

https://dspace.org/

Adsorption of Phenols onto Fly Ash

Bada, Samson Oluwaseyi

2008-07-18T10:43:53Z
http://hdl.handle.net/10539/5095

Downloaded from a DSpace repository. https://dspace.org/

Adsorption of Phenols onto Fly Ash

Samson Oluwaseyi Bada

A dissertation submitted to the Faculty of Engineering and the Built Environment, University of the Witwatersrand, in fulfillment of the requirements for the degree of Masters of Science in Engineering.

Johannesburg, 2007

Declaration

I declare that this dissertation is my own unaided work. It is being submitted for the degree of Masters of Science in the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other University.

Signature: S.O Bada

……..

November 2007

ABSTRACT

Organic wastewaters have always been a problem due to their increasing toxic threat to humans and the environment. The removal of organic compounds has become an important issue due to stringent measures introduced by various countries to enforce regulations concerning wastes originating from petrochemical industries. Hence, wastewater containing such compounds must be treated.

In this research, the adsorptive capacity of an unclassified (class F) South Africa Coal Fly Ash (SACFA) originating from a power plant was evaluated for the removal of phenol, 2-Nitrophenol and 4-Nitrophenol from aqueous solutions. Fly ash generated in the Lethabo Power Station was collected and tested for its use as a low-cost adsorbent. Batch studies were performed to evaluate the effects of various experimental parameters such as adsorbent dosage, initial pH (pH_o), and contact time on the removal of these three adsorbates. The equilibrium isotherms for the adsorption of the adsorbates on the SACFA were analyzed by the Freundlich and Langmuir models at pH 2.22. The desorption of the adsorbates from the FA surface was also carried out using 30 ml of distilled water at 307 K.

Fixed bed column tests were undertaken to study and evaluate the dynamic adsorption behaviour of phenol/FA through a dynamic column approach. The performance of a small - scale fixed bed column containing FA was evaluated using 20 mg/l of phenol concentrations. The column with 20 mm diameter, studied bed depths of 30, 40 and 50 mm and flow rate of 3.0 ml/min was used in order to obtain experimental breakthrough

curves. The bed depth service time (BDST) model was used to analyze the experimental data and the design parameters like adsorption capacity, adsorption rate and service time at 30% and 70% breakthrough. BDST was also extended by predicting service times of columns operated under different influent concentrations and flow rates and these theoretical values were compared with the experimental values.

The rate of adsorption follows first order kinetics before attaining equilibrium with the sorption rate (K_{ad}) obtained for adsorption on FA being the highest for 4-nitrophenol ($7.0X10^{-3}$ h^{-1}). The adsorption isotherm indicates that the Freundlich model effectively fits the experimental data for the adsorbates better than the Langmuir model, with 4-Nitrophenol having the highest adsorption capacity of 6.51 X 10^{-2} mg/g, 2-Nitrophenol 6.00 X 10^{-2} mg/g and phenol 6.31 X 10^{-2} mg/g. SACFA was found to adsorb 90.2% of phenol, 88.9% of 2-Nitrophenol and 92.6% of 4-Nitrophenol at an initial concentration of 20 mg/l. The desorption studies suggested that the desorption of 4-Nitrophenol was the most difficult out of the three adsorbates to be desorbed. The desorption efficiency was 17.9% for phenol, 18.8% for 2-Nitrophenol and 10.2% for 4-Nitrophenol by using 30 ml distilled water at 300 rpm for 22 h.

The studies showed that SACFA can be used as an efficient adsorbent material for removal of organic compounds from water and wastewater.

DEDICATIONS

This thesis is dedicated to God, my parents and Sisters

ACKNOWLEDGEMENTS

The thought that this research will be a success right from the start had filled my heart with such purpose and gave me the inspiration to strive so I can achieve success in all am attracted to. My life has been touched and influenced by so many people.

First, I would like to sincerely acknowledge my major supervisor, Prof J.H. Potgieter, my deepest gratitude for all your guidance, constructive suggestions and support through my graduate program. Thank you for teaching me how to become a researcher. Expressed appreciation is also due to Prof S.S. Potgieter-Vermaak, for the enormous time, insightful criticisms and patient encouragement aided in the completion of my experiment and writing of this thesis. My gratitude also goes to Prof R.A. Kruger, I gratefully acknowledge your advice, guidance and for supplying the Fly Ash used for this project.

Special thanks to Oluwagbenga Johnson for helping out in changing my samples during my dynamic column test. I would also like to acknowledge my fellow post-grads students, Afolabi Ayo Samuel and Saka Abdulkareem as well as post-docs, Peter Olubambi, for being there for me at all times.

Without the advice and encouragement from many relatives, friends and colleagues this dissertation would not have been possible. Special thanks to my mom and dad, I do appreciate all you did. I would also like to thank my siblings, my sisters, Mr Omosehin, my nieces, OmoT and nephews.

Finally, to my close friends who have offered such precious emotional support that will never be forgotten. My thanks go especially to Tony, Ayo, Debbie, Dayo, Gbucell and S.O.J.

CONTENTS

CONTENTS **Page**

DECLARATION……..ii

ABSTRACT…… iii

DEDICATION……..v

ACKNOWLEDGEMENTS……vi

CONTENTS……..viii

LIST OF FIGURES.....xii

LIST OF TABLES.....xvii

LIST OF SYMBOLS…….....xx

1 Introduction……...1

1.1 Background and Motivation……...1

1.2 Justification…….....4

1.3 Problem Statement…….....4

1.4 Hypothesis…….....6

1.5 Objectives of the Research…….....6

1.6 Lay-Out of the Thesis…….....7

2 Introduction…….....9

2.1 Existing Technologies……10

2.2 Adsorbents…….....14

2.2.1 Adsorbents Used For Waste Water Clean-Up…….....16

2.2.1.1 Fly Ash.....16

2.2.1.2 Activated Carbon.....19

2.2.1.3 Activated Alumina……..20

2.2.1.4 Peat……21

2.2.1.5 Zeolite……22

2.2.1.6 Rice Husk…….....23

2.2.2 Fly Ash and Activated Carbon for the removal of phenol and its derivates ……..24

2.2.2.1 Fly Ash for the Removal of Phenol and Its Derivatives…….....24

2.2.2.2 Activated Carbon for the Removal of Phenol and Its Derivatives ….....26

2.3 Removal of Inorganic Compounds Using Fly Ash……..28

2.3.1 Heavy Metals and Metalloids.……29

2.3.2 Inorganic Anions.……..29

2.3.3 Dyes Removal.……30

2.4 Adsorbates……..31

2.4.1 Phenol……31

2.4.2 Nitrophenols……...33

2.4.3 2-Nitrophenol……34

2.4.4 4-Nitrophenol……35

2.5 Concluding statements……....37

3 Materials and Methods…….....39

3.1 Materials…….....39

3.1.1 Adsorbate Material……..39

3.1.2 Adsorbent……40

3.2 Equipment for Characterization and Analytical Analysis …….……..40

3.3 Experimental Procedure……...40

3.3.1 Mineralogical Methods Used For the Classification of Fly Ash……...40

3.3.2 X-ray Diffraction Analysis…….....41

3.3.3 Scanning Electron Microscopy (SEM) Analysis……41

3.3.4 X-ray Fluorescence Spectroscopy Analysis……...41

3.3.5 Particle Size Distribution Analysis……42

3.3.6 Specific Surface Area Analysis……..42

3.3.7 Quantitative Chemical Analysis……43

3.4 Experimental Methods……..43

3.4.1 Characterization Studies……43

3.4.2 CFA Morphology……...44

3.4.3 XRD analysis……..45

3.4.4 Quantitative Elemental Analysis Studies……46

3.4.5 Particle Size Distribution……..47

3.4.6 Specific Surface Analysis……...48

3.4.7 Batch Studies…….....48

3.4.8 Desorption Studies…….....49

3.4.9 Dynamic Column Test…….51

4 Results and Discussion……..53

4.1 Effect of Contact Time……..53

4.2 Dynamic Adsorption…….55

4.3 Influence of pH……..58

4.4 Effect of FA Loading……60

4.5 Adsorption Isotherm…….62

4.5.1 Phenol Adsorption…….62

4.5.2 2-Nitrophenol Adsorption……..65

4.5.3 4-Nitrophenol Adsorption……..67

4.6 Desorption studies……..72

4.6.1 Effect of FA Loading……..74

4.7 Dynamic Column Studies……..75

4.7.1 Effect of bed depth on breakthrough…….78

4.7.2 Data Evaluation…….78

4.7.3 Design of adsorption column for different concentration……..80

4.7.4 Design of adsorption column for different flow rate.....82

4.7.5 Comparison…….....83

4.8 Summary……..84

5 Conclusions and Recommendation……...86

5.1 Conclusions……86

5.2 Recommendations…….89

6 References……...90

APPENDIX A: Batch Studies Data……105

APPENDIX B: Adsorption Isotherm Plots……115

APPENDIX C: Dynamic Column Studies Data……128

APPENDIX D: Dynamic Column Studies Plots……131

LIST OF FIGURES

Figure **Page**

Fig 1.1: Solution Part to Wastewater Treatment, Using an Adsorption approach……...8

Fig 2.1: Molecular structure of adsorbates……37

Fig 3 1 & 3.2: SEM micrographs of Fly Ash…….44

Fig 3.3: X-ray diffraction pattern of Lethabo Coal Fly Ash……..45

Fig.3.4: Particle size distribution profile for Lethabo Coal Fly Ash…….47

Fig 3.5: Experimental diagram of down-flow packed column……..52

Fig 4.1: Effect of contact time on the amount of Phenol, 2-Nitrophenol and 4-Nitro-phenol removed from aqueous solution with FA. Operating conditions: Co; 20 mg/l, RPM; 300, FA; 20g and Volume; 30 ml……55

Fig 4.2: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of phenol studied at concentration of 20mg/l……...56

Fig 4.3: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 2-Nitrophenol studied at concentration of 20mg/l……..57

Fig 4.4: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 4-Nitrophenol studied at concentration of 20mg/l……..57

Fig 4.5: Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at pH 2.22, Co; 20 mg/l and different loading weight of FA (5-40) g…….59

Fig 4.6: Effect of pH on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at pH 5.98,C_o; 20 mg/l and different loading weight of FA (5-40) g……..59

Fig 4.7: Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at pH 2.22, C_o; 20 mg/l and different loading weight of FA (5-40) g……...61

Fig 4.8: The linearized Freundlich Adsorption Isotherm for Phenol with FA…….….64

Fig 4.9: The linearized Langmuir Adsorption Isotherm for Phenol with FA……64

Fig 4.10: The linearized Freundlich Adsorption Isotherm for 2-Nitrophenol with FA ……66

Fig 4.11: The linearized Langmuir Adsorption Isotherm for 2-Nirophenol with FA. ……66

Fig 4.12: The linearized Freundlich Adsorption Isotherm for 4-Nitrophenol with FA. ……68

Fig 4.13: The linearized Langmuir Adsorption Isotherm for 4-Nirophenol with FA. ……68

Fig 4.14: Influence of adsorbent dosage on the desorption of phenol from FA……72

Fig 4.15: Influence of adsorbent dosage on the desorption of 2-Nitrophenol from FA. ……73

Fig 4.16: Influence of adsorbent dosage on the desorption of 4-Nitrophenol from FA. ……73

Fig 4.17: Breakthrough curves for Phenol Adsorption at 30 & 70 % concentration remaining……76

Fig 4.18: BDST plot at 30 % breakthrough point for Phenol Adsorption determined from a theoretical approach……77

Fig 4.19: BDST plot at 70 % breakthrough point for Phenol Adsorption determine from a theoretical approach……77

Fig 4.20: Comparison of BDST model predictions based on C_o: 20 mg/l with calculated BDST for phenol adsorption with C_o: 30 mg/l……..82

Fig B.1: Standard curve for phenol concentrations (10-30) mg/l at 269.0 nm…….115

Fig B.2: Standard curve for phenol from the mixture of 2-Nitrophenol and 4- Nitrophenol concentrations (10-30) mg/l at 269.0 nm…….115

Fig B.3: Standard curve for 2-Nitrophenol from the mixture of phenol and 4-Nitrophenol concentrations (10-30) mg/l at 277.5 nm…….116

Fig B.4: Standard curve for 4-Nitrophenol from the mixture of phenol and 2- Nitrophenol concentrations (10-30) mg/l at 320.5 nm…….116

Fig B.5: Effect of adsorbent dosage on the removal of phenol from 2-Nitrophenol and 4 -Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of FA (5-40) g……117

Fig B.6: Effect of adsorbent dosage on the removal of 2-Nitrophenol from phenol and 4 -Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of FA (5-40) g……117

Fig B.7: Effect of adsorbent dosage on the removal of 4-Nitrophenol from phenol and 2-Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of FA (5-40) g……118

Fig B.8: Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4-Nitr ophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of FA (5-40) g ……..……118

Fig B.9: Effect of pH on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at (pH 5.98),C_o; 20 mg/l and different loading weight of FA (5-40) g……119

Fig B.10: Effect of contact time on the amount of Phenol, 2-Nitrophenol and 4-Nitrophenol removed from aqueous solution with FA. Operating condition Co; 20 mg/l, RPM; 300, FA; 20g and Volume; 30 ml…….119

Fig B.11: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of phenol studied at concentration of 20mg/l……..120

Fig B.12: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 2-Nitrophenol studied at concentration of 20mg/l……..120

Fig B.13: Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 4-Nitrophenol studied at concentration of 20mg/l……..121

Fig B.14: The linearized Freundlich Adsorption Isotherm for Phenol with FA…….121

Fig B.15: The linearized Freundlich Adsorption Isotherm for 2-Nitrophenol with FA. …….122

Fig B.16: The linearized Freundlich Adsorption Isotherm for 4-Nitrophenol with FA. …….122

Fig B.17: The linearized Langmuir Adsorption Isotherm for Phenol with FA……..123

Fig B.18: The linearized Langmuir Adsorption Isotherm for 2-Nirophenol with FA …….123

Fig B.19: The linearized Langmuir Adsorption Isotherm for 4-Nitrophenol with FA. …….124

Fig B.20: The linearized Freundlich Desorption Isotherm for Phenol with FA……..124

Fig B.21: The linearized Freundlich Desorption Isotherm for 2-Nitrophenol with FA. …….125

Fig B.22: The linearized Freundlich Desorption Isotherm for 4-Nitrophenol with FA. …….125

Fig B.23: Influence of adsorbent dosage on the desorption of phenol from FA……126

Fig B.24: Influence of adsorbent dosage on the desorption of 2-Nitrophenol from FA. …….126

Fig B.25: Influence of adsorbent dosage on the desorption of 4-Nitrophenol from FA. …….127

Fig D.1: Breakthrough curves for Phenol Adsorption at 30 & 70 % concentration remaining…….131

Fig D.2: BDST plot at 30 % breakthrough point for Phenol Adsorption determined from actual Experimental data…….132

Fig D.3: BDST plot at 30 % breakthrough point for Phenol Adsorption determined from theoretical approach……132

Fig D.4: BDST plot at 70 % breakthrough point for Phenol Adsorption determined from actual Experimental data…….133

Fig D.5: BDST plot at 70 % breakthrough point for Phenol Adsorption determined from theoretical approach……133

Fig D.6: Comparison of BDST model predictions based on C_o: 20 mg/l with calculated BDST for phenol adsorption with C_o: 30 mg/l……..134

LIST OF TABLES

Table **Page**

Table 2.1 Uses and Physicochemical Properties of Phenol, 2-Nitrophenol and 4-Nitrophenol……..36

Table 3.1 Composition of CFA as determined by XRF analysis (mass %)……...46

Table 4.1: Freundlich and Langmuir adsorption isotherm parameters……..70

Table 4.2: A Comparison of Freundlich and Langmuir Constants for phenol adsorption reported in the Literature…….71

Table 4.3: Freundlich adsorption and desorption isotherm parameters…….74

Table 4.4: Adsorption and desorption efficiencies of phenol, 2-Nitrophenol and 4-Nitro phenol at maximum FA loading……...75

Table 4.5: % Adsorbate removal at breakthrough contact time of 2 hours……...80

Table 4.6: Comparison of theoretical and experimental adsorption capacity at 30% and and 70% breakthrough of initial adsorbates concentration……...80

Table 4.7: 30% breathrough time for experimental data based on 20 mg/l with calculated data for adsorbates adsorption with 30 mg/l…….81

Table 4.8: 30% breathrough time for theoretical data based on 3.0 ml/min with calculated data for adsorbates adsorption with 1.5 ml/min……...83

Table 4.9: Output-design parameters, data and constants for batch and dynamic Test …….85

TableA.1. Standard for phenol at concentrations (10-30) mg/l at 269.0 nm…….105

TableA.2. Standard curve for phenol from the mixture of 2-Nitrophenol and 4-Nitro-

phenol concentrations (10-30) mg/l at 269.0 nm……..105

TableA.3. Standard curve for 2-Nitro phenol from the mixture of phenol and 4-Nitro phenol concentrations (10-30) mg/l at 277.5 nm…….....106

TableA.4. Standard curve for 4-Nitro phenol from the mixture of phenol and 2-Nitro phenol concentrations (10-30) mg/l at 320.5 nm……..106

TableA.5. Effect of FA dosage selected on each of the adsorbate, (pH: 2.22)……..107

TableA.6. % Removal of each adsorbate at pH: 5.98.……..….107

TableA.7. Contact time experiments data for CFA using phenol, 2-Nitrophenol and 4-Nitrophenol at pH: 2.15…….....108

TableA.8. Contact time experiments data for % phenol, 2-Nitrophenol and 4-Nitrophenol removal using CFA at pH: 2.15……..108

TableA.9. Kinetic removal of phenol, 2-Nitrophenol and 4-Nitrophenol at 20 mg/l concentration at pH: 2.15……..109

TableA.10. Adsorption Isotherm data for Freundlich Model at different FA loading (5-35) g for phenol adsorption……...109

TableA.11. Adsorption Isotherm data for Freundlich Model at different FA loading (5-35) g for 2-Nitrophenol adsorption……..110

TableA.12. Adsorption Isotherm data for Freundlich Model at different FA loading (5-35) g for 4-Nitrophenol adsorption……..110

TableA.13. Adsorption Isotherm data for Langmuir Model at different FA loading (5-35) g for phenol adsorption……..111

TableA.14. Adsorption Isotherm data for Langmuir Model at different FA loading (5-35) g for 2-Nitrophenol adsorption……..111

TableA.15. Adsorption Isotherm data for Langmuir Model at different FA loading (5-35) g for 4-Nitrophenol adsorption……..112

TableA.16. Desorption Efficiency data of CFA from phenol, 2-Nitrophneol and 4-Nitrophenol with H_2O……...112

TableA.17. Desorption Isotherm data for Freundlich Model at different FA loading for Phenol adsorption……113

TableA.18. Desorption Isotherm data for Freundlich Model at different FA loading for 2-Nitrophenol adsorption……113

TableA.19. Desorption Isotherm data for Freundlich Model at different FA loading for 4-Nitrophenol adsorption……114

TableA.20. t-Test Report to show difference between Phenol and 2-Nitrophenol…….114

Table C.1 Input data for design calculations…….128

Table C.2. Breakthrough Times for Phenol Adsorption……..129

Table C.3. Breakthrough time for phenol (h) at BDST of 30 % & 70 %.....130

LIST OF SYMBOLS

b	Langmuir constant related to adsorption energy (L/mg)
C_o	Initial adsorbate concentration (mg/l)
C_e	Final aqueous phase concentration (mg/l)
K_f	Freundlich constants (mg/g)
K_a	BDST adsorption rate constant $\left(L/mg.h\right)$
K_{ad}	Adsorption rate constant for the adsorption equilibrium $(\min^{-1})$
n	Adsorption intensity (L/mg)
N_o	BDST adsorption capacity per unit bed volume (mg/L)
Q_e	Solid phase equilibrium concentration (mg/g)
Q_i	Desorbed adsorbate amount (mg/g)
Q_m	Maximum adsorption capacity (mg/g)
Q_t	Adsorbate adsorbed by adsorbent at time t (mg/g)
t_b	Breakthrough time at desired concentration (h)
V	Linear flow velocity of the feed to bed $(ml/\min)$
l	Volume of adsorbate (ml)

CHAPTER I

1.0 Introduction

1.1. Background and Motivation

The volumes of organic wastes generated in our society and the cost of their disposal has continued to increase, and this poses a challenge to chemical engineers to develop improved, cost effective and environmentally safe disposal and treatment methods. The toxicity of these organic compounds (phenol and nitro-phenols) makes their removal necessary. Phenolic compounds had been classified as high priority pollutants by the US Environmental Protection Agency due to their extensive impact on the deterioration of the water environment (EPA, 1984). They are products and raw materials of the following industries: petrochemical, oil refinery, plastic, explosives, azo dyes, pigments, leather, paint, pharmaceutical, coking plant, steel and pesticides industries (Uberoi *et al.*, 1997; Srivastava *et al.*, 2006). The improper discharge of these compounds in water bodies over a long period can cause the deterioration of water environments, while its intake by both human and animals causes liver and kidney damage, central nervous system impairment, diarrhoea and excretion of dark urine (Sarkar and Acharya, 2006).

The need to find a suitable means of managing organic wastes generated in our society and the cost of their disposal, has lead to this present study of utilizing South Africa Coal Fly Ash (SACFA) as an adsorbent for removing phenolic compounds from wastewater. Treatment methods available for organic waste include: granular activated carbon processes and reverse osmosis, anaerobic processes, the electro-Fenton method, combined applications of flotation and coagulation processes, stripping and oxidation. All of these are used in treating organic and

inorganic wastes of a variety of plants (Charest *et al.*, 1999; Chon *et al*., 1999; Vandevivere *et al.*, 1998). Most of these methods suffer from some drawbacks, such as high capital and operational cost, regeneration cost, and problem of residual disposal.

Liquid – phase adsorption has been shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, adsorbent cost, effectiveness and the availability of a wide range of adsorbents. Activated carbon is often the preferred adsorbent for the removal of organic compounds due to its high adsorption capacity (Stoeckli *et al.*, 2001; Haghseresht *et al.*, 2002; Singh *et al.*, 2002). However, it suffers from some drawbacks, such as high cost and the irreversible nature of adsorption (Rengaraj *et al.*, 2002). The non economical and the difficulty in regeneration of some high cost adsorbent such as granular activated carbon (GAC) are drawback faced when an adsorbent after adsorption are irreversible/ or not regenerated for another application. Hence, the disposal of an adsorbent as a waste after adsorption is not an economic option unless the adsorbent is of a very low cost. These drawbacks had lead many researchers to investigate the use of more cost effective and alternative adsorbents like peat, fly ash, rice husk, saw dust, clay, carbonized bark, zeolites, graphite and bottom ash for removal of organic compounds from wastewater (Srivastava *et al.*, 1997; Edgehill and Lu Max 1998; Yousef *et al.*, 1999; Bertoncini *et al*., 2000, and Rengaraj *et al.*, 2002).

The potential of fly ash as a natural adsorbent for adsorption had been investigated by Banerjee *et al*. (1995), Akgerman and Zardkoohi (1996), Ahmaruzzaman and Sharma (2005) and Sarkar and Acharya (2006)**.** Their work identified the potential for removing phenol and its analogues with fly ash and prompted this research into the use of South Africa fly ash as an alternative

adsorbent for their adsorption from wastewaters.

Previous research into the removal of organic compounds such as phenol and its analogues from contaminated wastewaters by coal fly ash (Sarkar and Acharya, 2006; Akgerman and Zardkoohi, 1996) indicated that phenol displayed a much higher affinity for coal fly ash than its analogues do. However, in another study on the adsorption of phenolic compounds onto fly ash by Ahmaruzzaman and Sharma (2005), it was found that phenol had the least affinity for coal fly ash among similar aromatic analogues used. These discrepancies in the adsorptive capacity of phenols and its analogues can be attributed to the differences in the surface properties, particle size, adsorbates properties and origin of the coal fly ash used.

The removal of nitro-substituted phenols had also been investigated and the results show that adsorption occurs due to the surface properties possessed by the coal fly ash (Singh and Nayak, 2004). In addition, Sarkar *et al.* (2003) investigated the kinetics of adsorption of some priority phenolic compounds, such as, 1, 2-dihydroxybenzene, 1, 3- dihydroxybenzene and 1-hydroxy-4-nitrobenzene onto fly ash where the process was found to consist of both surface adsorption and pore diffusion with external transport that mainly governs the rate-limiting process.

Among the chlorophenol, 2-chlorophenol and 2, 4-dichlophenol investigated and adsorbed by coal fly ash, it was found that the adsorbed amount of chlorophenol was influenced by a high specific surface area, high carbon content and the fine particle size of the coal fly ash (Kao *et al.,* 2000). Organic compounds with three different functional groups normally found in petrochemical waste effluent had been investigated by Banerjee *et al.* (1995), and the results showed that their adsorption depends on the molecular weight and polarity of the targeted

organic compounds in the wastewater.

In most of these studies, the fly ash was not properly classified, nor its properties given. In none of the open literature, could evidence be found of a study on the adsorption capacity and its application to organic compounds for SACFA. It is not unreasonable to expect SACFA to behave differently than many of those reported in the open literature, as far as its adsorptive properties are concerned, because it depends on the origin of the coal and the conditions of combustion prevailing during its formation. SACFA was studied fairly extensively for the removal of heavy metals from multi-component solutions by Potgieter and Potgieter-Vermaak (2006), and it was seen that SACFA responded differently but successfully to the uptake of the different heavy metal ions compared to other fly ashes.

1.2. Justification

Various techniques have been investigated for adsorption of organic and inorganic wastes by fly ash over the past years. Several research studies had been reported on the characterization of fly ash and adsorption of inorganic wastes using fly ash. None have been recorded on the adsorption of phenol, 2-Nitrophenol and 4-Nitrophenol using South African fly ash. Hence, it was decided to embark on this investigation

1.3. Problem Statement

A stabilization process involves the conversion of contaminants in waste to less hazardous forms through chemical and physical binding reactions (Core Consultative Committee, 2003). It can be achieved by several different means: chemical treatments (i.e. precipitation or passivation), chemically modifying the surfaces of the wastes, increase in the specific surface

area of the adsorbent thereby reducing its particle size for adsorption (Wang *et al.*, 2005) and higher agitation speed to increase the mass transfer kinetics of different constituents of the adsorbates onto the CFA (Kurma et al., 2004). The liquid-phase adsorption process provides an alternative amongst these available stabilization processes due to its effectiveness, cheapness, and environmental friendliness. It also has the capability to adsorb both organic and inorganic components within wastes.

The adsorption rate and the percentage organic pollutant adsorbed onto SACFA was compared with reported values from the literature and found to be different. The characterization of SACFA, specific surface area, influence of solution pH, adsorbent dosage and nature of adsorbate were therefore studied in order to determine its effects on the adsorption uptake of these organic pollutants (Cooney, 1999).

The nature of the organic compounds considering their molecular weight, polarity and functional groups will also affect their affinity to adsorp onto fly ash. Coupling these factors with empirical design procedures based on the data obtained from adsorption equilibrium tests from both batch and dynamic column operations can be used to predict the absorber size, performance, and affinity of organic compounds onto fly ash. A projected solution path to the proposed system is shown in Figure 1.1 to present an outline of adsorption theory, problem related to adsorption and mechanism associated with sorption process.

This research study is therefore aimed at investigating parameters that would favour the use and suitability of South African fly ash for the treatment of organic wastewater containing phenol and selected derivatives thereof by using the liquid adsorption stabilization process.

1.4. Hypothesis

South Africa coal fly ash (SACFA), classified as a Class F CFA, would be applied as an adsorbent to adsorb and retain various organic compounds typically generated and disposed of by the petrochemical industries considering some of the parameters affecting adsorption. In this study it is proposed that South Africa FA can be applied instead of granulated activated carbon (GAC) as adsorbent for C6 organic compounds. Furthermore, the adsorption process may differ significantly from those studied before due to the unique compositional and surface characteristics of the SACFA.

1.5. Objectives of the Research:

The objectives of this research are to:

a. Investigate the effectiveness of the SACFA to adsorb selected organic compounds during batch and dynamic column treatment processes.
b. Investigate the effects of adsorbent dosage, organic pollutant concentration and the contact time during batch and dynamic treatment methods.
c. Determine the breakthrough point for a dynamic column operated under different bed depths and flow rates in order to evaluate its performance.
d. Compare the adsorption rate/affinity of phenol for CFA in both batch and dynamic treatment methods.
e. Determine the applicability of Freundlich, Langmuir and the Bed Depth Service Time (BDST) approach to estimate design parameters characterizing the performance of the batch and the dynamic column tests.
f. Determine the adsorption kinetics of the various phenolic compounds onto SACFA

1.6. Lay-Out of the Thesis

The dissertation starts in chapter two with the literature review of the existing different technologies for treating organic wastewaters and the application of liquid phase adsorption processes as a suitable treatment method for the removal of organic compounds. The utilization of other adsorbents was also discussed with detailed focus on the properties of SACFA and the application of the CFA in the field of adsorption.

Detailed experimental methods used for the adsorption of organic compounds are discussed in chapter three. The characterization results obtained are presented and the approach of both batch and dynamic studies to adsorption also discussed. The uses, toxicity and physicochemical properties of the adsorbates (phenol, 2-Nitrophenol and 4-Nitrophenol) are discussed thoroughly.

Chapter four discusses the results obtained from the adsorption of organic compounds onto SACFA. Batch test was used to obtained equilibrium time required for the adsorbent (CFA) to reach adsorption equilibrium and a dynamic test was used to determine the equation which can be used to estimate the size of bed column required for wastes removal. The desorption results was also presented with details of the effects of pH, contact time and adsorbent loading on adsorption.

The dissertation is concluded in chapter five which contains the conclusions drawn and recommendations for future work.

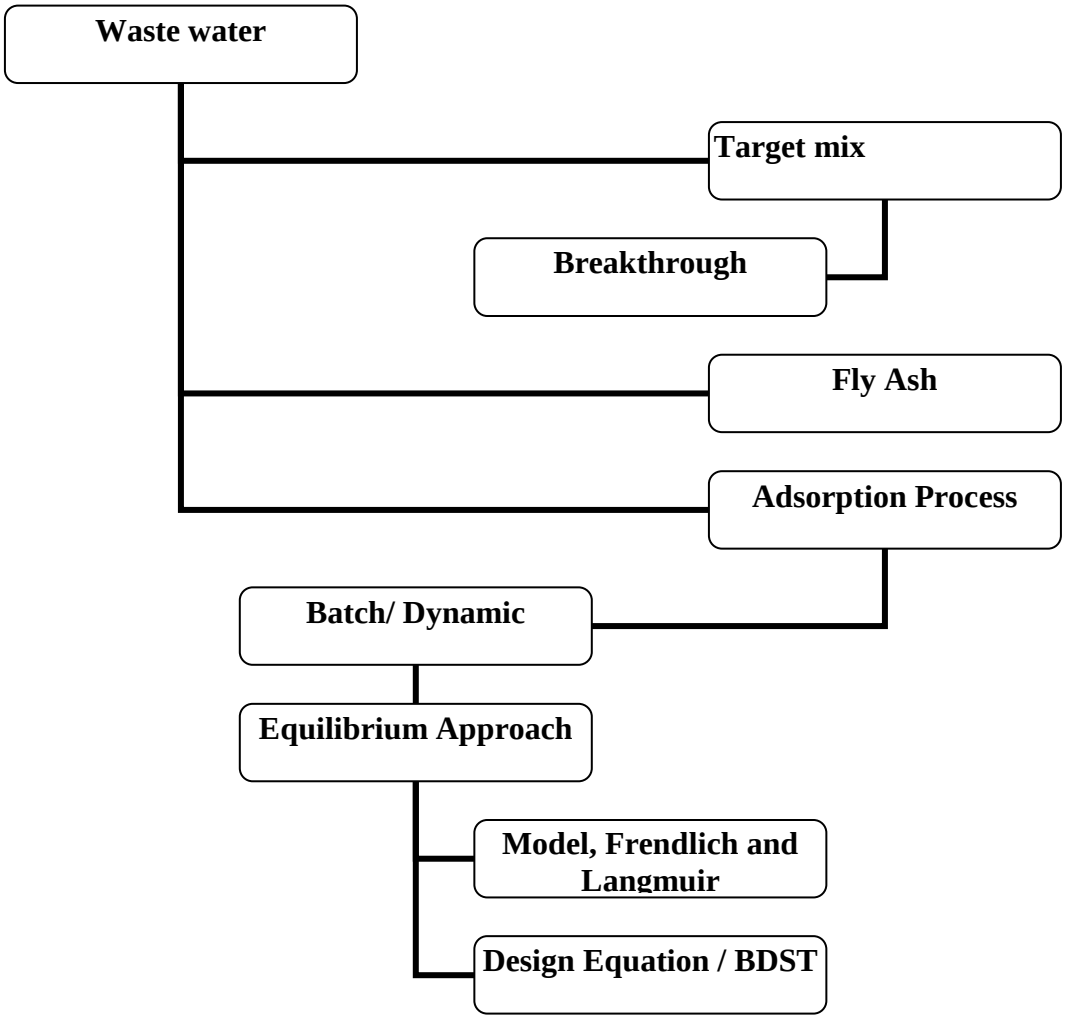


Figure 1.1. Solution to Wastewater Treatment, Using an Adsorption approach

CHAPTER II

Literature Survey

2.0. Introduction

The industrial growth in the chemical industry, specifically the petrochemical industry in the Southern Durban area of South Africa, had lead to substantial contamination of surface and ground waters by different organic compounds and exported refined petroleum products over the past decades (Butler and Hallowes, 2002). The high toxicity of these compounds and increasingly stringent treatment standards being introduced all over the world make their removal absolutely necessary. Wastewaters from these plants are highly variable in composition and their disposal is always a matter of great concern since they are considered high priority pollutants due to the deterioration of the water environment they cause and the considerable risk they pose to aquatic organisms. This was one of the reasons why the Department of Water and Forestry promulgated a regulation whereby industries are required to treat their effluents, and funded monitoring programmes and ecological impact studies to evaluate the environmental effects of their discharge (DWAF, 1993).

Quality control and assessment of abandoned landfill leachates are some of challenges facing the field of wastewater management (Smidt and Lechner, 2005). The application of different technologies, such as biological treatment (viz, air stripping, tricking filter, anaerobic processes), chemical oxidation, granular activated carbon processes and reverse osmosis, the electro-Fenton treatment method and sonochemistry (ultrasononic treatment) are some of the options to treat organic containing and dye wastewaters (Kornaros and Lyberatos, 2006; Kurniawan *et al.*, 2006; Ince *et al.*, 2001; Charest *et al.*, 1999, Chon *et al.*, 1999; Vandevivere *et al.*, 1998).

