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Regeneration potential of activated petroleum coke for application in oil sands process-affected water

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Abstract

Cost effective regeneration of spent adsorbent is crucial for large scale application of adsorption as a viable separation process. While adsorption studies are abundant in literature, systematic and comprehensive regeneration studies are seldom reported in literature. A proprietary activated carbon from petroleum coke was used for the removal of model naphthenic acids (NAs) and organic compounds from oil sands process-affected water (OSPW). A systematic and comprehensive study was conducted to regenerate the adsorbents. Methanol with aqueous NaOH (pH adjusted to around 12) was applied to regenerate the spent commercially available granular activated carbon (GAC) and activated petroleum-coke (APC). Optimization of solvent volume, solvent pH, regeneration time, and agitation speed was evaluated in preliminary batch experiments. Higher adsorption capacity and regeneration efficiency were achieved for APC due to higher mesoporous surface area during the treatment of two model compounds (2-naphthoic acid and diphenylacetic acid) and NAs rich OSPW than that of the GAC. Thereafter, the optimum regeneration scheme was applied in continuous column operations for recycling the adsorbents. Although, the bed adsorption capacity decreased dramatically after first cycle, the capacity could be stabilized after 2 repeated adsorption-desorption cycles. The regenerating solvent (methanol) was recovered effectively (maximum 90% recovery ratio) using vacuum distillation. Moreover, Na-salts of NA were recovered, which have some commercial applications. A desorption kinetics model was also developed which would be useful for future scaling up of the process.

Keywords

Naphthenic acids, OSPW, Adsorption-desorption, 2-naphthoic acid, Diphenylacetic acid, Methanol, Activated carbon, Activated petroleum coke, Solvent recovery, Solubility, Solvent extraction, Kinetic modeling.

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Abbreviations

AC	activated carbon
ACN	acetonitrile
ANOVA	analysis of variance
APC	activated petroleum coke
BET	Brunauer-Emmett-Teller
BOD	biochemical oxygen demand
BTEX	benzene, toluene, ethylene and xylene
CCD	central composite design
COD	chemical oxygen demand
DOC	dissolved organic carbon
GAC	granular activated carbon
GC-MS	gas chomatography – mass spectrophotometry
HPLC	high performance liquid chomatography
h	hour
NA	naphthenic acid
NOM	natural organic matter
OSPW	oil sands process affected water
PAC	Powdered activated carbon
PAHs	Polycyclic aromatic hydrocarbons
pH_{pzc}	pH resulting in the point of zero charge
PTFE	polytetrafluoroethylene
pzc	point of zero charge
rpm	revolutions per minute
RSM	response surface methodology
SEM	scanning electron microscope
TOC	total organic carbon
TDS	total dissolved solid
UV	ultra violet
UV-VIS	ultra violet – visible spectroscopy

List of symbols

β	regression coefficient
δ	boundary layer thickness (m)
a_w	surface area per unit mass of spent adsorbent $\left(\frac{m^2}{Kg}\right)$
C_b	concentration of ‘*b*’ (NAs) molecules in the bulk phase of solvent $\left(\frac{Kg}{m^3}\right)$
C_b^*	concentration exists inside the boundary layer $\left(\frac{Kg}{m^3}\right)$
C_0	initial solute concentration (mg/L)
C_e	equilibrium solute concentration (mg/L)
D_b	diffusion co-efficient of ‘*b*’ (NAs) molecules $\left(\frac{m^2}{Sec}\right)$
e	errors obtained randomly
i	linear coefficient
j	quadratic coefficient
J_b	mass flux of ‘*b*’ (NAs) molecules existing in the stagnant film area $\left(\frac{Kg}{Sec}\right)$
k_b	mass transfer co-efficient $\left(\frac{m}{Sec}\right)$
k_n	number of parameters studied and optimized in the experiment
k	proportionality constant, or regeneration rate constant (sec^{-1})
K_f	Freundlich constant [(mg/g)/(mg/L)$^{(1/n)}$]
K_L	Langmuir adsorption constant (L/mg)
n	nonlinear index
Q	amount of adsorbate per unit mass of adsorbent (mg/g)
Q_0	initial adsorption capacity (mg/g)
Q_e	equilibrium adsorption capacity (mg/g)
Q_m	maximum adsorption capacity (mg/g)
R	regeneration efficiency (%)
R^2	coefficient of determination
t	time (sec, or h, or min)
V	volume of solution (mL or L)
W	amount of adsorbent (g)

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Chapter 1

1 Introduction

1.1 Background and motivation

Large volume of oil sands process-affected water (OSPW) is being generated annually during bitumen extraction from Canadian tar sands industry and being stored in tailing ponds creating serious environmental issues due to leaking and spillage of contaminated water to the ecosystem. On the other hand, chemicals such as naphthenic acids (NAs), which are the main contributor to OSPW toxicity [1-6], have several industrial values if they can be recovered from OSPW.

Recently, carbon based adsorption process using commercial activated carbon (AC) or AC derived from petroleum coke to treat the OSPW [7-12] has been reported. Petroleum coke is a waste product that has potential use as activated carbon for many applications.

Activated carbon (AC), a highly porous adsorbent is widely used to eliminate various organic compounds from industrial and municipal wastewater effluents. The pores, channels and other void spaces of AC provide high surface area to adsorb organics either by physisorption or chemisorption from wastewater. After reaching its maximum capacity for adsorption, AC must either be disposed of or be regenerated. The regeneration of AC for finite number of cycles increases the cost-efficiency of the process and typically is conducted in the industry, and the viability of the carbon adsorption process is determined by the cost and ease of regeneration.

Naphthenic acids (NAs) produced during bitumen extraction in oil sands industries are a major environmental concern [13]. Hence, effluents from bitumen extraction processes are not allowed to be discharged directly. AC is one of the most common adsorbents that has been used in the treatment of oil sands process-affected water (OSPW) for removing NAs and other organics [12, 14-16]. AC can therefore be used once or regenerated to restore its adsorptive capacity after being spent or exhausted. Recovery of valuable products such as

NAs during regeneration can make the process more economical and provide environmental incentives such as retrieval of NAs from OSPW.

Spent AC can be regenerated using a variety of methods, but the process fundamentals are essentially the same. In most processes, regeneration is accomplished by subjecting the exhausted carbons to conditions that shift the adsorption equilibrium in favor of desorption. The relative ease of regeneration is dependent upon the type of adsorption (physical or chemical). For physisorption, this shift can usually be accomplished by heating, lowering the pressure, or washing with solvent. In the case of chemisorption, a supply of energy greater than the sorptive force is required to break the strong ionic or covalent bonds [17].

The most commonly applied carbon reactivation technique is thermal regeneration. However, 5 – 15 wt% of carbon is lost by burning off in each regeneration cycle; causing a loss of adsorptive capacity [18]. Also, thermal regeneration technique is not economically sustainable due to high temperature requirement which makes the process energetically expensive [17]. Moreover, it is not feasible to recover adsorbates during thermal regeneration.

On the other hand, solvent regeneration facilitates the adsorbates on the activated carbon to be removed due to the preferential solubility of the adsorbate in the selected solvent. This process does not require any other energy source such as elevated temperature, UV and ultrasonic radiation. Loss of carbon is also minimal compared to that of thermal regeneration [19]. Solvent regeneration method enables the recovery of useful adsorbates from the regenerating solvent by using distillation or extraction. At the same time, the spent solvent can also be easily recycled for the next regeneration cycle. It can be done on site reducing mobility challenges and cost. Both organic and inorganic solvents can be used for adsorbent regeneration [20].

While there is an enormous body of literature available on various adsorption processes involving numerous adsorbents, adsorbate, and effluents, not much work has been reported on the regeneration of spent carbons. Most of the regeneration processes are typically conducted in industrial facilities with proprietary methods and are seldom reported. Organic solvents have been used extensively in some investigations to extract the adsorbates during desorption [21-25]. Tamon et al. investigated their regeneration of spent AC in industrial wastewater treatment by N, N-dimethylformamide, N, N-dimethylacetamide, ethanol, methanol, acetone, 2, 4-dioxane, tetrahydrofuran, trimethylamine, toluene and benzene, and they found 80% regeneration efficiency of AC after five regeneration cycles using ethanol and toluene [26]. Mohamed et al. revealed that the bound NAs by activated carbon were desorbed efficiently (88% removal of NAs on the fourth cycle) with methanol [27]. On the other hand, inorganic solvents such as HCl, H_2SO_4, H_3PO_4, NaOH and NaCl possess oxidizing powers while acting act as desorbing agent [28, 29].

It is important to regenerate the spent carbon by desorbing the accumulated adsorbates and restore the original porous structure with little or no damage to the carbon itself to reuse the carbon for multiple adsorption-regeneration cycles.

Recent research focuses on developing high capacity AC to treat NAs rich OSPW. However, study on regenerating the spent carbon using suitable solvent based on controlling factors which are favorable for achieving higher regeneration efficiency is lacking in literature. Determination of optimum operating conditions including regeneration time, mixing, pH, temperature and solvent properties such as volatility, molecular weight and toxicity are required for continuous use of adsorbents in both batch and column operations, which are the objectives of this research. The separation of the adsorbate (naphthenic acids) and the solvent after regeneration is another objective in order to increase the economics of the process.

Chapter 2

2 Literature review

2.1 Oil sands process-affected water

Most of the deposited heavy crude oil is found in Athabasca oil sands, located in northern Alberta. It covers almost 42,000 km^2 and produces over 700 billion barrels of bitumen per day [30]. Bitumen extraction utilizes hot water based separation process during open-pit mining – a commercial mining approach to extract useful mineral or rock deposits from the surface of sand, cinder and gravel.

During the bitumen extraction, large volumes of contaminated water known as oil sand process-affected water (OSPW) are generated. OSPW is a suspension of solids, unrecovered bitumen and other large organics and is referred to as tailing water. More than 0.65 m^3 of contaminated water is generated per ton of oil sands during hot water extraction [31]. The OSPW is harmful for the environment as it contains various amount of toxic compounds such as saturated hydrocarbons with long chain alkyl groups attached to bi- to tetracyclic cores, polycyclic aromatic hydrocarbons (PAHs), and naphthenic acids (NAs) besides releasing various toxic volatile organic compounds [30].

2.1.1 Chemical composition of OSPW

Chemical composition of the organics found in OSPW includes a variety of compounds such as asphaltenes, benzene, creosols, nitriles, humic and fulvic acids, phenols, phthalates, PAHs, toluene, methane and naturally occurring radioactive minerals [2, 32]. The concentration of dissolved organic carbon (DOC), chemical oxygen demand (COD), and biochemical oxygen demand (BOD) in OSPW is shown in Table 2.1. NAs are reported to exhibit high toxicity among the other carboxylic acids [33, 34]. There is inadequate information regarding other organics present in OSPW that may also be responsible for OSPW toxicity. Based on several investigation, less than 50% of the organic portion in OSPW originated from NAs. Other organic compounds in OSPW, such as PAHs and BTEX may also contribute to the toxicity [6, 35-39]. Additionally, higher levels of inorganic ions transform the toxicity of both organic compounds and metals and accelerate the antagonistic (resistant to) or synergistic (acting together) reactions among different compounds [40-42].

Table 2-1 Measured chemical composition of tailing ponds [46].

Variable	References			
	Small et al. (2012) [9]	Allen (2008) [2]	Allen (2008) [43]	Holowenko et al. (2000) [44]
pH	8.65	8.2	--	8.1 - 8.5
Conductivity (mS)	3.4	--	--	--
TDS (mg/L)	--	2221	1900-2200	12.5-47.7 (g/100g)
Alkalinity (mg $CaCO_3$/L)	578.1	--	--	
Bicarbonate (mg/L)	--	775	--	960 – 1240
DOC (mg/L)	46.55	58 - 67	--	--
BOD (mg/L)	--	25-70	--	--
COD (mg/L)	--	86-350	--	--
Naphthenic acids (mg/L)	60.35	--	50-70	61 – 88
Bitumen (mg/L)	--	--	25-7500	0.62 – 3.1
Oil & Grease (mg/L)	--	9-92	--	--
Na^+ (mg/L)	680.35	659	--	438 - 895
Ca (mg/L)	--	17	--	3.4 – 7.3
Cl^- (mg/L)	535.7	540	80-720	127 – 634
$SO_4{}^{2-}$(mg/L)	219.35	218	230-290	2 – 173
NH_4^+(mg/L)	6.6	--	--	6.7 – 10
NH_3 (mg/L)	--	14	3-14	--
Al (µg/L)	36	--	--	--
Ni (µg/L)	9	--	--	--
Mo (µg/L)	276.65	--	--	--
Mn (µg/L)	25.55	--	--	--
Mg (mg/L)	8	--	--	2.6 – 9.7
Cu (µg/L)	171.5	--	--	--
Pb (µg/L)	8.1	--	--	--
V (µg/L)	11.1	--	--	--
K (mg/L)	--	--	--	9.1 – 18.5

“--”: Data are not available in literature.

2.1.2 Model compounds in OSPW

OSPW is a complex mixture of many potentially toxic organic compounds and the precise composition of OSPW is not known. A rough estimation was made to pick out NAs that have been used as alternatives to mimic OSPW composition in recent studies. These compounds were used for calibration of analytical equipment or for environmental and toxicological studies. The commonly used NA model compounds are tabulated in Table 2.2 below.

Table 2-2 List of compounds identified in OSPW [46]

No.	Name of compounds found in OSPW	Formula	Molecular Weight
1.	Ethanoic, Acetic Acid	$C_2H_4O_2$	60
2.	Butanedioic, Succinic acid [4, 45]	$C_4H_6O_4$	118
3.	Cyclopentane carboxylic acid	$C_6H_{10}O_2$	114
4.	Hexanoic acid [4, 45]	$C_6H_{12}O_2$	116
5.	Benzoic acid [46]	$C_7H_6O_2$	122
6.	Cyclohexanecarboxylic Acid [4, 45-48]	$C_7H_{12}O_2$	128
7.	1,4-Cyclohexanedicarboxylic acid [4, 45]	$C_8H_{12}O_4$	128
8.	3-methyl-1-cyclohexanecarboxylic acid [48]	$C_8H_{14}O_2$	142
9.	Trans-4-methyl-1-cyclohexane carboxylic acid [48]	$C_8H_{14}O_2$	142
10.	4-methyl-1-cyclohexane carboxylic acid [48]	$C_8H_{14}O_2$	142
11.	Adipic acid [4, 45]	$C_6H_6O_4$	142
12.	3-Cyclohexanepropionic acid [1, 46, 49]	$C_9H_{16}O_2$	156
13.	4-Methycyclohexaneacetic acid (4MACH, Sigma-Aldrich) [50]	$C_9H_{18}O_2$	158
14	Cyclohexane butyric acid (4 cyclohexylbutanoic acid) [49, 51]	$C_{10}H_{18}O_2$	170
15.	4-propylcyclohexanecarboxylic acid [47]	$C_{10}H_{18}O_2$	170
16.	Citronellic acid [52]	$C_{10}H_{18}O_2$	170
17.	Decanoic acid [4, 45, 53]	$C_{10}H_{20}O_2$	172
18.	2-Naphthoic acid [1, 46, 54]	$C_{11}H_8O_2$	172
19.	1-Methyl-1-cyclohexanecarboxylic acid [1, 47, 48]	$C_8H_{14}O_2$	172
20.	1,2,3,4-tetrahydro-2-naphthoic acid [47]	$C_{11}H_{12}O_2$	176
21.	1-adamantane carboxylic acid [47, 49, 52]	$C_{11}H_{16}O_2$	180
22.	Cyclohexanepentanoic acid [4, 45, 47, 49, 53]	$C_{11}H_{20}O_2$	184
23.	Trans-4-tert-butylcyclohexanecarboxylic acid [47]	$C_{11}H_{20}O_2$	184

24.	1-adamantaneacetic acid [47]	$C_{12}H_{18}O_2$	194
25.	Trans-4-pentylcyclohexane carboxylic acid [46, 47]	$C_{12}H_{22}O_2$	198
26.	Cyclohexylsuccinic acid [4, 45]	$C_{10}H_{16}O_4$	200
27.	Lauric Acid; dodecanoic acid [51]	$C_{12}H_{24}O_2$	200
28.	12-hydroxydodecanoic acid [47]	$C_{12}H_{24}O_3$	216
29.	(4-cyclohexylphenyl)acetic acid	$C_{14}H_{18}O_2$	218
30.	4-Heptyl benzoic acid [46]	$C_{14}H_{20}O_2$	220
31.	3,5-Dimethyladamantane-1-acetic acid	$C_{14}H_{22}O_2$	222
32.	Dicyclohexylacetic acid [47]	$C_{14}H_{24}O_2$	224
33.	Diphenylacetic acid	$C_{14}H_{12}O_2$	212
34.	4-Pentylbicyclo octane-1-carboxylic acid	$C_{14}H_{24}O_2$	224
35.	12-Methyltridecanoic acid	$C_{14}H_{28}O_2$	228
36.	Myristic acid	$C_{14}H_{28}O_2$	228
37.	(±)-6-Hydroxy-2,5,7,8-tetramethylchomane-2- carboxylic acid	$C_{14}H_{18}O_4$	250
38.	(3aR)-(+)-Sclareolide	$C_{16}H_{26}O_2$	250
39.	Palmitoleic acid [48]	$C_{16}H_{30}O_2$	254
40.	Hexadecanoic, Palmitic acid [51]	$C_{16}H_{32}O_2$	256
41.	2-Hexyldecanoic acid [47]	$C_{16}H_{32}O_2$	256
42.	Linolenic acid [48]	$C_{18}H_{30}O_2$	278
43.	Linoleic acid [48]	$C_{18}H_{32}O_2$	280
44.	Stearic acid [51]	$C_{18}H_{36}O_2$	284
45.	1-pyrenebutyric acid [47]	$C_{20}H_{16}O_2$	288
46.	12-hydroxysteric acid [47]	$C_{18}H_{36}O_3$	300
47.	Abietic acid [47]	$C_{20}H_{30}O_2$	302
48.	Arachidonic acid [48]	$C_{20}H_{32}O_2$	304
49.	Phytanic acid [52]	$C_{20}H_{40}O_2$	312
50.	cis-4,7,10,13,16,19-Docosahexaenoic acid [48]	$C_{22}H_{32}O_2$	328
51.	5-beta-cholanic acid [47, 51]	$C_{24}H_{40}O_2$	360
52.	Nervonic acid [48]	$C_{24}H_{46}O_2$	366
53.	12-oxochenodeoxycholic acid [47]	$C_{24}H_{38}O_5$	406

2.1.3 Naphthenic acids in OSPW

Heavy oil reserves including bitumen are available in crude oils which have been transformed though the modification of light and less complex components in the reservoir by a combination of biodegradation, thermal degradation, water washing, loss of volatiles, and inorganic oxidation [55, 56]. It was assumed that bitumen was originally derived from rich organic deposits of a previous marine environment where subsequent degradation of petroleum hydrocarbons has caused the formation of carboxylic acids including NAs [1, 57, 58].

NAs are a complex group of organics including saturated aliphatic, monocyclic and polycyclic alkanes with carboxylate aliphatic side chains of various lengths [1, 59-61]. These compounds are biodegradable in spite of their surfactant properties that are highly responsible for aquatic toxicity [61]. The portion of NAs in crude oil can differ from 0 to 4% (w/w) depending on the topographical position of the petroleum reserve [62]. For example, the ranges were found between 1 and 2% in the Athabasca oil sands [63]. The portion of carboxylic acid is around 2% for un-refined Athabasca bitumen in which almost 90% of tricyclic acids are found in NAs fraction [63]. Eventually, NAs are concentrated from 20 to 120 mg/L in the tailings pond over time [1].

2.1.4 Chemical and physical properties

NAs are commonly defined by general chemical formula $C_nH_{2n+z}O_2$ where n is the carbon number, and Z represents the number of hydrogen lost during the structural ring formation, this can either be zero or a negative integer. Besides, cyclic NAs are substituted with alkyl groups (a small methyl or ethyl group). For example, the formation of saturated hydrocarbon chains of NAs occurs due to Z = 0, where Z = -2, -4 and -6 forms monocyclic bicyclic and tricyclic NAs, respectively [64-66]. Typical structures of NAs along with their Z series are shown in Figure 2.1.

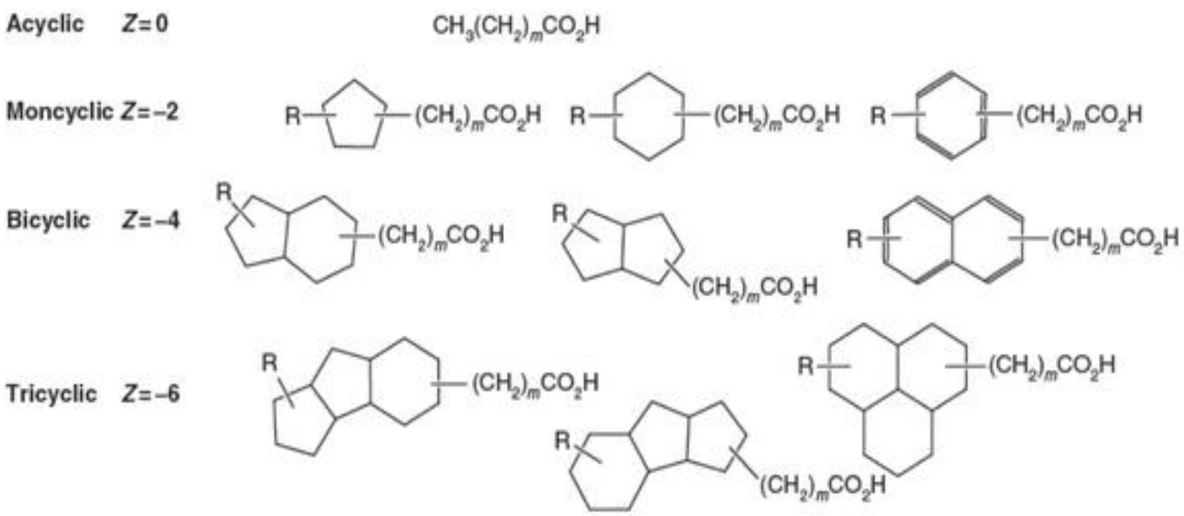


Figure 2-1 Typical structures of NAs, where 'R' is an alkyl group and 'm' is a variable describing the carboxyl side-chain length.

It shall be noted that, in addition to the aliphatic compounds as shown in the above Figure, NAs can be aromatic compounds too. A complex combination of NAs containing numerous individual NA compounds with a wide range of molecular weights exists in OSPW. It is difficult to analyze numerous isomers having similar physical and chemical properties though conventional analytical techniques within a specific group of carbon number and Z series [67].

NAs are usually stable, non-volatile, highly viscous liquids with a boiling point ranging between 250 and 350 °C and show high solubility in organic solvents and oils; besides they show low water solubility up to 50 mg/L at pH 7. Chemically, NAs perform like usual carboxylic acids with dissociation constants between 10^{-5} and 10^{-6} where pKa values are found between 5 and 6. Solubility of NAs in water depends on pH and solubility increases with increasing pH [1, 68-71]. Furthermore, due to both hydrophilic and hydrophobic constituents of NAs, they have properties similar to natural surfactants such as polarized aggregate arrangement and micelle formation [70, 71].

2.1.5 Aquatic toxicity

NAs composition and toxicity are dependent on the source and variable test conditions [71]. Issues those are responsible for toxicity such as temperature, salinity, hardness, and the presence of additional contaminants may rise or decline the sensitivity to NAs [72]. As a result, aquatic toxicity data and results should be considered carefully.

OSPW covers a complex mixture of organic and inorganic compounds and NAs contain the most toxic portion to many organisms such as plants, rat, fish, amphibians, snails, zooplankton, and bioluminescent bacteria [1, 61, 67, 73-78]. Membrane disruption and the disruption of osmotic homeostasis to aquatic organisms occur due to the surfactant features of NAs [79, 80]. NAs have been suspected as endocrine-disrupting constituents in other investigations [69, 79, 81].

The serious toxicity of matured OSPW held in various experimental test ponds on-site is generally removed within 1 to 2 years, whereas the disappearance of chronic toxicity takes about 2 to 3 years [82]. The link between the persistence, selective biodegradation, and associated toxicity of complex NAs mixtures remains unclear due to the lack of available analytical techniques required for the complete separation and identification of the numerous, closely related compounds.

2.1.6 Commercial applications of NAs

NAs are extremely toxic to both flora and fauna of aquatic life produced during bitumen extraction from Canadian tar sands. On the other hand, NAs are useful materials for commercial applications. NAs enhance water resistance and adhesion of concrete; increase high pressure resistance of drilling oils, and prevent foaming in jet fuel. They are very good wood preservative to prevent fungus growth in wood, preserve and act as flame retardant in fabric, increase insecticide solubility by acting as an emulsifier, catalyze rubber vulcanization, stabilize vinyl resins, and catalyze production of alkyl and polyester resins. Also the salts of NAs (alkali naphthenates) are applied as both emulsifying and demulsifying agents [1, 68]. The global naphthenic acid market is estimated to be worth US$ 110 million by the end of 2020.

2.2 Classification of activated carbon (AC)

AC contains highly established internal surface area and porosity that can exhibit a large capacity for adsorbing contaminants from liquids and gases [83]. Production of AC can be accomplished by either a thermal or a chemical process [84]. Common raw materials come from peat, coal, wood, lignite and nut shells. Recently, petroleum coke is utilized as a raw material for AC though modification [7, 12, 85]. Two types of AC such as granular AC (GAC) and powdered AC (PAC) are commercially available in the market. Usually, the size of GAC ranges from 40 mesh (0.425 mm) to 8 mesh (2.36 mm); whereas the size of PAC is around 325 mesh (0.025 mm) [86].

GACs are prepared though activation of carbonaceous materials and crushed to an appropriate size, followed by palletization (through pressing or extrusion) into pellets of different shapes prior to carbonization. In general, GACs are regarded as comparatively smaller pore diameters carbon with smaller internal surface areas, compared with PAC [87]. However, PAC is normally produced by activating carbon materials and grinding to obtain the proper size. Depending on the method of grinding, the shape of the particles may differ which affects its adsorptive properties [87]. In general, PAC is characterized by relatively large pore diameters and huge internal surface areas.

2.3 Applications of AC

Porous carbon was first applied in around 2000 B. C. when the Egyptians used it as an adsorbent for medicinal and purification process [83]. Commercially AC was being used since early 1900’s in sugar refinery industries. Nowadays, GACs have various applications in the pharmaceutical, food, chemical and petroleum industries besides the treatment of wastewater from municipal and industries. Basically, AC is efficient to remove pesticides, aromatic hydrocarbons, detergents, phenols and their derivatives and carcinogenic compounds [87]. PAC with fine particles has less diffusional resistance and is useful for adsorption from solutions. Usually PAC is used in combination with coagulation as it is difficult to separate PAC from the liquid effluent as well as regeneration of the PAC [87]. GAC is used extensively for gas treatment beside adsorption of liquids. It is more effective for packed bed column adsorption for continuous or cyclic process since pressure drop can be controlled by adjusting the particle size distribution and it also facilitates the regeneration process [87].

2.4 Carbon properties related to adsorption

The adsorption by AC depends on the physical and chemical properties including surface area, pore size distribution and ability to adsorb selected pollutant compounds. Surface area of carbon is correlated with its porous structure [88]. Each of the pores has its precise function during adsorption. Micro-pores are significant since they provide the greater surface area found deep under the surface of carbon. Micro-pores deliver adsorption sites for small molecules and facilitate chemisorption as they have higher adsorption energies [89]. The meso-pores are suitable for adsorption of larger molecules and act as transport arteries to the micro-pores. The large macro-pores contribute insignificant adsorption capacity to surface area, but allow adsorbate molecules to pass rapidly deep inside the pores. Pore size differs significantly based on materials and methods of activation [89]. AC needs large surface area or pore size/volume to adsorb the larger molecules since the smaller micro-pores are unreachable for them. Usually, pore forms by burning off the carbon during activation [90]. N_2 isotherm (at 77 K) analysis is commonly used to estimate the total surface area and pore volume of AC.

Adsorption rate is dependent on the approachability of pore structure of the adsorbent and size of the adsorbate molecules. Particle size of the adsorbent may affect the adsorption rate, but not adsorption capacity [87]. The external surface area possesses only a small portion of the total surface area of AC particles. Typically, carbon surface is non-polar [91] and it is activated by oxidizing gases such as CO_2, O_2 and steam though the formation of carbon-oxygen complexes. The formation of different complexes depends on the temperature of the activation process. Low temperature (200-500 °C) activation forms acidic surface oxides such as phenolic hydroxyl, carboxyl and lactic groups [92]. On the other hand, high temperature (800-1000 °C) develops basic oxides that are good for adsorption of organic acids [93].

2.5 Adsorption studies to treat NAs

Many investigations have been conducted to determine the adsorption ability of various types of soil and clays for NAs in hydrological systems such as aquifers for environmental studies [50, 94, 95]. Adsorption of model compounds of NAs on many adsorbents was studied by Azad et al. [96], and they found that both AC and Ni-based alumina played a significant role to eliminate 40 – 50 percent of total organic carbon (TOC), respectively. For instance, the adsorption capacity of Ni-Al_2-O_4 (10.7% Ni loading) for NAs was about 20 mg TOC/g adsorbent. However, total dissolved solids (TDS) decreased the adsorption of NAs on both adsorbents, as expected due to the masking effects [96].

Small et al. stated the scopes of activation parameters for making AC from both delayed and fluid coke. Although the adsorption properties of activated coke for NA were mediocre compared to that of commercial ACs [9], the adsorption capacity for activated petroleum coke was 515.2-588.8 mg/g (lower than that of a commercial AC being as high as 870.4 mg/g), much greater than that of non-activated petroleum coke being reported as 0.214-0.223 mg/g [9], or 0.39-0.86 mg/g [7]. Leaching of heavy metals from coke into treated water was also detected. Another review found that the treatment of OSPW with 22 % by weight of hot petroleum coke produced treated water that was non-harmful to Vibrio Fischeri [12].

