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Combined Granular Activated Carbon And UV/H_2O_2Processes For The Treatment Of Pharmaceutical Wastewater

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COMBINED GRANULAR ACTIVATED CARBON AND UV/H_2O_2 PROCESSES FOR THE TREATMENT OF PHARMACEUTICAL WASTEWATER

by

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Abstract

Combined Granular Activated Carbon and UV/H_2O_2 Processes for the Treatment of Pharmaceutical Wastewater

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The treatment of pharmaceutical wastewater was performed at the lab scale using UV/H_2O_2, process granular activated carbon (GAC) adsorption, and their combination to investigate the total organic carbon (TOC) removal efficiency for different inlet TOC loadings and treatment times. Experimental study revealed that GAC adsorption alone had 81% efficiency in TOC removal in 10 *min* breakthrough time for flow rate of 0.6 *L/min* with granular activated carbon dosage of 333.33 *mg*Activated Carbon*/L*, whereas UV/H_2O_2 process alone showed 26 and 29% TOC reduction at with 21.7 *g/L* H_2O_2 concentration with 254 and 185 *nm* wavelength lamps at 6 *h* hydraulic retention time, respectively, with average feed concentration (TOC) of 1,755.75 *mg*C*/L* and COD of 5,214.6 *mg/L* at 25 ± 5º*C*. Experimental results showed that the optimum H_2O_2 dosage for the UV/H_2O_2 process was 1:2 stoichiometric COD: H_2O_2 molar ratio to achieve up to 26 and 29% TOC reduction for two wavelengths 254 and 185 *nm*, respectively. The UV/H_2O_2 process showed a better efficiency at pH 3.12 (original pH condition of the wastewater) resulting 26-29% TOC reduction efficiency than that at pH 12.01 which resulted 15-20% TOC reduction efficiency. The Bohart-Adams rate constants (K_{AB}) and maximum adsorption capacity of carbon (N_o) from column breakthrough studies for synthetic pharmaceutical wastewater at 81% breakthrough were found to be 7.10×10^{-3} *L/(min.mg*C) and 1.06×10^{3} *mg*C*/L*, respectively.

In combined processes, it was found that GAC adsorption followed by desorption of contaminants from GAC by steam and UV_{254}/H_2O_2 treatment of the condensed steam led to 81% of TOC removal from the wastewater. Out of 358.73 *mg*C/*L* of TOC desorbed 88.1% of TOC was degraded in the UV_{254}/H_2O_2 treatment was degradation. Total operating costs of GAC adsorption followed by desorption of contaminants from GAC by steam and UV_{254}/H_2O_2 treatment of the condensed steam were found to be \$11/*L*. While the pre-treated wastewater by UV_{254}/H_2O_2 treatment followed by GAC adsorption, along with desorption of contaminants from GAC using steam and UV_{254}/H_2O_2 treatment of the condensed steam, led to an overall 81% TOC removal and 75.1% of TOC degradation using UV_{254}/H_2O_2 process. The cost of this combined treatment was found to be \$6/*L* of wastewater treated which led to an economical saving of \$5/*L* with respect to the combined TOC removal and degradation efficiency achieved. The savings predictions were achieved due to the less carbon dosage requirement and ability of UV/H_2O_2 process to degrade the TOC present in the wastewater.

Based on single and combined treatments, the minimum total cost and time for 81% TOC removal were determined for the combination of UV_{254}/H_2O_2 treatment followed by GAC adsorption, along with desorption of contaminants from GAC using steam and UV_{254}/H_2O_2 treatment of the condensed steam. The overall minimum cost and minimum time were found to be \$6/*L* of wastewater treated and 114.5 *h*, respectively. The treatment parameters and conditions for treating 30 *L* of the synthetic pharmaceutical wastewater were at an average feed concentration of TOC = 1,755.75 *mg*C/*L* and COD = 5,214.6 *mg/L* leading to TOC = 333.5 *mg*C/*L* of the effluent concentration which was near to the industrial effluent disposal level in Canada.

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Kiran. K. Shah

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a	empirical constants for Langmuir equation, *mg*C/*mg*Activated Carbon, (Equation 2.1)
b	empirical constants for Langmuir equation, *L/mg*C,(Equation 2.1)
B_1	DO of seed control before incubation, *mg/L*, (Equation C.2)
B_2	DO of seed control after incubation, *mg/L*, (Equation C.2)
$BOD_{5,in}$	BOD_5 concentration of influent wastewater sample, *mg/L*, (Equation C.1and 3.2)
$BOD_{5,out}$	BOD_5 concentration of effluent wastewater sample, *mg/L*, (Equation C.1and 3.2)
COD_{in}	*COD* concentration of influent wastewater sample, *mg/L*, (Equation 3.3)
COD_{out}	*COD* concentration of effluent wastewater sample, *mg/L*, (Equation 3.3)
C_e	equilibrium concentration of TOC in the solution after adsorption, *mg*C/*L*, (Equation 2.1)
C	concentration of effluent wastewater sample, *mg*C/*L*, (Equation 2.5)
C_o	concentration of influent wastewater sample, *mg*C/*L*, (Equation 2.5)
D_1	DO of a diluted sample immediately after preparation, *mg/L*, (Equation C.1)
D_2	DO of a diluted sample after 5 days incubation at 20°*C*, *mg/L*, (Equation C.1)
f	ratio of the volume of seed solution in GGA test to the volume of seed solution in seed control, (Equation C.2)
k	rate constant, $M^{-1}s^{-1}$, (Equation 2.6-2.12)
K_{AB}	Bohart -Adams rate constant, *L/(min.mg*C*)* , (Equation 2.5)
K_f	Freundlich capacity factor, *(mg*C/*mg*Activated Carbon*)/ (L/mg*C*))* $^{1/n}$, (Equation 2.3)

N_o	maximum adsorbent capacity, *mg*C/*L*, (Equation 2.5)
1/n	Freundlich intensity parameter (*dimensionless*), (Equation 2.3)
P	decimal volumetric fraction of sample used (*dimensionless*), (Equation C.1)
s	Standard deviation, (Equation B.2)
$SE_{\bar{x}}$	Standard error of the mean, (Equation B.3)
t	time, *min*, (Equation 2.5)
TOC_{in}	*TOC* concentration of influent wastewater sample, *mg*C/*L*, (Equation 3.1)
TOC_{out}	*TOC* concentration of effluent wastewater sample, *mg*C/*L*, (Equation 3.1)
v	superficial linear velocity, *m/s*, (Equation 2.5)
V	volume of sample*, L*
$\bar{x}$	Samples mean, (Equation B.1)
x/m	mass of adsorbate/mass of adsorbent, *mg*C/*mg*Activated Carbon, (Equation 2.1)
z	carbon bed height, *m*, (Equation 2.5)

Abbreviation

AC	Activated Carbon
ABR	Anaerobic Biological Reactor
AOP	Advanced Oxidation Process
BAF	Biological Activated Filter
BAT	Best Available Technology
BET	Brunauer-Emmet-Teller
BCT	Best Control Technology
BOD	Biochemical Oxygen Demand

BOD_5	Biochemical Oxygen Demand in 5 days
CWA	Clean Water Act
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
EBCT	Empty Bed Contact Time
EPA	Environmental Protection Agency
GAC	Granular Activated Carbon
GC	Gas Chromatography
GGA	Glucose-glutamic acid
HPLC	High-Performance Liquid Chromatography
HR	Higher Range
HRT	Hydraulic Retention Time
LPM	Litre per Minute
LR	Lower Range
MS	Mass Spectrometry
MTZ	Mass Transfer Zone
N.A	Not Applicable
N/A	Not Available
NOM	Natural Organic Matter
NDIR	Non- Dispersive Infra-Red
NSPS	New Source Performance Standards
PAC	Powdered Activated Carbon
PPCP	Pharmaceutical and Personal Care Product

RH	Target Compound
STPS	Sewage Treatment Plants
SCF	Seed Correction Factor
ThOD	Theoretical Oxygen Demand
TN	Total Nitrogen
TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solid
TVS	Total Volatile Solid
UV	Ultraviolet
VOC	Volatile Organic Carbon
WTP	Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION

Pharmaceutical drugs are vital substances due to their therapeutic effects. Their use is increasing ever since they were discovered. To meet the growing demands, the industrialization of pharmaceutical and personal care products is increasing exponentially. The global production of pharmaceutical was around 502 million *Kg/yr* in 2005 (Vrgtech, 2006). It had been expected that the global market grew by 4 - 6% in 2010 (IMShealth, 2010). Because of the nature of the production technologies of the pharmaceuticals, large quantities of wastewater and process water are generated in the pharmaceutical industries. Currently, as the world's population is increasing, there is an increase in water usage for drinking, urban, agricultural, and industrial purposes. Thus, the wastewater needs to be treated and restored back to its original quality. Since wastewaters or process waters generated by the pharmaceutical industries cannot be minimized because of the existing production technologies, effective end-of-pipe methods should be taken into consideration (Mizsey, 1994).

Generally, there are several engineering options for achieving the treatment of wastewaters. According to several environmental protection agencies, the biological treatment is generally more effective than physical and chemical processes due to the ability of microorganisms to degrade the contaminants present in the wastewater. But in some cases, the biological treatment cannot be accomplished due to recalcitrant and bioresistant components present in wastewater. Hence, physical-chemical processes provide a solution and as a result, they are usually implemented as primary treatment (Getzer, 2002; Belis *et.al*, 2004). Among several chemical treatments, advanced oxidation processes (AOPs) such as UV/H_2O_2 have been

found to be smart alternatives for the treatment of wastewater containing bioresistant compounds successfully. AOPs are technologies for the production of highly reactive intermediates, mainly hydroxyl radicals (˙OH), which are able to oxidize most organics in water. During the UV photolytic process, the UV light with the wavelength energy of more than bond energy can break the bonds directly. On the other hand, in UV/H_2O_2 process, the UV light at 185 or 245 *nm* is combined with H_2O_2 to generate ˙OH radicals, where these radicals react with organic pollutants to produce CO_2 and H_2O in case of complete mineralization. AOPs alone are very expensive to achieve complete mineralization of organic pollutants (Pérez *et al.*, 2002). Among various physical separation processes, the granular activated carbon (GAC) adsorption is widely used for the removal of volatile and bioresistant organic materials present in wastewater. Organic pollutants passed through packed columns containing GAC are adsorbed on the surface of carbon particles. The organic waste deposited on the carbon can be removed (carbon regeneration) by incinerating the exhausted carbon or by passing solvent through the exhausted carbon that would desorb the pollutants. Thus, a combination of UV/H_2O_2 and GAC adsorption process would give a cheaper option for total organic reduction from wastewater containing refractory organics.

Combined processes are promising alternatives for industrial wastewater treatment; therefore, more and more experiments are performed to support their industrial applications (Dewulf *et al.*, 2001; Kruithof *et al.*, 2003). Process optimizing the treatment is necessary to achieve a cost effective treatment method. Therefore, an appropriate design should not only consider the ability of the combination to degrade organics but also to obtain desired results in cost effectiveness.

Therefore, the aim of this research work is to investigate the reduction and degradation of TOC found in high strength industrial pharmaceutical wastewater at a predefined TOC removal efficiency of 81% (based on the efficiency obtained when combined experiments were done so as to have a common platform to compare the results), by using GAC adsorption alone, UV/H_2O_2 alone, and their combination. The following experiments were conducted:

1. Adsorption of pharmaceutical waste contaminants on GAC surface and desorption of the contaminants from the exhausted carbon by steam. It is hypothesised that the desorption process would result in the production of concentrated wastewater which helps in easy handling and high in concentration so that economical removal treatment is possible. Based on the results obtained, optimised design parameters of the GAC adsorption column and Bohart-Adams model parameters were determined.
2. Photolytic degradation of pharmaceutical waste by 254 and 185 *nm* UV lights in combination with H_2O_2. Based on the results established, optimum H_2O_2 dosage, optimum pH, and treatment time were determined.
3. Combination of GAC adsorption and UV_{254}/H_2O_2 treatment in different sequences for the treatment of pharmaceutical wastewater. Based on the results obtained, optimum carbon and H_2O_2 dosage, treatment time, and regenerant (in this case steam) requirement were determined.

Cost analysis for all the treatment processes, was done based on the results obtained by conducting the above set of experiments.

CHAPTER 2

LITERATURE REVIEW

This chapter is divided into two parts. The first part deals with general information on pharmaceutical wastewater including its characteristics and by-products, environmental impacts and health effects, and regulations and guidelines for its disposal. The treatment technologies for pharmaceuticals wastewater and compounds/solvents found in pharmaceutical wastewater are also summarized in this section. A brief discussion of the treatment technologies used in this study is described in the second part of this chapter.

2.1. Introduction

Most modern environmental regulations insist on industrial companies to pertain preventive environmental policy. In the pharmaceutical industry, conversely, the manufacturing of an active ingredient cannot facilitate the technology to be changed fundamentally. In this case, instead of preventive environmental policy, the attention is focused on the treatment of the wastes. Industries manufacturing pharmaceutical drugs and personal care products also contribute a large amount of organic recalcitrant waste which is as high as 43,090 *mg/L* in chemical oxygen demand (COD) and 20,062 *mg/L* in biological oxygen demand (BOD) (Murthy *et al.*, 1984). This adds up more contaminants to the surface and underground water supplies, thus less fresh water is available. The quality of our water, therefore, is becoming as much of a concern as the quantity. Passage of Federal Water Pollution Control Act Amendments of 1972, as amended in 1977 and 1978 (Clean Water Act, CWA), stimulated the principle objective, which was: "To restore and maintain the chemical-physical and biological integrity of the nation's water" (Metcalf and Eddy, 2003).

Pharmaceutical industries produce a wide variety of products using both inorganics and organics as raw materials, the latter being synthetic or of vegetable and animal origin (Kincannon and Esfandi, 1980). The pharmaceutical and personal care products range from antiepileptic to antibiotics, β-blockers to steroids, analgesic to antidepressants, and enzyme inhibitor such as herbicides, pesticides, and disinfectants. Even in a single pharmaceutical industry, producing varieties of drugs using different processes, the waste generated would differ from one process to another. Most of the wastes generated by these industries are toxic to biological life and are highly acidic or basic in nature depending on the drug manufactured. They contain recalcitrant organics which are hard to degrade using standard biological treatment processes.

Active pharmaceutical ingredients, surfactants, personal care products, or substances with endocrine-disrupting activity are also among the compounds which are found in lakes, sewage lines, rivers, and sea (Heberer, 2002; Daughton; Ternes, 1999). Several analytical methods such as gas chromatography (GC), high-performance liquid chromatography (HPLC) separation or mass spectrometry (MS) detection have been used to measure pharmaceuticals ($\mu g/L$) in sewage treatment plants (STPs) (Metcalf and Eddy, 2003; Stumpf *et al.*,1999; Ternes, 1998), rivers (Heberer, 2002; Kolpin *et al.*, 2004), sea, lakes, and groundwater (Metcalf and Eddy, 2003). Aquaculture industries and run-offs from farms also play a significant role in the presence of drugs in the environment (Calamari *et al*., 2003). Various parameters often used to characterize the wastewater are COD, BOD_5 (measured @ 20^oC after 5 days of incubation), total dissolved solids (TSS), total volatile solids (TVS), dissolved oxygen (DO), total organic carbon (TOC), pH, temperature, and total solids (TS).

2.2. Characteristics of Pharmaceutical Wastewater

Pharmaceutical wastewater are characterised mainly in five types depending on the drug manufacturing industry as:

1. alkaline waste stream;
2. acidic waste stream;
3. waste generated by allopathic manufacturing industry;
4. waste generated by pharmaceutical manufactured using biological processes; and
5. beef-liver extraction process industries.

The characteristics of the these waste streams are listed in Table 2.1. The wastes generated by sulpha drug industries are usually acidic type with very low pH of 3-6 (Wang *et al.,* 2006). Whereas the penicillin manufacturing industry generates waste which is very high in BOD_5 with a pH of 7-10. The beef-liver extraction process wastewater also has a BOD_5 as high as 16,000 *mg/L*. Apart from the waste generated from industries, the water bodies also contain small amount of various pharmaceutical drugs which are present in small magnitude, but have a large impact on the ecosystem as listed in Table 2.2. Concerns have been raised for the potential selection of resistant bacterial strains that may confer cross-resistance to other antimicrobial agents and for the potential harm to the environment.

Table 2.1. Typical characteristics of pharmaceutical wastewater (Wang *et al.,* 2006; Murthy *et al.,* 1984).

Industry	**Flow Rate (m^3/ *day*)**	**pH**	**Total Solids (*mg/L*)**	**BOD_5 at 20^oC (*mg/L*)**	**COD (*mg/L*)**	**Total alkalinity as $CaCO_3$ (*mg/L*)**
Alkaline waste stream of a synthetic drug plant	1,710	2.3–11.2	11825–23265	2,980–3,780	5,480–7,465	624–5630
Condensate waste stream of a synthetic drug plant	1,570–2,225	7–7.8	2,742–4,150	754–1,385	1,604–2,500	424–520
Acid waste stream of a synthetic drug plant	435	0.4–0.65	18,650–23,880	2,920–3,260	7,190–9,674	29,850–48,050 (acidity)
Pharmaceutical industry wastewater producing allopathic	N/A	6.5–7.0	300–400 (Suspended)	1,200–1,700	2,000–3,000	50–100
Beef- liver extraction process	N/A	5–6.3	16,500–21,600	11,400–16,100	17,100–24,200	3,800–4,350
Typical spent stream of biological production	15,000	7.3–7.6	4,000–8,500	1,000–1,700	N/A	N/A

N/A – not available.

Table 2.2. Pharmaceutical compounds analyzed in water samples and their general use (Wang *et al.,* 2006; Nikolaou *et al.*, 2007). (ST = Sewage Treatment)

Compound	Common Name	Concentration in ST Plant (*μg/L*)	Concentration in Hospital Effluents (*μg/L*)	Usage
Acetaminophen	Tylenol	N/A	0.5–29	Over-the-counter analgesic
Atenolol	N/A	N/A	0.1–122	B- blocker
Carbamazapine	Tegretol	1625	0.03–0.07	Management of epilepsy, bipolar disorder
Clofibric acid	N/A	361	N/A	Nicotine metabolite
Diclofenac	N/A	273–2134	0.06–1.9	N/A
Erythromycin	E-Mycin	886	0.01–0.03	Antibiotic
Gemfibrozil	Lopid	2366	N/A	Antihyperlipidemic
Ibuprofen	Advil	2134	1.5–151	Over-the-counter analgesic
Metoprolol	N/A	777	N/A	Antidiabetic
Miconazole	Micatin, Monistant	N/A	1.8–9.4	Antifungal agent
Ranitidine	Zantac	N/A	0.4–1.7	Acid reducer
Sulfamethoxazole	Component of bactrim	128	N/A	Antibiotic
Triclosan	N/A	0.01–0.02 0.2–2.7	N/A	Antibacterial and antifungal
Trimethoprim	Component of bactrim	154	0.01–0.03	Antibiotic

2.3. Fate and Pathway for Entry of Pharmaceutical Waste in Environment

The pharmaceutical chemicals range from non-prescribed and prescribed drugs, antibacterial agents, and surfactants are commonly found in household products. Pharmaceutical and personal care products (PPCP) and their metabolites are introduced into the environment via a number of routes, the primary route being the discharge of the treated and untreated wastewater from hospitals, industrial units, and intensive animal-breeding farms to rivers as illustrated in Figure 2.1. Also after ingestion by humans, pharmaceutical drugs are excreted as initial molecules, water-soluble conjugates, or metabolites, and thus, freely enter the influent of municipal wastewater treatment plants (WTPs). Due to their polar structure, most pharmaceutical and personal care products are not totally removed by sewage treatment plants (Nikolaou *et al.*, 2007). These are among the compounds, in the class of emerging contaminants, whose fate in the wastewater treatment process has received an increased attention in past years because of both their availability in the aquatic environment and health related issues.

2.4. Potential Hazards of Pharmaceutical Contaminants in Environment

Pharmaceutical residues in the environment have potential toxic effects. The significant difference in the concentration (i.e. ranging from $\mu g/L$ to mg/L) of the pharmaceutical compounds, fragrances, and their occurrence is found with respect to different geographical areas (Heberer, 2002). There is an increasing attention on pharmaceutical residues as potential pollutants due to the fact that they often have similar physio-chemical behaviour such as other harmful xenobiotics which are persistent or produce adverse effects. In addition, by contrast with regulated pollutants, which often have longer environmental half-lives, their continuous introduction in the environment may make them pseudopersistents.

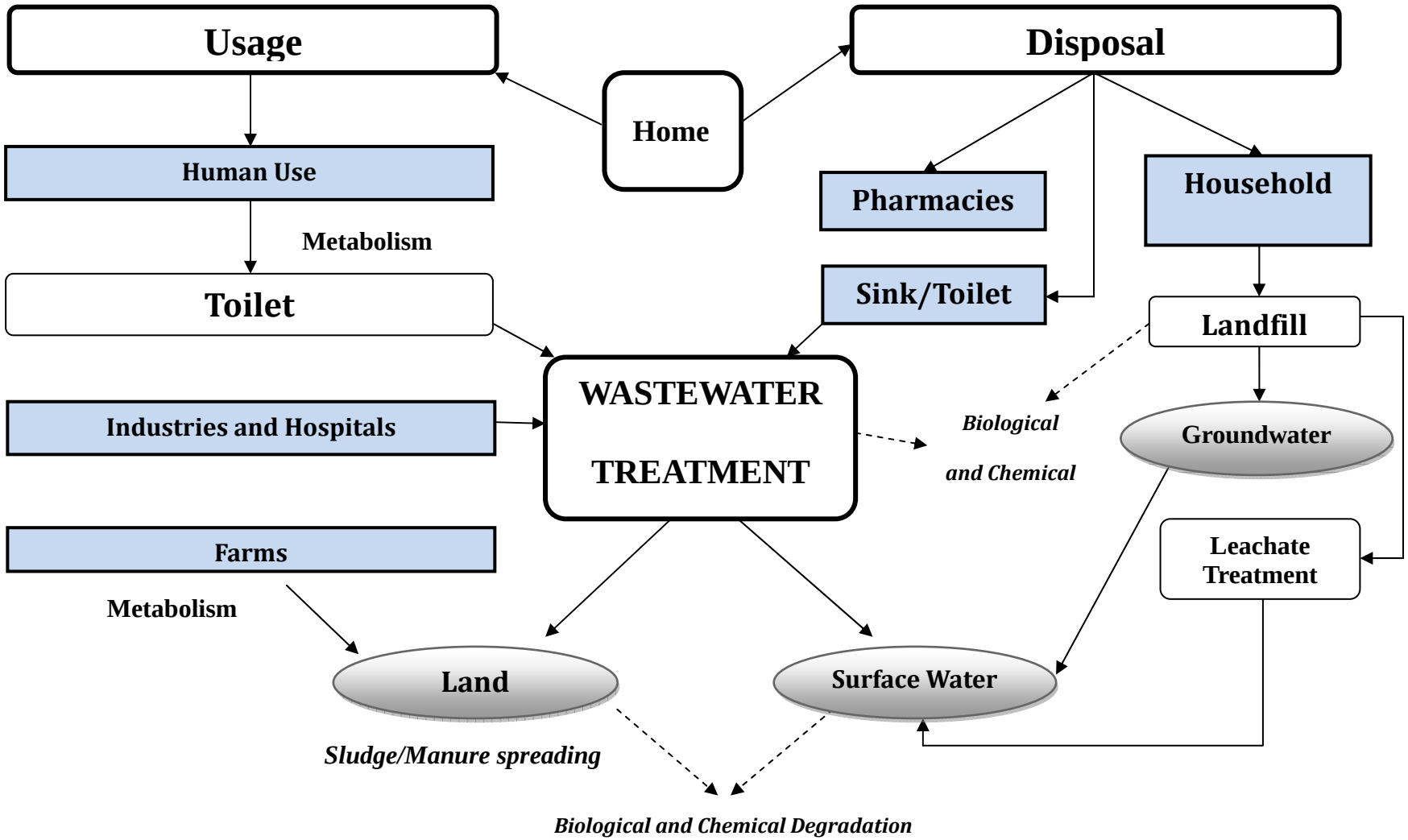

Figure 2.1. Sources and fate of pharmaceutical compounds in the environment (adapted from Nikolaou *et al.*, 2007).

Pharmaceutical residues and/or their metabolites are usually detected in the environment at trace levels, but even low concentration levels (*μg/L* or *mg/L*) can induce toxic effects. So far, an important negative impact is the case of antibiotics and steroids that cause resistance in natural bacterial population or endocrine disruption (Nikolaou *et al.*, 2007). The interest in these environmental effects has resulted in an increase of the research activities toward the development of new treatment methods. Their removal can be attributed not only to the biodegradation, but also to the adsorption onto solid surfaces**.** As a result, this has led to their occurrence being reported in water treatment effluents, rivers and lakes, and more rarely in groundwater (Ollers *et al.*, 2001; La Farre *et al*., 2001; Jones-Lepp *et al.*, 2004; Kolpin *et al*., 2004; Hirsch *et al.*, 1998; Hirsch *et al.*, 1999; Stan and Heberer, 1997; Stackelberg *et al.*, 2004).

Besides, these substances can also imply an important pollution source for the soil if the primary and secondary sludge (to which they are adsorbed) are spread on land. Studies have shown that the transformation processes for active pharmaceutical compounds can vary in wastewater treatment works depending on the composition of the sewage, weather conditions, and the design and operation of the treatment processes (Stumpf *et al.*, 1999; Kolpin *et al.*, 2002; Ternes *et al*., 2002). The overall removal rates using conventional biological treatments, AOPs, and granular activated carbon published in the open literature vary strongly within a range of 20 – 90% removal efficiency (Stumpf *et al.*, 1999; Kolpin *et al.*, 2002; Ternes *et al*., 2002). In Germany, the removal efficiencies by clarification and biological aerators are reported in the range from 10 to 90% depending on the nature of the compounds (Ternes, 1998). In Brazil, removal efficiencies for pharmaceutical polar compounds using activated sludge and bio-filtration treatment varied from 12 to 90%, where the efficiencies obtained in activated sludge

processes were higher than those in biofilters (Ternes *et al.*, 1999). In China, around 97.8% of COD were removed by anaerobic biological reactor (ABR) and aerobic treatment (Zhou *et.al,* 2006).

2.5. Regulations and Discharge Parameters of Pharmaceutical Wastewater Effluents

There is a certain degree of contaminant level in the discharge effluent of water to be maintained. To maintain the discharge effluent quality, the government makes rules and regulations that every industry has to abide by to meet the satisfactory conditions. Since 1980, the water-quality improvement by CWA 1970s has been continued, but the emphasis has been shifted to the definition and the removal of constituents that may cause long term health effects and environmental impacts (CWA, 1987). The required degree of the treatment has been increased significantly and the additional treatment objectives and goals have been added to better serve the purpose of contaminants' removal from water. Important federal regulations are Clean Water Act, (CWA, 2006), Water Quality Act (1987), and Total maximum daily load Section 303(d) of CWA (CWA, 1987).

A complete detail of the final effluent limitations and standards for the pharmaceutical manufacturing is given in the guidelines (EPA, 1998). These regulations establish effluent limitation guidelines and standards under the CWA including best conventional pollutant control technology (BCT) and best available technology (BAT) economically achievable for existing direct dischargers, new source performance standards (NSPS) for new direct dischargers, and pre-treatment standards for existing and new indirect dischargers (PSES and PSNS).

Recommendations for effluent quality of wastewater disposed by federal institutions are shown in Table 2.3. Any new setup subject to the pharmaceutical industry and its subpart must achieve the performance standards mentioned in Table 2.4.

2.6. Technologies for Pharmaceutical Wastewater Treatment

As pharmaceutical industries manufacture variety of compounds, they employ an array of wastewater treatments with respect to the waste generated. The wastewater generated not only varies in composition, volume, and raw materials used, but also on the season, time, and place. Thus, the treatment methods strive to get the effluent quality as set by the governing federal/state government.

The unit operations involved in the treatment can be broadly classified as (Wang *et al.,* 2006):

1. physio-chemical treatment / pre-treatment;
2. chemical /biological treatment (or combined);
3. advance oxidation treatments;
4. integrated treatments.

Various treatment processes and their combinations adapted by the industries are as follows (Wang *et al.,* 2006):

- Activated sludge process
- Trickling filter
- Anaerobic filtration / Anaerobic hybrid reactor
- Oxidation ponds/Aerated lagoons
- Extended aeration
- Powdered activated carbon combined with activated sludge process

Table 2.3. Recommended wastewater discharge standards by federal facilities in Canada (Correctional services of Canada, 2000).

Regulated Parameters	**Wastewater Disposal Path**	**Effluent Discharge Limit (unless otherwise specified) (*mg/L*)**
BOD_5	Freshwater, lakes, slow flowing stream	5
	River, streams and estuaries	20
	Shoreline	30
Fecal coliforms		100/100 *mL*
Total coliforms count		1,000/100 *mL*
Total suspended solids (TSS)	Freshwater, lakes, slow flowing stream	5
	River, streams and estuaries	20
	Shoreline	30
Reactive chlorine [Cl]		0.01 or current detection limit
pH		4-9
Phenol (mono and dihydric)		0.02
Oils and grease		5
Ammonia (NH_3)		1
Nitrates (NO_3, NO_2 in form of N)		10
Phosphorous (P)		1
Sulphur (S)		0.5
Temperature	ambient temperature changes no more than 1^oC	

Table 2.4. Regulation for any new pharmaceutical industry set-up (EPA, 1998).

Regulated parameter	**Effluent Limitations (*mg/L*)**	
	Maximum Daily Discharge	**Average Monthly Discharge**
BOD_5	267	111
TOC	320	216
COD	1675	856
Ammonia (as N)	84.1	29.4
Acetone	0.5	0.2
4-Methyl-2-pentanone (MIBK)	0.5	0.2
Isobutyraldehyde	1.2	0.5
n-Amyl acetate	1.3	0.5
n-Butyl acetate	1.3	0.5
Ethyl acetate	1.3	0.5
Isopropyl acetate	1.3	0.5
Methyl formate	1.3	0.5
Amyl alcohol	10.0	4.1
Ethanol	10.0	4.1
Isopropanol	3.9	1.6
Methanol	10.0	4.1
Methyl Cellosolve	25.0	10.2
Dimethyl Sulfoxide	91.5	37.5
Triethyl Amine	250.0	102.0
Phenol	0.05	0.02
Benzene	0.05	0.02
Toluene	0.06	0.02
Xylenes	0.03	0.01
n-Hexane	0.03	0.02
n-Heptane	0.05	0.02
Methylene chloride	0.9	0.3
Chloroform	0.02	0.01
1,2-Dichloroethane	0.4	0.1
Chlorobenzene	0.15	0.06
o-Dichlorobenzene	0.15	0.06
Tetrahydrofuran	8.4	2.6
Isopropyl ether	8.4	2.6
Diethyl amine	250.0	102.0
Acetonitrile	25.0	10.2
Cyanide	33.5	9.4
pH	6-9	6-9

- Granular activated carbon process
- Biomembrane reactor /Membrane filtration/ Ion exchange
- Advance oxidation technologies.

The physio-chemical treatment, such as coagulation, helps in reducing the COD by 46% and sulphur concentration by 32% at pH 8 with initial COD of 11,800 – 13,200 *mg/L* (Raj and Anjaneyulu, 2005). Major pharmaceutical industries opt for conventional biological processes for treating their wastewater as it is cheaper than other treatment methods with a reduction of COD by 85 - 98%, depending on the waste compounds present.

Powdered activated carbon sludge is one of the technologies with 89% efficiency for removal of priority pollutants such as nitro-aniline, nitro phenols, and chloroethanes with initial TOC concentration of 387 *mg*C/*L* (Kincannon and Esfandi, 1980). Tertiary treatments such as granular activated carbon have proven to adsorb even the recalcitrant compounds along with the volatile organic carbon and other chloroorganic family compounds with COD removal efficiency of 80-95% and colour removal of nearly 99% (Pelech *et al,* 2005).

Advanced oxidation technologies such as Fenton/H_2O_2, UV/H_2O_2, ozonation, and photolytic reaction have been proven to treat pharmaceutical wastewater with initial COD between 670-2,500 *mg/L* giving 67 - 78% COD removal efficiency (Höfl *et al.*, 1997). The photoFenton (H_2O_2/Fe^{2+}/Solar) process has attracted much attention due to 95% COD removal efficiency, by the oxidation of organic chemicals (COD 25,600 *mg/L*) present in the pharmaceutical wastewater (Bhaskaran and Kanmani, 2007). They are an alternative way for treatment of high organic compounds and recalcitrant. They are costly if used as a sole treatment for large scale wastewater treatment plants (Pérez *et al.*, 2002). Therefore, an integration of

biological, physical, and chemical processes would provide an optimized wastewater treatment option in treating wastewater which is not readily biodegradable (Tabrizi and Mehrvar, 2006).

An integrated treatment of biological/chemical and advanced oxidation processes has gained a lot of interest recently giving a result of 95% removal of linear alkyl benzene (LAS) from wastewater containing 100 *mg*LAS/*L* and 92% COD removal from phenolic wastewater with initial COD of 233 *mg/L* (Tabrizi and Mehrvar, 2006; Hamad *et al.*, 2005). A summary of various treatments for pharmaceutical wastewater is given in Table 2.5. It can be concluded from Table 2.5 that biological, adsorption, AOP as well as combination of biological and AOP processes provide excellent removal efficiency up to 99% COD and BOD from the pharmaceutical wastewater and are feasible methods of treatment. But, so far there is little information on adsorption/desorption processes to concentrate the organic pollutant and then treat them with AOP treatment or vice versa.

2.7. GAC Adsorption Process for the Treatment of Pharmaceutical Wastewater

The activated carbon treatment method has been limited to drinking water for many years but it has gained more attention in the past decades for its use in wastewater treatment. It is used as an additional treatment for wastewater to meet the discharge standards ever since the Safe Drinking Water Act of 1974 was implemented (Wang *et al.*, 2006). Granular activated carbon is very well known for its adsorption capacity of a wide range of pollutants as found to be successful in achieving the required effluent quality of the wastewater. Few pollutants, namely phenol, chloroorganics, aniline, benzoic acid, methyl *ter*-butyl ether, and others are removed with

Table 2.5. Selected treatment processes for pharmaceutical wastewater.

Wastewater Type	Method	Conditions	Removal Efficiency	References
from equalization tank of bulk drug pharmaceutical unit	aerobic oxidation	COD = 8,480 ± 414.73 *mg/L* BOD = 4,800 ± 316.23 *mg/L* HRT = 2 - 4.5 *days*	80% COD 80 - 96.5% BOD for COD < 4000 *mg/L* 45% COD 75% BOD for COD 5000 - 7000 *mg/L*	Raj and Anjaneyulu, 2005
from a drug plant (o-nitrophenol, 2-nitrophenol (2-NP), 4- nitrophenol (4NP), 1,1,2- trichloroethance (TCE), 1,1-dichloroethylene (DCE), phenol	activated sludge,	TOC = 387 *mg*C*/L*	72.4% TOC Phenol, 2-NP, 4-NP, TCE, DCE	Kinconnon and Esfandi, 1980
acetonitrile, acrylonitrile and benzonitrile in pharmaceutical wastewater	batch activated sludge bioreactor	Activated sludge of a pharmaceutical wastewater treatment plant and adapted through providing acetonitrile as the sole carbon and nitrogen source for their growth. VSS of 2 *g* L^{-1}. initial acetonitrile conc. 0.5-10 *g* L^{-1}	0.083 *g* acetonitrile / (*g* VSS. *h*), 0.0074 *g* acrylonitrile/ (*g* VSS. *h*) or 0.0029 *g* benzonitrile/ (*g* VSS. *h*)	Li *et al.,* 2007

from Northeast Pharmaceutical Company Ltd., China	hydrolysis acidification/activated sludge/BAF process	N/A	up to 90% COD up to 90% BOD_5	Liu *et al*, 2007
high strength organic pharmaceutical wastewater	hydrolytic acidification-anaerobic-aerobic biochemical process	COD = 12,000 – 18,000 *mg/L* BOD_5 = 4,000 – 8,000 *mg/L*	97.6% COD	Wang *et al.*, 2007
antibiotic pharmaceutical wastewater	multi-stage biochemistry-coagulation process	COD = 8,256.6 *mg/L* NH_3-N = 374.4 *mg/L*	94.4% COD 99% NH_3-N	Ning *et al.*, 2007
from a drug plant	membrane bioreactor	COD = 800–11,800 *mg/L* BOD_5 = 100–6,350 *mg/L*	95% COD 99% BOD	Chang *et al.*, 2008
from a drug plant	solar photoFenton oxidation in series with sequencing batch reactor (SBR)	BOD = 4,890 *mg/L* COD = 25,600 *mg/L* H_2O_2/Fe^{2+} = 15:1 H_2O_2/COD = 18:1	93% BOD 95% COD	Bhaskaran and Kanmani, 2007
from a drug plant (o-nitrophenol, 2-nitrophenol (2-NP), 4- nitrophenol (4NP), 1,1,2- trichloroethance (TCE), 1,1-dichloroethylene (DCE))	powdered activated carbon activated (PAC) sludge	TOC = 387 *mgC/L*	89.7% TOC Phenol, 2-NP, 4-NP, TCE, DCE	Kinconnon and Esfandi, 1980

from a drug plant	PAC fed biological treatment	COD = 7,030 *mg/L* BOC = 2,830 *mg/L* TOC = 1,930 *mg*C/*L* HRT = 3*days*	86.8 - 92.8% COD	Center *et al.*, 1985
from a drug plant (o-nitrophenol, 2-nitrophenol (2-NP), 4- nitrophenol (4NP), 1,1,2- trichloroethance (TCE), 1,1-dichloroethylene (DCE), phenol)	GAC Column	TOC = 387 *mg*C/*L*	43.9% TOC Phenol, 2-NP, 4-NP, TCE, DCE	Kinconnon and Esfandi, 1980
lake water containing organic micropollutant	GAC	TOC = 10.10 *mg*C/*L*	90% TOD	Guzzella *et al.*, 2002
chloroorganic compounds	GAC	C_o = 500 *mg/L*	99% Initial conc.	Pelech *et al.*, 2005
synthetic aniline and sulfanilic acid	GAC	TOC Sulfanilic = 138 *mg*C/*L* TOC Aniline = 380 *mg*C/*L* GAC dose = 50,000 *mg*Carbon/*L*	Aniline @ pH > 7 Sulfanilic Acid @ pH < 7	Faria *et al.*, 2008
benzene and toluene	GAC	C_o = 200 *mL/L*	34 *g* C_6H_6 /100 *g* GAC 64 *g* $C_6H_5CH_3$/100 *g* GAC	Lillo-Rodenas *et al.*, 2005
benzene	GAC	C_o = 768 *mL/L*	20 *g*/100 *g* GAC	Chiang *et al.*, 1999
methylene chloride	GAC	C_o = 0.007 *mg/L*	14 *g/g* GAC	Kye *et al.*, 1997

from a drug plant	Fenton-coagulation process	COD = 992 *mg/L* BOD_5 = 60 *mg/L* H_2O_2/COD = 0.27 H_2O_2/Fe^{2+} = 3:1 t= 30 *min*	73% COD	Mei-yan *et al.*, 2006
effluent of a pharmaceutical production facility	H_2O_2/Fe(II)	Sample 1 COD = 670 *mg/L* Sample 2 COD = 2,500 *mg/L*	81.34% COD 18% COD	Höfl *et al.*, 1997
effluent of a pharmaceutical production facility	ozonation/U	Sample 1 COD = 670 *mg/L* Sample 2 COD = 2,500 *mg/L*	66.41% COD 78% COD	Höfl *et al.*, 1997
effluent of a pharmaceutical production facility	H_2O_2/UV	Sample 1 COD = 670 *mg/L* Sample 2 COD = 2,500 *mg/L*	62.68% COD 40% COD	Höfl *et al.*, 1997
from a drug plant (o-nitrophenol, 2-nitrophenol (2-NP), 4- nitrophenol (4NP), 1,1,2- trichloroethance (TCE), 1,1-dichloroethylene (DCE), phenol)	resin column	TOC = 387 *mg*C/*L*	15% TOC 72.3% 2-NP 65.8% 4-NP	Kinconnon and Esfandi, 1980
p-nitrophenol, *m*-aminophenol	desorption from GAC	C_o = 1,000 *mg/L*	The capacity decreases to 80% after 7pH	Moreno-Castilla *et al.*, 1995
chloroorganic compounds	desorption from GAC using steam	C_o = 682 *mg/L*	96% initial conc.	Pelech *et al.*, 2005

phenolic wastewater	combined GAC and UV/H_2O_2	Phenol C_o. = 40 *mg/L* H_2O_2 = 5×10^{-3} M GAC dose = 1,000 *mg*Carbon*/L*	87.5% TOC 92.5% Mineralization of desorbed waste from GAC	Ince and Apikyan, 2000
phenolic wastewater	combined GAC and UV/H_2O_2	COD = 233 *mg/L* H_2O_2 = 100 *mg/L* GAC dose = 12,500 *mg*Carbon*/L*	91.41% COD	Hamad *et al.*, 2005
lake water containing organic micropollutant	combined GAC and UV/H_2O_2	TOC = 2.63 *mg*C*/L*	70% TOC	Guzzella *et al.*, 2002
perchloroethylene (PCE), trichloroethane (TCE), and other pollutants	UV/ H_2O_2 or ozonation followed by GAC	N/A	95% PCE and TCE	Lee *et al.*, 1995
disinfection byproducts (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs)	combined biological activated carbon and UV/H_2O_2	N/A	52% TOC	Toor and Mohseni, 2007
synthetic phenol and aniline wastewater	PAC with aerobic bioreaction	TOC = 380-390 *mg*C*/L*	99% TOC	Orshansky and Narkis 1997
synthetic pharmaceutical wastewater	Combined GAC and UV/H_2O_2 along with desorption process	TOC = 1755.5*mg/L* GAC dosage = 166.66 *mg*Carbon*/L* H_2O_2 = 21.7 *g/L*	81% TOC	This study

N/A- not available.

an efficiency of 99% when treated individually. This technology has a high capital investment and operational cost involved. There are serious amendments and researches done to optimize the cost factor and increase the efficiency of the process (Knappe *et al.*; 1992, Qi *et al.*, 1992; Waer *et al.*, 1992). It has been found that the use of powdered activated carbon is more effective when combined with the other treatment processes such as activated sludge (Wang *et al.*, 2006). From the present study, removal efficiency of compounds mixture is to be found out using adsorption method. The activated carbon works on the same principle of adsorption, which is the binding of molecules or particles to carbon surface. This binding can be due to a weak force of attraction, such as Vander Waals, ionic and dipole-quadrapole force, or a chemical reaction forming new types of electronic bonds (ionic or covalent), which are known as physical or chemical adsorption, respectively (Wang *et al.*, 2006). The attraction/reaction of a substance in a solution (adsorbate) to an activated carbon particle (adsorbent) occurs in three distinct steps (Figure 2.2):

1. Film diffusion: transfer of adsorbate from solution to the surface of adsorbent,
2. Pore diffusion: transfer of adsorbate from the surface of adsorbent to the adsorption site inside the pore, and
3. Attachment of adsorbate to the surface of the adsorbent.