2.1. Existing Technologies

Chemical oxidation treatment of organic compounds is a process performed on a wastewater either to prepare a specific contaminant for removal or to selectively modify the toxicity of a pollutant by altering its chemical form. This kind of process requires the utilization of powerful chemical oxidizers in order to remove and destroy organic pollutants within polluted wastewaters (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 with 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 wastewater treatment method for removing resistant organic compounds after the bulk removal of the compound has been accomplished by less expensive processes. Ozone oxidation occurs either by the generation of the hydroxyl radicals due to ozone decomposition and subsequent attack by the radicals on the pollutant or direct electrophilic attack of the ozone molecule of the pollutants (Kurniawan *et al*., 2006). The use of ozone as an oxidant does not create any secondary pollutants in the environment when compared to the carcinogenic halogenated hydrocarbons 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 due to its slow reaction rates with organic compounds and its slow self-decomposition. Nevertheless, its ability to remove organic compounds depends on an intermediate association to yield hydroxyl radicals, $OH^{\cdot}$ and $HO_2^{\cdot}$ (Neyens and Baeyens, 2003), and these hydroxyl radicals are

responsible for the removal of organic compounds from aqueous solution (Pera-Titus *et al.*, 2004).

Potassium permanganate is also a strong oxidant and readily reacts with impurities such as Fe^{2+}, Mn^{2+}, S^{2-} , phenol and radio-active contaminants, but the efficiency of its application as an oxidant can be improved by combining it with several other methods. For instance, potassium permanganate can be used to complete the removal of iron and manganese in a wastewater subjected to aeration treatment (Weber, 1972).

Highly toxic organic compounds in wastewater such as phenol can be quantitatively mineralized or degraded to carbon dioxide and water or transformed to less harmful compounds with a strong hydroxyl radical (Al-Kdasi *et al.*, 2004). The oxidation reactions in the wastewater solution can be initiated by the H_20_2 or ozone, producing free radicals which rapidly react with the targeted organic compounds. The strength of an oxidant and the oxidation conditions determined the intermediate oxidation products formed after this reaction (Weber, 1972). In addition, formation of unwanted products will lead to further treatment which is not economical due to the increase in oxidation time and the cost of oxidizing agent used. Chemical oxidation processes are more economical when the concentrations of the organics to be removed are very low (Lagrega *et al.*, 1994).

The biological treatment process 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, aerobic and anaerobic digestion are by far the most feasible cost effective processes for

removing organic and inorganic compounds from wastewaters (Kornaros and Lyberatos, 2006). The most popular treatment method utilized in the United States is the convectional treatment method which includes coagulation, reverse osmosis, chemical oxidation, sonochemical treatment, filtration and an electrochemical method (Lagrega *et al.*, 1994).

Air stripping is a phase change process that 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 transfering 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 stripper unit. This process is not practicable when the concentration of the pollutant has a low Henry's law constant (Hass and Vamos, 1995) less than 100 atmosphere. The treatment of acrylonitrile – butadiene – styrene (ABS) resin wastewater was carried out using air stripping methods based on economical and environmental considerations. Chang *et al*. (2006) utilized the combination of air stripping and biodegradation for the removal of BOD from wastewater using a laboratory – scale submerged membrane bioreactor (ASMBR).

A trickling filter is a biological process developed for treating combined effluent wastewater and it is operated aerobically, either continuously or in sequencing batch reactor operation mode. This process takes place in a dynamic column/reactor consisting of bacterial supporting growth material (silica gravel), feed wastewater and the filter. Kornaros and Lyberatos (2006) confirmed that convectional biological treatment methods for treating organic compounds are not the most effective means of removing pollutants generated from organic synthesis operations, such as dyes. This is due to the fact that the improper population of microbial, high

recalcitrant presence and high concentration of toxic organic compounds (Kornaros and Lyberatos, 2006).

Sonochemistry is the study of chemical reactions and mass transfer rates within a liquid phase under different ultrasonic conditions. The use of ultrasound to treat organic wastewater involves the destruction of targeted pollutants either directly through activating their thermal decomposition or indirectly through the production of oxidation species, such as hydroxyl radicals (Ince *et al.*, 2001). The removal of pollutants depends on the process operating parameters such as frequency, pH, dissolved gases, reactor geometry, chemical reagents and catalyst used (Kidak and Ince, 2006). Petrier *et al.* (1998**)** carried out an investigation on the dechlorination of 4- chlorophenol at 500 kHz, while Lin and Ma (1999) investigated the effects of initial solute concentration, pH and $FeSO_4$ on the decomposition of 2-chlorophenol in aqueous solution containing a chemical oxidant (H_2O_2) with varying ultrasonic conditions. They found that the rate of decomposition were 6.6 times and 9.8 times larger respectively at pH = 3 than at pH = 11 and the effect was found to be insignificant when compared with H_2O_2 addition without the presence of ultrasound.

The application of granular activated carbon (GAC) processes has proved to be one of the most effective processes for the treatment of organic wastewaters, heavy metals and the removal of dyes (Kumar *et al.*, 2004). However, the utilization of activated carbon as an adsorbent in developing countries had been limited due to some economic drawbacks, such as high capital and operational costs, regeneration cost and problems associated with residual disposal. These shortcomings have stimulated interest in South Africa to investigate the feasibility of using cheaper materials (CFA) in treating organic wastewaters.

The alternative approach to these existing technologies for the removal or managing organic wastes generated in our society is the stabilization of organic wastes using a liquid-phase adsorption process. Liquid – phase adsorption has been shown to be highly efficient for the removal of organic compounds as well as heavy metals from the waste effluents due to its simplicity and the availability of a wide range of adsorbents (Akgerman and Zardkoohi, 1999 and Ahmaruzzaman and Sharma, 2005). The potential of fly ash as a natural adsorbent for adsorption had also been investigated (Banerjee *et al*., 1995 and Sarkar and Acharya, 2006)**.** While Banerjee *et al*. (1997) explored the use of fly ash derived from bituminous coal for the adsorption of o-xylene and concluded that the rate of o-xylene adsorption onto FA to be very high, Kao *et al.* (2000) also utilized class F fly ash but with higher S.S.A ranging from 5 to 42 m^2/g to the CFA used in this study to remove cholorophenol from aqueous water and concluded that FA has a significant capacity for the adsorption of organic compounds. Each of these authors identified the potential for removing organic compounds with fly ash and this prompted the research into the use of South Africa fly ash as an alternative adsorbent for the adsorption of organic compounds from wastewaters.

2.2. Adsorbents

The simplicity, as well as the ease of operation with the application of low cost and readily available adsorbents (CFA) in wastewater treatment had lead to an extensive research for the application of liquid-phase adsorption process for the removal of organic pollutants. The utilization of FA in the wastewater treatment process would serve as an economically viable solution to the increasing toxic threat to the environment and the fact that it has a huge potential of replacing activated carbon or zeolites for adsorption in water pollution treatment.

Fly ash is relatively abundant in South Africa and consists of predominantly inorganic residues produced from pulverized coal. A research reported by Dijkema (2006), estimated that more than 30 million metric tons of fly ash are produced in South Africa annually, while it was estimated in the year 2000 that about 349 Mt of this resource was generated worldwide (WCI, 2000).

Cheaper materials had been found by researchers as potential substitutes and adsorbents to overcome the problems associated with activated carbon for the removal of organic pollutants. These adsorbents are peat and bentonite (Viraraghavan *et al.*, 1998), rice husk, rice husk ash and rice husk silica (Mahvi *et al.*, 2004), zeolites (Norberg,1999), rubber seed coat pine wood based activated carbon (Tseng *et al.*, 2003), rubber seed coat (Rengaraj *et al.*, 2002), bagasse and word charcoal (Mukherjee *et al*., 2007), clays and fertilizer wastes, pillared clays and mesoporous alumina (Konstantinou *et al.*, 2000), carbonized slash pine bark (Edgehill and Lu Max, 1998) and kenaf (Han, 1999), all of which have been evaluated for use as adsorbents.

In this research, South Africa Coal Fly Ash (SACFA) had been proposed as an adsorbent instead of activated carbon (AC). In addition, previous successful applications have been reported by several local researchers (Potgieter – Vermaak *et al*., 2006; Potgieter – Vermaak *et al.*, 2005; Reynolds, 2005; Matjie *et al.*, 2004; Woolard *et al*., 2002) on the uses of SACFA for soil amendment, removal of inorganic anions, stabilization and solidification, removal of inorganic compounds, as source of metal oxides and also for other higher value applications in the polymer industries.

The application of SACFA in this research for the uptake of organic compounds generated

from petrochemical wastewaters is therefore considered a distinctive new investigation due to the fact that the SACFA had not been used for the adsorption of organic compounds from industrial wastewaters previously.

2.2.1. Adsorbents Used For Waste Water Clean-Up

2.2.1.1. Fly Ash

Coal firing power thermal stations are still the main source of power generation in South Africa and these stations are situated in close vicinity to the coal fields. Sasol, which is one of the Africa's major producers of chemicals and liquid fuels and Eskom, the major power utility in South Africa are some of the biggest consumers of coal in South Africa with Sasol utilizing 28 million tons of coal for its gasification process at Sasol synfuels in Secunda and 6 million tons at Sasol Infrachem for Sasolburg. These plants generated 7 million tons of gasification ash and 1.5 million tons of fly ash respectively in 2005 (Matjie *et al.*, 2005).

South Africa currently produces more than 33 million tons of fly ash per annum and these huge quantities of FA are utilized for soil amendment, construction purposes, as an extender and pozzolan for cement and concrete applications, and as adsorbent for inorganic wastes (Kruger, 2002).

Previous research conducted on South African fly ashes includes an investigation on the surface properties of an ultra fine fly ash used in the polymer industry (Potgieter – Vermaak *et al.*, 2005), the use of fly ash in cement (Helmuth, 1987) and work on the feasibility of SACFA as a pre-treatment agent for acid mine drainage (Potgieter – Vermaak *et al.*, 2006) and it utilization for the removal of phosphate from aqueous solution (Agyei *et al.*, 2002). Matjie *et*

al. 2004 also investigated the extraction of alumina from low rank class F South African coal ash.

Fly ash is the powdery residue obtained by the separation of the solids from the flue gases of furnace fired with the pulverized coal. It is also known as a complex heterogeneous material and as the finest coal combustion residue (0.2-90μm) formed during the transformation of mineral matter present in coal particles after combustion. More so, poor combustor efficiency and the improper quality control in maintaining the particle size of the pulverized coal feed into the combustors can also leads to a wide distribution of char, semi coke or coked carbon of large dimension (90-300μm) in the ash generated (Tomeczek and Palugnoik, 2002). These particles are collected using a variety of methods such as mechanical collectors, electrostatic precipitators, fabric filters and wet scrubbers (Lee Daniels *et al.*, 2002).

The detailed chemical characteristics of fly ash can be explained based on its mineralogical composition which depends largely on its geological features related to formation, origin of coal, decomposition of coal and combustion condition (Vassilev and Vassileva, 1996; Singh and Kolay, 2002). The mineralogy of fly ash is closely related to the minerals entrained in the coal and several different minerals have been identified as part of fly ash. The major phases presents in the fly ash are mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anhydrite ($CaSO_4$), hematite (Fe_2O_3), lime (CaO) and an amorphous aluminosilicate (Alonson and Wesche, 1991; Goodarzi, 2005). However, the formation of these phases depends on the type of coal used during combustion. In addition, the mineral contents of the FA are found responsible for its applications as fillers in polymer, refractory materials, as soil ameliorant and as an adsorbent for inorganic removal from wastewaters (Kruger and Kruger, 2005; Sarkar and

Acharya, 2006).

The chemical composition of fly ash is determined from the source of coal used during combustion, combustion conditions and variation in composition with particle size (Lee Daniels *et al.*, 2002). The major elements in fly ash are Si, Al and Fe with smaller concentration of S, Ca, Mg and with oxygen as the main constituent in the form of various minerals. Trace elements present in the ash includes Pb, Zn, Cr, Ag, As, Cd, Ni and other minor metals (Goodarzi, 2005).

The particle size analysis, specific surface area determination (BET), density and porosity of fly ash are some of the factors that influence the reactivity of fly ash for adsorption processes. Ashes obtained through electrostatic precipitators are finer, while ash collected through mechanical means are coarser. The surface area analysis is one of the factors used to determine the adsorption capacity of any adsorbent, and has been found to increase with the decrease in the particle size of the fly ash (Sarkar *et al.*, 2006). The ash obtained from the burning of bituminous coal is found to be finer than that produced by the burning of lignite coal (Tolle *et al.*, 1982). This was also observed by Sarkar *et al*. (2006) who found that the higher sum total of (SiO_2, $Al_6Si_2O_{13}$ and Fe_3O_4) for bituminous coal, its silica content which apparently increases with decrease particle size, low carbon content and the melting of the higher aluminious siliceous material present in bituminous coal are responsible for the generation of ashes with finer particles than that of non bituminous coal.

In general, fly ash has low bulk density (1.01 – 1.43 g/cm^3), specific gravity (1.6 – 3.1 g/cm^3) while, 65-90 % of fly ash of silt loam texture have particles with diameters of less than 100 μm

(Roy *et al.*, 1981).

2.2.1.2. Activated Carbon

Activated carbon (AC) had been proven to be an effective and excellent adsorbent for the removal of a wide variety of organic and inorganic compounds from wastewater. The earliest application of activated carbon as an adsorbent dated back to centuries with the discovery that carbonaceous materials could be utilized for the removal of tastes, colours and odours from wastewater (Cooney, 1999). It is now a widely used adsorbent in water treatment technology for the removal of volatile organic compounds and dyes from industrial textiles wastewaters. It has remarkably high specific surface areas which range between 500 to 1500 m^2/g, random imperfect highly porous structure and widely different range of surface functional groups (Yin *et al.*, 2007).

Many references had been cited in the literature containing information regarding the production of activated carbon. Almost any carbon material can be used to produce activated carbon by a wide range of methods, which include thermal decomposition of various charred or carbonaceous materials, microwave pyrolysis, acidic treatment and controlled activation (Crittenden, 1998). The raw materials used in making activated carbon include hard wood, coals, coal tar, carbon black, rice husks, baggase ash, fertilizer waste slurry, saw dust, lignine, and coconut shell (Edgehill and Lu Max, 1998; Critttenden, 1998; Mukherjee *et al.*, 2007). The properties of the activated carbon formed through the conversion of carbonaceous materials depend extensively on the nature and origin of the raw material used, and the properties of the desired activated carbon depend on the activation time, temperature profile and activation steps. An increase in the activation time also leads to an increase in the size of the pores

generated and the internal surface area formed (Cooney, 1999). In addition, the surface of an AC adsorbent is essential non polar but surface oxidation by heating at around 300 ^{0}C or by chemical treatment may cause a slight polarity to occur with hydrophilic property which can be used to advantage in the adsorption of polar adsorbates (Crittenden, 1998).

Particle size is an important factor when specifying AC for a particular application, because smaller particles size causes more pressure drop across a carbon bed. The purity of the AC depends on the level of the ash present in the carbon material. The ash is the inorganic residue left when a sample of the carbon material is heated in a furnace. The ash constituents of a coal – based carbon is made up of silica, iron, calcium, magnesium and alumina. Mineral acids are used to remove some of the ash before the carbon is being utilized in the treatment of wastewater (Cooney, 1999).

2.2.1.3. Activated Alumina

Activated alumina had been used in the treatment of wastewater and its adsorption capability for the removal of both organic and inorganic compounds was found to be favoured by a specific surface area, pore structure, ionic strength and chemical inertness (Misra, 1986). It can be produced from the mixtures of amorphous and gamma alumina prepared by the dehydration of $Al(OH)_3$ under low-temperatures of 300-600 ^{0}C, with surface areas in the range of 250 – 350 m^2/g (Crittenden and Thomas, 1998).

Research conducted on the use of microporous alumina pillared montmorillonite (clay) and mesoporous alumina aluminium phosphate as adsorbents had shown successful removal of 2,4-chlorophenol, 2,4,6- trichlorophenol, pentachlorophenol, and also pesticides such as: molinate,

propazine and atrazine from waster water (Konstantinou *et al.*, 2000). The removal efficiency of the pillared clay material for the herbicide was found to be higher than that of the mesoporous aluminium phosphate due to the substitution of the alkyl lateral chains of the aluminium phosphate during the sorption of s-triazines and the increase of P/Al ratio during the adsorption of propachlor. Activated alumina was recommended for the removal of most inorganic compounds due to its affinity for inorganic anions with efficiency up to 100% for the uptake of As (V), Se (VI) and F^- (Faust and Aly, 1999).

2.2.1.4. Peat

Peat and other biomass materials have been used previously in the treatment of wastewater containing heavy metals and organic compounds. Peat is a yellow to dark brown residue, which occurs during the first stage of coal formation. It is composed of partly carbonizing materials such as decayed trees and peats bogs that have accumulated in water–saturated environments and swamps (Spedding, 1988). The main constituents of peat moss are lignin, humic acid and cellulose. In addition, the surface functional groups of peat include aldehydes, carboxylic acids, ketones, alcohols, ethers and phenolic hydroxides, which are all involved in the adsorption of pollutants. In addition, its polar nature is responsible for its specific adsorption potential for dissolved metals and polar organic compounds.

Peat moss has the natural ability to retain moisture because of its high water holding capacity and its specific adsorption capability for polar organic compounds and dissolved metals (Boardsell *et al.*, 1997). Viraraghavan and Alfaro (1998) investigated the effectiveness of using peat in removing phenol from organic wastewaters. The adsorption of phenol on peat was found to be optimum at the pH of 4.0 to 5.0, while the equilibrium data was well fitted by the

Freundlich model and yielded a removal capacity of 46.1% of phenol from an initial concentration of 1 mg/l. Shiskowski and Viraraghavan (1993) used peat to remove chromium with removal efficiencies of 94% and 96.6% from a packed column of 500 mm with influent concentrations ranging from 0.348 mg/l to 0.619 mg/l. Viraraghavan and Kapoor (1995) also used peat to remove mercury present in raw wastewater and this lasted for 5 h due to the present of other contaminants which interfered with the mercury sorption.

2.2.1.5. Zeolites

The drawback suffered by activated carbon due to its high regeneration cost and production cost has lead to the application of zeolites as an alternative adsorbent. Zeolites are a group of natural or synthetic hydrated aluminosilicate minerals which contain both alkaline and alkali-earth metals. It has been used as an adsorbent, molecular sieve, ion-exchangers and catalysts in the past decades, because their chemical properties and large effective surface area gives them superior adsorptive qualities (Metes *et al*., 2004). There are several types of zeolites such as MCM-22, ZSM-5, ZSM-22, BETA, and Y. Their adsorption equilibrium had been studied by Denayer *et al.* (1998), and these equilibrium studies showed that the synthetic zeolites have higher adsorption capacity than the natural zeolites for the removal of ink, dyes and polluted wastewater. Zeolite BETA was first synthesized in 1967 by Mobil but its configuration was only determined in 1988 (Treacy and Newsman, 1988). It has a large pore structure and it is widely used as catalyst support and adsorbent for separating mixtures consisting of aromatic compounds (Norberg and Su, 1999).

The adsorptive capacity of Na–Y and Ni/Na–Y zeolites as an adsorbents had been evaluated for the adsorption of phenol and chlorophenol isomers from aqueous solutions (in the

concentration range 0.6–48 mmol/dm^3) at 293 ± 3 K by Okolo *et al.* (2000). The experimental adsorption isotherms were regressed using Langmuir and Freundlich Model where, the Langmuir Model provided a better fit for Na–Y and Freundlich Model providing a good fit for the Ni/Na–Y data. Both zeolites exhibited similar effectiveness but, at lower phenol concentrations, Na–Y does deliver appreciably higher removal efficiencies than Ni/Na–Y zeolites.

2.2.1.6. Rice Husk

Rice husk is a known biomass available worldwide with annual production exceeding 100 million tons yearly (Grisdanurak *et al*., 2003). The main constituents of rice husk are ash, lignin and cellulose (Govinda *et al.,* 1980). Its chemical composition varies depending on the soil chemistry, geological location, climatic variation and type of fertilizer applied during growth. It is used in power plants as low–value fuel and on burning produces 14-20% ash which contains 80-95% silica in the crystalline form and minor amounts of metallic elements (Chandrasekhar *et al.,* 2003).

The adsorptive capacity of rice husk silica had been evaluated by Grisdanurak *et al*. (2003) and its adsorption capacity for chlorinated volatile organic compounds was found to be higher than that of commercial mordenite and activated carbons. It has been utilized for solving disposal problems and also as an adsorbent in treating organic wastewaters. The adsorption potential of this biomass for adsorbing phenol from aqueous solution was found to be depended on the pH, contact time and the initial phenol concentration. This result shows that phenol was adsorbed to a lesser extent at higher pH values. Phenol forms salts, which readily ionize leaving negative charge on the phenolic group while, its present on the adsorbent prevents the removal of

phenolate ions. In addition, the percentage adsorption of phenol for this test also decreases as the initial phenol concentration increases. The adsorption capacity determined for this test was 0.886 mg/g for phenol and the equilibrium data was fitted successfully by the Freundlich model (Mahvi *et al.*, 2004).

2.2.2. Fly Ash and Activated Carbon for the removal of phenol and its derivatives

2.2.2.1. Fly Ash for the Removal of Phenol and Its Derivatives

Recently, fly ash has been used in the adsorption of organic compounds from waste streams, and especially phenolic compounds. Akgerman and Zardkoohi (1996) investigated the adsorption of phenol, 3-chlorophenol and 2, 4-dichlorophenol from wastewater onto fly ash with phenol having the highest adsorption affinity for fly ash. The Freundlich isotherm was used in the modeling of the data obtained from the equilibrium experiments. The adsorbed amount of phenol onto the fly ash was 67 mg/g, 20 mg/g for 3-chlorophenol and 22 mg/g for 2, 4-dichlorophenol. The effectiveness of fly ash, bentonite and peat as less expensive adsorbent for the removal of phenol from wastewater has been examined by Viraraghavan and Alfaro (1998). The batch test indicated that the optimum pH for the adsorption of phenol on fly ash was between 4.0 and 5.0 at 294 ± 1^0K. The Freundlich Model fitted the data on the adsorption of phenol on peat and betonite very well whereas the Langmuir isotherm described the sorption of phenol on fly ash. Fly ash was found to adsorb 41.6% of phenol from the initial concentration of approximately 1 mg/l as compared to the concentration of 20 mg/l used in this study. This concentration differences might be responsible for the lack of agreement between the models used in fitting the data obtained when using SACFA and this particular test. Das and Patnaik (2005) also explored the adsorptive capacity of blast furnace flue dust (BFD) and slag for removal of phenol. They found that the equilibrium adsorption of phenol onto BFD

and slag were attained after 8 h of contact time. The removal efficiency of 75% and 90% were achieved for slag and BFD respectively. Both Freundlich and Langmuir isotherm models well fitted to the adsorption data obtained from the equilibrium experiments.

The potential of fly ash as a substitute for activated carbon was examined by Aksu and Yener (1999). The results obtained showed that the capacity of fly ash for adsorption of phenol depends on the initial pH and phenol concentration. The maximum adsorption capacity for phenol was found to be 27.9 mg/g at an initial concentration of 100 mg/l. The application of Freundlich model for the phenol sorption data obtained showed a good fit. The kinetics of adsorption of priority organic compounds such as phenol, o-hydroxyphenol, m-hydroxyphenol, and 4-nitrophenol onto fly ash were studied by Sarkar *et al.* (2003). The rate of adsorption was found to be of a complex nature and controlled by both pore diffusion and surface adsorption. Through evaluation of the ultimate adsorption data obtained from the concentration range studied found that the external transport is the main rate – limiting process. The adsorptive capacities of fly ash as a potential adsorbent for the same species were studied by Singh and Nayak (2004). The adsorbent particle size, pH, solute concentration and temperature all played a role in the adsorption of these solutes. It was observed that an increased amount of the nitro-phenols was adsorbed with a decrease in the fly ash particle size, lower pH, increasing concentration and temperature. The adsorption of phenol and its analogues from contaminated water onto fly ash has been investigated by Sarkar and Acharya (2006). The efficiency of removal was favoured at lower solute concentration, smaller particle size of fly ash, increased agitation time and speed, and increase dose of fly ash. The equilibrium data showed a better correlation to the Langmuir isotherm model. The process was also found to be spontaneous and endothermic in nature.

2.2.2.2. Activated Carbon for the Removal of Phenol and Its Derivatives

A great deal of research has been performed on the adsorption of phenols and its other analogues onto activated carbon. Adsorption isotherms for twelve mono-,di-, and trichlorophenols from aqueous solutions on wood-based and lignite-based carbons have been studied (Colella and Armenante, 1998). The Freundlich Model was effectively used to model these data while, the Langmuir Model was found to have a very poor fit. Initial concentrations ranging from 100 to 4,000 mg/l were tried for this adsorption isotherm studies. The adsorptive capacity for activated carbon in adsorbing 2,4-DCP was found to be 502 mg/g. Particle size did not appear to play a significant role on chlorophenol adsorption; although, larger particles were associated with a slightly diminished adsorption capacity. Adsorption data for the removal of phenol from aqueous solution onto activated carbon produced from rubber seed coat (RSCC) were generated by Rengaraj *et al.,* (2002b). The Freundlich Model was successfully used to model these data and the adsorption of phenol onto RSCC was found to follow the first order reversible kinetics. It was observed that 96% of the ultimate adsorption occurs within the first 3 h of contact followed by a very slow approach to the final equilibrium concentration which suggest a possible saturation of the adsorbent.

The adsorption of phenol onto activated carbon-commercial grade (ACC) and laboratory grade (ACL) have been studied by Srivastava *et al.,* (2006). The adsorption was found to followed pseudo-second order kinetics with the ACL having higher adsorption rate than the ACC. Adsorption isotherms over a wide range of concentrations ranging from 75 mg/l to 300 mg/l onto activated carbon at optimum pH of 6.5 were generated. The Redlich-Peterson Model was found to have a better fit for phenol removal on all the asorbents. An interesting conclusion

was made that the higher percentage of phenol removal onto ACC and ACL was possible provided that the initial concentration of phenol in the solution was low.

The extent of adsorption of 3-chlorophenol from water was determined by using a carbon obtained from burning of rice straw (RC). The adsorption capacities were found to be higher for the Langmuir model than the Freundlich Model. The adsorption capacity determined by data-fitting to the Langmuir model was 14.2, 12.9, 11.4 and 4.9 mg/g at pH 4, 6, 8 and 10, respectively. The adsorption was presumed by Wang *et al*. (2007) to occur primarily on the surface of the carbon fraction of RC, as silica was expected to be highly hydrophilic. They suggested that rice-straw-based carbon be used at low-to-neutral pH as an adsorbent for chlorophenols because adsorption decreased with increasing pH due to increased deprotonation of surface functional groups of RC and dissociation of chlorophenols.

Isotherms for phenols adsorption onto activated carbon were generated and the Freundlich Model was found to fit the experimental data (Mukherjee *et al.*, 2007). The adsorptive capacity was found to be 1.037 mg/g (C_o = 30 mg/l) and 1/n to be 8.69 while, at a C_o = 50 mg/l, the adsorption capacity was 2.45 mg/g and 1/n to be 1.51. It was also found that the solution pH under the given test conditions slightly affected the phenol removal by the AC. The adsorption equilibria of aqueous 2, 4- dichlorophenol onto activated carbon fiber (ACF) activated by static air were studied by Wang *et al.* (2007). Langmuir Model was found to best fit the data out of Freundlich, Redlich-Peterson and Toth models used to fit the experimental data. The adsorption kinetics was found to follow the pseudo second-order, activation energy was calculated to be 40.90 kJ/mol, and the thermodynamic parameters, ΔH and ΔS, were estimated to be −5.82 kJ/mol and 0.07 kJ/(mol K), respectively, suggesting that the adsorption was

exothermic. The positive value of the force implies the increased randomness at the solid/solution interface in the adsorption of 2, 4-DCP onto ACF.

The adsorption of 2-chlorophenol onto thermally activated carbons and chemically activated powdered carbons (PAC) have been studied (Aktas and Cecen, 2007). The Freundlich and Langmuir Model were successfully used to model the data obtained. However, Langmuir Model indicates a higher adsorption capacity of 2-chlorophenol onto thermally activated carbons and chemically activated powdered carbons than the Freundlich Model. The thermally activated carbons have a better adsorption capacities of 250 mg/g and 270 mg/g compared to 86.5 mg/g and 60.4 mg/g obtained from the Freundlich Model. The Langmuir model also indicated that the chemically activated powdered carbons had adsorption capacities of 140.8 mg/g and 256.4 mg/g compared to 13.6 mg/g and 8.2 mg/g obtained from the Freundlich Model. The authors found that the difference in the adsorption capacities for these adsorbates was almost certainly caused by their activation method, which resulted into different surface characteristics.

2.3. Removal of Inorganic Compounds Using Fly Ash

There are many research reports on work that have been carried out in the field of adsorption techniques for the removal of toxic metal ions, pollutants in air, organic compounds, dye adsorption, and inorganic anions in wastewater using fly ash as adsorbent. Malerius and Werther (2003) investigated the removal of mercury from a sewage sludge incineration plant using fly ash as adsorbent. The data obtained were well fitted by the Langmuir equation. Sen and De (1987) also used fly ash in removing mercury from aqueous solution and results obtained showed that fly ash was comparable in its adsorption abilities with powdered

activated carbon. Adsorption of organic gas such as toluene vapour on fly ash was investigated by Rovatti *et al.* (1988). They found that fly ash obtained after thermal activation treatment, offered satisfactory adsorption performance for toluene vapour.

2.3.1. Heavy Metals and Metalloids

The application of fly ash for removing heavy metals date back as early as 1975, when its effectiveness as a low cost adsorbent was evaluated for removing chromium ions such as Cr^{6+} and Cr^{3+}. The adsorption capacity of fly ash for Cr^{6+} was first conducted by Panday *et al.* (1984) and Dasmahapatra *et al.* (1996). They found that fly ash removal efficiency increases at a lower pH, with particle size having no significant effect on the adsorption. Adsorption data for $Cr^{6+}$and Hg^{2+}onto FA were also generated by Banerjee *et al.* (2004). The adsorption capacity of FA was found to be 1.379 mg/g for $Cr^{6+}$and 11.00 mg/g for Hg^{2+}. The removal of Zn^{2+} and Cd^{2+} from wastewater was investigated using lignite-based fly ash and activated carbon. The result shown that fly ash was as effective as activated carbon with the adsorption efficiency increasing with an increase in concentration, dosage of fly ash and temperature.

Isotherms for the removal of Cu, Ni, Zn, Cd and Pb onto fly ash and fly ash/lime mixing were obtained by Ricou *et al.* (1999) and the results indicate that the adsorption removal capacity increased with increasing pH. Adsorption equilibrium studies to determine the removal characteristics of Zn^{2+}onto fly ash were conducted by Weng and Huang (2004). The results showed that the amount of Zn^{2+} adsorbed increases as the concentration and pH of the solution increase with a final total removal efficiency of 99%. The adsorptive capacity was found to be in the range of 1.04×10^{-6} to 1.15×10^{-5} mol Zn^{2+} /g of adsorbent and adsorption was favourable at low ionic strength, high pH and high temperature. Pb^{2+} and Cd^{2+} had been

removed from wastewater through the application of hydrothermal treated fly ash known as zeolites, and an adsorption capacity of 95.6mg was found for the cesium/g-zeolite, while lead/g-zeolite was estimated to be 70.5mg (Mimura *et al.,* 2001).

2.3.2. Inorganic Anions

The removal of phosphate had been investigated by Grubb *et al*. (2001) using batch equilibration tests. The result obtained showed that the uptake of phosphate onto fly ash is attributed to the formation of insoluble iron and aluminium phosphate at low to medium pH values. The rate and efficiency of phosphate removal by fly ash, slag and ordinary Portland cement (OPC) were studied by Agyei *et al.* (2002). Adsorption data was well fitted by the Frumkin isotherm and slag was found having a higher adsorption capacity than fly ash. The solution pH, temperature, concentration and reaction times plays an important role in the adsorption of fluoride from wastewater using fly ash. Chaturvedi *et al.* (1999) reported that the removal of fluoride is favourable at low concentrations, high temperature and acidic pH.

2.3.3. Dyes Removal

The utilization of fly ash in removing dyes from textile wastewater was first investigated by Khare *et al.* (1987). They reported that the adsorption of Victoria blue (dye) from wastewater, with the maximum adsorption achieved at pH 8. The adsorption process was found to be predominantly diffusion controlled, while the equilibrium isotherm fit the Langmuir model of adsorption well. A calcium-rich fly ash had been used as adsorbent for the removal of Congo red dye under different conditions. It was observed that the maximum adsorption obtained was between 93% and 98%. under the studies conditions. The adsorption isotherm was well fitted by the Freundlich and Dubinin- Radushkevich models (Acemioglu, 2004).

Wang *et al.* (2004) had reported the use of treated and non-treated fly ash for the removal of methylene blue and basic dye from a wastewater solution. The adsorption capacity for acid treated fly ash was found to be 2.4 x 10^{-5} mol/g, while non-treated fly ash showed an adsorption capacity of 1.4 x 10^{-5} mol/g. (Wang *et al*., 2005) in another investigation also found that the porous unburned carbon in the fly ash was responsible for the adsorption of the dye, and not the fly ash itself.

Adsorption studies were also carried out on the use of fly ash as low-cost adsorbent for the uptake of dyes by Mohan *et al.* (2002). Adsorption of the dye from aqueous solution was found to be a function of the high solution pH while the particle size of the fly ash was inversely proportional to the adsorption rate. The Freundlich model was found to provide a better fit than the Langmuir adsorption isotherm. Ramakrishna and Viraraghavan (1997) investigated the adsorption of acid dyes using peat, fly ash, bentonite and steel plant slag. The result obtained showed a higher uptake of the acid dye for the bentonite and peat than the fly ash and steel plant slag. In addition, the adsorption capacity was found comparable to the adsorption of acid and basic dyes removed by granular activated carbon.

2.4. Adsorbates

2.4.1. Phenol

Phenols belong to a class of organic compounds with aromatic functional groups and are similar in structure to the more common herbicides and insecticides, which resist biodegradation. Pure phenol consists of white or clear acicular crystals and at 41 ^{0}C it congeals into a solid that can be liquefied by mixing with a very small amount of water. It has a

characteristic sweet, medicinal, or tar–like odour. Phenols are very soluble in water and its odour threshold is 0.04 ppm (U.S.EPA, 1981). In the presence of chlorine in drinking water, phenols form chlorophenol, which has a medicinal taste that is quite pronounced, and objectionable (Mahvi *et al.*, 2004). The main sources of phenols are in the wastewaters of chemical and allied industries. However, it is an important raw material and product of the following industries: coking plants and pesticides industries (Srivastava *et al.*, 2006).

The USEPA reported phenol in their 1993 Toxic Release Inventory as one of the top twenty-five chemicals most discharged by the US industries (Zappi *et al.*, 2000). Phenols are considered high priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to both humans and animals. The effects of phenol in humans are similar to those produced in animals. Systemic absorption causes central nervous system impairment, liver and kidney damage, difficulty in swallowing, anorexia, headache, fainting, dark urine and other mental disturbances (Farwell and Hunt, 1988; Sarkar and Acharya, 2006). Phenols are listed on many target regulatory lists as a contaminant of primary interest. The Ministry of Environment and Forests (MOEF), Government of India and EPA USA, have listed phenol and phenolic compounds on the priority – pollutants catalogue. The US Environmental Protection Agency (EPA) had instituted a regulation for lowering phenol content in the wastewater to less than 1.0 mg/l (Banat *et al*., 2000). In addition, MOEF has set a maximum concentration level of 1.0 mg/l of phenol in industrial wastewaters for safe release into surface waters, while the World Health Organization (WHO) recommend a threshold permissible concentration of phenol in drinking water as 0.001mg/l (WHO, 1984).

