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Treatment of Oil Sands Process-Affected Water Using Activated and Surface Modified Petroleum Coke for Organic Compounds Recovery

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A thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemical and Biochemical Engineering

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Abstract

Each day large volumes of oil sands process-affected water (OSPW) are being produced during the extraction of bitumen in oil sands industry in northern Alberta. OSPW contains different polyaromatic hydrocarbons which not only are the major source of toxicity in OSPW, but also create operational problems such as corrosion of the equipment during bitumen recovery process. Therefore, these compounds need to be removed prior to the recycle of the OSPW. In this research, petroleum coke (PC) as an abundant, inexpensive adsorbent was selected as an adsorbent for recovery of chemicals from OSPW. The surface area and adsorption capacity of PC were increased through several processes such as KOH activation, surface modification, and optimization. The Box-Behnken design and response surface methodology were employed to optimize KOH activation parameters for the production of activated petroleum coke (APC). APC adsorbent with a BET surface area of $1726 \text{ m}^2/\text{g}$ and total pore volume of 0.85 cc/g was produced at the optimum activation conditions (KOH/coke mass ratio of 3.0, activation temperature $790 \text{ }^\circ\text{C}$, and activation time 3.47 hr). The produced APC at optimum condition was tested in batch and bench scale continuous adsorption column for adsorption of model compounds and treatment of OSPW. Furthermore, two different amination processes including a single stage treatment with ammonia gas at an elevated temperature and a two-step treatment of nitration followed by reduction were adopted. The results showed an excellent adsorption capacity for the model NAs and OSPW at $\text{pH} = 4.0$. Ammonia treatment was more effective on improvement of adsorption capacity than the nitration followed by reduction method. The results of the PLS model shows that the pH of the solution and the NH_3 surface modification are the most important contributors that affect the adsorption capacity of APC. The result of this study provides an effective treatment method for OSPW by using APC. The TOC of OSPW could be reduced by 96 percent after a two steps treatment including pH adjustment and adsorption by APC. The APC could be regenerated easily using a solution of methanol and sodium hydroxide and could be reused in several cycles.

Keywords:

Oil sands process-affected water, Naphthenic acids, Adsorption, Petroleum coke, KOH activation, Surface modification, Optimization, Box-Behnken design, Batch and Column study, Projection to latent structure modelling

Co-Authorship Statement

Chapter 3: Preparation of activated petroleum coke for removal of naphthenic acids model compounds: Box-Behnken design optimization of KOH activation process

Authors: Hojatallah Seyedy Niasar, Hanning Li, Sreejon Das, Tirumala Venkateswara Rao Kasanneni, Madhumita B. Ray, Chunbao (Charles) Xu

Design of experiments and statistical analysis suggested by Dr. Charles (Chunbao) Xu was performed by Hojatallah Seyedy Niasar. The activated petroleum coke at different condition was prepared by Dr. Hanning Li and Hojatallah Seyedy Niasar. The prepared activated petroleum coke was tested in batch experiments by Hojatallah Seyedy Niasar. The BET analysis was conducted by Fang (Flora) Cao, and the SEM images were taken by Hojatallah Seyedy Niasar. All the steps from design of experiment to the writing was supervised by Dr. Madhumita Ray and Dr. Charles (Chunbao) Xu. Furthermore, the final version of the draft was revised and edited by Dr. Madhumita Ray and Dr. Charles (Chunbao) Xu.

Chapter 4: Surface Amination of Activated Carbon and Petroleum Coke for the Removal of Naphthenic Acids and Treatment of Oil Sands Process Water (OSPW)

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The experiments related to activation of petroleum coke were conducted by Dr. Hanning Li and Hojatallah Seyedy Niasar. The adsorption batch experiments were conducted by Hojatallah Seyedy Niasar with the help and supervision of Dr. Tirumala Venkateswara Rao Kasanneni. Also, Dr. Tirumala Venkateswara Rao Kasanneni was involved on writing and analysis of obtained surface modified adsorption data. The final version of the draft was revised by Dr. Madhumita Ray and Dr. Charles Xu. This work has been published in “*Chemical engineering journal*”.

Chapter 5: Continuous column adsorption of naphthenic acids from real and synthetic oil sands process-affected water (OSPW) using commercial and activated petroleum coke (APC)

Authors: Hojatallah Seyedy Niasar, Sreejon Das, Madhumita B. Ray, Chunbao (Charles) Xu

The experiments were designed by Hojatallah Seyedy Niasar under supervision of Dr. Charles (Chunbao) Xu and Dr. Madhumita Ray. The experiment setup was designed and assembled by Sreejon Das and Hojatallah Seyedy Niasar. The adsorption and desorption experiment data were obtained by Hojatallah Seyedy Niasar and Sreejon Dar respectively. The analysis of fresh and exhausted adsorbents was conducted by Fang (Flora) Cao. The work was done in consultation with and under the supervision of Dr. Madhumita Ray and Dr. Charles (Chunbao) Xu. This study was revised by both mentioned professors to the final version.

Chapter 6: Application of projection to latent structures (PLS) model to the adsorption of model naphthenic acids by raw and surface modified activated petroleum coke

Authors: Hojatallah Seyedy Niasar, Madhumita B. Ray, Stanislav Ivanov, Chunbao (Charles) Xu

The batch experiment data collected in chapters 3 and 4 was used to develop a projection to latent structures (PLS) model by Hojatallah Seyedy Niasar and Stanislav Ivanov. The results and discussion was conducted by Hojatalaah Seyedy Niasar and Dr. Madhumita Ray and Dr. Charles (Chunbao) Xu were revised the initial draft to the final format.

Acknowledgments

Through the past four years of my PhD, lots of people have helped me to successfully finish this work, whom without their help this work would have been much harder or even impossible to complete.

Foremost, I would like to show my sincere gratitude to my supervisors Professor Charles (Chunbao) Xu and Professor Madhumita (Mita) B. Ray for their continuous support, immense knowledge, and valuable guidance. I will always look at them as my mentors. At times when I saw my supervisors hard at work late at nights, I learned that success is not accidental; it needs ambition and sacrifice. I will forever appreciate the conversations we have had about non research-related topics, about life and success.

During the past four years, I met people who supported me in the lab and also out of campus. I wish to deeply thank Fang (Flora) Cao, Fate Hashemi, Dr. Zhongshun (Sean) Yuan, Dr. Tirumala Venkateswara Rao Kasanneni, and Dr. Hanning Li who greatly helped me in experiments and data analysis. I would like to express my sincere appreciation to my friends, Alfredo Martinez-Iglesias, Sreejon Das, Amin Jabery, Vahid Vajihinejad, Saber Ayatollahi, Manoli Kiryakos, Olufemi popoola, Nazanin Afghan, and Arman Abtahi who supported me not only in my studies but also in my everyday life during the past four years.

I would like to show my special thanks to my wife, Vida Rahmani, who was always been by my side and has supported me. During the past four years, she was also busy with her PhD studies at McMaster University and it was only during the weekends that I could go back to Hamilton and we were able to spend time together. This was hard for both of us, especially for her. I want to deeply thank her for her understanding and her support. I wish to extend my sincere gratitude to my mother-in-law and father-in-law, Razieh Radfar and Dr. Hamidreza Rahmani for their encouragement and full support, not only during the past four year, but since the time that we met.

Last but not least, I would like to show my heartfelt appreciation to my parents, whom without their love, sacrifice, encouragement, and support, I would not have reached this stage of my life. I will never forget their hard work and the sacrifices they have made so I can pursue my dreams and proceed my education. All I really aim for in life is demonstrating the love I have for them by making them proud of me.

I would also like to mention that this research would not have been possible without the kind financial support provided by the University of Western Ontario Graduate Studies, the Department of Chemical and Biochemical Engineering at the University of Western Ontario (Teaching Assistantship, Graduate Research Scholarship), and Ontario Graduate Scholarships. Support from our industrial partner, NEWALTA Company is also greatly acknowledged.

Hojatallah Seyedy Niasar

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July 2017

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Nomenclature

Symbol	Meaning	Unit
b	Sips adsorption constant	$(L/mg)^{(1/n)}$
C	Concentration	mg/L
F	Flow rate	mL/min
$K_{dif.}$	Intra-particle diffusion constant	$mg/g \text{ min}^{0.5}$
K_f	Freundlich adsorption constant	$(mg/g) / (mg/L)^{(1/n)}$
K_L	Langmuir adsorption constant	L/mg
K_{Th}	Thomas rate constant	mL / (min mg)
m	Mass	gram
Q	Adsorption capacity	mg/g
Q_m	Maximum adsorption capacity	mg/g
S	Surface area	m^2/g
T	Temperature	$^{\circ}C$
t	Time	Minute
V	Volume	Liter

Abbreviations

AC	Activated carbon
APC	Activated petroleum coke
CAC	Commercial activated carbon
CP	Cyclohexanepentanoic acid
CSS	Cyclic steam simulation
FTIR	Fourier transform infrared
GC/MS	Gas chromatography mass spectroscopy
HPLC	High pressure liquid chromatography
ICP	Inductively coupled plasma
MR	Molar refractivity
MV	Molecular volume
NAs	Naphthenic acids
OSPW	Oil sands process-affected water
PAH	Polycyclic aromatic hydrocarbon
PC	Petroleum coke
PCA	Principal component analysis
PLS	Projection to latent structure
PSA	Polar surface area
RMSEE	Root mean squared error of estimation
RSM	Response surface methodology
SAGD	Steam assisted gravity drainage
SEM	Scanning electron microscopy
SPE	Squared prediction error
TOC	Total organic carbon

Chapter 1

1 General introduction

The main objective of this research was to provide an efficient treatment method for the recovery of organics such as naphthenic acids (NAs) and polycyclic aromatic hydrocarbons (PAHs) from Alberta's oil sands process-affected water (OSPW) by adsorption utilizing cost effective and applicable adsorbents derived from petroleum coke. The challenge with petroleum coke (PC) as an adsorbent is however its low adsorption capacity due to its low surface area^{1,2}. In this research, the surface area and adsorption capacity of PC were increased through several processes such as activation, surface modification, and optimization, and the activated petroleum coke (APC) was used as a adsorbent for NAs in batch tests with model compounds and OSPW. Furthermore, the produced APC at optimum condition was tested in a bench scale continuous adsorption column for treatment of OSPW. The regeneration capability of the APC was tested, and a mathematical model was developed to describe the process.

1.1 Background

1.1.1 Athabasca's oil sands extraction process

Alberta has the third largest proven oil reserve after Saudi Arabia and Venezuela in the world³. This large amount of oil reserve is in the form of oil sands, and it makes the extraction process difficult and costly. There are several extraction methods, and the most common ones are open pit mining and in-situ operations (such as cycle steam stimulation, steam assisted gravity drainage, vapor extraction process). In open pit mining operation, the bitumen needs to be washed out from sands particles with hot water which contains a mixture of chemical additives⁴. Different studies reported different values for the required amount of fresh water for surface mining operation of oil sands. For example, McQueen *et al.*⁵ reported about 1.6 barrel of fresh water for extraction of each barrel of crude oil.

Other researchers have reported a value of approximately 2-2.5 barrels of fresh water for extraction of 1 barrel of bitumen⁶. Oil sands mining operations are licensed to take 445 million m³ of water per year from the Athabasca River⁷. At least 90% of this water ends up as OSPW, a toxic wastewater in tailings ponds⁸.

Annually, a large volume of OSPW is accumulated in the tailings ponds in Alberta, Canada, covering more than 50 square kilometers and can be seen from space⁸ (Figure 1.1). Based on the zero discharge policy⁹⁻¹², the extraction companies cannot drain this wastewater into the environment, and it needs to be treated prior to discharge.



Figure 1.1: Tailings ponds at Athabasca region, Alberta, Canada (Image taken from Google Maps at April 21, 2017)

1.1.2 Oil sand process-affected water (OSPW) characterization

Analysis of OSPW shows that it contains a group of organic acids known as NAs, PAHs, chlorides and assorted heavy metals with other organic and inorganic compounds¹³. The classic general chemical formula for NAs is $C_nH_{2n+Z}O_2$, where n represents the carbon number and Z is zero or a negative even integer (-2, -4, -6, ...) that indicates the hydrogen shortage in the formulation because of ring formation^{14,15}.

Because of the large numbers of compounds present in NAs in OSPW, their analysis by mass spectroscopy produces a huge amount of data¹⁴. There are several different methods for presenting the results of NAs analysis in the literature. Some researchers present the

mass spectrum with the relative ion intensities on the y-axis, and the m/z values on x-axis. In another form of presentation, the relative intensity of each ion is plotted vs. the carbon number¹⁴. John *et al.*¹⁶ (1998) presented data in tables with carbon numbers ranging from 10 to 29 and the relative intensity of each m/z value in the cell corresponding to the appropriate carbon and Z numbers. Nowadays, these results are more commonly presented as three dimensional plots^{14,17,18}. An example of such 3D plot is shown in Figure 1.2.

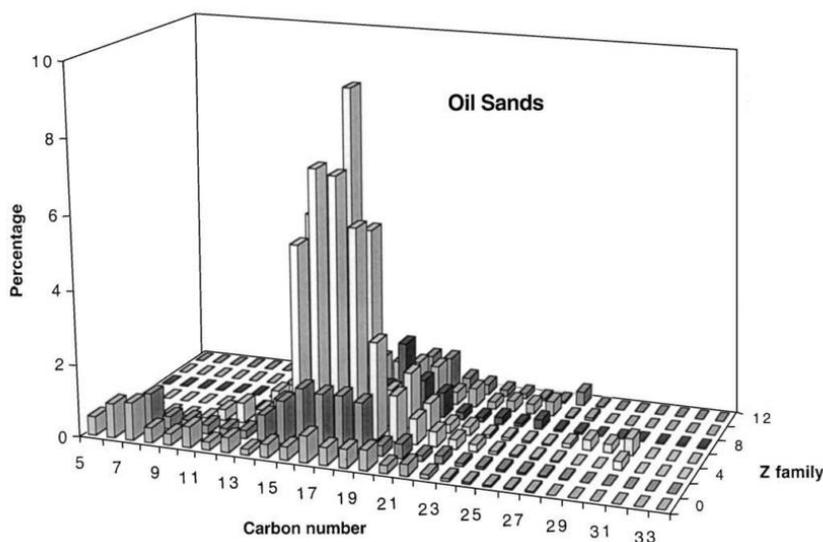


Figure 1.2 : Results for analysis of NAs in an OSPW presented in 3D plot format, reproduced from Zhao *et al.*¹⁹.

In addition to NAs, asphaltenes, benzene, creosols, cyanide, humic acid, fulvic acids, phenols, phthalates, PAHs, toluene are other compounds commonly present in OSPW¹⁰.

1.1.3 Necessity of OSPW treatment and recycling

Existence of NAs and PAHs compounds, in particular the former, causes toxicity for OSPW. Most of this toxicity is because of NAs^{6,18,20-22} which should be removed from OSPW. There is a risk for leaching of these toxic chemicals to the fresh surface and underground water resources. Furthermore, existence of this chemicals in OSPW causes equipment corrosion in the downstream processes for water recycling and reuse¹⁷. Therefore, these compounds should be removed before any further recycling and reuse of

the water. Additionally, NAs have industrial applications such as wood preservation reagents, flame retardants in fabric, and de-foaming chemical in jet fuels^{19,23}. Therefore, recovery of these valuable chemicals could offset part of the OSPW treatment cost.

1.1.4 OSPW treatment methods

Different methods such as advanced oxidation²⁴⁻²⁶, membrane processing^{9,27}, biological treatment^{11,15}, photocatalytic degradation^{28,29}, and adsorption^{2,13} have been studied for removal of fine particles and chemical compounds from OSPW. These technologies have failed to operate in large scale because of technical challenges such as fouling, relative poor performance, and high treatment costs. Recently, petroleum coke (PC), a waste by-product generated from oil sands bitumen upgrading processes, has demonstrated to be an inexpensive precursor for activated carbon (AC) materials as adsorbent for treatment of industrial wastewaters. The use of PC and activated PC (APC) as adsorbents has brought renewed attention to the cost-effective OSPW treatment^{2,13,30}.

1.2 Research objectives

Objective-1: Production and characterization of APC materials

The first objective was to convert the oil sands petroleum coke (supplied by Suncor Corp.) to APC materials. APC was prepared by chemical activation method. The activation was carried out in a horizontal tubular furnace operated at various conditions (KOH/Coke ratio, temperature, and reaction time). The activation conditions were optimized using the Box-Behenken experimental design, and response surface methodology (RSM), in order to maximize the adsorption of NA model compounds at different pHs in batch tests.

Objective-2: Surface modification and application of APC materials as adsorbents for recovery of organics from OSPW

In the second phase of the project, the surface of the produced APC materials was modified by two different amination methods in order to enhance the surface basicity and

hence selectivity of APC on removal of NAs in OSPW. Two different amination processes including a single stage treatment with ammonia gas at an elevated temperature and a two-step treatment of nitration followed by reduction were investigated. The performance of surface modified APC was tested on removal of NA model compounds, i.e., 2-naphthoic acid, diphenylacetic acid, and 1,4-cyclohexanepentanoic acid. The performance of the APC materials after surface modification in removal of model NA compounds was tested in terms of the adsorption kinetics and equilibrium isotherms, and compared with that of a commercial AC.

Objective-3: Design and operation of a bench-scale continuous adsorption column and desorption of NAs from synthetic and real OSPW

In the third phase of this project, a continuous adsorption column was designed and assembled, and used for adsorption tests employing the as-produced APC materials with the highest adsorption capacity based on the batch tests results from the previous phases of the project. The objective of this phase of the project was to examine the performance of the as-produced APC in a continuous adsorption system. For this purpose, breakthrough curves for the as-produced APC were obtained at various operation conditions. Furthermore, the obtained breakthrough curves were fitted to Thomas, Yoon-Nelson, and Adams-Bohart models to obtain better understanding of the adsorption mechanism. Also, the spent APC was regenerated by methanol solvent in several cycles to measure the recyclability and reusability of the APC material in continuous treatment of OSPW.

Objective-4: Development of an adsorption model for the NA adsorption on APC identifying important parameters of adsorbate and adsorbent

Developing a projection to latent structure (PLS) model to investigate the effect of molecular properties of model NAs such as polarizability, carbon, hydrogen and oxygen number, pKa, pi-bond number, molecular weight and molecular volume, number of H-bonding acceptor and donor sites, and refractivity, as well as the APC surface properties

such as total, meso and micro pore surface area, and its different surface modification on removal of NAs from OSPW.

1.3 Research approach and methodology

1.3.1 Petroleum coke activation and surface modification

The first objective of this research was to convert raw petroleum coke with low surface area to a highly porous activated petroleum coke (APC) as an adsorbent with high capacity for NAs removal from OSPW. For this purpose, a chemical activation approach using potassium hydroxide was selected. In this method, raw petroleum coke, KOH and deionized water were mixed together in specific mass ratio. After that, the slurry was put in an ultrasonic bath for 30 minutes and then left overnight to let the KOH solution penetrate to the skeletal structure of petroleum coke. In the next step, the slurry was heated up in a horizontal tubular reactor, as schematically shown in Figure 1.3, to the specific temperature and desired length of time. The experiment was conducted under nitrogen flow to prevent air oxidation. After that, the furnace was turned off and the solids were cooled down under nitrogen flow to ambient temperature. In the next step, the prepared solid samples were washed with HCl solution to remove the ash and potassium-contained in the solids. After that, the washed solid samples were dried in an oven at 120 °C overnight in air. Then, the prepared activated petroleum coke (APC) samples were stored in sealed glass containers for analysis and the adsorption tests.

For surface modification by the creation of nitrogen containing functional groups on the surface of the carbon-based adsorbent, two different techniques were employed. In the first method, ammonia gas was blown at high temperature through the surface of the adsorbent powder in a horizontal tubular reactor, as schematically shown in Figure 1.3, and the resulted adsorbent samples were designated as adsorbent-NH₃.

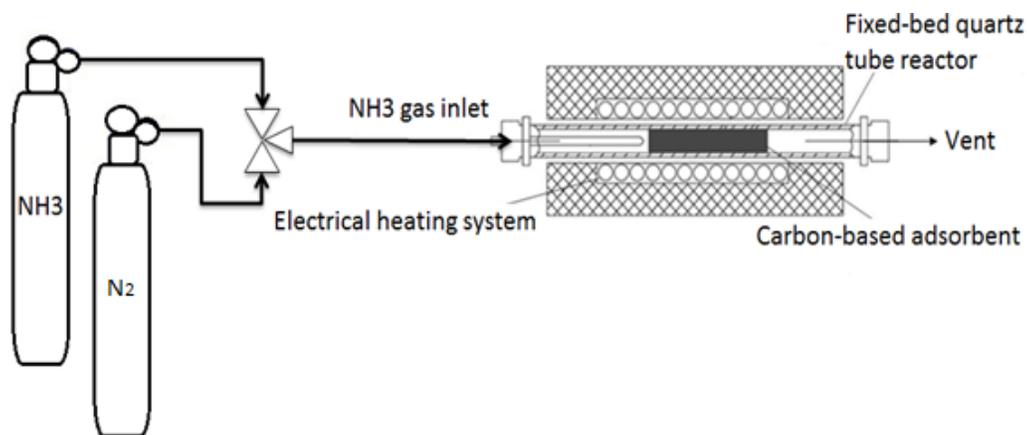


Figure 1.3: Horizontal tubular reactor setup for activation and surface modification of petroleum coke

In the second method of surface modification, procedure originally proposed by Abe *et al.*³¹ was used for amination of AC and APC. In this method, fuming nitric acid was added dropwise to a mixture of AC or APC, acetic anhydride, and concentrated sulfuric acid under continuous stirring while maintaining the temperature below 5 °C using ice-water. The reduction of nitrated AC or APC was carried out in nitrogen atmosphere in the presence of Milli-Q water, aqueous ammonia, and sodium hydrosulfite as the reducing agent. Finally, the modified AC or APC was washed, dried, and stored in glass containers for further tests. The adsorbent samples prepared by this method were named as adsorbent-NH₂.

1.3.2 Batch adsorption studies

Adsorption batch experiments were carried out on an Orbital Shaker. The unit was operated at 170 rpm (the agitation speed chosen based on some preliminary tests to ensure elimination of mass transfer resistance) and the temperature within the unit was kept at room temperature (23 °C). The adsorption kinetics experiments were carried out using 500 mL Erlenmeyer flasks, filled with a constant 175 mL volume of solutions. In adsorption kinetics studies, a same adsorbent loading of 70 mg was used. In isotherm adsorption equilibrium experiments, different adsorbent loadings were used for the same volume of the tested solution of same initial concentration. The model NA compounds were analyzed on a High Pressure Liquid Chromatography (HPLC) system. A Dionex

ICS-3000 was used in HPLC configuration to detect the naphthenic acids using an Acclaim Fast LC Column 120 C18 (3 × 75 mm). A Shimadzu 5000A TOC analyzer with an ASI-5000 auto sampler was used to measure the total organic carbon (TOC) contents of real OSPW samples.

The isotherm adsorption curves for each tested model compound fitted to Langmuir, Freundlich, and Sips models to investigate the mechanism of adsorption. The Langmuir adsorption model is based on bellow assumptions:

- The surface of adsorbent is homogeneous
- All sites are equivalent
- Monolayer coverage
- There are no interactions between adsorbed molecules

The assumptions which Freundlich model is based on are as below:

- The adsorption sites on the surface are not equivalent
- There is non-homogeneous adsorption
- There are interactions between adsorbed molecules on the surface
- Multilayer adsorption

Based on which model fits the isotherm data the best, the mechanism of adsorption was determined.

1.3.3 Continuous column adsorption studies

The adsorption column used in this study was a glass tube with a silica support, and an inner diameter of 1 cm. The adsorbent was packed uniformly in the column, and the top and the bottom zones were packed with small glass beads of 2 mm diameter in order to minimize the end effects and to maintain a uniform distribution of liquid. Samples were collected from outlet stream at the top of the column at various time intervals. The performance of each adsorption test was measured by obtained breakthrough curve. Two identical columns were operated simultaneously for two different adsorbents: commercial activated carbon (CAC) and APC. Figure 1.4 shows the setup used for the column adsorption studies. The solutions were pumped with two peristaltic pumps, and the flow

of the liquid (at a flow rate of 2.5 mL/min) was chosen upward to minimize any possible dead zone and channeling through the packed bed.



Figure 1.4: Continuous column adsorption setup

1.4 Thesis overview

Chapter 1 states the problems caused by oil sands process affected water (OSPW) and briefly introduces its occurrence, necessity and possible treatment methods. The objectives of this research are outlined, and general research methodologies to achieve those objectives have been briefly described. Furthermore, the thesis structure has been outlined at the end of this chapter.

Chapter 2 details review of literature regarding the OSPW, its characterization, and potential usages and environmental risks, as well as different treatment methods, in particular the treatment method based on adsorption process. This chapter explains the potential use of petroleum coke as a precursor for production of a highly porous activated carbon as a possible adsorbent for treatment of OSPW. Different activation methods and surface modification techniques reported by different researchers are summarized in this chapter.

Chapter 3 focuses on optimization of the KOH chemical activation process for production of APC adsorbents from PC. Box Behnken design was employed to determine the optimum operating parameters for KOH activation process, including temperature, KOH/Coke ratio and treatment time, in order to maximize the adsorption of model compounds of naphthenic acids (cyclohexanepentanoic acid, 2-naphthoic acid and diphenylacetic acid). The other objective of this part of research was to track sulfur and heavy metals such as vanadium, nickel and cobalt in PC before and after activation, as well as any possible leaching of these compounds from the APC adsorbents during the adsorption process.

Chapter 4 discusses the effects of surface modification on adsorption properties of the activated carbon-based adsorbents including a commercial activated carbon (CAC) and the activated petroleum coke (APC). Two different amination techniques including a single stage treatment (using ammonia gas at elevated temperatures) and a two-step method (via nitration followed by reduction) were investigated, aiming at better adsorption efficiencies of the surface modified activated carbon-based adsorbents for naphthenic acids (2-naphthoic acid, diphenylacetic acid, and 1,4-cyclohexanedicarboxylic acid) and better reduction of TOC in real OSPW.

Chapter 5 describes the column adsorption performance of the APC produced at the optimum activation condition for removal of organics from both synthetic solutions of NA model compounds and real OSPW. Regeneration of the exhausted adsorbents and the recovery of the adsorbed chemicals such as NAs were also studied.

Chapter 6 Investigates the effect of molecular properties of model NAs such as polarizability, carbon, hydrogen and oxygen number, pKa, pi-bond number, molecular weight and volume, number of H-bonding acceptor and donor sites, and refractivity, as well as the APC surface properties such as total, meso and micro pore surface area, and its different surface modification on removal of NAs from OSPW by using projection to latent structure (PLS) model.

Chapter 7 summarizes the main findings and conclusions of this research and suggests future work that needs to be conducted for large scale industrial applications of APC as adsorbents for OSPW treatment.

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Chapter 2

2 Literature review

This chapter summarizes previous literature studies related to the oil sands process-affected water (OSPW): its occurrence, compositions, toxicity, and treatment methods. In this chapter, two main bitumen extraction methods in oil sands industry are explained with more focus on open pit mining method that produces a huge volume of contaminated water known as OSPW. Furthermore, different techniques along with their strengths and weaknesses in analysis of OSPW have been summarized, with focus on gas chromatography mass spectroscopy (GC/MS). Details regarding the adsorption treatment method are summarized to explain the reasons behind selecting adsorption as a treatment method appropriate for treatment of OSPW. Petroleum coke as an inexpensive and abundantly available by-product of oil sands upgrading process was introduced as a potential adsorbent for OSPW adsorption treatment. Advances in petroleum coke activation and surface modification were reviewed. At the end, the published results related to continuous adsorption of OSPW were reviewed, based on which the knowledge gaps and necessity for further research were discussed.

2.1 Bitumen extraction in oil sands industry

Canada has the third largest reserved crude oil (mainly in oil sands) in the world after Saudi Arabia and Venezuela¹. The main Canadian oil sands reserves are located in the province of Alberta and cover an area of about 142,000 km², where the oil sands reserves are estimated to be about 170 billion barrels¹. Figure 2.1 shows the Canadian land impacted by oil sands industry.

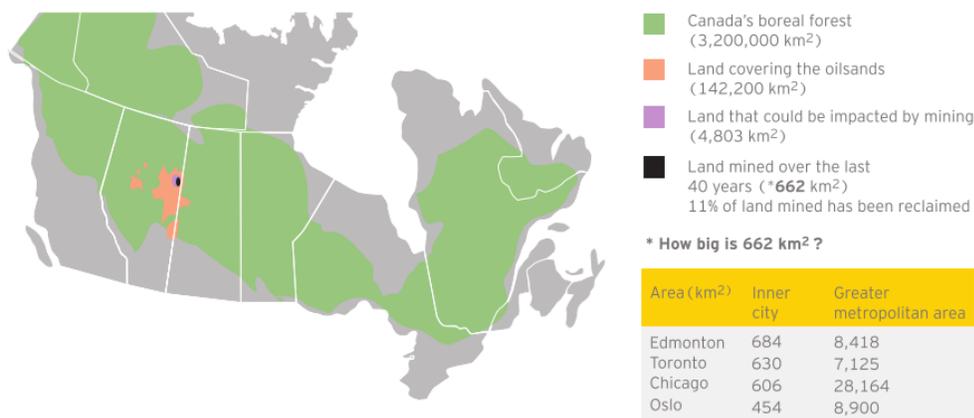


Figure 2.1: Canada's land impacted by oil sands industry. (Source: Canadian association of petroleum production²)

Two main bitumen extraction methods in oil sands industry are open pit mining and in-situ extraction methods. The latter includes technologies such as steam assisted gravity drainage (SAGD), cyclic steam simulation (CSS), steam flood, in-situ combustion and cold heavy oil production with sand (CHOPS), etc.³. In both of these methods, a huge volume of water is needed for extraction of oil which ends up as contaminated water in tailings ponds⁴. For instance, Dadashi Forshomi *et al.*⁵ reported that about 2-4 m³ of fresh water is needed for extraction of 1 m³ of bitumen in SAGD process. The same amount of water is required in open pit mining. Toor *et al.*⁶ reported that between 2 and 2.5 m³ of fresh water is needed for extraction of 1 m³ of synthetic crude oil in open pit mining method. In general, surface mining method contributes about 20% of bitumen extraction and SAGD accounts for the remaining 80%⁷. By 2010, the volume of tailings ponds in the Athabasca oil sands region was estimated over 840 million cubic meters⁸.

2.1.1 Open pit mining

In the open pit mining, an alkaline hot water solution is used to separate the bitumen from sands particles⁴. After the oil sands are mixed with the alkaline hot water (40-85 °C), the mixture is allowed to settle down and the particles are separated with water from the bottom of the settling tank and the bitumen is collected from the top as froth. About 80 to 90 percent of bitumen can be recovered through this process³. This process results in a large volume of waste water, a mixture of fine particles, water and residual bitumen⁹.

2.1.2 In-situ extraction

The main in-situ extraction technology is steam assisted gravity drainage (SAGD) that has been approved to be a promising technique for extraction of bitumen from oil sands deposit¹⁰. This method is used for oil sands reservoirs which are too deep to mine. In SAGD method, parallel horizontal wells are drilled into the oil sands deposit. Steam with 75-80% quality at 7000-11,000 kPa pressure⁵ is injected into the upper horizontal well and released into the deposit to reduce the viscosity of the bitumen. The fluid bitumen drains to the lower horizontal well where the bitumen and produced water from the condensed steam are collected. Then the bitumen emulsion, a mixture of oil, water, sands and clay minerals, is pumped to the surface. In the next stage the bitumen is separated in a same way of open pit mining in settling tanks. It is estimated that over the next 15 years, an increase of 2.9 million barrels of oil per day will be produced with the SAGD operation¹¹. The oil sands reserves in western Canada are located in three major deposits in northern Alberta. The most developed region is Athabasca-Wabiskaw oil sands deposits with several of oil sands companies located in the town of Fort McMurray. The second region is located in Cold Lake region in the eastern part of the Alberta's province, and the third region is located in Peace River basin in northwestern Alberta. These three regions cover 225,308 km² and hold proven reserves of 1.75 trillion barrels of bitumen together². The active extraction sites with color-identified extraction method have been shown in Figure 2.2.

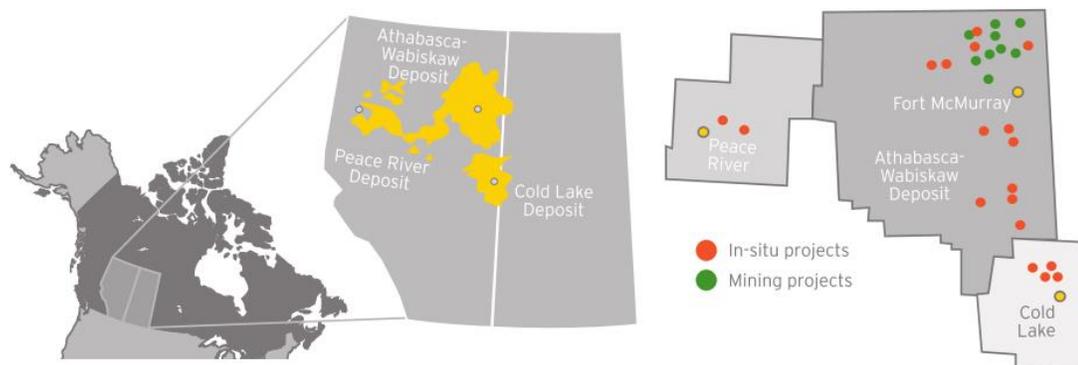


Figure 2.2: Active bitumen extraction sites using in-situ and open pit mining in western Canada's sedimentary basin²

2.2 Oil sands process-affected water (OSPW), occurrence, characterization and necessity for treatment

The water used during the bitumen extraction process in oil sands industry ends up as contaminated water in tailings ponds known as oil sands process affected water (OSPW)¹²⁻¹⁴. This wastewater contains fine particles, clay, residual bitumen, process additives, trace heavy metals, solvents, and the organic compounds that are released to the water during the extraction process^{3,15-17}. Figure 2.3 shows different bitumen extraction steps in open pit mining method.



Figure 2.3: Surface mining's extraction steps, a) Exploration¹⁸, b) Separation cell¹⁸, c) OSPW tailings ponds¹⁹

Table 2.1 shows general characteristics of OSPW.. Naphthenic acids (NAs), polyaromatic hydrocarbons (PAHs)³, residual petroleum hydrocarbons²⁰, and inorganics such as metals, sodium, chloride, and sulfate ions²¹, as well as suspended solids are the main pollutants in OSPW. Existence of these complex chemicals in OSPW, makes the recovering of water for recycling process costly. These chemicals create problems such as corrosion in steam generation units. Furthermore, based on the zero discharge policy²¹⁻²⁴, extraction companies are not allowed to drain this wastewater into the environment. In addition, existence of NAs in OSPW causes toxicity for the aquatic ecosystem as well²⁵.

Table 2.1: General characteristics of OSPW.

<i>Variable</i>	<i>Small et al.</i> ²⁶	<i>Allen et al.</i> ²³	<i>Allen et al.</i> ²⁷	<i>Holowenko et al.</i> ²⁸
pH	8.6-8.7	8.2	-	8.1 - 8.5
TDS (mg/L)	-	1900-2221	1900-2200	12.5 - 47.7 (g/100g)
DOC (mg/L)	39.1-54	58 - 67	-	-
BOD (mg/L)	-	< 10-70	-	-
COD (mg/L)	-	86-973	-	-
NAs (mg/L)	-	50-70	50-70	61 – 88
Bitumen (mg/L)	NA ^a	-	25-7500	0.62 – 3.1
Oil & Grease (mg/L)	NA	9-92	-	-
NH_4^+ (mg/L)	6.4-6.8	-	-	6.7 – 10
NH ₃ (mg/L)	-	14	14	-
Al (µg/L)	25.7-47.3	0.07-0.5	-	-
Ni (µg/L)	6.9-11.1	0.006-2.8	-	-
Mo (µg/L)	264.5-290	-	-	-
Mn (µg/L)	22.1-29	-	-	-
Mg (mg/L)	NA	-	-	2.6 – 9.7
Cu (µg/L)	152.7-190.3	0.002-0.9	-	-
Pb (µg/L)	6.8-9.4	-	-	-
V (µg/L)	5.3-16.9	-	-	-

^aNot available

2.2.1 Naphthenic acids

Naphthenic acids (NAs) are a complex mixture of naturally occurring aliphatic, alicyclic and aromatic carboxylic acids³. NAs are naturally occurring in some waters and rivers that are in contact with oil sands reserves in Alberta, Canada. The concentration of NAs are reported in the range of 0.1- 0.9 mg/L in different locations of the Athabasca river²⁹.

The classical chemical formula for NAs is $C_nH_{2n+z}O_2$, where n represents the carbon number and Z is zero or a negative, even integer (-2,-4,-6,...) that shows the hydrogen shortage in the molecule because of ring formation²⁸⁻²⁹. Some molecular structures of classical NAs have been shown in Figure 2.4.

