Summer 8-31-2023

Removal of Diclofenac Pharmaceutical Residues from Wastewater

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Removal of Diclofenac Pharmaceutical Residues from Wastewater

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A Thesis submitted in partial fulfillment of the requirements for the degree of

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Spring 2023

Declaration of Authorship

I Fatma Hisham Marawan Aly declare that this thesis titled, "Removal of Diclofenac pharmaceutical waste from wastewater" and the work presented in it are my own. I confirm that:

- This work was done wholly or mainly while in candidature for a research degree at this University.
- Where any part of this thesis has previously been submitted for a degree or any other qualification at this University or any other institution, this has been clearly stated.
- Where I have consulted the published work of others, this is always clearly attributed.
- Where I have quoted from the work of others, the source is always given. With the exception of such quotations, this thesis is entirely my own work.
- I have acknowledged all main sources of help.
- Where the thesis is based on work done by myself jointly with others, I have made clear exactly what was done by others and what I have contributed myself.

Signed:

Fatma Hisham Aly

Date:

Summer 2023

Dedication

This Work is dedicated to.

My Dear Parents

My beloved Husband

My dear Sisters

Acknowledgments

In the name of Allah and above all, Alhamdulillah for giving me the strength and patience to complete this work after spending several years working on this research. I was blessed to work with two of the greatest mentors who guided me and helped me in every single step, I was so lucky to work under the supervision of Dr. Ahmed El Gendy and Dr. Mohamed El Zayat who made my master's journey a wonderful trip. Also, I'm very thankful to all the people who give me unyielding support, assistance, and encouragement to finish this dissertation, and I hope I do not forget any of them in this acknowledgment.

I would like to express my deep appreciation to my parents who gave me all the support and motivation to finish this work. My best thanks to my mother who always prays for me. I am very proud of my Father who does not abandon giving me his valuable advice and support. I wish to thank them for supporting me throughout my whole life. I wish also to thank my sisters, Engy and Sara, for never forgetting me in their prayers as I wish them all the best in their career and life.

I'm very thankful to my advisors Dr. Ahmed El Gendy and Dr. Mohamed El Zayat for all their great efforts and sincere advice throughout this work. Their technical advice and contribution were unique and shall never be forgotten. I would like to tell them that I have learned a lot from them and that this work would have never been done without their guidance, help, and continuous support.

I am very thankful to my beloved husband who encouraged me to finish this work and was always beside me. He was my main motive to finish my degree. May Allah fulfill our life with joy, happiness, and love.

I am deeply grateful for Suez Cement Company for sponsoring me through my journey of graduate school at the American University in Cairo. I would like to thank the company for believing in me and allowing me to continue my studies with their continues support and assistance. I am also deeply thankful for the American University in Cairo for providing me with the research grant (R41) which helped me to finish my research with kind and continuous support.

I would like to thank Madinaty WWTP administration for their help and support. Special thanks to Eng. Khaled El Deek and Eng. Medhat Mamdouh for their continuous assistance. Moreover, I want to express my appreciation to VBAG Company operators specially Eng. Yehia and Dr. Rehab.

I hope also not to forget to thank all the professors and doctors who taught me during my academic courses, especially Dr. Ahmed El Gendy, Dr. Mohamed El Zayat, Dr. Mohamed Hamdy Nour, Dr. Salah El Haggar, and Dr. Mohamed Emam.

I want to express my deep sincere and gratitude to Eng. Mohamed El Sisi and Eng. Zahraa for their help in the laboratory and for their valuable advice. Moreover, I would also like to thank all my colleagues for their cooperation throughout.

Abstract

As diseases worldwide and in Egypt are increasing by time, developing, and producing new medicines is massively expanding. The use of pharmaceutical compounds is rising worldwide. Diclofenac compound is used in plenty of different kinds of drugs as a nonsteroidal anti-inflammatory drug "NSAID" treating inflammation, osteoarthritis and rheumatoid. Due to excessive exposure to diclofenac -from humans and animals, large amounts are found in the water streams and the environment. Most of the conventional treatment methods is not capable of the complete removal of the diclofenac. Therefore, most of it is thrown back into the water bodies badly affecting the environment, forming a closed loop of diclofenac consumption unintentionally. The more diclofenac used, the more it can cause serious endangerments to the environment, not only aquatic life but also human beings. Therefore, the diclofenac was put on the EU Water Framework Directive watch list. Adsorption studies conducted in batch mode and continuous flow mode reactors demonstrated the ability of removal diclofenac compound from wastewater using activated carbon material. For the purpose of determining adsorption isotherms, a batch adsorption experiment has been carried out, while column design experiments were assessed through a lab scale column design including three variables: initial diclofenac concentration (3 – 20 mg/l), bed height (3.3 – 7.5 cm) and feed flow rate (3 – 6 ml/min). The research conducted that Langmuir isotherm was a better isotherm fit than Freundlich. It also proved that the higher the bed height in column experiments the higher the percentage removal of diclofenac, reaching 93% at bed height 7.5 cm. Therefore, the optimum and sustainable method to remove the diclofenac compound from its primary source -at wastewater treatment plants- is studied using activated carbon in two different operating modes to protect the environment before the contamination reaches any natural stream and causes further damage.

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Acronyms

AC	Activated Carbon
AOX	Halogenated Organic
BOD	Biological Oxygen Demand
BTX	Benzene, Toluene, and Three Xylene Isomers
COD	Chemical Oxygen Demand
DCF	Diclofenac
DW	Distilled Water
EBCT	Empty Bed Contact Time
EU	European Union
GAC	Granular Activated Carbon
HLR	Hydraulic Loading Rate
LPO	Lipid PerOxidation
MF	Microfiltration
NF	Nanofiltration
PAC	Powdered Activated Carbon
PZC	Point of Zero Charge
RBC	Rotating Biological Contactor
RO	Reverse Osmosis
SBR	Sequencing Batch Reactors
SS	Suspended Solids
UF	Ultrafiltration
UV	Ultra Violet
WTP	Water Treatment Plant
WWTP	Wastewater Treatment Plant

Chapter 1. **Introduction and Objectives**

1.1 **Introduction**

Diclofenac (DCF) compound is a nonsteroidal anti-inflammatory drug used mainly to relieve pain, inflammation, and joint stiffness caused by arthritis (National Center for Biotechnology Information, 2023). It is prescribed for a variety of specialties including otolaryngology, surgery, pediatrics, neurology, and gynecology. It can be found in different forms to be taken including liquid, tablets, and ampoule. Diclofenac has different forms of medications for different uses; some of them being Voltaren, Cataflam, and Cambia (Durbin, Diclofenac, 2020). Cataflam is commonly used as a pain killer, especially for menstrual cramps. Voltaren is used to medicate symptoms of osteoarthritis or rheumatoid arthritis. Also used to treat ankylosing spondylitis and osteoarthritis of the knees and hands (Durbin, Voltaren, 2020). Moreover, Cambia medicine is used to treat inflammation, headaches, or migraines (Durbin, Diclofenac, 2020). These medications and others are very commonly used as forms of DCF compound.

DCF is mainly taken as an oral form; only six percent is taken applied over skin (S.Schmidt, et al, 2018). Around 70% of the DCF taken orally is excreted by the patients in urine and the rest are excreted as feces. It is estimated that only 21–40% is removed in wastewater treatment plants, resulting in a possibility of 3/4 of the consumed DCF entering the water cycle (S.Schmidt, et al, 2018).

Due to all these reasons, the diclofenac is added in the watch list of the EU Water Framework Directive (Directive 2013/39/EU) (Directive, 2013). It is important to measure DCF concentrations in water bodies because some studies show high percentages of DCF compound worldwide (I .López, et al, 2019).

Some DCF values worldwide were examined; for example, the concentration in the Erft River, in Germany was reported to be 15.03 µg /l (P. Sathishkumar, et al, 2020). Moreover, in Nigeria, DCF concentration was found to reach 57.16 µg/l in an irrigation canal (P. Sathishkumar, et al, 2020).

Diclofenac could easily endanger aquatic life with its existence in water bodies. It was found

that the brown trout experienced severe harm in the liver, gills, and kidneys at exposure to 50 µg/l concentration of DCF (L. Lonappan, et al, 2016). Also, some analysis on rainbow trout showed tissue damage and accumulation of DCF in muscle tissues, kidneys, and liver at a concentration of 1 µg/l. It was proven that at concentration of 250 ng/l (0.25 µg/l) of DCF damage to tissues may occur (L. Lonappan, et al, 2016).

Moreover, Linson L., in 2016, illustrated that the vultures experienced collapse after harvesting corpses containing DCF. Therefore, DCF veterinary medicines were banned from south Asian countries after a noticeable decrease in the vulture population, and it was reported that the population started to increase after the ban. Not enough research is conducted to assure the exact safe values of DCF exposure; however, a lot of studies condemned minimal concentration exposure to DCF compound in the long run for fish and animals (L. Lonappan, et al, 2016).

A.M. Fareed investigated the presence of Diclofenac in the Nile river-In the Rosetta branch- and they revealed that the maximum concentration of DCF in the river was 19.393 µg/l which can affect aquatic life drastically (A.M. Fareed, et al, 2018). Finally, there are many ways for diclofenac compound to reach the water bodies; therefore, proposing an easy and cost-sufficient removal method is now vital to resolve such a problem and save the ecosystem.

1.2 **Problem Statement**

The main wastewater treating technologies in Egypt used in wastewater treatment plants are Conventional Activated Sludge, Trickling Filter, Oxidation Ditches, Constructed Wetlands, Rotating Biological Contactor (RBC), Sequencing Batch Reactors (SBR), and Modified Septic Tank (Abdallah, 2014). It was found that conventional activated sludge treatment method removed only 50% of diclofenac from wastewater (B. Tiwari, et al, 2017).

As diclofenac sodium compound is found in the Egyptian water streams. And it can affect negatively on the environment including flora, fauna, and eventually human beings, it is vital to figure out methods to treat this problem from its roots to preserve the Egyptian's natural sources and eliminate any possible dangers in the future.

The Guiding research question is: How could we treat the wastewater from diclofenac sodium material sustainable and cost-effective solution.

The proposed solution is to treat wastewater from the pharmaceutical compound in wastewater treatment plants before it immerges into the water streams and directly or in directly come back to the water cycle increasing its concentration and contamination possibilities. Also, to monitor the health and environmental impacts of such contaminant into water streams.

1.3 **Objectives**

Inspired by all the previous research and the serious damage that can be caused by the increase in DCF concentration in the environment. The main objectives for the research are:

1. To find the most sustainable method to remove DCF compound from its primary source -Wastewater by using activated carbon material.

2. To study the adsorption mechanism for DCF by the activated carbon in treated wastewater in different modes.

3. To investigate the most energy saving method to remove DCF compound from its primary source -Wastewater by using activated carbon material with the least amount of energy and materials.

4. To study different adsorption methods for DCF compound from wastewater (batch mode and continuous flow mode).

The work in the thesis will follow the following sequence:

1. Determination of the adsorption characteristics and mechanism of the activated carbon by adsorption studies using diclofenac in wastewater as the adsorbate.

2. Using two different modes of application for treatment, namely, continuous flow columns and completely mixed batch reactors.

3. Using diclofenac contaminated wastewater with different concentrations and Activated carbon quantities to study the adsorption mechanism in batch mode experiments.

4. Using diclofenac contaminated wastewater with different concentrations, flow rates, and activated carbon bed heights to study the adsorption mechanism in continuous flow mode experiments.

1.4 Thesis Outline

The thesis is organized as follows:

- Chapter two includes a literature review on activated carbon together with an explanation of the production process. Also, the definition of diclofenac sodium compound and its various uses and occurrence in the environment. The work of plenty of researchers in the field of removal of diclofenac compound from water to compare the results obtained from various removal methods. Moreover, the chapter includes a summary of research on diclofenac sodium adsorption by activated carbon in both batch and continuous flow mode systems.

- Chapter three includes the experimental method applied and the materials and methods used to determine and evaluate the diclofenac adsorption by activated carbon.

- Chapter four contains the results and discussion of the data obtained from the experiments.

- Chapter five includes a summary of the important findings, including recommendations for further studies.

Chapter 2. **Literature review**

2.1 Introduction

Diclofenac pharmaceutical compound is used as an anti-inflammatory drug utilized mainly to relieve pain, inflammation, and joint stiffness caused by arthritis. It is titled as a "contaminant of emerging concern" and was put on the Watch List of EU Decision for year 2015/495. Its existence in rivers and treated wastewater effluent have enlarged the concerns (G. McEneff, et al, 2014). Wastewater treatment plants effluents can affect the aquatic systems directly causing an increase in diclofenac concentration in rivers (P. Sathishkumar, et al, 2020). Many researchers have reported the toxicity of diclofenac on aquatic animals. Exposure of relatively small quantities of diclofenac (30 ηg/l) for 90 minutes can decrease the level of Lipid PerOxidation (LPO) in fish which can cause further malformations and developmental alterations and eventually affects the quality of fish (P. Sathishkumar, et al, 2020). Therefore, researchers are searching for methods to remove the diclofenac compound from the water stream avoiding the reach of the compound to the nature causing harm to biota.

2.2 Pharmaceutical Constituents in wastewater

Concerns regarding the effects of drugs on the environment have grown recently. Pharmaceuticals constitute a sizable group of developing organic micropollutants that are persistent contaminants in the environment and cannot be effectively eliminated by standard treatment techniques (K.O. K'oreje, et al, 2016).. Pharmaceutical substances were regarded as environmental pollutants in the aquatic environment around 40 years ago (A.M. Botero-Coy, et al, 2018). Naproxen is an analgesic that is used to treat pain and inflammation was detected in Algiers with concentrations up to 9585 ng/l in wastewater and 228.3 ng/l in the surface water. It was also detected in the Nile River in Egypt with concentration up to 21.189 µg/l (A.M. Fareed, et al, 2018). It was found that Naproxen can affect microorganisms amount of chlorophyll, carotenoids, and enzymatic activity when exposed to concentrations from 50 µg/l. (I. Pacheco, et al, 2019). Moreover, Ibuprofen was also noticed in the Nile River in Egypt with concentration up to 19.95 µg/l. It has been reported that WWTPs in Spain recorded

concentration of 13.74 µg/l. In zebra fish, it is reported that exposure to ibuprofen from 5 µg/l negatively affects the growth rate and causing improper response to external stimuli (I. Pacheco, et al, 2019). Also, progesterone which is used in female fertility treatment was found with noticeable concentrations in water samples in France detected in the Rhône-Alpes region with concentrations up to 199 ng/l. It was found that exposure of small quantities of progesterone (10 ng/l) can affect the excellence and quantity of fertilized eggs of fish causing decrease in reproductive rates in the species (I. Pacheco, et al, 2019).

Finally, Diclofenac has been reported in different water and wastewater streams worldwide, it is used as an analgesic drug which is used for pain relief for inflammatory rheumatic and certain non-rheumatic conditions. P. Sathishkumar in 2020 formed a table collecting recorded values of diclofenac across the globe. Among 88 surface water records diclofenac records classified as follows, 28 samples recorded values less than 1 µg/l, 32 samples recorded values between 0.1 – 0.5 µg/l, 8 samples recorded values between 0.5 – 1 µg/l, and 20 samples recorded values more than 1 µg/l (P. Sathishkumar, et al, 2020). Unfortunately, diclofenac affects animals and plants negatively. A. Margalida in 2017, revealed that by using a mathematical model it was shown that diclofenac causes up to 6389 deaths for vultures in Europe per year. Also, chlorophyll alterations were detected in duckweed Lemna minor after exposure to 100 µg/l of diclofenac (M. Kummerová, et al, 2016).

Diclofenac is found in numerous wastewater treatment plant's effluent around the world. Unfortunately, the conventional wastewater treatment process does not achieve high removal percentages for diclofenac removal from wastewater which causes returning diclofenac compound back to the environment (M. Rosset, et al, 2019). It was revealed that diclofenac was detected in 83% of the collected samples in European wastewater effluents. The biological treatment of urban wastewater only removes 5% of the diclofenac compound (M. Rosset, et al, 2019). Diclofenac removal efficiency ranges between 2%−60% only (J.Wang, et al, 2016).

2.2.1. Diclofenac

Diclofenac is a nonsteroidal anti-inflammatory drug which is used for pain relief for inflammatory rheumatic and certain non-rheumatic conditions. Drugs containing diclofenac compound are one of the doctors first choice to prescribe due to its effective treatment for acute and chronic inflammatory and painful cases (P.A. Todd, et al, 1988). Phenylbutazone first appeared in 1952 after salicylic acid which was the first nonsteroidal anti-inflammatory agent. Modifications were made in order to increase the activity and tolerability of the anti-inflammatory drug (Alfred R. Sallmann, 1986). Researchers found that the effective anti-inflammatory drug should have three main characteristics which are: partition coefficient of approximately 10, two aromatic rings twisted in relation to each other, and acidity constant between 4 and 5. Diclofenac achieved the three main characteristics with an acidity constant of 4.0 and a partition coefficient of 13.4 (Alfred R. Sallmann, 1986).

The chemical formula and molar mass of diclofenac is shown in Figure 2-1.

Diclofenac

- Chemical Formula: $C_{14}H_{11}Cl_2NO_2$
- Molar mass: 296.1 g/mol

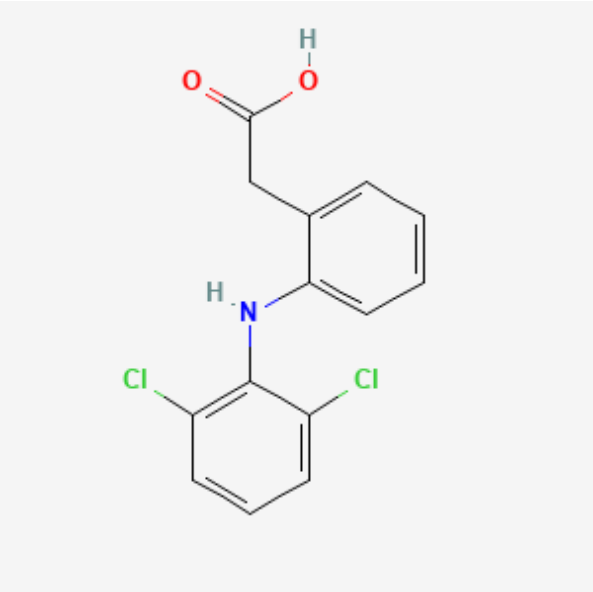

Figure 2-1: Chemical Structure Depiction of Diclofenac Compound (National Center for Biotechnology Information, 2023)

Two types of diclofenac drugs are made, diclofenac potassium and diclofenac sodium. The main difference between both is the speed of drug absorption into the blood. Diclofenac potassium is known to be absorbed within an hour while diclofenac sodium could take from 2 to 4 hours to be absorbed. Therefore, in chronic situation diclofenac sodium is used in reducing inflammation, and in fast paced situations for quick pain relief drugs containing diclofenac potassium is recommended (R. Altman R, et al, 2015).

Diclofenac Sodium (NCBI, 2023; A. Abo El Naga , et al, 2019)

- Chemical Formula: $C_{14}H_{10}Cl_2NNaO_2$
- Molar mass: 318.1 g/mol
- Melting point: 283–285 °C
- Water solubility: 0.00482 mg/

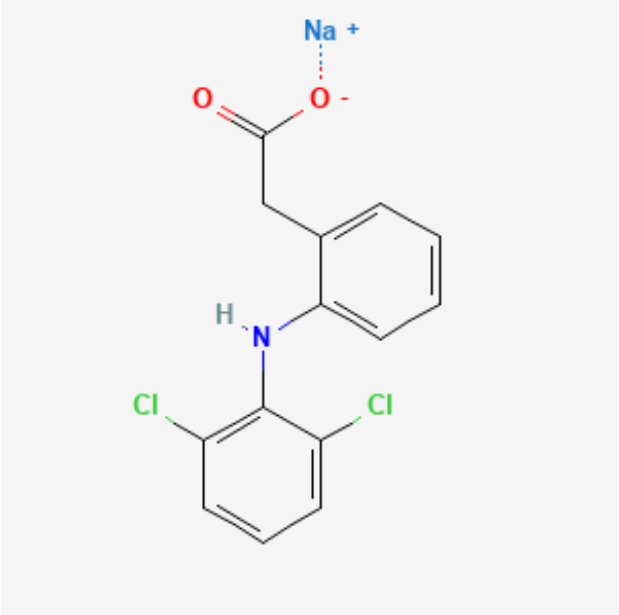

Figure 2-2:Chemical Structure Depiction of Diclofenac Sodium Compound (NCBT, 2023)

2.3 Methods of Diclofenac Occurrence in water cycle

Diclofenac drug is widely used for various medical purposes. Diclofenac is commonly used by humans and even animals as drugs. Diclofenac medication taken orally is excreted either in urine or feces with percentages rage from 65-70% and 20-30% respectively. One of the forms of diclofenac are salves and, in this case, only 6 percent of diclofenac is absorbed by the skin and the remining 94 percent is washed-off (S. Schmidt,et al, 2018). The metabolism of diclofenac is mediated by two processes glucuronidation and oxidative biotransformation. The oxidative metabolism of diclofenac is catalyzed by two enzymes: CYP2C9 and CYP3A4.

Diclofenac is then metabolized to four metabolizes which are then excreted in the form of glucuronide and sulfate conjugates, mainly in the urine (approximately 60%) but also in the bile (approximately 35%) and about 1% is excreted as diclofenac (R. Kasperek, et al,2015).

There can be many ways for pharmaceutical compounds to reach the water surfaces and even drinking water when not considered to treat. Most of diclofenac intake by human and veterinary routes eventually ends up in landfills and wastewater treatment plants. Moreover, diclofenac can reach the wastewater treatment plant directly from pharmaceutical factories (L. Lonappan, et al, 2016). Figure 2-3 shows cycle of the diclofenac or any other pharmaceutical compound from the intake process to the drinking water taps.

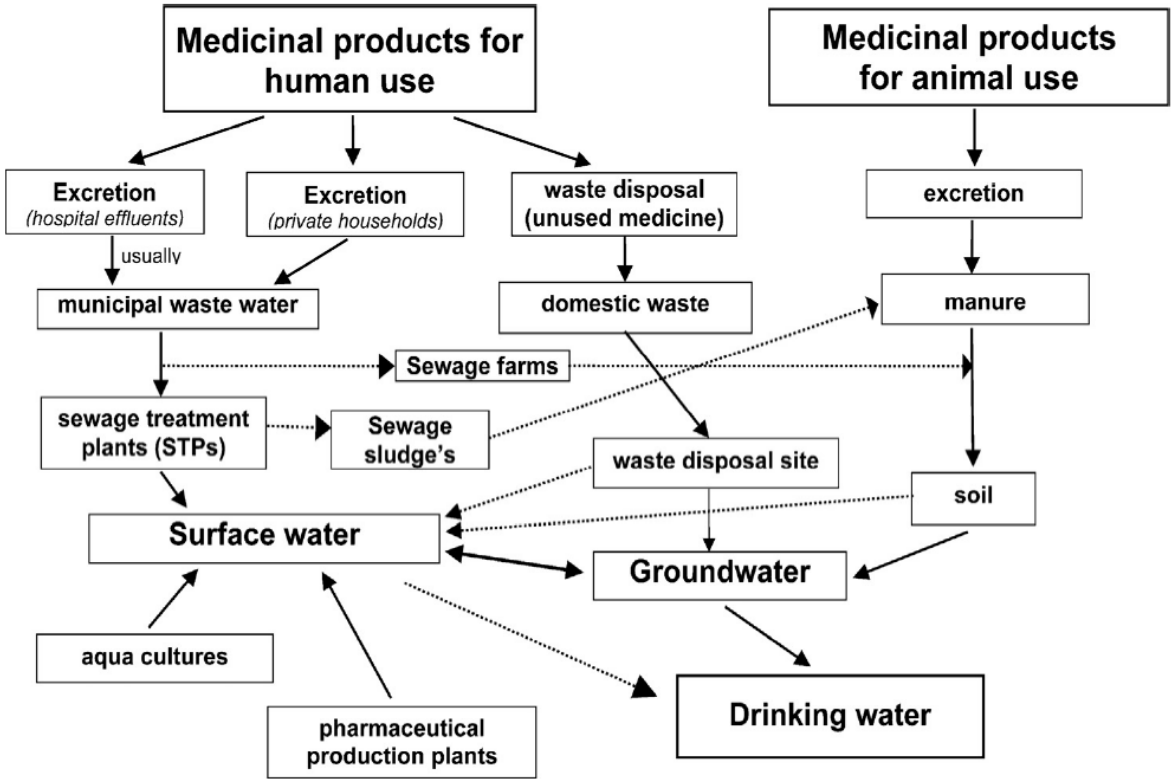

Figure 2-3: Possible Sources and Pathways for the Occurrence of any Pharmaceutical Residues to the aquatic environment (S.O. Ganiyu, et al, 2015) adapted from (N. Rosman, et al, 2018)

2.4 Diclofenac Existence in Environment

Diclofenac has been reported in different water and wastewater streams worldwide. It is reported to be found in canals, lakes, streams, rivers, drains, and estuaries. Reports recorded the occurrence of diclofenac substances in the aquatic environment, values of diclofenac were reported in surface water, drinking water, ground water, seawater, and wastewater. Some examples for diclofenac values recorded worldwide are as follows; the concentration in the Erft River, in Germany was reported to be 15.03 µg/l, and in Nigeria DCF concentration was found to reach 57.16 µg/l in an irrigation canal (P. Sathishkumar, et al, 2020). P. Sathishkumar in 2020 formed a table collecting recorded values of diclofenac across the globe. Among 88 surface water records diclofenac records classified as follows, 28 samples recorded values less than 1 µg/l, 32 samples recorded values between 0.1 – 0.5 µg/l, 8 samples recorded values between 0.5 – 1 µg/l, and 20 samples recorded values more than 1 µg/l (P. Sathishkumar, et al, 2020).