Modification of carbon surface chemically [97, 98] and though formation of bio-films [99] were found to increase adsorption rates for AC. However, the adsorption capacity and kinetics of adsorption decreased by surface fouling due to the deposition of oil and metal hydroxides, bacteria, and natural occurring organic matter (NOM) [100]. Solution pH could play an important role to change the adsorption properties [98]. Acidification of OSPW could effectively increase the adsorption capacity of NAs effectively [2].

Adsorption is also dependent on the point of zero charge (pzc), an important parameter to determine the performance of adsorbent capacity [101-107]. Carbon surface, possessing either acidic or basic character can affect the solution pH though exchanging ions [104]. The surface charge of an AC is fairly related to solution pH. At a certain pH the surface turns to be neutrally charged which is defined as pH_{PZC}. There are numerous established approaches to determine the pzc of carbon surface applying such as pH drift method or zeta potential measurement [101, 102, 106, 107].

There are thee mostly used adsorption systems in industry to treat the wastewater such as fixed-bed, pulsed-bed and fluidized-bed. These systems treat the effluent by passing water continuously though the bed either upward or downward with significant residence time during adsorption process. An optimum flow rate is mandatory depending on the rate of adsorption by AC.

2.5.1 Fixed-bed

In fixed-bed column adsorption, wastewater enters from the top of the column over a fresh bed of adsorbent. The adsorption zone of the bed moves downward until the adsorbent comes to the saturation point when the effluent concentration is equal to the influent concentration. The area where concentration decreases from the initial value to zero is the adsorption or mass transfer zone [108, 109]. The advantage of a downward flow in a fixed-bed is that the filtration of suspended solids and adsorption take place at the same time. On the other hand, periodic backwashing is necessary to control head loss due to the deposition of suspended material on the adsorbent surface [87, 110].

2.5.2 Pulsed-bed

In a pulsed-bed, liquid passes in though the bottom of the adsorbent bed and comes out at the top. At periodic intervals, the flow of effluent is stopped and spent carbon is detached from the bottom. Less than 10% of spent adsorbent is pulsed at any one time in this process. Virgin or regenerated carbon is incorporated to the top of the adsorption system [87]. The system is operated with countercurrent flow of the influent and solid adsorbent where the concentrated solution meets the spent adsorbent first while the virgin adsorbent contacts the lowest concentrations of solution, which maximizes the driving force needed for adsorption [87]. Thus, this system utilizes the total adsorption capacity of the nearly spent adsorbent.

2.5.3 Fluidized-bed

Fouling or plugging of the fixed or pulsed bed by deposition of suspended materials from the wastewater is a common problem during operation. To eliminate the problem, fluidized-bed adsorption is a promising alternative way to treat the effluent water [111]. This type of adsorption bed improves the mass transfer and mixing significantly due to turbulent flow. Moreover, adsorbed organic molecules increase the density of the adsorbent; hence spent adsorbents move to the bottom part of the bed and facilitate the removal of spent adsorbent [87, 112].

2.6 Regeneration of spent carbon adsorbents

AC is extensively used in many process industries for wastewater treatment due to high surface area and pore volume [113]. The pores of AC are varied such as micro-pores (≤ 2 nm), meso-pores (2-50 nm) and macro-pores (50-10000 nm) [114]. Different sizes and structures of pores in AC control the degree of adsorption. Decrease in pore size of AC increases the surface area and facilitates adsorption effectively. The micro-pores provide the site for primary adsorption and usually become congested before the meso-pores and macro-pores [115].

AC possesses large surface area which is enough to adsorb a good number of adsorbate materials on its surface [116]. The adsorption capacity of a AC is considered based on several factors such as amount of contaminant adsorbed per unit mass of carbon, concentration of contaminant in the effluent stream to be treated, and empirical factors pertinent to the contaminant [117]. The usual practices for spent adsorbent are regeneration and ultimate disposal. Reusing and regenerating spent carbon are considered as sustainable approaches to the environment, reducing the cost of replacing the spent adsorbents. Regeneration processes reverse the adsorption equilibrium towards desorption. Conventionally, regeneration methods are broadly classified as thermal, biological, chemical/solvent processes (Table 2.3). Other techniques are also considered in this review.

2.6.1 Thermal regeneration

Thermal methods are commonly used for regeneration of the spent adsorbents. In this method, organic substances adsorbed on the surface of AC are removed in a heated furnace by oxidation at 800-1000 °C. Thermal regeneration of spent adsorbents involves thee steps: drying, baking (pyrolysis of adsorbates), and reactivation (oxidation of the residue from the adsorbate). The process can be conducted in multiple-hearth furnaces, rotary kilns, or fluidized-bed furnaces [91]. Problems associated with thermal treatment of spent AC are the loss of 5-10% of carbon due to oxidation and attrition, loss in adsorption capacity caused by changes in the pore structure of the carbon, requiring elevated temperature which is also associated with high energy cost as well as air pollution problems associated with the off gasses [118, 119]. Magne and Walker [118] and Ferro et al. [120] reported that thermal regeneration of spent carbon contaminated with phenol did not restore total adsorption capacity. These studies showed that phenol adsorbed by both physisorption and chemisorption. During regeneration, the physically adsorbed phenol desorbed thermally; however, the chemically adsorbed phenol was pyrolyzed forming carbon deposits at the high temperatures before it was desorbed. As a result, the total surface area as well as the surface area accessible to phenol decreased [120]. In addition to thermal regeneration, other methods include wet-air oxidation, biological, chemical/solvent, electrochemical and ultrasonic regeneration.

2.6.2 Wet-air oxidation

Wet-air oxidation is an aqueous phase oxidation process that uses molecular oxygen as an oxidant. The process operates at temperatures from 125 °C to 320 °C and pressures from and 0.5-20.3 MPa [121]. Oxidation conditions vary, depending on whether partial or complete oxidation is desired. The loss of adsorption capacity was attributed to surface oxidation as well as the formation of carbon-oxygen complexes on the surface of the carbon.

2.6.3 Biological regeneration

Biological regeneration of spent carbon is essentially appropriate to adsorbates that are biodegradable when the exhausted adsorbent is exposed to active microorganisms with localized actions [122-124]. This type of regeneration is typically used in the textile industries with effluents that are easily degraded under biological conditions. Though, the regeneration process is slow due to low rate but the process is moderately economical. The limitation of this method is the fact that not all adsorbates are biodegradable which limits its large scale use for industrial pollutants [125].

2.6.4 Electrochemical regeneration

The electrochemical regeneration of spent carbon consists of removal of molecules adsorbed on the carbon surface of the adsorbent with the use of an electric current in an electrochemical cell. Electrochemical regeneration represents an alternative to thermal regeneration commonly used in wastewater treatment applications.

Passing a current though the electrochemical cell can stimulate impurity desorption. Ions produced on the electrodes modify local pH conditions in the divided cell that affect the adsorption equilibrium and have been shown to encourage desorption of organic contaminants such as phenols from the carbon surface [126, 127]. Investigations on cathodic regeneration have revealed 85% regeneration efficiencies for adsorbed phenols during 4 hours of regeneration with applied currents between 10-100 mA [126]. The anode is the oxidizing electrode and consequently has a lower localized pH during electrolysis which also stimulates desorption of some organic pollutants. Regeneration efficiencies of AC in the anodic partition are lower than that achievable in the cathodic section by 5-20% for the same regeneration time and currents [128]. In electrochemical regeneration, efficiency decreases over subsequent cycles as a result of pore blockages and damage to adsorption sites by the applied current [129]. There are a very limited number of commercially available electrochemical regeneration systems for carbon-based adsorbents.

2.6.5 Ultrasonic regeneration

Cleaning, destruction and extraction of pollutants by ultrasound are possible due to physical and chemical phenomena taking place within the aqueous solution. The regeneration of spent AC by ultrasonic irradiation is due to the generation of physical and thermal effects of ultrasound. The regeneration of spent AC by using ultrasound has been studied to desorb trichloroethylene at 20 kHz [130]. Ultrasound wave in aqueous solution creates high acoustic energy cavitation though the formation, growth and implosive breakdown of bubbles in liquid. The breakdown of the bubbles generates very high local temperatures and pressures at the inside and interface of the collapsing bubbles. This occurrence dissociates water molecules and produces OH radicals, also generating high speed micro-jets and high pressure shock waves initiating the high-velocity inter-particle collisions [131-133]. Ultrasound also generates acoustic vortex micro-streaming with the pores of the solid particles in addition to solid–liquid interface [134]. It can be concluded that desorption by ultrasound can be an alternative technique to classical methods used for the regeneration of exhausted AC. However, ultrasonicated regeneration always requires the presence of a solvent.

2.6.6 Chemical/Solvent regeneration

Chemical regeneration is a process in which adsorbates are removed from the spent adsorbent by reacting with suitable chemical reagents. In general, two types of reagents are used: those with oxidizing ability and those with solubilizing ability. Subsequent washing with a solvent such as water is required to remove the regenerating agent from the carbon surface. Chemical regeneration exhibits several advantages over thermal regeneration. The process can be done in situ which eliminates losses due to pumping, transport, and repacking. Additionally, carbon loss due to burn-off is eliminated and the recovery of adsorbates is possible by using subsequent treatment methods such as distillation [135, 136]. The drawbacks associated with chemical regeneration include the high cost of reagents, danger of pollution from hazardous chemicals, and incomplete regeneration. The efficiency of regeneration is dependent primarily on the solubility of the adsorbate in the regenerating solvent. Additionally, since most industrial wastewater contains a heterogeneous mixture of adsorbates, multiple regenerants may be required.

Organic solvents are carbon-based solvents; they range from alcohols, esters, ethers, ketones, amines and other hydrocarbons. They are typically used in dissolving materials to create solutions or in extracting a substance from another. They are classified based on their structure and functional groups such as aromatic hydrocarbons, aliphatic/non-aromatic hydrocarbons and carbon compounds of varying functional groups such as carbonyls, alcohols, ethers and halocarbons. A variation in pH also influences the regeneration efficiency of the adsorbate on AC, which can best be explained with the weakening of the electrostatic forces between the carbon surface and the organics [105].

Table 2-3 Summery of spent carbon regeneration techniques.

Regeneration Techniques	Regeneration Treatment	Comments
Thermal reactivation [137-140]	a) By pyrolysis and burning-off of adsorbed organic substances. b) Adsorbent drying at approximately 105 °C (221 °F). c) High temperature desorption and decomposition (500–900 °C or 932–1,652 °F) under an inert atmosphere. d) Residual organic gasification by an oxidizing gas (steam or carbon dioxide) at elevated temperatures (800 °C or 1,470 °F)	a) In order to avoid igniting the carbon, it is heated to about 800 °C in a controlled atmosphere. This is the widely used method and regenerates the carbon very well, with two disadvantages: it requires considerable investment in either a multiple-hearth furnace and it causes high carbon losses. b) Thermal regeneration is a high energy-consumption process due to the required high temperatures making it both an energetically and commercially expensive process.
Chemical/solvent regeneration [26, 141, 142]	a) Organic solvents such as methanol, ethanol, n-pentane, methylene dichloride, and ethyl ether are the most commonly used to regenerate exhausted AC. b) In general, two types of reagents are used: those with oxidizing ability and those with solubilizing ability. c) pH of the solvent plays an important role in determining the regeneration efficiency.	a) The process can be done in situ which eliminates losses due to pumping, transport, and repacking. b) Recovery of adsorbates is possible by using subsequent treatment methods such as distillation. c) The loss of carbon and adsorption capacity is minimum compared to that of thermal regeneration technique.
Biological /Microbial regeneration [123, 124, 143]	a) Spent carbon is exposed to active microorganisms with localized actions. b) Technique that may use membranes, biphasic reactors, UV photolysis, and many others bio-reactors. c) A packed bio-filter with spent carbon was evaluated to extract the adsorbate materials.	a) The main advantages associated with the use of biofiltration are related to its set-up, maintenance, and operating costs that are usually lower and less harmful for the environment than conventional processes like thermal reactivation. b) The reaction is slow in terms of process rate and the limitation of this method is the

		fact that not all adsorbates are biodegradable which limits its use on a wide scale for industrial pollutants.
Electrochemical regeneration [126-129, 144, 145]	a) Once the adsorptive capacity of the AC bed has been spent by the adsorption of contaminant molecules, the carbon is transferred to an electrochemical cell (to either the anode or the cathode) in which electrochemical regeneration can occur. b) Current applied though the electrochemical cell can stimulate impurity desorption. c) Ions produced on the electrodes modify local pH conditions in the divided cell will affect the adsorption equilibrium and encourage desorption of organic contaminants such as phenols from the carbon surface.	a) Electrochemical regeneration of AC is feasible at a laboratory scale as regeneration efficiencies up to 80% were achievable during the regeneration of phenol-loaded or natural organic matter-loaded spent carbons. b) In this process, efficiency decreases over subsequent cycles as a result of pore blockages and damage to adsorption sites by the applied current. c) It has limitation for commercial utilization.
Ultrasonic regeneration [130-134]	a) Ultrasound wave in aqueous solution creates high acoustic energy cavitation though the formation, growth and implosive breakdown of bubbles in liquid. b) The breakdown of the bubbles generates very high local temperatures and pressures at the inside and interface of the collapsing bubbles.	a) The ultrasonic regeneration showed a possibility as an alternative to thermal regenerations of AC. b) This process is relatively new, needing more investigations.
Wet air oxidation [121, 146-148]	a) Slurry (10% w/v) of spent carbon in distilled water was oxidized by wet oxidation in the temperature range of 150-250 °C using oxygen partial pressures between 0.69-1.38 MPa in an autoclave. b) It was observed that the regeneration mainly occurred due to the oxidation of the adsorbates taking place on the surface of AC.	a) It was possible to regenerate the spent GAC and PAC with an efficiency of 98%. b) SEM studies of the regenerated carbon showed widening of the pores and loss of structure between the adjacent pores as compared with the virgin adsorbent.

For solvent regeneration method of particular interest in this thesis, regeneration efficiency depends on the molecular weight and size of the solvent molecules. The smaller size of solvent can easily penetrate into the carbon adsorption sites to remove the adsorbates [149].

Therefore, organic solvents smaller in molecular weight than the target adsorbate are more suitable for regeneration of spent adsorbents. Martin et al. investigated the influence of various solvents such as carboxylic acids, alcohols and chloromethane on the regeneration efficiency of adsorbates of varying molecular size, structure and properties of [25], where 25-50 mL of the solvent was used to regenerate 150 mg of the spent carbon adsorbent after adsorption of phenol, aniline, benzyl alcohol, benzaldehyde and nitrobenzene.

Ferro–Garcia et al. also studied the regeneration of AC exhausted by chlorophenols (ortho-chlorophenol and meta-chlorophenol), using solvents of acetone, methanol, ethanol or benzene. A low regeneration efficiency was achieved for benzene among the other solvents possibly due to larger aromatic structure of benzene [120]. Besides molecular weight, solubilizing power of solvent plays an important role in the physical displacement of the adsorbate molecules from the carbon surface [149].

In a study of batch desorption of phenol from AC, nineteen solvents were tested, including dimethyl formamide, 95% ethanol, acetone, toluene, benzene, ethyl acetate, dioxane, n-butanol, 2-propanol, isoamyl alcohol, methanol, chloroform, tetracholoroethane, dichloroethane, carbon disulfide, formaldehyde, carbon tetrachloride, distilled water and acetic acid, where ethanol produced the maximum regeneration efficiency at 88.3%.

Polarity is the ability of a solvent to separate electric charge in the molecule; this determines the effectiveness of the solvent in contact with its target solute enhancing its dissolving capacity. Polar solvents possess uneven distribution of charges and can dissolve a material of a similar polarity [141]. In addition, toxicity and the costs are also important factors considering the selection of a solvent for regeneration. Solvent regeneration of spent adsorbents followed by recovery of the solvent and adsorbate possibly with atmospheric temperature and pressure or vacuum distillation can make the process more economical.

2.7 Objectives of this work

Although, adsorption and regeneration of spent adsorbents have been investigated in many studies with various adsorbents including activated carbon, the regeneration of spent adsorbent for NAs recovery has never been reported in public literature. In an earlier study in our group, [14, 15] commercial granular activated carbon (GAC) and a proprietary activated petroleum coke (APC) demonstrated to be effective for the removal of model NAs and organics from real OSPW. However, the regeneration of the spent adsorbents was not studied, which is the overall objective of this work. The specific objectives of the work were to (i) determine suitable solvents for regeneration of the spent adsorbents of GAC and APC, (ii) determine the optimum regeneration conditions using batch studies, (iii) determine regeneration efficiency and performance of the spent AC in repetitive batch and column adsorption-desorption, (iv) determine the recovery potential for the NAs, and (v) develop desorption kinetic model for the regeneration process.

Chapter 3

3 Experimental

This chapter describes the experimental setup, experimental and analytical methods used during this study.

3.1 Materials and methods

In this study, experiments were conducted with two types of activated carbon. One is a commercial granular activated carbon (GAC), and another is activated petroleum coke (APC), prepared from petroleum coke using proprietary activation methods [14].

3.1.1 Granular activated carbon (GAC) and Activated petroleum coke (APC)

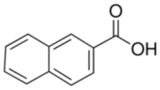
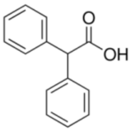
Initially, commercial activated carbon such as GAC (Norit ROW 0.8 SUPRA, CAS Number: 7440-44-0) purchased from Sigma-Aldrich Canada Co. (Oakville, Ontario, Canada) was used for adsorption experiments. About 2 g of GAC was washed with 400 mL Milli-Q water to remove fines.in a 1 L Erlenmeyer flask, agitated for 20 min in a MaxQ 4000 Bench-top Orbital Shaker (Thermo Scientific) at 180 rpm. The wash-water was decanted along with any GAC that did not sink to the bottom of the flask. Two additional cycles of rinsing were conducted until no fines were found in the supernatant. Once completed, the water was decanted and the carbon was dried in a heated oven at 110 ° C for 3 h, the dried GAC stored in a sealed glass jar and placed in a desiccator. The moisture of the dried carbon in use was then assumed to be negligible and the amount of carbon used in the experiments was on a dry basis.

The petroleum coke (PC) was supplied by NEWALTA Corporation (Burlington, ON). The PC was chemically activated with KOH. Briefly, in each activation test, about 6 g of fresh PC was mixed with sufficient amount of water containing 20 g analytical grade KOH (VWR company, Canada) to make a solution. The solution was ultra-sonicated for 30 min and kept overnight to facilitate the penetration of KOH solution inside the skeletal structure of PC. Subsequently, the well-mixed solution was heated in a tubular furnace with nitrogen flow at 100 mL/min and a heating rate of 20 °C/min up to 700 °C (maintained for 3 h). The activated petroleum coke 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 for more than 12 hours and the dried sample was stored in a sealed glass jar, and placed in a desiccator prior to adsorption and regeneration tests.

3.1.2 Preparation of NAs solution and OSPW

Two model compounds from Table 2.2 are selected for this study and their properties are presented in Table 3.1. They are characterized based on molecular weight, pKa and molecular structure. Chemical structure of 2-naphthoic acid and its behavior similar to the acidic compounds are most often come upon in crude oils [46]. Diphenylacetic acid shows its aromaticity beside acidic properties and to be used as a comparison with 2-naphthoic acid. Both diphenylacetic acid and 2-naphthoic acid are bicyclic acids, which are abundant in both oil sands and petroleum derived NA mixtures [52].

Table 3-1 Selected model NAs compounds

Model compounds	**Formula**	**Molecular weight**	**pKa**	**Chemical structure**
2-Naphthoic acid Source: VWR, CAS Registry No: 93-09-04	$C_{11}H_8O_2$	172	4.20[a]	
Diphenylacetic acid Source: Sigma-Aldrich, CAS Registry No: 117-34-0	$C_{14}H_{12}O_2$	212	4.72[a]	

[a] Value obtained from SciFinder chemical database.

The model naphthenic acid compounds (2-naphthoic acid and diphenylacetic acid) in crystal form were purchased from Sigma–Aldrich Company (Oakville, Canada). The solubility of the model NAs is not available in literature and was determined in the laboratory through conventional precipitation method to be approx. 50 mg/L for 2-naphthoic acid, and about 100 mg/L for diphenylacetic acid. Therefore, the initial concentration of these two model compounds used as single compound in all experiments was 40 mg/L. To make the acidic solutions, the appropriate amount of acid was first weighed with a Metrohm Toledo

AB304-S/FACT, and subsequently transferred to a volumetric flask. The flask was partially filled with Milli-Q water and the solution was stirred on a hot plate at 70 °C for 48 h. Thereafter, the solution was allowed to stir for another 24 h at room temperature after which Milli-Q water was added to make the desired concentration. The OSPW was obtained from Suncor Energy, Alberta. The OSPW was kept in a container for over six months, while the suspended particles from the raw OSPW settled. Total organic carbon (TOC) and pH of the supernatant were measured prior to the adsorption experiments.

3.1.3 Solvent selection

Solubility of the adsorbate (in this case, NAs) in the regenerating solvent is obviously the most important parameter for efficient regeneration [24]. Solubility test was conducted using the conventional precipitation method of Klevens, 1950 [150]. The commercial NAs are in solid form and soluble in organic solvents [1]. HPLC-grade solvents, i.e., methanol, ethanol, ethylene glycol, acetone, ethyl ether, isopropanol, methylene dichloride, and acetonitrile all purchased from VWR (VWR International, Mississauga, Canada) were investigated to determine solubility of the NAs. Known amounts of NAs were added gradually in the selected solvents by thoroughly mixing in an orbital shaker until equilibrium (almost an hour) was reached at room temperature, and the NAs were precipitated. The saturated solution was centrifuged at 3500 rpm for 30 min to isolate the precipitated solute, and the supernatant was carefully withdrawn using a pipette and diluted to analyze the NAs concentration in the HPLC.

Eight different solvents were screened for determining the preliminary feasibility of these solvents for regeneration of the spent carbon adsorbents. The physical properties of the solvents, such as solubility, molecular weight, boiling point, are listed in Table 3.2. The commercial price of these solvents are also provided in Table 3.2. It can be seen that methanol is the lowest price (0.94 – 2.03 $/gal), followed by ethanol, ethyl ether, methylene dichloride, etc. Methanol also has the lowest molecular weight (32.04 g/mole), which is one of the major factors for molecular diffusion into the micro-pores of the target adsorbents. Moreover, methanol can easily wash out the NAs molecules from the carbon sites during desorption because it has shown comparatively higher solubility (results are described below) for the model naphthenic acids compared to other solvents. Additionally, methanol shows relatively low toxicity and inflammability making it a suitable regenerating solvent. In addition, its comparatively lower boiling point (64.7 °C) makes it easy to recover methanol for recycling in large-scale adsorption applications.

Table 3-2 Solvent selection criteria for regeneration of activated carbon

Solvents	Commercial price (USD) [a]	Molecular Weight (g/mole)	Boiling Point (°C)	Solubility (g/L) of model NAs
Methanol	0.94-2.03 ($/gal)	32.04	64.7	63
Ethanol	2.11-2.79 ($/gal)	46.07	78.37	60.58
Ethylene glycol	5.43-7.27 ($/gal)	62.07	197.3	3.56
Acetone	5.72-7.45 ($/gal)	58.08	56	4.38
Ethyl ether	2.7 ($/gal)	74.12	34.6	50.8
Iso-propanol	6.45-8.90 ($/gal)	60.1	82.6	58.34
Methylene dichloride	4-4.81 ($/gal)	84.93	39.6	8.4
Acetonitrile	5.9- 6.81 ($/gal)	41.05	82	18.4

3.1.4 OSPW and NAs analysis

Total organic carbon (TOC) content in OSPW was measured in a Shimadzu 5000A TOC analyzer with an ASI-5000 auto sampler A Dionex HPLC-IC (ICS-3000) was used in an isocratic HPLC configuration to detect the model naphthenic acids using an Acclaim Fast LC Column 120 C18, 3 × 75 mm. For 2-naphthoic acid and diphenylacetic acid, the mobile phase was 60% acetonitrile (ACN) and 40% water (milli-Q). Acidification of the mobile phase to pH 2.15 was performed in order to ensure that the acids were in molecular form during analysis. This pH was above the minimum recommended pH for the C18 column. The mobile phase was stirred in a 2 L beaker and sulfuric acid was slowly added until the pH was 2.15. The mobile phase was then filtered using a vacuum filtration apparatus with a 0.20 µm, 47 mm polytetrafluoroethylene (PTFE) disk filter to remove any insoluble contaminants that may be present within the sulfuric acid. Prior to any analysis the HPLC system was initialized and allowed to equilibrate for 60 min or until the baseline was stable. Upon completion of an analysis, the column was rinsed with 20% ACN-water solution in order to wash out the acidic mobile phase, which could deteriorate the column over long exposure.

A UV-VIS-NIR spectrophotometer, Shimadzu UV-3600, was used to scan over the UV-VIS range to determine the λ_{max} for the model NAs to be used in the HPLC UV-diode array detector. Two Starna Far UV Quartz Cells (Mandel Scientific Company Inc.) of 3.5 mL were used to determine the absorption spectra of the model naphthenic acids. 2-naphthoic acid and diphenylacetic acid showed a peak for the carboxyl moiety and a triple peak for the benzene rings which agree with literature values [151]. The maximum peak for the benzene moiety was found to occur at 280 nm, while that for the carboxyl moiety occurred at 188 nm. Therefore, 200 nm was used in the UV-VIS detector of the HPLC for the two model NAs.

3.2 Batch adsorption and regeneration experiment

3.2.1 Batch adsorption

The experiments were conducted in three steps: (1) adsorption of model compounds (2-naphthoic acid and diphenyl acetic acid) on GAC and APC; (2) selection of effective solvent for regeneration and process optimization; (3) regeneration of spent carbon by solvent extraction in optimum conditions. All batch adsorption experiments were performed in 500 mL Erlenmeyer flasks using 0.1 g of GAC or APC in 250 mL Milli-Q water solution of a model NA with initial concentration of 40 mg/L, or OSPW with initial TOC concentration of 40 mg/L, at pH 4.0 or 8.0. The flasks were shaken vigorously at 250 rpm using a MaxQ 4000 Bench-top Orbital Shaker (Thermo Scientific) for 24 h (a time previously determined to be adequate for adsorption equilibrium to be established) at room temperature. The solution was then vacuum filtered using high quality silicone treated filter paper (150 mm × 100 circles, Whatman International Ltd, Maidstone, England,) in order to remove the carbon for the analysis of dissolved NAs in water.

3.2.2 Batch regeneration

The schematic of the regeneration scheme is shown in Figure 3.1. The separated spent carbon adsorbent on the filter paper was placed in a beaker and a known volume of solvent (methanol and aqueous NaOH) was added. Prior to the desorption test, pH of methanol was adjusted with aqueous sodium hydroxide (VWR International, Mississauga, Canada) and monitored by measuring the pH using an pH meter (± 0.01 pH) (Orion Star A111). Central composite design (CCD) and response surface methodology (RSM) were applied in this study to optimize the two most significant operating variables for regeneration: solvent dosage (mL) and amount of aqueous NaOH (mg) using 2-naphthoic acid as the model compound. The Mini Tab Software (version 17) was used for the statistical design of experiments and data analysis. Different combinations of methanol and aqueous NaOH used for the regeneration of the spent carbon are shown in Table 3.3.

Table 3-3 CCD and results for the study of two experimental variables for regeneration of spent carbon using 2-naphthoic acid

Batch no.	A: Solvent Dosage, mL (code)	B: NaOH, mg (code)	Regeneration Efficiency (%)*
1	40 (-1)	4.0 (+1)	87.21
2	80 (+1)	2.4 (-1)	69.65
3	60 (0)	1.6 (-1.414)	60.11
4	20 (-1.414)	3.2 (0)	62.46
5	100 (+1.414)	3.2 (0)	60.02
6	80 (+1)	4.0 (+1)	78.04
7	40 (-1)	2.4 (-1)	71.29
8	60 (0)	3.2 (0)	84.42
9	60 (0)	3.2 (0)	87.03
10	60 (0)	3.2 (0)	86.57
11	60 (0)	3.2 (0)	85.31
12	60 (0)	3.2 (0)	86.90
13	60 (0)	4.8 (+1.414)	83.16

*Each batch represents the average regeneration efficiency (%) obtained using three replicates.

All regeneration experiments were carried out in triplicates, and relative errors in concentration of the adsorbate are less than 5%, indicating excellent reproducibility of the experiments, so the average values are reported in this work. The spent carbon was mixed with solvent and shaken in covered conical flasks in the orbital shaker at 250 rpm for 9 h, which was found to be the desorption equilibrium time confirmed by preliminary tests. Samples from desorption experiments were filtered through 0.45 µm nylon syringe filters prior to the analysis of desorbed concentrations of NAs using HPLC.

The regeneration efficiency is calculated as:

$$Regeneration\ efficiency\ (\%) = \frac{Q_0 - Q_r}{Q_0} \times 100 \tag{1}$$

Where, Q_0 is the quantity of adsorbate (NAs) adsorbed per unit weight of adsorbent and Q_r is the quantity of adsorbate per unit weight of adsorbent remained after regeneration.