There are many phenolic compounds found in industrial wastewater which are potentially toxic to humans and aquatic life. One of them, 2, 4- Dichlorophenol is a solid at room temperature and is a high volume feed stock used for the production of herbicides and some other chemicals. It is not used outside industrial applications. Nevertheless, small quantities may be present when chlorination changes other phenolic compounds into 2-4 dichlorophenol (Agency for Toxic Substances and Disease Registry, 1992). Table 2.1 lists the key physical and chemical properties of phenol and figure 2.1 illustrates its chemical structure

2.4.2. Nitrophenols

Nitrophenols belong to the family of nitro-compounds with a general structural formula RNO_2. Nitrophenols are common by-products of many industrial processes and among the most frequent organic pollutants in agricultural wastewaters. The nitrophenols are formed in air as a result of the atmospheric photochemical reactions of several aromatic compounds formed from anthropogenic sources (Toxic Release Inventory, 1992). They are classified as compounds exhibiting moderate to high toxicity in the aquatic environment and are also characterized as one of the most challenging classes of contaminants requiring removal from wastewater streams (Mohammad *et al.*, 1996). They are six carbon cyclic molecules used as an intermediate for the synthesis of a number of organophosphorus pesticides, explosives, azo dyes, pigments, wood preservatives, pharmaceuticals, rubber chemicals (Uberoi *et al.*, 1997).

Nitrophenols are bioplasmic poisonous compounds which pose significant health risks as they are physiologically active and potentially carcinogenic. In addition, they could restrain micro-organism growth, thus decreasing the self-purifying ability of water. They are found in about

14 out of 1177 hazardous waste sites on the National Priority List being identified by the EPA (Uberoi *et al*., 1997) and as the EPA evaluate more sites the number of sites at which nitrophenol are found also increases. The USEPA had listed 2-NP, O-NP, 4-NP and 2, 4-DNP among the nitrophenols on the Priority Pollutants List and also recommends their concentrations in natural waters to be below 10 ng/l (Haghighi-Podeh *et al.*, 1995).

2.4.3. 2-Nitrophenol

2-Nitrophenol is a light yellow solid with a peculiar aromatic smell. It is slightly soluble in cold water and its main sources are industrial manufacturing and processing plants. Manufacturing and processing industries release an estimated total of 14,969 kg of 2-Nitrophenol into the air, 113.4 kg in water and 9,752 kg disposed off in off-site landfills (TRI, 1992). In addition, 2-Nitrophenols are found in the treated waste waters from the following industries: iron and steel manufacturing (nitrophenols formed during the coke making process); electrical/electronic components production, rubber processing and pharmaceutical manufacturing (EPA, 2000). It is used mainly as an intermediate for the production of dyestuffs, pigment, rubber chemicals, and fungicides. Small quantities are used as an acid-base indicator and as an inhibition for the degradation of glucose by Pseudomonas fluorescences (Spero, 2000). It may be released to the environment in wastewater and as a fugitive emission during its production and use as a chemical intermediate (Patnaik and Khoury, 2004). Therefore, humans are solely responsible for the presence of this chemical in the environment.

2.4.4. 4-Nitrophenol

4- Nitrophenol, also known as p-Nitrophenol, is a colourless to slight yellow crystalline material with very little odour, moderately toxic pollutant that is moderately soluble in cold water and denser than water. 4-Nitrophenol is produced either by the catalytic hydrolysis of 4-nitrochlorbenzene or by the reaction of dilute HNO_3 on phenol and subsequent steam distillation to separate the 4- from the 2- isomer (HSDB, 1989). It is an important fine chemical intermediate, serving as a precursor for pesticides and pharmaceutical products which had been selected by the EPA (2000) as one of the persistent, bioaccumulative and toxic (PBT) chemicals. The frequent application of this chemical for agriculture, industrial and defense purposes had lead to its presence in water bodies with an estimated 3,175 kg disposed of by underground injection and 113.4 kg disposed of in off-site landfills by industries (TRI, 1992). Technologies such as aerobic, anaerobic biodegradation process, advanced oxidation processes and adsorption have been used to remove 4-nitrophenol from domestic and industrial effluents (Karim and Gupta, 2003).

Table 2.1. Listed the key physical and chemical properties of the adsorbates.

Figure 2.1. Illustrates the chemical structure of adsorbates.

Table 2.1 Uses and Physicochemical Properties of Phenol, 2-Nitrophenol and 4-Nitrophenol.

Parameter	Phenol	2-Nitrophenol	4-Nitrophenol
Uses	Wood preservative, weed killer, synthetic resins, Costmetic surgery, and anticeptic TCP component	Production of dyes, rubber chemicals, fungicide and an acid indicator.	Production of N-4-aminophenol, insecticides, leather tanning, dyestuffs and oxydianiline.
Molar mass g/mol	94.11	139.11	139.11
Solubility in water (g/100ml)	8.30	0.26	1.52
Melting point (^{0}C)	40.5	46-46	113-114
Boiling point(^{0}C)	210	216	297

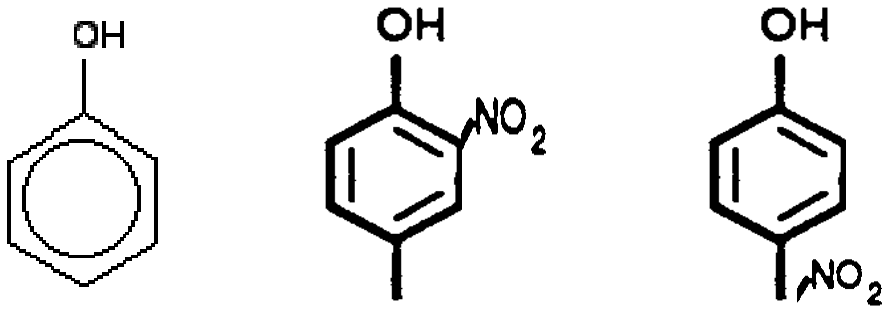


Figure 2.1. Molecular structure of adsorbates.

Physical and Chemical Properties of Phenol, 2-Nitrophenol and 4-Nitrophenol (www.Wikipedia.org); (www.inchem.org); (TRI, 1992); (HSDB, 1989).

2.5. Concluding statements

Several adsorbents have been proposed in the literature for the removal of organic compounds from solution. These cheaper carbonaceous materials, including FA containing unburnt C, have been used successfully for mercury and removal of toxic ions and organic constituents from wastewater. SACFA has been investigated and utilized for many applications, but not for the removal of organic compounds from wastewater. Various authors had also previously investigated the influence of variables such as adsorbent dosage, contact time, initial concentration and initial pH on the adsorption of phenolic compounds, and therefore it is very important to consider these parameters for the removal of organic compounds using SACFA.

From the research conducted by Aksu and Yener (2001) the adsorption capacity of the fly ash

and dried activated sludge for the removal of phenol was shown to be a function of initial phenol concentration and initial pH of the solution. More so, the effect of various parameters such as pH, adsorbent particle size and phenol concentration were investigated for the removal of nitro-substituted phenols by Singh and Nayak (2004). Their result shows that phenols adsorption increases with decreasing adsorbent particle size. This result was also observed by Sarkar *et al*. (2005), where the decrease in the particle size of fly ash leads to an increase in its surface area. The removal of nitro-phenols was also found to increase with increasing concentration and this was due to the increase in the concentration gradient between the solute and the solid phase, and the high degree of interaction between nitro-phenols and the adsorbents. As the pH of the solution decreases the adsorption capacity of the adsorbents for phenols also increases. This occurred due to the dissociation of phenol into anions which are repulsed by the negatively charged surface of the adsorbent. All these parameters are also investigated in the course of this study.

CHAPTER III

3.0 Materials and Methods

3.1. Materials

The material used for this project work includes:

(i) Adsorbates: Phenol, o- Nitrophenol and p-Nitrophenol

(ii) Solvent: Distilled water.

(iii) Adsorbent: Coal Fly Ash.

3.1.1. Adsorbate Material

The composition of the synthetically prepared aqueous solutions used in this research was similar to that generated by the petrochemical and coal conversion, phenol producing industries. The stock solution was prepared by diluting the required quantities of phenol, 2-Nitrophenol and 4-Nitrophenol of AnalR grade supplied by Merck Chemical Ltd., South Africa, in the same volume of distilled water to obtain adsorbate solutions of various initial concentrations (C_o) in the range of 10 mg/l – 30 mg/l.

Fresh solutions were prepared on a daily basis with the initial concentration of the adsorbate calculated before the start of any experiment. The pH value for the aqueous solution containing the mixture of phenol, 2- Nitrophenol and 4-Nitrophenol (10 mg /l – 30 mg /l) was 6.67 before being adjusted to 2.22 and 5.98 with diluted HCl and NaOH solutions for the adsorption test. All the pH measurements were done with a pH meter (827 pH Lab, Metrohm). Each flask was capped and inverted 3 times to mix the contents thoroughly and then allowed to stabilize for 10-15 minutes in the pyrex conical flask until isotherm experiments for both batch and column studies were performed.

3.1.2 Adsorbent

Fly ash is the fine powdery residue obtained by separating the solids from the flue gases during the combustion of coal. The fly ash utilized in this investigation was a low grade Coal Fly Ash (CFA) obtained from Lethabo power station in South Africa, collected using an electrostatic precipitator. The pH of the sample was measured after 2.5 g of CFA was mixed with 10 ml of distilled water and shaken at 35 ºC for 24 h and then the slurry was filtered and the pH was measured by a pH meter as 11.01. The physico-chemical characteristic of the adsorbent was determined using standard procedures and the sample stored inside a desicator until experiments were performed.

3.2. Equipment for Characterization and Analytical Analysis

The equipment used for this project work included: Scanning Electron Microscope (SEM) model Jeol JSM840; X-Ray Diffractometer model Phillips PW 1830 X "Pert PRO Diffractometer with a Cu-anode from PANalytical; X-ray Fluorescence Spectrometer using Magi $^{//}$X Pro XRF spectrometer from PANnalytical; N_2 absorption surface area analyzer (Micromeritics TriStat 3000 Instrument Corp); Mastersizer 2000 of Malvern Instruments Ltd; Labcon platform shaking incubator (Model FSIM-SPO16); Whatman microfiber filters; pH meter (827 pH Lab, Metrohm); UV-VIS spectrophotometer (SQ-4802 Double Beam); analytical balance; Quartz Cuvettes and Pyrex Glass Conical flasks.

3.3. Experimental Procedure

3.3.1. Mineralogical Methods Used For the Classification of Fly Ash

The techniques needed for the characterization of fly ash requires the knowledge of its chemical composition and physical properties of the ash, such as the particle size, specific

surface area and phase composition. In order to obtain a best possible information the physico-chemical characterization of the SACFA a combination of SEM (Scanning Electron Microscopy), X-ray diffractometry (XRD), X-Ray Fluorescent spectrometry (XRF), TriStat 3000 analyzer and Malvern particle size distribution analyser were used by employing standard procedures.

3.3.2. X-ray Diffraction Analysis

The mineralogical composition of the fly ash was determined by the X-ray diffraction analyses for the qualitative evaluation of the common and predominant phases within the ash. The phase identification of the representative samples of the fly ash which is in a powdery form, were determined by the X-ray diffractometry using a Phillips PW 1830 diffractometer with a Cu-anode. The diffractometer was operated at 40 kV and 40 mA for 1 h over the range of 2θ from 0^O to 80^O and the identification was carried out with High Score Plus software.

3.3.3. Scanning Electron Microscopy (SEM) Analysis

The Scanning Electron Microscopy (SEM) model Jeol JSM840 was used to determine the morphological and qualitative characteristics of the ash. The SEM was operated at the accelerating voltage of 20 keV for mineral analysis of representative samples in order to provide information on the physical properties of the ashes. The fly ash sample was carbon coated in order to make its surface conductive.

3.3.4. X-ray Fluorescence Spectroscopy Analysis

Quantitative analysis of the major elements within the candidate CFA with particle size less than 99 µm (obtained by sieving) was determined by X-ray Fluorescence Spectroscopy, using

a Magi $^{//}$X Pro XRF spectrometer from PANalytical. The sample was placed in an aluminum cup and hydraulically pressed into pellets under very high pressure of 20 tonnes for 60 seconds. This was done to ensure sample integrity under the vacuum and a consistent surface to receive the X-rays. Quantitative analysis was carried out with the Magi $^{//}$X Pro XRF spectrometer at 40 kV and 40 mA, using IQ^{+} "Standardless" analysis.

3.3.5. Particle Size Distribution Analysis

The particle size of the fly ashes was measured using a laser based particle size analyzer, namely a Mastersizer 2000 of Malvern Instruments Ltd. It utilizes Fraunhofer diffraction of light formed by particles with a diameter larger than the incident laser beam wavelength. A combination of an optical filter, lens and photo detector coupled with a computer loaded with Mastersizer software enables one to compute the particle size distribution from the diffraction data and store it as volume percentage against the particle size.

3.3.6. Specific Surface Area Analysis

The specific surface area of the fly ash was obtained using a TriStat 3000 analyzer (Micromeritics Instrument Corp) with N_2 adsorption at - 196 ºC. The sample was first degassed at 200 ºC for 4 h. TriStat 3000 is an automated gas analyzer which contains three ports, allowing up to three samples to be analyzed simultaneously. The TriStat 3000 system consists of the TriStar analyzer, a SmartPrep degasser which is used for samples preparation, a vacuum pump and a control module for entering analysis and report options.

3.3.7. Quantitative Chemical Analysis

The concentration changes of the individual compounds in the solutions were determined by means of UV-VIS spectrophotometry (SQ-4802 Double Beam). The maximum absorbances for each solute from the highest standard solution prepared were found using scanning spectrophotometry at the respective wavelength maxima λ_{max}. The λ_{max} used were 269 nm, 277.5 nm and 320.5 nm for phenol, 2-Nitrophenol and 4-Nitrophenol, respectively. The calibration plot of absorbance versus concentration for all the standards showed a linear working range up to 30 mg/l (see appendix A.1-A.4) with correlation coefficient ≥ 0.99. Therefore, the supernatant solutions obtained after adsorption were also analyzed using the same wavelengths.

3.4. Experimental Methods

3.4.1. Characterization Studies

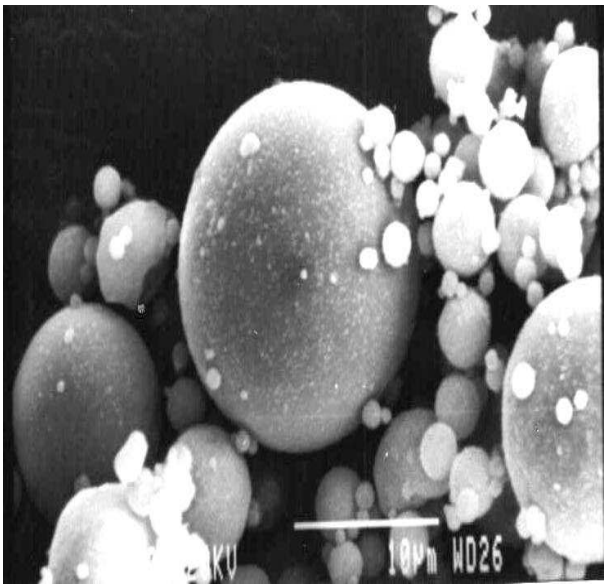
The chemical and physical characteristics of fly ash depend strongly on the geological origin of the coal, coal type, and combustion conditions (Singh and Kolay, 2002). Beneficiation techniques such as cyclone separation is used to separate fly ash in various fractions in order to optimize its application, increase its value and minimize disposal cost. The knowledge of fly ash mineralogy, environmental taxes encouraging recycling and the quality needed in the market-place create opportunities for research into the modification and exploitation of the unique chemistry of fly ash (Kruger and Kruger, 2005).

Adsorption, being a surface phenomenon, depends on the high specific surface area, narrow particle size distribution and the porosity of an adsorbent. Kao *et al.* (2000) observed that the larger the specific surface area, the higher the carbon content, and the finer the particle size of

the fly ash, the greater its adsorption capacity will be.

3.4.2. CFA Morphology

Lethabo CFA exhibited a similar morphology to those of other pulverized CFAs as reported in the literature (Goodarzi, 2005). The investigation reveals that most of the particles present in the fly ash are spherical in shape with a relatively smooth surface. Fig.3.1 shows sub-angular and spherical particles with relatively smooth grains consisting of quartz, while fig.3.2 shows clusters of iron (Fe-oxide) particles formed due to partial decomposition of pyrite and with dark quartz inclusions. Similar results were obtained from the investigation conducted by Matjie *et al.* (2005) on Sasol ashes.



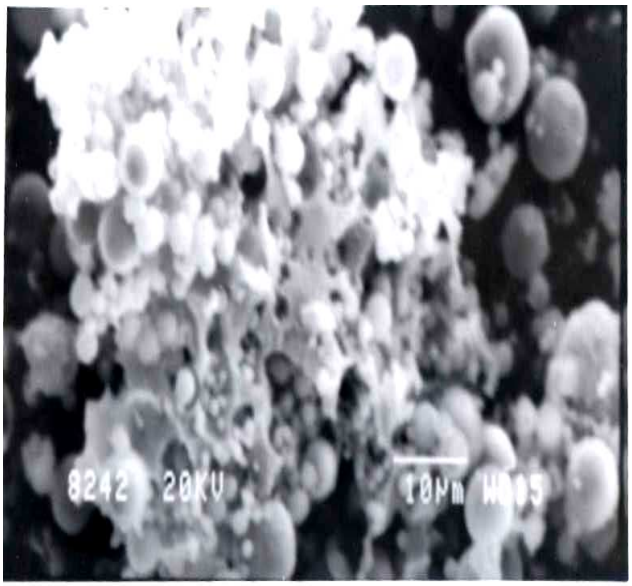


Figure 3.1 and 3.2. SEM micrographs of Coal Fly Ash

3.4.3. XRD analysis

The diffractogram (Figure 3.3.) shows the X-ray diffraction pattern for particle size ≤ 99 μm. It was found that the FA consisted of mullite, quartz, hematite and small amounts of calcium oxide with large characteristic peaks of quartz (SiO_2). This result is similar to that reported for a fly ash investigated by Sarkar *et al*. (2006). The intensity of quartz is very strong, with mullite forming a chemically stable and dense layer. The low calcium oxide intensity is characteristic of Class-F CFA, and similar to the result reported by Giere *et al*. (2003).

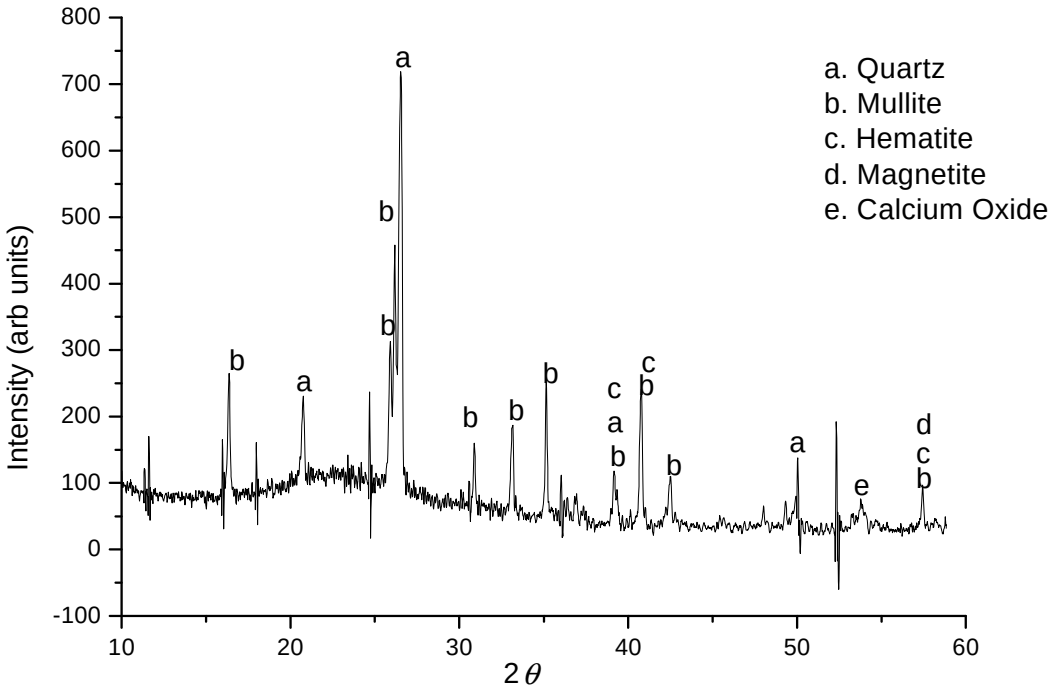


Figure 3.3. X-ray diffraction pattern of Lethabo FA

3.4.4. Quantitative Elemental Analysis Studies

The results of the X-ray fluorescence quantitative analysis of the elements in the CFA are shown in Table 3.1. The result shows that this CFA is a class F fly ash. The sum of SiO_2, Al_2O_3 and Fe_2O_3 content in the CFA was found to be greater than 70%, while its CaO content was lower than 5% (ASTM, 1994)**.** Minor elements within the CFA were also identified by the XRF and the results reveal that trace elements like Ti, Sr, and Ba are also present.

Table 3.1

Composition of CFA as determined by XRF analysis (mass %)

Element as oxide	Weight %
SiO_2	53.24
Al_2O_3	34.26
CaO	4.01
Fe_2O_3	2.87
MgO	1.23
TiO_2	1.32
K_2O	0.65
P_2O_5	0.54
Na_2O	0.40
S	0.304
Ba	0.113
Sr	0.071
Loss on ignition (unburnt C + moisture)	1.35

3.4.5. Particle Size Distribution

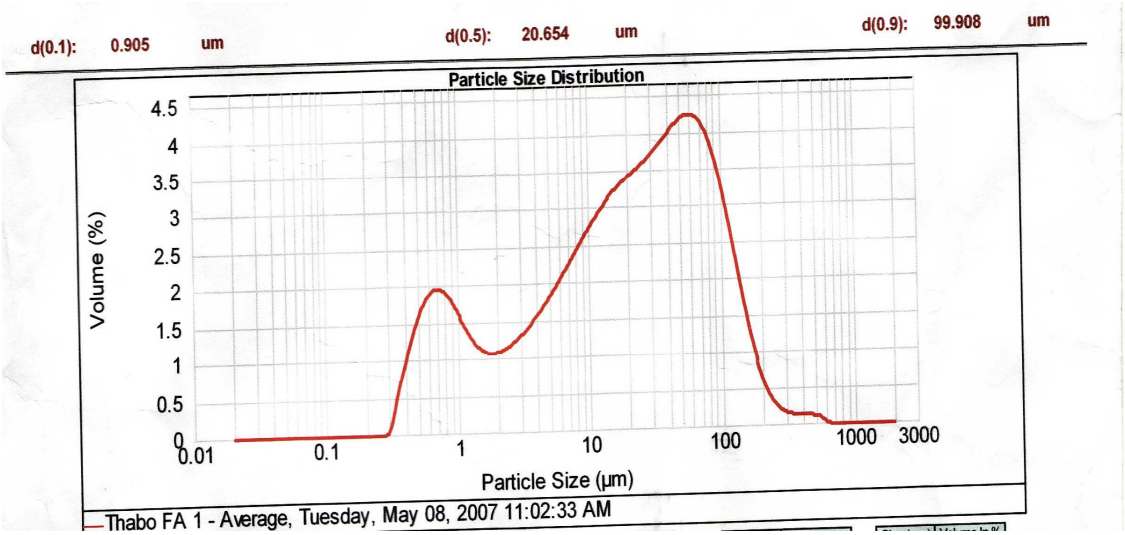


Figure 3.4. Particle size distribution profile for an unclassified Lethabo Coal Fly Ash.

The grain size distribution of Lethabo CFA (fig 3.4.) can be grouped as a Normal – Gaussian particle size distribution with nodes in the region of 50- 90 µm and 0.7 - 1 µm. The particle size of the CFA used for the experiment was found to be on average less than 99 µm. The observed particle size distribution is typical of an unclassified fly ash and indicates that the material consists of a coarser as well as finer fraction. From the point of view of utilization, it has been reported that CFA with particle sizes of less than 45 µm is useful as filler and cement extender (Kruger, 1997).

Bhargava and Sheldarkar (1993b) observed that for effective adsorption small particle sizes and large surface areas are required for high adsorbate removal at equilibrium. Kao *et al.* (2000) confirmed that the larger the specific surface area and the finer the particle size distribution of adsorbent, the greater its adsorption capacity and interaction with an adsorbate.

3.4.6. Specific Surface Analysis (S.S.A)

The N_2 adsorption gave the specific surface area (S_{BET}) and pore volume for the CFA used in this analysis as 1.279 m^2/g and 0.001437 cm^3/g, respectively. This result can be compared with those reported by Viraraghavan and Alfaro (1998) where the S.S.A of the FA used in adsorbing phenol from wastewater was within the range of 1.5 – 1.7 m^2/g and possessed an adsorption capacity for phenol in the range of 0.015 to 0.100 mg of phenol per gram of adsorbent. However, the S.S.A. for this CFA is in contrast with the result reported by Kao *et al*. (2000), who found that specified FAs typically have S.S.A ranging from 5 to 42 m^2/g, and with difference particle size ranging from 53 to 212 µm

3.4.7. Batch Studies

These experiments were performed to determine the equilibrium time required for the adsorbent (fly ash) to reach adsorption equilibrium. The adsorbates used are mixture of phenol, 2-Nitrophenol and 4-Nitrophenol which are common phenolic compounds found in the wastewaters released into the aquatic environment by industries such as petrochemical, coal tar and steel industries. These compounds are potentially toxic to humans and aquatic life. Kinetic tests using a mixture of these three adsorbates were performed on SACFA. The batch technique was used because of its simplicity to obtain equilibrium data. The initial solute mixes were taken and analyzed to determine the initial concentrations of the solutes before mixing with the CFA. For each adsorption data point, a 30 ml aliquot of the adsorbate solution having an initial phenol, 2-Nitrophenol and 4-Nitrophenol concentration of 20 mg/l each with varying quantities of 30 ml/20 g were introduced into a series of 250 ml Pyrex conical flasks at temperature of 298 K and pH of about 2.22, adjusted with HCl solution respectively. The conical flasks were placed and shaken in a Labcon platform shaking incubator (Model FSIM-

SPO16) to attain equilibrium after about 22 h of contact time and at a constant stirring speed of 300 rpm. The samples were covered throughout the experiment and the supernatant solution filtered after different time intervals of agitation through Whatman microfiber filters. The concentration of the filtrate left were then determined using UV-VIS spectrophotometry (SQ-4802 Double Beam).

Data obtained from the adsorption isotherm tests was used in determining the adsorption capacity of the fly ash. A laboratory batch adsorption test at equilibrium will not give accurate data for design of a fly ash adsorption system. Column tests are required to accomplish this and this is one advantage that column tests have over a batch approach. The equilibrium adsorption uptake and percentage removal of phenol from the aqueous solution q_e (mg/g) was determined or calculated using the following relationship:

$$\text{Amount adsorbed } q_e = \frac{(C_0 - C_e)V}{W} \qquad (3.1)$$

(mg of adsorbate / g of adsorbent).

$$\%\ \text{removal } q_e = \frac{100(C_0 - C_e)}{C_0} \qquad (3.2)$$

Where C_0 is the initial sorbate concentration (mg/l), C_e the equilibrium sorbate concentration (mg/l), V is the volume of solution (l) and w is the mass of the adsorbent (g).

3.4.8. Desorption Studies

The first part of this work involves the adsorbability of the phenolic compounds onto CFA. All the CFA samples (5-40) g loaded with the adsorbates were dried in a desiccator for 3 days. The

second phase in the research dealt with the determination of the desorbabilities or reversibility of phenolic compounds adsorbed onto the CFA. The desorption studies were conducted in 250 ml Pyrex conical flasks containing water at a temperature of 307 K, shaken at 300 rpm to attain equilibrium at 22 h.

Desorption efficiency of the various adsorbates were determined using the batch technique, where a known mass of CFA initially contacted with phenol, 2-Nitrophenol and 4-Nitrophenol as in adsorption experiments were mixed with 30 ml of distilled water and agitated until equilibrium was reached as in the original adsorption test. After desorption the concentration in the liquid phase was analyzed. A series of desorption tests involving the eight different CFAs loaded with the adsorbates during the adsorption test now produced the experimental data in Table A.12. After each consecutive desorption step, the new adsorbates amount on each of the CFAs was determined from (q_i), which is calculated by,

$$q_i = \frac{X_a - \Sigma(X_d)_i}{W} \qquad (3.3)$$

Where X_a is the initial adsorbate loading on the CFA (mg), X_d is the mass of adsorbate desorbed after each *ith* desorption step (mg) and W is the weight of CFA used in each desorption test (g).

$$\text{DE (\%)} = \frac{C_d V_d}{W_a q_e} X\ 100 \qquad (3.4)$$

Where C_d is the desorbed adsorbate concentration of desorption solution (mg/l), V_d the volume of the desorption solution (l), W_a the mass of pre-adsorbed adsorbent (g) and q_e is the

amount of adsorbate pre-adsorbed on adsorbent (mg/g).

3.4.9. Dynamic Column Test

In dynamic column adsorption, the wastewater continuously enters and leaves the column, so that the fly ash in the column meets fresh solution each time. Hence, adsorption takes place due to the changes in the concentration of the organic wastes as the mass transfer zone moves through the bed. This condition does not exist in a batch isotherm test procedure. The dynamic column test provides the necessary information for the scale-up data useful for industrial system designs and minimizes adsorbent usage by maximizing its utilization.

The feasibility of using fly ash as an adsorbent depends on the good flow of influent through it when running simple isotherms. A Perspex glass column used in this phase of the work was of length 550 mm and internal diameter of 20 mm. The column was operated under down flow conditions, which allow the influent to be gravity fed and also ensures that the bed remains packed and steady during the entire operation, thereby resulting in maximum contact between the fly ash and the feed organic compounds. The setup for this continuous flow studies is shown in figure 3.5. The pump used for the test was a Vera Manostat pump with a variable flow rate from 1 to 345 ml/min. Precision digital speed control was used to accurately maintain the flow rate through silicon tubing. The influent flow rate from the pump through the column was calibrated using a graduated cylinder and stop clock. The organic solution was pumped from a cylindrical glass serving as the influent reservoir.

The column was packed with 20 mm borosilicate glass beads between two supporting layers at different bed depths. CFA masses of 10, 15 and 20 g were added to yield different bed heights

of 30, 40, and 50 mm respectively, while the process was performed at a flow rate of 3 ml/min and 20 mg/l initial solute concentration. Wire mesh filter was used as the supporting layers to keep the glass beads in position and to support the fly ash. Effluent concentrations were monitored as a function of time for each column and the breakpoint for breakthrough curves generated for each bed depth were selected at 30% and 70% of the influent concentration remaining to determine the BDST equation which can be used to evaluate any desired effluent quality.

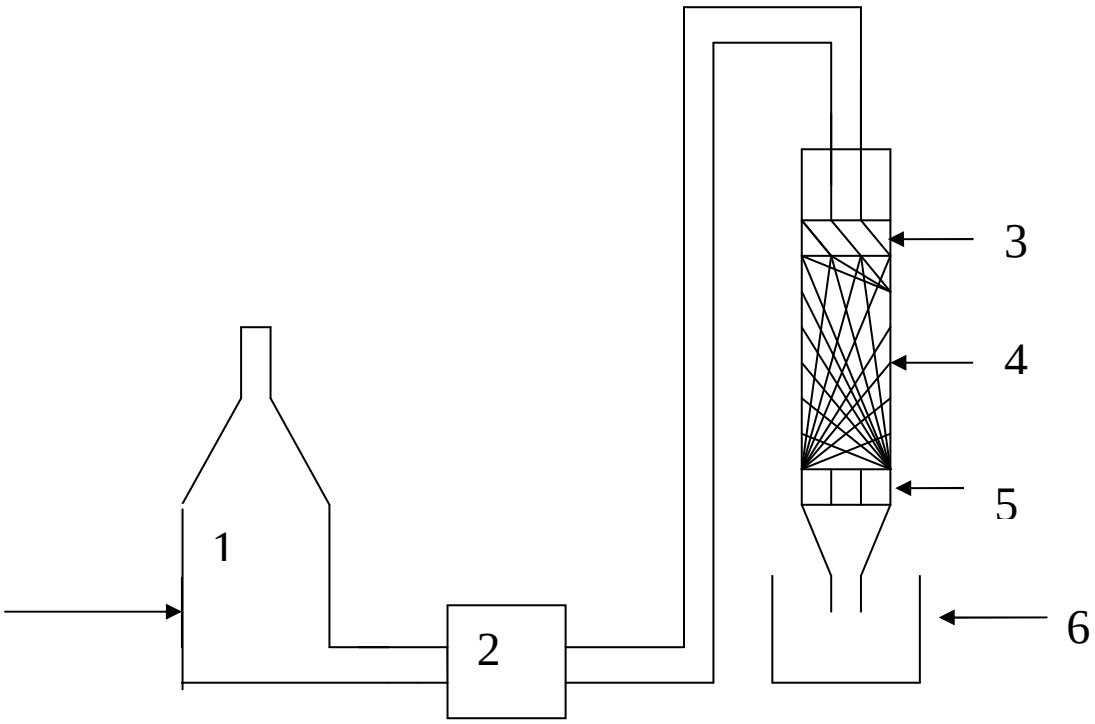


Figure 3.5. Experimental diagram of down-flow packed column. (1) 20 mg/l adsorbate solution, (2) peristaltic pump, (3) glass beads, (4) FA, (5) glass beads, (6) effluent waste water.

CHAPTER IV

4.0 Results and Discussion

Kinetic experiments were conducted to investigate the rate constants of adsorption for phenol, 2-Nitrophenol and 4-Nitrophenol onto SACFA. The amounts of adsorbates removed by SACFA were also evaluated for in these studies, while the theoretical adsorption capacity of the CFA at all final concentrations of phenol, 2-Nitrophenol and 4-Nitrophenol in aqueous solution were calculated using Freundlich constants (K_f and $1/n$) and Langmuir constants (b and Q_m). The Langmuir model was used to fit the set of adsorption experimental data in tables A.13, A.14 and A.15. The equilibrium constants for the Freundlich model were determined from set of experimental data in tables A.10, A.11 and A.12. The reversibility of adsorption was also investigated to estimate the extend of desorption of phenolic compounds of CFA.