S. Schmidt in 2018 analyzed water samples in Berlin, Germany, and reported values for diclofenac compound in Teltowkanal canal. Teltowkanal canal recorded 2.1 µg/l as a maximum value of diclofenac in the canal. Moreover, other researchers reported values of diclofenac in Taff and Ely Rivers in Wales. It was reported that diclofenac recorded 85 ng/l as a maximum concentration in Taff River, and it reordered 261 ng/l as a maximum concentration in Ely River (B. Kasprzyk-Hordern, et al, 2010).

Groundwater is one of the most reliable sources of water around the world. Groundwater cannot be recharged on its own, but it should be recharged from other sources. The major source of contamination is farming, polluted surface water sources, and leaching from landfills (T. Kivits, et al, 2018). Relatively high concentrations of diclofenac were notices in groundwater samples (13.48 µg/l) in Nigeria. Internationally, diclofenac compound is detected in wells in various locations like India, Luxembourg, Poland, France, Germany, Spain, and Serbia. The concentrations of diclofenac ranged from 2.5 ng/l to 13.48 µg/l (J. Kapelewska, et al, 2018; P. Sathishkumar, et al, 2020). Groundwater from a municipal solid waste monitoring well from landfill leachate in north-eastern Poland was analyzed and diclofenac concentration ranged from 0.15– 2.77 µg/l (J. Kapelewska, et al, 2018). Moreover,

diclofenac has been detected in France, it was found in groundwaters with concentration of 9.7 ng/l (E. Vulliet, et al, 2011).

Drinking water quality cannot be compromised; distinctive attention has been focused on quality of drinking water either from taps or mineral water. Diclofenac has been detected in treated drinking water in countries such as Japan, Sweden, Spain, and France. Research in France investigated drinking water in Rhône-Alpes region scanning pharmaceutical compounds. It detected a maximum value of diclofenac which reached 56 ng/l in drinking water sourced from surface water (E. Vulliet, et al, 2011). Also, Spain researchers detected levels of diclofenac in mineral waters and tap water at average concentration of 18 ng/l and 25 ng/l, respectively (E. Carmona, et al, 2014).

Due to the growth of population in coastal areas around the world, many pollutants found their way to oceans and seas. Researchers have found that diclofenac has been detected in coastal areas in many regions worldwide. In the Red Sea in Saudi Arabia coast. A. Ali, et al, (2018) detected one of the highest recorded values for diclofenac in sea waters which is 10.2 µg/l of diclofenac in the red sea near the city of Jeddah (A. Ali, et al, 2018). Diclofenac was detected on coasts in various regions. In Ireland, diclofenac was also detected with concentrations from 0.06 µg/l to 0.46 µg/l in the east coast and from 0.24 µg/l to 0.55 µg/l in the west coast (G. McEneff, et al, 2014). The occurrence of diclofenac compound in seawater is assured in the following regions: the Baltic Sea, the Aegean Sea, and the Eleusine Gulf in Eastern Mediterranean Sea, Santos Bay with values up to 9.2 ng/l, 14 ng/l, and 16.3 ng/l, 19.4 ng/l respectively (P. Sathishkumar, et al, 2020).

Wastewater treatment plants (WWTPs) are designed to treat pathogens and organic substances before the wastewater integrates with the environment. Pharmaceutical compounds like diclofenac are not detected in the WWTPs discharge as there are no guidelines or restrictions for diclofenac concentrations in wastewater. Unfortunately, this caused the existence of many organic compounds in the treated wastewater effluent (J. Kapelewska, et al, 2018). There are many reported concentrations of diclofenac in influent and effluent of WWTPs. These concentrations depend on various parameters, for example, the population rate, discharge rate per capita, intake rate per capita, and pharmaceutical consumption of

diclofenac (P. Sathishkumar, et al, 2020).

Diverse research is being conducted to measure the diclofenac concentrations in influent and effluent of WWTPs until this day. G. McEneff in 2014 had detected levels of diclofenac in two WWTPs in Ireland. The first WWTP used secondary treatment followed by tertiary treatment using UV for disinfection. Values ranging from 0.31 µg/l -1.69 µg/l were found for diclofenac in the effluent wastewater. The second WWTP is a secondary treatment facility which recorded values ranging 0.45 µg/l – 2.63 µg/l of diclofenac (G. McEneff, et al, 2014). Studies about diclofenac's existence in WWTPs are numerous. In Wales, diclofenac was measured in Cilfynydd WWTP's influent and effluent. Diclofenac values ranged from 26 – 257 ng/l in the influent of the WWTP and 33 – 142 ng/l in the effluent of the treatment plant (B. Kasprzyk-et al, 2010). Another research conducted in Poland showed differences between inlet and exit values of diclofenac in three different WWTPs. J. Kapelewska in 2018 detected diclofenac concentrations ranges from <0.003 µg/l – 11.72 µg/l in inlet and from 0.02 µg/l – 3.18 µg/l.

P. Sathishkumar in 2020 summarized a table of WWTP influent and effluent diclofenac detection values. Diclofenac values were detected in WWTP effluent all over the world, in India, Spain, Ireland, Turkey, Mexico, Greece, and Germany with values of 25.68 µg/l, 3.91 µg/l, 2.63 µg/l, 1.4 µg/l, 2.5 µg/l, 3.3 µg/l, 6.3 µg/l, respectively. Detected values of diclofenac from studies ranges from <10 ng/l in China to 836 µg/l in Pakistan. (S. Schmidt, et al, 2018; K. Singh, et al, 2020; G. McEneff, et al, 2014; S. Sari, etal, 2014; J. Rivera-Jaimes, et al, 2018; A. Stasinakis, et al, 2012). In Egypt, a study was conducted to evaluate the water quality in Nile River, Rosetta branch. Fifteen pharmaceutical compounds were detected including diclofenac. Diclofenac was detected in 5 points in Rosetta branch. The highest diclofenac value detected was 19.393 µg/l while the lowest was 0.442 µg/l (A. Fareed, et al, 2018).

2.5 Diclofenac Environmental Effect

The main concern for the release of diclofenac and other compounds in the environment is their potential of bioaccumulation in living organisms. The nature of diclofenac can lead to its direct existence in the environment and into our food chain (G. McEneff, et al, 2014). Studies have shown that diclofenac existence in aquatic life can cause toxicity for animals even in small

concentrations (ng/l). Moreover, Diclofenac has been detected in aquatic organisms and wild animals (P. Sathishkumar, et al, 2020).

2.5.1. Diclofenac effect on Animals

In some south Asian countries like India, Nepal, Pakistan, and Bangladesh the diclofenac was banned for veterinary uses due to the rapid decline in Gyps Vultures population (Balmford, 2013). However, after the ban the population of the vultures increased normally (Balmford, 2013). Moreover, other toxicity incidences in vultures were detected in Europe (A. Margalida, et al, 2017). A. Margalida, et. al (2017) revealed that by using a mathematical model it was shown that diclofenac causes from 715 – 6389 deaths for vultures in Europe per year. Another study on rat tissues declared that a diclofenac sodium dose of 1.07 mg/kg taken twice a day for 5 days had negative effects on bursting pressures of the colonic anastomoses and hydroxyproline contents of perianastomotic tissues of rats (A. Inan, et al, 2006).

2.5.2. Diclofenac effect on Aquatic life

Diclofenac toxicity in many aquatic animals have been evaluated by many researchers, it was found that it could easily endanger aquatic life with its existence in water bodies (P. Sathishkumar, et al, 2020). The brown trout for example experienced severe harm in the liver, gills, and kidneys at exposure to 50 µg/l concentration of diclofenac (L. Lonappan, et al, 2016). Also, some analysis on rainbow trout showed tissue damage and accumulation of diclofenac in muscle tissues, kidneys, and liver at a concentration of 1 µg/l (L. Lonappan, et al, 2016). Moreover, it was proven that damage to fish tissues may occur after diclofenac exposure with concentration starting 250 ng/l (0.25 µg/l) (L. Lonappan, et al, 2016). Diclofenac was found to reduce the hepatosomatic index (HSI) in freshwater fish which causes in reduction of testosterone levels of fish (I. Guiloski, et al, 2015). A decrease in the level of lipid peroxidation was discovered after exposure to 30 ng/l of diclofenac for 90 minutes in Zebrafish embryo (P. Sathishkumar, et al, 2020).

2.5.3. Diclofenac effect on Plants

Diclofenac was also reported to be found in plant's roots and shoots (B. Bartha, et al, 2014). At exposure of 10 µg/l of diclofenac Alfalafa leaves experienced suppression of iron-superoxide dismutase (FeSOD) gene expression (A. Christou,et al, 2016). Chlorophyll alterations were detected in duckweed Lemna minor after exposure to 100 µg/l of diclofenac (M. Kummerová, et al, 2016). Finally, research had conducted that diclofenac compound have negative cytotoxic and genotoxic effects on various plants (P. Sathishkumar, et al, 2020).

2.6 Diclofenac Removal Techniques

There are numerous methods for water and wastewater treatment worldwide. Different types of water treatment include coagulation, flocculation, and filtration. Moreover, wastewater treatment can involve many steps according to the usage of water after treatment. Different treatment methods include activated sludge, extended aeration, moving bed biofilm reactor, oxidation ditches, trickling filters, and others. Much research aimed to record the occurrence of diclofenac before and after water and wastewater treatment to assess the removal efficiency. Research in Wales was conducted to measure the influent and effluent values for many pharmaceutical compounds including diclofenac in two different WWTPs (Cilfynydd and Coslech). Cilfynydd and Coslech WWTPs are utilizing two different wastewater treatment processes trickling filter beds and activated sludge, respectively. It was shown that the value of diclofenac removal efficiency in Coslech WWTP reached approximately 57.3%, and 44.7%in Cilfynydd WWTP. (B. Kasprzyk-Hordern, et al, 2010).

Different treatment methods for wastewater achieve the desired effluent water quality; however, wastewater treatment does not measure pharmaceutical compounds values. Diclofenac removal efficiencies in different treatment methods were measured in research to evaluate the water and wastewater quality. It was found that Membrane bioreactor (MBR) removed only 32% of diclofenac from wastewater and conventional activated sludge removed 50%. (B. Tiwari, et al, 2017). Moreover, in Colombia diclofenac's removal efficiency was recorded to be than 20% in Salitre WWTP, which depends on chemical treatment. Also, it recorded less than 40% removal efficiency of diclofenac in Antioquia WWTP which treats

wastewater using primary treatment coupled with a stabilization process with sludge. (A. Botero-Coy, et al, 2018)

As shown in the literature, it has been proved that conventional wastewater treatment methods are uncapable of fully eliminating the diclofenac compound from wastewater. Therefore, advanced treatment processes such as membranes should be observed for higher removal rates in terms of pharmaceutical compounds removal. Membranes are characterized by the driving force applied to the process, including microfiltration (MF), nanofiltration (NF), ultrafiltration (UF), and reverse osmosis (RO). Their main differences are due to different pore sizes for each membrane type. The MF is the membrane with the largest pore size while NF and RO have the smallest pore size. N. Rosman in 2018 reported removal percentages for the diclofenac using the four membrane types. It showed that the MF and UF removed less than 20% of diclofenac from water, while NF removed 50 – 80%, and RO removed more than 80% of the pharmaceutical compound. (N. Rosman,et al, 2018)

After summarizing research from literature, a graph comparing removal efficiencies for diclofenac compound in water and wastewater was conducted to compare different removal percentages for different treatment processes as shown in Figure 2-4.

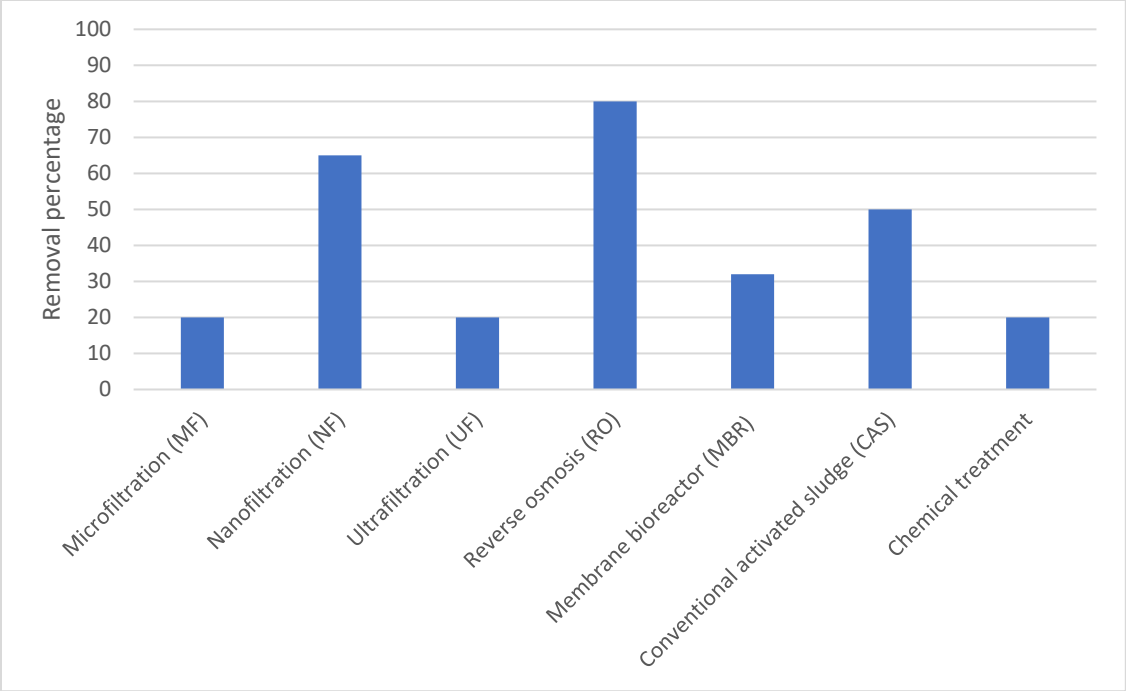

Figure 2-4: Graph Comparing Diclofenac Removal Efficiencies for different Treatment Processes.

There are many researchers who are trying to find the optimum and most cost-efficient treatment solution for pharmaceutical compounds. One of the virally studied pharmaceutical compounds among the rest enlisted compounds in the EU watch list is diclofenac compound (J. Sousa, 2018). Activated sludge treatment is one of the most common treatment methods for wastewater, it was shown that it removes from 9 – 60% of diclofenac in different conditions (B. Kasprzyk-Hordern, et al, 2010). Table 2-1 shows a variety of diclofenac removal percentages using different technologies.

Table 2-1: Diclofenac Removal Percentages Using Different Technologies.

#	Pharmaceutical Compound	Influent Value (ng/l)	Technology Used	Type of Water	Removal Percentage (%)	Reference
1.	Diclofenac	$20*10^6$ - $70*10^6$	Primary treatment, Orbal oxidation ditch, and UV disinfection	Wastewater	10 - 60	(J. Wang, et al, 2016)
2.	Diclofenac	$10*10^6$ - $40*10^6$	Electron beam	Artificial aqueous solution combined with a biological aerated filter	~100	(S. He, et al, 2014)
3.	Diclofenac	580	Bardenpho process	Wastewater	80	(J. Wang, et al, 2016)
4.	Diclofenac	4000	MBR	Synthetic sewage.	15 ± 7.2%	(Y. Xiao, et al, 2017)

#	Pharmaceutical Compound	Influent Value (ng/l)	Technology Used	Type of Water	Removal Percentage (%)	Reference
5.	Diclofenac	100	PAC (Powdered activated carbon)	Surface water	40	(J. Wang, et al, 2016)
6.	Diclofenac	$300*10^6$	PAC (molecularly imprinted polymer)	DI Water	>90	(C. Dai, et al, 2011)
7.	Diclofenac	5800	PAC (Powdered activated carbon)	WWTP effluent	80	(J. Wang, et al, 2016)
8.	Diclofenac	$1*10^6$	GAC (Granular activated carbon)	Synthetic Drinking water	99.7	(E.Rigobello, et al, 2013)
9.	Diclofenac	$10*10^6$	Graphene	Synthetic water	97	(J. Wang, et al, 2016)
10.	Diclofenac	-	Activated sludge treatment	Wastewater	9 - 60	(B. Kasprzyk-Hordern, et al, 2009)
11.	Diclofenac	$1*10^9$	Citrus-waste biomass (Adsorption)	Deionized water	99.7	(A Angosto, et al, 2020)

#	Pharmaceutical Compound	Influent Value (ng/l)	Technology Used	Type of Water	Removal Percentage (%)	Reference
12.	Diclofenac	100	PAC (Powdered activated carbon)	Synthetic water	100	(J. Wang, et al, 2016)
13.	Diclofenac	$20 *10^6$ - $100*10^6$	Granular activated carbon (size particles between 2.00 and 2.38 mm)	Distilled water	92.7	(M. de Franco, et al, 2018)
14.	Diclofenac	$100*10^6$	Thermo-plasma expanded graphite	Distillated water	>70	(Cuccarese, Marco, et al, 2021)
15.	Diclofenac	$5*10^6$ - $30*10^6$	Isabel grape bagasse	Distillated water	20	(Márjore Antunes, et al, 2012)
16.	Diclofenac	$10*10^6$ - $30*10^6$	AC from cocoa pod husks	Distillated water	76 – 93.6	(Fatima Mansour, et al, 2018)

#	Pharmaceutical Compound	Influent Value (ng/l)	Technology Used	Type of Water	Removal Percentage (%)	Reference
17.	Diclofenac	$1*10^6$ - $100*10^6$	Sewage sludge	Distillated water	80 - 99	(M. Elshikh, et al, 2022)

2.7 Adsorption

2.7.1. Adsorbents

The adsorption process is considered one of the best alternatives for the removal of organic pollutants from water because can be easily designed, have a relatively low cost, and easy to operate. During the adsorption process hazardous products are not formed which can happen in different treatment methods. It is a simple process which depends on the accumulation of organic pollutants on the surface of the absorbent. There are many materials that can be used as adsorbents. For example: expressive waste generation from agricultural, food waste, and wooden products are all attractive options for adsorbents that can be used for organic pollutants removal (H. Quesada, et al, 2019). Adsorbents can be classified into four classifications, adsorbents that can be found in nature, thermally treated adsorbents, chemically treated adsorbents, and Activated carbon. Adsorbents can be used in nature after a simplified washing pretreatment, or chemically treated, after washing with chemicals to remove unwanted organic and inorganic matter existing on the surface. Adsorbent can also be thermally treated, by using heat, increasing the surface area, and breaking the less stable bonds and releasing the volatile fraction of the material. It is found that activated carbon material had the higher adsorption capacity among the four categories, followed by chemically or thermally treated adsorbents and, finally, in natura materials (H. Quesada, et al, 2019).

2.7.1.1. Activated Carbon

Activated carbon adopts adsorption process in purifying gaseous or liquid matters. Adsorption is a process that depends on compiling the gaseous or liquid matters on the surface of the solid absorbent. Physical attractive forces between molecules known as "Van-der-Waals forces" are the reason behind the adsorption phenomenon as there are no chemical reactions involved. The adsorption process can be assessed in terms of rate of adsorption and the magnitude of the adsorbent. And the efficiency of the adsorbent is determined by the type of Activated carbon, the particle size of Activated carbon "Granular or Powder", the pore size, and the particles distribution. (V. Agrawal, et al, 2017)

Activated carbon is one of the oldest adsorbents used worldwide for removal of liquid or

gas organic and inorganic contaminants. Charcoal, which is the ancestor of activated carbon, is the one of the oldest adsorbents known in water purification. The ancient Egyptians were aware of the adsorption properties of wood charcoal 1500 before Christ where they used it for medical purposes (McDOUGALL, 1991). Charcoal properties were discovered by Scheele in 1773 for gases treatment, then in 1786 he discovered its properties in decolorizing the solutions. Afterwards Lowitz, started removal of bad odors from water using charcoal from 1789 to 1790. But in 1900 the chemist Ostreijko from Sweden developed the commercial activated carbon by using chemical and thermal methods for activation. The first time to produce a chemical activated carbon using zinc chloride was in 1914 in an Austrian plant (A. Bhatnagar, et al, 2013).

Activated carbon is carbon-based materials extracted from carbon rich materials such as wool, coal, and coconut that consists of well-developed internal pore structure. Activated carbon is characterized by its high surface area, internal pore structure, and its capacious porosity (A. Bhatnagar, et al, 2013). It is a material consisting of pure carbon and it is known for its powerful adsorption capabilities due to the porous structure and the large surface area that can reach 1500 m^2/gm. Therefor it is used as an efficient adsorbent that purifies and disinfects liquid or vapor matters with reasonable economical aspects (V. Agrawal, et al, 2017). It is a highly porous carbonaceous compound with volume of pores that can be greater than 0.2 ml/g (McDOUGALL, 1991).

The Structure of the activated carbon is like the graphite structure. Activated carbon is composed of tiny graphite platelets with diameters from 20 to 100 Å which form the open cavities/ pores of molecular dimensions (McDOUGALL, 1991). Activated carbon is an exclusive material as it is filled with voids the size of molecules. These pores contain huge van der Waals forces which are the reason for the adsorption process although they are spaces of zero electron density. The porosity of activated carbon can be classified according to the size of the activated carbon pores, and there are three main groups as follows. (H. Marsh, et al, 2006).

- Microporosity where width of pores is less than 2.0 nm.
- Mesoporosity where width of pores is between 2.0 – 50 nm.
- Macroporosity where width of pores is greater than 50 nm.