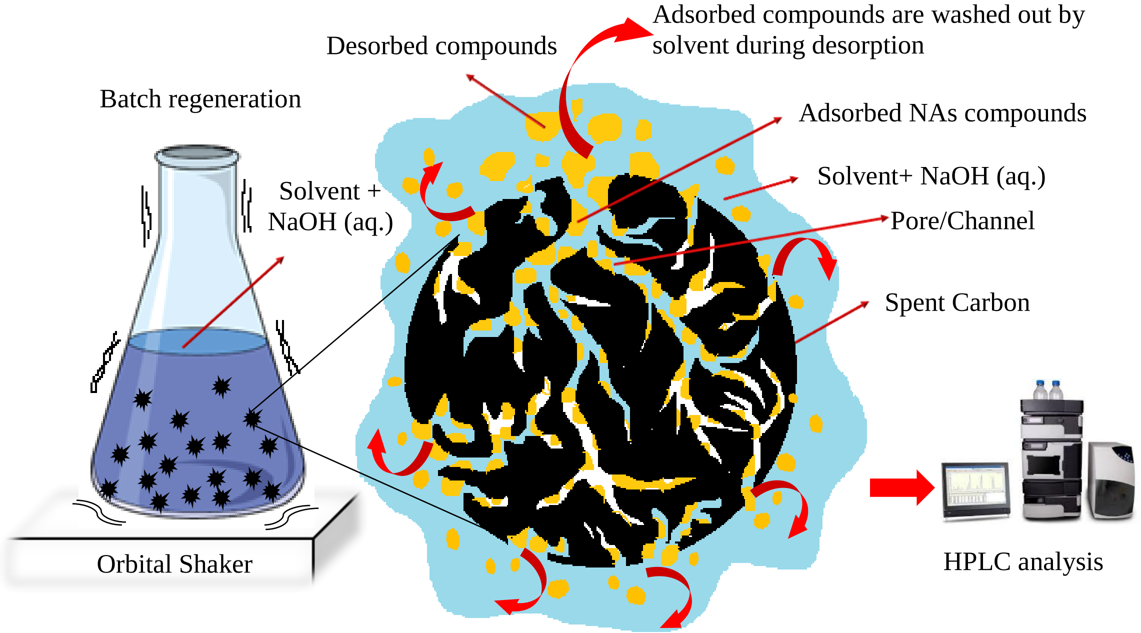


Figure 3-1 Typical batch regeneration process with solvent

3.3 Solvent recovery for repeating regeneration cycles

Regeneration solvent recovery makes the system more economically viable as the separated solvent can be recycled for further regeneration. The boiling points of NAs are in the range of 160-198 °C, whereas the boiling points of the tested solvents vary in the range of 35-197 ^{o}C, with majority of the solvents having boiling point below 100 °C. Therefore, distillation/condensation can be applied easily for solvent recovery besides the recovery of model compounds. In this experiment, solvent recovery was conducted in a Liebig condenser (Figure 3.2). The highly concentrated remaining solution after distillation was dried, and the dried mass (Na-salt of naphthenic acids) was weighed, followed by dissolution in water. Thereafter, HPLC analysis was conducted to confirm the recovery of the extracted compounds. The collected solvent was further used in next cycle of regeneration of the spent carbon adsorbents.

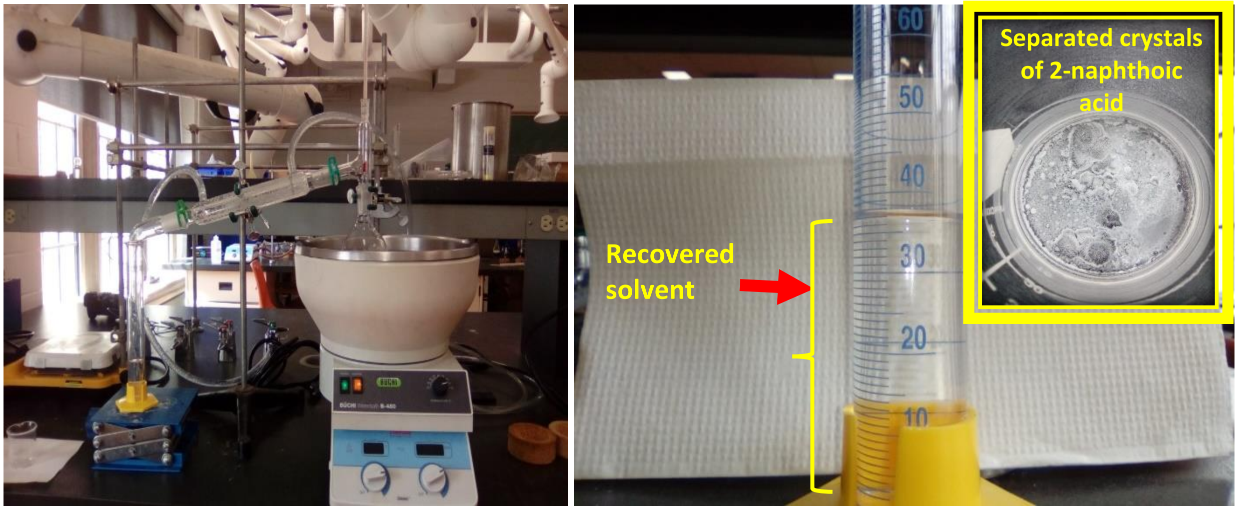


Figure 3-2 Typical solvent and adsorbate recovery using Liebig condenser after batch regeneration.

3.4 Continuous column regeneration of spent carbon

The adsorption and desorption experiments were carried out in both batch and continuous (packed-bed) systems. Figure 3.3 depicts the schematic of a packed-bed glass column (1 cm i.d. and 20 cm long) used for adsorption/regeneration cycles. Typically, the column was packed with about 0.5 g of fresh adsorbent particles (d $\leq$ 200 μm) with a bed height of 5 cm. During the continuous column regeneration cycle, the optimal regenerant solution (determined from the batch tests mentioned above) was continuously fed to the bottom of the spent column by a positive-displacement pump (Masterflex, Model 77200-62, Cole-Parmer Instrument Company, USA) equipped with adjustable flow capability.

The breakthrough curve was first determined at 300 K and 2.5 mL/min flowrate of water solution of 40 mg/L of NAs. The column adsorption capacity was then calculated from the breakthrough curve. In the desorption and regeneration process, the spent carbon bed was washed initially with milli-Q water and thereafter by solvent at a flow rate of 2.5 mL/min at 300 K. Effluent samples were then analyzed in the HPLC periodically. The column regeneration was continued until the effluent concentration of the NAs reached a low concentration of 1 mg/L. After the desorption process, the remaining solvent was removed from the regenerated carbon bed with superheated steam passing at 413 K.

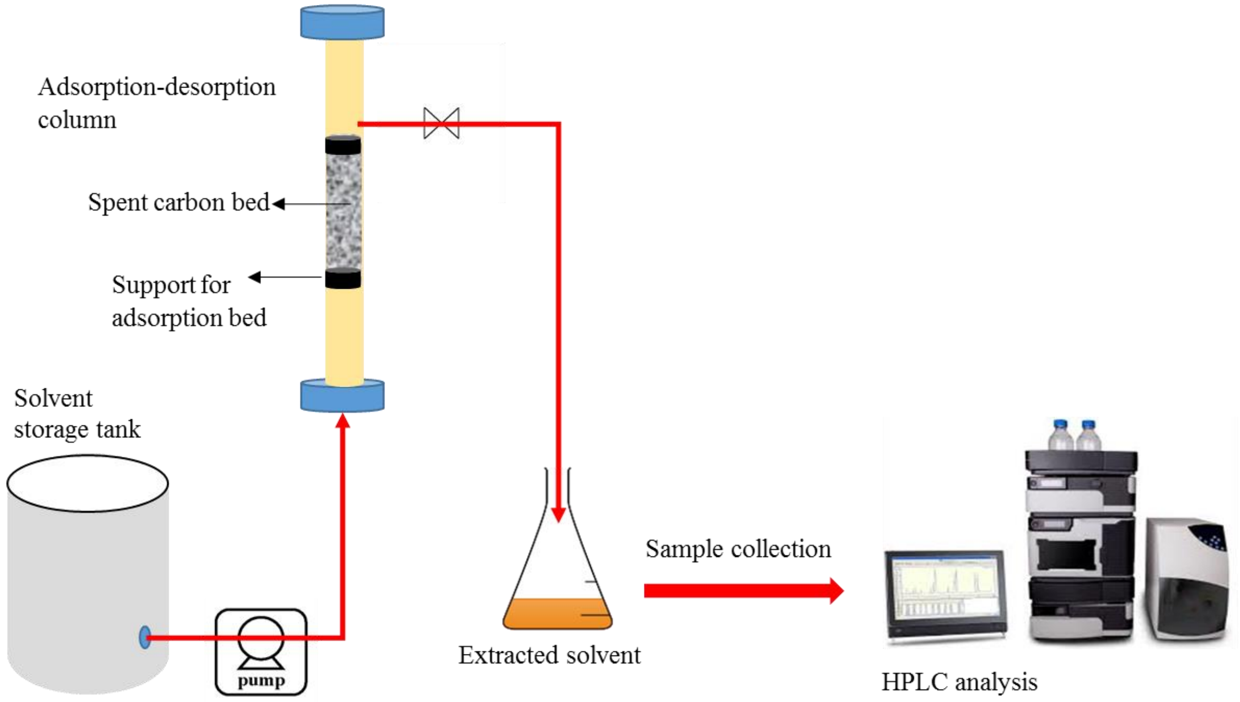


Figure 3-3 Packed-bed column for continuous adsorption and regeneration of adsorbents

Chapter 4

4 Results and Discussions

A series of regeneration experiments was conducted to investigate the ability of various solvents to regenerate the spent carbon adsorbents and recover the adsorbed naphthenic acids (NAs). This chapter first presents the results of batch desorption of both model NAs and real OSPW dissolved compounds. Thereafter, the results of the column study conducted with model compounds and real OSPW are reported. All the results presented in this chapter are average values obtained from experiments carried out in triplicates with error less than 5%. Effects of controlling parameters on regeneration efficiency, performance of repetitive adsorption/regeneration cycles, recovery of both solvent and adsorbates (NAs), and surface characteristics of the carbon adsorbents are discussed in this chapter.

4.1 Solvent selection based on solubility

Organic solvents such as alcohols, esters, ethers, ketones, amines and other hydrocarbons are usually used in dissolving or extracting organic compounds [19, 20, 141, 142]. Solvents with smaller molecules can easily penetrate into the micro-pores of a adsorbent to extract/displace the adsorbate molecules during regeneration [26, 149]. Hence, organic solvents with smaller molecular weight compared to that of the target adsorbate are potentially effective in regenerating spent adsorbents. Polarity of the solvent also determines its contact efficiency with the target adsorbate as well as the adsorbent surface. Solvent selection must also meet other constraints such as the solvent can be easily removed from the adsorbent, solubility of the adsorbates in the solvent, and is environmentally green and cost effective [26].

Since the solubility of model NAs in selected solvent is not available in open literature, initial solubility experiments were conducted using conventional precipitation method. The results shown in Figure 4.1 indicate that NAs are highly soluble in both methanol and ethanol, followed by isopropanol and ethyl ether. In terms of NAs, 2-naphthoic acid shows higher solubility than diphenylacetic acid in most of the organic solvents. For example, conventional precipitation method shows that methanol gets saturated with 2-naphthoic acid at approximately 300 g/L, whereas, diphenylacetic acid reaches the saturation point at about 260 g/L because the lower pKa value of 2-naphthoic acid (4.20) makes it deprotonated easier than diphenylacetic acid with higher pKa value (4.72), the proton affinity of methanol is considerably high at 761 kJ/mol, making it a good solvent for the NAs.

Based on the data presented (Table 3.1) on molecular weight, flammability, boiling point, price and toxicity, methanol has been found to be the most suitable solvent and was chosen for developing the optimum regeneration scheme for the carbon based adsorbents.

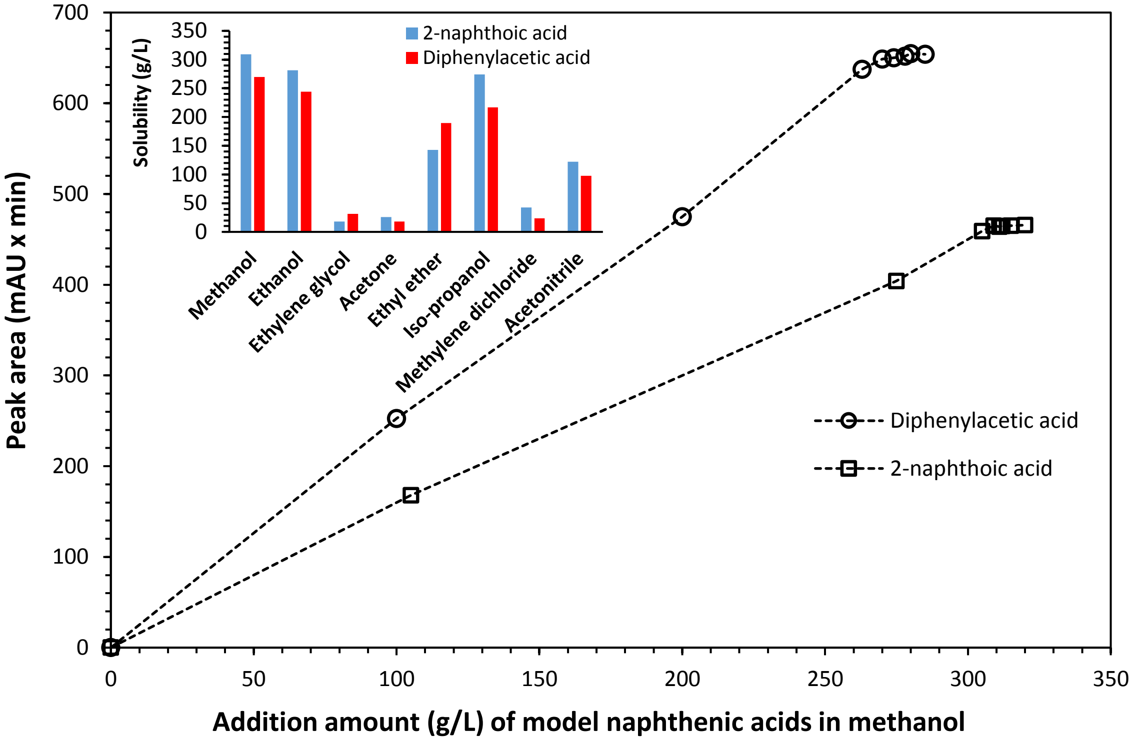


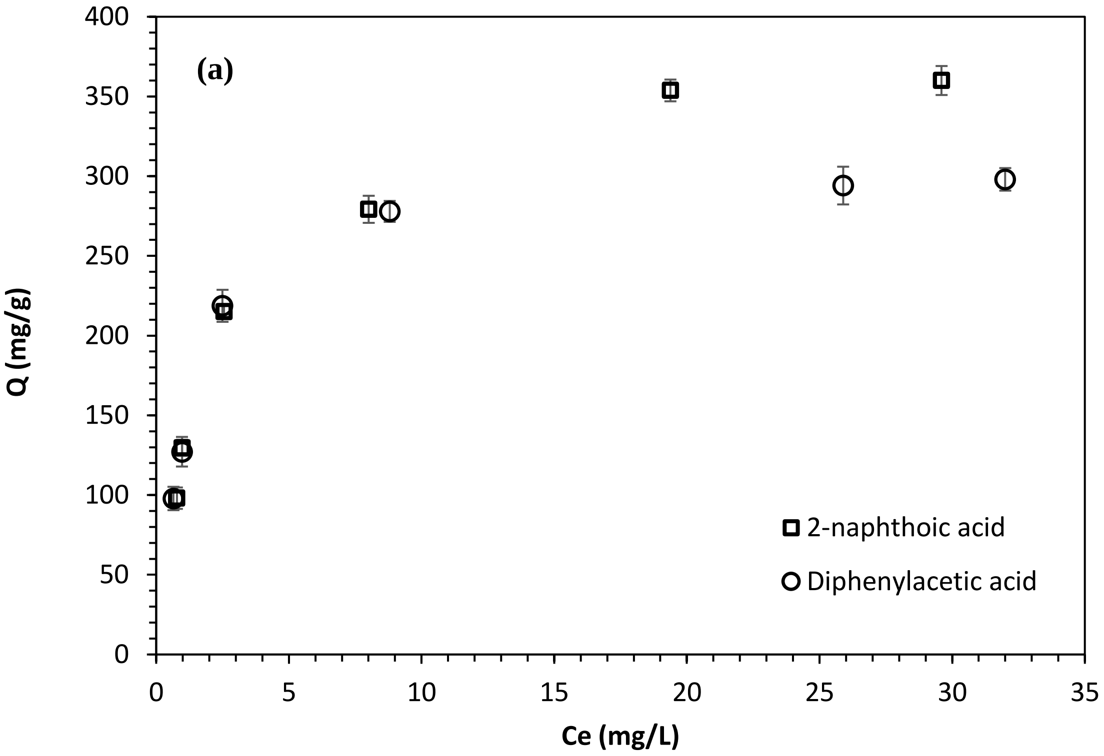
Figure 4-1 Variation of HPLC peak area with addition amount of 2-naphthoic acid or diphenylacetic acid in methanol. The curve levels-off at the saturation concentration or solubility of the model compound in the solvent.

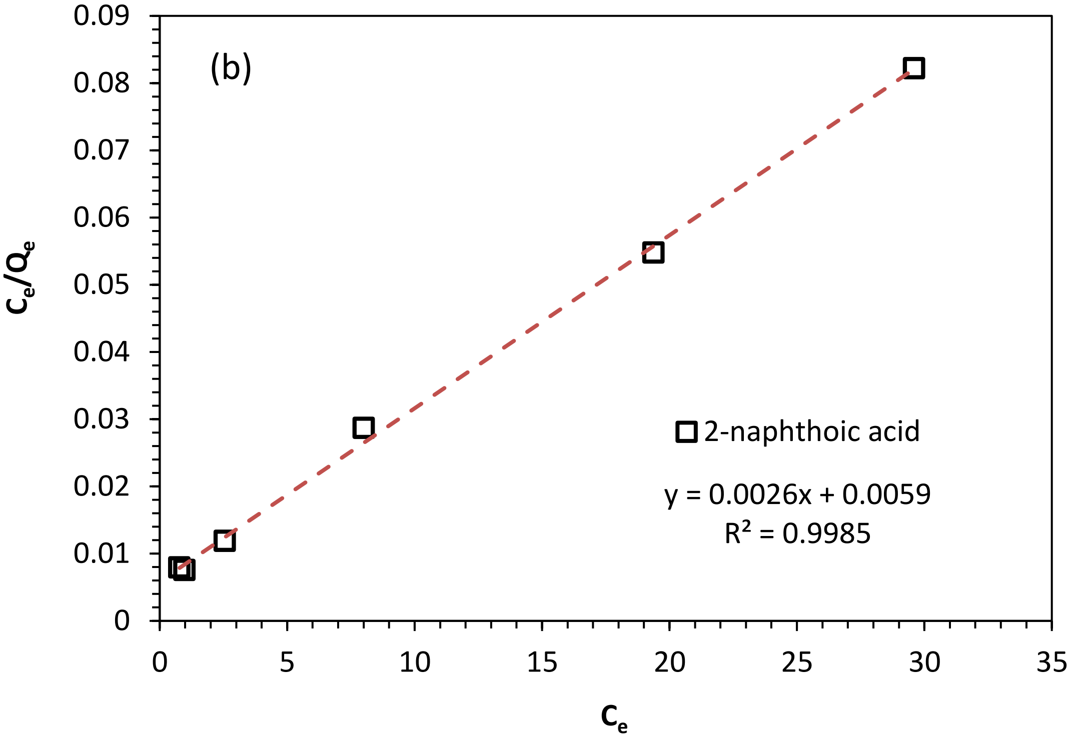
4.2 Batch adsorption isotherm

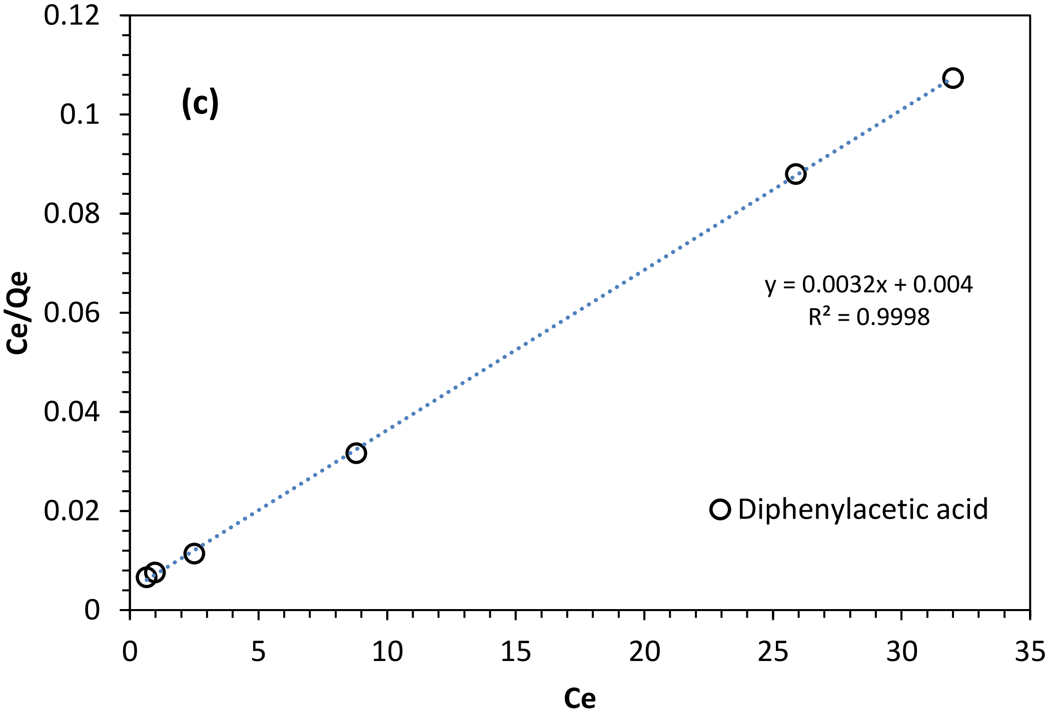
Batch adsorption experiments with the two model compounds were conducted using different doses of GAC and APC. Although, adsorption of NAs on GAC and APC increases with decreasing solution pH, as was reported in our previous study [14], batch adsorption tests were conducted only at pH 8.0, since the pH of OSPW is approximately 8.0. Equation 2 was used to determine the adsorption isotherm parameters for the two model compounds, i.e., 2-naphthoic acid and diphenylacetic acid.

$$Q_e = \frac{V \times (C_0 - C_e)}{W} \tag{2}$$

Where, Q_e is the equilibrium adsorption capacity (mg/g), V is the volume of solution (L), C_0 and C_e are the initial and equilibrium concentrations of adsorbate (mg/L), respectively, and W is the amount of adsorbent (g). The representative adsorption isotherm for APC has been illustrated in Figure 4.2 for the two model NAs.




(b)
C_e/Q_e
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0
5
10
15
20
25
30
35
C_e
□ 2-naphthoic acid
y = 0.0026x + 0.0059
R² = 0.9985


(c)
Ce/Qe
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
Ce
y = 0.0032x + 0.004
R² = 0.9998
○ Diphenylacetic acid

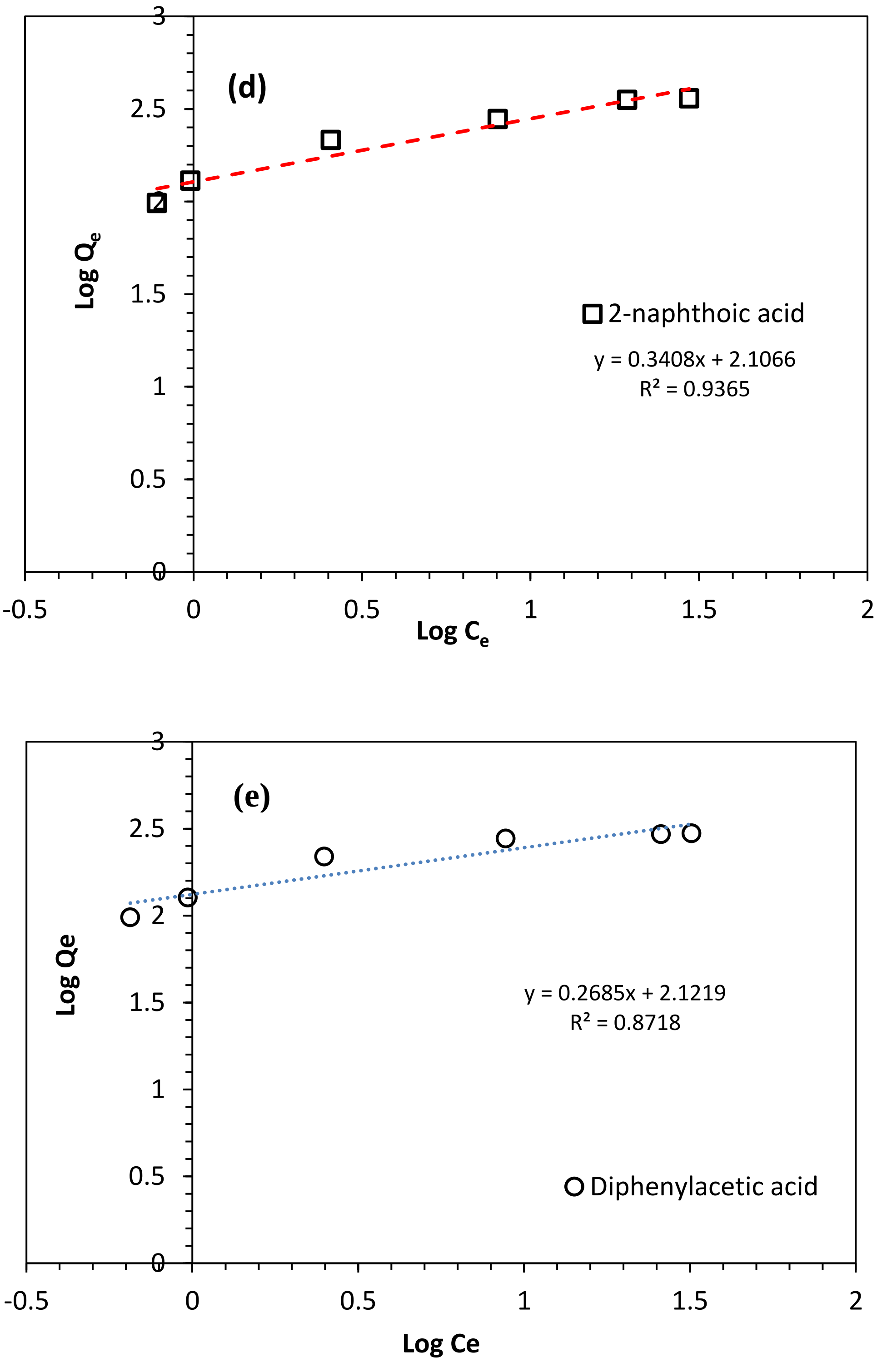


Figure 4-2 (a) Adsorption isotherm of 2-naphthoic acid and diphenylacetic acid by APC, (b) Linear form of Langmuir adsorption isotherm model for 2-naphthoic acid

by APC, (c) Linear form of Langmuir adsorption isotherm model for diphenylacetic acid by APC, (d) Linear form of Freundlich adsorption isotherm model for 2-naphthoic acid by APC, (e) Linear form of Freundlich adsorption isotherm model for diphenylacetic acid by APC (initial concentration of each model compound: 40 mg/L; volume of solution: 175 mL; solution pH: 8.0 and shaking speed: 250 rpm; adsorption equilibrium was reached within 48 h).

The adsorption isotherm data were plotted using Langmuir and Freundlich models (Table 4.1) as shown in Figures 4.2 b-e. The proposed Langmuir assumptions are given below:

1. Fixed number of vacant or adsorption sites are available on the surface of solid.
2. All the vacant sites are of equal size and shape on the surface of adsorbent.
3. Each site can hold maximum of one molecule and a constant amount of heat energy is released during this process.
4. Dynamic equilibrium exists between adsorbed molecules and the free molecules.

$$\mathrm{A(g)} + \mathrm{B(S)} \underset{\text{desorption}}{\overset{\text{Adsorption}}{\rightleftharpoons}} \mathrm{AB}$$

5. Adsorption is monolayer or unilayer.

The proposed Freundlich assumptions are given below:

1. The heat of adsorption is many instances decreases in magnitude with increasing extent of adsorption.
2. This decline in heat of adsorption is logarithmic, implying that adsorption sites are distributed exponentially with respect to adsorption energy.
3. This isotherm does not indicate an adsorption limit when coverage is sufficient to fill a monolayer.

Langmuir model fitted the experimental data well for both NA model compounds, but the Freundlich model did not fit the experimental data well for these two compounds.

Table 4-1 Adsorption isotherm models with their linear forms [154]

Adsorption isotherm model		Linear equation
Langmuir	$Q_e = Q_m\left(\frac{K_L C_e}{1 + K_L C_e}\right)$	$\frac{C_e}{Q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m}$

Freundlich	$Q_e = K_f C_e^{1/n}$	$\log(Q_e) = log(K_f) + \frac{1}{n} log(C_e)$

Note: 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), n is the nonlinear index and K_f is the Freundlich adsorption constant [(mg/g)/(mg/L)$^{(1/n)}$].

The isotherm parameters of Langmuir and Freundlich models for 2-naphthoic acid and diphenylacetic acid are listed in Table 4.2. The order of maximum experimental adsorption capacity for APC was: 2-naphthoic acid > diphenylacetic acid (Table 4.3). Compounds with benzene ring in their structure adsorbed more by APC due to $\pi - \pi$ interation between benzene ring of the compound and the adsorbent surface [14].