4.1. Effect of Contact Time

Figure 4.1 presents the results for the effect of contact time on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol from aqueous solution at an initial concentration of 20 mg/l. It can be seen that the amount of all the adsorbates adsorbed onto CFA increases with time and about 75.6%, 74.2% and 89.2% of phenol, 2-Nitrophenol and 4-Nitrophenol had been removed within the first fifteen minutes of agitation respectively. This is as a result of the large number of vacant surface sites existing on the surface of the CFA that are available for adsorption during the initial agitation stage. It is obvious from Figure 4.1 that the profile for the adsorbates is a single, smooth, and continuous curve. The profile shows that after a lapse of time there exist a repulsive force between the adsorbates in the bulk phase and the adsorbent due to the

non availability of more vacant sites for adsorption onto the CFA. The adsorption capacity (Q_t) generally increases with the increase in contact time and the adsorption equilibrium reached values as high as 2.39 X 10^{-2} mg/g, 2.33 X 10^{-2} mg/g, and 2.74 X 10^{-2} mg/g for phenol, 2-Nitrophenol and 4-Nitrophenol respectively after 360 min of agitation. Further increases in adsorption capacity after the first 360 min of contact time, will be dependent on the creation of some fresh internal surfaces (Giles *et al.*, 1974). Allen (1987) stated that further interaction of the adsorbate and the adsorbent cannot continue indefinitely without irreparable damage to the adsorbent. 4-Nitrophenol was found to adsorb more than phenol due to its lower solubility in aqueous solution and because the more non-polar an organic compound, the lesser its affinity for solvent and the higher its adsorption affinity by the adsorbent (Cooney, 1999). The adsorption capacity for phenol was found to be slightly higher than that of 2-Nitrophenol and this show that solubility is not all important in this system because if solubility was to be the controlling factor then 2-Nitrophenol would have had a higher adsorption affinity for CFA than phenol because of its lower solubility in water than phenol. The t-test result showed that phenol adsorption is significantly higher $\left(t_{0.05} Stat\ df\left(8\right) 19.532 > t_{0.05} Table\ df\left(8\right) 2.306\right)$ than that of 2-Nitrophenol (as shown in Table A.20). In addition, the difference in adsorption behaviour of phenol, 2-Nitrophenol and 4-Nitrophenol might be due to the different affinities of the three phenolic species for the reactive functional groups in the CFA. A similar result was reported by Denizli *et al.* (2002) where adsorption capacity for phenol and 4-nitrophenol on microbeads were found to be greater than that of 2-Nitrophenol.

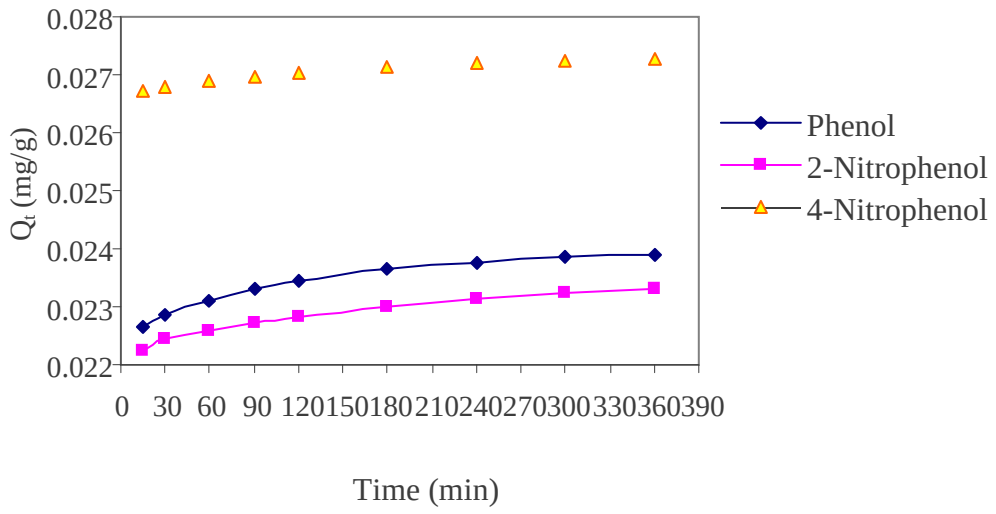


Figure 4.1. Effect of contact time on the amount of Phenol, 2-Nitrophenol and 4-Nitrophenol removed from aqueous solution with CFA. Operating conditions: C_o; 20 mg/l, RPM; 300, CFA; 20g and Volume; 30 ml.

4.2. Dynamic Adsorption

This study provides information on the mechanism of adsorption which is highly important for the efficiency of the adsorption process. The data from the kinetic adsorption of phenol, 2-Nitrophenol and 4-Nitrophenol onto CFA was modelled by the pseudo first-order Lagergren equation. The result shows that the rate constant followed the first order rate expression given by Lagergren and Svenka (1898). Figures 4.2, 4.3 and 4.4 show a linear plot of $\log(q_{e-}q_t)$ versus t for the phenol, 2-Nitrophenol and 4-Nitrophenol adsorption studied at a concentration of 20 mg/l. The value for K_{ad} was calculated from the slope of linear plots for the CFA using the Lagergren equation:

$$\log(q_e - q) = \log q_e - \frac{k_{ad}}{2.303} t, \qquad (4.1)$$

The values of K_{ad} (h^{-1}) were calculated at 307 K and different times considering the slopes of the individual linear plot of log ($q_e - q$) versus t. The value of K_{ad} was found to be $1.2X10^{-3}$ h^{-1} for phenol, $1.0X10^{-3}$ h^{-1} for 2-Nitrophenol and $7.0X10^{-3}$ h^{-1} for 4-Nitrophenol. Comparing the K_{ad} values 0.221 h^{-1} and 0.3592 h^{-1} for phenol and 4-Nitrophenol respectively as reported by Ahmaruzzaman and Sharma (2005), it can be observed that the values obtained in this study were lower and this signifies that the SACFA has a lower affinity for these adsorbates which is consistent with the lower adsorption (K_f values) observed for these adsorbates as compared to that reported by the authors mentioned above.

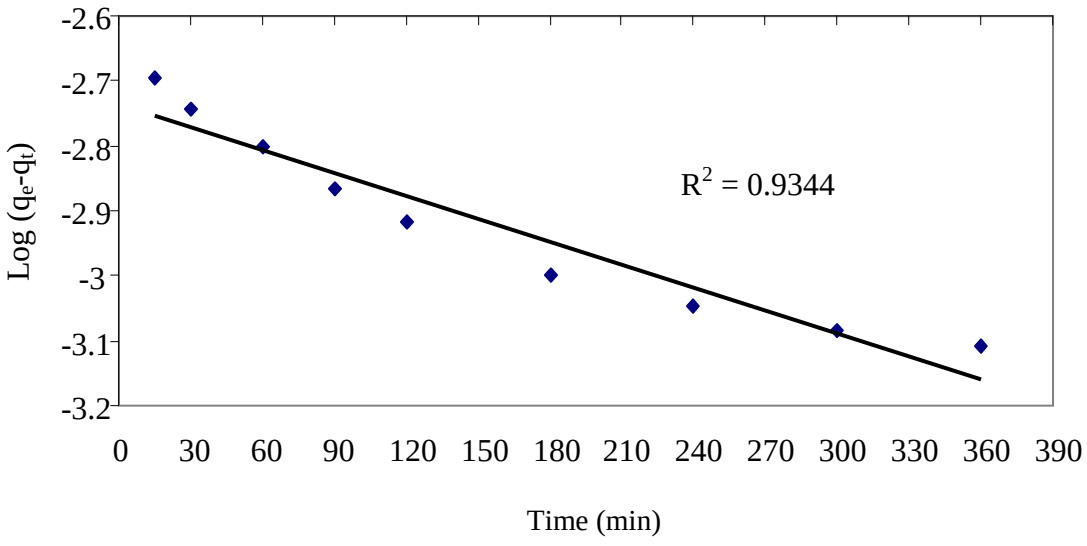


Figure 4.2. Linear plot of $\log(q_e - q_t)$ versus t for the kinetic removal of phenol studied at concentration of 20mg/l.

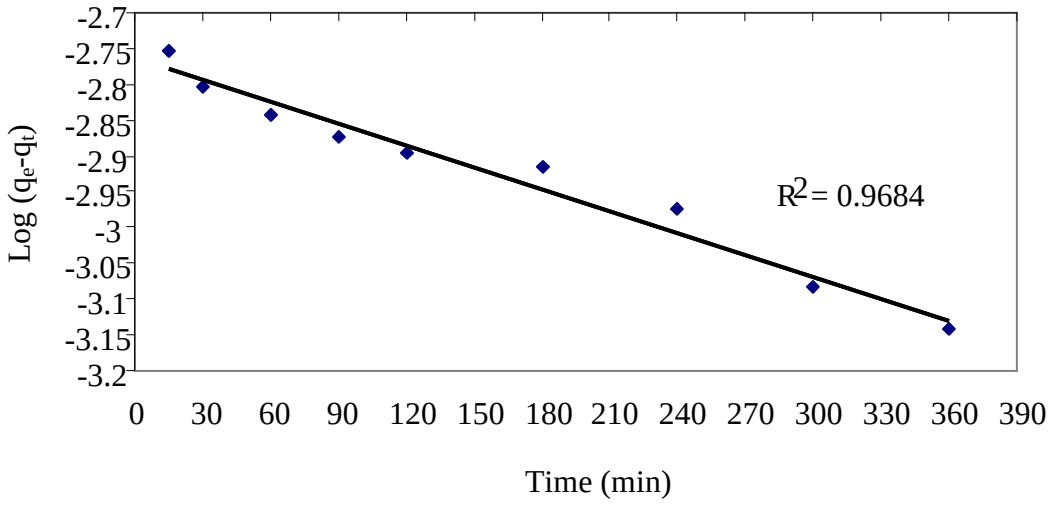


Figure 4.3. Linear plot of $\log(q_e - q_t)$ versus t for the kinetic removal of 2-Nitrophenol studied at concentration of 20mg/l.

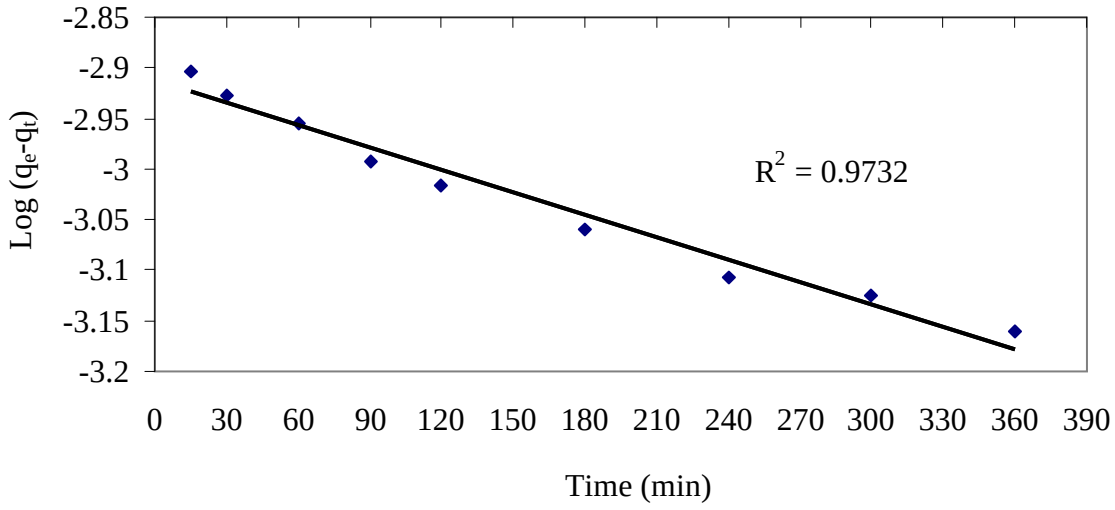


Figure 4.4. Linear plot of $\log(q_e - q_t)$ versus t for the kinetic removal of 4-Nitrophenol studied at concentration of 20mg/l.

4.3. Influence of pH

The pH of the solution was found to influence the adsorption of the adsorbates on CFA. The degree of adsorption of these adsorbates onto the CFA surface is primarily influenced by the surface charge on the CFA, which in turn is influenced by the solution pH. Figure 4.5 and 4.6 shows the % removal of the adsorbates on CFA at two different pH values. It can be seen that the % amount of the adsorbates removed increases as the pH decreases. At a pH of 2.22, the adsorption changes and the % adsorbates removed are more than that at a pH of 5.98. At lower pH values, however, dissociation into $C_6H_5O^-$ will be repressed, resulting in less repulsion between the negative surface charge of the CFA and the anion. Therefore, more phenol would be adsorbed at the pH of 2.22 than 5.98. The sorption of 2-nitrophenol and 4-Nitrophenol with pK_a values of (7.23) and (7.15), respectively followed the same trend. Similar results were reported by Kao *et al.* (2000) for the removal of chlorophenols from aqueous solution by fly ash and the adsorptive removal of phenol by bagasse, fly ash and activated carbon. Srivastava *et al.* (2006) found that an increase of adsorption occurred at lower pH values. This result suggested that the % uptake of phenol and substituted phenols on CFA follows the order: 4-Nitrophenol > Phenol > 2-Nitrophenol for this particular system. This order is in contrary to the result reported by Calace *et al.* (2002) where phenol was found to adsorb more than 4-Nitrophenol and 2-Nitrophenol; and did not seem to relate to chemical characteristic alone because if adsorption was related to pH for the system then, 4-Nitrophenol would have adsorbed more than phenol considering their pK_a values.

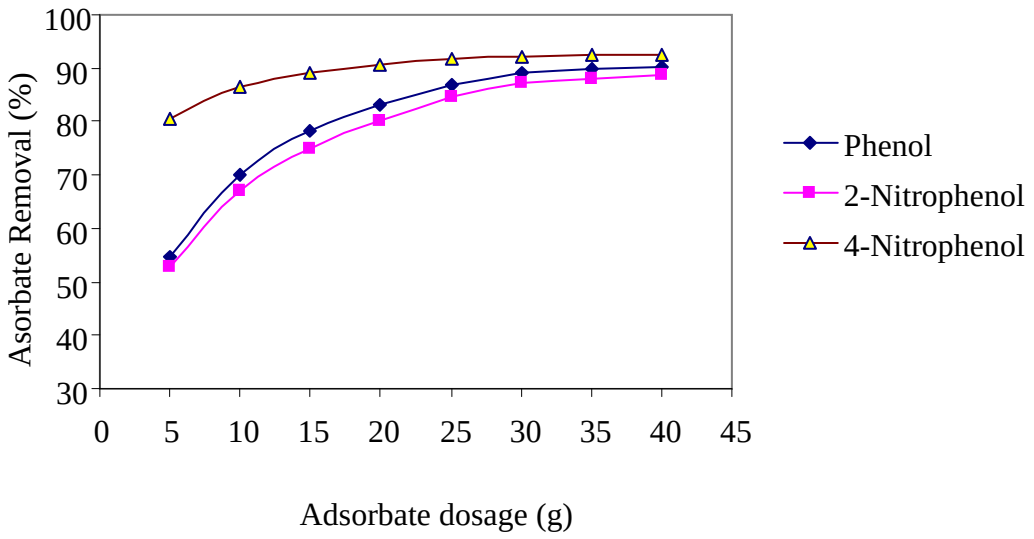


Figure 4.5. Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4-Nitro-phenol at pH 2.22, t; 22 h, C_o; 20 mg/l and different loading weight of CFA (5-40) g.

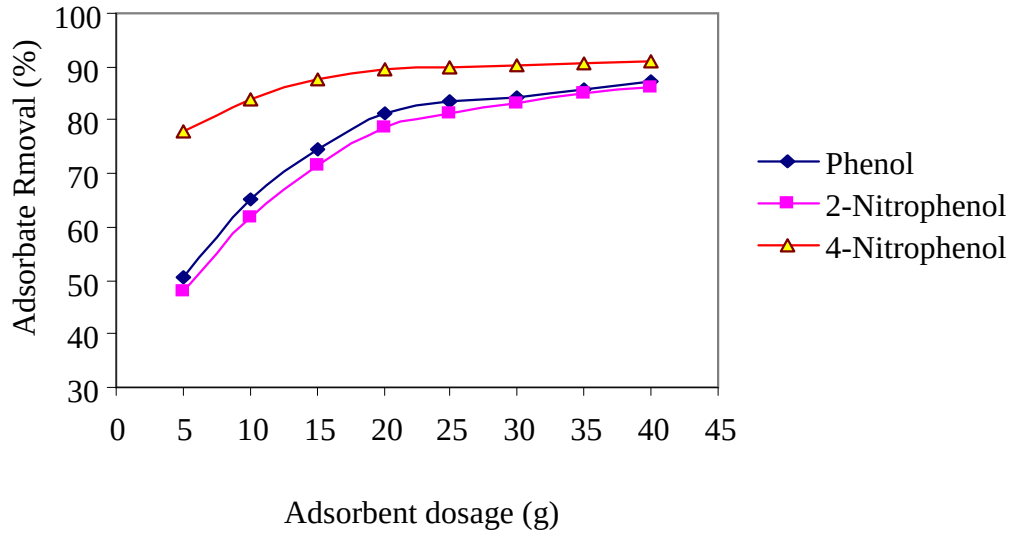


Figure 4.6. Effect of pH on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at pH 5.98, t; 22 h, C_o; 20 mg/l and different loading weight of CFA (5-40) g.

4.4. Effect of CFA Loading

The equilibrium adsorption experiments were conducted by contacting FA at 307 ^{0}K, an initial adsorbate concentration of 20 mg/l, CFA loading range 5-40 g with the solution for 22 h. Figures 4.7, 4.8, & 4.9 show the effect of CFA loading on the % removal of phenol, 2-Nitrophenol and 4-Nitrophenol. It can be seen from these figures that as the CFA loading increases from 5 g to 40 g, the percentage removal of adsorbates increases. For phenol, the % adsorbed increases from 54.7% to 90.2%, for 2-Nitrophenol it increases from 52.6% to 88.9% and for 4-Nitrophenol it increases from 80.4% to 92.6% under the same operating conditions. This result is in contrast with the % amount of phenol adsorbed onto AC with S.S.A of 598 m^2/g. Rengaraj *et al.* (2002a) reported an adsorption of 96% of phenol from initial concentration of 30 mg/l, agitation time of 24 h with a minimum AC dosage of 2.5 g, as compared to the 40 g of CFA used for this experiment. However, it could be compared with the findings by Gupta *et al.* (1998) which reported that as the adsorbent dosage is being double the uptake of phenol increases by 3 % while in the case of 4-Nitrophenol, the adsorption goes up by 3.5 %.

The higher affinity of CFA for 4-Nitrophenol was expected due to its lower solubility in water than phenol, and its higher adsorption onto CFA than 2-Nitrophenol may be attributed to its lower dissociation constant. The major contributing factor that may be responsible for the higher adsorption of 4-Nitrophenol than 2-Nitrophenol for this system may be attributed to the lower dissociation constant value of 4-Nitrophenol (pK_a 7.15) than 2-Nitrophenol (pK_a 7.23). The ionization of 4-Nitrophenol, being more acidic than 2-Nitrophenol, is much affected at lower pH of aqueous solution compared to 2-Nitrophenol. Therefore, phenolic compounds with smaller pK_a values have a higher attractive force or affinity for the positive charged

surface of the FA which resulted into higher adsorption of 4-Nitrophenol than both phenol and 2-Nitrophenol. Similar result was reported by Sarkar and Acharya (2006) when 125 mg/l phenol concentration, 1 g per 0.050 litre of FA dosage with pK_a 9.9 adsorbed better onto FA than o-hydroxyphenol with pK_a 10.2. The other major factor that may be responsible for the higher adsorption of 4-Nitrophenol onto CFA than 2-Nitrophenol had been discussed in section 4.1.

The increase in adsorption with increasing adsorbent dosage can be attributed to the increase in the surface area and the availability of more adsorption sites provided by the CFA. In addition, as the quantities of CFA dosage increases the removal of all the adsorbates till their uptake becomes very low due to the saturation of the adsorbent and their removal tends to be constant. This was also found by Batabyal *et al.* (1995).

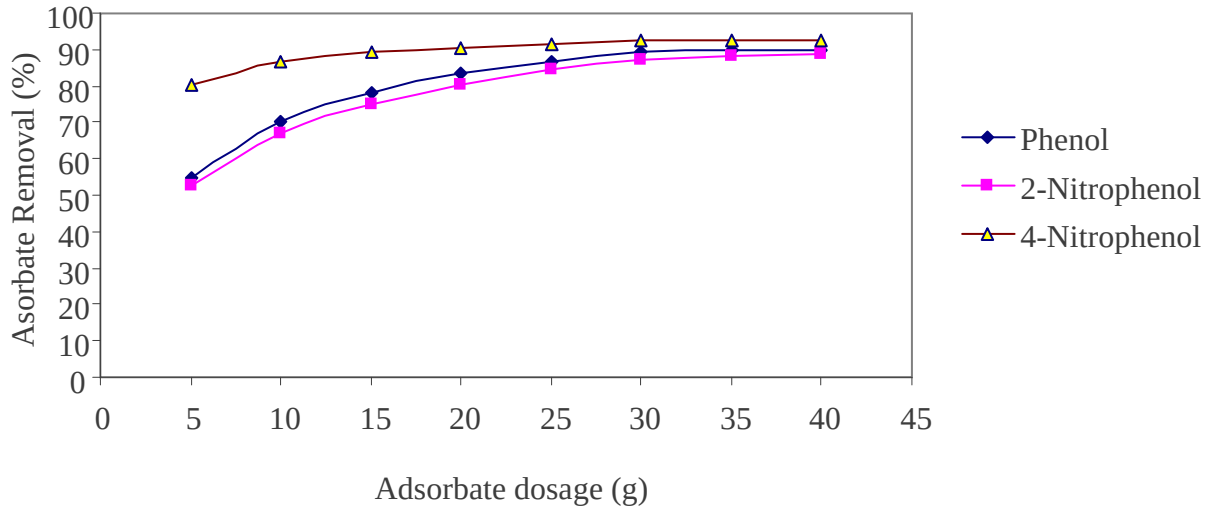


Figure 4.7. Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4 Nitrophenol at pH 2.22, C_o; 20 mg/l, t; 22 h and different loading weight of CFA (5-40) g.

4.5. Adsorption Isotherm

The equilibrium adsorption isotherm is of importance in the design of adsorption systems. The set of experimental results as presented in tables A.10 to A.15, were fitted with the Freundlich and Langmuir model. Adsorption isotherms were obtained and the adsorptive capacity interpreted using both models:

$$\text{Log}\, Q = \log K + {}^{1}\!/\!_{n} \log C_e \qquad (4.2)$$

The parameter K_f and $1/n$ were obtained by linearly regressing each set of experimental data using the equation above.

$$\frac{1}{Q} = \frac{1}{Q_m} + \left(\frac{1}{bQ_m}\right)\left(\frac{1}{C_e}\right) \qquad (4.3)$$

According to Equation (4.3), a plot of ${}^{1}\!/\!_{Q}$ versus ${}^{1}\!/\!_{C_e}$, should yield a straight line. The slope is ${}^{1}\!/\!_{Q_m}$ and the intercept of ${}^{1}\!/\!_{bQ_m}$. These two values will enable one to calculate the two constants for Langmuir model b and Q_m, where the constants are related to the energy of adsorption and capacity, respectively.

4.5.1. Phenol Adsorption

The Freundlich (K_f and $1/n$) and Langmuir constants (b and Q_m) determined from the adsorption isotherms for phenol (figs.4.10 & 4.11) in wastewater containing 2-Nitrophenol and

4-Nitrophenol on CFA are shown in Tables A.10 & A.13. The correlation coefficient values determined for each of the adsorption isotherms indicates that the Freundlich model effectively fits the experimental data better than the Langmuir model and the value for 1/n was found to be less than 1 for the CFA, which suggested favourable uptake of the phenol on CFA (A.17). The Freundlich and Langmuir constants for CFA from the removal of phenol from 2-Nitrophenol and 4-Nitrophenol were calculated by regressing the isotherm data with the initial concentration of 20 mg/l.

The adsorption capacity for phenol at the maximum residual concentration was calculated using the Freundlich constants (K_f and $1/n$) at an initial concentration of 20 mg/l of phenol and the value obtained was 6.3 X 10^{-2} mg/g. The adsorption capacity for phenol when applying Langmuir constant under the same conditions was found to be 5.91 X 10^{-2} mg/g. The K value determined for FA on the adsorption of phenol from the solution was found to be higher than that of 2-Nitrophenol and lower when compared to 4-Nitrophenol within the same concentration ranged studied.

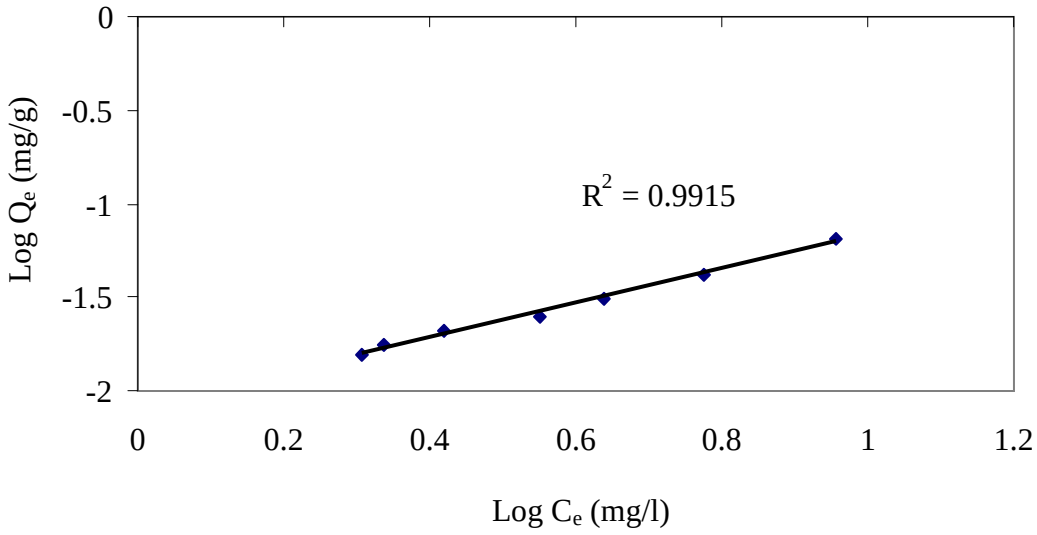


Figure 4.8. The linearized Freundlich Adsorption Isotherm for Phenol in 2-Nitrophenol and 4-Nitrophenol mixtures with CFA.

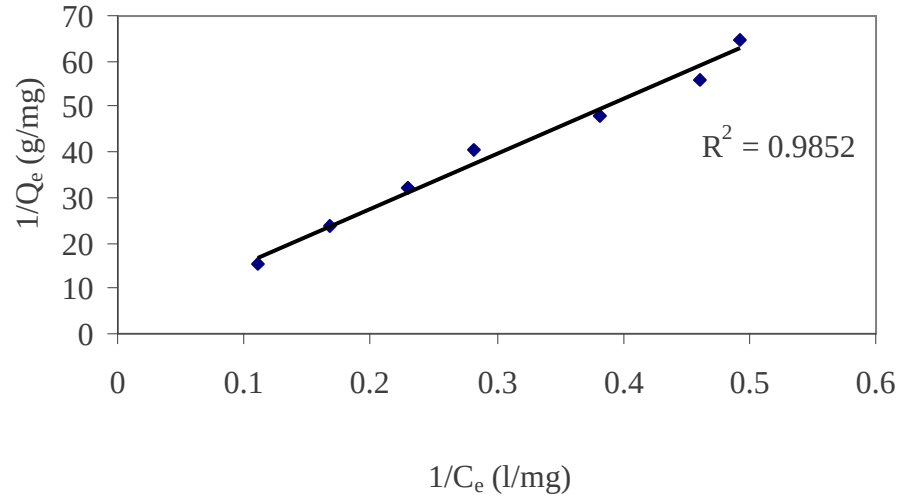


Figure 4.9. The linearized Langmuir Adsorption Isotherm for Phenol in 2-Nitrophenol and 4-Nitrophenol mixtures with CFA

4.5.2. 2-Nitrophenol Adsorption

The Freundlich and Langmuir constants determined from the adsorption isotherms for 2-Nitrophenol in wastewater containing phenol and 4-Nitrophenol on CFA are shown in Table A.17. The value of the correlation coefficient (0.98) for the regression indicates that Freundlich Model adequately fits the experimental data. Freundlich constants for CFA for the removal of 2-Nitrophenol were determined by regressing isotherm data with 20 mg/l initial concentration. The Freundlich adsorption isotherm data and plot are shown in Table A.11 and Figure 4.12, respectively. Table A.14 and Figure 4.13 show the Langmuir adsorption isotherm data and plot, respectively.

The adsorption capacity for 2-Nitrophenol at the maximum residual concentration was calculated using the Freundlich constants (K_f and $1/n$) at initial concentration of 20 mg/l for the adsorbates and the value obtained was 6.00 X 10^{-2} mg/g. The adsorption capacity for 2-Nitrophenol when applying Langmuir constant under the same condition was found to be 5.63 X 10^{-2} mg/g. 2-Nitrophenol has a lower adsorption affinity for CFA than phenol within the concentration range studied. The higher adsorption capacity for phenol than 2-Nitrophenol for this system might be as a result of the molecular mass and the simple structure of phenol compared to 2-Nitrophenol. This result is in agreement with the removal of phenols and 2-Nitrophenols from aquatic systems reported by Denizli *et al.* (2001). The decrease in the molecular mass of the organic solutes which also decreases their molecular dimension favours the uptake of a smaller molecular adsorbate within the same or dissimilar class of compound (Cooney, 1999). This shows that molecular mass and simple structure of the phenol is important for its uptake in an aqueous system. The possible explanation for the higher adsorption of 4-Nitrophenol than 2-Nitrophenol had been discussed in sections 4.1 and 4.4.

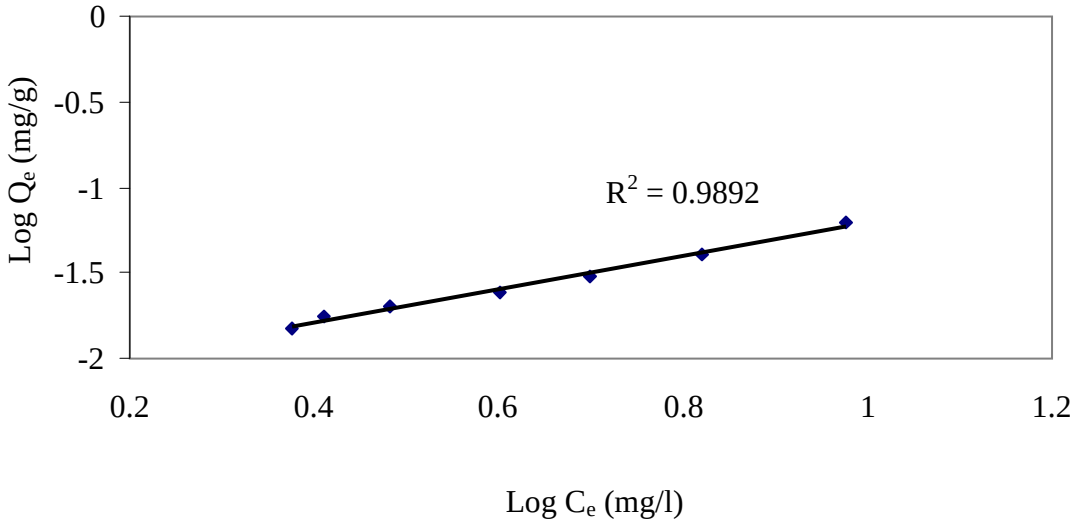


Figure 4.10. The linearized Freundlich Adsorption Isotherm for 2-Nitrophenol with CFA.

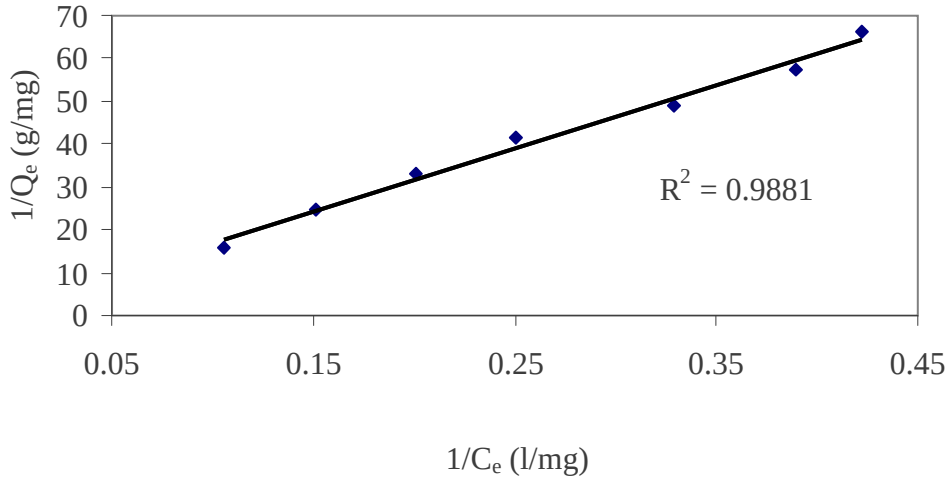


Figure 4.11. The linearized Langmuir Adsorption Isotherm for 2-Nitrophenol with CFA.

4.5.3. 4-Nitrophenol Adsorption

The value of the correlation coefficient (greater than 0.97) for the regression indicates that Freundlich model adequately fits the experimental data. Freundlich constants (K_f and$1/n$) for CFA for the removal of 4-Nitrophenol were determined by regressing isotherm data with 20 mg/l initial concentration. The Freundlich adsorption isotherm data and plot are shown in Table A.12 and Figure 4.14, respectively. Table A.15 and Figure 4.15 show the Langmuir adsorption isotherm data and plot, respectively.

The adsorption capacity for 4-Nitrophenol at the maximum residual concentration was calculated using the Freundlich constants (K_f and $1/n$) at an initial concentration of 20 mg/l for the adsorbates and the value obtained was 6.51 X 10^{-2} mg/g. The adsorption capacity for 4-Nitrophenol when applying Langmuir constant under the same condition was found to be 1.79 X 10^{-2} mg/g. 4-Nitrophenol has the highest adsorption affinity for CFA followed by phenol and 2-Nitrophenol within the concentration range studied.

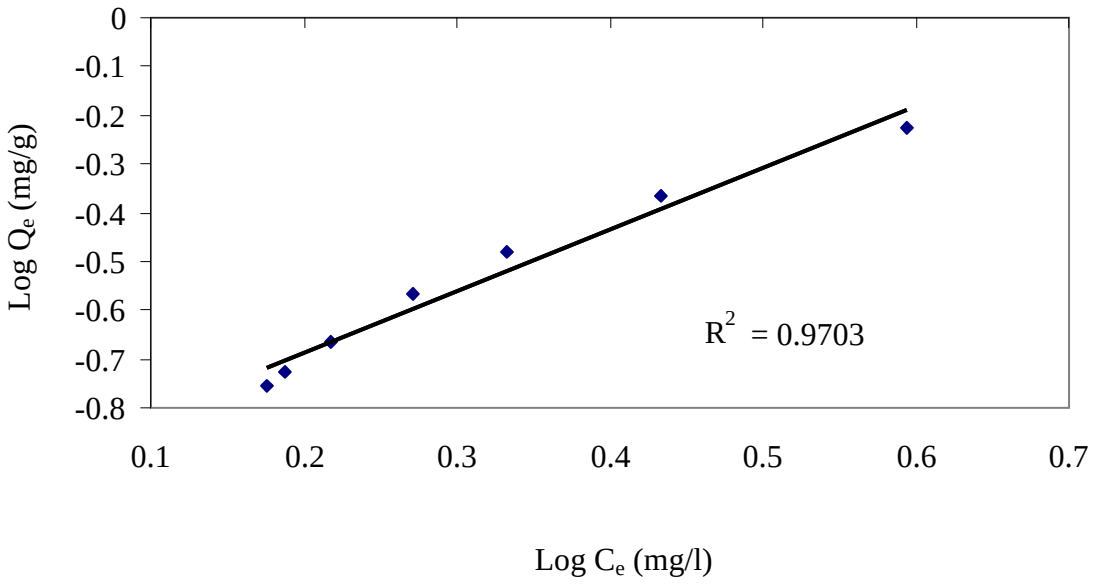


Figure 4.12. The linearized Freundlich Adsorption Isotherm for 4-Nitrophenol with CFA.