The activation of carbon is the most important step to produce activated carbon, and the activation process can occur chemically or physically. (McDOUGALL, 1991).

a) Chemical Activation

Chemical activation is a single step process which is a wet-chemical process. And its purpose is to convert the uncarbonized cellulosic material (for example: wood) into activated carbon. It depends on activating agents that could be phosphoric acid, sulphuric acid, or zinc chloride. There are chemicals that have common strength as dehydrating agents that are suggested to be used as agents like suggested for use include sodium carbonate, sodium and calcium hydroxide, calcium, ferric iron, the chloride salts of magnesium, calcium, and aluminum. (McDOUGALL, 1991)

The process is relatively simple as it involves mixing the agent and the carbon-based material (wood) with each other forming a paste. This paste is dried in a kiln with temperatures between 200 – 650 °C. Due to high temperature and by the aid of the dehydrating agent the raw material transforms into activated carbon with a permeable structure and large surface area. (McDOUGALL, 1991)

b) Physical Activation

Physical activation must include two steps to be completed. The first step is carbonization of the raw material, and its mainly by heating the material in an inert atmosphere to a temperature less than 700 °C. This step mainly reduces the volatile content of the raw material, it is desirable to achieve more than 80% of fixed carbon content. Also, the carbonization process causes rearrangement of carbon atoms to form graphite like structures which forms the extended surface area and the porous structure. The second step includes an oxidizing agent which can be air, steam, or Carbon dioxide CO_2 that should be heated with the previously heated raw material in temperature between 800 – 1100 °C. The active oxygen in the agent burns away the reactive components of the carbon skeleton as carbon dioxide and carbon monoxide. (McDOUGALL, 1991)

There are many types of activated carbon that can be efficient as adsorbents, based on the raw materials, the use intent, and the production process. There are four main types of activated carbon available in the markets. Granular activated carbon known as (GAC),

powdered activated carbon known as (PAC), tablet form activated carbon, and finally sheets of activated carbon. The two most popular forms are GAC and PAC as they are easily found in markets. However, there are some differences between them. GAC mainly consists of irregularly shaped particles with sizes that range from 0.2 to 5 mm approximately. While PAC is in a powder format with size less than 0.075 mm. Both have high surface area for adsorption, but GAC is more used in water filtration and PAC is more used in food de-colorization. The main merit of GAC is that it can easily be regenerated unlike the PAC which can be hard and challenging to regenerate. If activated carbon is to be used in a treatment plant/ process the type should be chosen according to the available equipment. If the process equipment includes equipment like belt press or filter press that can remove the PAC from the filtrate, then PAC can be a good choice. And if other reactors are found then mostly the GAC would be the preferred type as it forms less dust in operation and avoids cake formation.

All the forms of activated carbon can be extracted from different carbon-based materials like Wood, coal, and coconut shells. The comparison between each is based on the purpose of use and the economic status, some of which are described below.

a) *Coconut shells based Activated Carbon.*

Coconut shell carbons are signatured with their large internal surface areas characterized by micropores. It is best known for the low dust emission during the production process. It is attractive for water and some critical air applications, and Coconut shell based activated carbons are considered a high quality renewable and ecofriendly raw material.

b) *Coal based Activated Carbon.*

This type of Activated carbon is generated from coal. It has a large surface area characterized by micropores and mesopores. It is known for its low cost and consistent density. However, it is not considered as a green raw material.

c) *Wood based Activated Carbon.*

The wood based activated carbon has a large surface area characterized by micropores and mesopores. It also has exquisite decolorizing properties due to its signature porosimetry.

Moreover, it is considered to be a renewable source of raw material. There are many applications for activated carbon as an adsorbent material, these applications apply in many fields like water treatment, air and gas, mining, food, and beverage.

a) Water treatment

In early years activated carbon was used to dechlorinate drinking water for better drinking water quality. Afterwards, it became widely used in groundwater rehabilitation, and treatment of wastewater removing toxic materials from water. Moreover, treatment of landfill seepage and decolorization of liquids are major applications for activated carbon. It is used as a strong sorbent for pollutants, chemical oxygen demand compounds (COD) and halogenated organic compounds (AOX) are reported to be removed by activated carbon adsorbent. Research has shown that activated carbon can remove up to 95.4% of COD (A. Nayl, et al, 2017). Nevertheless, pharmaceutical compounds removal using activated carbon has been popular and proven as one of the best removal materials for its low cost and high efficiency. The percentage removal efficiency of naproxen, ketoprofen, and ibuprofen have recorded 90.45%, 88.4& and, 70.07% respectively. Diclofenac compound also reported a removal percentage of 93% using activated carbon. (M. Rosset, et al, 2019)

b) Air and gas

Activated carbon has been successfully used in odor control systems for years. It has been used for natural gas purification and in removal of H_2S gas (in wastewater treatment plants or industrial odor control) and BTX (Benzene, toluene, and three xylene isomers). It also can be used in waste incineration plants for the elimination of dioxins and heavy metals. Activated carbon can be used in removal of toxic waste in air conditioning, exhaust, and ventilation. Moreover, it can be used in gas masks and cigar filters.

c) Mining

Activated carbon is commonly used in mining purposes as it is used to recover gold metal which is a very precious metal. It is needed in separation of carbon from cyanide phase which is one of the final stages of mining. High quality activated carbon should be used in the gold extraction operation process to reduce fines and recover more gold.

d) Food and beverage

In the food and beverage industry the vital usage of activated carbon is purifying and decolorization. Activated carbon is effective in removing patulin which is toxic and is a polyketide lactone that is found often in apples spoiled by P.expansum or in products such as apple juice. It is also known for its color modifications by removal of organic impurities. A major field of application for adsorption technology is the treatment of liquids, including sugar solutions, glucose, fruit concentrates, vegetable oils and fats.

2.7.2. Adsorption Performance

There are many adsorption mechanisms that have been studied including the characterization of adsorbent during the adsorption process, the modeling of the adsorption equilibrium data, density functional theory calculation, and molecular dynamics study. However, the adsorption modeling the most used methos as it provides data like the maximum adsorption capacity which is substantial for the evaluation process (J. Wang, et al, 2020).

There are many Adsorption Isotherm such as the Langmuir linear model (1916, 1918), the Freundlich model (1906), the Sips model (1948), the Temkin model (1940), and the Brunauer, Emmett, Teller (BET) model (1938), Bohart-Adams (1920), and Yan (2001), and two of the most used are the Langmuir and Freundlich isotherm models. (J. Wang, et al, 2020; M.de Franco, et al, 2018).

2.7.2.1. Langmuir Isotherm Model

Langmuir isotherm model is a linear model that assumes only one molecular layer can be reached. There are some assumptions that Langmuir used in forming the isotherm model, these assumptions are listed below. (K. Hammond, et al, 2013)

- The adsorption and desorption rates are equal at equilibrium.
- The surface consists of a two-dimensional array of similar adsorption pores.
- The probability of absorbing on or desorbing from a pore is unrelatable with the number of nearby molecules.

- The vapor phase adheres to the ideal gas law.
- Adsorption is monolayer.

The Langmuir linear Isotherm equation has the following form.

The linear model (Henry's law) has the following form:

$$qe = \frac{q_{max} \times K \times C_e}{1+(K \times C_e)}$$ (Langmuir, 1918) Equation 2.1: Langmuir Isotherm Equation

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_{m \times K_L}}\right) \times \frac{1}{Ce}$$ Equation 2.2: Langmuir linear model

Where qe (mg/g) is the adsorbed amount at equilibrium and Ce (mg/l) is the adsorbate concentration at equilibrium. And K (L/g) is the partition coefficient.

2.7.2.2. Freundlich Isotherm Model

Freundlich isotherm model represents a nonlinear adsorption phenomenon and it's known to be more accurate dealing with low concentrations. The Model assumes that the sorption happened on more than one layer. (JianlongWang, XuanGuo, 2020)

The Freundlich Isotherm equation has the following form.

$$qe = K_f \times Ce^{1/n}$$ (Freundlich, 1906) Equation 2.3: Freundlich Isotherm Equation

$$\log qe = \log K_f + \frac{1}{n} \log Ce$$ (J. Wang, et al, 2020) Equation 2.4: Freundlich linear model

Where qe (mg/g) is the adsorbed amount at equilibrium and Ce is the adsorbate concentration at equilibrium. While Kf (1/n. mg1-1/n / g) and n are Freundlich coefficients.

If n= 1 then Freundlich model will result a linear model.

2.8 Diclofenac Removal by Adsorption

Ahmed O. Abo El Naga in 2019 studied the removal of diclofenac compound using sugar cane bagasse activated carbon due to its high absorbance characteristics. Experiments have been implemented using different amounts of diclofenac concentrations and activated carbon material. It was shown that the more the sugar cane bagasse activated carbon the more adsorption occurs up to 0.4 g/l, as there were no noticeable differences beyond this value. Moreover, the increase in the diclofenac concentration was shown to decrease robustly on the activated carbon adsorption capacity. The research indicated a comparison between Freundlich and Langmuir models to determine which model provides the best fit. The comparison illustrated that Langmuir model provided the best fit with a correlation coefficient R^2 equals 0.987. Also, Ahmed O. Abo El Naga in 2019, addressed the reusability of the sugar cane bagasse activated carbon by simply rinsing the material with acetone and drying it in a vacuum oven. The experiments showed that even after repeating the regeneration process for 5 times the adsorption efficiency retained about 92.4% of its adsorption capacity. (A. Abo El Naga , et al, 2019).

R. Baccar M. Sarrà in 2012 examined the removal of several pharmaceutical materials including the diclofenac compound using olive-waste cakes based activated carbon. Diclofenac was measured using an HPLC equipped with a UV detector at 230 nm. They investigated the consequences of pH and different temperatures on the adsorption of materials. According to R. Baccar M. Sarrà in 2012, there is no effect on the adsorption of the pharmaceutical compounds from 4 – 40 °C. Although this paper did not discuss the removal efficiency of the diclofenac compound using the activated carbon, it emphasized that the best fit equilibrium adsorption was obtained using Langmuir model with R^2 equals to 0.967. The pseudo-second-order kinetic model was the model that the adsorption process for the diclofenac chemical followed. The adsorption kinetics of various adsorbates have been examined. (R. Sarrà , et al, 2012)

Marcela A. E. de Franco in 2018 studied the diclofenac removal using activated carbon. Diclofenac was measured using UV-vis spectrophotometer. Using two approaches, the batch process and the fixed-bed column process, initial diclofenac concentration, activated carbon quantity, and volumetric flow rate were evaluated to optimize the conditions of

removal efficiency. Marcela A. E. de Franco's in 2018 research showed that the more activated carbon in the column the more time it needs to reach saturation in the breakthrough curve. Moreover, experimental data illustrated that Yan equation showed the highest determination coefficients R^2 0.9842 while the quantity of activated carbon in column was more precisely predicted by Thomas equation. In this research the initial diclofenac concentration, feed flow, and weight of adsorbent ranged between 20 – 100 mg/l, 3 – 5 ml/min, and 0.5 – 1.5 g respectively. The increase in the initial concentration and flow rate of diclofenac, but the decrease in the increase in activated carbon, has been shown to be the least breakthrough time. Adsorption equilibrium showed that the Freundlich model is the most suitable to describe the isotherms behavior (M. de Franco, et al, 2018). Table 2-2 summarizes diclofenac removal percentages using different types and doses of activated carbon.

Table 2-2: Diclofenac Removal Percentages Using Activated Carbon with different Approaches.

#	Activated Carbon	Source	Initial Diclofenac concentration	Removal Percentage (%)	Reference
1.	0.25 – 1 g/L	Sugar cane bagasse	50 – 250 mg/L	45 - 95	(A. Abo El Naga , et al, 2019).
2.	0.2 – 0.9 g/L	Olive-waste cake	14.8 mg/L	80 - 92	(R. Sarrà , et al, 2012)
3.	5 – 10 g/L	NA Commercial	20 – 100 mg/l	90 - 95	(M. de Franco, et al, 2018).

2.9 Research Motivation

The Guiding research question is: What is the most suitable method/ approach that can be used to successfully remove diclofenac sodium material from wastewater before entering the water cycle again after treatment. The suggested solution is to remove the diclofenac sodium material from the point source which is the wastewater treatment plant using high quality activated carbon using one of two approaches: continuous flow mode, or batch mode.

Wastewater treatment plant's effluent contaminants can easily emerge back into the water cycle if not treated properly. Therefore, treating contaminants like pharmaceutical compounds from the wastewater treatment plant is the most convenient method to avoid entering the water cycle and affecting plants, aquatic life, and humans.

Diclofenac was found in numerous wastewater treatment plant's effluent around the world and the conventional wastewater treatment process does not achieve high removal percentages for diclofenac removal from wastewater which causes returning diclofenac compound back to the environment (M. Rosset, et al, 2019). It was important to search for methods to remove the diclofenac compound from wastewater treatment plants before it emerges back to the environment.

Adsorption is known to be one of the most promising methods for contaminants removal because it has many advantages. The adsorption process is not complicated to design and work with, has relatively low cost, and it is possible to regenerate adsorbents (M. Rosset, et al, 2019). Moreover, using adsorption to remove pharmaceuticals is an extremely promising technique due to its convenience when used for different treatment processes (R. Sarrà, 2012). Activated carbon is a very popular and commonly used adsorbents because it can be obtained from many natural resources and easy to operate with. It also have a porous structure and large surface area that can reach 1500 m^2/gm.

Chapter 3. **Materials and Methods**

3.1 Background

This chapter describes the selection of materials, experimental methods, and experimental work carried out at the Environmental Department of the American University in Cairo. The experiments described in this chapter were performed to evaluate the efficiency of diclofenac removal by activated carbon. Various experiments were performed to determine the adsorption capacity and kinetics of activated carbon. Two sets of experiments were run: a fully mixed batch reactor and a continuous column. Both systems were used for water and wastewater treatment, depending on the specific application.

Experiments were performed in duplicate. One is used as a fully mixed batch reactor and the other as a continuous flow column. Both systems are commonly used in sewage treatment plants. Column experiments are important for a clear understanding of the dynamics and kinetics of the adsorption process. In addition, surface titration experiments were performed to get an overview of the surface charge properties of diclofenac sodium and activated carbon used in these experiments.

3.2 Materials and Reagents

3.2.1. Wastewater

Wastewater used in the laboratory experiments is secondary treated wastewater from Madinaty WWTP in Cairo. Madinaty WWTP is a four phases treatment plant with total capacity of 160,000 m^3/day, only two phases are currently in operation with capacity of 40,000 m^3/day each. The treatment method of the treatment plant is based on activated sludge treatment. The treatment plant consists of three stages, the first stage is the pretreatment which consists of screens, aerated grit and grease removal tank, and primary sedimentation tanks. The pretreatment stage is designed to remove 35% of the biological oxygen demand (BOD) and 60% of the suspended solids (SS) of the wastewater in the treatment plant.

The second stage is the biological treatment which consists of aeration tanks and secondary

clarifiers. The activated sludge process depends on high concentration of microorganisms, basically bacteria, protozoa and fungi, which are left to produce loose clumped mass of fine particles that are kept in suspension by stirring and aeration, aiming to remove organic matter by settling via the sedimentation tanks from wastewater. In Madinaty WWTP, four aeration tanks and two sedimentation tanks were operating for each phase. The final stage in the wastewater treatment is the tertiary treatment. Sand filters are used in the tertiary treatment accompanied by the chlorination tank for disinfection purposes.

Wastewater samples were withdrawn from the outlet of the secondary settling tanks. Treated wastewater used in the experiments were from the outlet of the treated water from the secondary sedimentation tank. More than 40 liters were needed for the trials and the final experiments. Treated wastewater was filtered prior to experiments using filtered glass and a vacuum pump to remove any suspended particles that can affect the experiment.

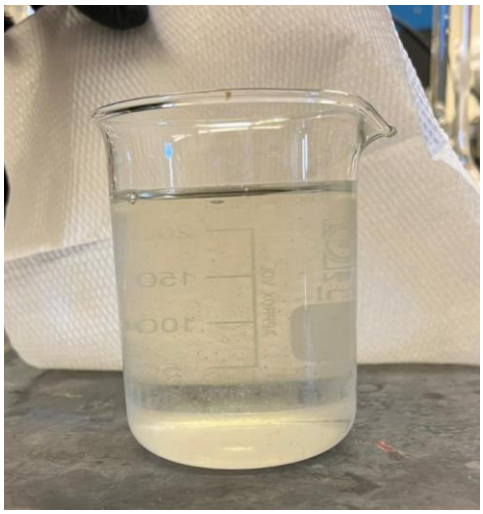

Figure 3-1: Wastewater before Filtration

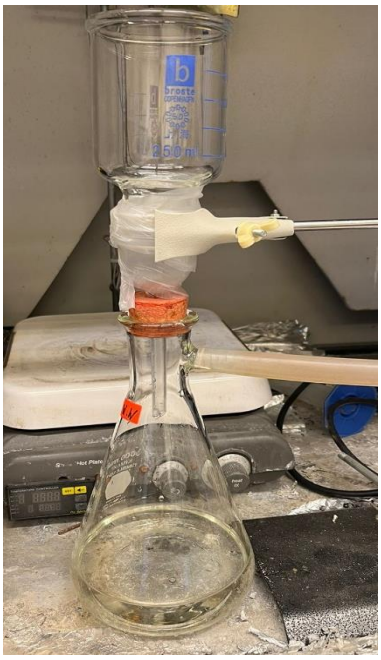

Figure 3-2: Filtration of Wastewater Using Filtered Glass and Vacuum Pump.

3.2.2. Diclofenac sodium

Diclofenac sodium standard (10 grams) was purchased from Sigma-Aldritch (Germany) with assay ≥98%. The standard is a white to off-white colored powder. And it was used to prepare a standard curve for diclofenac sodium on the measuring apparatus.

A concentrated solution of diclofenac sodium with concentration of 400 mg/l was prepared using 20 mg of diclofenac sodium powder (weighed using Kern analytical balance "Model ALJ 220-4"). dissolved in 500 ml in deionized water (DW) produced from water treatment unit (Nano pure UV, USA by Barnstead- "Model 7148") shown in Figure 3-6. Experimental standard solutions were prepared according to the concentrations specified in the literature for the detection limit of the measuring apparatus and the range of given experiment by diluting the diclofenac concentrated solution as follows:

- 100 mg/l: 6.25 ml of concentrated solution added to 18.75 ml of DW.
- 80 mg/l: 5 ml of concentrated solution added to 20 ml of DW.
- 50 mg/l: 3.125 ml of concentrated solution added to 21.875 ml of DW.

- 30 mg/l: 1.875 ml of concentrated solution added to 23.125 ml of DW.
- 20 mg/l: 1.25 ml of concentrated solution added to 23.75 ml of DW.
- 10 mg/l: 0.625 ml of concentrated solution added to 24.375 ml of DW.
- 8 mg/l: 0.5 ml of concentrated solution added to 24.5 ml of DW.
- 5 mg/l: 0.3125 ml of concentrated solution added to 24.6875 ml of DW.
- 1 mg/l: 0.0625 ml of concentrated solution added to 24.9375 ml of DW.
- 0.5 mg/l: 0.03125 ml of concentrated solution added to 24.96875 ml of DW.

Different diclofenac sodium concentrations were spiked in the wastewater to prepare diclofenac sodium contaminated wastewater. In order to simulate the actual situation that occurs in the wastewater treatment plant the commercial medicine containing diclofenac sodium material was used to spike the wastewater in all the experiments. Diclofenac sodium containing medicine was purchased from local pharmacies in Egypt "Voltaren SR, by Novartis", Figure 3-3.

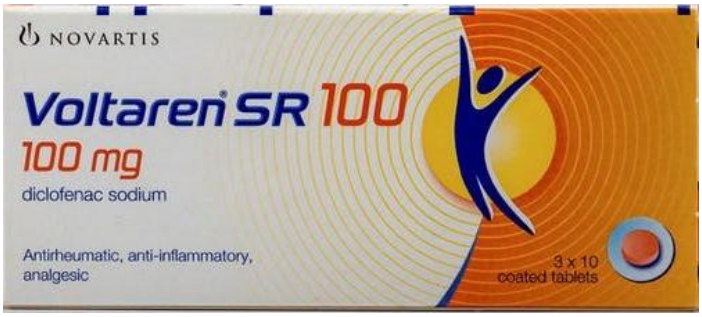

Figure 3-3: Voltaren SR 100 mg

Two tablets with concentration 100 mg each were grinded using a mortar and a pestle, the powder was added to 500 ml of DDW creating a solution with concentration of 400 mg/l. For each different experiment the concentration of diclofenac sodium was added as follows.

$$C_1 \times V_1 = C_2 \times V_2$$ Equation 3.1: Concentration and volume linear equation

Where C_1 is the concentration of concentrated solution and C_2 is the desired concentration for each experiment. V_1 is the volume needed from the concentrated solution and V_2 is volume of

prepared wastewater. Different concentrations were prepared for each experiment as follows.

- 10 mg/l: 975 ml of wastewater and 25 ml of concentrated solution was added to it.
- 8 mg/l: 980 ml of wastewater and 20 ml of concentrated solution was added to it.
- 5 mg/l: 987.5 ml of wastewater and 12.5 ml of concentrated solution was added to it.
- 2 mg/l: 995 ml of wastewater and 5 ml of concentrated solution was added to it.
- 1 mg/l: 997.5 ml of wastewater and 2.5 ml of concentrated solution was added to it.
- 0.8 mg/l: 998 ml of wastewater and 2 ml of concentrated solution was added to it.
- 0.5 mg/l: 998.75 ml of wastewater and 1.25 ml of concentrated solution was added to it.

3.2.3. Activated Carbon

Granular activated carbon (size fraction between 1 and 3 mm) was supplied by Sigma-Aldritch (Germany). The activated carbon was rinsed with distilled water to remove any excess carbon powder and impurities, then it was dried at 110 ℃ for 6 h, afterwards it was kept in a sealed bottle for further use. The quality level of the purchased activated carbon is 200 and its' biological source is peat. Also, the surface area for the activated carbon is 875 m^2/g. The activated carbon weight used in each experiment is weighed using Kern analytical balance (Model ALJ 220-4), Figure 3-6.

3.2.4. Sample analysis

Samples were analyzed using the Ultraviolet (UV–visible) spectrophotometry method. The prepared concentrations created the following calibration curve for diclofenac sodium. A ten-point standard calibration was employed prior to the analysis of the samples in each experiment. The exactness measure for calibration standard can be demonstrated by the comparing relationship coefficient (R^2). A high R^2 value was obtained which reached 0.9999 (almost 1) as indicated in Figure 3-4.

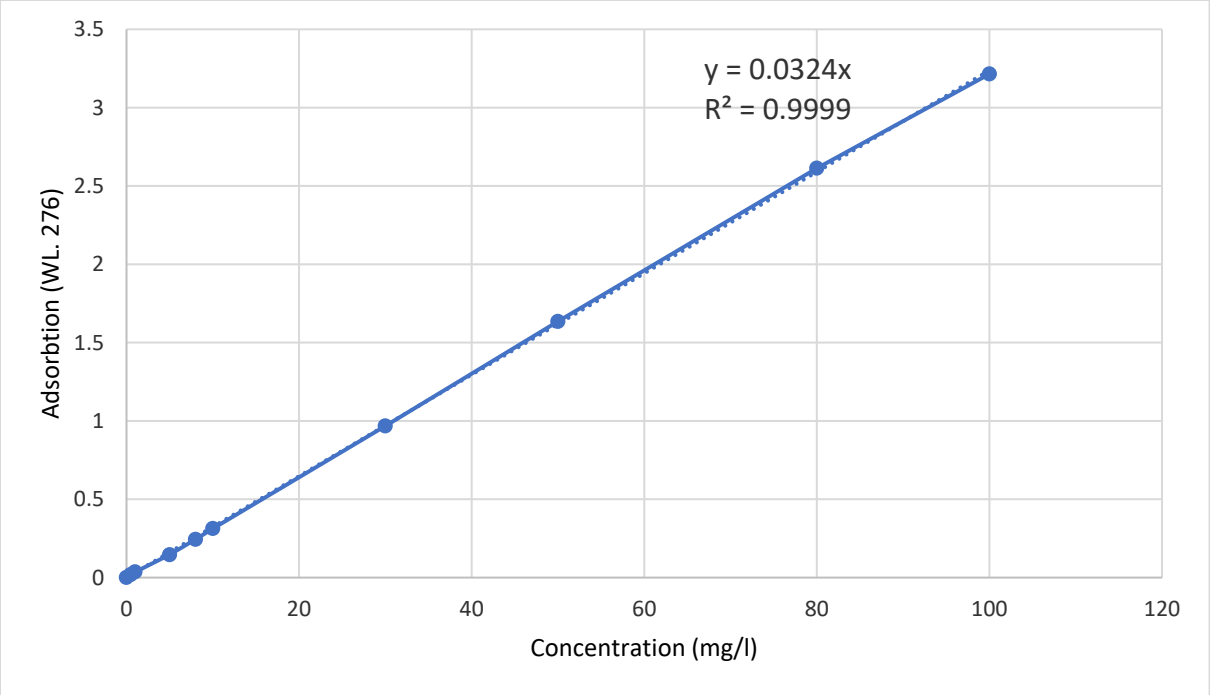

Figure 3-4: Calibration Curve of Diclofenac Sodium using Ultraviolet–Visible (UV – Vis) Spectrophotometer.