Table 4-2 Langmuir and Freundlich adsorption model parameters

2-naphthoic acid					
Adsorption isotherm model	**Isotherm parameters**				
Langmuir	pH	K_L	Q_m (mg/g)	Q_m(experimental)	R^2
	8.0	0.44	384.61	360	0.998
Freundlich	pH	K_f		n	R^2
	8.0	127.82		2.93	0.936
Diphenylacetic acid					
Adsorption isotherm model	**Isotherm parameters**				
Langmuir	pH	K_L	Q_m (mg/g)	Q_m(experimental)	R^2
	8.0	0.8	312.5	298	0.999
Freundlich	pH	K_f		n	R^2
	8.0	132.12		3.73	0.871

Table 4-3 Maximum experimental adsorption capacity (Q_{max}) of GAC and APC adsorbents [18]

Model NAs	**Adsorbent**	**Q_{max} (mg/g) at pH = 8.0**
2-naphthoic acid	APC	360
Diphenylacetic acid		260
2-naphthoic acid	GAC	189
Diphenylacetic acid		40

APC has higher BET specific surface area 1705±20 m^2/g compared to GAC (1372±27 m^2/g), however, APC performed significantly better than GAC due to its higher mesoporous area (1372±22 m^2/g for APC compared to 634±19 m^2/g for GAC), facilitating the diffusion of NAs in the pores of the adsorbent.

4.3 Batch regeneration

Preliminary desorption experiments were conducted in batch system with model compounds to evaluate the two most important parameters, i.e., the volume and pH of the solvent, which potentially control the regeneration process. Additionally, mixing and regeneration time also will have some effect on the efficiency of regeneration. Since the batch regeneration tests were conducted on an orbital shaker, the mixing speed of the shaker and time were optimized in preliminary experiment. Repetitive batch adsorption/regeneration experiments were conducted for the recovery of solvent and adsorbate compounds in each cycle. Finally, the batch regeneration experiment was conducted for real OSPW under the same operating conditions obtained from the tests with model compounds.

4.3.1 Effects of solvent volume

The optimization of solvent volume for the regeneration of spent carbon was conducted with GAC to minimize the number of experiments. Several literature studies found that phenol extraction from spent carbon increased by increasing the volume of pure acetone and methanol, as expected [141, 152]. In this experiment, the effects of solvent volume on the extraction of 2-naphthoic acid from GAC can be seen in Figure 4.3. The experiments were conducted with 0.1 g of spent carbon adsorbent with different volumes of solvent. It can be seen that the efficiency increased with the increasing methanol volume, but the regeneration efficiency of only methanol is fairly low, ranging from 7.42-19.72. Although, NAs exhibited excellent solubility in methanol, use of only methanol seems to be inefficient for regenerating spent carbon with NAs.

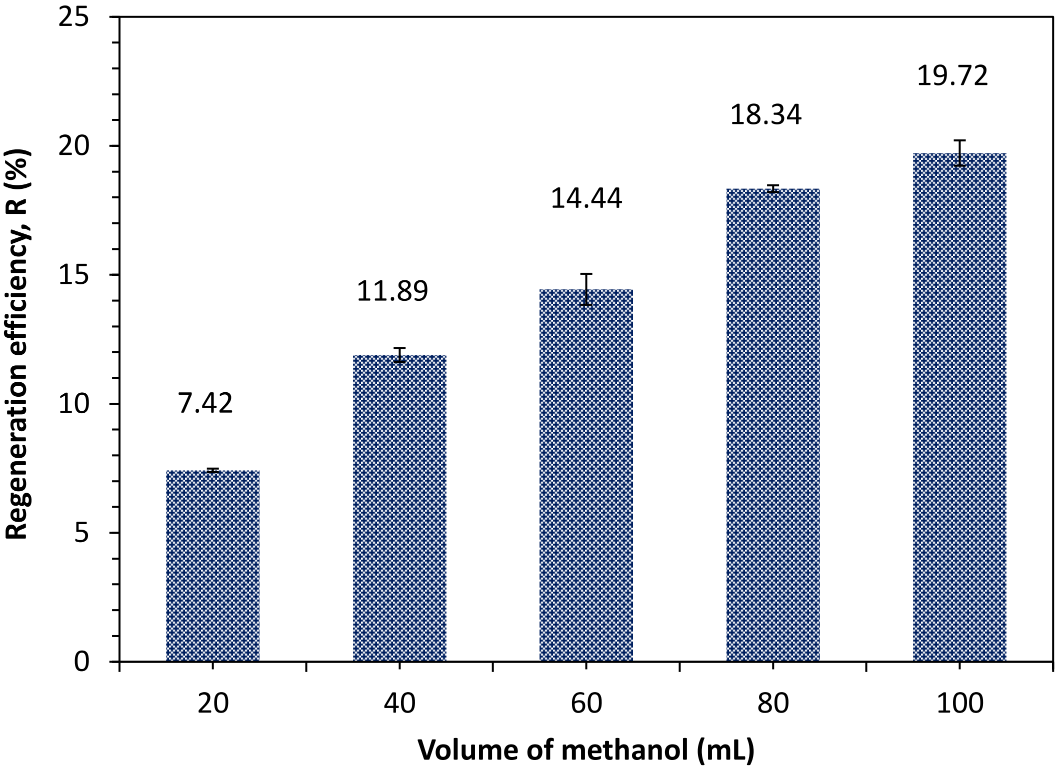
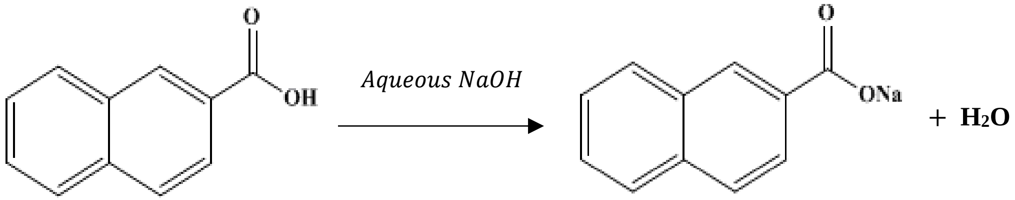


Figure 4-3 Effects of different volumes of pure methanol on batch regeneration of spent GAC with 92 mg/g capacity. Adsorption of 2-naphthoic acid: carbon loading = 0.1 g, agitation speed = 250 rpm, agitation time = 24 h, and temperature = 298 K.

4.3.2 Effects of desorbing agent and pH

The above regeneration experiments indicated that pure methanol was not efficient enough to extract 2-naphthoic acid from GAC. Soluble forms of the adsorbate can be obtained by pH control or the use of reactive regenerant. Since the NAs are acidic, increasing the pH of the solvent might be beneficial for deprotonation of the acid. pH will have impact on the surface charge distribution. Adsorbates that are difficult to solubilize or are very strongly bound to the surface, reduced affinity for the adsorbent though a change in surface charge can be used to improve the regeneration efficiency [20]. The pK_A values of the NAs (2-naphthoic acid and diphenylacetic acid) are 4.14, and 4.72, respectively. It was found that the maximum adsorption on activated carbon occurred in acidic pH indicating that protonated NAs adsorbed well on the activated carbon with a pZc value around 9.2 due to hydrophobic interactions between positively charge carbon surface and NAs. Therefore, it is hypothesized that the addition of a base such as aqueous NaOH may improve the performance of regeneration using methanol due to the following reaction:



Based on the stoichiometric reaction between 2-naphthoic acid and aqueous NaOH, initially 2.32 mg of NaOH (aq.) was determined to be sufficient based on the adsorption capacity of the spent carbon. Thereafter, methanol can easily wash out the released sodium 2-naphthoate molecules form the carbon adsorption sites.

The estimation of stoichiometric aqueous NaOH loading is given below:

$$\frac{Desorbing\ agent\ (mg)}{Spent\ carbon\ (g)} = \frac{MW_{Desorbing\ agent}\ \left(\frac{g}{mole}\right)}{MW_{Adsorbate}\ \left(\frac{g}{mole}\right)} \times Adsorption\ capacity\ \left(\frac{mg}{g}\right) \tag{3}$$

Here, MW = Molecular weight

It was found that the presence of desorbing agents such as HCl and NaOH improved the regeneration efficiency in solvent regeneration technique [153]. Addition of aqueous NaOH increased the regeneration efficiency of methanol significantly and the results are shown in Figure 4.4 (a). The batch experiments were conducted with ~2.4 mg of aqueous NaOH and different volumes of methanol to regenerate 0.1 g of spent carbon with 89.5~91 mg/g adsorption of 2-naphthoic acid. A significant enhancement in the regeneration efficiency (approximately 70%) was observed with 40 mL methanol; however, with further increasing methanol volume to 60-100 mL, the regeneration efficiency remained almost constantly. Thereafter, the experiments were conducted with 40 mL methanol by varying the dosage of aq. NaOH, and the results are shown in Figure 4.4 (b). There is an optimum NaOH loading or maximum pH beyond which regeneration efficiency is decreased.

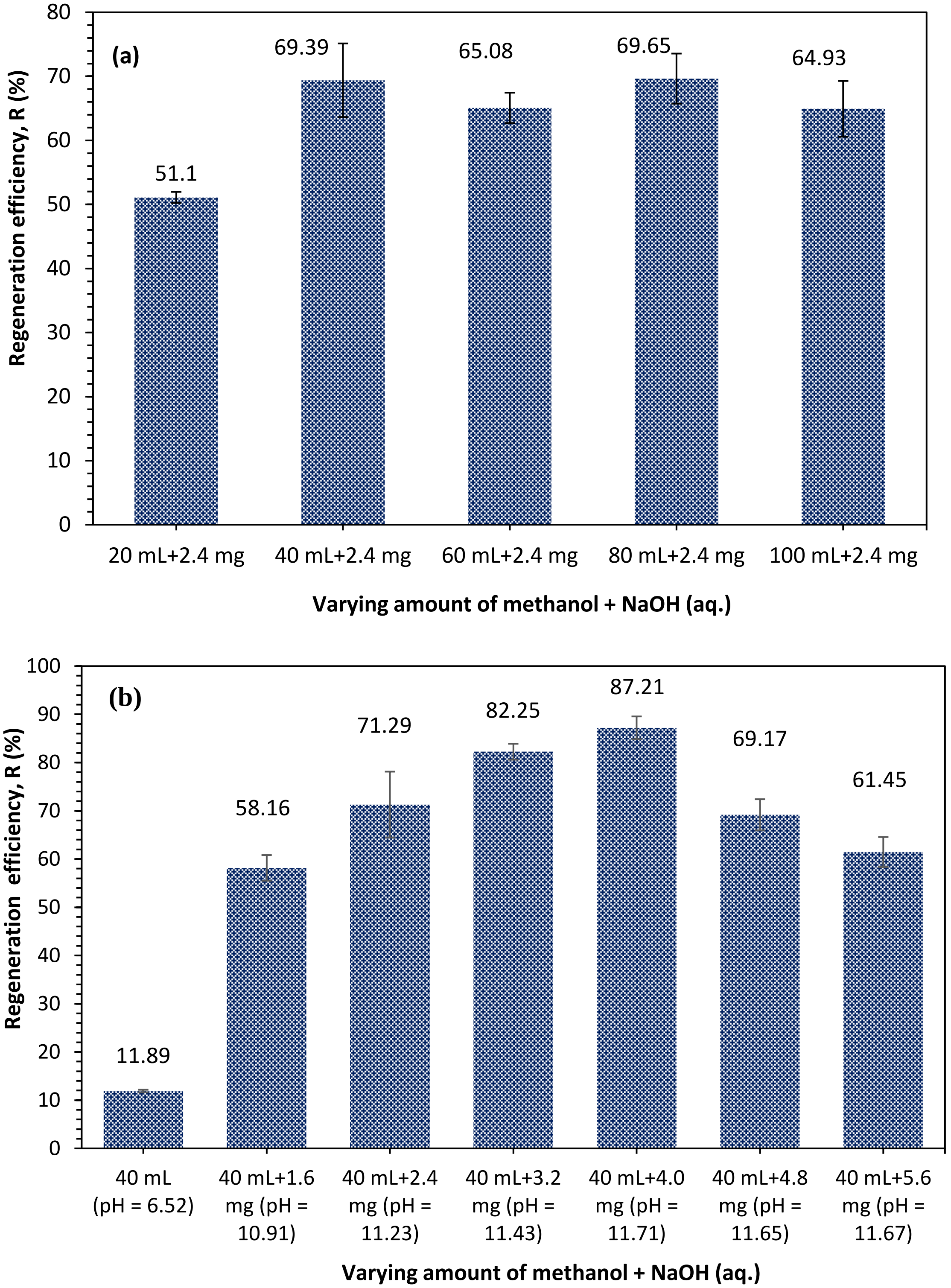


Figure 4-4 (a) Effects of the addition volume of the desorbing agent (methanol + NaOH) on regeneration of spent GAC with 91 mg/g capacity of 2-naphthoic acid, (b)

effects of pH on the regeneration of spent carbon with 89.5 mg/g capacity of 2-naphthoic acid. Carbon loading: 0.1 g, agitation speed: 250 rpm, agitation time: 24 h, and temperature: 298 K.

It can be seen that increasing NaOH dosage or pH value with the fixed methanol volume, the regeneration efficiency increased, and the maximum regeneration efficiency of 87.2% was obtained at pH 11.71. Beyond this point, the regeneration efficiency decreased by increasing the pH further. It was assumed that using excess aqueous NaOH may cause the deposition of highly concentrated Na–salts of 2-naphthoic acid inside the carbon channels, which would block the pores of the carbon, hence reducing the regeneration efficiency.

4.3.3 Optimization of dosages based on statistical analysis

From the results of the experiments with single variables as reported in earlier sections, it was seen that the regeneration efficiency did not change proportionally with the amount of solvent used, although the amount of NAs in methanol was far below the solubility limit of NAs indicating the complex chemistry of the process. Therefore, the central composite design (CCD) and response surface methodology (RSM) were used to optimize the two most significant operating variables: solvent dosage (mL) and addition amount of aqueous NaOH (mg) with batch experiments. The Mini Tab Software (version 17) was used for the statistical design of experiments and data analysis. The aim of this study was to determine the lowest amount of methanol and NaOH to achieve cost-effective regeneration of the spent APC after OSPW adsorption treatment for recovery of NAs and other organics. Accordingly, methanol dosages from 20 – 100 mL and NaOH 1.6– 4.8 mg were used. Table 3.3 shows the CCD in the form of a 3^2 full factorial design with four additional repeat experiments (batch number 9 – 12). Both the independent variables and their coded values (in parentheses), as well as the obtained regeneration efficiency for each batch experiment, are presented in the Table. The coded values for solvent dosage (A) and aq. NaOH (B) were set at five levels: – 1.414 (minimum), – 1 (low), 0 (medium), + 1 (high), and + 1.414 (maximum). In order to obtain the optimum solvent dosage and addition amount of NaOH, regeneration efficiency, R (%) was investigated as the response. The quadratic equation model for the optimal conditions is shown in Equation 4 [154]:

$$Y = \beta_0 + \sum_{i=1}^{k_n} \beta_i X_i + \sum_{i=1}^{k_n} \beta_{ii} X_i^2 + \sum_{i_{i\leq j}}^{k_n} \sum_{j}^{k_n} \beta_{ij} X_i X_j + \cdots + e \tag{4}$$

Where i represents the linear coefficient, j indicates the quadratic coefficient, β denotes the regression coefficient, k_n is the number of parameters studied and optimized in the experiment and e represents the errors obtained randomly.

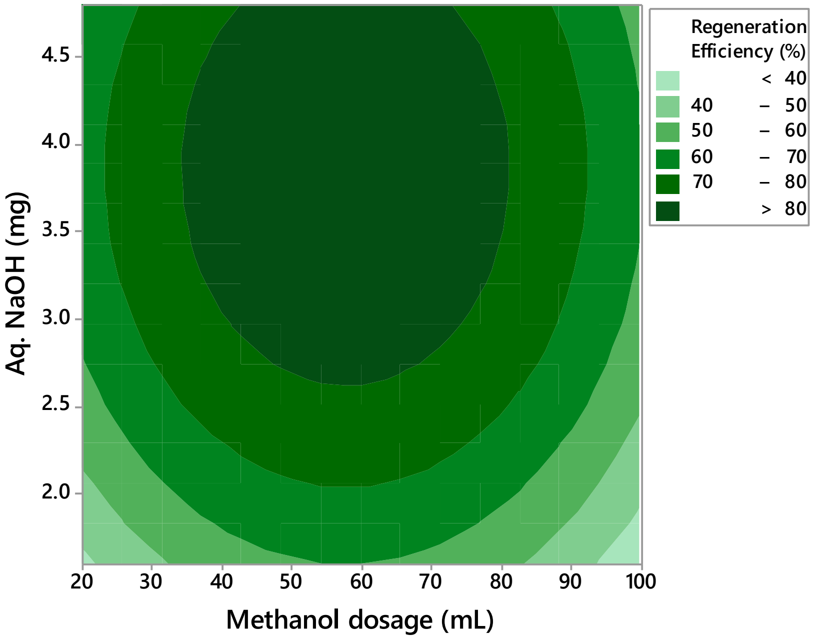
For the graphical presentation of data, analysis of variance (ANOVA) was used to achieve the correlation between the process variables and the response. The goodness of fit of the polynomial model is indicated by the coefficient of determination (R^2). Model terms were analyzed by the $P - value$ (probability). Three-dimensional surface plots and their respective contour plots were obtained to evaluate the optimum region based on two parameters.

The CCD shown in Table 3.3 develops the mathematical equation where the responses (Y) were calculated as a function of solvent dosage (A) and dosage of NaOH (B) as shown in Equation 5. The obtained results were evaluated by using ANOVA analysis to know the goodness of fit of the model.

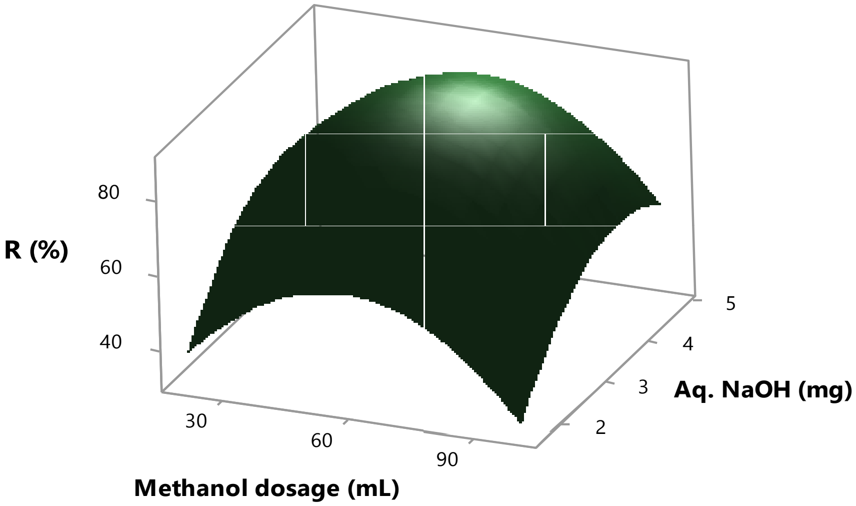
$$Y = -46.74 + 1.793A + 43.31B - 0.015A^2 - 5.621B^2 \tag{5}$$

The data presented in Table 3.3 show that the model is important since the $P - value$ (probability) was less than 0.05 [154]. The regression coefficient (R^2) provides the total difference in the response predicted by the model. In this study, R^2 value is 97.79% with the adjusted R^2 (96.69 %), indicating a reasonable fit of the quadratic model to the experimental data [155].

Regeneration efficiency, R (%) *vs* aqueous NaOH dosage (mg), solvent dosage (mL) plots are represented in Figure 4.5 with response surface and circular contour plots. The plots are approximately symmetrical to re-confirm the optimum conditions for maximum efficiency as seen earlier in the single parameter experiments. The two-dimensional surface plot analysis represents the responses on the solvent and NaOH dosage plane. These plots display concentrated curve around the center showing > 80% regeneration efficiency. As displayed in the plots, the maximum responses (R ~ 87%) can be obtained at two different optimum conditions (at methanol dosage-to-NaOH ratio of 40 mL:4 mg and 60 mL:3.2 mg, respectively), where the experimental pH values were similar around 11.71. Similar results can be found in three-dimensional contour plot. It is obvious that using less solvent for maximum regeneration would make the regeneration process more economical viable. As a result, the methanol dosage-to-NaOH ratio of 40 mL:4 mg was chosen in this work for further investigation.



(a) Design expert scheme: response surface plot



(b) Design expert scheme: contour plot

Figure 4-5 Design–expert plots; (a) response surface and (b) contour plot to optimize the methanol and NaOH dosages for extraction of 2-naphthoic acid from the spent GAC.

4.3.4 Influence of shaking speed on batch study

In batch regeneration experiments, shaking is crucial to eliminate the effects of mass transfer limitation due to external surface diffusion. The influence of agitation on desorption efficiency of the spent carbon was investigated by varying the shaking speed at 200, 250 and 300 rpm, while keeping the volume of solvent, spent GAC carbon loading, pH, temperature and contact time constant. The effects of agitation are shown in Figure 4.6, where the regeneration efficiency of the GAC spent carbon generally increased with increasing shaking speed from 200 to 300 rpm. The results show that the increasing shaking speed facilitates the solvent extraction of 2-naphthoic acid and shaking rate in the range of 250–

300 rpm was sufficient for minimizing the mass transfer resistance due to the external surface diffusion in the batch experiments. As such, the shaking speed of 250 rpm was selected for further experiments.

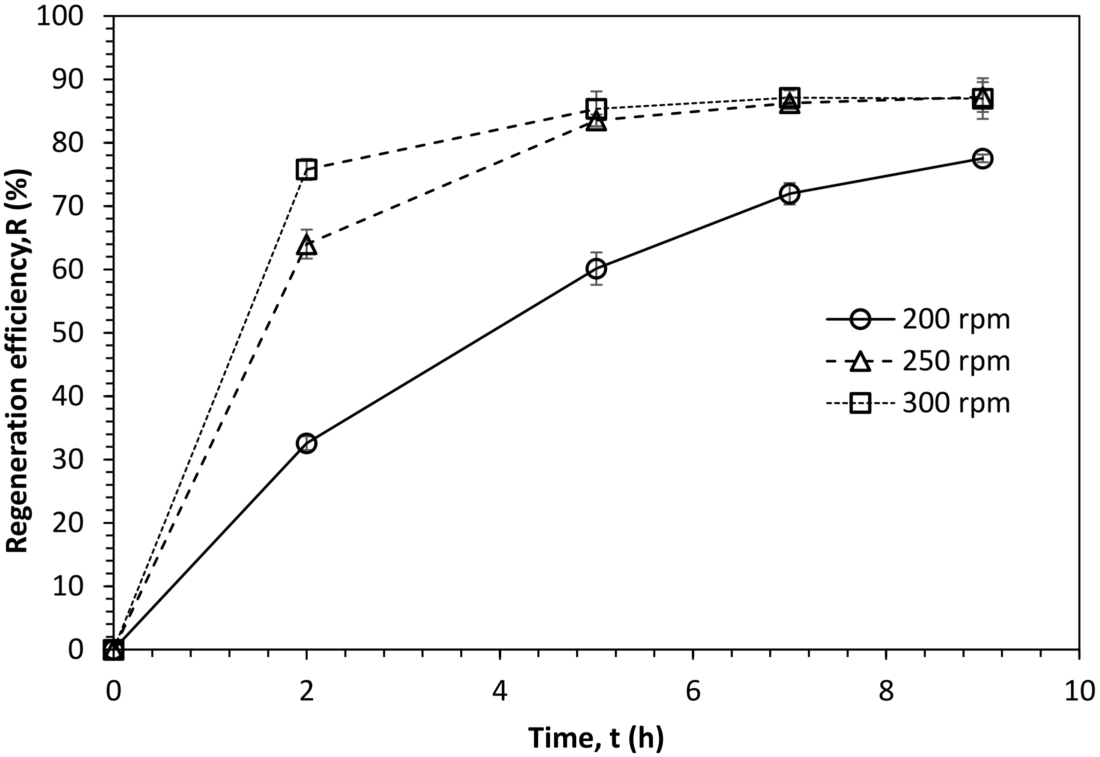


Figure 4-6 Effects of shaking speed on regeneration efficiency of spent GAC with 89.5 mg/g capacity of 2-naphthoic acid. Spent GAC loading = 0.1 g, Methanol volume = 40 mL, pH = 11.71, and Temperature = 298 K.

4.3.5 Effects of regeneration time

Based on the assumption that the rate of regeneration would be proportional to the difference between the initial amount of the adsorbed compound on spent carbon and the amount remaining on the spent carbon after regeneration, at any time [125]. This correlation is represented mathematically as,

$$-dq_r/dt = kq_r \tag{6}$$

$$\frac{dq_r}{q_r} = -kdt \tag{7}$$

Integrating Equation 6 with boundary conditions; when t = 0, then $q_r = q_0$

$$ln(q_r/q_0) = -kt \tag{8}$$

$$(q_r/q_0) = e^{-kt} \tag{9}$$

$$\frac{q_0 - q_r}{q_0} = 1 - e^{-kt} \tag{10}$$

$$\frac{q_0 - q_r}{q_0} \times 100 = 100(1 - e^{-kt}) \tag{11}$$

The values of k (proportionality constant/ regeneration rate constant) can be determined from the experimental data illustrated in Figure 4.7. The regeneration efficiency is expressed as,

$$R\ (\%) = 100(1 - e^{-kt}) \tag{12}$$

Where, q_0 (t = 0) and q_r (t = t) are the amount of adsorbate (mg) per gram of carbon. R (%) is defined as, $R\ (\%) = \left(1 - {}^{q_r}/_{q_0}\right) \times 100$. The regeneration rate constant (k) can be determined from experimental data under various operating conditions.

In this work, the effect of regeneration time was investigated at optimum solvent loading, pH, and shaking speed. The regeneration efficiency reaches equilibrium after almost 5 h of operation in case of both model compounds. Based on experimental data, the operating time was selected as roughly 5-6 h to complete the batch regeneration. Estimated linear regression equations based on kinetic data are given below: $-\ln\left({}^{q_r}/_{q_0}\right) = 0.395\ t$, and $-\ln\left({}^{q_r}/_{q_0}\right) = 0.292\ t$ for 2-naphthoic acid and diphenylacetic acid desorption, respectively. The 1st order kinetic model equations are well fitted with the experimental data (R^2

= 0.95 and 0.93 for 2-naphthoic acid and diphenylacetic acid, respectively). The determined rate constant indicate that the rate of regeneration was higher for 2-naphthoic acid (0.395 h $^{-1}$) than that of diphenylacetic acid (0.292 h $^{-1}$).

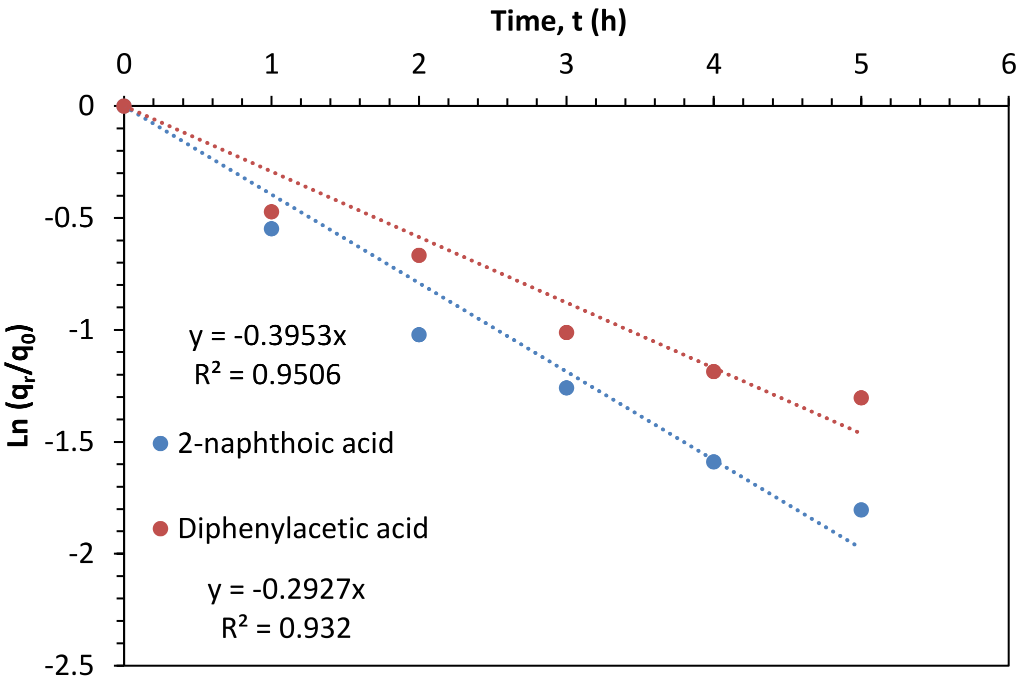


Figure 4-7 Ln (q_r/q_0) vs time for GAC with 89.5 mg/g adsorption of 2-naphthoic acid and 78.8 mg/g adsorption of diphenylacetic acid. Spent carbon loading: 0.1 g, solvent volume: 40 mL, solvent pH: 11.71, agitation speed: 250 rpm, temperature: 298 K. Symbols: experimental measurement data, and lines: kinetic modeling results.

4.3.6 Solvent recycling and recovery of model compounds

The experiment conducted in this section makes the regeneration process more economically viable because the solvent is recycled for use in the regeneration to minimize wastes while reducing transportation and disposal costs and hence the overall operation costs of the OSPW treatment process. The previously optimized solvent volume (40 mL) was used in each batch regeneration of 0.1 g of spent carbon. Table 4.4 summarizes the solvent and compound recovery efficiency in each cycle for 2-naphthoic acid. As displayed in the Table, after 1st cycle regeneration of GAC activated carbon, approximately 7.80 mg sodium salts of 2-naphthoic acid was detected in the 40 mL of exhausted methanol, where the average concentration of 2-naphthoic acid was measured to be 195.12 mg/L. Subsequently, the exhausted solvent was distilled using distillation-condensation process, where about 36 mL of the methanol solvent was recovered, i.e., about 90% methanol recovery efficiency. After drying the bottom product, about 6.38 mg of sodium salt of 2-naphthoic acid solids was retrieved, namely 82% 2-naphthoic acid salt recovery efficiency in the 1st cycle. As shown in Table 4-4, in the 5 cycles of regeneration operations tested, the recovery efficiencies for the methanol solvent and the 2-naphthoic acid salt were approx. 86-92% and 73-84%, respectively. Therefore, our work demonstrated that most of the dissolved NAs can be recovered from the solvent. The salts of NAs (alkali naphthenates) are valuable commercial products as both emulsifying and demulsifying agents [68].