2.7.1. Properties of activated carbon

Activated carbon (AC) is prepared from various materials such as wood, peat, coconut shell, lignite, bituminous coal, and petroleum residues. GAC is produced using bituminous coal or lignite whereas, PAC from coconut shells, saw dust, or virgin coal. The adsorption capacity of the AC depends on the surface area that the particle offers for adsorption of the organic pollutants. Usually, the specific surface area of the activated carbon varies from 500 -1,400 m^2/g. Table 2.6 describes selected properties of activated carbon.

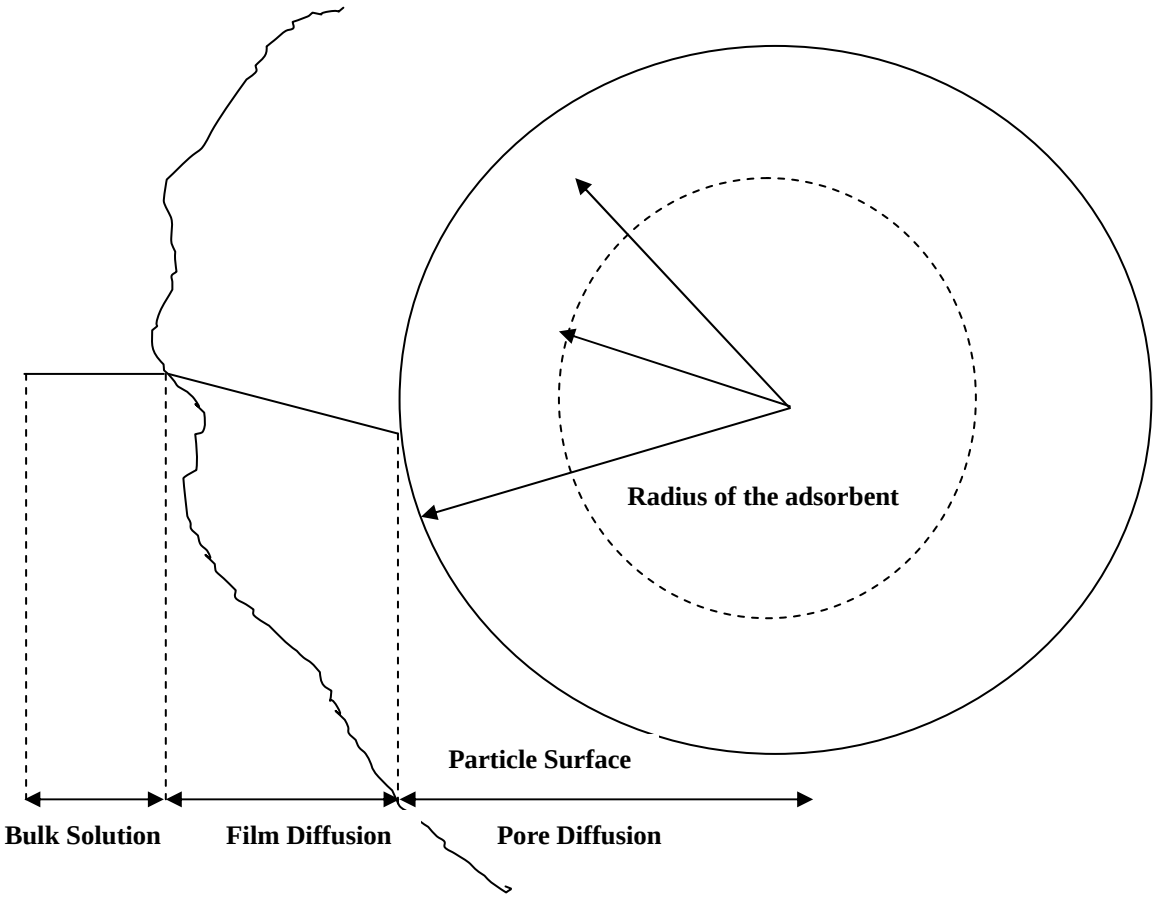

Figure 2.2. Transport mechanism of a substance (adsorbate) from the bulk solution onto an activated carbon particle (adsorbent).

Table 2.6. Properties of activated carbon (adapted from EPA, 1991).

Properties	Importance	Values used in this study[(a)]
Particle Size	Rate of adsorption increases as particle size decreases. Head loss through packed column increases as particle size decreases.	4-12 mesh size
Pore Volume	Measure of total macropore and micropore volume within the carbon particles. Measured in cm^3/g.	1
Specific Surface Area	A measure of the area available for adsorption. The larger the surface area, the greater the adsorptive capacity. Measured by determining the amount of nitrogen adsorbed by the carbon and reported as m^2/g.	625
Iodine Number	Refers to the milligrams of iodine adsorbed during the standard test. Measures the volume present in pores from 10 to 28 Å in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing low molecular-weight substances. It is reported as *mg/g*.	N/A
Abrasion Number	Measures the ability of carbon to withstand handling and slurry transfer. This property is of limited value because measuring techniques are not reproducible.	75-85
Molasses Number	Refers to milligrams of molasses adsorbed during standard test and measures the volume in pores greater than 28 Å in diameter. The molasses number specification is generally only used in color removal applications, and is not a valid specification requirement for water treatment and is reported in *CG*	75
Bulk Density	Useful in determining the volume occupied by a given weight of carbon and reported as g/cm^3.	0.38

(a) EMD Chemicals MSDS, 2010

N/A-not available

2.7.2. Adsorption isotherms

Various mathematical models are proposed to support the adsorption mechanisms of activated carbon. The quantity of adsorbate that can be adsorbed is a function of the characteristics and the concentration of the adsorbate and the temperature. Based on these fundamental relations, the two most widely accepted isotherms are Freundlich and Langmuir models. The former one is an empirical relationship while the latter is based on theoretical assumptions. The Langmuir isotherm is based on the mono layer adsorption concept and assumes that adsorption is reversible. Langmuir isotherm is defined by Equation (2.1) (Wang *et al.*, 2006)

$$x/m = \frac{abC_e}{1 + bC_e} \tag{2.1}$$

where:

x/m = mass of adsorbate (TOC) adsorbed per unit mass of dry adsorbent (*mg*C/*mg*Activated Carbon),

C_e = equilibrium concentration of adsorbate (TOC) in solution after adsorption (*mg*C/*L* of solution),

a = maximum adsorption capacity of carbon (*mg*C/*mg*Activated Carbon)

and b = empirical constant (*L* of solution/*mg*C).

Empirical constants a and b can be determined by plotting m/x versus $1/C_e$ as shown in Figure 2.3(a). For higher concentration, re-arranged linear form of Langmuir isotherm, Equation (2.2) is used (Figure 2.3(b) Wang *et al.*, 2006). The adsorption of methylene chloride followed a Langmuir isotherm and its desorption from the carbon surface, using high temperature nitrogen purge gas, did not affect the time required for regeneration (Kye *et al.*,1997).

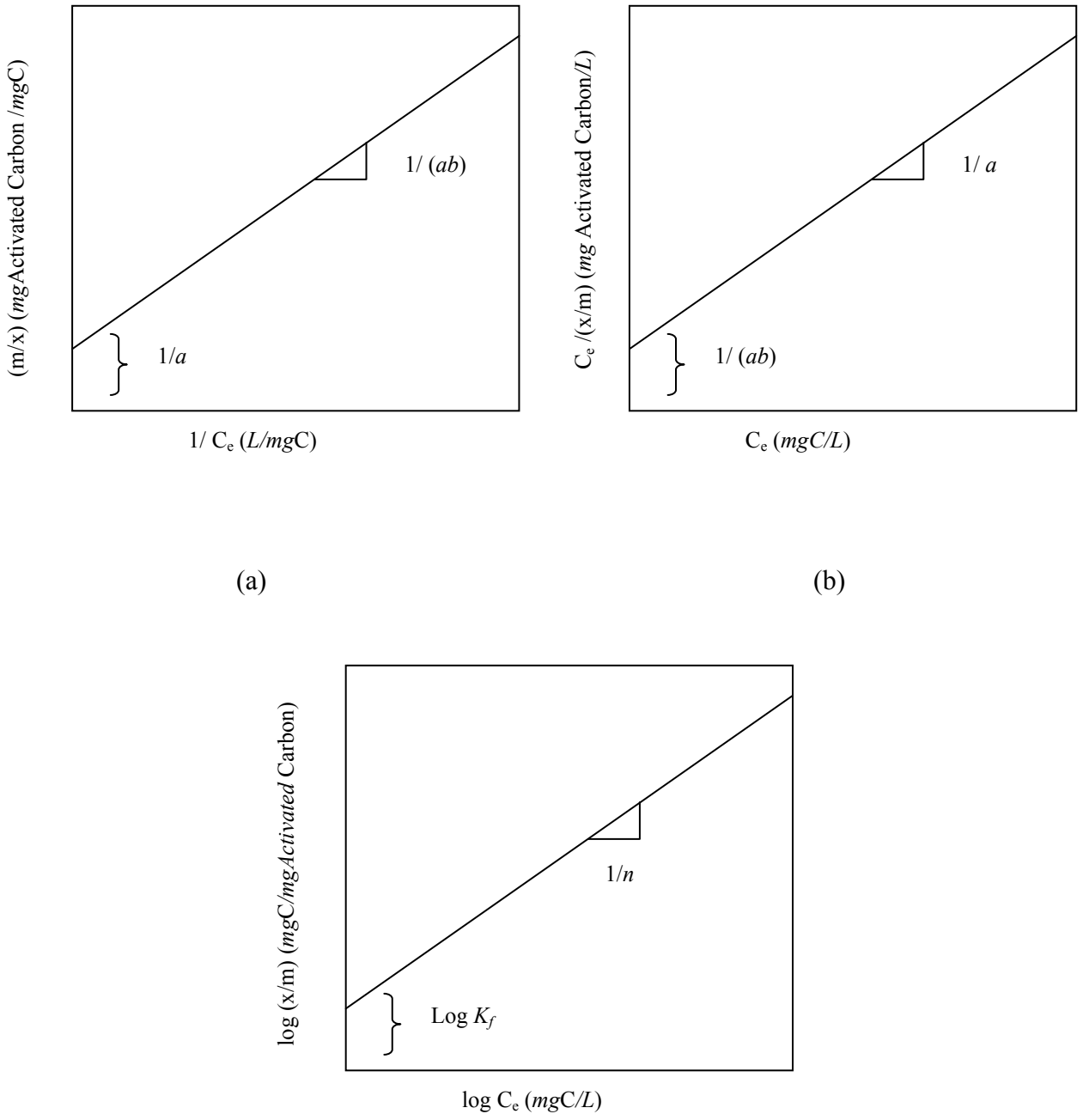

Figure 2.3. Adsorption isotherms for (a) Langmuir for lower concentration data, (b) re-arranged Langmuir for high concentration data, and (c) Freundlich (adapted from Wang et al., 2006).

$$\frac{C_e}{x/m} = \frac{1}{ab} + \frac{C_e}{a} \tag{2.2}$$

The Freundlich isotherm found in 1912 is described by Equation (2.3) (Wang *et al.*, 2006):

$$x/m = K_f C_e^{1/n} \tag{2.3}$$

where:

x/m = mass of adsorbate (TOC) adsorbed per unit mass of adsorbent (*mg*C/*mg*Activated Carbon),

K_f = Freundlich capacity factor ((*mg*C/*mg*Activated Carbon)/(*L*/*mg*C))$^{1/n}$,

C_e = equilibrium concentration of adsorbate in solution after adsorption, (*mg*C/*L*),

1/n = Freundlich intensity parameter.

The constants K_f and *n* can be determined by plotting log x/m versus log C_e as shown in Figure 2.3(c).

A significant research has been done to predict GAC capacity for organics' adsorption using Freundlich isotherm. Qi *et al.* (1992) compared the adsorption capacity of dichloromethane, tetrachloroethylene, and trichloroethylene with the isotherm predicted values. It was found that there was an agreement between experimental and predicted values. Stephen *et al* (1983) worked on evaluating GAC adsorptive capacity and found that pulverizing GAC greatly reduced the contact time required to reach equilibrium and thus, prevented the biodegradation of adsorbate.

General rules of thumb, uses, and caveats that are helpful in isotherm interpretation are as

follows (Engineering Designs, 2001)

1. A flat isotherm curve indicates a narrow Mass Transfer Zone (MTZ), meaning that the GAC generally adsorbs contaminants at a constant capacity over a relatively wide range of equilibrium concentrations. Given an adequate capacity, carbons exhibiting this type of isotherm will be very cost effective and adsorption system design will be simplified owing to a shorter mass transfer zone.
2. A steep isotherm curve indicates a wide MTZ, with the adsorption capacity increasing as equilibrium concentration increases. Carbons exhibiting this type of isotherm curve tend to be more cost effective.
3. A change in isotherm slope generally occurs for wastes that contain several compounds with variable adsorption capacities. An inflection point occurs when one compound is preferentially adsorbed over another and desorption occurs, so that the preferentially adsorbed compound can utilize sites previously used by less adsorbable compounds.

Liquid phase isotherms are useful screening tools as follows (Engineering Designs, 2001):

1. to determine if adsorption is a viable technology,
2. to calculate the equilibrium capacity or approximate capacity at breakthrough so that a preliminary estimate of carbon usage can be made,
3. to determine the relative difficulty to remove individual contaminants if single-constituent isotherms are used, and the identity of the initial breakthrough compound,
4. to determine changes in equilibrium adsorption capacity relative to the concentration of contaminants in the waste stream, and the effects of changes in waste stream concentration,
5. to determine the maximum amount of contaminant that can be adsorb by GAC at a given

concentration, and

6. the relative efficiencies of different types of carbons to identify which should be used for dynamic testing.

Adsorption capacity is influenced by many factors such as flow rate, feed concentration, bed height, temperature, and pH (liquid phase) (Metcalf and Eddy, 2003).

2.7.3. Activated carbon adsorption kinetics

2.7.3.1. Mass transfer zone

The sorption area of the GAC bed is called mass transfer zone (MTZ). As the water containing pollutants passes through the bed whose depth is equal to the MTZ, the concentration of the pollutants in water cannot further be decreased in the region before the MTZ. The MTZ will move in the direction of the flow until the exhaustion of the bed. Typically, when the effluent concentration reaches above 5% of its inlet concentration, the carbon bed is said to have achieved its breakthrough point. A schematic diagram of MTZ moving through a column is shown in Figure 2.4. The length of MTZ is a function of hydraulic loading rate of the water to be treated and the concentration of pollutants in the water (Metcalf and Eddy, 2003).

2.7.3.2. Breakthrough capacity

In practice, the breakthrough capacity $(x/m)_b$ of a column is a percentage of a theoretical adsorption capacity (x/m) of the carbon found from the isotherms. Usually, the breakthrough capacity is calculated as 25 – 50% of theoretical adsorption capacity as shown in Equation (2.4) (Metcalf and Eddy, 2003).

$$Theoritical\ adsorption\ capacity\ = \frac{Breakthrough\ time\ \times Flow\ rate \times Feed\ Concentration}{Mass\ of\ Adsorbent\ in\ Bed} \qquad (2.4)$$

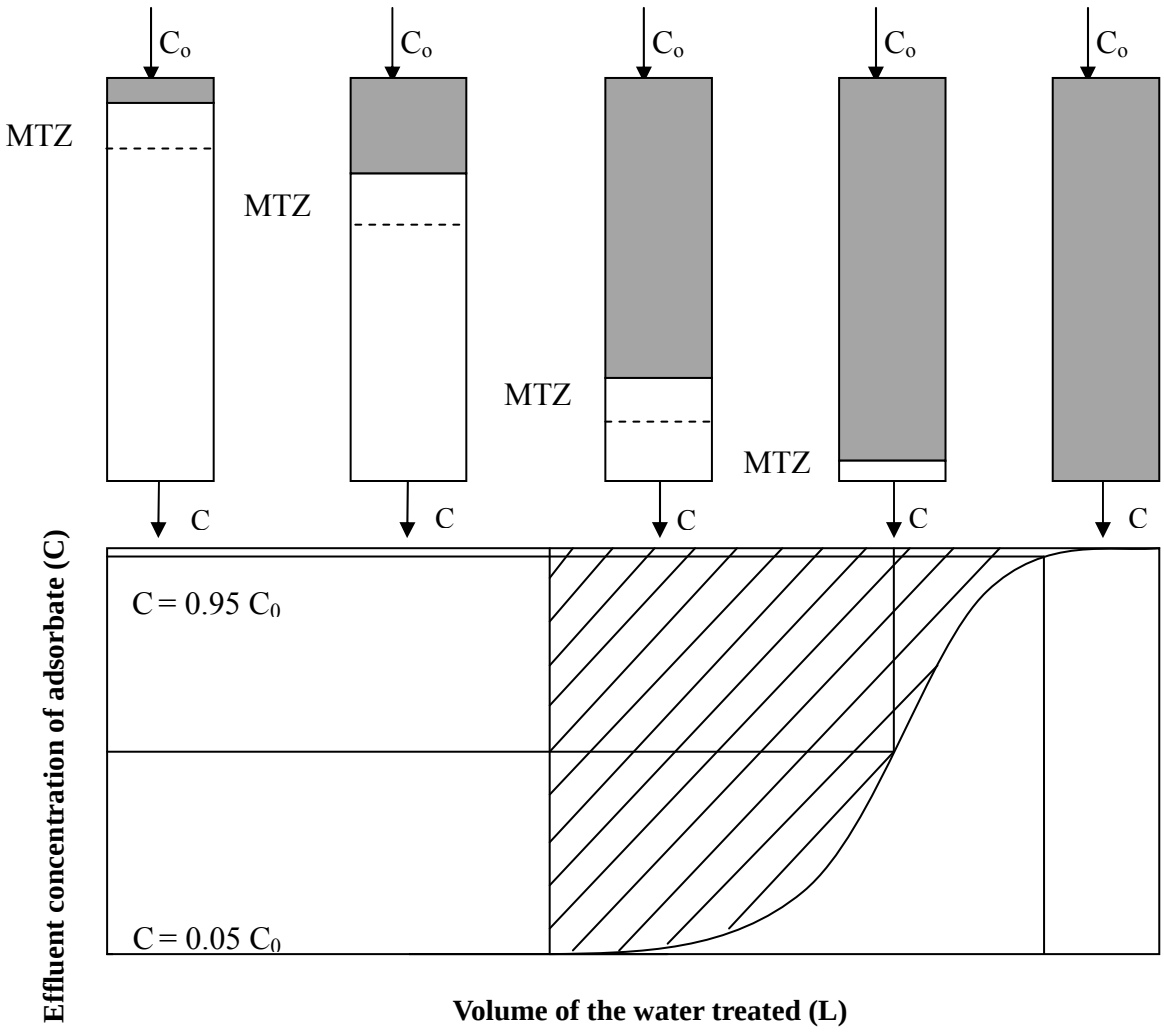

Figure 2.4. Schematic diagram of mass transfer zone and column breakthrough (adapted from Metcalf and Eddy, 2003).

where; break through time = [*min*]; flow rate = [*L/min*]; Feed Concentration = [*mg/L*]; Mass of adsorbent in the bed= [*mg*Activated Carbon]; Breakthrough capacity = [*mg/mg*Activated Carbon].

2.7.4. Fixed-bed adsorption model

Few mathematical models have been developed to calculate the important parameters used in the design of fixed bed column absorbers as well as to describe the column breakthrough curves. The most commonly used model is Bohart -Adams model. Bohart -Adams established a fundamental equation that describes the relationship between concentration profile (C/C_o) and the time for the adsorption of chlorine on charcoal in a fixed bed column (Bohart and Adams, 1920). This model assumes that the adsorption is proportional to both residual capacity of the activated carbon and the concentration of the sorbing species. The Bohart -Adams model Equation (2.5) is used to describe the initial part of the breakthrough curve (Hamdaoui, 2006; Han et al., 2008).

$$\frac{C}{C_o} = exp\left(K_{AB}C_o t - K_{AB}N_o\left(\frac{z}{v}\right)\right) \tag{2.5}$$

By taking the natural logarithm of both sides, it can be rearranged as follows

$$ln\ \frac{C}{C_o} = K_{AB}C_o t - K_{AB}N_o\left(\frac{z}{v}\right) \tag{2.6}$$

where:

C = effluent wastewater concentration in TOC (*mg*C/*L* of solution);

C_o = influent wastewater concentration in TOC (*mg*C/*L* of solution);

K_{AB} = Bohart -Adams kinetic constant (*L/(mg*C *min*));

N_o = maximum adsorption capacity of the adsorbent (*mg*C adsorbed/*L* of solution);

t = time to breakthrough point (*min*);

z = carbon bed height (m);

v = superficial velocity (m/min).

In 2005, Goel *et al*. performed the adsorption experiment of Lead (II) on activated carbon for the determination of Bohart-Adams constant to predict the breakthrough time for the pilot column as presented in Table 2.7. The Bohart-Adams constant N_o and K_{AB} were found to be 525 *mg*C adsorbed*/L* of solution and 0.022 *L/(mg*C *min*), respectively.

Table 2.7. Results of Bohart-Adams modeling for the prediction of pilot scale lead removal column (adapted from Goel *et al*., 2005).

Inlet Concentration *mg/L*	**Hydraulic loading rate (*L/min.m*^{2})**	**Breakthrough point**	**Predicted time (*min*)**	**Observed time (*min*)**	**Breakthrough capacity of GAC (*mg/g*Activated *C*arbon)**
6	82.1	60%	3900	4320	3

2.7.5. Desorption process/Activated carbon regeneration

The goal of a treatment process is to get an end pipe solution. Once the activated carbon reaches the maximum adsorption capacity, it no longer adsorbs pollutants. Earlier, the exhausted carbon were incinerated or buried. The incineration of the waste leads to air pollution and other health effects. An economical way to use carbon adsorption technique is to regenerate / reactivate the exhausted carbon, back or near to its adsorption capacity, by using efficient methods. The methods that are used to regenerate the exhausted carbon are either the treatment of carbon with chemicals which oxidize the pollutants captured in the pores of the carbon, steam backwashing which drags the volatile pollutants out with ease, solvents which leach the carbon, and finally biological degradation of the pollutants using microbial culture.

The desorption/regeneration process depends on the time and the temperature at which the exhausted carbon is activated. It was found that the GAC capacity was returned to that of the virgin activated carbon at a temperature of $850^{o}C$ in 15 *min* (Pelech *et al.,* 2005). Hand *et al.,* (1984) found that typically 4 – 10% of carbon is lost during the regeneration process. Many papers are published in support of regenerated exhausted carbon (Hand *et al.,* 1984; Munoz *et al.*, 2007; Moreno *et al.*, 1995), as treatment of any waste has to be an end pipe solution rather than merely transferring the waste from one carrier to another. The regeneration of the GAC is either done in-situ or collected from different locations and sent to a regeneration facility.

As mentioned earlier, various technologies have been developed for the regeneration of exhausted activated carbon using steam and chemicals. Volatile organic compounds (VOC) such as dichloromethane and trichloroethane are very well adsorbed on carbon and their removal efficiency from the wastewater is around 95-98%. Experiments conducted for desorption of these VOCs using steam at $300^{o}C$ have shown up to 99% removal efficiency (Pelech *et al.,* 2005). Carbon loaded with calcium could regenerate GAC with properties close to the virgin carbon by reducing the time and the temperature of the regeneration process (Knappe *et al.*, 1992). Biological regeneration of carbon is also practised, as it combines both the biological and physiochemical processes and thus, reduces the regeneration cost. Liang *et al.* (2007) proved that the biological activated carbon (BAC) was effective to remove 89% of both toluene and H_2S from the toluene - H_2S gas mixture.

2.7.6. Design parameters

The choice between powdered activated carbon (PAC) and granular activated carbon (GAC) selection is based on the following factors (Wang *et al.*, 2006):

1. Type of existing equipment: PAC is added as slurry to the wastewater and is removed by successive treatment processes along with the waste sludge. Thus, its use is limited to surface water treatment with existing filters; whereas GAC is used in fixed bed adsorbers. It is usually placed between gravity filters and final disinfection step.
2. Projected carbon usage: The effective carbon use per water volume treated is much lower for GAC than the dose of PAC required attaining the same removal. Thus, PAC is generally preferred in seasonal or intermittent contamination case or where a lower carbon dosage rate is required.
3. Desired effluent quality and variability of flow rate and pollutant concentration: This choice is directly dependent on the adsorption capacity of the carbon and effective carbon surface utilized during the adsorption process and can be obtained from the isotherm studies and physical properties of the carbon.
4. Contact time: It is the time by which the wastewater is in contact with the activated carbon and largely depends on the flow rate of the influent wastewater. The contact time of GAC adsorber is usually 5- 30 *min* while for PAC it is 0.5-1 *day*.
5. Disposal: On exhaustion of activated carbon adsorption capacity, GAC can be regenerated and reused before disposal whereas PAC (and some GAC) is normally just disposed off.

Factors affecting the adsorption performances are molecular structure, solubility, pH, temperature, and adsorption of mixed solutes. A comparative study for GAC columns used in industrial wastewater treatment experiments to obtain column dimensions is summarized in Table 2.8. It is desirable to have large height to diameter (H: D) ratio, because the percent utilization of maximum capacity of absorbent increases with this ratio (Reynolds and Richards, 1995).

Table 2.8. Comparison of height to diameter ratio for various GAC columns**.**

Type of Water	**Height (H)*mm***	**Diameter (D) *mm***	**Carbon Bed Height (H_b) *mm***	**H: D Ratio**	**H_b: D Ratio**	**References**
Pink water	4900	510	3400	9.6:1	6.6:1	Doll and Frimmel (2005)
Synthetic wastewater	N/A	50	300	N/A	6:1	Andreozzi *et al.*(2002)
Industrial wastewater	250	25	N/A	10:1	N/A	Huber *et al.* (2003)
Wastewater	900	40	480	22.5:1	12:1	Nikolaou *et al.*(2007)
Drinking water	205	9	N/A	22.7:1	N/A	Guzzella *et al.* (2002)
Drinking water	1400	4500	N/A	0.31:1	N/A	Guzzella *et al.* (2002)
Synthetic wastewater	N/A	140	1000	N/A	7.1:1	Chang *et al.* (2007)
Synthetic wastewater	N/A	110	1000	N/A	9.1:1	Chang *et al.* (2007)
Synthetic wastewater	N/A	40	419	N/A	10.5:1	Chang *et al.* (2007)
Synthetic wastewater	N/A	40	432	N/A	10.8:1	Chang *et al.* (2007)
Aqueous system	400	20	N/A	20:1	N/A	Snyder *et al.* (2004)
Aqueous system	800	100	N/A	8:1	N/A	Snyder *et al.* (2004)
Lake water	300	25	N/A	12:1	N/A	Snyder *et al.* (2007)
Pharmaceutical wastewater	N/A	50	260	N/A	5.2:1	Ternes *et al.* (2005)
Pharmaceutical wastewater	N/A	365	285	N/A	0.8:1	Ternes *et al.* (2005)
Pharmaceutical wastewater	900	120	850	7.5:1	7:1	This study

N/A – not available

2.8. Advanced Oxidation Processes (AOPs)

AOPs are emerging technologies which have been of a great interest in water and wastewater treatment since past several decades. They are promising technologies for treating wastewater containing recalcitrant and inhibitory organics, microbes, and contaminants from surface and groundwater. AOP works on the principle of chemical oxidation of organic compounds into simpler form of molecules without generating any secondary waste disposal problem or transferring them to another medium. The versatility of AOPs is also enhanced by different generation methods of free radicals. Many AOPs use O_2, O_3, or hydrogen peroxide (H_2O_2) as an oxidant to generate free radicals required to destroy the organic compounds. Mostly, H_2O_2 is used to generate hydroxyl radicals ($^{\bullet}OH$) in presence of UV light with wavelength 254 *nm* or less. Major reactions involved in UV/H_2O_2 process are listed in Reactions (2.7) to (2.13). These reactions are by no means a comprehensive list of all the reactions that take place in a UV/H_2O_2 process (Beltran *et al.*, 1999; Grenjak, 2006; Johnson and Mehrvar, 2008).

$$H_2O_2 + h\nu \xrightarrow{\varphi_1} 2\,{}^{\bullet}OH \qquad \varphi_1 = 0.5 \text{ mol photon}^{-1} \qquad (2.7)$$

$$H_2O_2 + {}^{\bullet}OH \xrightarrow{k_1} HO_2{}^{\bullet} + H_2O \qquad k_1 = (1.4\text{-}4.5) \times 10^7\, M^{-1}s^{-1} \qquad (2.8)$$

$$2\,{}^{\bullet}OH \xrightarrow{k_2} H_2O_2 \qquad k_2 = (5.0\text{-}8.0) \times 10^9\, M^{-1}s^{-1} \qquad (2.9)$$

$$2HO_2^{\bullet} \xrightarrow{k_3} H_2O_2 + O_2 \qquad k_3 = (0.8\text{-}2.2) \times 10^6\, M^{-1}s^{-1} \qquad (2.10)$$

$$HO_2{}^{\bullet} + {}^{\bullet}OH \xrightarrow{k_4} H_2O + O_2{}^{\bullet} \qquad k_4 = 1.4\times 10^{10}\, M^{-1}s^{-1} \qquad (2.11)$$

$$RH + {}^{\bullet}OH \rightarrow \text{intermediates} \xrightarrow{k_5} CO_2 + H_2O \qquad \text{RH = pollutant; } k_5 \text{ varies} \qquad (2.12)$$

$$RH + h\nu \rightarrow \text{intermediates} \xrightarrow{\varphi_2} CO_2 + H_2O \qquad \text{RH = pollutant; } \varphi_2 \text{ varies} \qquad (2.13)$$

In 1996, Kerzhentsev *et al.* reported that most organic compounds can be completely mineralized and converted into CO_2, H_2O, NO_3^-, NH_4^+, and SO_4^{2-} by irradiation in the presence of TiO_2. Moreover, nitrogen-containing molecules are mineralized into NH_4^+ and mostly into NO_3^- (Kerzhentsev *et al.*, 1996). Ammonium ions are relatively stable and their proportion depends mainly on the initial oxidation degree of nitrogen and on the irradiation time in the presence of air (Ioannis *et al.*, 2003).

The most common AOPs are UV, UV/H_2O_2, UV/O_3, Fenton/H_2O_2, photo-Fenton/H_2O_2, O_3, O_3/H_2O_2, TiO_2/UV (photocatalysis), UV/O_3/H_2O_2, and TiO_2/UV/H_2O_2 processes. Different methods produce different types of free radicals depending on the oxidants used. Table 2.9 shows various types of radicals generated by different processes. The intermediates formed during the advanced oxidation treatment are different depending on target pollutants. Table 2.10 shows AOP treatment methods used for few pharmaceutical compounds.

Table 2.9. Types of radicals generated in advanced oxidation processes (Gulyas *et al*., 1997).

Process	**Free radicals produced**
UV/ H_2O_2, UV/O_3, UV/O_3/ H_2O_2, O_3, O_3/ H_2O_2, H_2O_2/Fe^{2+} (Fenton process), H_2O_2/ Fe^{2+} (photo Fenton), TiO_2/UV (photocatalysis), TiO_2/UV/ H_2O_2	$^{\bullet}OH$
UV/ H_2O_2, UV/O_3, UV/O_3/ H_2O_2, O_3, O_3/ H_2O_2,	$HO_2^{\bullet}$
UV/O_3, UV/O_3/ H_2O_2, O_3, O_3/ H_2O_2,	$HO_3^{\bullet}$
UV/O_3, UV/O_3/ H_2O_2, O_3, O_3/ H_2O_2,	$O_2^{\bullet}$

Table 2.10. Example of advanced oxidation processes used for the treatment of few pharmaceutical compounds found in waste water.

Compound	Treatment Methods	Conditions	Degradation Product	Efficiency	References
Benzene	flash photolysis	N/A	Phenol	N/A	Baulch *et al.*, 1988
Aniline	electrochemical oxidation	C_o = 0.001 *M* T= 81 *h*	Maleic acid and CO_2	76.1	Chung and Park,2000
4- Aminophenol	ozonation	O_3 dose = 5.3 *g/h* C_o. = 10 *mmol/L* T = 10 *min*	Acetic acid	72%	He *et al.*, 2007
Aniline	photocatalytic oxidation using TiO_2	C_o = 0.4 *mg/L* T = 7 *h*	No C_6H_6 ring in the end product	84.7	Li and Zhong, 2005

N/A- not available

2.8.1. Factors affecting the UV/H_2O_2 performance

2.8.1.1. Presence of carbonate species

Bicarbonate and carbonate ions present in the background water matrix scavenge hydroxyl radicals and reduce the reaction rates with organics according to Reactions (2.14) to (2.16) (Johnson and Mehrvar, 2008).

$$HCO_3^- + {}^{\bullet}OH \xrightarrow{k_6} CO_3^{\bullet -} + H_2O \qquad k_6 = 2\times10^7\ M^{-1}s^{-1} \qquad (2.14)$$

$$CO_3^{2-} + {}^{\bullet}OH \xrightarrow{k_7} CO_3^{\bullet -} + OH^- \qquad k_7 = 3.7\times10^8\ M^{-1}s^{-1} \qquad (2.15)$$

$$CO_3^{\bullet -} + H_2O_2 \xrightarrow{k_8} HCO_3^- + HO_2^{\bullet} \qquad k_8 = 8.2\times10^5\ M^{-1}s^{-1} \qquad (2.16)$$

2.8.1.2. Presence of natural organic matter

Natural organic matters (NOM) present in the background water matrix scavenge hydroxyl radicals and reduce the reaction rate with target compound (Trussel Tech, 2010). Reaction (2.12) is applicable to NOM reaction with hydroxyl radical when RH is replaced by NOM.

2.8.1.3. pH

The pH has a significant effect on the oxidation pathway and the end products. The pH dictates the level at which certain ions important to AOPs are present, including carbonate ion, bicarbonate ion, and the anion of hydrogen peroxide ($OH_2^{\bullet -}$) (Crittenden *et al.,* 2005). The pH affects the charge on target organics if they are weak acids or bases and in some cases the ionic form has a rate constant one or two orders of magnitude higher than that of the molecular form (Trussel Tech, 2010).

It has been observed that the UV/H_2O_2 process for COD removal from the wastewater of oil recovery industry (initial COD concentration = 1050 *mg/L*, COD: H_2O_2 = 1:2, pH = 3, temperature = 39 - 43^oC) showed that almost 90% of the COD could be removed (Dincer *et al.*, 2008). Aromatic compounds (initial COD concentration = 8,034 *mg/L*, pH = 8.7, time = 4 *h*) are easily degraded via ozonation at pH 3 and 8 with average COD removal efficiencies of 57% (pH 8) to 60% (pH 3) (Arslan and Balcioglu, 2002).

2.8.1.4. UV lamp technology

There are two types of lamps commonly applied in the AOPs for destruction of target compounds (Trussel Tech, 2010):

a. Low pressure UV (LPUV) lamps

b. Medium pressure UV (MPUV) lamps.

LPUV lamps may be either low intensity or high intensity lamps. LPUV lamps emit UV light only at a wavelength of 254 *nm*. MPUV lamps emit energy over 200 through 400 *nm* range but only the 200 to 300 *nm* is important in the UV/H_2O_2 process because hydrogen peroxide only absorbs UV light at wavelengths less than 300 *nm* (Crittenden *et al.,* 2005). LPUV lamps generate UV light more efficient than MPUV lamps. MPUV lamps can operate at a higher power input so fewer lamps may be needed, but the power requirements are greater for each lamp (Reynolds and Richards, 1995).

2.8.1.5. Concentration of oxidants

Most studies (Table 2.5) show that there is an optimum concentration of the oxidants, such as H_2O_2 and O_3, under which the performance of the treatment process is maximized and

reaches to 90% pollutant removal efficiency. The concentration of H_2O_2 oxidants above optimum value does not further enhance the performance of the process but, in turn, has an inhibitory effect on the degradation of pollutants. In Fenton reaction, the extent and the rate of the degradation process are also increased by increasing oxidation concentrations (Parra *et al.*, 2000). The amount of the H_2O_2 required to satisfy 1 *g* (chemical) oxygen demand of the pollutant/contaminant can be calculated using stoichometry to be 2.125 *g* of H_2O_2, as shown below. This stoichometry equivalence is used as a base to initiate the optimization procedure of H_2O_2 (calculation shown in Appendix D).