3.3 Equipment and supplies

3.3.1. Equipment

Samples were analyzed using the Ultraviolet (UV–visible) spectrophotometry method, using Shimadzu Corporation (Model UV–1650) equipment, at the wavelength of absorbance, 276 nm. The range of detection was starting from 0.5 mg/l to 100 mg/l.

Figure 3-5: Shimadzu Ultraviolet–Visible (UV – Vis) Spectrophotometer (Model UV-1650)

- **Analytical Balance:** with measuring capability from 0.1 mg up to 220 gm. It was applied for weighing activated carbon, diclofenac sodium standards, Diclofenac sodium medicine. Type Kern analytical balance (Model ALJ 220-4) Figure 3-6.
- **Water Treatment Unit:** Nano pure UV, USA by Barnstead (Model 7148) Figure 3-6.
- **JAR Tester:** used in batch experiments and it's paddle speed ranges from 5 – 300 rpm and it is manufactured by PHIPPS and BIRD in USA (Model PB-700) Figure 3-7.
- **pH Meter:** pH electrode manufactured by ADWA Italy (Model AD8000) Figure 3-11.
- **Magnetic Stirrer:** Model (Lab companion – HP-2000) Figure 3-9.
- **Peristaltic Pump:** Peristaltic Pump with flow rate from 1 to 110 ml/min (Masterflex pump – Model 77800-60) Figure 3-9.

Figure 3-6: Nano pure UV Water Treatment Unit and Kern Analytical Balance

3.3.2. Glass ware and suppliers

lab wares that was used frequently were rinsed with a 10% nitric acid solution followed by DW before use. The list of supplies used during the experimental work is as follows:

- Volumetric flasks (class A): 5 ml to 1000 ml volumes.
- Glass beakers: 50 ml to 2000 ml capacities.
- Disposable plastic pipits: 1 ml to 10 ml.
- Glass column locally manufactured.
- Whatman filter paper with pore size 0.45 micron.
- Filtered support base glass.

3.4 Laboratory experiments

3.4.1. Batch Rate Experiments

This set of experiments was designed with the following objectives:

1. To monitor the change of diclofenac contaminated wastewater as a function of time.
2. To investigate the impact of various activated carbon dosages on diclofenac absorption from wastewater.
3. To use various diclofenac concentrations to track the kinetics of the activated carbon adsorption.
4. To confirm the equilibrium time for varying experimental conditions.

These set of experiments were carried out in glass beakers using 200 ml of wastewater spiked by the diclofenac sodium compound from the medicine (Voltaren SR) with different concentrations. The setup is represented in Figure 3-7. The experiments are shown in Table 3-1.

Table 3-1: Batch rate Experiments

Experiment Number	Activated Carbon dose (g)	Diclofenac concentration (mg/l)	Reaction Time (Minutes)
1.	1	0.5	50
2.	1	1	58
3.	1	3	80
4.	1	5	100
5.	1	8	145
6.	1	10	170
7.	0.5	0.5	76
8.	0.5	1	104

Experiment Number	Activated Carbon dose (g)	Diclofenac concentration (mg/l)	Reaction Time (Minutes)
9.	0.5	3	245
10.	0.5	5	345
11.	0.5	8	800
12.	0.5	10	1200
13.	0.5	13	1400
14.	0.5	17	1400
15.	0.5	20	1400
16.	0.2	5	1400
17.	0.2	8	1400
18.	0.2	10	1400
19.	0.2	13	1400
20.	0.2	17	1400
21.	0.2	20	1400
22.	0.1	0.5	210
23.	0.1	1	1300
24.	0.1	3	1400
25.	0.1	5	1400
26.	0.1	8	1400
27.	0.1	10	1400
28.	0.1	13	1400
29.	0.1	17	1400
30.	0.1	20	1400

The steps of the experiment were as follows:

1. Filter the appropriate amount of Wastewater using filtered glass mentioned above.

2. Preparation of the 200 ml diclofenac solution in a beaker, by diluting diclofenac solution (400 mg/l) to the filtered wastewater to reach the designed concentration for each

experiment.

3. Measure pH before each experiment.

4. Start mixing at a fixed speed (20±2 rpm) using the jar test apparatus (PHIPPS &BIRD, PB-700 JARTESTER).

5. Addition of the desired weight of granular activated carbon at time zero.

6. Collection of 4 ml samples from the beaker at different time intervals.

7. Analysis for each sample by UV-vis spectrophotometer.

8. Return sample back to the beaker to maintain the same volume in the beaker for Isotherm calculations.

Note: A trial experiment was implemented with DW as trials before using real treated wastewater to assess the elimination of diclofenac using the used activated carbon.

Figure 3-7: Jar Test Apparatus Used for Mixing Different Concentrations.

3.4.2. Column Experiments

This set of experiments had been intended for the following purposes:

1. To confirm the equilibrium time for varying experimental conditions.

2. To monitor the change of diclofenac effluent concentration as a function of time.

3. To determine the adsorption capacity of the activated carbon before breakthrough.

4. To determine the impact of some characteristic's column parameters. For example, the empty bed contact time and the Hydraulic Loading Rate (HLR) on diclofenac adsorption in fixed beds.

A glass column was manufactured in a local glass workshop with the requested dimensions (internal diameter 1.2 cm, total height 18 cm). Also, an outlet nozzle was requested to easily take samples from, and a glass mesh was designed with holes to hold the activated carbon and pass water at the same time, column shown in Figure 3-8. These set of experiments were carried out in a glass column with an internal diameter 1.2 cm with different bed heights. Wastewater is spiked by the diclofenac sodium compound from the medicine (Voltaren SR) with different concentrations, different activated carbon weights, and different pump flow rates. The setup is presented in Figure 3-8. The experiments are illustrated in the Table 3-2.

Table 3-2: Column Experiments

Experiment Number	Activated Carbon dose (g)	Diclofenac concentration (mg/l)	Flow rate (ml/min)
1.	1	10	3
2.	1	10	4
3.	1	10	6
4.	1	20	3
5.	1	10	3
6.	1	8	3

Experiment Number	Activated Carbon dose (g)	Diclofenac concentration (mg/l)	Flow rate (ml/min)
7.	1	5	3
8.	1	3	3
9.	1.7	10	3
10.	1.5	10	3
11.	1	10	3

The steps of the experiment were as follows:

1. Activated carbon is weighed and soaked in distilled water 24 hours before each experiment.

2. Filter the appropriate amount of Wastewater using filtered glass mentioned above.

3. Preparation of the spiked wastewater solution in a 2 L glass beaker, by diluting the diclofenac stock solution (400 mg/l) to filtered wastewater to reach the designed concentration for each experiment.

4. Influent solution beaker is put on a magnetic stirrer on lowest speed (Lab companion – HP-2000)

5. Measure pH before each experiment.

6. Packing column with glass wool, activated carbon and glass beads as shown in Figure 3-8.

7. Covering the glass column and the influent solution beaker with foil to avoid sunlight exposure.

8. Passing DW using a pump (Masterflex pump – Model 77800-60) for an hour to remove any carbon particles from the system.

9. Remove DI Water from the column and plug the spiked wastewater into the system.

10. Start time zero when diclofenac spiked wastewater solution pass through the silicon tube until reached the activated carbon.

11. Collection of samples at the specified times for influent and effluent wastewater.

12. Analysis for each sample by the UV-vis spectrophotometer.

Note: Most of the experiments were implemented with DW as trials before using real treated wastewater.

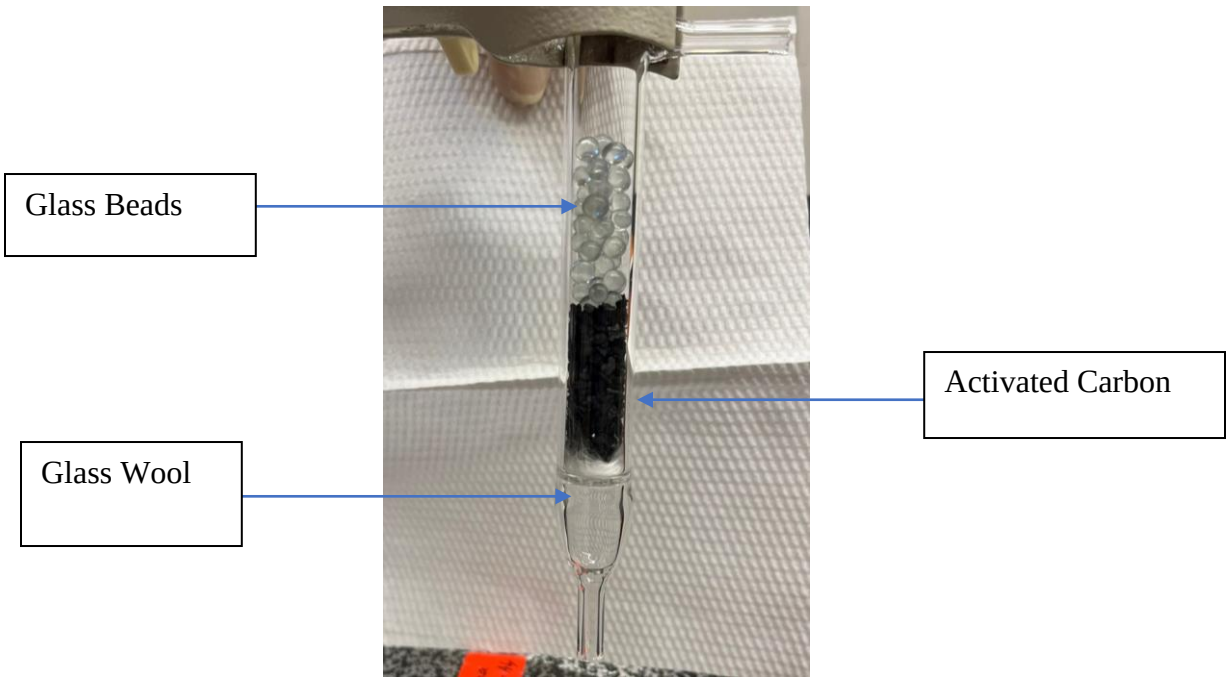

Figure 3-8: Activated Carbon Column Components.

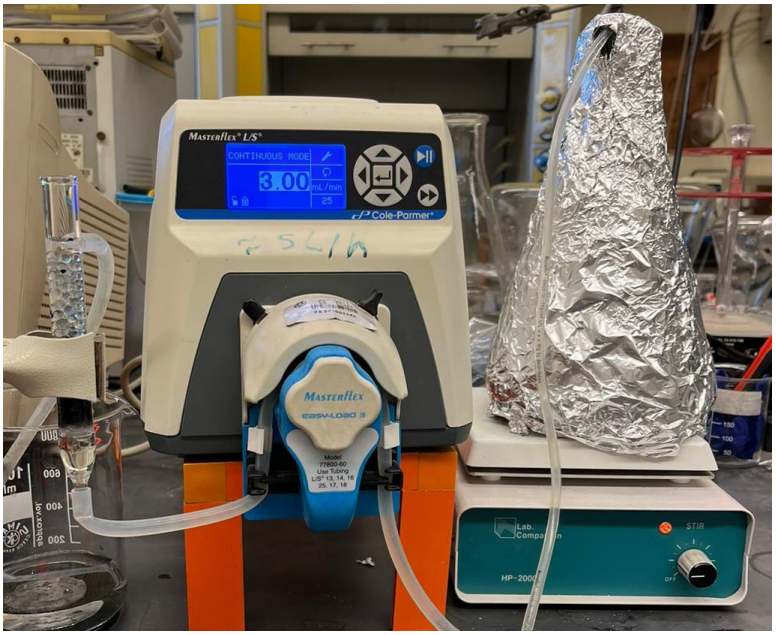

Figure 3-9: Column experiment setup

3.4.3. Surface Titration Experiment

To determine the surface charge properties, diclofenac sodium powder and activated carbon samples were titrated potentiometrically. To achieve the desired concentration of 10 gm/L in this study, 1 g of diclofenac sodium powder and activated carbon were suspended at room temperature in a beaker containing 100 ml of DW. Prior to titration, the mixture was continuously stirred and purged with ultra-pure nitrogen gas to remove CO_2, which could have interfered with an acid-base titration. To precisely adjust the pH, standard HNO_3 (of assay about 99%) and NaOH were added. A pre-calibrated ADWA (Model AD8000) pH meter and probe were used to determine the pH (Figure 3-11).

As an ionic background, $NaNO_3$ was used to standardize the solution. Each solution's pH was gradually increased by adding NaOH, while its pH was gradually decreased by adding HNO_3. To lessen the effects of dilution, less than 5% of the sample volume (5 ml) of acid and base were added. The pH was measured in 0.1 increments for both acid and base. To investigate the effect of background concentration on the surface charge of the diclofenac sodium powder and the activated carbon, two ionic backgrounds (0.01M and 0.001M) were used.

The steps of the experiment were as follows:

1. To create a 0.1 M solution, 8.5 g of $NaNO_3$ were added to 1L of DW.

2. To create a 0.1 M solution, 2 g of NaOH were added to 500 ml of DW.

3. To create a 0.1 M solution, 3.2 g of HNO_3 (assay 99%) were added to 500 ml of DW.

4. Diluting the stock solution used in the first step to the desired molarities as follows:

    - Add 10 ml from the $NaNO_3$ stock solution (0.1 M) into 100 ml DW to reach 0.001M.

    - Add 1 ml from the $NaNO_3$ stock solution (0.1 M) into 100 ml DW to reach 0.001M.

5. 100 ml from the ionic background ($NaNO_3$ with 0.1 M) was taken and then 1 gm activated carbon was added. The solution was stirred and purged continuously by nitrogen gas while measuring the pH.

6. In order to reach 5% of the total volume of the solution (5 ml), 0.1 ml of 0.1 M NaOH was added. Every 0.1 ml, the pH was measured.

7. On the other side, The HNO_3 used was 0.1 M. Up until 5% of the total volume of the solution (5 ml), 0.1 ml was added. Each 0.1 ml was used to measure the pH.

8. The experiment was duplicated for ionic background 0.001.

9. The experiment was repeated for Diclofenac sodium (1 gram of 100 mg tablets).

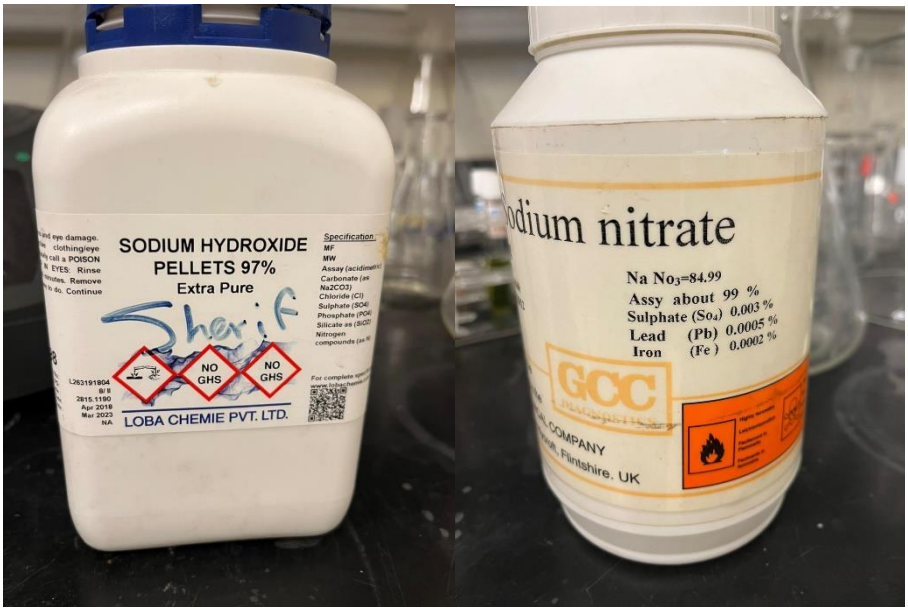

Figure 3-10: Chemicals Used Sodium Hydroxide and Sodium Nitrate.

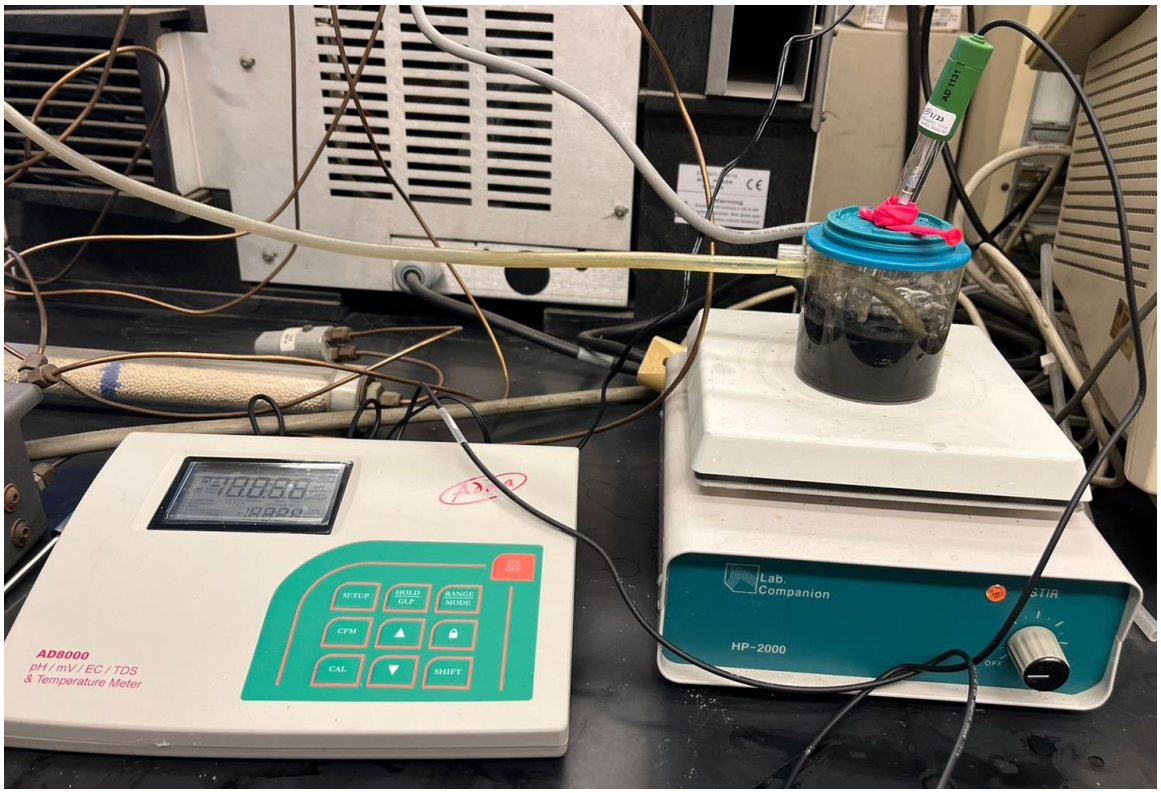

Figure 3-11: Surface titration experiment setup

Figure 3-12: Nitrogen Gas Cylinder

3.5 Laboratory analysis

3.5.1. Diclofenac sodium Analysis

Samples contaminated with diclofenac were analyzed using the Ultraviolet (UV–visible) spectrophotometry method, using Shimadzu Corporation (Model UV–1650) equipment, at the wavelength of the highest absorbance, 276 nm. The range of detection started from 0.5 mg/l to 100 mg/l. Calibration with blank wastewater samples were performed as blank samples before each reading.

The percent removal of diclofenac sodium was determined using the following equation:

$$Removal\ Percentage\ = \left(1 - \frac{C}{Co}\right) \times 100$$ Equation 3.2: Removal Percentage Equation

Where:

C: the final diclofenac concentration (mg/l)

C_o: the initial diclofenac concentration (mg/l)

The calculation for the adsorbed phase concentration was as follows:

$$q\ = (Co - c) \times \frac{V}{W}$$ Equation 3.3: Adsorbed Concentration Equation

Where:

q: the adsorbed quantity of diclofenac per gram of activated carbon (mg/g)

C: the final diclofenac concentration (mg/l)

C_o: the initial diclofenac concentration (mg/l)

V: the volume of the solution, L

W: the weight of dry sorbent, gm

3.5.2. Quality control and Assurance

A crucial and vital component of any research endeavor is quality assurance. Any QA plan should aim to ensure that trustworthy and valid methods are applied while gathering and processing research data. The exact steps taken to guarantee that the process's quality stays within acceptable bounds are known as quality control. The term "quality assurance" refers to the precise procedures used to evaluate the effectiveness of the quality control program in achieving the objectives for the laboratory data.

According to the U.S. EPA method, quality control and quality assurance (QC / QA) procedures were used with the analyses. (USEPA, Environmental Measurements and Modeling, 2003):

- During the analysis, the instrument calibration was checked using the laboratory control standard (calibration verification standard).

- The calibration blank is a zero standard and is used to automatically zero the instrument.

- A method blank (also referred to as a reagent blank) is a sample of reagent solution that has been handled exactly like a sample, including exposure to all glassware, equipment, and reagent. It is used to determine whether there is any interference in the reagent, setting, or lab equipment.

- More than 5 points of calibration standards were used to represent the calibration line. If the correlation coefficient (R^2) is higher than 0.999, the calibration was considered acceptable.

3.6 Sorption Isotherm Model

The term "adsorption isotherm" refers to the steady-state equilibrium relationship between the amount of adsorbate per unit of adsorbent (Qeq) and the equilibrium concentration of adsorbate in the solution (Ceq).

Adsorption modeling may enable us to assess the amount to which an adsorption system can be enhanced, as well as determine the ideal operating conditions for the system.

3.6.1. Langmuir Isotherm

The Langmuir linear Isotherm equation has the following form.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m \times K_L}\right) \times \frac{1}{Ce}$$ Equation 3.4: Langmuir linear model

Where qe (mg/g) is the adsorbed amount at equilibrium and Ce (mg/l) is the adsorbate concentration at equilibrium. And K (L/g) is the partition coefficient.

3.6.2. Freundlich Isotherm

The Freundlich Isotherm equation has the following form.

$$\log qe = \log K_f + \frac{1}{n} \log Ce$$ Equation 3.5: Freundlich linear model

Where qe (mg/g) is the adsorbed amount at equilibrium and Ce is the adsorbate concentration at equilibrium. While Kf (1/n . mg1-1/n / g) and n are Freundlich coefficients.

If n= 1 then Freundlich model will result a linear model.

Chapter 4. **Results and Discussion**

4.1 Batch Rate Experiments

Batch Adsorption rate experiments were conducted using different doses of activated carbon (0.1 – 1 gm) and different concentrations of diclofenac (0.5 – 20 mg/l) in wastewater. The purpose of this was to investigate diclofenac adsorption using the batch system which is applied in many full-scale treatment systems.

4.1.1. Effect of Sorbent Dose

The dose of the sorbent is one of the crucial adsorption parameters. The sorbent dose has a direct impact on the effectiveness of the adsorption mechanism. The batch equilibrium experiment was carried out using various adsorption doses to ascertain the impact of the activated carbon different concentrations on the adsorption process; 0.5 mg/l, 1 mg/l, 2.5 mg/l, and 5 mg/l (Weight of diclofenac/ Volume of wastewater) (W/V), with different initial diclofenac concentrations ranging from 0.5 mg/l to 20 mg/l with contact time of approximately 24 hours. Table 4-1 shows the different doses and concentrations used.

Percentage of diclofenac removal from spiked wastewater was calculated at equilibrium to assess the performance of the different activated carbon doses in terms of removal of diclofenac from wastewater. It was shown that the higher the activated carbon dose (gm/l) the higher the removal rate for the diclofenac sodium compound. The amount of drug adsorbed at equilibrium was also calculated to measure the quantity of diclofenac adsorbed at equilibrium at the different activated carbon doses. Qeq (mg/g) was calculated from the following equation:

$$qe = \frac{(Co - Ce) \times V}{M}$$ Equation 4.1: Adsorption at Equilibrium Equation

Where: where C_o and C_e (mg/l) are the initial and equilibrium phase of diclofenac concentrations, respectively, V the volume of the wastewater solution (L), and M is the mass of the activated carbon used for each dose (g).