Table 4-4 Recovery efficiency of methanol solvent and 2-naphthoic acid per cycle. Solvent volume: 40 mL, pH: 11.71, operating time: 6-7 h, agitation speed: 250 rpm, temperature: 298 K, and spent GAC carbon loading: 0.1 g.

No. of cycle	Solvent recovery (mL)	Solvent recovery efficiency	Desorbed 2-naphthoic acid salt (mg)	2-naphthoic acid salt recovery (mg)	2-naphthoic acid salt recovery efficiency
Cycle -1	36	**90.0%**	7.80	6.38	**82.0%**
Cycle -2	36.7	**92.0%**	7.00	5.89	**84.1%**
Cycle -3	34.5	**86.2%**	6.47	5.42	**83.7%**
Cycle -4	35	**87.5%**	5.82	4.26	**73.1%**
Cycle -5	36.2	**90.5%**	5.29	4.43	**83.7%**

Similarly, in the 5 cycles of regeneration operations tested for diphenylacetic acid, the recovery efficiencies for the methanol solvent and the diphenylacetic acid salt were approx. 86% – 91% and 76% – 80%, respectively as shown in Table 4-5.

Table 4-5 Recovery efficiency of methanol solvent and diphenylacetic acid per cycle. Solvent volume: 40 mL, solvent pH: 11.71, operating time: 6-7 h, agitation speed: 250 rpm, temperature: 298 K, and spent GAC carbon loading: 0.1 g.

No. of cycle	Solvent recovery (mL)	Solvent recovery efficiency	Desorbed diphenylacetic acid salt (mg)	Diphenylacetic acid salt recovery (mg)	Diphenylacetic acid salt recovery efficiency
Cycle -1	34.3	**86.0%**	6.02	4.72	**78.0%**
Cycle -2	35.4	**88.5%**	5.10	4.08	**80.0%**
Cycle -3	36.1	**90.2%**	4.44	3.41	**76.8%**

Cycle -4	34.8	**87.0%**	4.06	3.17	**78.1%**
Cycle -5	35.6	**89.0%**	3.63	2.83	**78.0%**

4.3.7 Repeated adsorption–regeneration at optimum conditions

Cycles of batch adsorption and desorption experiments were repeated at the optimal desorption conditions as reported in the previous Section: for adsorption, 250 mL of 40 mg/L of 2-naphthoic acid or diphenylacetic acid and 0.1 g of GAC loading were used; for regeneration, 40 mL of methanol with NaOH at pH 11.71 as regenerating solvent and 250 rpm agitation. Figure 4.8 illustrates the adsorption capacity of GAC and regeneration efficiency as a function of the number of regeneration cycle. In the first cycle, the average adsorption capacity of GAC for both model compounds was 89.25 mg/g and 79.45 mg/g, respectively, and the average regeneration efficiency was approx. 87% and 76% for 2-naphthoic acid and diphenyl acetic acid, respectively. The adsorption capacity and the regeneration efficiency dropped to 62-72 mg/g and 58-73%, respectively for the two NA model compounds.

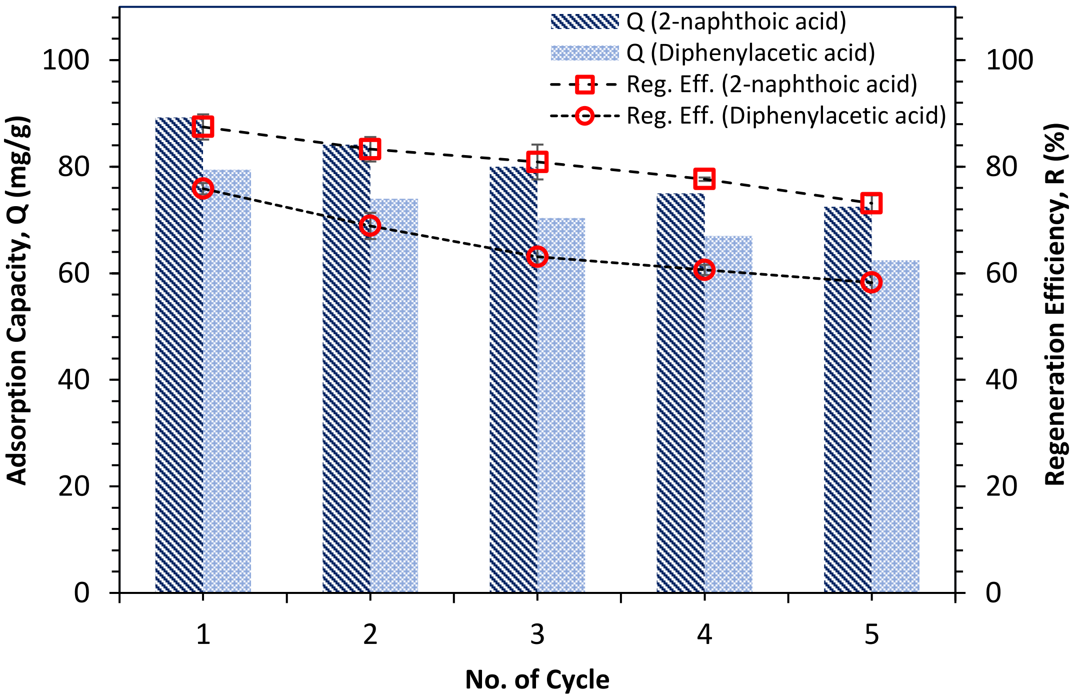


Figure 4-8 The adsorption capacity and regeneration efficiency in repeated batches of adsorption-regeneration cycles at the optimal conditions with GAC for 2-naphthoic acid and diphenylacetic acid. Adsorption conditions: carbon loading = 0.1 g, pH of 2-naphthoic acid or diphenylacetic acid solution was 8.0, volume of solution =

250 mL, shaking speed = 250 rpm, temperature = 298 K. Regeneration conditions: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent GAC loading = 0.1 g.

Just for checking the performance of APC in the repeated batches of adsorption-regeneration cycles, we performance similar tests as discussed in the above Figure 4.8, except for using 0.05g APC in both adsorption and regeneration batches and operating the adsorption tests at pH = 4.0 with APC (instead of pH 8.0 for GAC). The results are presented in Figure 4.9. As expected, the results in Figure 4.9 show comparatively higher adsorption capacity of APC than that of GAC (Figure 4.8) in all adsorption cycles owing to not only the higher meso-porous surface area of APC than that of GAC but also the lower pH value used in the tests with APC. The adsorption capacity of APC (at pH 4.0) was about 199 mg/g for 2-naphthoic acid and 176 mg/g for diphenylacetic acid in the first adsorption cycle, compared to 89.25 mg/g for 2-naphthoic acid and 79.45 mg/g for diphenyl acetic acid with GAC (pH 8.0). The average regeneration efficiency was also higher with APC, being approx. 96% and 81% for 2-naphthoic acid and diphenyl acetic acid, respectively in the first cycle. The APC adsorption capacity and regeneration efficiency were both reduced as similarly observed with GAC (in Figure 4.8), e.g., the regeneration efficiency was reduced to 79% and 67% after fifth regeneration cycle for 2-naphthoic acid and diphenylacetic acid, respectively.

Figure 4.8 and 4.9 show that the initial pH of adsorption (pH = 8.0 and 4.0) of model naphthenic acids did not impact significantly on desorption efficiency, although at pH 4.0 the adsorption capacity was higher through surface charge distribution which facilitates the extraction of more adsorbates (NA compounds) using a certain amount of methanol.

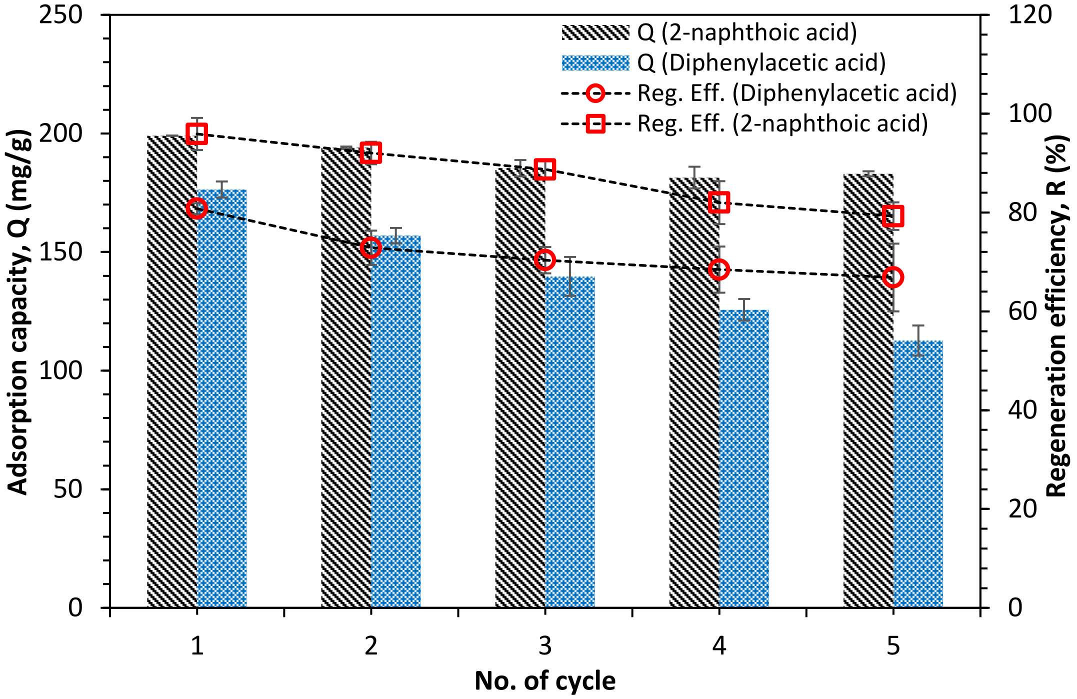


Figure 4-9 The adsorption capacity and regeneration efficiency in repeated batches of adsorption-regeneration cycles at the optimal conditions with APC for 2-naphthoic acid and diphenylacetic acid. Adsorption conditions: carbon loading = 0.05 g, pH of 2-naphthoic acid or diphenylacetic acid solution was 4.0, volume of solution = 250 mL, shaking speed = 250 rpm, temperature = 298 K. Regeneration conditions: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent APC carbon loading = 0.05 g.

4.3.8 Surface properties of the spent and regenerated carbon adsorbent

The textural properties of the fresh GAC and APC adsorbents (BET specific surface area, Micro-pore area, Meso-pore area, Total pore volume and Average pore size) were analyzed by N_2 isothermal adsorption (at 77 K), and the results are summarized in Table 4.6. The highly porous structure of the two carbon adsorbents was confirmed by SEM images as illustrated in Figure 4.10.

Table 4-6 Textural properties of the fresh GAC and APC adsorbents[a]

Adsorbent	BET specific surface area, m^2/g	Micro-pore area, m^2/g	Meso-pore area, m^2/g	Total pore volume, cc/g	Average pore size, nm
GAC	1372±27	766±11	634±19	0.7	2
APC	1705±20	353±16	1372±22	0.85	2.1

a. Determine by N_2 isothermal adsorption (at 77 K).

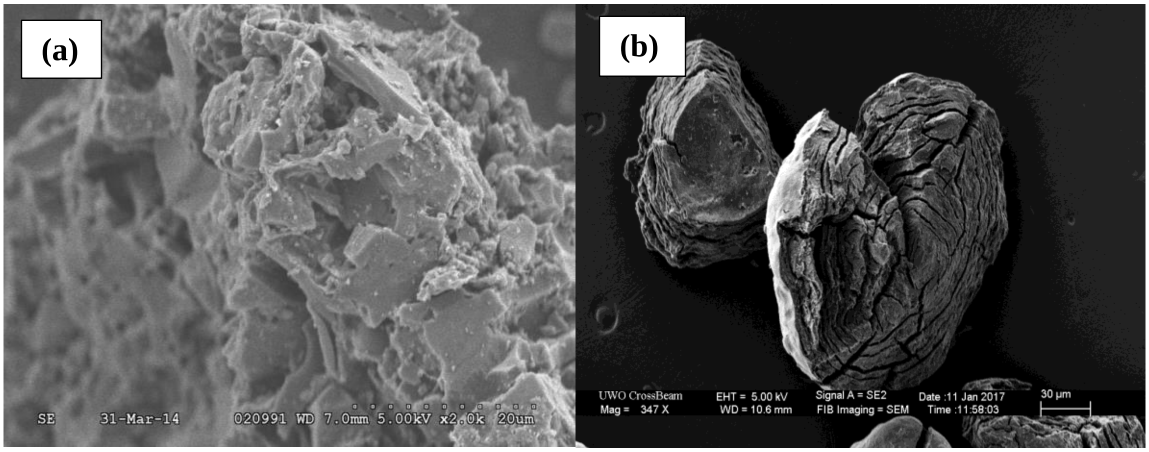
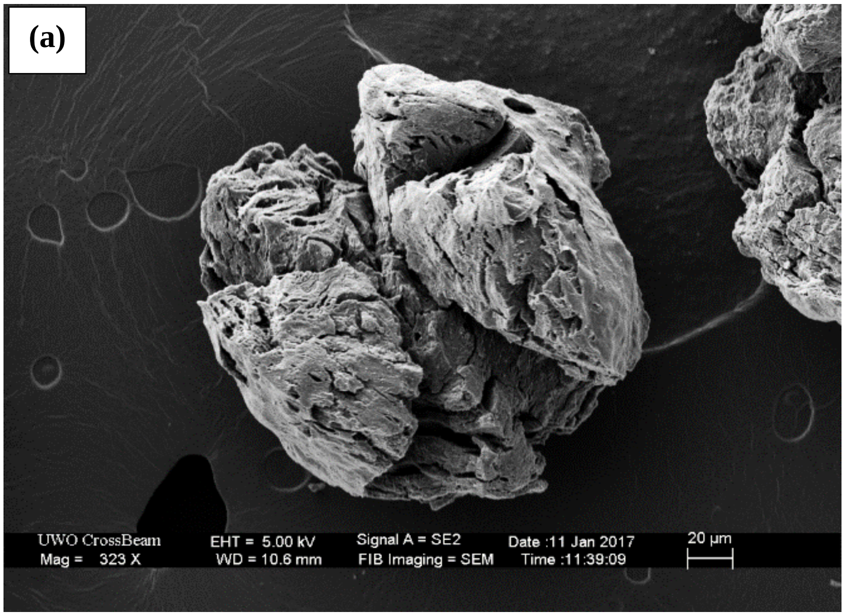


Figure 4-10 SEM images of fresh adsorbents of (a) GAC, (b) APC.

Compared with APC, GAC has a higher microporous area with slightly lower average pore size (Table 4.6). The BET specific surface area of the commercial APC used in this study is about 1705±20 m^2/g, and the surface area of spent carbon after the 5th adsorption cycle was reduced to 1276±18 m^2/g, whereas after the regeneration it increased to 1569±31 m^2/g, i.e., about 8 % loss in surface area after the 5th cycle treatment. The SEM images of spent and regenerated APC adsorbent after 5th cycle are shown in Figure 4.11 (a) and 4.11 (b); respectively. When comparing the SEM images of the spent and regenerated APC particles (Figure 4.11) with that of the fresh APC (as shown previously in Figure 4.10), some pore blocking may be observed, especially the micro-pores, which accounts for the loss of BET surface areas of the spent and regenerated APC particles. Table 4.7 indicates the evidence of the loss of micro-pores of APC after 5th regeneration cycle. Similar observation can be obtained with the spent and regenerated GAC adsorbent after 5th cycle.

Table 4-7 Textural properties of APC after 5th regeneration cycle compared with the fresh APC

Type of carbon	BET specific surface area, m^2/g	Micro-pore area, m^2/g	Meso-pore area, m^2/g
Fresh APC	1705±20	353±16	1372±22
APC after 5th regeneration cycle	1569±31	196±20	1324±27



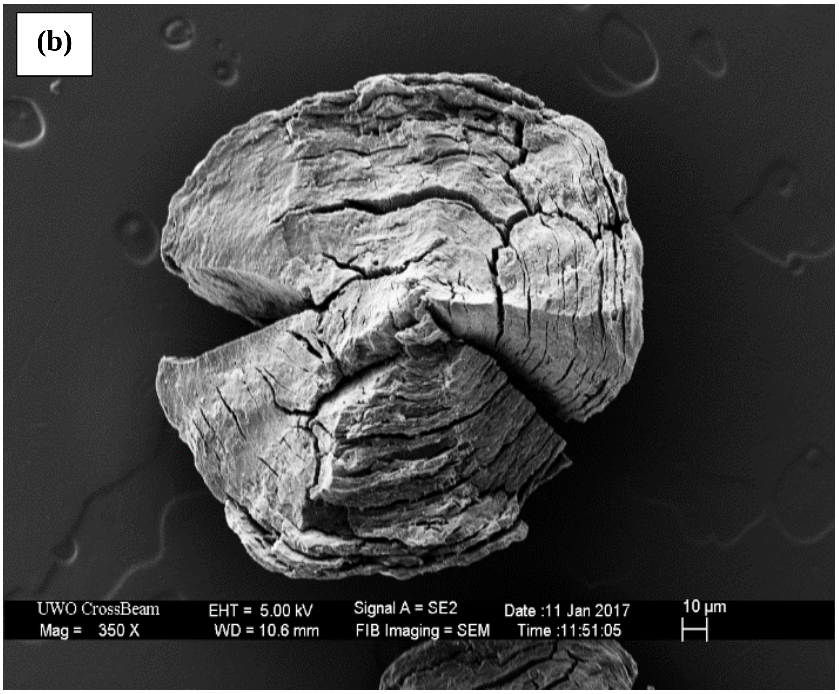


Figure 4-11 SEM images of APC after fifth adsorption-regeneration cycle for 2-naphthoic acid treatment: (a) spent adsorbent, (b) regenerated adsorbent.

4.3.9 Mathematical modeling

A mass transfer model was developed to describe the desorption process. A desorption process commonly consists of the following steps: desorption of the adsorbate from the surface of the adsorbent, diffusion of the adsorbate out of the internal pores of the adsorbent into the external surface of the adsorbent particle, and diffusion of the adsorbate through the external surface into the solvent bulk phase. In this study, to simply the modeling work, we combined the internal and external diffusion into diffusion of the desorbed adsorbate across a boundary layer around the surface of the adsorbent particles directly into the bulk phase. The following assumptions were considered in developing the model (Figure 4.12):

- a stagnant film or boundary layer exists around the surface of the adsorbent particle.
- diffusion occurs throughout the boundary layer from the interface of the adsorbent to solvent bulk phase.
- instantaneous diffusion occurs though the boundary layer.

- initially before starting desorption (t = 0), the concentration of the adsorbate in the stagnant film around the surface of the adsorbent and the bulk is zero.
- complete desorption is assumed in this system.

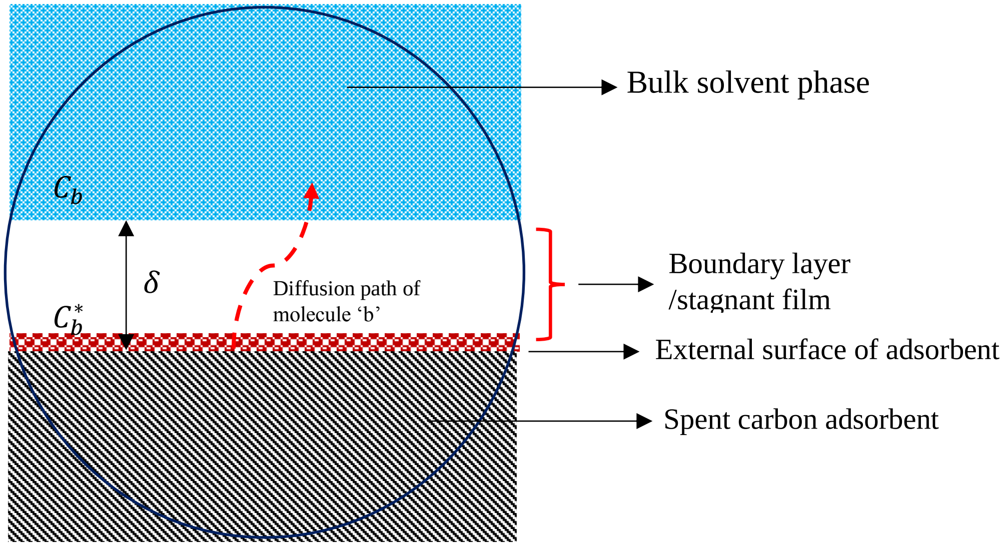


Figure 4-12 Schematic of diffusion controlled desorption though the stagnant film/boundary layer adjacent to the external surface of spent carbon adsorbent and desorption process of NA molecules.

Diffusion of the absorbate molecules during desorption is due to the concentration gradient. The net diffusion from the adsorbent surface to the bulk phase is written as:

$$J_b = Wa_w \frac{D_b}{\delta}(C_b^* - C_b) \tag{13}$$

Or,

$$J_b = Wa_w k_b (C_b^* - C_b) \tag{14}$$

Here,

J_b = Mass transfer of 'b' (NAs) molecules across the stagnant film $\left(\frac{kg}{Sec}\right)$.

a_w = Surface area per unit mass of spent adsorbent $\left(\frac{m^2}{kg}\right)$.

Wa_w = Total area of spent adsorbent (m^2).

W = mass the adsorbent particle

D_b = Diffusion co-efficient of 'b' (NAs) molecules $\left(\frac{m^2}{Sec}\right)$.

δ = Boundary layer thickness (m).

$k_b = \frac{D_b}{\delta}$ = Mass transfer co-efficient $\left(\frac{m}{Sec}\right)$

In the boundary layer the diffusion occurred at a high rate and there exists a concentration $\left(\frac{kg}{m^3}\right)$, which is C_b^*.

C_b = Concentration of 'b' (NAs) molecules in the bulk phase of solvent $\left(\frac{kg}{m^3}\right)$.

$C_b^* - C_b$ = Concentration gradient inside the stagnant film/boundary layer $\left(\frac{kg}{m^3}\right)$.

Mass change of the 'b' (NAs) molecules per unit time in the regenerating solvent can be defined as:

$$J_b = V\frac{dC_b}{dt} \tag{15}$$

Rearrangement of equations (14) and (15),

$$V\frac{dC_b}{dt} = Wa_w k_b(C_b^* - C_b) \tag{16}$$

Or,

$$\frac{dC_b}{(C_b^* - C_b)} = \frac{Wa_w k_b}{V}dt \tag{17}$$

Integrating equation (17) with boundary conditions, when t = 0; $C_b = 0$ and when t = t; $C_b = C_b$.

$$-[ln(C_b^* - C_b)]_0^{C_b} = \frac{Wa_w k_b}{V}[t]_0^t \tag{18}$$

Or,

$$lnC_b^* - ln(C_b^* - C_b) = \left(\frac{Wa_w k_b}{V}\right)t \tag{19}$$

Or,

$$\ln\left(\frac{C_b^*}{C_b^* - C_b}\right) = \left(\frac{Wa_w k_b}{V}\right)t \tag{20}$$

At any time, rate of desorption is equal to rate of increase in adsorbate concentration in solvent. Applying the law of conservation of mass, the concentration of NAs molecules in the boundary layer/stagnant film (C_b^*) at a given moment, t during the batch experiment is calculated by the following relation,

$$-W\frac{dQ}{dt} = +V\frac{dC_b}{dt} \tag{21}$$

Or,

$$-WdQ = +VdC_b \tag{22}$$

Or,

$$-W\int_{Q=Q_m}^{Q=0} dq_a = +V\int_{C_b=0}^{C_b=C_b^*} dC_b \tag{23}$$

Or,

$$-W[-Q_m] = VC_b^* \tag{24}$$

Or,

$$C_b^* = \frac{Q_m \times W}{V} \tag{25}$$

For evaluating the unknown constant value of C_b^* and $a_w k_b$, the kinetics of batch desorption process were conducted in which the necessary operating parameter W and V are known and experimental parameters Q_m and $C_b = \int(t)$ are measured.

The following procedure was adopted to determine the desorption parameters:

- a_w and k_b were determined from the slope $\left(\frac{W a_w k_b}{V}\right)$ of the equation (20).
- Mass transfer co-efficient $\left(k_b = \frac{D_b}{\delta}\right)$ was determined by the measured surface area (a_w) of adsorbent.

Figure 4.13 represents the kinetic study of batch regeneration of spent GAC for 2-naphthoic acid in three different shaking speeds to determine the mass transfer co-efficient during desorption. The resultant data are plotted in Figure 4.14 based on Equation (20) for three individual shaking speeds, which showed mass transfer co-efficient (k_b) increased with increasing shaking speed. The mass transfer/diffusion co-efficient of 2-naphthoic acid during regeneration is measured since W, V and a_w are the known parameters for individual speed. The desorption model parameters are e presented in Table 4.8. As expected, shaking speed influences the mass transfer coefficient of the adsorbate molecules during desorption with methanol. The mass transfer co-efficient is comparatively higher for higher shaking speed of 250 rpm and 300 rpm $\left(1.38 \times 10^{-7} and\ 1.46 \times 10^{-7} \frac{m}{Sec}; respectively\right)$ than that of lower speed such as 200 rpm $\left(7.85 \times 10^{-8} \frac{m}{Sec}\right)$. The estimated mass transfer coefficient can be used to quantify the mass transfer between methanol and GAC carbon adsorbent used in this study. Quantifying the mass transfer co-efficient allows for design and manufacture of equipment for the adsorption-regeneration NAs recovery process for OSPW treatment.

Table 4-8 Desorption model parameters at different agitation speeds during batch regeneration of GAC with about 100 mg/g of adsorbed 2-naphthoic acid. Mass of the spent GAC, W = 0.1 g, volume of methanol, V = 40 mL (0.00004 m^3), and pH = 11.71.

Agitation speed (rpm)	Weight of spent GAC, W (g)	Surface area of GAC, $a_w \left(\frac{m^2}{g}\right)$	Slope, $\frac{Wa_wk_b}{V}$ $\left(\frac{1}{Sec}\right)$	Mass transfer co-efficient, $k_b = \frac{D_b}{\delta}\left(\frac{m}{Sec}\right)$	R^2
200	0.1	1372±27	0.275	7.85×10^{-8}	0.98
250	0.1	1372±27	0.483	1.38×10^{-7}	0.98
300	0.1	1372±27	0.513	1.46×10^{-7}	0.96

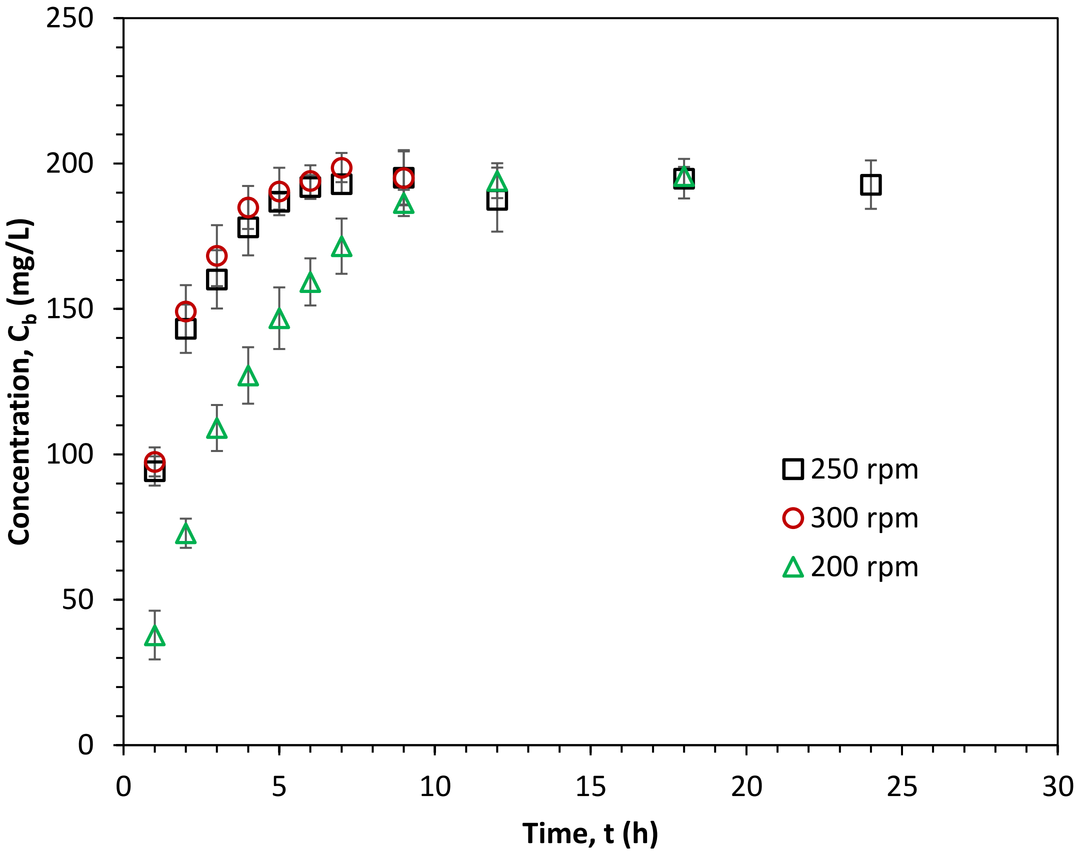


Figure 4-13 Concentration of the adsorbate during batch regeneration of spent GAC with about 100 mg/g of adsorbed 2-naphthoic acid. Mass of the spent GAC, W = 0.1 g, volume of methanol, V = 40 mL (0.00004 m^3), and pH = 11.71.