1 *g* COD = 1 *g* of O_2 = 0.03125 *mol* of O_2 = 0.0625 *mol* equivalent of H_2O_2 = 2.125 *g* of H_2O_2

Optimal concentration of H_2O_2/contaminant (mole H_2O_2 / mole of contaminant) between molar ratios of 10 to 100 has been proposed by some researchers (Bhaskaran and Kanmani, 2007; Parra *et al.*, 2000). There was also 80% decrease in the inhibition effect when 32 cm^3 H_2O_2 was added to 1,000 cm^3 textile wastewater. The excess H_2O_2 reacts with $^{\bullet}OH$, competing with contaminant present in the wastewater of interest, as shown in Reaction (2.8), hence decreasing the efficiency of the treatment (Stanislaw and Gonera, 1999).

Also, relatively high hydrogen peroxide dosages compared to the O_3/ H_2O_2 process are needed for the UV/H_2O_2 process to generate sufficient quantities of hydroxyl radicals because hydrogen peroxide does a poor job absorbing UV light (Crittenden *et al.,* 2005), especially compared to NOM and iron if they are present. Higher H_2O_2 dosages produce significant amounts of residual H_2O_2 that must be removed from water. The chemical cost of H_2O_2 needs to be balanced against the energy costs of the UV lamps when evaluating an appropriate UV/H_2O_2 process (LPUV or MPUV) for a given application.

2.8.1.6. Photolysis of hydrogen peroxide

Photolysis is a process in which compounds absorb photons and the energy released drives oxidation processes induced by light. The photolysis rate of a compound can be estimated based on its light absorption rate and quantum yield (Crittenden *et al*., 2005). The extinction coefficient represents the phenomenon that as wavelength decreases, more photons are absorbed (Aquafine, 2009). It is the photolysis of hydrogen peroxide that generates the hydroxyl radicals that drive the UV/H_2O_2 according to the Reaction (2.7):

Studies have also shown that UV lamp of 185 *nm* wavelength would break water molecules to ˙OH radicals by lysing the water molecule (Cal Water, 2010). While 254 *nm* radiation can travel effectively through water for almost a meter, 185 *nm* radiation, because of its interaction with water molecules, loses much of its strength after several centimetres (Aquafine, 2009).

2.8.1.7. Reactivity of the target compound with hydroxyl radicals.

The general reaction for destruction of a target compound (contaminant) in an AOP is shown in Reaction (2.12) (Beltran *et al.*, 1999) where:

$$RH + {}^{\bullet}OH \rightarrow \text{intermediates} \xrightarrow{k_5} CO_2 + H_2O \qquad \text{RH = target compound; } k_5 \text{ varies} \qquad (2.12)$$

The second order hydroxyl radical rate constant is an indication of how the AOP reactions will proceed. AOP reactions tend to be quite rapid with second order hydroxyl radical rate constants on the order of 10^8 to 10^{10} *L/mole.s*. The higher the second order hydroxyl radical rate constant, the more amenable the compound is to reduction by an AOP (Crittenden *et al*., 2005). A sampling of second order hydroxyl radical rate constants is provided in Table 2.11.

Table 2.11. Second order hydroxyl radical rate constant, $k_{\cdot OH}$, of several compounds

Compounds	**Second Order Hydroxyl Radical Rate Constant, $k_{\cdot OH}$, $M^{-1}s^{-1}$ (adapted from Crittenden *et al.*, 2005)**
1,4- dioxane	2.8×10^9
2-methylisoborneol (MIB)	8.2×10^9
Geosmin	1.4×10^9
Methyl tert-butyl ether (MTBE)	1.6×10^9
1,2- dichloroethane	2.0×10^9
HCO_3^-	8.5×10^9
CO_3^-	3.9×10^9
NOM	3.0×10^9 - 4.5×10^9

Although the second order rate constants of bicarbonate ion, carbonate ion, and NOM are typically lower than those of the target compounds, their concentrations are often several orders of magnitude higher than the target compounds, increasing the importance of the presence of these species in the background water matrix (Mehrvar *et al.*, 2001).

2.8.1.8. Treatment time

The information on the toxicity and the biodegradability of the intermediates helps to determine the optimum treatment time. In 2000, Parra *et al.* reported that during the first hour of the UV/H_2O_2 treatment process, there was the formation of intermediates which were more toxic ($1/EC_{50}$ = 0.3 *mg*C/ *L*, where EC_{50} is half maximal effective concentration which is used as a measure of drug's potency) than the initial compounds; metobromuron and isoproturon ($1/EC_{50}$ = 0.06 *mg*C/ *L*) and it was sharply decreased with an increase in the treatment time.

An optimum contact time is necessary not only to increase the efficiency of the process, but also to minimize the operational cost (Stasinakis, 2008). It is reported that 60% of the total operation cost is due to the higher consumption of electricity without beneficial effect in efficiency during the Fe^{+2}/H_2O_2/UV process (Parra *et al.*, 2002).

Based on the literature review, biological process is a common process to degrade the concentrated pharmaceutical wastewater; however it is a slow process and could take up to months. Dilution of the wastewater is necessary to prevent shock load on the microorganisms. It is difficult to apply remediation methods to highly concentrated sulpha drug wastewater. Compositions of pharmaceutical drugs present in the wastewater are also hazardous and toxic if left untreated even in the amount range of μg and has an impact on the aqua culture. UV/H_2O_2 (process which mineralizes the contaminants to CO_2 and H_2O) and GAC (process which removes desired amount of contaminant) could be used as an ex-situ remediation method. To date, limited studies have been performed on the treatment of pharmaceutical wastewater using GAC and UV/H_2O_2 methods.

CHAPTER 3

MATERIALS, METHODS, AND EXPERIMENTAL SETUP

3.1. Materials

3.1.1. Synthetic pharmaceutical wastewater composition

The synthetic wastewater was based on a composition found in the study of Patil *et al.* (1962) as shown in Table 3.1. The chemicals and their concentrations used in this study to replicate the wastewater characteristics found in the literature are listed in Table 3.2. 4-Aminophenol and sulfanilic acid were stored in a storage cabinet at room temperature while all other chemicals were stored in an inflammable liquid cabinet away from heat source (below $20^{o}C$) and were used as received.

Table 3.1. Characteristics of an untreated synthetic drug waste(Wang, 2006).

Compounds	Concentration (*mg/L*)
p-amino phenol, p-nitrophenolate, p-nitrochlorobenzene	150-200
Amino-nitrozo, amino-benzene, antipyrene sulfate	170-200
Chlorinated solvents	600-700
Various alcohols	2,500 – 3,000
Benzene, Toluene	400 – 700
4 amino-benzene sulfonic acid (sulfanic acid)	800 – 1,000
Sulfa drugs	400 – 700
Analogous substances	150 – 200
Calcium chloride	600 – 700
Sodium chloride	1,500 – 2,500
Ammonium sulfate	15,000 – 20,000
Calcium sulfate	800 – 21,000
Sodium sulfate	800 – 10,000

Table 3.2. Composition of the synthetic pharmaceutical wastewater used in this study.

Compound	Molecular Formula	Molecular Weight (*g/mol*)	Amount (*mg/L*)	Manufacturer	Purity as provided by manufacturer
4-Aminophenol	$C_6H_4OHNH_2$	109.13	150	Alfa Aesar	98%
Aniline	$C_6H_5NH_2$	93.13	170	J.T. Baker	100%
Methyl chloride	CH_2Cl_2	84.93	600	EMD Chemicals	99.8%
Methanol	CH_3OH	32.04	2500	BDH Chemicals	99.8%
Benzene	C_6H_6	78.1121	400	EMD Chemicals	99%
Sulfanilic Acid	$C_6H_4NH_2SO_3H$	173.19	800	Alfa Aesar	98%

The estimated total organic carbon of synthetic wastewater based on the theoretical total organic carbon was 1,952 *mg*C*/L* (as shown in Appendix A). Distilled water was used to prepare the synthetic wastewater. To investigate the characteristics of initial synthetic wastewater, the pH value and the concentrations of COD, BOD_5, TOC, and TN were measured. The pH of the synthetic wastewater was 2.91 ± 0.8. Nominal COD, BOD_5, TOC, and TN of the synthetic wastewater were measured to be 5,475.37 ± 470; 1,935 ± 8; 1,705 ± 253; and 98.5 ± 14 *mg/L* in this study. The results are compared with literature values in Table 3.3. The physical properties of all chemicals are shown in Table 3.4

Table 3.3. Characteristics of synthetic pharmaceutical wastewater.

Characteristics	Literature values	Values in this study
COD (*mg*O_2/*L*)	4,000 – 5,194[a]	4,005 – 5,945
BOD_5 (*mg*O_2/*L*)	1,920 – 2,522[a]	1,926 – 2,492
TOC (*mg*C/*L*)	1,762[a] – 1,998[b]	1,452 – 1,958
TN (*mg*N/*L*)	109.47[b]	85 - 112
pH	2.9 - 7.6[a]	2.11 - 3.17

[a] Patil *et al*., (1962).
[b] Theoretical calculation based on the amount of chemicals used in the synthetic wastewater as shown in Appendix A.

Table 3.4. Physical properties of the chemicals found in synthetic pharmaceutical wastewater. (Yaws, 1999; Moreno-Castilla *et al.*, 1995; Orshansky and Narkis, 1997; Chinang *et al.*, 1999**)**

Compounds	**CAS No.**	**Molecular Formula**	**Appearance**	**Vapour Pressure at 20^{o}*C* *(mm Hg)***	**Boiling Point (^{o}*C*)**	**Molecular Weight (*g/mol*)**	**Solubility (*mg/L* in water) at 25^{o}*C***	**Density (*g/mL*) at 25^{o}*C***	**UV Intermediates**	**Adsorption Capacity (*g*/100 *g*Activated Carbon)**
4- Aminophenol 98%	123-30-8	C_6H_7NO	crystalline powder	N/A	284	109.13	15,000	1.13	acetic acid	17.8 at 25^{o}*C* from 1,000 *mg/L*
Aniline 99%	62-53-3	C_6H_7N	colorless oily liquid	0.6	184.13	93.13	34,160	1.018	maleic acid	12.66 at 25^{o}*C* from 1200 *mg/L*
Methylene Chloride 99.8%	75-09-2	CH_2Cl_2	colorless liquid	350	39.75	84.93	19,380	1.318	N/A	N/A
Methanol 99.9%	67-56-1	CH_3OH	colorless liquid	97	64.7	32.04	10,00,000	0.787	formaldehyde	33.9 at 25^{o}*C* from 2200 *mg/L*
Benzene 98%	71-43-2	C_6H_6	colorless liquid	74.6	80.1	78.11	1,755	0.873	maleic acid oxalic acid	20 at 30^{o}*C* from 617 *mL/L*
Sulfanilic Acid 98%	121-57-3	$NH_2C_6H_4SO_3H$	transparent crystals/ white powder	N/A	decompose at 288˚*C*	173.19	10,000 at 20^{o}*C*	1.49	N/A	N/A

N/A - not applicable

3.1.2. Granular activated carbon

Granular activated carbon was purchased from EMD Chemicals. Carbon granules were of 4-12 mesh size, pore volume 1 *mL/g*, specific surface area of 625 m^2/g, and specific density of 1.5 with respect to water (Table 2.6). They were stored in a well-ventilated storage cupboard .

3.1.3. Hydrogen peroxide

Hydrogen peroxide solution was purchased from EMD Chemicals and was used as received. It was 30% *w/w* in water with the molecular weight of 34.04 *g*/*mol* and the density of 1.11 g/cm^3.

3.1.4. 1 *N* NaOH solution

The 1 *N* NaOH solution using NaOH (99%, EMD Chemicals) (CAS#1310-73-2) was prepared by dissolving 1 *mole* NaOH in distilled water and diluted to 1 *L* in a volumetric flask. It was stored in an inflammable liquid cabinet away from heat source (below 20^oC).

3.1.5. 1 *N* H_2SO_4 solution

The 1 *N* H_2SO_4 solution, (99%) (CAS#7664-93-9) was purchased from EMD Chemicals and was used as received. It was stored in an inflammable liquid cabinet away from heat source (below 20^oC).

3.1.6. GAC pre-treatment

For every batch of pre-treatment, 4 *Kg* of fresh carbon were heated up to 170^oC in an FD series Binder-World oven with forced convection for 25 *min* to remove any volatile impurities

and was allowed to cool down for 30 *min*. The carbon was then soaked in distilled water for about 10-15 *min* to remove any carbon powder produced due to abrasion. This pre-treated carbon was used in all adsorption experiments.

3.1.7. Chemicals for TOC-TN analysis

Potassium hydrogen phthalate commonly known as KHP ($KHC_8H_4O_4$, 99.99%), potassium nitrate (KNO_3, 99.9%), and phosphoric acid (H_3PO_4, 99.99%) (BDH Chemicals, purchased from VWR International) were used for the calibration of total organic carbon (TOC) and total nitrogen (TN) analyzer. These chemicals were stored in a cold and well ventilated space. Potassium hydrogen phthalate (KHP) was used as an organic carbon source for TOC calibration. KHP was dried in an oven at 105º*C* for 2 *h* prior to the preparation of the standard stock solution and stored in a desiccator. For preparation of 4,000 *mg*C/*L* of KHP standard stock solution, an accurate 8,500 *mg* of KHP were dissolved in distilled water and was diluted to 1 *L*. A series of working standard solutions, covering the expected range of sample concentrations such as 1-4,000 *mg*C/*L* were prepared by accurately diluting 4,000 *mg*C/*L* of standard stock solution with distilled water. Both stock and working standard solutions were caped and stored at 2-8º*C* in a refrigerator.

Potassium nitrate (KNO_3) was used as a nitrogen source for TN calibration. Potassium nitrate was dried in an oven at 80º*C* and cooled in a desiccator at 25º*C*. 7.222 *g* KNO_3 were dissolved in distilled water and diluted to 1 *L* to prepare 1,000 *mg*N/*L* of KNO_3 standard stock solution. A series of working standard solutions covering the expected range of sample concentrations such as 1-200 *mg*N/*L* were prepared by accurately diluting the 1,000 *mg*N/*L*

standard stock solution with distilled water. Both stock and working standard solutions were caped and stored at 2-8º*C* in a refrigerator. 20% *v/v* phosphoric acid was prepared by diluting 20 *mL* of pure phosphoric acid to 80 *mL* distilled water. It was prepared fresh immediately before use.

3.1.8. Chemicals for BOD_5 analysis

3.1.8.1 Nutrients for biological oxygen demand analysis

A solution, which is called dilution solution in Standard Methods 5210B (APHA, 1998), contains the reagents of phosphate buffer solution, magnesium sulphate solution, calcium chloride solution, and ferric chloride solution. Other reagents used for BOD_5 tests include acid and alkali solutions, nitrification inhibitor, and glucose-glutamic acid solution. The solutions of phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride were stored in a refrigerator at 4º*C* after preparation. All reagent solutions were prepared as follows:

- Phosphate buffer solution : 8.5 *g* KH_2PO_4, 21.75 *g* K_2HPO_4, 33.4 *g* $Na_2HPO_4 \cdot 7H_2O$, and 1.7 *g* NH_4Cl were dissolved in approximately 500 *mL* of distilled water and were diluted to 1 *L*. The pH was adjusted to 7.2 using 1 *N* sulphuric acid or 1 *N* sodium hydroxide solution.
- Magnesium sulphate solution: 22.5 *g* $MgSO_4 \cdot 7H_2O$ were dissolved in distilled water and was diluted to 1 *L*.
- Calcium chloride solution: 27.5 *g* $CaCl_2$ were dissolved in distilled water and was diluted to 1 *L*.
- Ferric chloride solution: 0.25 *g* $FeCl_3 \cdot 6H_2O$ were dissolved in distilled water and was diluted to 1 *L*.

- Glucose-glutamic acid (GGA) solution: reagent grade glucose and glutamic acid were dried at 103º*C* for 1 *h*. 150 *mg* of glucose and 150 *mg* of glutamic acid were dissolved in distilled water and were diluted to 1 *L*. The standard solution of glucose-glutamic acid (GGA) was prepared to check dilution water quality, seed effectiveness, and analytical technique. They were prepared fresh immediately before use.

Nitrification inhibitor: 2-chloro-6-trichloromethyl pyridine was used as received (Hach Co.). Detailed procedure to carry out the BOD_5 test is explained in Section 3.4.4.

3.1.8.2. Seed source for BOD_5 analysis

One capsule of commercial polyseed (Polyseed®, InterLab® Supply) contains 100 *mg* of special microbial culture capable of degrading industrial and municipal wastewater. Polyseed solution was prepared by adding one polyseed capsule into a container filled with 500 *mL* distilled water. This solution was aerated using an aeration stone for 30 *min* and then settled for 15 minutes before use. The mixture was prepared fresh before use. Detailed explanation of its use in the BOD_5 analysis is given in Section 3.4.4.

3.1.9. Chemicals for COD analysis

Potassium hydrogen phthalate (KHP, $KOCOC_6H_4COOH$) with 99.9% purity (J.T. Baker), was used to prepare the standard solution for the COD analysis and was stored in a refrigerator at 2-4º*C*. For the preparation of 10 *g*COD/*L* standard stock solutions, KPH was pre-dried in an oven to a constant weight at 110º*C*, then 8.5034 *g* KPH, measured by a Mettler M3 Fisher Scientific microbalance with an accuracy of ±1 μg, were dissolved in distilled water and diluted to 1 *L*. A series of working standard solutions, covering the expected range of sample concentrations such

as 100 - 4,500 *mg*COD/*L* were prepared by accurately diluting the 10 *g*COD/*L* of standard stock solution with distilled water. Both stock and working solutions were stored in a refrigerator at 4º*C*.

Reagents required for COD analysis come in pre-packaged and premixed COD vials (Bioscience Inc.) based on method number 5220 of Standard Methods (APHA, 1998). COD vials with the range 100-4,500 *mg*COD/*L* were employed in this study. The chemical compositions of pre-packaged and premixed COD vials used for the COD analysis are shown in Table 3.5. The vials were stored at 2-10º*C*. Detailed explanation of the COD analysis procedure is given in Section 3.3.6.

Table 3.5. Chemicals compositions of a fresh COD vial as received.

Chemicals	**%volume present in 100-4,500 *mg*COD/*L* range vial**
sulphuric acid (H_2SO_4, 1 mg/m^3, CAS# 7664-93-9)	54
potassium dichromate ($K_2Cr_2O_7$, 0.0235 *mg/L* as Cr^{+6}, CAS# 7778-50-9)	0.14
silver sulphate ($AgSO_4$, 0.01 mg/m^3 as Ag, CAS# 10294-26-5)	0.29
mercuric sulphate ($HgSO_4$, 0.05 mg/m^3 as Hg, CAS# 7783-35-9)	0.43
sulfamic acid (NH_2SO_3H, CAS# 5329-14-6)	0.0001
water (H_2O, CAS# 7732-18-5)	54.8601

3.1.10 Hydrogen Peroxide Checkit

Hydrogen peroxide CHECKIT (Lovibond) was used to determine the concentration of

H_2O_2 in solution. The CHECKIT unit has three compartments, which functions as both a sample container and a comparator in a compact unit. The outer compartments are used for the analysis of low (0.2-2 *mg/L*) and high (10-10 *mg/L*) concentrations of H_2O_2. The middle compartment is used as a reference. It was filled with the water to be tested without addition of any reagent tablet in order to compensate for any inherent color or turbidity present in the sample. Three types of reagent tablets are part of this CHECKIT: LR (lower range), HR (high range), and acidifying tablet, which are used to detect the concentration of H_2O_2 in the sample.

To measure H_2O_2, each compartment was filled to the 10 *mL* mark with the sample water. A LR reagent tablet was added to the low range compartment and HR and the acidifying tablet were added to the high range compartment. The tablet was crushed with a clean stirring rod and the stopper was placed. The unit was inverted several times until the tablets were fully dissolved. Next, it was allowed to stand for 2 *min*. Then, CHECKIT was given a final shake and the colour produced was compared against the standards using daylight. The resulting sample colour was visually matched with the coloured plastic foils to indicate the concentration of the H_2O_2 present in the water sample. For example, if the colour of the water sampled was unchanged when the tablets were added to the sample water in the kit, the solution did not contain H_2O_2 in the range of detection (<0.2 *mg/L*). If the colour changes to pink, then the solution contains H_2O_2. For example, if the colour of the sample is dark orange, based on the nomenclature of the kit, the concentration of H_2O_2 of the sample is in the range of 100 *mg/L*. In contrast, if the colour of sample changes to light pink, the concentration is in the range of 0.2 *mg/L*.

3.2. Experimental Set-up

This section describes the adsorption, photochemical, and their combined processes. Experimental set up and analytical techniques for each process are described separately.

3.2.1. Experimental set-up for GAC adsorption/desorption process

The schematic diagram of the adsorption using granular activated carbon (GAC) is shown in Figure 3.1. The height to the diameter (H/D) ratio of the columns for wastewater treatment according to the previous studies (Table 2.8) ranged from 3.12:1 – 22:1. The two columns used in this study were 90 *cm* in height (H), 12 *cm* in diameter (D), and 85 *cm* in bed height (z), each with H/D = 7.5:1, indicating that the selected dimensions of the columns would be reliable to carry the pilot scale adsorption studies for the synthetic wastewater treatment. The volume of water in each column was 5 *L* without carbon and 4.5 *L* with activated carbon having porosity of 0.9 (Appendix F). The height of carbon bed in each column was 85 *cm* and the column had two supporting layers, of steel wire mesh at top and bottom, for the activated carbon bed. The column was packed with 2 *Kg* granular activated carbon from the top of the GAC column, before installation (Section 3.1.2). The total volume of the feed tank was 120 *L* with minimum 20 *L* water for operation. The dimensions of the feed tank were 58 *cm* in height, 58 *cm* in width, and 58 *cm* in length.

The synthetic wastewater, with the composition and characteristics as shown in Tables 3.2 and 3.3, was pumped into the GAC column using a proportioning pump (520-A-N5, Neptune). In order to mix the wastewater in the feed tank, the wastewater was recirculated to the feed tank for 15 *min*. The flow rate of the feed (*L/min*) was adjusted using a flow meter,

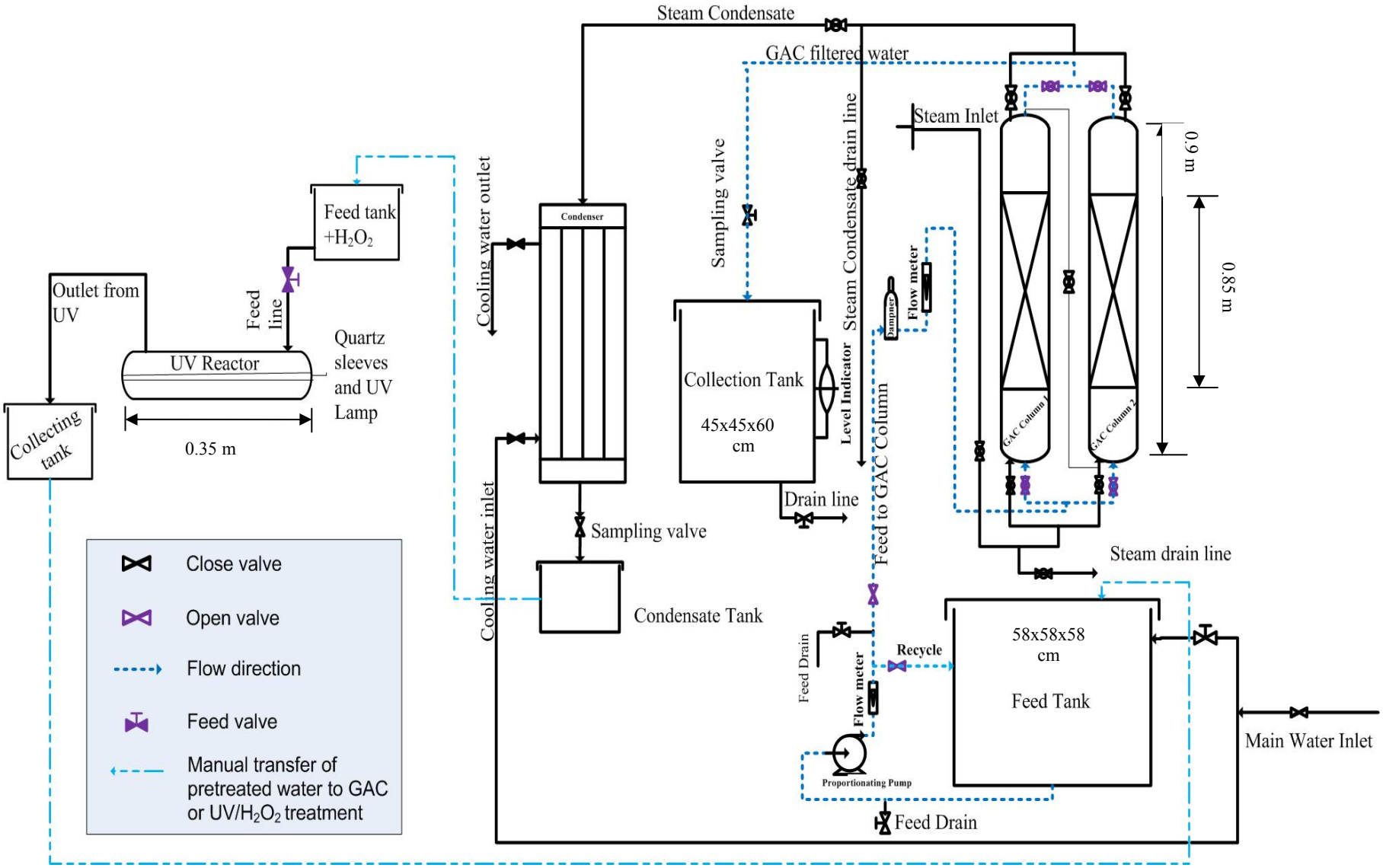

Figure 3.1. Schematic diagram of GAC adsorption and UV/H_2O_2 processes.

purchased from VWR International. The treated wastewater from the GAC column was discharged into a collecting tank with dimensions of 60 *cm* in height, 45 *cm* in width, and 45 *cm* in length. Treated wastewater samples were taken from sampling valves located above the collecting tank and from the collecting tank itself. During the desorption process, the steam was passed through the column, regulated by adjusting pressure monitored by a pressure gauge (range 0-35 *KPa*) using a ball valve. The steam from the column was condensed using a condenser by passing it through a copper tube immersed in water. The condenser had shell height of 45 *cm* and diameter of 20 *cm*. There were 20 copper cooling coils used with a diameter of 1.27 *cm* and total length of 15.24 *m*. The condensed steam was collected in the collecting tank with the capacity of 14 *L*, where the samples were taken from the sampling port located at the bottom of the condenser.

3.2.2. Experimental set-up for UV/H_2O_2 process

The experiments were performed in a 1.35 *L* stainless steel UV photoreactor (Siemens, SL-1S), with the outer diameter of 8 *cm* and the length of 35 *cm* (Figure 3.1). A low pressure UV (185 or 254 *nm*) lamp, covered with a quartz sleeve, was inserted into the center of the photoreactor. The lamp was 3.8 *cm* in diameter, 35 *cm* in length, and had a 17 *W* output power. The feed tank had a total volume of 14 *L* with the minimum 10 *L* water in the tank for operation.

The feed tank was placed at a height above the photoreactor so that the feed entered the reactor by gravity. The feed flow rate was adjusted using a valve (in the range of 22.5-3.75 *mL/min*) according to the hydraulic retention time (HRT) selected. The adjusted feed flow was confirmed before and after the experiments and maintained constant. The feed tank was maintained at 10 *L* during the entire experimental runs. A collection tank was placed at the exit of

the photoreactor with a holding capacity of 14 *L*. Prior to the start of the experiments, the synthetic wastewater mixed with the appropriate dosage of H_2O_2 solution was filled in the feed tank. Also, the UV lamps were switched on 15 *min* prior to the start of the experiments in order to make sure that the intensity of the lamp was uniform throughout the photoreactor (UV Process, 1995). Two sets of experiments were performed using 185 and 254 *nm* UV lamps. After performing one set of experiments with 185 *nm* UV lamp, the lamp was switched off and the feed flow to the photoreactor was stopped. Then, the UV photoreactor was drained and washed thoroughly by distilled water. The 185 *nm* wavelength UV lamp was removed from the reactor along with the quartz sleeve. The outer surface of the sleeve was also thoroughly washed with distilled water. The lamp was then replaced with the 254 *nm* UV lamp to continue the second set of experiments.

3.3. Analytical Techniques

The temperature, pH, TOC, TN, BOD_5 and COD were measured using the following analytical techniques.

3.3.1. Temperature and pH measurements

The pH was measured by a potentiometric pH meter using a glass indicator electrode and a reference electrode. The pH meter used in these experiments was model $230A^+$ from Thermo Orion, in which the indicator and reference electrodes were combined in one. The buffers of pH 4 and 7 were used to calibrate the meter before pH measurements. Those two buffers were chosen in the expected sample ranges. During pH measurements, the temperature was also displayed automatically. The calibration determined if the electrode was calibrated properly and was checked before testing samples.

3.3.2. Dissolved oxygen (DO)

Dissolved oxygen (DO) of the BOD_5 samples of influent and effluent wastewater (Appendix C) were measured by a dissolved oxygen meter (YSI 58 Dissolved Oxygen Meter, YSI Inc.) equipped with a BOD bottle probe (YSI 5750 Non-Stirring BOD Bottle Probe, YSI Inc.). The membrane of the probe was replaced during each calibration. The probe was filled with electrolyte solution and then the membrane was replaced and fixed over the probe avoiding any air bubbles using an "O" ring. The DO meter was first adjusted to zero readings and then it was calibrated using the air-saturated water by adjusting the DO reading to a corrected calibration value. The DO meter was calibrated before every test. Air-saturated water was obtained by aerating water for at least 15 *min* at a constant temperature which was measured through the temperature measurement function of the DO meter. A corrected calibration value was determined using the calibration value, (99%) at Toronto's altitude (76 meters above sea level). For example, the DO value at 76 *m* of sea level 58 is 8.92 *mg/L* at 21^oC, and then the corrected calibration value was calculated to be $8.92 \times 99\% = 8.47$ *mg/L*.

3.3.3. TOC/TN measurements

The TOC was measured by a Tekmar Dohrmann's Apollo 9000 TOC/TN analyzer. The analyzer uses combustion (680 to 1000^oC) with a patented reusable platinum catalyst for the lowest detection limit while maximizing TOC recovery. The Non-Dispersive Infra-Red (NDIR) detector in the Apollo 9000 TOC Analyzer is sensitive for very low levels of 4 *mg*C/*L* TOC which directly and specifically measures the carbon dioxide generated by the oxidation of the organic carbon in the sample. The chemiluminescence detector measures the TN content of the sample. Any potential interference is removed by in-line scrubbers or

filters as the sample gas is swept to the detector.

The analyzer is able to measure TOC and TN simultaneously for the same sample with an optional module. It can measure TOC between 4-25,000 *mg*C*/L* range and TN from 0-200 *mg*N*/L* range. Approximately 15-40 *mL* sample was filled in a sampling vial and was placed in the auto sampler. Through running TOC Talk software (version 3.5), the TOC and TN standard calibration analysis were carried out using the working standard solutions. The TOC (Figure 3.2 and 3.3) and TN (Figure 3.4 and 3.5) calibration curves for the range of 1-4,000 *mg*C*/L* and 1-200 *mg*N*/L* were obtained for analyzing TOC and TN concentrations, respectively. Measurement of each sample was repeated in triplicate and an average value was reported as the TOC/TN reading. A response factor of the instrument correlates the raw counts to a known amount of organic carbon in the standard. The calibrations of the TOC and TN curves were done once during the 9 month experimental study period.

The steps during the TOC/TN analysis (Apollo 9000 TOC/TN Analyzer Operation Manual, 2009) are described as follows:

1. Sampling: Samples were injected into the analyzer with the help of an automated syringe from the sampling bottle. The sample injection valve automatically selects the appropriate sample volume for the optimum measuring range.
2. Inorganic Carbon (IC) detection: 20% phosphoric acid was added to lower the pH so that inorganic carbon was sparged off as CO_2. This was measured to get IC content and to ensure that it was not carried over into the TOC.

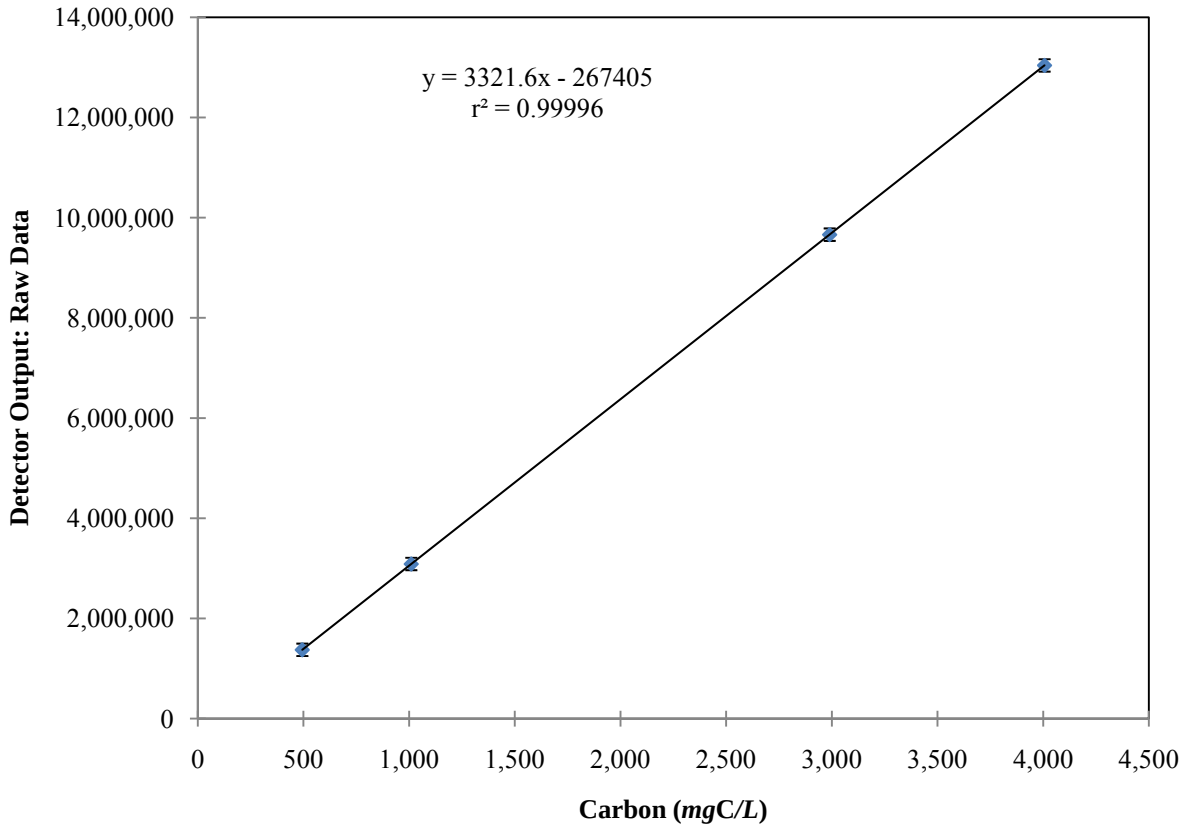

Figure 3.2. TOC calibration curve plotted for output raw data from the detector versus the amount of organic carbon present, for the range of 1 - 4,000 *mg*C/*L*. Here y represents the raw counts from the detector and x represents the amount of carbon present in *mg*C/*L*. A response factor of the instrument correlates the raw counts to a known amount of carbon in the standard and the software converts it into *mg*C/*L* respectively.

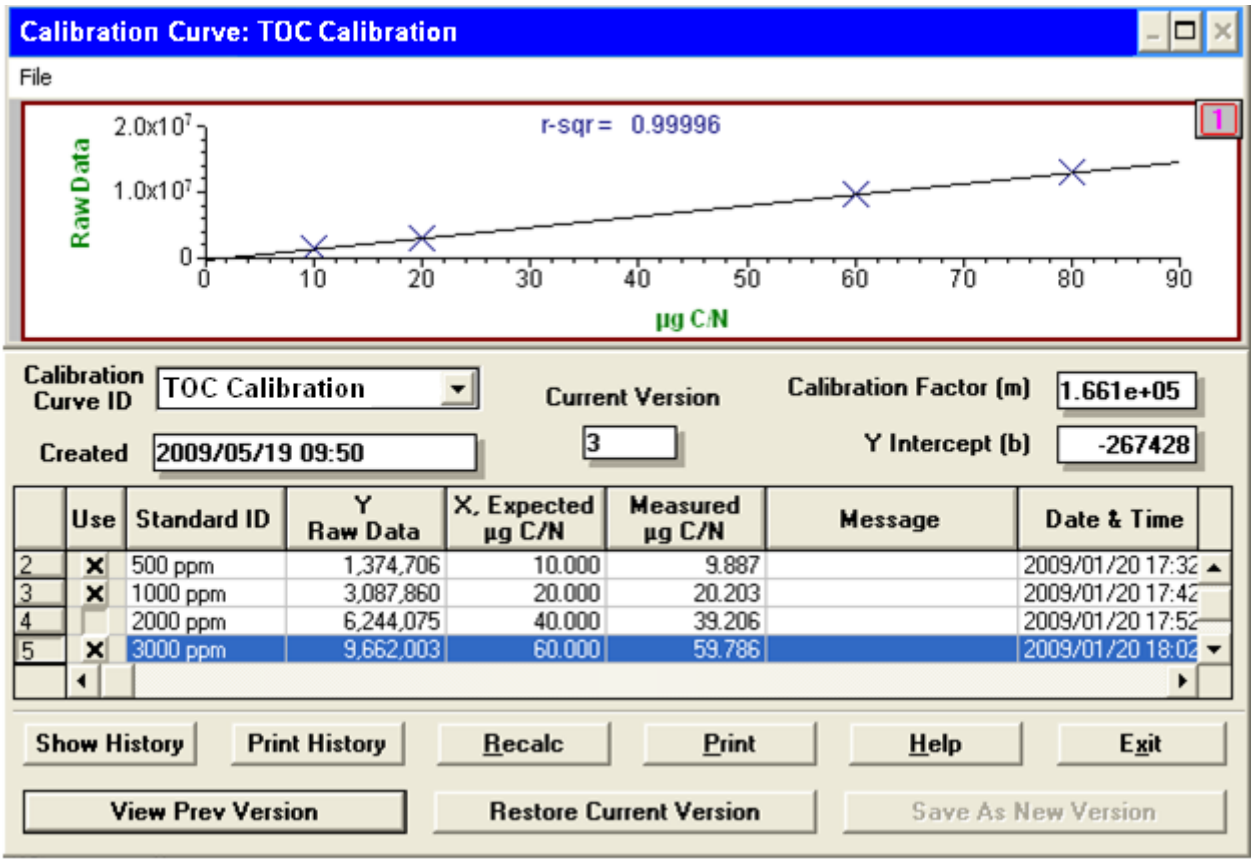

Figure 3.3. Snapshot of the TOC calibration curve for the range 0 - 60 μgC from Apollo 9000 TOC/TN analyzer.

