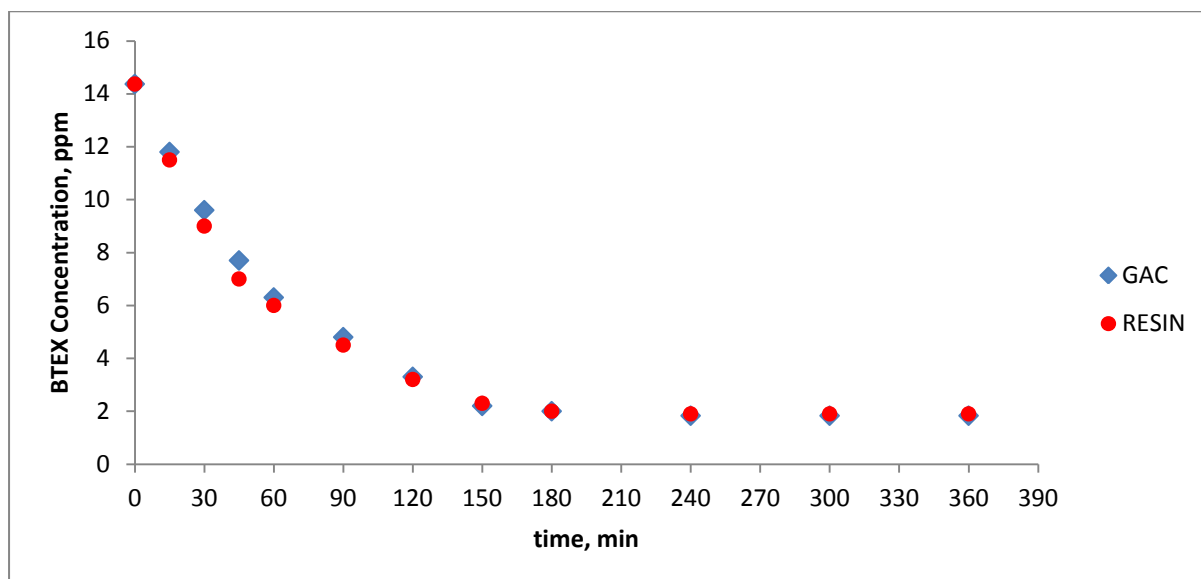


Figure 4.7: Long Term BTEX adsorption on two types of adsorbent (0.25g of PAD 910 polystyrenic resin and GAC in 25ml of simulated waste water)

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

Table 4.2: Global rate parameters for short term BTEX adsorption onto PAD 910 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

Table 4.3: Global rate parameters for long term BTEX adsorption onto GAC

Model	Benzene	Toluene	Ethylbenzene	m;-p-Xylene	o-Xylene
Pseudo 1st Order					
k_1 (min ⁻¹)	0.11	0.32	0.18	0.19	0.10
q_{e1} (mg/g)	0.14	0.15	0.29	0.28	0.24
r^2	0.933	0.925	0.951	0.986	0.984
Pseudo 2nd Order					
k_2 (g.mg ⁻¹ .min ⁻¹)	0.89	0.4	0.19	0.38	0.51
q_{e2} (mg/g)	1.44	3.15	0.12	0.34	0.33
r^2	0.991	0.995	0.989	0.995	0.997
Elovich					
b (g.mg ⁻¹)	2.68	9.25	1.69	53.56	73.23
a (mg.g ⁻¹ .min ⁻¹)	2.15×10^{13}	1.99×10^{30}	2.23×10^5	∞	∞
r^2	0.622	0.624	0.452	0.834	0.792

Global parameters for short term BTEX adsorption onto GAC were similar to short term onto resin and long term BTEX for PAD 910 resin were also similar to long term onto GAC results, hence not reported.

Obviously, the Elovich model does not fit the experimental data adequately as shown by the low correlation coefficient hence it was discarded 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 Figure 4.8 (b) has been chosen as the most fitting model for this study based on the following reasons.

- A plot of the predicted residual concentration at the different sampling time versus the experimental measured residual concentration for all kinetics adsorption experiments for both models in Figure 4.8, showed that pseudo-second order represents the experimental values better for the whole concentration range.
- One way ANOVA was used to validate the effect of pseudo first and second order 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 Figure 4.8 (a) while there is no significant difference in Figure 4.8 (b).

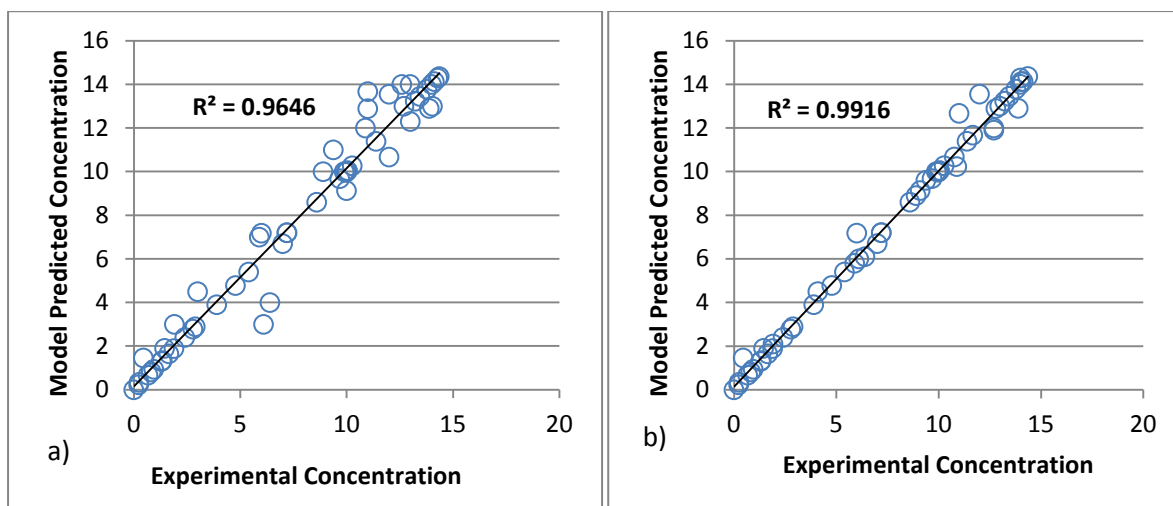


Figure 4.8: Validation of Kinetic Model Choice a) pseudo-first order; b) pseudo-second order

- 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 yield 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 hence they were not reported.
- Moreover, the values of equilibrium quantity adsorbed obtained by the pseudo-first order model were at times comparably lower than the values obtained from the experiment unlike the values obtained by the pseudo-second order.

As such, the pseudo-second order is the only reported model. According to Ho and McKay (2000), the pseudo-second order model is based on the sorption capacity of the adsorbent, i.e. the vacant sites and chemi-sorption assumption. The parameters obtained by the pseudo-second order model showed that the resin performed best in terms of the rate constant. The high fraction and mesopore of the PAD polystyrenic resin is likely to be responsible from its high rate constant, which is relatively consistent with the underlying assumption of the importance of vacant sites for a pseudo-second order process. However it was found to be different from the adsorption onto GAC. The high mesopore volume and fraction in the resin provides ease of access for the BTEX molecules to diffuse into the inner surface of sorbents. These results were in agreement with the work published by Valderrama et al. (2007), who also observed that a more mesoporous adsorbent had about a hundred times greater rate

constant than the granular activated carbon in the competitive adsorption of aromatic hydrocarbons.

It was also confirmed that the adsorption process was extremely fast within the first 45 mins in both cases, which was followed by a slower transport stage. It suggested a shift of the BTEX molecule transport regime from macropore/mesopore 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 both GAC and PAD 910 polystyrenic resin and the concentration-time dependence plots are shown in Figure 4.9.

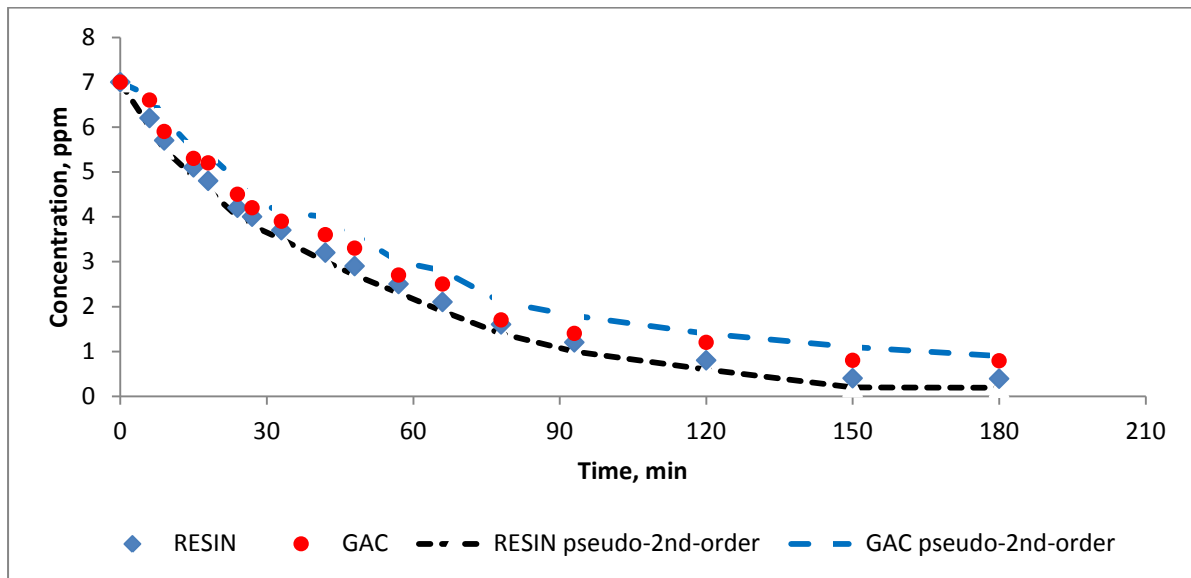


Figure 4.9: Short Term BTEX adsorption on two adsorbents (0.25g of PAD 910 polystyrenic resin and GAC in 25 ml of simulated waste water).

Since the time scale for the short term study is small, evidently q_e parameters would not be a true reflection of the quantity adsorbed at equilibrium, which is the reason why they were not reported in this case. In order to obtain the rate parameter in terms of the residual concentration in the aqueous phase, rather than the quantity adsorbed, the pseudo-second order equation in equation 2-3 was written in terms of concentration C and the equilibrium concentration C_e . Integrating with boundary conditions of $C = C_0$ at $t = 0$, $C = C_t$ at time t were applied. When assuming that C_e tends to zero, the linear equation 4-1 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 4.4.

$$\frac{1}{c_t} = k'_2 t + \frac{1}{c_0} \quad (4-1)$$

Table 4.4: 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
Pseudo 2nd Order (GAC)					
k'_2 (L.mg ⁻¹ .min ⁻¹)	0.68	0.54	0.31	0.15	0.81
r^2	0.967	0.990	0.933	0.956	0.978

With regards to the rate constant k'_2 obtained, the sequence was PAD 910 polystyrenic resin then granular activated carbon. The sequence was accepted since the mesopore volume sequence is $0.052 \text{ cc/g} > 0.041 \text{ cc/g}$ for PAD 910 polystyrenic resin and GAC respectively. The results were consistent with the observation obtained in the long term adsorption experiments. This was also confirmed by other researchers who have observed the beneficial effect of a higher mesoporous volume/fraction on the adsorption rate of pollutants generally from an aqueous phase (Valderrama et al., 2007, Mastral et al., 2003, Han et al., 2000, Lei et al., 2006).

With the other assumptions of intra-particle diffusion limiting the adsorption process, the Homogeneous Particle Diffusion Model (HPDM) and the Weber-Morris Model were to test the validity of the assumption and also gain further insight into the adsorption process. As summarized in section 2.6.2.2, a linear regression analysis of the left-hand-side of equation 2-10 versus time yields the mass transfer parameter K from which the effective diffusion coefficient D_e could be obtained from the HPDM. On the other hand, a linear regression of q_t versus $t^{0.5}$ yields the intra-particle rate constant k_i , with constant C , which measures the resistance to the diffusion process. In both models, a high correlation coefficient gives evidence to the validity of the other assumption of intra-particle diffusion limitation.

Figure 4.10 and 4.11 shows the linear regression for the HPDM and the Weber-Morris plot for both adsorbents (PAD 910 polystyrenic resin and granular activated carbon).

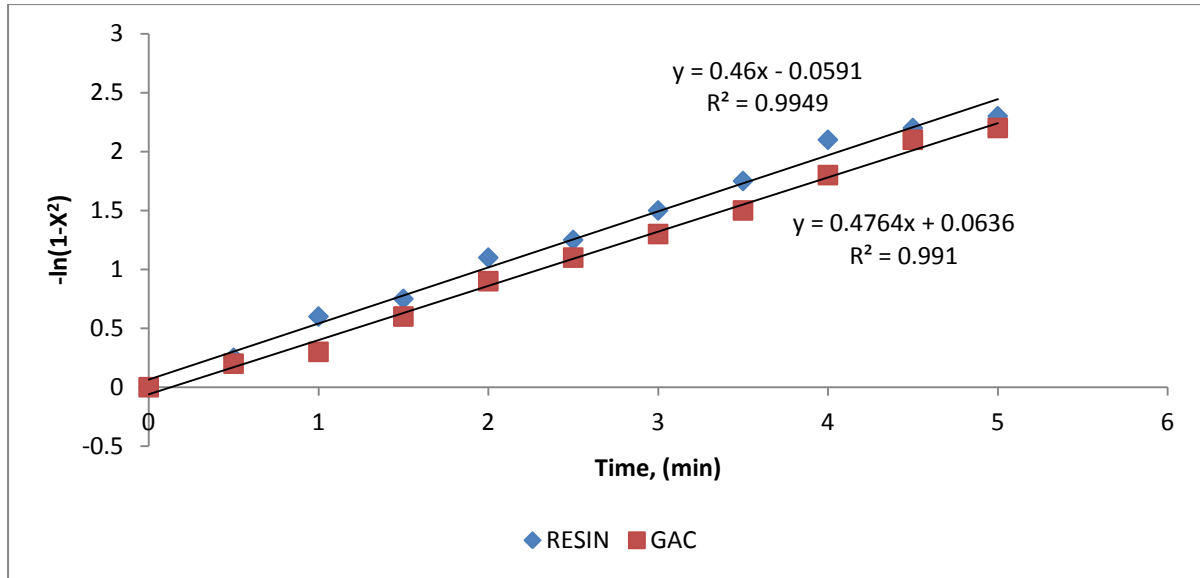


Figure 4.10: HDPM Regression of BTEX adsorption onto PAD 910 polystyrenic resin and granular activated carbon.

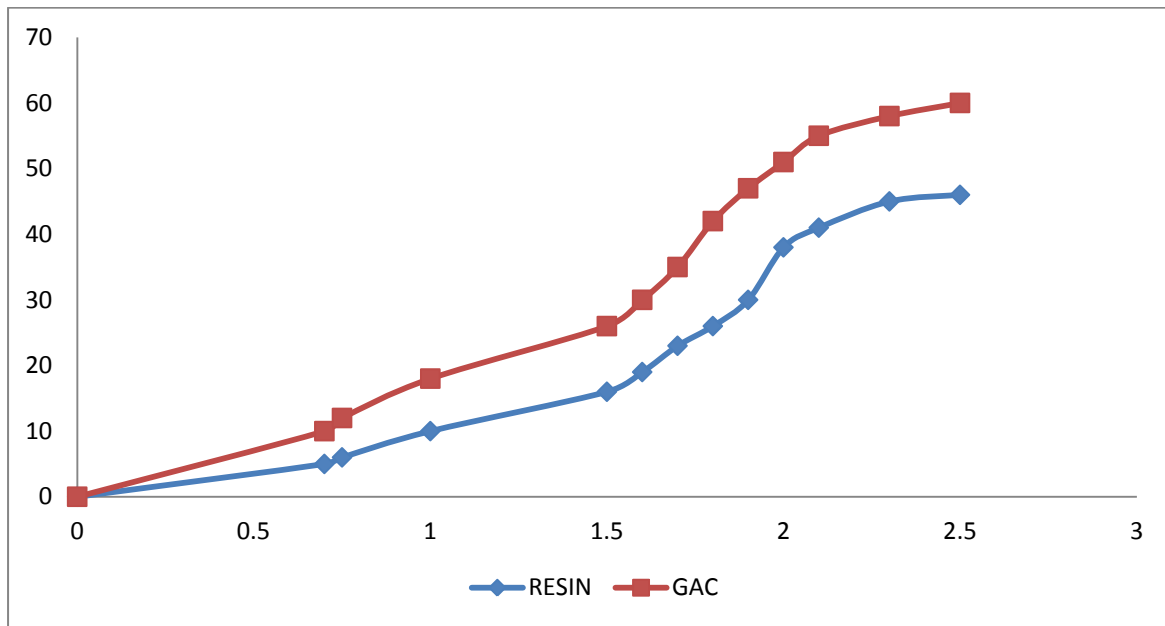


Figure 4.11: Weber-Morris plot of BTEX adsorption onto PAD 910 polystyrenic resin and granular activated carbon

When eliminating the initial first minute of adsorption, which is the time taken before intra-particle diffusion and surface adsorption start taking place on the Webber-Morris plot both adsorbents exhibit a two stage linear section. This represents a regime of macropore/mesopore mass transport which is represented by an intra-particle transport parameter k_{id1} before transition into a second regime of mass transport through the micropore channel which is represented by an intra-particle transport parameter k_{id2} to the adsorption sites. This observation was also made by some researchers (Hall et al., 2009, Valderrama et

al., 2008, Cabal et al., 2009). The diffusion parameters that were obtained from the diffusion model are given in Table 4.5.

Table 4.5: Diffusion parameters for PAD 910 polystyrenic resin and GAC.

Adsorbent	HPDM*			Weber-Morris			
	2K= slope (min ⁻¹)	D _e (m ² /s)	r ²	k _{id1} (mg.g ⁻¹ .min ^{-1/2})	r ²	k _{id2} (mg.g ⁻¹ .min ^{-1/2})	r ²
PAD 910	0.12	5.01 X 10 ¹²	0.97	14.2	0.96	5.1	0.97
GAC	0.22	2.12 X 10 ¹²	0.95	12.4	0.93	4.8	0.96

*All samples were screened to relatively the same size range

Both the homogeneous particle diffusion model and the Weber-Morris intra-particle diffusion model suggests the importance of BTEX molecules diffusion through the pore channels since there was a high correlation of the adsorption experimental data. The effective diffusivity calculated from HPDM followed a close trend as the parameters obtained from the pseudo-second order model, which gave further evidence of the importance of mesoporosity in the adsorption process. Daifullah and Girgis (2002) reported diffusion coefficients of the order of 10⁻¹² for BTEX adsorption onto granular activated carbon, which suggested that the diffusion through resin is faster than granular carbon as a result of a larger surface area for the adsorption process. It is important to note that, since the diffusion coefficient should not be affected by the surface area of the adsorbent, but rather by factors such as the porosity of the adsorbent, size of the adsorbate, temperature and viscosity of the media. This then suggests that, parameters obtained by the HPDM might be very much related to flux and not necessarily to an intrinsic value of diffusion coefficient.