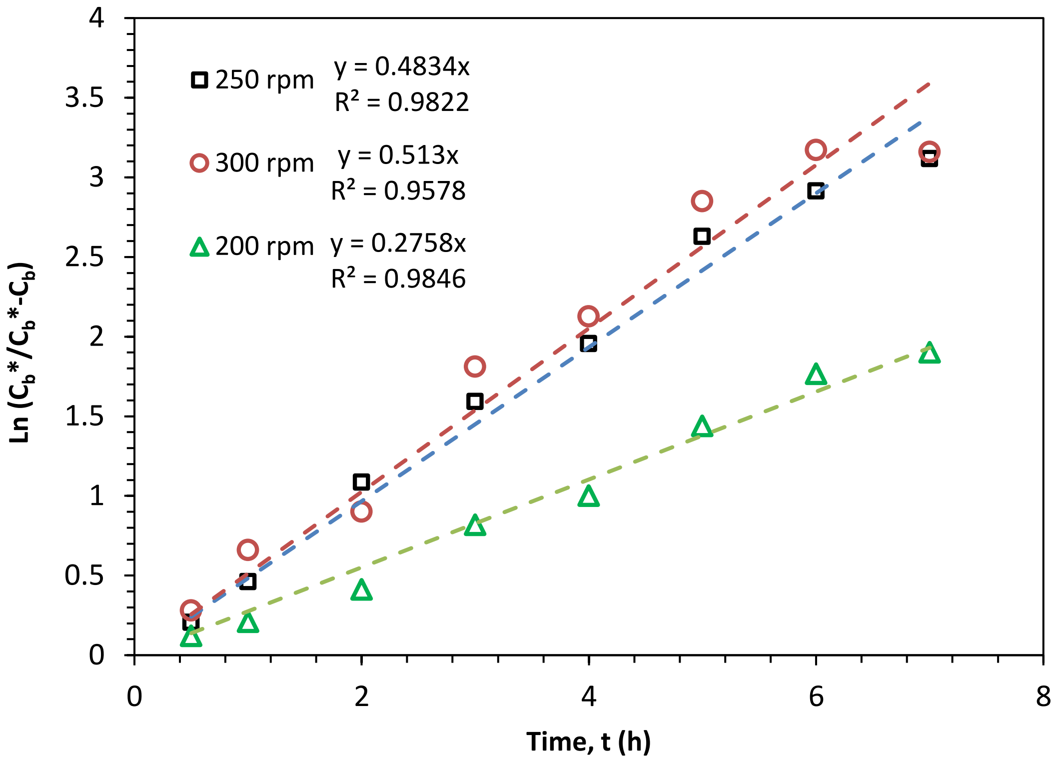


Figure 4-14 Linear relationship to determine the mass transfer co-efficient during batch regeneration of spent GAC with 100 mg/g adsorbed 2-naphthoic acid. Mass of the spent GAC, W = 0.1 g, volume of methanol, V = 40 mL (0.00004 m^3), and pH = 11.71.

4.3.10 Batch regeneration of spent APC for OSPW treatment

OSPW is a complex mixture of chemicals. Experiments were also conducted to determine the efficiency of methanol to regenerate the spent APC carbon adsorbent in OSPW treatment. TOC removal was used to determine the adsorption performance of APC at pH 4.0. Although, the original pH of OSPW from Suncor, Alberta, Canada was almost 8.5, the adsorption experiments were conducted at low pH 4.0 in order to achieve better removal of TOC. The results shown in Figure 4.15 are from the repetitive adsorption – regeneration cycles with APC for TOC removal from OSPW. First cycle of adsorption shows the average adsorption capacity of APC for OSPW was 171.4 mg TOC/g. A small loss of the adsorption capacity (by 16%) was observed after the fifth cycle. In each cycle, the spent APC was regenerated using 40 mL of methanol whose pH was adjusted to 11.71 with aqueous

NaOH. After regeneration, the extracted solution was diluted with the same volume of Milli-Q water, and then methanol was separated from the extracted solution by evaporation and collected by condensation. The remaining solution was analyzed to obtain the concentration of TOC. In first cycle, the average regeneration efficiency of APC was about 76%, and it dropped slightly to 65% after the fifth cycle.

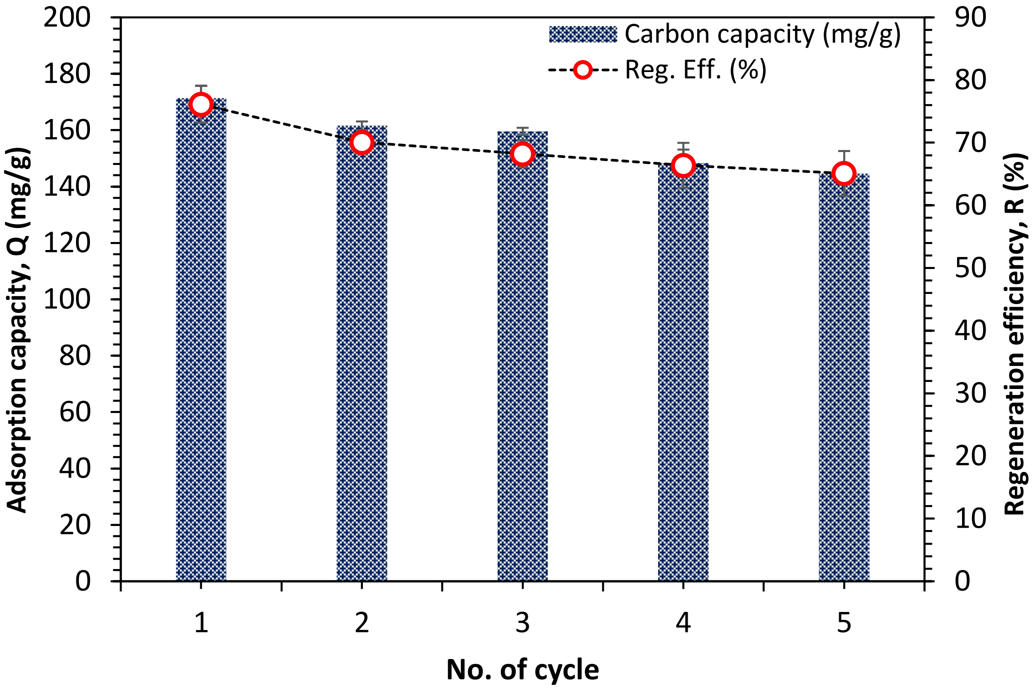


Figure 4-15 The adsorption capacity and regeneration efficiency in repeated batches of adsorption-regeneration cycles with APC for OSPW treatment. Adsorption conditions: carbon loading = 0.05 g, pH of OSPW was adjusted to 4.0, volume of solution = 250 mL, shaking speed = 250 rpm, temperature = 298 K. Regeneration conditions: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent APC carbon loading = 0.05 g.

4.4 Continuous-flow fixed-bed column study

From the above batch regeneration experiments, pure methanol with pH 11.71 was found to be quite effective for both spent GAC and APC saturated with NA model compounds

(2-naphthoic acid and diphenylacetic acid), as well as for the spent APC after OSPW treatment for TOC removal. In this part of work, a series of adsorption-desorption experiments were conducted in continuous-flow fixed bed column packed with 0.5 g GAC or APC activated carbons. Adsorption only occurs in a particular region of the bed, known as the mass transfer zone, which moves though the bed. The factors that determine the arrangement of the fixed-bed column include total feed flow rate, allowable pressure drop, energy demands, length of the mass transfer zone, method of adsorbent regeneration, and the capital investment. After adsorption of NAs, the regeneration of carbon bed was also conducted in the continuous-flow fixed-bed column system at the optimal conditions as determined in the previous batch adsorption tests, i.e., with methanol and NaOH mixture (pH 11.71). According to Tamon et al. [26], a lower flow rate of solvent increases the contact time, which facilitates the column regeneration. On the hand, however, a larger flow rate with a smaller possible total volume of the regeneration solvent is more economically attractive [26]. Based on our preliminary experiments, a suitable flowrate, 2.5 mL/min, was chosen in this work for the water solution and solvent flows in both adsorption and regeneration cycles in the continuous-flow fixed bed column.

4.4.1 Adsorption breakthrough curve

Typical adsorption breakthrough curves for different cycles that occurred during the adsorption of 2-naphthoic acid and diphenylacetic acid in the fixed bed column of APC particles (0.5g for 2-naphthoic acid or 1.0 g for diphenylacetic acid) are shown in Figure 4.16. After the break point, the bed started to be saturated and the outlet solute concentration increased rapidly, eventually approaching the inlet concentration as the entire bed is eventually saturated. For instance, with the 2-naphthoic acid the breakthrough occurred after 2000 min (or over 30 h) on-stream in cycle-1. In cycles 2-4 with regenerated APC packed-bed however the breakthrough occurred in a shorter time (<1000 min) on-stream. The bed adsorption capacity can be determined from the adsorption breakthrough curve. The steepness of the breakthrough curve determines the extent to which the capacity of an adsorbent bed can be utilized. Thus, the shape of the curve is very important in determining the length of the adsorption bed.

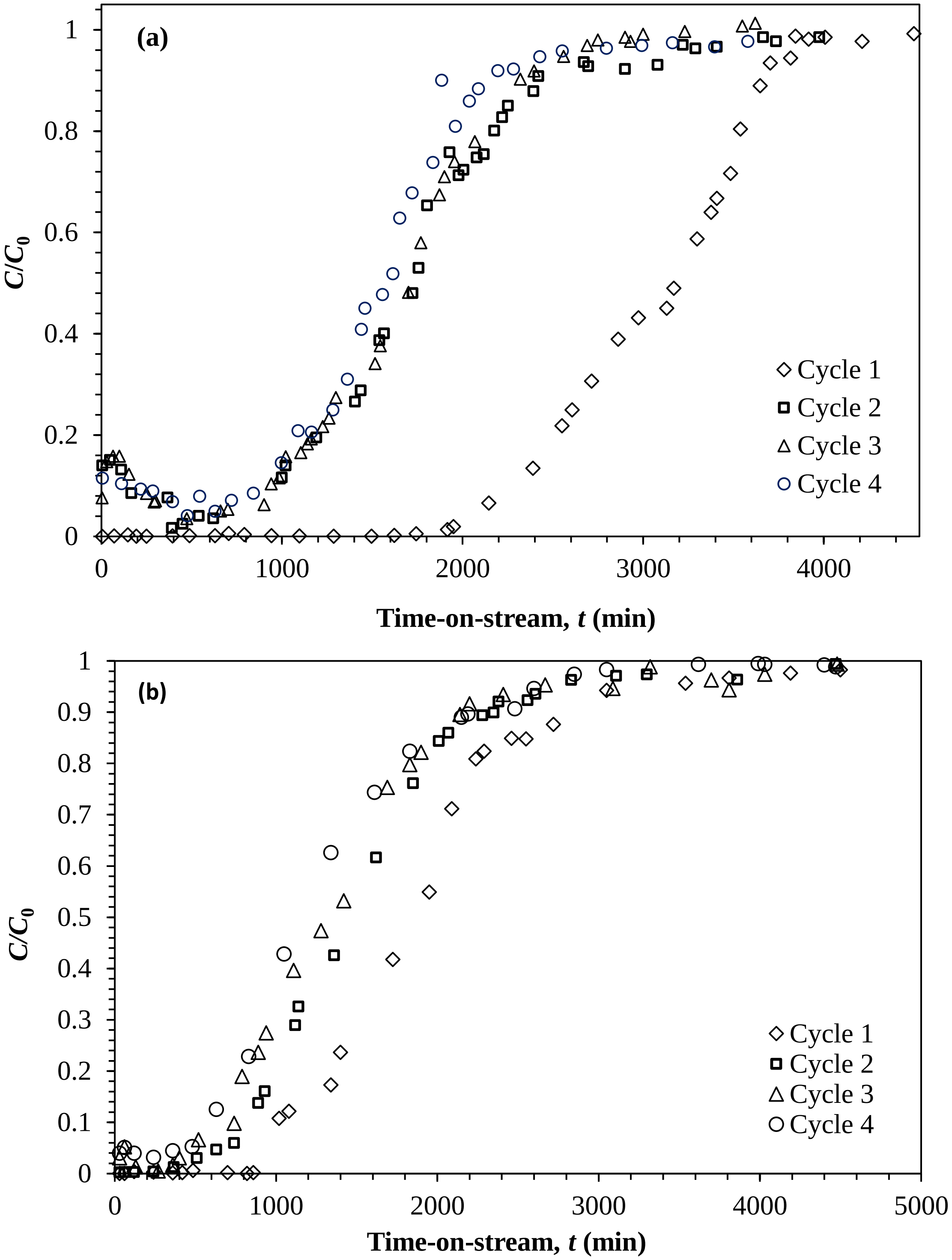
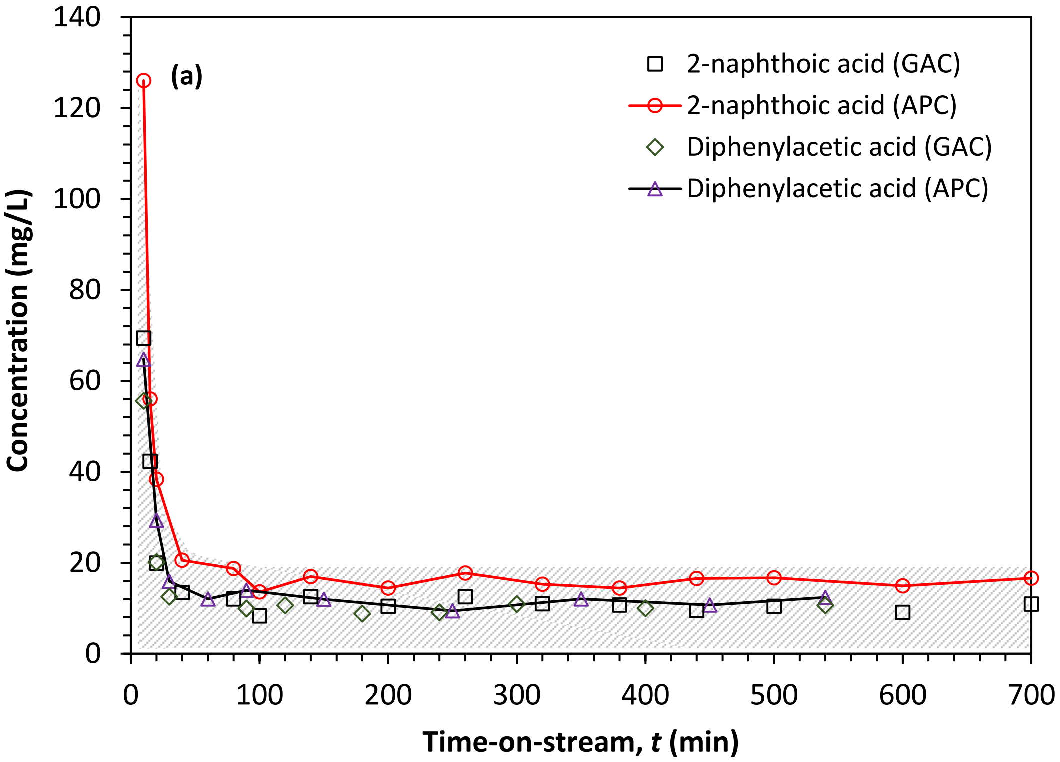


Figure 4-16 Typical absorption breakthrough curves during adsorption of (a) 2-naphthoic acid and (b) diphenylacetic acid in continuous-flow fixed-bed column of

APC (0.5 g for 2-naphthoic acid or 1.0 g for diphenylacetic acid), represented by the ratio of outlet to inlet solute concentration as a function of time-on-stream. Adsorption parameters:, temperature = 298 K, flow rate of the solution = 2.5 mL/min, pH = 4.0

4.4.2 Continuous-flow fixed-bed desorption

Typical desorption curves with methanol (pH = 11.71) are shown in Figure 4.17 (a).where the concentration of the desorbed 2-naphthoic acid and diphenylacetic acid from both spent GAC and APC in the first cycle are plotted with the time-on-stream. As shown in the Figure, very high NAs concentration was obtained in methanol within the first 1-2 h and most of the desorbed NAs was extracted by methanol. The amount of desorbed NAs can be calculated from the area under the desorption curves. Figure 4.17 (a) shows plots of desorption concentrations of the two NAs model compounds vs. time-on-stream where the areas under the desorption curves confirm the amounts of extracted NAs (i.e., 195 mg/g and 297 mg/g for extraction of 2-naphthoic acid with GAC and APC; respectively, and 143 mg/g and 165 mg/g for extraction diphenylacetic acid with GAC and APC; respectively). The amounts of extracted NAs were also estimated by multiplication of concentrations and the total volume of the water solution after the desorption experiments, obtaining the amounts of extracted NAs to be 193 mg/g and 298 mg/g for 2-naphthoic acid with GAC and APC, respectively, and 144 mg/g and 168 mg/g for diphenylacetic acid with GAC and APC; respectively. The values are quite similar with those estimated with the areas under the desorption curves. Figure 4.17 (b) plots the desorbed concentrations of 2-naphthoic acid and diphenylacetic acid as a function of the volume of methanol consumed in the continuous-flow solvent regeneration of the spent GAC and APC in a fixed-bed column.


(a)
2-naphthoic acid (GAC)
2-naphthoic acid (APC)
Diphenylacetic acid (GAC)
Diphenylacetic acid (APC)
Concentration (mg/L)
Time-on-stream, t (min)
0
20
40
60
80
100
120
140
0
100
200
300
400
500
600
700

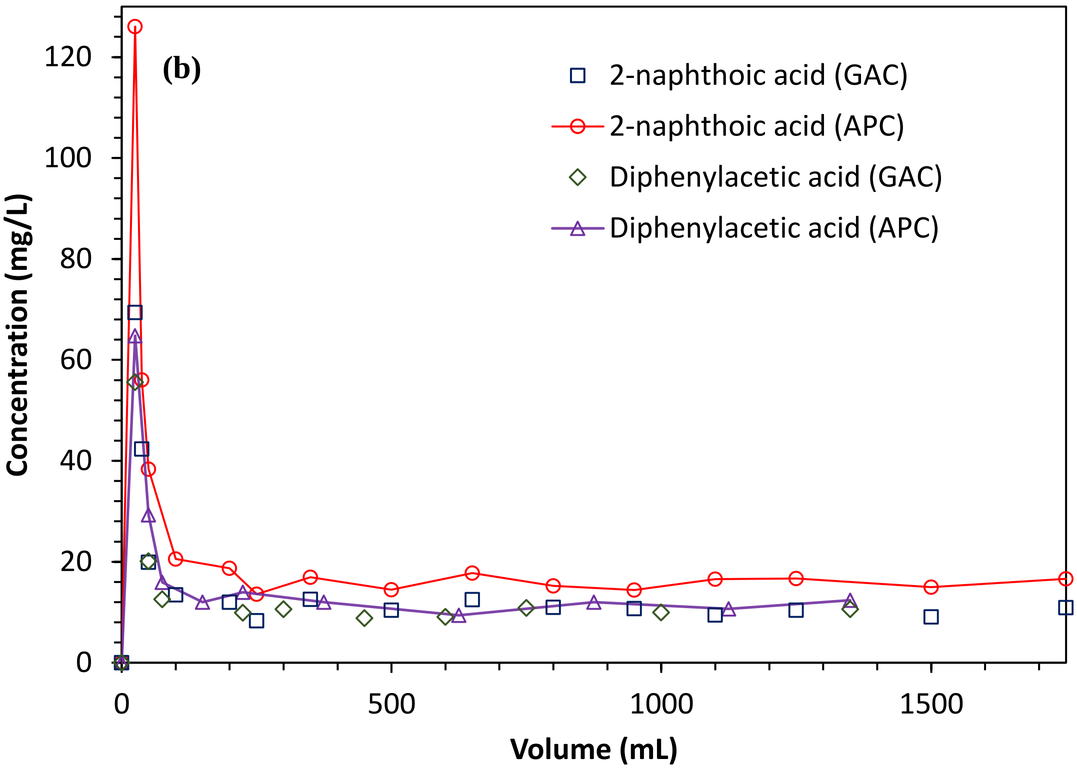


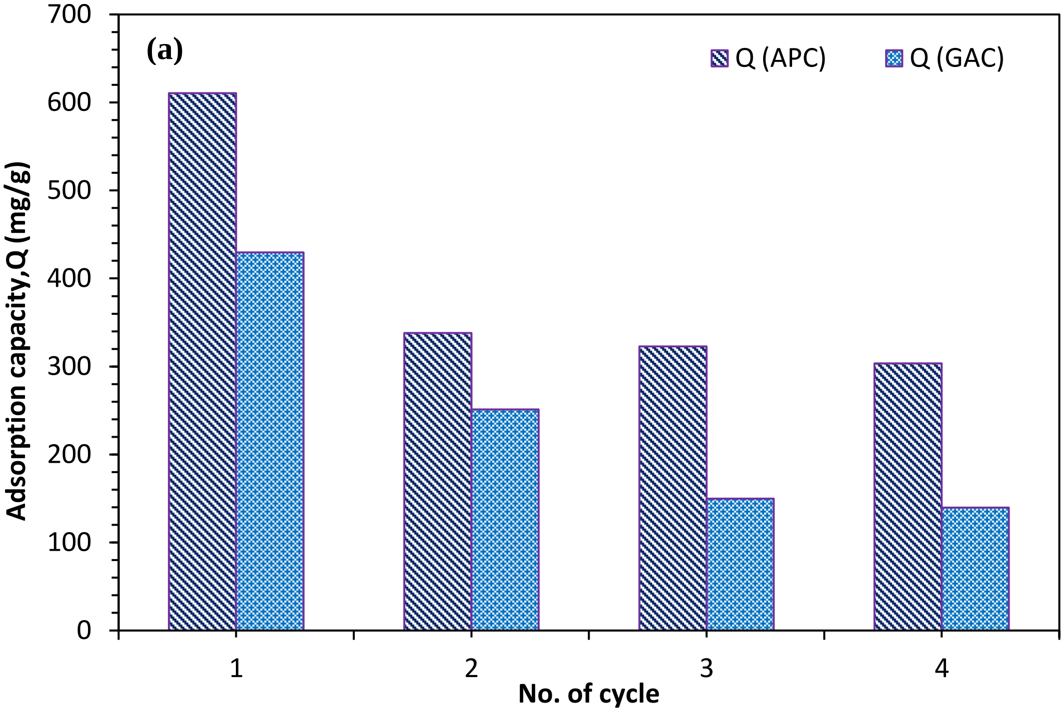
Figure 4-17(a) Concentration curves of desorbed 2-naphthoic acid and diphenylacetic acid in methanol (pH = 11.71) during the first cycle of desorption from spent carbon (GAC and APC); (b) Concentration curves of desorbed 2-naphthoic acid and diphenylacetic acid as a function of the volume of methanol consumed in the continuous-flow solvent regeneration of the spent GAC and APC in a fixed-bed column in first cycle. Adsorption and regeneration conditions: flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading in the packed bed column = 0.5 g for 2-naphthoic acid and = 1.0 for diphenylacetic acid.

4.4.3 Continuous-flow fixed-bed adsorption – regeneration cycle

The regeneration efficiencies of the repeated adsorption – regeneration cycles for 2-naphthoic acid are shown in Figure 4.18. After complete column regeneration, milli-Q water was passed though the column to wash out the regenerant solution before the next adsorption cycle. The adsorption of 2-naphthoic acid was conducted with both GAC and APC at two different pH (4.0 and 8.0). The results shown in Figure 4.18 (a) indicate that pH = 4.0 shows much higher adsorption capacity for both GAC (430, 251, 150, and 140 mg/g) and

APC (611, 388, 323, and 303 mg/g) during the first, second, third and fourth consecutive adsorption cycles, respectively. On the other hand, in Figure 4.18 (b), the adsorption capacity for 2-naphthoic acid at pH = 8.0 was found comparatively lower for GAC (137, 126, 112, 117 mg/g) and for APC (195, 143, 135, 129 mg/g) in the four repeated cycles, respectively. The adsorption capacity of adsorbents is highly dependent on solution pH, and the capacity was found to decrease with increasing pH, which was the case for both the model NAs tested. The naphthenic acids are mostly deprotonated at pH =8.0, and the surfaces of GAC and APC used in this study are positive at pH = 8.0 with $pH_{pzc} > 9.0$, which would promote the electrostatic interaction between the model NAs and the activated carbon surface. On the other hand, at low pH of 4.0, both the naphthenic acids are protonated and the surfaces of the activated carbons are also positive, not favorable for the electrostatic interaction between the model NAs and the activated carbon surface. Therefore, hydrophobic interaction rather than electrostatic interaction between the model NAs and the activated carbon surface seems to be more dominant mechanism for adsorption of the NAs by activated carbon adsorbents. The results also clearly indicate that APC has much higher adsorption capacity for adsorption of NA model compounds than GAC, likely due to its higher mesoporous area (Table 4.6).

It is interesting to see that the loss in adsorption capacity after the first cycle of adsorption and regeneration was more than the successive cycles for both types of carbon adsorbents. In addition, the loss was higher in pH 4.0 compared to that at pH 8.0. It is probably due to the fact that adsorption is stronger at low pH, hence making it more difficult for complete regeneration. In order to understand the reason behind the decline in adsorption capacity after solvent regeneration, the regenerated activated carbon was characterized by textural properties analysis (using N_2 isothermal adsorption) during batch repetitive adsorption – regeneration cycles. Solvent regeneration did not change the surface area, pore volume, and average pore size of the adsorbents, therefore the decrease in adsorption capacity after the solvent regeneration was not caused by the change in pore structure of the regenerated adsorbents, rather due to the blockage of the active site by the incomplete desorption of adsorbate molecules [142]. The capacity decreases very slowly in the successive cycles for both types of carbon adsorbents. As is shown in Figure 4.18 (b), the adsorption capacity approaches to almost stable value (GAC→112 mg/g and APC→135 mg/g) after two repetitive adsorption – regeneration cycles. On the other hand, in Figure 4.18 (a), the adsorption capacity was found almost steady at 303 mg/g and 140 mg/g for APC and GAC, respectively after three consecutive adsorption – regeneration cycles.



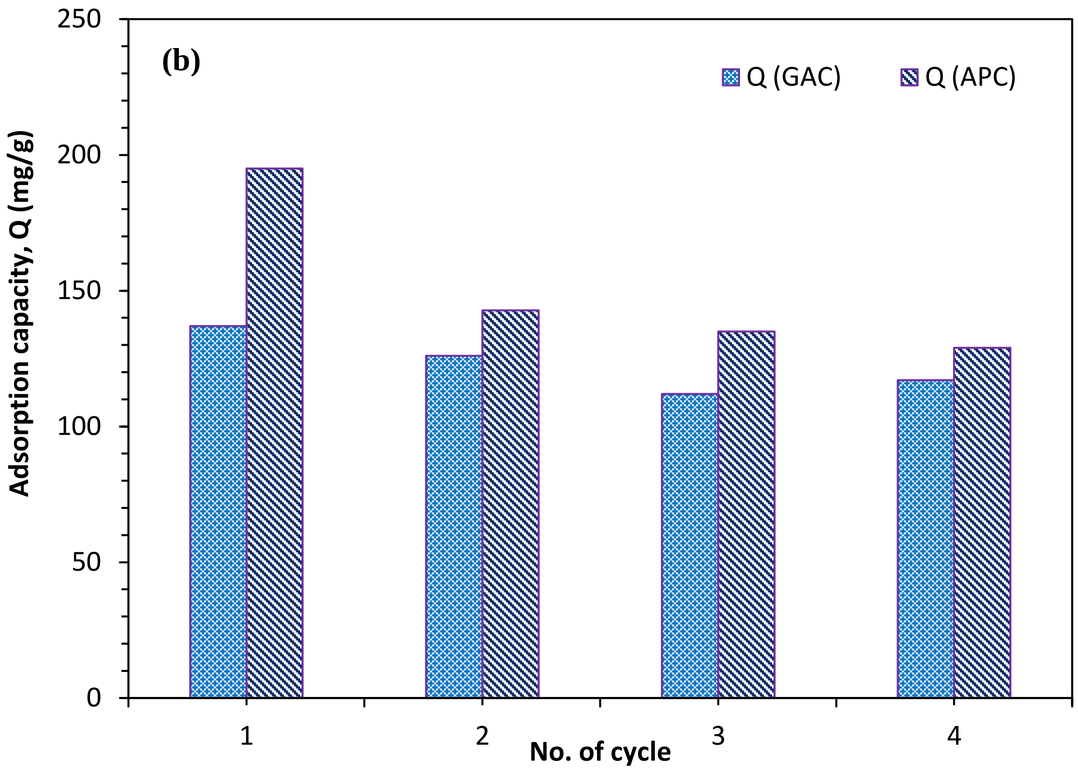
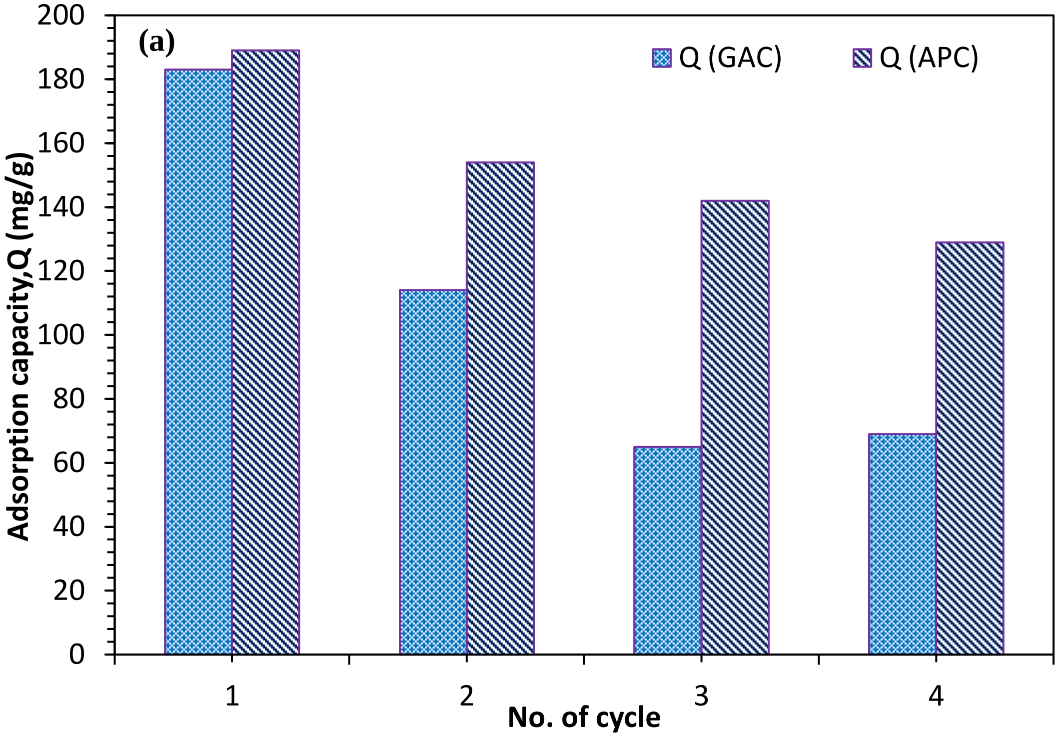


Figure 4-18 Repeated fixed bed column adsorption-regeneration cycles for 2-naphthoic acid removal from water solution at (a) pH = 4.0 and (b) pH = 8.0 using both GAC and APC (0.5 g loading). Adsorption parameters: flow rate of 2-naphthoic acid solution = 2.5 mL/min. Regeneration parameters: solvent (methanol) at pH = 11.71, operating time = 700 min, flow rate = 2.5 mL/min, and temperature = 298 K

Similarly, the adsorption was performed with diphenylacetic acid solution at two different pH (4.0 and 8.0) as shown in Figure 4.19. The adsorption capacity of diphenylacetic acid on both GAC and APC surface was lower than that of 2-naphthoic acid in each cycle (Figure 4.18). From Figure 4.19, the adsorption capacity for diphenylacetic acid at pH = 4.0 is much higher than that of pH = 8.0 with both GAC and APC. Similar to 2-naphthoic acid, continuous adsorption of diphenyl acetic acid also demonstrated similar behavior such as (i) loss of capacity was more in the first cycle of regeneration, and (ii) the loss in capacity was more when adsorption was conducted at pH 4.0 than that at pH 8.0.