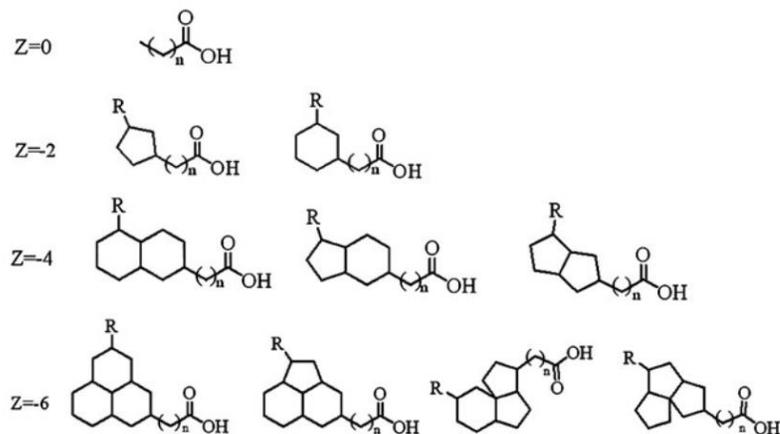
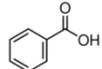
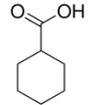
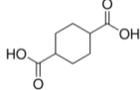
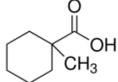
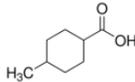
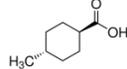
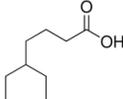
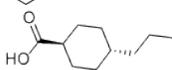
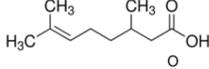
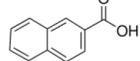
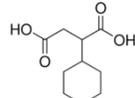
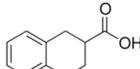
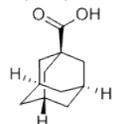
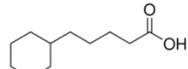
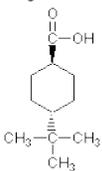


Figure 2.4: Structure of classical NAs (Reproduced from Mohamed *et al.*³¹)

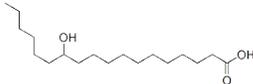
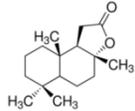
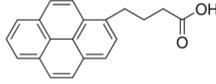
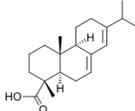
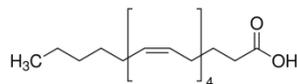
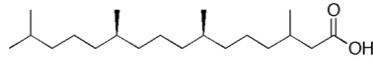
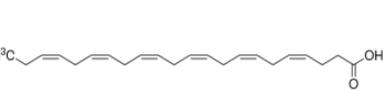
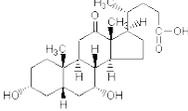
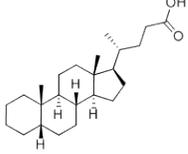
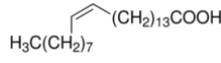
Recently numerous aromatic NAs were identified in OSPW owing to advancements in analytical techniques OSPW^{3,28–31,33}. Other atoms such as sulphur and nitrogen have also been identified. Although most analyses and characterizations still focus on the classical NAs, it has been observed that more than 50% of the compounds in the extracts of OSPW are not classical NAs³. Based on this finding, a revised version of the classical NAs formula for oxygenated naphthenic acids along with numerous other formulas for non-oxygen heteroatoms were proposed³. Table 2.2 presents the model NAs that have been frequently used in various literature studies in recent past.

Table 2.2: List of model NA compounds frequently used in various literature studies

	Name	Formula	MW	Structure
1	Ethanoic, Acetic Acid	C ₂ H ₄ O ₂	60	
2	Butanedioic, Succinic acid ^{37, 38}	C ₄ H ₆ O ₄	118	
3	Cyclopentane carboxylic acid	C ₆ H ₁₀ O ₂	114	
4	Adipic acid ^{37, 38}	C ₆ H ₆ O ₄	142	
5	Hexanoic acid ^{37, 38}	C ₆ H ₁₂ O ₂	116	

6	Benzoic acid ³⁹	C ₇ H ₆ O ₂	122	
7	Cyclohexanecarboxylic acid ^{37, 38, 32, 40, 39}	C ₇ H ₁₂ O ₂	128	
8	1,4-Cyclohexanedicarboxylic acid ^{37, 38}	C ₈ H ₁₂ O ₄	128	
9	1-Methyl-1-cyclohexanecarboxylic acid ^{32, 40, 29}	C ₈ H ₁₄ O ₂	172	
10	3-methyl-1-cyclohexanecarboxylic acid ³²	C ₈ H ₁₄ O ₂	142	
11	4-methyl-1-cyclohexanecarboxylic acid ³²	C ₈ H ₁₄ O ₂	142	
12	trans-4-methyl-1-cyclohexanecarboxylic acid ³²	C ₈ H ₁₄ O ₂	142	
13	3-Cyclohexanepropionic acid ^{29, 39, 17}	C ₉ H ₁₆ O ₂	156	
14	cyclohexane butyric acid (4-cyclohexylbutanoic acid) ^{17, 41}	C ₁₀ H ₁₈ O ₂	170	
15	4-propylcyclohexanecarboxylic acid ⁴⁰	C ₁₀ H ₁₈ O ₂	170	
16	Citronellic acid ⁴²	C ₁₀ H ₁₈ O ₂	170	
17	Decanoic acid ^{37, 38, 43}	C ₁₀ H ₂₀ O ₂	172	
18	2-Naphthoic acid ^{29, 1, 39}	C ₁₁ H ₈ O ₂	172	
19	Cyclohexylsuccinic acid ^{37, 38}	C ₁₀ H ₁₆ O ₄	200	
20	1,2,3,4-tetrahydro-2-naphthoic acid ⁴⁰	C ₁₁ H ₁₂ O ₂	176	
21	1-adamantane carboxylic acid ^{40, 17, 42, 44}	C ₁₁ H ₁₆ O ₂	180	
22	Cyclohexanepentanoic acid ^{37, 38, 40, 17, 43}	C ₁₁ H ₂₀ O ₂	184	
23	trans-4-tert-butylcyclohexanecarboxylic acid ⁴⁰	C ₁₁ H ₂₀ O ₂	184	

24	1-adamantaneacetic acid ⁴⁰	C ₁₂ H ₁₈ O ₂	194	
25	trans-4-pentylcyclohexane carboxylic acid ^{39, 40}	C ₁₂ H ₂₂ O ₂	198	
26	12-hydroxydodecanoic acid ⁴⁰	C ₁₂ H ₂₄ O ₃	216	
27	Lauric Acid; dodecanoic acid ⁴¹	C ₁₂ H ₂₄ O ₂	200	
28	4-Heptyl benzoic acid ³⁹	C ₁₄ H ₂₀ O ₂	220	
29	3,5-Dimethyladamantane-1-acetic acid	C ₁₄ H ₂₂ O ₂	222	
30	Dicyclohexylacetic acid ⁴⁰	C ₁₄ H ₂₄ O ₂	224	
31	Diphenylacetic acid	C ₁₄ H ₁₂ O ₂	214	
32	4-Pentylbicyclo[2.2.2]octane-1-carboxylic acid	C ₁₄ H ₂₄ O ₂	224	
33	12-Methyltridecanoic acid	C ₁₄ H ₂₈ O ₂	228	
34	(±)-6-Hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid	C ₁₄ H ₁₈ O ₄	250	
35	2-Hexyldecanoic acid ⁴⁰	C ₁₆ H ₃₂ O ₂	256	
36	(4-cyclohexylphenyl)acetic acid	C ₁₄ H ₁₈ O ₂	218	
37	Myristic acid	C ₁₄ H ₂₈ O ₂	228	
38	hexadecanoic, Palmitic acid ⁴¹	C ₁₆ H ₃₂ O ₂	256	
39	Palmitoleic acid ³²	C ₁₆ H ₃₀ O ₂	254	
40	Linolenic acid ³²	C ₁₈ H ₃₀ O ₂	278	
41	Stearic acid ⁴¹	C ₁₈ H ₃₆ O ₂	284	
42	Linoleic acid ³²	C ₁₈ H ₃₂ O ₂	280	

43	12-hydroxysteric acid ⁴⁰	$C_{18}H_{36}O_3$	300	
44	(3aR)-(+)-Sclareolide	$C_{16}H_{26}O_2$	250	
45	1-pyrenebutyric acid ⁴⁰	$C_{20}H_{16}O_2$	288	
46	Abietic acid ⁴⁰	$C_{20}H_{30}O_2$	302	
47	Arachidonic acid ³²	$C_{20}H_{32}O_2$	304	
48	Phytanic acid ⁴²	$C_{20}H_{40}O_2$	312	
49	cis-4,7,10,13,16,19-Docosahexaenoic acid ³²	$C_{22}H_{32}O_2$	328	
50	12-oxochenodeoxycholic acid ⁴⁰	$C_{24}H_{38}O_5$	406	
51	5-beta-cholanic acid ^{40, 41}	$C_{24}H_{40}O_2$	360	
52	Nervonic acid ³²	$C_{24}H_{46}O_2$	366	
53	4-Methycyclohexaneacetic acid (4MACH, Sigma-Aldrich) ⁴⁵	$C_9H_{18}O_2$	158	

2.2.2 Corrosivity

Presence of NAs in OSPW leads to corrosivity of this wastewater towards process equipment^{29,46,47}. The carboxyl groups of these chemicals are able to react with metals and create functionalities that accelerate corrosion process^{8,48}. Most of the NAs occur in their sulfide forms which are mainly responsible for the corrosive behavior of OSPW⁴⁸. Corrosion due to the existence of NAs in OSPW is one of the main concerns for petroleum industry, which limits the choice of materials and makes it hard to recycle and reuse the OSPW⁴⁸. Operation temperatures between 220 and 400 °C accelerate the corrosion rate²⁹. At temperatures above 400 °C, NAs decompose and create a protective

film that prevents corrosion²⁹. The possible reaction mechanism between NAs and metallic ions suggested by Chakravarti *et al.*⁴⁹ is shown in **Figure 2.5**.

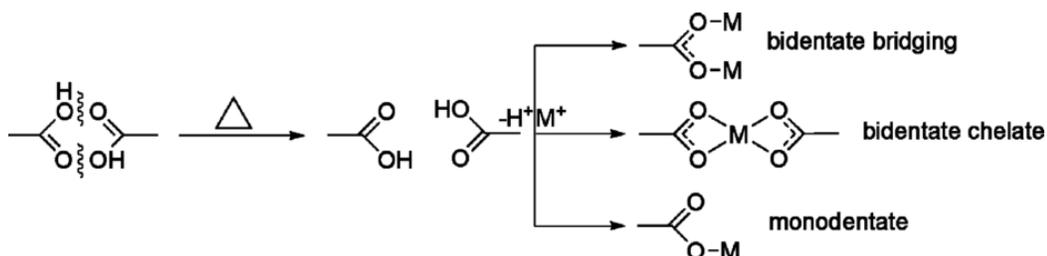


Figure 2.5: Possible mechanistic pathway for corrosive behavior of NAs, Reprinted with permission from Chakravarti *et al.*⁴⁹. Copyright (2013) American Chemical Society.

Based on the corrosive behavior of NAs, these chemicals are needed to be removed before any recycling and further use of OSPW.

2.2.3 Toxicity

The other problem with OSPW that requires this wastewater to be treated before any further use or returning to the environment is its toxicity^{42,50}. The toxicity of OSPW has regularly been ascribed to NAs⁵¹, while it might also be due to other chemicals like PAHs, and metals that exist in OSPW^{42,51}. These chemicals are toxic to the aquatic organisms, mammals, and birds⁵². According to Scarlett *et al.*⁵², effects of 54 NAs, together with six alkylphenols, were modelled for a range of environmental and human toxicity related endpoints using ADMET predictorTM software. In addition to the models, experimental CALUX® assays were performed on seven tricyclic diamondoid acids. Most of the NAs modelled were predicted to have lethal median concentrations (LC50) >100 μM for the three aquatic species modelled. Polycyclic acids containing a single aromatic ring were found to be the most toxic. Some of these compounds were predicted to be carcinogenic (based on rat and mouse models) with human estrogenic and androgenic activity, which could disrupt human reproductive processes. Therefore, by

removing NAs from OSPW, not only the corrosive behavior of the wastewater will be reduced, but also the tailings could be returned into the natural ecosystems.

2.2.4 Characterization of NAs

Different analytical methods have been established for NAs identification; however, all methods tend to be semi-quantitative, and lack the ability to identify individual isomers in the extract of OSPW³. Positive and negative electrospray ionization⁵³, GC/MS⁵⁴, liquid chromatography–accurate mass time-of-flight mass spectrometry³², high performance liquid chromatography (HPLC)²⁹, Fourier transform infrared (FTIR) spectroscopy are some commonly used methods. GC/MS analysis of NAs is one of the most promising methods. Due to the high boiling point of NAs and organics in OSPW, a sample preparation and a derivatization step to reduce the boiling point of NAs is needed before GC/MS analysis. Different types of derivatization methods such as alkylation, silylation, and acylation⁵⁵ are possible. Silylation is the most common derivatization technique, and the common reagents are trimethylchlorosilane (TMCS), trimethylsilylimidazole (TMSI), N-methyl-trimethylsilyltrifluoroacetamide (MSTFA), N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) and N-(t-butyltrimethylsilyl)-N-methyltrifluoroacetamide (MTBSTFA)⁵⁶.

2.2.5 Commercial applications for NAs

Despite being a part of oil extraction waste, NAs are commercially available and they have different applications⁵⁷. There are some techniques for extraction of NAs from oil cuts for commercial uses. For instance, the distilled petroleum cut between 200 and 370 °C is washed with an alkaline aquatic solution to extract NAs. The formed NAs salts are acidified to bring them back to their acid form²⁹. NAs have found different applications as an additive in different materials, such as improving water resistance and adhesion of concrete; increasing high pressure resistance of drilling oils, preventing foaming in jet fuel, preventing fungus growth in wood, preserving and acting as flame retardant in fabric, increasing insecticide solubility by acting as an emulsifier, catalyzing rubber vulcanization, stabilizing vinyl resins, and catalyzing production of alkyl and polyester

resins, etc.²⁹ A specific application of NAs is copper naphthenate - an environmentally safe wood preservative that has growing market⁵⁴.

2.3 Treatment methods

Technologies for tailings treatment could be divided into two major categories, applied and research stages. In research stage, different methods such as advanced oxidation⁵⁸⁻⁶⁰, membrane processes^{22,61,62}, biological treatment^{21,30,63-65}, photocatalytic degradation^{15,66}, and adsorption^{4,52,67-69} have been investigated for removal of fine particles and chemical compounds from OSPW. Some of the most commonly used treatment methods, in both applied and research stages, are presented below.

2.3.1 Centrifuge System

Currently, some oil sands extraction companies, e.g., Syncrude's Mildred Lake Mine in Mildred Lake, Alberta, use centrifugation method to separate suspended solids from OSPW⁷⁰. The centrifugal method used by Syncrude can achieve slurry with solids content up to 60 wt% through the application of centrifugal force. This process is cost efficient, and the separation of solids from water is efficient and fast, but the method is limited to removal of only suspended solids from OSPW, not dissolved organics or toxicity²³. The positive aspects of centrifugation are the reliability of cake water content under different weather, and feed conditions, and have the ability to operate for most of the year, but capital cost and large-scale deposition of cake are the primary concerns⁷⁰.

2.3.2 Ozonation

Ozonation method is one of the most common oxidation methods studied for OSPW treatment, especially for toxicity removal^{58,71,72}. In this method, ozone from an ozone generator is bubbled through OSPW. After stripping the remaining water with nitrogen to remove any excess ozone, a considerable portion of toxic chemicals are removed from the tailing water⁷³. Applications of this method require investment and operation of ozonation equipment in the industry, so the cost of implementing an ozonation system would be extensively high⁷².

2.3.3 Natural Wetlands

Natural wetlands perform many functions that are both beneficial to wildlife and processes involving water filtration. As water flows through a wetland, the suspended solids become trapped by vegetation and settle down. Other pollutants are transformed to less soluble forms taken up by plants or become inactive. Wetland plants foster the necessary conditions for microorganisms to live there. These microorganisms can transform and remove pollutants from the water. This method can be used in conjunction with tailing ponds to eliminate toxins in a biological way that is beneficial to the surrounding environment. The disadvantages of wetlands include large land area requirements, the need for a preliminary treatment before the wastewater can be treated by the system, seepage of toxic chemicals, and the need of a long retention time. For example, the average residence time of Suncor OSPW in natural wetland is about 5 weeks⁶. The wetland approach would be worse than current tailing pond structures since it has no engineered dams to prevent seepage. Coagulation and flocculation

Coagulation is one of the methods that has been tested for remediation of OSPW⁴⁶. In this process, a synthesized chemical or polymer coagulant is added to a fluid to cause small suspended particles to bind together to form larger ‘flocks’ so that the process of sedimentation occurs at a faster rate. The combined weight of the dirt particles and the flock become heavy enough to sink to the bottom during sedimentation. This technique can be used with other OSPW treatment methods, for complete treatment of OSPW as only suspended and colloidal particles are removed by coagulation.

2.3.4 Membrane process

Among available technologies, the membrane pre-filtration by low pressure-driven membranes, such as microfiltration and ultrafiltration, have been commonly used to remove particles, colloids, and turbidity for municipal and industrial wastewater treatment⁷⁴. Kim *et al.*⁷⁴ however believe that the membrane processes is not efficient in treatment of OSPW due to their high susceptibility to fouling.

2.3.5 Adsorption

In an adsorption process, the toxic chemicals can be removed and reused safely. This leaves cleaner wastewater that is easier and safer to recycle. Adsorption is one of the most efficient methods in removal of organics as well as inorganic pollutants from wastewater^{75,76}. In general, two main modes of adsorption are physisorption and chemisorption. In chemisorption the adsorbate chemically bonds with the surface functional groups of the adsorbent, while in physisorption the interaction between adsorbate and adsorbent is weaker such as in dipole-dipole interaction and hydrogen bonds. Two main factors that affect the adsorption behavior of an adsorbent are its surface area and functionality. Among existing adsorbents, activated carbon has been recognized as one of the most popular and cheapest adsorbents in water and wastewater treatment⁷⁷. Researchers have been trying to produce AC from different precursors such as wood, biomass, biochar, coconut shell, and petroleum coke, etc.⁷⁸. The disadvantage of this method is the contaminated adsorbent which being accumulated after adsorption and needed to be handled in a safe and proper method.

Table 2.3 summarizes different adsorbents that have been used for OSPW treatment.

Table 2.3. Different adsorbents that have been used for OSPW treatment

	OSPW or model compounds	Adsorbents	References
1	DOC of OSPW	Oil sand coke	Small <i>et al.</i> ²⁶
2	Commercial NAs	Clays (Na-montmorillonite, Na-kaolinite, and Na-illite)	Zou <i>et al.</i> ⁷⁹
4	Mixture of alkylated cyclopentane carboxylic acids	Biomass and biochar	Iranmanesh ⁸⁰
5	1,4-cyclohexanedicarboxylic acid, diphenylacetic acid, 2-naphthoic acid	Commercial AC	Martinez-Iglesias <i>et al.</i> ⁸¹
6	OSPW	Biomass-based biochar	Bhuiyan <i>et al.</i> ⁸²
7	OSPW	Coal based activated carbon	Shahinoor Islam <i>et al.</i> ⁸³
8	OSPW	Petroleum coke	Zubot <i>et al.</i> ⁸⁴
9	Single-ring model naphthenic acid	Petroleum coke-derived activated carbon	Sarkar ²⁵
10	OSPW	Raw petroleum coke	Gamal El-Din <i>et al.</i> ⁴

2.3.6 Biological methods

Different biological methods have been investigated for remediation of OSPW. Lari *et al.*⁸⁵ used *Daphnia magna* for OSPW treatment, which only removed 29% of dissolved components. Furthermore, previous studies using planktonic cells have shown poor NAs treatability⁷³. The biological treatment takes a long period of time (days and weeks) and also the toxic compounds that are present in OSPW might decrease the efficiency of the biodegradation process. As such, it was found that NAs are poorly biodegraded in the tailings ponds of many oil sands companies⁷².

In industrial scale, most of the work has been done on fine particle or solids separation for tailings ponds through technologies such as composite tailings and non-segregating tailings, thickened tailings⁸⁶, in-line thickening with accelerated dewatering, centrifuged mature fine tailings (MFT), wetland reclamation, and coke or water capped MFT for solid separation from MFT⁸⁷. However, these technologies remove solids only while the chemicals such as NAs that cause corrosivity and toxicity of the OSPW are still present and need to be removed. Attempts to recover bitumen from the tailing ponds were largely unsuccessful. Skimming bitumen from the tailings ponds is no longer practiced due to its high operating costs and difficulties in dealing with the froth produced. Therefore, there is an urgent need for an improved method to remove NAs and residual bitumen from oil sands tailings.

Among the mentioned methods for chemicals removal, adsorption has attracted much interest of different groups of researchers. Gamal El-Din *et al.*⁴ studied the combination of ozonation treatment method with petroleum coke adsorption for remediation of NAs. Their result showed that the elimination of NAs by petroleum coke adsorbent is more effective than that by the ozonation method. Adsorption using petroleum coke, a relatively inexpensive and abundant material, after activation as an adsorbent, has brought renewed attention for OSPW reclamation^{67,88,89}.

2.3.7 Current treatment methods in oil sands industry

At the moment Suncor and Syncrude using two different technologies for recovery and recycling of OSPW. The Suncor technology called tailings reduction operations, which in

this method a polymer is being mixed with OSPW as a flocculants and then the mixture depositing in a thin layer and allowing it to dry. In the other method which developed by Syncrude Company, mature fine tailings being centrifuged and solid and fine particles being separated by centrifuge forces. The weakness of both mentioned methods is their weakness on removal of dissolved chemicals which are the main source of corrosively and toxicity of OSPW. The advantage of proposed treatment method in this study is removal and recovery of these dissolved chemicals.

The advantages and disadvantages of all above mentioned methods are summarized in Table 2.4.

Table 2.4. Advantage and disadvantage of different OSPW treatment methods

Treatment method	Advantages	Disadvantages
Centrifugation	Cost efficient and fast, inexpensive operation	Limited to removal of only suspended solids
Ozonation	Efficient on toxicity removal	Costly process, needs a large capital investment
Natural wetland	Inexpensive operation cost, not sensitive to the pH of the OSPW	Needs long retention time, requires a large area and land size
Membrane process	Compact process with small footprint	Highly susceptible to fouling, costly operation process
Adsorption	Efficient and inexpensive process, able to recover chemicals	Production of exhausted adsorbent as waste product
Biological methods	Mild operating conditions	Not effective, sensitive to the pH of OSPW

2.4 Recent advances in OSPW treatment by adsorption

Surface area, pore size distribution, and surface functional groups are the major factors that define the adsorption properties of an adsorbent. The functionality of an adsorbent is one of the main factors that specify its adsorption behavior⁹⁰⁻⁹². The presence of heteroatoms like oxygen, nitrogen, hydrogen and phosphorus on the surface of an

activated carbon adsorbent would alter the surface chemistry of the adsorbent⁹³. Usually several forces are involved in the adsorption of organic compounds on the surface of carbonaceous adsorbents. Interactions between the aromatic ring and the *p* electrons of the graphenes, electron donor-acceptor interactions between the aromatic ring and the non-acidic surface sites, electrostatic attractive or repulsive interactions between the charged carbon surface and the ions in the solution are among the most important interactions⁹⁴. The surface charge of an adsorbent is a function of pH of the solution. At point of zero charge the surface will show a neutral charge. Point of zero charge is thus another factor that affects the adsorption behavior of an adsorbent⁹⁵⁻¹⁰¹.

Recent studies focused on using petroleum coke, another by-product of the oil industry, as an inexpensive, and abundantly available adsorbent for reclamation of OSPW^{90,91}. At the end of 2012, as much as 77 million tons of petroleum coke was stockpiled only in Alberta¹⁰⁴. Each year, several million tons of oil sands coke are produced as a by-product of bitumen upgrading in Alberta, Canada⁸⁸. Petroleum coke is a potentially viable adsorbent that can be used to treat OSPW to a sufficient quality for its reuse or return to the environment⁶⁷. The forces that affect the adsorption process with petroleum coke can be categorized in two different types: physical forces (such as dipole moments, short range repulsive interactions, polarization forces, hydrogen bonds), and chemical forces as a result of the electrons redistribution between the solid surface and the adsorbed atoms⁹⁴. However, the adsorption capacity and efficiency of petroleum coke are generally low due to its low surface area. It is expected that the adsorption capacity could be increased by increasing the surface area of petroleum coke through some activation processes.

To enhance the surface area and hence the adsorption capacity and efficiency of petroleum coke, several activation techniques have been established of petroleum coke. Activation methods such as acidic treatment¹⁰⁵⁻¹⁰⁷, base treatment^{108,109}, plasma⁷⁷, microwave^{77,110-112}, ozone^{113,114}, thermal⁷⁷, and impregnation¹¹⁵⁻¹¹⁷ are some of those activation methods. In general, the activation processes could be categorized into two main groups, chemical and physical activation.

The high adsorption capacity of carbon-based adsorbents is attributed to their high surface functional groups, microporous structure and high surface area¹¹⁸. There are different surface functional groups on the surface and edges of carbonaceous adsorbents such as carboxyl, carbonyl, phenol, quinone, and lactone groups¹¹⁹. The active sites in carbonaceous adsorbents are in the form of edges, dislocations and discontinuities that could facilitate chemical reactions with other molecules. As a result, the adsorption behavior (efficiency, capacity, and selectivity, etc.) cannot be interpreted based on surface area and pore size distribution alone. Adsorbents with the same surface area but produced by different methods might exhibit significantly different adsorption behavior¹¹⁸.

The existence of nitrogen-containing functional groups (Figure 2.6) on the carbon surface generally provides basic properties of the surface, which could theoretically enhance the interactions between adsorbent and acid molecules^{92,120–123}, e.g., via dipole-dipole, H-bonding, and covalent bonding, etc. There are several ways to introduce nitrogen to the surface of carbonaceous adsorbents, such as amine treatment, nitric acid treatment and some other nitrogen containing molecule reactions¹¹⁴.

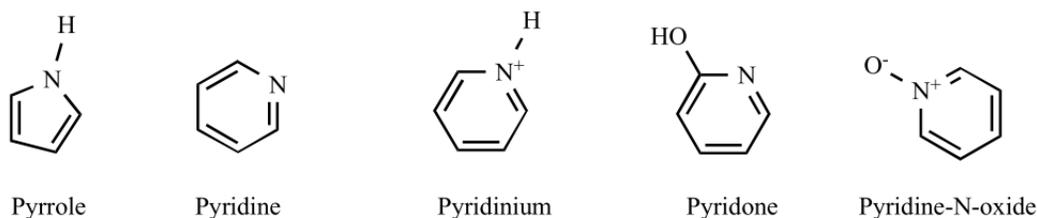


Figure 2.6: Possible nitrogen containing functional groups in carbonaceous material¹²⁴. (Adapted from *Carbon Journal*, Vol. 33, Pels *et al.*, Evolution of nitrogen functionalities in carbonaceous materials during pyrolysis, page 1641-1653, Copyright 1995, with permission from Elsevier)

Most properties of activated carbon (AC), such as its catalytic and adsorption properties, are related to its surface functional groups¹¹⁴. The modification of these groups for a desirable application is an important area of research. There are different techniques for improvement of surface activity and selectivity of AC materials.

Oxidization is one of the surface modification methods of carbonaceous adsorbents. Through oxidization, the concentration of oxygen containing groups in the surface increases and it changes the acidic properties of the surface. For example, activated carbon with low oxygenated acidic surface groups has the best adsorption capacity for benzene and toluene¹¹⁴. Oxidization by sulfuric acid is an effective method to increase the oxygen-containing groups of AC, but this method needs concentrated acid and post-treatment to remove the extra remaining acid¹¹⁴. Figueiredo *et al.* in 1999 found that the oxidization in the gas phase mainly increases the concentration of hydroxyl and carbonyl surface groups, while oxidations in the liquid phase increases the concentration of carboxylic acids¹¹⁹. In another study, Chen *et al.* found that surface oxidation predominantly increased the concentration of carboxylic and phenolic surface groups¹¹⁷. Acid treatment is generally used to oxidize the carbon surface; it enhances the acidic characteristic, increases hydrophilic properties and removes the minerals. Moreover, acid treatment has a significant effect on surface area and functional groups of carbonaceous adsorbents¹²⁵.

Opposite to the oxidization treatment which improves the acidic properties of AC, the ammonization improves its basic properties¹¹⁴. The nitrogen containing surface functional groups improve the adsorption of acidic molecules on the surface of AC¹¹⁴. The basic characteristics of an AC were a result of treatment by ammonization and were introduced by groups such as C-H, C=N groups, amino, cyclic amides, nitrile groups and pyrrole-like structure¹¹⁴.

In this thesis work, two different amination techniques were employed to introduce nitrogen-containing functionality on the surface of activated petroleum coke (APC) and commercial AC for increasing their adsorption properties towards NAs. The two different methods used were: (1) a one-step process, ammonia gas was used directly at elevated temperature to introduce -NH_2 group on the surface of the adsorbents, and (2) a two-step process consisting of an electrophilic substitution to introduce nitrate group, followed by reduction of the nitrate to NH_2 . The performance of these adsorbents after different amination modifications in adsorption removal of NA model compounds and TOC from real OSPW will be discussed in Chapter 4.

2.5 Summary of the literature review

The important findings of the literature review can be summarized in the following:

- Canada has the third largest oil reserves (mainly oil sands) in the world after Saudi Arabia and Venezuela.
- In the oil sands extraction process, the bitumen is washed out from clay and sands with an alkaline hot water solution, which creates a contaminated wastewater known as oil sands process affected water (OSPW). Oil sands industry produces a large volume wastewater that should be recovered and recycled as per the zero discharge policy. Generally, in either in-situ extraction process or open pit mining process, about 2-4 m³ of fresh water is needed for extraction of 1 m³ of bitumen.
- NAs in different forms have different commercial applications such as improving water resistance and adhesion of concrete, increasing high pressure resistance of drilling oils, preventing foaming in jet fuel, preventing fungus growth in wood, preserving and acting as flame retardant in fabric, increasing insecticide solubility by acting as an emulsifier, catalyzing rubber vulcanization, stabilizing vinyl resins, and catalyzing production of alkyl and polyester resins.
- Current operating oil sands companies are trying to separate the clay and fine particles from OSPW, while the dissolved chemicals such as NAs and PAHs are still present in the treated water. Existence of NAs causes toxicity of this water to the aquatic ecosystem and corrosivity to the pipelines and equipment. As such, these chemicals need to be removed before recycling and recovery of OSPW.
- Until now, different treatment methods, such as advanced oxidation, membrane processes, biological treatment, photocatalytic degradation and adsorption, have been investigated for removal of chemical compounds from OSPW. However, none of these methods is used in industrial scale. Among these mentioned

methods, adsorption has attracted increasing attention of both academia and industry.

- Petroleum coke is an inexpensive and widely available adsorbent that can be used to treat OSPW for removal of NAs, PAH and other chemicals. Each year, several million tons of petroleum coke are produced as a by-product of oil sands bitumen upgrading. The challenge with petroleum coke is its low surface area and hence adsorption capacity that could be increased through activation.
- The existence of nitrogen-contained functional groups on the surface of a carbon-based adsorbent generally provides basic properties, which could enhance the interaction between the adsorbent and acid molecules such as NAs, and hence improve the adsorption performance of the adsorbent.

2.6 Knowledge gaps and project objectives

Based on the literature review, currently oil sands industry has focused on treating OSPW by technologies such as centrifugation or coagulation and natural precipitation for solid particles separation only. There is no treatment method industrially realized by far in oil sands industry for cost-effective removal of the toxic dissolved chemicals in OSPW such as NAs and PAHs. The knowledge gaps of the OSPW treatment are summarized below:

- The existing methods for OSPW treatment are mainly for solid particles separation only, but do not remove its toxicity and corrosivity, and because of that, the treated OSPW needs to be diluted by fresh water before recycling or returning into the natural ecosystems.
- By far there is no study for recovery of organics such as NAs and PAHs from tailing ponds.
- There is no industrially realized treatment technology for removal of dissolved chemicals in OSPW.

- There is no comprehensive and optimization study on applying petroleum coke or activated petroleum coke as a widely available and inexpensive adsorbent for OSPW treatment.
- There is no comprehensive method and analytical techniques for chemical analysis of OSPW.
- Effects of pre-treatment of OSPW, such as pH adjustment, on OSPW treatment were not investigated.
- There is no research on regeneration of adsorbents after adsorption treatment of NAs model compounds or real OSPW.
- There is no research on purification of mixed recovered organics from OSPW by adsorption treatment.

Based on the above knowledge gaps, the overall objective of this project was to develop a cost-effective adsorption process utilizing activated petroleum coke (APC) as inexpensive but efficient adsorbent for treatment of OSPW in such a way that dissolved chemicals such as NAs are recovered and the treated water can be recycled back to the extraction process. Specifically, the objectives of the project are to:

- (1) Produce activated petroleum coke (APC) by chemical activation using KOH to increase the specific surface area and porosity of the petroleum coke;
- (2) Optimize the activation parameters using Box-Behnenken design of experiments and RSM to maximize the adsorption capacity of the produced APC for NAs;
- (3) Develop surface modification techniques to improve the selectivity and adsorption capacity of the produced APC;
- (4) Investigate the adsorption performance of APC in a continuous column for NA model compounds removal, as well as real OSPW treatment;

- (5) Investigate cost-effective methods for regeneration of the used adsorbents after the adsorption treatment.

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Chapter 3

3 Preparation of activated petroleum coke for removal of naphthenic acids model compounds: Box-Behnken design optimization of KOH activation process

Abstract

This study employed Box-Behnken design and response surface methodology to optimize activation parameters for the production of activated petroleum coke (APC) adsorbent from petroleum coke (PC) to achieve highest adsorption capacity for three model naphthenic acids. Activated petroleum coke (APC) adsorbent with a BET surface area of 1726 m²/g and total pore volume of 0.85 cc/g was produced at the optimum activation conditions (KOH/coke mass ratio) of 3.0, activation temperature 790 °C, and activation time 3.47 hr). Effects of the activation parameters on the adsorption performances (adsorption capacity and kinetics) were investigated. With the APC obtained at the optimum activation condition, the maximum adsorption capacity of 451, 362, and 320 (mg/g) was achieved for 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid (CP), respectively. Although, generally APC adsorbents with a higher specific surface area and pore volume provide better adsorption capacity, the textural properties (surface areas and pore volume) are not the only parameters determining the APC adsorbents' adsorption capacity. Other parameters such as surface functionalities play effective roles on the adsorption capacity of the produced APC adsorbents for NAs. The KOH activation process, in particular the acid washing step, distinctly reduced the sulfur and metals contents in the raw PC, decreasing the leaching potential of metals from APC adsorbents during adsorption.

Keywords: Petroleum coke; KOH activation; Optimization; Naphthenic acids; Adsorption capacity; Leaching of metals

3.1 Introduction

Each year, several million tonnes of oil sands process-affected water (OSPW) is produced from the bitumen extraction process in Alberta, Canada¹. More than 3 barrels of fresh water is required for the production of every barrel of bitumen². There are different kinds of organic compounds in OSPW such as polyaromatic hydrocarbons (PAHs), bitumen, and naphthenic acids (NAs). NAs are the main source of toxicity of OSPW^{3,4} and need to be removed before process water can be discharged in the aquatic environment.

Petroleum coke (PC) is an inexpensive by-product of petroleum industry that can be used to produce highly porous activated carbon^{5,6} for treatment of OSPW. The main problem of PC is its high sulfur content⁵, presence of heavy metals, and low surface area. Different researchers have attempted to use PC with or without activation for removal of organics from wastewaters^{5,7-11}, where research efforts have been made in PC activation in order to maximize its surface area and minimize the sulfur and heavy metal contents. Activation of PC has been realized by either chemical or physical method¹². The chemicals such as KOH¹³⁻¹⁵, H₃PO₄ or CaCl₂¹⁶, ZnCl₂ and H₂SO₄¹⁷, and NaOH¹⁸ are the most common agents used in activation of carbonaceous precursors. Although the detailed mechanism of chemical activation of carbonaceous material is not fully understood yet^{19,20}, in general, chemical activation by alkalis consists of solid–solid or solid–liquid reactions involving the hydroxide reduction and carbon oxidation to generate porosity. During the reactions, CO, CO₂ and H₂ evolution was observed¹⁹. Also, potassium may form –OK groups by the oxidation of cross-linking carbon atoms, and the formation of surface groups in the edge of the lamellae would cause the separation of carbon lamellae²⁰. The other mechanism of KOH activation of PC could be dehydration of KOH into K₂O at elevated temperatures, and then reduced into metallic potassium by carbon. Metal potassium then intercalates into pseudo-graphitic layers to develop the porosity after washing the treated carbon with HCl and water to completely remove residual K, K₂O, K₂CO₃, and KOH²¹. Furthermore, existence of volatile compounds in PC might cause formation of pores at elevated temperatures during the activation process²¹.

The objective of this study was to determine the optimum conditions of the KOH activation process for PC in order to maximize the adsorption capacity of naphthenic acids model compounds. KOH was selected as the agent for PC activation because of its effectiveness,

availability and cost²². Produced APC adsorbents exhibited significant adsorption capacities for the removal of model NAs^{6,23}. The APC has the potential to be used in many processes such as wastewater treatment^{5,6,9}, decolourization, gas separation, catalysts for oxidative reactions and reductive reactions, etc.¹⁷.

The main objective of this research was to obtain the optimum parameters (i.e., temperature, KOH/coke ratio, and the activation time) for the KOH activation process for PC using surface response methodology (SRM) in order to maximize the adsorption of naphthenic acid model compounds. A Box-Behnken design was employed to find the optimum condition of the process. The obtained APC adsorbents were then tested for adsorption of three naphthenic acid model compounds (cyclohexanepentanoic acid, 2-naphthoic acid, and diphenylacetic acid) and adsorption capacity was chosen as the objective function in the optimization. There is the possibility of metal ions and organics leaching out from APC⁵, therefore, another objective of this work was to track the sulfur and heavy metals such as vanadium, nickel, and cobalt in PC before and after activation, as well as possible leaching of these metals and other organics during the adsorption process. To this end, the sulfur and heavy metal contents of PC were measured before and after activation, and the water phase after the adsorption process was analyzed for composition of metal ions and the dissolved organics concentration (DOC).