Table 4-1: Effect of Activated Carbon Dose on Diclofenac Adsorption

	Activated Carbon Dose 0.5 (g/l)		Activated Carbon Dose 1 (g/l)		Activated Carbon Dose 2.5 (g/l)		Activated Carbon Dose 5 (g/l)	
Initial Diclofenac Concentration (mg/l)	Percentage removal (%)	Qeq (mg/g)	Percentage removal (%)	Qeq (mg/g)	Percentage removal (%)	Qeq (mg/g)	Percentage removal (%)	Qeq (mg/g)
20*	21.331	8.703704	45.537	9.290	83.812	6.839506	-	-
17	23.181	7.814338	47.039	7.799	86.861	5.85608	-	-
13	27.828	7.592593	52.715	7.191	94.244	5.142706	-	-
10*	29.712	5.740741	58.796	5.880	97.717	3.824216	100	2
8*	31.679	4.732272	63.059	5.045	100	3.148163	100	1.6
5	34.093	3.325086	65.476	3.395	100	1.925926	100	1
3	35.417	2.098765	-	-	100	1.17284	100	0.4
1	73.684	1.728395	-	-	100	0.395062	100	0.2
0.5	100.000	1.234568	-	-	100	0.197531	100	0.1

* Marked concentration are concentrations selected to be presented graphically.

Figures from Figure 4-1 to Figure 4-3 show how the adsorption dose affects the ability to absorb diclofenac. The increase in adsorption dose from 0.5 gm/l to 5 gm/l is obvious resulting in increasing the uptake of diclofenac compound.

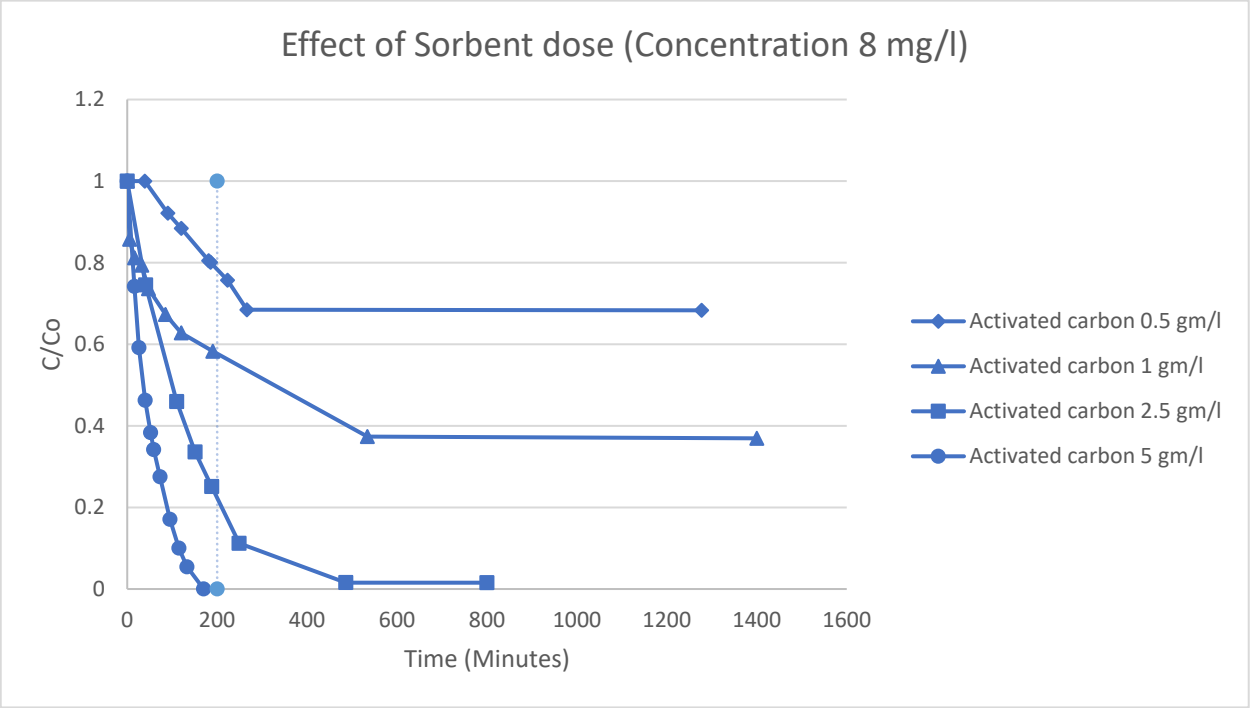

Figure 4-1: Effect of Different Sorbent Doses with Diclofenac Concentration 8 mg/l

As clearly seen from the graph the more sorbent added to the same volume of diclofenac spiked wastewater the more the adsorption capacity. It is shown that at the same time the percentage removal differs dramatically from one sorbent dose to another using the same concentration. For example, at time 200 minutes the removal percentage using activated carbon 5 gm/l was 100% and decreases as the activated carbon dose decreases reaching approximately 22% with activated carbon dose of 0.5 gm/l. Figure 4-2 and Figure 4-3 show different diclofenac concentrations used. Concentrations 8 mg/l, 10 mg/l, and 20 mg/l were chosen as it shows different variety of activated carbon doses results as small doses reach 100% percentage removal in very short duration needing less activated carbon doses (> 0.5 mg/l) to be able to calculate the adsorption at equilibrium. At higher doses (5mg/l) achieved 100% removal percentage for all the concentrations from 0.5 mg/l to 10 mg/l,

therefore it was chosen not to be used in higher concentrations.

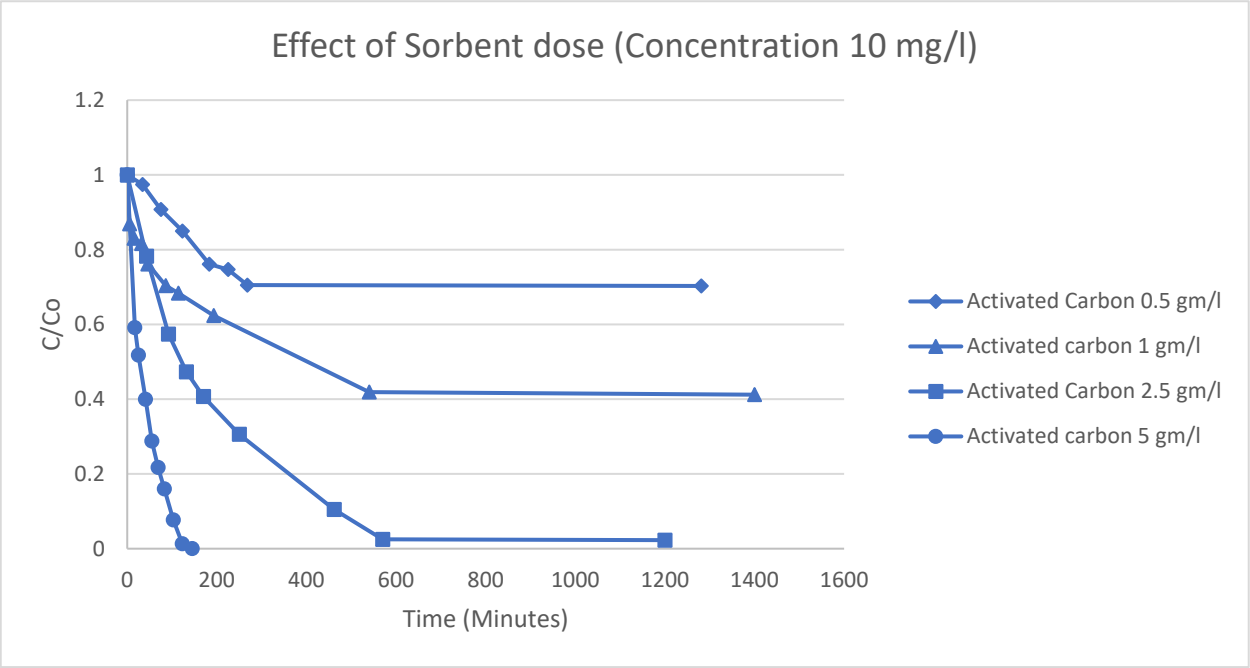

Figure 4-2: Effect of Different Sorbent Doses with Diclofenac Concentration 10 mg/l

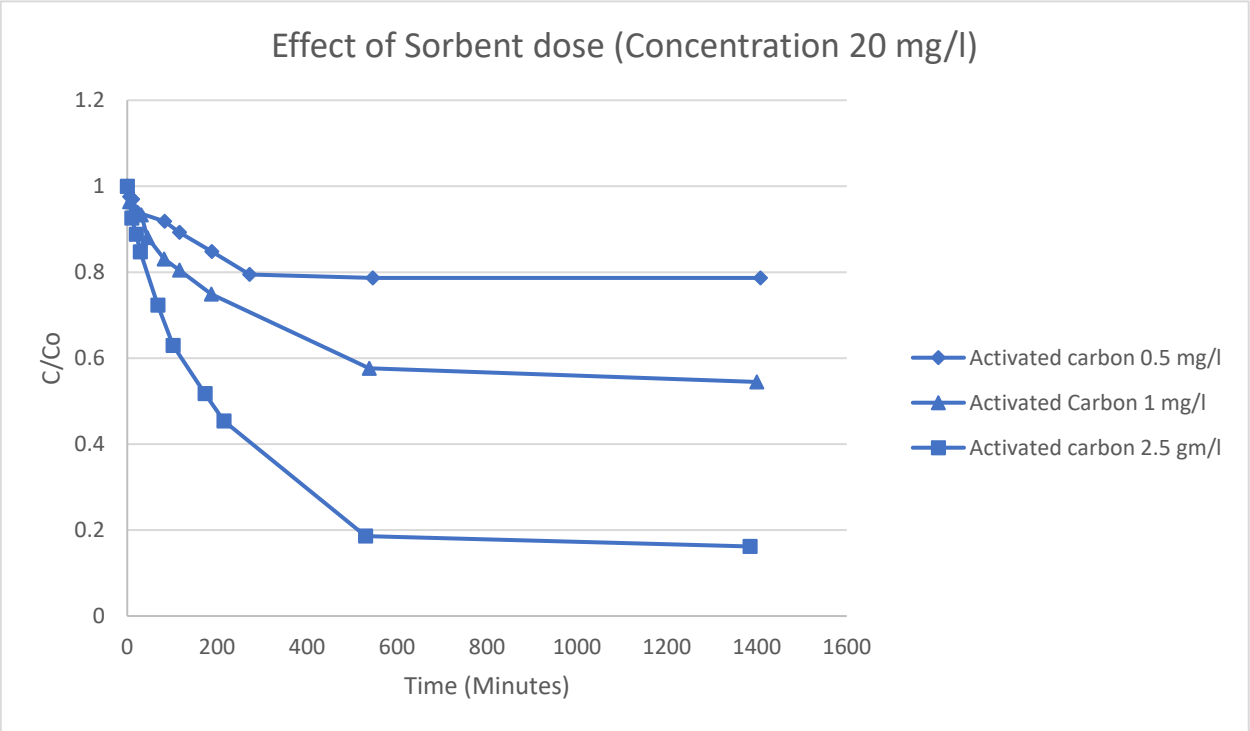

Figure 4-3: Effect of Different Sorbent Doses with Diclofenac Concentration 20 mg/l

4.1.2. Effect of Initial Diclofenac Concentration

The initial Diclofenac concentration, which serves as the sorption dose concentration, is crucial because it affects the ratio of sorbent to sorbate in the system, which has an impact on the effectiveness and sorption capacity.

The batch equilibrium experiments were conducted using various Diclofenac concentrations: 0.5, 1, 5, 8, 10, 13, 17, and 20 mg/l, with various activated carbon doses: 0.5, 1, 2.5, and 5 g/l, to determine the impact of the initial Diclofenac concentration on the adsorption mechanism. The calculated contact time from the earlier experiments in equilibrium was also used. At higher doses (5mg/l) achieved 100% removal percentage for all the concentrations from 0.5 mg/l to 10 mg/l, therefore it was chosen not to be used in higher concentrations.

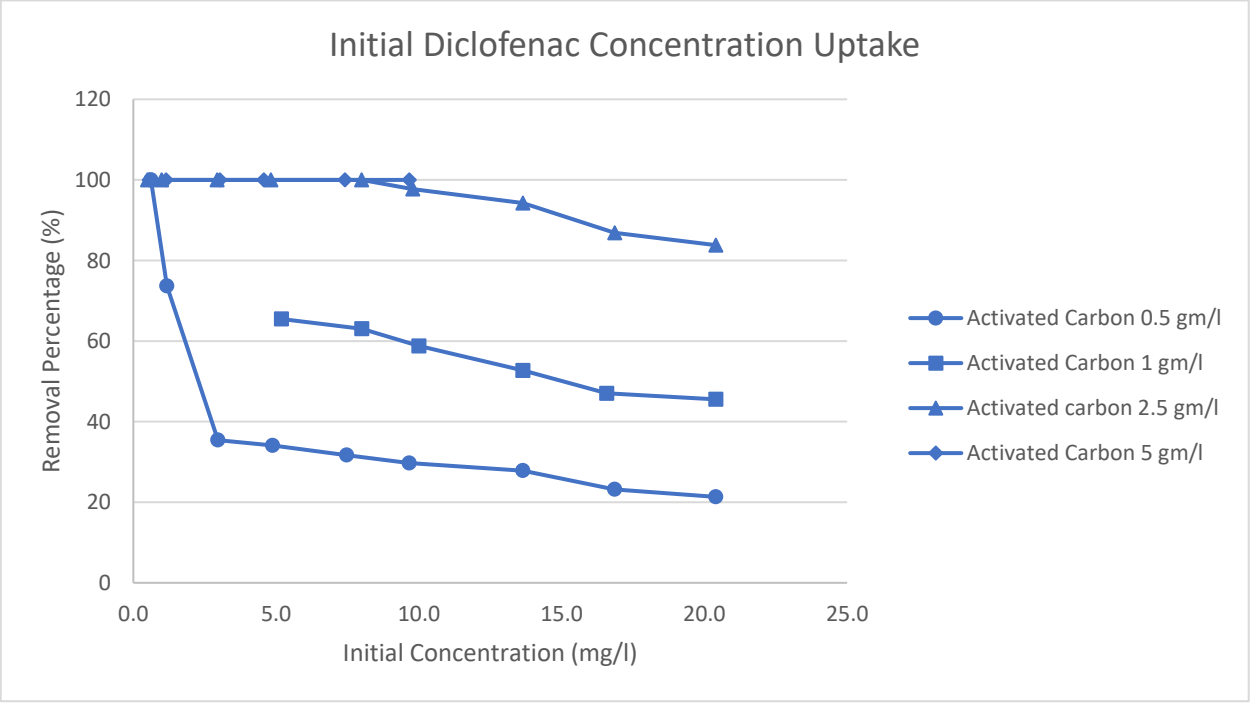

Figure 4-4: Initial Diclofenac Concentration Uptake

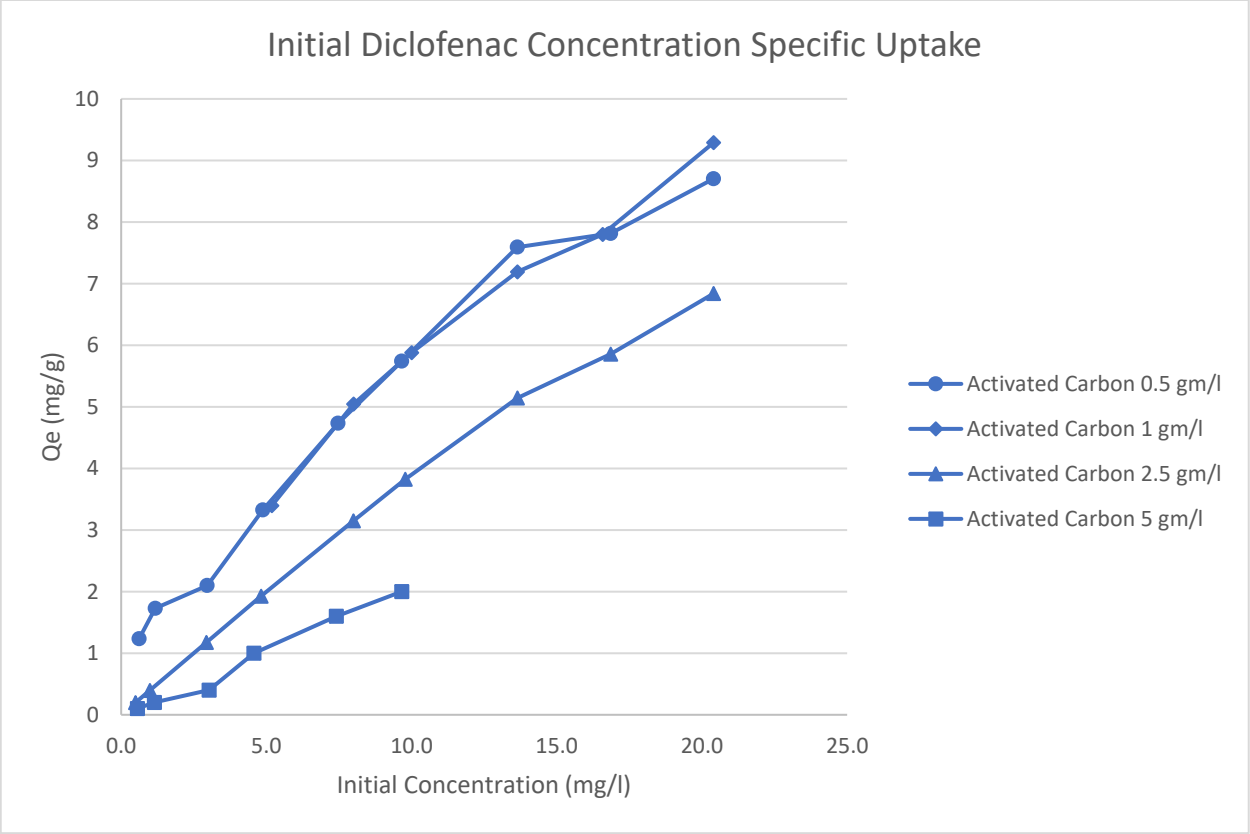

Figure 4-5: Initial Diclofenac Concentration Specific Uptake

The effect of the initial Diclofenac concentration on the activated carbon's capacity for adsorption and its specific uptake is shown in Figure 4-5. It is clear from Figure 4-4 and Figure 4-5 that the activated carbon to diclofenac ratio affects both the adsorption uptake efficiency and the sorption capacity (Qeq), as determined from earlier experiment runs for the sorbent dose effect. The initial concentration of diclofenac has an inverse relationship with the removal efficiency (% removal). The removal efficiency decreases as the amount of diclofenac increases, while the specific absorption increases if binding sites are present.

4.1.3. Effect of Contact Time

Since the necessary contact time depends on the system behavior, it is essential to determine the required contact time to reach equilibrium. The duration of equilibrium sorption was calculated using the batch equilibrium experiments. The activated carbon doses of 0.5, 1, 2.5, and 5 g/l were used in the batch equilibrium experiments along with

spiked wastewater solutions of 0.5, 1, 3, 5, 8, 10, 13, 17, and 20 mg/l of diclofenac. At intervals ranging from three minutes to twenty-four hours, the percentage of diclofenac uptake was measured. According to the findings', activated carbon has a quick adsorption mechanism.

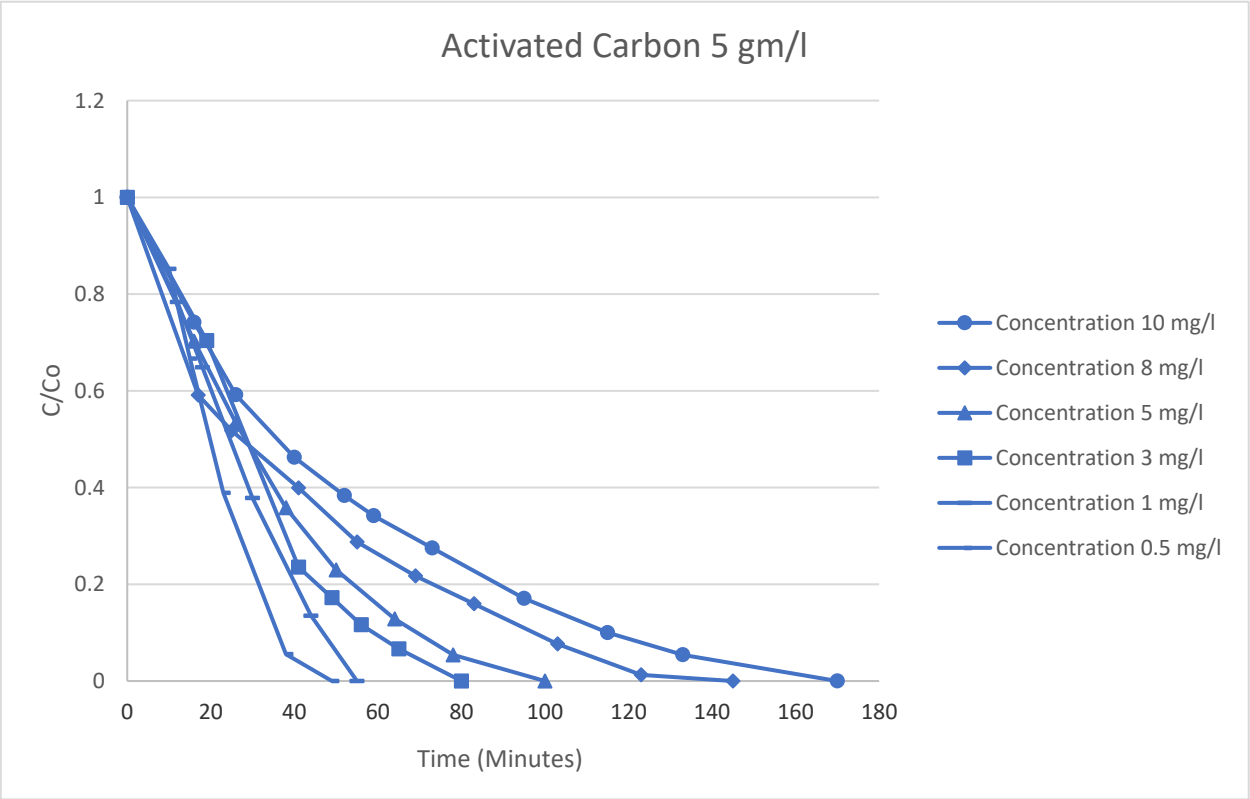

Figure 4-6: Batch Adsorption Rate of 5 gm/l Activated Carbon with Different Concentrations of Diclofenac Sodium Concentrations (0.5 – 10 mg/l)

At sorbent dose of 5 gm/l where 1 gram of activated carbon was added to 200 ml of diclofenac spiked wastewater solution, the higher the dosage of activated carbon the faster the adsorption rate of diclofenac for all concentrations. All concentrations reached 100% removal rate of diclofenac at different times. At concentrations 1 mg/l and 3 mg/l the time of adsorption was reduced by more than 47% and 68%, respectively, after doubling the activated carbon dosage from 2.5 to 5 mg/l.

At low initial concentration of 0.5 mg/l the removal uptake reaches its optimum at 50 minutes. While when the concentration increases the removal takes more time where it

reaches 170 minutes at 10 mg/l with the same sorbent concentration. Also, the contact time increases with the increase of the concentration noticeably in a non-linear pattern. For example, at concentration 5 mg/l the contact time at equilibrium was 100 minutes while at concentration 10 mg/l the contact time at equilibrium was 170 minutes, approximately, this indicates that doubling the concentration does not mean doubling the contact time to be reached at equilibrium.