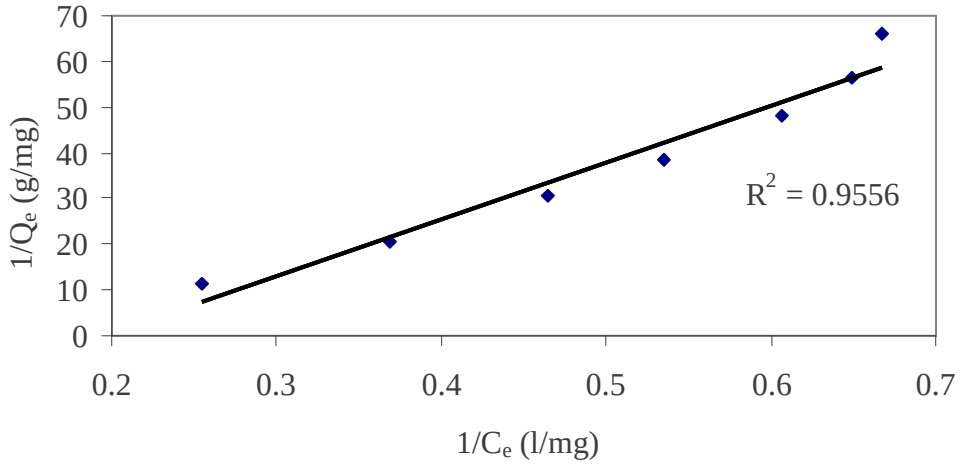


Figure 4.13. The linearized Langmuir Adsorption Isotherm for 4-Nirophenol with CFA.

The higher adsorption affinity of CFA for 4-Nitrophenol was expected due to its lower solubility in water than phenol. 4-Nitrophenol is moderately soluble in cold water and denser than water (1.52 g/100 ml), while the solubility of 2-Nitrophenol in water is (0.26 g/100 ml)

and phenol with (8.3 g/100 ml) under the same condition (25 ^{0}C). Both 2-Nitrophenol and 4-Nitrophenol have the same molecular weight, and therefore it seems that solubility is not the overriding important factor for this test when considering the higher amount of 4-Nitrophenol adsorbed onto CFA compared to 2-Nitrophenol. The result is in agreement with the findings of Denizli *et al.* (2001) where more 4-Nitrophenol was found to adsorb onto microbeads than 2-Nitrophenol. The other major adsorption mechanism that may be responsible for the higher uptake of 4-Nitrophenol than both 2-Nitrophenol and phenol are already been discussed in section 4.1 and 4.4

The adsorption capacity of the adsorbent used in this investigation was found to be lower than that of many other FAs and GAC. The main reason could be the high surface area of GAC which is usually in the range of 500-1500 m^2/g (Yin *et al.*, 2007). In addition, the surface area of the FA and AC reported by Srivastava *et al.* (2006) for the uptake of phenol were 168.39 m^2/g and 336.60 m^2/g respectively. Samla coal and residue coal with specific surface areas of 135.30 m^2/g and 165.07 m^2/g were used respectively for the adsorption of phenolic compounds from wastewater.

Nitrogen adsorption gave the specific surface area (S_{BET}) for the CFA used in this analysis as 1.279 m^2/g, which is similar to the result reported by Viraraghavan and Alfaro (1998) where the S.S.A of the FA used in adsorbing phenol from wastewater was within the range of 1.5 – 1.7 m^2/g. In view of the fact that surface areas of GAC and CFA used for this test are considerably different, the amount (mg) of adsorbates adsorbed by SACFA are expected to be lower when compared to activated carbon and other FAs with higher specific surface areas. The adsorption results from this study were compared to those previously found by other

authors (Table 4.2) and the value of K_f was found to be significantly higher for the phenol-SACFA system in comparison to phenol-rice husk and phenol-coke breeze described by Mahvi *et al.* 2004. Also, the constant K_f value obtained for this system was in contrast to the result reported by Viraraghavan and Alfaro (1998) for phenol-bentonite and phenol-peat systems. The adsorption capacity for phenol varies widely among the different adsorbents, thus again underlining the necessity and importance to characterise and investigate each adsorbent intended for pilot or plant use.

Table 4.1. Freundlich and Langmuir adsorption isotherm parameters.

	Freundlich constants			Langmuir constants		
Adsorbates	K(mg/g)	n(L/mg)	R^2	Q_m(mg/g)	b(L/mg)	R^2
Phenol	0.0082	1.083	0.9915	0.284	0.029	0.9852
2-Nitrophenol	0.0066	1.025	0.9892	0.461	0.015	0.9881
4-Nitrophenol	0.115	1.267	0.9703	0.110	0.0415	0.9556

Operating conditions: Temperature, T = 307 K; Speed of agitation = 300 RPM, pH = 2.220; C_0 = 20 mg/l.

Table 4.2: A Comparison of Freundlich and Langmuir Constants for phenol adsorption reported in the Literature.

Adsorbent	Adsorbate	Langmuir		Freundlich		Adsorption capacity (mg/g)	Ref
		Q_m (mg/g)	b(L/mg)	K(mg/g)	n(L/mg)		
Coke breeze	Phenol	0.172	0.00150	0.917	0.350	0.180	Ahmaruzzaman and Sharma, 2005
Petroleum coke	Phenol	6.010	0.00267	0.259	2.41	6.00	Ahmaruzzaman and Sharma, 2005
Rich Husk	Phenol	0.0022	30.7	0.00092	5.13		Mahvi *et al.*, 2004
Rice Husk Ash	Phenol	0.886	5.15	0.00092	1.75	0.886	Mahvi *et al.*, 2004
Phanerochaete biomass	2, 4-dichlorophenol			0.187	1.21		Wu Juan *et al.*, 2006
Peat	Phenol			0.201	0.21		Srivastava *et al.*, 2006
Peat	Phenol			4.6×10^{-10}			Viraraghavan and Alfaro, 1998
Bentonite	Phenol			0.0362	0.64		Srivastava *et al.*, 2006
Bentonite	Phenol			5.1×10^{-8}			Viraraghavan *et al.*, 1998
Coal Fly Ash.	2, 4-dimethyl phenol	2.730	0.00917	1.88	1.77	0.780	Batabyal *et al.*,1995
Fly Ash	Phenol	13.16	0.0129	0.8787	2.25		Sarkar *et al.* 2006
Fly Ash	Chlorophenol			3.76	208.33		Kao *et al.*, 2000
Bagasse FA.	Phenol			0.003	4.66		Mukherjee *et al.* 2007.
SACFA	Phenol 2-Nitrophenol 4-Nitrophenol	0.284 0.461 0.110	0.029 0.015 0.042	0.0082 0.0066 0.1150	1.083 1.025 1.267	0.063 0.060 0.065	Present work

4.6. Desorption studies

The adsorption-desorption efficiencies shown in Figures 4.16, 4.17, & 4.18 and Table A.18 reveal that the desorption of 4-Nitrophenol from CFA was more difficult than 2-Nitrophenol, and its adsorption was more irreversible than that of phenol and 2-Nitrophenol on the adsorbent. The irreversibility of adsorption in this case implies that the dominant adsorption mechanism is the high-energy bonding to specific functional groups on the surface of the CFA and resulted in a degree of chemisorption. This test shows that 4-Nitrophenol was adsorbed with a higher adsorption efficiency of 92.6 % compared to both phenol 90.2 % and 2-Nitrophenol 88.9 %. The desorption efficiency for 2-Nitrophenol was 18.8 % when using 30 ml of distilled water to desorbed phenol from CFA. Hence, from the initial concentration of 20 mg/l of the adsorbates, 20 g of CFA adsorbed 16.45 mg/l of phenol, 16.01 mg/l of 2-Nitrophenol and 18.13 mg/l of 4-Nitrophenol from the solution. The concentration for the three adsorbates released after replacing the supernatant solution with distilled water for the desorption test were 3.00 mg/l for phenol, 3.04 mg/l for 2-Nitrophenol and 1.92 mg/l for 4-Nitrophenol.

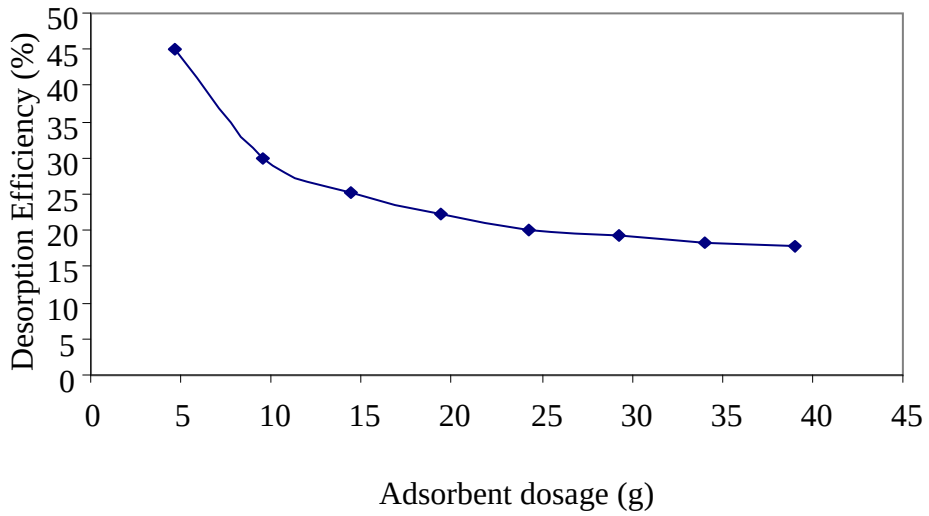


Figure 4.14. Influence of adsorbent dosage on the desorption of phenol from CFA.

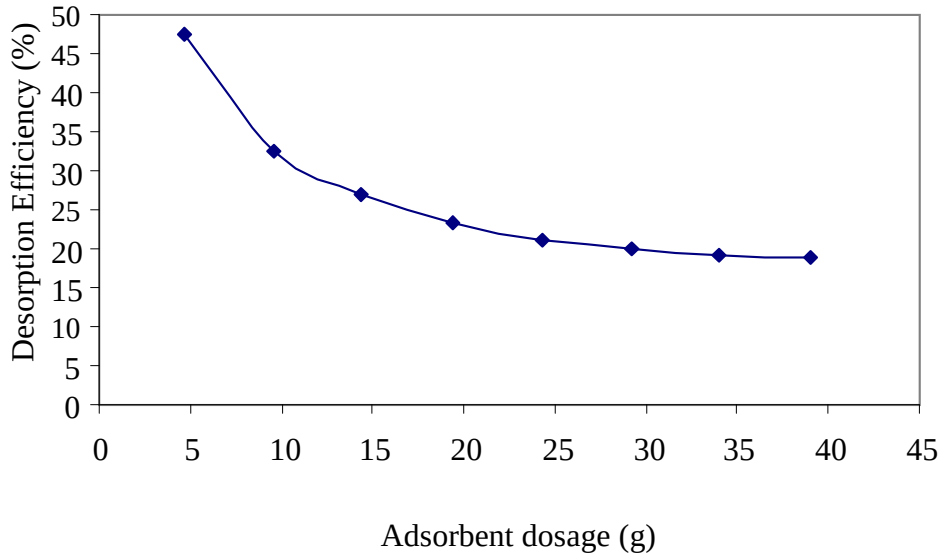


Fig 4.15. Influence of adsorbent dosage on the desorption of 2-Nitrophenol from CFA.

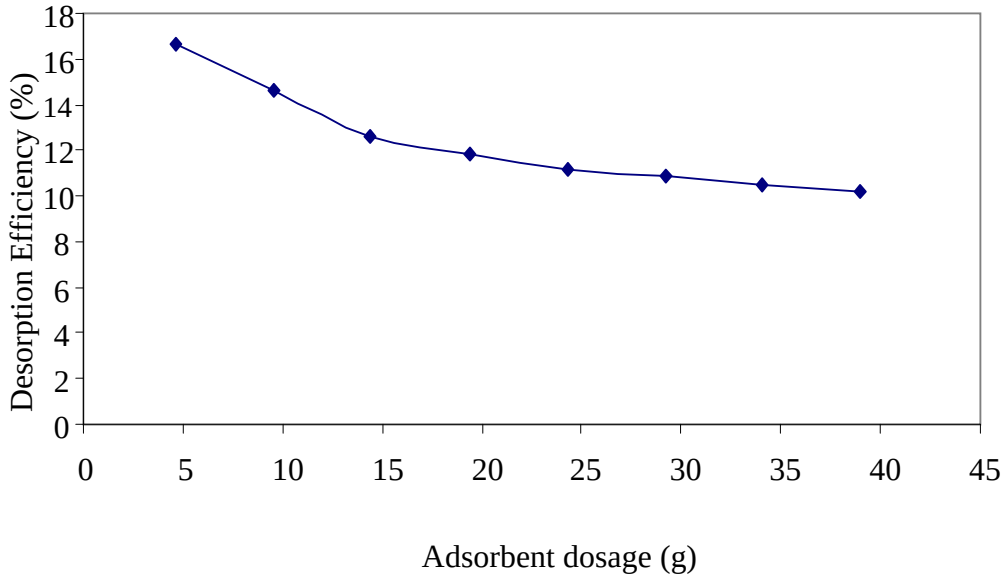


Fig 4.16. Influence of adsorbent dosage on the desorption of 4-Nitrophenol from CFA.

4.6.1. Effect of FA Loading

The results showed that higher adsorbent dosages resulted in lower degrees of irreversibility. In other words, the reversibility of the adsorbates bonded with the CFA was found to decrease during desorption as the adsorbent dosage increases. A similar result was reported by Ha and Vinitnantharat (2000) for the removal of phenol and 2-4-dichlorophenol in a biological activated carbon system. Higher desorption efficiency at lower adsorbent dosage observed in this test may be attributed to less available sites for bonding to specific functional groups on the surface of the CFA. Aktas and Cecen (2006) also reported that this effect might be as a result of the higher numbers of micropores and mesopores present in larger adsorbent dosage with greater adsorption energies than an adsorbent in a smaller dosage.

Table 4.3. Freundlich adsorption and desorption isotherm parameters

Adsorbates	Adsorption Freundlich constants			Desorption Freundlich constants		
	K (mg/g)	n(L/mg)	R^2	K (mg/g)	n (L/mg)	R^2
Phenol	0.0082	1.083	0.9915	0.177	1.111	0.9992
2-Nitrophenol	0.0066	1.025	0.9892	0.180	1.123	0.9995
4-Nitrophenol	0.115	1.267	0.9703	0.001	0.167	0.9714

Operating conditions: Temperature, T = 307 K; Speed of agitation = 300 RPM; Contact time = 22 h; H_20 solution = 0.03 l

Table 4.4. Adsorption and desorption efficiencies of phenol, 2-Nitrophenol and 4-Nitrophenol at maximum FA loading

Adsorbates (mg/l)	Desorption Efficiency (%)	Adsorption Efficiency (%)
Phenol	17.9	90.2
2-Nitrophenol	18.8	88.9
4-Nitrophenol	10.2	92.6

4.7. Dynamic Column Studies

Batch isotherms do not give precise scale-up data for the design of an adsorber. The practical applicability of CFA to adsorbed adsorbates was established in the dynamic column tests. The experimental breakthrough curves for the adsorption of phenol in a column packed with CFA at different bed heights are shown in Figure 4.19 and Table C.2 which provide the experimental column result for service time against % adsorbates remaining.

Influent concentrations of 20 mg/l were used for all the column experiments. The adsorption capacity per unit bed volume (N_o) 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 30% occurs when the concentration of the effleunt is 30% of the influent concentration (20 mg/l) and 70% breakthrough occur when the concentration of the effluent is 70% of the influent concentration. The lines through the data points in Figure 4.17 is the BDST

curve of 30% and 70% breakthrough under actual experimental conditions, while the BDST calculated equation for 30% and 70% breakthrough are shown in Figure 4.18 and 4.19. Since the flow rate is constant for all the bed heights and the area between the ordinate and the breakthrough curve gives the concentration of the adsorbate removed over the test time, the amount of adsorbate removed per gram of adsorbent was calculated from the breakthrough curve area by dividing the total amount of adsorbate removed by the mass of the adsorbent in the column.

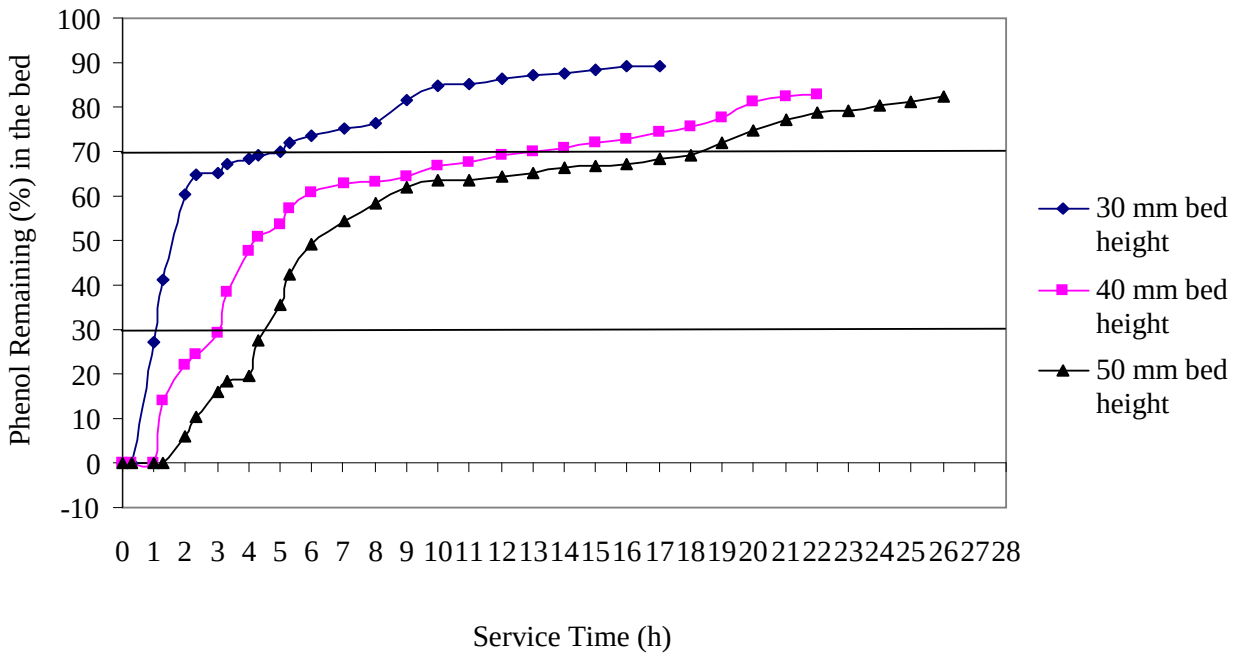


Figure 4.17. Breakthrough curves for Phenol Adsorption at 30 & 70 % concentration remaining.

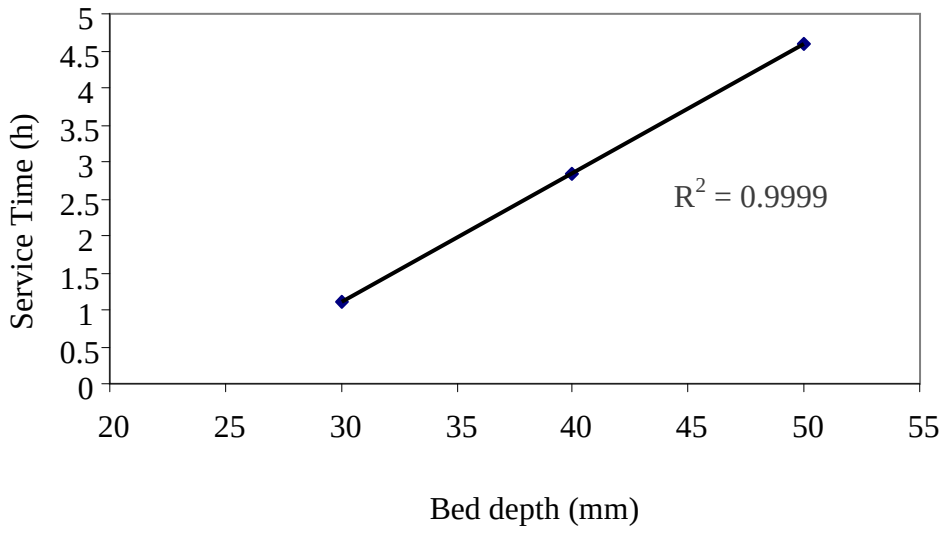


Figure 4.18. BDST plot at 30 % breakthrough point for Phenol Adsorption determined from a theoretical approach.

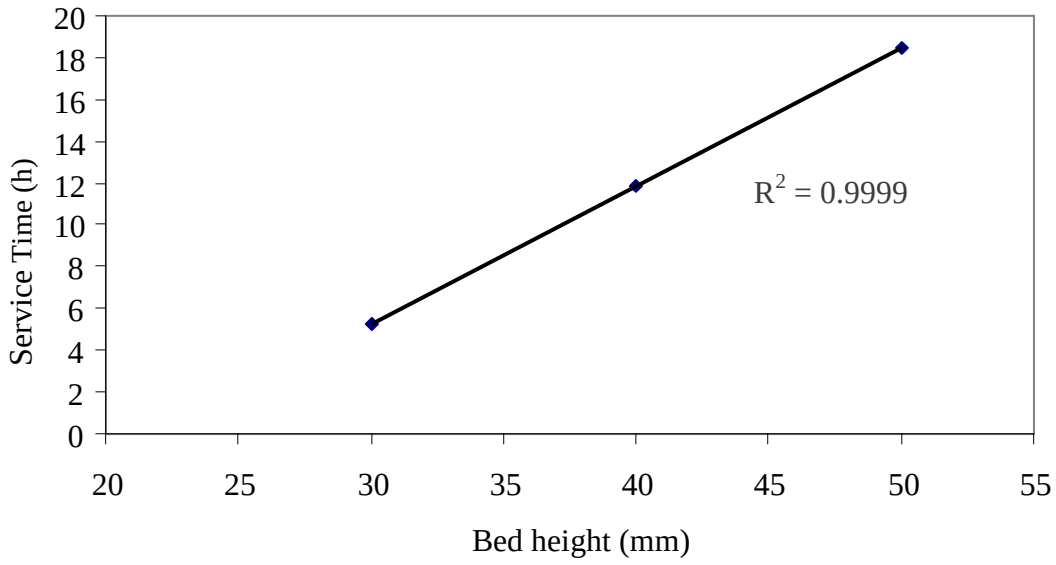


Figure 4.19. BDST plot at 70 % breakthrough point for Phenol Adsorption determine from a theoretical approach.

4.7.1. Effect of bed depth on breakthrough

The adsorption capability of CFA was tested at various bed depths of 30, 40 and 50 mm, with a 3.0 ml/min flow rate and 20 mg/l initial adsorbate concentration. The bed depths were obtained after the columns were packed with FA of 10 g, 15 g and 20 g respectively. Fig 4.17 above shows the combined breakthrough curves for the % adsorbates remaining in the column versus service time for different bed heights at constant flow rate of 3.0 ml/min. The breakthrough time, t_b, for phenol was found to increase with increased bed depths at 30% and 70% BDST. (See Table C.3).

From this study, it was confirmed from the 30% and 70% 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 a large influent concentration is to be treated. 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 30 to 50 mm, which means that the breakthrough curve becomes steeper as the bed depth decreases. Therefore, higher percentages of phenol are 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 X 10^{-2} l/mg-h for phenol.

4.7.2. 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 are shown in Appendix C and the data of the breakthrough curves are shown in Appendix D.

The breakthrough time at 70% is considerably higher than that of 30% for phenol at a 50 mm bed height for the breakthrough points investigated. This is due to the ability of the CFA to retain adsorbate efficiently within the column as the loading increases.

The adsorption capacity (N_o) were calculated for both 30% and 70% breakthrough and from the actual experimental data obtained. Table 4.6 shows that the CFA had higher adsorption capacity per unit bed volume for 70% breakthrough than 30% breakthrough for phenol. 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 70% theoretical and actual capacity as compared to the better correlation between the 30% theoretical and actual capacity may be from the fact that the Bohart/Adams equation which is based on BDST theory assumes a rectangular isotherm instead of 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 CFA for phenol at 20 mg/l for actual experimental values and theoretical values was found to be greater than the capacity determined from batch adsorption data. Hence, this result shows that this CFA had a better adsorption affinity for organic compounds comparable to the result of the FA 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 coal used by these authors had a higher specific surface area than the SACFA.

Table 4.5. % Adsorbate removal at breakthrough contact time of 2 hours.

Bed height (mm)	Phenol Removal (%)
30	37.7
40	78.0
50	93.8

Table 4.6. Comparison of theoretical and experimental adsorption capacity at 30% and 70% breakthrough of initial adsorbates concentration.

Adsorbates	N_o (mg/l)	Theoretical Capacity, (mg/g)	Actual Capacity, (mg/g)
Phenol (30%)	10.5	0.53	0.56
Phenol (70%)	39.6	1.98	0.98

4.7.3. Design of adsorption column for different concentration

The column design parameters obtained from the earlier test with 3 ml/min, initial concentration of 20 mg/l and bed depths of 30, 40, and 50 mm can be used for the design of this new adsorption column with a new influent concentration of 30 mg/l. 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 tests:

$$New\ slope = Old\ \text{slope}\left(\frac{V_{old}}{V_{new}}\right) \tag{4.4}$$

$$New\ b = Old\ \text{b}\left(\frac{C_{o,old}}{C_{o,new}}\right)\frac{\ln\left[\left(C_{o,new}/C_b\right)-1\right]}{\ln\left[\left(C_{o,old}/C_b\right)-1\right]} \tag{4.5}$$

The plot in figure 4.20 represents the results of phenol adsorption with an initial concentration of 30 mg/l against the original C_o of 20 mg/l. The predicted BDST equations for the 30 mg/l influent concentration of phenol can be found in fig.4.20. The equation was based on the new slope and new intercept derived from the BDST equation for 20 mg/l feed concentration. The increase in the influent concentration of the adsorbates from 20 mg/l to 30 mg/l also leads to the 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 20 mg/l concentration. The breakthrough times corresponding to 30% actual concentration of 20 mg/l and the calculated 30 mg/l can be found in table 4.7

Table 4.7. 30% breathrough time for experimental data based on 20 mg/l with calculated data for adsorbates adsorption with 30 mg/l.

Bed height (mm)	Service Time (h) Phenol	
	20 mg/l	30 mg/l
30	1.00	0.74
40	3.00	1.91
50	4.50	3.08

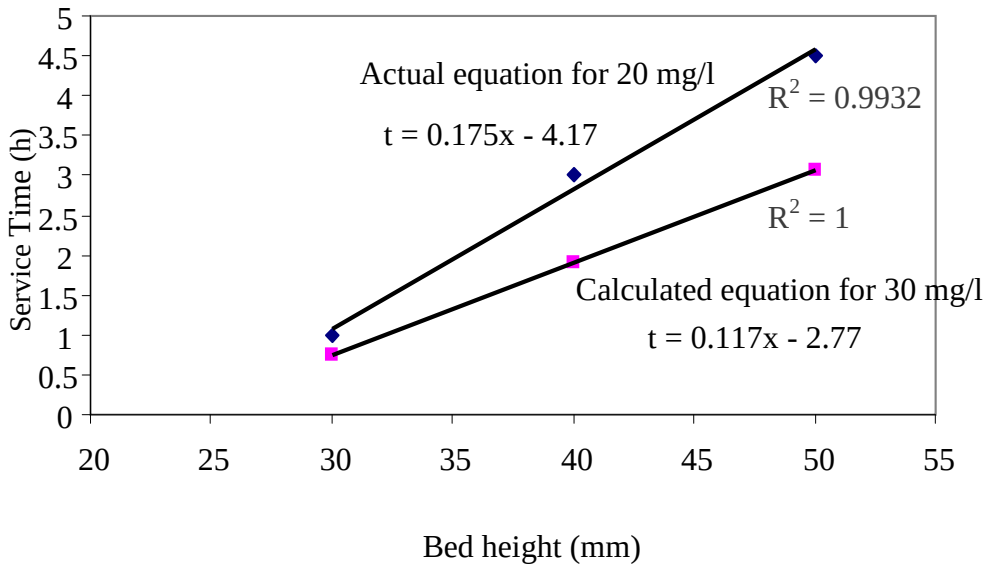


Figure 4.20. Comparison of BDST model predictions based on C_o: 20 mg/l with calculated BDST for phenol adsorption with C_o: 30 mg/l.

4.7.4. Design of adsorption column for different flow rate

The initial concentration of 20 mg/l, flow rate of 3 ml/min and bed depths of 30, 40, and 50 mm was used for the design of a new adsorption column at a flow rate of 1.5 ml/min. The breakthrough times which correspond to 30% actual concentration of 20 mg/l (Table 4.8) 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 (4.4), while the breakthrough time, which is a linear function of the bed depth, was determined from the equation below for the three bed depths;

$$t_b = \frac{N_0 \mathrm{D}}{\sum \mathrm{C}_0 v} - \frac{1}{KC_0} \ln\left(\frac{C_0}{C_b} - 1\right) \qquad (4.6)$$

Table 4.8. 30% breathrough time for theoretical data based on 3.0 ml/min with calculated data for adsorbates adsorption with 1.5 ml/min

Bed height (mm)	Service Time (h) Phenol	
	1.5 ml/min	3.0 ml/min
30	6.30	1.10
40	9.85	2.85
50	13.35	4.60

4.7.5. Comparison

In comparing the adsorption capacity of the SACFA with the values in the literature (Table 4.1) the physico-chemical characteristics of the various adsorbents in respect to the CFA used for this test had to be considered. The nature and composition of FA are found to be influenced by the coal origin and the existing burning conditions under which it was formed. Therefore, it is to be expected that these ashes should have different adsorption capacities for the uptake of adsorbates.

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 FA as compared to the CFA used in this test. Hence, the chemical composition of their FA belongs to the same class F as the SACFA used in this test. The carbon percentages of their FAs are found to be in the range of 0.81 to 3.73 % which is comparable to the 1.35 % used in this test. More so, their S.S.A was found to be in the range of 1 to 6 m^2/g compared to 1.279 m^2/g for CFA. The FA used by Banerjee *et al.* (1995) and CFA used for this test are almost of the same equal

parameters which might be responsible for the lower affinity of the adsorbates for the FA and the CFA. The adsorption capacity for the FA used by Sarkar *et al.* (2005) was found to be much higher than the CFA used in this test. Furthermore, the result was also in contract with the findings of Ahmaruzzaman and Sharma (2005) and this is due to the fact that the coal ash used had a higher specific surface area within the range of 96.44 and 312.56 m^2/g than the SACFA used in this test. According to this result, SACFA with S.S.A of 1.279 m^2/g and pore volume of 0.001437 cm^3/g seems to perform fairly well in comparison to the rubber activated carbon with S.S.A of 596 m^2/g used for adsorbing phenol by Rengaraj *et al.* (2002b). In addition, it is also difficult to compare the adsorption capacity that are reported because the chemical and structural properties of the adsorbents, adsorbates properties and the initial concentration of the phenolic species all determine the affinity of the adsorbent for the adsorbates.

4.8. Summary

The adsorption isotherms and the calculated adsorption capacities show that the SACFA possesses the ability to remove the test adsorbates from water. The adsorption capacity for the adsorbates based on Freundlich constants were found to be 4-Nitrophenol > phenol > 2-Nitrophenol. That is, CFA had the highest adsorption capacity for 4-Nitrophenol within the concentration range studied. This work also shows that contact time of 360 minutes is sufficient for equilibrium to be established between the adsorbates and the adsorbent, but equilibrium time depends on the type of adsorbates and adsorbent used. The contact time of the adsorbates onto CFA are also comparable to the result from Rengaraj *et al.* (2002a, b) who reported that a contact time of 2 hours was used on the adsorption of phenol onto palm seed activated carbon. An equilibrium time of 22 hr was used in this study to obtained experimental

data used in evaluating the adsorption capacity of the CFA.

Table 4.9. Output-design parameters, data and constants for batch and dynamic Test.

Parameters	Phenol	2-Nitrophenol	4-Nitrophenol
Adsorption Capacity (mg/g)	0.063	0.060	0.065
Rate constant [K_{ad} ($\min^{-1}$)]	$1.2X10^{-3}$	$1.0X10^{-3}$	$7.0X10^{-3}$
Adsorption Efficiency (%)	90.2	88.9	92.6
Desorption Efficiency (%)	17.9	18.8	10.2
Adsorption Capacity (mg/g) at breakthrough (30%)	0.56		
Adsorption rate constant $\left(L/mg.h\right)$	1.02 X 10^{-2}		
Adsorption Capacity (mg/g) at breakthrough (70%)	0.980		
Adsorption rate constant $\left(L/mg.h\right)$	2.91 X 10^{-3}		

CHAPTER V

5.0 Conclusions and Recommendation

5.1 Conclusions

In this research the ability of SACFA as a natural adsorbent was studied. The CFA used for this study was generated from Lethabo power plant with a specific surface area (S_{BET}) of 1.279 m^2/g, pore volume 0.001437 cm^3/g and particle size less than 99 µm, respectively. Its properties had been compared with some of the FA used by other authors (Sarkar *et al.*, 2006; Kao, *et al*., 2000; Viraraghavan and Alfaro, 1998) from the literature in the text of this thesis while, its adsorption capacity for the test adsorbates and similar organic compounds from the literature was also compared in the text and on Table 4.2.

The difference in the adsorption capacity of the CFA used in this test and the Baggasse fly ash used by Gupta *et al.* (1998) for the adsorption of nitrophenols might be as a result of the differences in the S.S.A of both adsorbents, particle size, initial concentration of the phenolics in solution, the existence of other species that may compete with the phenolic species of interest for adsorbent active site or the pH range of the solutions. All these parameters that determine the adsorption rate of an adsorbent makes it difficult in comparing the adsorption capacity that are reported.

Kinetic experiments was also carried out and the data from the kinetic adsorption of phenol, 2-Nitrophenol and 4-Nitrophenol onto FA were modelled using the Lagergren pseudo first-order approach. Adsorption isotherm data were determined for Phenol, 2-Nitrophenol and 4-Nitrophenol onto coal fly ash using a batch test method. Varying quantities of SACFA (5-40) g with an initial adsorbate concentration of 20 mg/l were used to determine the Freundlich

constants (K and 1/n) and Langmuir constants (Q_m and b). The batch approach was also used to determine the desorption efficiency of phenol, 2-Nitrophenol and 4-Nitrophenol. Continuous column studies were performed to compare the adsorption capacity of phenol onto CFA in a continuous column process with the capacity obtained from batch studies.