3.2 Material and methods

3.2.1 Materials and Chemicals

The Syncrude petroleum coke (PC), used in this study as the precursor of activated carbon adsorbents, was supplied by NEWALTA Corporation (Burlington, ON). The raw PC has a BET surface area of $<15 \text{ m}^2/\text{g}$ and a total pore volume of $<0.01 \text{ cm}^3/\text{g}$. The chemicals such as KOH, 2-naphthoic acid, HPLC-grade acetonitrile were purchased from VWR Company, (Mississauga, ON, Canada) and diphenylacetic acid, cyclohexanepentanoic acid, sulfuric acid 98%, hydrochloric acid 37%, perchloric acid 70%, and nitric acid 70% from Sigma-Aldrich, Canada. All chemicals were ACS reagent-grade and used without further purification. The basic properties of the selected model naphthenic acids are shown in Supplementary Table S 3.1.

3.2.2 Petroleum coke activation

Potassium hydroxide (KOH) was used as the chemical agent for activation of PC. KOH and PC at different mass ratios were mixed together with adequate amount of water to make a thick slurry. The mixture was heated in an electric tubular furnace at approx. 20°C/min up to a specific temperature for a specific period of time in nitrogen flow (5 mL/min). After the specific activation time elapsed, the reactor was cooled down to room temperature in presence of nitrogen gas, followed by washing the activated petroleum coke (APC) with HCl (37%) to remove the excess potassium hydroxide as well as some ash components. Then the sample was washed with sufficient amount of distilled water until the pH of the filtrate was equal to the pH of distilled water. In the next step, the washed APC was dried in air at 110 °C, then cooled down and stored in a sealed sample container for further use.

3.2.3 Surface characterization

A Nova 1200E, surface area and porosity analyzer (QuantaChrome Co.) was used to measure the pore size distribution and specific surface area of the prepared samples. SEM images were taken on an LEO (Zeiss) 1540×B FIB/SEM microscope at UWO nanofabrication facility. This system was equipped with a sample transfer airlock, allowing rapid sample changes without disrupting the high vacuum of main chamber. The samples were coated with a thin layer of Osmium metal with a Filgen OPC80T Osmium Plasma coater before imaging by SEM. The Osmium film would enhance the secondary electron yield, prevent sample charging and reduce damage to delicate materials from the electron beam during imaging.

3.2.4 ICP analysis

ICP was applied for metal analysis of the PC samples before and after activation. In sample preparation, about 1 g of solid sample was grounded with a mortar-pestle. Then, 800 mg of grounded sample was weighed and put in a 250 mL beaker and mixed with 10 mL (70 wt.%) nitric acid under gentle heating, followed by the addition of 8 mL (70 wt.%) perchloric acid until the solution became colorless. After cooling, 30 mL of water was added, followed by gentle heating for 10 minutes. After the solution was cooled down, the volume of the solution was adjusted to 100 mL with MilliQ water. Subsequently, the solution was filtered through a 0.45 µm

filter to remove any particulate matters. Finally, 12 mL of particle-free sample was used for ICP analysis.

3.2.5 Leaching test

In order to investigate leaching of any organic or inorganic compounds from the APC, about 1 g of the APC material was weighed and mixed with 250 mL MilliQ water under stirring for 24 hours. DOC and ICP analyses were then performed to measure the organics and metals leached from APC adsorbents. Only, the APC samples which had very high adsorption capacity were tested for leaching.

3.2.6 Design of experiments and Statistical analysis

The Box-Behnken design (Supplementary Figure S 3.1) was employed to optimize the PC activation parameters such as activation temperature, KOH/coke mass ratio and activation time. For each parameter, three levels were selected: such as temperature, 650, 750, and 850 °C, KOH/coke ratio, 1, 2, and 3, and time of activation, 60, 120, and 180 minutes. The ranges of parameters were chosen based on previous studies in the literature^{6,22,24–26} as well as our own preliminary studies, and presented in Supplementary Table S 3.2. In this design, 14 samples of APC (Table 3.1) were prepared and tested for the adsorption of three model NA compounds. A reduced cubic model (aliased) was considered in analysis of variance (ANOVA) for statistical analysis. The maximum adsorption of the model compounds tested with the produced APC adsorbent was considered as the response factor.

Based on the optimization results, the spent adsorbent (the optimum sample with the highest adsorption capacity for NAs model compounds) was further analysed for the sulfur and heavy metals content to determine any possibility of leaching of these elements during the adsorption process.

3.2.7 Adsorption of NA model compounds

The adsorption performance of all produced APC adsorbents was tested in batch experiments. In a typical test, the adsorption was performed in a 500 mL Erlenmeyer flask with 350 mL model compound solution placed in an orbital shaker at 170 rpm and 23 °C. The initial concentration of all model compounds was fixed at 40 mg/L and the pH was adjusted to 6.0 by adding either 0.1

M NaOH or HCl. For the kinetic studies, 3 mL samples were taken and analyzed at different time intervals between 1 min to 24 hours. For the isotherm equilibrium tests, different amounts of APC adsorbent were used in 350 mL of the model compound solutions, and shaken for 48 hours to make sure that the adsorption equilibrium was reached. The mixtures were then filtered using 0.45 μm nylon syringe filters prior to the analysis on an HPLC and UV-Spectrophotometer depending on the concentration.

3.3 Results and discussions

3.3.1 Characterization of the produced APC

Textural properties:

The Box-Behnken matrix of the output responses vs. the activation parameters and the textural properties of the obtained APC adsorbents are presented in Table 3.1. BET surface area, meso-pore and micro-pore surface area, and total pore volume of all the prepared APC materials are presented. The properties are strongly dependent on the activation parameters (KOH/coke mass ratio, temperature and time), and the BET surface area of the obtained APC ranges from 240 (KOH/PC = 1 w/w, 650°C and 120 min) to 1474 m^2/g (KOH/PC = 3 w/w, 750°C and 180 min), while the total pore volume ranges from 0.165 cm^3/g (KOH/PC = 1 w/w, 650°C and 120 min) to 0.679 cm^3/g (KOH/PC = 2 w/w, 650°C and 180 min). These textural properties were used to model the experimental data and predict the adsorption capacity of APC in different conditions. The modeling results are presented later in Section 3.4.

Table 3.1: The Box-Behnken matrix of the output responses vs. the activation parameters and the textural properties of the obtained APC adsorbents

	Coded values			Actual values					Output response				
	X ₁	X ₂	X ₃	KOH/ PC ratio (w/w)	T (°C)	Time (min)	S _{BET} (m ² /g)	Meso- pore (m ² /g)	Micro- pore (m ² /g)	Total pore (cm ³ /g)	Q _{2-naph.} (mg/g)	Q _{Diph.} (mg/g)	Q _{CP} (mg/g)
1	-1	-1	0	1	650	120	243	204	39.6	0.165	83	46	66
2	-1	+1	0	1	850	120	769	566	112.4	0.312	345	167	155
3	0	-1	+1	2	650	180	347	308	39.6	0.166	105	61	122
4	0	0	0	2	750	120	1216	1152	104.8	0.405	274	183	247
5	0	+1	-1	2	850	60	1070	953	117.2	0.472	370	211	197
6	-1	0	+1	1	750	180	1006	885	121.6	0.453	274	285	200
7	0	-1	-1	2	650	60	867	780	87.4	0.283	292	154	242
8	0	0	0	2	750	120	1314	1213	101.2	0.459	278	219	246
9	-1	0	-1	1	750	60	612	568	43.2	0.188	210	146	123
10	+1	+1	0	3	850	120	789	685	104.2	0.385	345	257	151
11	0	+1	+1	2	850	180	768	677	91.0	0.310	202	165	176
12	+1	-1	0	3	650	120	1247	1009	238.3	0.483	292	127	266
13	+1	0	-1	3	750	60	1408	1136	271.5	0.631	275	216	189
14	+1	0	+1	3	750	180	1474	1303	171.5	0.679	436	291	320

Chemical composition:

CHNS and ash compositions of the raw PC and the APC produced at the optimum conditions (KOH/coke = 3 w/w, time= 3.47 hours, and temperature = 790 °C) are presented in Table 3.2. As it can be seen, the carbon content is slightly increased in APC sample, while hydrogen, nitrogen, sulfur and ash contents are decreased slightly, as expected.

Table 3.2: PC characterization before and after activation (KOH/coke = 3 w/w, Time= 3.47 hours, and Temperature = 790 °C)

	PC	APC
Carbon content (wt%)	89.5	90.6
Hydrogen content (wt%)	3.9	1.1
Nitrogen content (wt%)	2.7	2.1
Sulfur content (wt%)	0.46	0.34
Ash content (wt%)	5.7	4.3

Scanning electron microscopy (SEM):

The SEM images of the raw PC and various APC products obtained at various conditions are illustrated in Figure 3.1.

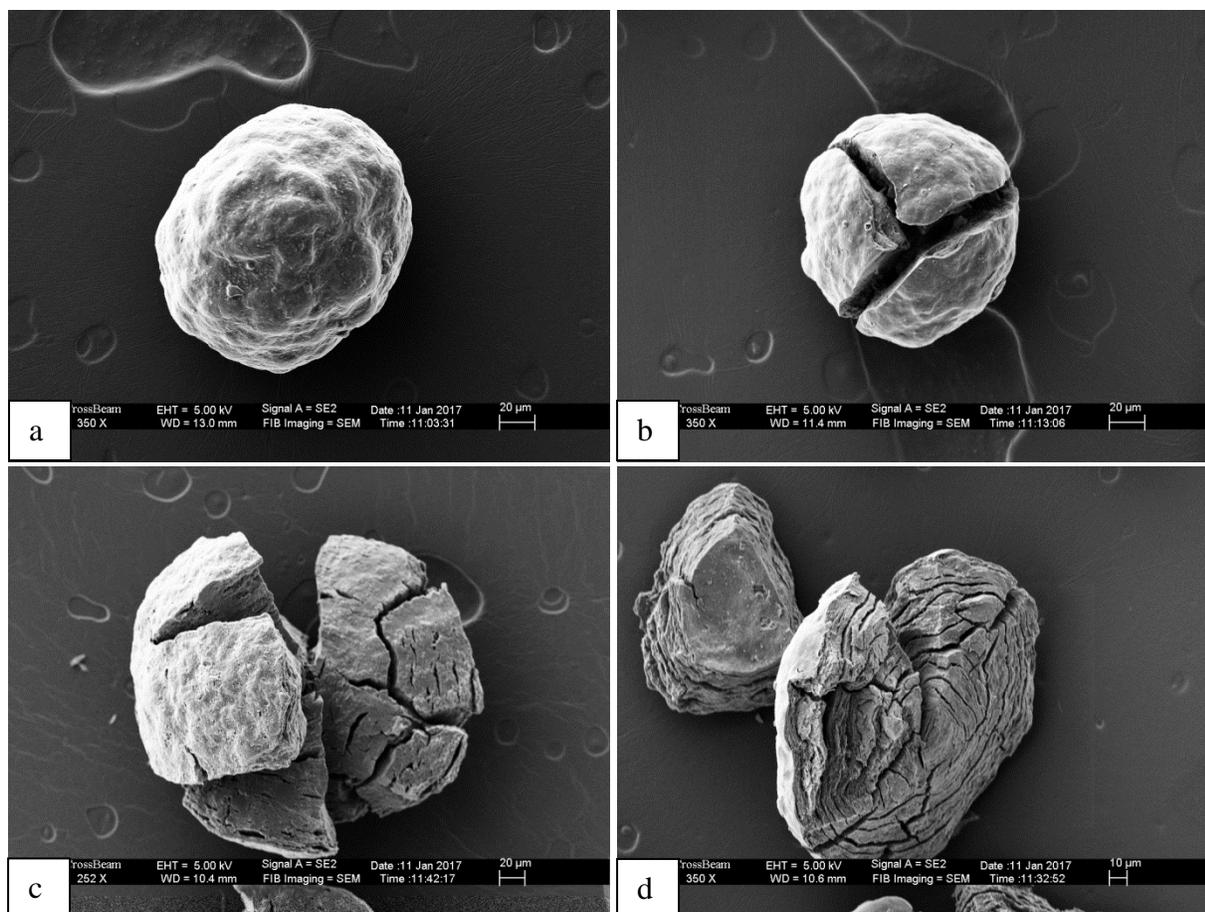


Figure 3.1: The SEM images of raw PC (a), APC (KOH/coke = 2 w/w, 3 h, 650 °C) (b), APC (KOH/coke ratio = 2 w/w, 2 h, 750 °C) (c) and APC (KOH/coke ratio = 3 w/w, 3 h, 750 °C) (d).

Figure 3.1 demonstrated that KOH activation of PC produced APC materials with macro-/micro-cracks and onion-like structure, greatly improving surface area and porosity of the APC products. The BET surface areas of the APC products increased from 12 m²/g (raw PC) to 347 m²/g (KOH/coke = 2 w/w, 3 h, 650 °C), and 1314 m²/g (KOH/coke = 2 w/w, 2 h, 750 °C) and 1474 m²/g (KOH/coke ratio = 3 w/w, 3 h, 750 °C). A higher KOH/coke mass ratio, longer activation time and higher temperature appear to be positive for generation of APC with higher surface area. However, interestingly the effect of temperature on specific surface area is not monotonic, e.g., activation of PC at 850 °C led to reduced surface area and total pore volume (Table 3.1). A possible reason could be the collapse of micropores or graphitization of the carbon structure at

such a high temperature, both leading to a decrease in the specific surface area of activated carbon products^{27,28}.

3.3.2 Isotherm results

The adsorption capacities of all prepared adsorbents for three tested naphthenic acid model compounds are presented previously in Table 3.1. To obtain the capacity of an APC adsorbent for a NA model compound, the isotherm equilibrium of the compound was obtained by adding different amounts of the adsorbent in 350 ml solution with initial concentration of 40 mg/L of the NA compound. After 48 hours of shaking, samples were taken and analyzed by HPLC for 2-naphthoic acid (2-naph.) and diphenylacetic acid (diph.) and UV-Spectrophotometer for cyclohexanepentanoic acid, respectively. Obtained Q_e values (mg/g) versus equilibrium concentration (C_e) are plotted. Some representative isotherm equilibrium results of the NA model compounds with the APC adsorbent (KOH/coke ratio of 2 w/w, 850°C, 3 h) are shown in Figure 3.2. The isotherm data of 2-naphthoic acid and diphenylacetic acid fitted well with both Langmuir and Freundlich models, while the isotherm data of cyclohexanepentanoic acid fitted the Sips model better. For example, the Langmuir model fitted the isotherm data for 2-naphthoic acid and diphenylacetic acid with $R^2 = 0.99$ and 0.98 , respectively. Sips model is typically applied for heterogeneous adsorption²⁹. For cyclohexanepentanoic acid, the Sips model fitted the isotherm data better than the other two models with $R^2 = 0.7$. Unlike the two other NAs with aromatic structure, cyclohexanepentanoic acid has an alicyclic structure with low polarity. Benzene ring in the structure of NAs could create a pi-pi interaction with the adsorbent forming a mono-layer. However, the adsorption of cyclohexanepentanoic acid on APC at pH 6.0 may involve both electrostatic attraction between carboxyl anion and positive surface and the hydrophobic interactions between the APC and the adsorbate molecules.

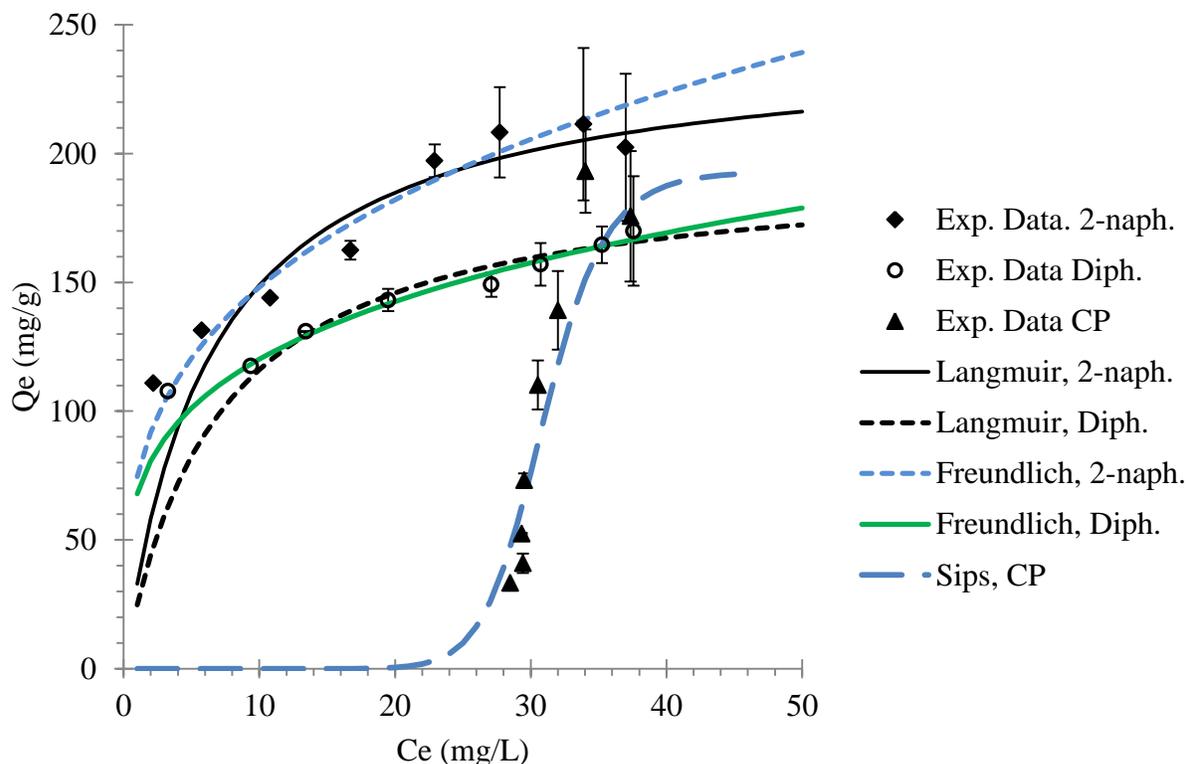


Figure 3.2: Adsorption isotherm of three NA model compounds with the APC adsorbent (KOH/coke ratio of 2 w/w, 850°C, 3h).

The capacity of obtained APC adsorbents for the removal of NAs is much greater than the typical values reported by researchers in literature. For example, Zubot et al. (2012) reported a capacity of less than 1 mg/g for untreated PC for the removal of organics from OSPW. Obviously, KOH activation has improved the PC surface significantly.

3.3.3 Response surfaces

Response surfaces for the adsorption capacity of APC adsorbents for various NA model compounds were created by SigmaPlot version 12.5 as shown in Figure 3.3. As illustrated in Figure 3.3, different model components show different adsorption behaviours on the APC adsorbents. To have better illustration of the effects of the independent factors in the activation process, the contour plots of maximum adsorption capacity versus activation parameters (activation temperature, time, and KOH/Coke ratio) for three NA model compounds (2-naphthoic

acid, Diphenylacetic acid, and Cyclohexanepentanoic acid) are presented in Supplementary Figure S 3.2.

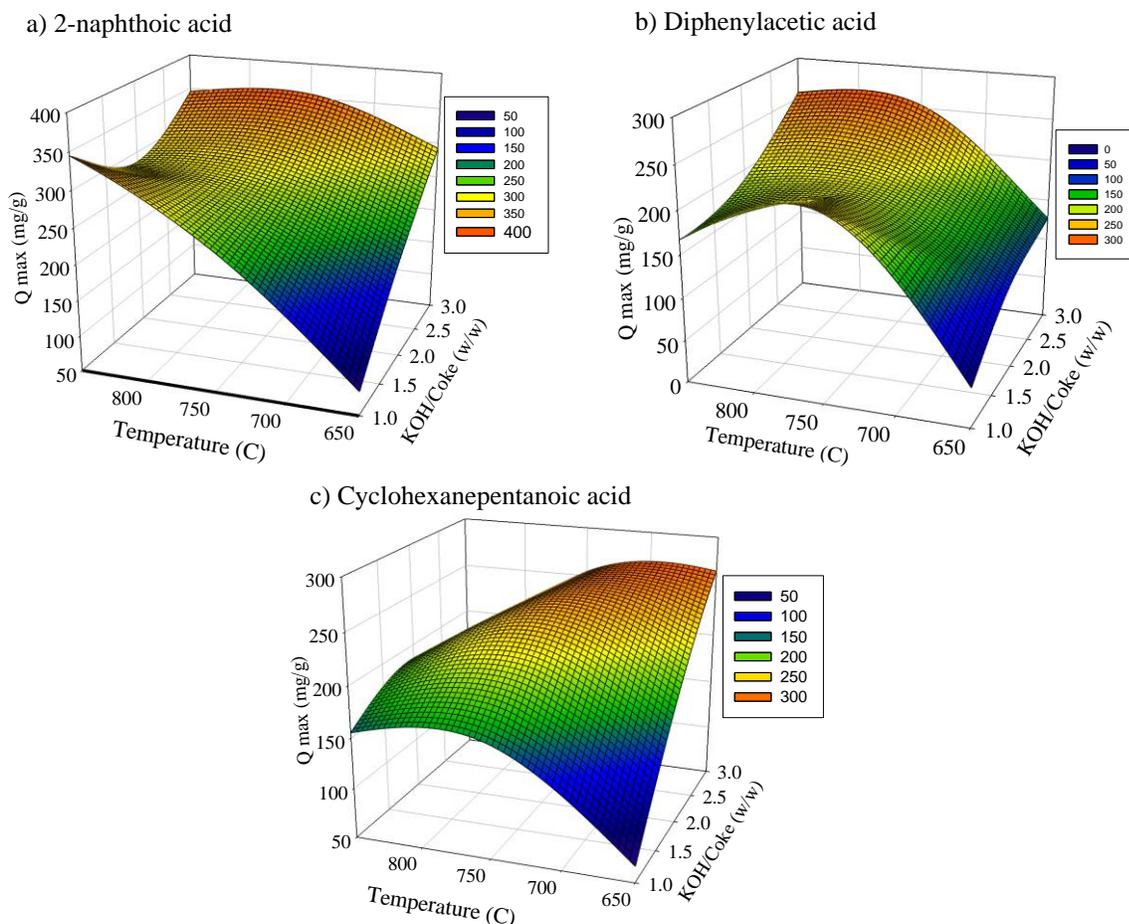


Figure 3.3: Surface response of experimental maximum adsorption capacity Q_{\max} (mg/g) of three NA model compounds on APC adsorbents prepared under different conditions (temperature and KOH/coke mass ratio)

From Figure 3.3, all three NA model compounds, i.e., diphenylacetic acid, 2-naphthoic acid and cyclohexanepentanoic acid, have similar behaviour on the APC adsorbents prepared at lower temperature (less than 750 °C). At activation temperature < 750 °C, the adsorption capacity for all these compounds increased by increasing the KOH/coke ratio as well as increasing the temperature from 650 to 750 °C. In contrast, the APC adsorbents prepared at > 750 °C, adsorption of all compounds, in particular cyclohexanepentanoic acid, exhibited a different behaviour: the adsorption capacity reduced with further increasing the activation temperature

from 750 to 850 °C. This could be due to the loss of some functional groups on the adsorbent responsible for adsorption of the NA compounds when prepared at 850 °C. The relative intensity of functional groups such as hydroxyl and carbonyl decrease at elevated temperature³⁰. Another possible reason could be that activation of PC at 850°C led to reduced surface area as well as total pore volume (Table 3.1) caused by the collapse of micropores or graphitization of the carbon structure at such high temperature^{27,28}. The reduced surface area and micropores would result in a decrease in adsorption capacity of the adsorbent.

In all circumstances, the KOH/coke ratio shows a positive effect on the adsorption capacity of the prepared APC adsorbents, i.e., the adsorption capacity generally increases with the increasing KOH/coke ratio due to higher surface area and pore volume for the APC at this condition (Table 3.1).

Main effects: The main effects plots, as shown in Figure 3.4, were drawn by plotting the mean adsorption capacity of the APC adsorbents for the three NA model compounds vs. the activation parameters (KOH/coke ratio, time of activation, and temperature). From the main effects plots, similar conclusions (as drawn from the response surface and contour plots) can be obtained. For instance, for all three model compounds the adsorption capacity increased with increasing the KOH to PC ratio from 1 to 3. This improvement in adsorption capacity was more significant when the ratio increased from 2 to 3 for the aromatic model compounds. By increasing the activation temperature from 650 °C to 750 °C, the adsorption capacity of APC adsorbents for all three NA model compounds increased, and the increase was more pronounced for the two aromatic NA compounds than of cyclohexanepentanoic acid. However, further increasing the activation temperature from 750 to 850 °C, the mean adsorption capacity for 2-naphthoic acid increased from 290 mg/g to 315 mg/g, while it reduced slightly from 220 mg/g to 200 mg/g for diphenylacetic acid, and it reduced from 220 mg/g to 170 mg/g for cyclohexanepentanoic acid. Compared to the KOH/coke ratio and activation temperature, effect of activation time on the adsorption capacity of the obtained APC was less significant.

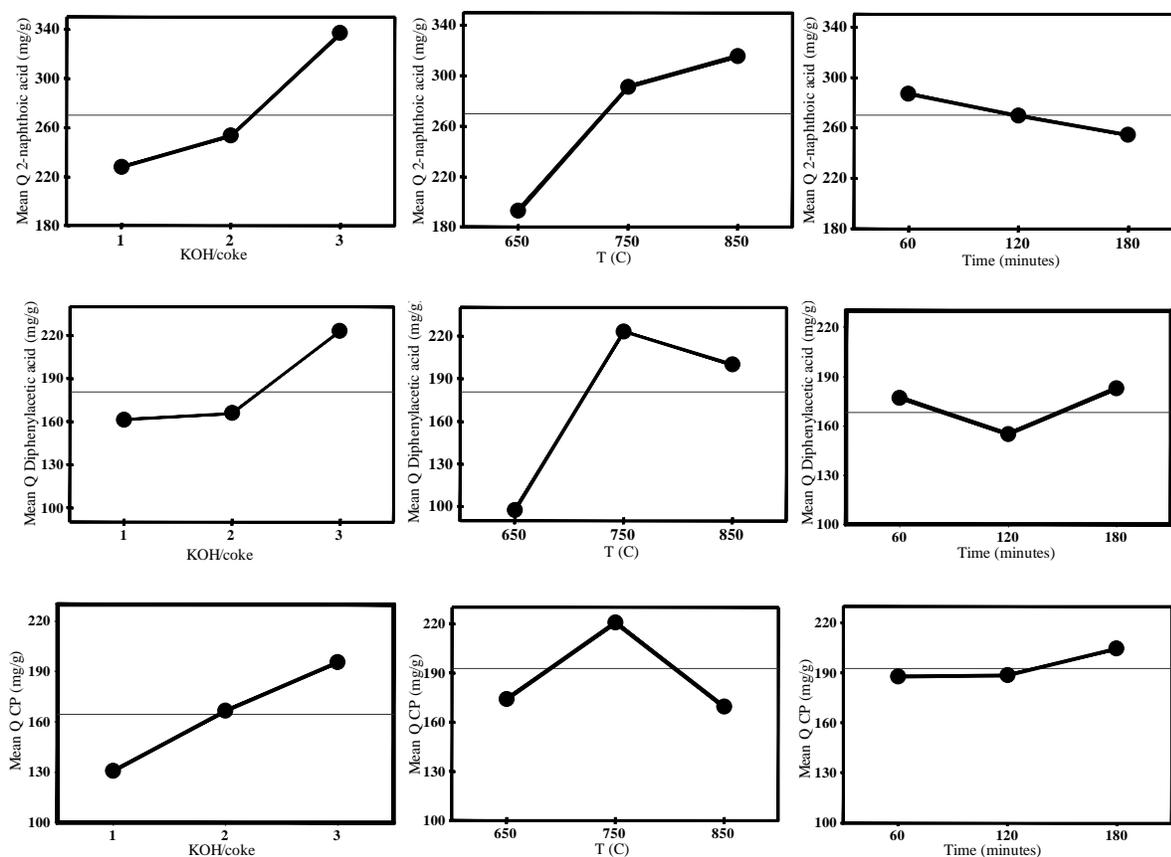


Figure 3.4: The main effects plots for the mean adsorption capacity of the APC adsorbents for three NA model compounds

3.4 Modeling

The adsorption capacity results were modeled by the *Design Expert* software in order to predict the optimum condition for maximizing the adsorption for all three NA model compounds, i.e., 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid, as shown in the following equations (1), (2) and (3), respectively. In these equations, the A, B and C are the coded terms for KOH/coke mass ratio, activation temperature, and activation time, respectively. The terms in these equations with P-value < 0.05 were selected as the significant terms. For instance, for 2-naphthoic acid, A, B, C, AB, AC, A², B², A²B, A²C are significant model terms.

2-naphthoic acid:

$$Q \text{ (mg/g)} = 280.69 + 54.50 \times A + 43.75 \times B - 88.75 \times C - 52.25 \times A \times B + 24.25 \times A \times C + 20.04 \times A^2 - 36.46 \times B^2 + 35.00 \times A^2 \times B + 145.00 \times A^2 \times C \quad (\text{Eq.1})$$

Diphenylacetic acid:

$$Q \text{ (mg/g)} = 218.43 + 30.87 \times A + 51.5 \times B - 34.75 \times C - 69.93 \times B^2 + 88.25 \times A^2 \times C \quad (\text{Eq.2})$$

Cyclohexanepentanoic acid:

$$Q \text{ (mg/g)} = 248.67 + 47.75 \times A - 6.50 \times B - 35.25 \times C - 51.00 \times A \times B + 13.50 \times A \times C + 24.75 \times B \times C - 32.71 \times A^2 - 56.46 \times B^2 - 7.96 \times C^2 + 87.25 \times A^2 \times C + 8.75 \times B \times C^2 \quad (\text{Eq.3})$$

In equation 1 and 3, the coefficient of A and B factors are positive, while the coefficient of AB factor negatively contribute the adsorption capacity. It illustrates that increasing KOH/coke ratio and temperature at the same time could negatively affect the adsorption behaviour of 2-naphthoic acid and cyclohexanepentanoic acid. Such behaviour was observed at higher temperature (Figure 3.4). For example, increasing activation temperature from 750 to 850 °C reduced the adsorption capacity due to collapse of pore structure and losing functionalities that might be responsible for removal of these two model compounds.

The analysis of variance (ANOVA) results for the modeling are presented in Table 3.3.

Table 3.3: Analysis of variance (ANOVA) for the fitted models

Source	SS ^a	Df ^b	MS ^c	F-Value	P-Value
a) 2-naphthoic acid response:					
Model	1.205E+05	9	13390	126.5	< 0.0001
Residual	529.4	5	105.88		
Lack of Fit	198.8	3	66.25	0.4	0.7700
Pure Error	330.7	2	165.33		
Core Total	1.210E+5	14			
b) Diphenylacetic acid:					
Model	63379.4	5	12675.88	16.54	0.0003
Residual	6896.34	9	766.26		
Lack of Fit	6152.34	7	878.91	2.36	0.3294
Pure Error	744.00	2	372.00		
Core Total	70275.73	14			
c) Cyclohexanepentanoic acid:					
Model	62566.57	11	5687.87	414.5	0.0002
Residual	41.17	3	13.72		
Lack of Fit	12.5	1	12.5	0.87	0.4490
Pure Error	28.67	2	14.33		
Core Total	62607.73	14			

^aSum of squares, ^bDegree of freedom, ^cMean square

For 2-naphthoic acid the model equation (Eq. 1) fits the experimental results very well, with $R^2=0.996$ and $R^2_{Adj}=0.988$. The Model F-value of 126.46 implies the model is significant, as shown in Table 3.3. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. For diphenylacetic acid (Eq. 2), R^2 and R^2_{Adj} were 0.902 and 0.847, respectively. The Model F-value of 16.54 implies the model is significant. There is only a 0.03% chance that a "Model F-Value" this large could occur due to noise. The obtained model for prediction of cyclohexanepentanoic acid (Eq. 3) adsorption fitted experimental data well with the R^2 and R^2_{Adj} of 0.999 and 0.997, respectively.

The predicted values using the above model equations versus experimental values for all the NA model compounds are plotted in Figure 3.5, which show good predicatbility of the developed models.

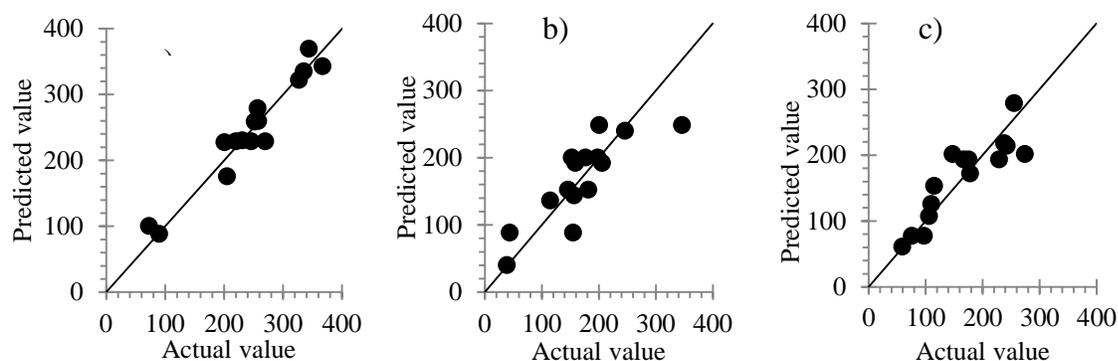


Figure 3.5: The predicted vs. experimental adsorption values (mg/g) for all NA model compounds tested, i.e., 2-naphthoic acid (a), diphenylacetic acid (b) and cyclohexanepentanoic acid (c)

The model predicted that KOH/coke mass ratio = 3, activation temperature = 790 °C, and activation time = 3.47 hrs are the optimum PC activation conditions to achieve the maximum adsorption capacity of the APC for all three NA model compounds tested. The maximum capacity as predicted by the models are 478, 337, and 333 (mg/g) for 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid, respectively, while the experimental values obtained with the APC at the optimum conditions were 451.3, 362.2, and 319.6 (mg/g), respectively, as shown in Table 3.4.

Table 3.4: The predicted and experimental values obtained with the APC adsorbents prepared at the optimum activation conditions (values are in mg/g)

Response	Prediction	SE ^a Mean	95% CI ^b Low	95% CI High	SE Prediction	95% PI ^c Low	95% PI High	Experimental Value
Q _{2-naph.}	478.4	12.36	446.7	510.2	16.1	437.1	519.8	451.3
Q _{Diph.}	337.4	24.61	281.8	393.1	37.0	253.7	421.2	362.2
Q _{CP}	333.2	5.8	314.7	351.6	6.90	311.3	355.1	319.6

^aStandard Error, ^bConfidence interval, ^cPrediction interval

The APC adsorbent prepared at the optimum activation conditions showed that it has a very high BET surface area and total pore volume of 1726 m²/g and 0.85 cc/g respectively. In order to relate the textural properties of the produced adsorbent and their adsorption capacity for NAs, the obtained data for adsorption capacity of the APC adsorbents for the NA model compounds tested were modeled as a function of their surface area, meso and micro pore area, and the total pore volume (as presented previously in Table 3.1). The best fitted equations using ProMV software are presented as Eqs (4), (5) and (6) for 2-naphthoic acid, diphenylacetic acid, and cyclohexanepentanoic acid, respectively.

$$Q_{2\text{-naphthoic acid}} = 21.32 \times \text{Pore volume (cc/g)} + 0.257 \times \text{Mesopore (m}^2\text{/g)} + 0.084 \times \text{Micropore (m}^2\text{/g)} + 0.071 \times S_{\text{BET}} \text{ (m}^2\text{/g)} \quad (\text{Eq. 4})$$

$$Q_{\text{Diphenylacetic acid}} = 15.45 \times \text{Pore volume (cc/g)} + 0.186 \times \text{Mesopore (m}^2\text{/g)} + 0.061 \times \text{Micropore (m}^2\text{/g)} + 0.052 \times S_{\text{BET}} \text{ (m}^2\text{/g)} \quad (\text{Eq. 5})$$

$$Q_{\text{Cyclohexanepentanoic acid}} = 16.84 \times \text{Pore volume (cc/g)} + 0.203 \times \text{Mesopore (m}^2\text{/g)} + 0.067 \times \text{Micropore (m}^2\text{/g)} + 0.056 \times S_{\text{BET}} \text{ (m}^2\text{/g)} \quad (\text{Eq. 6})$$

The relative average error of the above fitted models (Eqs 4-6) were calculated to be 35%, 32%, and 32% for 2-naphthoic acid, diphenylacetic acid, and cyclohexanepentanoic acid, respectively. Such large errors of the models suggest that the textural properties (surface areas and pore volume) are not the only parameters determining the APC adsorbents' adsorption capacity, although higher quotients for pore volume and mesopore indicate the importance of creating such adsorbents for larger molecules like naphthenic acids. Other parameters such as surface functionalities play effective roles on the adsorption capacity of the produced APC adsorbents for NAs, more research in this regard is needed.

3.4.1 Kinetic study

For better understanding of the adsorption kinetics, kinetic data were also obtained and fitted to pseudo-first, pseudo-second and Weber-Morris models. As an example, Figure 3.6 shows the adsorption kinetic data and fitted curves based on different kinetic models for all three NA model compounds with the APC sample (activation conditions: KOH/PC mass ratio of 1.0, 850°C, 2 h). For the entire duration of experiments, the adsorption kinetic data fitted the second order model

the best for all three compounds, suggesting that the adsorption was chemisorption controlled. These results are in a good agreement with the results of our previous study²³.

Weber-Morris model, as given in Eq. (7), is a model to simulate adsorption systems that are controlled by diffusion.

$$q_t = K_{\text{dif}}t^{0.5} \quad (\text{Eq.7})$$

Where q_t is the adsorption capacity of the adsorbent (mg/g), K_{dif} is intra-particle diffusion rate constant (mg/g min^{0.5}).