It was confirmed from the Weber-Morris transport parameters that, the order of the transport rate was higher in the first transport regime than in the second transport regime, i.e. $k_{id1} > k_{id2}$ in both cases. This is consistent with the explanation behind a very fast initial rate followed by slow stage diffusion. Terzyc and Gauden (2002) also described the same phenomenon in their study on the sorption of dissolved organic matter. The lower performance, in terms of kinetics that was shown by granular activated carbon compared to the resin was attributed to the pore structure, making accessibility of the BTEX molecules more difficult in the kinetic experiments.

4.2.4 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 0.25g of PAD 910 polystyrenic resin. The concentration-time dependence plot is shown in Figure 4-12.

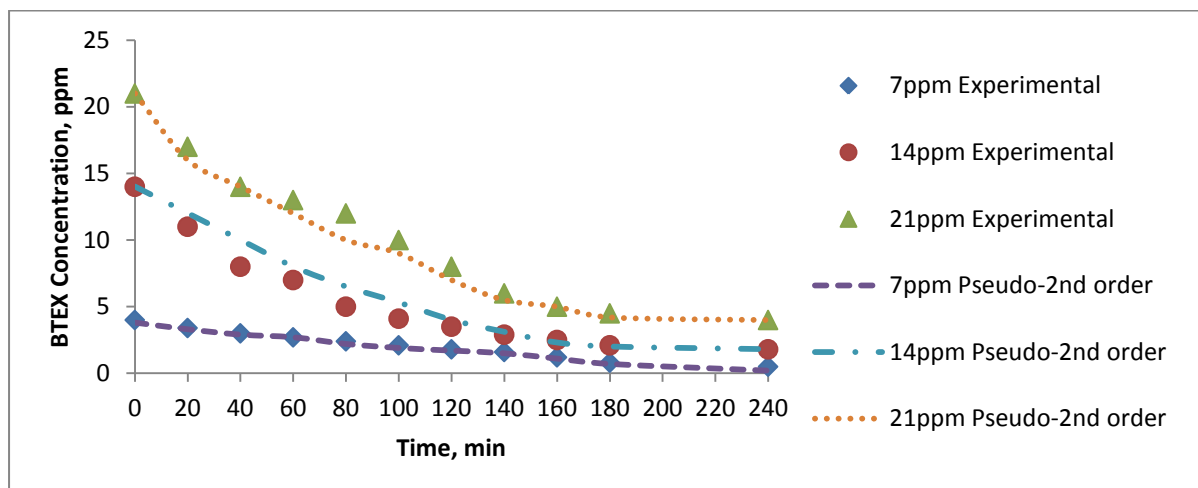


Figure 4.12: Effect of Initial BTEX concentration on adsorption onto PAD 910 polystyrenic resin.

Rate parameters obtained from the experimental data are highlighted in Table 4.6, while Figure 4.13 shows the typical sorption data curves for the effect of initial BTEX concentration on the quantity of BTEX adsorbed per time.

Table 4.6: Rate parameters for initial BTEX concentration effect on the adsorption process

Pseudo-2 nd order Model	7ppm	14ppm	21ppm
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

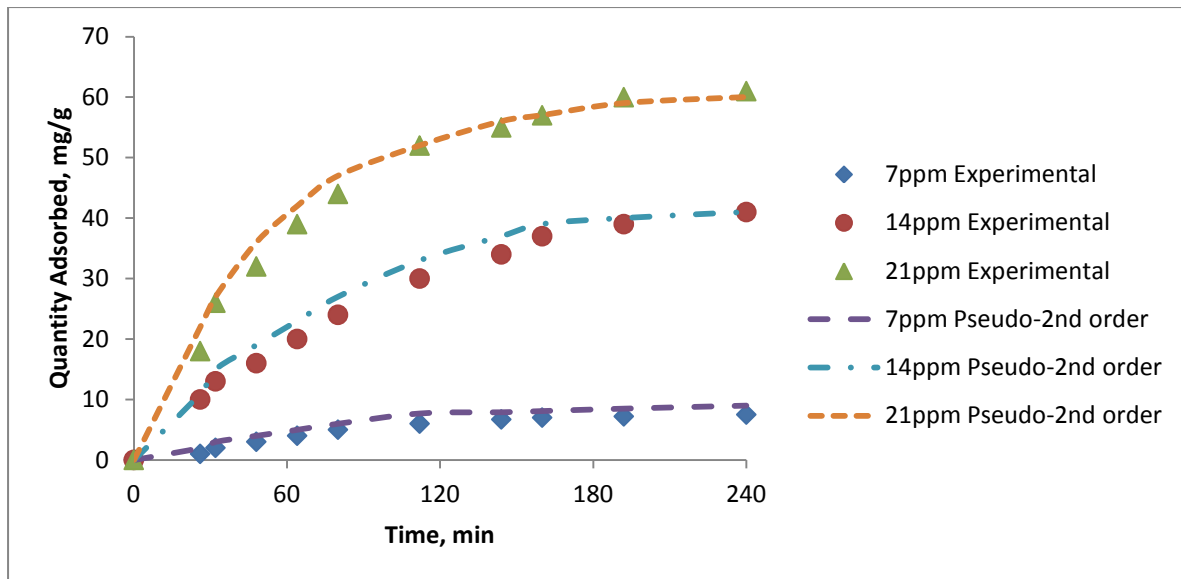


Figure 4.13: Plot of BTEX sorbed capacity versus time showing initial concentration effect

Table 4.6 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 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 Figure 4.13 shows that a larger quantity is adsorbed at higher concentration which is logical because of the greater amount of BTEX available in the aqueous system. It can also be confirmed from Figure 4.11 that the initial concentration influenced the contact time required to reach equilibrium.

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 $h_0 = kC_0^n$. 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.

The experimental data were fitted to the homogeneous particle diffusion model (HPDM) in order to investigate the hypothesis that the diffusion parameter, D_e obtainable from the model may not be an intrinsic effect of diffusivity but only an apparent measure of flux. Table 4.7 shows the HPDM parameters and it also shows the dependence of the D_e on initial concentration. It is also important to note that, since diffusion coefficient is not a function of the initial concentration of the adsorbing species, these results shows that the obtained mass transfer parameter from HPDM is a reflection of flux and not intrinsic effective diffusivity. The parameter further shows a positive correlation as the rate constant with BTEX concentration, further showing the likely hood of it being a reflection of flux.

Table 4.7: Diffusion parameters for the effect of initial concentration on BTEX adsorption

Initial Concentration	2K = Slope (/min)	D_e (m ² /min)	r^2
7ppm	0.0623	6.23×10^{-13}	0.98
14ppm	0.1112	1.02×10^{-11}	0.95
21ppm	0.1234	1.20×10^{-11}	0.99

4.2.5 Effect of adsorbate

A comparative study of the non competitive adsorption of benzene, toluene, ethylbenzene and isomers of xylene onto resin was done over a short period as well as a long period and the concentration-time dependence plots were produced in Figure 4.14 and 4.15.

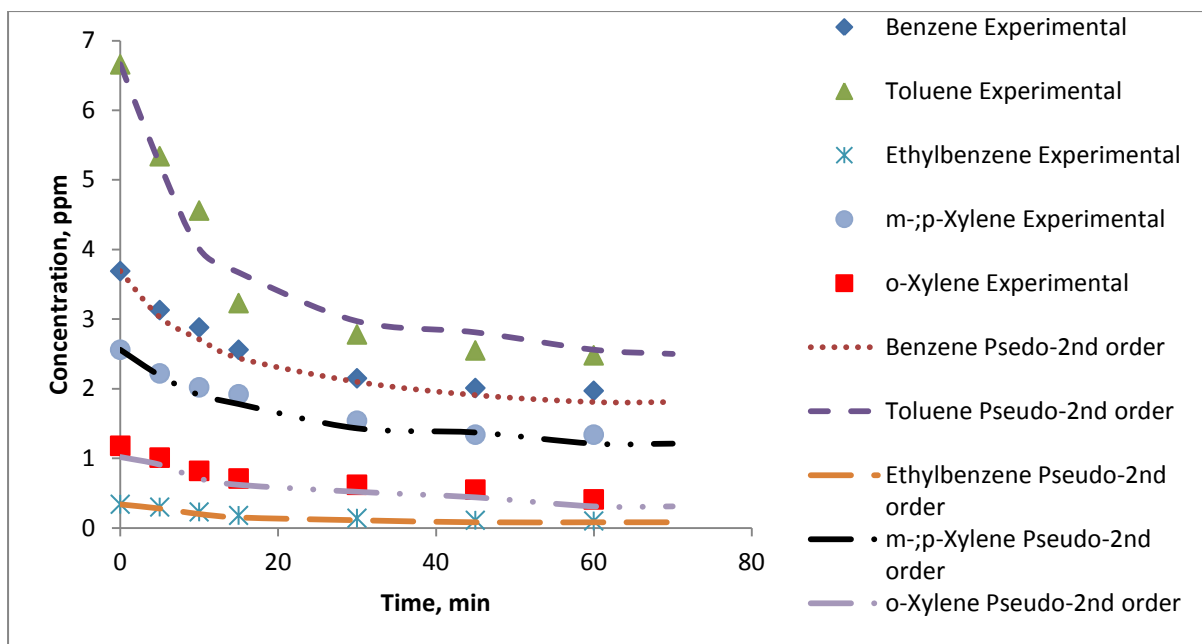


Figure 4.14: Adsorption of BTEX compounds over a short period (0.25g of PAD 910 polystyrenic resin, 25 ml simulated wastewater with 3.69 ppm Benzene, 6.66 ppm Toluene, 0.34 ppm Ethylbenzene, 2.56 ppm m;p-Xylene and 1.18 ppm o-Xylene)

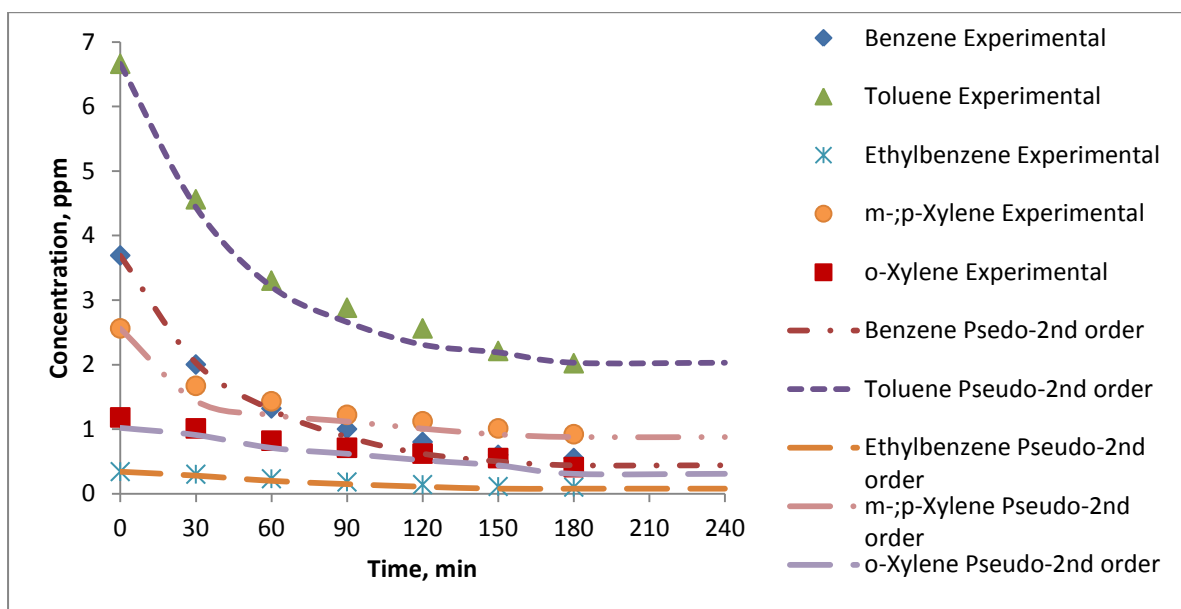


Figure 4.15: Adsorption of BTEX compounds over a long period (0.25g of GAC, 25 ml simulated waste water with 3.69 ppm Benzene, 6.66 ppm Toluene, 0.34 ppm Ethylbenzene, 2.56 ppm Ethylbenzene, 2.56 ppm m;p-Xylene and 1.18 ppm o-Xylene)

Table 4.8: Rate Parameters for adsorption of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene for short period

Pseudo-2 nd order Model	Benzene	Toluene	Ethylbenzene	m-;p-Xylene	o-Xylene
k'_2 (L.mg ⁻¹ .min ⁻¹)	0.44	0.22	0.034	0.17	0.11
r^2	0.91	0.97	0.98	0.90	0.92

Table 4.9: Rate parameters of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene for long period

Pseudo-2 nd order Model	Benzene	Toluene	Ethylbenzene	m-;p-Xylene	o-Xylene
k'_2 (L.mg ⁻¹ .min ⁻¹)	0.34	0.18	0.031	0.11	0.08
r^2	0.96	0.98	0.98	0.97	0.99

The parameters obtained from the study are presented in Table 4.8 and 4.9. Benzene being the smallest of the four compounds in terms of molecular weight and dimension, 78 g/mol against 107 g/mol expectedly transported faster than the other compounds, which is consistent with the theory of diffusive transport for both the long term and the short term process. The rate constant for the long term experiment was much lower than that obtained for the short term for all the BTEX compounds, which further demonstrates that the initial stage of the adsorption process is much faster followed by the second slow transport of BTEX molecules through the micropores to the ‘active sites’.

Using both the HPDM and Weber-Morris plots, the diffusion parameters were obtained for these two sets of studies which are presented in Table 4.10. It is noticeable from Table 4.9, that the trend of the HPDM parameter seemed to change depending on the time regime studied. As it was explained earlier in this section under the effect of concentration, the diffusion parameter from HPDM is reflective of flux. However, during a shorter contact period, the rate seemed to be independent of aromatic size, but rather dependent on the partition coefficient ($\log k_{ow}$) of the aromatic hydrocarbons (BTEX) due to the interfacial processes, with $\log k_{ow}$ of xylene greater than that of benzene (3.12 against 2.20).

Table 4.10: Diffusion parameters for the adsorption of Benzene, Toluene, Ethylbenzene, m-;p-Xylene and o-Xylene

Adsorbate	HPDM		HPDM		Weber-Morris (short term)		Weber-Morris (long term)	
	(short term)		(long term)					
	D _e (m ² /min)	r ²	D _e (m ² /min)	r ²	k _{id} (mg.g ⁻¹ .min ^{1/2})	r ²	k _{id} (mg.g ⁻¹ .min ^{1/2})	r ²
Benzene	3.45X10 ⁻¹²	0.97	2.11X10 ⁻¹³	0.96	2.13	0.95	0.42	0.97
Toluene	2.34X10 ⁻¹¹	0.98	3.21X10 ⁻¹³	0.92	3.13	0.99	0.31	0.95
Ethylbenzen	3.67X10 ⁻¹¹	0.82	1.02X10 ⁻¹³	0.9	1.23	0.98	0.44	0.88
m-;p-Xylene	2.12X10 ⁻¹¹	0.87	1.98X10 ⁻¹³	0.88	1.01	0.91	0.67	0.83
o-Xylene	1.89X10 ⁻¹³	0.96	3.91X10 ⁻¹³	0.96	1.36	0.07	0.13	0.93

For the aqueous phase system, an equivalent of Fick's law could be written for the adsorption process at the carbon/water interface as:

$$\text{Flux} = (\text{Mass Transfer Coefficient})(\text{Change in BTEX concentration}) \quad (4-2)$$

$$\text{Which can be written as: } \text{Flux} = \text{MTC} * (C_{\text{bulk}} - C_{\text{interface}}) \quad (4-3)$$

Where the flux through the adsorbent/water interface would be equivalent to the adsorption rate per interfacial area and since the same adsorbent was used, it could be assumed that the rate is equivalent to flux. The mass transfer coefficient is equivalent to the diffusivity of the BTEX through the water medium via the interface, and is dependent on the molecular size of the BTEX compound. The interfacial concentration, $C_{\text{interface}}$ is however dependent on the partition coefficient. The octanol-water partition coefficient is identical to the carbon-water partition coefficient and could be written according to the equation:

$$k_{ow} \equiv k_{AC/W} = \frac{C_{\text{interface},AC}}{C_{\text{interface},water}} \quad (4-4)$$

Since $C_{\text{interface}, AC}$ is constant, as $k_{AC/W}$ increased, the $C_{\text{interface},water}$ decreased. Thus, a possible explanation for the change trend for the HPDM parameter from a short study to a long term study would be a change in the dominant term in equation 4-3. It seems like there is a transition from an interfacial process dominant regime during which case, the interfacial BTEX hydrocarbon concentration was more dominant in driving the adsorption process

during the short contact period, to a diffusive transport dominant phase, during which the mass transfer coefficient is more dominant in driving the adsorption process during the long term study.

On contrary, the intra-particle diffusion rate parameter obtained from the Weber-Morris plot does highlight the importance of BTEX compound size in the transport of the molecules through the pore channels, highlighting the ease of diffusion of the smaller isomers of xylene over the other compounds. As with the global rate parameter, it is observed both from the HPDM and Webber-Morris model that the parameters reduced from short term study to long term study, suggesting the shift of diffusion from the easier accessible mesopore volume of the resin through the deeper less accessible pore volumes to the ‘active sites’.

4.3 Adsorption Isotherm Study

Over a twenty four hour contact time with two adsorbents (GAC and PAD 910 polystyrenic resin) in a shaker maintained at 180 rpm, the BTEX adsorption isotherms were studied. The experimental data were fitted to the Langmuir, Freundlich and the linearized Dubin-Radushkevich (D-R) isotherm models. However, only the Langmuir parameter was used in the discussion of the BTEX compounds capacity due to limitation inherent in the Freundlich model because there is no practical limit to the adsorption capacity due to the $1/n$ th power of concentration. Moreover, Site (2001) concluded that the Langmuir isotherm model is the most useful in representing the adsorption of aromatic compounds onto carbons. The mean free energy parameter, E from the D-R model was used to further understand the mechanism of adsorption.

4.3.1 Effect of internal diffusion

The adsorption isotherm of BTEX at 25⁰C onto granular activated carbon and PAD 910 polystyrenic resin was studied and the experimental data with the Langmuir model fitted plot is shown in Figure 4.16.