The relevance of this study is the fact that it can be used as a tool to determine the feasibility of using low cost adsorbents (CFA) to treat waters contaminated with Phenol, 2-Nitrophenol and 4-Nitrophenol. Due to the lower adsorption capacity of the CFA, the adsorbent requirements for the candidate adsorbents will be higher when compared to GAC. This will lead to larger adsorbent bed volumes required for treatment when the CFA adsorbents are used. In order to accommodate large volumes of adsorbent to treat an influent with the CFA adsorbents, larger equipment will be required. The long term benefits such as the low adsorbent cost requirements and the possibility of regenerating the spent CFA should also be considered during design operation. Since, the desorption test conducted with water in this test is fairly closed to the result obtained by Sarkar *et al*. (2006) where there is no release of phenolic from the FA into the water.

The calculated CFA 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 CFA required, but the actual adsorption capacity will vary according to the various adsorption parameters. The engineering applications would also be carried out under different conditions and the pH of the influent will also be varied. From the findings in this research, it is already been known that if the pH of the waste water is higher than the pK_a value of the adsorbates, there will be lesser adsorption due to dissociation of the adsorbate molecules. Also, the CFA

requirements should be seen as a function of the influent and effluent concentration required. Therefore, pilot scale experiments using the same operating conditions be carried out with the same waste water stream prior to design scale up.

The following conclusions can be drawn from this research work:

1. The equilibrium between the phenol, 2-Nitrophenol and 4-Nitrophenol in the solution and FA surface was basically achieved between the first 15 and 60 minutes of agitation respectively, after which the process approached equilibrium.
2. More than 75%, 74% and 89% of phenol, 2-Nitrophenol and 4-Nitrophenol were adsorbed within the first fifteen 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.
4. The pH was found to be a significant factor which affects the adsorption capacity of the organic compounds in solution. At a pH of 2.22, the percentage adsorbates removed are more than that at pH of 5.98, as indicated in figures 4.5 and 4.6
5. 4-Nitrophenol has the highest adsorption capacity among the adsorbates studied onto the SACFA.
6. The adsorption capacities of the studied adsorbates are significantly lower than the capacity of GAC for these adsorbates, as indicated in published literature.
7. The equilibrium adsorption data is better fitted by the Freundlich adsorption model than the Langmuir model for the three adsorbates, as indicated by correlation coefficient values obtained for both approaches.
8. The adsorption capacity of CFA determined from the removal of phenol during a

continuous column process was found to be higher than that determined from the batch adsorption capacity.

9. The desorption of 4-Nitrophenol from FA was found to be more difficult and more irreversible than that of 2- Nitrophenol and phenol.
10. The very low desorption of 4-Nitrophenol indicates that chemisorption might be occurring between the active sites of fly ash and functional groups of phenolates.
11. It was shown the SACFA generated from Lethabo power plant can be successfully utilized as an adsorbent for the removal of phenol, 2-Nitrophenol and 4-Nitrophenol from wastewater.

5.2. Recommendations

It is recommended that more work should be carried out on how to improve the adsorption capability of SACFA by subjecting it to physical and chemical treatments in order to increase its specific surface area and to promote the development of micropores within the CFA, as these treatments are known to change adsorption capacity. A comparison with fly ashes from different power stations to gauge their suitability and efficiency for removal of phenol from waste streams might also prove to be very interesting and potentially very useful, especially with the view of their proximity to potential treatment and application sites. In addition, a thorough pilot scale experiment using the same operating conditions should be conducted with the same wastewater effluents and adsorbent prior to design scale up.

References

Acemioglu,B. (2004). Adsorption of Congo red from aqueous solution onto calcium rich fly ash. *Journal of Colloid Interface Science,* Vol. 274, 371-379.

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.

Agency for Toxic Substances and Disease Registry (1992). Toxicological Profile for 2,4-Dichlorophenol. Atlanta, Georgia: US Department of Health and Human Services, Agency for Toxic Substances and Disease Registry, *DHHS (ATSDR) publication*. No.TP-91/14.

Agyei, N.M., Potgieter, J. H. and Strydon C.A. (2002). The removal of phosphate ions from aqueous solution by fly ash, slag, ordinary ement and related blends. *Cement and Concrete Research,* Vol. 32, 1889-1897.

Ahmaruzzaman, M., Sharma, D.K. (2005). Adsorption of phenols from wastewater. *Journal of Colloid and Interface Science,* Vol. 287, 14-24.

Akgerman, A., Zardkoohi, M. (1996). Adsorption of phenol from wastewater by peat, fly ash and bentonite. *Journal of Chemical Engineering, Data,* 41, 185-187.

Aksu, Z., Yener, J. (1999). A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents. *Waste Management,* Vol. 21, 695-702.

Aktas, O., Cecen, F. (2006) Effect of type of carbon activation on adsorption and its reversibility. *Journal of Chemical Technology and Biotechnology,* Vol. 81, 94-101

Allen, S.J. (1987). Equilibrium adsorption isotherms for peat. *Fuel,* Vol. 66, 1169-1175.

Alonso JL, Wesche K. (1991). Charaterization of fly ash. In: Wesche K, editor. Fly ash in co-Ncrete properties and performance. RILEM report, Vol. 7,3-23

Al-Kdasi, A., Idris, A. and Saed, K., Guan, C.T. (2004). Treatment of textile wastewater by advanced oxidation processes- a review, *Global Nest International Journal*, Vol. 6 (3), 226-234.

ASTM C 618 94. (1994). Specification for coal fly ash and raw calcined natural pozzolan for use as a mineral admixture in Portland cement concrete. *Annual Book of ASTM Standards*, Vol. 4.02, 296-298.

Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O. (2000). Adsorption of phenol by bentonite. *Environmental Pollution*, Vol. 107, 391-398.

Banerjee, K., Cheremisinoff, P.N. and Cheng, S.L. (1995). Sorption of organic contaminants by fly ash in a single solute system. *Environmental Science and Technology*, Vol. 29, 2243-2251.

Banerjee, K., Cheremisinoff, P.N. and Cheng, S.L. (1997). Adsorption Kinetics of o-xylene by Fly Ash. *Water Research,* Vol. 31, 249-261.

Banerjee, S.S., Joshi, M.V. and Jayaram, R.V. (2004). Removal of Cr (VI) and Hg(II) from aqueous solution using fly ash and impregnated fly ash. *Separation Science and Technol*ogy, Vol. 39, 1611-1629.

Batabyal, D., Sahu, A., and Chaudhuri, S.K. (1995). Kinetics and mechanism of removal of 2,4-dimethylphenol from aqueous solutions with coal fly ash. *Separations Techno logy,* Vol. 5, 179-186.

Bertoncini, C., Odetli, H. and Bottani, E.J. (2000). Computer simulation of phenol physisorption on graphite. *Langmuir*, Vol.16, 7457-7463.

Bhargava, D.S., Sheldarkar, S.B. (1993b). Use of TNSAC in phosphate adsorption studies and relationships. Effects of adsorption operating variables and related relationships. *Water Research*, Vol. 27(2), 313-324.

Boardsell, D.V., Nichols, D.G., Jones, D.L. (1997). Physical Properties of Nursery Potting mixture. *Scientia Horticulturae,* Vol. 11, 1-8

Bohart, G.S., Adams, E.Q. (1920). Some aspects of the behaviour of charcoal towards chlorine. *Journal of the Chemical Society*, Vol. 42, 523-529.

Butler, M., Hallowes, D. (2002). Corporate Accountability in South Africa: The petrochemical industry and air pollution.

Calace, N., Nardi, E., Petronio, B.M. and Pietroletti, M. (2002). Adsorption of phenols by papermill sludges. *Environmental Pollution,* Vol. 118, 315-319.

Chandrasekhar, S., Satyanarayana, K.G., Pramada, P.N., Raghavan, P. and Gupta, N. (2003). Processing, properties and applications of reactive silica from rice husk-an overview. *Jour nal of Material Science,* Vol. 38, 3159-3168.

Chang, Y.C., Chang, J.S., Lin, Y.W., Erdei, L. and 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.

Chaturvedi, A.K., Yadava, K.P., Pathak, K.C. and Singh, V.N. (1999). Defluoridation of water by adsorption of fly ash. *Water, Air Soil Pollution*, Vol. 49, 51-61.

Charest, A., Bisallon, J.G., Lepine, F. and Beaudet, R. (1999). Removal of phenolic compounds from a petrochemical effluent with a methanogenic consortium. *Canadian Journal of Microbiology*, Vol. 45, 235-241.

Chon, S.S., Huang, Y.H., Lee, S.N., Huang, G.H. and Huang, C.P. (1999). Treatment of high strength hexamine–containing wastewater by electro-Fenton method. *Water Research*, Vol. 33, 751-756.

Colella, L.S., Armenante, P.M. (1998). Adsorption Isotherms for Chlorinated Phenols on Ac-

tivated Carbon. *Journal of Chemical Engineering*, Vol. 43, 573-579.

Cooney, David.O. (1999). Adsorption design for wastewater Treatment, Lewis Publisher, Washington, D.C. USA

Crittenden, B., and Thomas, W.J. (1998). Adsorption Technology and Design. Butterworth-Heinemann Publishers, Oxford, Great Britain.

Core Consultative Committee on Wastes (2003). New and Better Hazardous Waste Treatment Technologies in WA. First forum briefing paper 5.

Das, C.P., and Patnaik, D.K. (2005). Removal of phenol by industrial solid waste, Practice Period. *Hazardous Toxic Radioactive Waste Management,* ASCE 9 (2), 135-140.

Dasmahapatra, G.P., Pal, T.K., Bhadra, A.K., Bhattacharya, B. (1996). Studies on the separate-on characteristics of hexavalent chromium from aqueous solution by fly ash. *Separation Science and Technol*ogy, Vol. 31, 2001-2009.

Denayer, J.F., Souverijins, W., Jacobs,P.A., Martens, J.A. and Baron, G.V.(1998). High- Temperature low-pressure adsorption of branched C-5-C-8 alkanes on zeolite beta, ZSM-5, ZSM-22, Zeolite Y, and Mordenite. *Journal of Physical Chemistry, Vol.* B 102 (23), 4588-4597.

Denizli, A., Okan, G., and Ucar, M. (2002). Dye-Affinity Microbeads for Removal of Phenols and Nitrophenols from Aquatic Systems. *Journal of Applied Polymer Science,* Vol. 83, 2411-2418.

Department of Water Affairs and Forestry (1993). South African Water Quality Guildelines. Volume 3: Industrial Use.

Dijkema, L.P. Private communication, Johannesburg: July, 2006.

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.

Environmental Protection Agency, 1984. Methods 604, Phenols in Federal Register, October 26, Part VIII, 40, CFR, 58, USA.

Faust, S.D., Aly, O.M. (1999). Chemistry of water treatment, 2nd edition Lewis Publisher, Washington, D.C, USA.

Farwell, J.K., Hunt, S. (1988). Environmental Toxicology: Organic Pollutants, Halsted Press John Wiley & Sons, N.Y, Page 398.

Fettig, J., Stapel, H., Steinert, C. and Geiger, M. (1996). Treatment of landfill leachate by preozonation and adsorption in activated carbon columns. *Water Science Technology*, Vol. 26, 381-388.

Giere, R., Carleton, L.E. and Lumpkin, R.G. (2003). Micro- and nanochemistry of fly ash from a coal-fired power plant. *American Mineralogist*, Vol. 88, 1853-1865.

Giles, H., Smith, D., and Huitson, A. (1974). A general treatment and classification of the solute adsorption isotherm (II). *Journal of Colloid Interface Science*, Vol. 47, 766-778.

Goodarzi, F. (2005). Charateristic and composition of fly ash from Canadian coal- fired power plants. *Fuel*, Vol. 85, 1418-1427.

Grisdanurak, N., Chiarakorn, S. and Wittayakun, J. (2003). Utilization of mesoporous molecular sieves synthesized from natural source rice husk silica for chlorinated volatile organic compounds (CVOCs) Adsorption. *Korean Journal of Chemical Engineering*, Vol. 20 (5), 950-955.

Grubb, D.G., Guimaraes, M.S. and Valencia, R. (2001). Phosphate immobilization using an acidic type F fly ash. *Journal of Hazardous Materials*, Vol. 76, 217-236.

Gupta, V.K., Sharma, S., Yadav, I.I. and Mohan, D. (1998). Utilization of Bagasse Fly Ash Generated in the Sugar Industry for the Removal and Recovery of Phenol and p-Nitrophenol from wastewater. *Journal of chemical Biotechnology*, Vol. 71, 180-186.

Ha, S.R., Vinitnantharat, S. (2000). Competitive removal of phenol and 2, 4-dichlorophenol in biological activated carbon system. *Environmental Technology*, Vol. 21, 387-396.

Haas, C. N., Vamos, J.R. (1995). Hazardous and Industrial Waste Treatment. Prentice-Hall Inc., New York, New York.

Haghighi-Podeh, M.R., Bhattavhaya, S.K. and Mingo, Q. (1995). Effects of nitrophenols on acetate utilizing methanogenic system. *Water Research*, Vol. 29(2): 391.

Haghseresht, F., Nouri, S. and Lu, G.Q. (2002). Effects of solute ionization on the adsorption of aromatic compounds from dilute aqueous solution by activated car- bon. *Langmuir*, Vol 18, 1574-579.

Han, J.S. (1999). Stormwater filtration of toxic heavy water ionsusing Lignocellulosic materials selection process, fiberization, chemical modification and material formation. US Department of Agriculture, Forest service, Forest products laboratory, Madison, Wisconsin, U.S.A.

Hazardous Substances Data Bank. (1989). National Library of Medicine. National Toxicology Information Program, Bethesda, MD. September 11, 1989.

Helmuth, R. (1987). Fly ash in cement and concrete, Portland Cement Association, Skokie, pp 36-61.

Ince, N.H., Tezcanli, G., Belen, R.K. and Apikyan, I.G. (2001). Ultrasound as a catalyzer of aq ueous reaction systems: the state of the art and environmental applications. *Applied Catalysis B; Environmental*, Vol. 29, 167-176.

Kao, P.N., Tzeng, J.H., and Huang, T.L. (2000). Removal of chlorophenols from aqueous solution by fly ash. *Journals of Hazardous Materials*, Vol. 76, 237-249.

Karim, K., Gupta, S.K. (2003). Continuous biotransformation and removal of nitrophenols under denitrifying conditions. *Water Research*, Vol. 37, 2953-2959.

Khare, S.K., Pandy, K.K., Srivastava, R.M. and Singh, V.N. (1987). Removal of Victoria blue

from aqueous solution by fly ash. *Journal of Chemical Technology and Biotechnology,* Vol. 38, 99-104.

Kidak, R., Ince, N.H. (2006). Ultrasonic destruction of phenol and substituted phenols: A review of current research. *Ultrasonic Sonochemistry,* Vol. 13, 195-199.

Konstantinou, I.K., Albanis, T.A., Petrakis, D.E. and Pomonis, P.J. (2000). Removal of Herbicides from aqueous solutions by Adsorption on Al-pillared clays, Fe-Al pillared clays and mesoporous Alumina Aluminum Phophates. *Water Research,* Vol. 34, 3123-3136.

Kornaros, M., Lyberatos, G. (2006). Biological treatment of wastewaters from a dye manufacturing company using a trickling filter. *Journal of Hazardous Materials,* Vol. 136, 95-102.

Kruger, R.A. (2002). South African Coal Ash Association, Personal Communication, Johannesburg.

Kruger, R.A., Kruger, J.E. (2005). Historical development of coal ash utilization in South Africa, International ash utilization symposium and the world coal ash Conference, Policy 3.

Kumar, N., Byggningsbacka, R. and Korpi, M. (2002). Synthesis and characterization of Pd-MCM-22 and Pt-SAPO-11 catalysts for transformation of *n*-butane to aromatic hydrocarbons. *Applied Catalysis A-General,* Vol. 227 (1-2), 97-103.

Kumar, V.K., Subanandam, K., Ramamurthi, V. and Sivanesan, S. (2004). GAC Sorption Process: Problems and Solutions. http://www.eco-web.com/cgi- local/sfc?a=/editorial/index.html.html&b=/editorial /040319.html (Cited, 10 February 2006).

Kurniawan, T.A., Chan, G.Y.S. and Lo, W.H. (2006). Radicals-catalyzed oxidation reactions for degradation of recalcitrant compounds from landfill leachate. *Chemical Engineering Journal,* Vol. 125, 35-57.

Lagergen, S., Svenka, K., Vetenskapsakad., (1898). *Handl,* 24.

LaGrega, M., Buckingham, P., Evans, J., and the Environmental Resources Management Gro-

up, (1994). Hazardous Waste Management, McGraw-Hill Publisher, New York, USA.

Lee Daniels, W., Stewart, B., Haering, K. and Zipper, C. (2002). The Potential for Beneficial Reuse of Coal Fly Ash in Southwest Virginia Mining Environments. Page 1-19. www.ext.vt.edu/pubs/mines/460-134/460-134.html. (Cited, 08 March, 2006).

Lin, J.G., Ma, Y.S. (1999). Magnitude of effect of reaction parameters on 2- Chlorophenol decomposition by ultrasonic process. *Journal of Hazardous Matter,* B 66, 291-305.

Mahvi, A.H., Maleki, A. and Eslami, A. (2004). Potential of rice husk and rice husk ash for phenol removal in aqueous systems. *American Journal of Applied Science,* Vol.1 (4), 321-326

Malerius, O., Werther, J. (2003). Modeling the adsorption of mercury in the flue gas of sewage Sludge incineration. *Chemical Engineering Journal*, Vol. 96, 197-205.

Matjie, R.H., Ginster, M., Van Alphen, C., and Sobiecki, A. (2005). Detailed Characterization of Sasol Ashes. http://whocares.caer.uky.edu/wasp/AshSymposium/AshLi-braryAgenda.asp#2005. (Cited, 19 September 2006).

Matjie R.H., Bunt, J.R. and Van Heerden. (2004). Extraction of alumina from coal fly ash generated from a selected low rank bituminous South Africa coal. *Mineral Engineering*, Vol.18, 299-310.

Metes, A., Kovacevic, D. and Vujevic, D. (2004). The role of Zeolites in wastewater treatment of printing inks. *Water Research,* Vol. 38 (14-15), 3373-3381.

Mimura, H., Yokota, K., Akiba, K. and Onodera, Y. (2001). Alkali hydrothermal synthesis of Zeolites from coal fly ash and their uptake properties of cesium ion. *Journal of Nuclear Science and Technology*, Vol. 38, 766-772.

Misra, C. (1986). Industrial Alumina Chemical, in: Monograph, 184, *America Chemical Society*, Washington, DC, USA.

Mohammad, R., Podeh, H. and Bhattacharya, S.K. (1996). Fate and toxic effect of nitrophenols

on anaerobic treatment systems. *Water Science Technol*ogy, Vol. 34 (5-6), 345-350.

Mohan, D., Singh, K.P., Singh, G. and Kumar, K. (2002). Removal of dyes from wasterwater using fly ash, a low-cost adsorbent. *Industrial Engineering and Chemical Research*. Vol. 41, 3688-3695.

Mukherejee, S., Kumar, S., Misra, A.K. and Fan, M. (2007). Removal of phenols from waster environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal*, Vol. 129, 133-142.

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.

Norberg, V., Su, B.L. (1999). Toward a better understanding on the benzene location in sodium exchanged-Beta zeolite: An in-situ infrared study of molecular recognition. *Material Resea rch Society*, 12th International Zeolite Conference, pp 167-174.

Panday, K.K., Prasad, G. and Singh, V.N. (1984). Removal of Cr (VI) from aqueous solutions by adsorption on fly ash-wollastonite. *Journal of Chemical Technology and Biotechnology*, Vol. 34A, 367-374.

Patnaik, P., Khoury, J.N. (2004). Reaction of phenol with nitrite ion: Pathways of formation of nitrophenols in environmental waters. *Water Science Technology*, Vol. 38(5), 206-210.

Pera-Titus, M., Garcia-Molina, V., Banos, M.A., Gimenez, J. and Esplugas, S. (2004). Degradadtion of chlorophenols by means of advanced oxidation processess: a general review, *Applied Catalysis B; Environmental*, Vol. 47, 219-256.

Petrier, C., Jiang, Y. and Lamy, M.F. (1998). Ultrasound and Environment: Sonochemical destruction of chloroaromatic derivatives. *Environmental Science and Technology*, Vol. 32, 1316-1318.

Potgieter, J.H., Potgieter-Vermaak, S.S. (2006). A Comparison of the Adsorption of Heavy M-

etals from Multicomponent Solutions onto Industrial Clay and Fly Ash, International Confere rence on Coal Ash, October 2-4 2006, Pretoria, South Africa.

Potgieter-Vermaak, S.S., Potgeiter, J.H., Kruger, R.A., Spolnik, Z., and Van Grieken, R (2005). A characterisation of the surface properties of an ultra fine fly ash (UFFA) used in the polymer industry. *Fuel*, Vol. 82, 2295-2300.

Potgieter-Vermaak, S.S., Potgieter, J.H., Monama, P. and Gieken Van. R. (2006). Comparison of limestone,dolomite and fly ash as pre-treatment agents for acid mine drainage. *Minerals Engineering*, Vol. 19, 454-462.

Ramakrishna, K.R., Viraraghavan, T. (1997). Dye removal using low cost adsorbent. *Water Science Technology*, Vol. 36, 189-196.

Reynolds, K. (2005). The utilization of Ash wall for the Control and Treatment of Acid Mine Drainage, World of Coal Ash Conference, Lexington, Kentucky, April11-25, 2005, USA.

Rengaraj, S., Moon, S.H., Sivabalan, R., Arabindoo, B. and Murugesan, V. (2002a).Agricultural solid waste for the removal of phenol from waster and wastewater by palm seed coat activated carbon. *Waste Management*, Vol. 22, 543-548.

Rengaraj, S., Moon, S.H., Sivabalan, R., Arabindoo, B., and Murugesan, V. (2002b). Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat. *Journal of Hazardous Materia ls*, Vol. B 89, 185-196.

Ricou, P., Lecuyer, I. and Le Cloirec, P. (1999). Removal of Cu^{2+}, Zn^{2+}, and Pb^{2+} by adsorption onto fly ash and fly ash/lime mixing. *Water Science and Technology*, Vol. 39, 239- 247.

Rovatti, M., Peloso, A. and Farraiolo, G. (1988). Susceptibility to regeneration of fly ash as an adsorbent material. *Resource Conservation and Recycling*, Vol. 1, 137-143.

Roy, W.R., Thiery, R.G., Schuller, R.M. and Suloway, J.J. (1981). Coal Fly Ash: A Review of the Literature and Proposed Classification System with Emphasis on Environmetal Impacts.

Environmental Geology Notes 96. Illinois State Geology Survey. Champaign, IL.

Sarkar, M., Acharya, P.K. and Bhattacharya, B. (2003). Modelling the adsorption kinetics of some priority organic pollutants in water from diffusion and activated energy parameters. *Journal of Colloid Inteface Science*, Vol. 266, 28-32.

Sarkar, M., Acharya, K.P., and Bhattacharya, B. (2005). Removal characteristics of some priority organic pollutants from water in a fixed bed fly ash column. *Journal of chemical Technology and Biotechnology*, Vol. 80, 1349-1355.

Sarkar, A., Bassu, A.K., Udaybhanu, G. and Rano, R. (2006). A comprehensive characterization of fly ash from a thermal power plant in Eastern India. *Fuel*, Vol. 87, 259-277.

Sarkar, M., Acharya, K.P. (2006). Use of fly ash for the removal of phenol and its analogues from contaminated water. *Waste Management*, Vol. 26, 559-570.

Sen, A.K., De, A.K. (1987). Adsorption of mercury from wastewater by fly ash. Wat*er Research*, Vol. 21, 885-888.

Shiskowski, D.M., Viraraghavan, T. (1993). Removal of chromium from waste-water by peat filters. *Journal of Environmental Science*, Vol. 28 (5), 967-981.

Singh, D.N., Kolay, P.K. (2002). Simulation of ash-water interaction and its influence on ash characteristic. *Progress in Energy and Combustion Science*, Vol. 28 (3), 267-299.

Singh, B.K., Nayak, P.S. (2004). Sorption equilibrium studies of toxic nitro-substituted phenols on fly ash. *Adsorption Science and Technology*, Vol. 22, 295-310.

Singh, P.K., Mohan, D., Singh, G. and Kumar, K. (2002). Removal of dyes from wastewater using fly ash, a low-cost adsorbent. *Industrial and Engineering Chemistry Research*, Vol. 41, 3688-3695.

Sismanoglu, T., Pura, S. (2001). Adsorption of aqueous nitrophenols on clinoptilolite. *Colloids & Surfaces. A*: *Physicochemical Engineering Aspects*, Vol. 180, 1-6.

Smidt, E., Lechner, P. (2005). Study on the degradation and stabilization of organic matter in waste by means of thermal analyses. *Thermochimica Acta*, Vol. 438, 22-28.

Spedding, P.J. (1988). Review of the inorganic geochemistry of peats and peatland waters. *Fuel*, Vol. (67) 7, 883-900.

Spero, J., Devito, B. and Theodore, L. (2000). Regulatory Chemicals Handbook (Chemical Industries). Marcel Dekker Publishers, UK.

Srivastava, V.C., Swamy, M.M., Mall, I.D., Prasad, B. and Mishra, I.M. (2006). Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, Kinetic and Thermodynamics. *Colloids and Surfaces*, Vol. 272, 89-104.

Srivastava, S.K., Tyagi, R., Pal, N., and Mohan, D., (1997). Process development for removal of substituted phenol by carbonaceous adsorbent obtained from fertilizer waste. *Environment Engineering*, Vol. 123, 842-851.

Stoeckli, F., Lopez –Ramon, M.V. and Moreno-Castilla, C. (2001). Adsorption of phenolic compounds from aqueous solutions by activated carbons described by the Dubinin- Astakhov equation. *Langmuir* 17, 3301-3306.

Tolle, D.E., Arthur, M.F. and Pomeroy, S.E. (1982). Fly ash used for Agriculture and Land Reclamation: A critical literature Review and Identification of Additional Research Needs. Columbus. Ohio. RP-1224-5.

Tomeczek, J., Palugnoik, H. (2002). Kinetics of mineral matter transformation during coal combustion. *Fuel*, Vol. 81 (10), 1251-1258.

Toxic Release Inventory. (1992). Toxicological profile for Nitrophenols: 2-Nitrophenols and 4-Nitrophenols. Washington, D.C. Office of Toxic substances.

Treacy, M.M.J., Newsman, J.M. (1988). 2 New 3-Dimensional 12-ring Zeolite frame works of which Zeolite Beta is a disordered intergrowth. *Nature*, Vol. 332, 249-251.

Tseng, R.L., Wu, F.C. and Juang, R.S. (2003). Liquid – phase adsorption of dyes and phenols using pinewood –based activated carbons. *Carbon,* Vol. 41, 487-495.

Uberoi, V., Bhattavhaya, S.K. and Mingo, Q. (1997). Toxicity and degradability of nitrophenols in anaerobic systems. *Water Environment Research*. Vol. 69(2): 146.

United States Environmental Protection Agency.(1981). Treatability manual. Vol.1 EPA 600/2-82-oola. Office of Research and Development, Washington, DC.

US Environmental Protection Agency, Release and pollution prevention report, 2000.

Vandevivere, P.C., Bianchi, R. and Verstraete, W. (1998). Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *Journal of Chemical Technology and Biotechnology*, Vol. 72, 289-302.

Vassilev, S.V., Vassileva, C.G. (1996). Mineralogy of combustion wastes from coal-fired power stations. *Fuel Processing Technology*, Vol. 47, 261-280.

Vempati, R. K., Yousuf, M. A., Chinthala, A. K. and Cocke, D. L. (1995). Solidification/Stabilization on Toxic metal wastes using coke and coal combustion by-product. *Waste Management,* Vol. 15, 433-440.

Viraraghavan, T., Alfaro, F. (1998). Adsorption of phenol from wastewater by peat, fly ash and bentonite. *Journals of Hazardous Materials,* Vol. 57, 59-70.

Viraraghavan, T., Kapoor, A., (1995). Adsorption of mercury from waste-water by Peat. *Journal of Environmental Science,* Vol.30 (3), 553- 566.

Wang, S., Boyjoo, Y., Choueib, A. and Zhu, J. (2004). Utilization of fly ash as low cost adsorbents for dye removal. *Chemeca*, 26-2S9 September, Sydney.

Wang, S., Boyjoo, Y., and Zhu, J. (2005). Sonochemical treatment of fly ash for dye removal from wastewater. *Journals of Hazardous Materials,* Vol. B126, 91-95.

Wang, S. l., Tzou, Y.M., Lu, Y.H. and Sheng, G. (2007). Removal of 3-chlorophenol from wa-

er using rice-straw-based carbon. *Journal of Hazardous Material,* Vol. 147, 313-318.

Wang, J.P., Feng, M.H. and Yu, H.Q. (2007). Analysis of adsorption characteristic of 2, 4-dic dichlorophenol from aqueous solutions by activated carbon fiber. *Journal of Hazardous Material,* Vol. 144, 200-207.

Weber, W.J. Jr. (1972). Physiochemical processes for water quality control. Wiley – Interscience, John Wiley & Sons Inc, New York, USA.

Weng, C.H., Huang, C.P., (2004). Adsorption characteristic of Zn(II) from dilute aqueous solutions by fly ash. *Colloids & Surfaces. A*: *Physicochemical Engineering Aspects,* Vol. 247, 137-143.

Woolard, C.D., Strong, J. and Erasmus, C.R. (2002). Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams. *Applied Geochemistry*, Vol. 17, 1159-1164.

World Coal Institute. (2000). Electricity generated from coal, http://www.wci-coal.com.(Cited, 17 Febuary, 2007).

World Health Organization. (1984). Guildlines for Drinking Water Quality, Vol.1. World Health Organization, Geneva, Page 85.

Wu, J., Yu, Han-Qing. (2006). Bisorption of 2, 4-dichlorphenol from aqueous solution by Phanerochaete chrysosporium biomass: Isotherms, Kinetics and thermodynamics. *Journals of Hazardous Materials,* Vol. B 137, 498-508.

Yin, Y. C., Aroua, M.K. and Wan Daud, W.M. (2007). Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. *Separation andPurification Technology,* Vol. 52, 403-415.

Yousef, R.I., Tutunji, M.J., Derwish, G.A.W. and Musleh, S.M. (1999). Chemical and structural properties of Jordanian Zeolite tuffs and their admixture with urea and thiourea: potential

scavengers for phenolic compounds in aqueous medium. Journal of Colloid Interface Science, Vol. 348-359.

Zappi, M.G., Aycock, K., Subramani, A. and Tavai, A.S. (2000). Development of Kenaf based bisorptive water treatment process. Technical Interim Report, Project Number1434-HQ-96-GR-O2679-20, Water Resources Research Institute, Mississippi State University.

APPENDIX A

Batch Studies Data

TableA.1. Standard data for phenol at concentrations (10-30) mg/l at 269.0 nm.

Concentration (mg/l)	Absorbance
10	0.159
15	0.237
20	0.319
25	0.392
30	0.472

TableA.2. Standard data for phenol from the mixture of 2-Nitrophenol and 4-Nitrophenol concentrations (10-30) mg/l at 269.0 nm.

Concentration (mg/l)	Absorbance
10	0.719
15	1.112
20	1.484
25	1.881
30	2.269

TableA.3. Standard data for 2-Nitro phenol from the mixture of phenol and 4- Nitrophenol concentrations (10-30) mg/l at 277.5 nm.

Concentration (mg/l)	Absorbance
10	0.798
15	1.243
20	1.679
25	2.135
30	2.684

TableA.4. Standard data for 4-Nitro phenol from the mixture of phenol and 2- Nitrophenol concentrations (10-30) mg/l at 320.5 nm.

Concentration (mg/l)	Absorbance
10	0.817
15	1.273
20	1.733
25	2.212
30	2.671

TableA.5. Effect of CFA dosage selected on each of the adsorbates (pH: 2.22).

CFA dosage (g)	Phenol Removal (%)	2-Nitrophenol Removal (%)	4-Nitrophenol Removal (%)
5	54.7	52.7	80.4
10	70.2	66.9	86.5
15	78.3	75.0	89.3
20	83.3	80.3	90.7
25	86.9	84.8	91.8
30	89.2	87.2	92.3
35	89.9	88.2	92.5
40	90.2	88.9	92.6

TableA.6. % Removal of each adsorbate at pH: 5.98.

CFA dosage (g)	Phenol Removal (%)	2-Nitrophenol Removal (%)	4-Nitrophenol Removal (%)
5	50.5	47.8	77.9
10	65.3	61.7	83.9
15	74.7	71.6	87.6
20	81.3	78.6	89.4
25	83.5	81.3	89.9
30	84.3	83.0	90.4
35	85.9	85.2	90.7
40	87.4	86.0	90.9

TableA.7. Contact time experiments data for CFA using phenol, 2-Nitrophenol and 4-Nitrophenol at pH: 2.15.

Time (min)	Phenol [Qt (mg/g)]	2-Nitrophenol [Qt (mg/g)]	4-Nitrophenol [Qt (mg/g)]
15	0.02267	0.02225	0.02674
30	0.02288	0.02244	0.02681
60	0.02310	0.02258	0.02688
90	0.02331	0.02272	0.02697
120	0.02346	0.02284	0.02703
180	0.02367	0.02300	0.02714
240	0.02378	0.02315	0.02721
300	0.02385	0.02325	0.02724
360	0.02390	0.02330	0.02726

TableA.8. Contact time experiments data for % phenol, 2-Nitrophenol and 4-Nitrophenol removal using CFA at pH: 2.15.

Time (min)	Phenol Removal (%)	2-Nitrophenol Removal (%)	4-Nitrophenol Removal (%)
15	75.6	74.2	89.2
30	76.3	74.8	89.4
60	77.0	75.3	89.6
90	77.7	75.8	89.9
120	78.2	76.2	90.1
180	78.9	76.7	90.5
240	79.3	77.2	90.7
300	79.5	77.5	90.8
360	79.7	77.7	90.9

TableA.9. Kinetic removal of phenol, 2-Nitrophenol and 4-Nitrophenol at 20 mg/l concentration at pH: 2.15.

Time (min)	Phenol log [Q_e-Q_t]	2-Nitrophenol Log [Q_e-Q_t]	4-Nitrophenol Log [Q_e-Q_t]
15	-2.6968	-2.7520	-2.9031
30	-2.7447	-2.8027	-2.9263
60	-2.8027	-2.8416	-2.9547
90	-2.8649	-2.8745	-2.9914
120	-2.9154	-2.8945	-3.0159
180	-2.9978	-2.9154	-3.0605
240	-3.0457	-2.9727	-3.1079
300	-3.0836	-3.0836	-3.1249
360	-3.1079	-3.1427	-3.1612

TableA.10. Adsorption Isotherm data for Freundlich Model at different CFA loading (5-35) g for phenol adsorption.