From Figure 3.6, the intra-particle diffusion rate constant (K_{dif}) for the APC adsorbent tested for 2-naphthoic acid was obtained at 13.63, much higher than those of diphenylacetic acid ($K_{\text{dif}} = 8.3$) and cyclohexanepentanoic acid ($K_{\text{dif}} = 8.7$). These results suggest that 2-naphthoic acid diffuses faster in the pores of the APC adsorbent and reaches saturation earlier than the other two compounds, which may be explained by its more compact molecular structure, facilitating the intra-diffusion in the adsorbent pores. As shown in the Figure 3.6, Weber-Morris model fits well to the initial 30 minutes of adsorption data, implying that the intra-particle diffusion could be the rate controlling step in the initial step of adsorption process.

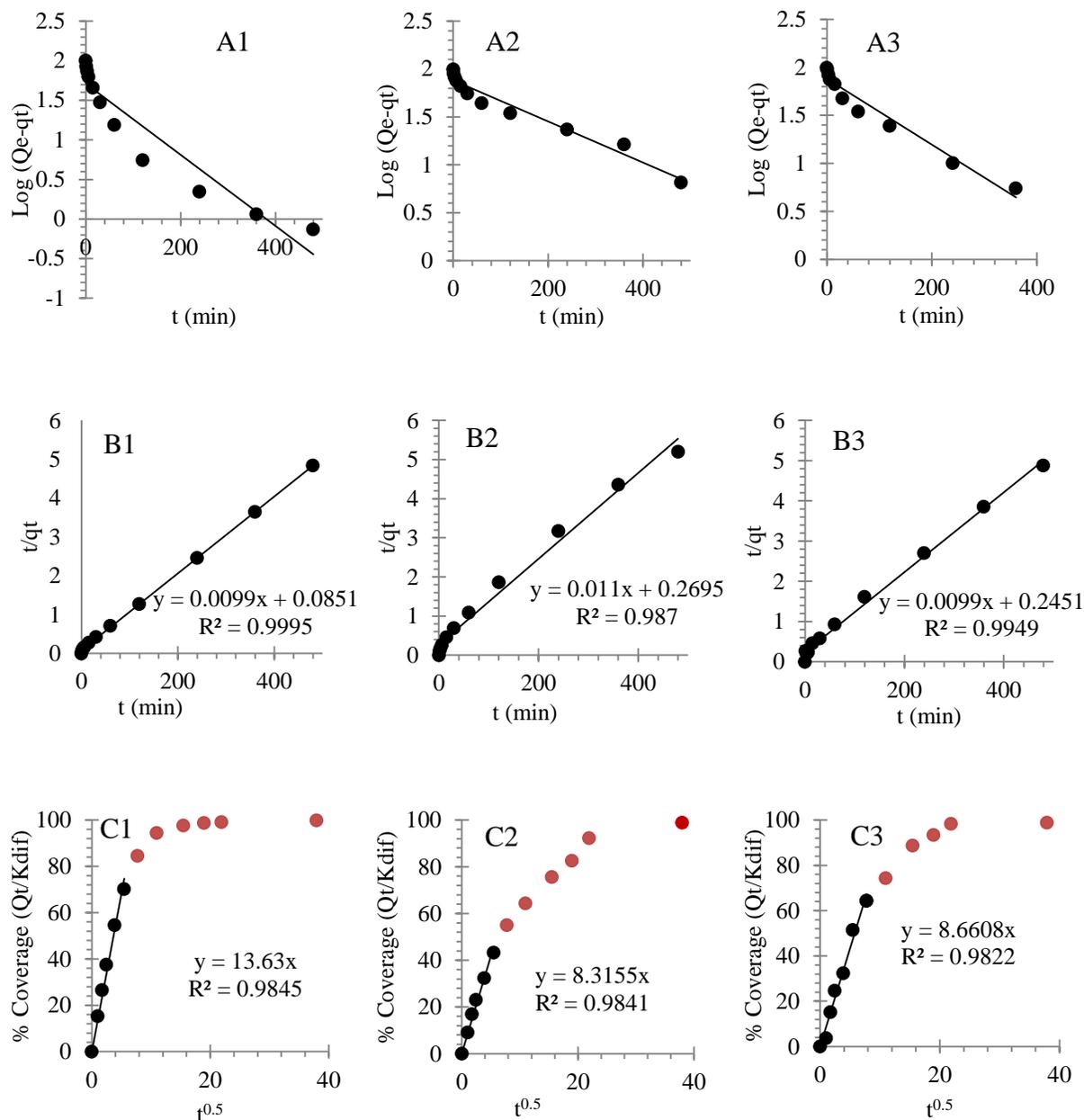


Figure 3.6: Adsorption kinetics data and fitted curves based on different kinetic models with the APC sample (activation conditions: KOH/PC mass ratio of 1.0, 850°C, 2 h) (A: Pseudo-first order, B: Pseudo-second order, C: Weber-Morris model, Subscripts 1, 2 and 3 refers to 2-naphthoic acid, diphenylacetic acid, and cyclohexanepentanoic acid, respectively.)

3.4.2 Leaching test

One of the main concerns regarding the application of APC as adsorbent in water and wastewater treatment processes is the leaching of metals such as vanadium³¹, molybdenum and nickel⁵, manganese, iron and chromium¹⁷. In order to investigate the metal leaching behavior of the APC adsorbent during adsorption, ICP analysis of raw PC, APC and the leachate from the APC was conducted, and the results are presented in Table 3.5. These results clearly show that the quantity of metals in the raw PC was significantly reduced during the KOH activation process. For example, the concentration of Al, Co, Fe, V, Cr, Mn and Mg in the raw PC was reduced from 62.7, 0.1, 57.8, 10.2, 0.12, 2.0 and 6.1 ppm, and it is attributed to the acid washing step of the activation process. Furthermore, the ash content of PC was measured before and after activation, as shown previously in Table 3.2. The ash content of the raw PC reduced from 5.7% (PC) to 4.3% (APC), which supports the above ICP analysis results showing noticeable reduction in sulfur and metals contents of the PC during activation. As presented in Table 3.5, the leachate from the APC (24 hours of shaking of produced APC adsorbent in MilliQ water) contains undetectable amounts of metals, suggesting negligible leaching of metals from the APC during the adsorption process.

3.5 Conclusions

(1) Petroleum coke (PC) with a BET surface area of $<15 \text{ m}^2/\text{g}$ and a total pore volume of $<0.01 \text{ cc/g}$ can be activated to produce highly porous adsorbents by KOH activation. Activated petroleum coke (APC) adsorbent with a BET surface area of $1726 \text{ m}^2/\text{g}$ and total pore volume of 0.85 cc/g was produced at the optimum activation conditions (KOH/coke mass ratio of 3.0, activation temperature $790 \text{ }^\circ\text{C}$ and time 3.47 hrs). With the APC obtained at the optimum activation conditions, the maximum adsorption capacity of 451, 362, and 320 (mg/g) was achieved for 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid, respectively.

(2) The adsorption capacity of APC adsorbents for all three NA model compounds increased by increasing KOH/coke mass ratio or by raising the activation temperature up to $750 \text{ }^\circ\text{C}$. Further increasing the activation temperature from 750 to $850 \text{ }^\circ\text{C}$ produced APC adsorbents with reduced adsorption capacity for diphenylacetic acid and cyclohexanepentanoic acid. Compared to the KOH/coke ratio and activation temperature, effect of activation time on the adsorption capacity of the obtained APC was less significant.

(3) Generally APC adsorbents with a higher specific surface area and pore volume give better adsorption capacity. However, the textural properties (surface areas and pore volume) are not the only parameters determining the APC adsorbents' adsorption capacity. Other parameters such as surface functionalities also play important roles on the adsorption capacity of the produced APC adsorbents for NAs.

(4) The KOH activation process, in particular the acid washing step, could significantly reduce the sulfur and metals contents present in the raw PC, and no significant leaching of metals from the APC adsorbents occurred.

3.6 Acknowledgements

The authors would like to acknowledge funding from NSERC and Newalta (Terrapure) Corporation via a CRD grant, as well as NSERC Discovery Grants awarded to co-authors (C. Xu and M. Ray). The authors are also indebted to Dr. Shahzad Chatha and Mrs. Fang Cao for their great assistance in samples preparation and analysis.

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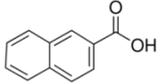
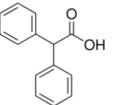
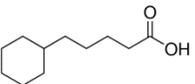
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3.8 Supplementary information for chapter 3

Table S 3.1: Basic properties of the selected model naphthenic acids (NAs) tested in this study.

Name:	Formula:	MW:	pKa:	Structure:
2-naphthoic acid CAS No.: 93-09-04	C ₁₁ H ₈ O ₂	172.18	4.2 ¹	
Diphenylacetic acid CAS No.: 117-34-0	C ₁₄ H ₁₂ O ₂	212.24	4.72 ¹	
Cyclohexanepentanoic acid CAS No.: 5962-88-9	C ₁₁ H ₂₀ O ₂	184.28	N/A ²	

¹Value obtained from SciFinder (<https://scifinder.cas.org/>) chemical database, calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (1994–2015 ACD/Labs).

²Not available

Table S 3.2: Variables, their real and coded values in Box-Behnken design

Variable	Unit	Symbol	Coded and real level of variables		
			-1	0	1
KOH/coke	-	X ₁	1	2	3
Temperature	°C	X ₂	650	750	850
Time	Min	X ₃	60	120	180

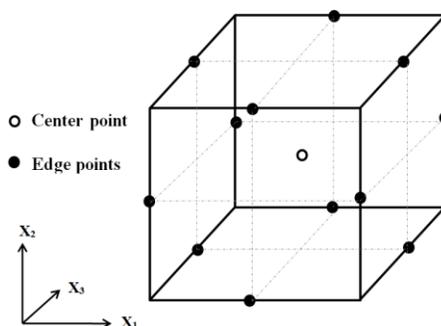


Figure S 3.1: Schematic of the Box-Behnken design for K= 3 (K is number of factors)

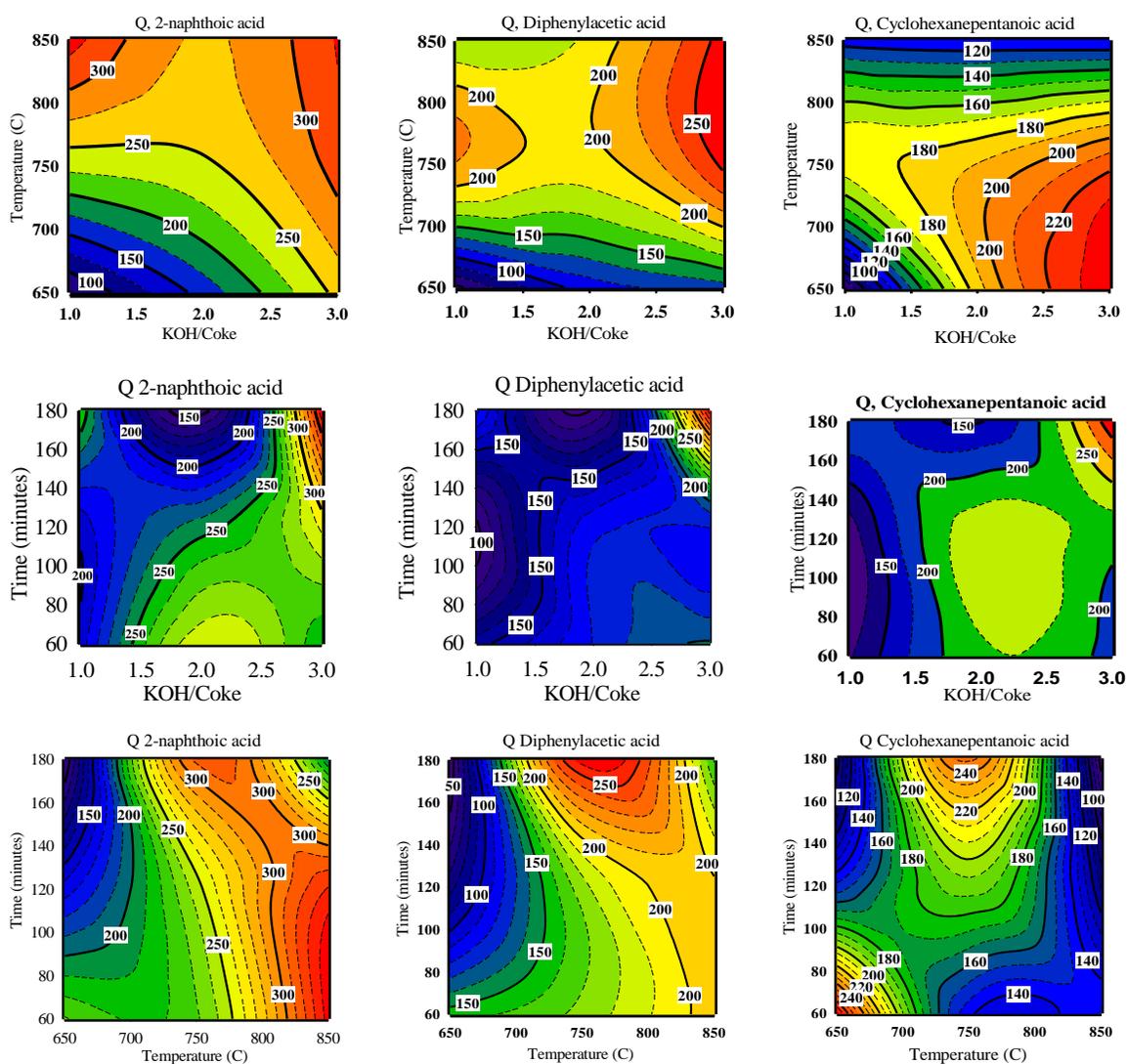


Figure S 3.2: Contour plots of maximum adsorption capacity versus activation parameters for the NA model compounds tested.

Chapter 4

4 Surface Amination of Activated Carbon and Petroleum Coke for the Removal of Naphthenic Acids and Treatment of Oil Sands Process-affected Water (OSPW)

Abstract

To enhance the removal of model naphthenic acids (NA) from synthetic wastewater and removal of organics in oil sands process-affected water (OSPW) by adsorption, surfaces of commercial charcoal-derived activated carbon (AC) and proprietary petroleum coke-derived activated carbon (PAC) were modified. Two different amination processes including a single stage treatment with ammonia gas at an elevated temperature and a two-step treatment of nitration followed by reduction were adopted. All adsorbents showed excellent capacity for the model NAs and OSPW at low pH (≤ 4.0). Ammonia treatment was more effective on improvement of adsorption capacity than the nitration followed by reduction method. The effect was more significant for commercial activated carbon compared to PAC, especially for multi-component adsorption at pH 8.0. The kinetics of adsorption improved significantly by the surface modification methods indicating great potential for these adsorbents in continuous column operation.

Keywords: Activated carbon, Petroleum coke activated carbon, KOH activation, Surface amination, Naphthenic acids, Oil sands process-affected water

4.1 Introduction

Each day large volumes of oil sands process-affected water (OSPW) are being produced during the extraction of bitumen in oil sands industry in northern Alberta^{1,2}. OSPW contains different polyaromatic hydrocarbons (PAHs), bitumen, as well as naphthenic acids (NAs)^{3,4}, which not only are the major source of toxicity in OSPW⁵⁻⁸, but also create operational problems such as corrosion of the equipment during bitumen recovery process⁹. A recent report indicates that about 720 billion liters of OSPW that were produced during the extraction of bitumen from Canadian oil sands industry have been stored in tailing ponds covering approximately 170 kilometer square¹⁰. Water treatment and management strategies are urgently needed for OSPW recycling in order to reduce the withdrawal of fresh water from the Athabasca River and to permit the safe release of treated OSPW to the receiving environment by removing these compounds¹¹.

Until now, different methods such as advanced oxidation¹², membrane processes¹³, biological treatment¹⁴, and adsorption^{3,15} have been tested for the removal of organics including naphthenic acids from OSPW. Although efficient, membrane processes are highly susceptible for fouling in treating OSPW¹⁶. In addition, filtration methods are not cost effective due to large pressure heads needed to treat large volumes of contaminated water. Biological treatments although cost-effective, are often slow, and toxic compounds present in OSPW affect the efficiency and survival of the microorganisms. NAs are poorly biodegraded in the holding ponds in the field¹⁷. Among all the different treatment methods, adsorption has gained significant attention due to its efficiency and fast removal rates³. Recent studies on petroleum coke (PC), a relatively inexpensive and abundant feedstock, used as an adsorbent after activation, have brought renewed attention to the use of adsorption processes for OSPW treatment^{15,18,19}. Gamal El-Din et al.³ demonstrated that adsorption using PC followed by ozonation is an efficient process of removing NAs from OSPW.

PC based adsorption processes have been used for treatment of a wide variety of wastewaters²⁰⁻²². However, raw PC has low surface area and consequently low adsorption capacity. Various surface activation methods have been adopted for increasing the specific surface area and porosity, and customization of PC surface characteristics

depending on the properties of the compounds to be adsorbed. Most of the earlier research used chemical activation methods using KOH or some other alkali metal hydroxides^{23,24}. Although, microporous surface area and micropore volume are important factors for adsorption, surface functionality and solution pH play significant roles in determining the equilibrium adsorption capacity of polar compounds such as naphthenic acids. The existence of nitrogen-containing functional groups on the surface of adsorbent generally provides basic properties, which improves removal of polar compounds such as organic acids, due to dipole-dipole interactions, H-bonding and covalent bonding^{25,26}.

There are several ways of introducing nitrogenous groups on the carbonaceous adsorbents including chemical activation using urea-formaldehyde, melamine-formaldehyde, tetraethylenepentamine (TEPA), direct treatment of surface with nitrogen containing reagents such as ammonia and amines, and the surface impregnation with amine-containing compounds with varying success depending on the nature of adsorbates^{20,23}.

The objective of this research is to enhance removal of naphthenic acids from synthetic solution using surface modified activated carbon adsorbents. Two types of activated carbon adsorbents were used, a commercial activated carbon (AC), and a proprietary petroleum coke activated carbon (PAC). Two different methods were used to introduce nitrogen-containing functionality on the surface of both AC and PAC: (1) a one-step process where direct ammonia gas was used to introduce -NH_3 group on the surface, and (2) a two-step process including an electrophilic substitution to introduce nitrate group, followed by reduction of the nitrate to NH_2 . The adsorption performances of the surface modified AC and PAC by these two methods were compared in removal of 3 model naphthenic acids from pure water, and removal of total organic carbon (TOC) from real oil sand process-affected water (OSPW).

4.2 Material and Methods

4.2.1 Materials

The commercial activated carbon (AC) used in this study was an extruded activated charcoal (Norit ROW 0.8 SUPRA) (CAS Number: 7440-44-0), purchased from Sigma-Aldrich Canada Co. The petroleum coke (PC) and the oil sands process-affected water (OSPW) were supplied by NEWALTA Corporation (Burlington, ON). The chemicals such as KOH, 2-Naphthoic acid, 1,4-cyclohexanedicarboxylic acid, HPLC grade acetonitrile were purchased from VWR company. Diphenylacetic acid was purchased from Sigma-Aldrich Canada Co. The properties of the selected model naphthenic acids such as solubility and K_{ow} values were provided in a previous publication¹⁰. Milli-Q water was obtained from a Milli-Q Integral A10 purification system (Millipore SAS, 67120 Molsheim, France).

4.2.2 Experimental Methods

PAC production from petroleum coke:

For KOH activation of PC, about 6 g of raw PC was mixed with adequate amount of water containing 20 g KOH (analytical grade) to make a slurry. The slurry was ultrasonicated for 30 min and left overnight for KOH solution to penetrate the skeletal structure of PC. Thereafter, the well-mixed slurry was heated in 100 mL/min nitrogen flow in a tubular furnace at a heating rate of 20 °C/min up to 700 °C and kept at this temperature for 3 h. The petroleum-coke derived activated carbon (PAC) was cooled to ambient temperature using nitrogen, and washed with 5% HCl to remove the ash, residual KOH and other potassium-containing compounds, followed by washing with Milli-Q water until the pH of wash water reached neutral. The washed samples were dried in an oven at 120 °C overnight in air and stored in sealed glass containers prior to the analysis and use.

Surface modification of AC and PAC:

About 5 g of AC or PAC was placed in a custom-made quartz tube reactor and nitrogen was passed through the reactor to completely displace oxygen in the reactor, followed by

heating of the sample to 700 °C for 3 h in a 10 ml/min flow of ammonia gas. Ammonia gas modified samples were designated as AC-NH₃ and PAC-NH₃, respectively.

For the second method of surface modification, a two-step process was adopted²⁷. In this method, 5 g of AC or PAC, 20 ml acetic anhydride and 10 ml concentrated sulfuric acid were placed in a three-neck flask. Fuming nitric acid was added dropwise in the mixture with continuous stirring for 5 h and keeping the temperature below 5 °C using ice-water. The mixture was kept at room temperature for another 19 h for complete reaction. Subsequently, nitrated AC or PAC was washed with Milli-Q water and dried in an oven at 105 °C in air for 24 h. The reduction of nitrated PAC was carried out in a 1000 mL flask in nitrogen atmosphere in presence of Milli-Q water, 28 wt% aqueous ammonia, and sodium hydrosulfite (reducing agent), under stirring at room temperature for 24 h. Finally, the modified AC and PAC were washed with Milli-Q water and dried at 105°C and stored in glass container for further tests. The produced adsorbents are denoted as AC-NH₂ or PAC-NH₂, respectively.

Analytical Methods:

A Nova 1200E, BET analyzer (QuantaChrome Co.) was used to characterize the textural properties (e.g., the pore size distribution and specific surface area) of the raw and modified adsorbents. The particle size of the adsorbents was determined using Helos/BR laser diffraction analyzer (Sympatec GmbH, Germany). X-ray Photoelectron Spectroscopy (XPS) analyses were carried out for Carbon 1s and Nitrogen 1s with a Kratos Axis Nova spectrometer using a monochromatic Al K (alpha) source (15mA, 14kV). The instrument work function was calibrated for binding energy (BE) of 83.96 eV for the Au 4f_{7/2} line for metallic gold, and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p_{3/2} line of metallic copper. The Kratos charge neutralizer system was used on all specimens. High resolution analyses were carried out with an analysis area of 300 x 700 microns and pass energy of 20 eV. Spectra have been charge corrected to the main line of the carbon 1s spectrum set to 284.5 eV and were analysed using CasaXPS software.

A Dionex ICS-3000 was used in an HPLC configuration to detect the naphthenic acids using an Acclaim Fast LC Column 120 C18 (3 × 75 mm). The mobile phase used was an acetonitrile (ACN)/water mixture with varying solvent ratios depending on the model NAs. The mobile phase consisted of 60% ACN and 40% Milli-Q water for 2-naphthoic acid and diphenylacetic acid, and 53% ACN and 47% MQ water for 1,4-cyclohexanedicarboxylic acid. The mobile phase was acidified with sulfuric acid to pH 2.15, in order to ensure that the acids in the samples were in their protonated form. The acidified mobile phase was filtered using a vacuum filtration apparatus with a 47 mm polytetrafluoroethylene (PTFE) disk filter with pore size of 0.20 μm. A Shimadzu 5000A TOC analyzer with an ASI-5000 auto sampler was used to measure the total organic carbon (TOC) contents of the samples.

The point of zero charge (pH_{pzc}) of the adsorbents was determined using the pH drift method due to its simplicity and wide applications. About 50 mL of 0.1 M NaCl solution was adjusted to pH values between 3 and 11, by adding either HCl or NaOH 0.1 and 0.01 M. Then 0.15 g of adsorbent was added to the vials containing NaCl solution. The vials were then flushed with nitrogen gas, capped, and placed in the orbital shaker at 170 rpm for approximately 32 hr at room temperature (23 °C). After which the vials were opened and the pH values were recorded. The final pH was plotted against the initial pH, and the point where $\text{pH}_{\text{initial}} = \text{pH}_{\text{final}}$ was taken to be the point of zero charge.

Batch Adsorption Experiments:

All batch adsorption experiments were performed in 500 mL Erlenmeyer flasks, using 175 mL of solution placed in an orbital shaker at 170 rpm and 23 °C. Initial tests illustrated that the adsorption equilibrium was reached within 48 h. Therefore, for the kinetic experiments, ten samples of 1 mL were taken at different time intervals between 5 min-48 h. Samples were filtered using 0.45 μm nylon syringe filters prior to the analysis on the HPLC. In typical tests, 70 mg adsorbent was added to 175 mL of the solution containing the model naphthenic acids with initial concentration at 40 mg/L either as single compound or as a mixture of three, each at same (40 mg/L) initial concentration. The pH values for most experiments were natural pH (4.1- 4.2) of 40 mg/L of naphthenic

acids or adjusted to $\text{pH} = 8$, which is close to the pH of real OSPW. Duplicate experiments were carried out at each condition, and the results presented are the average of two experiments. The differences in concentration at different time intervals between two experiments varied between 0.5% -7% indicating excellent reproducibility of the experiments.

4.3 Results and Discussion

4.3.1 Surface characterization of all the adsorbents

Chemical activation of raw PC using KOH significantly increased the surface area of raw PC. The surface area of PC increased from $12 \pm 0.2 \text{ m}^2/\text{g}$ to $1443 \pm 13 \text{ m}^2/\text{g}$ for the PAC after KOH activation, mainly due to the formation of mesopores ($\approx 1004 \text{ m}^2/\text{g}$). The pore size of the PC increased from 1.2 to 2.1 nm for PAC. The SEM images of PC before and after KOH activation are shown in Figure 4.1, a and b respectively.

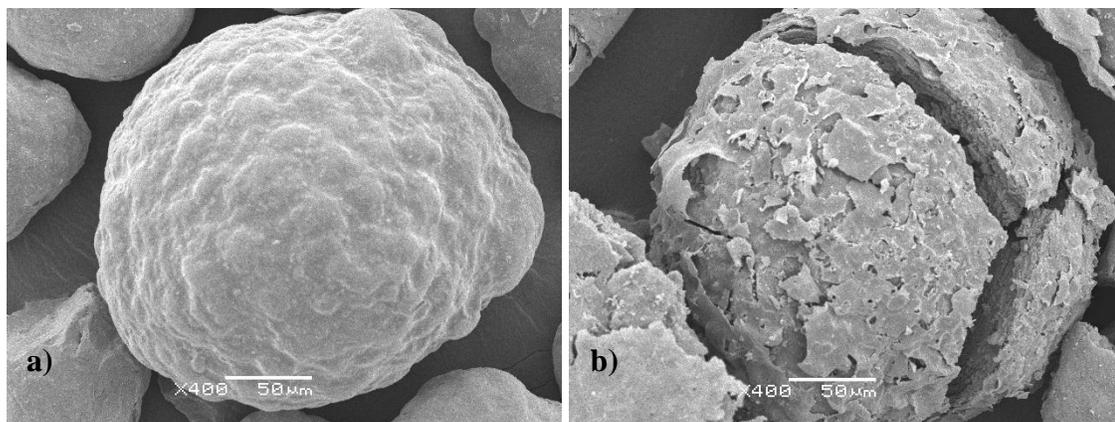


Figure 4.1: SEM images of PC before (a) and after (b) activation

The total surface area of commercial activated carbon (AC) is $1399 \pm 27 \text{ m}^2/\text{g}$, which is slightly lower than that of PAC ($1443 \pm 13 \text{ m}^2/\text{g}$). While, AC has higher microporous area with slightly lower average pore size, PAC has higher mesoporous area with higher pore size than AC. Surface activation with ammonia ($-\text{NH}_3$) and amination ($-\text{NH}_2$) treatment caused decrease in specific surface area of both AC and PAC, as presented in Table 4.1.

Table 4.1: Comparison of textural properties of AC and PAC with and without surface modification.

Sample name	Micropore area (m ² /g)	Mesopore area (m ² /g)	Total area (m ² /g)	Micropore volume (cm ³ /g)	Total pore volume (cm ³ /g)	Pore size (nm)
AC	766	634	1399± 27	0.3	0.7	2.0
AC-NH ₂	520	435	955± 7	0.3	0.5	2.0
AC-NH ₃	778	488	1266± 23	0.4	0.6	2.0
PC	12	0	12± 0.2	0	~0	1.2
PAC	439	1004	1443± 13	0.2	0.8	2.1
PAC-NH ₂	277	689	967± 8	0.1	0.5	2.1
PAC-NH ₃	254	770	1024± 7	0.1	0.5	2.1

The decrease was more for AC/PAC–NH₂ than AC/PAC–NH₃, probably due to the collapse of pore structure and clogging of the pores during the two-steps amination (-NH₂) treatment [27], as evidenced by the reduced pore volume in these surface modified carbon materials. Both AC and PAC lost about 33% of surface area in the 2-step amination process.

The XPS spectra of PAC and NH₃ modified PAC are shown in Figure 4.2, which demonstrate reduction in various oxygen-containing groups (O-C=O, C=O, C-OH, and C-O-C) in the PAC-NH₃ sample, accompanied by increasing aromatic amine (C-NH₂, binding energy 400.5 eV), imine or pyridinic and pyrrolic nitrogen (C=N-, 398.4 eV) functionality. It thus suggests that thermal decomposition of the oxygen-containing functional groups would create active sites for introduction of nitrogen-containing functional groups such as aromatic amine and imine (or pyridinic and pyrrolic nitrogen) on the surface, as observed earlier in literature²⁸.

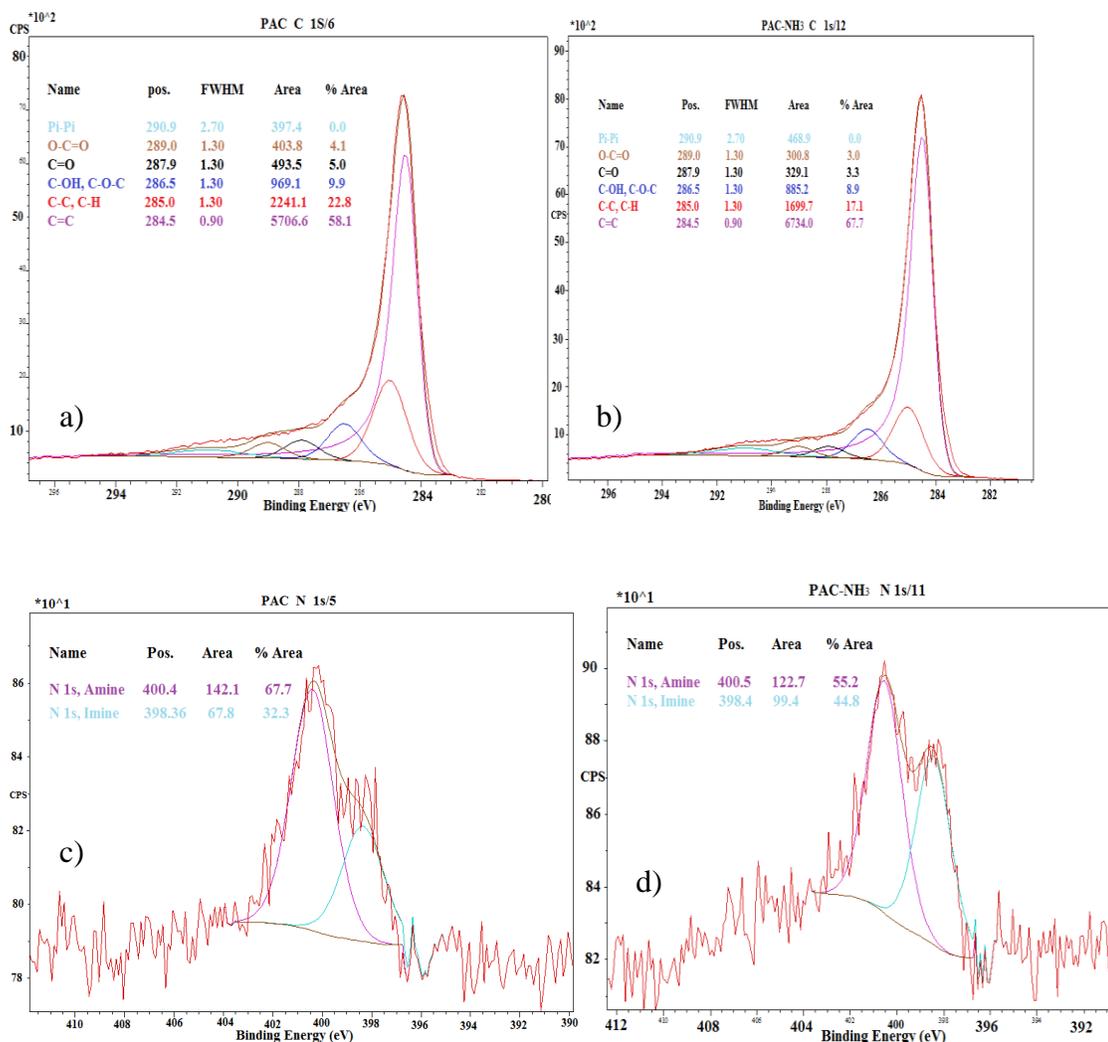


Figure 4.2: XPS analysis of PAC (a: Carbon 1s, c: Nitrogen 1s) and PAC-NH₃ (b: Carbon 1s, d: Nitrogen 1s)

Point of zero charge for an adsorbent dictates the pH dependent polarity of the surface, which could affect adsorption of polar compounds on the surface. The point of zero charge values of the adsorbents were measured by pH drift method and are presented in Figure 4.3. As expected, with KOH treatment the point of zero charge increased from 5.9 for PC to 7.8 for PAC, and the ammonia treatment increased the pzc of PAC further from 7.8 to 9.5. The original pzc of commercial AC is approximately 9.5, with ammonia treatment it increased to 11, as expected.

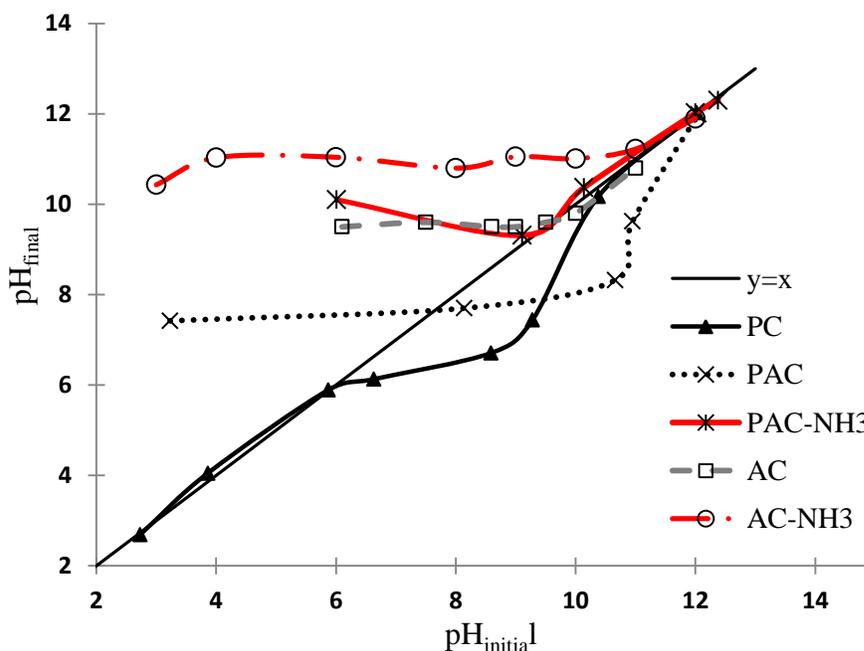


Figure 4.3: Point of zero charge for AC and PAC adsorbents and their ammonia modified samples

4.3.2 Batch adsorption of model naphthenic acids by various adsorbents

Batch adsorption experiments were conducted using different doses of PC, PAC, AC, and surface modified AC and PAC adsorbents. The experiments were conducted with both pure NAs individually and in the mixture. The natural pH of 40 mg/L of NA solutions is between 4.1 and 4.2, and initial experiments were conducted at the natural pH without controlling the pH. Since the pH of the suspended particles free OSPW is about 8.0, batch adsorption experiments were also conducted at pH 8.0 to evaluate the performance of the adsorbents. Eq. (1) was used to determine the adsorption isotherm parameters for the three model compounds.

$$Q_e = \frac{V \cdot (C_0 - C_e)}{m} \quad (\text{Eq.1})$$

Where, Q_e is adsorption capacity at equilibrium (mg/g), V is the volume of solution (L), C_0 and C_e are the initial and equilibrium concentrations of adsorbate, respectively (mg/L), and m is the mass of adsorbent (g).

4.3.2.1 Comparison of PC, PAC, and AC

The significant improvement in adsorption performance of KOH activated PC (PAC) compared to PC can be seen in Figure 4.4. For all three model NAs owing to much greater surface area and total pore volume of PAC ($1443 \pm 13 \text{ m}^2/\text{g}$ and $0.8 \text{ cm}^3/\text{g}$) compared to PC ($12 \pm 0.2 \text{ m}^2/\text{g}$ and $\sim 0 \text{ cm}^3/\text{g}$). On the other hand, with comparable surface area that of the commercial AC ($1399 \pm 27 \text{ m}^2/\text{g}$), PAC performed significantly better than AC due to its higher mesoporous area ($1004 \text{ m}^2/\text{g}$ for PAC, and $634 \text{ m}^2/\text{g}$ for AC). With comparable water solubility, pK_a , and molecular weight, all three NAs have shown very similar affinities to PC and PAC. At $\text{pH} \approx 4.1$, all three NAs would remain mostly un-dissociated, thus adsorption of NAs occurs mainly due to van der Waals forces, hydrophobic interactions, and hydrogen bonding.