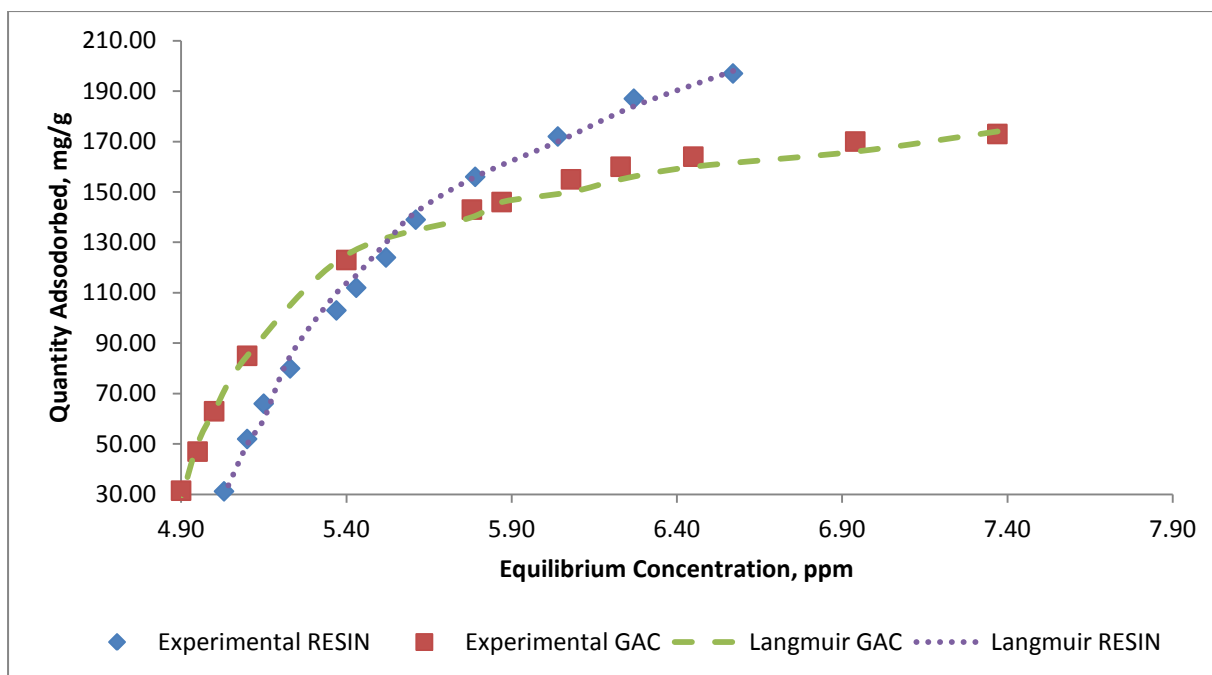


Figure 4.16: BTEX adsorption isotherm on GAC and PAD 910 polystyrenic resin at 25⁰C (0.25 g adsorbent in 25 ml simulated wastewater of initial concentration range: 7 – 15 ppm)

The isotherm parameters from the Langmuir and D-R models are highlighted in Table 4.11. From the maximum adsorption capacity parameter q_e obtained from the Langmuir model, it is evident that there is a direct correlation between this parameter and the specific surface area of the adsorbent. The commercial PAD 910 polystyrenic resin which has the highest SSA of 670 m²/g had the highest capacity, while the low surface area activated carbon which has the lower SSA of 580 m²/g also had a lower BTEX capacity. 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 this adsorption - ‘active sites’ is expectedly proportional to the SSA. However, on normalizing the maximum adsorption capacity by the SSA, the influence of the pore size distribution is demonstrated.

Table 4.11: BTEX adsorption isotherm parameters for Two Different Adsorbents GAC and Resin

Adsorbent	Langmuir				Linear D-R			
	K_L (L/mg)	q_m (mg/g)	SSA Normalized q_m (mg/m ²)	r^2	$\beta \times 10^8$ (mol ² /J ²)	q_D (mg/g)	E (kJ/mol)	r^2
GAC	0.44	110.2	0.27	0.99	4.12	40.34	3.28	0.91
RESIN	0.79	78.9	0.66	0.95	1.77	63.23	5.21	0.98

It is important to note that, the normalized adsorption capacity was higher for the resin than the GAC (0.66 vs 0.27 mg/m²) which suggests that this resin has a better potential as the adsorbent for removing BTEX compounds. It is expected that the normalized adsorption capacity is controlled by surface chemistry and porous structure of the activated carbon. With BTEX size being 9.1Å*7.3Å*3.8Å, any pore below 10Å might be inaccessible to the BTEX molecules. According to the structural analysis of the adsorbents, there are about 62.3% (~0.32 cc/g) of the pores in resin and 36.6% (~0.09 cc/g) in GAC. This explains why the normalized adsorption capacity was higher in PAD 910 polystyrenic resin (with accessible pore volume of about 0.30 cc/g). The positive correlation of the porosity on the adsorption equilibrium capacity of BTEX was also observed by Dorea et al. (2007).

The other parameter obtained from the Langmuir model, k_1 i.e. Langmuir adsorption constant related to the adsorption energy is indicative of the intensity of the adsorption process according to Site (2001) could indeed be related to the partition coefficient at equilibrium as equal to the ratio of the adsorbate concentration in the solid phase at equilibrium, to the solute concentration in the aqueous phase at equilibrium. This parameter consistently followed the trend observed of the adsorption rate constant, further suggesting the importance of mesopore volume/fraction in driving the adsorption process. It could however also be argued that this parameter is a function of the hydrophobicity of the carbon surface.

4.3.2 Effect of adsorbate

Figure 4.17 shows the adsorption isotherm data obtained from a comparative competitive study of the equilibrium adsorption of benzene, toluene, ethylbenzene and isomers of xylene with the adsorption conditions, while the parameters are tabulated in Table 4.11.

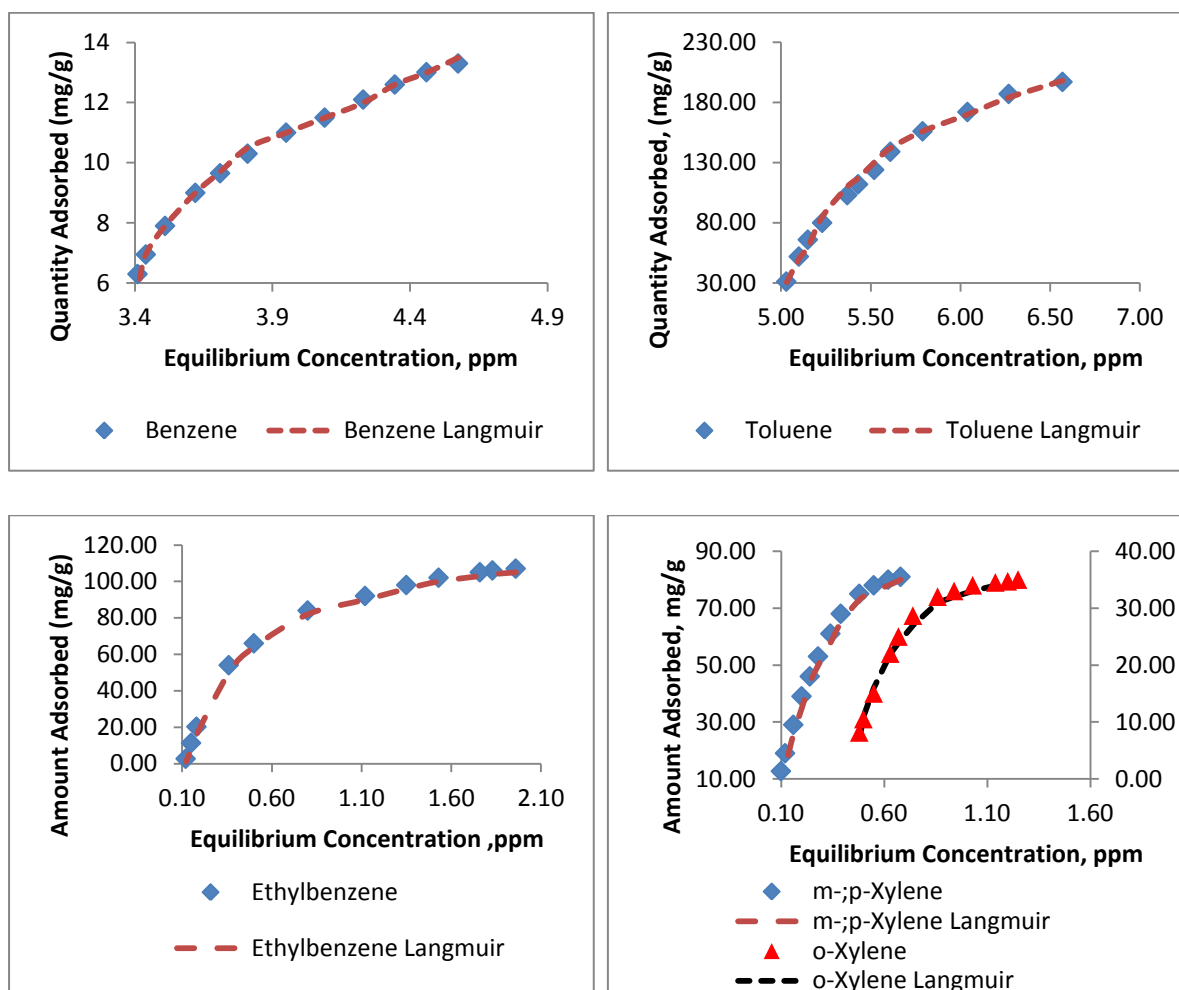


Figure 4.17: Benzene, Toluene, Ethylbenzene and Xylene Adsorption isotherm on PAD 910 polystyrenic resin at 25⁰C (0.25 g in 25 ml simulated wastewater of initial concentration range: 0.1 – 7 ppm)

Table 4.12: 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
ETHYLBEN	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

As demonstrated in Table 4.12, the equilibrium capacity of the PAD 910 polystyrenic resin used was greater for toluene. Compared to the other compounds, toluene has a smaller size which makes it easier for its molecules to diffuse into more micropores for 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 inaccessible 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.

On the contrary, the adsorption coefficient, K_L was observed to be much higher for xylene. This further highlights the relationship between this adsorption coefficient to the partition coefficient at equilibrium as being equal to the ratio of the sorbate concentration in the solid phase at equilibrium, to the solute concentration in the aqueous phase at equilibrium. In addition to that Chiou et al. (1979) observed that an inverse relationship exists for organic compounds between sorption coefficients and solubilities.

4.3.3 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 Figure 4.18 while the parameters obtained from the isotherm models are given in Table 4.13. 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 attach to carbon surface oxygen groups through hydrogen bonding and may 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.

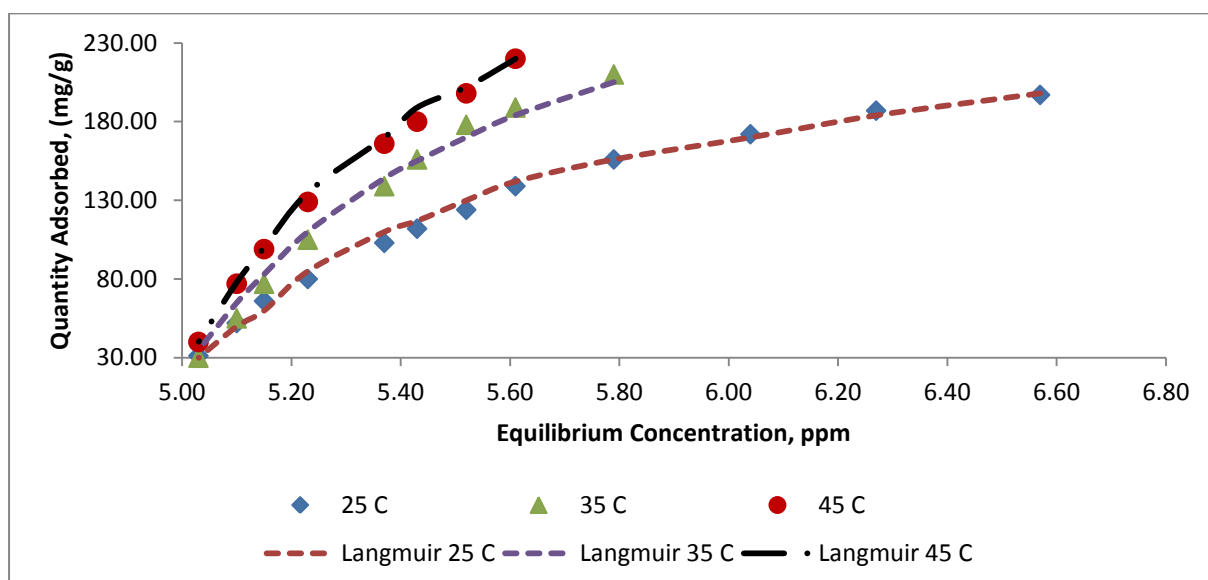


Figure 4.18: BTEX Adsorption Isotherm on PAD 910 polystyrenic resin at different temperature (0.25 g adsorbent in 25 ml simulated wastewater on initial concentration range: 0.34 – 15 ppm)

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 on 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

temperature of 35⁰C and 45⁰C, which could have been used to normalize the equilibrium capacities.

Table 4.13: BTEX adsorption isotherm parameters at different temperatures

Temp. ⁰C	Langmuir				Linear D-R			
	K_L (L/mg)	q_m (mg/g)	SSA Normalized q _m (mg/m ²)	r²	β X 10⁸ (mol ² /J ²)	q_D (mg/g)	E (kJ/mol)	r²
25	0.6	198	0.87	0.97	4.27	44.96	3.45	0.97
35	0.62	210	1.22	0.99	2.93	62.49	3.74	0.96
45	0.53	220	1.62	0.99	3.29	55.21	4.12	0.9

4.3.4 Thermodynamic analysis of BTEX adsorption

The mean free energy of adsorption E in kJ/mol was obtained according to Equation 2-19 from 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 – 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:

$$\Delta G^0 = -R \times T \times \ln K_l \quad (4-5)$$

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 -20.3kJ/mol to – 36.6kJ/mol,

indicating the likely spontaneity of the adsorption process as expected. Similarly, the (ΔG^0) is also equivalent to:

$$\Delta G^0 = \Delta H^0 - T \times \Delta S^0 \quad (4-6)$$

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:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \times T} \quad (4-7)$$

Table 4.14, highlights the thermodynamics properties obtained by linear regression of K_L values obtained from the temperature study against $1/T$, according to equation 4-7.

Table 4.14: Thermodynamics properties of the adsorption of BTEX onto PAD 910 polystyrenic resin

Temperature, K	K_L L/mol	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/mol	r^2
298	6.98E4	-20.3	-4.67	69.34	0.88
308	6.45E4	-26.12	-4.17	62.19	0.84
318	5.77E4	-36.6			

The small positive value 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 alliance with the 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 in the literature review section, 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 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).

4.4 Adsorption Dynamic Column Studies

Batch isotherms do not give precise scale-up data for the design of an adsorption column. The practical applicability of GAC and/or PAD 910 resin to adsorbed adsorbates was investigated and established in a dynamic column study. The experimental breakthrough curves for the adsorption of BTEX in a column packed with GAC and PAD 910 resin at different bed heights are shown in Figure 4.19 and 4.20.

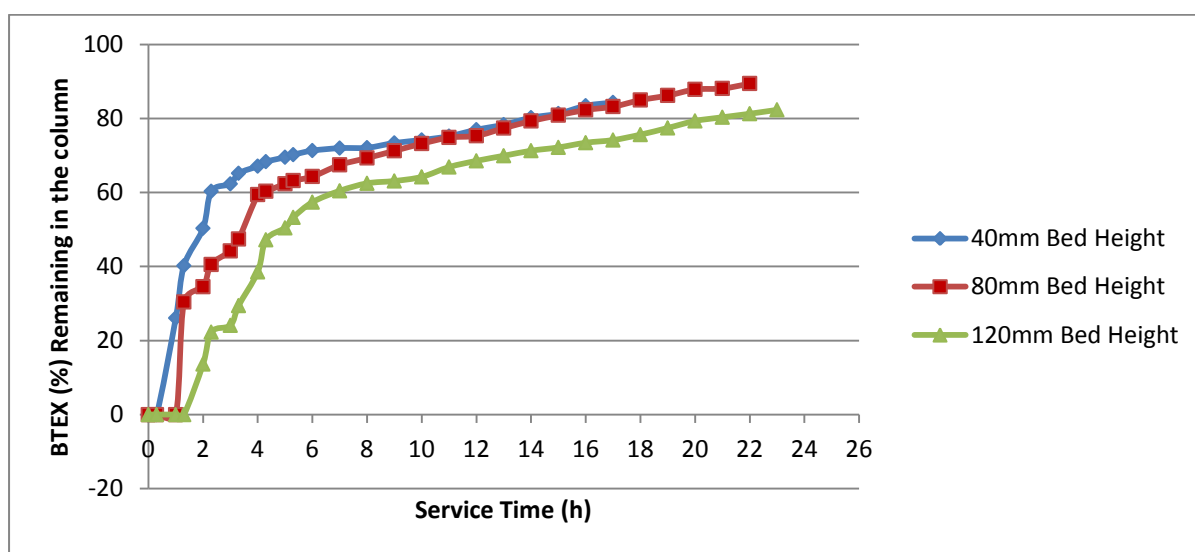


Figure 4.19: Breakthrough curves for benzene BTEX onto GAC

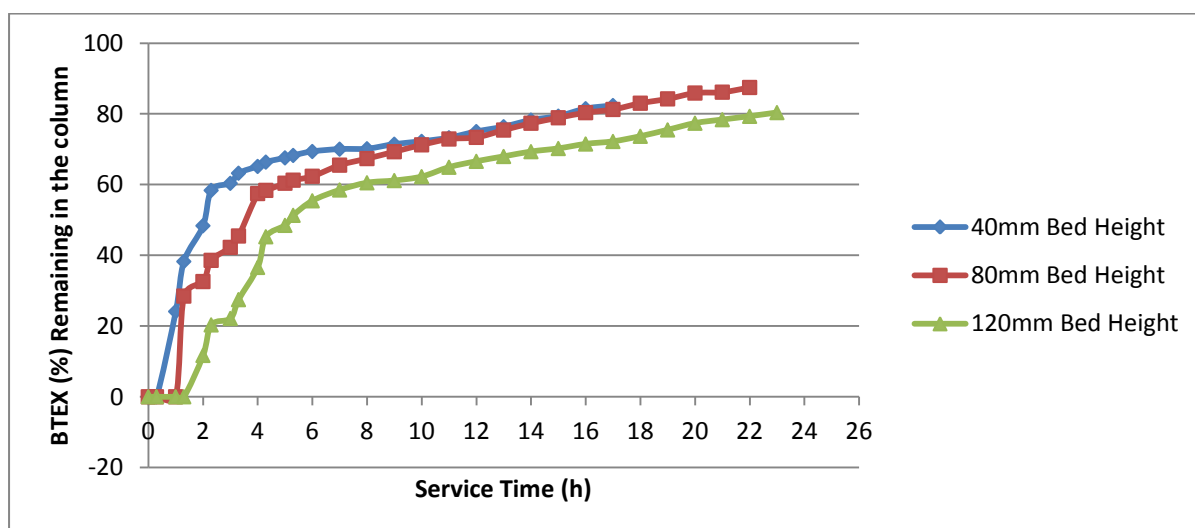


Figure 4.20: Breakthrough curves for BTEX onto PAD 910 polystyrenic resin

Influent concentrations of 14.43 mg/L for BTEX were used for all the column experiments. The adsorption capacity per unit bed volume (N_0) and adsorption rate constant (K) are estimated by making use of the Bed Depth Service Time (BDST) equation. Breakthrough is defined as the point where a specified amount of the influent is detected in the effluent (Lagrega et al., 1994). A breakthrough of 20% on both columns occurs when the concentration of the effluent is 20% of the influent concentration (~15mg/L) and 60% breakthrough occur when the effluent is 60% of the influent on GAC and PAD 910 polystyrenic resin column.