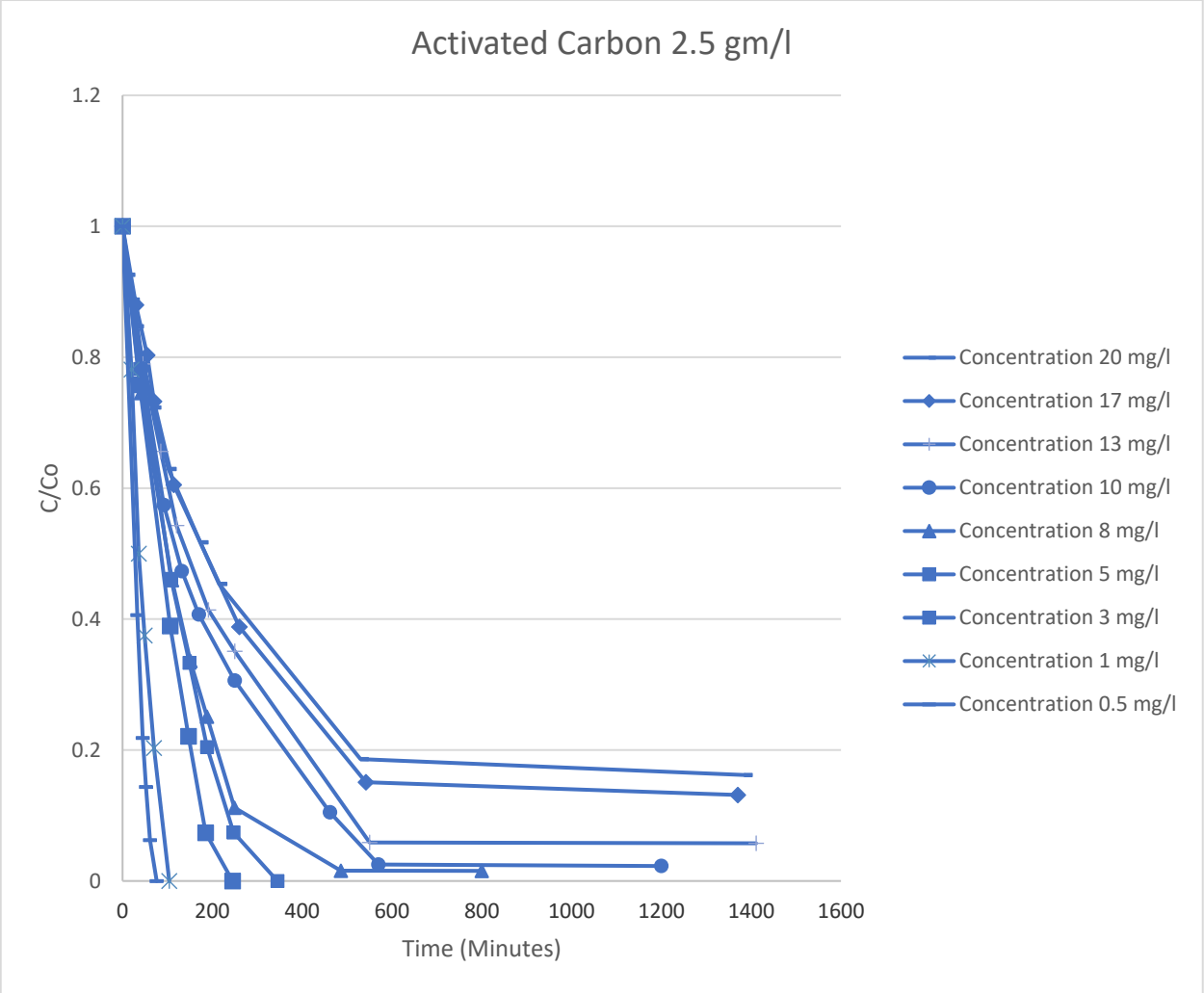

Figure 4-7: Batch Adsorption Rate of 2.5 gm/l Activated Carbon with Different Concentrations of Diclofenac Sodium (0.5 - 20 mg/l)

As expected, in Figure 4-7, the rate of diclofenac removal increased slower than the previous dosage. Concentrations of diclofenac from 0.5 – 5 mg/l were completely

removed. Concentrations from 8 – 20 mg/l reached more than 80% removal rate at approximately 600 minutes. The pattern shows that the higher the diclofenac concentration the slower the adsorption occurs at same time. Lower doses of activated carbon (1 mg/l and 0.5 gm/l) is used to evaluate the removal efficacies in different concentrations shown in Figure 4-8 and Figure 4-9.

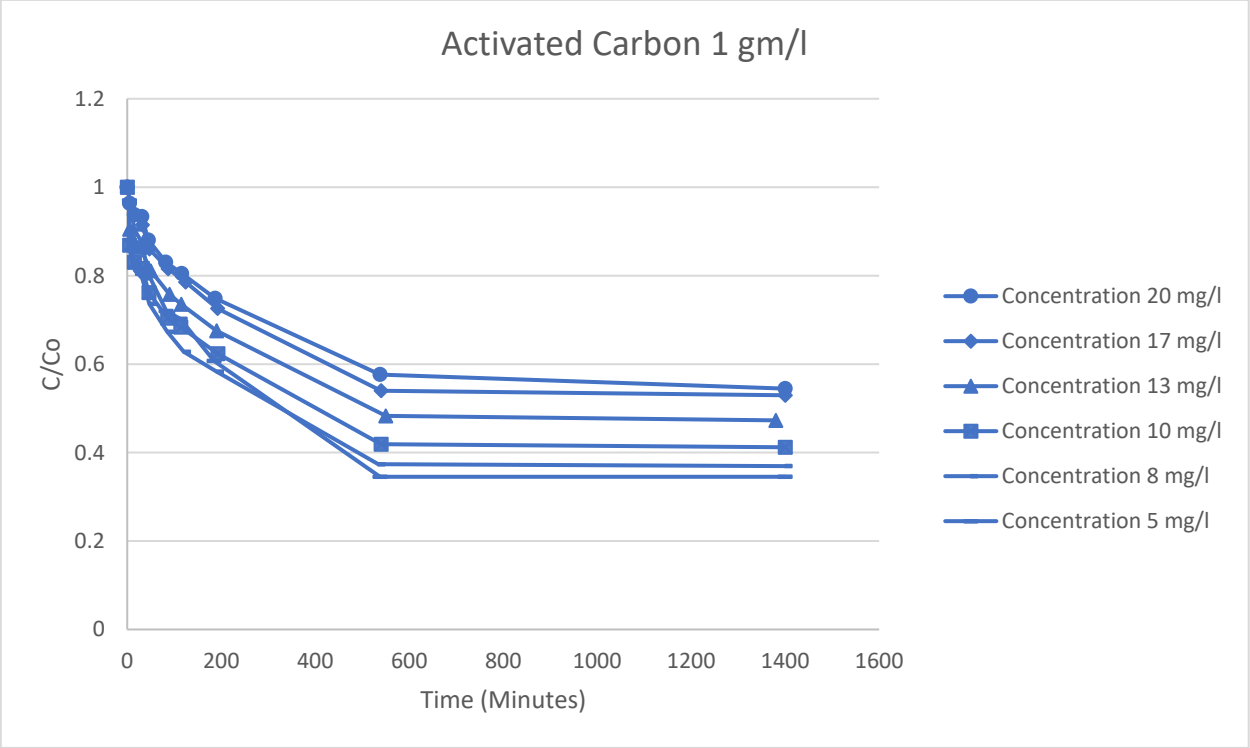

Figure 4-8: Batch Adsorption Rate of 1 gm/l Activated Carbon with Different Concentrations of Diclofenac Sodium (5 - 20 mg/l)

Figure 4-8 demonstrates that the first 185 minutes of the experiment's runs are when diclofenac adsorption occurs at a high rate. Most of the concentrations used exceeded 30% removal after 200 minutes and the removal slowly decreases until it reaches 540 minutes where concentrations reached equilibrium concentration. For example, at initial concentration 20 mg/l after 540 minutes the concentration reached 11.4 mg/l. Concentrations from 5 mg/l to 20 mg/l were removed by the activated carbon with percentages from 65% to 47%, respectively. Moreover, Ce/Co decreases at the same equilibrium time when compared with the 2.5 gm/l dose. For example, for doses 2.5 mg/l

and 1 mg/l at initial concentration 20 mg/l equilibrium was reached at approximately 540 minutes for both doses.

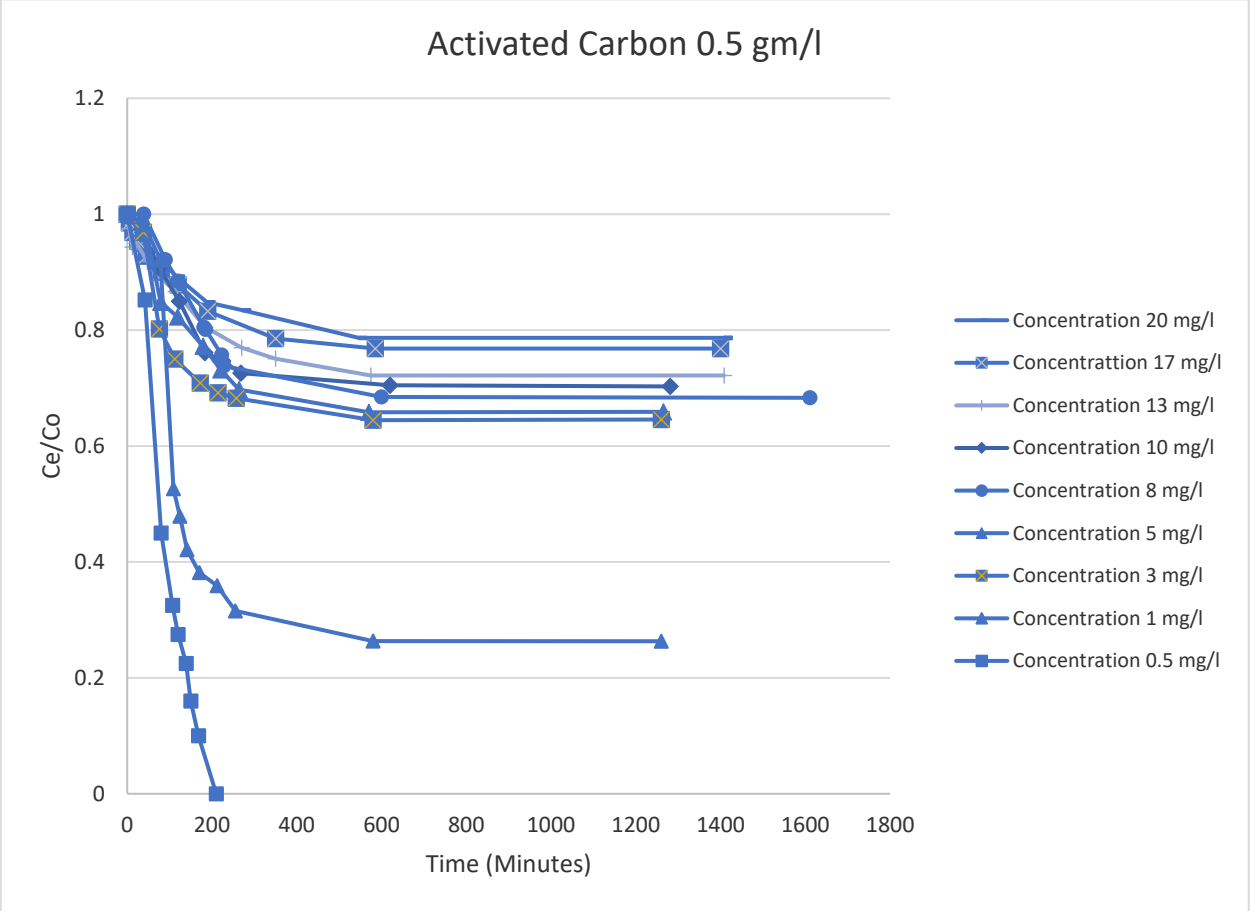

Figure 4-9: Batch Adsorption Rate of 0.5 gm/l Activated Carbon with Different Concentrations of Diclofenac Sodium (0.5 - 20 mg/l)

A wide range of concentrations were used to study the specific uptake of the activated carbon in relation to the contact time, as shown in Figure 4-9. As expected, the lower the activated carbon dose the less the removal percentage of the diclofenac from wastewater by the activated carbon. It can be clearly conducted that the less the activated carbon dose used the more time taken to the diclofenac to be completely adsorbed. The small concentration 0.5 mg/l was fully removed from the diclofenac wastewater solution in 210 minutes which is the higher contact time needed compared to the activated carbon dosage of 2.5 mg/l and 5 mg/l. While the remaining concentrations reached equilibrium at approximately 600 minutes. At dose 0.5 gm/l the removal percentages from concentration

3 mg/l to 20 mg/l reached 45% to 25%, respectively. The least removal percentage was recorded at concentration 20 mg/l (25%) while the highest removal percentage was recorded at concentration 1 mg/l (75%). The smaller concentration (0.5 mg/l) took 76% less time from using dosages 0.5 to 5 mg/l of activated carbon with same conditions and took 35% less time by using dosages from 2.5 to 5 mg/l.

4.2 Adsorption Isotherm

Knowing adsorption capacity and identifying the system's important operational conditions is of great importance, to be able to achieve maximum efficiency. In addition, we might be helped by adsorption isotherms to increase the adsorption mechanism. For the purpose of this work, two isotherm models have been selected: Freundlich and Langmuir Isotherms.

4.2.1. Freundlich Isotherm

Freundlich isotherm model represents a nonlinear adsorption phenomenon, and it is known to be more accurate dealing with low concentrations. The Model assumes that the sorption happened on more than one layer (JianlongWang, XuanGuo, 2020). The Equation is as follows:

$$qe = K_f \times Ce^{1/n} \quad \text{(Freundlich, 1906)}$$

$$\log qe = \log K_f + \frac{1}{n} \log Ce \quad \text{(J. Wang, et al, 2020)}$$

Where K_f and n are Freundlich constants which integrate all factors affecting the adsorption process, such as adsorption capacity and intensity of adsorption.

The equilibrium data resulting from the batch equilibrium experiment runs were fitted with Freundlich Isotherm model. The Freundlich adsorption isotherm of Diclofenac sodium compound using activated carbon are shown in Table 4-2 and Table 4-5 . The linear plot of the Freundlich equation is depicted in Figure 4-10 through Figure 4-12, and

Table 4-6 lists the adsorption parameters that were calculated from these figures. The adsorption rate and strength are measured by the parameters Kf and 1/n.

Table 4-2. The linear plot of the Freundlich equation is depicted in Figure 4-10 through Figure 4-12, and Table 4-6 lists the adsorption parameters that were calculated from these figures. The adsorption rate and strength are measured by the parameters Kf and 1/n.

Table 4-2: Freundlich Adsorption Isotherm of Diclofenac Sodium using Activated Carbon (0.5 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	Log Ce	Log Qe
0.1	2.96	1.91	0.2	2.10	0.28	0.32
0.1	4.88	3.21	0.2	3.33	0.51	0.52
0.1	7.47	5.10	0.2	4.73	0.71	0.68
0.1	9.66	6.79	0.2	5.74	0.83	0.76
0.1	13.64	9.85	0.2	7.59	0.99	0.88
0.1	16.85	12.95	0.2	7.81	1.11	0.89
0.1	20.40	16.05	0.2	8.70	1.21	0.94

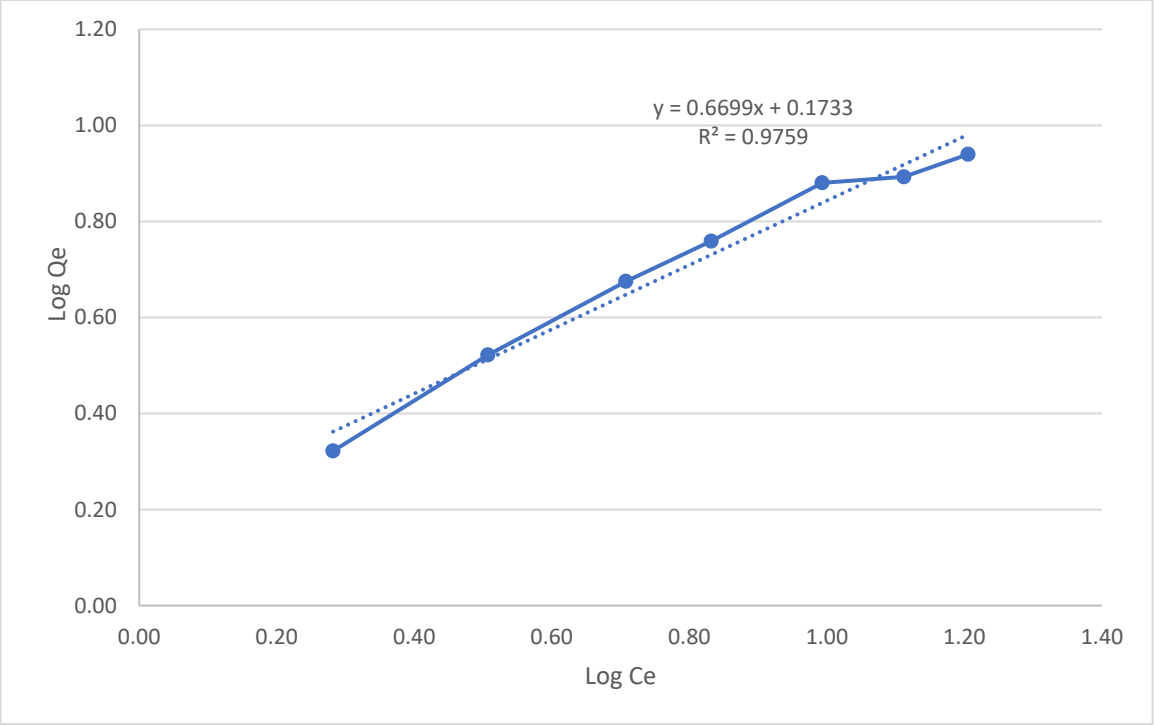

Figure 4-10: Freundlich Adsorption Isotherm for Diclofenac Sodium Adsorption (0.5 gm/l Activated Carbon)

Table 4-3: Freundlich Adsorption Isotherm of Diclofenac sodium using activated carbon (1 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	Log Ce	Log Qe
0.2	5.2	1.790	0.2	3.395	0.25	0.53
0.2	8.0	2.955	0.2	5.045	0.47	0.70
0.2	10.0	4.120	0.2	5.880	0.61	0.77
0.2	13.6	6.451	0.2	7.191	0.81	0.86
0.2	16.6	8.781	0.2	7.799	0.94	0.89
0.2	20.4	11.111	0.2	9.290	1.05	0.97

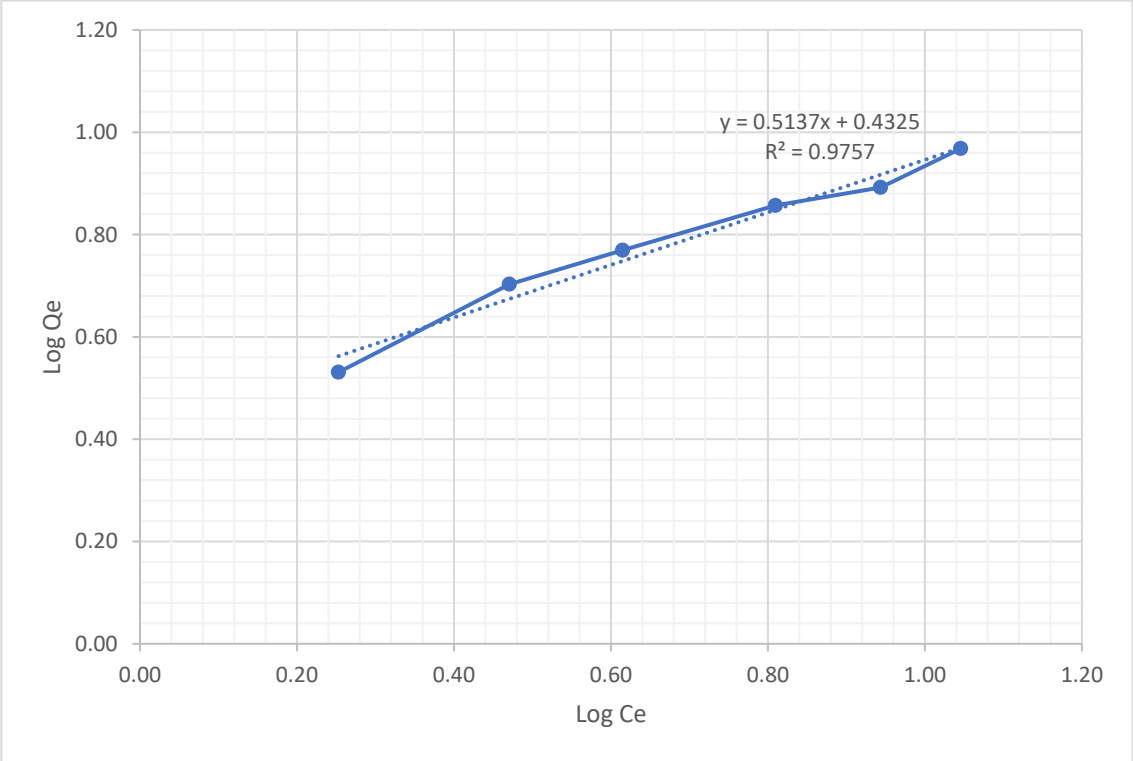

Figure 4-11: Freundlich Adsorption Isotherm for Diclofenac Sodium Adsorption (1 gm/l Activated Carbon)

Table 4-4: Freundlich Adsorption Isotherm of Diclofenac sodium using activated carbon (2.5 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	Log Ce	Log Qe
0.5	7.99	0.12	0.2	3.15	-0.91	0.50
0.5	9.78	0.22	0.2	3.82	-0.65	0.58
0.5	13.64	0.79	0.2	5.14	-0.11	0.71
0.5	16.85	2.21	0.2	5.86	0.35	0.77
0.5	20.40	3.30	0.2	6.84	0.52	0.84

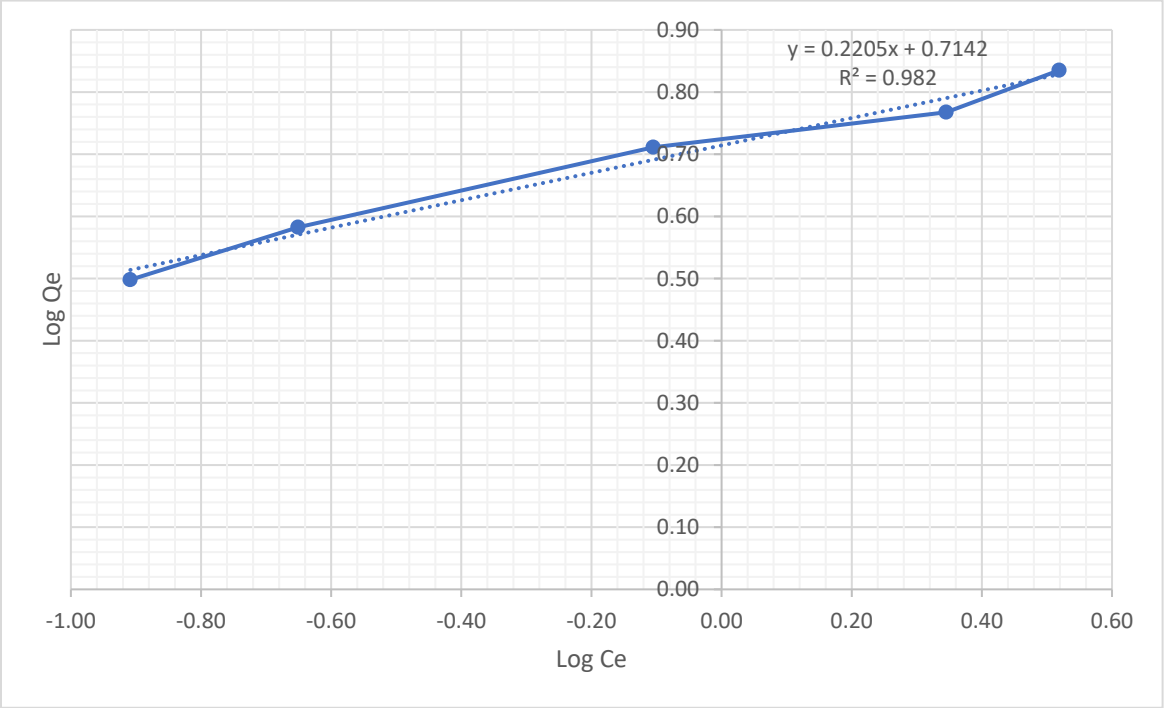

Figure 4-12: Freundlich Adsorption Isotherm for Diclofenac Sodium Adsorption (2.5 gm/l Activated Carbon)

Table 4-5: Freundlich Adsorption Parameters using Activated carbon.