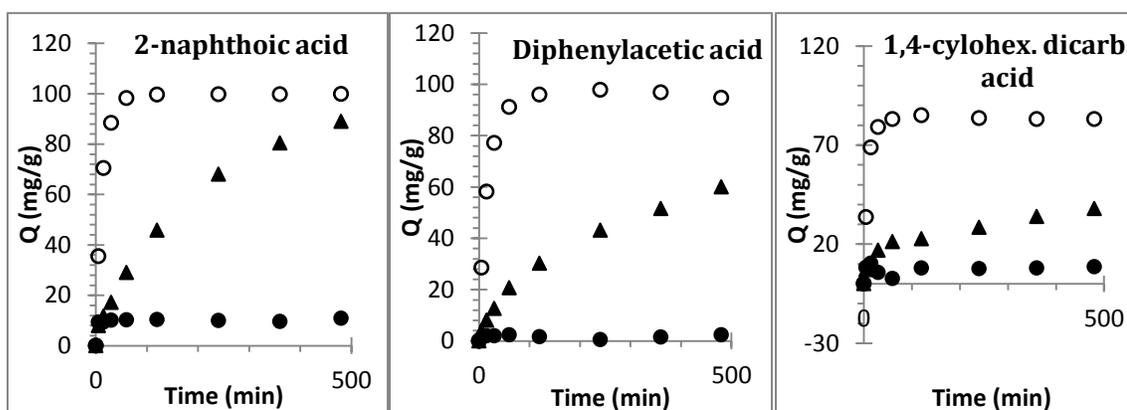


Figure 4.4: Batch adsorption of 2-naphthoic acid (a), diphenylacetic acid (b) and 1,4-cyclohexanedicarboxylic acid (c) by AC (▲), PC (●) and PAC (○), (70 mg adsorbent; initial concentration of each model compound =40 mg/L; volume of the solution= 175 mL, pH =4.1- 4.2; duplicate experiments)

The adsorption isotherm data were plotted using Langmuir, Freundlich and Sips models (Equations of these models are shown in Table 4.2). In most cases, although Langmuir and Freundlich models fitted the experimental data well for the single compound as well as for the mixtures, Freundlich model fitted experimental data better at higher equilibrium concentration. 1,4-cyclohexanedicarboxylic acid followed a co-operative adsorption mechanism due to the formation of hydrogen bonds and was not represented

well by the chosen isotherm models¹⁰. The isotherm parameters of Langmuir and Freundlich models for all adsorbents are listed in Table 4.3. The order of adsorption capacity for AC and PAC was: 2-naphthoic acid > diphenylacetic acid > 1,4-cyclohexanedicarboxylic acid. Compounds with benzene ring in their structure adsorbed more by AC and PAC due to π - π interaction between benzene ring of the compound and the adsorbent surface.

Table 4.2: Different isotherm models with their linear forms*

	General form	Linear form
Langmuir	$q_e = q_m \frac{K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$
Freundlich	$q_e = K_f C_e^{\frac{1}{n}}$	$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$
Sips	$q_e = q_m \frac{b (C_e)^{1/n}}{1 + b (C_e)^{1/n}}$	$\ln \frac{q_e}{q_m - q_e} = \frac{1}{n} \ln(C_e) + \ln(b)$

*(where q_e is the amount of adsorbate that can be adsorbed by unit mass of adsorbent (mg/g), q_m is the monolayer adsorption capacity (mg/g), K_L is the Langmuir adsorption constant (L/mg), C_e is the equilibrium concentration of the adsorbate (mg/L), K_f is the Freundlich adsorption constant ((mg/g)/ (mg/L)^(1/n)), and b is the Sips adsorption constant (L/mg)^(1/n)).

Table 4.3: Isotherm parameters of Langmuir and Freundlich models

			Langmuir				Freundlich		
			K_L	q_m (model)	q_m (experiment)	R^2	K_f	n	R^2
2-naphthoic acid	pH= 4	AC	3.3	189	189	1.0	123.4	7	0.96
		AC-NH ₂	0.9	208.3	214	0.98	135.6	9.2	0.86
		AC-NH ₃	1.2	294.1	298	0.99	164.3	5.7	0.98
		PAC	0.8	666.7	679	0.99	271.6	3.7	1.0
		PAC-NH ₂	0.9	384.6	365	1.0	163.8	3.6	0.95
		PAC-NH ₃	0.2	476.2	428	1.0	117.4	2.6	0.95
	pH= 8	AC	0.3	153.8	152	0.98	75.9	5.6	0.9
		AC-NH ₂	0.4	175.4	168	1.0	84.7	5.1	0.86
		AC-NH ₃	0.2	270.3	255	0.99	82.8	3.2	0.99
		PAC	0.3	294.1	284	0.97	124.1	4.8	0.90
		PAC-NH ₂	0.0	200.0	105	0.80	13.8	1.6	0.90
		PAC-NH ₃	0.6	344.8	330	0.99	147.4	4.0	0.98
Diphenylacetic acid	pH= 4	AC	7.0	89.3	87	0.99	78.7	16.2	0.67
		AC-NH ₂	0.3	119.0	117	0.99	44.5	3.7	0.88
		AC-NH ₃	2.8	135.1	135	1.0	101.7	12.1	0.83
		PAC	2.0	204.1	200	1.0	126.6	6.8	0.94
		PAC-NH ₂	0.3	129.9	120	0.95	51.7	4.1	0.67
		PAC-NH ₃	0.2	175.4	159	0.97	64.0	4.0	0.94
	pH= 8	AC	-0.5	35.8	40	0.96	37.2	33.6	0.02
		AC-NH ₂	-1.2	45.5	50	0.93	36.9	13.8	0.16
		AC-NH ₃	0.3	131.6	100	1.0	64.4	5.5	0.86
		PAC	0.2	156.3	130	0.99	59.5	4.1	0.89
		PAC-NH ₂	-0.7	90.1	100	0.98	97.8	-	0.0
		PAC-NH ₃	0.4	192.3	185	0.99	88.7	4.9	0.99
1,4-cyclohexane-dicarboxylic acid	pH= 4	AC	-0.1	19.2	60	0.8	183.6	-2.1	0.5
		AC-NH ₂	0.1	106.4	80	0.91	95.0	-11	0.62
		AC-NH ₃	1.7	144.9	206	0.70	112.6	11	0.13
		PAC	0.3	111.1	121	0.83	78.7	15	0.12
		PAC-NH ₂	1.0	81.3	80	0.92	72.5	39.5	0.03
		PAC-NH ₃	0.3	111.1	100	1.0	72.1	10.5	0.42
	pH= 8	AC	-0.1	5.6	148	0.71	-	-	-
		AC-NH ₂	0.0	-	70	0.02	0.8	0.8	0.50
		AC-NH ₃	0.0	-	70	0.14	0.9	0.8	0.8
		PAC	0.0	-	65	0.17	0.8	0.8	0.70
		PAC-NH ₂	0.0	-	63	0.32	0.1	0.5	0.74
		PAC-NH ₃	0.0	-	112	0.80	0.0	0.3	0.92

The adsorption capacity of all adsorbents highly depended on solution pH, and the capacity decreased with increasing pH; this was true for almost all NAs either in a single compound solution or in a mixture. At pH 8, all three NAs are expected to be mostly deprotonated, and although the surfaces of most adsorbents used in this study are still positive ($pH_{pzc} > 8.0$), lower adsorption at pH = 8 than at pH = 4 implies that NAs were adsorbed mainly by hydrophobic interaction rather than by electrostatic interaction. For the model NAs, Freundlich model constant, n , is greater than 1 for all tested adsorbents indicating non-homogeneous, multilayer adsorption on these adsorbents.

4.3.2.2 Effect of surface modification of AC and PAC

The equilibrium adsorption of the 3 model NAs using different adsorbents is compared in Figure 4.5. The maximum capacity (Q_{max}) of all the adsorbents for three model components individually and in the mixture are presented in Table 4.4 for the unmodified and surface modified AC and PAC adsorbents for both pH 4 and 8.

Table 4.4: Maximum experimental adsorption capacity (Q_{max}) of the unmodified and surface-modified AC and PAC adsorbents

		Q_{max} (mg/g)		Q_{max} (mg/g)	
		Natural pH ($\approx 4.1-4.2$)		pH=8	
		Single comp.	Mixture	Single comp.	Mixture
2-naphthoic acid	AC	305	189	182	152
	AC-NH ₂	200	214	150	168
	AC-NH ₃	425	298	194	255
	PAC	776	679	360	284
	PAC-NH ₂	545	365	275	105
	PAC-NH ₃	693	428	413	330
Diphenylacetic acid	AC	300	87	142	40
	AC-NH ₂	200	117	93	50
	AC-NH ₃	377	135	200	100
	PAC	624	200	260	130
	PAC-NH ₂	450	120	225	100
	PAC-NH ₃	600	159	364	185
1,4-cyclohexanedicarboxylic acid	AC	430	60	300	148
	AC-NH ₂	250	80	100	70
	AC-NH ₃	350	206	251	70
	PAC	566	121	399	65
	PAC-NH ₂	390	80	286	63
	PAC-NH ₃	601	100	490	112

It can be seen that PAC at natural pH exhibits better adsorption performance for all three naphthenic acids, with the highest capacity for 2-naphthoic acid, as compared to the commercial AC. Comparing the Q_{\max} values (200-776 mg/g) for PAC and AC with literature values for various adsorbate-adsorbent combinations, NAs are removed very effectively with the carbonaceous adsorbents at pH 4. For example, the reported Q_{\max} for adsorption of 2,4-dichlorophenol by Mn-modified AC was 244 mg/g²⁹, or 158 mg/g for adsorption of phenol by H₃PO₄-modified PC³⁰. As expected, removal of NAs in a single compound solution was significantly higher than that in the mixture of NAs, due to competitive adsorption.

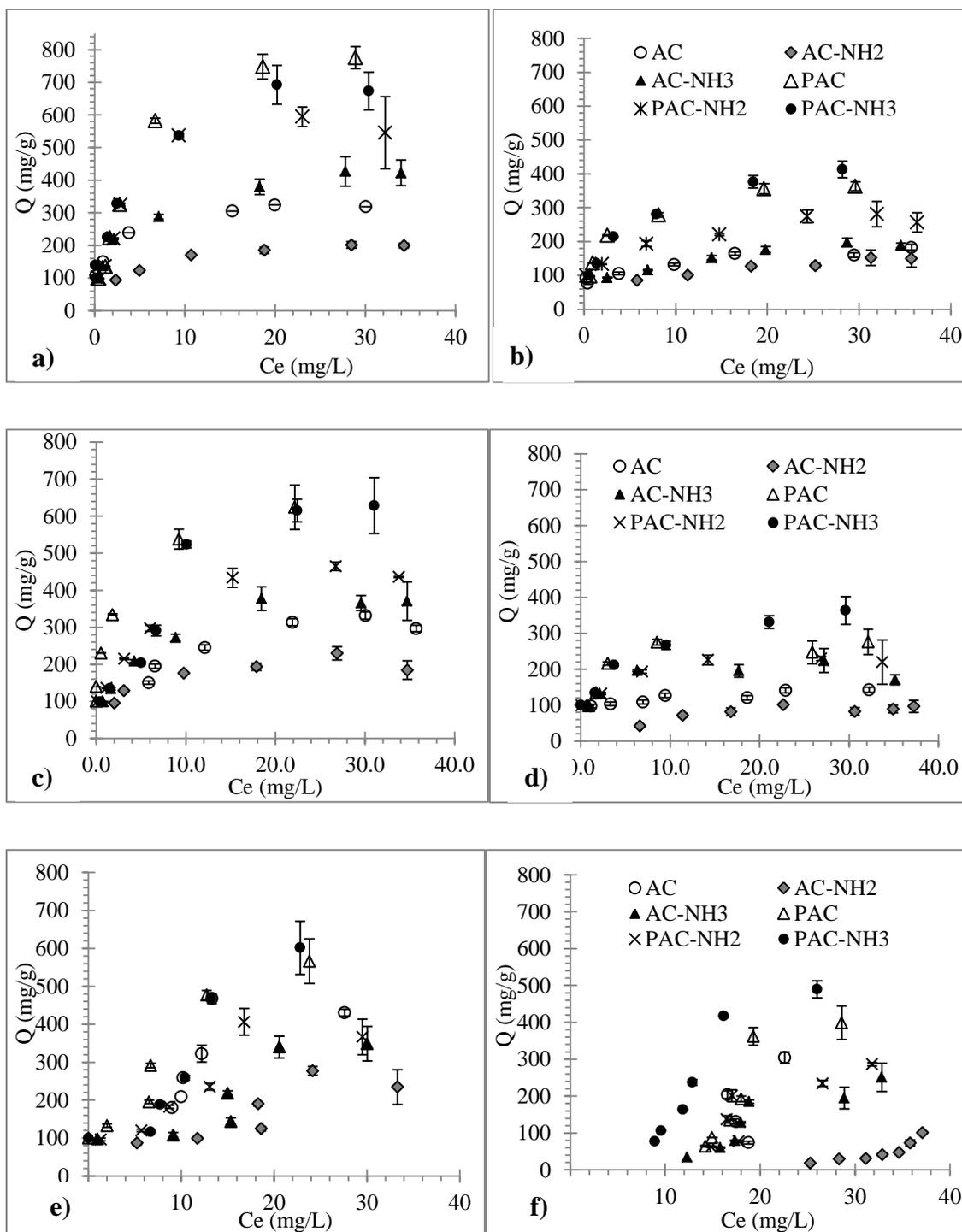


Figure 4.5: Adsorption isotherms of 2-naphthoic acid, a) natural pH, b) pH=8; Diphenylacetic acid, c) natural pH, d) pH=8 and 1,4-cyclohexanedicarboxylic acid, e) natural pH, f) pH=8 on various adsorbents (AC \circ , AC-NH₂ \diamond , AC-NH₃ \blacktriangle , PAC Δ , PAC-NH₂ \times , PAC-NH₃ \bullet)

It can be seen from Figure 4.5 and Table 4.4 that surface activation using the one-step ammonia treatment improved the adsorption capacity for three NAs on AC in most cases at both pH values except for 1,4-cyclohexanedicarboxylic acid in the mixture and at a higher pH. The effect of surface modification on PAC was not very significant, as in many cases the adsorption performance of modified PAC decreased, likely due to the loss of PAC surface area during modification. Large macroporous area of untreated PAC is more conducive for internal diffusion of large NA molecules with only exception of 1,4-cyclohexanedicarboxylic acid which showed slightly better performance with modified PAC. 1,4-cyclohexanedicarboxylic acid undergoes cooperative adsorption, where, solute molecules tend to be adsorbed packed in rows or clusters, which is typically found with planar aromatic molecules such as benzene and naphthalene. Although 1,4-cyclohexanedicarboxylic acid is not planar, hydrogen bonding between molecules played a role in making a 3D supra-molecular architecture, allowing much better adsorption of 1,4-cyclohexanedicarboxylic acid¹⁰. As expected, adsorption capacity of all tested adsorbents was lower for each model compound in mixture compared to pure compound adsorption due to competitive adsorption. For example, Q_{\max} of PAC for pure 2-naphthoic acid, diphenylacetic acid, and 1,4-cyclohexanedicarboxylic at pH 4.1 were 776, 624, and 566 mg/g, respectively, while these values were reduced to 630, 200 and 121 mg/g in the mixture, respectively, as given in Table 4.4.

4.3.3 Kinetics of adsorption

Adsorption kinetics in porous adsorbent are significantly controlled by the external mass transfer, internal pore diffusion, molecular weight and structure of adsorbate. As the kinetic experiments were conducted at the earlier optimized rpm of 170, the effect of external mass transfer can be considered insignificant in this case. The adsorption kinetics results of all three NAs in the single-compound solution and in the mixture at natural pH (=4) are shown in Figure 4.6. It can be seen that in almost all cases, adsorption rate was much faster with PAC and the surface modified PACs compared to AC and surface modified AC for all three NAs. For instance, the concentration of 2-naphthoic acid, diphenylacetic acid and 1,4-cyclohexanedicarboxylic acid reduced from 40 mg/l to 0, 1.6 and 6 mg/l, respectively after 2 hours of mixing with PAC, while these values were

21, 28 and 31 mg/l for AC. The PAC based adsorbent reached the 90% of maximum adsorption capacity within 30 min, compared to ≈ 480 min for AC. The superb adsorption kinetics at PAC surface are due to the higher mesoporous area and bigger pore size for the PAC-based adsorbents than the AC-based adsorbents, leading to faster internal pore diffusion of the NAs. The layered structure of PAC also could facilitate adsorption by reducing steric hindrance between adsorbate molecules.

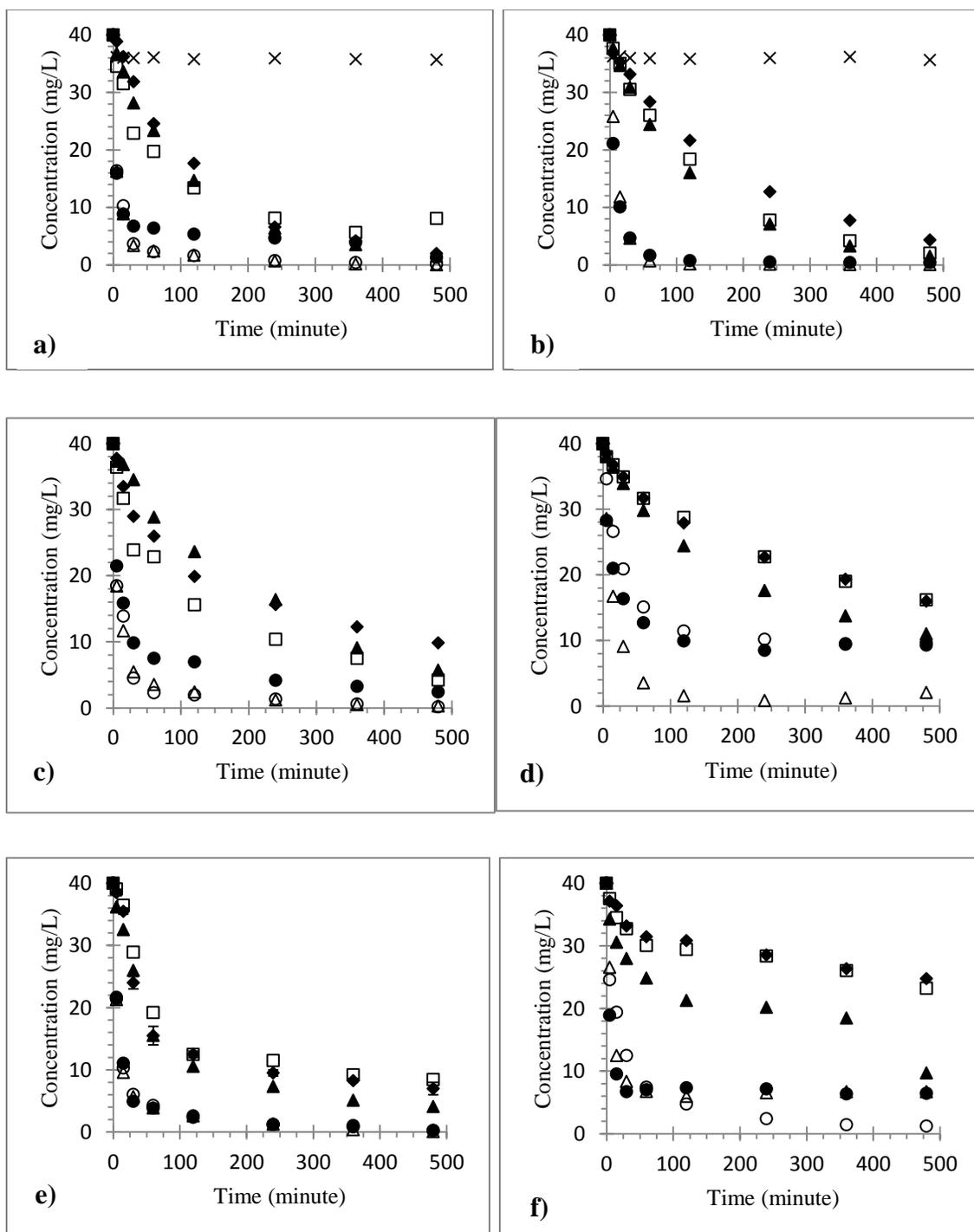


Figure 4.6: Kinetics of adsorption for a) pure 2-naphthoic acid, b) 2-naphthoic acid in mixture, c) pure diphenylacetic acid, d) diphenylacetic acid in mixture, e) pure 1,4-cyclohexanedicarboxylic acid, and f) 1,4-cyclohexanedicarboxylic acid in mixture, with various adsorbents (PC ×, AC ♦, AC-NH₂ □, AC-NH₃ ▲, PAC Δ, PAC-NH₂ ●, PAC-NH₃ ○)

The surface modification methods at natural pH did not significantly affect the kinetics of PAC based adsorbents, while they have moderate to significant effect on the AC-based adsorbents. These can be seen better employing a time constant (the time to reach 63.2% of the maximum capacity), as plotted for various adsorbents in Figure 4.7. As shown previously, the ammonia and amination modification treatments increased the point of zero charge values of AC significantly from 9.5 to 11, while the changes in point of zero charge values for PAC were moderate. The effect of surface modification on kinetics of adsorption was more significant at pH 8, when all the NAs are completely dissociated. With a higher point of zero charge value, the adsorbent has a higher surface positive charge which increases the interaction between anions of NAs and the positive surface, thus accelerating the adsorption kinetics³¹.

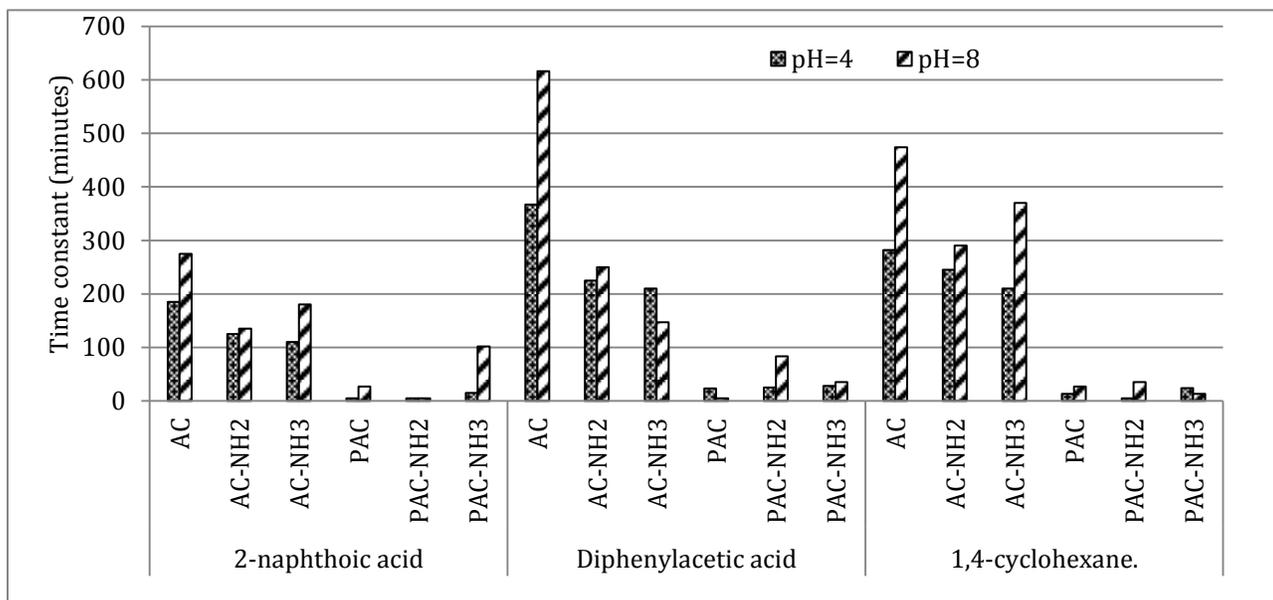


Figure 4.7: Time constant (min) of the unmodified and surface-modified AC and PAC adsorbents on adsorption of three model compounds in single compound solution at pH= 4 or pH=8

In single compound experiments, the time constants for PAC, PAC-NH₂ and PAC-NH₃ are between 0 (unquantifiable) to 100 minutes, while these values are much higher for AC, AC-NH₂ and AC-NH₃ ranging from 110 to 617 minutes. Both surface amination

methods reduced the adsorption time constant values of AC for all model compounds in pH= 4 and pH= 8. For example, the time constant value for adsorption of 2-naphthoic acid by AC in natural pH was 185 min, while this value was reduced to 125 min and 110 min for AC-NH₂ and AC-NH₃, respectively.

The kinetic data were fitted to pseudo-first and pseudo-second order models to determine the mechanism of adsorption. A representative graph for the adsorption of 2-naphthoic acid by PAC at its natural pH is shown in Figure 4.8. The parameters of two kinetic models for all model compounds under different adsorption conditions are presented in Table 4.5.

The pseudo-second order model fitted the kinetics data better than first-order model in most cases, indicating chemisorption controlling the adsorption process^{32,33}. As reported previously, NAs were adsorbed onto the basal plane of the carbonaceous adsorbent by π -electron dispersion²⁰. The improved adsorption rate on surface modified AC is not due to physical transport processes such as internal diffusion as pore size of the surface modified adsorbents remained unaltered, while the total surface area actually decreased. The enhanced kinetics probably is due to greater electrostatic interactions via sharing of electrons between the benzene ring or dissociated NA compounds and basal plane of AC. By introduction of nitrogen-containing functional groups on the surface of adsorbents, higher π -electron density was generated in basal plane of the aminated AC or PAC due to the delocalization of free electrons in the pyridinic and pyrrolic nitrogen (or imine). Although, the capacity of the surface modified PAC decreased, faster kinetics of the modified adsorbent offset this negative effect in continuous column operation. Faster kinetics implies a sharper breakthrough curve, reducing the cycle time increasing the throughput per unit of adsorbent.

Table 4.5: Parameters of the pseudo-first and pseudo-second order kinetic models

		Pseudo-first order				Pseudo-second order				
		k_1	$q_{e,cal}$ (mg/g)	Δq (%)	R^2	k_2	$q_{e,cal}$ (mg/g)	Δq (%)	R^2	
2-naphthoic acid	pH= 4	AC	0.004	88.3	-11.7	0.996	0.0001	104.2	4.2	0.997
		AC-NH ₂	0.0037	68.7	-31.3	0.919	0.0001	103.1	3.1	0.998
		AC-NH ₃	0.0046	72.4	-27.6	0.966	0.0002	103.1	3.1	0.998
		PAC	0.0041	5.3	-94.7	0.41	0.0037	100	0	1
		PAC-NH ₂	0.0041	8.9	-91.1	0.58	0.0038	100	0	1
		PAC-NH ₃	0.0037	18.2	-81.8	0.54	0.001	100	0	1
	pH= 8	AC	0.0016	83.9	-16.1	0.96	0.0001	104.2	4.2	0.99
		AC-NH ₂	0.0014	61.4	-38.6	0.667	0.0001	100	0	0.995
		AC-NH ₃	0.0018	72.2	-27.8	0.862	0.0001	103.1	3.1	0.997
		PAC	0.0027	32.5	-67.5	0.702	0.0006	100	0	1
		PAC-NH ₂	0.009	56.7	-43.3	0.956	0.009	101	1	0.999
		PAC-NH ₃	0.0021	58.8	-41.2	0.788	0.0002	102.0	2	0.999
Diphenyl-acetic acid	pH= 4	AC	0.0021	94.8	-5.2	0.996	0	107.5	7.5	0.983
		AC-NH ₂	0.003	48.5	-51.5	0.997	0.0001	94.4	-5.6	0.992
		AC-NH ₃	0.0025	81.9	-18.1	0.974	0.0001	105.3	5.3	0.997
		PAC	0.0009	15	-85	0.09	0.0007	98	-2	0.998
		PAC-NH ₂	0.0011	18.2	-81.8	0.13	0.0007	98	-2	0.998
		PAC-NH ₃	0.0021	2.5	-97.5	0.407	0.0006	100	0	0.999
	pH= 8	AC	0.0007	89.1	-10.9	0.97	0	102	2	0.9
		AC-NH ₂	0.0004	79.4	-20.6	0.947	0.0001	100	0	0.995
		AC-NH ₃	0.0023	9.06	-90.9	0.957	0	102	2	0.996
		PAC	0.0027	6.7	-93.3	0.4	0.0057	100	0	1
		PAC-NH ₂	0.002	52.4	-47.6	0.9	0.0002	102	2	0.995
		PAC-NH ₃	0.0011	20.7	-79.3	0.31	0.0005	99	-1	0.999
1,4-cyclo-hexane-dicarboxy-lic acid	pH= 4	AC	0.001	78.9	-21.1	0.944	0.0001	102	2	0.98
		AC-NH ₂	0.001	75	-25	0.91	0.0001	101	1	0.984
		AC-NH ₃	0.001	74.9	-25.1	0.932	0.0001	102	2	0.988
		PAC	0.001	10.9	-89.1	0.156	0.0001	100	0	0.999
		PAC-NH ₂	0.003	8.3	-91.7	0.543	0.0033	100	0	1
		PAC-NH ₃	0.0025	11.7	-88.3	0.35	-0.001	93.5	-6.5	0.998
	pH= 8	AC	0.003	138	38	0.85	0	172	72	0.76
		AC-NH ₂	0.0014	84.7	-15.3	0.93	0.0001	102	2	0.97
		AC-NH ₃	0.003	94.8	-5.2	0.99	0	78	-22	0.38
		PAC	0.0027	30.9	-69.1	0.72	0.0007	97	-3	0.999
		PAC-NH ₂	0.0014	22.9	-77.1	0.154	0.0005	99	-1	0.998
		PAC-NH ₃	0.0016	5	-95	0.16	0.001	82	-18	0.999

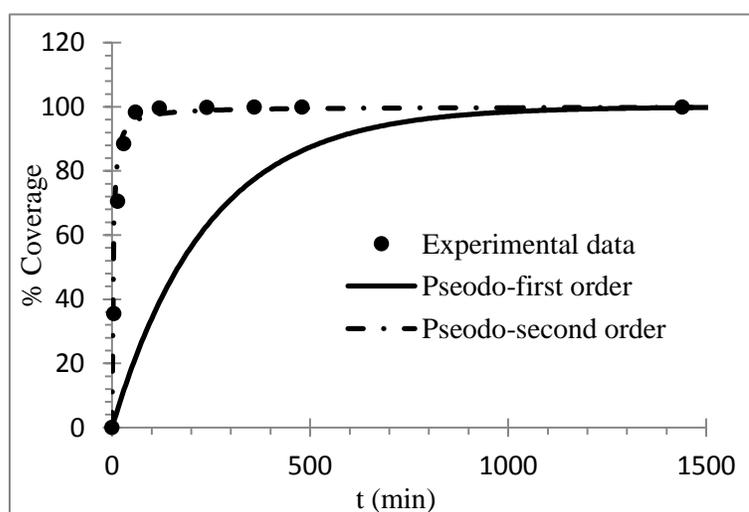
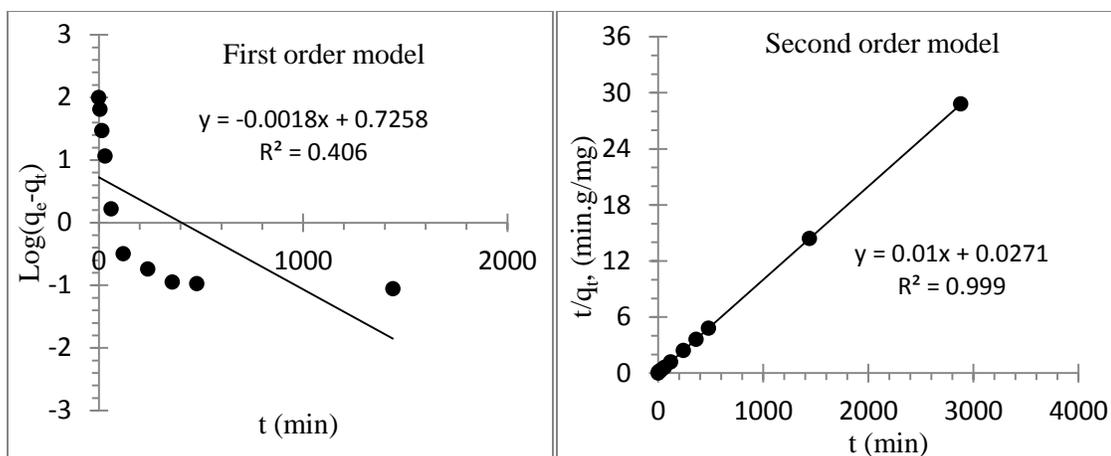


Figure 4.8: Modeling of the adsorption of 2-naphthoic acid on PAC (pH= 4) using the first and second order kinetic models

4.3.4 Total organic carbon (TOC) removal of real OSPW by AC and PAC

Experiments were also conducted to determine the efficacy of AC and PAC to remove the dissolved organic compounds from the supernatant of OSPW obtained from Syncrude, Alberta, Canada. Since the GC-MS analysis of OSPW indicated myriads of compounds, the TOC removal was used as an indicator for evaluating the adsorption performance. Although, the original pH of OSPW was around 8.5, adsorption experiments were conducted at various initial pH adjusted by using either 0.1 M HCl or 0.1M NaOH. The results (Figure 4.9) illustrate that almost 80-85% TOC in OSPW could

be removed at pH 2, increasing to 99% removal at pH= 3.5. Both AC and PAC had comparable performances in TOC removal in the pH range 2-5, albeit a better performance was shown by PAC at pH 5-6, while the AC exhibited better TOC removal at higher pH 8-9. AC has a higher pH_{pzc} value compared to PAC indicating greater positive surface of AC at pH 8.0. Similar to NAs, a higher pH of the solution led to a reduced TOC removal for both PC and PAC. A reduced TOC removal at higher pH suggests that hydrophobic interaction plays a more important role in adsorbing organics from OSPW than electrostatic interactions indicating that surface modifications to increase negative surface polarity may not be necessary for OSPW treatment using activated carbon based adsorbents. Preliminary experiments with ammonia and amination modified AC and PAC adsorbents for the treatment of OSPW indicate good capacity at low pH and inferior capacity at pH 8 supporting this hypothesis. Similar to model compounds, the kinetics of adsorption of the organics in OSPW may be affected positively by surface amination, however, thorough parametric studies are presently being conducted to confirm this.

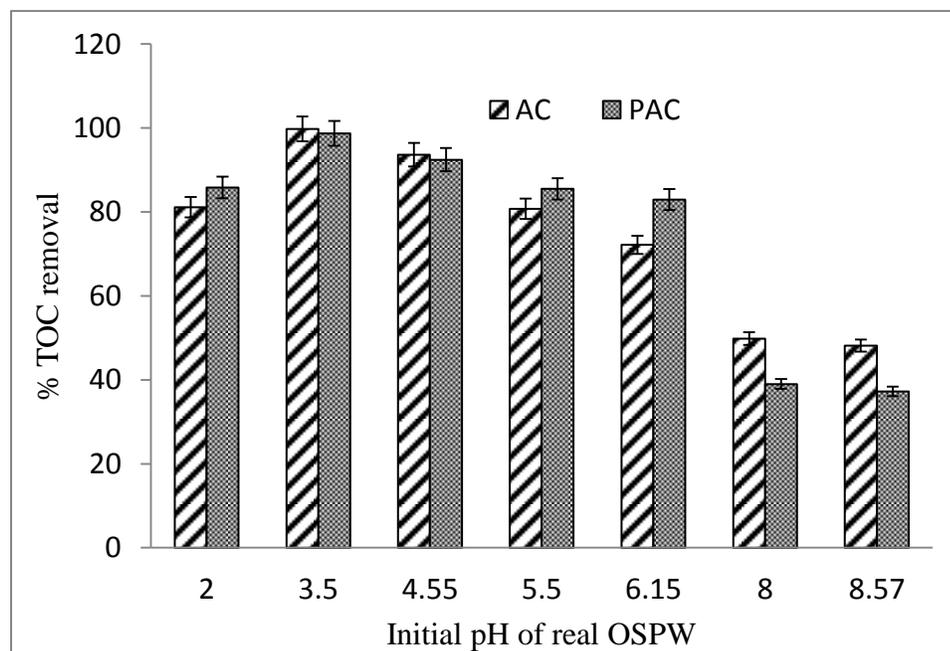


Figure 4.9: Effects of initial pH on TOC removal of OSPW (Initial TOC = 129 mg/L, Adsorbent loading = 1 g/L)

4.4 Conclusions

- (1) KOH activation of petroleum coke produced highly mesoporous activated carbon (PAC) with total surface area of $1443 \pm 13 \text{ m}^2/\text{g}$, which showed superior adsorption performance for the removal of 3 model naphthenic acids compared to commercial granular activated carbon (AC) with Q_{max} ranging from 200-776 mg/g at pH 4.0.
- (2) The adsorption of 3 model naphthenic acids by AC and PAC followed the order: 2-naphthoic acid > diphenylacetic acid > 1,4-cyclohexanedicarboxylic acid. Compounds with benzene ring in their structure adsorbed more due to π - π interaction between benzene ring of the compound and the adsorbent surface.
- (3) The treatment of AC and PAC by ammonia gas is more effective compared to amination for increasing their adsorption capacity for the model NAs in mixture at pH 8.
- (4) Although equilibrium capacity of the modified adsorbents decreased somewhat, two techniques employed (one-step ammonia treatment and two-step amination treatment) for surface modification improved the adsorption kinetics of the NA model compounds for all conditions, more significantly for AC than PAC. For example, the time to reach 63.2% of the equilibrium capacity for 2-naphthoic acid adsorption reduced by 33% and 41% for AC-NH₂ and AC-NH₃, respectively. The effect was more significant at pH 8 and in mixture, showing the effectiveness of surface treatment for real OSPW treatment.
- (5) The adsorption capacity of all adsorbents highly depended on the solution pH, and the capacity decreased with increasing pH, irrespective of single or multi-compound adsorption. The NAs were adsorbed mainly by hydrophobic interaction rather than by electrostatic interaction.
- (6) Pseudo-second order kinetics model fitted the experimental data in most cases indicating chemisorption on all adsorbents.
- (7) Both PAC and AC could remove almost 99% of the TOC in OSPW at pH 3.5, although only 50% TOC removal occurred at pH 8, the natural pH of OSPW.