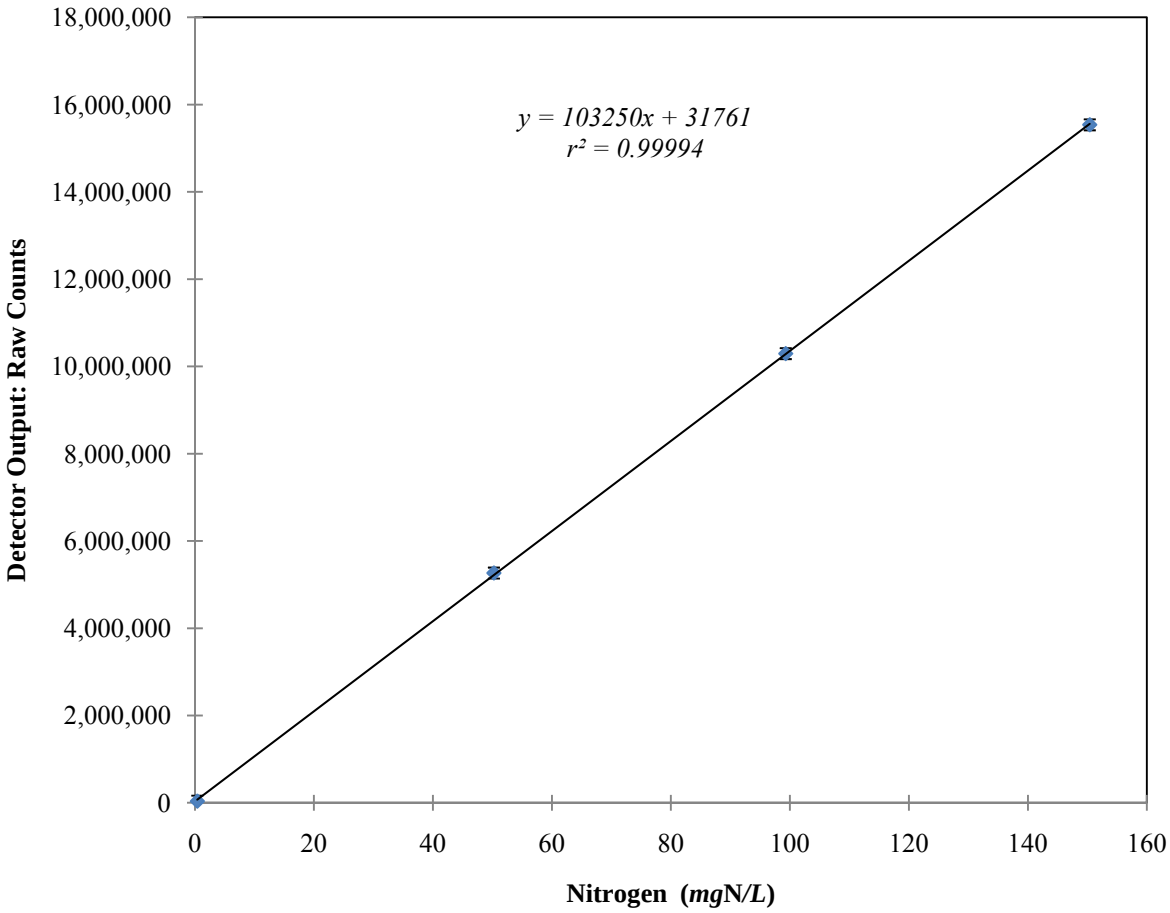

Figure 3.4. TN calibration curve plotted for output raw data from the detector versus the amount of nitrogen present, for the range of 1-200 *mg*N/*L*. y represents the raw counts from the detector and x represents the amount of nitrogen present *mg*N/*L*. A response factor of the instrument correlates the raw counts to a known amount of nitrogen in the standard and the software converts it into *mg*N/*L* respectively.

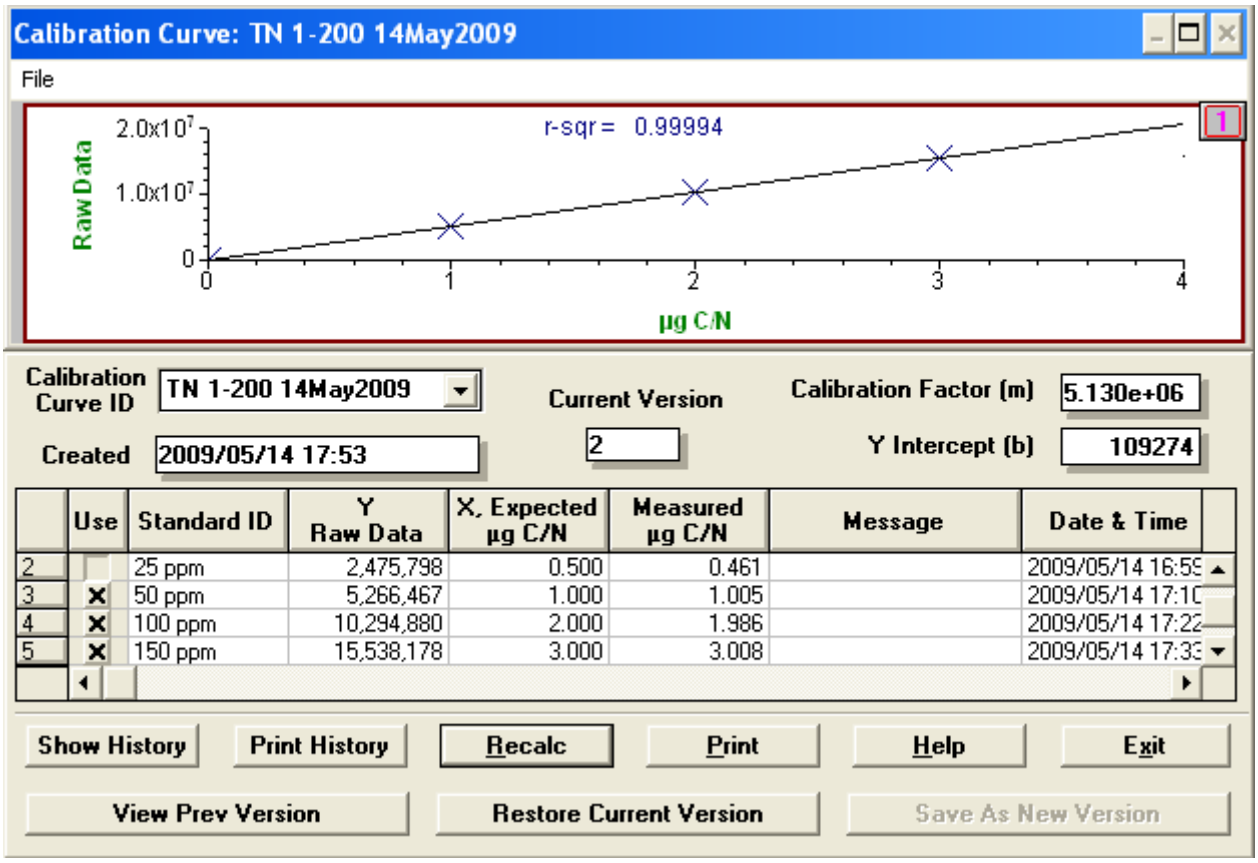

Figure 3.5. Snapshot of TN calibration curve for the range of 0 - 4 μgN from Apollo 9000 TOC/TN analyzer.

3. Oxidation: The high temperature combustion method was used to achieve the total and complete oxidation of the samples, including organic carbon to CO_2 and nitrogen compounds to nitric oxide (NO) in the combustion chamber.
4. TOC measurement: Carrier gas (purified air) sweeps sample gas containing CO_2, nitric oxide, and water vapour out of the combustion furnace. The sample then travels through tubing, cooled by a fan to condense water vapour and finally to water trap where water was collected. Then the sample gas passes through a semi-permeable Nafion® tube to further remove any moisture. This moisture free sample gas was then passed through the corrosive scrubber to remove any halides and finally to the NDIR-detector. Here, the CO_2 was measured and the result was displayed as Total Organic Carbon (*mg*C*/L*).
5. TN measurement*:* The sample gas from the NDIR-detector is directed towards nitrogen module where the nitric oxide is then reacted with ozone to produce excited state of nitrogen dioxide ($NO_2^{\cdot}$) that emits light when it decays to its ground state. This emitted light is measured with chemiluminescence detector (CLD) and correlated to specific amount of TN in the sample and was displayed as Total Nitrogen (*mg*N*/L)*.
6. Cleaning: Before introducing a sample, Apollo 9000 automatically rinses the syringe to eliminate any contaminants that may interfere with the testing process. This rinsing occurs through a loop sequence where the syringe is filled and discarded with distilled water.

TOC removal efficiency was determined by Equation (3.1).

$$TOC\% = \frac{(TOC_{in} - TOC_{out})}{TOC_{in}} \times 100\% \quad (3.1)$$

where,

TOC_{in} is *TOC* concentration of influent wastewater sample, *mg*C/*L*; and TOC_{out} is *TOC* concentration of effluent wastewater sample, *mg*C/*L*.

TN removal efficiency was determined by Equation (3.2).

$$TN\% = \frac{(TN_{in} - TN_{out})}{TN_{in}} \times 100\% \quad (3.2)$$

where,

TN_{in} is *TN* concentration of influent wastewater sample, *mg*N/*L*; and TN_{out} is *TN* concentration of effluent wastewater sample, *mg*N/*L*

3.3.4. BOD_5 measurements

Dilution water was prepared by adding 1 *mL* of each phosphate buffer, magnesium sulphate, calcium chloride, and ferric chloride per *L* of distilled water. The dilution water was placed in an incubator (C25KC, Classic Incubator Shaker, New Brunswick Scientific Co.) for 24 *h* at 20^{o}*C* and was aerated using an aeration stone for 1 *h* before use. 1 *mL* of each sample of the synthetic wastewater, 2 *mL* aerated polyseed solution, and 0.16 *g* nitrification inhibitor was added into 300 *mL* BOD bottle. Two blanks were prepared by filling with aerated dilution water to roughly check the quality of unseeded dilution water and the cleanliness of the BOD bottles. Three seed controls were prepared by adding 10, 15, and 20 *mL* of polyseed solution into separate 300-*mL* BOD bottles. A magnetic stirrer bar was used to stir the solution in each BOD bottle to make it homogenous during DO measurements and then all BOD bottles were filled with the aerated dilution water up to the middle of the bottles' neck.

Initial DOs of all samples including wastewater samples, the blanks, and the seed controls were first measured by a BOD bottle probe (YSI 5750 Non-Stirring BOD Bottle Probe, YSI Inc.) connected to an YSI 58 DO meter with mild agitation before incubation. All BOD bottles were incubated in the incubator at $20^{o}C$ for 5 days. The 5-day DOs of all samples were measured and their BOD_5 values were calculated. A sample calculation is shown in Appendix C. The BOD_5 removal efficiency was determined by Equation (3.3).

$$BOD_5\% = \frac{\left(BOD_{5,in} - BOD_{5,out}\right)}{BOD_{5,in}} \times 100\% \tag{3.3}$$

where $BOD_{5,in}$ is BOD_5 concentration of influent wastewater sample, *mg/L*; and $BOD_{5,out}$ is BOD_5 concentration of effluent wastewater sample, *mg/L*.

3.3.5. UV spectrophotometer

A UV spectrophotometer (Ultrospec 1100 pro UV/Vis Spectrophotometer, Biochrom Ltd.) was used for the quantification of color in terms of absorbance. The spectrophotometer had the ability to measure the absorbance, percent transmission, and concentration values. It measures the absorbance of samples based on the amount of light passed through a sample relative to a blank. While percent transmission mode measures the amount of light that has passed through a sample relative to a blank, it displays the result as a percentage. The concentration mode is used when a conversion factor is known, and it is required to convert the absorbance measurement for a sample at a specific wavelength into a concentration. The wavelength 600 *nm* was used for high range COD measurements. The light sources are tungsten halogen and deuterium arc (Ultrospec 1100 pro). The instrument has a one cell compartment.

The detector was from single solid state silicon photodiode. The cell was a standard rectangular quartz cell (optical glass). The cell's volume was 5 *mL* and had a polytetrafluoroethylene (PTFE) cover.

3.3.6. COD measurements

The COD was used to measure the amount of oxygen required to oxidize the organics in a solution by a powerful chemical oxidant. This oxidation is usually occurred by potassium dichromate in acidic solution. The drawbacks of this method are as follows (Eckenfelder, 2000):

1. COD cannot oxidize aromatics such as benzene and volatile straight-chain aliphatic compounds; therefore, they are not measured in the COD tests. The measured COD therefore underestimates the theoretical oxygen demand (ThOD).
2. Some reduced substances, such as sulphides, sulphites, and ferrous iron would be also oxidized and measured as COD. Therefore, the COD values are overestimated in this case.

The COD tests were carried out using the closed refluxed method. This method is based on the oxidation of organics by a mixture of $K_2Cr_2O_7$ and sulphuric acid (APHA, 1998). Potassium dichromate is a strong oxidizing agent under acidic conditions (acidity is usually achieved by the addition of sulphuric acid). The reaction of potassium dichromate with organic compounds is given by as follows:

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \rightarrow nCO_2 + \left(\frac{a+8d-3c}{2}\right)H_2O + cNH_4^+ + 2dCr^{3+} \qquad (3.4)$$

where,

$d = 2n/3 + a/6 - b/3 - c/2.$

In the process of oxidizing the organic substances found in water samples, potassium dichromate is reduced, forming Cr^{3+}. The amount of Cr^{3+} is determined when oxidization is complete and it is used as an indirect measure of the organic contents of the water samples. In the colorimetric method (closed reflux), oxygen consumption is measured against standards at 600 *nm* with a spectrophotometer explained in Section 3.3.5.

The COD reactor (Bioscience, Inc.) was preheated to 150 ± 2^oC prior to the preparation of the vials. The reagent vials (Bioscience Inc) were uncapped and 0.5 *mL* of sample solution or working standard solution (for 100 – 4,500 *mg/L* range vials) was carefully added from the side of the vial. Then, the vial was shaken manually to mix well. COD standards and a blank (distilled water) were processed exactly the same as the samples. COD vials containing sample, COD standard and blank were heated in the COD reactor for 2 h at 150 ± 2^oC, and then they were removed from the reactor and were placed in a rack until they are cooled and any suspended precipitate in the vials was settled. 5 *mL* of the vial sample was placed in a rectangular quartz cell to carry out the absorbance test in the UV spectrophotometer (Ultrospec 1110 Pro, Biochrom Ltd.) one by one to measure their COD under a standard curve covering the expected range of sample concentrations. Each sample was measured in triplicate and their average value was reported as the COD reading in *mg/L*. If samples could not be tested within 5 *h* of collection, they were preserved with concentrated sulphuric acid to a pH no greater than 2 so as to reduce the rate of microbiological growth, which can cause sample contamination or degradation and were refrigerated at 4^oC until analysis. The software, SWIFT II 1000, installed in a computer connected to the spectrophotometer (Section 3.3.5), was used for COD analysis. A

wavelength of 600 *nm* for COD range 100-4,500 *mg/L* was set and absorbance was zeroed by a blank. A standard curve for this COD range was generated by Run>Standards to get the absorbance readings of a series of standards with known COD concentrations. Each replicate of the standards was measured and stored, and the mean values were calculated. A standard curve (Figure 3.6) was then constructed using the mean absorbance values. The standard curve showed linearity between absorbance values and known standards concentrations and was displayed in a graph view, with the results of samples superimposed upon it. An unknown COD concentration was measured using the software by opening the file menu and clicking on "Standards", and then hit Run menu button to click "Samples". Samples were only run after the standard curve was created. Each replicate of a sample was measured and compared with the standard curve. Each sample's result was displayed as it was collected. The COD standard curve was calibrated every 6 months. The COD removal efficiency was determined by Equation (3.5).

$$COD\% = \frac{(COD_{in} - COD_{out})}{COD_{in}} \times 100\% \quad (3.5)$$

where COD_{in} is COD concentration of influent wastewater sample, *mg/L*; and COD_{out} is COD concentration of effluent wastewater sample, *mg/L*.

3.4. Experimental Procedures

3.4.1. Batch test: GAC isotherm

Different amount of granular activated carbon (0-75 *g*) was added to five bottles each containing 100 *mL* synthetic pharmaceutical wastewater to allow the adsorption of wastewater ingredients on its surfaces. These bottles were placed in a shaker at 150 *rpm* for 3 days. Usually, one day contact time is adequate for complete adsorption (Wang *et al.*, 2006). Samples were then filtered using a filter paper. The inlet and filtered sample TOC concentrations were then

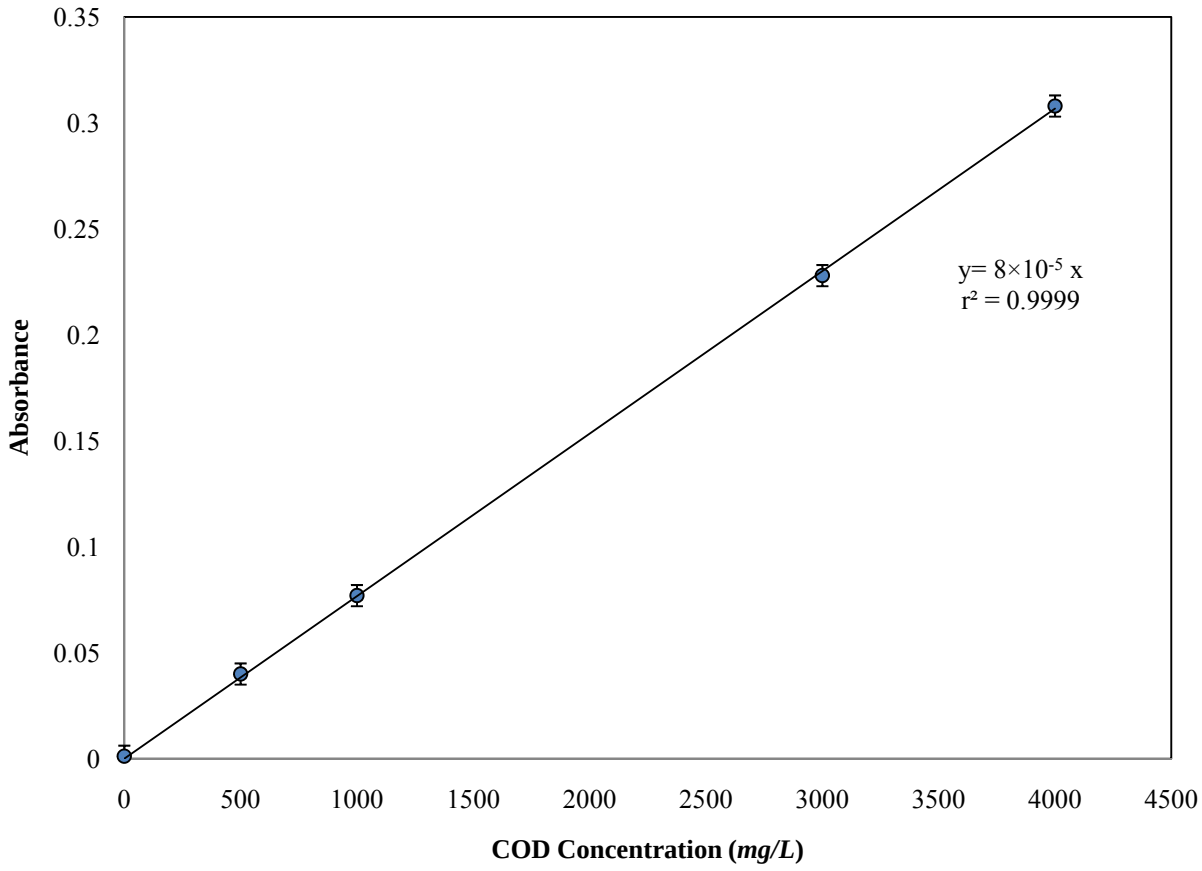

Figure 3.6. COD standard curve plotted for measured absorbance against known COD concentration for the range of 100-4,500 *mg*COD/*L*, where y respresents the Absorbance measured and x represents the COD concentration in *mg*/*L*.

measured. Impurities were removed and mass (*mg*) of TOC adsorbed per unit *g* activated carbon (x/m) were calculated for all eight samples. The TOC results were reported as filtered sample concentrations (C_e). Respective plot of impurities adsorbed per unit gram carbon (x/m) versus filtered sample concentration (C_e) was generated to find isotherm constants as explained in Section 2.7.2.

3.4.2. GAC column adsorption process

3.4.2.1. Adsorption of pharmaceutical wastewater on GAC

Single GAC column (Figure 3.1) was charged with synthetic pharmaceutical wastewater in an up flow steady state mode at a volumetric flow rate of 0.4, 0.6, and 0.8 *L/min*. The bed depth was 85 *cm* with an average feed TOC concentration of 1,755.5 and 853.6 *mg*C/*L* to study the effects of the flow rate. Experiments were also conducted with an average feed TOC concentration of 1,755.5 *mg*C/*L*, volumetric flow rate of 0.6 *L/min,* and bed depths of 10, 20, and 30 *cm*. The effluent water samples (10 *mL* each) from the column were collected at 5-10 *min* time intervals and were analyzed for TOC, TN, pH, and COD. The temperature was 24 ± 2^{o}C and the pH was 3.2 ± 0.2 in all experiments. Treated water was collected and its volume was recorded. Column breakthrough point and adsorption capacity of the carbon for different flow rates were calculated to find the optimum flow rate. Bohart-Adams model parameters were calculated using the TOC data obtained for different bed heights at the optimum flow rate of 0.6 *L/min* (Section 4.1.2.1). The Bohart-Adams model was validated to predict the breakthrough point for a scale up column. The removal efficiencies of TOC, TN, and COD of the synthetic pharmaceutical wastewater were determined for the GAC adsorption in series, with the feed TOC concentration of 1,912.5 *mg*C/*L* and the flow rate of 0.6 *L*/*min*. After completion of each adsorption experiment, the carbon was either regenerated or discarded and the bed was refilled

with fresh GAC.

3.4.2.2. Desorption of impurities from GAC

After the exhaustion of the GAC by pharmaceutical waste, the desorption process was carried out to remove the impurities adsorbed on the activated carbon. The column desorption was studied by using steam at the temperature 115±5^{o}C and the pressure of 30 *KPa*. The steam was passed through the GAC adsorption column continuously for 60 *min* at the flow rate of 0.15 *L/min*. Cold water in the condenser was set at an optimum flow rate of 3.6 *L/min* (a value below or above this cold water flow rate resulted in either uncondensed steam or no further change in the condensed steam temperature T = 20 ± 2 ^{o}C). The condensed steam samples (10 *mL*) were collected at certain time intervals to measure the TOC, TN, COD, and pH. The condensed steam was collected and its volume was measured. The desorption efficiencies, in terms of *mg*C desorbed from the exhausted activated carbon/*L* of wastewater treated, were determined.

3.4.3. Photolytic (UV/ H_2O_2) process alone

Photolytic process alone was operated continuously at the HRT of 1, 2, 3, 4, 5, and 6 *h* for both 185 and 254 *nm* UV lamps, with the TOC loading rates of 324-1,945 *mg*C*/(L.h)*. The amount of H_2O_2 added to the synthetic wastewater was calculated based on different ratios of H_2O_2 to the inlet COD (*mg/L*) reading of the inlet synthetic wastewater. This mixture was allowed to flow through the photoreactor operated with 254 *nm* wavelengths UV lamp. The same procedure was also carried out by using 185 *nm* wavelength UV lamp. The H_2O_2 dosages of 2.125 – 6.375 *mg*H_2O_2*/mg*COD were supplied to the synthetic wastewater for each HRT.

For every experiment corresponding to HRT of 1 to 6 *h* for both lamps, the treated

samples of wastewater (10 *mL*) were collected to measure the concentrations of TOC and TN. The temperature and pH of the wastewater samples were also measured. The removal efficiencies of TOC, COD, and TN for the treatment of the synthetic pharmaceutical wastewater were determined. The optimal H_2O_2 dosage in the photoreactor was also determined. After determining the optimum H_2O_2 dosage, UV/H_2O_2 runs were carried out at inlet pH 7 and 12.01, for HRT of 1, 2, 3, 4, 5, and 6 *h* for both lamps, respectively, with the TOC loading rates of 314-1,945 *mg/(L.h)*. The pH values were adjusted to 7 and 12.01 by adding less than 1 *mL* of 1*N* NaOH (as mentioned in Section 3.1.4). If the pH went higher than the required value, less than 1 *mL* of 1*N* H_2SO_4 (Section 3.1.5) was added to balance the pH.

3.4.4. Combined GAC adsorption and UV_{254}/H_2O_2 processes

Experiments with combination of UV_{254}/H_2O_2 process followed by the GAC adsorption process were conducted to see if there was any improvement in the TOC and COD removal efficiencies compared to individual processes. The TOC loading rates were 652.66 *mg/(L.h)* for UV_{254} photoreactor and 135.2 *mg/*(*L.h*) for GAC column of the combined processes. The synthetic wastewater was passed through UV_{254} photoreactor, with an optimum dosage of 4.25 *mg*H_2O_2/*mg*COD at an HRT of 3*h*.

30 *L* of effluent water from the UV_{254} photoreactor was collected and manually transferred to the GAC column feed tank. It was then passed through the GAC adsorption column for 20 and 60 *min* at the flow rate of 0.6 *L/min*. Desorption process was then carried out on the exhausted activated carbon by passing saturated steam (115 ± 5^oC) at the flow rate of 0.15 *L/min* for 60 *min*. Cold water for the condenser was adjusted at a flow rate of 3.6 *L/min*. The condensed steam was collected and a sample (10 *mL*) was taken for TOC, COD, and TN analyse.

The UV/H_2O_2 process was performed on the condensed steam, using the optimum 4.25 *mg*H_2O_2/*mg*COD, to mineralize the impurities desorbed from the carbon for an HRT of 1 and 2 *h*. A 10 *mL* sample was taken for TOC, COD, TN, temperature, and pH analyses. The TOC and TN removal efficiencies of the combined processes for the treatment of the synthetic pharmaceutical wastewater were determined.

In another set of experiment the pharmaceutical wastewater was treated with GAC adsorption treatment. Then desorption process was carried out, to which UV_{254}/H_2O_2 treatment was conducted on the condensed steam to observe the efficiency of the combined processes for the treatment of synthetic pharmaceutical wastewater. The GAC column was operated at a flow rate of 0.6 *L/min* for average feed TOC concentration of 1,755.5 *mg*C/*L* for 10 *min* (at 81% breakthrough). The effluent water from the column was collected and a sample (10 *mL*) was taken for COD, TOC, and TN. On completion of the adsorption process, the exhausted activated carbon was regenerated by passing saturated steam, at 115 ± 5^oC, with the flow rate of 0.15 *L/min* for 60 *min*. The cold water for the condenser was set at a flow rate of 3.6 *L/min*. The condensed steam was collected and a sample (10 *mL*) was taken for TOC, COD, and TN analyses. The UV_{254}/H_2O_2 process was performed on the condensed steam, using optimum 4.25 *mg*H_2O_2/*mg*COD dosage (i.e. 1:2 stoichiometric COD: H_2O_2 (*w/w*) ratio as found in Section 4.2.2) to mineralize the impurities desorbed from the carbon with an HRT of 1 and 2 *h,* respectively. A 10 *mL* sample was taken for TOC, COD, and TN analyses. The TOC and COD removal efficiencies of the combined processes for the treatment of the synthetic pharmaceutical wastewater were also investigated.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents the results of the granular activated carbon adsorption (GAC), photochemical process (UV/H_2O_2), and their combination for the treatment of synthetic pharmaceutical wastewater.

4.1. Adsorption Treatment of Synthetic Pharmaceutical Wastewater by GAC Alone.

Isotherms and column adsorption models were evaluated to get an idea of the adsorption mechanisms of the pharmaceutical wastewater on the GAC and to design the scale-up column for the treatment process.

4.1.1. Prediction of GAC adsorption isotherm model for pharmaceutical wastewater based on batch test data

Isotherm models are usually used to establish the capacity of an adsorbent when the solution reaches equilibrium. In this study, two classic isotherm models, Freundlich and Langmuir (Section 2.7.2), were examined to find the appropriate isotherm for the pharmaceutical wastewater on GAC.

4.1.1.1. Langmuir isotherm model

The experimental data for the batch adsorption of pharmaceutical wastewater were fitted to Langmuir isotherm model using Equation (2.1) as follows:

$$\frac{x}{m} = \frac{abC_e}{1 + bC_e} \tag{2.1}$$

Rearranging Equation (2.1), one gets:

$$\frac{m}{x} = \frac{1}{ab}\frac{1}{C_e} + \frac{1}{a} \tag{4.1}$$

x/m = mass of TOC adsorbed per unit mass of dry activated carbon, (*mg*C/*mg*Activated Carbon)

C_e = equilibrium concentration of TOC in solution after adsorption, (*mg*C/*L* of solution)

a = maximum adsorption capacity of activated carbon, [*mg*C/*mg*Activated Carbon]; and b = empirical constant, (*L* of solution/*mg*C).

The adsorption data for pharmaceutical wastewater were plotted as shown in Figure 4.1. Figure 4.1 shows a linear relationship between *m/x* and $1/C_e$ as expected in the Langmuir adsorption isotherm (Equation 4.1). The value of the coefficient of determination, r^2, for the pharmaceutical waste was found to be 0.992, indicating a good fit of the monolayer Langmuir model to the adsorption of waste on GAC. Langmuir constants, *a* and *b*, were obtained from the linear regression as shown in Table 4.1. The maximum uptake (x/m) of the carbon was found to be 1.85×10^{-3} *mg*C/*mg*Activated Carbon for initial TOC intake of 1,489.5 *mg*C/*L*.

Table 4.1. Langmuir isotherm constants for pharmaceutical wastewater adsorption at 25º*C*.

Adsorbate	**Langmuir Model**		
	Constant *a* (*mg*C/*mg*Activated Carbon)	Constant *b* (*L*/*mg*C)	r^2
Pharmaceutical Wastewater	1.85×10^{-3}	1.07×10^{-3}	0.992

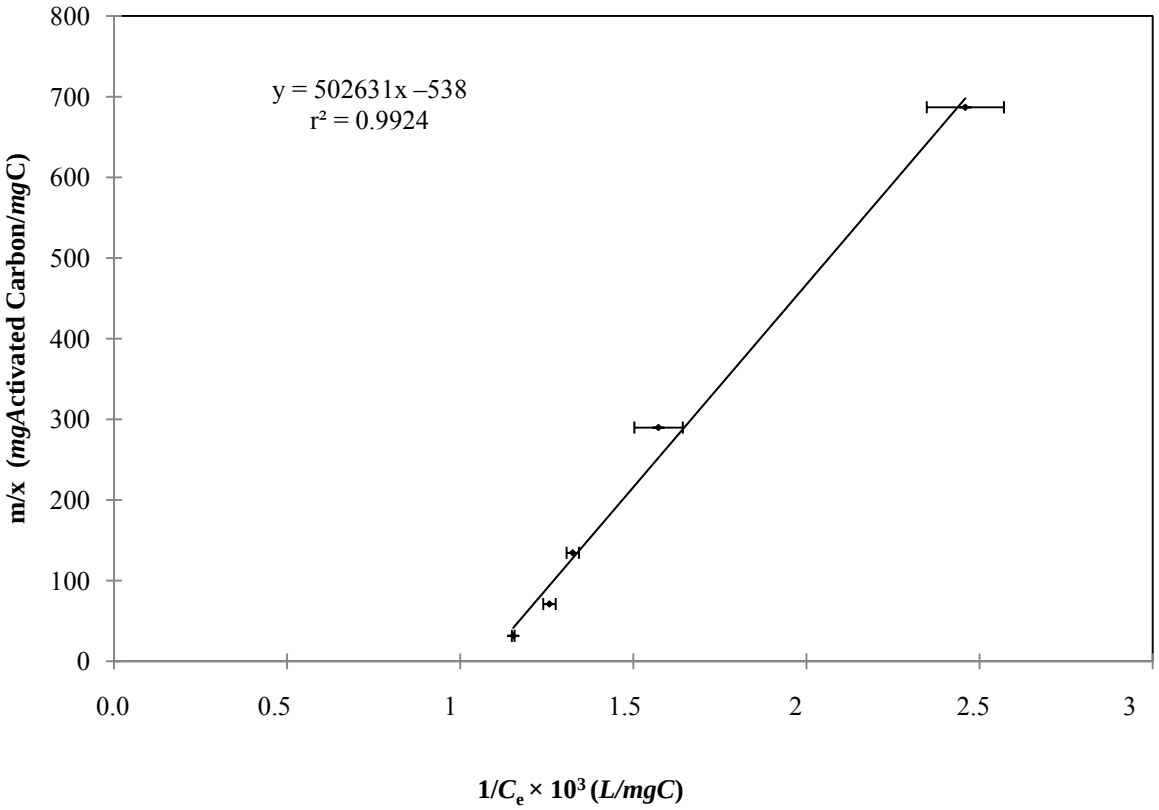

Figure 4.1. Testing Langmuir isotherm model for the amount of adsorbate/amount of activated carbon versus equilibrium concentration for batch adsorption data of pharmaceutical wastewater on GAC at 23^{o}C, where y represents *mg*Activated Carbon/*mg*C and x represents inverse of equilibrium concentration (*L*/*mg*C). Initial Conditions: TOC = 1,498.5 *mg*C/*L* and pH 3.18.

4.1.1.2. Freundlich isotherm model

The experimental data were also fitted to the Freundlich isotherm model as follows:

$$x/m = K_f C_e^{\frac{1}{n}} \tag{2.3}$$

By taking logarithm of both sides of Equation (2.3):

$$log\ x/m = log\ K_f + \frac{1}{n}\ log\ C_e \tag{4.2}$$

where:

x/m= amount of TOC adsorbed per unit mass of activated carbon, (*mg*C/*mg*Activated Carbon)

K_f= Freundlich capacity factor, ((*mg*C/*mg*Activated Carbon)/(*L*/*mg*C))$^{1/n}$

C_e = equilibrium concentration of TOC in solution after adsorption, (*mg*C/*L*)

$\frac{1}{n}$ = Freundlich intensity parameter.

The solid curve in Figure 4.2 represents log x/m versus log C_e which according to Equation (4.2) should be a linear curve. But from Figure 4.2, it is visible that the adsorption data do not fit well with the Freundlich isotherm curve. Based on the r^2 value, the Langmuir model, r^2 = 0.992, fits well to the experimental results. Therefore the pharmaceutical wastewater obeys the Langmuir adsorption isotherm model and indicates GAC would provide monolayer and homogenous adsorption of the pharmaceutical wastewater. A steep isotherm curve indicates a wide mass transfer zone with the adsorption capacity increasing as equilibrium concentration increases. Carbon exhibiting this type of isotherm curve tends to be more cost effective (Engineering Design, 2001). Few available literature values for the isotherm constants are shown in Table 4.2. The parameters of the isotherm equations of the individual component would be difficult to compare with the results obtained because the isotherm data are collected

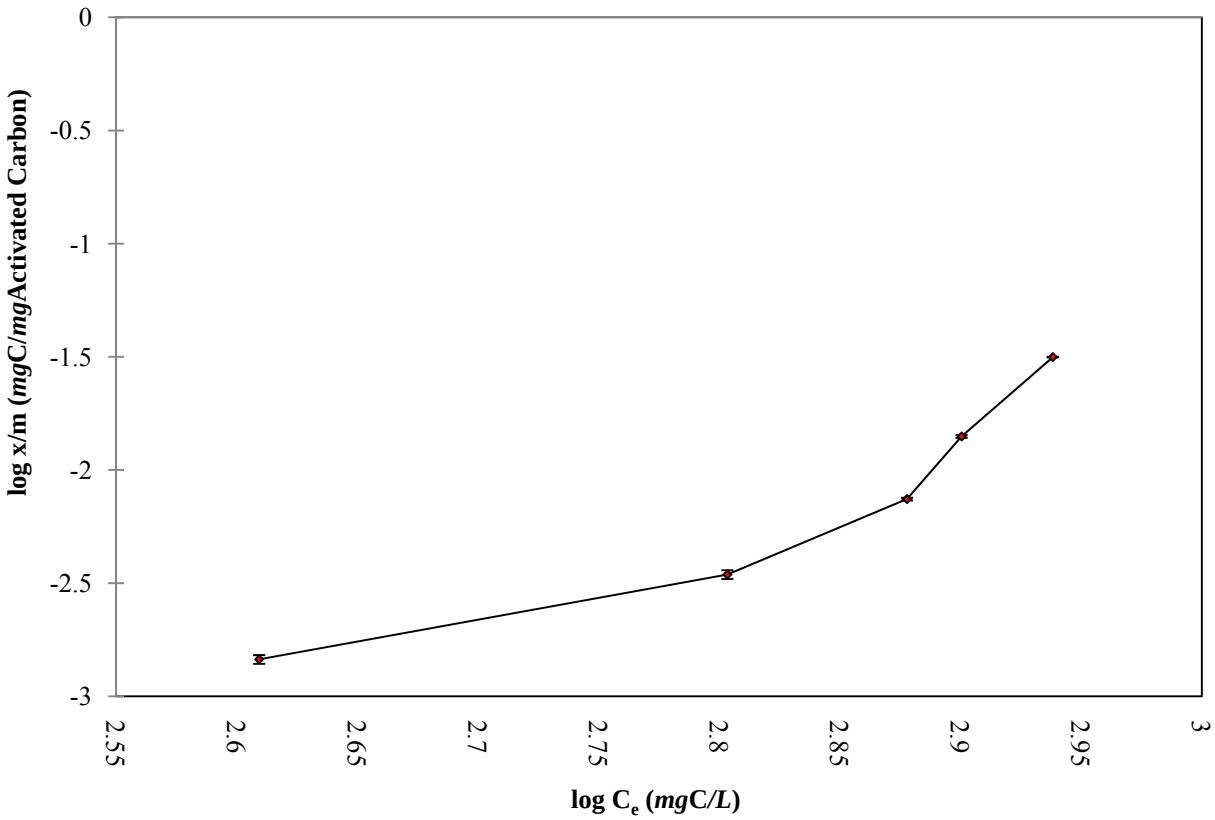

Figure 4.2. Testing of Freundlich isotherm model for batch adsorption of pharmaceutical wastewater on GAC using data of amount of TOC absorbed per amount of activated carbon versus equilibrium concentration. Average feed TOC = 1,498.5 *mg*C/*L,* T = 23º*C* and pH = 3.18.

Table 4.2. Literature values for adsorption constants of Langmuir and Freundlich isotherm models

Compounds	Conditions	Freundlich constants			Langmuir Constants			References
		K_f ((*mmol/g*Activated Carbon) (*L/mg*))$^{1/n}$	*1/n*	r^2	*a* (*mmol/g*)	*b* (*L/mmol*)	r^2	
benzene	inlet conc. = 50, 250, 450,and 750 *mg/L*, Activated Carbon (AC) Fabric	0.75	0.19	0.7786	2.416	2.26	0.8935	Singh *et al*., 2002
hexane	inlet conc. = 10, 100, 200, and 450 *mg/L*, AC Fabric	1.3	0.08	0.967	2.417	5.08	0.9514	Singh *et al*., 2002
aniline	inlet conc. = 10-500 *mg/L*, Norit GAC 1240 PLUS, pH3.	0.32	0.125	0.496	0.38	9	0.693	Faria *et al*., 2008
sulfanilic acid		0.58	0.143	0.957	0.6	20	0.617	Faria *et al*., 2008
benzenesulfonic acid		0.49	0.77	0.550	0.52	20	0.457	Faria *et al*., 2008
benzoic acid	inlet conc. = 1.72 × 10^{-4} *mol/L*, pH 4.15, AC cloth	8.83	0.361	0.9955	2.97	15.8	0.9764	Ayeanci and Duman, 2006
salicylic acid	inlet conc. =.75 × 10^{-4} *mol/L*, pH 3.62, AC cloth	6.26	0.61	0.98	3.03	10.1	0.9896	Ayranci and Duman, 2006
4 amino benzoic acid	inlet conc. = 1.73 × 10^{-4} *mol/L*, pH 7, AC cloth	0.601	0.290	0.9916	0.2	552	0.9847	Ayranci and Duman, 2006
Pharmaceutical wastewater	**inlet conc. = 1498.5 *mg*C/*L*, pH 3.18, GAC**	**N/A**	**N/A**	**N/A**	**1.85 × 10^{-3} (*mg/mg*)**	**1.07 × 10^{-3} (*L/mg*)**	**0.992**	**This study**

under different conditions: pH, temperature, type of adsorbent, and the form of adsorbate species.

Based on the Langmuir isotherm results (constants *a* and *b*), adsorption is a viable technology and a rough estimate of the amount of activated carbon (*m*) required for treating pharmaceutical wastewater could be predicted. From the calculations shown in Appendix D, in order to obtain 320 *mg*C/*L* of effluent TOC (C_e) of the pharmaceutical wastewater (according to the discharge limits set by the government regulations, (Table 2.3 and Table 2.4) using the Langmuir isotherm model equation, approximately 1.07 *Kg* of carbon per litre of pharmaceutical wastewater would be required. This estimated activated carbon value was used to design the column test.