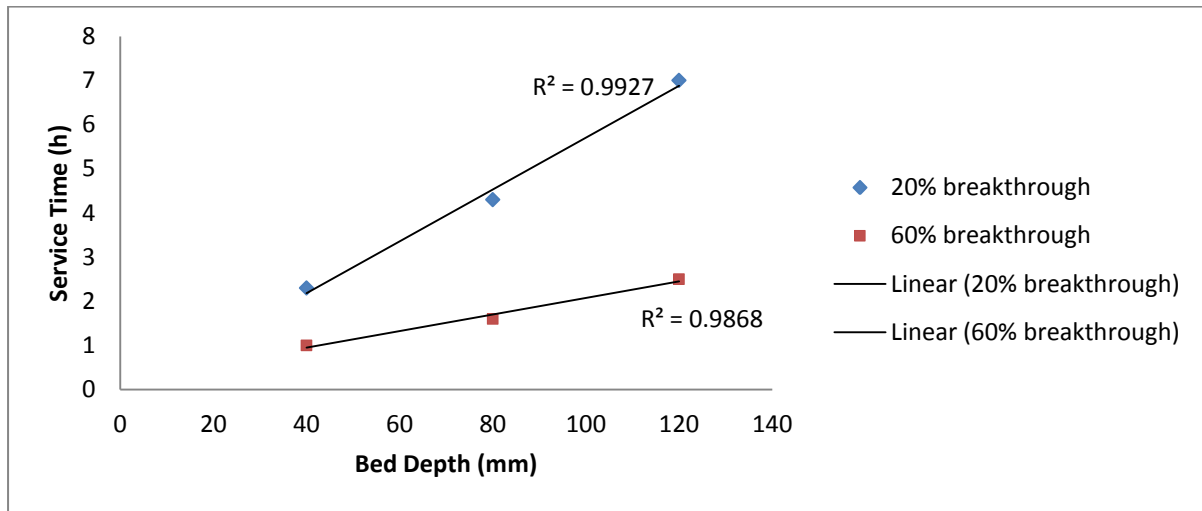


Figure 4.21: BDST plot for BTEX adsorption onto GAC, determined from a theoretical approach

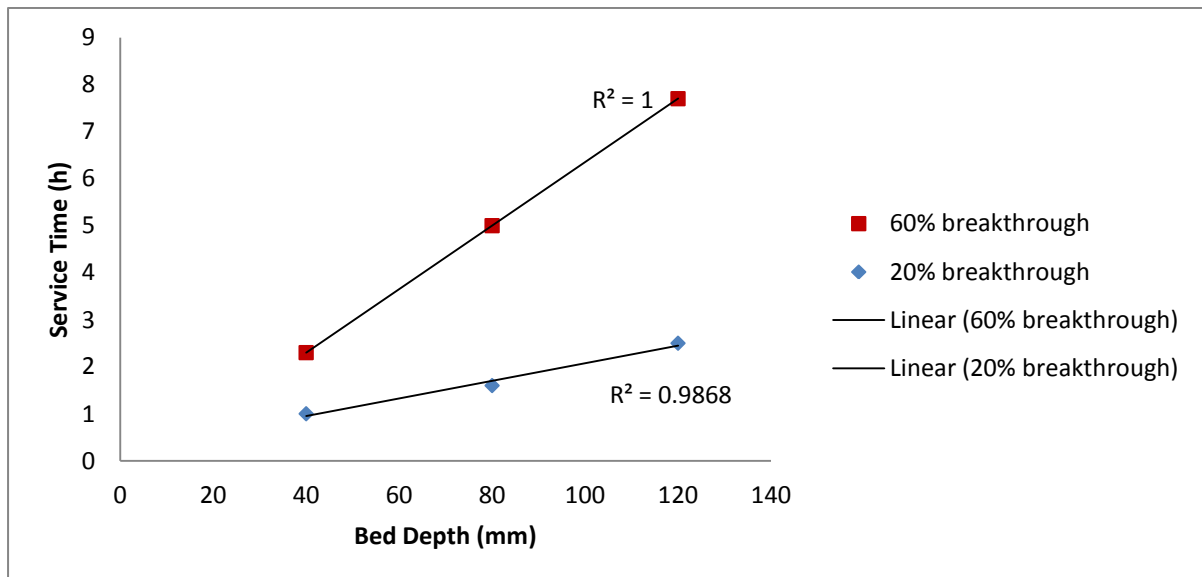


Figure 4.22: BDST plot for BTEX adsorption onto PAD 910 polystyrenic resin determined from a theoretical approach.

4.4.1 Effect of bed depth on breakthrough

The adsorption capability of GAC and PAD 910 resin was tested at various bed depths of 40 mm, 80 mm and 120 mm, with a 6 ml/min flow rate and 14.43 mg/L BTEX concentration. The bed depths were obtained after the columns were each packed with GAC and PAD 910 polystyrenic resin of 17 g, 36 g and 55 g. Fig 4.21 and 4.22 above shows the combined breakthrough curves for the % adsorbates remaining in the column versus service time for different bed heights at a constant flow rate of 6 ml/min. The breakthrough time, t_b , for BTEX was found to increase with increased bed depths at 20% and 70% BDST, (see Table D4).

For this study, it was confirmed from the 20% and 60% breakthrough that the increase in the bed depth increases breakthrough time t_b and that the use of a single column is not applicable in a case where the influent concentration that is to be treated is high. In addition, the slope of the S-curve from t_b to the point of exhaustion is found to decrease as the bed depth increases from 80 mm to 120 mm, which means that the breakthrough curve becomes steeper as the bed depth decreases. Therefore there is a higher percentage of BTEX removed from the wastewater due to the increase in the bed depth of the packed column. The adsorption rate constant (K_a); which characterizes the rate transfer of the adsorbates from the liquid phase onto the solid was found to be 1.02×10^{-2} l/mg-h for benzene, 0.98×10^{-2} l/mg-h for toluene, 1.23×10^{-2} l/mg-h for ethylbenzene and 1.11×10^{-2} l/mg-h for xylene.

4.4.2 Data evaluation

BDST equation is based on the work by Bohart and Adams (1920) which stated that the breakthrough time is a linear function of the bed depth. The continuous column studies data and the data of the breakthrough curves are shown in Appendix E. The breakthrough time at 60% is considerably higher than that of 20% for BTEX at 120 mm bed height for the breakthrough points investigated. This is due to the ability of the resin to retain adsorbate efficiently within the column as the loading rate increases.

The adsorption capacity (N_0) was calculated for both 20% and 60% breakthrough and from the actual experimental data obtained. Comparing Table 4.16 with Table 4.17 it is evident that PAD 910 polystyrenic had higher adsorption capacity per unit bed volume for 60% breakthrough than 20% breakthrough for BTEX. The same table also compares the theoretical adsorption capacity determined using the BDST parameters to actual experimental adsorption capacity obtained during continuous packed column operation. The lack of

agreement between the 60% theoretical and actual capacity as compared to the better correlation between the 20% theoretical and actual capacity may be from the fact that Bohart and Adams (1920) equation which is based on BDST theory assumes a rectangular isotherm instead of a curved isotherm assumed by real systems (Cooney, 1999). Adak et al. (2006) reported a similar case where there was a difference between the experimental and theoretical breakthrough curves due to the assumption that the isotherm followed a different model.

The capacity of PAD 910 polystyrenic resin for BTEX at 14.47 mg/l for actual experimental values and theoretical values was found to be greater than the capacity determined from batch adsorption data. Hence, the result shows that this resin has a better adsorption affinity for organic compounds comparable to the result of adsorbent used by Banerjee et al. (1995). In addition, the result is in contrast with the result reported by Ahmaruzzaman and Sharma (2005) and this is due to the fact that the adsorbents used by these authors had a higher specific surface area than GAC used in this study.

Table 4.15: % Adsorbate removal at a breakthrough contact time of 4 hrs

Bed Height (mm)	Benzene % Removal	Toluene % Removal	Ethylbenzene % Removal	m-;p-Xylene % Removal	o-Xylene % Removal
40	30.1	37.7	35.4	34.4	32.3
80	66.0	78.0	75.4	74.5	76.3
120	91.2	93.8	92.4	91.3	91.0

Table 4.16: Comparison of theoretical and experimental adsorption capacity at 20% breakthrough of initial adsorbate concentration

Adsorbates	N_0 , (mg/l)	Theoretical Capacity, (mg/g)	Actual Capacity, (mg/g)
Benzene	2.45	0.52	0.58
Toluene	3.33	0.44	0.49
Ethylbenzene	0.23	0.22	0.23
m-; p-Xylene	1.23	0.12	0.18
o-Xylene	0.45	0.09	0.11

Table 4.17: Comparison of theoretical and experimental adsorption capacity at 60% breakthrough of initial adsorbate concentration

Adsorbates	N_0 , (mg/l)	Theoretical Capacity, (mg/g)	Actual Capacity, (mg/g)
Benzene	1.23	1.98	0.99
Toluene	1.46	1.23	0.66
Ethylbenzene	0.12	1.11	0.87
m-; p-Xylene	0.19	1.09	0.22
o-Xylene	0.08	0.03	0.10

4.4.3 Design adsorption column for different concentrations

The column design parameters obtained from the earlier test with 6 ml/min, initial concentration of 14.47 ppm and bed depths of 40, 80 and 120 mm can be used for the design of the new adsorption column with a new influent concentration of ~30 ppm. A new BDST equation was developed with new slope and intercept due to the changes in the concentration. This new equation for a change in concentration is developed from the equation below instead of running additional experiments:

$$\text{New Slope} = \text{Old slope} \left(\frac{V_{old}}{V_{new}} \right) \quad (4-8)$$

$$\text{New } b = \text{Old } b \left(\frac{C_{0,old}}{C_{0,new}} \right) \frac{\ln[(C_{0,new}/C_b)-1]}{\ln[(C_{0,old}/C_b)-1]} \quad (4-9)$$

The plot in Figure 4.21 represents the results of BTEX adsorption with initial concentration of 30 ppm against the original C_0 of 14.47 ppm. The predicted BDST equations for the 30 mg/l influent concentration of BTEX are demonstrated in Figure 4.21. The equation was based on the new slope and the new intercept derived from the BDST equation for 14.47 mg/l feed concentration. The increase in the influent concentration of the adsorbates from 14.47 mg/l to 30 mg/l also leads to a decrease in the breakthrough times, which is to be expected. The predicted point for the 30 mg/l concentration can be seen to match the three different bed heights obtained from the 14.47 mg/l concentration. The breakthrough times corresponding to 20% actual concentration of 14.47 mg/l and the calculated 30 mg/l is obtained in Table 4.17.

Table 4.18: 20% breakthrough time for experimental data based on 14.47 mg/l with calculated data for adsorbates adsorption with 30 mg/l

Bed Height (mm)	Service Time (hr)	
	At 14.57 mg/l	At 30.0 mg/l
40	2.01	1.11
80	4.01	2.92
120	6.53	5.55

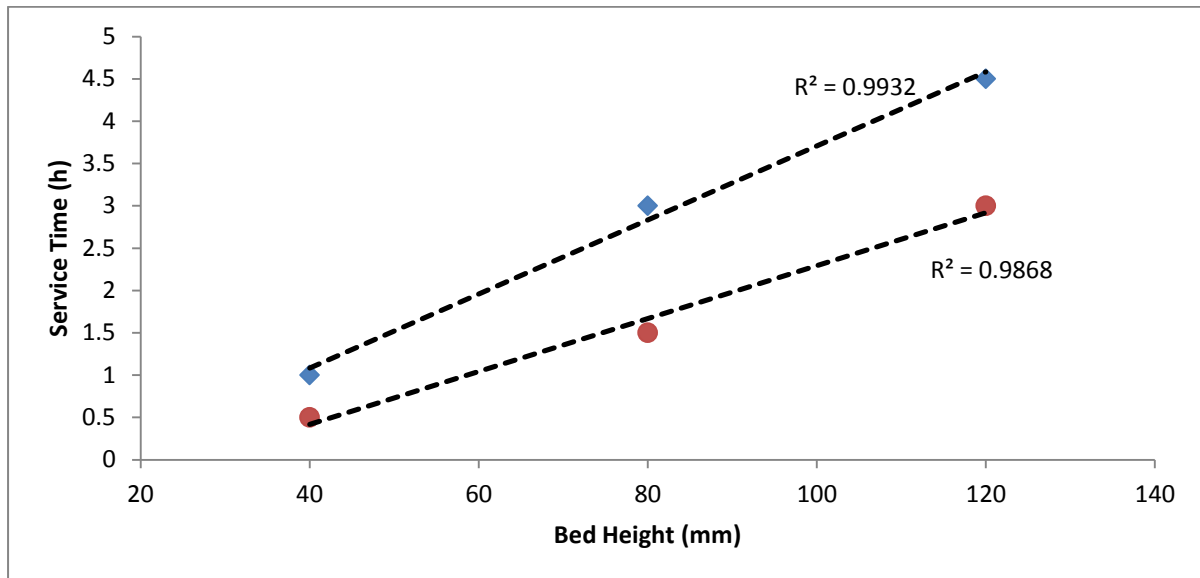


Figure 4.23: Comparison of BDST model predictions based on $C_0 = 14.47$ mg/l with calculated BDST for BTEX adsorption with $C_0 = 30$ mg/l

4.4.4 Design of adsorption column for different flow rate

The initial concentration of 14.47 ppm, flow rate of 6 ml/min and bed depths of 40, 80 and 120 mm was used for the design of a new adsorption column at a flow rate of 6 ml/min. The breakthrough times which correspond to 20% actual concentration of 14.47 ppm was obtained from the new BDST equation which was developed from the new slope. The rate constant (K_a) is not affected by a change in flow rate because the solid-phase mass transfer resistance is usually the dominant factor. The new slope for a change in flow rate was

developed from equation 4-8, while the breakthrough time, which is a linear function of the bed depth, was determined from the equation below for the three bed depths:

$$t_b = \frac{D N_0}{\Sigma C_0 v} - \frac{1}{K C_0} \ln \left(\frac{C_0}{C_b} - 1 \right) \quad (4-10)$$

Table 4.19: 20% breakthrough time for theoretical data based on 6 ml/min with calculated data for adsorbates adsorption with 3 ml/min

Bed Height (mm)	Service Time (hr)	
	At 3.0 ml/min	At 6.0 ml/min
40	5.30	1.23
80	10.23	3.67
120	14.23	5.34

4.4.5 Comparison

Adsorption capacity from the dynamic column test reported by Banerjee et al. (1995) had shown that all the adsorbates removed had a lower adsorption affinity for GAC as compared to PAD 910 polystyrenic resin used in this study. However, it could be noted that, the chemical composition of the GAC does not belong to the same class as the polystyrenic resin used in this study. The resin SSA was found to be in the range of 0.27 to 1.67 m²/g which is comparable to 1.3 m²/g for GAC used in this study. The adsorbent used by Banerjee et al. (1995) and the resin used in this study are almost of the same equal parameters which might be responsible for the lower affinity of the adsorbates for the PAD 910 polystyrenic resin and GAC. The adsorption capacity for the adsorbent used by Sarkar and Acharya (2006) was found to be higher than the resin used in this study. Furthermore, the result was in contrast with the findings of Ahmaruzzaman and Sharma (2005) and this is due to the fact that their adsorbents had a higher surface area than the one in this study.

5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The competitive adsorption of benzene, toluene, ethylbenzene and isomers of xylene, as representatives of aromatic hydrocarbons, onto granular activated carbon and PAD 910 polystyrenic resin from aqueous phase has been studied in terms of kinetics, equilibrium isotherms and dynamic column study. Commercial granular activated carbon and polystyrenic resin was used without any prior treatment in order to investigate the effect of varying original adsorbents properties on BTEX adsorption and the performance of the adsorbents.

The PAD 910 polystyrenic resin had a better performance compared to the GAC. The difference in adsorption capacity of the GAC used in this study and the granulated natural zeolite for the adsorption of BTEX used by Laleh et al. (2011) might be as a result of the differences in the SSA of both adsorbents, particle size, initial concentration of BTEX in the aqueous solution, the existence of other species that may compete with the BTEX species of interest for adsorbent active sites or the pH range of the solution. All of the parameters that determine the adsorption rate mentioned above make it difficult in comparing the adsorption capacity that is reported in this study with previous studies. The porous structure of the PAD 910 polystyrenic resin made this adsorbent to be more accessible to the BTEX molecules hence it was better when compared to GAC in this study.

The batch equilibrium study was done to investigate the underlying factors that influence the rate of adsorption onto PAD 910 polystyrenic resin and GAC. However, the study focused more on the PAD 910 polystyrenic resin since it performed better than GAC and also the fact that there is no documented and published literature for this type of adsorbent for this particular application. The derivative of this study aimed at generating data and documenting the influence of identified factors for the PAD 910 polystyrenic, which can be used for process modelling. BTEX adsorption was best described by the pseudo-second order model which is based on the vacant sites and chemisorption assumptions. Mesoporous adsorbent had a higher rate of BTEX removal, demonstrating the importance of accessibility to the active sites which are vacant. The high correlation of the adsorption experimental data to both the homogeneous particle diffusion model and the intra-particle diffusion model suggests the importance of BTEX molecules diffusion through the pore channels during the adsorption process. A positive dependence of rate parameters on the initial BTEX concentration was

observed, consistent with the theory of diffusive transport control as stated by Febrianto et al. (2009).

Under the conditions studied, the adsorption process appeared to be two-staged: a fast stage for about 45 minutes, followed by a much slower and longer second stage. The intra-particle diffusion model suggests the two-stage process is likely due to the faster macropore diffusion and the slower micropore diffusion. In both cases, the diffusion rate was more favoured by the BTEX smaller size in consistence with diffusive transport theory. Interestingly, there was a negative dependence of adsorption rate on the amount of carbonyl oxygen groups on the carbon surface especially as the contact time increased. This may likely be due to the formation of the donor-acceptor complex as the carbonyl groups are being exhausted, thus causing a steric hindrance for further BTEX adsorption.

The significance of this study is the fact that it can be utilized as a tool to determine the feasibility of using a low cost adsorbent (PAD 910 polystyrenic resin) to treat water contaminated with benzene, toluene, ethylbenzene and isomers of xylene. Due to the lower adsorption capacity of the PAD 910 polystyrenic resin, the adsorbent requirements for the nominated adsorbents will be higher when compared to GAC. 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 resin, it means larger equipment is required. The long term benefits such as lower adsorbent cost and regeneration possibilities should be considered during the design operation phase.