4.5 Acknowledgements

The authors would like to acknowledge the funding from NSERC and NEWALTA Corporation via a CRD grant and Fang Cao for her great assistance in analyzing the samples.

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Chapter 5

5 Continuous column adsorption of naphthenic acids from synthetic and real oil sands process-affected water (OSPW) using carbon-based adsorbents

Abstract

In this study, an activated petroleum coke (APC) and a commercial activated carbon (CAC) were used in a continuous adsorption column for removal of model naphthenic acids and organics from real oil sands process-affected water (OSPW). Diphenylacetic acid and 2-naphthoic acid, as two naphthenic acid (NA) model compounds, were removed completely by the APC in the continuous operation. Due to the complex nature of organics in OSPW (Figure S 5.1), total organic carbon (TOC) was measured to determine the effectiveness of OSPW treatment with the activated carbon adsorbents. The percent removal of TOC from OSPW at its natural pH= 8 by APC was only 25%, whereas acidification at pH 4 followed by APC adsorption removed 96% of the initial TOC. When compared to the CAC, the APC showed an average of 20% higher organics removal. The experimental breakthrough curves were better fitted by Thomas model in comparison to Adams-Bohart and Yoon-Nelson models.

Keywords: Activated carbon, Activated petroleum coke, Oil-sands Process Affected Water, Naphthenic acids, Adsorption, Continuous column, Breakthrough curves, Modeling.

5.1 Introduction

Alberta has the third largest proven oil reserve after Saudi Arabia and Venezuela in the world ¹. This large amount of oil reserve is in form of oil sands, which makes the extraction process difficult and costly. Annually a large volume of oil sands process-affected water (OSPW) is stockpiled during the extraction of bitumen from the oil sands ². Based on zero discharge policy,

this wastewater should be stored in the tailing ponds for treatment and recycling³. The presence of organic chemicals such as poly aromatic hydrocarbons (PAHs) and naphthenic acids (NAs) in OSPW is of concern due to their negative impact on the environment. The NAs can react with the salts present in OSPW, and produce complexes which could create corrosion in boilers and refining instruments¹ during recycling of OSPW. Furthermore, NAs are the major source of toxicity of OSPW with a risk of contamination of underground and surface water resources⁴. Therefore, these compounds need to be removed prior to the recycle of the OSPW. On the other hand, offsetting the treatment cost partially, recovering NA salts from OSPW has economical benefits due to their many industrial uses. NAs enhance water resistance and adhesion of concrete, increase high-pressure resistance of drilling oils, prevent foaming in jet fuel, prevent fungus growth in wood, be a flame retardant in fabric, increase insecticide solubility, catalyze rubber vulcanization, stabilize vinyl resins, and catalyze production of alkyl and polyester resins^{5,6}. Alkali naphthenates are applied as both emulsifying and demulsifying agents.

Different physico-chemical methods have been applied for treatment and remediation of OSPW such as centrifugation, coagulation-flocculation, membrane filtration⁷, adsorption⁸, advanced oxidation⁹, and remediation in wetlands³. Among all these methods, adsorption processes have significant potential for large-scale application due to their ability (i) to use inexpensive raw material or waste by-product as adsorbent, (ii) to recover valuable adsorbates, and (iii) their easy operation and scaling-up.

Recently, petroleum coke (PC), a waste from petroleum industry was used as adsorbent for OSPW treatment¹⁰⁻¹². Different type of adsorbents such as biomass-based biochar⁸, activated carbon¹³, modified biopolymer¹, polymers and Clays¹⁴ were also tested for removal of organic compounds from OSPW.

In our previous study¹⁵, petroleum coke was converted to activated petroleum coke (APC) with a very high surface area of 1726 m²/g and large pore volume of 0.85 cc/g. The APC demonstrated to be highly effective for removing model naphthenic acids in synthetic wastewater in batch adsorption at different operating conditions. The objective of this study was to test the performance of APC for removal of organics from a real OSPW stream from Alberta in a continuous column operation, and determine the regeneration efficiency of exhausted adsorbent

in repeated cycles. In addition, adsorption of model naphthenic acids by APC in the column was also conducted. The results of this research could be used for designing a large-scale continuous treatment scheme for OSPW treatment.

5.2 Materials and methods

5.2.1 Chemicals and adsorbents

Diphenylacetic acid (99%, CAS Number: 117-34-0) was purchased from Sigma-Aldrich Canada. 2-naphthoic acid (98%, CAS Number: 93-09-4) was purchased from VWR Company, Canada. OSPW was obtained from Alberta's oil sands extraction site through Suncor Energy, Alberta, Canada. Sulfuric acid, sodium hydroxide, HPLC-grade acetonitrile and methanol, and potassium hydroxide were purchased from VWR Company. The Syncrude petroleum coke was obtained from NEWALTA Corporation (Burlington, ON), and was activated using KOH at elevated temperature based on our previous study¹⁵. The activated petroleum coke (APC) has BET specific surface area of 1705 ± 20 m²/g, micro-pore area of 353 ± 16 m²/g, meso-pore area of 1372 ± 22 m²/g and total pore volume of 0.85 cc/g. Commercial activated carbon (CAC) used in this work was, Norit ROW 0.8 SUPRA (CAS Number: 7440-44-0), produced by Cabot Corporation (Boston, MA, USA). The CAC used has the following textural properties: BET specific surface area of 1399 m²/g, micro-pore area of 766 m²/g, meso-pore area of 634 m²/g and total pore volume of 0.7 cc/g. To eliminate the effects of particle size on adsorption, both APC and crushed CAC were sieved with mesh sieve No. 60 (i.e., < 0.25 mm diameter) in order to have similar particle size. *Escherichia coli* and *Micrococcus luteus* cultures were purchased from MerlanScientific, (Mississauga, ON, On, Canada).

5.2.2 Continuous adsorption column setup

A glass tube with inner diameter of 1 cm, and length of 20 cm, equipped with quartz support was used as the adsorption column. The flow of the solution was fixed at 2.5 mL/min by a peristaltic pump. The flow was upward in order to avoid any channeling, and minimizing the dead zone in the column. In each test, about 0.5-1 g carbon adsorbent was packed in the column as uniformly as possible. In order to minimize the end effects and to have a uniform distribution of liquid, the top and the bottom zones of the column were packed with 2 mm glass beads. Effluent samples were collected at the top of the column at regular time intervals. The column operation was

continued until the outlet concentration reached the inlet concentration which was considered as the column saturation point. Regeneration of the spent adsorbent was conducted using an earlier optimized method of regeneration developed by Das (2017)¹⁶, where methanol with 0.01 wt% NaOH (pH 11.7) was used for regeneration of the spent carbon. The extracted model compounds and organic compounds from OSPW were recovered by evaporating the solvent in a rotary evaporator. The evaporated methanol was then condensed and recovered for use in the next regeneration cycle. A total of four cycles of adsorption and regeneration were conducted.

5.2.3 Analytical methods

A Dionex ICS-3000 was used in an HPLC configuration to measure the concentration of naphthenic acids. An acclaim fast LC column 120 C18 (3 × 75 mm) was used for separation of the compounds using a mobile phase of a mixture of 40% MilliQ water and 60% (v/v) acetonitrile. The flow rate of the mobile phase was set to 1.2 mL/min. The mobile phase was acidified with sulfuric acid to pH 2.15 in order to ensure that the acids in the samples were in their protonated form. The acidified mobile phase was filtered using a vacuum filtration apparatus with a 47 mm polytetrafluoroethylene disk filter with pore size of 0.45 μm. A UV detector was used and the peaks were measured at 260 nm. A preliminary GC-MS analysis showed the presence of numerous compounds in OSPW. Due to this complex nature, instead of identifying individual compounds, total organic carbon (TOC) of the OSPW was measured using a Shimadzu 5000A TOC analyzer with an ASI-5000 auto sampler. A Nova 1200E, BET analyzer (QuantaChrome Co.) was used to measure the pore size distribution and specific surface area of the raw and regenerated adsorbents. The Fourier transform infrared spectroscopy (FTIR) was conducted to determine the functional groups of fresh and exhausted adsorbents.

5.2.4 Column performance

The performance of each adsorbent was evaluated by analyzing its breakthrough curve, which is the ratio of outlet to inlet concentration versus operation time. The amount of adsorbate on the carbon at t min can be calculated using equation 1.

$$q_t = \frac{F \times C_i}{1000} \int_{t=0}^{t=t} \left(1 - \frac{C_t}{C_i}\right) dt \quad (\text{Eq. 1})$$

Where, q_t is the amount of adsorbate (model NAs) adsorbed (mg) after t min, F is the flow rate of the solution (mL/min), C_i and C_t are the inlet and outlet concentration (mg/L) of the adsorbate, and C_t is the outlet concentration at time t . The same formula was used to calculate the TOC removal from real OSPW by replacing the C with TOC. Equation 2 was used to calculate the capacity of the adsorbent. The m in equation 2 refers to the total mass of adsorbent in the column.

$$q_{bed} \left(\frac{mg}{g} \right) = \frac{q_{total}(mg)}{m(g)} \quad (\text{Eq. 2})$$

In this work the obtained breakthrough curves were fitted to Adams-Bohrat¹⁷, Yoon-Nelson¹⁸ and Thomas¹⁹ models. Thomas model is shown by equation 3.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp \left[\frac{K_{Th} q_0 x}{v} - K_{Th} C_0 t \right]} \quad (\text{Eq. 3})$$

Where, K_{Th} is Thomas rate constant ($\text{mL min}^{-1} \text{ mg}^{-1}$), q_0 is equilibrium adsorption capacity (mg/g), x is the amount of adsorbent in the column (g), C_0 and C_t (g/L) are the concentration in the influent and effluent at time t , respectively, and v is the flow rate (mL/min). By linearizing the Thomas model and fitting with $\ln \left(\frac{C_0}{C_t} - 1 \right)$ vs. time, the parameters of the model were obtained. The linear form of Thomas model is shown by equation 4.

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \frac{K_{Th} q_0 x}{v} - K_{Th} C_0 t \quad (\text{Eq. 4})$$

The Adams-Bohart model is shown in equation 5.

$$\frac{C_t}{C_0} = \exp \left(K_{AB} C_0 t - \frac{K_{AB} N_0 Z}{v} \right) \quad (\text{Eq. 5})$$

Where, C_0 and C_t are concentration of the adsorbate in the influent and effluent at time t (g/L), respectively, N_0 is the saturated adsorption capacity per column volume (g/L), K_{AB} is the mass transfer coefficient ($\text{L g}^{-1} \text{ min}^{-1}$), Z is the bed depth (cm), v is the flow rate (mL/min). The linear form of this model is shown in equation 6.

$$\ln \left(\frac{C_t}{C_0} \right) = K_{AB} C_0 t - \frac{K_{AB} N_0 Z}{v} \quad (\text{Eq. 6})$$

The Yoon-Nelson was the third model was used to fit the breakthrough data. This model and its linearized form are presented by equations 7 and 8, respectively.

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp [K(\tau - t)]} \quad (\text{Eq. 7})$$

$$\ln \left(\frac{C_t}{C_0 - C_t} \right) = Kt - K\tau \quad (\text{Eq. 8})$$

Where, K is the rate constant (l/min), τ is the time required for 50% adsorbate breakthrough (min), and t is the sampling time (min). The Thomas model is based on two assumptions: firstly, the adsorption is limited by mass transfer at the interface, not by the chemical interactions between adsorbate and adsorbent, secondly, the experimental data should follow Langmuir isotherm and second-order kinetics²⁰. The Adams-Bohart model is based on the assumption that the adsorption rate is controlled by external mass transfer²¹. The Yoon-Nelson model has a more simple form than other models. Also, this model requires no detailed data concerning the characters of adsorbate and adsorbent, as well as the parameters of the fixed bed²². The performances of Thomas and Yoon-Nelson models in fitting the data are the same, but Thomas model provides more details about the adsorption parameters. For example, Thomas model could predict the maximum adsorption capacity as reported in Table 5.2. The calculated parameters of the models are presented in Table 5.2.

5.3 Results and discussion

5.3.1 Evaluation of APC breakthrough curves

Dynamics of a continuous column adsorption process can be determined by its breakthrough curves. It provides relevant information about the key parameters for the design, operation and optimization of the continuous adsorption process²³. Initially, the performances of CAC and APC on the removal of two model compounds 2-naphthoic acid and diphenylacetic acid in water solution (pH=4.0) were determined and the results are presented in Figure 5.1.

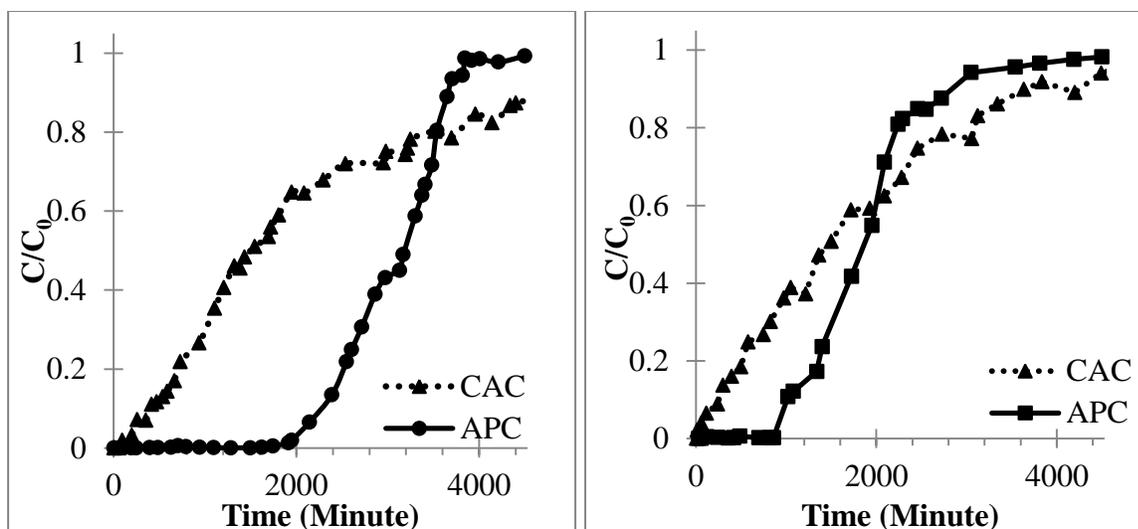


Figure 5.1: Breakthrough curves of the first cycle for removal of 2-naphthoic acid (a), diphenylacetic acid (b), by CAC and APC in water solution (pH=4.0)

The column study results show that APC performed better as compared to CAC. For example, one gram of APC could treat about 6.1 L of 2-naphthoic acid solution to an effluent with > 85% reduction in the adsorbate concentration (i.e., $C/C_0 = 0.15$), while to achieve the same quality of the effluent, one gram of CAC could only treat 1.5 L of the 2-naphthoic acid solution. With the model compound of diphenylacetic acid, both CAC's and APC's performance was inferior; for 85 % reduction in the adsorbate concentration, the APC and CAC adsorbents could treat only 3.1L and 0.9 L diphenylacetic acid solution, respectively. This was expected from the batch kinetic studies presented in Chapter 4²⁴, which showed the maximum adsorption capacity, Q_{max} (mg/g), for CAC and APC for 2-naphthoic acid was 153.8 (mg/g) and 284 (mg/g), respectively, while for diphenylacetic acid these values were much lower, being 35.8 (mg/g) and 156.3 (mg/g), respectively.

On the other hand, when raw OSPW at pH=8.0 was treated by the column packed with APC and CAC, the TOC removal was not significant, with a removal efficiency of only 25% and 18% by APC and CAC, respectively. The reason could be because of higher solubility of NAs in alkaline wastewater²⁵. In addition, our earlier work with model NAs and CAC (Martinez- Iglesias et al., 2015) demonstrated that adsorption of model compounds was significantly greater at a lower pH value (pH 2-4) due to positive surface of the carbon adsorbents and that electrostatic interaction

could be the dominant mechanism of adsorption. Based on this, the pH of OSPW was reduced from around 8 to 4 to reduce the solubility of acid extractable organics, as evidenced by the observation that a part of soluble organics was precipitated from the solution in the feed tank. Furthermore, reducing the pH of OSPW from around 8 to 4 could also enhance the adsorption capacity of the carbons because OSPW at a lower pH would lead to a more positively charged surface of APC and CAC adsorbents. Thus, in this work all adsorption tests were conducted at both pH 4 and pH 8, whose results will be discussed in the following sections.

Furthermore, the effect of ionic strength on removal of 2-naphthoic acid was investigated. The results showed that the molar ratio of sodium, calcium, and magnesium chloride, up to 3 molar does not have any significant effect of adsorption capacity of APC (Figure S 5.2).

5.3.2 Regeneration

A solvent regeneration method was used for the regeneration of spent carbon adsorbents. In this work, solvent regeneration was considered among other regeneration methods because valuable organic chemicals like NAs could be extracted and recovered after adsorption process. The other advantages of solvent regeneration are the rapid in-situ regeneration, without the need for carbon handling and the energy cost as required for thermal regeneration, and the associated air pollution problem. Among the available solvents, methanol was chosen because of its high volatility and low price¹⁶. However, only methanol was not effective enough for regeneration of carbon adsorbents. By adding a small amount of alkali such as aqueous NaOH, sodium salts of naphthenic acids were formed which have higher solubility than the un-protonated NAs, hence enhancing desorption and regeneration of NAs from spent adsorbents.

An optimization study was performed in batch experiments to determine the optimum addition amount of alkali aqueous NaOH in methanol solvent or pH value of methanol for regeneration, it was determined that pH 11.7 was the optimal pH level to obtain the highest regeneration efficiency. The regeneration of the spent carbons in this work was conducted for four adsorption-regeneration cycles, all in methanol at pH = 11.7, while the adsorption with the fresh or regenerated carbon adsorbent was operated at both pH pH 4 and 8 at room temperature. The

maximum adsorption capacity and regeneration efficiency of CAC and APC for during the 4 repeated adsorption-regeneration cycles tested solutions (with the NA model compounds or real OSPW at pH 4 and 8 are presented in Table 5.1.

Table 5.1: The maximum adsorption capacity (Q_{\max} , mg/g) and regeneration efficiency (%RE) of CAC and APC during the 4 repeated adsorption-regeneration cycles tested solutions (with the NA model compounds or real OSPW at pH 4 and 8.

		pH= 4				pH= 8			
		CAC Q_{\max}	%RE ^a	APC Q_{\max}	%RE	CAC Q_{\max}	%RE	APC Q_{\max}	%RE
2-naphthoic acid	Cycle 1	430	90	611	95	137	81	195	93
	Cycle 2	251	87	338	93	125	78	143	90
	Cycle 3	150	85	323	92	112.5	73	135	85
	Cycle 4	140	82	303	90	117	70	129	84
Diphenylacetic acid	Cycle 1	183.5	78	188.5	89	53.5	65	76.5	76
	Cycle 2	113.5	74	154.0	85	33.0	63	63.0	72
	Cycle 3	65.0	73	141.5	82	27.5	59	55.5	70
	Cycle 4	68.5	69	129	83	23.5	56	50.5	67
OSPW (TOC)	Cycle 1	368	73	441	86	116	69	168	77
	Cycle 2	298	69	379	84	104	65	137	78
	Cycle 3	279	71	351	80	89	62	97	73
	Cycle 4	214	64	306	79	84	61	89	71

^aRegeneration efficiency in methanol at pH 11.7

The results showed much higher adsorption capacity and regeneration efficiency for APC compared to CAC in all cases, which could be owing to larger specific surface area and mesopore structure as well as other functionality properties of the APC adsorbent. The APC has a layer by layer structure and more mesopores²⁴ which would facilitate diffusion of the adsorbate

molecules inside the inner surface area, and for the same reason, enhance removal of the adsorbed chemicals by the solvent during the regeneration process. Both the adsorption capacity and the regeneration efficiency of either adsorbent for diphenylacetic acid were less than those for 2-naphthoic acid in all cases. For example, the regeneration efficiency for diphenyl acetic acid in the first cycle with CAC after adsorption at pH=4 was 78%, while this value was 90% for 2-naphthoic acid. The possible reasons for higher adsorption capacity and regeneration efficiency for 2-naphthoic acid could be due to its lower molecular weight, lower solubility in water and higher solubility in methanol compared to those of diphenylacetic acid. In general, the regeneration efficiency for exhausted CAC and APC for organics in OSPW was lower than that of the two NA model compounds, perhaps due to strong chemisorption of some of the OSPW on the adsorbents.

Moreover, the results as shown in Table 5.1 also indicate that the regeneration efficiency was lower in the cycles after adsorption at pH 8.0 (lower adsorption capacity) than that after adsorption at pH 4.0 (larger adsorption capacity) for both CAC and APC, which can actually be expected because the larger amount of the adsorbate in an adsorbent would lead to a larger desorption rate in the regeneration operation.

5.3.3 Modelling of the column adsorption

Thomas, Adams-Bohart, and Yoon-Nelson models were used to fit the experimental breakthrough curves for APC and CAC adsorbents. Both Thomas and Yoon-Nelson models fit the experiment data well for both APC and CAC. It should be noted that Thomas and Yoon-Nelson models are essentially identical. Thomas model indicates the adsorption to be limited by external mass transfer in the column, not by the chemical forces between adsorbent and adsorbate. This is particularly reasonable for APC that has higher mesoporous area which facilitates the internal diffusion. The summary of the fitted parameters are presented in Table 5.2.

Figure 5.2 shows the experimental breakthrough curves (represented by data points) for adsorption removal of 2-naphthoic acid, diphenylacetic acid, and TOC of OSPW with APC in four adsorption-regeneration cycles, and the fitted curves using Thomas and Adames-Bohart models.

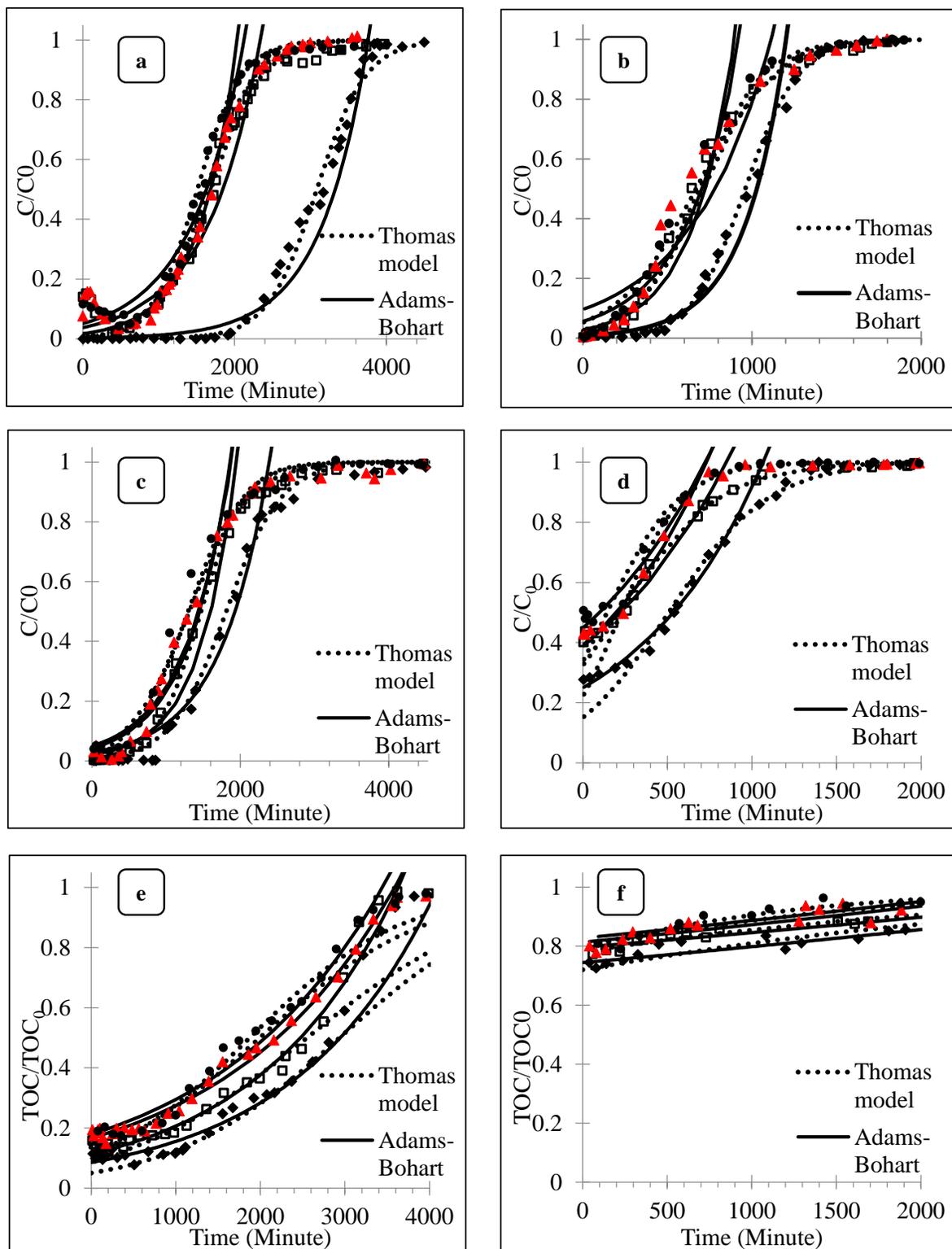


Figure 5.2: Column adsorption performance of APC in four adsorption-regeneration cycles for removal of model NA compounds and TOC of OSPW, and the fitted curves using Thomas and Adams-Bohart models. a) 2-naphthoic acid at pH= 4, b) 2-naphthoic acid at pH= 8, c) diphenylacetic acid at pH= 4, d) diphenylacetic acid at pH= 8, e) OSPW at pH= 4, f) OSPW at pH= 8, (♦: Cycle 1, □: Cycle 2, ▲: Cycle 3, ●: Cycle 4)

The experimental breakthrough curves showed better column performance at pH= 4 compared to pH= 8 for 2-naphthoic acid, diphenylacetic acid, and OSPW. This observation was in agreement with our batch adsorption results¹⁵. For 2-naphthoic acid solution at pH=8, the C/C_0 starts to rise after 1.25 L of the solution was flowed through the column. After 700 minutes of column performance, the C/C_0 value reached 0.15. However, at pH =4, it took a much longer time (about 2450 min) when C/C_0 reached the same value. Since the p_{zpc} of both carbons are greater than 9.0, at lower pH such as pH = 4, the surface of adsorbent becomes more positively charged, which could facilitate the adsorption of a NA compound (remaining protonated at a low pH), noting that at a low pH electrostatic interactions are the dominant mechanism of adsorption of chemicals on carbon adsorbents.

The “ τ ” value predicted by Yoon-Nelson model, is defined as the time required for 50% adsorbate breakthrough (min). As shown in Table 5.2), τ was 1053 minutes at pH=8, while this value was 3080 minutes at pH=4 for removal of 2-naphthoic acid by APC, which means that the APC could work almost three times longer at pH= 4 compared to pH= 8 to reach its 50% adsorption capacity.

As shown in Figure 5.2, for diphenylacetic acid at pH= 8, the C/C_0 never came below 0.25, while in contrast, at pH 4, the C/C_0 of breakthrough curve started from 0 and it took 2450 minutes to reach 0.15. It clearly reveals that the adsorbent has a much greater adsorption capacity at a lower pH for both diphenylacetic acid and 2-naphthoic acid. The results as shown in the Figure also indicate that the APC adsorbent has a lower adsorption capacity for diphenylacetic acid compared to that for 2-naphthoic acid, which could be due to its larger molecular size (weight) compared to 2-naphthoic acid, making it more difficult to diffuse into the internal pores of the adsorbent.

The column adsorption treatment of OSPW by APC for TOC removal showed different behaviour compared with the adsorption removal of the model NA compounds. In the column adsorption treatment of OSPW, the TOC_{out}/TOC_{in} started from a high value around 0.75 at $t = 0$ for OSPW at its natural pH= 8. However, after adjusting the pH of OSPW to 4, the TOC_{out}/TOC_{in} started from a small value less than 0.1. It should be noted that some organics in OSPW precipitated in the feed tank when the pH was adjusted to 4.0 (the initial TOC of OSPW reduced from 250 mg/L to 75 mg/L by simply adjusting the pH from 8 to 4). Therefore, the organics

burden to the adsorbent bed was lower at a lower pH. Nonetheless, the APC had a better adsorption performance at a lower pH, and its maximum adsorption capacity for removal of TOC in OSPW was 168 mg/g at pH 8, compared with 441 mg/g at pH=4.

Unlike those for the adsorption removal of 2-naphthoic acid and diphenylacetic acid, the experimental breakthrough curves for removal of TOC in OSPW by APC were fitted better to Adams-Bohart model (Table 5.2), suggesting that the interactions between the organics in OSPW and the surface functional groups of APC material play dominating role in the adsorption process, where the interactions could be forces like hydrogen bonding, dipole-dipole, and hydrophobic interactions.

As clearly shown in Figure 5.2, the adsorption capacity of APC did reduced after some repeated adsorption-regeneration cycles, but did not drop significantly for the regenerated APC after OSPW treatment, while this drop was much more significant for the 2-naphthoic acid and diphenylacetic acid. The APC in OSPW treatment could be more effectively regenerated using solution of methanol and sodium hydroxide (at pH = 11.7) although the adsorption capacity of APC was reduced by 31% after 3 repeated adsorption-regeneration cycles, but it appeared to be stabilized after 3 cycles. As mentioned previously, during regeneration by desorption it is possible that the sodium salt of 2-naphthoic acid or diphenylacetic acid precipitated in the APC carbon adsorbent and blocked its active mesoporous surface, causing significant loss in APC's adsorption capacity. After the 2-3 cycles, however, the reductions in adsorption capacity for all tested solutions were less than the initial drop between the first and second cycles.

On the other hand, after the first cycle a small drop follow by a steady increase in the adsorbate concentration at the column exit was noticed at the beginning of each cycle for all tested solutions, which was believed to result from the remaining adsorbate from the previous cycle. This can be avoided by washing the column with distilled water for a sufficiently long time after each regeneration process prior to the next cycle of adsorption.

Table 5.2: Thomas, Adams-Bohart, and Yoon-Nelson model parameters for fixed bed adsorption removal of 2-naphthoic acid, diphenylacetic acid, and TOC of OSPW at pH= 4, and pH= 8 by CAC and APC

		Adsorbent	Thomas model				Adams-Bohart		Yoon-Nelson		
			K_{Th}	q_{model}	q_{exp}	R^2	K_{AB}	R^2	K_{YN}	τ (min.)	R^2
2-naph.	pH= 4	CAC	0.02	332.0	429.7	0.94	0.008	0.71	0.0007	1660.0	0.94
		APC	0.10	615.9	610.6	0.97	0.060	0.86	0.0039	3079.7	0.97
	pH= 8	CAC	0.05	103.6	137.0	0.98	0.015	0.88	0.0018	518.0	0.98
		APC	0.17	210.7	195.0	0.98	0.100	0.84	0.0066	1053.5	0.98
Diph.	pH= 4	CAC	0.03	199.9	183.5	0.93	0.010	0.61	0.0010	1999.0	0.93
		APC	0.08	181.0	188.5	0.97	0.043	0.80	0.0031	3042.4	0.97
	pH= 8	CAC	0.08	44.0	53.5	0.96	0.018	0.85	0.0032	437.0	0.96
		APC	0.08	53.0	76.5	0.97	0.020	0.89	0.0033	530.0	0.97
OSPW	pH= 4	CAC	0.03	338.0	367.6	0.86	0.010	0.98	0.0011	1780.4	0.86
		APC	0.03	406.0	441.0	0.86	0.015	0.95	0.0013	2139.2	0.86
	pH= 8	CAC	0.02	110.5	115.9	0.98	0.001	0.88	0.0006	2296.3	0.98
		APC	0.01	154.9	168.0	0.80	0.002	0.87	0.0005	1886.2	0.80

As mentioned earlier, a commercial activated carbon (CAC) was also tested in the column operation. The maximum adsorption capacity ($q_{exp.}$, mg/g) of 2-naphthoic acid by CAC during the four cycles is compared with APC, as shown in Table 5.2. The obtained results showed a much better performance for APC compared to CAC, which could be attributed to the larger specific surface area and meso-pore area of APC (1705 and 1372 m²/g, respectively) than those of CAC (1399 and 766 m²/g, respectively). The column adsorption performance of CAC in four adsorption-regeneration cycles for removal of model NA compounds and TOC of OSPW is illustrated in Figure 5.3, where the fitted curves using Thomas and Adams-Bohart models are also shown. Similarly as shown before with the APC, Thomas model fitted the experimental data for the two NA model compounds at both pH= 4 and 8 better than Adams-Bohart model, for the TOC removal from OSPW, the Adams-Bohart model worked better than Thomas model, which imply that the adsorption of NA model compounds could be mostly controlled by diffusion, while both diffusion and chemical interaction between the adsorbent and adsorbate might play a role in the TOC removal from OSPW.

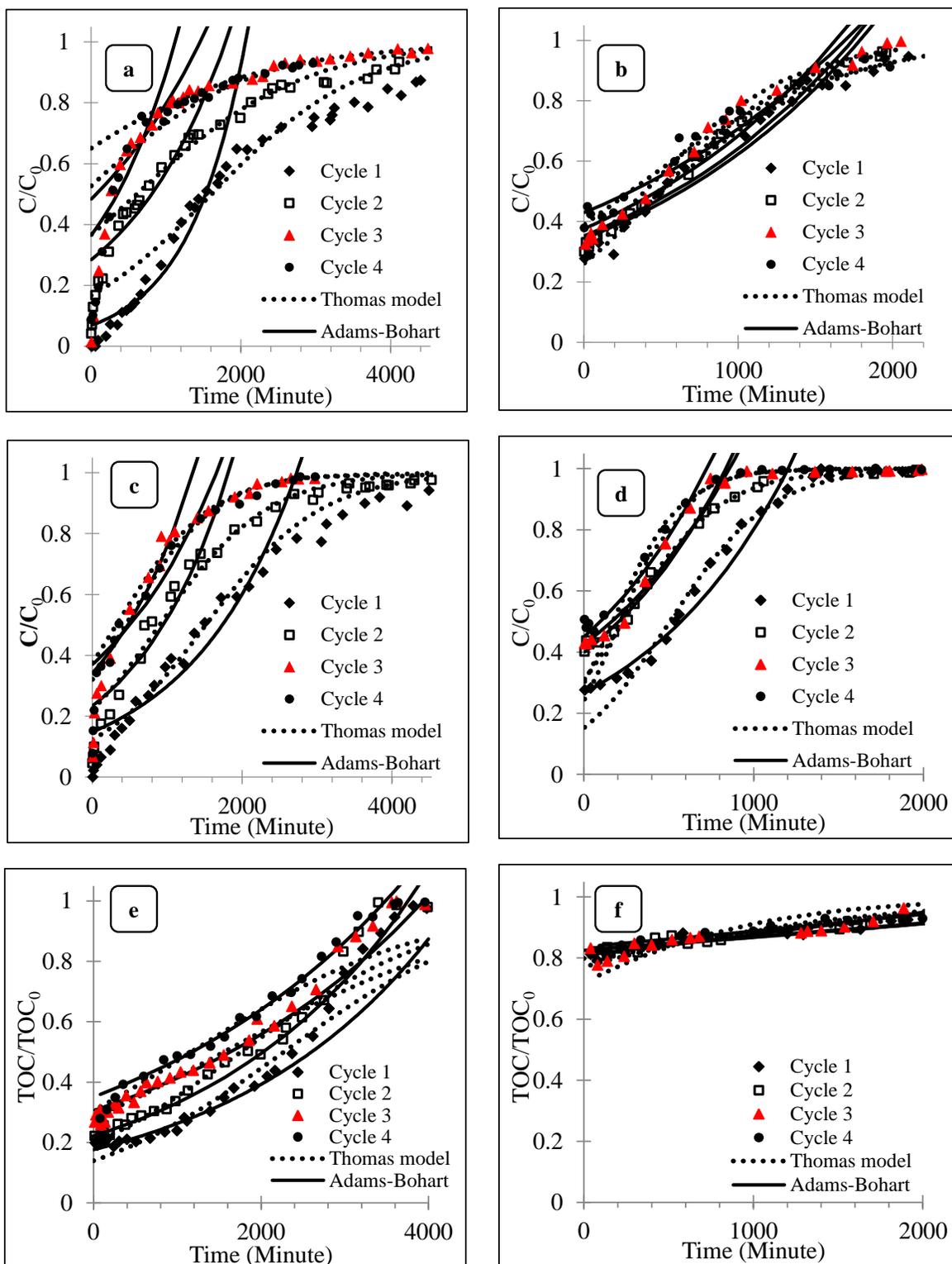


Figure 5.3: Column adsorption performance of CAC in four adsorption-regeneration cycles for removal of model NA compounds and TOC of OSPW, and the fitted curves using Thomas and Adams-Bohart models. a) 2-naphthoic acid at pH= 4, b) 2-naphthoic acid at pH= 8, c) diphenylacetic acid at pH= 4, d) diphenylacetic acid at pH= 8, e) OSPW at pH= 4, f) OSPW at pH= 8.

The FTIR spectra of the functional groups on the surface of the fresh, exhausted and regenerated APC in the OSPW treatment were recorded, and some typical spectra are shown in Figure 5.4.