4.1.2. GAC column test results

In this section, a series of experiments were carried out to find the effects of operating variables such as hydraulic loading rate, the bed height, and the feed concentration on the dynamic mode adsorption capacity by the pilot column test. The scale-up evaluation was carried out using the optimized parametric conditions obtained from pilot column studies.

4.1.2.1. Effects of hydraulic loading rate

Column experiments were conducted in the bed with the height of 0.85 *m,* cross sectional area of 0.011 m^2, average TOC feed concentration of 1,755.5 *mgC/L*, and hydraulic loading rate (HLR) ranging from 36.3 - 72.7 $L/(min.m^2)$. Figure 4.3 shows that the breakthrough time (at 50%) decreases from 40 to 18 *min*, as HLR increases from 36.3 to 72.7 $L/min\ m^2$. The maximum adsorption capacity is found to be 7.90 *mg*C/*g*Activated Carbon at 54.5 $L/(min.m^2)$ as shown in Table 4.3. The variation in the breakthrough curve and adsorption capacity may be explained on the basis of mass transfer fundamentals. An increase in the hydraulic loading rate causes an

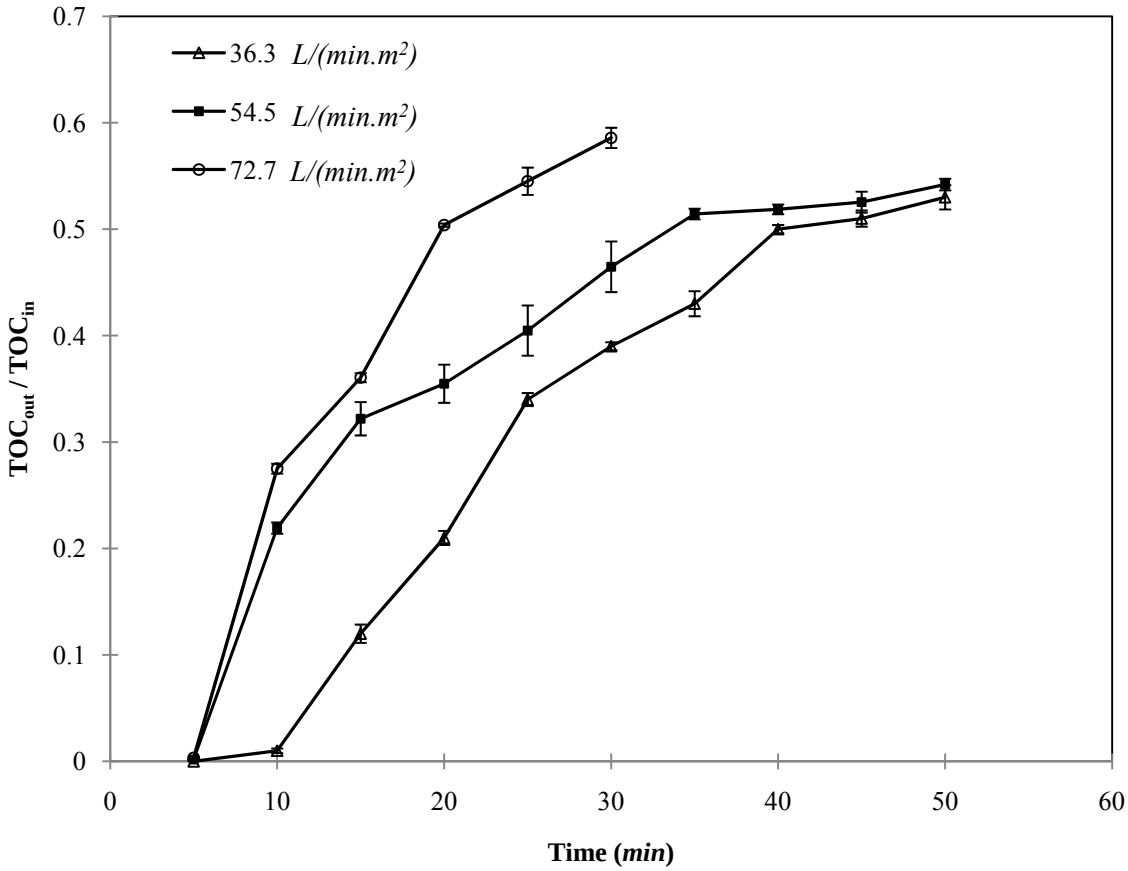

Figure 4.3. Breakthrough curve for different hydraulic loading rates at constant bed height of 0.85 *m* and average feed TOC concentration of 1,755.5 *mg*C/*L*.

increase in zone speed, resulting in a decrease in the time required to achieve the breakthrough, that is less time is available for diffusion of the pollutants on to the active carbon sites(Treybal, 1980).

Table 4.3. Column adsorption capacity at various operating conditions (at 50% breakthrough concentrations) from pilot column experimental studies.

	Feed TOC concentration (*mg*C/*L*)	**(50%) Breakthrough time (*min*)**	**Bed Height (*m*)**	**Flow rate (*L/min*)**	**Hydraulic loading rate ($L/min.m^2$)**	**Adsorption Capacity (*mg*C/*g*Activated Carbon)**
	1767.1	40	0.85	0.4	36.3	7.07
Optimum	**1755.5**	**30**	**0.85**	**0.6**	**54.5**	**7.90**
	1723.6	18	0.85	0.8	72.7	6.21
	1776.2	2.5	0.10	0.6	54.5	3.34
	1828.5	8.5	0.20	0.6	54.5	3.26
	1797.6	11.5	0.30	0.6	54.5	3.65
	856.5	60	0.85	0.6	54.5	0.11

4.1.2.2. Effect of bed height

Breakthrough experiments were conducted at the activated carbon bed heights of 0.1, 0.2, 0.3, and 0.85 *m* at the average feed TOC concentration of 1,755.5 *mgC/L* and the optimized hydraulic loading rate of 54.*5* $L/(h.m^2)$ (0.6 *L/min*) as shown in Table 4.3 (the maximum adsorption capacity). Experiments on the effects of bed height showed a decrease in minimum effluent concentration with increase in bed height, keeping other parameters constant. The minimum effluent concentration is defined as the average concentration of the pharmaceutical wastewater at the column outlet (or effluent) in initial constant phase. Figure 4.4 shows that the minimum effluent concentration decreases rapidly from 337 *mgC/L* for a bed height of 0.1 *m* to 1.41 *mgC/L* for 0.85 *m* bed height. The increase in the total adsorptive capacity of the bed resulted in a decrease in the solute

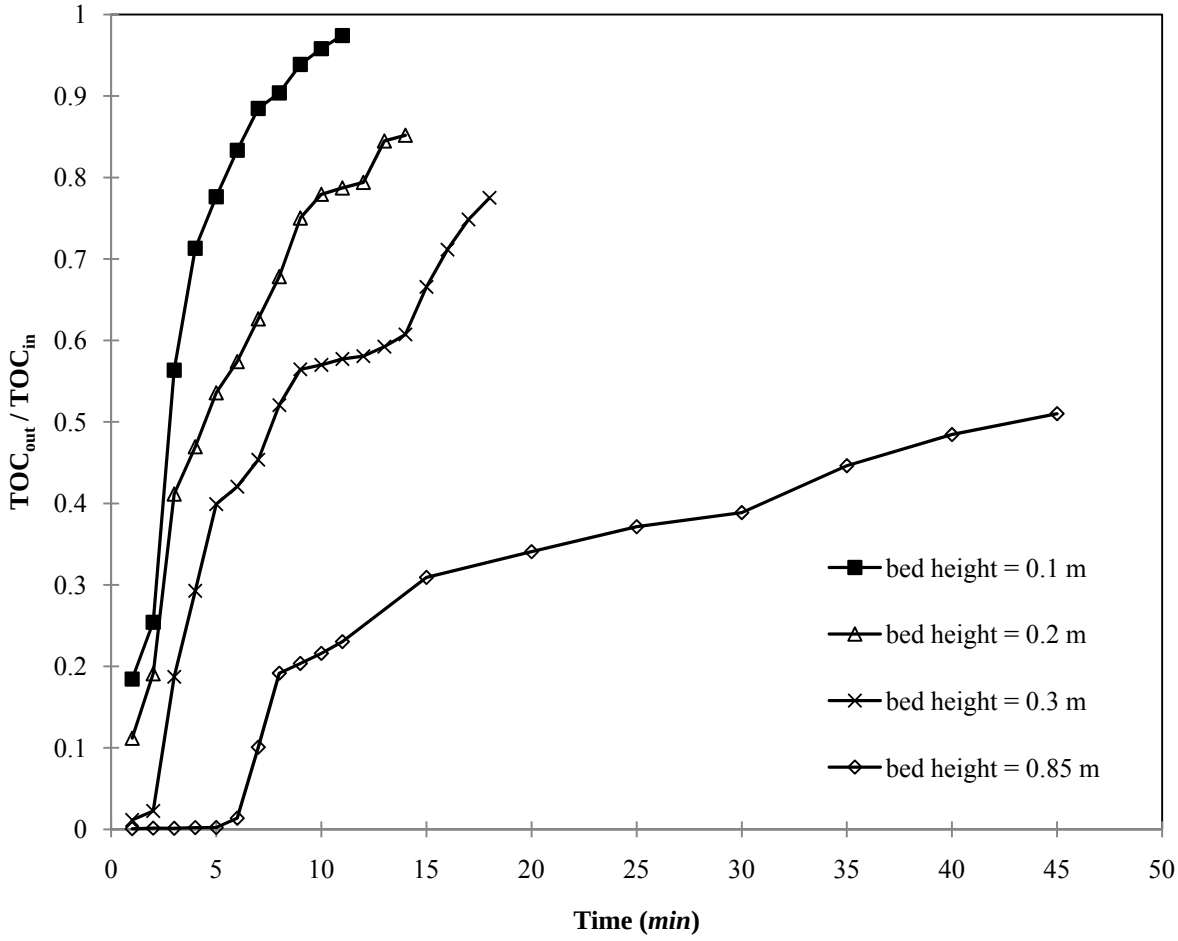

Figure 4.4. Breakthrough curve for different bed heights at constant hydraulic loading rate of 54.5 *L/ (min.m^2)* and average feed TOC concentration of 1,755.5 *mg*C/*L*. It also is in agreement with the H_b:D range mentioned in Section 2.7.6.

concentration in the effluent. Based on the maximum adsorption capacity of 7.9 *mg*C/*g*Activated Carbon and the literature value of the column dimensions (Section 3.2.1), 0.85 *m* bed height was chosen as the optimized bed height for the rest of the experiments.

4.1.2.3. Effect of feed concentration

The change in the initial feed concentration of the pharmaceutical wastewater had a significant effect on the breakthrough curve as illustrated in Figure 4.5. The higher the initial feed concentration is, the smaller the breakthrough time is. These results demonstrate that the change of concentration gradient affects the saturation rate and the breakthrough time; in other words, the diffusion process is concentration dependent. As the feed concentration increases, the TOC loading rate of the pharmaceutical wastewater increases, so does the driving force for mass transfer, which results in a decrease in the adsorption zone length (Patrick *et al.,* 2002). The net effect is an appreciable increase in adsorption capacity of pharmaceutical wastewater as presented in Table 4.3.

4.1.3. Column Study Results: Bohart -Adams model

Bohart -Adams model is based on the surface reaction theory (Reynolds and Richards, 1995) and it assumes that equilibrium is not instantaneous; therefore, the rate of sorption is proportional to the fraction of sorption capacity still remaining on the adsorbent (Muraleedharan *et al.*, 1994). The Bohart–Adams model, Equation (2.6), is used to predict the performance of continuous adsorption columns:

$$ln\left(\frac{C}{C_o}\right) = K_{AB}\, C_o t - \, K_{AB} N_o \left(\frac{z}{v}\right) \tag{2.6}$$

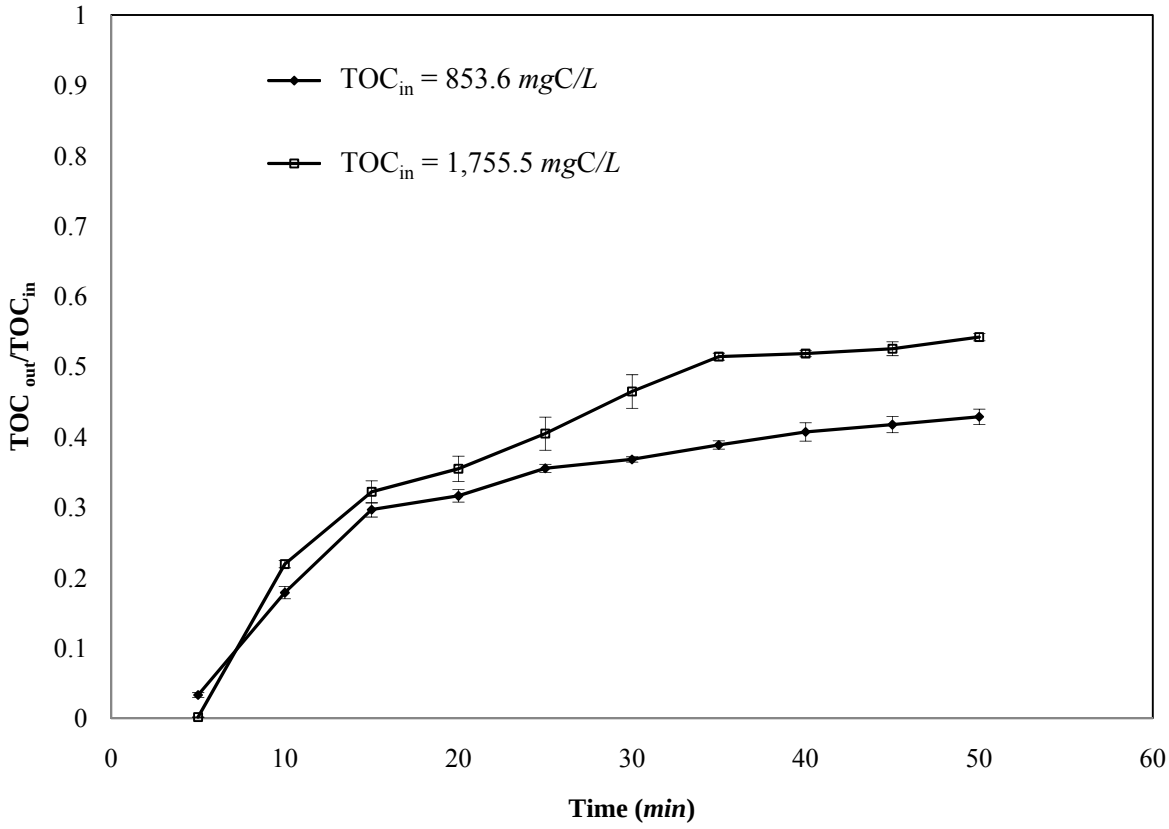

Figure 4.5. Breakthrough curve for two feed concentrations at constant bed height of 0.85 *m* and hydraulic loading rate of 54.5 $L/(min.m^2)$.

Solving Equation (2.6) for t

$$t = \frac{1}{C_o K_{AB}} ln\left(\frac{C}{C_o}\right) + \frac{N_o}{C_o}\left(\frac{z}{v}\right) \quad (4.3)$$

A simplified form of the Bohart-Adams Model, Equation (4.3) is:

$$t = a\,z + b \quad (4.4)$$

where

$$a = \frac{N_o}{C_o}\left(\frac{1}{v}\right) \quad (4.5)$$

$$b = \frac{1}{C_o K_{AB}} ln\left(\frac{C}{C_o}\right) \quad (4.6)$$

Iso-removal lines (plots of time versus bed height for a specific removal percentage) as shown in Figure 4.6 plotted for linear superficial velocity of 0.055 *m/min* (volumetric flow rate 0.6 *L/min*) for three different bed heights 0.1, 0.2 and 0.3 *m* with the average feed TOC concentration of 1,755.5 *mg*C/*L*. The breakthrough time at desired breakthrough concentrations exhibit linearity with the bed depth. From the slope (*a*) and intercept (*b*) of the respective lines, the adsorption capacity (N_o) and the rate constant of adsorption (K_{AB}) can be calculated, respectively. The calculated constants for the Bohart-Adams model for the adsorption of pharmaceutical wastewater on to the GAC are presented in Table 4.4. These data were used in the scaling up design of the column.

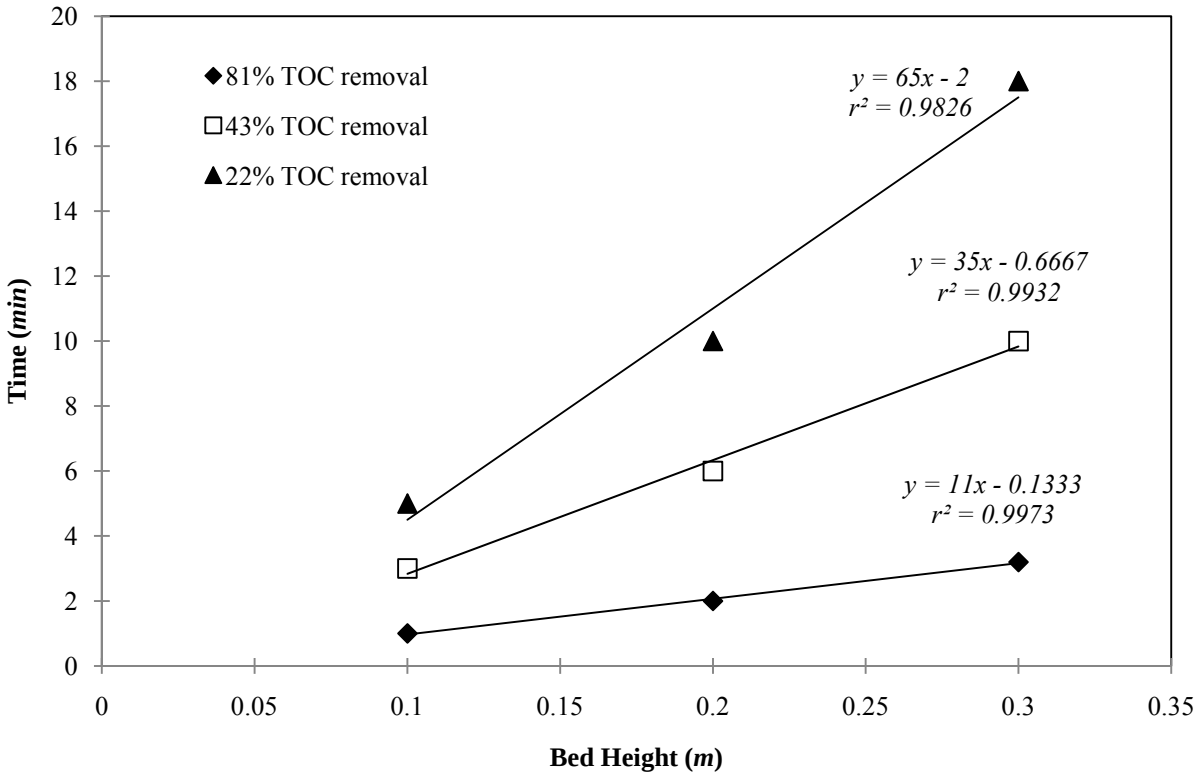

Figure 4.6. Iso-removal lines for 22, 43 and 81% breakthrough for different bed height at average feed concentration of 1,755.5 *mg*C/*L* and hydraulic loading rate of 54.5 $L/(min.m^2)$: Bohart-Adams modeling at mini-column studies. *y* represents the time required to achieve respective %TOC removal and *x* represents given bed height condition.

Table 4.4. Constants of Bohart-Adams model for the adsorption of pharmaceutical wastewater onto GAC column.

Iso-removal percentage (%)	$\frac{C}{C_o}$	***a*** ***(min/m)***	***b*** ***(min)***	N_o ***(mgC/L)***	K_{AB}**(Eq.(4.4))** ***(L/mgC.min)***	r^2
22	0.78	65	-2	6.28×10^3	7.08×10^{-5}	0.9932
43	0.57	35	-0.6667	3.38×10^3	4.80×10^{-4}	0.9826
81	0.19	11	-0.1333	1.06×10^3	7.10×10^{-3}	0.9973

From Figure 4.6, for a particular iso-removal line (corresponding to Equation 4.4), the necessary bed height for a pre-selected time period can be directly calculated for a defined breakthrough concentration (Muraleedharan *et al*., 1994). The slope constant for a different flow rate (a_{new}) can be directly calculated by multiplying the original slope (a_{old}) by the ratio between the original linear flow rate (v_{old}) and the new linear flow rate (v_{new}) (Hutchin, 1973) as follows:

$$a_{new} = a_{old}\left(\frac{v_{old}}{v_{new}}\right) \quad \textbf{(}4.7\textbf{)}$$

Similarly the equation developed for one concentration can be modified to apply for another concentration (Hutchin, 1973):

$$a_{new} = a_{old}\left(\frac{C_{old}}{C_{new}}\right) \quad \textbf{(}4.8\textbf{)}$$

$$b_{new} = b_{old}\left(\frac{C_{old}}{C_{new}}\right)\frac{ln\,C - ln\,C_{new}}{ln\,C - ln\,C_{old}} \quad \textbf{(}4.9\textbf{)}$$

where, C_{old} and C_{new} are the original and the new feed concentrations. Thus, developed model and the constants evaluated can be employed for the design of adsorption columns over a range of feasible flow rates and concentrations.

4.1.4. Prediction of breakthrough time for GAC column using Bohart-Adams' model

Residence time is an important parameter for developing a model for a continuous flow system (Chang *et al.,* 2007). The longer the residence time is, the better the performance is. In the present system, the highest residence time was achieved either by increasing the height of the column or by decreasing the linear flow rate through the column, both of which increased the contact time. An optimum hydraulic loading rate of 54.5 $L/(min.m^2)$ was chosen based on the results of the column study. Scale-up experiments were done based on the geometric dimensions and operating parameters obtained in the column study and are tabulated in Table 4.5. The Bohart-Adams parameters, K_{AB} (adsorption rate constant) and N_o (dynamic adsorption capacity), calculated from the pilot column study were used to predict the breakthrough time of the scale up column in this study. Since a column with larger diameter and height than that of the pilot column was not available for conducting experiments in the laboratory, experiments were done by increasing the height of the column twice as that of pilot, changing the initial TOC concentration of the wastewater and conducted in series to predict the breakthrough time using the Bohart-Adams model.

The GAC adsorption process was carried out in two GAC columns operated in series to treat the pharmaceutical wastewater with the TOC inlet concentration of 1,912.5 *mg*C*/L*. The

wastewater was passed through columns with the flow rate of 0.6 *L/min.*

Table 4.5. Geometric and operating parameters in the GAC columns.

Design parameters	Column 1	Column 2
Internal Diameter (*m*)	0.06	0.06
Cross Section Area (m^2)	0.011	0.011
Height (*m*)	0.9	1.8
Operating parameters		
Flow rate (*L/min*)	0.6	0.6
Height of Column(*m*)	0.85	1.7
Carbon (*g*)	2,000	4,000
TOC Concentration (*mg*C/*L*)	1,755.5	1,912.5
% Efficiency Expected	81%	81%

Breakthrough curves (Figure 4.7) were plotted for columns in series with the total 1.7 *m* bed height (containing total 4 *Kg* of adsorbent) and at hydraulic loading rates of 54.5 $L/(min.m^2)$. The breakthrough capacity, Q, expressed in *mg* of TOC adsorbed per *g* of activated carbon was calculated using Equation (2.4). Results obtained from the pilot study are summarized in Table 4.6 and sample calculations are shown in APPENDIX F.

$$Breakthrough\ Capacity(Q) = \frac{Breakthrough\ time\ \times Flow\ rate \times Feed\ Concentration}{Mass\ of\ Adsorbent\ in\ Bed} \qquad (2.4)$$

The predicted breakthrough time for 54.5 $L/(min.m^2)$ hydraulic loading rate was in close proximity to that of the observed, thus validating the applicability of the model.

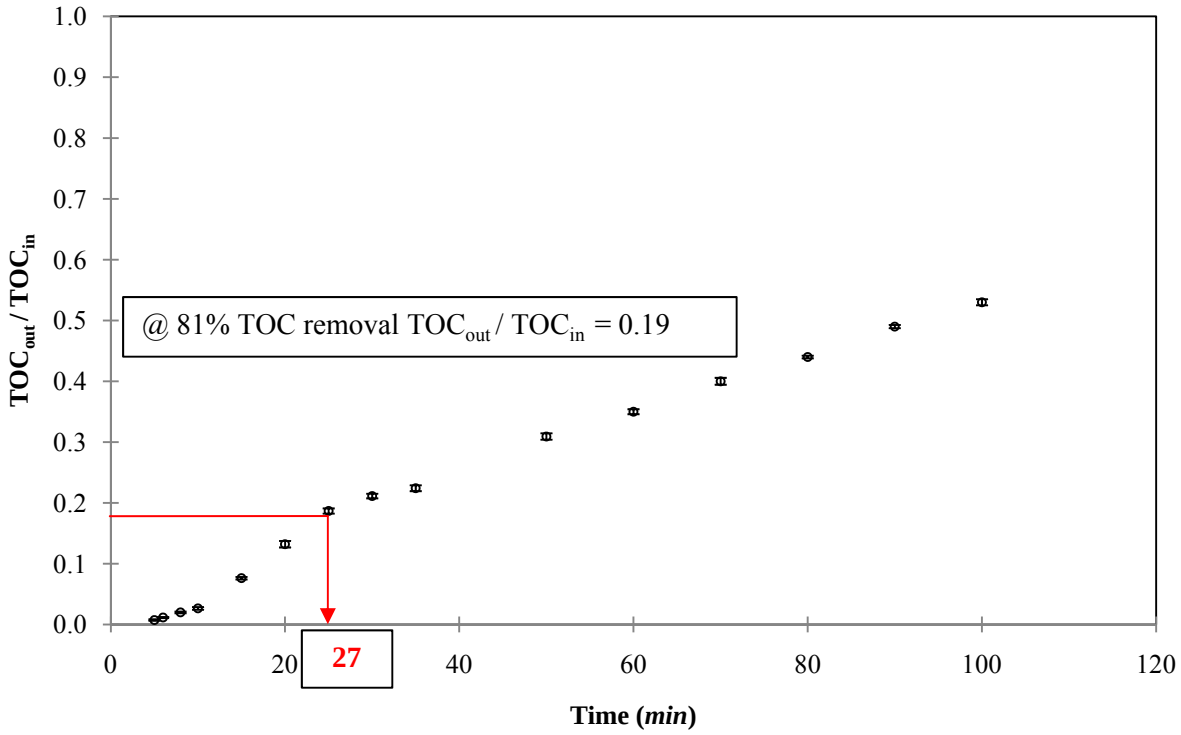

Figure 4.7. Breakthrough curve for hydraulic loading rate 54.5 *L/*(*min.m*^{2}), 1.7 *cm* bed height (two columns in series), feed concentration TOC = 1,912.5 *mg*C/*L* and an influent pH of 3.18 for 81% TOC removal efficiency. 27 *min* was the observed breakthrough time.

Table 4.6. Results of Bohart-Adams modeling for prediction for pharmaceutical wastewater treatment using scale up column

Scale up run	Inlet Concentration (*mg*C/*L*)	Hydraulic loading rate ($L/min.m^2$)	Breakthrough point	Predicted time (*min*)	Observed time (*min*)	Breakthrough capacity of GAC (*mg*C/*g*Activated Carbon)
GAC performed in series	1,912	54.50	81%	17	27	7.75

4.1.5. Desorption process

The data collected while operating single GAC adsorption column with radius of 0.06 *m* and height of 0.85 *m* at 46% TOC breakthrough and 0.6 *L/min* flow rate for the pharmaceutical wastewater are tabulated in Table 4.7. The observed breakthrough time was 50 *min*.

Table 4.7. TOC and TN values for single column GAC adsorption and desorption process.

Adsorption Process			
Type of water	**TOC (*mg*C/*L*)**	**TN (*mg*N/*L*)**	**COD(*mg/L*)**
Inlet Stream	1,755.5	85.4	5,343.1
GAC treated	951.5	40.9	3,522.6
% Efficiency (Adsorption process)	46	52.1	34.1
Desorption Process			
GAC condition	**TOC (*mg*C/*L* of wastewater treated)**	**TN (*mg*N/*L* of wastewater treated)**	**COD (*mg/L* of wastewater treated)**
After adsorption	804.2	44.8	1,820.6
After desorption	158.7	7.0	460.2
% Efficiency (Desorption process)	19.7	15.7	25.2

Figure 4.8 shows the graph of TOC, TN, and COD removal from the pharmaceutical wastewater when treated with GAC adsorption. It was hypothesised that the desorption process would result in the production of concentrated wastewater which helps in easy handling and high in concentration so that economical removal treatment is possible. To investigate further, the above mentioned 46% breakthrough adsorption run was selected to study the desorption portfolio. After the breakthrough time of 50 *min*, adsorption process was stopped and the extra pharmaceutical wastewater inside the column was drained leaving GAC loaded only with adsorbed contaminants from the pharmaceutical wastewater. The desorption was carried out by passing steam at 115 ± 5^{o}C and 30 *KPa* through the exhausted GAC column in upward direction at the flow rate of 0.15 *L/min* and then the condensed steam (regenerant) was collected (Section 3.4.2.2). The steam flow rate was set less the sorption flow rate 0.6 *L/min* so that the volume of the regenerant collected is less, supporting the hypothesis. TOC concentration of the condensed steam was monitored at different time intervals as shown in Figure 4.9.

It was observed that the desorption cycle took 1 *h*, after which further desorption was negligible. The total volume of the condensed steam collected at 1 *h* was 9 *L* compare to 30 *L* original volume of the feed wastewater. The maximum TOC concentration of pharmaceutical wastewater was obtained at a contact time of 6 *min* and recorded as 1,824.2 *mg*C/*L*, which is 1.03 times the influent TOC concentration of the pharmaceutical wastewater. The volume of the regenerant collected was as low as 0.34 times the feed volume but did not result high in concentration as assumed. The removal efficiency desorption process was calculated as follows, where a = TOC or TN:

$$\%\ removal\ of\ a = \frac{total\ mg\ of\ a_{out}}{total\ mg\ of\ a_{in}} \times 100\% \tag{4.10}$$

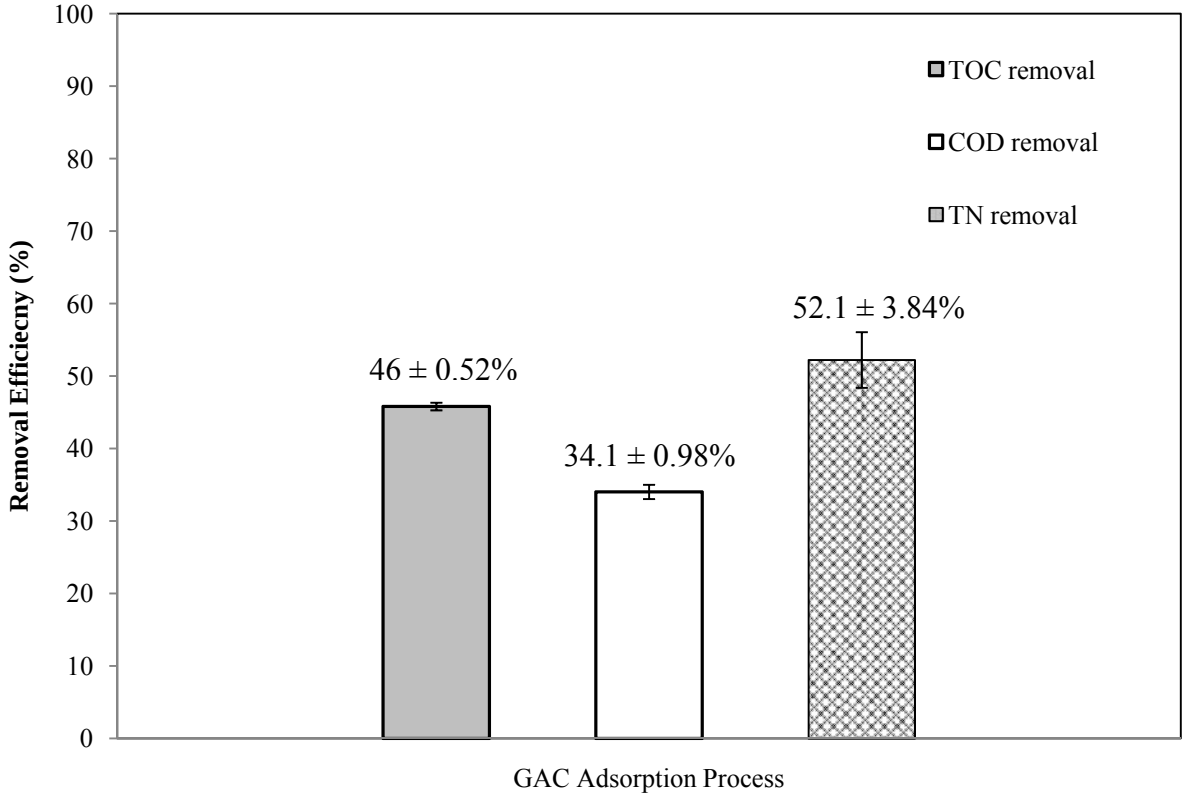

Figure 4.8. Removal efficiency of TOC, COD, and TN during the GAC adsorption process operating with single column having radius of 0.06 *m* and height of 0.85 *m* at 46% breakthrough and 0.6 *L/min* flow rate for feed TOC concentration = 1,755.5 *mg*C/*L* and TN concentration = 85.4 *mg*N/*L* of the pharmaceutical wastewater. Breakthrough time was 50 *min.*

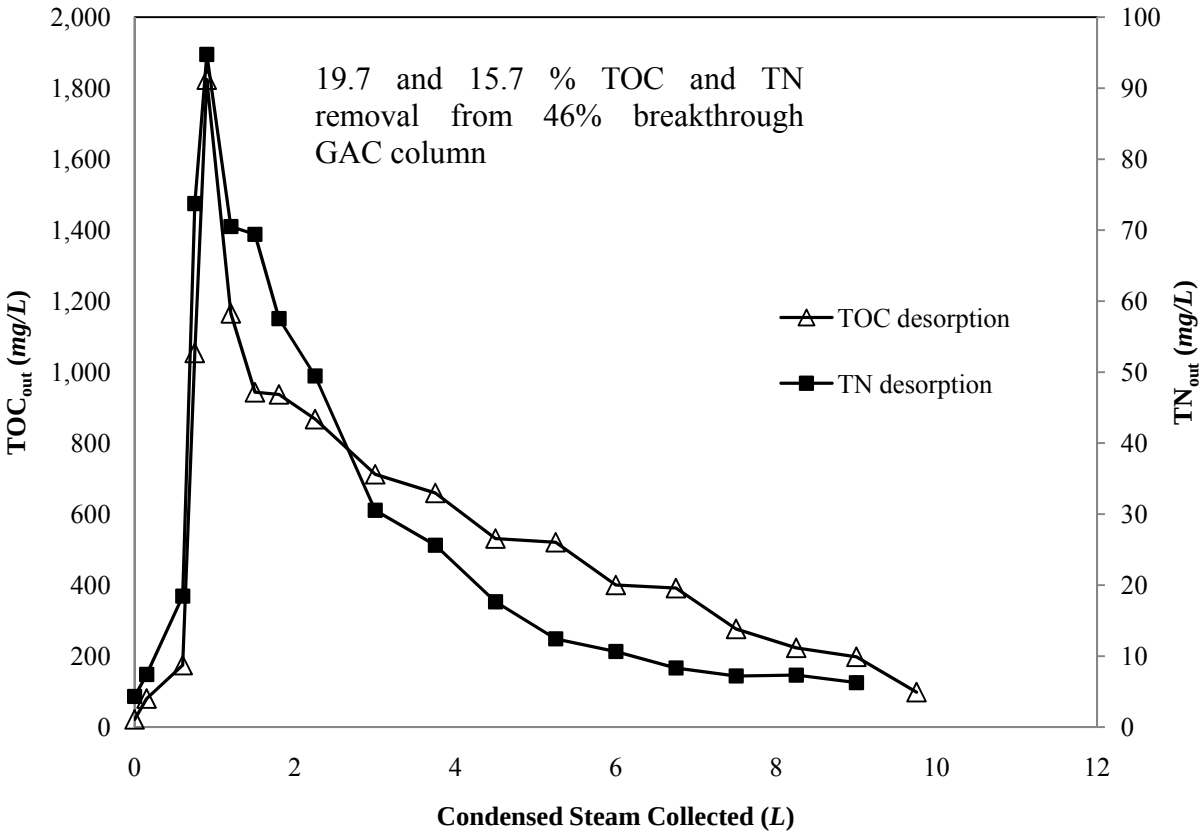

Figure 4.9. Desorption profile of contaminants from GAC surface in terms of TOC and TN present in condensed steam collected. Adsorption operated with single column having radius of 0.06 *m* and height of 0.85 *m* at 46% breakthrough and 0.6 *L/min* flow rate for feed TOC concentration = 1,755.5 *mg*C/*L* and TN concentration = 85.4 *mg*N/*L* of the pharmaceutical wastewater. Breakthrough time for adsorption was 50 *min*. Desorbing agent: steam @ 115 ± 5^{o}*C,* flow rate: 0.11 *L/min,* bed depth: 0.85 *m,* ID of column: 0.06 cm.

The TOC and TN desorption efficiency calculated was about 19.7% and 15.8% from GAC using steam. Low TOC and TN removal efficiencies may be due to high boiling point (higher than $120^{o}C$) of chemicals present in the pharmaceutical wastewater (Table 3.4).

The regenerant (condensed steam) collected during desorption run and the degradation of the TOC content will be further explained in experiments performed in Section 4.3.

4.1.6. pH and temperature during experiments

During the experiments, the pH and temperature of the wastewater sample were measured. Figure 4.10 presents the pH results of the adsorption experiments performed at two different feed TOC concentrations of 853.5 and 1,755.5 *mg*C/*L*, respectively. As shown in Figure 4.10, the pH values were increased during the initial phase of the process and eventually returned back to the inlet pH value. The increase in pH during the initial phase can be attributed to the fact that the acidic impurities, such as sulfanilic acid and 4 aminophenol, present in the pharmaceutical wastewater (Section 3.1.1) are being removed from the wastewater in the presence of granular activated carbon, which also is in agreement with the kinetics of Langmuir adsorption process mentioned in Section 4.1.1.1. It was found that the pH returns back to the inlet pH between 3- 3.7 which can be attributed to the fact of carbon column breakthrough where outlet TOC concentration are almost the same as the inlet. The temperature during the GAC operational period had no significant changes and was maintained between 23 and $26^{o}C$ which were close to the room temperature at each testing.