(a)
Q (GAC)
Q (APC)
Adsorption capacity,Q (mg/g)
0
20
40
60
80
100
120
140
160
180
200
1
2
3
4
No. of cycle

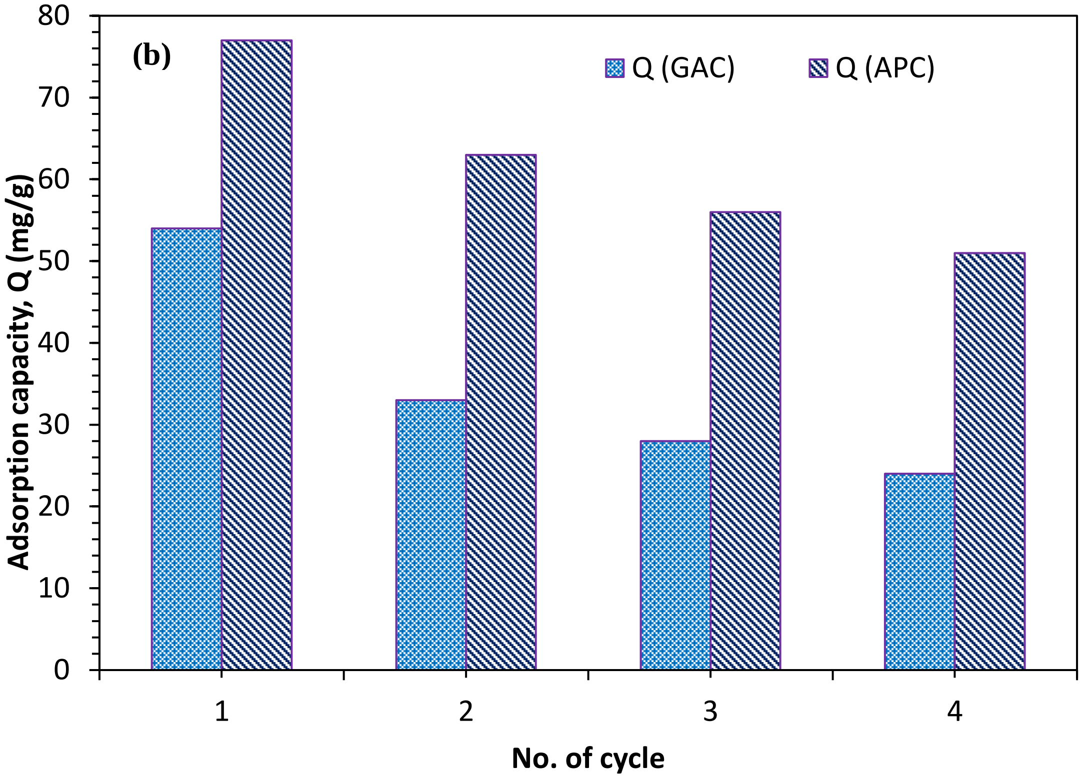


Figure 4-19 Repeated fixed bed column adsorption-regeneration cycles for diphenylacetic acid removal from water solution at (a) pH = 4.0 and (b) pH = 8.0 using both GAC and APC (1.0 g loading). Adsorption parameters: flow rate of diphenylacetic acid solution = 2.5 mL/min. Regeneration parameters: solvent (methanol) at pH = 11.71, operating time = 540 min, flow rate = 2.5 mL/min, and temperature = 298 K

In this part of the study, the repeated adsorption – regeneration cycles were also conducted for real OSPW treatment. The apparent color of extracted solutions of organics from OSPW and the 2-naphthoic acid model compound during desorption test in the fixed-bed column studies confirms the regeneration of spent carbon by methanol (Figure 4.20). The adsorptive capacity of the adsorbent (GAC and APC) in the column was evaluated by flowing the OSPW through the column continuously for 9 h. Since, the actual composition of OSPW is too complex to be determined, in this work the total organic carbon (TOC) of OSPW was measured to determine the performance of the adsorption process. It appears in Figure 4.21 (a) that the total loss of adsorption capacity over four adsorption – regeneration cycles was 47% and 28% for GAC and APC, respectively. Almost same results were found in Figure 4.21 (b), where the total loss of adsorption capacity over four adsorption – regeneration cycles was 41% and 30% for both GAC and APC; respectively. These results indicate that the adsorption capacity of APC can be recovered to a higher level than that of GAC by solvent regeneration, or in other words, the APC has better regenerability than GAC.

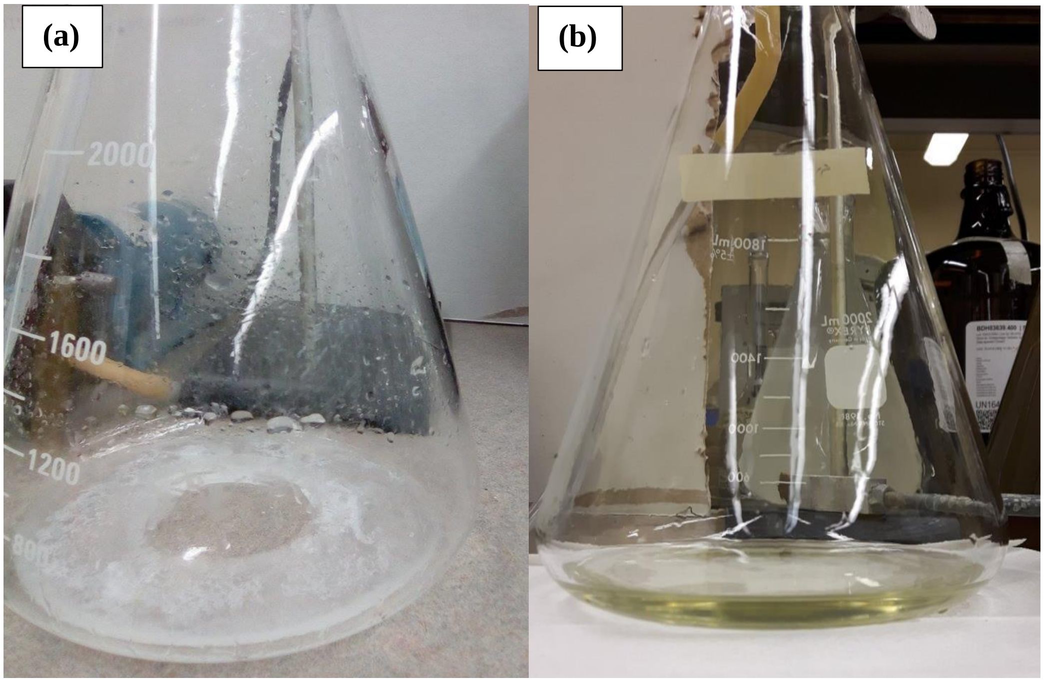


Figure 4-20 Apparent color of extracted solutions is the evidence for the methanol extracted (a) 2-naphthoic acid model compound and (b) organics from real OSPW during solvent regeneration of 2-naphthoic acid and OSPW in fixed-bed column with a flow of methanol at pH = 11.71.

Figure 4.21 (a) and (b) show the adsorption capacity as a function of the adsorption – regeneration cycle. As before with pure naphthenic acids model compounds, the capacity of APC for OSPW was higher than that of GAC, and the capacity was significantly higher at pH 4.0 compared to that at pH 8.0 due to the presence of naphthenic acids in OSPW.

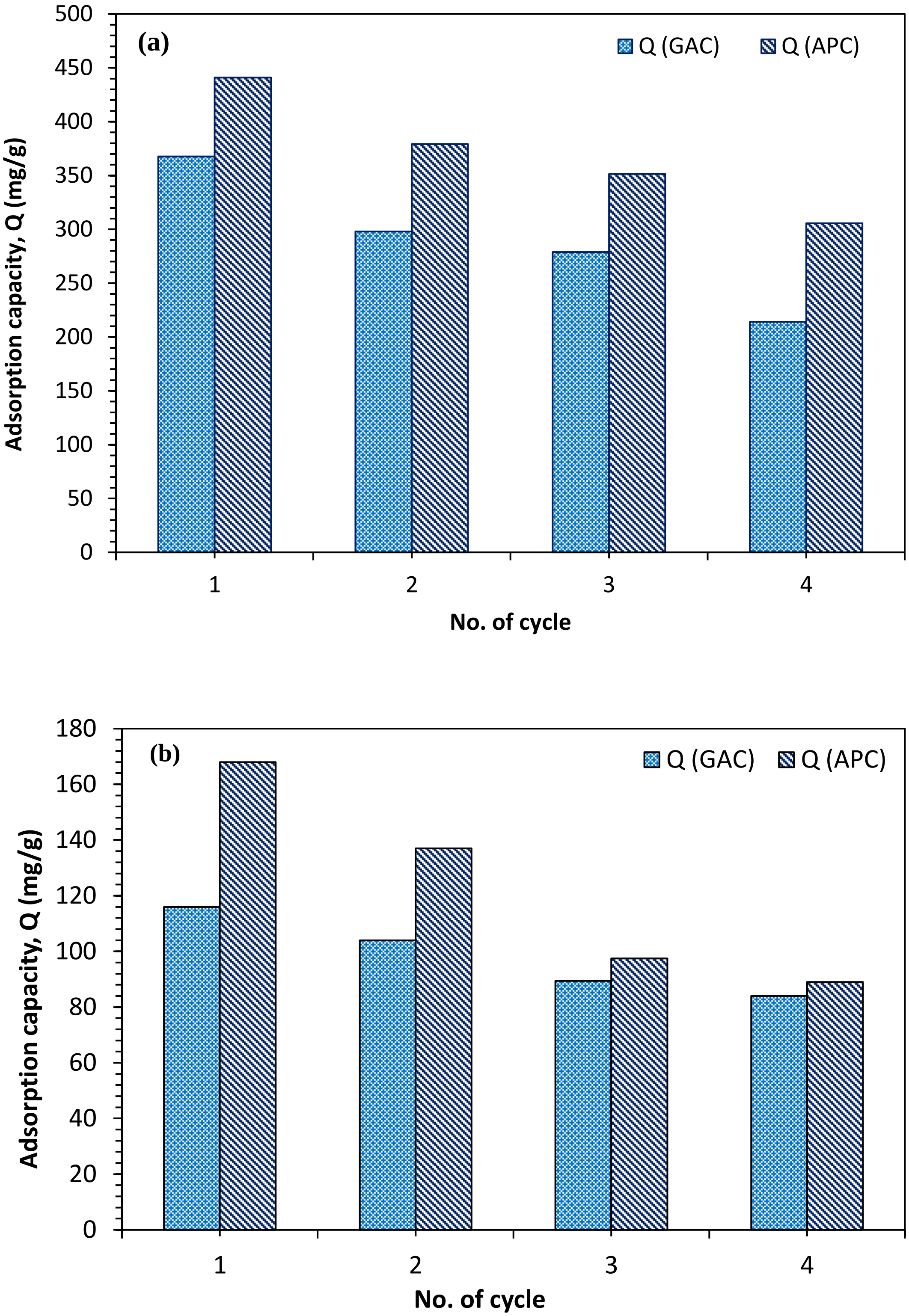


Figure 4-20 Repeated fixed bed column adsorption-regeneration cycles for OSPW treatment at (a) pH = 4.0 and (b) pH = 8.0 using both GAC and APC (0.5 g loading).

Adsorption parameters: flow rate of diphenylacetic acid solution = 2.5 mL/min. Regeneration parameters: solvent (methanol) at pH = 11.71, operating time = 540 min, flow rate = 2.5 mL/min, and temperature = 298 K

4.4.4 Solvent recycling and recovery of model compounds in the continuous-flow fixed-bed regeneration

After fixed-bed regeneration of spent carbon with methanol, the extracted solution was treated in the same way as in the batch regeneration process to recover the solvent and the adsorbate, and some representative results are presented in Table 4.9. During the extraction of 2-naphthoic acid from the fixed-bed spent APC, approximately 291 mg sodium 2-naphthoate was present in 1.75 L of exhausted methanol solution. Using, simple condensation process, about 1.62 L of methanol was retrieved in the first cycle. The results indicate that almost 90 – 93% methanol can be recovered from the different regeneration cycles. Rest of the methanol (bottom product) was left inside the flask, containing the desorbed sodium 2-naphthoate. After drying the bottom product, maximum 260 mg sodium 2-naphthoate was retrieved in the 1st cycle, i.e., 89% recovery efficiency. As shown in Table 4.9, approximately 73 – 91% of sodium 2-naphthoate were recovered in four different regeneration cycles.

Table 4-9 Solvent and adsorbate recovery in each regeneration cycle

No. of cycle	Recovered Solvent (L)	Solvent recovery efficiency	Desorbed 2-naphthoic acid salt (mg)	2-naphthoic acid salt recovery (mg)	2-naphthoic acid salt recovery efficiency
Cycle -1	1.62	**93.0%**	290.88	259.46	**89.2%**
Cycle -2	1.61	**92.3%**	157.69	134.80	**85.5%**
Cycle -3	1.58	**90.8%**	149.24	135.92	**91.0%**
Cycle -4	1.57	**90.0%**	136.99	100.26	**73.2%**

Fixed-bed regeneration parameters: adsorption capacity of the spent APC carbon was 610.66, 338.02, 322.87, and 303 mg/g in four successive cycles, methanol solvent pH was 11.71, operating time was 700 min, flow rate was 2.5 mL/min, about 1.75 L solvent is used to regenerate the spent carbon bed, temperature was 298 K, and loading of spent APC was 0.5 g in each cycle.

As mentioned above, the mixtures of NAs and other organic compounds can also be separated from the OSPW by using distillation column, although it is still challenging to identify and separate individual compounds from the complex mixture of OSPW.

Chapter 5

5 Conclusions & Recommendations

Adsorption is an established technology for removal of dissolved organics from various effluents. Although, there are numerous studies on evaluating various adsorbents and adsorption processes, very little research has been reported on the regeneration and recycling of the spent adsorbent. In this work, regeneration of two types of adsorbents based on activated carbon, a commercial granular activated carbon (GAC), and an activated petroleum coke (APC) was evaluated for the desorption of model naphthenic acids as well as organics from real oil sand process affected water (OSPW). Regenerated adsorbents were used for multiple adsorption cycles in both batch and continuous adsorption. Following conclusions are obtained.

5.1 Conclusions

- Among several suitable solvents, methanol was selected in batch tests involving desorption of model NAs (2-naphthoic acid and diphenylacetic acid) from spent carbons. Solubility of 2-naphthoic acid and diphenylacetic acid in methanol was determined experimentally based on precipitation method, and it was much higher than other solvents tested. In addition, methanol was selected based on low price, boiling point, and molecular weight.

- Although, solubility of the model NAs was quite high in methanol, desorption of NAs from the spent carbon adsorbents using only methanol was not efficient making the process economically not viable. Addition of aqueous NaOH to methanol drastically improved the batch desorption of naphthenic acids from spent carbon (GAC and APC) due to the formation of Na-salt of the acids. The optimum conditions for batch regeneration for 0.1 g of spent GAC were determined to be pH 11.71, methanol loading of 40 mL, shaking speed at 250 rpm, temperature at 298 K and regeneration time of 6-7 h.

In batch experiment, methanol and aq. NaOH mixture could regenerate the spent carbons several times without significant reduction in the adsorption capacity. The loss in carbon capacity was found to be 8.86%, 36% and 15.66% for APC during 2-naphthoic acid, diphenylacetic acid and OSPW treatment, respectively, which signifies stable adsorption capacity after five adsorption cycles. However, the loss of GAC capacity was found to be 19% and 22% during the treatment of 2-naphthoic acid and diphenylacetic acid, respectively after the fifth adsorption cycle. As such, the adsorption capacity of APC can be recovered to a higher level than that of GAC by solvent regeneration, or in other words, the APC has better regenerability than GAC.

- The methanol and aq. NaOH mixture did not change the surface structure and area of the activated carbon, the loss in adsorption capacity was due more for stronger adsorption of the naphthenic acids and OSPW organics.

- Methanol is fairly volatile and can be easily separated from the exhausted solution by a simple distillation process due to the wide difference in the boiling point of methanol (65 °C) and NAs (> 250 °C). The purified solvent was used for further regeneration of the spent carbon. About 86% to 92% of methanol was retrieved during the five cycles of batch regeneration process. About 73% to 84% adsorbate (Na-salt of the naphthenic acids) was recovered during the five cycles of batch desorption process.

- A mass transfer model for desorption of adsorbate molecules from the surface of the adsorbent into bulk phase of the solvent was developed based on adsorbate diffusion though the stagnant layer around the adsorbent particles. The desorption kinetics data were fitted to the model equations and the estimated mass transfer co-efficient was 1.55×10^{-7}, 2.68×10^{-7} and 2.84×10^{-7} m/sec for the batch regeneration process under 200 rpm, 250 rpm and 300 rpm agitation speed, respectively.

- Based on batch regeneration results, the continuous-flow fixed-bed column study was conducted by using the optimum conditions. Adsorption at pH = 4.0 gives the better adsorption capacity than pH = 8.0. Highest adsorption capacity of about 611 mg/g, 189 mg/g and 441 mg-TOC/g for 2-naphthoic acid, diphenylacetic acid and OSPW was obtained during the adsorption with APC at pH = 4.0, respectively. Total loss in carbon capacity after five cycles was about 50%, 32% and 30% for APC for 2-naphthoic acid, diphenylacetic acid and OSPW treatment, respectively. The regeneration efficiency for

APC in first cycle was about 95%, 89% and 86% during the extraction of 2-naphthoic acid, diphenylacetic acid and OSPW, respectively.

5.2 Recommendations

Recommendations for future work are provided below:

- An area of interest that needs to be investigated is the impact of temperature on desorption process, as temperature decreases the forces of attraction of the adsorbate and adsorbent.

- The effects of process variables such as flow rate, pH, and presence of background organics, packing of the carbon should be tested for continuous column desorption.

- The mechanism of drastic loss in activity in the first regeneration cycle should be studied for more efficient regeneration.

- A cost analysis should be conducted comparing regeneration and disposal of spent carbon adsorbents.

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Appendices

Appendix A: Raw data (batch regeneration of spent carbon)

Table A- 1: Determination of solubility saturation point of 2-naphthoic acid and di-phenylacetic acid in methanol (Figure 4.1)

2-naphthoic acid with methanol				
2100 mL times dilution				
Concentration (g/L)	Original dosage (amount of 2-naphthoic acid/volume of methanol)	5 µL solution has been taken and added 10.5 mL solvent	Concentration (mg/L)	peak area
0	0		0	0
105	525 mg/5mL		50	75.25
275	1375 mg/5mL		130.95	197.09
305	1525 mg/ 5mL		145.23	218.58
309	1545 mg/ 5mL		147.14	221.46
311	1555 mg/5 mL		148.09	220.31
312	1560 mg/ 5mL		149	221.08
315	1575 mg/5 mL		150	219.89
320	1600 mg/5mL		152.38	221.44
Diphenylacetic acid with methanol				
2100 mL times dilution				
Concentration (g/L)	Original dosage (amount of diphenylacetic acid/volume of methanol)	5 µL solution has been taken and added 10.5 mL solvent	Concentration (mg/L)	peak area
0	0		0	0
100	500 mg/5mL		47.61	171.87
200	1000 mg/5mL		95.23	343.79
263	1315 mg/ 5mL		125.23	452.09
270	1350 mg/ 5mL		128.57	464.15
274	1370 mg/5 mL		130.47	463.3
278	1390 mg/ 5mL		132.38	464.18
280	1400 mg/5 mL		133.33	463.91
285	1425 mg/5mL		135.71	463.54

Table A- 2: Batch adsorption experiment of (a) 2-naphthoic acid (b) diphenylacetic acid on APC to determine the adsorption isotherm (Initial concentration of each model compound = 40 mg/L; volume of the solution = 175 mL; solution pH = 8.0;

adsorption equilibrium was reached within 48 h; and shaking speed = 250 rpm.) [Figure 4.2]

(a) 2-naphthoic acid				
Batch	Initial concentration, C_0 (mg/L)	Equilibrium concentration, C_e (mg/L)	Carbon dosage (g)	Adsorption capacity, Q_{max} (mg/g)
1	40	0.78	0.07	98.04
2	40	0.98	0.05	129.64
3	40	2.56	0.03	215
4	40	8.01	0.02	279.21
5	40	19.38	0.01	353.77
6	40	29.6	0.005	360
(b) Diphenylacetic acid				
Batch	Initial concentration, C_0 (mg/L)	Equilibrium concentration, C_e (mg/L)	Carbon dosage (g)	Adsorption capacity, Q_{max} (mg/g)
1	40	0.65	0.07	97.84
2	40	0.97	0.05	127.17
3	40	2.5	0.03	218.69
4	40	8.8	0.02	277.9
5	40	25.89	0.01	294.11
6	40	32	0.005	298

Table A- 3: Sample peak obtained during HPLC analysis for batch regeneration of spent GAC with different dosages of pure methanol. (Adsorption capacity of spent carbon: about 92 mg/g, carbon loading: 0.1 g, agitation speed: 250 rpm, agitation time: 24 h, and temperature: 298 K.) [Figure 4.3]

Adsorption capacity : 0.1 g of activated carbon contains 9.2 mg of 2-naphthoic acid			
a. 20 mL methanol			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
50.82	33.76	7.34	7.42
51.94	34.50	7.50	
51.34	34.11	7.41	
b. 40 mL methanol			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
42.48	28.22	12.27	11.89
40.52	26.92	11.70	
40.43	26.86	11.67	
c. 60 mL methanol			

Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
31.38	20.84	13.59	14.44
34.43	22.87	14.91	
34.2	22.72	14.81	
d. 80 mL methanol			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
31.56	20.96	18.23	18.34
31.59	20.98	18.25	
32.07	21.30	18.52	
e. 100 mL methanol			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
28.25	18.76	20.40	19.72
26.7	17.73	19.28	
26.99	17.93	19.49	

Table A- 4: Sample peak obtained during HPLC analysis for batch regeneration of spent GAC with methanol and NaOH (aq.) solution to understand the effect of desorbing agent on regeneration efficiency (Adsorption capacity of spent carbon: about 91 mg/g, carbon loading: 0.1 g, agitation speed: 250 rpm, agitation time: 24 h, and temperature: 298 K.) [Figure 4.4 (a)]

Adsorption capacity : 0.1 g of activated carbon contains 9.1 mg of 2-naphthoic acid			
a. 20 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D. E. (%)
356.52	236.87	52.05	51.10
351.33	233.42	51.3	
342.16	227.33	49.96	
b. 40 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D. E. (%)
233.01	154.81	68.04	69.39
216.16	143.61	63.12	
263.69	175.19	77	
c. 60 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D. E. (%)
156.08	103.69	68.36	65.08
146.2	97.13	64.04	

143.46	95.31	62.84	
d. 80 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D. E. (%)
128.69	85.5	75.16	69.65
115.32	76.61	67.34	
113.78	75.59	66.45	
e. 100 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D. E. (%)
89.17	59.24	65.09	64.93
96.14	63.87	70.18	
81.56	54.18	59.53	

Table A- 5: Sample peak obtained during HPLC analysis for batch regeneration of spent GAC with different pH of methanol (Adsorption capacity of spent carbon: about 89.5 mg/g, carbon loading: 0.1 g, agitation speed: 250 rpm, agitation time: 24 h, and temperature: 298 K) [Figure 4.4 (b)]

Adsorption capacity : 0.1 g of activated carbon contains 8.95 mg of 2-naphthoic acid			
a. 40 mL methanol + 1.6 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
206.5	137.19	61.31	58.16
184.62	122.66	54.82	
196.48	130.54	58.34	
b. 40 mL methanol + 2.4 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D.E. (%)
271.14	180.14	80.5	71.29
233.01	154.81	69.18	
216.16	143.61	64.18	
c. 40 mL methanol + 3.2 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D.E. (%)
275.43	182.99	81.78	82.25
271.13	180.13	80.5	
284.49	189.01	84.47	
d. 40 mL methanol + 4.0 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D.E. (%)
293.96	195.31	87.29	87.21

283.79	188.55	84.27	
303.29	201.50	90.06	
e. 40 mL methanol + 4.8 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D.E. (%)
218.35	145.07	64.83	69.17
236.21	156.93	70.13	
244.4	162.37	72.56	
f. 40 mL methanol + 5.6 mg NaOH (aq.)			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency (%)	Average D.E. (%)
207.13	137.61	61.5	61.45
219.73	145.98	65.24	
193.98	128.88	57.6	

Table A- 6: Extraction of 2-naphthoic acid from spent carbon (GAC) by methanol during kinetic study of batch regeneration in thee different shaking speed. (Regeneration parameters: adsorption capacity = 89.5 mg/g for 2-naphthoic acid, solvent volume = 40 mL, solvent pH = 11.71, operating temperature = 298 K, and spent carbon loading = 0.1 g in each batch.) [Figure 4.6, and Figure 4.12]

Shaking speed: 200 rpm			
2 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
109.77	72.93	32.59	32.51
105.18	69.88	31.23	
114.12	75.82	33.88	
5 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
210.14	139.61	62.39	60.13
206.96	137.50	61.45	
190.4	126.50	56.53	
7 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
234.26	155.64	69.56	71.94
245.42	163.05	72.87	
247.15	164.20	73.38	
9 hours regeneration			

Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
258.3	171.61	76.69	77.53
263.17	174.85	78.14	
261.92	174.01	77.77	
Shaking speed: 250 rpm			
2 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
208.92	138.80	62.03	64.00
211.34	140.41	62.75	
226.37	150.40	67.21	
5 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
285.74	189.84	84.84	83.53
278.71	185.17	82.75	
279.55	185.73	83.00	
7 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
294.3	195.53	87.38	86.22
286.72	190.49	85.13	
290.16	192.78	86.15	
9 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
293.96	195.30	87.28	87.20
283.79	188.55	84.26	
303.29	201.50	90.05	
Shaking speed: 300 rpm			
2 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
248.39	165.03	73.75	75.78
255.16	169.52	75.76	
262.13	174.15	77.83	
5 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
274.89	182.63	81.62	85.32
297.5	197.65	88.33	
289.63	192.43	86.00	

7 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
289.47	192.32	85.95	87.11
291.91	193.94	86.67	
298.77	198.50	88.71	
9 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
297.29	197.51	88.27	86.97
303.43	201.59	90.10	
278.03	184.72	82.55	

Table A- 7: Kinetic study of model compounds (2-naphthoic acid and diphenylaceteic acid) desorption from spent GAC. (Regeneration parameters: adsorption capacity = 89.5 mg/g for 2-naphthoic acid and 78.8 mg/g for diphenylacetic acid, solvent volume = 40 mL, solvent pH = 11.71, agitation speed = 250 rpm, operating temperature = 298 K, and spent carbon loading = 0.1 g in each batch). [Figure 4.7]

2-naphthoic acid extraction from spent GAC			
1 hour regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
134.89	89.62	40.05	42.13
146.13	97.08	43.38	
144.71	96.14	42.96	
2 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
208.92	138.8	62.03	64.00
211.34	140.41	62.75	
226.37	150.4	67.21	
3 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
230.9	153.4	68.55	71.58
251.46	167.07	74.66	
240.91	160.06	71.53	
4 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
266.08	176.78	79	79.59