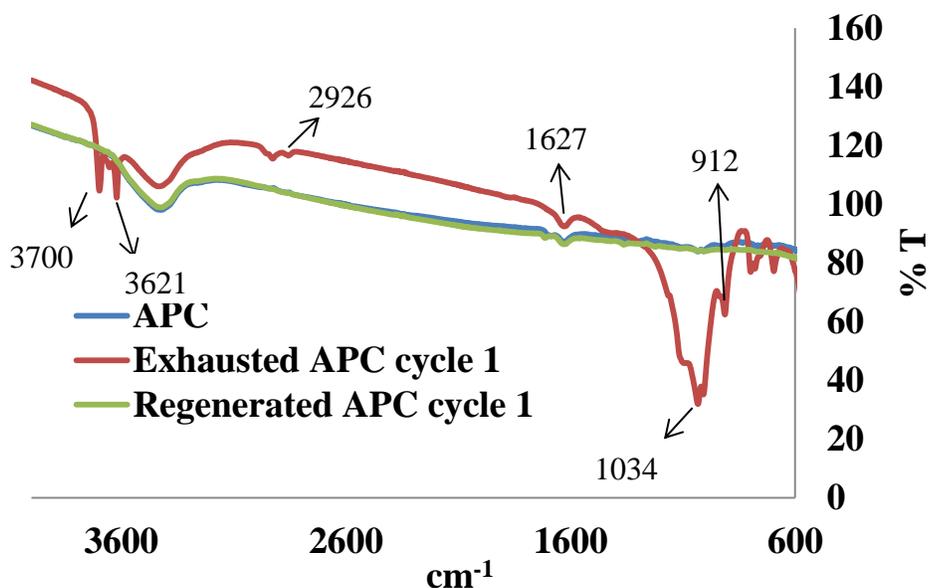


Figure 5.4: FTIR spectra of the fresh, exhausted and regenerated APC in OSPW treatment (cycle 1).

The FTIR analysis, as shown above in Figure 5.4, revealed some major changes in the functional groups on the surface of exhausted APC after each adsorption-regeneration cycle for OSPW treatment. The peak at 3700 cm^{-1} is indicative of adsorbed organics with carboxyl groups on the surface of APC after the OSPW adsorption treatment. While, the peak at 2926 cm^{-1} could be attributed to the aliphatic C-H bond, and the peak at 1034 cm^{-1} —C—OH stretching or carboxylic anhydrides. The intensity of all peaks except for 1627 cm^{-1} (aromatic C=C bond that could be attributed to the aromatic structure of the APC) reduced significantly after regeneration, which suggesting a good removal of the adsorbed organic compounds by the solvent (methanol) regeneration. While the peaks observed in FTIR spectra are representative of many different classes of organic compounds, the exhausted adsorbent after NAs adsorption have similar spectra, indicating their potential presence in OSPW.

Based on the results of this work, an OSPW treatment process based on column adsorption with APC was proposed for large-scale applications as shown in Figure 5.5.

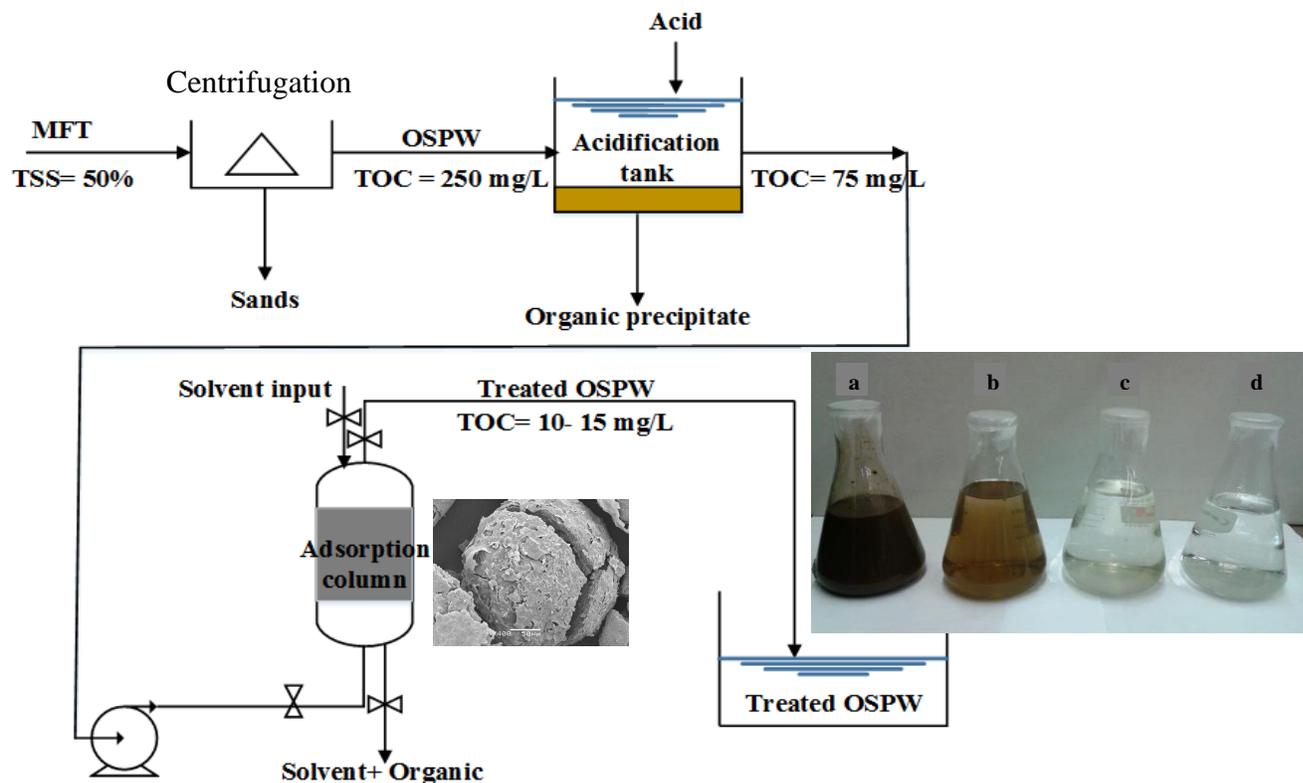


Figure 5.5: Proposed OSPW treatment process based on column adsorption with APC for large-scale applications; Pictures of raw OSPW sample from MFT (a) and OSPW samples after centrifugation at 3500 g (b), adjustment pH to 4 and followed by centrifugation (c), and column adsorption treatment with APC (d).

In the first step, the suspended particles were removed from the mature fine tailing water (Erlenmeyer a in Figure 5.5) using centrifugation process. The TOC of OSPW after centrifugation and removal of solid particles was 250 mg/L (Erlenmeyer b in Figure 5.5). The TOC was reduced to 75 mg/L by adjusting the pH of OSPW from 8 to 4 due to precipitation of the organics (Erlenmeyer c in Figure 5.5). The pH-adjusted OSPW was then pumped through the fixed-bed column and the TOC of output solution (Erlenmeyer d in Figure 5.5) was reduced to a value less than 10 mg/L. A TOC reduction of 96%, which is a significant step in OSPW treatment occurred and the treated water could meet the regulations to be released to the environment, or being recycled back to the extraction process.

5.4 Conclusion

The study provides an effective treatment method for recovery of naphthenic acids (NAs) and removal of TOC from OSPW using column adsorption with activated petroleum coke (APC) as a novel adsorbent. The TOC of OSPW could be reduced by 96% after multi-steps treatment including centrifugation, pH adjustment and column adsorption with APC. The APC could be regenerated using a solution of methanol and sodium hydroxide and could be reused for several cycles although the adsorption capacity of APC was reduced by 31% after 3 repeated adsorption-regeneration cycles, but it appeared to be stabilized after 2-3 cycles. The fresh and regenerated APC performed better than the commercial activated carbon (CAC) for all compounds/solutions tested, in particular at $\text{pH} \leq 4.0$. With both carbon-based adsorbents (APC and CAC), Thomas model fitted the experimental data for the two NA model compounds at both $\text{pH} = 4$ and 8 better than Adams-Bohart model, for the TOC removal from OSPW, the Adams-Bohart model worked better than Thomas model, which imply that the adsorption of NA model compounds could be mostly controlled by diffusion, while both diffusion and chemical interaction between the adsorbent and adsorbate might play a role in the TOC removal from OSPW.

5.5 Acknowledgements

The authors would like to acknowledge funding from NSERC and Newalta (Terrapure) Corporation via a CRD grant, as well as NSERC Discovery Grants awarded to co-authors (C. Xu and M. Ray). The authors are also indebted to Mrs. Fang Cao for her great assistance in samples preparation and analysis.

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5.7 Supplementary information for chapter 5

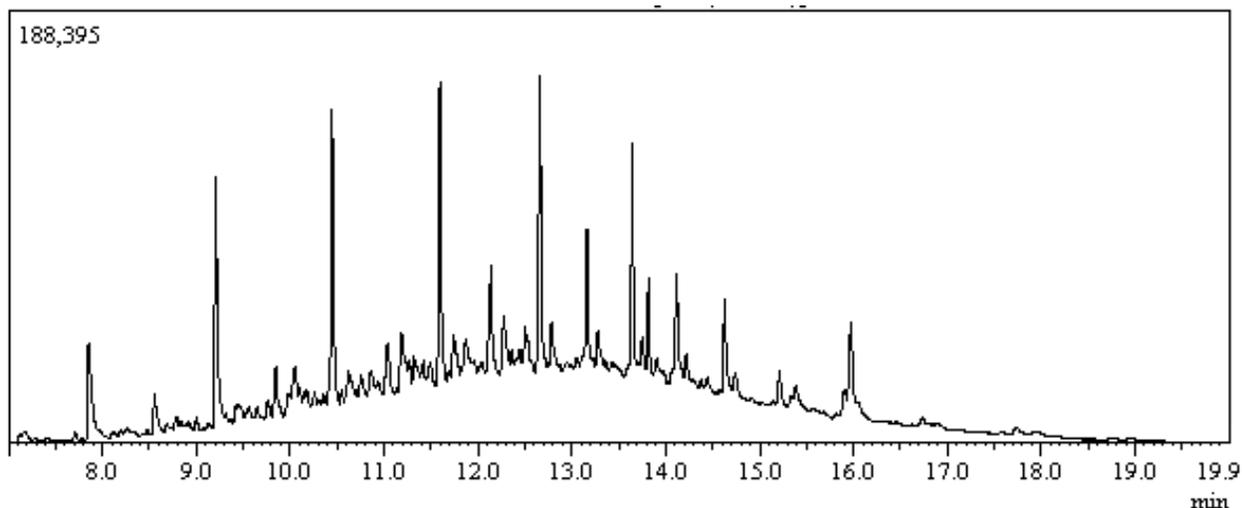


Figure S 5.1: The GC/MS spectra for OSPW after solvent extraction and derivatization

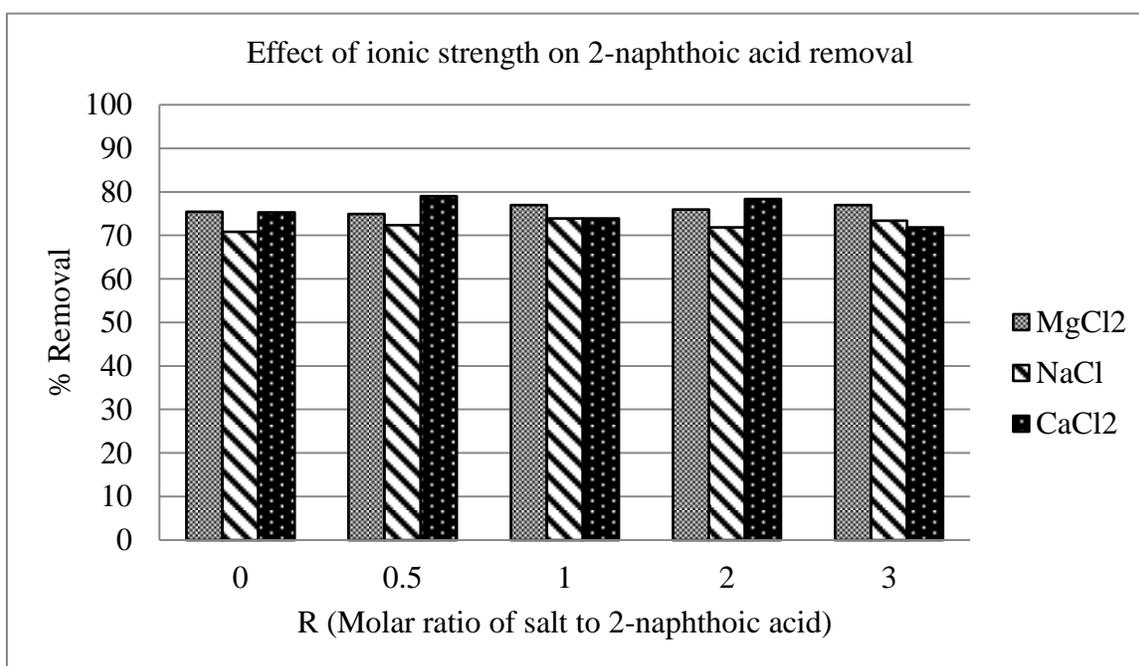


Figure S 5.2: Effect of ionic strength on removal of 2-naphthoic acid by activated petroleum coke

Chapter 6

6 Application of projection to latent structures (PLS) model to the adsorption of model naphthenic acids by activated petroleum coke with and without surface modification

Abstract

For the first time, projection to latent structure (PLS) modeling was applied to investigate the effects of molecular properties of model naphthenic acids' (NAs), and the surface parameters of activated petroleum coke (APC) on adsorption removal of NAs by APC. The effect of surface amination, and the pH of the solution was investigated in this study. The results of this study demonstrate that the PLS model has a good predictability for both the kinetic and isotherm adsorption parameters on NAs adsorption removal by APC. The results of the PLS model show that the pH of the solution and the NH_3 surface modification are two important contributors that affect the adsorption capacity of APC the most. The results of PLS kinetic parameters illustrate that the kinetic of NAs adsorption by APC is mainly controlled by the surface properties of adsorbent rather than the molecular properties of the adsorbate. By increasing the ratio of mesopore to micropore surface area, the time constant would be reduced and the adsorption process would be faster. The kinetic modeling data suggest that the mechanism of the adsorption varied in different adsorption processes and more than one mechanism could be involved.

6.1 Introduction

Projection to latent structure (PLS) model could interpret as principal component analysis (PCA), but with different objective functions. In PCA, the latent variables are calculated in the way that explains the best the input matrix "X"; while in PLS, the latent variables

being calculated in the way that fit the “X” in the way that gives the best prediction for outputs matrix “Y”¹. In PLS model, the data are being projected to lower dimension latent variable spaces where the most effective parameters lie. By doing this, the amount of information required to explain the output data will be reduced significantly. Therefore, the most effective information will be concentrated in the initial latent variables and the last latent variables will only represent less important variables and probably just noise². The PLS method creates a model just based on those parameters which have the most contribution to the outputs (the initial latent variables) and eliminates those variables that has less contribution and just represent the noise and irrelevant data¹. The objective function of PLS method is to optimize the predictability of dependent variable (Y matrix) rather than best fit the independent parameters¹.

Another powerful aspect of this method is handling the missing data^{2,3}. These missing data can be automatically calculated based on the available data sets. Multivariate analysis, also known as latent variable modeling, is a statistical data modeling that provides unique approaches over other classical empirical models like multiple linear regression and neural network⁴. The PLS model shows how the combination of “X” variables affects the output. The latent variable method was selected in this work because of its ability to rapidly extract required information from a large number of data sets, deal with missing information and high dimension data sets, and handle low signal to noise ratio.

The adsorption data obtained from our previous research study⁵ was used to establish the presented PLS model. Diphenylacetic acid, 2-naphthoic acid, 1,4-cyclohexanedicarboxylic acid, and cyclohexanepentanoic acid were studied as four NA model compounds. The NAs’ properties which were considered in the presented PLS model are carbon (C#), hydrogen (H#) and oxygen number (O#), pKa, pi-bond number (Pi#), molecular weight (MW) and volume (MV), number of H-bonding acceptor (H-acceptor) and donor (H-donor) sites, molar refractivity (MR) and polarizability of the model compounds, as well as total, meso and micro pore surface areas of the adsorbents. In addition, the effects of two different approaches for surface modification of the APC, as well as the pH of the solution were investigated. More details of these two surface

modification approaches are explained in section 6.2. The values of the above-mentioned parameters for all tested model NAs compounds are presented in Table 6.1.

Table 6.1: The considered properties of the tested NA model compounds in the PLS model^a

	2-naphthoic acid ⁶	Diphenylacetic acid ⁷	1,4-cyclohexanedicarboxylic acid ⁸	Cyclohexanepentanonic acid ⁹
C#	11	14	8	11
O#	2	2	4	2
H#	8	12	12	20
Pi#	6	7	2	1
MW	172.18	212.25	172.18	184.27
MV	155	199.28	156.66	196.84
pKa	4.2	4.7	4.5	5.1
PSA	37.3	37	75	37
H-acceptor	2	2	4	2
H-donor	1	1	2	1
MR	51	61.8	39.9	52
Polarizability	20.2	24.5	15.8	20.8

^aThese values were obtained from national center for biotechnology information, PubChem compound database.

In adsorption process, the electrostatic interactions between adsorbent and adsorbate play an important role in both the isotherm and the kinetic of the process. To investigate the effects of these interactions, some related parameters such as polarizability, refractivity, H-bonding acceptor and donor sites, polar surface area (PSA), and number of pi bonds of the model compounds were considered as the input of PLS model. PSA is defined simply as the surface of the molecule that is polar¹⁰. Molecules are adsorbed by their polar sites onto the polar sites of the APC adsorbent surface.

All used kinetic and isotherm data to establish the presented PLS model were measured in batch experiments as discussed in the previous chapters. Furthermore, the effects of surface amination on adsorption properties of APC were investigated. Two different amination methods were investigated, whose detailed process and results are presented in

our previous work⁵. The APC sample modified with ammonia gas was designated as “NH₃”, and the APC modified by a two-step nitration and reduction processes was denoted as “NH₂”. For the output “Y” matrix, the maximum adsorption capacity, Q_{\max} (mg/g), and the maximum adsorption capacity per unit surface area were considered as two isotherm output variables. For the kinetic data, “ k ” and “ n ”, as the Bangham’s kinetic model constants were selected to investigate the adsorption kinetic mechanism.

There are huge amounts of characterization data for adsorbents and adsorbates that sometimes are correlated. Therefore, by using appropriate statistical models the essential parameters could be identified¹¹. Sometimes, the affective information lies not in any specific parameter, but in how two or several variables are changing in respect to each other. In PLS model, the data are being processed in a way to find the most affective data and it eliminates less meaningful factors. There are few studies in literature that have applied PLS to find the effects of adsorbate molecular properties and adsorbent surface characteristics like meso and micro pore surface areas on adsorption isotherms and kinetics of the adsorbents. In the present study, for the first time, PLS model was applied to screen the most correlated characterization parameters of model NAs for their adsorption removal by APC, and identify the most relevant factors on adsorption kinetic and isotherm. This method of modeling avoids any variance coming from undetected differences between adsorbates and adsorbents, and gives a more precise evaluation of the effects of each factor on the “Y” matrix. In total, 18 different variables that cover the physical and chemical properties of adsorbates and adsorbents were considered in building the presented PLS model.

6.2 Experimental methods

The Syncrude petroleum coke was obtained from NEWALTA Corporation (Burlington, ON), and was activated using KOH at elevated temperature based on our previous study⁵. A Nova 1200E, BET analyzer (QuantaChrome Co.) was used to measure the textural properties of the obtained activated petroleum coke (APC). The APC used in this work

has BET specific surface area of 1705 ± 20 m²/g, micro-pore area of 353 ± 16 m²/g, meso-pore area of 1372 ± 22 m²/g and total pore volume of 0.85 cc/g.

The surface of the APC was aminated by two different methods. In the first method, the ammonia gas was passed through a packed bed of APC particles at elevated temperature in nitrogen atmosphere. This experiment was performed in a horizontal tubular furnace. For the second method of surface modification, a two-step process, nitration and then reduction was applied to create NH₂ groups on the surface of APC. More details of these two surface modification methods were given in our previous publish work⁵.

All the data to build the presented PLS model were obtained by batch adsorption experiments. For the kinetic study, ten samples were taken at different time intervals until reaching the plateau part of the kinetic curve. Samples were filtered using 0.45 μm nylon syringe filters prior to the analysis on the HPLC. For each kinetic test, 70 mg adsorbent was added to 175 mL of the solution containing the model NAs with initial concentration of 40 mg/L. Then, the obtained kinetic data were fitted to Bangham's model to obtain “*n*” and “ln(*k*)” as the two kinetic parameters for interpretation of the kinetic mechanism. For the isotherm results, different APC loadings were used to obtain the equilibrium concentration after 48 hrs of adsorption under shaking. The initial concentration of model NAs was adjusted to 40 mg/L. Then, by obtaining the isotherm equilibrium curves, the maximum adsorption capacities were calculated.

A Dionex ICS-3000 was used in an HPLC configuration to detect the naphthenic acids using an Acclaim Fast LC Column 120 C18 (3 × 75 mm). The mobile phase used was an acetonitrile (ACN)/water mixture. The mobile phase was acidified with sulfuric acid to pH 2.15, in order to ensure that the acids in the samples were in their protonated form.

6.2.1 Data preprocessing for PLS modeling

The first step of PCA modeling is to center and scale the raw data. Centering by using equation 1, which removes any bias terms by subtracting the mean value of each variable from each data point of that variable.

$$X_{k, \text{center}} = X_{k, \text{raw}} - \text{mean}(X_{k, \text{raw}}) \quad (\text{Eq. 1})$$

Then the data was scaled by dividing them by their standard deviation according to Equation 2.

$$X_{k, \text{scaled}} = \frac{X_{k, \text{center}}}{\text{Standard deviation}(X_{k, \text{center}})} \quad (\text{Eq. 2})$$

By doing these preprocessing steps, each column of data set will center to zero and will have a standard deviation equal to 1. These preprocessing steps will not change the interpretation of the final results. ProSensus' latent variable modeling software (ProMV) was used to apply PLS model in order to investigate the effects of adsorbent properties and adsorbate characteristics on adsorption of model NAs by raw and surface modified APC.

Adsorption kinetic

The Bangham model (Equation 3) was used to investigate the adsorption mechanism. Bangham model is the generalized form of Weber-Morris model¹². The data was fitted to the logarithmic form of Bangham model (Equation 4) to obtain the Bangham constants “ k ”, and “ n ” from the intercept and slope of the fitting line respectively.

$$Q_t/Q_{\text{max}} = k \times t^n \quad (\text{Eq. 3})$$

$$\ln(Q_t/Q_{\text{max}}) = \ln(k) + n \ln(t) \quad (\text{Eq. 4})$$

Which Q_t is the adsorbed compound per each gram of adsorbent at time “ t ”, and “ k ” and “ n ” are Bangham's constants. The values of the “ n ” implies which mechanism controls the adsorption process.

6.3 Results and discussion

The kinetic data were fitted to Bangham's model and the model's constants, " $\ln(k)$ " and " n ", along with time constant (time required to reach 63.2% of the maximum adsorption capacity) were considered as the output kinetic data to interpret the adsorption mechanism. Furthermore, the absolute maximum capacity (Q_{\max}) and the maximum adsorption capacity per unit of the total surface area (Q_{\max}/St) were considered as the isotherms output data, in order to eliminate the influence of surface reduction during the surface modification process.

6.3.1 Accuracy of the model

The accuracy of PLS model to fit the "X" data is shown by R^2X , and the accuracy of "Y" prediction is shown by Q^2Y . In PLS model, the first latent component represents the data the most, and the role of the next latent variables is being reduced in order. The model fit capability for X matrix (R^2X), Y matrix (R^2Y), and model prediction capability (Q^2Y) of the PLS model with seven components obtained 0.94, 0.69, and 0.63 respectively (Figure 6.1(a)). The R^2X in PLS model represents how well the model fits X data. The R^2 and Q^2 values for each of the Y variables are shown in Figure 6.1(b). By looking at Figure 6.1(a), it is clear that the initial three components fit the data significantly, and by adding component number 4, 5, 6 or 7, the R^2 and Q^2 did not change significantly. The R^2 and Q^2 of this model represent a good fitting and prediction capability. For example, the R^2 and Q^2 of presenting model are 0.65 and 0.60 for Q_{\max} . These values for other output measurements are presented in Figure 6.1(b).

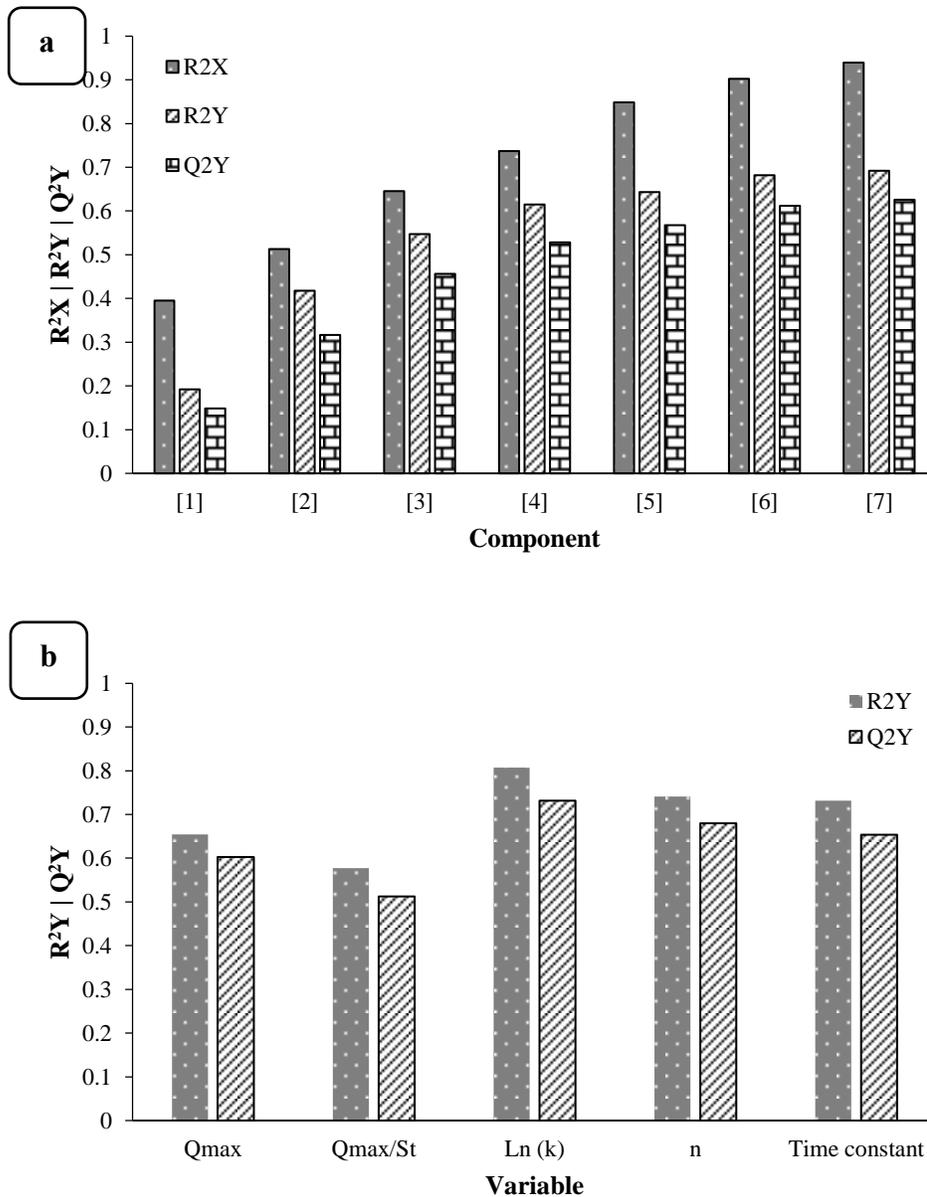


Figure 6.1: Cumulative R^2X , R^2Y , and Q^2Y for each of the latent variable components of the PLS model (a); R^2 and Q^2 for each of the Y variables (b)

6.3.2 Correlation-loading plots

The correlation-loading plots of the initial latent variables explain the most significant correlations between X matrix and the output data (Y matrix). Figure 6.2 shows the loading plots of the initial three latent variables. It is a positive aspect of the PLS method that represents the X and Y variables in a same loading plot graph.

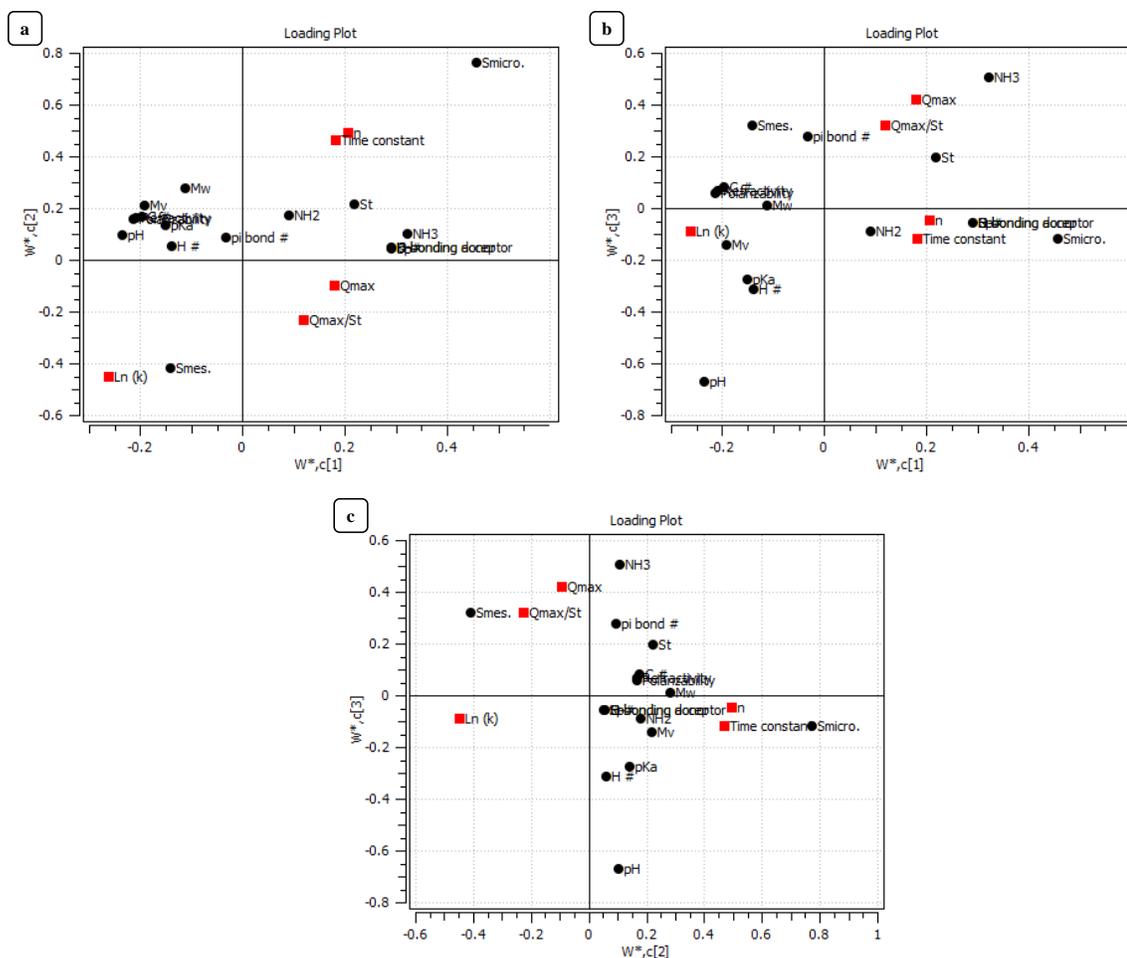


Figure 6.2: Correlation-loading plot for the studied parameters on adsorption of NA model compounds by APC

In the correlation-loading plot, factors that create clusters or located in a same quarter are highly correlated. For example in Figure 6.2(a), pKa , pH , MW , and MV have made a cluster, and it means that these variables are affecting the output matrix “Y” in a same direction. Also, because the Q_{max} and $\text{Q}_{\text{max}}/\text{St}$ are located on the opposite sides of the loading plot, it means that those variables (pKa , pH , MW , and MV) affect the maximum adsorption capacity negatively. In addition, because Q_{max} and $\text{H-bonding acceptor}$ and donor factors are the same side of the first latent variable, it means that they are positively correlated. By increasing the number of $\text{H-bonding acceptor}$ and donor sites, the maximum adsorption capacity would be increased. It was found that, 1,4-cyclohexanedicarboxylic acid that has more H-bonding donor and acceptor sites in its

molecule structure, has higher adsorption potential compared with other tested NA model compounds. The H-bonding acceptor and donor for 1,4-cyclohexanedicarboxylic acid are 4 and 2 respectively, while these values were 2 and 1 for the other tested compounds. Furthermore, the loading plots illustrate that surface modification with ammonia (NH_3), and the number of H-bonding acceptor and donor sites have positive impact on Q_{max} in general.

In addition, the correlation-loading plots illustrate that there is a positive relationship between time constant and micro-pore surface area ($S_{\text{micro.}}$) of the APC. Also, because the time constant and mesopore surface area ($S_{\text{mes.}}$) are located in two opposite quarters of the loading plot, it means that these parameters are negatively correlated. In other words, by increasing the mesopore surface area of the APC, the time constant will reduce and vice versa.

6.3.3 Coefficient plots

The coefficient plots (Figure 6.3 and Figure 6.4) show the contribution of each X matrix variables to the output data (Y matrix). The coefficient plots for isotherm output parameters shown in Figure 6.3. The isotherm output parameters which were considered here are the maximum adsorption capacity (Q_{max}), and the maximum adsorption of the unit surface area (Q_{max}/St). The coefficient plots show that three significant parameters that affect the both considered isotherm parameters the most are the same, and those parameters are: pH of the solution, surface amination with ammonia gas, and surface areas (total, meso and micro pore) of APC. It shows that the surface amination by ammonia gas (NH_3) and mesopore surface area ($S_{\text{mes.}}$) have the most positive impact on the adsorption capacity, and the pH and the micropore surface area ($S_{\text{micro.}}$) have the most negative impact on the adsorption capacity. Surface amination positively increased the adsorption capacity of APC because of creating amine groups on the surface that increase the interactions between the NA model compounds and the surface of the APC⁵. The pH has a negative effect on the adsorption capacity, likely because of less positive charge of the APC's surface at elevated pHs. The coefficient plots of isotherm variables show that the surface properties of the APC and the pH of the solution are the most effective parameters to define the adsorption capacity of the APC. Furthermore, the plots illustrate

that such parameters as carbon number, oxygen number, hydrogen number, polarizability, and refractivity are less effective parameters on defining the maximum adsorption capacity.

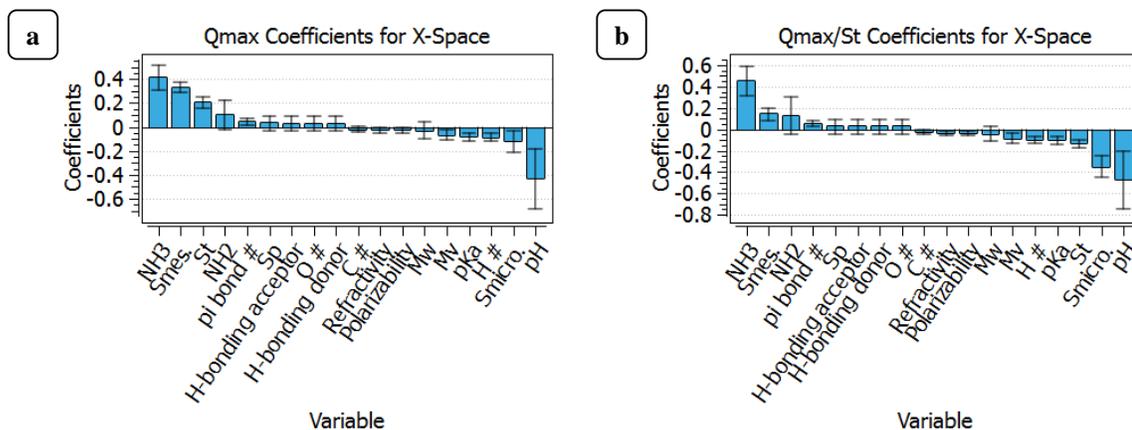


Figure 6.3: Coefficients plot showing the effects of each X variable on adsorption isotherm parameters; (a) Q_{\max} , (b) Q_{\max}/St .

The coefficient plots for kinetic output parameters are shown in Figure 6.4. From the kinetic coefficient plots, it can be concluded that the surface properties of APC have the most significant contribution to the kinetic of the adsorption process. For instance, the mesopore surface area ($S_{\text{mes.}}$) has negatively contributed to the time constant, while micropore surface area ($S_{\text{micro.}}$) has positively affected it. It means that by increasing the mesopore surface area the kinetic of the adsorption would be much faster. Furthermore, the kinetic coefficient plots show that the effects of physical properties of model NA compounds on the adsorption kinetic by APC material could be neglected.