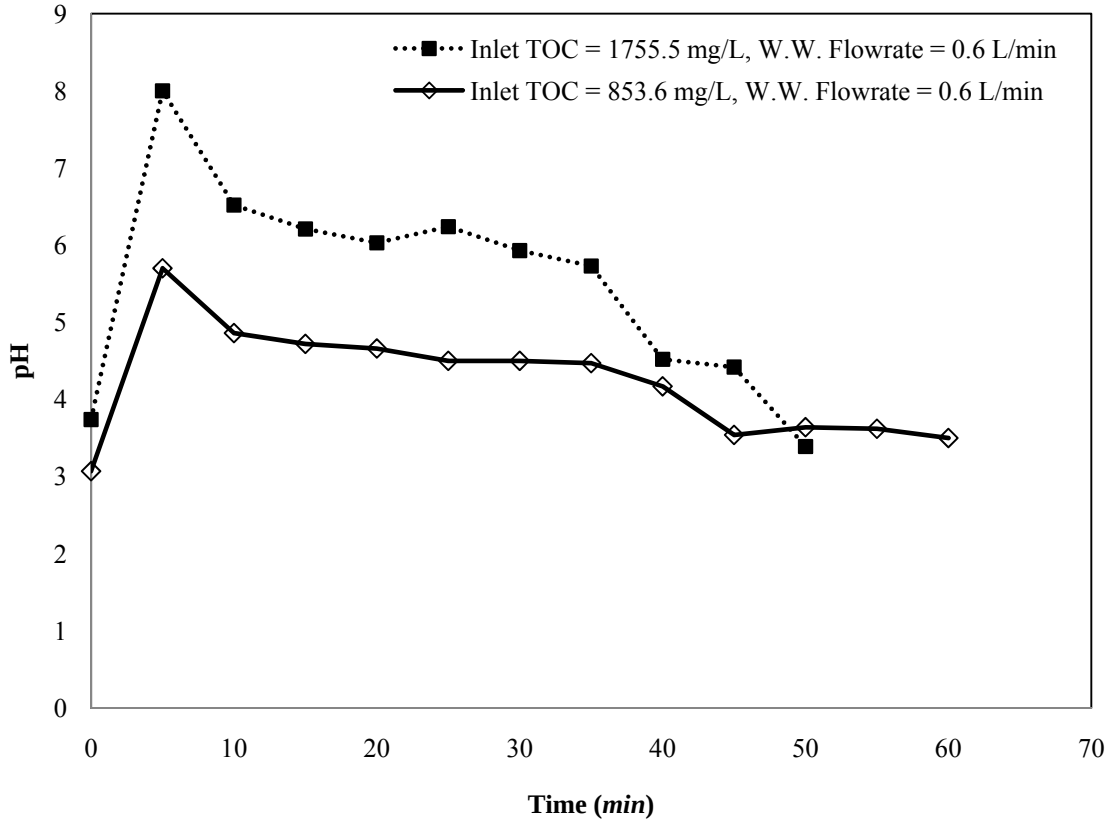

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Figure 4.10. pH during the GAC adsorption process with different feed TOC concentration, adsorption operated with single column radius of 0.06 *m* and height of 0.85 *m* at 46% breakthrough and 0.6 *L/min* flow rate for feed TOC concentration = 1,755.5 *mg*C/*L* and TN concentration = 85.4 *mg*N/*L* of the pharmaceutical wastewater. Breakthrough time for adsorption was 50 *min*.

4.2 Photolytic Treatment of Synthetic Pharmaceutical Wastewater

All experiments for this process were conducted in continuous mode for the treatment of pharmaceutical wastewater using 185 and 254 *nm* wavelength UV lamps at various mass ratios of H_2O_2 concentrations to the inlet COD concentrations (Section 2.8.1.5).

4.2.1 Photochemical treatment of pharmaceutical wastewater by UV light alone

Several experiments were conducted using 185 and 254 *nm* wavelenght UV lamps with different flow rates. In these experiments, wastewater was passed through the UV photoreactor in the presence of the UV only. Samples (10 *mL*) from the UV reactor, at different HRT and UV wavelengths, were taken and analysed immediately. The ranges of the wastewater flow rate were varied from 3.75-22.5 *mL/min* which corresponded to 1-6 *h* HRT.

Figure 4.11 illustrates the TOC reduction of the pharmaceutical wastewater with respect to different residence times for both wavelengths. It was observed that as HRT was increased from 1 to 6 *h*, the TOC removal rate was increased from 12.1 to 23.2% for 254 *nm* while 13.4 to 26.5% for 185 *nm*, respectively. This is due to the fact that as the HRT is increased, the UV absorbance increases. Moreover, the 185 *nm* light has capacity to break the water molecule present in the wastewater into readily reactive hydroxyl radicals (˙OH) (Aquafine UV, 2009). So it was assumed that the property of ˙OH radicals would accelerates the destruction process of the organics present and in turn, increases the TOC removal. From Figure 4.11, it is observed that the TOC removal rate were 2-5% higher when 185 *nm* wavelength was used in comparision to that of 254 *nm* wavelenght UV lamp.

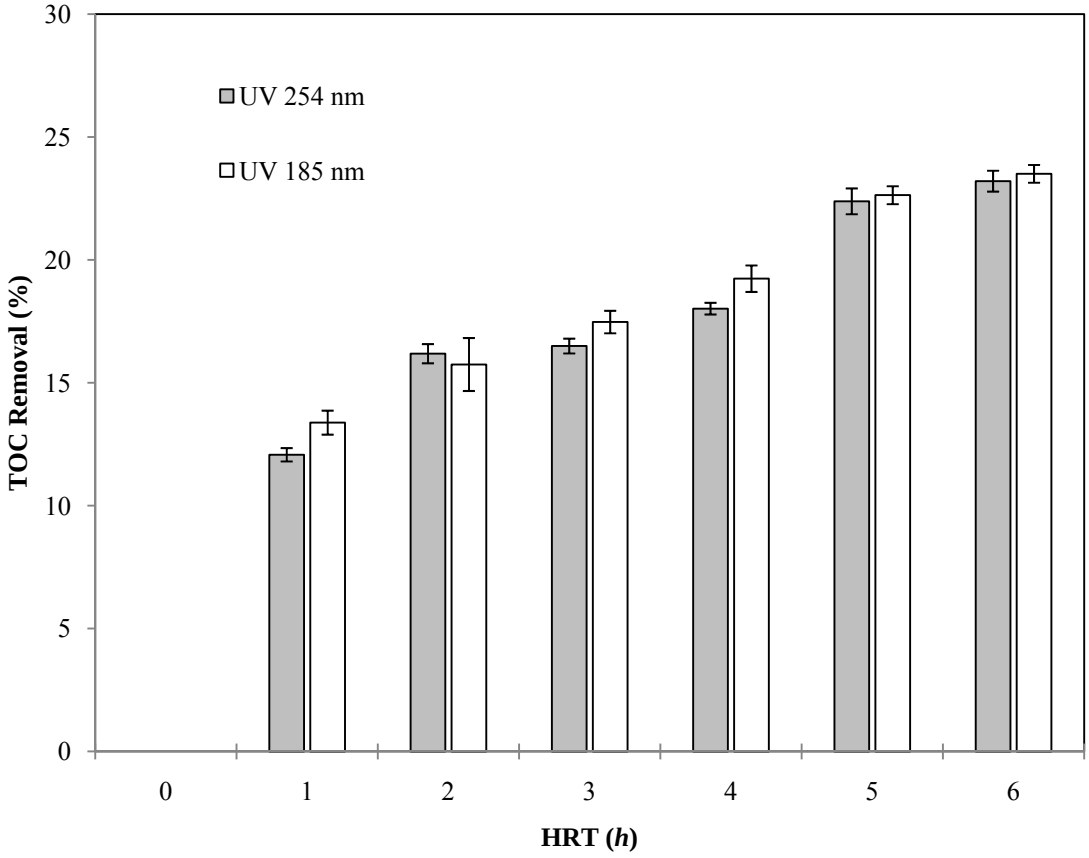

Figure 4.11. Relationship between TOC removal efficiency and hydraulic residence time for two different type of UV lamps used in the UV process with no H_2O_2. Average inlet concentration of TOC = 1,824 *mg*C/*L*, COD = 5,124.5 *mg/L*, pH = 3.12, and T = 24±2^{o}*C*.

4.2.2 Optimimal experimental value of H_2O_2 for the degradation of pharmaceutical wastewater

The UV alone could degrade the TOC of the wastewater up to a maximum of 23.2% for 254 *nm* while 26.5% for 185 *nm* in 6 *h* HRT. In this section, experiments were conducted to investigate the effects of H_2O_2 on the photolytic degradation of the synthetic pharmaceutical wastewater in the presence of UV light. In order to accelerate the degradation process, a sufficient H_2O_2 is essential so that it can absorb UV light and generates hydroxyl radicals. Figure 4.12 and Figure 4.13 illustrates that the addition of H_2O_2 rapidly increases the TOC removal efficiency of pharmaceutical wastewater. It can be observed that for 1 *h* HRT with 4.25 *mg*H_2O_2/*mg*COD, the TOC removal rate approximately matches the rate when the treatment was done with UV light alone for 6 *h* HRT. The addition of 4.25 *mg*H_2O_2/*mg*COD in 6 *h* could degrade TOC in the pharmaceutical wastewater up to 26.5% and 29.5% for 254 and 185 *nm*, respectively, while increasing the ratio of H_2O_2 concentration: feed COD concentration above this level led to a decrease in TOC removal rate. Thus, optimum concentration of H_2O_2 was found to be about 4.25 *mg*H_2O_2/*mg*COD. The reasons to support the decrease in TOC removal rate at higher than optimum H_2O_2 concentrations are:

- Auto-oxidation of H_2O_2 into O_2 and H_2O according to the reaction below (Ledakowicz and Gonera, 1999):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad (4.11)$$

- The excess of H_2O_2 reacts with $^{\bullet}OH$ competing with pollutants and hence, decreasing the efficiency of the treatment (Ledakowicz and Gonera, 1999).

$$H_2O_2 + {}^{\bullet}OH \xrightarrow{k_1} HO_2{}^{\bullet} + H_2O \qquad k_1 = (1.4 - 4.5) \times 10^7\ M^{-1}s^{-1} \qquad (2.8)$$

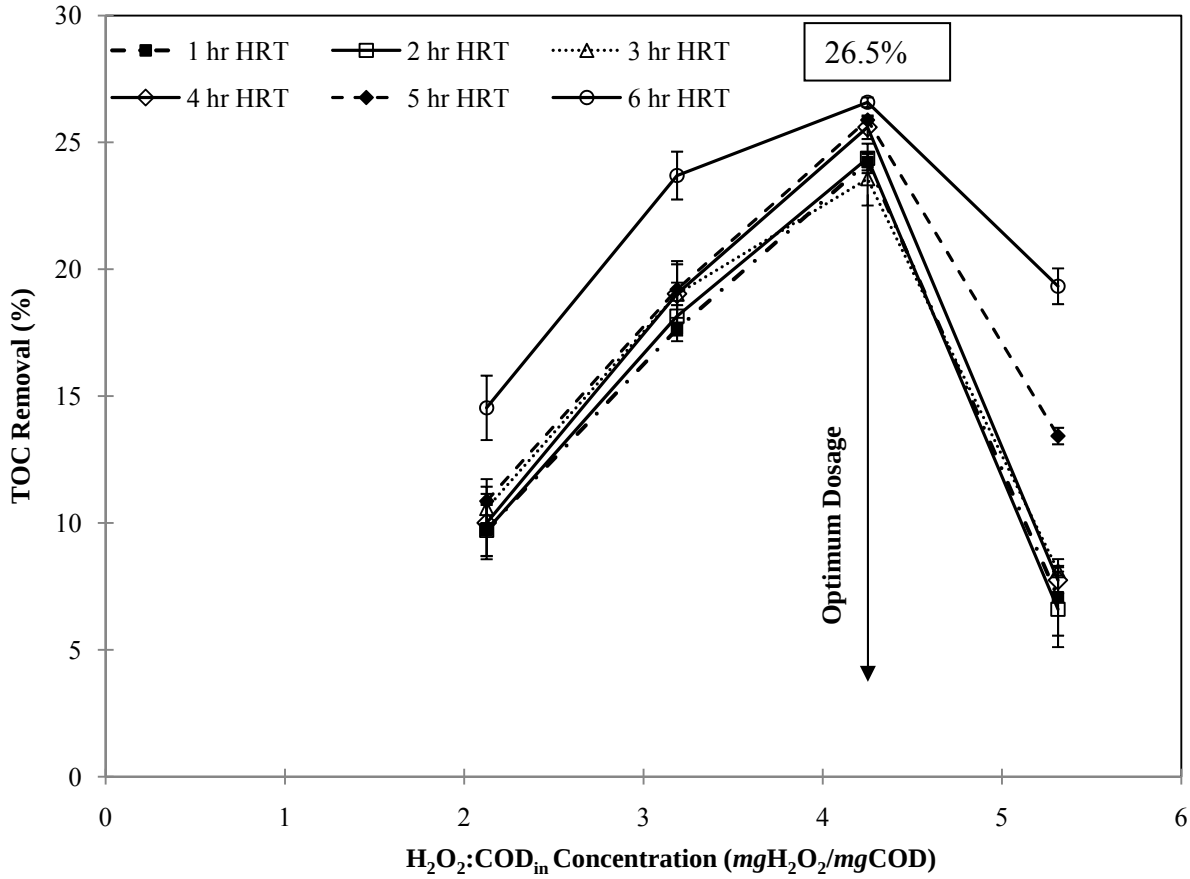

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Figure 4.12. Effect of H_2O_2 concentration on TOC removal of pharmaceutical wastewater. 4.25 *mg*H_2O_2/*mg*COD was found to be the optimum dosage when using 254 *nm* wavelength UV lamp for pharmaceutical wastewater having average inlet conditions of TOC = 1,824 *mg*C/*L*, COD = 5,124.5 *mg/L*, pH = 3.12 and temperature about 24±2^oC.

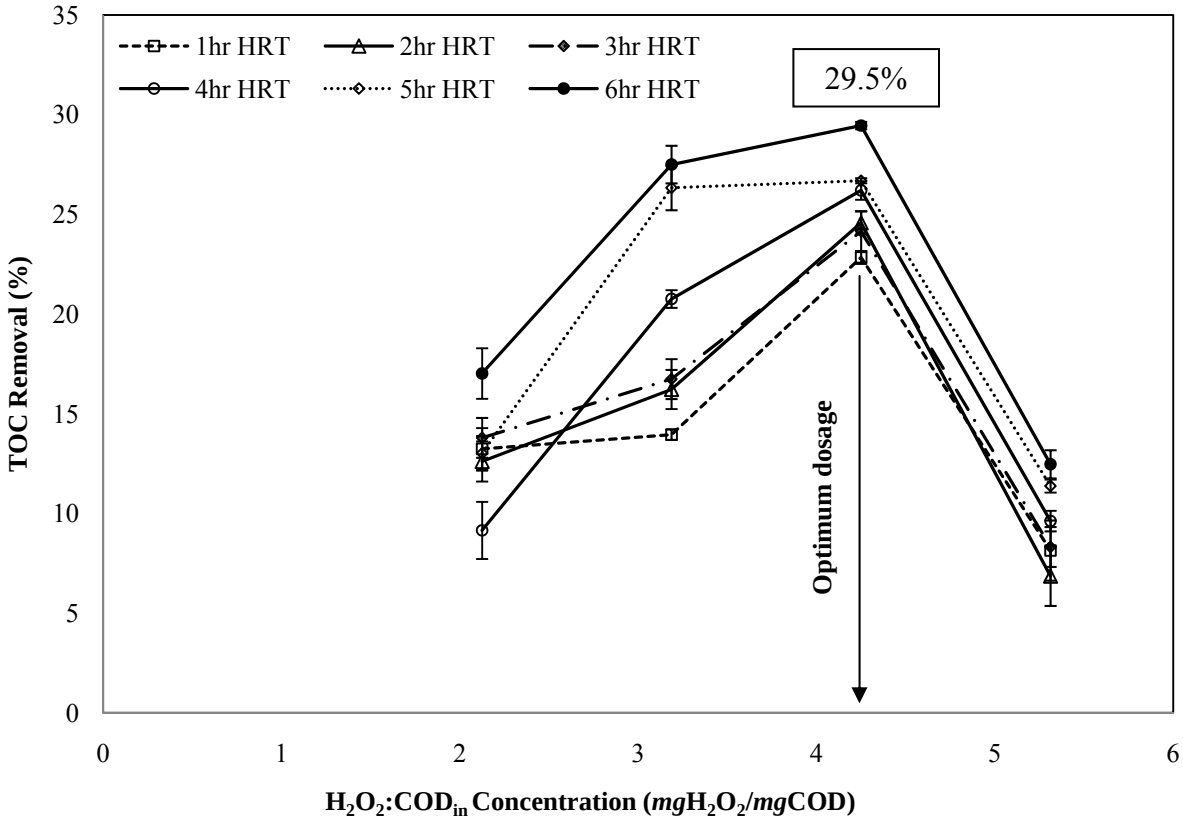

Figure 4.13. Effect of H_2O_2 concentration on TOC removal of pharmaceutical wastewater. 4.25 *mg*H_2O_2/*mg*COD was found to be the optimum dosage when using 185 *nm* wavelength UV lamp for pharmaceutical wastewater having average inlet conditions of TOC = 1,824 *mg*C/*L*, COD = 5,124.15 *mg/L*, pH = 3.12 and temperature about 24±2^{o}*C*.

4.2.3 Photolytic degradation of pharmaceutical wastewater by using UV alone, optimum concentration of H_2O_2, and their combination

The TOC removal from the pharmaceutical wastewater was compared for three different conditions shown in Figure 4.14 as follows:

1. Optimum concentration of 4.25 *mg*H_2O_2/*mg*COD alone
2. UV/H_2O_2 at optimum concentration of 4.25 *mg*H_2O_2/*mg*COD
3. UV alone

Experiments for optimum H_2O_2 alone and UV alone were carried out for an HRT of 6 *h* while UV/H_2O_2 at optimum concentration of 4.25 *mg*H2O2/*mg*COD was carried out at HRT of 1 *h*. It was observed that the wastewater treated with UV/H_2O_2 at optimum concentration of 4.25 *mg*H_2O_2/*mg*COD could remove TOC up to 26.5% and 29.5% for 254 and 185 *nm*, respectively, while TOC removed by optimum H_2O_2 alone and UV alone were 10.3% and 23.2% - 26.5% respectively. Samples treated with UV/H_2O_2 at optimum concentration of 4.25 *mg*H_2O_2/*mg*COD had an increase in TOC removal of more than 5-10% than that of UV or H_2O_2.

4.2.4 Effects of pH on removal of TOC from pharmaceutical wastewater using UV/H_2O_2 process

Experiments by UV/H_2O_2 process with optimum H_2O_2 were conducted to treat pharmaceutical wastewater under three different initial pH conditions. The pH of the inlet was set at 7 and 12.01, respectively, for two runs (Section 3.4.3).

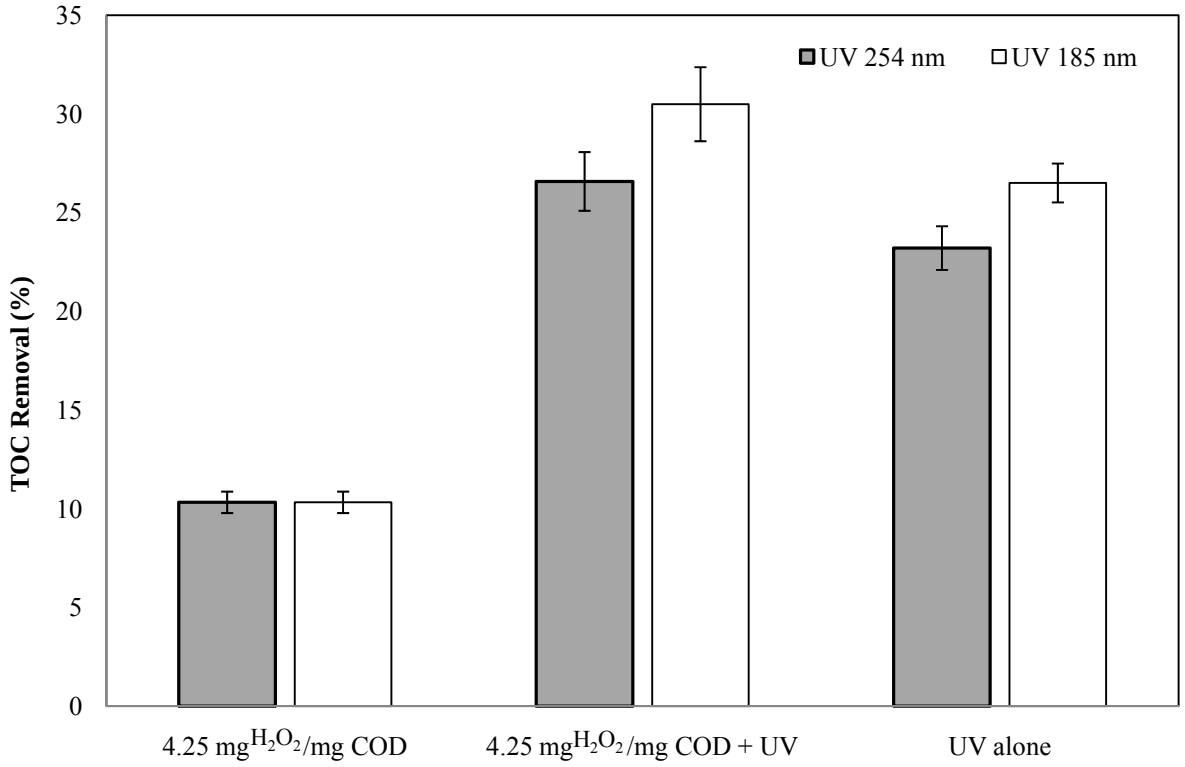

Figure 4.14. Comparison of the TOC degradation for three different conditions: Optimum concentration of 4.25 *mg*H_2O_2*/mg*COD alone; UV/H_2O_2 at optimum concentration of 4.25 *mg*H_2O_2*/mg*COD, and UV alone. Average inlet concentration of the wastewater was TOC = 1,824 *mg*C*/L,* COD = 5,124.5 *mg/L*, pH = 3.12, T = 24 ± 2^oC, and HRT = 6 *h.*

Figure 4.15 and Figure 4.16 illustrate the effects of pH on the removal efficiency of TOC by UV/H_2O_2 process using 254 and 185 *nm* UV lamps, respectively. These figures show that as the pH value of the inlet wastewater increases from 3.12 to 12.01, the TOC removal rate decreases by 17 – 19 % for both types of UV lamps. At lower pH of the solution, i.e. pH 3, the production of hydroxyl radical is optimized (Daifullah and Mohamed, 2004). In addition, the dissociated form of hydrogen peroxide (HO_2^-)(Christensen et al., 1982) in alkaline solution reacts with hydroxyl radicals more than two orders of magnitude faster than that of hydrogen peroxide and therefore it decreases the oxidation efficiency by consuming hydroxyl radicals according to the following reactions (Equation 4.4 and 2.8, Johnson and Mehrvar, 2008):

$$HO_2^- + {}^{\bullet}OH \xrightarrow{k_6} HO_2{}^{\bullet} + OH^- \qquad k_6 = 7.5\times10^9\, M^{-1}s^{-1} \qquad (4.12)$$

$$H_2O_2 + {}^{\bullet}OH \xrightarrow{k_1} HO_2{}^{\bullet} + H_2O \qquad k_1 = (1.4 - 4.5)\times10^7\, M^{-1}s^{-1} \qquad (2.8)$$

The reaction rate constant for the HO_2^- with hydroxyl radical is higher ($7.5 \times 10^9\ M^{-1}s^{-1}$) compared to the reaction rate constant ($(1.4 - 4.5) \times 10^7\ M^{-1}s^{-1}$) for hydrogen peroxide with hydroxyl radical. From the experimental results, it was concluded that at pH 3, the TOC removal was 17-19% higher than the TOC removal than that achieved at 12 pH, for pharmaceutical wastewater considered in this study at both wavelengths. Therefore, all the UV/H_2O_2 experiments in this study were conducted at the original pH of the wastewater (i.e. pH = 3; without any pH adjustments of the raw wastewater). However, the lower pH may cause a discharge issue. The discharge of industrial wastewater to the environment must have a pH in the range of 6 - 9 (Correctional Service Canada, 2003). In the event if UV/H_2O_2 is used as a treatment method, prior to discharge of treated water, it has to be neutralized.

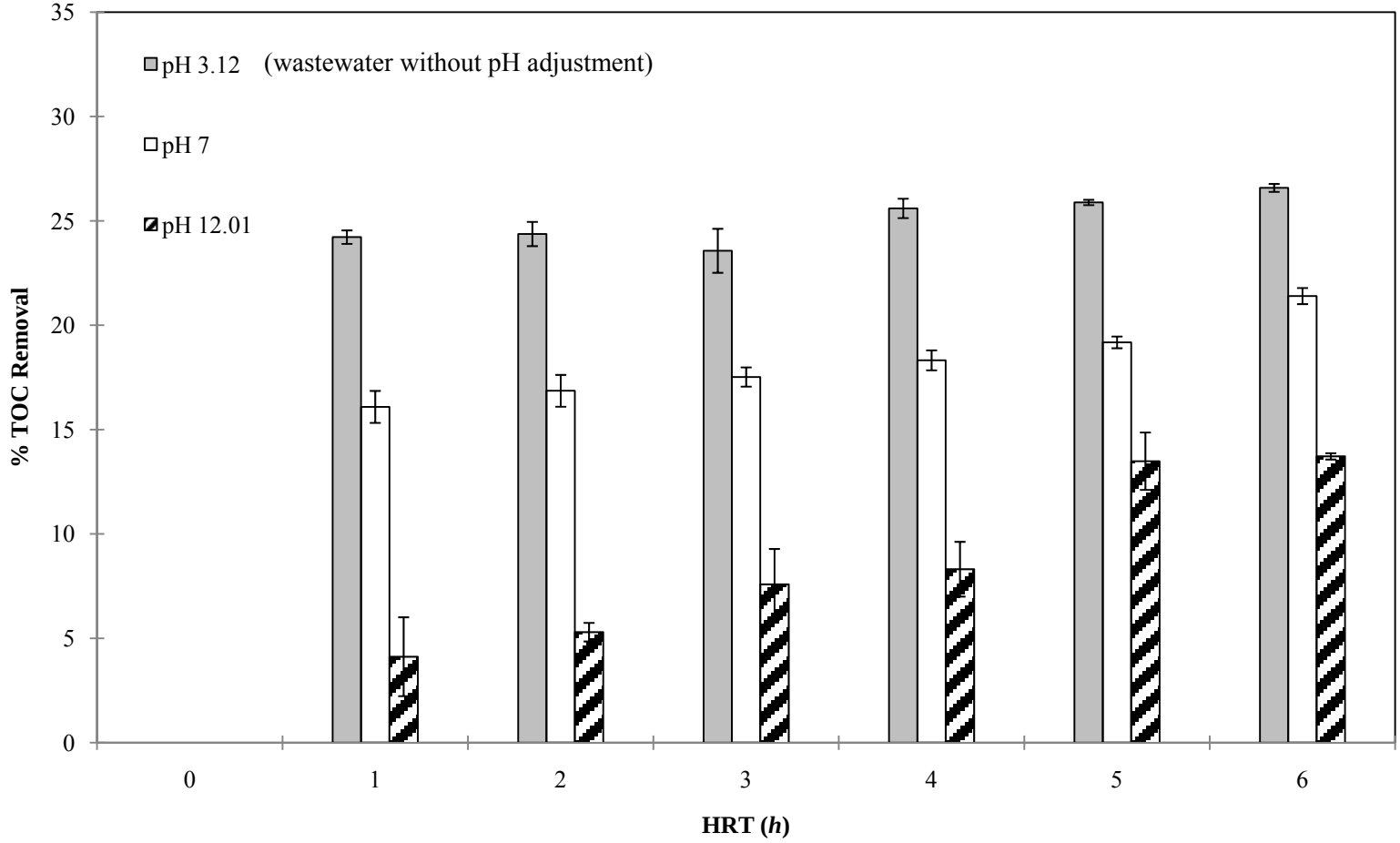

Figure 4.15. Dependency of pH on UV/H_2O_2 treatment using 254 *nm* wavelength UV lamp and optimum 4.25 *mg*H_2O_2/*mg*COD with average inlet conditions of TOC = 1,824 *mg*C/*L*, COD = 5,124.15 *mg/L*, and T = 24 ± 2^oC.

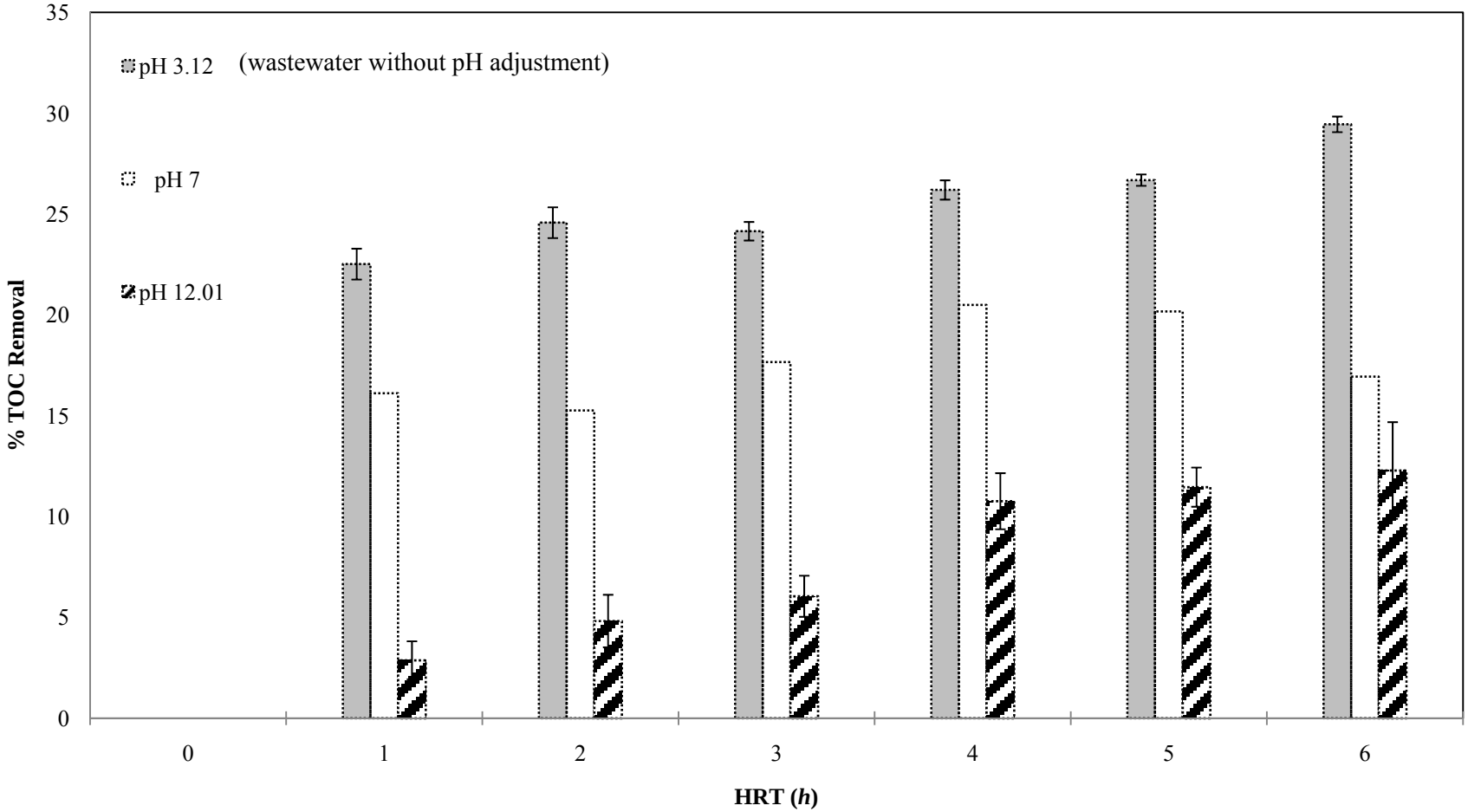

Figure 4.16. Dependency of pH on UV/H_2O_2 treatment using 185 *nm* wavelength UV lamp and optimum 4.25 *mg*H_2O_2/*mg*COD with average inlet conditions of TOC = 1,824 *mg*C/*L*, COD = 5,124.15 *mg/L*, and T = 24 ± 2^oC.

4.2.5 Changes in total nitrogen content during the optimized UV/H_2O_2 experiments

Experiments were conducted to see the effects of nitrogen removal (TN) in the photolytic degradation. Figure 4.17 illustrates that there was no significant change in total nitrogen measured in the samples after UV/H_2O_2 treatment. This may be due to the fact that the UV/H_2O_2 process is only capable of degrading nitrogenous compounds to NH_4^+ or mostly to NO_3^- (Section 2.8) at higher concentration and not to molecular form N_2 and thus, it can be measured by the TN analyzer as TN present in the wastewater sample. To better understand the nitrogen reaction chemistry, experiments with different nitrogen concentration should be performed along with intermediate identification to analyze the treatment efficiency of the process.

4.2.6 Impact of H_2O_2 on COD and BOD_5 tests

The impact of H_2O_2 on COD was tested by performing COD tests on the inlet wastewater samples, one with H_2O_2 and another without any H_2O_2. It was observed that the sample with H_2O_2 exerted an excessive amount of oxygen for chemical oxidation in comparison to the samples without H_2O_2. Figure 4.18 illustrates the COD requirement of both samples and as it can be observed, the difference is significantly high in the range of 4,000 *mg/L*. Therefore, residual H_2O_2 can interfere with COD measurement and overestimates a higher COD value due to its reaction with dichromate. As explained in Section 3.3.6, the reaction of potassium dichromate with organic compounds (in absence of H_2O_2) is given by Reaction (3.4):

$$C_nH_aO_bN_c + dCr_2O_7^{2-} + (8d+c)H^+ \rightarrow nCO_2 + \left(\frac{a+8d-3c}{2}\right)H_2O + cNH_4^+ + 2dCr^{3+} \qquad (3.4)$$

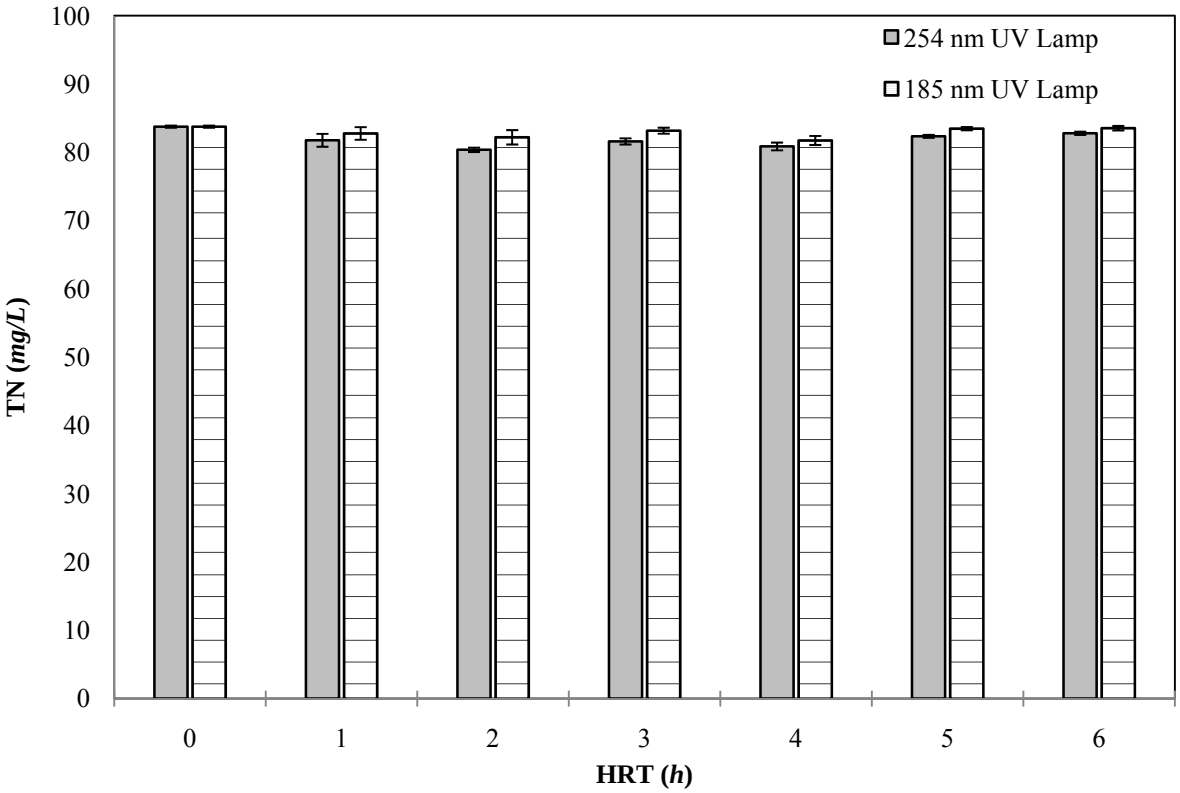

Figure 4.17. Total nitrogen content during the UV/H_2O_2 treatment using 185 and 254 *nm* wavelength UV lamps and optimum 4.25 *mg*H_2O_2/*mg*COD with average inlet conditions of TOC = 1,824 *mg*C/*L*, COD = 5,124.15 *mg/L,* TN = 84 *mg*N/*L*, pH = 3.2, and T = 24 ± 2^oC.

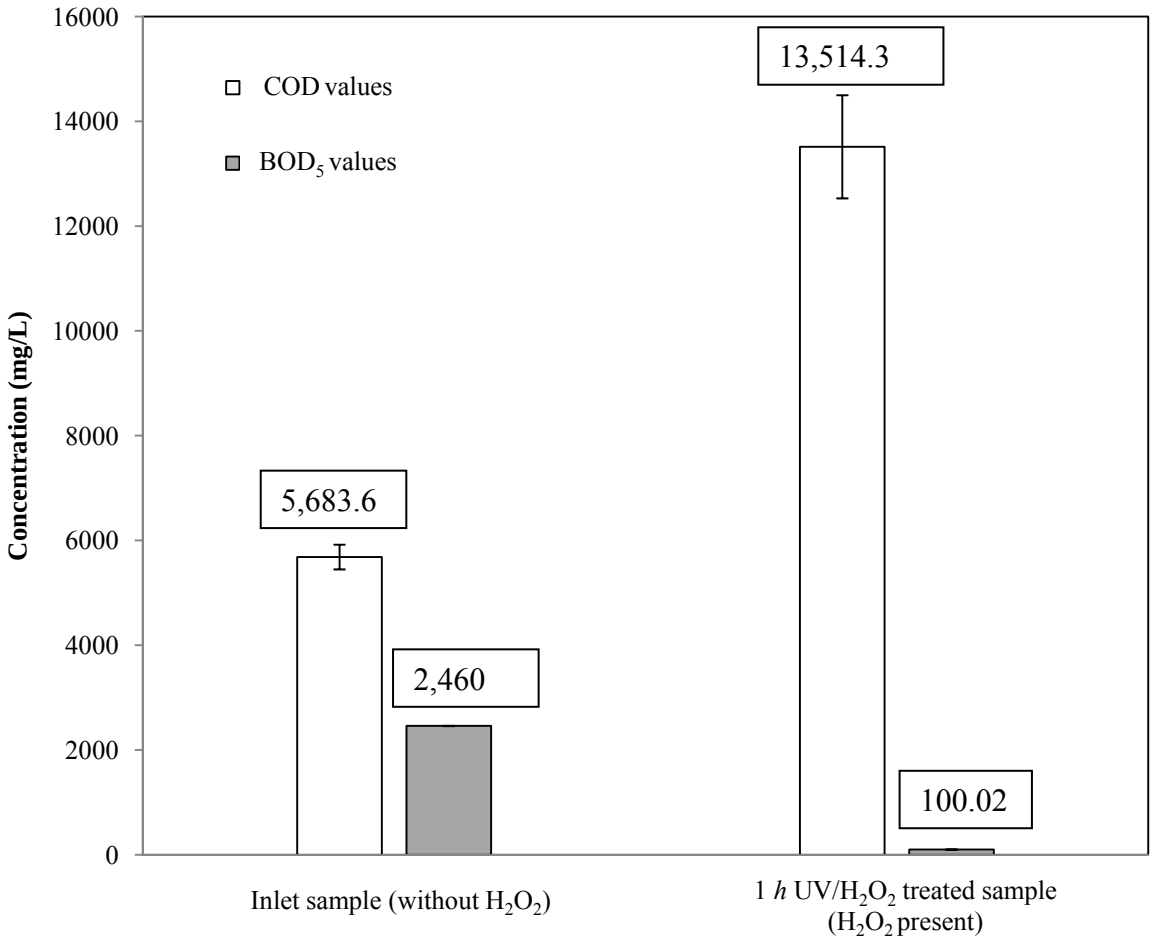

Figure 4.18. Effect of H_2O_2 on COD and BOD_5 measurement. Average feed condition: TOC = 1,824 *mg*C/*L*, COD = 5,124.5 *mg/L*, TN = 84 *mg*N/*L*, T = 24^oC, and pH = 3.2. H_2O_2 dosage = 4.25 *mg*H_2O_2/*mg*COD

where,

$$d = 2n/3 + a/6 - b/3 - c/2$$

When COD analysis of sample containing H_2O_2 was performed, the colour of the solution turned into green due to the reaction of H_2O_2 with potassium dichromate acidified by sulphuric acid. This is due to the formation of Cr_3^+ ions from the reduction of potassium dichromate as shown in Reaction (4.14) and reductive ability of H_2O_2 to reduce potassium dichromate (Lin *et al*., 1999). Thus, H_2O_2 interfered with the COD analysis.

$$Kr_2Cr_2O_7 + 3H_2O_2 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4) + 7H_2O + 3O_2 \quad (4.13)$$

Moreover, Figure 4.18 illustrates the BOD_5 of the inlet samples (Appendix B) with and without H_2O_2. It was observed that samples with H_2O_2 consume less oxygen as compared to the sample without H_2O_2 in the BOD_5 tests. The reason is the inhabitant characteristics of H_2O_2 which hinders the bacterial activity (Ito *et al*., 1998). Thus, residual H_2O_2 can inhibit bacterial growth in the BOD_5 tests and hence misjudge the actual BOD_5 reading.