The calculated PAD 910 polystyrenic resin required for pilot design will be based on the given influent concentration and the plant conditions. Although the required adsorption capacities give an estimate of the PAD 910 polystyrenic resin required, the actual adsorption capacity will vary according to the various adsorption parameters. Sarkar and Acharya (2006) concluded from their research that if pH of the waste water is higher than the pK_a value of the adsorbates, then there will be lesser adsorption due to dissociation of the adsorbate molecules. Therefore, the engineering applications would also be carried out under different conditions and the pH of the influent will also be varied. Moreover, the PAD 910 polystyrenic requirements should be seen as a function of the influent and effluent concentration required. Therefore, pilot scale experiments using the same operating conditions were carried out with the same waste water stream prior to design scale up.

Adsorption Isotherm

The total BTEX quantity adsorbed at equilibrium seemed to be more dependent on the specific surface area (SSA) of the adsorbent than on the mesopore volume, likely due to the number of 'active sites' for the adsorption to take place. However, on normalizing the quantity adsorbed by the SSA, the contribution of the mesopore volume becomes more evident, suggesting part of the micropores may not be accessible to BTEX due to steric hindrance. Toluene had a greater adsorption capacity than xylene which is larger in size, which further supports the argument of steric hindrance, hence a need to consider the mesopore fraction/volume while choosing a suitable adsorbent for target BTEX remediation.

Further supporting the electron-donor-acceptor mechanism, there was a positive dependence of the quantity adsorbed on the total oxygen functional groups. 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 small 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.

Although the thermodynamic analysis shows an exothermic process, there was a positive dependence of the quantity adsorbed with temperature. A possible explanation is the reduced steric hindrance at higher temperatures due to the increased diffusivity of BTEX molecules. In addition, the positive temperature effect is consistent with the chemisorptions process.

The following conclusions can be drawn from this study:

1. The equilibrium between benzene, toluene, ethylbenzene and isomers of xylene in the solution and PAD polystyrenic resin surface was achieved between the first 45 and 90 minutes of the agitation respectively, after which the process approached equilibrium.
2. More than 95%, 88%, 50%, 84% and 90% of benzene, toluene, ethylbenzene and xylenes were adsorbed onto the PAD polystyrenic resin within the first 60 minutes of agitation respectively, after which there was a slow approach to equilibrium.
3. The amount of adsorbate adsorbed was found to increase with an increase in the adsorbent dosage for both GAC and PAD polystyrenic resin.

4. Toluene has the highest adsorption capacity among the adsorbates studied onto PAD polystyrenic resin and GAC.
5. The adsorption capacities of the studied adsorbates are lower than the capacity of GAC for these adsorbates indicated in the published literature.
6. The adsorption capacity of PAD polystyrenic resin determined from the removal of BTEX during a continuous column process was found to be higher than that determined from the batch adsorption capacity.
7. 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.
8. The equilibrium adsorption data is better fitted by the Langmuir adsorption model than the Freundlich adsorption model for the two adsorbates, as indicated by correlation coefficient values obtained for both approaches.

5.2 Recommendations

- **Templating.** Since it has been found that the mesoporous volume and fraction of the PAD polystyrenic resin used as an adsorbent greatly influence both kinetics and isotherms of BTEX adsorption, it would be interesting to produce a treated PAD 910 polystyrenic resin precursor using the template method to investigate the feasibility of producing a more effective adsorbent. For further studies; a pitch and KOH template is recommended to increase the pore volume of the PAD 910 polystyrenic resin.
- **Solubility effect.** Herein, it was found that the temperature effect on the adsorption might have been as a result of the solubility contribution. Unfortunately, there was no solubility data available at the temperature studied. It would be interesting to lower the temperature studied in order to be able to effectively normalize the adsorption capacity with the solubility at the studied temperature.
- **Mechanism.** To further understand the role of hydrogen bonding in the mechanism of BTEX adsorption, a further characterization of carbon (i.e. polarity index, pH at point of zero charge) and effect of system pH may be required.
- It is recommended that more work needs to be done on how to improve the adsorption capability of PAD 910 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 are proven to change adsorption capacity.

- Thorough pilot scale experiments using the same operating conditions should be conducted with the same waste water effluent and adsorbents prior to design scale-up.

6 REFERENCES

- ADAK, A., BANDYOPADHYAY, M. & PLA, A. 2006. Fixed bed column study of crystal violet (C.I. basic violet 3) dye from aquatic environment by surfactant-modified alumina. *Dyes and Pigments*, Vol. 69, 245 - 251.
- AHARONI, C. & UNGARISH, M. 1977. Kinetics of activated chemisorption. Part 2. Theoretical models. *Journal of Chem. Soc. Faraday Trans.*, Vol. 73, 456 -464.
- AHMARUZZAMAN, M. & SHARMA, D. K. 2005. Adsorption of phenols from wastewater. *Journal of Colloid and Interface Science*, Vol. 287, 14 - 24.
- AHN, S., WERNER, D., KARAPANAGIOTI, H. K., MCGLOTHLIN, D. R., ZARE, R. N. & LUTHY, R. G. 2005. Phenanthrene and Pyrene Sorption and Intraparticle Diffusion in Polyoxymethylene, Coke and Activated Carbon. *Environmental Science Technology*, Vol. 39, 6516 - 6526.
- AIVALIOTI, M., PAPOULIAS, P., KOUSAITI, A. & GIDARAKOS, E. 2012. Adsorption of BTEX, MTBE, and TAME on natural and modified diatomite. *Hazardous Materials*, 207-208, 117-127.
- AIVALIOTI, M., VAMVASAKIS, I. & GIDARAKOS, E. 2010. BTEX and MTBE adsorption on to raw and thermally modified diatomite. *Hazardous Materials*, 178, 136-143.
- AKGERMAN, A. & ZARDKOOHI, M. 1999. Adsorption of phenol from wastewater by peat, fly ash and bentonite. *Journal of Chemical Engineering, Data*, 41, 185 - 187.
- ALLEN-KING, R. M., GRATHWOHL, P. & BALL, W. P. 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments and rocks. *Advanced Water Resources*, Vol. 25, 985 - 1016.
- ALLEN, S. J. 1987. Equilibrium adsorption isotherms for peat. *Fuel*, Vol. 66, 1169 - 1175.
- ASHFORD, R. D. 1994. *Ashford's dictionary of Industrial Chemicals*, London: Wavelength Publishers, Ltd.
- ASHTON, P. J. 2002. Avoiding conflicts over Africa's water resources. *Ambio*, 31, 236-242.
- ASHTON, P. J. & HAASBROEK, B. 2002. Water demand management and social adaptive capacity: a South African study. In: Turton, A.R., Henwood, R. (Eds), *Hydropolitics in the developing world: A Southern African Perspective. African Water Issues Research Unit (AWIRU)*.
- ASHTON, P. J. & RAMASAR, V. 2002. Water and HIV/AIDS: Some strategic considerations for Southern Africa. *Hydropolitics in the Developing World: A Southern African Perspective. African Water Issues Research Unit (AWIRU)*, 22 - in press.
- ATASOY, E., DOGEROGLU, T. & KARA, S. 2004. The Estimation of NMVOC Emission from an urban-scale wastewater treatment plant. *Water Research*, Vol. 38, 3265 - 3274.
- BAKER, F. S., MILLER, C. E., REPIK, A. J. & TOLLES, E. D. 1992. *Activated carbon*.
- BALAN, C., BILBA, D. & MACOVEANU, M. 2009. Studies on Chromium (III) removal from aqueous solution by sorption on sphagnum moss peat. *J. Serb. Chem. Soc.*, Vol. 74 (8-9), 953 - 964.
- BALL, W. P. & ROBERTS, P. V. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. *Environmental Science and Technology*, Vol. 25, 1223-1249.
- BANERJEE, K., CHEREMISINOFF, P. N. & CHENG, S. L. 1997. Adsorption Kinetics of o-xylene by Fly Ash. *Water Research*, Vol. 31, 249 - 261.
- BANERJEE, K., CHERMISINOFF, P. N. & CHENG, S. L. 1995. Sorption of organic contaminants by fly ash in a single solute system. *Environment Science and Technology*, Vol. 29, 2243 - 2251.
- BANSAL, R. C., DONNET, J. B. & STOECKLI, F. 1998. *Active carbon. Marcel Dekker, Inc.*
- BATTELLE 1992. The development of a Fluidized Bed Technique for the Regeneration of Powdered Activated Carbon. *Washington: US Department of the Interior*.
- BIELEFELDT, A. R. & STENSEL, H. D. 1999. *Water Research*, 33.
- BOHART, G. S. & ADAMS, E. Q. 1920. Some aspects of the behavior of charcoal towards chlorine. *Journal of Chemical Society*, Vol. 42, 523 - 529.
- BRINDLE, K. & STEPHENSON, T. 1996. The application of membrane biological reactors, for the treatment of wastewaters. *Biotechnology. Bioengineering*, 49, 601-610.

- BURROWS, A., HOLMAN, J., PARSONS, A., PILLING, G. & PRICE, G. 2009. *Chemistry: Introduction inorganic, organic and physical chemistry*, Oxford University Press.
- BYRD, J. 1998. Characteristics Infrared Absorption Frequencies.
- CABAL, B., ARIA, C. O., PARRA, J. B. & PIS, J. J. 2009. Kinetics of Naphthalene Adsorption on Activated Carbon: Comparison between Aqueous and Organic Media. *Chemosphere*, Vol. 76, 433-438.
- CARDINAL, L. J. & STENSTROM, M. K. 1991. Enhanced bio-degradation of polyaromatic hydrocarbons in the activated sludge process. *Research Journal - WPCF*, 63, 950-957.
- CAVALCANTI, J. V. F. L., ABREU, C. A. M., BENACHOUR, M. & BARAUNA, O. S. 2012. *Removal of Effluent from Petrochemical Wastewater by Adsorption Using Organoclay*, InTech.
- CHANG, C., HOLL, W., ULMER, M., CHEN, Y. & GROB, H. 2004b. Adsorption Kinetics of Polyethylene Glycol from aqueous solution onto activated carbon. *Water Research*, Vol 30 (10), 2559 - 2570.
- CHANG, M. K., VOICE, T. C. & CRIDDLE, C. S. 1993. *Biotechnology. Bioengineering*, 1057-1065.
- CHANG, Q., WEI, B. G. & HE, Y. D. 2009. Capillary pressure method for measuring lipophilic hydrophilic ratio of filter media. *Chem. Eng. Journal*, Vol. 150 (2-3), 323-327.
- CHANG, Y. C., CHANG, J. S., LIN, Y. W., ERDEI, L. & VIGNESWARAN, S. 2006. Quantification of air stripping and biodegradation of organic removal in acrylonitrile-butadiene-styrene (ABS) industry wastewater during submerged membrane bioreactor operation. *Desalination*, Vol. 191, 162 - 168.
- CHENG, C., PHILLIPS, D. & ALKHADDAR, R. M. 2005. Treatment of spent metalworking fluids. *Water Research*, 17, 4051-4063.
- CHERN, J.-M. & CHIEN, Y.-W. 2002. Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves. *Water Research*, 36, 647-655.
- CHIEN, S. H. & CLAYTON, W. R. 1980. Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption in Soils. *Soil. Science. Am. Journal*, Vol. 44, 265-268.
- CHIOU, C. T., PETERS, L. J. & FREED, V. H. 1979. A physical concept of soil-water equilibria for non-ionic organic compounds. *Journal of Science*, Vol. 206, 831 - 832.
- COONEY, D. A. 1999. *Adsorption design for wastewater treatment.*, Lewis Publisher.
- CORNEL, P. & SONTHEIMER, H. 1986. *Chemical Engineering Science*, 41, 1791-1800.
- COSTA, A. S., ROMAO, L. P. C., ARAUJO, B. R., LUCAS, S. C. O., MACIEL, S. T. A., WISNIEWSKI JR., A. & ALEXANDRE, M. R. 2012. Environmental strategies to remove volatile aromatic fractions (BTEX) from petroleum industry wastewater using biomass. *Bioresource Technology*, 105, 31-39.
- COUGHLIN, R. & EZRA, F. S. 1968. Role of surface acidity in the adsorption of organic pollutants on the surface of carbon. *Environment Science and Technology*, Vol. 2, 291-297.
- CRITTENDEN, J. C., TRUSSELL, R. R., HAND, D. W., HOWE, K. J. & TCHOBANOGLOUS, G. 2000. *Water Treatment Principles and Design*, MWH.
- CROOK, E. H., MCDONNELL, R. P. & MCNULTY, J. I. 1978. *Industrial Engineering*, 14, 113-118.
- DAIFULLAH, A. A. M. & GIRGIS, B. S. 2002. Impact of surface characteristics of activated carbon on adsorption of BTEX. *Journal of Colloid and Surfaces*.
- DOREA, H. S., BISPO, J. R. L., ARAGAO, K. A. S., CUNHA, B. B., NAVICKIENE, S., ALVES, J. P. H., ROMAO, L. P. C. & GARCIA, C. A. B. 2007. Analysis of BTEX, PAH's and metals in the oilfield produced water in the State of Sergipe, Brazil. *Microchemistry*, 85, 234.
- DRIVER, A., MAZE, K., LOMBRAD, A. T., NEL, J., ROUGET, M., TURPIE, J. K., COWLING, R. M., DESMET, P., GOODMAN, P., HARRIS, H., JONAS, Z., REYES, B., SINK, K. & STRUSS, T. 2004. National Spatial Biodiversity Assessment 2004: Priorities for Biodiversity Conservation in South Africa. *South African National Biodiversity Institute*, Strelitzia 17.
- DUBININ, M. M. 1960. The Potential Theory of Adsorption of Gases and Vapors for Adsorbents with Energetically Non-Uniform Surfaces. *Chem. Rev*, Vol. 60, 235 - 241.

- DWIVEDI, C. P., SAHU, J. N., MOHANTY, C. R., RAJ MOHAN, B. & MEIKAP, B. C. 2007. Column performance of granular activated carbon packed bed for Pb(II) removal. *Journal of Hazardous Materials*, Vol. 156, 596 - 603.
- EDGEHILL, R. A. & LU MAX, G. Q. 1998. Adsorption characteristics of carbonized bark for phenol and pentachlorophenol. *Journal of Chemical Technology and Biotechnology*, Vol. 71, 27 - 34.
- EL-DIB, M. A. 1975. Adsorption of Sevin and Baygon on Granular Activated Carbon. *Water Research*, Vol. 9, 975.
- EVERETT, D. H. 1971. Manual of Symbols and Terminology for Physiochemical Quantities and Units. *Butterworths and Pure Applied Chemistry*, 21 (1).
- FALKENMARK, M. 1994. The dangerous spiral: near future risks for water related eco-conflicts. Proceedings of the ICRC Symposium Water and War: Symposium on Water in Armed Conflicts, International Committee of the red cross, Montreux, Swi.
- FEBRIANTO, J., KOSASIH, A. N., SURNASO, J., JU, Y., INDRASWATI, N. & ISMADJI, S. 2009. Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies. *Journal of Hazardous Materials*, Vol. 162, 616 - 645.
- FETTIG, J., STAPEL, H., STEINERT, C. & GEIGER, M. 1996. Treatment of landfill leachate by preozonation and adsorption in activated carbon columns. *Water Science Technology*, 26, 381-388.
- FINLAYSON-PITTS, B. J. & PITTS, J. N. 1997. Tropospheric Air Pollution: Ozone, Airborne Toxics, Polycyclic Aromatic Hydrocarbons and Particles. *Particle Science*, Vol. 276, 1045 - 1051.
- FREUNDLICH, H. 1926. *Colloid and Capillary Chemistry* Matheun, London.
- FURUYA, E. G., CHANG, H. T., MIURA, Y. & NOLL, K. E. 1997. *Separation and Purification Technology*, 11, 68-78.
- GILES, H., SMITH, D. & HUITSON, A. 1974. A general treatment and classification of the solute adsorption isotherm (II). *Journal of Colloid and Interface Science*, Vol. 88, 1853 - 1865.
- GOU, Y. & ROCKSTRAW, D. A. 2007. Physiochemical Properties of Carbons Prepared from Pecan Shell by Phosphoric Acid Activation. *Bioresource Technology*, Vol. 98, 1513 - 1521.
- GRAHAM, N., CHEN, X. G. & JAYASEELAM, S. 2001. *Ozonation of Drinking Water and of Wastewater.*, New York, Wiley-VCH.
- GUNAY, A., ARSLANKAYA, E. & TOSUN, I. 2007. Lead removal from aqueous solution by natural and pretreated clinoptilolite: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, Vol. 146, 362 - 371.
- HAAS, C. N. & VAMOS, J. R. 1995. *Hazardous and Industrial Waste Treatment*, Prentice-Hall Inc.
- HALL, S., TANG, R., BAEYENS, J. & DEWIL, R. 2009. Removing Polycyclic Aromatic Hydrocarbons from Water by Adsorption on Silica Gel. *Polycyclic Aromatic Compounds*, Vol. 29, 160-183.
- HAN, S., SOHN, K. & HYEON, T. 2000. fabrication of a new nanoporous carbons through silica templates and their application to the adsorption of bulky dyes. *Chemistry of Materials*, Vol. 12(11), 3337 - 3341.
- HART, H. & SCHUETZ, R. D. 1966. *Organic Chemistry*, Houghton Mifflin Company, Boston.
- HASANY, S. M. & CHAUDHARY, M. H. 1996. Sorption potential of hare river sand for the removal of antimony from acidic aqueous solution. *Appl. Rad. Isot.*, No. 47, 467 - 471.
- HELFFERICH, F. 1962. *Ion Exchange*, New York, McGraw Hill.
- HILL, A. V. 1910. The possible effects of the aggregation of the molecules of haemoglobin on its dissociation curves. *Journal of Physiol.*, (London), iv - vii.
- HO, Y. S. & MCCAY, G. 2000. The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat. *Water Research*, Vol. 34 (3), 735 - 742.
- HO, Y. S. & MCKAY, G. 1998. Sorption of Dye from Aqueous Solution by Peat. *Chem. Eng. Journal*, Vol. 70(2), 115 - 124.
- HO, Y. S., PORTER, J. F. & MCKAY, G. 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: copper, nickel and lead single component systems. *Journal of Water Air Soil Pollution*, Vol. 141, 1 - 33.