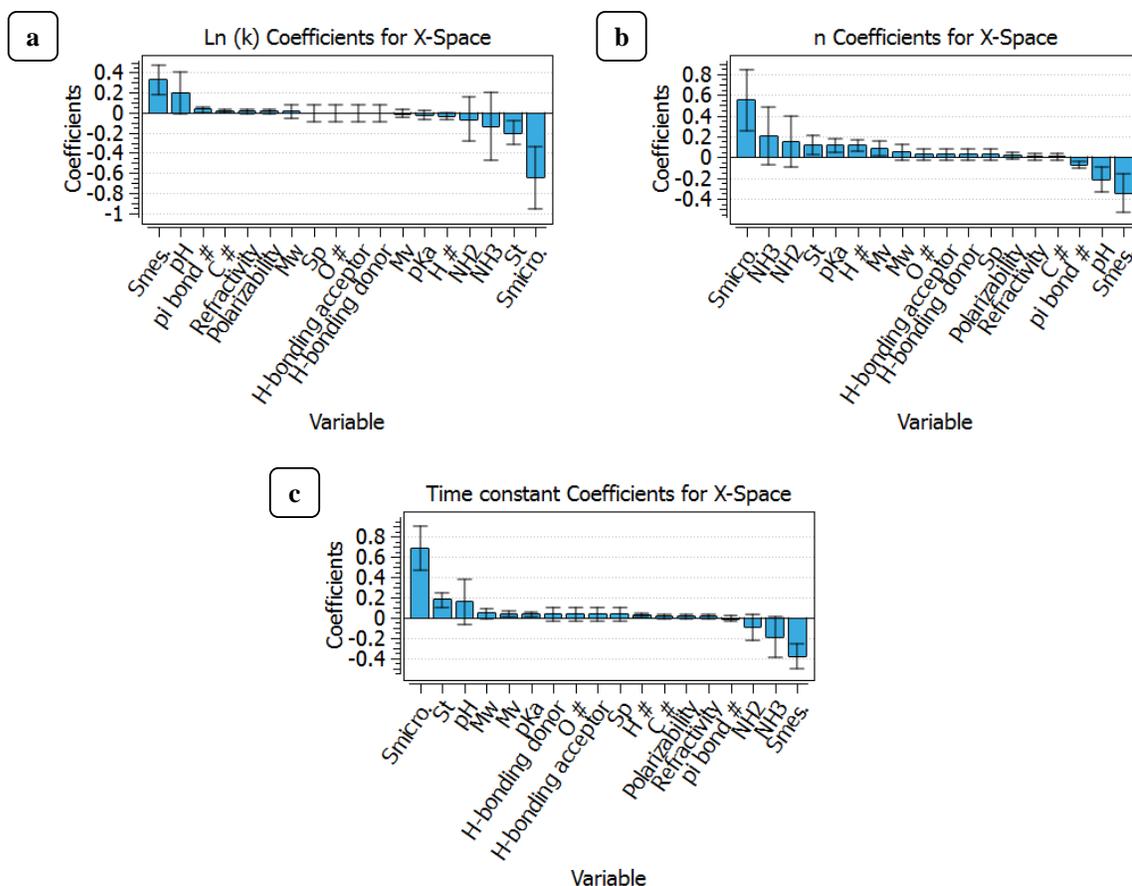


Figure 6.4: Coefficients plots showing the effects of each X variable on the adsorption kinetic parameters; (a) Ln (*k*), (b) *n*, and (c) time constant

6.3.4 Predictability

One of the common weaknesses of the most prediction models is their limitation on a specific space of the input variables. Most of the models could not predict the output parameters accurately out of their defined region. However, unlike most of the prediction models, the PLS model provides a natural way of checking for validity of any input before predicting the outputs³. For prediction of any new point, the first thing that needs to be checked is the distance of the new point from latent variable space. The distance of xi data point from the latent variable space in the X space is called the squared prediction error (SPE-X) and being calculated by Equation 5. The “j” changes for all dimensions of the X space.

$$\text{SPE}_i = \sum (x_{ij} - \text{average}(x_{ij}))^2 \quad (\text{Eq. 5})$$

Figure 6.5 (a) shows the squared prediction error for X space, and as seen, all the data points fall below the 99% confidence interval, which means the modeled relationships between the X variables are well capable of predicting the behaviors of the Y parameters. Another parameter that needs to be checked for any new data point before prediction is hotelling. The hotelling's T^2 values are presented in Figure 6.5(b), and all the data point have fallen below 0.95 confidence interval.

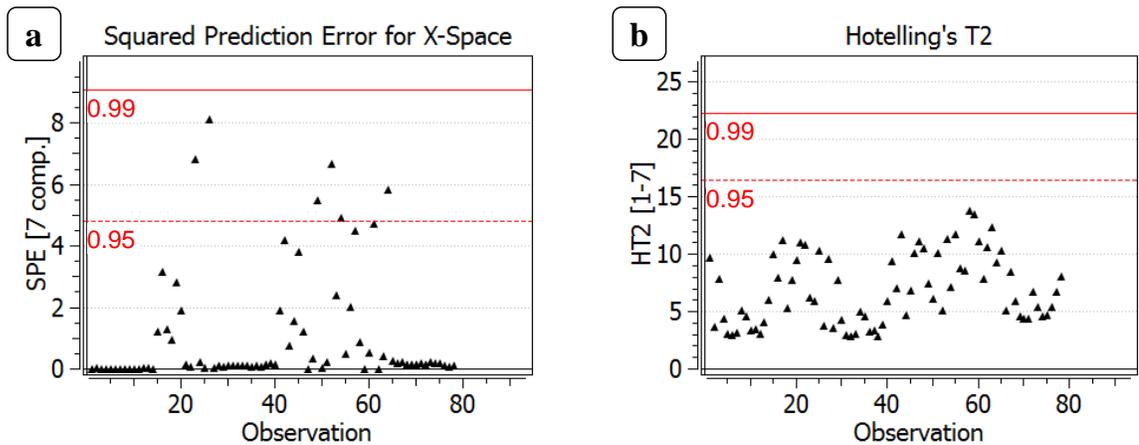


Figure 6.5: Squared prediction error (SPE) values for the observations (a), and hotelling (b).

If any of data points of SPE and T^2 fall above the confidence level, those variables should be eliminated in building the PLS model or someone should investigate the reason why that variable has fallen out of confidence interval level. In the present case, all the data points were located below the 99 percent confidence interval.

Figure 6.6 (a) to (e) compares the experimental values and model predicted values of “Y” matrix variables.

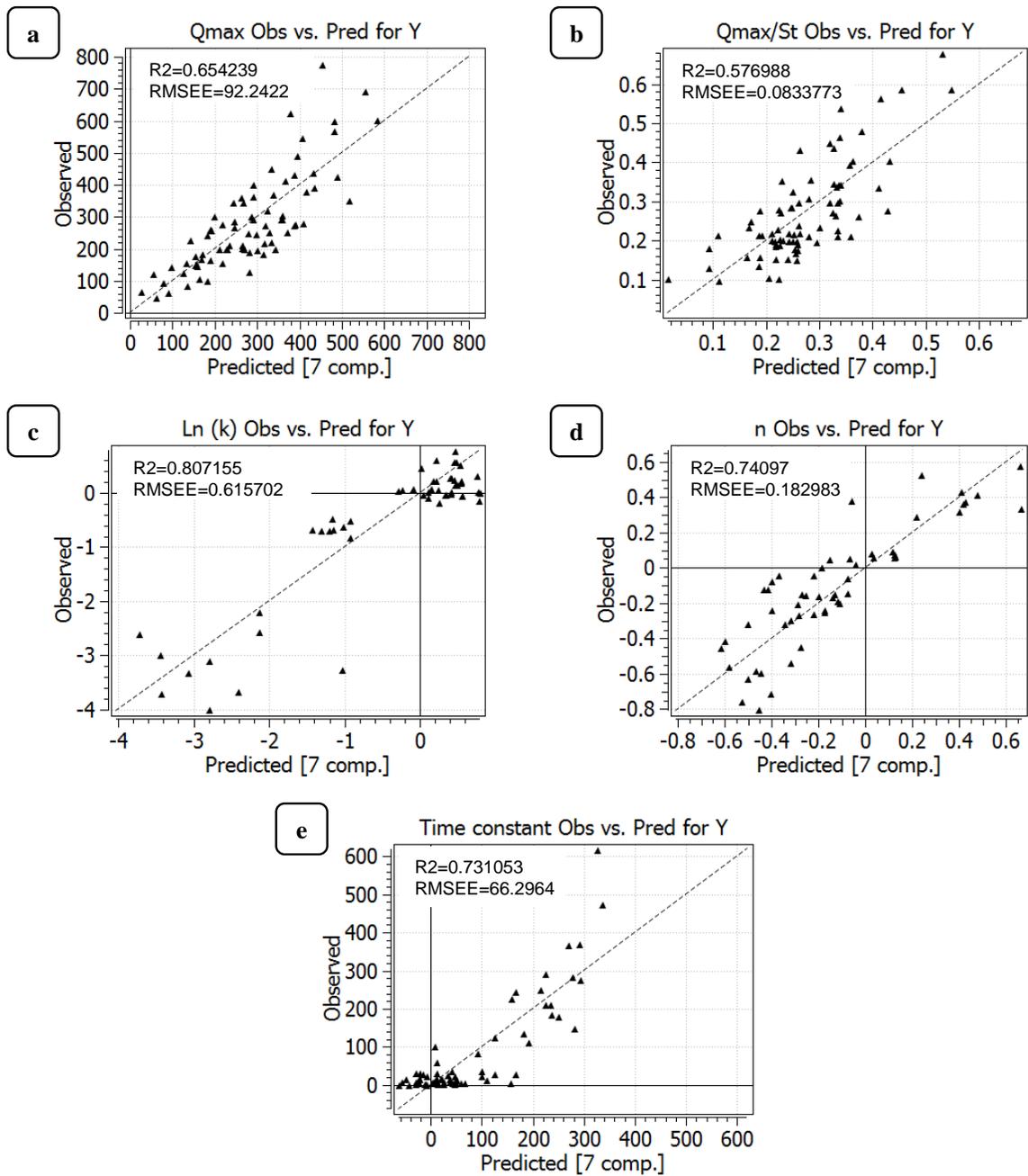


Figure 6.6: Observed vs. predicted plots for Q_{\max} (a), Q_{\max}/St (b), $\ln(k)$ (c), n (d), and time constant (e).

The root mean squared error of estimation (RMSEE) represents a standard deviation of the Y variable, and is calculated by Equation 6.

$$\text{RMSEE} = \sqrt{\left(\frac{\sum_i^N (Y_i - Y_{i_{\text{predicted}}})^2}{N} \right)} \quad (\text{Eq. 6})$$

Which: N is the number of data points.

RMSEE is the standard deviation of the prediction errors, and the unit of RMSEE is the same as the unit of the y-variable. Residuals are a measure of how far from the regression line to the data points are. In other words, it tells how concentrated the data is around the line of best fit. The RMSEE for Q_{max} is 92.2, which is acceptable in the data ranging between 0 to 800 for Q_{max} . The RMSEE value for time constant was 66 minutes, acceptable too considering the data ranging between 0 to 600 minutes. In average the RMSEE of Y variables was calculated to be less than 15 percent of data ranging of each Y variable, which can be considered a small threshold in adsorption process.

6.3.5 Contour plots

The contour plots of isotherm output variables are presented in Figure 6.7. Each contour plot was drawn as a function of two main contribution factors. For isotherm variables (Q_{max} and Q_{max}/St), the pH of the solution and the surface amination of APC are the main contributors, as previously seen in coefficient plots (Figure 6.3).

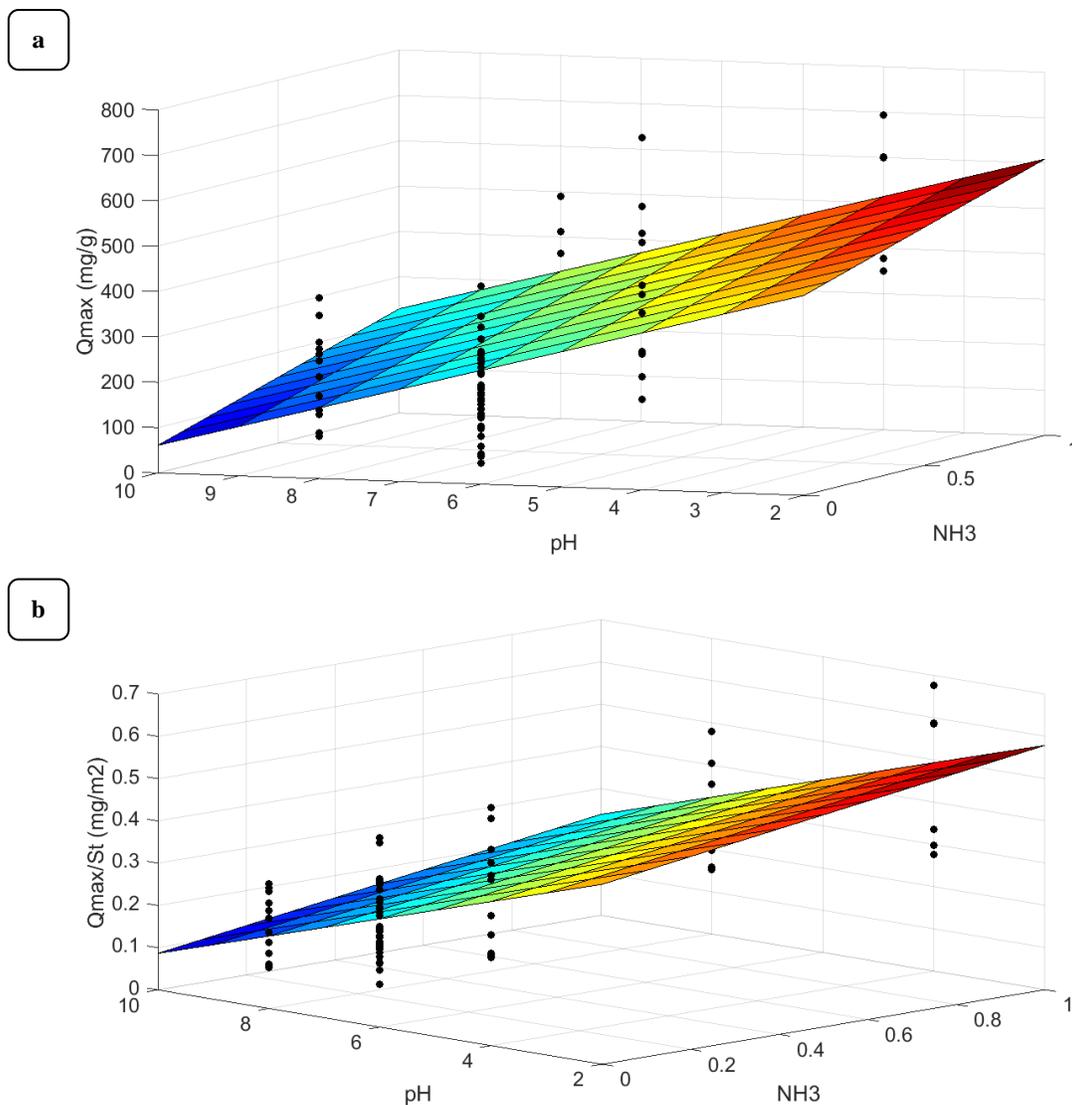


Figure 6.7: Contour surface plots from the PLS model as functions of the main two contributing factors and the experimental data for isotherm output parameters: Q_{\max} (a), and Q_{\max}/St (b).

The contour surface plots of the kinetic variables (“ n ”, $\ln(k)$, and time constant) are presented in Figure 6.8. These contour plots show the plane that was fitted to the experimental data by just using the main two contribution factors. The scattered data in these plots represent the experimental observed data, and their distance from the contour surface is an indication of the prediction abilities of the model. Figure 6.8(a) illustrates the contour plot of variances in $\ln(k)$ as a function of meso and micro pore surface area

as two main contributing factors. This contour plot shows how the mesopore surface area is positively affecting the $\ln(k)$ and micropore surface area negatively. Plot in Figure 6.8 (b) shows the Bangham model's " n " constant. In a specific case, when the " n " is equal to 0.5, Bangham model represents the Webber and Morris model. When the " n " is equal to 0.5, it means that the diffusion controls the adsorption process. The obtained results show that " n " is falling between -1 and 0.5, which means that diffusion is not the only mechanism that controls the adsorption of model NAs by APC. The roles of meso and micro surface area as the two main contribution factors on time constant are presented in Figure 6.8 (c). This plot shows the opposite direction of meso and micro pore surface area on the time constant value, suggesting that the mesopore surface area is the most contribution factor for reducing the time constant value and enhancing the kinetic of the adsorption of NAs by APC.

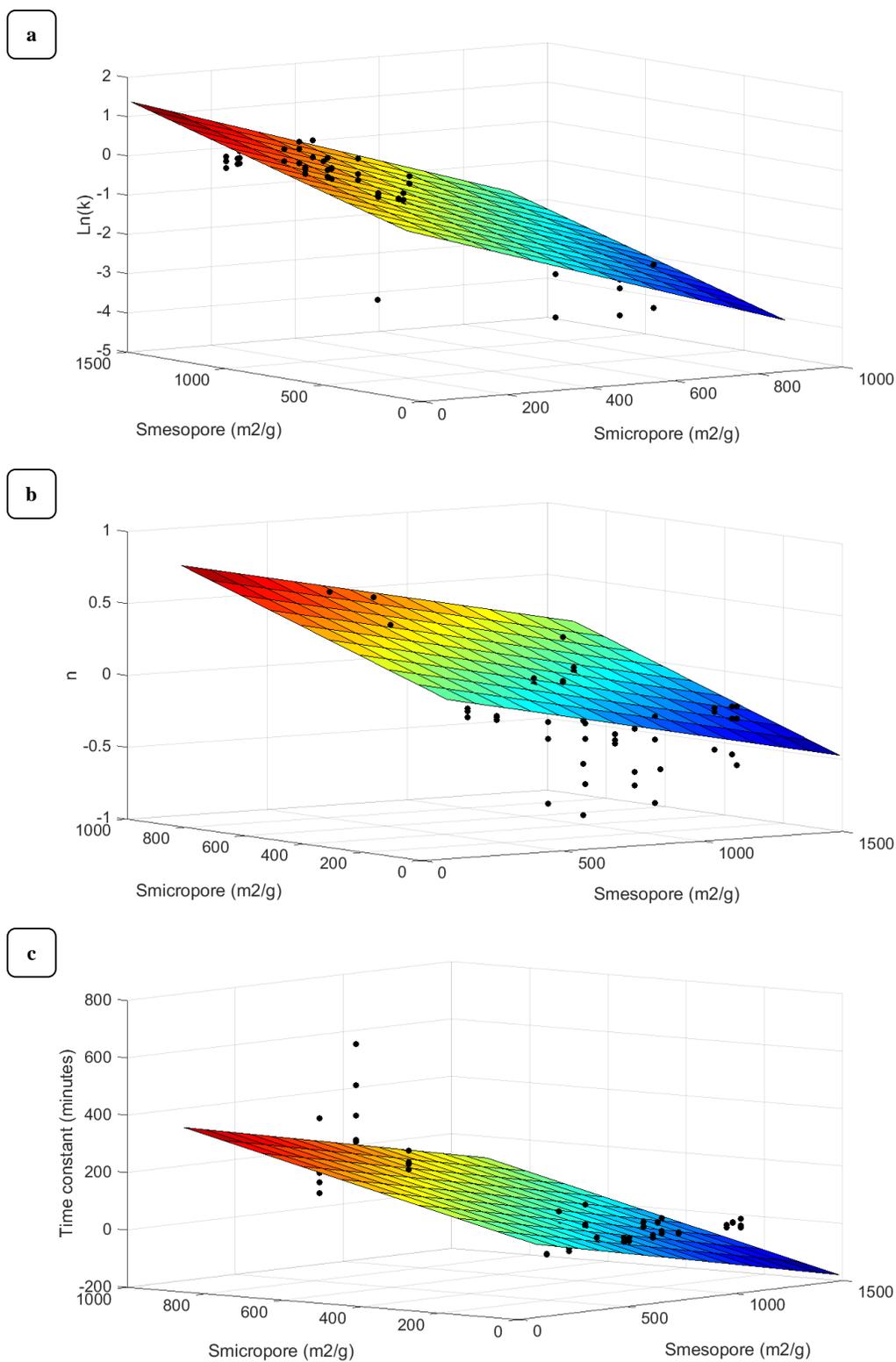


Figure 6.8: Contour surface plots from the PLS model as functions of the main two contributing factors and the experimental data for kinetic output parameters: $\ln(k)$ (a), n (b), and time constant (c).

6.4 Conclusions

It can be concluded that the PLS model has a good predictability for the kinetic and isotherm adsorption parameters on NAs adsorption removal by APC. Using seven latent variables, the R square of the PLS model obtained 0.94 and 0.69 for X and Y spaces, respectively, with the Q^2Y of 0.64. It was found that the amination of APC by ammonia gas is a more effective surface modification approach than the two-step nitration and reduction process for increasing the adsorption capacity of APC. Furthermore, the results of the PLS model show that the pH of the solution and the NH_3 surface modification are two important contributors that affect the adsorption capacity of APC the most. In addition, the loading plots suggest that the molecular properties of NAs such as MW, MV, carbon number, and oxygen number, are making a cluster and hence highly correlated, but have less effect on the APC's adsorption capacity for NAs.

The results of PLS kinetic parameters illustrate that the kinetic of NAs adsorption by APC is mainly controlled by the surface properties of adsorbent rather than the molecular properties of the adsorbate. It was found that the molecular properties of the tested NAs have less contribution to the kinetic of the adsorption. By increasing the ratio of mesopore to micropore surface area, the time constant would be reduced and the adsorption process would be faster. Furthermore, the kinetic modeling data suggest that the mechanism of the adsorption varied in different adsorption processes and more than one mechanism could be involved.

6.5 Acknowledgement

The authors would like to gratefully acknowledge NSERC and NEWALTA Company for funding support and ProSensus Inc. for generous permission to use ProMV software. The authors would like to thank Vida Rahmani for her help and advice on using ProMV software for PLS modelling.

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Chapter 7

7 Conclusions, recommendations, and future works

7.1 General conclusion

The purpose of this study was to create an efficient and scalable treatment method for removal of organic compounds from oil sands process-affected water (OSPW) by using petroleum coke as a cheap byproduct of the oil sands industry. The current treatment methods only focus on separating the clay and fine particles from OSPW, while the dissolved chemicals such as NAs and PAHs are still in the water and create problems such as toxicity for the aquatic ecosystem. Existence of NAs causes this wastewater to be corrosive as well; and for this reason, these chemicals need to be removed before recycling and recovery of OSPW. The main target chemicals for recycling were naphthenic acids (NAs) and polycyclic aromatic hydrocarbons (PAHs). Among available treatment methods, adsorption was selected because of its potential to recover organics from the OSPW, inexpensive treatment method, and availability of adsorbent in the site. Petroleum coke was selected as a precursor for (activated carbon) AC production, due to its availability in the contaminated site and its inexpensive price. Petroleum coke was chemically activated in order to increase its adsorption properties. The experiments began with testing a commercial AC for creating a base point of comparison for activated petroleum coke's (APC) performance.

Among activation techniques, a chemical activation using KOH was selected because of its low cost and high efficiency. Furthermore, different surface modification methods were conducted to increase the selectivity and capacity of the produced APC in removal of organics from OSPW. Two different amination processes including a single stage treatment with ammonia gas at elevated temperature, and a two-step treatment (nitration followed by reduction reactions) were adopted.

In the initial step of this research, the focus of the study was on removal of model compounds such as 2-naphthoic acid, diphenylacetic acid, and 1,4-cyclohexanedicarboxylic acid from a synthetic OSPW solution. Produced APC was tested in batch experiments to measure its adsorption capacity on NA model compounds removal. The effect of the pH and ionic strength of the solution was tested. In the next phase, the KOH activation of petroleum coke was optimized. The Box-Behnken design was employed to optimize the PC activation parameters such as activation temperature, KOH/coke mass ratio, and activation time. For each parameter, three levels were selected: 650, 750, and 850 °C for temperature, 1, 2, and 3 for KOH/coke ratio, and 60, 120, and 180 minutes for activation duration were selected.

In the next part of the experiments, the focus was on running a continuous treatment column using APC for removal of model compounds from synthetic OSPW as well as organics from real OSPW. Furthermore, the exhausted APC was regenerated by an alkaline methanol solution to measure the regeneration potential of APC. In all stages, the equilibrium isotherms and adsorption kinetics were measured and fitted into different available models such as Adams-Bohart, Yoon-Nelson, and Thomas to investigate the adsorption mechanism and the behavior of APC.

In the last part of this study, a PLS model was developed based on the obtained adsorption isotherms and kinetic data to investigate the role of molecular properties of NA model compounds as well as the surface properties of APC on the adsorption process.

The following detailed conclusions could be drawn from this research:

- Oil sands petroleum coke could be converted from a low value byproduct of upgrading process to an added value adsorbent with a high surface area after KOH activation at elevated temperature. After the KOH activation, the surface area of PC was increased from a value around 12 m²/g to 1443 m²/g, mainly due to the formation of mesopore (≈1004 m²/g) surface area. In addition, the pore size of the PC increased from 1.2 to 2.1 nm after KOH activation, which makes it easier for NA model compounds to diffuse and reach the inner surface area.

- Two different amination processes including a single stage treatment with ammonia gas at elevated temperature and a two-step, nitration followed by reduction, were adopted. All tested adsorbents showed higher adsorption capacity for removal of model NAs, as well as organic content from the OSPW at lower pH. Ammonia treatment was more effective on improvement of adsorption capacity than the nitration followed by reduction method. The effect was more significant for commercial activated carbon compared to APC, especially for multi-component adsorption at pH 8.0. Surface activation with ammonia (-NH_3) and amination (-NH_2) treatment caused decrease in specific surface area of both AC and PAC. The decrease was more for AC/PAC- NH_2 adsorbent than AC/PAC- NH_3 adsorbent, probably due to the collapse of pore structure and clogging of the pores during the amination (-NH_2) treatment, as evidenced by the reduced pore volume in the surface modified carbon materials. Both AC and APC lost about 33% of surface area in the 2-step amination process. The treatment of AC and APC by ammonia gas was more effective for increasing their adsorption capacity for the model NAs in mixture at pH 8. In general, the equilibrium capacity of the surface modified adsorbents decreased. Surface modification improved the adsorption kinetics of the NA model compounds more significantly for AC than APC. For example, the time to reach 63.2% of the equilibrium capacity (time constant) of AC for removal of 2-naphthoic acid was reduced 33% and 41% for AC- NH_2 and AC- NH_3 , respectively. The effect was more significant at higher pH. The adsorption capacity of all adsorbents highly depended on the pH of the system, and the capacity decreased with increasing pH, irrespective of single or multi-compound adsorption. In batch experiments, both APC and AC could remove almost 99% of the TOC of OSPW at pH 3.5, with a much lower removal of 50% at pH 8, the natural pH of OSPW.
- Box-Behnken design and response surface methodology was applied to optimize activation parameters for the production of activated petroleum coke (APC). The objective function was to maximize the adsorption capacity of APC for removal of three tested model naphthenic acids (2-naphthoic acid, diphenylacetic acid, and 1,4-cyclohexanedicarboxylic acid). Activated petroleum coke with a BET surface

area of 1726 m²/g and total pore volume of 0.85 cc/g was produced at the optimum activation conditions: KOH/coke mass ratio equal to 3.0, activation temperature equal to 790 °C, and activation time of 3.47 hours. The obtained APC at optimum condition was tested in batch experiments to measure the adsorption capacity on removal of three NA model compounds. The maximum adsorption capacity of 451, 362, and 320 (mg/g) was achieved for 2-naphthoic acid, diphenylacetic acid and cyclohexanepentanoic acid, respectively. The optimization results illustrated that the APC with higher surface area and pore volume provide better adsorption capacity. Furthermore, the textural properties such as surface area and pore volume are not the only parameters that determine the adsorption capacity. Other parameters such as surface functionalities play effective roles on the adsorption capacity of the produced APC adsorbents for NAs. The adsorption capacity of APC for all three tested NA model compounds increased by increasing KOH/coke mass ratio or by raising the activation temperature up to 750 °C. Further increasing the activation temperature from 750 to 850 °C, produced APC with lower adsorption capacity for diphenylacetic acid and cyclohexanepentanoic acid. Compared to the KOH/coke ratio and activation temperature, effect of activation time on the adsorption capacity of the obtained APC was less significant.

- The inductively coupled plasma (ICP) analysis results clearly show that the quantity of metals in APC was significantly reduced after the KOH activation process. For example, the concentration of Al, Co, Fe, V, Cr, Mn, and Mg in the raw PC was reduced from 62.7, 0.1, 57.8, 10.2, 0.12, 2.0, and 6.1 ppm to 19.3, 0.03, 12.6, 1.19, 0.06, 0.26, and 1.76, respectively. This reduction could be attributed to the acid washing step of the activation process. Furthermore, the ash content of PC was reduced after KOH activation, which supports the ICP analysis results showing noticeable reduction in sulfur and metal contents of the PC during activation. Furthermore, no significant release of metals from the APC was observed during the leaching test.
- The obtained activated petroleum coke at optimum condition and also the commercial activated carbon were used in a continuous adsorption column for

removal of organics from model and synthetic OSPW. Diphenylacetic acid and 2-naphthoic acid, as two NA model compounds, were removed completely by the APC in a continuous adsorption system. The treatment of OSPW by APC showed that total organic carbon (TOC) of OSPW could be reduced from a value close to 250 mg/L to a value less than 15 mg/L after a pH adjustment step and APC column treatment. The APC could not remove the TOC of OSPW at its natural pH= 8 and only removed 25% of it. At pH= 4, about 96 percent of the TOC was removed after a pH adjustment step and APC column treatment. The TOC of OSPW reduced to 75 mg/L after pH adjustment to 4 and it reduced to 10 mg/L after column treatment. The Thomas, Adams-Bohart, and Yoon-Nelson models were used to fit the obtained breakthrough curves for APC and commercial activated carbon. The results showed that Thomas model best fits the experiment data related to APC adsorbent. This means that the adsorption is limited by mass transfer and not by the chemical forces between adsorbent and adsorbate. Treated OSPW meets the environmental regulations and could be released to the environment or recycled back to the bitumen extraction process. Furthermore, APC could be regenerated by a solution of methanol and sodium hydroxide and can be reused in several cycles. The adsorption capacity of APC was reduced by 31% after three times of regeneration. While the Thomas model was the best fit for the obtained breakthrough curves for removal of 2-naphthoic acid and diphenylacetic acid, the Adams-Bohart model was the best model in predicting the breakthrough curve of TOC removal from OSPW.

- Projection to latent structure (PLS) method was used to investigate the effect of molecular properties of model NAs such as polarizability, carbon, hydrogen and oxygen number, pKa, pi-bond number, molecular weight and volume, number of H-bonding acceptor and donor sites, and refractivity, as well as the APC surface properties such as total, meso and micro pore surface area, and its different surface modification on removal of NAs from OSPW. The maximum adsorption capacity for the isotherms and the Bangham's kinetic model constants ("K" and "n") for the adsorption kinetic mechanism were further investigated with the PLS model. The obtained R^2X and Q^2Y of the PLS model were 0.94 and 0.63,

respectively. The coefficient plots of the PLS model showed that the three most significant parameters which affect the isotherm parameters are pH of the solution, surface amination with ammonia gas, and surface area of APC. For the isotherm results, the PLS model shows that the pH of the solution and the surface characteristics of the APC define the adsorption capacity. Furthermore, the results of the PLS kinetic variables illustrate that the kinetic of NAs adsorption by APC is mainly controlled by the surface properties of the adsorbent rather than the molecular properties of the adsorbate.

7.2 Contributions and novelty

Based on the obtained results, the contributions and novelty of this study could be summarized as followed:

- Increasing the surface area of oil sands petroleum coke at elevated temperature during KOH activation after a thermal pretreatment
- Removing NA model compounds from batch and continuous systems using APC
- Optimizing KOH activation parameters such as KOH/coke ratio, temperature, and activation time for maximizing the adsorption of model NAs by APC
- Surface amination of APC and commercial activated carbon for improving the adsorption of NAs from synthetic and real OSPW
- Demonstrating the pH effect as one of the main contribution factors for OSPW treatment and removal of organics by APC
- Demonstration of ionic strength as an insignificant factor for removal of NA model compounds by APC
- Reducing the TOC of OSPW from a value around 250 mg/L to a value about 10 mg/L after pH adjustment and APC column treatment

- Regenerating exhausted APC by an alkaline methanol solution after OSPW treatment
- Proposing a novel three steps treatment of tailing ponds: centrifugation, pH adjustment, and APC adsorption column treatment, reducing the TOC of OSPW from a value close to 250 to a value about 10 mg/L
- Demonstrating molecular properties of model NAs as an insignificant factor, compared to surface properties of APC, for adsorption of model NAs

7.3 Recommendations and future works

This study has covered the required laboratory experimentations for creating a novel treatment of OSPW. The proposed treatment method was tested in batch as well as bench scale continuous column systems. For real applications and scale up, following suggested work is required:

- The particle size of produced APC is about 100 micrometer which creates a considerable pressure drop in a continuous column. For this reason, produced APC needs to be pelletized for its applications in larger scales.
- More purification of recovered organics from OSPW after adsorption process is needed. Recovered NAs from OSPW are a mixture of different chemicals and need to be purified for further applications.
- There is no comprehensive method for analysis of OSPW and still some uncertainties exist in this area. More research needs to be conducted for improving the OSPW analysis techniques.
- More studies are needed for pre-treatment of OSPW. In this work, the effect of pH adjustment on OSPW treatment was investigated. Other pre-treatments such as coagulation and flocculation might help the removal efficiency of dissolved organics from OSPW.

- Other APC surface modification techniques might be helpful in increasing the adsorption capacity of NAs and efficiency on NAs removal from OSPW. A surface amination at low temperature, in a way that does not cause collapse of micro and meso pore structure, could be an effective method.
- Cost analysis for APC production, OSPW treatment by the proposed method, and regeneration of exhausted APC should be performed. The cost analysis should cover the capital and operation costs, as well as profitability of the proposed treatment method.
- An optimization study is needed for regeneration of exhausted APC with different solvents at various operating conditions.
- For determining the significant factors in treatment of OSPW by the adsorption process, more NA model compounds need to be tested in order to achieve a more precise PLS model with higher prediction capabilities

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7.1.1 Permission for Chapter 4

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7.2 Appendix B: Resume

HOJATALLAH SEYEDY NIASAR

COURSES PASSED IN THE PhD PROGRAM:

- Mathematical methods in Engineering, Mark: **99/100**
- Advanced particles and fluidization, Mark: **98/100**
- Statistical process analysis, Mark: 93/100
- Risk assessment and management, Mark: 93/100
- Engineering Planning and Project management, Mark: 82/100
- Green fuels and chemicals, Mark: 85/100

SKILLS:

- Wastewater specialist:
 - Experimental-based researcher for more than 6 years as a graduate student in chemical engineering by focusing on environmental sustainability, wastewater treatment, and renewable energy
 - Design and manufacture of wastewater treatment facilities such as yeast production's wastewater and oil sands process-affected water in bench and pilot scales
 - Work with analytical equipment such as HPLC, GC, GC-MS, TOC, COD, SEM-EDX, and UV spectrophotometer
- Experiment design and data processing:
 - Expert in Minitab and Design Expert software for experiment design
- Leadership and teamwork:
 - Instructed and led dozens of fourth year undergraduate students in chemical process plant design course at Chemical and Biochemical Engineering Department, University of Western Ontario
 - Worked effectively in teams with postdoctoral fellows, fellow graduate and undergraduate students in experimental-based research projects to decrease projected timelines
 - Supervised and trained multiple interns at various university levels in wastewater treatment and water research at University of Western Ontario
- Self-motivated, problem-solver, and critical thinker

EDUCATION:

Doctor of Philosophy (PhD):	2013-2017
Chemical Engineering, University of Western Ontario, London, ON	
Master of Science (MSc):	2008-2010
Chemical Engineering, Isfahan University of Technology	
Bachelor of Science (BSc):	2004-2008
Chemical Engineering, University of Kashan	

WORK EXPERIENCE:

Graduate Research Assistant	Sept. 2013-Aug. 2017
University of Western Ontario, London, ON	

- Recovery of organics from oil sands process-affected water and tailings with novel highly porous activated carbon-based adsorbents produced from petroleum coke

Graduate Teaching Assistant

Sept. 2013-Apr. 2017

- Instructed dozens of students by explaining theoretical methodologies and lab procedures, brain storming, answering questions, and assisting in problem solving for chemical process plant design course and fundamentals of biochemical and environmental engineering
- Conducted weekly meetings focused on problem solving in feasibility and profitability of chemical plants, design and mass/energy calculation of various plant units, drawings of PFD and P&ID, as well as safety concerns, risk assessment and mitigation strategies
- Scored and judged reports (scientifically and grammatically), and invigilated quizzes and final presentation sessions.

Graduate Research Assistant

Sept. 2008-July 2010

Isfahan University of Technology

- Pretreatment and detoxification of yeast production's wastewater in order to increase biogas production

Graduate Teaching Assistant

Sept. 2008-July 2010

Isfahan University of Technology

- Assisted students in microbiology lab for basic understanding of biochemical principles such as staining, aseptic technique, bacterial cell culture, bacteriological examination of water and wastewater, bacterial transformation, and enzyme kinetics
- Marked and commented on reports and quizzes.

AWARDS:

- Ontario Graduate Scholarship (OGS), May 2016

SELECTED PUBLICATIONS:

- **Niasar, H.S.**, Li, H., Kasanneni, T.V.R., Ray, M.B., Xu, C.C. *Surface amination of activated carbon and petroleum coke for the removal of naphthenic acids and treatment of oil sands process-affected water*. Chem. Eng. J. 293, 189–199 (2016).
- Martinez-iglesias, A., **Seyedy Niasar, H.**, Xu, C. C. & Ray, M. B. *Adsorption of Model Naphthenic Acids in Water with Granular Activated Carbon*. Adsorption Sci. Technol. 33, 880–894 (2015).

CONFERENCE PAPERS:

- **Hojat Seyedy**, Jing Wan, Sreejon Das, Chunbao Xu, and Madhumita B. Ray, “*Development of Treatment Train based on Green Technologies for Removal and Recovery of Naphthenic Acids from Oil-Sand Process Affected Wastewater*”, 5th International Congress on Green Process Engineering, Mont Tremblant, QC (June 2016)
- **Hojat Seyedy**, A. Martinez-Iglesias, H. Li, M. Ray, C. Xu, “*Study of activated and functionalized petroleum coke as an adsorbent for removal of naphthenic acids from synthetic oil sands process water*”, 64th Canadian Chemical Engineering Conference, Niagara Falls, ON (October 2014)2