The excess H_2O_2 could be removed by adding bovine liver catalyst, corresponding to the amount of H_2O_2 present, if H_2O_2 present is less than 200 *mg/L* (Ito *et al*., 1998). Tests were performed to detect the amount of H_2O_2 left as residual in the sample as mentioned in Section 3.1.10. It was found that as soon as the tablets were added to the sample, the sample would turn dark brown and did not match any of the colour coding presented on the calibrated plastic foil (Section 3.1.10). This indicated that the concentration of H_2O_2 was higher than 100 *mg/L*. Thus, the catalyst required to remove such large quantity of H_2O_2 was high and is very expensive. Due

to this fact, there was no BOD_5 and COD test performed for any of the UV/H_2O_2 treated samples.

4.3 Combination of UV/H_2O_2 and GAC Adsorption Processes

From the above set of experiments at selected conditions, it was observed that the UV/H_2O_2 process gave maximum of 26% - 29% TOC removal from the pharmaceutical wastewater using either 185 or 254 *nm* UV lamp at an HRT of 6 *h,* while GAC process gave 3 times higher TOC removal (i.e. 81%) in 10 *min* breakthrough time at the flow rate of 0.6 *L*/*min* (as shown in Table 4.8). The aim of any treatment process is to degrade the contaminants present in the wastewater and convert them to inorganic (CO_2, H_2O, N_2), nontoxic, and less molecular weight compounds. But, from the above experiments, it was observed that 81% of TOC (contaminants) were transferred from one phase (wastewater) to another (GAC) during the adsorption process, while only 26% of TOC was actually degraded/ eliminated from the wastewater using UV/H_2O_2 process. Also, the desorption of TOC left on the exhausted activated carbon was carried out using steam which resulted in transfer of 19% TOC (contaminants) from carbon to condensed steam.

Thus, experiments were performed to see how the TOC present in the regenerant (condensed steam) and UV/H_2O_2 treated water could be eliminated using the combination of the above two processes. The pre-treated wastewater by UV_{254}/H_2O_2 was fed to the GAC process to see if there was an improvement in the TOC removal, treatment time, as well as activated carbon and H_2O_2 dosage required (Section 3.4.4) and vice versa. Also, the steam condensate collected during the desorption process was passed through UV/H_2O_2 to calculated the TOC and TN removal efficiencies.

Table 4.8.Optimised results obtained in GAC and UV_{254}/H_2O_2 processes individually from Section 4.1 and 4.2. L= length, ID = inner diameter, OD = outer diameter, and italic *L* = litres of wastewater treated. Sample Calculation shown in APPENDIX G.

Process	**Column/Reactor dimension (*m*)**	**Inlet average TOC loading (*mg*C/*L*)**	**TOC removal efficiency (%)**	**Dosage**	**Time (*min*)**	**Flow rate (*L*/*min*)**	**To treat 30*L* wastewater**	
							Treatment time (*min*)	**Total dosage (*Kg*)**
UV_{254}/H_2O_2	L = 0.35 OD = 0.08 ID = 0.038	1,824	26	21.7 gH_2O_2/L	HRT = 300	3.75×10^{-3}	8,000	H_2O_2 = 0.651
GAC Adsorption	L = 0.9 ID = 0.06 bed height = 0.85	1,755.5	81	333.3 *g*Activated Carbon/*L*	Break-through time = 10 at 6 *L*	0.6	50	GAC = 10

4.3.1 UV_{254}/H_2O_2 followed by GAC adsorption treatment along with UV/H_2O_2 treatment of the regenerant from the desorption process.

Simplified flowchart of the combined UV_{254}/H_2O_2 followed by GAC adsorption treatment process as shown in Figure 4.19. Wastewater treated by UV/H_2O_2 as mentioned in Section 4.2, at an optimum H_2O_2 concentration of 4.25 mgH_2O_2/mgCOD and HRT of 3 *h* and 6 *h*, had not more than 3% difference in the TOC removal efficiency for both 185 and 254 *nm* UV lamps. Thus, wastewater treated with UV_{254}/H_2O_2 (hereafter defined as Stage 1 of this combined process) at an HRT of 3 *h* was fed to the GAC column to study the breakthrough point and combined effect of both processes. Conditions and parameters used for the GAC adsorption process (defined as Stage 2 of the combined process) are listed inTable 4.9.

It was found that the GAC column had 75.1% breakthrough at flow rate of 0.6 *L*/*min* in 20 *min* from Figure 4.20. The overall TOC removal efficiency of the UV_{254}/H_2O_2 followed by GAC adsorption was 81%. The desorption of the contaminant from the GAC (defined as stage 3 of the combined process) was carried out in the column using steam at the conditions mentioned in Table 4.9 and the results were plotted in Figure 4.20. It was observed that only 10.1% of TOC was recovered from the GAC during the desorption process which, again might be due to high boiling point (higher than 120^oC) of chemicals present in the wastewater pretreated by UV_{254}/H_2O_2. Furthermore, the regenerant (condensed steam) collected during desorption cycle was treated with UV_{254}/H_2O_2 (defined as stage 4 of the combined process) at optimum conditions mentioned in Table 4.9. It was observed that 82% of the TOC present in the condensed steam was eliminated in 2 *h* HRT.

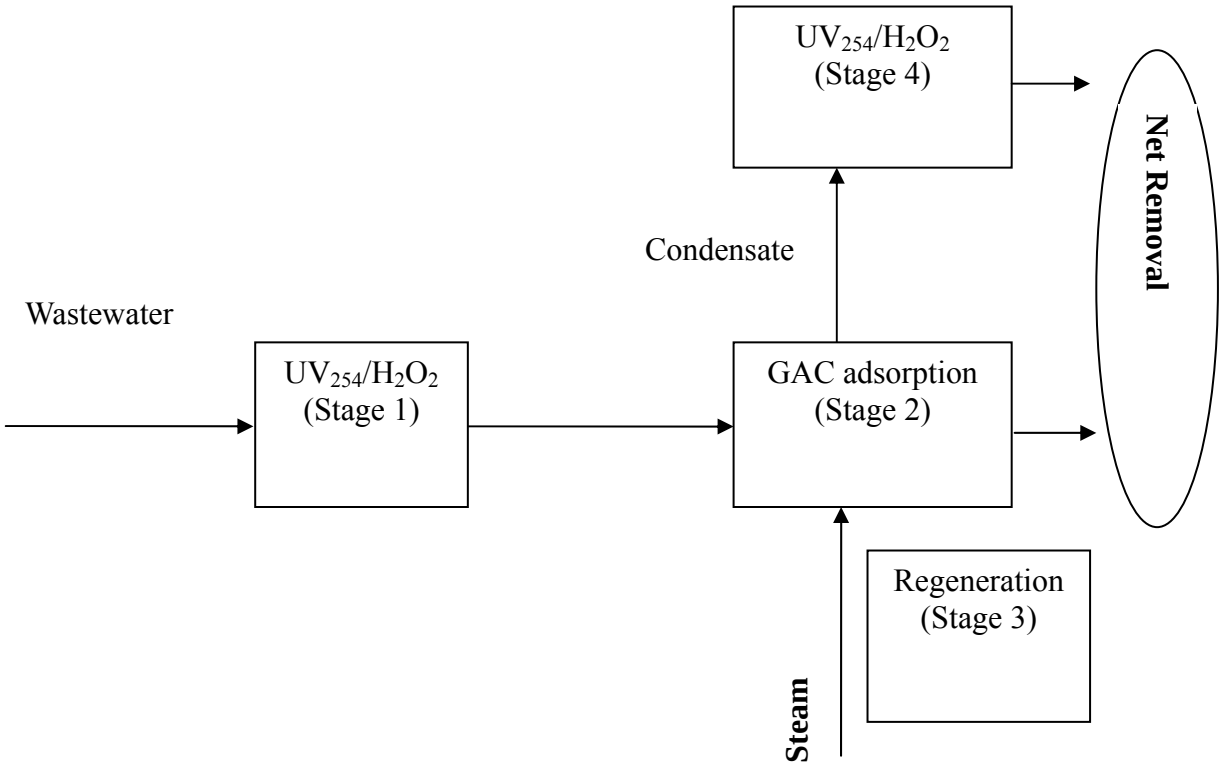

Figure 4.19. Flowchart of the combined UV_{254}/H_2O_2 followed by GAC adsorption treatment process.

Table 4.9. Results obtained from UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 treatment of regenerant from the desorption process. L= length, ID = inner diameter, OD = outer diameter, T = temperature, P = pressure, and italic *L* = litres of wastewater treated. Sample calculation shown in APPENDIX G.

Process		**Column/Reactor dimension (*m*)**	**Inlet average TOC loading (*mg*C/*L*)**	**TOC removal efficiency (%)**	**Dosage**	**Time (*min*)**	**Flow rate (*L/min*)**	**To treat 30*L* wastewater**		
								Treatment time (*min*)	**Total dosage (*Kg*)**	**Net TOC removal efficiency (%)**
Combined UV_{254}/H_2O_2 + GAC adsorption along with Desorption + UV_{254}/H_2O_2	**Stage 1** UV_{254}/H_2O_2	L = 0.35 OD = 0.08 ID = 0.038	1,856.2	23.6	21.7 gH_2O_2/L	HRT = 180	7.5×10^{-3}	4,000	H_2O_2 = 0.651	81
	Stage 2 GAC adsorption	L = 0.9 ID = 0.06 bed height = 0.85	1,418.5	75.1	166.65 *g*Activated Carbon/*L*	Breakthrough time = 20 at 12 *L*	0.6	50	GAC = 5	
	Stage 3 Desorption (Regeneration of GAC)	L = 0.9 ID = 0.06 bed height = 0.85 Steam condition T = 115±5 ^oC P = 30 *KPa*	1,066.5 (present on GAC)	10.1	0.75 *L* steam/*L*	60 *min*	0.15 *L* steam/*min*	150	Steam = 22.5	10.1
	Stage 4 Desorption + UV_{254}/H_2O_2	L = 0.35 OD = 0.08 ID = 0.038	107.7	82	0.9 gH_2O_2/L	HRT = 120	11.2×10^{-3}	**To treat 22.5 *L* of condensed steam**		82
								2,009	H_2O_2 = 0.020	

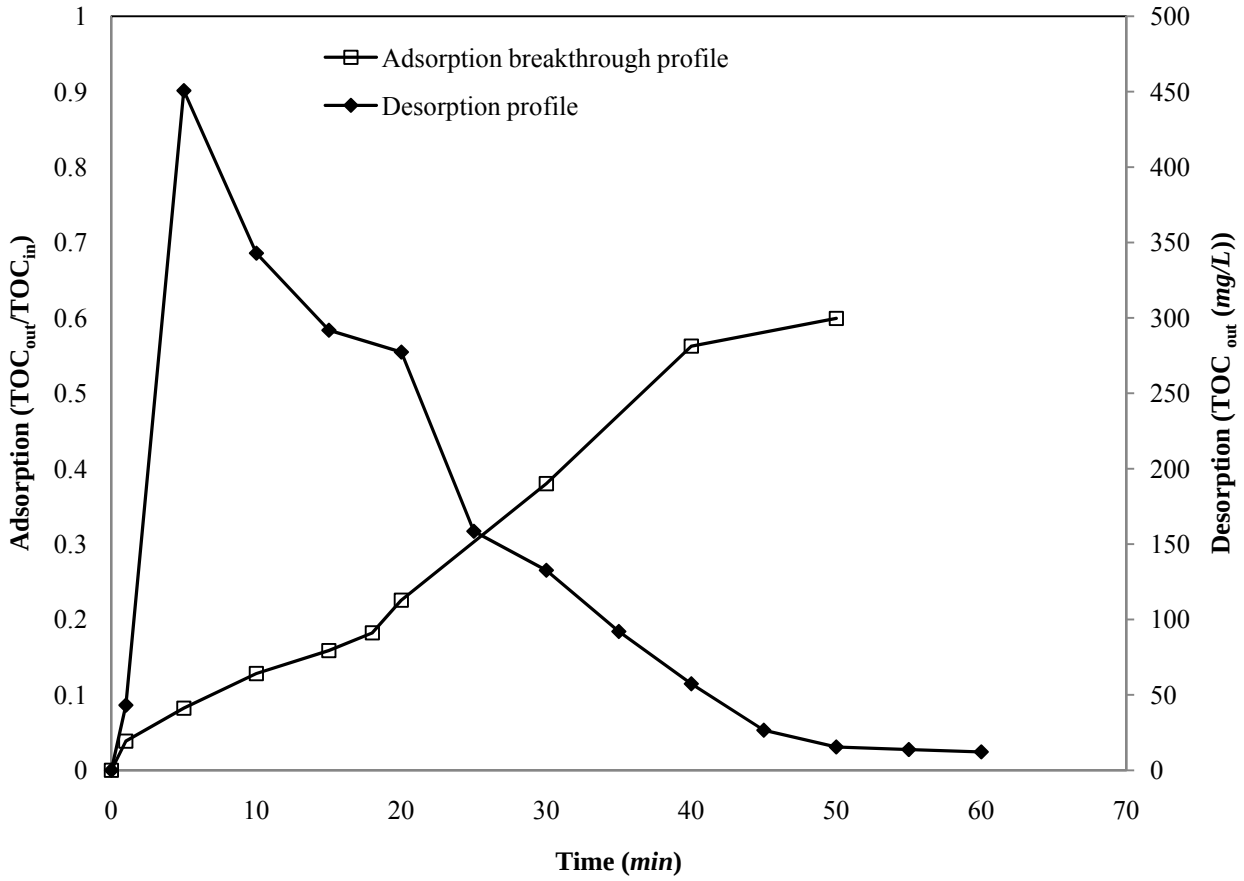

Figure 4.20. Adsorption and desorption profile (in terms of TOC) of pharmaceutical wastewater using combination of UV_{254}/H_2O_2 + GAC adsorption treatment processes along with desorption of contaminants from exhausted GAC and its treatment with UV_{254}/H_2O_2 process. The average inlet concentration of the wastewater was TOC = 1,856.23 *mg*C/*L*, COD = 5,224.04 *mg*/*L*, pH = 3.32, and T = 24 ± 2^oC.

There was no significant change in the TN removal during both of the UV_{254}/H_2O_2 process performed while GAC adsorption had 83% of TN removal and desorption process could recover only 4.2% of TN present on the exhaust carbon. Figure 4.21 illustrates overall TOC and TN removal of UV_{254}/H_2O_2 + GAC process, using combination of UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 treatment of the regenerant, from the pharmaceutical wastewater. This combination process will be further analysed on the basis of cost and removal efficiency obtained in Section 4.4.

4.3.2 GAC adsorption treatment along with UV_{254}/H_2O_2 treatment of the regenerant from the desorption process.

From the adsorption experiments (Section 4.1.2), it was found that 81% of removal efficiency could be achieved by using appropriate dosage of fresh GAC. The aim of the GAC adsorption treatment along with UV_{254}/H_2O_2 treatment of the regenerant as shown in the Figure 4.22, was to eliminate the contaminants in the wastewater by assuming that 100% of TOC would be recovered from the exhausted activated carbon using steam, giving condensate concentration (in terms of TOC and TN) more and volume less than that of the feed wastewater.

Experiments were performed by treating pharmaceutical wastewater with GAC adsorption at 81% TOC breakthrough. The contaminants from the exhausted activated carbon were desorbed using steam at $115 \pm 5^{o}C$ and to further eliminate the contaminants desorbed, condensate collected was then treated with UV_{254}/H_2O_2 at an HRT of 2 *h*.

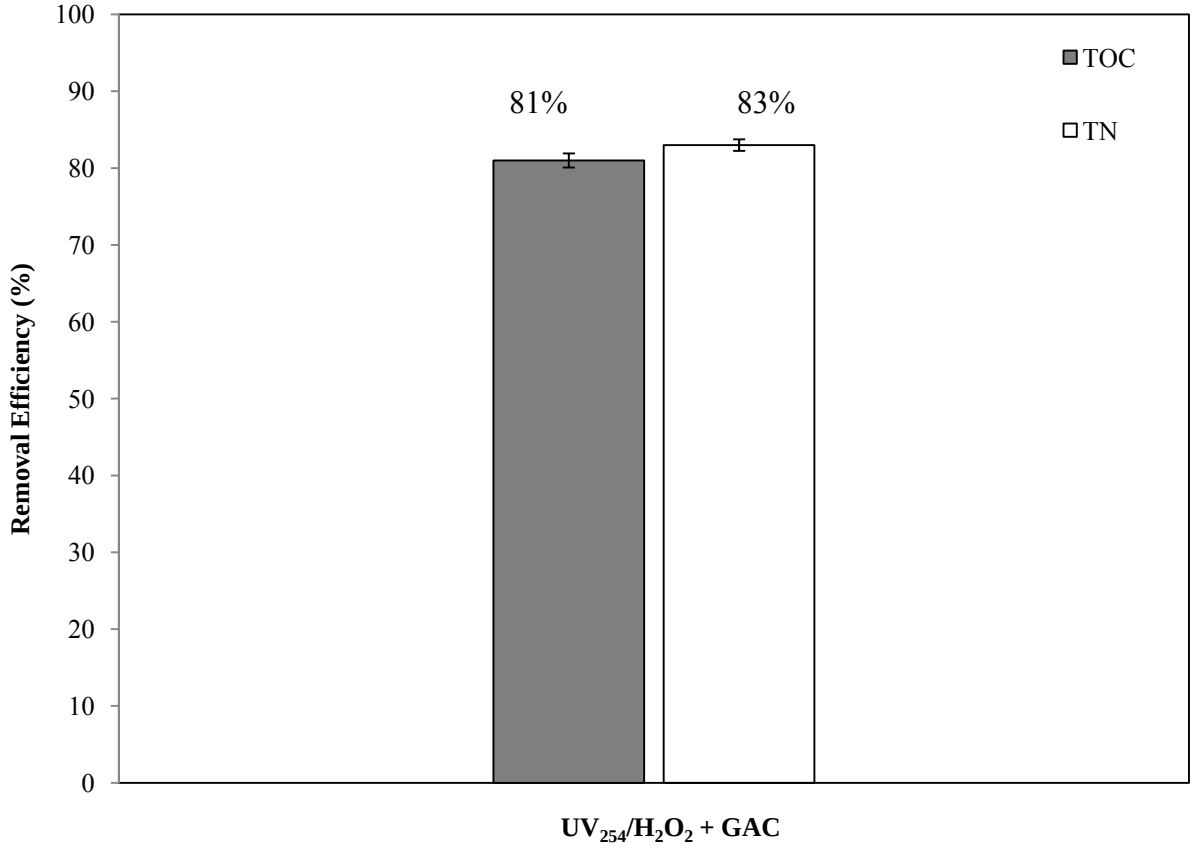

Figure 4.21 TOC and TN removal during UV_{254}/H_2O_2 + GAC process (Stage 1 and 2) using combination of UV_{254}/H_2O_2 + GAC adsorption treatment processes along with desorption of contaminants from exhausted GAC and its treatment with UV_{254}/H_2O_2 process. The average inlet concentration of the wastewater was TOC = 1,856.23 *mg*C/*L*, COD = 5,224.04 *mg*/*L,* TN = 103.3 *mg*N/*L*, pH = 3.32, and T = 24 ± 2^{o}*C*.

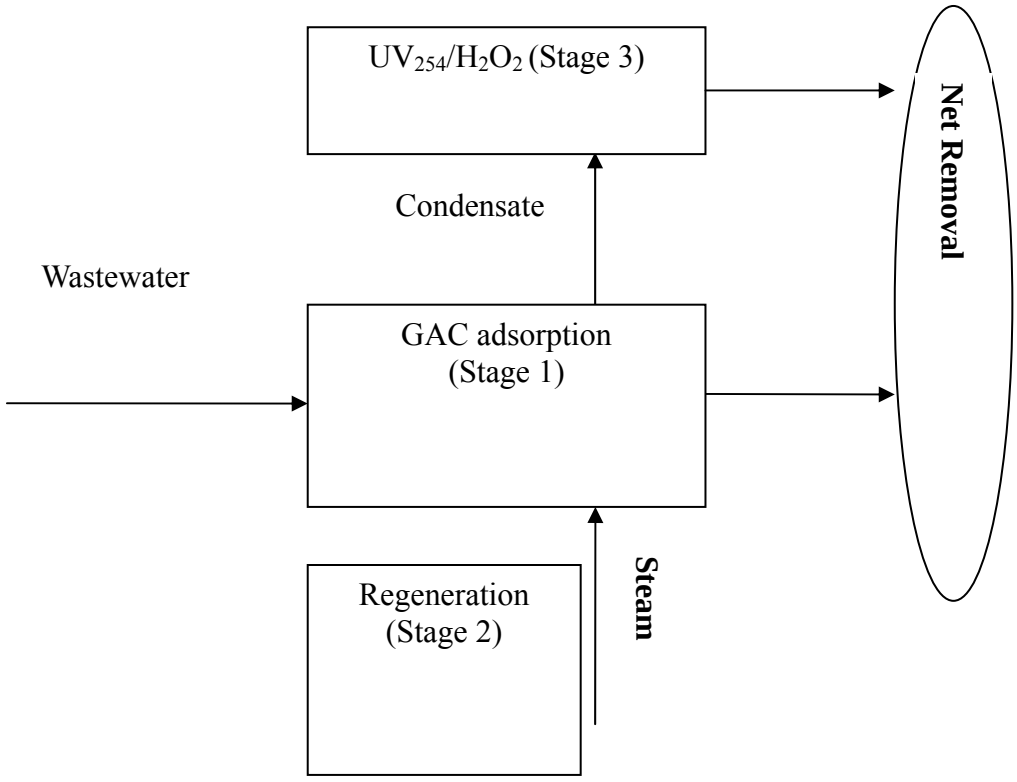

Figure 4.22. Flowchart of GAC adsorption treatment along with UV_{254}/H_2O_2 treatment of the regenerant processes.

The parameters and inlet conditions used for the GAC adsorption treatment along with UV_{254}/H_2O_2 treatment of the regenerant are listed in Table 4.10 and adsorption/ desorption profile results are plotted in Figure 4.23. It was observed that the GAC adsorption alone could treat 81% and 90.3% of TOC and TN present in the wastewater, respectively. The desorption process led to 26% TOC recovery which was higher by 1.3 to 1.6 times than the recovery made during desorption of GAC column with breakthrough of 40% (Section 4.1.5) or desorption process (Stage 3) of the combined UV_{254}/H_2O_2 + GAC adsorption treatment processes along with desorption of contaminants from exhausted GAC and its treatment with UV_{254}/H_2O_2 process in Section 4.3.1.

This might be due to the fact that less TOC was accumulated while operating the GAC column at 81% breakthrough than that of 40% breakthrough and also the possible intermediates (Table 2.10: phenol, maleic acid, acetic acid) formed during the UV_{254}/H_2O_2 process might be of higher boiling point than that the steam temperature used. It was in accordance with the hypothesis and UV_{254}/H_2O_2 treatment was performed on the regenerant (steam condensate) accordingly to further eliminate the contaminants. There was negligible change in the TN removal efficiency for the UV_{254}/H_2O_2 process on regenerant. The overall TOC and TN % removal efficiency results of the combined process are shown in Figure 4.24.

Table 4.10. GAC adsorption treatment along with UV_{254}/H_2O_2 treatment of regenerant from the desorption process for the pharmaceutical wastewater. L= length, ID = inner diameter, OD = outer diameter, T = temperature, P = pressure, and italic *L* = litres of wastewater treated.

Process		**Column/Reactor dimension (*m*)**	**average TOC loading (*mg/L*)**	**Efficiency (%)**	**Dosage**	**Time (*min*)**	**Flow rate (*L/min*)**	**To treat 30*L* wastewater**	
								Treatment time (*min*)	**Total dosage (*Kg*)**
Combined GAC adsorption along with Desorption + UV_{254}/H_2O_2 of regenerant from the desorption process	**Stage 1** GAC adsorption	L = 0.9 ID = 0.06 bed height = 0.85	1,755.5	81	333.35 *g* Carbon/*L*	Breakthrough time = 10 at **6 *L***	0.6	50	GAC = 10
	Stage 2 Desorption	L = 0.9 ID = 0.06 bed height = 0.85 Steam condition T = 115±5 ^oC P = 30 *KPa*	1,420 (present on GAC)	26	1.5 *L* steam/*L*	60 *min*	0.15 *L* steam/*min*	300	Steam = 45
	Stage 3 UV_{254}/H_2O_2 of regenerant from the desorption process	L = 0.35 OD = 0.08 ID = 0.038	358.7	88.1	2.55 gH_2O_2/L	HRT = 120	11.2×10^{-3}	**To treat 45 *L* of condensed steam**	
								4017	$H_2O_2 = 0.12$

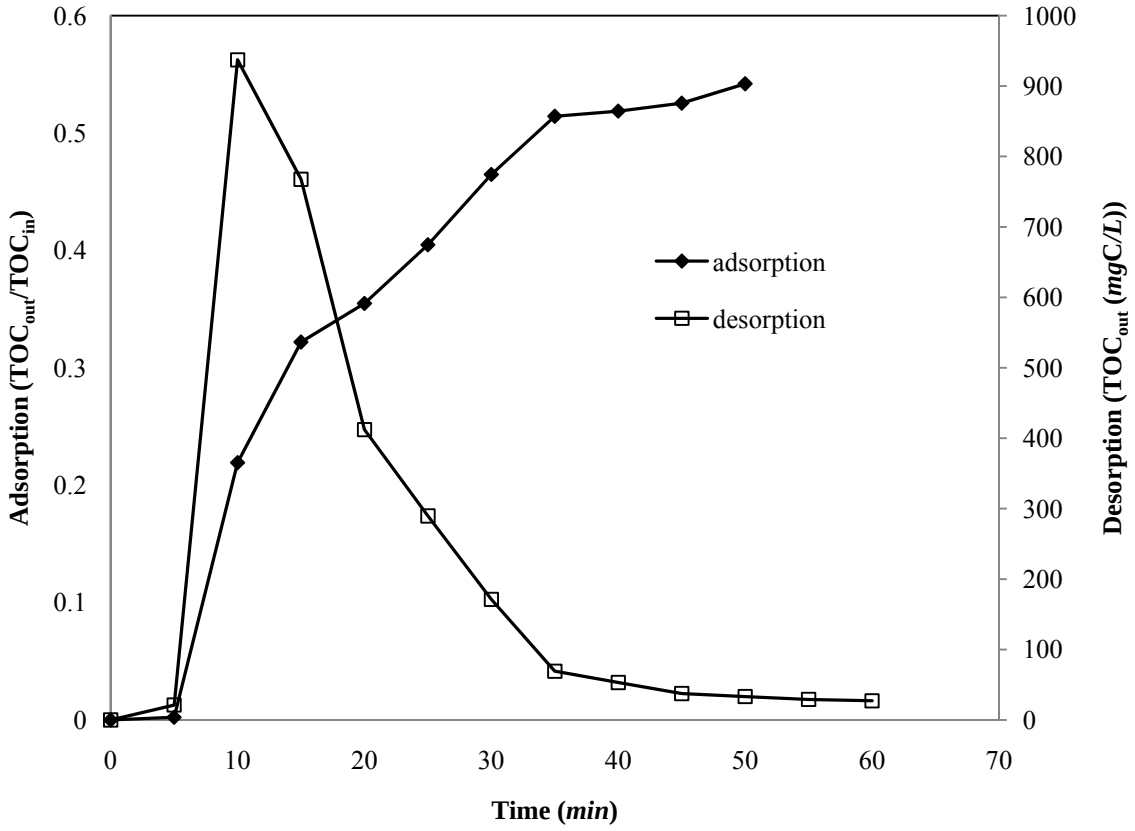

Figure 4.23. Adsorption and desorption profile (in terms of TOC) of pharmaceutical wastewater using combination of GAC treatment processes along with desorption of contaminants from exhausted GAC and its treatment with UV/H_2O_2 process. The average inlet concentration of the wastewater was TOC = 1,755.5 *mg*C/*L*, COD = 5,343.2 *mg*/*L*, pH = 3.32, and 24 ± 2^oC.

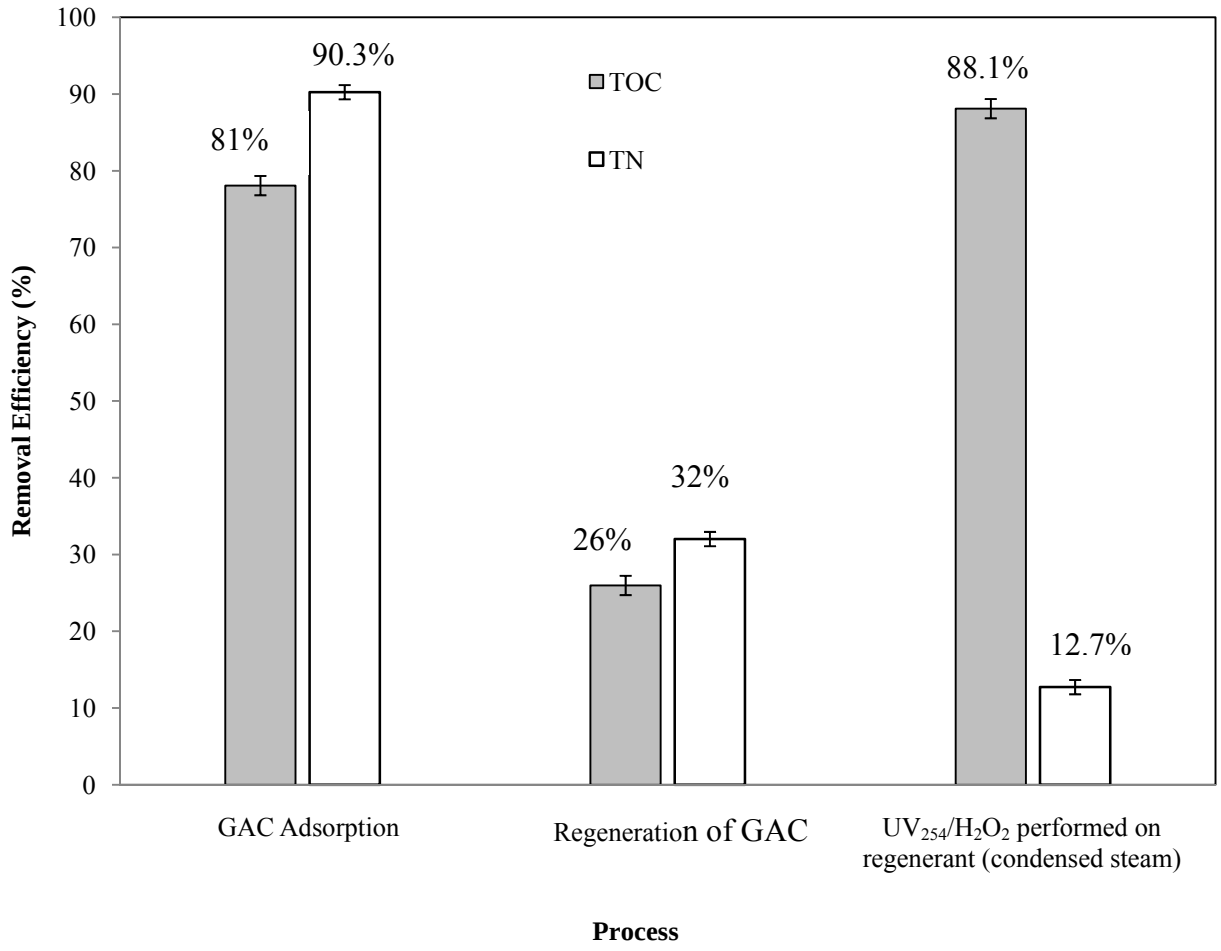

Figure 4.24. Overall TOC and TN removal from the pharmaceutical wastewater using combination of GAC treatment processes along with desorption of contaminants from exhausted GAC and its treatment with UV/H_2O_2 process. The average inlet concentration of the wastewater for the GAC treatment was TOC = 1,755.5 *mg*C/*L*, COD = 5,343.2 *mg*/*L,* TN = 85.5 *mg*N/*L*, pH = 3.32, and 24 ± 2^oC.

4.4 Cost Analysis of the Treatment Processes.

In this section, the costs for all processes at the optimum conditions on the basis of 30 *L* of pharmaceutical wastewater treatment were analyzed to obtain the most cost effective treatment processes.

Operation and material costs were considered for lab scale studies only. Calculations were based on the amount of chemicals used, the amount of electricity consumed during the treatment period, and the amount of steam required for desorption process. Operating cost for all processes were calculated per litre of wastewater treated.

It was found that to treat 30 *L* of raw wastewater by adsorption process alone required 10 *kg* of activated carbon and electricity for 1 *h* to operate the proportionating pump of 1/2 *hp* at 30% efficiency. To treat 30 *L* wastewater by UV/H_2O_2 process, it required 0.6 *L* H_2O_2 and electricity for 133.5 *h*. The combined process of UV_{254}/H_2O_2 + GAC along with desorption of contaminants from the exhausted carbon and UV/H_2O_2 treatment of the desorbed water required 5 *kg* of activated carbon, electricity for about 1 *h* to operate the proportionating pump of 1/2 *hp* at 30% efficiency and 111 *h* to treatment time using 17 *W* UV lamp, 50 *lb* of steam for desorption process, and 0.61 *L* of H_2O_2. Whereas the GAC adsorption along with desorption of contaminants from the exhausted carbon and UV_{254}/H_2O_2 treatment of the desorbed water required 0.26 *L* of H_2O_2, electricity for about 45 *h* using 17 *W* UV_{254} lamp and 1 *h* to operate the proportionating pump of 1/2 *hp* at 30% efficiency and about 100 *lb* of steam for desorption process. Cost of the process was calculated based on Equation (4.15):

$$\text{Cost of treatment } \left(\frac{\$}{L}\right) = \frac{\text{Material cost + Electricity cost + Steam cost}}{\text{Litre of wastewater treated}} \quad (4.14)$$

where, Material cost = cost of H_2O_2 and/or cost of GAC.

Electricity cost = cost related to pump and/or UV lamp.

The cost of H_2O_2 was taken as 24.25 *$/L* (VWR International, 2009), electricity was 7.5 *c/KWh* (Canada Energy, 2010), steam was 1 *$/1000 lb* (US Dept. of Energy, 2009) and carbon was 32.68 *$/kg* (VWR International, 2009).

4.4.1 Cost of GAC treatment for 30 *L* wastewater

Based on the information stated in Section 4.4, the cost of GAC adsorption treatment using Equation (4.16) was 10.9 *$/*L giving 81% TOC removal efficiency from the pharmaceutical wastewater. The average inlet concentration of TOC and COD were 1,755.75 *mg*C*/L* and 5,343.2 *mg/L*, respectively, with flow rate of 0.6 *L /min* (**Table 4.8**).

$$\text{Cost } \left(\frac{\$}{L}\right) = \frac{326.8 \text{ (Material cost)} + 0.02 \text{ (Electricity cost)}}{30 \text{ (Litre of wastewater treated)}} \quad (4.15)$$

$$= \frac{326.82}{30} \quad = 10.9 \left(\frac{\$}{L}\right)$$

From the analysis, it can be concluded that the cost of the adsorption process majorly depends on the GAC dosage. The GAC dosage for a particular wastewater treatment depends on the adsorption model for the selected wastewater and the effluent quality of wastewater required (section 4.1). Also the contaminants present in the wastewater transfers from one phase (wastewater) to another (GAC) which in case of a high strength wastewater, it is not a recommendable treatment process if used as a sole treatment process.

4.4.2 Cost of UV_{254}/H_2O_2 process at optimum condition

Based on the highest TOC removal efficiency obtained during UV/H_2O_2 process (Section 4.2.2), the optimum H_2O_2 concentration was found to be 4,250 $mgH_2O_2/(gCOD\ L)$, for which the given feed COD condition was 2.71 gH_2O_2/L, for an optimum HRT of 6 *h*. The average feed TOC concentration was 1,824 *mg*C/*L*, COD concentration of 5,124.15 *mg/L*, pH = 3.12, and temperature about 24±2 ^oC. UV/H_2O_2 process (both with 185 and 254 *nm* UV lamps) gave about 26.5% TOC reduction under optimum conditions (Figure 4.12 and Figure 4.13). Cost of UV/H_2O_2 process at optimum condition and highest TOC removal of 26.5% were calculated using the information in Section 4.4 and Equation (4.17).

$$\text{Cost}\left(\frac{\$}{\text{L}}\right) == \frac{47.77\ (\text{Material cost}) + 0.17\ (\text{Electricity cost})}{30\ (\text{Litre of wastewater treated})} \tag{4.16}$$

$$= \frac{47.9}{30} = 1.6\left(\frac{\$}{L}\right)$$

From the cost analysis of the UV/H_2O_2 process, it is observed that the cost is highly dependent on the amount of 30% *v/v* H_2O_2 dosage used for the treatment and not on the electricity consumption since the cost for electricity consumption is as low as 5¢/*L* of wastewater treated.

4.4.3 Cost of combined UV_{254}/H_2O_2 and GAC process at optimum condition

Based on the results obtained from Table 4.9 and Table 4.10 for the combined processes, the cost for the treatment was calculated and listed in Table 4.11 and Table 4.12 using Equation. (4.15).

Table 4.11. Cost analysis of combined UV_{254}/H_2O_2 + GAC adsorption along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) process

Process Requirements	Total Consumption (based on 30 *L* of wastewater treatment)	Conversion	Total Consumption for 30 *L* wastewater treatment (after necessary unit conversion)	Cost/Consumption	Total Cost for 30 *L* wastewater treatment
		UV_{254}/H_2O_2			
H_2O_2	0.651 *Kg*	density of H_2O_2 = 1.11 *Kg/L*	0.59 *L*	24.250 *$/L*	$14.235
electricity	66.5 *h*	Power output of UV lamp = 0.017 *KW*	1.13 *KWh*	0.075 *$/KWh*	$0.085
		GAC ADSORPTION			
pump	0.833*h*	Power output of pump = 0.378 *KW*	0.31*KWh*	0.075 *$/KWh*	$0.023
activated carbon	5 *Kg*		5.00 *Kg*	32.680 *$/Kg*	$163.4
		DESORPTION			
steam	22.5 *Kg*	1 *Kg* = 0.0022 *Klb*	0.05 *Klb*	1 $/*Klb*	$0.050
		UV_{254}/H_2O_2			
H_2O_2	0.020 *Kg*	density of H_2O_2 = 1.11 *Kg/L*	0.02 *L*	24.250 *$/L*	$0.437
electricity	33.5 *h*	power output of UV lamp = 0.017 *KW*	0.57 *KWh*	0.075 *$/KWh*	$0.042
				Total	***$*178.26**

Table 4.12. Cost analysis of combined GAC adsorption along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) process.