- HORSFALL, M. & SPIFF, A. I. 2005. Equilibrium sorption study of Al^{3+} , Co^{2+} and Ag^{2+} in aqueous solutions by fluted pumpkin (*Telfairia occidentalis* HOOK) waste biomass. *Acta Chim. Slov.* 52, 174 - 181.
- IUPAC 1985. Report Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity. *Pure and Applied Chemistry*, No. 57 (4), 603 - 619.
- JIANG, B., ZHANG, Y., ZHOU, K. & CHEN, S. 2008. Effects of Chemical Modification of Petroleum Cokes on the Properties of the Resulting Activated Carbon. *Fuel*, Vol. 87, 1844 - 1848.
- JUDD, S. 2006. *The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Waste water treatment*, Elsevier, Amsterdam.
- KIM, Y., KIM, C., CHOI, I., RENGRAJ, J. & YI, J. 2004. Arsenic removal using mesoporous alumina prepared via a templating method. *Environmental Science Technology*, Vol. 38, 924 - 931.
- KOOPAL, L. K., VAN RIEMSDIJK, W. H., DE WIT, J. C. M. & BENEDETTI, M. F. 1994. Analytical isotherm equation for multicomponent adsorption to heterogeneous surfaces. *Jornal of Colloid Interface Science* 166, 51 - 60.
- KORNAROS, M. & LYBERATOS, G. 2006. Biological treatment of wastewater from a dye manufacturing company using trickling filter. *Journal of Hazardous Materials*, Vol. 136, 95 - 102.
- KURNIAWAN, T. A., CHAN, G. Y. S. & LO, W. H. 2006. Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. *Chemical Engineering Journal*, Vol. 125, 35-57.
- LAGERGREN, J. & SVENSKA, K. 1898. Vetenskapsakademiens Handlingar.
- LAGREGA, M., BUCKINGHAM, P., EVANS, J. & GROUP, T. E. R. M. 1994. *Hazardous Waste Management* McGraw-Hill Publisher,.
- LALEH, S., ALI, T., HOSSEIN, K., GHOLAMREZA, N. B., ALI, A. A., SHAPOOR, N. & MOHAMMAD, A. 2011. Adsorption of BTEX on Surfactant Modified Granulated Natural ZEolite Nanoparticles: Parameters Optimizing by Applying Taguchi Experimental Design Method. *Clean - Soil, Air, Water Journal*, Vol 39 (10), 939 - 948.
- LAMBIOTTE, A. 1942. Process of continous carbonation of cellulosic materials. *US patent #2,289,917*.
- LANGMUIR, I. 1916. The Adsorption of Gases on Plane Surface of Glass, Mica and Platinum. *Journal of Am. Chem. Soc.*, No. 40, 1361 - 1368.
- LEE, C., CHAO, H. & LEE, J. 2004. Effects of organic Solutes Properties on the volatilization processes from water solutions. *Water Research*, Vol. 38, 365 - 374.
- LEE, S. C., CHIU, M. Y., HO, K. F., ZOU, S. C. & WANG, X. 2002. Volatile Organic Compounds (VOCs) in Urban Atmosphere of Hong Kong. *Chemosphere*, Vol. 48, 375 - 382.
- LEI, S., JUN-ICHI, M., HIROFUMI, K. & KATSUMI, K. 2006. Effects of mesopores on adsorption rate of methylene blue molecules on activated carbon fibers. *Nippon Kagakkai Keon Yokoshu*, Vol. 86(1), 453.
- LI, L., QUINLIVAN, P. A. & KNAPPE, N. U. 2005. Predicting adsorption isotherms for aqueous organic micropollutants from activated carbon and pollutant properties. *Environmental ScienceTechnology*, Vol. 39, 3393 - 3400.
- LIN, S. H. & HUANG, C. Y. 1999. Adsorption of BTEX from aqueous solution by macro reticular resins. *Hazardous Materials*, 70, 21-30.
- LIN, S. H. & WU, Y. F. 1996. *Environmental Technology*, 17, 175 - 183.
- LIVIA, B. 2010. Semi-arid Areas. *International Institute for Sustainable Development (IISD)*, www.iisd.org.
- LONG, C., LI, A., HU, D., LIU, F. & ZHANG, Q. 2008. Description of Adsorption Equilibrium of PAHs on Hypercrosslinked Polymeric Adsorbent Using Polanyi Potential Theory. *China Series B: Chemistry*, Vol. 51 (6), 586 - 592.

- LOZANO-CASTELLO, D., LILLO-RODENAS, M. A., CAZORLA-AMOROS, D. & LINARES-SOLANO, A. 2001. Preparation of Activated Carbon from Spanish Anthracite I. Activation by KOH. *Carbon*, Vol. 39, 741 - 749.
- MALLEVIALLE, J., P.E., O. & WIESNER, M. R. 1996. *Water treatment membrane processes*, McGraw-Hill.
- MANES, M. & HOFER, L. J. E. 1969. Application of the polanyi adsorption potential theory to adsorption from solution on activated carbon. *Journal of Physical Chemistry*, Vol. 73, 584 - 590.
- MASTRAL, A. M., GARCIA, T., MURILLO, R., CALLEN, M. S., LOPEZ, J.M. & NAVARRO, M. V. 2003. Measurements of polycyclic aromatic hydrocarbon adsorption in activated carbons at very low concentrations. *Ind.Eng.Chem.Res*, Vol. 42, 155 - 161.
- MATHUR, A. K., MAJUMDER, C. B. & CHATTERJEE, S. 2007. Combined removal of BTEX in air stream by using mixture of sugar cane bagasse, compost and GAC biofilter media. *Hazardous Materials*, 148, 64-74.
- MATTSON, J. S. & MARK, H. B. 1971. Activated carbon. *New York: Dekker*.
- METCALF & EDDY 2004. *Waste Water Engineering Treatment and Reuse*, McGraw Hill.
- MOHAN, D., GUPTA, V. K., SRIVASTAVA, S. K. & CHANDER, S. 2001. Kinetics of Mercury Adsorption from Wastewater using Activated Carbon Derived From Fertilizer Waste. *Colloids and Surfaces*, Vol 177 (2-3), 169 - 181.
- NEYENS, E. & BAEYENS, J. 2003. A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, Vol. B98, 33-50.
- NOLL, K. E., GOUNARIS, V. & HOU, W. S. 1994. Adsorption Technologies for Air and Water pollution control.
- OPEC 2011. The impact of recent events on the oil market. . *Organisation of the Petroleum Exporting Countries (OPEC)*.
- PERA-TITUS, M., GARCIA-MOLINA, V., GIMENEZ, J. & ESPLUGAS, S. 2004. Degradation of chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B; Environmental*, Vol. 47, 219 - 256.
- PEREZ-MARIN, A. B., MESEGUER ZAPATA, V., ORTUNO, J. F., AGUILAR, M., SAEZ, J. & LLORENS, M. 2007. Removal of cadmium from aqueous solutions by adsorption onto orange waste. *Journal of Hazardous Materials*, Vol. B139, 122 - 131.
- PODOLL, R. T., IRWIN, K. C. & PARISH, J. H. 1989. Dynamic studies of naphthalene sorption on soil from aqueous solution. *Chemosphere*, Vol. 18 (11-12), 2399 - 2412.
- RINGOT, D., LERZY, B., CHAPLAIN, K., BONHOURE, J. P., AUCLAIR, E. & LARONDELLE, Y. 2007. In vitro biosorption of ochratoxin A on the yeast industry by-products: comparison of isotherm models. *Bioresource Technology*, 98, 1812 - 1821.
- RODRIGUEZ, J. F. & LINARES, S. A. 1989. Chemistry and physics of carbon: a series of advances. *Marcel Dekker, Inc.*
- SAHU, J. N. 2009. Performance of modified multi-stage bubble column reactor for lead (II) and biological oxygen water using activated rice huck. *Journal of Hazardous Materials*.
- SARKAR, M. & ACHARYA, P. K. 2006. Use of fly ash for the removal of phenol and its analogues from contaminated water. *Waste Management*, Vol. 26, 559 - 570.
- SCHOLES, R. 2001. Global Terrestrial Observing System: Regional Implementation Plan for Southern Africa. *GTOS*, 21.
- SCHOLZ, W. & FUCHS, W. 2000. Treatment of oil contaminated wastewater in a membrane bioreactor. *Water Research*, 34, 3621-3629.
- SINNOT, R. K. 1999. *Chemical Engineering Design*.
- SIPS, R. 1948. Combined form of Langmuir and Freundlich equations. *Journal of Chem. Phys.*, Vol. 16, 490 - 495.

- SITE, A. D. 2001. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants: A review. *Journal of Physical Chemistry. Ref. Data*, Vol. 30, No. 1, 187 - 438.
- SMAKHTIN, V., ASHTON, P. J., BATCHELOR, A., MEYER, R., MAREE, J. P., MURRAY, M., BARTA, B., BAUER, N., TERBLANCHE, D. & OLIVIER, J. 2001. Unconventional water supply options in South Africa: possible solutions or intractable problems? *Water International*, 26, 314-334.
- STOECKLI, F. 1990. Microporous carbons and their characterization: the present state of art. *Carbon*, Vol 28, 1-6.
- SUZUKI & MOTOYUKI 1990. *Adsorption Engineering*, Kodansha, Tokyo.
- TEMKIN, M. I. & PYZHEV, V. 1940. Kinetics of ammonia synthesis on promoted iron catalyst. *Acta Phys. Chim.*, USSR 12, 327 - 356.
- TERZYK, A. P. & GAUDEN, P. A. 2002. the simple procedure of the calculation of diffusion coefficient for adsorption on spherical and cylindrical adsorbent particles - experimental verification. *Journal of Colloid and Interface Science*, Vol. 249, 256 - 261.
- TURPIE, J. K., MARAIS, C. & BLIGNAUT, J. N. 2008. The working for water programme: Evaluation of payments for ecosystem services mechanism that addresses both poverty and ecosystem service delivery in South Africa. *Ecological Economics*, 788-798.
- USEPA 2010. evaluation of impacts to underground sources of drinking water by hydraulic fracturing of coalbed methane reservoirs. . *Report no. EPA 816-R-04-003*, US Environmental Protection Agency, Office of Groundwater and Drinking Water, USA.
- VALDERRAMA, C., CORTINA, J. L., FARRAN, A., GAMISANS, X. & LAO, C. 2007. Kinetics of Sorption of Polyaromatics Hydrocarbons onto Granular Activated Carbon and Macronet Hyper-Cross-Linked Polymers (MN200). *Journal of Colloid Interface Science*, Vol. 310 (1), 35 - 36.
- VALDERRAMA, C., GAMISANS, X., DE LAS HERAS, X., FARRAN, A. & CORTINA, J. L. 2008. Sorption Kinetics of Polycyclic Aromatic Hydrocarbons Removal Using Granular Activated Carbon: Intraparticle Diffusion Coefficients. *Journal of Hazardous Materials*, Vol. 157 (2-3), 386 - 396.
- VIJAYARAGHAVAN, K., PADMESH, T. V. N., PALANIVELU, M. & VELAN, M. 2006. Biosorption of nickel (II) ions onto *Sargassum wightii*: application of two-parameter and three parameter isotherm models. *Hazardous Materials*, Vol. B133, 304 - 308.
- VINOD, V. P. & ANIRUDHAN, T. S. 2003. Adsorption behavior of basic dyes on the humic acid immobilized pillared clay. *Water* Vol. 150 (1-4), 193 - 217.
- WEBER, W. J. J. 1972. *Physiochemical processes for water quality control*.
- WEBER, W. J. J. & BENJAMIN, M. V. 1980. *Fundamental Concepts for Application of Activated Carbon in Water and Wastewater Treatment*, Ann Arbor Sc. Michigan.
- WEBER, W. J. J. & MORRIS, J. C. 1963. Kinetics of Adsorption on Carbon from Solution *J.Sanit.Eng.Div.*, ASCE 89, 31 - 59.
- WHITESIDE, A. & SUNTER, C. 2000. AIDS:The challenge for South Africa. . *Human and Rousseau*, South Africa 179.
- WU, C. C. & GSCHWEND, P. M. 1988. Sorption Kinetics of Hydrophobic Organic Compounds to Natural Sediments and Soils. *EPA600J86517; PB9014985*.
- YADAV, J. S. & REDDY, C. A. 1993. Degradation of benzene, toluene, ethylbenzene and xylenes (BTEX) by the Lignin-Degrading Basidiomycete *phanerochaete chrysosporium*. *Applied and Environmental Microbiology*, Vol. 59, no. 3, 765 - 762.
- YANG, B. W., CHANG, Q., HE, C. & ZHANG, Y. 2007. Wettability study of mineral wastewater treatment filter media. *Chem. Eng. Process*, Vol. 46 (10), 975 - 981.
- YANG, R. T. 2003. *Adsorbents: Fundamentals and Applications*, Wiley and Sons, New Jersey.
- YOON, I. & PARK, C. 2002. Effects of Gas Flow Rate, Inlet Concentration and Temperature on Biofiltration of Volatile Organic Compounds in a Peat-Packed Biofilter. *Journal of Bioscience and Bioengineering*, Vol.93 No. 2, 165 - 169.
- YU, L. & ZHANG, Q. 2006. Preparation of Adsorbents made from sewage sludges for organic materials from wastewater. *Journal of Hazardous Materials*, B137, 359-366.

- ZELDOWITSCH, J. 1934. Über den Mechanismus der katalytischen oxydation von CO an MnO_2 . *Acta Physicochim*, URSS, 364-449.
- ZHOU, H. & SMITH, D. W. 2002. Advanced technologies in water and waste water treatment. *Environmental Engineering Science*, 1, 247-264.
- ZUNCKEL, K., VENJONOKA, J. J., BRUNKE, E. G., PRETORIUS, O., KOOISIALEE, A., RAGHUNANDAN, A. & VAN TIENHOVEN, A. M. 2004. Surface ozone southern africa: Synthesis of Monitoring results during the cross Border Air Pollution Assessment Project. *Atmospheric Environment*, Vol. 38, no. 36, 6139 - 6147.

APPENDIX A: EQUIPMENT



Figure A.1: *Labcon* oven



Figure A.2: *Stuart* Platform Orbital Shaker



Figure A.3: *Perkin Elmer Turbo Mass System GC-MS*



Figure A.4: *Perkin Elmer FTRI Spectrophotometer*

APPENDIX B: Adsorption Porous Structure Measurement

B1. Micropore volume and mesopore surface area calculation

A linear plot (t-plot) of the volume of nitrogen adsorbed against the calculated thickness, t was employed to obtain the micropore volume, V_{mic} and the mesopore surface area, S_{mes} within the thickness range 4 – 7.4 Å. The intercept, i and the slope, s of the t-plot were used in obtaining the micropore volume and mesopore surface area according to the expressions:

$$V_{mic} = i * 0.00123 \quad (\text{in cc/g}) \quad \text{B1}$$

$$S_{mes} = s \times 12.56 \quad (\text{in m}^2/\text{g}) \quad \text{B2}$$

Since micropores contributes negligibly to the BET total surface area, the micropore surface area obtained by deducting the mesopore surface area from the BET total surface.

B2. Average pore radius calculation

Since the contribution of pores not filled below a relative pressure of 1 negligible to the total pore volume and the surface area of the sample, the average pore size radius (r_{ave}) could be estimated from the total pore volume and the BET total surface area. By assuming that all pores are cylindrical, the total pore volume and the BTE total surface area could be expressed as:

$$V_t = \pi r_{ave}^2 L \quad \text{B3}$$

$$\text{And} \quad S_{BET} = 2\pi r_{ave} L \quad \text{B4}$$

,where L is the mean pore length. Thus, the average pore size radius was calculated by dividing equation B3 by equation B4 to yield:

$$r_{ave} = \frac{2*V_t}{S_{BET}} \quad \text{B5}$$

APPENDIX C: BTEX Calibration Curves

Table C.1: Benzene concentration GC-MS calibration data

Conc., ppm	Peak Area Ratio		
	Run 1	Run 2	Mean Ratio
1	0.075670	0.083542	0.079606
3	0.123213	0.085393	0.104303
3.2	0.010749	0.267005	0.138877
3.7	0.012377	0.289457	0.150917
5	0.049880	0.308873	0.179376
6	0.203449	0.210635	0.207042
8	0.253468	0.245262	0.249365

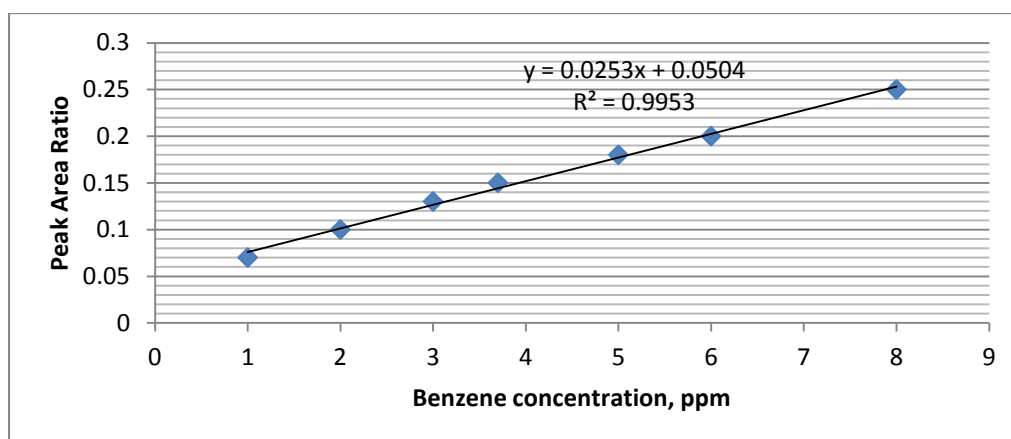


Figure C.1: Benzene concentration GC-MS curve

Table C.2: Toluene concentration GC-MS calibration data

Conc., ppm	Peak Area Ratio		
	Run 1	Run 2	Mean Ratio
2	0.012436	0.075635	0.044035
3.5	0.153213	0.069693	0.111453
6	0.206782	0.213457	0.210119
6.66	0.273909	0.224518	0.249214
7.5	0.298745	0.276379	0.287562
8	0.337678	0.290635	0.314156
9	0.356782	0.345262	0.351022

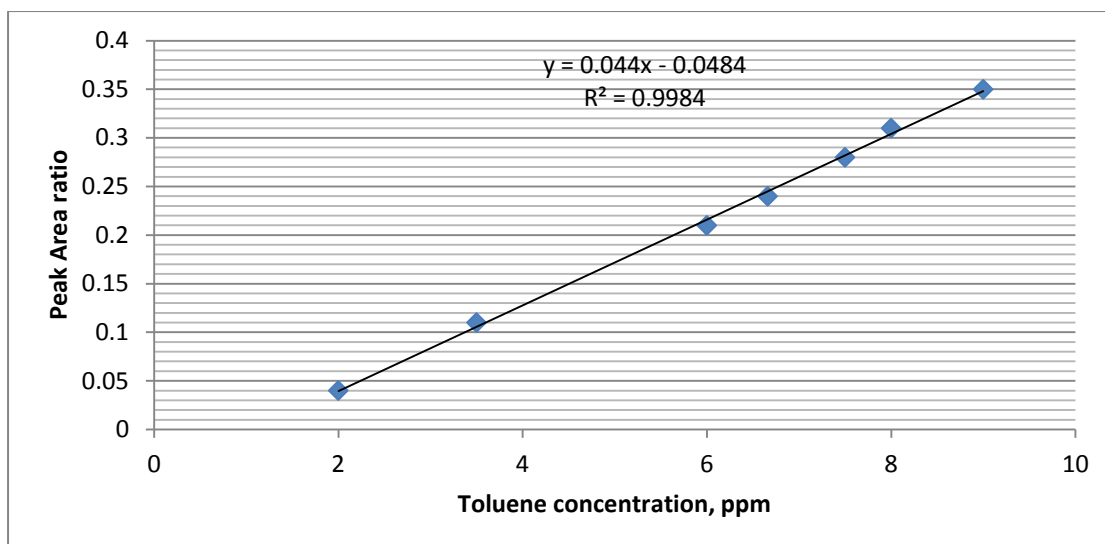


Figure C.2: Toluene concentration GC-MS calibration curve

Table C.3. Ethylbenzene concentration GC-MS calibration data

Conc., ppm	Peak Area Ratio		
	Run 1	Run 2	Mean Ratio
0.1	0.06040441	0.03770433	0.04905437
0.2	0.08725598	0.04838763	0.06782181
0.3	0.09349824	0.09467925	0.09408875
0.34	0.02051392	0.20563458	0.11307425
0.5	0.14567389	0.14267345	0.14417367
0.85	0.23045013	0.27451987	0.252485
1	0.18612959	0.39358394	0.28985677