CFA (g)	C_e (mg/l)	Q_e (mg/g)	Log C_e (mg/l)	Log Q_e (mg/g)
5	9.06	0.0656	0.9571	-1.1828
10	5.96	0.0421	0.7753	-1.3755
15	4.35	0.0313	0.6385	-1.5045
20	3.55	0.0247	0.5502	-1.6077
25	2.62	0.0209	0.4183	-1.6808
30	2.17	0.0178	0.3365	-1.7489
35	2.03	0.0154	0.3075	-1.8125

Initial Phenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.11. Adsorption Isotherm data for Freundlich Model at different CFA loading (5-35) g for 2-Nitrophenol adsorption.

CFA (g)	C_e (mg/l)	Q_e (mg/g)	Log C_e (mg/l)	Log Q_e (mg/g)
5	9.47	0.0632	0.9764	-1.1994
10	6.61	0.0402	0.8202	-1.3961
15	4.99	0.0300	0.6981	-1.5226
20	3.99	0.0240	0.6010	-1.6195
25	3.04	0.0204	0.4829	-1.6914
30	2.57	0.0174	0.4099	-1.7587
35	2.37	0.0151	0.3748	-1.8207

Initial 2-Nitrophenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.12. Adsorption Isotherm data for Freundlich Model at different CFA loading (5-35) g for 4-Nitrophenol adsorption.

CFA (g)	C_e (mg/l)	Q_e (mg/g)	Log C_e (mg/l)	Log Q_e (mg/g)
5	3.93	0.0886	0.5944	-0.2260
10	2.71	0.0485	0.4330	-0.3635
15	2.15	0.0328	0.3324	-0.4783
20	1.87	0.0260	0.2718	-0.5657
25	1.65	0.0208	0.2175	-0.6626
30	1.54	0.0177	0.1875	-0.7270
35	1.50	0.0152	0.1761	-0.7543

Initial 4-Nitrophenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.13. Adsorption Isotherm data for Langmuir Model at different CFA loading (5-35) g for phenol adsorption.

CFA (g)	C_e (mg/l)	Q_e (mg/g)	1/ C_e (l/mg)	1/ Q_e (g/mg)
5	9.06	0.0656	0.1104	15.2346
10	5.96	0.0421	0.1678	23.7417
15	4.35	0.0313	0.2299	31.9489
20	3.55	0.0247	0.2817	40.5269
25	2.62	0.0209	0.3817	47.9478
30	2.17	0.0178	0.4608	56.0853
35	2.03	0.0154	0.4926	64.9351

Initial Phenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.14. Adsorption Isotherm data for Langmuir Model at different CFA loading (5-35) g for 2-Nitrophenol adsorption

CFA (g)	C_e (mg/l)	Q_e (mg/g)	1/ C_e (l/mg)	1/ Q_e (g/mg)
5	9.47	0.0632	0.1056	15.8278
10	6.61	0.0402	0.1513	24.8942
15	4.99	0.0300	0.2004	33.3111
20	3.99	0.0240	0.2506	41.6406
25	3.04	0.0204	0.3290	49.1352
30	2.57	0.0174	0.3891	57.3724
35	2.37	0.0151	0.4219	66.1813

Initial 2-Nitrophenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.15. Adsorption Isotherm data for Langmuir Model at different CFA loading (5-35) g for 4-Nitrophenol adsorption.

CFA (g)	C_e (mg/l)	Q_e (mg/g)	1/ C_e (l/mg)	1/ Q_e (g/mg)
5	3.93	0.0886	0.2545	11.2841
10	2.71	0.0485	0.3690	20.6271
15	2.15	0.0328	0.4651	30.5250
20	1.87	0.0260	0.5348	38.5357
25	1.65	0.0208	0.6061	48.0031
30	1.54	0.0177	0.6494	56.6251
35	1.50	0.0152	0.6667	65.9196

Initial 4-Nitrophenol Concentration (C_o) = 20 mg/l

Volume (V) = 0.030 l

TableA.16. Desorption Efficiency data of CFA from phenol, 2-Nitrophneol and 4-Nitrophenol with H_2O.

Initial CFA dosage (Adsorption) g	CFA Dosage (Desorption) g	Phenol Desorption Efficiency (%)	2-Nitrophenol Desorption Efficiency (%)	4-Nitrophenol Desorption Efficiency (%)
5	4.634	45.1	47.5	16.7
10	9.577	29.9	32.4	14.7
15	14.403	25.2	26.9	12.6
20	19.373	22.3	23.4	11.8
25	24.305	20.1	21.1	11.2
30	29.217	19.3	20.0	10.9
35	34.036	18.4	19.2	10.5
40	39.009	17.9	18.8	10.2

TableA.17. Desorption Isotherm data for Freundlich Model at different CFA loading for Phenol adsorption.

CFA (g)	C_e (mg/l)	Q_i (mg/g)	Log C_e (mg/l)	Log Q_i (mg/g)
4.634	3.40	0.0488	0.5315	-0.2745
9.577	3.23	0.0339	0.5092	-0.2931
14.403	3.15	0.0260	0.4983	-0.3025
19.373	3.00	0.0210	0.4771	-0.3214
24.305	2.91	0.0180	0.4639	-0.3336
29.217	2.88	0.0153	0.4594	-0.3380
34.036	2.79	0.0134	0.4456	-0.3511

TableA.18. Desorption Isotherm data for Freundlich Model at different CFA loading for 2-Nitrophenol adsorption.

CFA (g)	C_e (mg/l)	Q_i (mg/g)	Log C_e (mg/l)	Log Q_i (mg/g)
4.634	3.39	0.0462	0.5302	-0.2756
9.577	3.28	0.0317	0.5159	-0.2875
14.403	3.18	0.0246	0.5024	-0.2989
19.373	3.04	0.0201	0.4829	-0.3162
24.305	2.95	0.0173	0.4698	-0.3281
29.217	2.90	0.0149	0.4624	-0.3350
34.036	2.84	0.0130	0.4533	-0.3436

TableA.19. Desorption Isotherm data for Freundlich Model at different CFA loading for 4-Nitrophenol adsorption.

CFA (g)	C_e (mg/l)	Q_i (mg/g)	Log C_e (mg/l)	Log Q_i (mg/g)
4.634	2.30	0.0891	0.3617	-1.0499
9.577	2.21	0.0472	0.3444	-1.3257
14.403	2.00	0.0330	0.3010	-1.4813
19.373	1.92	0.0251	0.2833	-1.6003
24.305	1.85	0.0204	0.2672	-1.6911
29.217	1.81	0.0171	0.2577	-1.7671
34.036	1.76	0.0146	0.2455	-1.8363

TableA.20. t-Test Report to show difference between Phenol and 2-Nitrophenol.

t-Test: Paired Two Sample for Means		
	Variable 1	*Variable 2*
Mean	0.0234	0.022835
Variance	1.97325E-07	1.36906E-07
Observations	9	9
Pearson Correlation	0.993839939	
Hypothesized Mean Difference	0	
df	8	
t Stat	19.53152574	
P(T<=t) one-tail	2.45383E-08	
t Critical one-tail	1.859548033	
P(T<=t) two-tail	4.90766E-08	
t Critical two-tail	2.306004133	

The t-test table showed that the adsorption of the two compounds are significantly higher for phenol $\left(t_{0.05}Stat\ df\left(8\right)19.532 > t_{0.05}Table\ df\left(8\right)2.306\right)$ than that of 2-Nitrophenol.

APPENDIX B

Adsorption Isotherm Plots

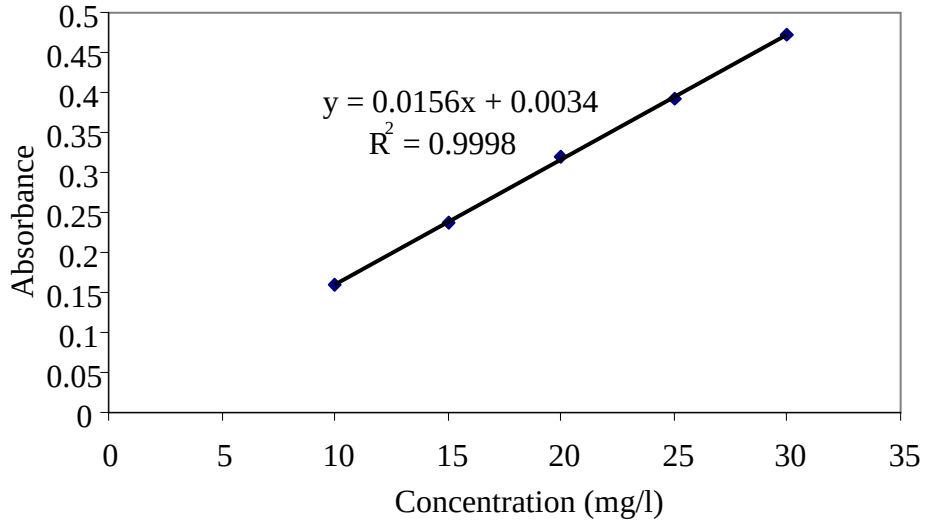


Figure B.1. Standard curve for phenol concentrations (10-30) mg/l at 269.0 nm

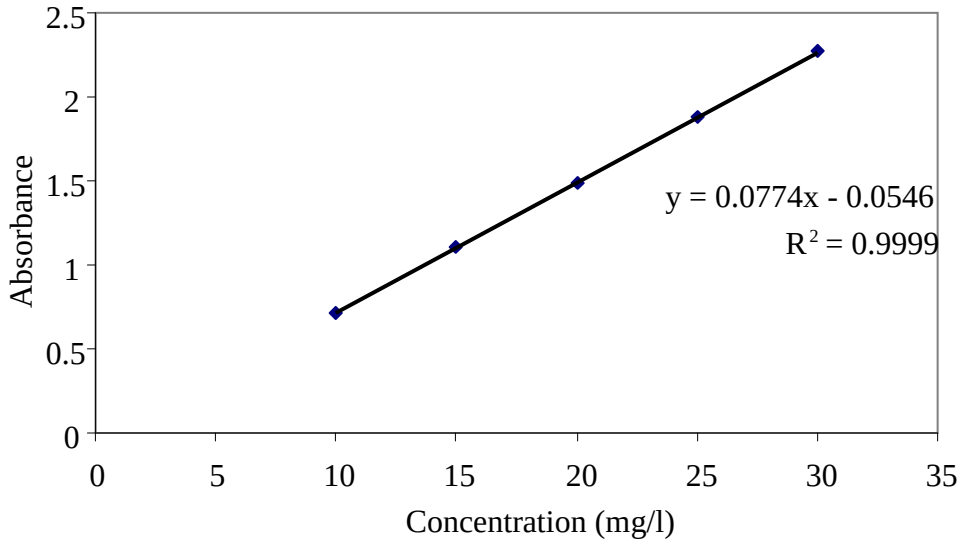


Figure B.2. Standard curve for phenol from the mixture of 2-Nitrophenol and 4-Nitrophenol concentrations (10-30) mg/l at 269.0 nm

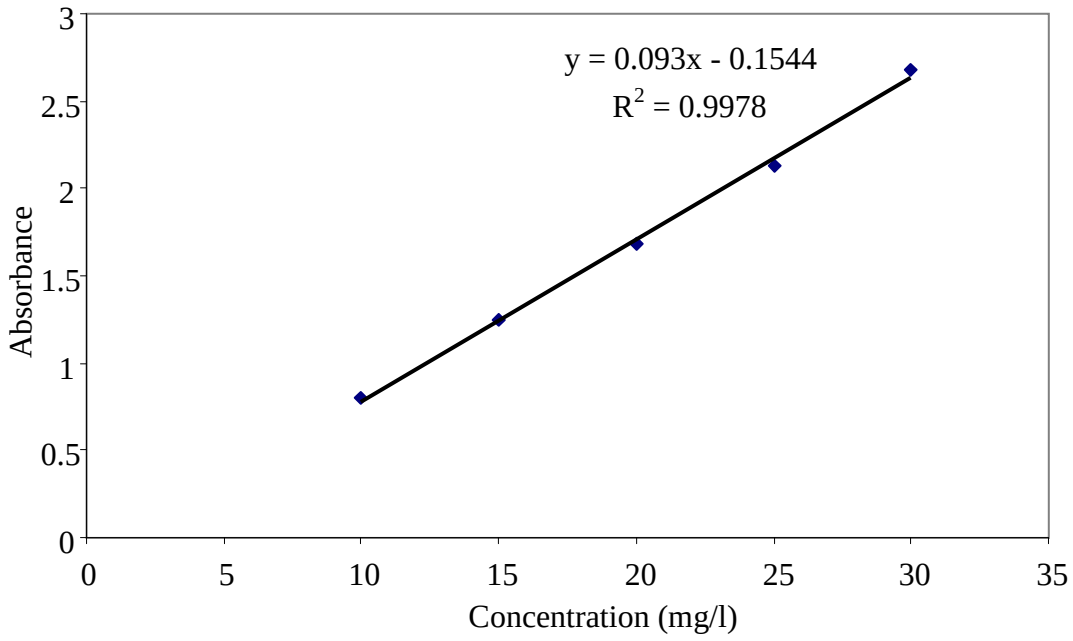


Figure B.3. Standard curve for 2-Nitrophenol from the mixture of phenol and 4-Nitrophenol concentrations (10-30) mg/l at 277.5 nm.

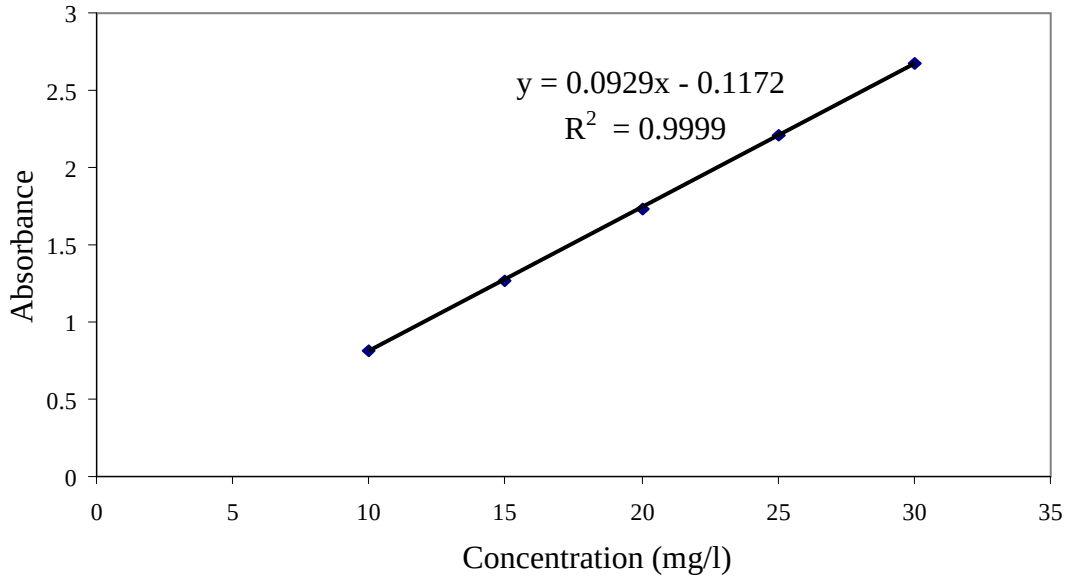


Figure B.4. Standard curve for 4-Nitrophenol from the mixture of phenol and 2-Nitrophenol concentrations (10-30) mg/l at 320.5 nm.

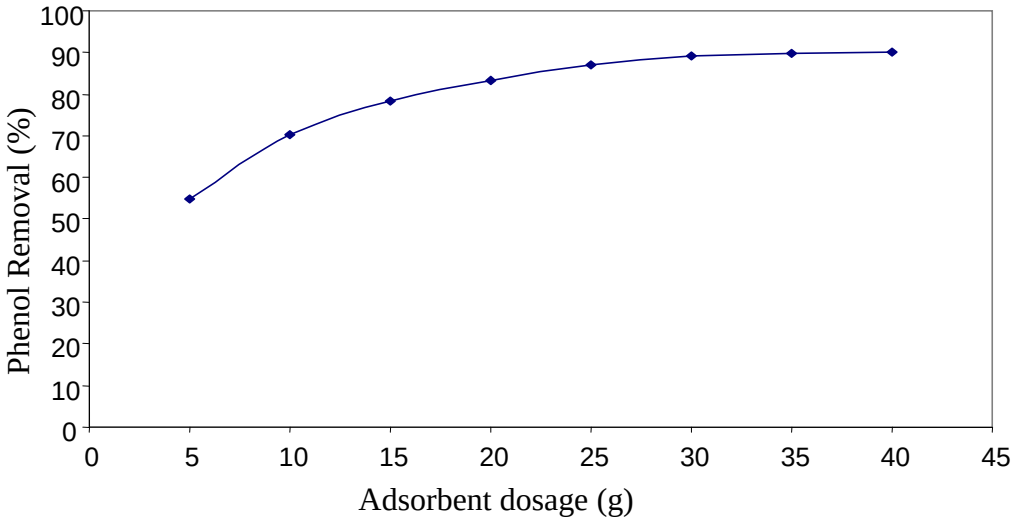


Figure B.5. Effect of adsorbent dosage on the removal of phenol from 2-Nitrophenol and 4-Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of CFA (5-40) g.

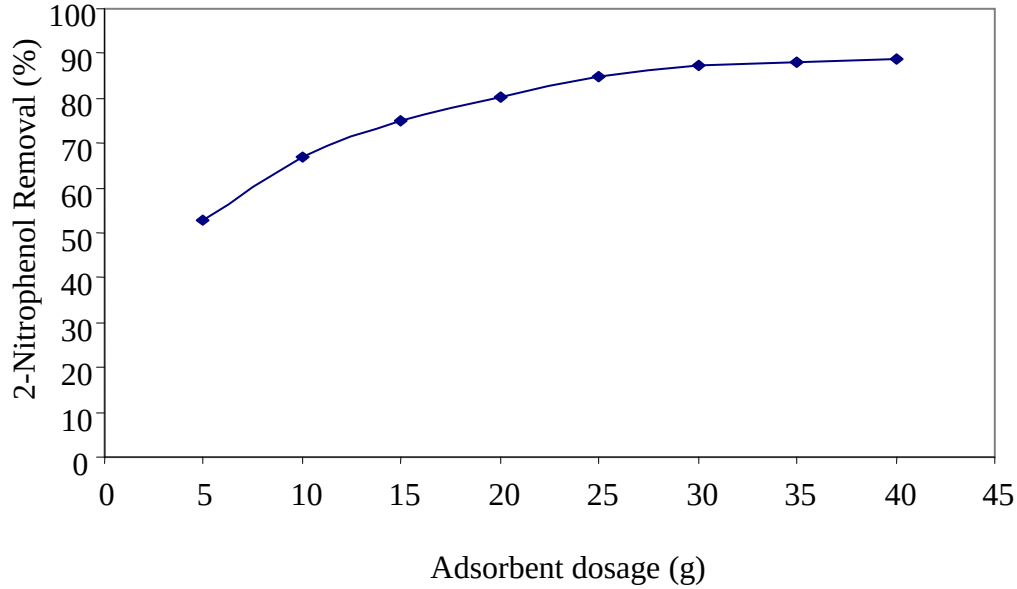


Figure B.6. Effect of adsorbent dosage on the removal of 2-Nitrophenol from phenol and 4-Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of CFA (5-40) g.

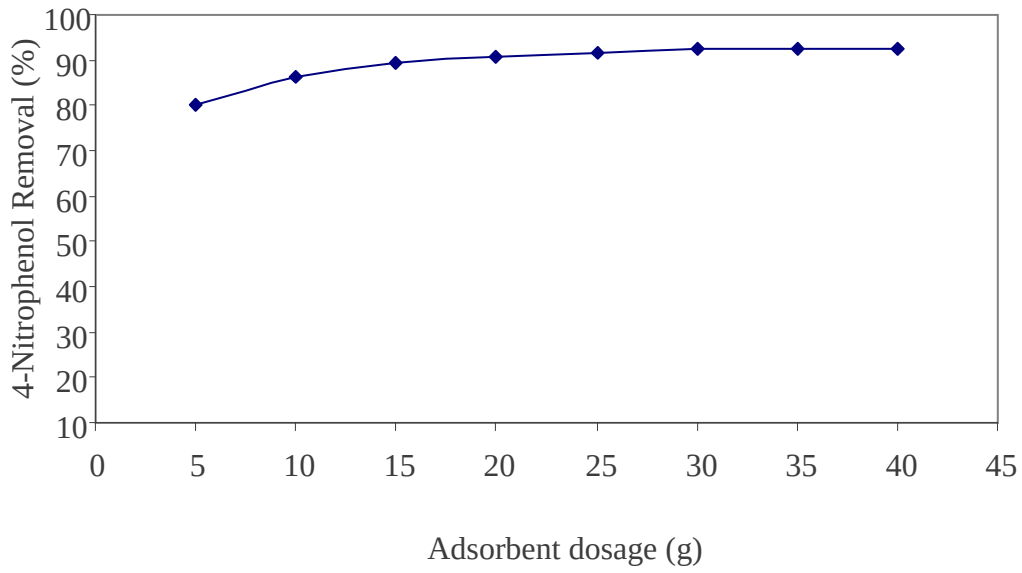


Figure B.7. Effect of adsorbent dosage on the removal of 4-Nitrophenol from phenol and 2-Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of CFA (5-40) g.

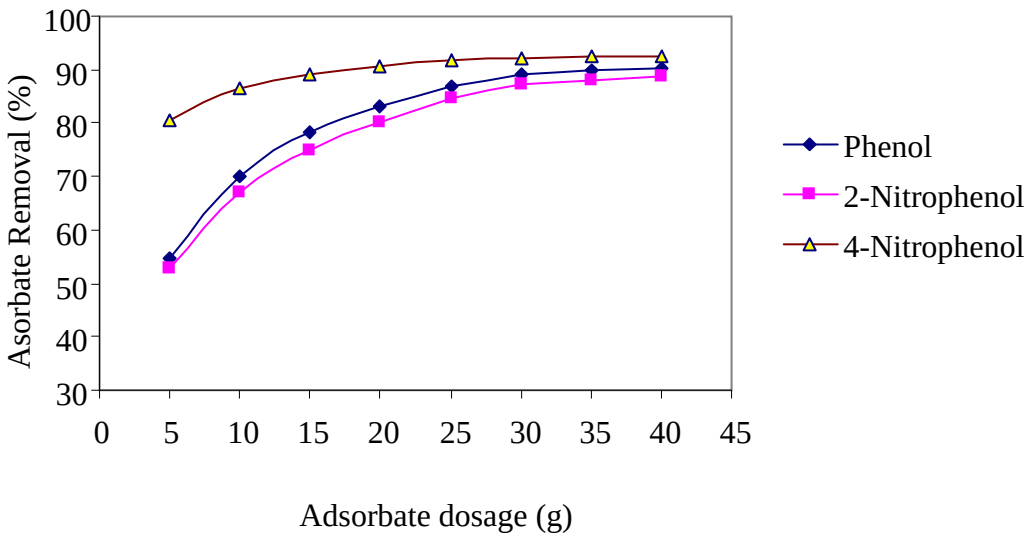


Figure B.8. Effect of adsorbent dosage on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at (pH 2.220),C_o; 20 mg/l and different loading weight of CFA (5-40) g.

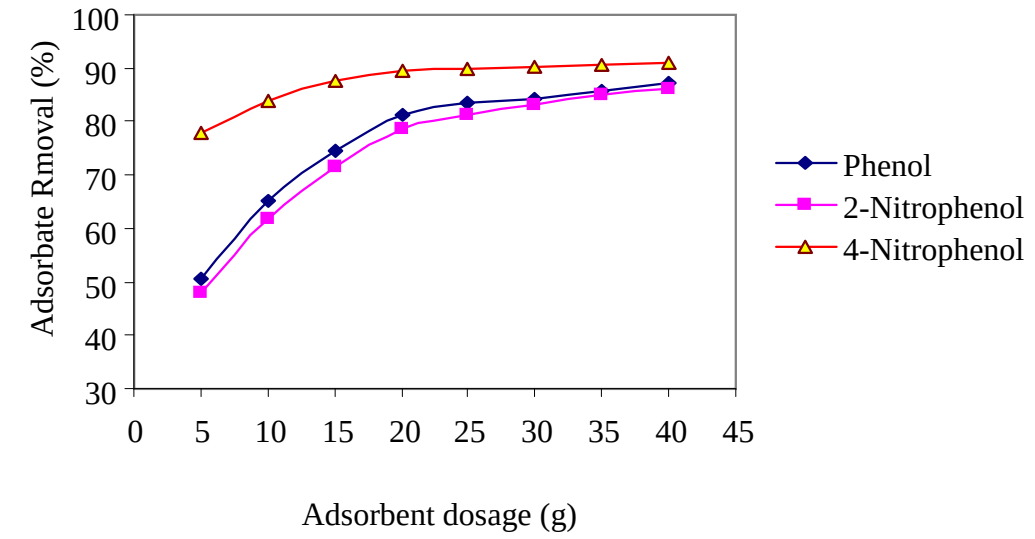


Figure B.9. Effect of pH on the removal of phenol, 2-Nitrophenol and 4-Nitrophenol at (pH 5.978),C_o; 20 mg/l and different loading weight of CFA (5-40) g

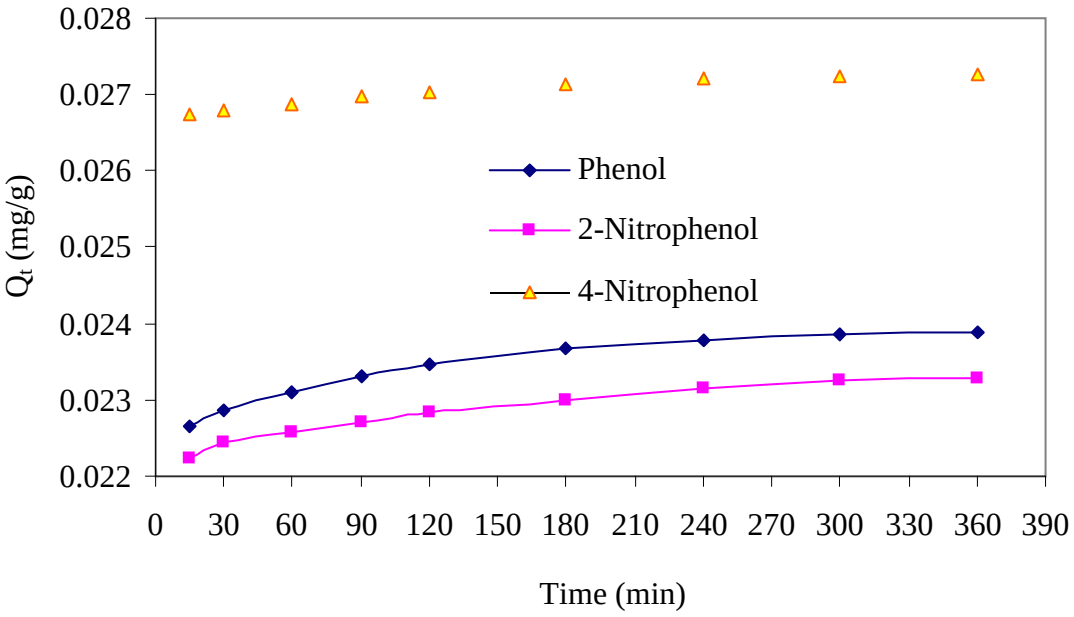


Figure B.10. Effect of contact time on the amount of Phenol, 2-Nitrophenol and 4-Nitrophenol removed from aqueous solution with CFA. Operating condition Co; 20 mg/l, RPM; 300, FA; 20g and Volume; 30 ml.

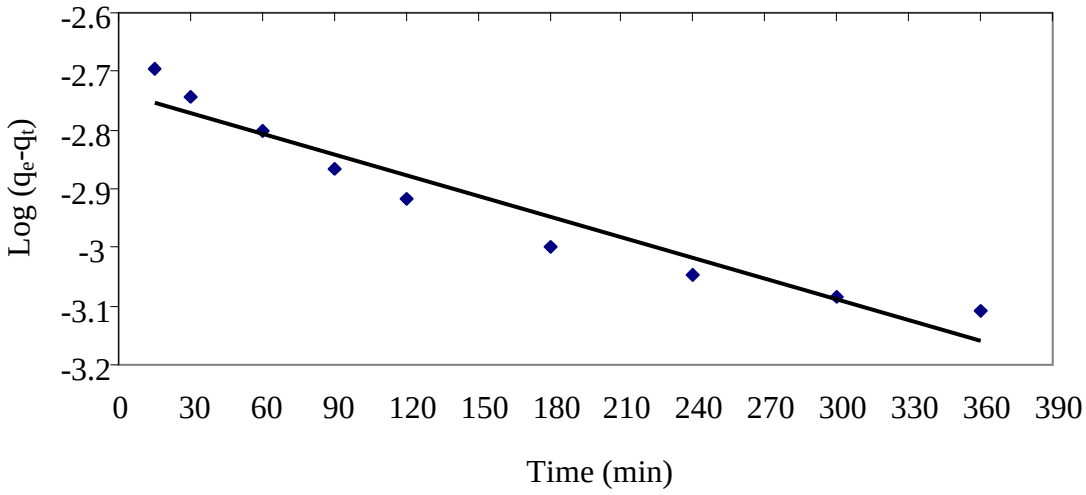


Figure B.11. Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of phenol studied at concentration of 20mg/l.

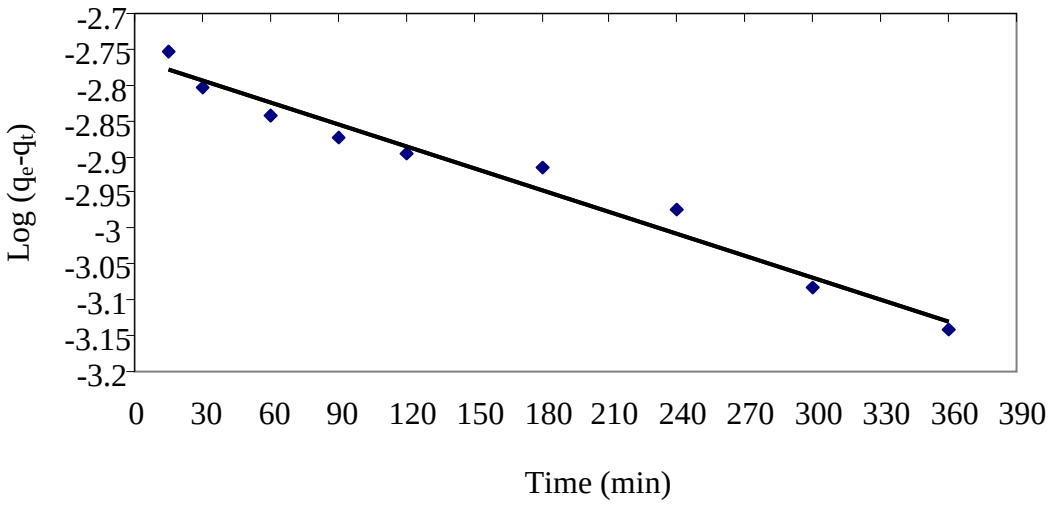


Figure B.12. Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 2-Nitrophenol studied at concentration of 20mg/l.

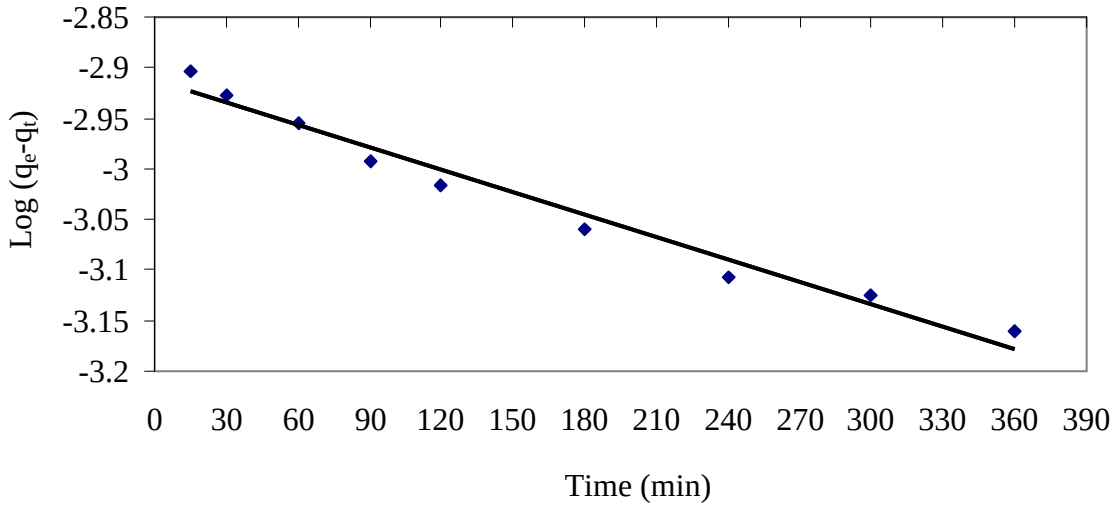


Figure B.13. Linear plot of $\log(q_{e-}q_t)$ versus t for the kinetic removal of 4-Nitrophenol studied at concentration of 20mg/l.

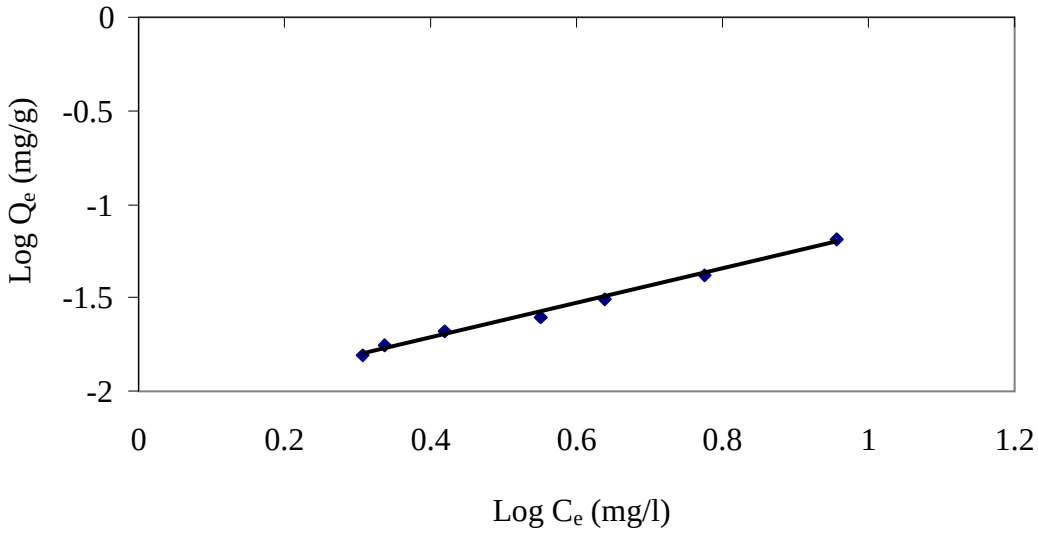


Figure B.14. The linearized Freundlich Adsorption Isotherm for Phenol with CFA.