Activated Carbon Doses (gm/l)	Log Kf	1/n	R^2	Kf	n
0.5	0.1733	0.6699	0.976	1.49	1.49
1	0.4325	0.5137	0.976	2.707	1.947
2.5	0.7142	0.2205	0.982	5.178	4.54

The linear correlation coefficients (R^2) show the fit between the experimental data and calculated linearized form of the isotherm equation. The higher the value of R2 the better the fit between the experimental and calculated data. Good linearity was obtained for Freundlich Isotherm as illustrated in Figure 4-10, Figure 4-11, and Figure 4-12 and summarized in Table 4-5.

4.2.2. Langmuir Isotherm

In the past, Langmuir has been used to rate the effectiveness of various sorbents. According to K. D. Hammond et al. (2013), This empirical model suggests monolayer adsorption, in which adsorption can only occur at a small number of localized, precise sites. The isotherm is used to determine both the equilibrium concentration of an element in its solid phase (qe, mg/g), as well as its equilibrium concentration in its aqueous phase (Ce, mg/l). The equation is as follows:

$$qe = \frac{q_{max} \times K \times C_e}{1+(K \times C_e)} \text{ (Langmuir, 1918)}$$

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_{m \times K_L}}\right) \times \frac{1}{Ce}$$

Where;

- Qe: is the mass of diclofenac sodium absorbed per gram of adsorbent.

- Ce: is the equilibrium concentration in liquid phase, (mg/liter)
- K_L: is the Langmuir constant, (liter/mg)
- Qm: Monolayer coverage, (mg of Diclofenac Sodium/gm of adsorbent)

The Langmuir isotherm model was used to fit the equilibrium data obtained from the batch equilibrium experiment runs. Table 4-6 and Figure 4-13 display the Diclofenac Langmuir adsorption parameters. Additionally, Table 4-6 provides an overview of the adsorption parameters and the linear plot of the Langmuir equation.

Table 4-6: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (0.5 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	1/q	1/Ce	Ce/Qe (gm/l)
0.1	2.96	1.91	0.2	2.10	0.48	0.52	0.91
0.1	4.88	3.21	0.2	3.33	0.30	0.31	0.97
0.1	7.47	5.10	0.2	4.73	0.21	0.20	1.08
0.1	9.66	6.79	0.2	5.74	0.17	0.15	1.18
0.1	13.64	9.85	0.2	7.59	0.13	0.10	1.30
0.1	16.85	12.95	0.2	7.81	0.13	0.08	1.66
0.1	20.40	16.05	0.2	8.70	0.11	0.06	1.84

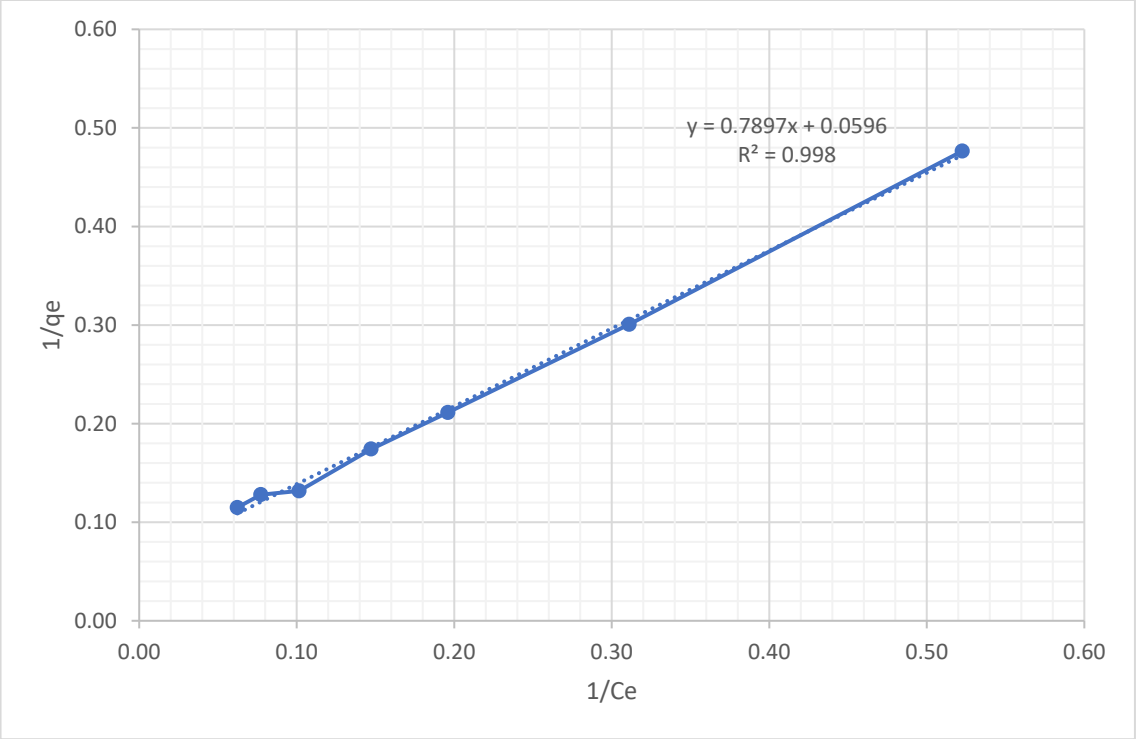

Figure 4-13: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (0.5 gm/l Activated carbon)

Table 4-7: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (1 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	1/q	1/Ce	Ce/Qe (gm/l)
0.2	5.2	1.790	0.2	3.395	0.29	0.56	0.53
0.2	8.0	2.955	0.2	5.045	0.20	0.34	0.59
0.2	10.0	4.120	0.2	5.880	0.17	0.24	0.70
0.2	13.6	6.451	0.2	7.191	0.14	0.16	0.90
0.2	16.6	8.781	0.2	7.799	0.13	0.11	1.13
0.2	20.4	11.111	0.2	9.290	0.11	0.09	1.20

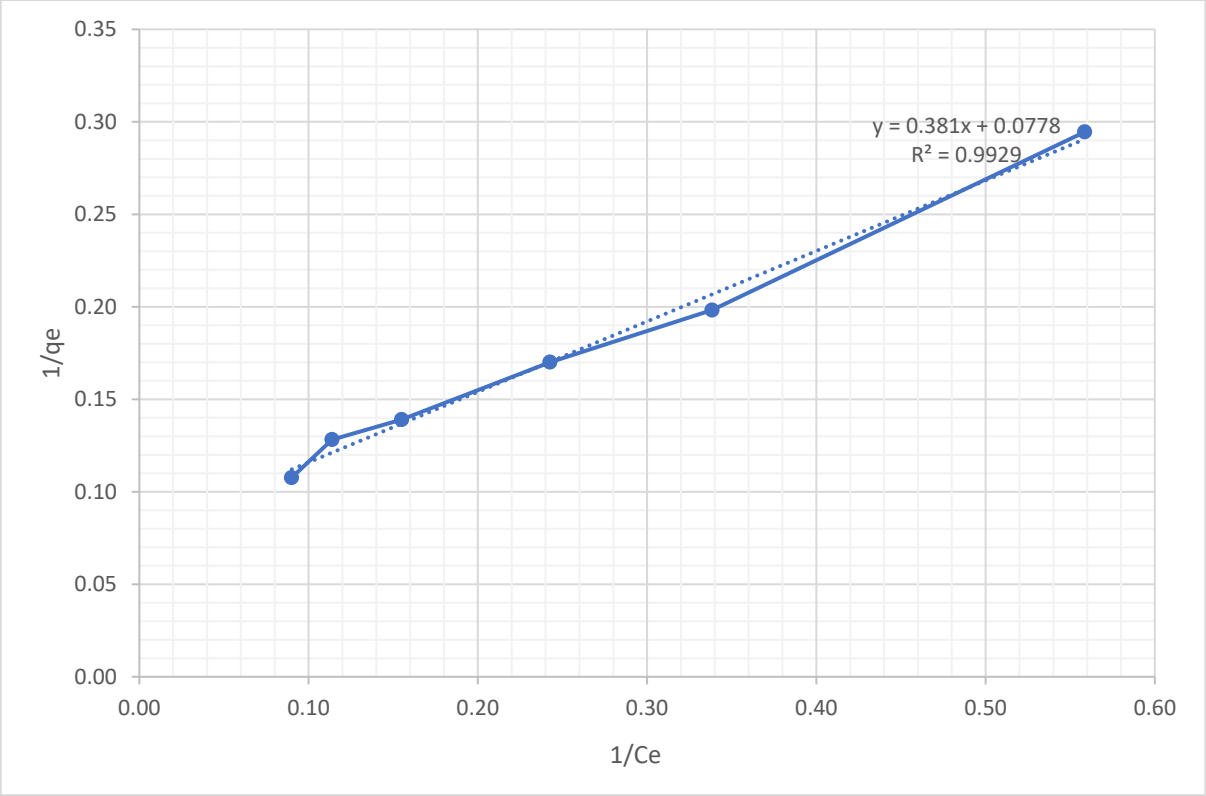

Figure 4-14: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (1 gm/l Activated carbon)

Table 4-8: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (2.5 gm/l Activated carbon)

Mass (gm)	Initial Conc. (Ci) (mg/l)	Equilibrium Conc. (Ce) (mg/l)	Volume (L)	Qe (mg/gm)	1/q	1/Ce	Ce/Qe (gm/l)
0.5	7.99	0.12	0.2	3.15	0.32	8.10	0.04
0.5	9.78	0.22	0.2	3.82	0.26	4.48	0.06
0.5	13.64	0.79	0.2	5.14	0.19	1.27	0.15
0.5	16.85	2.21	0.2	5.86	0.17	0.45	0.38
0.5	20.40	3.30	0.2	6.84	0.15	0.30	0.48

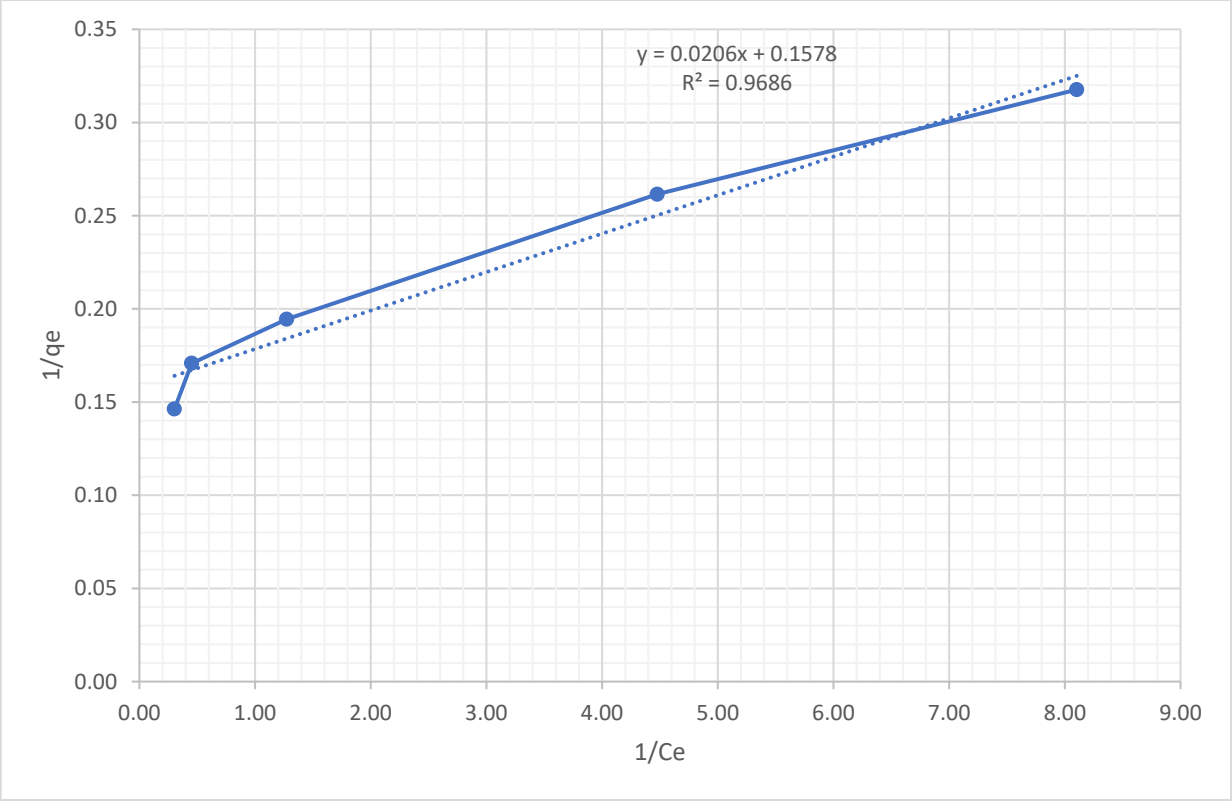

Figure 4-15: Langmuir Isotherm for the Adsorption for Diclofenac Sodium (2.5 gm/l Activated carbon)

Table 4-9: Langmuir Isotherm Parameters for Diclofenac Sodium Adsorption by Activated carbon.

Activated Carbon Doses (gm/l)	1/qm	1/qm . K_L	R^2	K_L	qm
0.5	0.0596	0.7897	0.998	0.0755	16.779
1	0.0078	0.381	0.9929	0.0204	128.205
2.5	0.1578	0.0206	0.986	7.6602	6.337

From the R^2 values, the fit to the Langmuir equation was better than that to the Freundlich. Moreover, the values of maximum adsorption capacity obtained using the Langmuir equation match better with the experimental data than those calculated by the Freundlich equation.

4.3 Column Experiments

As a baseline case to test the impact of bed height, initial diclofenac concentration, and flow rate on fixed bed behavior in subsequent column experiments, a column (with internal diameter 1.2 cm and 13 cm total height) was used with different initial diclofenac solution concentrations (3 – 20 mg/l), different bed heights (1 – 1.7 gm), and different flow rates (3 – 6 ml/min). The purpose of this was to investigate diclofenac adsorption using column system which is applied in many full-scale treatment systems.

4.1.1. Different Flow rates

For a meaningful comparison, the effluent concentrations should be compared with the bed volumes rather than the run time. The varied flow rates and run times are to the reason for this. Calculating the different bed volumes is shown as follows:

$$Bed\ Volume\ = \frac{Volume\ of\ wastewater\ Treated}{Volume\ of\ used\ Activated\ carbon} = \frac{Flowrate\ \left(\frac{ml}{min}\right) \times Time\ (Minutes)}{Volume\ of\ used\ Activated\ carbon}$$

The effluent diclofenac concentrations at various times and bed volumes are shown in Table 4-10 below. The amount of wastewater that has passed through the densely packed column of activated carbon is measured by the bed volume.

Table 4-10: Effluent Data for Column Experiments for Different Flow Rates

Flow rate (3 ml/min)			Flow rate (4 ml/min)			Flow rate (6 ml/min)		
Time (Hour)	**C_{eff}/Co**	**Bed Volumes**	**Time (Hour)**	**C_{eff}/Co**	**Bed Volumes**	**Time (Hour)**	**C_{eff}/Co**	**Bed Volumes**
0	0	0	0	0	0	0	0	0
10	0	0	10	0.146	9.278	10	0	0
20	0.4212	13.943	20	0.4482	20.618	20	0.6004	29.591
30	0.4988	22.234	30	0.5433	30.927	30	0.6628	44.387
50	0.5861	36.950	50	0.6791	51.545	55	0.7349	81.375
100	0.6458	67.626	100	0.7623	103.090	105	0.7779	155.353
150	0.6667	102.485	150	0.7670	164.944	160	0.7849	236.728
450	0.7123	313.728	450	0.7843	474.214	385	0.8095	569.627
600	0.7214	418.304	670	0.8014	685.548	625	0.8380	924.720
800	0.75	557.739	800	0.8214	824.720	780	0.8612	1154.05

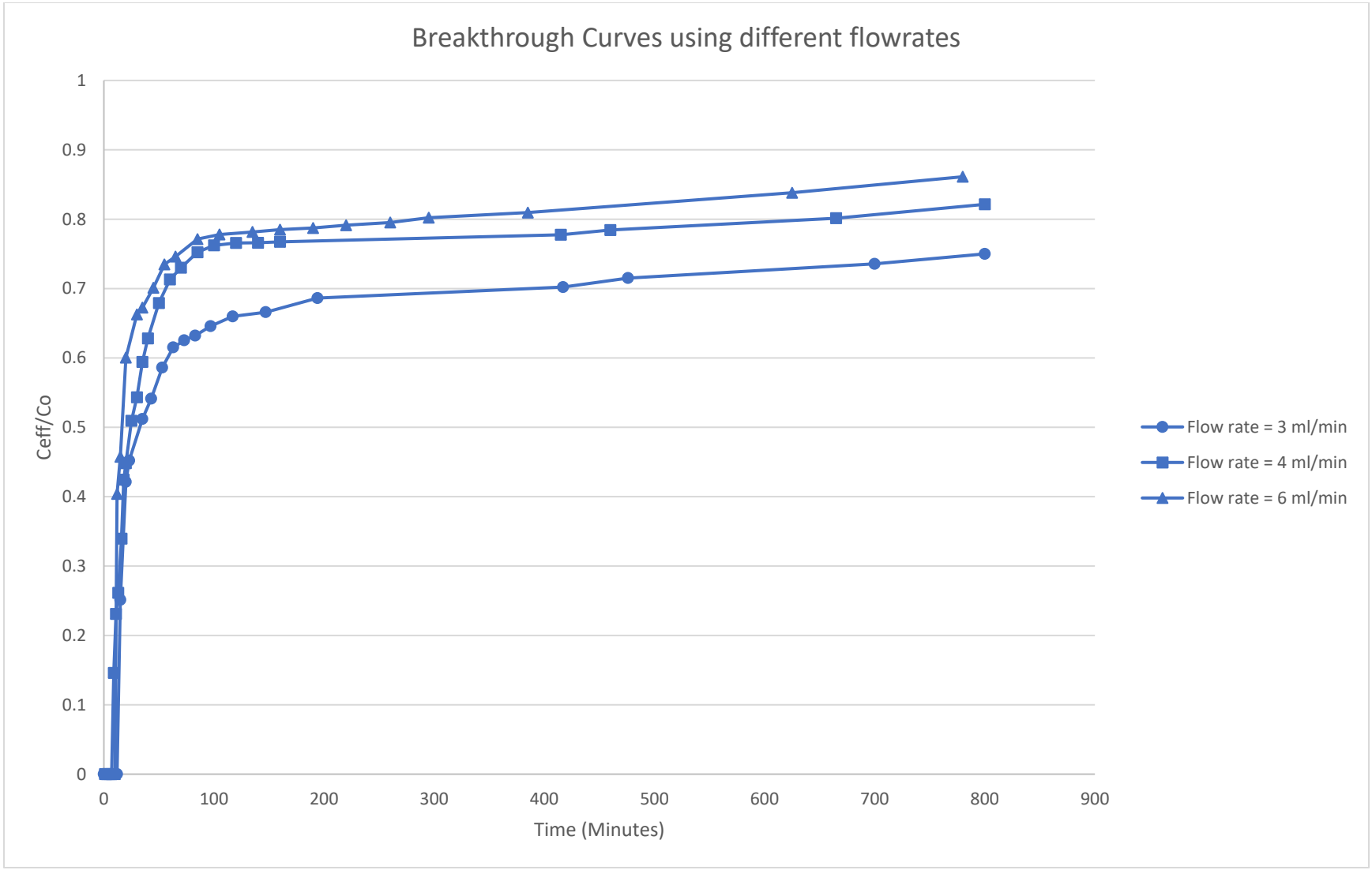

Figure 4-16: Breakthrough Curves using Different Flowrates

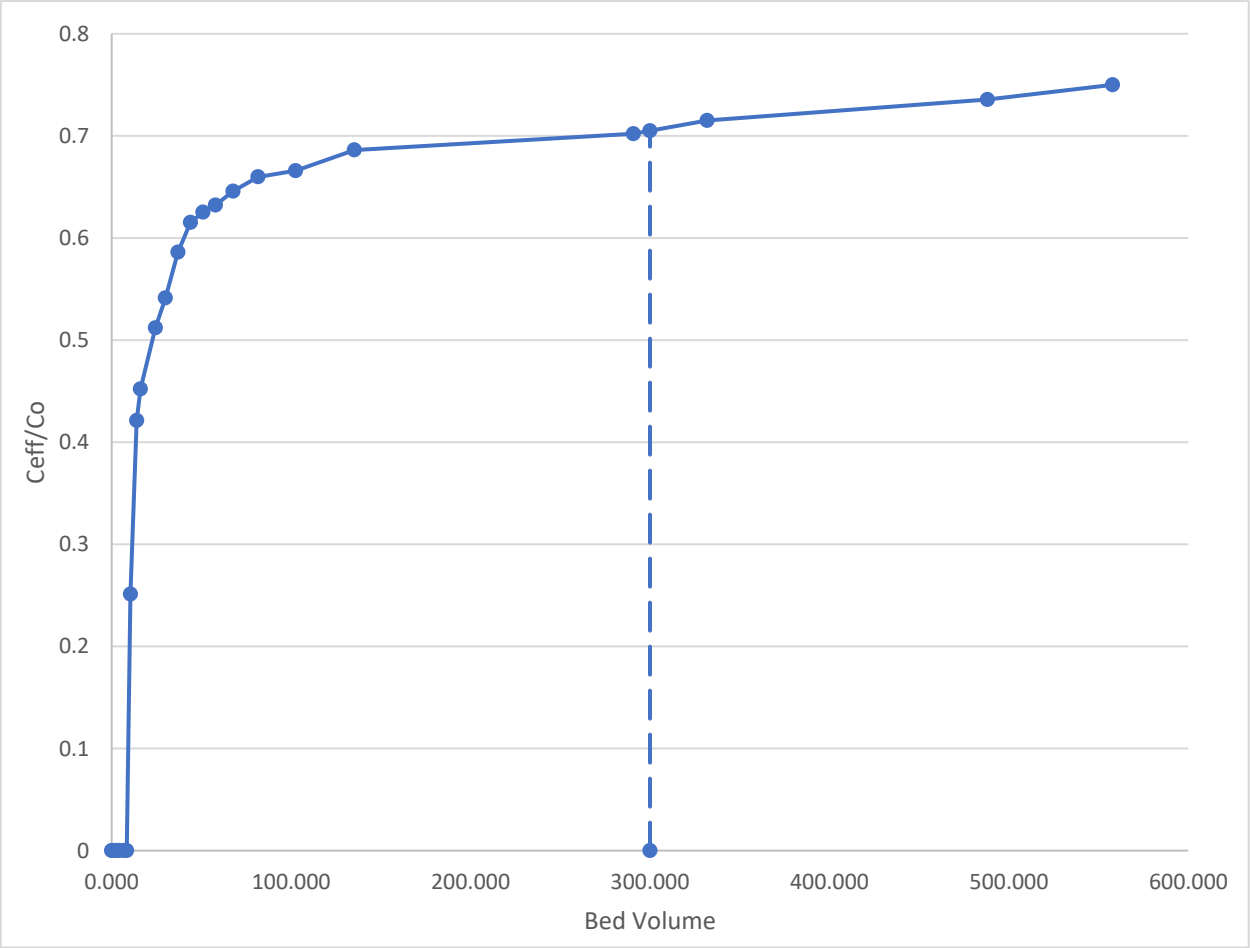

Figure 4-17: Breakthrough Curve of diclofenac versus Bed volumes (Initial concentration = 10 mg/l , Activated carbon = 1 grams, and flow rate = 3 ml/min)

Both Figure 4-17 and Figure 4-18 depicts the breakthrough of diclofenac sodium versus time and bed volumes. It is shown that effluent concentration reaches approximately 70% of the initial concentration after almost 7 hours. At bed volume 300 and time 417 minutes the curve started to flatten and slight changes were shown after words therefore this is considered the time of equilibrium of the column.