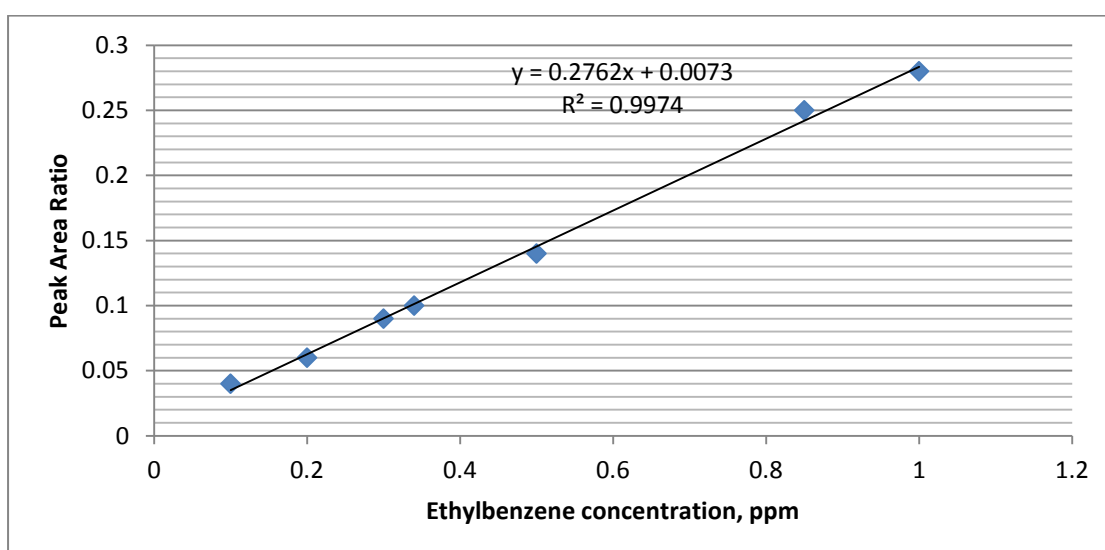


Figure C.3: Ethylbenzene concentration GC-MS calibration curve

Table C.4. m-;p-Xylene concentration GC-MS calibration data

Conc., ppm	Peak Area Ratio		
	Run 1	Run 2	Mean Ratio
1	0.29480262	0.16032288	0.22756275
1.5	0.32771634	0.23951897	0.28361766
2.2	0.34621956	0.35345698	0.34983827
2.57	0.38498819	0.37109824	0.37804322
3.3	0.40263878	0.4819126	0.44227569
4.5	0.55021987	0.5451832	0.54770154
5	0.57186533	0.5983453	0.58510531

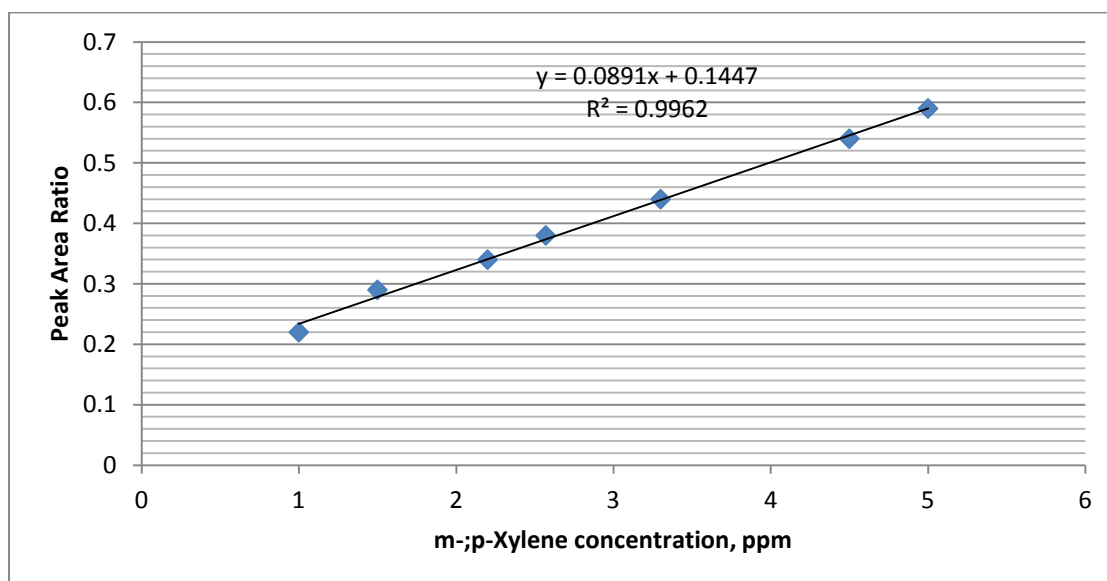


Figure C.4: m-; p- Xylene concentration GC-MS calibration curve

Table C.5. o-Xylene concentration GC-MS calibration data

Conc., ppm	Peak Area Ratio		
	Run 1	Run 2	Mean Ratio
0.5	0.03696269	0.04259659	0.03977964
0.8	0.08724156	0.0782411	0.08274133
1	0.10835262	0.10289356	0.10562309
1.2	0.14298353	0.12356278	0.13327315
2	0.21349832	0.213984	0.21374116
2.5	0.24873452	0.2534981	0.25111631
3	0.30430877	0.30012188	0.30221532

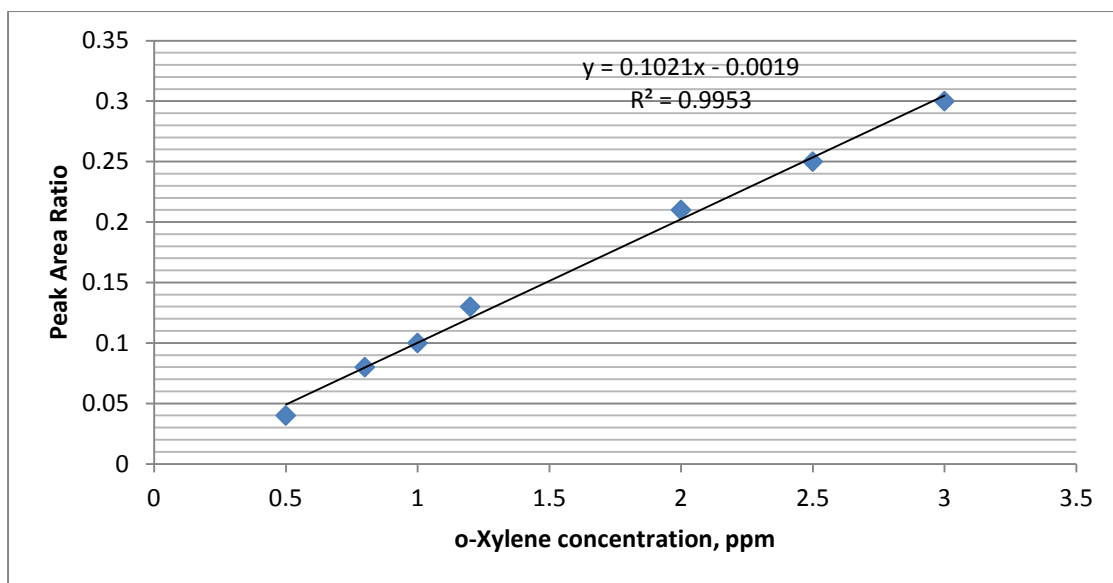


Figure C.5: o-Xylene concentration GC-MS calibration curve

APPENDIX D: Adsorption Data

D1. Short Term BTEX adsorption data on PAD 910 polystyrenic resin

Time, min	Benzene		Toluene		Ethylbenzene		m-;p-Xylene		o-Xylene	
	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm
0	0.1508	3.69	0.2492	6.66	0.1131	0.34	0.3771	2.56	0.1201	1.18
5	0.1145	3.13	0.1772	5.34	0.0942	0.3	0.3498	2.22	0.1104	1.01
10	0.0989	2.88	0.1541	4.56	0.0791	0.23	0.3019	2.02	0.0841	0.82
15	0.0861	2.56	0.1031	3.23	0.0564	0.18	0.2991	1.92	0.0775	0.71
30	0.0808	2.15	0.0941	2.78	0.0591	0.14	0.2864	1.54	0.0654	0.62
45	0.0881	2.01	0.0771	2.55	0.0507	0.11	0.2442	1.34	0.0443	0.55
60	0.0771	1.97	0.0641	2.48	0.04905	0.1	0.2442	1.34	0.0417	0.41

D2. Long Term BTEX Adsorption data on PAD 910 polystyrenic resin

Time, min	Benzene		Toluene		Ethylbenzene		m-;p-Xylene		o-Xylene	
	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm	Peak Ratio	Conc., ppm
0	0.1508	3.69	0.2492	6.66	0.1131	0.34	0.3771	2.56	0.1231	1.18
3	0.0956	2.01	0.1541	4.56	0.0942	0.30	0.2977	1.67	0.1104	1.01
6	0.0845	1.32	0.1092	3.31	0.0791	0.23	0.2471	1.43	0.0841	0.82
9	0.0745	1.01	0.0845	2.88	0.0564	0.18	0.2371	1.22	0.0775	0.71
12	0.0672	0.83	0.0743	2.56	0.0591	0.14	0.2373	1.12	0.0774	0.63
18	0.0441	0.61	0.0683	2.21	0.0507	0.11	0.2275	1.01	0.0397	0.54
24	0.0411	0.55	0.0567	2.02	0.0490	0.09	0.2114	0.92	0.0389	0.39

D3. Toluene adsorption data on surface GAC and PAD 910 polystyrenic resin

Time, min	GAC			RESIN		
	RUN 1 Conc., ppm	RUN 2 Conc., ppm	MEAN Conc., ppm	RUN 1 Conc., ppm	RUN 2 Conc., ppm	MEAN Conc., ppm
0	15.012	14.982	14.997	15.012	14.982	14.997
5	7.381	7.364	7.373	6.541	6.587	6.564
10	6.891	6.983	6.937	6.291	6.275	6.283
15	6.407	6.532	6.470	6.014	6.099	6.057
20	6.211	6.241	6.226	5.792	5.821	5.807
25	5.981	6.197	6.089	5.617	5.607	5.612
30	5.981	5.821	5.901	5.531	5.54	5.536
35	5.811	5.699	5.755	5.423	5.448	5.436
40	5.367	5.417	5.392	5.351	5.376	5.364
45	5.091	5.112	5.102	5.201	5.271	5.236
50	5.002	5.012	5.007	5.121	5.144	5.133
55	4.931	4.971	4.951	5.007	5.019	5.013
60	4.901	4.887	4.894	5.001	5.077	5.009

D4. Effect of initial BTEX concentration and adsorbate data onto PAD 910 polystyrenic resin

Time, min	BTEX at 7 ppm			BTEX at 14 ppm			BTEX at 21 ppm		
	RUN 1 Conc., ppm	RUN 2 Conc., ppm	MEAN Conc., ppm	RUN 1 Conc., ppm	RUN 2 Conc., ppm	MEAN Conc., ppm	RUN 1 Conc., ppm	RUN 2 Conc., ppm	MEAN Conc., ppm
0	3.992	4.002	3.997	14.181	14.003	14.092	21.098	21.003	21.051
5	3.412	3.521	3.467	11.341	11.112	11.227	17.891	17.771	17.831
10	2.981	3.002	2.992	8.123	8.111	8.117	14.231	14.689	14.460
15	2.671	2.773	2.722	7.133	7.111	7.122	13.256	13.987	13.622
20	2.411	2.491	2.451	5.091	5.009	5.050	12.122	11.999	12.061
25	2.111	2.119	2.115	4.112	4.033	4.073	10.234	10.345	10.290
30	1.876	1.887	1.882	3.578	3.449	3.514	8.035	8.567	8.301
35	1.678	1.689	1.684	2.911	2.912	2.912	6.124	6.099	6.112
40	1.213	1.231	1.222	2.551	2.489	2.520	5.789	5.013	5.401
45	0.897	0.879	0.888	2.145	2.119	2.132	4.509	4.675	4.592
60	0.534	0.543	0.539	1.799	1.812	1.806	4.015	4.018	4.017

D5. BTEX adsorption isotherm data on PAD 910 polystyrenic resin at different temperatures

Initial conc., ppm	25 ⁰ C			35 ⁰ C			45 ⁰ C		
	RUN 1 Conc., C _e ppm	RUN 2 Conc., C _e ppm	MEAN Conc., C _e ppm	RUN 1 Conc., C _e ppm	RUN 2 Conc., C _e ppm	MEAN Conc., C _e ppm	RUN 1 Conc., C _e ppm	RUN 2 Conc., C _e ppm	MEAN Conc., C _e ppm
1	0.032	0.035	0.034	0.039	0.041	0.040	0.011	0.014	0.013
3	0.189	0.987	0.588	0.112	0.187	0.150	0.198	0.199	0.199
6	4.509	4.897	4.703	3.009	3.125	3.067	2.981	2.891	2.936
9	4.198	4.097	4.148	2.981	2.987	2.984	2.881	2.789	2.835
11	3.987	3.876	3.932	2.781	2.77	2.776	2.578	2.567	2.573
15	3.122	3.129	3.126	2.671	2.611	2.641	2.198	2.091	2.145
17	2.918	2.981	2.950	2.451	2.498	2.475	1.987	1.786	1.887
18	2.467	2.567	2.517	2.234	2.153	2.194	1.378	1.476	1.427
19	2.109	2.001	2.055	1.983	1.981	1.982	1.309	1.299	1.304
21	1.981	1.876	1.929	1.876	1.834	1.855	1.202	1.218	1.210

D6. Mixing strength using PAD 910 polystyrenic resin

Mixing Strength rpm	Benzene (%)	Toluene (%)	Ethylbenzene Removal (%)	m-;p-Xylene Removal (%)	o-Xylene (%)
0	81	70	49	70	80
40	88	74	53	73	82
80	91	77	55	78	84
120	95	83	58	80	87
150	98	88	59	84	90
180	98	88	59	84	90

D7. Mixing strength using activated carbon

Mixing Strength rpm	Benzene (%)	Toluene (%)	Ethylbenzene (%)	m-;p-Xylene (%)	o-Xylene (%)
0	86	71	42	69	80
40	90	75	45	72	82
80	93	76	48	77	84
120	95	85	49	80	87
150	97	88	50	84	90
180	97	88	50	84	90

D8. Daily trade influent monitoring on line 1

Sample ID		Outfall Line 2 22/03/2011	Outfall Line 1 28/03/2011	Outfall Line 1 04/04/2011	Outfall Line 1 11/04/2011	Outfall Line 1 18/04/2011	Outfall Line 1 25/04/2011	Outfall Line 1 02/05/2011	Outfall Line 1 09/05/2011	Outfall Line 1 16/05/2011
Reference No.		11-144	11-144	11-158	11-170	11-177	11-197	11-197	11-202	11-218
Date analysed		2011/03/30	2011/03/30	2011/04/12	2011/04/29	2011/04/29	2011/05/06	2011/05/06	2011/05/16	2011/05/26
CAS No.:	Units	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre
(i)	Benzene	3400	690	510	2700	1400	3900	10 000	4 800	9200
(ii)	Toluene	5300	<100	790	3500	790	3100	10 000	2 900	11 000
(iii)	Ethylbenzene	150	<100	<100	<100	<100	<100	<100	180	35
(iv)	m,p-Xylene	3200	900	1100	2600	2200	2400	4000	3300	2900
(v)	o-Xylene	1900	600	550	1500	1300	1400	2000	1600	1600
	Total BTEX	13950	2190	2950	10300	5690	10800	26000	12780	24735

D9. Daily trade influent monitoring on line 2

Sample ID		Outfall Line 2 22/03/2011	Outfall Line 2 28/03/2011	Outfall Line 2 04/04/2011	Outfall Line 2 11/04/2011	Outfall Line 2 18/04/2011	Outfall Line 2 25/04/2011	Outfall Line 2 02/05/2011	Outfall Line 2 09/05/2011	Outfall Line 2 16/05/2011
Reference No.		11-144	11-144	11-158	11-170	11-177	11-197	11-197	11-202	11-218
Date analysed		2011/03/30	2011/03/30	2011/04/12	2011/04/29	2011/04/29	2011/05/06	2011/05/06	2011/05/16	2011/05/26
CAS No.:	Units	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre	µg/litre
(i)	Benzene	800	540	1200	7100	7800	3200	4400	4400	470
(ii)	Toluene	2900	1200	1200	13 000	20 000	3700	10000	9700	5700
(iii)	Ethylbenzene	150	<100	<100	120	380	<100	520	280	170
(iv)	m,p-Xylene	980	890	380	4400	6000	2000	2400	2500	1100
(v)	o-Xylene	560	650	270	2000	3100	1400	1400	1500	620
	Total BTEX	5390	3280	3050	26620	37280	10300	18720	18380	8060

APPENDIX E: Column Dynamic Studies Data

Table E.1: Input data for design calculations

Parameters	Values
GAC Surface area (m ² /g)	640
PAD 910 resin Surface area (m ² /g)	540
GAC Pore volume (cm ³ /g)	0.00088
PAD 910 resin Pore volume (cm ³ /g)	0.0016
GAC Maximum Particle size (μm)	1500
PAD 910 resin Maximum Particle size (μm)	1234
Solution pH	5.86
<i>Feed Concentration (mg/L):</i>	
BTEX	14.47
Adsorbent loading (g)	17/35/55
GAC and PAD 910 resin bed height (mm)	40/60/120
Column Internal Diameter (mm)	33

Table E.2: Breakthrough Times for benzene adsorption onto GAC

Service Time (h)	40mm Bed Height % benzene remaining	80mm Bed Height % benzene remaining	120mm Bed Height % benzene remaining
0	0	0	0
0.3	0	0	0
1	26.1	0	0
1.3	40.23	30.45	0
2	50.34	34.56	13.67
2.3	60.34	40.56	22.3
3	62.34	44.23	24.12
3.3	65.2	47.45	29.45
4	67.12	59.45	38.56
4.3	68.34	60.35	47.23
5	69.54	62.37	50.45
5.3	70.23	63.23	53.29
6	71.34	64.34	57.4
7	72	67.48	60.46
8	72.12	69.34	62.49
9	73.4	71.28	63.12
10	74.2	73.23	64.23
11	75.23	74.88	66.89
12	76.98	75.34	68.56
13	78.35	77.41	69.93
14	80.23	79.34	71.3
15	81.34	80.89	72.19
16	83.45	82.33	73.46
17	84.34	83.23	74.18
18		85	75.64
19		86.23	77.45
20		87.87	79.34
21		88.12	80.34
22		89.45	81.29
23			82.34
24			

Table E.3: Breakthrough times for benzene adsorption onto PAD 910

Service Time (h)	40mm Bed Height % benzene remaining	80mm Bed Height % benzene remaining	120mm Bed Height % benzene remaining
0	0	0	0
0.3	0	0	0
1	24.12	0	0
1.3	38.25	28.47	0
2	48.36	32.58	11.69
2.3	58.36	38.58	20.32
3	60.36	42.25	22.14
3.3	63.22	45.47	27.47
4	65.14	57.47	36.58
4.3	66.36	58.37	45.25
5	67.56	60.39	48.47
5.3	68.25	61.25	51.31
6	69.36	62.36	55.42
7	70.02	65.5	58.48
8	70.14	67.36	60.51
9	71.42	69.3	61.14
10	72.22	71.25	62.25
11	73.25	72.9	64.91
12	75	73.36	66.58
13	76.37	75.43	67.95
14	78.25	77.36	69.32
15	79.36	78.91	70.21
16	81.47	80.35	71.48
17	82.36	81.25	72.2
18		83.02	73.66
19		84.25	75.47
20		85.89	77.36
21		86.14	78.36
22		87.47	79.31
23			80.36
24			

Table E.4: Breakthrough time for benzene (h) at BDST of 20% and 60%

Bed Depth (mm)	GAC		PAD 910	
	Benzene 20% t_b (h)	Benzene 60% t_b (h)	Benzene 20% t_b (h)	Benzene 60% t_b (h)
40	1	2.3	0.7	3
60	1.6	4.3	1.5	5
120	2.5	7	2.3	8

APPENDIX F: Design Example

F1. Single stage batch adsorption system

Design of contained technologies for the remediation of BTEX have typically usually being based on parameters obtained from isotherms (Valderrama et al., 2008). Since the mean residence time in these technologies may be too short for complete equilibration, it is informative to apply kinetic parameters in obtaining design parameters for BTEX containment. The empirical and model correlations obtained in this study are used in obtaining a design equation for a single stage batch adsorption system for the containment of BTEX in effluent wastewater.