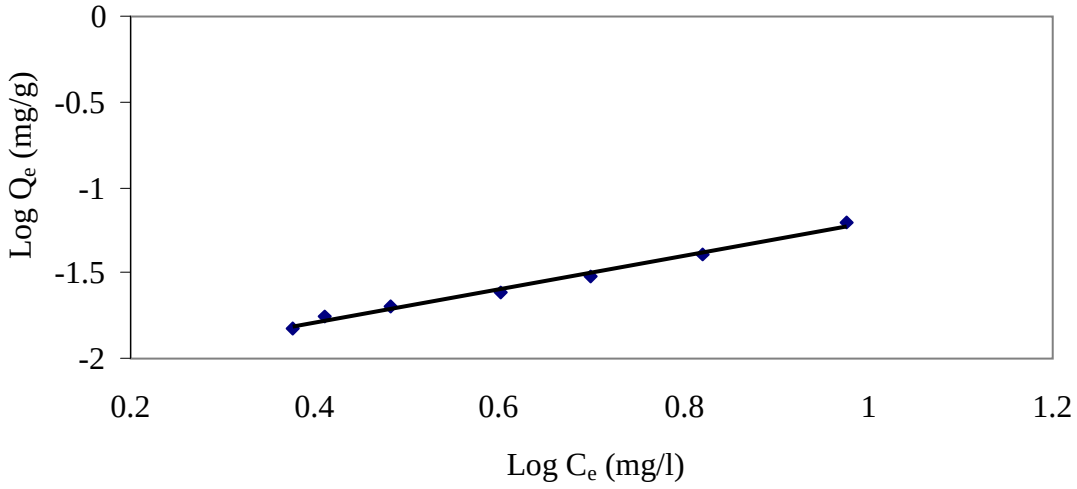


Figure B.15. The linearized Freundlich Adsorption Isotherm for 2-Nitrophenol with CFA.

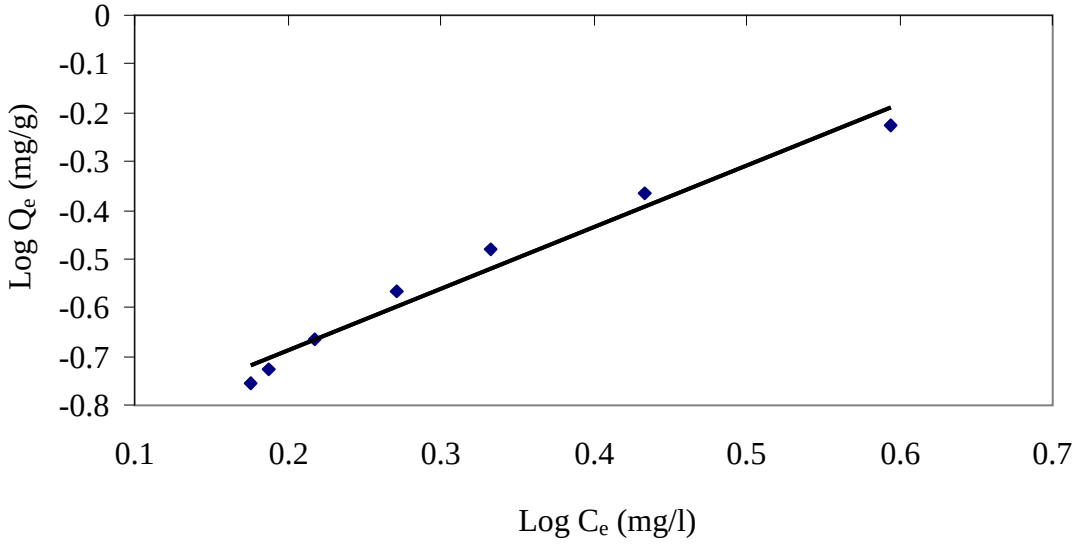


Figure B.16. The linearized Freundlich Adsorption Isotherm for 4-Nitrophenol with CFA.

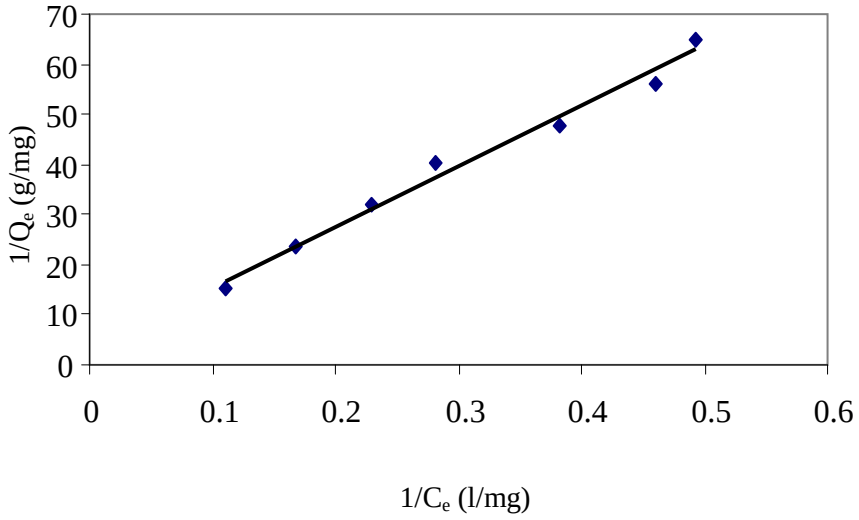


Figure B.17. The linearized Langmuir Adsorption Isotherm for Phenol with CFA.

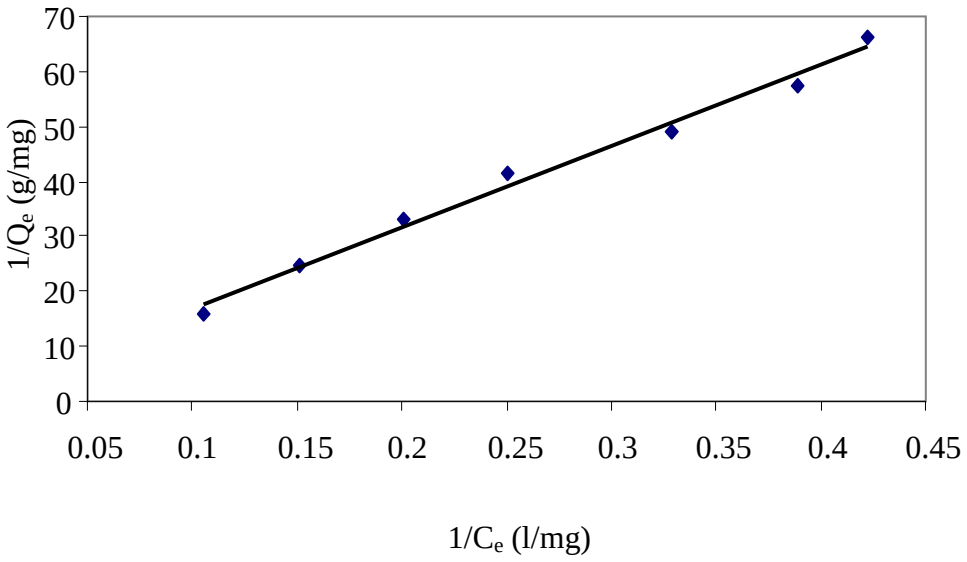


Figure B.18. The linearized Langmuir Adsorption Isotherm for 2-Nitrophenol with CFA.

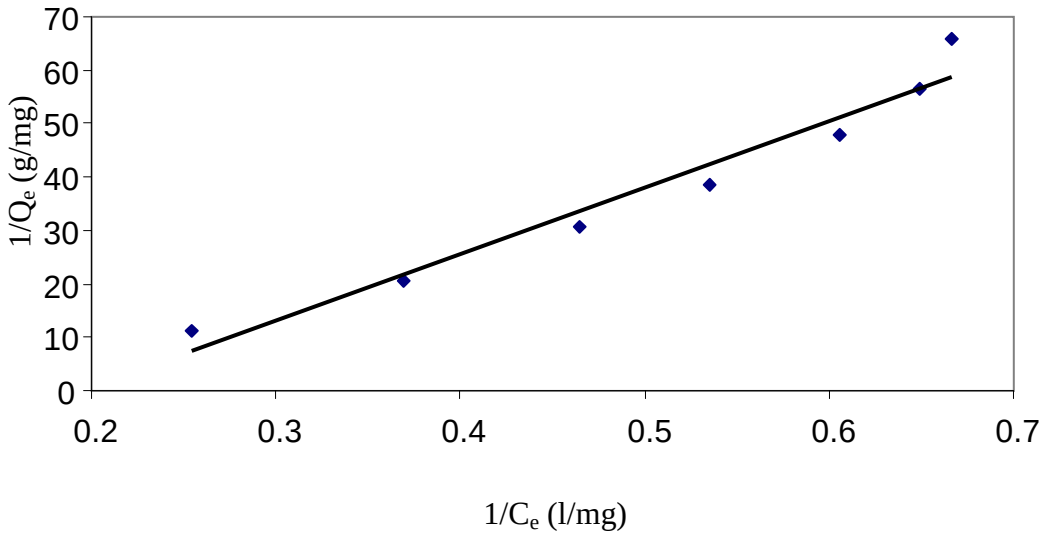


Figure B.19. The linearized Langmuir Adsorption Isotherm for 4-Nitrophenol with CFA.

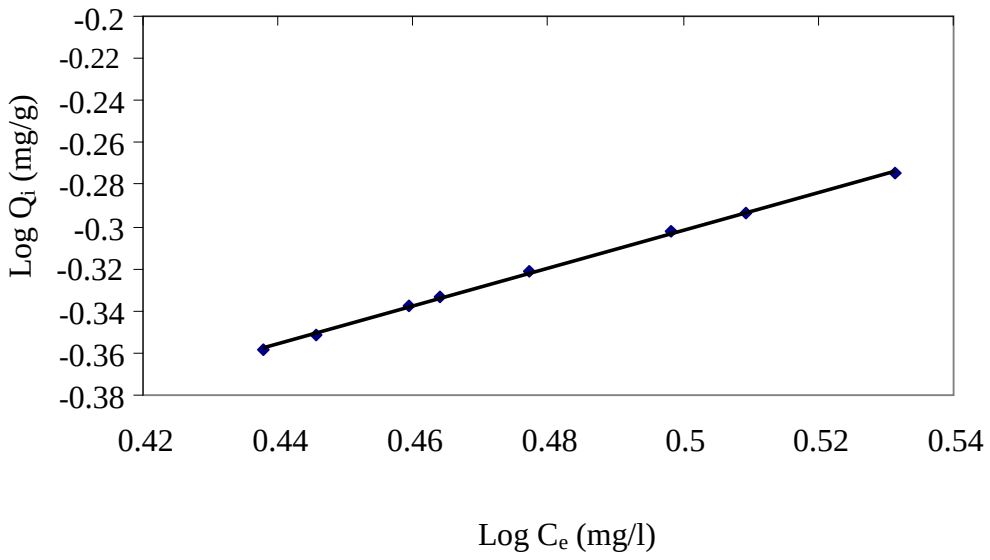


Fig.B.20: The linearized Freundlich Desorption Isotherm for Phenol with CFA.

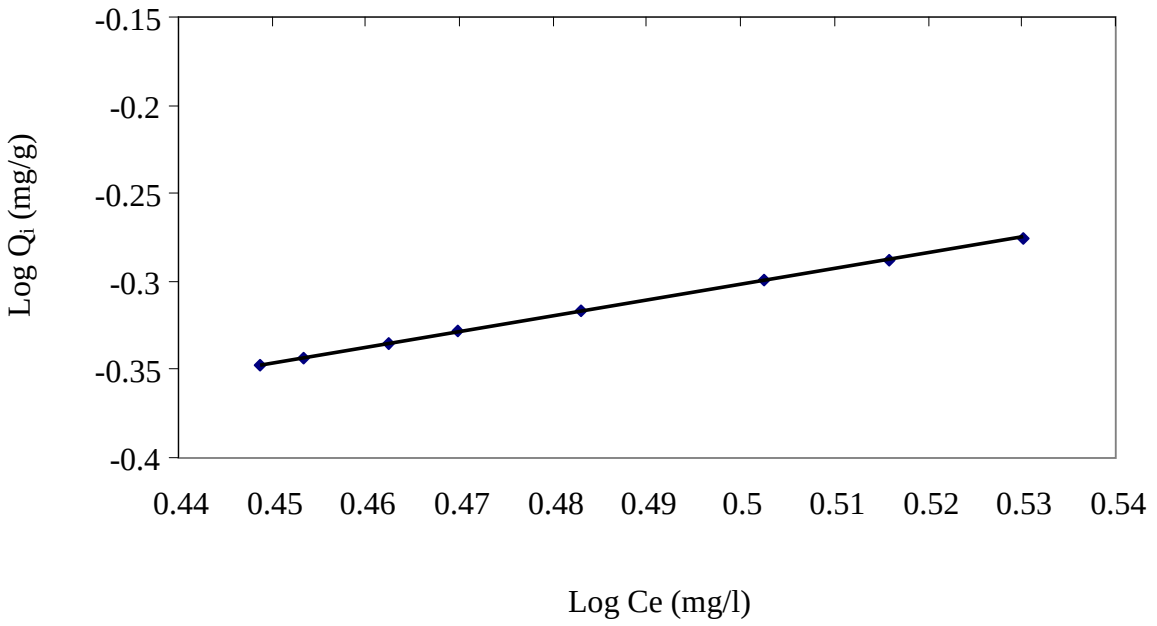


Figure B.21. The linearized Freundlich Desorption Isotherm for 2-Nitrophenol with CFA.

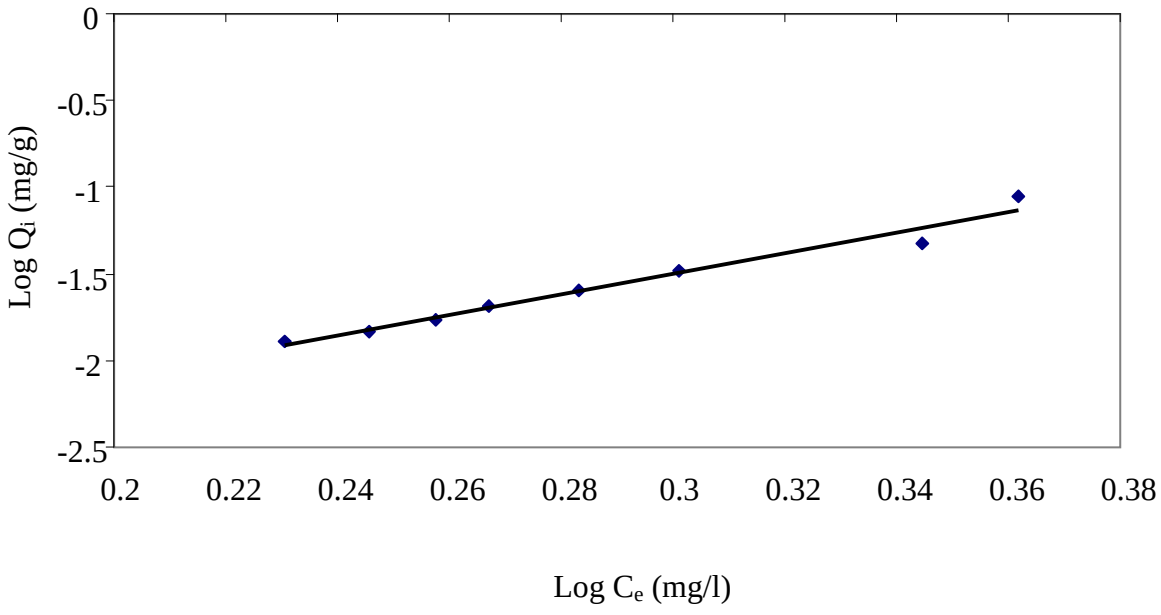


Figure B.22. The linearized Freundlich Desorption Isotherm for 4-Nitrophenol with CFA.

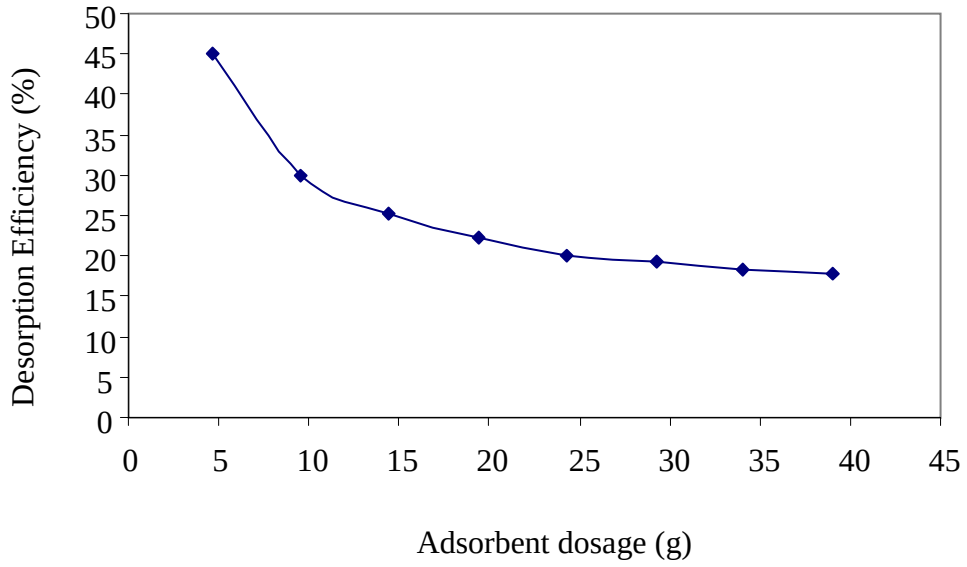


Figure B.23. Influence of adsorbent dosage on the desorption of phenol from CFA.

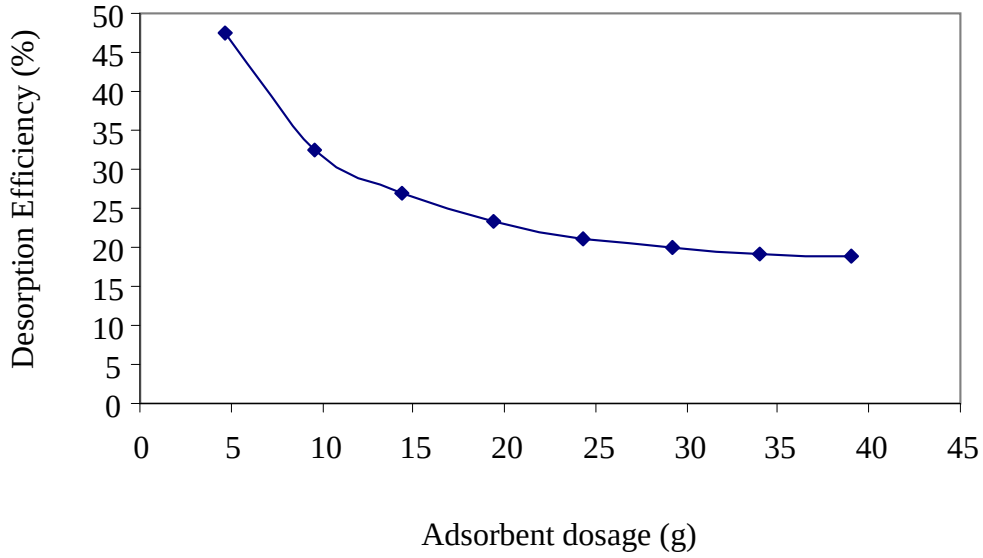


Figure B.24. Influence of adsorbent dosage on the desorption of 2-Nitrophenol from CFA.

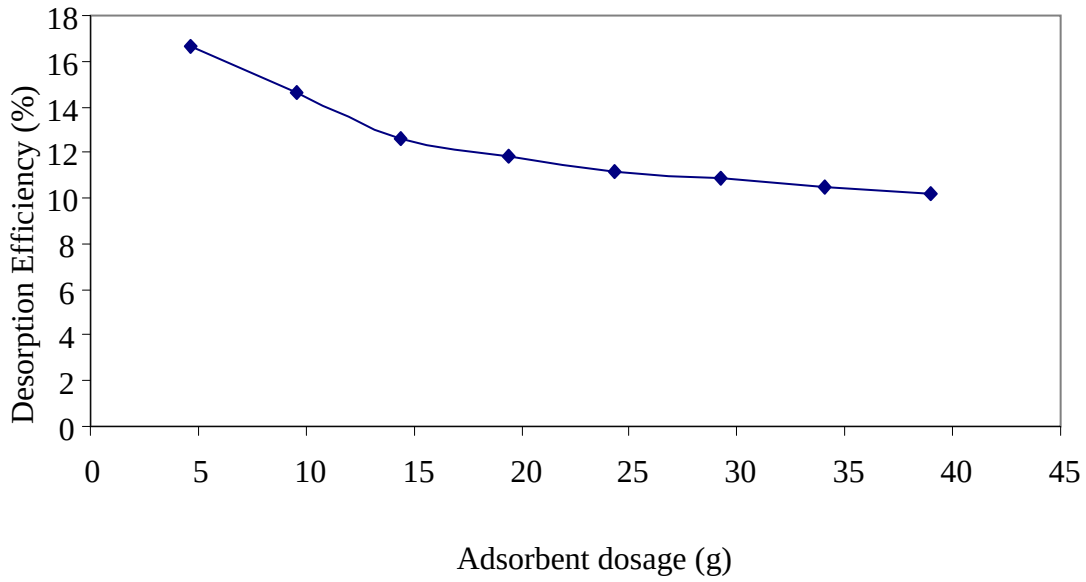


Figure B.25. Influence of adsorbent dosage on the desorption of 4-Nitrophenol from CFA.

APPENDIX C

Dynamic Column Studies Data

Table C.1

Input data for design calculations

Parameters	Values
BET Surface area (m^2/g)	1.279
Pore volume (cm^3/g)	0.001437
Maximum Particle size (µm)	< 99
Solution pH	2.22
Feed Concentration	20 mg/l
Adsorbent loading (g)	10/15/20
CFA bed height (mm)	30/40/50
Column Internal Diameter (mm)	20.00
Fluid flow rate (ml/min)	3.00

Table C.2. Breakthrough Times for Phenol Adsorption.

Service Time (h)	30 mm Bed height % Phenol Remaining	40 mm Bed height % Phenol Remaining	50 mm Bed height % Phenol Remaining
0	0	0	0
0.3	0	0	0
1	27.3	0	0
1.3	41.25	13.95	0
2	60.35	22	6.2
2.3	64.75	24.25	10.3
3	65.1	29.05	16
3.3	67.27	38.35	18.55
4	68.3	47.65	19.8
4.3	69.1	50.68	27.73
5	69.95	53.7	35.65
5.3	72.05	57.23	42.45
6	73.5	60.75	49.25
7	75.1	63	54.3
8	76.5	63.35	58.4
9	81.8	64.6	62.2
10	84.65	66.85	63.5
11	85.3	67.5	63.8
12	86.25	69.4	64.45
13	87.2	70.05	65.05
14	87.8	70.7	66.35
15	88.5	72	67
16	89.1	72.65	67.3
17	89.4	74.25	68.55
18		75.5	69.2
19		77.75	72.05
20		81.3	74.85
21		82.25	77.4
22		83	78.65
23			79.3
24			80.25
25			81.25
26			

Table C.3. Breakthrough time for phenol (h) at BDST of 30 % & 70 %

Bed depth (mm)	Phenol 30 % t_b (h)	Phenol 70 % t_b (h)
30	1.00	5.00
40	3.00	12.40
50	4.50	18.20

APPENDIX D

Dynamic Column Studies Plots

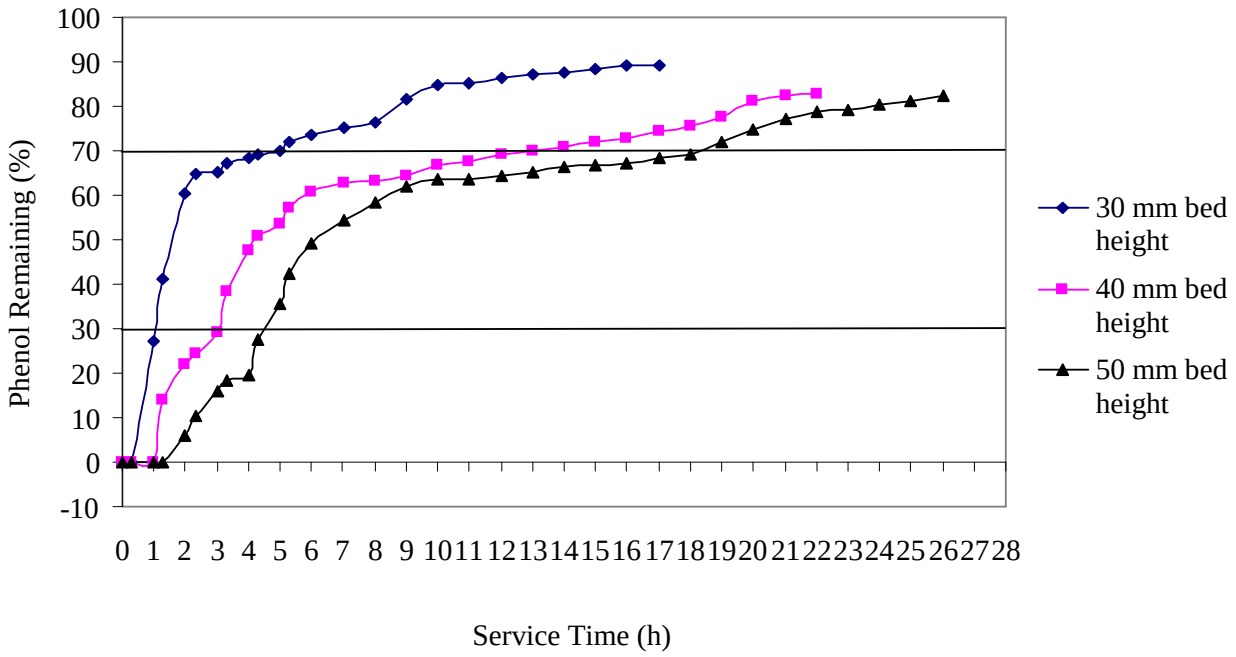


Figure D.1. Breakthrough curves for Phenol Adsorption at 30 & 70 % concentration remaining.

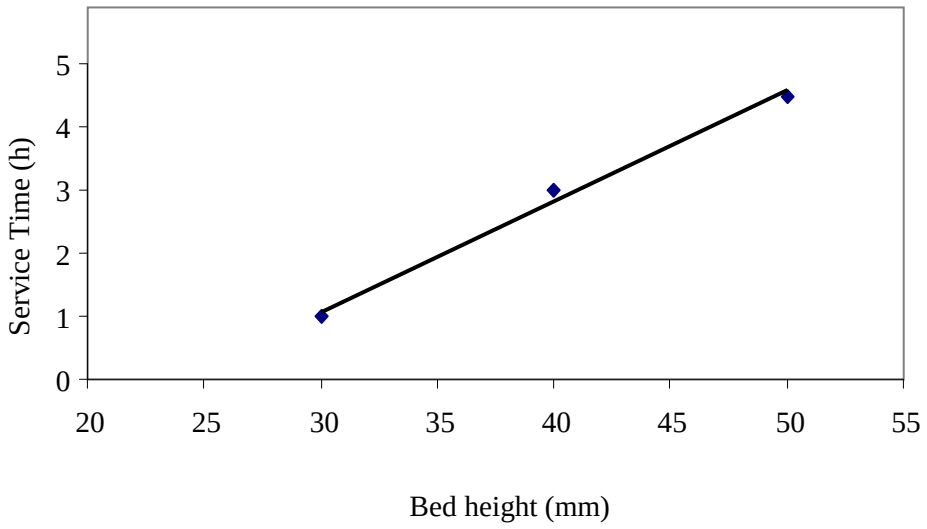


Figure D.2. BDST plot at 30 % breakthrough point for Phenol Adsorption determined from actual Experimental data.

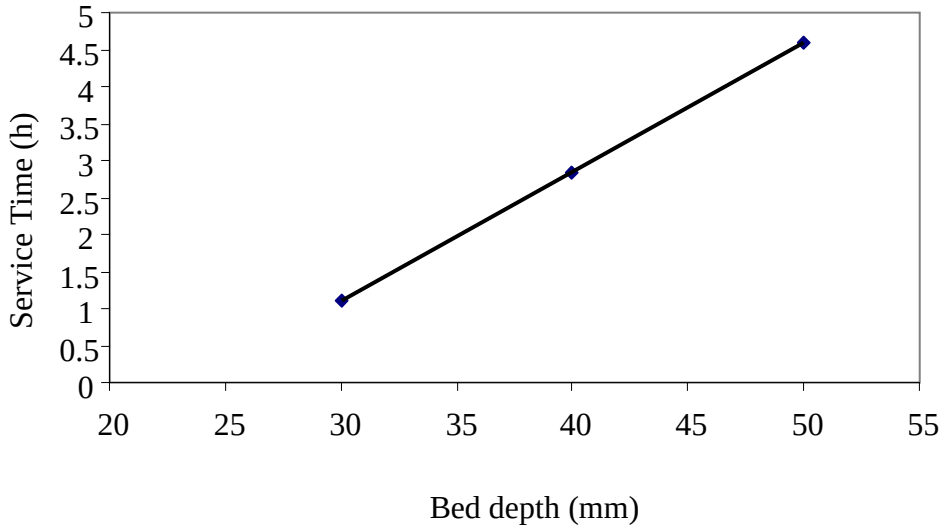


Figure D.3. BDST plot at 30 % breakthrough point for Phenol Adsorption determined from theoretical approach.

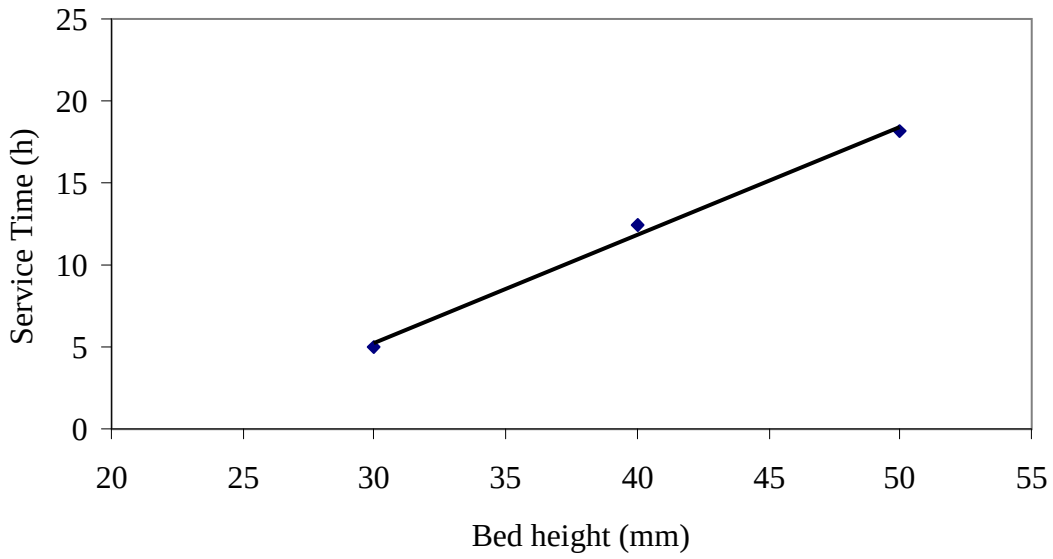


Figure D.4. BDST plot at 70 % breakthrough point for Phenol Adsorption determined from actual Experimental data.

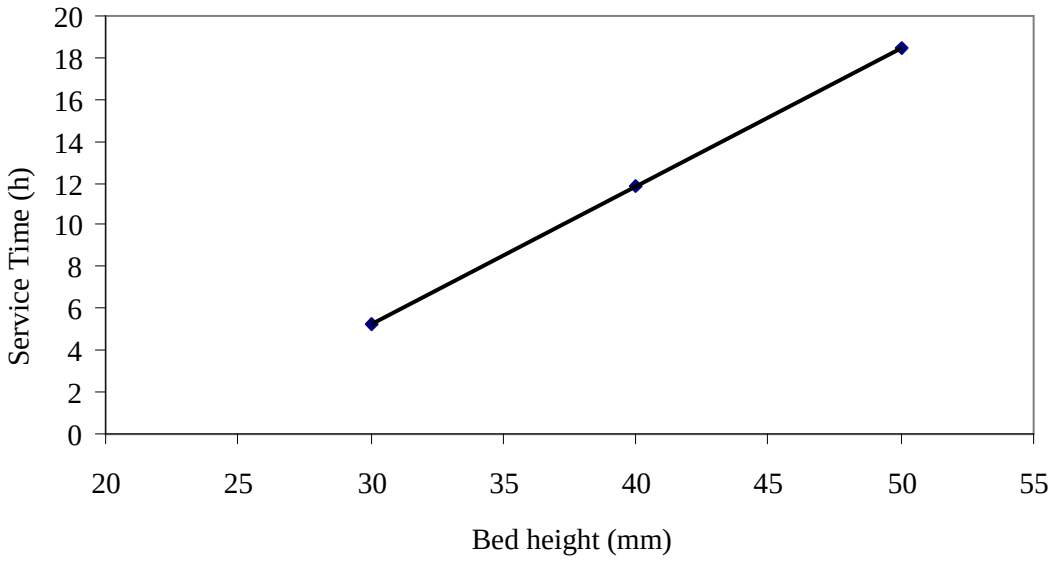


Figure D.5. BDST plot at 70 % breakthrough point for Phenol Adsorption determined from theoretical approach.

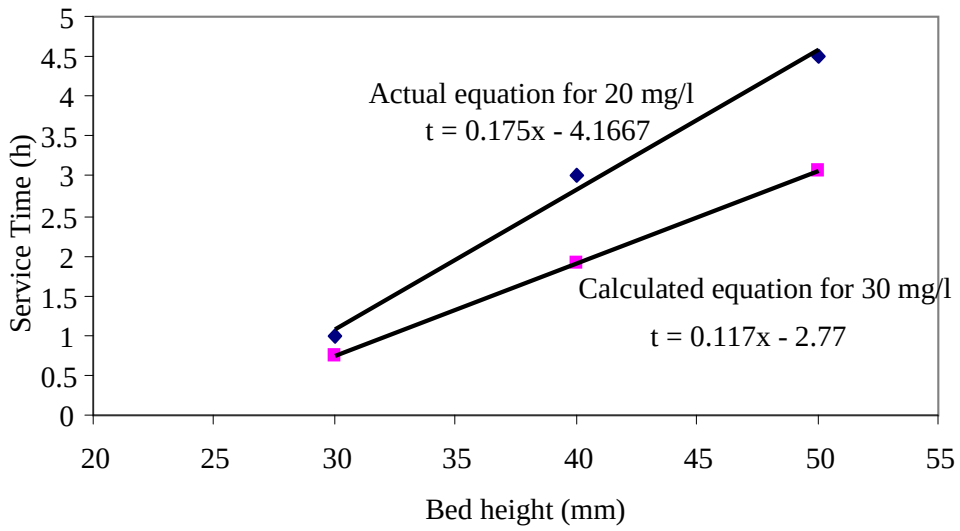


Figure D.6. Comparison of BDST model predictions based on C_o: 20 mg/l with calculated BDST for phenol adsorption with C_o: 30 mg/l.