Process requirements	**Total Consumption (based on 30 *L* of wastewater treatment)**	**Conversion**	**Total Consumption for 30 *L* wastewater treatment (after necessary unit conversion)**	**Cost/Consumption**	**Total Cost for 30 *L* wastewater treatment**
		GAC ADSORPTION			
pump	0.833 *h*	power output of the pump = 0.378 *KW*	0.31 *KWh*	0.075 *$/KWh*	$0.023
activated carbon	10 *Kg*		10 *Kg*	32.680 *$/Kg*	$326.8
		DESORPTION			
steam	45 *Kg*	1 *Kg* = 0.0022 *Klb*	0.10 *Klb*	1 *$/Klb*	$0.099
		UV_{254}/H_2O_2			
H_2O_2	0.12 *Kg*	density of H_2O_2 = 1.11 *Kg/L*	0.11 *L*	24.250 *$/L*	$2.62
electricity	66.95 *h*	power output of the UV lamp = 0.017*KW*	1.13 *KWh*	0.075 *$/KWh*	$0.085
				Total	**$329.62**

The cost of treatment processes at optimum conditions are compared in Table 4.13. Based on the aim of the experiment of reducing/ degrading contaminants from the wastewater and the efficiency calculated for different processes under consideration, it was found that GAC alone transferred 81% of TOC from the wastewater to the GAC surface costing $10.5/L while UV_{254}/H_2O_2 alone could degrade 26.5% of TOC from the wastewater costing approximate $0.5/L. Thus, GAC alone process was ruled out from the selection process as it just transferred waste from one phase to another. Combination of UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) could degrade 72% of TOC and resulted in overall 81% of TOC removal from wastewater which was 2.8 times higher than the UV_{254}/H_2O_2 process alone. Also another combination of GAC along with UV_{254}/H_2O_2 treatment of the regenerant gave 82% TOC degradation and resulted in 81% TOC removal from the wastewater. But, when the cost of both combined processes was compared, it was found that UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 of the regenerant was more cost effective ($6/*L*) than the other process under consideration which costs $11/*L*. Thus, from the results of %TOC degradation (not % TOC removal) versus cost of the treatment, it is found that the combined process of UV_{254}/H_2O_2 + GAC along with desorption of contaminants from the exhausted carbon and UV/H_2O_2 treatment of the desorbed water was the best suited treatment process from the four processes under study in terms of cost and TOC removal and degradation efficiency and it costs $6/*L* of wastewater treated giving TOC removal efficiency of 81% with total treatment time of 114.5 *h.* A graphical representation of percentage TOC removal efficiency and cost of treatment per *L* of wastewater is shown in Figure 4.25.

Table 4.13. Cost comparison for all processes based on the treatment of 30 *L* pharmaceutical wastewater.

Process	Cost affecting parameters	TOC Removal Efficiency (%)	% TOC degraded/ eliminated	Cost (*$/L of wastewater treated*)	Treatment time (*h*)
GAC	Activated Carbon, Electricity, Steam	81	0	10.9	0.83
UV_{254}/H_2O_2	H_2O_2, Electricity	26.6	26.6	0.48	133.5
UV_{254}/H_2O_2 + GAC + (UV_{254}/H_2O_2) *REG	H_2O_2, Activated Carbon, Electricity, Steam	81	72.8	6	114.5
GAC + (UV_{254}/H_2O_2) *REG	H_2O_2, Activated Carbon, Electricity, Steam	81	82.1	11	50.3

*REG = Regeneration

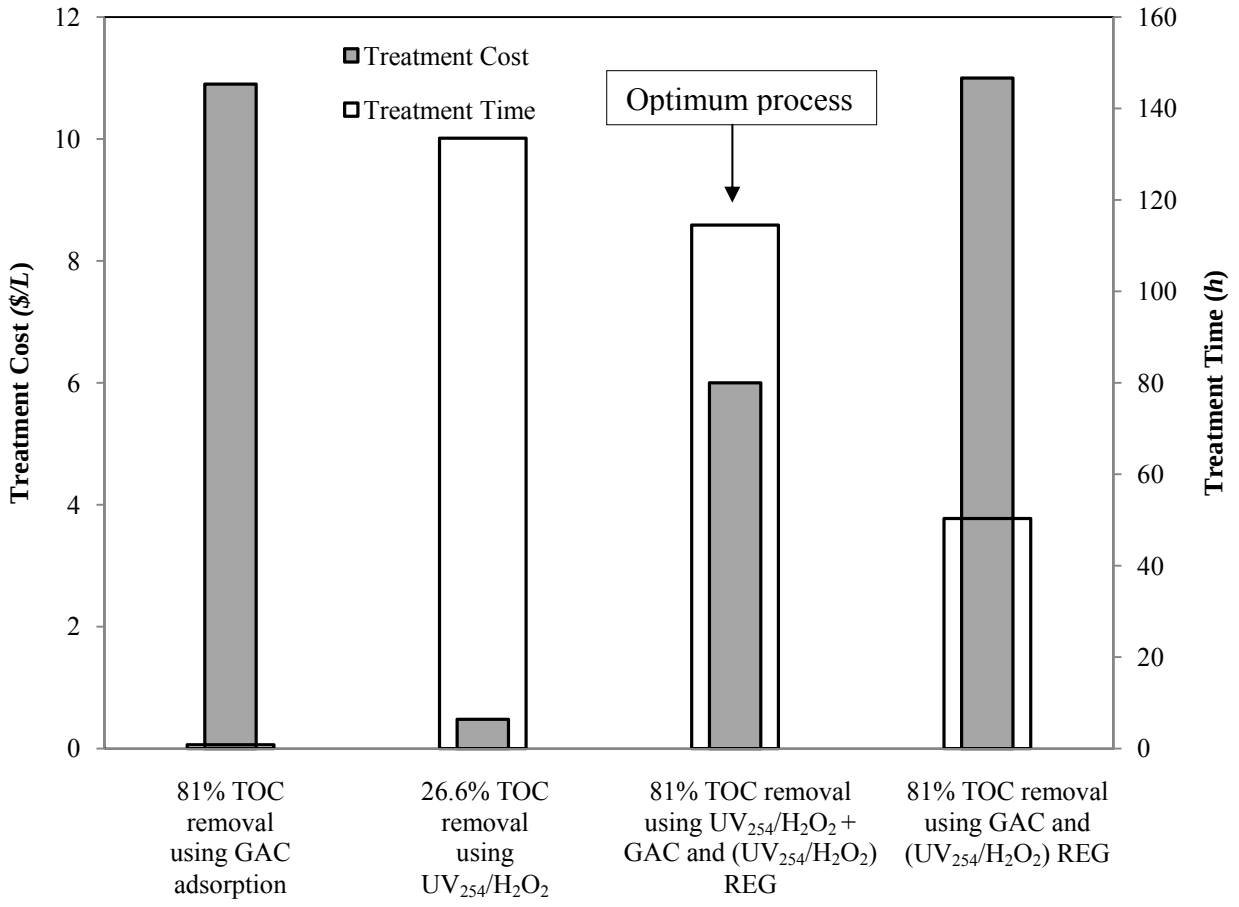

Figure 4.25. Comparison of cost and efficiency of GAC adsorption, UV_{254}/H_2O_2, and combination of UV_{254}/H_2O_2 and GAC process to treat 30 *L* of pharmaceutical wastewater, where, (UV_{254}/H_2O_2) REG in the graph is UV_{254}/H_2O_2 treatment of the condense steam.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The following conclusions are drawn from this study**:**

GAC Process Alone:

- From the batch experiments, it was concluded that the adsorption is a viable process for the pharmaceutical wastewater (with an average initial TOC_{in} = 1,498.5 *mg*C*/L*) and the monolayer adsorption on GAC follows the Langmuir adsorption isotherm. Based on the isotherm an approximate amount of GAC required for the continuous process was determined to be 1.03*Kg*Activated Carbon */L.*
- From the optimized single GAC column design, continuous adsorption experiments for removal of 81 ± 2% of TOC from the pharmaceutical wastewater (average TOC_{in}=1755.5 *mg*C*/L*) required breakthrough /service time of 10 *min* and activated carbon dosage of 333.33 *mg*Activated Carbon/*L*.
- From the continuous column adsorption experiments at different bed heights with flow rate of 0.6 *L/min*, the Bohart -Adams rate constant (K_{AB}) and maximum adsorption capacity of the carbon (N_o), for adsorption at 81% breakthrough of the carbon bed, was found to be 7.10×10^{-3} *L/(min.mg*C) and 1.06×10^{3} *mgC/L* for synthetic pharmaceutical wastewater of average feed TOC = 1,755.75 *mg/L*) using the Bohart -Adams model.
- Bohart – Adams model constants were evaluated based on pilot column studies. These

constants can be employed for the design of adsorption columns over a range of feasible flow rates and concentrations. Modeling of column data can successfully predict the adsorption behaviour of the same column with 1.7 *m* height (in series). The results show that adsorption process can treat 16.2 *L* of pharmaceutical wastewater containing 1,755.5 *mg*C/*L* TOC with 4 *Kg* of activated carbon and service time of 27 *min* at 81% TOC removal efficiency.

- Only 18-26% TOC of the pollutants from the exhausted carbon was recovered during the steam desorption process (at $115\pm5^{o}C$; $30KPa$). This can be due to the fact that the pollutants adsorbed on carbon had higher boiling point, and low pressure steam that was used did not transfer enough heat to desorb the pollutants from the carbon sites.

UV/H_2O_2 Process Alone

- The UV/H_2O_2 contributed to the degradation of the pharmaceutical wastewater. However, this process was slow. Under the irradiation from UV_{254} and UV_{185} lamp in the continuous photoreactor, the TOC degradation was 23 ± 0.5%
- The optimal concentration of H_2O_2 to degrade a pharmaceutical wastewater having 1,824 ± 72 *mg*C/*L* TOC and 5,124.5 ± 40 *mg*/*L* COD strength was found to be 4.25 *mg*H_2O_2/*mg*COD under the irradiation from UV_{254} and UV_{185} lamp.
- Experimental results demonstrated that a maximum TOC degradation of 26.6 ± 0.5% and 29.5 ± 0.3% of pharmaceutical wastewater occurred with optimum 4.25 *mg*H_2O_2/*mg*COD of H_2O_2 dosage, under the irradiation UV_{254} and UV_{185} in continuous flow photoreactor at optimum flow rate of 3.75 *mL/min* (6 *h* residence time).

- The continuous flow photodegration of pharmaceutical wastewater was performed at

three pH conditions; it was observed that the percentage TOC degradation was the highest at acidic conditions (pH 3 = original pH of the wastewater without adjustment).With the optimal quantity of H_2O_2 (4.25 *mg*H_2O_2/*mg*COD) and acidic pH, the maximum mineralization was 26.6 ± 0.5% and 29.5 ± 0.3% for UV_{254} and UV_{185} *nm*, respectively. However, the lower pH may raise environmental discharge issues. In fact, the discharge of industrial wastewater to the environment must have a pH in the range of 6-9.

Combined UV_{254}/H_2O_2 and GAC Processes

- UV_{254}/H_2O_2 pre-treated pharmaceutical wastewater in combination with GAC adsorption process (i.e. UV_{254}/H_2O_2 + GAC) was successful in treating the pharmaceutical wastewater. The TOC removal efficiency was increased from 26.58% (UV_{254}/H_2O_2) to 81% (UV_{254}/H_2O_2 + GAC) for optimum operating condition of 3 *h* HRT for UV_{254}/H_2O_2 and 20 *min* breakthrough time for the GAC bed.
- It was observed that the breakthrough time for the GAC adsorption process using the UV_{254}/H_2O_2 pre-treated wastewater was twice higher than the breakthrough time of the GAC adsorption column treating the raw pharmaceutical wastewater. This process improvement can be due to the reason that the possible intermediates (as mentioned in Table 3.2) formed during the UV_{254}/H_2O_2 treatment that were more readily adsorbed by the GAC than the pollutant present in the raw wastewater.
- UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) led to 78% TOC degradation and overall 81 % TOC removal efficiency at optimum conditions.

- GAC adsorption along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) was also successful in the degradation of pharmaceutical wastewater. It led to 82% TOC degradation and 81 % TOC overall removal efficiency at optimum conditions.
- Based on cost analysis versus % TOC degradation efficiency (and not % TOC removal), it was found that UV_{254}/H_2O_2 + GAC along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant) was competent to the other combination processes in terms of TOC degradation but costs half than that of the GAC adsorption along with UV_{254}/H_2O_2 treatment of the condensed steam (regenerant).

5.2. Recommendations

- Due to the volatile nature of the constituting compounds (benzene, methanol, and methyl chloride) in the pharmaceutical wastewater, further experiments should be performed to investigate the effect of volatility on the photodegradation results of pharmaceutical wastewater.
- Kinetic studies should be performed for UV_{185}/H_2O_2 to demonstrate the pseudo first order reaction.
- The main problem of COD and BOD_5 measurements during the photolytic treatment was due to the interference of residual H_2O_2 present. The amount of H_2O_2 could not be measured by the low range (0-100 *mg/L*) H_2O_2 check kit and thus it was removed by adding approximate amount of the bovine liver catalyst. Removal of residual H_2O_2 could be accomplished by using higher range H_2O_2 check kit (range 100-1000 *mg/L*) and catalyst (bovine liver).
- Although few possible reaction intermediates can be found in the literature, further

studies should be performed to identify the intermediate/by-products that are produced during the photodegradation of pharmaceutical wastewater. Measurements such as mass spectrometry, high pressure liquid chromatography, and/or gas chromatography can be performed on the UV/H_2O_2 treated samples to identify the intermediates produced during the UV/H_2O_2 process for a better understanding of the treatment process.

- The steam used for the desorption of contaminants from the exhausted activated carbon was at a maximum of 120^oC. It is suggested that the regeneration of the exhausted activated carbon should be done using steam at 200-500^oC (Knappe et al., 1992) which allows the pollutants temperature to reach close to their boiling point and thus facilitate the desorption process.

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APPENDICES

APPENDIX A.

Determination of TOC and TN of the synthetic pharmaceutical wastewater

The carbon source of the synthetic pharmaceutical wastewater, as mentioned in Section 3.1, was from six chemicals namely 4-aminophenol, aniline, methyl chloride, methanol, benzene, and sulfanilic acid whereas nitrogen source was from three chemicals namely 4-aminophenol, aniline, and sulfanilic acid as found in actual pharmaceutical wastewater. The calculated values of the total organic carbon (TOC) and total nitrogen (TN) of the raw synthetic pharmaceutical wastewater are based on these six chemicals as shown in Table A.1.

As a sample calculation, 170 *mg/L* aniline ($C_6H_5NH_2$) as calculation sample, the TOC as total *mg*C (in aniline)/*L* of wastewater and TN as total *mg*N (in aniline)/*L* wastewater are determined as follows:

$$\mathrm{TOC}_{\mathrm{Aniline}}\left(\frac{mg\mathrm{C}}{L}\right) = \frac{\text{Carbon Molar Mass (in aniline)}}{\text{Aniline Molar Mass}} \times \text{Amount of Aniline found in raw wastewater}\left(\frac{mg}{L}\right)$$

$$\mathrm{TOC}_{\mathrm{Aniline}} = \frac{6 \times (12.0107)}{93.1265}\left(\frac{mg\mathrm{C}}{mg\mathrm{Aniline}}\right) \times 170\left(\frac{mg\mathrm{Aniline}}{L}\right)$$

$$\mathrm{TOC}_{\mathrm{Aniline}} = 131.55\left(\frac{mg\mathrm{C}}{L}\right)$$

and

$$\mathrm{TN_{Aniline}}(mg\mathrm{N}/L)$$

$$= \frac{\text{Nitrogen Molar Mass (in aniline)}}{\text{Aniline Molar Mass}}$$

$$\times \text{Amount of Aniline found in raw wastewater} \left(\frac{mg}{L}\right)$$

$$\mathrm{TN_{Aniline}} = \frac{1 \times (14.0067)}{93.1265} \left(\frac{mg\mathrm{N}}{mg\text{Aniline}}\right) \times 170 \left(\frac{mg\text{Aniline}}{L}\right)$$

$$\mathrm{N_{Aniline}} = 25.56 \left(\frac{mg\mathrm{N}}{L}\right)$$

Thus, from Table A.1, the total concentrations of TOC and TN are estimated as follows:

$$TOC_{total} = 98.96 \left(\frac{mg\mathrm{C}}{L}\right) + 131.55 \left(\frac{mg\mathrm{C}}{L}\right) + 84.74 \left(\frac{mg\mathrm{C}}{L}\right) + 936.33 \left(\frac{mg\mathrm{C}}{L}\right) + 368.7 \left(\frac{mg\mathrm{C}}{L}\right) + 332.58 \left(\frac{mg\mathrm{C}}{L}\right)$$

$$\mathrm{TOC_{total}} = 1{,}952.77 \left(\frac{mg\mathrm{C}}{L}\right)$$

and

$$\mathrm{TN_{total}} = 19.24 \left(\frac{mg\mathrm{N}}{L}\right) + 25.56 \left(\frac{mg\mathrm{N}}{L}\right) + 64.67 \left(\frac{mg\mathrm{N}}{L}\right)$$

$$\mathrm{TN_{total}} = 109.47 \left(\frac{mg\mathrm{N}}{L}\right)$$

Table A.1. Theoretical values of TOC and TN of the pharmaceutical wastewater composition.

Compound	**Molecular Formula**	**Molecular Weight (*g/mole*)**	**Concentration in Raw Wastewater (*mg/L*)**	**TOC (*mg*C/*L*)**	**TN (*mg*N/*L*)**
4-Aminophenol	$C_6H_4OHNH_2$	109.13	150	98.96	19.24
Aniline	$C_6H_5NH_2$	93.13	170	131.43	25.56
Methyl chloride	CH_2Cl_2	84.93	600	84.74	0
Methanol	CH_3OH	32.04	2,500	936.33	0
Benzene	C_6H_6	78.11	400	368.7	0
Sulfanilic Acid	$C_6H_4NH_2SO_3H$	173.19	800	332.58	64.67
			Total theoretical value	1,952.77	109.47
			Total literature value (Patil *et al.,* 1962)	1,762-1,998	-

APPENDIX B.

Determination of standard deviation and relative error

The standard error of the mean was used as the error bar in this study. The sample standard deviation was used to analyze the accuracy of an experimental measurement for a finite set of experimental data. Sample mean ($\bar{x}$), sample standard deviation (s), and standard error of the mean ($SE_{\bar{x}}$) are determined as follows (Skoog *et al.*, 1998). Standard error of the mean is estimated by the sample estimate of the sample standard deviation divided by the square root of the total sample number.

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N} \quad \text{(B.1)}$$

$$s = \sqrt{\frac{\sum_{i=1}^{N} (x_i - \bar{x})^2}{N-1}} \quad \text{(B.2)}$$

$$SE_{\bar{x}} = \frac{s}{\sqrt{N}} \quad \text{(B.3)}$$

where x_i is the measurement values of sample i; and N is the total number of measurements. Thus the upper and lower limit of a sample reading can be given as:

$$Upper\ limit = \bar{x} + SE_{\bar{x}}$$

$$Lower\ limit = \bar{x} - SE_{\bar{x}}$$

For example, in Figure 4.12, the error bar for UV_{254} at 6 h was calculated to be 1.36. The feed TOC concentrations and % TOC removal of three samples were determined as shown in Table B.1 when treated with the UV/H_2O_2 process with H_2O_2 concentration of 1.125 mg H_2O_2/L of wastewater (Section 4.2.1) for an HRT of 6 h. Therefore, the mean, the sample standard deviation and standard error of the TOC concentrations and % TOC removal were calculated as follows:

Table B.1. TOC data for the standard error calculations

	TOC (*mg*C/*L*)	**% TOC Removal**
HRT (*min*)	0.00	6.00
Sample 1	1,947.42	16.80
Sample 2	1,828.75	12.09
Sample 3	1,697.10	14.71
Mean: x	1,824.42	14.53
Standard Deviation: s	125.20	2.36
Standard Error	72.30	1.36

Using Equation B.1, B.2, and B.3 we get:

$$\bar{x} = \frac{16.80 + 12.09 + 14.71}{3} = 14.53\ mg\mathrm{C}/L$$

$$s = \sqrt{\frac{(14.53 - 16.8)^2 + (14.53 - 12.09)^2 + (14.53 - 14.71)^2}{3 - 1}} = 2.36\ mg\mathrm{C}/L$$

$$SE_{\bar{x}} = \frac{2.36}{\sqrt{3}} = 1.36\ mg\mathrm{C}/L$$

Thus, the upper and lower limit of TOC reading of the sample under observation is given as:

Upper limit= $14.53 + 1.36\ mg\mathrm{C}/L$

and Lower limit= $14.53 - 1.36\ mg\mathrm{C}/L$

APPENDIX C.

Determination of BOD_5

BOD_5 (of only the influent wastewater Section 3.1) was determined using the equation based on 5210B Standard Methods (APHA, 1998).

$$\mathrm{BOD}_5 = \frac{(\mathrm{D}_1 - \mathrm{D}_2) - \mathrm{SCF}}{\mathrm{P}} \quad \text{(C.1)}$$

$$\mathrm{SCF} = (\mathrm{B}_1 - \mathrm{B}_2)\mathrm{f} \quad \text{(C.2)}$$

where:

D_1 is the DO of a diluted sample immediately after preparation, *mg/L*;

D_2 is the DO of a diluted sample after 5 days of incubation at 20^oC, *mg/L*;

SCF is seed correction factor, *mg/L*;

P is decimal volumetric fraction of sample used, where P = volume of sample/volume of BOD-bottle

B_1 is the DO of the seed control before incubation, *mg/L*;

B_2 is the DO of the seed control after incubation, *mg/L*; and

f is the ratio of the volume of polyseed solution in glucose-glutamic acid (GGA) test to the volume of polyseed solution in seed control.

For example, the influent BOD_5 concentration of the pharmaceutical wastewater was measured. Each 300-*mL* BOD bottle contained 1 *mL* of influent wastewater (*P*=1/300). The volume of polyseed solution used in glucose glutamic acid (GGA) check test was 4 *mL*. Three seed controls were prepared using 10, 15, and 20 *mL* of polyseed solution, respectively. A DO meter (YSI 58 Dissolved Oxygen Meter, YSI Inc.) and a BOD bottle probe (YSI 5750 Non-Stirring BOD Bottle Probe, YSI Inc.) were used to measure the DO of all samples. The DO of the dilution water (D_1) was measured to be 9.10 *mg/L*. The average D_2 of two diluted influent wastewater samples was 0.3 *mg/L*. The average D_2 value of the 3 seed controls measured by the DO meter and SCF values are showed in Table C.1.

Therefore, the influent BOD_5 of the wastewater in the GAC process was determined as follows.

$$BOD_5 = \frac{(9.10 - 0.3) - 0.6}{1/300} = 2{,}460\ mg/L$$

Table C.1. Calculation for SCF

Sample ID	Initial DO: B_1 (*mg/L*)	DO after 5 days: B_2 (*mg/L*)	f	SCF (*mg/L*)	Average of SCF (choose the value > 0.6-1.0 *mg/L*)*
Seed control 1	9.5	7.9	4/10 = 0.4	0.6	
Seed control 2	9.5	7.6	4/15 = 0.3	0.5	= (0.6+0.6)/2 = 0.6
Seed control 3	9.5	6.4	4/20 = 0.2	0.6	

*BOD_5 Training Videos provided by InterLab® Supply (http://polyseed.com/videos/index.php)

APPENDIX D.

H_2O_2 dosage calculation

H_2O_2 decomposes into H_2O water and O_2 oxygen on exposure to light (320 *nm* or higher) as shown below (LajChem and EMD Chemical MSDS for H_2O_2).

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

COD measures the oxygen demand of the sample to completely oxidize it into molecular form CO_2, H_2O, and NH_3. With both of the above information, we can calculate the ratio of COD to H_2O_2 using the stoichiometric balance between the Chemical Oxygen Demand (COD) of the sample to the moles of oxygen available from H_2O_2 which is established as follows:

$$1\ g\ \text{COD} = 1\ g\ \text{of}\ O_2 = \frac{1\ g}{32\ g/mole}\ O_2 = 0.03125\ mole\ of\ O_2$$

According to the stoichiometric, 2 *mole* H_2O_2 gives 1 *mole* O_2. So 2×0.03125 *mole* H_2O_2 will give 0.03125 *mole* of O_2 which is 0.0625 *mole* H_2O_2. Molecular formula of H_2O_2 is 34.014 *g/mole*. Thus,

$$1\ g\ \text{COD} = 1\ g\ \text{of}\ O_2 = \frac{1\ g}{32\ g/mole}\ O_2 = 0.03125\ mole\ of\ O_2 = 0.0625\ mole\ H_2O_2$$

and

$0.0625\ mole\ H_2O_2 = 0.0625\ mole \times 34\ g/mole\ H_2O_2 = 2.125\ g H_2O_2$

Thus COD to H_2O_2 ratio is 1: 2.125. This relation is used as the base for all other ratios of COD: H_2O_2 used in the experiments

For example, calculating H_2O_2 dosage for UV/H_2O_2 process of the pharmaceutical wastewater having average TOC of 1,824 *mg*C/*L* and COD of 5,124 *mg/L* at 1:2 stoichiometric COD: H_2O_2 ratio, the amount of H_2O_2 added per L of wastewater treated is calculated as follows:

For 1:2 stoichiometric ratio of COD: H_2O_2

1 *mg*COD = 2 × 2.125 *mg*H_2O_2 = 4.25 *mg*H_2O_2

So for 5,124 *mg*COD

= 5124 *mg*COD × 4.25 *mg*H_2O_2/ *mg*COD

= 21,777 *mg*H_2O_2

= 21.7 *g*H_2O_2

Thus, 21.7 *g*H_2O_2 is required per *L* of wastewater.

APPENDIX E.

Estimation of carbon dosage from isotherm data

Data obtained from batch tests were plotted in Figure 4.1 and the slope and intercept of the graph was equated to the Langmuir isotherm model to predict the Langmuir constants as follows:

Langmuir adsorption model as given in Equation (4.1):

$$m/x = \frac{1}{ab}\frac{1}{C_e} + \frac{1}{a} \tag{4.17}$$

where slope = 502.63×10^3 *mg*Activated Carbon/*L* and

intercept = 538 *mg*Activated Carbon/*mg*C from Figure 4.2.

$$a = \frac{1}{\text{intercept}}$$

$$= \frac{1}{538\ mg\text{Activated Carbon}/mg\text{C}}$$

$$= 1.85 \times 10^{-3}\ \ mg\text{C}/mg\text{Activated Carbon}$$

$$b = \frac{1}{\text{slope} \times a}$$

$$= \frac{1}{502.63 \times 10^3\ (mg\text{Activated Carbon}/L) \times 1.85 \times 10^{-3}\ (mg\text{C}/mg\text{Activated Carbon})}$$

$$= 1.07 \times 10^{-3}\ L/mg\text{C}$$

Now from the model parameters, the estimate amount of carbon required to treat pharmaceutical wastewater to an effluent concentration C_e in terms of TOC = 320 *mg*C/*L* was calculated to be:

$$\frac{m}{1498.5 - 320} = \frac{1}{1.85 \times 1.07 \times 10^{-6}} \times \frac{1}{1498.5} + \frac{1}{1.85\times10^{-3}}$$

$$m = 1.03\ Kg\text{Activated Carbon}/L$$

APPENDIX F

GAC porosity calculation:

A cylindrical column was set up, securing it to the stand with a clamp. GAC sample was added to the column, making sure the column did not leak any GAC particle out. The volume of the column V_t was determined by multiplying the height of the GAC bed by the cross-sectional area of the cylindrical column. Two 4 *L* graduated cylinder was filled with water. Slowly the water was added into the column containing the GAC sample till the 4 *L* mark on the column (i.e. void volume is filled with water). The volume of water added was denoted as V_v. Dividing V_v by V_t expressed the porosity value of the GAC sample.

Volume of the column measured (V_t) = 5 *L*

Volume of the water added to the column (V_v) = 4.5 *L*

$$\text{Porosity} = \frac{V_v}{V_t} \times 100$$

$$= \frac{4.5\ \text{L}}{5\ \text{L}} \times 100 = 0.9$$

APPENDIX G

Sample calculations.

GAC alone:

Hydraulic loading rate

HLR (as explained in Section 4.1.2.1) can be calculated for GAC adsorption process

carried out for flow rate = 0.4 L/*min*, column diameter = 0.06 *m* and cross sectional area of the column = 0.011m^2 in Table 4.3 as follows:

$$\text{HLR} = \frac{\text{flow rate}}{\text{cross section area}}$$

$$= \frac{0.4}{0.011}$$

$$= 36.3\ (L/min.m^2)$$

Adsorption capacity

Adsorption capacity is defined as amount of TOC adsorbed per unit amount of granular activated carbon supplied and can be calculated from the experimental results obtained in Table 4.3 as follows:

For 50% breakthrough at 40 *min*, feed TOC concentration of 1,767.1 *mg*C/*L*, bed height of 0.85 *m*, GAC amount of 2,000 *g*Carbon, and flow rate of 0.4 *L*/ *min*

$$\text{Adsorption Capacity} = \frac{\text{amount of TOC adsorbed}}{\text{amount of GAC supplied}}$$

$$= \frac{0.5 \times 1{,}767.1(mg\text{C}/L) \times 0.4(L/min) \times 40\ min}{2000\ g\text{Activated Carbon}}$$

$$= 7.07\ (mg\text{C}/g\text{Activated Carbon})$$

Boharts-Adam constant

Boharts-Adam constants N_o and K_{AB} were calculated from the Iso-removal lines in Figure 4.6. For a selected Iso-removal line of 81% in Figure 4.6 using Equation (4.5), slope (a) and intercept (b) were found out to be, a = 11 (*min*/*m*) and b = -0.1333 (*min*), having inlet TOC concentration of 1,755.5 *mg*C/*L*, flow rate of 0.6 *L*/*min* and cross sectional area of 0.011m^2.

Thus, equating Equation (4.6) with (a) and Equation (4.7) with (b), N_o and K_{AB} are estimated. Excel file was programmed to calculate the model constants as shown in Table 4.4 as follows:

$$a = \frac{N_o}{C_o}\left(\frac{1}{v}\right) \quad (4.18)$$

$$11(min/m) = \frac{N_o}{1{,}755.5(mgC/L)}\left(\frac{0.011(m^2) \times 1000(L)}{0.6(L/min) \times 1(m^3)}\right)$$

$$N_o = \frac{11 \times 1{,}755.5 \times 0.6 \times 1}{1{,}000 \times 0.011}$$

$$N_o = 1.06 \times 10^3 (mgC/L)$$

$$b = \frac{1}{C_o K_{AB}} \ln\left(\frac{C_o}{C}\right) \quad (4.19)$$

$$-0.1333(min) = \frac{1}{1{,}755.5(mgC/L) \times K_{AB}} \ln\left(\frac{1{,}755.5(mgC/L)}{333.5(mgC/L)}\right)$$

$$K_{AB} = \frac{1}{1{,}755.5(mgC/L) \times -0.1333(min)} \ln\left(\frac{1{,}755.5(mgC/L)}{333.5(mgC/L)}\right)$$

$$K_{AB} = 7.10 \times 10^{-3}\ (L/mgC.min)$$

Prediction of 81% breakthrough time using Boharts-Adam model for scale up column:

Using Equations (4.8), (4.9), and (4.10), a_{new} and b_{new} values were predicted and based on the new a and b values, the breakthrough time was predicted using Equation (4.5). Excel file was programmed to calculate the predicted values as shown in Table 4.6.

$$a_{new} = a_{old}\left(\frac{C_{old}}{C_{new}}\right) \quad (4.20)$$

$$a_{new} = 11\left(\frac{1{,}755.5}{1{,}912.5}\right)$$

$$a_{new} = 10.1$$

$$b_{new} = b_{old}\left(\frac{C_{old}}{C_{new}}\right)\frac{\ln C - \ln C_{new}}{\ln C - \ln C_{old}} \quad (4.21)$$

$$b_{new} = -0.1333\left(\frac{1{,}755.5}{1{,}912.5}\right)\ln\left(\frac{\ln 363.4 - \ln 1{,}912.5}{\ln 333.5 - \ln 1{,}755.5}\right)$$

$$b_{new} = -0.129$$

$$t = az + b$$

$$t = 10.1 \times 1.7 - 0.129$$

$$t = 17\ min$$

Table G.1. Calculation using excel sheet used for predicting 81% breakthrough.

Parameters	from Figure 4.6	Predicted values	Observed values	Mean absolute percentage error (%)
Bed height (*m*)	1.7	1.7	1.7	N.A
Flow rate (*L/min*)	0.6	0.6	0.6	N.A
TOC (*mg*C/*L*)	1775.5	1,912.5	1,912.5	N.A
a (*min/m*)	11	10.1	n/a	N.A
b (*min*)	-0.13	-0.13	n/a	N.A
Breakthrough t (*min*)	18.83	17	27	36

TOC removal efficiency

From the data presented in Table 4.7: average feed TOC = 1,755.5 *mg*C/*L* and TOC after adsorption process = 951 *mg*C/*L*.

TOC removal efficiency is calculated using Equation 3.1 as follows:

$$\%\text{TOC removal} = \frac{(TOC_{in} - TOC_{out})}{TOC_{in}} \times 100\% \quad (3.6)$$

$$= \frac{(1{,}755.5 - 951)}{1{,}755.5} \times 100\%$$

$$= 46\%$$

Desorption efficiency

From Table 4.7, it was observed that TOC conditions before and after desorption was measured as 804.2 *mg*C/*L* of wastewater treated and 158.7 *mg*C/*L* of wastewater treated, when adsorption was carried out at 0.6 *L*/*min* for 50 *min.* So, total volume of wastewater treated is calculated as = 0.6 *L*/*min* × 50 *min* = 30 *L.*

Thus, total *mg* of TOC before and after desorption is calculated as follow:

mg of TOC before desorption (on GAC) = 804.2 *mg*C/*L* × 30 *L* = 24,126 *mg*C

mg of TOC after desorption (removed from GAC) = 158.7 *mg*C/*L* × 30 *L* = 4,761 *mg*C

Thus, desorption efficiency is calculated using Equation (4.11).

$$\% \text{ removal of TOC} = \frac{\text{total } mg \text{ of TOC}_{out}}{\text{total } mg \text{ of TOC}_{in}} \times 100\% \tag{4.22}$$

$$= \frac{4{,}761\ mg\text{C}}{24{,}126\ mg\text{C}} \times 100\%$$

$$= 19.7\%$$

UV/H_2O_2 alone:

Flow rate calculation

Based on the HRT selected and volume of the reactor the flow rate was calculated as follow:

HRT selected = 6 *h*

Volume of the reactor = 1.35 *L*

$$\text{flow rate} = \frac{\text{Volume of the reactor}}{\text{HRT}}$$

$$= \frac{1.35\ L \times 1\ h \times 1{,}000\ mL}{6\ h \times 60\ min \times 1\ L}$$

$= 3.75\ mL/min$

Amount of H_2O_2 added

From APPENDIX D it was calculated that $21.7 g H_2O_2/L$ of wastewater is required when COD: H_2O_2 1:4.25 is used for the wastewater with COD = 5,124.15 *mg*/*L* and TOC = 1,824 *mg*C/*L*. As mentioned in Section 3.1.3, 30% *v*/*v* H_2O_2 was used. So to obtain 21.7 gH_2O_2 using the density of H_2O_2 as 1.11 *g*/*mL* (EMD Chemical MSDS for H_2O_2):

$$mL \text{ of } H_2O_2 = \frac{21.7\ g}{1.11\ g/mL}$$

$$= 19.55\ mL\ H_2O_2$$

Now in 100 *mL* 30% *v*/*v* H_2O_2 solution there is 30 *mL* H_2O_2. Thus, to obtain 19.55 *mL* H_2O_2, we require:

$$= \frac{19.55\ mL\ H_2O_2 \times 100}{30}$$

$$= 62.16\ mL \text{ of } 30\%\ v/v\ H_2O_2 \text{ solution}$$

UV_{254}/H_2O_2 + GAC along with desorption and UV_{254}/H_2O_2 treatment of the condensed steam:

Treatment time to treat 30 *L* of wastewater

During UV/H_2O_2 process as shown in Table 4.9, with flow rate = 7.5×10^{-3} *L*/*min* and HRT of 180 *min*,

$$\text{Treatment time for } 30\ L = \frac{\text{Total volume of wastewater treated}}{\text{Flow rate}}$$

$$= \frac{30\ L}{7.5\ \times 10^{-3}\ L/min}$$

$$= 4{,}000\ min$$

Based on each GAC adsorption run with flow rate = 0.6 *L*/*min* and breakthrough time of 20 *min* at 12 *L*, as shown in Table 4.9,

$$\text{Treatment time for } 30\ L = \frac{\text{Total volume of wastewater treated}}{\text{Flow rate}}$$

$$= \frac{30\ L}{0.6\ L/min}$$

$$= 50\ min$$

As breakthrough time is 20 *min* for each run, it conversely means 50/20 = 2.5 runs of GAC adsorption have to be carried out to treat 30 *L* wastewater. After each adsorption run, desorption process was performed and the results in Table 4.9 were obtained. Each desorption run at steam flow rate 0.15 *L*/*min* took treatment time 60 *min*. Since 2.5 adsorption runs were carried out to treat 30 *L* of wastewater,

$\text{Treatment time for } 30\ L = 2.5\ \times\ 60\ min$ = 150 *min*

Volume of condensed steam generated at end of each desorption cycle:

Volume of condensed steam = 0.15 *L*/*min* × 60 *min*

= 9 *L*.

UV_{254}/H_2O_2 process was carried out on the condensed steam from the desorption process at a flow rate of 11.2 × 10^{-3} *L*/*min* and HRT of 120 *min* as mentioned in Table 4.9. Since 2.5 desorption runs were carried out to treat 30 *L* of wastewater with GAC, total condensed steam collected was = 9 *L*/run × 2.5 run = 22.5 *L*.

$$\text{Treatment time for } 22.5\ L = \frac{\text{Total volume of condensed steam treated}}{\text{Flow rate}}$$

$$= \frac{22.5\ L}{11.2\ \times 10^{-3}\ L/min}$$

$$= 2{,}009\ min$$

GAC Dosage calculation:

Since 2.5 adsorption runs were carried out to treat 30 *L* of wastewater and each run used 2 *Kg* of GAC (Section 3.2.1). Thus,

Total amount of GAC = 2 *Kg*Activated Carbon/run × 2.5 run = 5 *Kg*Activated Carbon

$$\text{Dosage of GAC } = \frac{\text{Total amount of GAC used}}{\text{Total amount of wastewater treated}}$$

$$= \frac{5\ Kg \text{ Activated Carbon } \times\ 1{,}000\ g}{30\ L \times\ 1\ Kg}$$

$$= 166.6\ g\text{Activated Carbon}/L$$

Net TOC removal:

It is defined as net TOC removed during combined process of UV_{254}/H_2O_2 + GAC. From Table 4.9, inlet TOC to the UV_{254}/H_2O_2 process was 1,856.2 *mg*C/*L* while outlet TOC at the end of combined process, i.e. GAC was found to be 353.2 *mg*C/*L*. Thus,

$$\text{Net TOC removal} = \frac{\text{TOC}_{\text{in}} - \text{TOC}_{\text{out}}}{\text{TOC}_{\text{in}}}$$

$$= \frac{1856.2\ mg\text{C}/L \text{ - } 353.2\ mg\text{C}/L}{1856.2\ mg\text{C}/L}$$

$$= 81\ \%$$