In order to reduce the BTEX quantity from an effluent stream of volume V (l) with initial BTEX concentration of C_0 (ppm) to a target guideline concentration C_t (ppm), using a PAD 910 polystyrenic resin is to be used; the mass balance equation for the system is given by the equation:

$$V(C_0 - C_t) = M(q_t - q_0) \quad \text{E1}$$

Where: M = mass of sorbent required; V = volume of effluent to be treated; C_0 = initial effluent concentration; C_t = target effluent concentration at time t ; q_t = BTEX loading time at time t ; and q_0 = initial BTEX loading. At time $t = 0$, for a fresh adsorbent batch, $q_0 = 0$, thus equation E1 could be written as:

$$M = \frac{V(C_0 - C_t)}{q_t} \quad \text{E2}$$

A concentration time function could be obtained as described by (Ho and McKay, 1998) to obtain q_t within the studies concentration limits in this study. Expressing the equilibrium quantity adsorbed, q_e and initial sorption rate, h_0 as follows:

$$q_e = \frac{C_0}{A_q C_0 + B_q} \quad \text{E3}$$

$$h = \frac{C_0}{A_h C_0 + B_h} \quad \text{E4}$$

$$k = \frac{C_0}{A_k C_0 + B_k} \quad \text{E5}$$

Since the pseudo-second order rate law was more applicable in this study, substituting equations E3 to E5 into the rate law given in equation 2-4 for the obtained parameters from the effect on initial concentration study, the relationship of q_t , C_0 and t was obtained as:

$$q_t = \frac{C_0 t}{0.928 - 0.062 C_0 + (0.013 C_0 + 0.152) t} \quad \text{E6}$$

As such, the amount of adsorbent required to achieve the target BTEX concentration in the effluent can be obtained from a combination of equations E2 and E6. Furthermore, equation E6 could be used to determine the amount of BTEX adsorbed at any given concentration (within the studied range of 0.5 and 14.47 ppm) and contact time. The three-dimensional plot of equation 4-9 is shown in Figure F1.

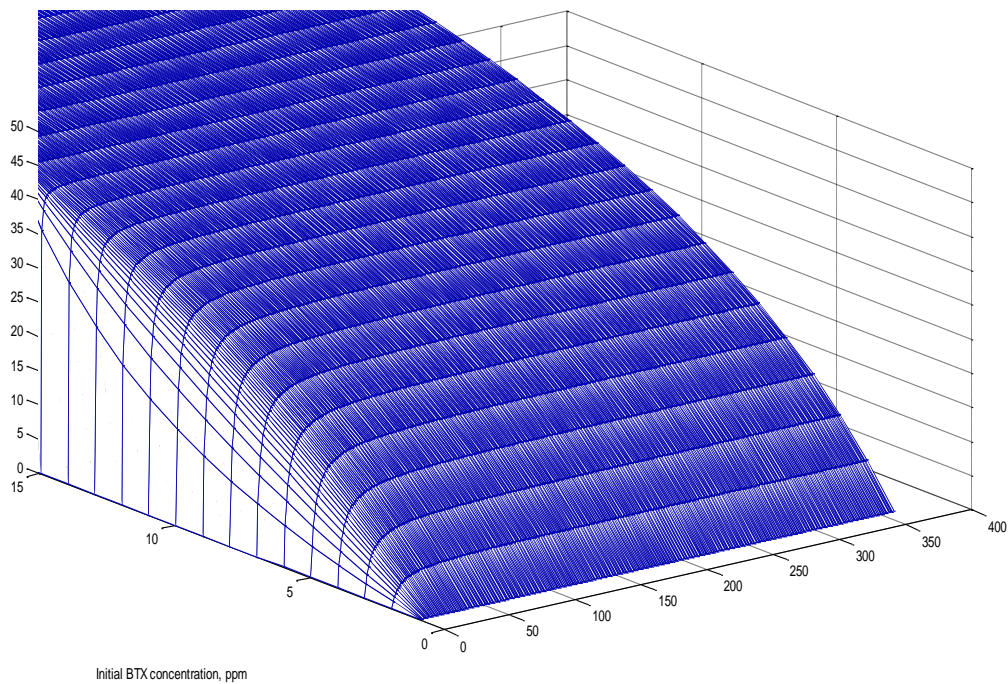


Figure F1: 3-d Plot of BTEX Quantity Adsorbed with Time and Initial Concentration

APPENDIX G

G1. ANOVA: Single Factor

DESCRIPTION					<i>Alpha</i> 0.05			
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Mean</i>	<i>Variance</i>	<i>SS</i>	<i>Std Err</i>	<i>Lower</i>	<i>Upper</i>
Conc1	46	392.97	8.542826	22.81524	1026.686	0.699055	7.134856	9.950796
Model Pred1	41	388.78	9.482439	20.91862	836.745	0.740455	7.985924	10.97895
Conc 2	48	336.78	7.01625	23.8715	1121.961	0.684337	5.639542	8.392958
Model Pred.	45	308.04	6.845333	22.06701	970.9483	0.70678	5.420912	8.269755

G2. ANOVA

<i>Sources</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P value</i>	<i>F crit</i>	<i>RMSSE</i>	<i>Omega Sq</i>
Between Groups	209.104	1	69.7013	3.10070	0.02811	2.65593	0.26651	0.03382
Within Groups	3956.34	176	22.4792					
	4165.44		23.2706					
Total	4	179	4					

APPENDIX H

H1. Acceptance of Trade effluent for Discharge into eThekweni Municipality sewer system

Large Works general quality limits are applicable when an industries effluent discharges in catchments leading to sewage works of greater than 25 Mℓ/d capacity. Small Works quality limits apply for catchments leading to sewage works with less than 25 Mℓ/d capacity.

GENERAL QUALITY LIMITS	LARGE WORKS > 25 Mℓ/d	SMALL WORKS < 25 Mℓ/d	UNITS
1. Temperature (°C)	< 44 °C	< 44°C	Degrees Celsius
2. pH	6 < pH < 10	6,5 < pH < 10	pH units
3. Oils, greases, waxes of mineral origin	50	50	mg/ℓ
4. Vegetable Oils, greases, waxes	250	250	mg/ℓ
5. Total sugar and starch (as glucose)	1 000	500	mg/ℓ
6. Sulphates in solution (as SO_4^{2-})	250	250	mg/ℓ
7. Sulphides, hydrosulphides (as S^{2-})	1	1	mg/ℓ
8. Chlorides (as Cl^-)	1 000	500	
9. Flouride (as F^-)	5	5	mg/ℓ
10. Phenols (as phenol)	10	5	mg/ℓ
11. Cyanides (as CN^-)	20	10	mg/ℓ
12. Settleable Solids	Charge	Charge	mℓ/ℓ
13. Suspended Solids	2 000	1 000	mg/ℓ
14. Total dissolved solids	[1 000]	[500] <u>3000</u>	mg/ℓ
15. Electrical Conductivity	-	400	mS/m
16. Anionic Surfactants	-	500	mg/ℓ
17. C.O.D.	Charge	Charge	mg/ℓ

GENERAL QUALITY LIMITS	LARGE WORKS	SMALL WORKS	UNITS
	> 25 Mℓ/d	< 25 Mℓ/d	
Heavy Metal Limits			
18. Copper (as Cu)	50	[5] <u>10</u>	mg/ℓ
19. Nickel (Ni)	50	[5] <u>10</u>	mg/ℓ
20. Zinc (Zn)	50	[5] <u>10</u>	mg/ℓ
21. Iron (Fe)	50	[5] <u>10</u>	mg/ℓ
22. Boron (B)	50	[5] <u>10</u>	mg/ℓ
23. Selenium (Se)	50	[5] <u>10</u>	mg/ℓ
24. Manganese (Mn)	50	[5] <u>10</u>	mg/ℓ
25. Lead (Pb)	20	5	mg/ℓ
26. Cadmium (Cd)	20	5	mg/ℓ
27. Mercury (Hg)	1	1	mg/ℓ
28. Total Chrome (Cr)	20	[5] <u>10</u>	mg/ℓ
29. Arsenic (As)	20	5	mg/ℓ
30. Titanium (Ti)	20	[5] <u>10</u>	mg/ℓ
31. Cobalt (Co)	20	[5] <u>10</u>	mg/ℓ
TOTAL METALS	100	20	mg/ℓ

SPECIAL LIMITATIONS

- 1 No calcium carbide, radio active waste or isotopes
- 2 No yeast & yeast wastes, molasses spent or unspent
- 3 No cyanides or related compounds capable of liberating HCN gas or cyanogen
- 4 No degreasing solvents, petroleum spirit, volatile flammable solvents or any substance which yields a flammable vapour at 21°C

H2. Acceptance of Trade Effluent for Discharge into Sea Outfall

No trade effluent shall be accepted for discharge into the sea outfall unless it complies with the following conditions. The effluent shall not contain concentrations of substances in excess of those stated below:-

SEA OUTFALL QUALITY LIMIT		UNITS
1. Temperature (°C)	44 °C	Degrees Celcius
2. pH	5,5 < pH < 9,5	
3. Settleable solids	2	ml/l
4. Oils, greases and waxes of mineral origin	50	mg/l
5. Arsenic (expressed as As)	5	mg/l
6. Cadmium (expressed as Cd)	1,5	mg/l
7. Total chromium (expressed as Cr)	3	mg/l
8. Copper (expressed as Cu)	3	mg/l
9. Lead (expressed as Pb)	5	mg/l
10. Mercury (expressed as Hg)	0,05	mg/l
11. Cyanides (expressed as CN ⁻)	10	mg/l
12. Nickel (expressed as Ni)	10	mg/l
13. Zinc (expressed as Zn)	20	mg/l
14. Sulphide (expressed as S ⁼)	1	mg/l
15. Sulphates in solution (expressed as SO ₄ ⁼)	250	mg/l

APPENDIX I
MATERIAL SAFETY DATA SHEET

I1. Activated Carbon

Section 01 - Chemical And Product And Company Information

Product Identifier Activated carbon (All Grades)
Product Use Water purification, gold recovery, and air scrubbing
Supplier Name..... Merck South Africa.
Prepared By..... . Merck South Africa
Preparation Date..... .February 16, 2009

Section 02 - Composition / Information on Ingredients

Hazardous Ingredients..... Activate Carbon 100%
CAS Number..... Activated Carbon 7440-44-0
Synonym (s)..... Activated granular carbon, activated powdered carbon, pelleted activated,carbon, activated charcoal, animal bone black

Section 03 - Hazard Identification

Inhalation..... Non-toxic though inhalation
Skin Contact / Absorption..... Not Available
Eye Contact..... Mechanical dust irritation
Ingestion.....Non-toxic though ingestion
Exposure Limits..... OSHA/PEL= 5mg/m³ as resp.
ACGIH/TLV= 10mg/m³ as total

Section 04 - First Aid Measures

Inhalation..... Remove victim to fresh air. Give artificial respiration only if breathing has stopped. If breathing is difficult, give oxygen. Seek medical attention.
Skin Contact / Absorption..... Remove contaminated clothing. Wash affected area with soap and water. Seek medical attention if irritation occurs or persists.
Eye Contact..... Flush immediately with water for at least 20 minutes. Forcibly hold eyelids apart to ensure complete irrigation of eye tissue. Seek medical attention.
Ingestion..... No known health effects. Seek medical attention if any problems are experienced.
Additional Information..... Not Available

Section 05 - Fire Fighting

Conditions of Flammability.....Non-combustible under normal circumstances. Once ignited, the fire generally burns slowly (smolder) with a dull glow and may be difficult to detect.

Means of Extinction..... Use water spray, alcohol foam, dry chemical or carbon dioxide.

Flash Point..... Not Applicable

Auto-ignition Temperature..... > 220°C

Upper Flammable Limit Not Applicable

Lower Flammable Limit..... Not Applicable

Hazardous Combustible Products.... Carbon monoxide, formaldehyde, and carbon dioxide. Contact with strong oxidizers (ozone, liquid oxygen) may cause rapid combustion.

Special Fire Fighting Procedures.....Wear NIOSH-approved self-contained breathing apparatus and protective clothing.

Explosion Hazards..... Airborne dust may create an explosion hazard.

Section 06 - Accidental Release Measures

Leak / Spill..... Wear appropriate personal protective equipment. Ventilate area. Stop or reduce leak if safe to do so. Prevent material from entering sewers. Vacuum or shovel spilled material and place in closed container for proper disposal.

Deactivating Materials..... Not Available

Section 07 - Handling and Storage

Handling Procedures..... Use proper equipment for lifting and transporting all containers. Use sensible industrial hygiene and housekeeping practices. Wash thoroughly after handling. Avoid all situations that could lead to harmful exposure.

Storage Requirements..... Store in a clean, well ventilated area away from oxidizers, acids, ignition sources, heat and combustible materials.

Section 08 - Personal Protection and Exposure Controls

Protective Equipment

Eyes..... Chemical goggles, full-face shield, or a full-face respirator is to be worn at all times when product is handled. Contact lenses should not be worn; they may contribute to severe eye injury.

Respiratory..... Respiratory protection is not normally required. If use creates dust formations, then a NIOSH-approved respirator with a dust cartridge is recommended. Wet activated carbon removes oxygen from air causing a severe hazard to workers inside confined spaces. Before entering such an area, sampling and work procedures for low oxygen levels should be taken (such as wearing a self-contained breathing apparatus).

Gloves..... Impervious gloves of chemically resistant material (rubber or PVC) should be worn. Wash contaminated clothing and dry thoroughly before reuse.

Clothing..... Body suits, aprons, and/or coveralls of chemical resistant material should be worn at all times. Wash contaminated clothing and dry thoroughly before reuse.

Footwear.....No special footwear is required other than what is mandated at place of work.

Other..... Not Available

Engineering Controls

Ventilation Requirements.....Mechanical ventilation (dilution or local exhaust), process or personnel enclosure and control of process conditions should be provided. Supply sufficient replacement air to make up for air removed by exhaust systems.

Other.....Emergency shower and eyewash should be in close proximity.

Section 09 - Physical and Chemical Properties

Physical State.....Solid

Odor and Appearance.....Black odourless particulate solid, pellet, or powder

Odor Threshold..... Not Applicable

Specific Gravity (Water=1)..... 0.25 – 0.60

Vapor Pressure (mm Hg, 20oC)..... Not Applicable

Vapor Density (Air=1).....Not Applicable

Evaporation Rate.....Not Applicable

Boiling Point..... Maximum 4000°C

Freeze/Melting Point..... > 3500°C

pH..... Not Applicable
Water/Oil Distribution Coefficient.....Not Applicable
Bulk Density..... > 400kg/m³
% Volatiles by Volume..... 0%
Solubility in Water.....Insoluble
Molecular Formula.....C
Molecular Weight.....12.011

Section 10 - Stability and Reactivity

Stability.....Stable under normal conditions.
Incompatibility.....Strong oxidizers such as ozone, liquid oxygen, chlorine, potassium permanganate.
Hazardous Products of Decomposition..Carbon monoxide may be generated in the event of a fire (especially with incomplete combustion in an enclosed space).
Polymerization.....Will not occur

Section 11 - Toxicological Information

Irritancy..... Not Available
Sensitization.....Not Available
Chronic/Acute Effects..... Not Available
Synergistic Materials..... Not Available
Animal Toxicity Data..... LD50(rat,oral): >10g/kg
LC50(rat, inhalation): >64.4mg/L
Carcinogenicity..... Not considered to be carcinogenic as per IARC, NTP, and OSHA.
Reproductive Toxicity.....Not Available
Teratogenicity..... Not Available
Mutagenicity.....Not Available

Section 12 - Ecological Information

Fish Toxicity.....Not Available
Biodegradability..... Not Available
Environmental Effects..... Not Available

Section 13 - Disposal Considerations

Waste Disposal..... Dispose in accordance with all federal, provincial,
and/or local regulations

including the Canadian Environmental Protection Act.

Section 14 - Transportation Information

TDG Classification

Class.....Not regulated

Group..... Not regulated

PIN Number.....Not regulated

Other..... Secure containers (full and/or empty) with suitable
hold down devices during shipment.

Section 15 - Regulatory Information

WHMIS Classification.....Not a controlled product

Revision Date.....December 19, 2013