271.89	180.64	80.73	
266.21	176.86	79.04	
5 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
285.74	189.84	84.84	83.53
278.71	185.17	82.75	
279.55	185.73	83	
6 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
292.23	194.15	86.77	85.77
284.72	189.16	84.54	
289.68	192.46	86.01	
7 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
294.30332	195.53	87.39	86.23
286.72599	190.50	85.14	
290.16105	192.78	86.16	
9 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
293.96655	195.31	87.29	87.21
283.79609	188.55	84.27	
303.29508	201.50	90.06	
12 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
298.34456	198.22	88.59	83.84
268.30467	178.26	79.67	
280.39472	186.29	83.26	
18 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
302.5	200.98	89.82	87.06
303.43	201.59	90.09	
273.72	181.85	81.27	
24 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
276.01671	183.38	81.96	86.15
292.04696	194.03	86.72	

302.28477	200.83	89.76	
Diphenylacetic acid extraction from spent GAC			
1 hour regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
156.029	43.22	21.93	23.32
162.744	45.08	22.88	
178.845	49.54	25.14	
2 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
264.26	73.2	37.15	37.58
224.477	62.18	31.56	
313.141	86.74	44.03	
3 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
339.639	94.08	47.75	48.65
377.906	104.68	53.13	
320.469	88.77	45.06	
4 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
481.047	133.25	67.63	63.63
449.928	124.63	63.26	
426.606	118.17	59.98	
5 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
470.686	130.38	66.18	69.44
511.661	141.73	71.94	
499.134	138.26	70.18	
6 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
486.318	134.71	68.38	72.83
502.852	139.29	70.70	
564.765	156.44	79.41	
7 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
521.949	144.58	73.39	75.79

541.986	150.13	76.20	
553.069	153.2	77.76	
9 hours regeneration			
Peak area	Concentration of methanol after regeneration (mg/L)	Desorption Efficiency, D.E. (%)	Average D.E. (%)
545.162	151.01	76.65	76.45
533.899	147.89	75.07	
552.13	152.94	77.63	

Table A- 8: Repeating batches of adsorption-regeneration cycles of 2-naphthoic acid. Regeneration parameters: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent carbon (GAC) loading = 0.1 g in each batch. [Figure 4.8]

Adsorption run	**Cycle – 1**		**Cycle – 2**		**Cycle – 3**		**Cycle – 4**		**Cycle – 5**	
	Peak area	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**
1.	6.16	4.09	10.59	7.03	10.3	6.84	15.61	10.37	17.38	11.54
2.	5.76	3.82	9.18	6.09	12.88	8.55	18.82	12.50	18.1	12.02
3.	7.52	4.99	8.9	5.91	13.15	8.73	10.53	6.99	14.25	9.46
Average concentration (mg/L)		**4.30**		**6.34**		**8.04**		**9.95**		**11.01**

Regeneration cycle: 1

Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	4.3 mg/L		Time	7 h
Average adsorption capacity, Q	89.25 mg/g		Shaking speed	250 rpm
Carbon loading	0.2 g		Spent carbon loading	0.1 g
Volume of untreated water	500 mL		Amount of 2-naphthoic acid on 0.1 g spent carbon	8.925 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	89.25%			

After spent carbon regeneration

Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
293.96	195.30	87.53	195.12	87.45
283.79	188.55	84.50		

303.29	201.50	90.31		
Regeneration cycle: 2				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	6.34 mg/L		Time	7 h
Average adsorption capacity, Q	84.15mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.1 g spent carbon	8.415 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	84.15%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
256.41	170.35	80.97	175.17	83.26
260.92	173.35	82.40		
273.66	181.81	86.42		
Regeneration cycle: 3				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	8.04 mg/L		Time	7 h
Average adsorption capacity, Q	80 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.1 g spent carbon	8.00 mg
Time	24 h			
Shaking speed	250 rpm			

Removal efficiency	80.00%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
254.88	169.34	84.67	161.76	80.88
244.72	162.59	81.29		
230.82	153.35	76.67		
Regeneration cycle: 4				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	9.95 mg/L		Time	7 h
Average adsorption capacity, Q	75.07 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.1 g spent carbon	7.507 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	75.07%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
219.17	145.61	77.58	145.73	77.65
218.35	145.07	77.29		
220.54	146.52	78.07		
Regeneration cycle: 5				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	11.01 mg/L		Time	7 h

Average adsorption capacity, Q	72.47 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.1 g spent carbon	7.247 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	72.47%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
197.94	131.51	72.58	132.49	73.13
204.99	136.19	75.17		
195.33	129.77	71.63		

Table A- 9: Repeating batch adsorption-regeneration cycles of diphenylacetic acid. Regeneration parameters: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent carbon (GAC) loading = 0.1 g in each batch. [Figure 4.8]

Adsorption run	**Cycle – 1**		**Cycle – 2**		**Cycle – 3**		**Cycle – 4**		**Cycle – 5**	
	Peak area	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**
1.	28.63	7.93	35.56	9.85	42.31	11.71	47.6	13.18	56.35	15.61
2.	27.62	7.65	37.19	10.29	44.87	12.43	49.84	13.80	51.12	14.15
3.	32.88	9.10	39.92	11.05	41.13	11.39	45.51	12.61	55.22	15.30
Average concentration (mg/L)		8.22		10.40		11.84		13.19		15.02
Regeneration cycle: 1										
Adsorption parameters					**Regeneration parameters**					
Initial concentration, C_0	40 mg/L				solvent volume	40 mL				

Final concentration, C	8.22 mg/L		Time	7 h
Average adsorption capacity, Q	79.45 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.1 g spent carbon	7.94 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	79.45%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
545.16	151	76.07	150.61	75.87
533.89	147.89	74.50		
552.13	152.94	77.04		
Regeneration cycle: 2				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	10.40 mg/L		Time	7 h
Average adsorption capacity, Q	74.0 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.1 g spent carbon	7.4 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	74.00%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
441.7	122.35	66.13		

456.92	126.56	68.41	127.44	68.89
481.69	133.42	72.12		
Regeneration cycle: 3				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	15.02 mg/L		Time	7 h
Average adsorption capacity, Q	70.4 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.1 g spent carbon	7.04 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	70.40%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
411.88	114.09	64.82	111.02	63.08
387.72	107.39	61.02		
402.82	111.58	63.39		
Regeneration cycle: 4				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	13.19 mg/L		Time	7 h
Average adsorption capacity, Q	67.02 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.1 g spent carbon	6.702 mg
Time	24 h			

Shaking speed	250 rpm			
Removal efficiency	67.02%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
359.17	99.49	59.37	101.57	60.62
373.35	103.41	61.72		
367.54	101.80	60.76		
Regeneration cycle: 5				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	15.02 mg/L		Time	7 h
Average adsorption capacity, Q	62.45 mg/g		Shaking speed	250 rpm
Carbon loading	0.1 g		Spent carbon loading	0.1 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.1 g spent carbon	6.245 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	62.45%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
337.94	93.60	59.95	90.93	58.24
330.59	91.57	58.65		
316.33	87.62	56.12		

Table A- 10: Repeating batch adsorption-regeneration cycles of 2-naphthoic acid. Regeneration parameters: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent carbon (APC) loading = 0.05 g in each batch. [Figure 4.9]

Adsorption run	**Cycle – 1 (pH = 4.0)**		**Cycle – 2 (pH = 4.0)**		**Cycle – 3 (pH = 4.0)**		**Cycle – 4 (pH = 4.0)**		**Cycle – 5 (pH = 4.0)**	
	Peak area	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**
1.	0.28	0.18	1.92	1.27	5.71	3.79	5.11	3.39	4.89	3.24
2.	0.29	0.19	1.6	1.06	3.18	2.11	7.47	4.96	5.01	3.32
3.	0.31	0.20	1.88	1.24	4.37	2.90	4.21	2.79	5.62	3.73
Average concentration (mg/L)		0.19		1.19		2.93		3.71		3.43

Regeneration cycle: 1				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	0.19 mg/L		Time	7 h
Average adsorption capacity, Q	199.05 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.05 g spent carbon	9.95 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	99.52%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
364.16	241.94	97.26	238.54	95.89
370.72	246.30	99.01		
342.25	227.39	91.41		

Regeneration cycle: 2				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	1.2 mg/L		Time	7 h
Average adsorption capacity, Q	194 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.05 g spent carbon	9.7 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	97.00%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
347.66	230.98	95.25	223.21	92.04
331.05	219.94	90.70		
329.19	218.71	90.19		
Regeneration cycle: 3				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	2.93 mg/L		Time	7 h
Average adsorption capacity, Q	185.35 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.05 g spent carbon	9.26 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	92.67%			

After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
316.4	210.21	90.80	205.40	88.72
301.25	200.15	86.45		
309.83	205.85	88.92		
Regeneration cycle: 4				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	3.71 mg/L		Time	7 h
Average adsorption capacity, Q	181.40 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.05 g spent carbon	9.07 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	90.72%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
297.84	197.88	87.27	185.90	81.98
261.55	173.77	76.63		
280.03	186.05	82.05		
Regeneration cycle: 5				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	3.43 mg/L		Time	7 h
Average adsorption capacity, Q	183 mg/g		Shaking speed	250 rpm

Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of 2-naphthoic acid on 0.05 g spent carbon	9.14 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	91.42%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
281.01	186.70	81.70	181.14	79.27
259.19	172.20	75.36		
277.73	184.52	80.75		

Table A- 11: Repeating batch adsorption-regeneration cycles of diphenylacetic acid. Regeneration parameters: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent carbon (APC) loading = 0.05 g in each batch. [Figure 4.9]

Adsorption run	**Cycle – 1 (pH = 4.0)**		**Cycle – 2 (pH = 4.0)**		**Cycle – 3 (pH = 4.0)**		**Cycle – 4 (pH = 4.0)**		**Cycle – 5 (pH = 4.0)**	
	Peak area	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**	**Peak area**	**Concentration (mg/L)**
1.	17.2	4.76	33.82	9.36	48.3	13.37	52.71	14.60	61.97	17.16
2.	14	3.87	31.46	8.71	47.08	13.04	58.1	16.09	69.11	19.14
3.	20.01	5.54	28.08	7.77	35.17	9.74	50.21	13.90	58.02	16.07
Average concentration (mg/L)		4.72		8.62		12.05		14.86		17.46

Regeneration cycle: 1				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	4.72 mg/L		Time	7 h

Average adsorption capacity, Q	176.36 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.05 g spent carbon	8.81 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	88.20%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
644.16	178.43	81.01	177.93	80.78
630.72	174.70	79.32		
652.25	180.67	82.03		
Regeneration cycle: 2				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	8.62 mg/L		Time	7 h
Average adsorption capacity, Q	156.90 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.05 g spent carbon	7.844 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	78.45%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
494.22	136.89	69.84	142.80	72.86
550.02	152.35	77.73		

502.41	139.16	71.00		
Regeneration cycle: 3				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	12.05 mg/L		Time	7 h
Average adsorption capacity, Q	139.73 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.05 g spent carbon	6.986 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	69.88%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
462.7	128.16	73.44	122.79	70.36
445.36	123.36	70.69		
421.81	116.84	66.95		
Regeneration cycle: 4				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	14.86 mg/L		Time	7 h
Average adsorption capacity, Q	125.66 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.05 g spent carbon	6.283 mg
Time	24 h			
Shaking speed	250 rpm			

Removal efficiency	62.85%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
384.91	106.62	67.91	107.46	68.44
357.17	98.93	63.01		
421.81	116.84	74.42		
Regeneration cycle: 5				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	17.46 mg/L		Time	7 h
Average adsorption capacity, Q	112.70 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of diphenylacetic acid on 0.05 g spent carbon	5.634 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	56.35%			
After spent carbon regeneration				
Peak area	**Concentration (mg/L)**	**Regeneration Efficiency (%)**	**Average concentration (mg/L)**	**Average regeneration efficiency (%)**
304.35	84.30	59.89	94.09	66.85
387.09	107.22	76.18		
327.68	90.76	64.48		

Table A- 12: Repeating batch adsorption-regeneration cycles of OSPW. Regeneration parameters: solvent volume = 40 mL, solvent pH = 11.71, operating time = 6-7 h, agitation speed = 250 rpm, temperature = 298 K, and spent carbon (APC) loading = 0.05 g in each batch. [Figure 4.14]

Adsorption run	Cycle – 1 (pH = 4.0)	Cycle – 2 (pH = 4.0)	Cycle – 3 (pH = 4.0)	Cycle – 4 (pH = 4.0)	Cycle – 5 (pH = 4.0)
	TOC (mg/L)	TOC (mg/L)	TOC (mg/L)	TOC (mg/L)	TOC (mg/L)
1.	5.62	7.3	8.01	10.68	11.49
2.	6.84	7.71	7.82	11.27	11.01
3.	4.7	8.04	8.44	9.03	10.77
Average concentration (mg/L)	5.72	7.68	8.09	10.33	11.09

Regeneration cycle: 1				
Adsorption parameters			Regeneration parameters	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	5.72 mg/L		Time	8 h
Average adsorption capacity, Q	171.40 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of TOC on 0.05 g spent carbon	8.57 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	85.70%			

After spent carbon regeneration			
TOC (mg/L)	Regeneration Efficiency (%)	Average TOC (mg/L)	Average regeneration efficiency (%)
169.63	79.17	163.06	76.11
165.04	77.03		
154.52	72.12		

Regeneration cycle: 2				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	7.68 mg/L		Time	8 h
Average adsorption capacity, Q	161.58 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of TOC on 0.05 g spent carbon	8.08 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	80.80%			
After spent carbon regeneration				
TOC (mg/L)		**Regeneration Efficiency (%)**	**Average TOC (mg/L)**	**Average regeneration efficiency (%)**
141.43		70.01	141.53	70.06
137.14		67.89		
146.02		72.29		
Regeneration cycle: 3				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		Solvent volume	40 mL
Final concentration, C	8.09 mg/L		Time	7 h
Average adsorption capacity, Q	159.55 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of TOC on 0.05 g spent carbon	7.98 mg
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	79.78 %			

After spent carbon regeneration				
TOC (mg/L)		**Regeneration Efficiency (%)**	**Average TOC (mg/L)**	**Average regeneration efficiency (%)**
136.94		68.64	136.11	68.23
141.04		70.70		
130.35		65.34		
Regeneration cycle: 4				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	10.33 mg/L		Time	7 h
Average adsorption capacity, Q	148.37 mg/g		Shaking speed	250 rpm
Carbon loading	0.05 g		Spent carbon loading	0.05 g
Volume of untreated water	250 mL		Amount of TOC on 0.05 g spent carbon	7.42
Time	24 h			
Shaking speed	250 rpm			
Removal efficiency	74.18%			
After spent carbon regeneration				
TOC (mg/L)		**Regeneration Efficiency (%)**	**Average TOC (mg/L)**	**Average regeneration efficiency (%)**
120		64.69	123.14	66.39
132.39		71.37		
117.05		63.10		
Regeneration cycle: 5				
Adsorption parameters			**Regeneration parameters**	
Initial concentration, C_0	40 mg/L		solvent volume	40 mL
Final concentration, C	11.09 mg/L		Time	7 h
Average adsorption capacity, Q	144.55 mg/g		Shaking speed	250 rpm

<table>
<tr><td>Carbon loading</td><td>0.05 g</td><td rowspan="5"></td><td>Spent carbon loading</td><td>0.05 g</td></tr>
<tr><td>Volume of untreated water</td><td>250 mL</td><td rowspan="4">Amount of TOC on 0.05 g spent carbon</td><td rowspan="4">7.23 mg</td></tr>
<tr><td>Time</td><td>24 h</td></tr>
<tr><td>Shaking speed</td><td>250 rpm</td></tr>
<tr><td>Removal efficiency</td><td>72.28%</td></tr>
<tr><td colspan="5">After spent carbon regeneration</td></tr>
<tr><td colspan="2">TOC (mg/L)</td><td>Regeneration Efficiency (%)</td><td>Average TOC (mg/L)</td><td>Average regeneration efficiency (%)</td></tr>
<tr><td colspan="2">124.77</td><td>69.03</td><td rowspan="3">117.67</td><td rowspan="3">65.10</td></tr>
<tr><td colspan="2">119.09</td><td>65.89</td></tr>
<tr><td colspan="2">109.15</td><td>60.39</td></tr>
</table>

Appendix B: Raw data (continuous regeneration of spent carbon)

Table B- 1: Concentration of desorbed 2-naphthoic acid in methanol during the first cycle of spent carbon (GAC) regeneration. Regeneration parameters: solvent (methanol) volume = around 1.75 L, solvent pH = 11.71, operating time = 700 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g. Adsorption parameter: Carbon loading = 0.5 g, flow rate of 2-naphthoic acid solution = 2.5 mL/min, pH of the solution = 4.0, and adsorption capacity = 430 mg/g [Figure 4.16 (a) and Figure 4.16 (b)]

1st Regeneration cycle: 2-naphthoic acid (GAC)					
Time	**Peak area**	**Diluted concentration (mg/L)**	5 µL solution/add 50 µL methanol (**10 times dilutions**)	volume (mL)	Area under the concentration curve
0	0	0.00		0	
10	104.1	69.41		25	279.36
15	63.48	42.33		37.5	155.65
20	29.89	19.93		50	333.67
40	20.15	13.44		100	509.04
80	18.02	12.02		200	203.11
100	12.44	8.29		250	417.02
140	18.83	12.56		350	689.14
200	15.62	10.42		500	687.74
260	18.76	12.51		650	705.14
320	16.49	11.00		800	651.33
380	16.07	10.72		950	605.72
440	14.21	9.48		1100	596.12
500	15.59	10.40		1250	973.19
600	13.6	9.07		1500	1000.20
700	16.4	10.94		1750	
		Total area under the curve (mg/L x min)			7806.41
		Total area under the curve X 10 (mg/L x min)			**78064.11**
		Amount of desorbed 2-naphthoic acid in 0.5 g GAC			**195.16 mg**
		Regeneration efficiency obtained from the area under the curve			**90.77 %**

Table B- 2: Concentration of desorbed 2-naphthoic acid in methanol during the first cycle of spent carbon (APC) regeneration. Regeneration parameters: solvent (methanol) volume = around 1.75 L, solvent pH = 11.71, operating time = 700 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g. Adsorption parameter: Carbon loading = 0.5 g, flow rate of 2-naphthoic acid solution = 2.5 mL/min, pH of the solution = 4.0, and adsorption capacity = 611 mg/g [Figure 4.16 (a) and Figure 4.16 (b)].

1st Regeneration cycle: 2-naphthoic acid (with APC)					
Time	**Peak area**	**Diluted concentration (mg/L)**		volume (mL)	Area under the concentration curve
0	0	0.00	5 µL solution/add 50 µL methanol (**10 times dilutions**)	0	
10	189.04	126.05		25	455.21
15	84.03	56.03		37.5	235.93
20	57.5	38.34		50	588.92
40	30.82	20.55		100	785.09
80	28.05	18.70		200	322.66
100	20.34	13.56		250	609.86
140	25.39	16.93		350	941.39
200	21.67	14.45		500	965.79
260	26.61	17.74		650	990.00
320	22.88	15.26		800	890.18
380	21.62	14.42		950	928.79
440	24.81	16.54		1100	996.20
500	24.99	16.66		1250	1580.98
600	22.43	14.96		1500	1578.32
700	24.91	16.61		1750	
		Total area under the curve (mg/L x min)			11869.31
		Total area under the curve X 10 (mg/L x min)			**118693.1**
		Amount of desorbed 2-naphthoic acid in 0.5 g GAC			**296.73 mg**
		Regeneration efficiency obtained from the area under the curve			**97.18 %**

Table B- 3: Concentration of desorbed Diphenylacetic acid in methanol during the first cycle of spent carbon (GAC) regeneration. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 540 min,

flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 1.0 g. Adsorption parameter: Carbon loading = 1.0 g, flow rate of diphenylacetic acid solution = 2.5 mL/min, pH of the solution = 4.0, and adsorption capacity = 184 mg/g [Figure 4.16 (a) and Figure 4.16 (b)].

1st Regeneration cycle: Diphenylacetic acid (GAC)					
Time	**Peak area**	**Diluted concentration (mg/L)**	5 μL solution/add 50 μL methanol (**10 times dilutions**)	volume (mL)	Area under the concentration curve
0	0	0.00		0	
10	201.06	55.59		25	378.61
20	72.8	20.13		50	163.37
30	45.37	12.54		75	674.47
90	35.94	9.94		225	308.62
120	38.47	10.64		300	583.64
180	31.89	8.82		450	536.85
240	32.83	9.08		600	598.98
300	39.38	10.89		750	1043.37
400	36.09	9.98		1000	1442.53
540	38.44	10.63		1350	
		Total area under the curve (mg/L x min)			5730.43
		Total area under the curve X 10 (mg/L x min)			**57304.35**
		Amount of desorbed Diphenylacetic acid in 1.0 g GAC			**143.26 mg**
		Regeneration efficiency obtained from the area under the curve			**77.86 %**

Table B- 4: Concentration of desorbed Diphenylacetic acid in methanol during the first cycle of spent carbon (APC) regeneration. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 540 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 1.0 g. Adsorption parameter: Carbon loading = 1.0 g, flow rate of diphenylacetic acid solution = 2.5 mL/min, pH of the solution = 4.0, and adsorption capacity = 189 mg/g [Figure 4.16 (a) and Figure 4.16 (b)].

1st Regeneration cycle: Diphenylacetic acid (with APC)					
Time	**Peak area**	**Diluted concentration (mg/L)**	5 μL solution/add 50 μL methanol (**10 times dilutions**)	volume (mL)	Area under the concentration curve
0	0	0.00		0	

10	234.32	64.79		25	470.59
20	106.07	29.33		50	226.29
30	57.61	15.93		75	419.35
60	43.5	12.03		150	389.95
90	50.52	13.97		225	778.98
150	43.39	12.00		375	1070.33
250	34.03	9.41		625	1072.41
350	43.54	12.04		875	1136.42
450	38.66	10.69		1125	1039.82
540	44.91	12.42		1350	
		Total area under the curve (mg/L x min)			6604.13
		Total area under the curve X 10 (mg/L x min)			**66041.33**
		Amount of desorbed Diphenylacetic acid in 1.0 g GAC			**165.10 mg**
		Regeneration efficiency obtained from the area under the curve			**87.35 %**

Table B- 5: Repeating column adsorption-regeneration cycles for 2-naphthoic acid removal. Regeneration parameters: solvent (methanol) volume = around 1.75 L, solvent pH = 11.71, operating time = 700 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g in each cycle for both GAC and APC. Adsorption parameter: carbon loading = 0.5 g, flow rate of 2-naphthoic acid solution = 2.5 mL/min, and pH of the solution = 4.0 during the treatment process by using both GAC and APC. [Figure 4.17 (a)]

No. of cycle	Adsorbent	Q_{max} (mg/g) at pH 4.0	Q_{max} for 0.5 g AC (mg)	Total volume of solvent (L)	Peak area	Concentration (mg/L)	Desorbed 2-naphthoic acid (mg)	Regeneration efficiency (%)
Cycle-1	GAC	429.74	214.87	1.75	164.06	109.39	191.44	89.1
	APC	610.66	305.33		249.11	166.10	290.68	95.20
Cycle-2	GAC	251.08	125.54		93.49	62.33	109.09	86.89
	APC	338.02	169.01		135.14	90.11	157.69	93.30
Cycle-3	GAC	149.79	74.895		54.84	36.56	63.99	85.44
	APC	322.87	161.43		128.11	85.42	149.49	92.60
Cycle-4	GAC	139.67	69.835		48.73	32.49	56.86	81.42
	APC	303.35	152.00		117.88	78.60	137.55	90.69

Table B- 6: Table B-6: Repeating column adsorption-regeneration cycles for 2-naphthoic acid removal. Regeneration parameters: solvent (methanol) volume = around 1.75 L, solvent pH = 11.71, operating time = 700 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g in each cycle for both GAC and APC. Adsorption parameter: carbon loading =

0.5 g, flow rate of 2-naphthoic acid solution = 2.5 mL/min, and pH of the solution = 8.0 during the treatment process by using both GAC and APC. [Figure 4.17 (b)]

No. of cycle	Adsorbent	Q_{max} (mg/g) at pH 8.0	Q_{max} for 0.5 g AC (mg)	Total volume of solvent (L)	Peak area	Concentration (mg/L)	Desorbed 2-naphthoic acid (mg)	Regeneration efficiency (%)
Cycle-1	GAC	137	69	1.75	56.9	37.81	55.89	81
	APC	195	98		91.81	61	90.82	93
Cycle-2	GAC	126	63		49.86	33.13	49.14	78
	APC	143	71		65.19	43.31	64.53	90
Cycle-3	GAC	112	56		41.87	27.82	40.88	73
	APC	135	68		58.45	38.84	57.8	85
Cycle-4	GAC	117	59		42.14	28	41.3	70
	APC	129	65		55.07	36.59	54.6	84

Table B- 7: Repeating column adsorption-regeneration cycles for diphenylacetic acid treatment. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 540 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 1.0 g in each cycle for both GAC and APC. Adsorption parameter: carbon loading = 1.0 g, flow rate of diphenylacetic acid solution = 2.5 mL/min, and pH of the solution = 4.0 during the treatment process by using both GAC and APC. [Figure 4.18 (a)]

No. of cycle	Adsorbent	Q_{max} (mg/g) at pH 4.0	Q_{max} for 1.0 g AC (mg)	Total volume of solvent (L)	Peak area	Concentration (mg/L)	Desorbed diphenylacetic acid (mg)	Regeneration efficiency (%)
Cycle-1	GAC	184	184	1.35	383.79	106.31	143.5	78
	APC	188.5	188.5		448.63	124.27	167.8	89
Cycle-2	GAC	113.5	113.5		224.60	62.21	84.0	74

	APC	154	154		350.05	96.96	130.9	85
Cycle-3	GAC	65	65		126.89	35.15	47.5	73
	APC	141.5	141.5		310.28	85.95	116.0	82
Cycle-4	GAC	68.5	68.5		126.39	35.01	47.3	69
	APC	129	129		286.32	79.31	107.1	83

Table B- 8: Repeating column adsorption-regeneration cycles for diphenylacetic acid treatment. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 540 min, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 1.0 g in each cycle for both GAC and APC. Adsorption parameter: carbon loading = 1.0 g, flow rate of diphenylacetic acid solution = 2.5 mL/min, and pH of the solution = 8.0 during the treatment process by using both GAC and APC. [Figure 4.18 (b)]

No. of cycle	Adsorbent	Q_{max} (mg/g) at pH 8.0	Q_{max} for 1.0 g AC (mg)	Total volume of solvent (L)	Peak area	Concentration (mg/L)	Desorbed diphenylacetic acid (mg)	Regeneration efficiency (%)
Cycle-1	GAC	53.5	53.5	1.35	92.99	25.76	34.8	65
	APC	76.5	76.5		155.48	43.07	58.1	76
Cycle-2	GAC	33	33		55.60	15.40	20.8	63
	APC	63	63		121.30	33.60	45.4	72
Cycle-3	GAC	27.5	27.5		43.39	12.02	16.2	59
	APC	55.5	55.5		103.89	28.78	38.9	70
Cycle-4	GAC	23.5	23.5		35.19	9.75	13.2	56
	APC	50.5	50.5		90.48	25.06	33.8	67

Table B- 9: Repeating column adsorption-regeneration cycles in OSPW treatment. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 9 h, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g in each cycle for both GAC and APC. Adsorption parameter: Carbon loading = 0.5 g, flow rate of OSPW = 2.5 mL/min, and pH = 8.0 during the treatment process by using both GAC and APC. [Figure 4.20 (a)]

No. of cycle	Adsorbent	Q_{max} at pH 8.0 (mg/g)	Q_{max} for 0.5 g AC (mg)	Total volume of solvent (L)	TOC (mg/L)	Desorbed TOC (mg)	Regeneration efficiency (%)
Cycle-1	GAC	116	58	1.352	29.60	40.0	69
	APC	168	84	1.344	48.13	64.7	77
Cycle-2	GAC	104	52	1.349	25.06	33.8	65
	APC	137	68.5	1.3	41.10	53.4	78
Cycle-3	GAC	89.4	44.7	1.345	20.61	27.7	62
	APC	97.5	48.75	1.348	26.40	35.6	73
Cycle-4	GAC	84	42	1.339	19.13	25.6	61
	APC	89	44.5	1.35	23.40	31.6	71

Table B- 10: Repeating column adsorption-regeneration cycles in OSPW treatment. Regeneration parameters: solvent (methanol) volume = around 1.35 L, solvent pH = 11.71, operating time = 9 h, flow rate = 2.5 mL/min, temperature = 298 K, and carbon loading = 0.5 g in each cycle for both GAC and APC. Adsorption parameter: Carbon loading = 0.5 g, flow rate of OSPW = 2.5 mL/min, and pH = 4.0 during the treatment process by using both GAC and APC. [Figure 4.20 (b)]

No. of cycle	Adsorbent	Q_{max} at pH 4.0 (mg/g)	Q_{max} for 0.5 g AC (mg)	Total volume of solvent (L)	TOC (mg/L)	Desorbed TOC (mg)	Regeneration efficiency (%)
Cycle-1	GAC	368	184	1.341	100.16	134.3	73
	APC	441	220.5	1.34	141.51	189.6	86
Cycle-2	GAC	298	149	1.33	77.30	102.8	69

	APC	379	189.5	1.32	120.59	159.2	84
Cycle-3	GAC	279	139.5	1.35	73.37	99.0	71
	APC	351.5	175.75	1.338	105.08	140.6	80
Cycle-4	GAC	214	107	1.348	50.80	68.5	64
	APC	305.7	152.85	1.335	90.45	120.8	79

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