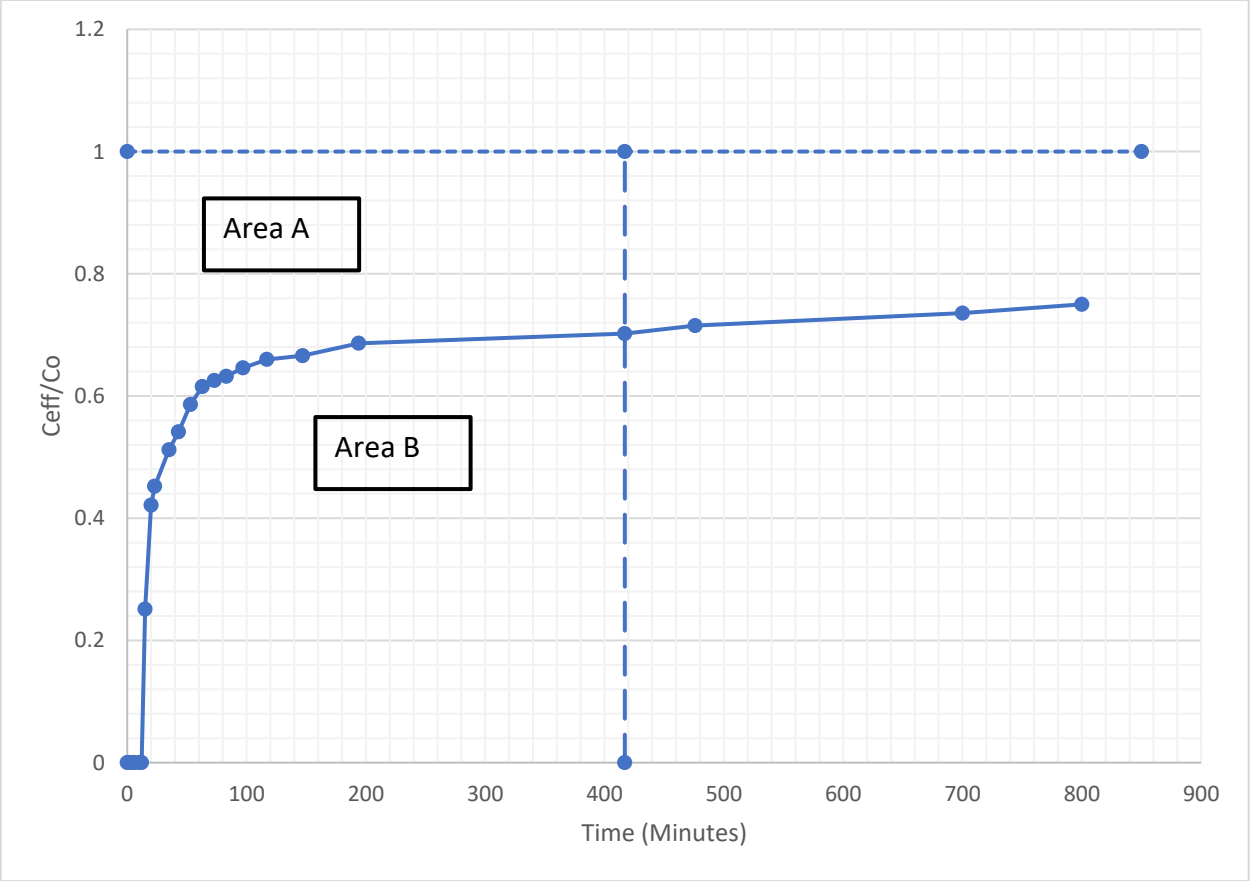

Figure 4-18: Effluent diclofenac Concentration versus Time (Initial concentration = 10 mg/l , Activated carbon = 1 grams, and flow rate = 3 ml/min)

The breakthrough curve is shown in Figure 4-17. The maximum breakthrough, where Ceff/Co was increasing until the experiment's end, is seen to occur above 300 bed volumes. Following were the calculations used to determine surface concentration at the end of the run:

F = flowrate = 0.0026 L/min (As calculated experimentally).

tf = Time until equilibrium = 417 minutes.

$$M\ Passing\ = (F\ \times tf \times Co) = 0.0026\ \times 417\ \times 10\ = 10.85\ mg$$

$$\frac{M\ ads}{M\ passing} = \frac{A}{A+B} = \frac{131}{232+131} = 0.36$$

$$M\ ads\ = \frac{A}{A+B} \times M\ passsing\ = 4.133\ mg$$

$$\text{Surface concentration at exhaustion}\ = \frac{M\ ads}{Mass\ of\ Activated\ carbon\ in\ column} = \frac{4.133}{1}$$

$$= 4.133\ mg/g$$

Where:

- A= Area corresponding to the adsorbed part.
- B= Area corresponding to the un-adsorbed part.
- M passing= Mass of diclofenac passing through the column
- M ads= Mass of diclofenac adsorbed by the activated carbon
- F= Volumetric diclofenac solution flow rate through the column (L/min)
- tf= Total time of the column run (minutes) until exhaustion
- C_o= Influent Concentration of diclofenac spiked wastewater (mg/l)

Area A and area B were calculated using a grid method to calculate the area under the curve in cm^2.

Given that the column is empty of packing, the Empty Bed Contact Time (EBCT) calculates the amount of time a fluid parcel spends inside the column. It can be calculated easily by dividing the column volume (in mL) by the liquid's volumetric flow rate (in mL/min).

The height of the column bed directly affects the EBCT. The bed size and volume, the hydraulic rating rate (mL/min /Area) and the EBCT were computed to establish the amount of time needed for wastewater recovery. When creating the bed column, the EBCT is seen to be crucial. The performance of the packed activated carbon is significantly impacted by the EBCT, making it a vital consideration for building the bed column.

- Empty bed contact time (EBCT)

- $EBCT = \frac{V}{Q} = \frac{Lbed}{\frac{Q}{A}} = {}^{3.73}/_{1.434} = 1.434\ minutes$

Where the Volume= the column area multiplies by the packed activated carbon length in the column=

$$\pi\, r^2\, x\, L = \pi \left(\frac{1.2}{2}\right)^2 (3.3) = 3.73\ cm^3$$

Hydraulic Loading Rate (HLR)= Design Flow divided by Cross Sectional Area

$$HLR = \frac{2.62}{\pi \times \frac{1.2^2}{2}} = 2.30\ cm/min$$

All the results of the column experiment are shown in the following Table 4-11.

Table 4-11: Analysis of the Column Experiment for initial concentration 10 mg/l, flowrate 3 ml/min, and Activated Carbon used = 1 gram

Parameter	Value
Breakthrough Bed Volumes	300
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	4.133
Hydraulic Loading rate (HLR) (cm/min)	2.30
Empty Bed Contact Time (EBCT) (minutes)	1.434

The contact time was changed in each experiment by changing the flowrates for each experiment (3, 4, and 6 ml/min) and keeping the same bed height and initial concentration.

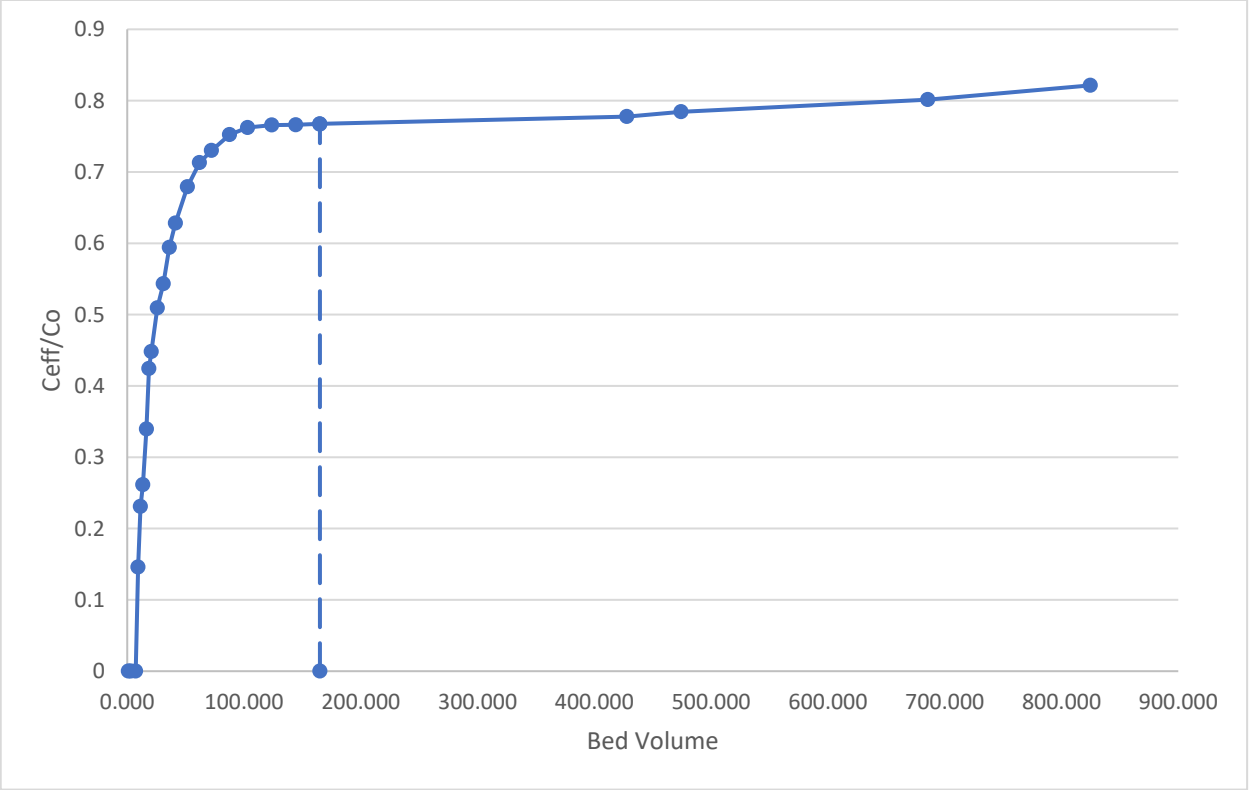

Figure 4-19: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 10 mg/l , Activated carbon = 1 grams, and flow rate = 4 ml/min)

Both Figure 4-19 and Figure 4-20 both depict the breakthrough of sodium diclofenac in relation to time and bed volumes. It is demonstrated that after almost 2.75 hours, the effluent concentration has reached nearly 77% of its initial value.

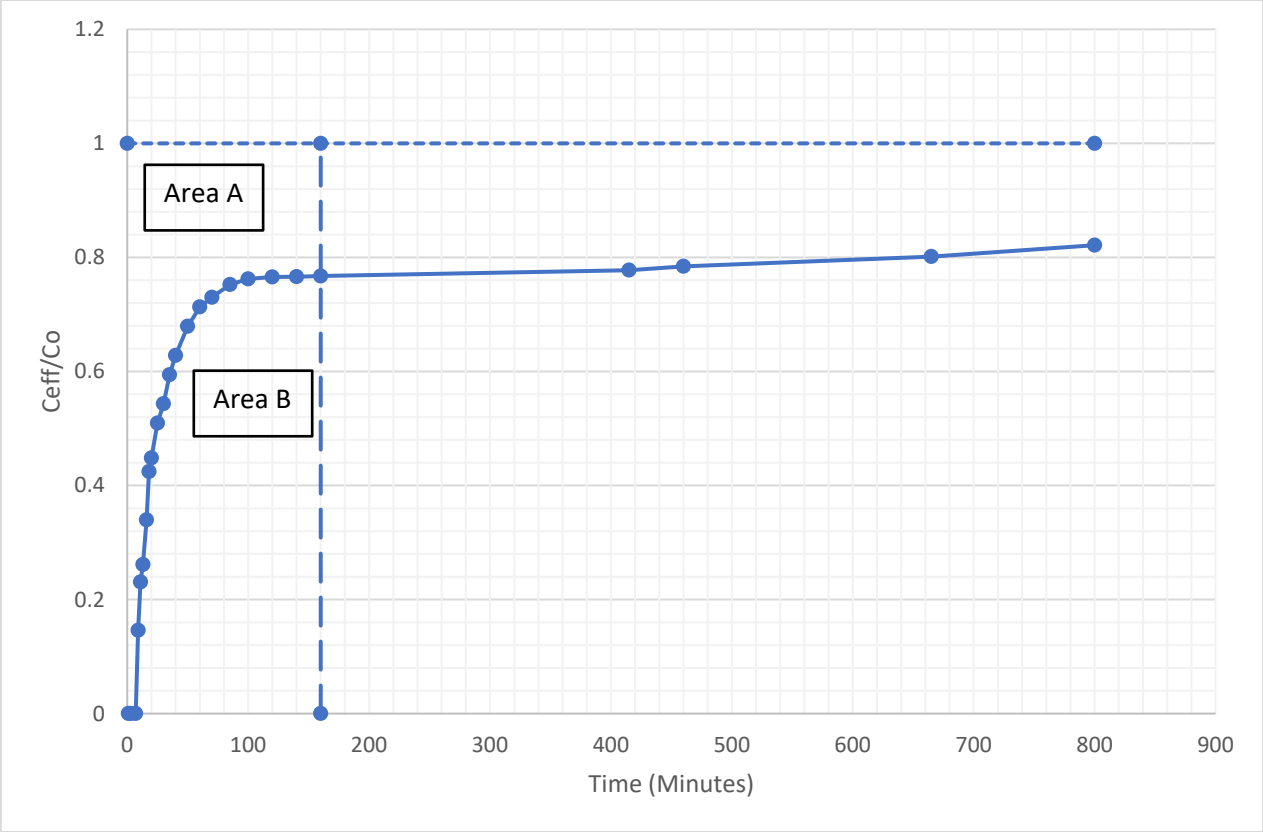

Figure 4-20: Effluent diclofenac Concentration versus Time (Initial concentration = 10 mg/l, Activated carbon = 1 grams, and flow rate = 4 ml/min)

$$M\ Passing\ = (F\ \times tf \times Co) = 0.0038\ \times 165\ \times 10\ = 6.34\ mg$$

$$\frac{M\ ads}{M\ passing} = \frac{A}{A+B} = \frac{65}{65+124} = 0.343$$

$$M\ ads\ = \frac{A}{A+B} \times M\ passsing\ = 2.18\ mg$$

$$\text{Surface concentration at exhaustion}\ = \frac{M\ ads}{Mass\ of\ Activated\ carbon\ in\ column} = \frac{2.18}{1}$$

$$= 2.18\ mg/g$$

$$EBCT\ = \frac{V}{Q} = \frac{Lbed}{\frac{Q}{A}} = {}^{3.73}/_{3.85} = 0.97\ minutes$$

$$HLR = \frac{3.85}{\pi \times \frac{1.2^2}{2}} = 3.40\ cm/min$$

Same calculation for the surface concentration was implemented as mentioned before for flow rate = 3 ml/min. Figure 4-20 summarizes the results of adsorbing diclofenac by the activated carbon material in a higher flowrate (flowrate = 4 ml/min). Table 4-12 summarizes the design-related calculations.

Table 4-12: Analysis of the Column Experiment for initial concentration 10 mg/l, flowrate 4 ml/min, and activated carbon used = 1 gram

Parameter	Value
Breakthrough Bed Volumes	165
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	2.18
Hydraulic Loading rate (HLR) (cm/min)	3.40
Empty Bed Contact Time (EBCT) (minutes)	0.97

As shown in the previous table the breakthrough bed volumes decreased as the flowrate increased and the EBCT also decreased as flowrate increase for this column experiment. Further experiments using higher flow rates, different bed heights, and different diclofenac concentrations were conducted to determine the behavior of the removal of diclofenac by the activated carbon.

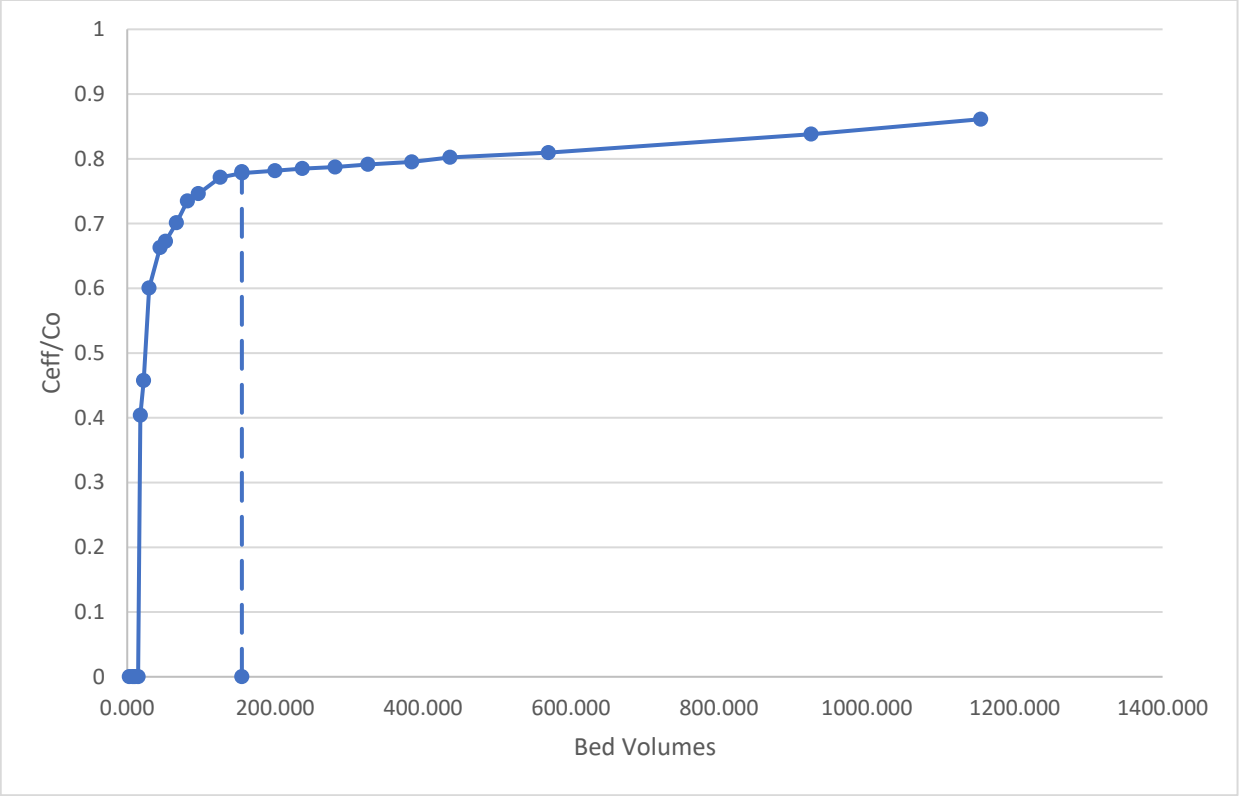

Figure 4-21: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 10 mg/l , Activated carbon = 1 grams, and flow rate = 6 ml/min)

Both Figure 4-21 and Figure 4-22 both depict the breakthrough of sodium diclofenac in relation to time and bed volumes. It is demonstrated that after almost 1.75 hours, the effluent concentration has reached nearly 79% of its initial value. Although the flowrate nearly doubled from 3 ml/min to 6 ml/min, it is shown that the breakthrough time was not doubled from flowrate 6 ml/min to 3 ml/min.

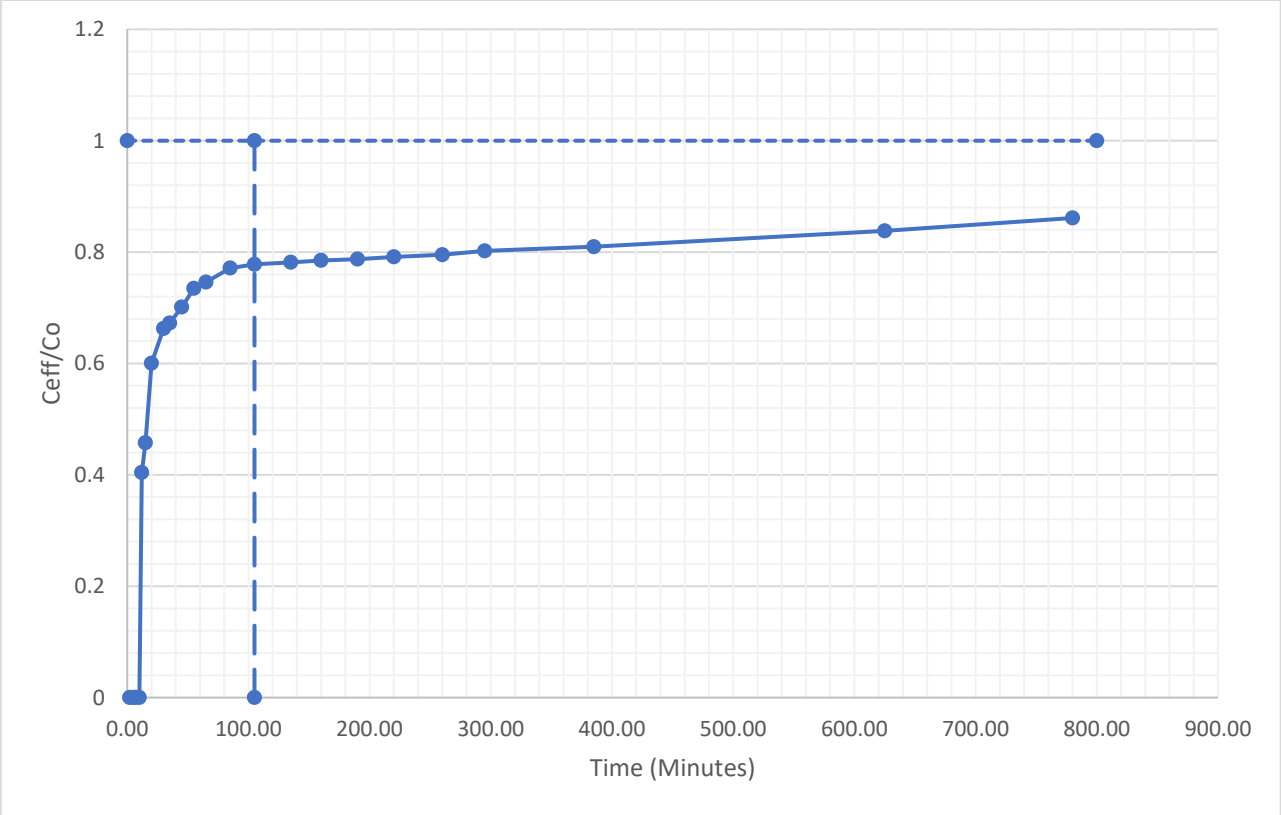

Figure 4-22: Effluent diclofenac Concentration versus Time (Initial concentration = 10 mg/l, Activated carbon = 1 grams, and flow rate = 6 ml/min)

$$M\ Passing\ = (F\ \times tf \times Co) = 0.0055\ \times 105\ \times 10\ = 5.798\ mg$$

$$\frac{M\ ads}{M\ passing} = \frac{A}{A+B} = \frac{46}{46+76} = 0.377$$

$$M\ ads\ = \frac{A}{A+B} \times M\ passsing\ = 2.186\ mg$$

$$\text{Surface concentration at exhaustion}\ = \frac{M\ ads}{Mass\ of\ Activated\ carbon\ in\ column} = \frac{2.186}{1}$$

$$= 2.186\ mg/g$$

$$EBCT\ = \frac{V}{Q} = \frac{Lbed}{\frac{Q}{A}} = {}^{3.73}/_{5.52} = 0.676\ minutes$$

$$HLR = \frac{5.52}{\pi \times \frac{1.2^2}{2}} = 4.88\ cm/min$$

Surface concentration calculations were performed as previously described for flow rates = 3 and 4 ml/min. Figure 4-22 summarizes the results of adsorbing diclofenac by the activated carbon material in a higher flowrate (flowrate = 6 ml/min). Table 4-12 summarizes the design-related calculations.

Table 4-13: Analysis of the Column Experiment for Initial Concentration 10 mg/l, flowrate 6 ml/min, and Activated Carbon used = 1 gram

Parameter	Value
Breakthrough Bed Volumes	155
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	2.186
Hydraulic Loading rate (HLR) (cm/min)	4.88
Empty Bed Contact Time (EBCT) (minutes)	0.68

As expected, it is obviously shown in the previous table the breakthrough bed volumes decreased as the flow rate increased and the EBCT also decreased as flowrate increase for this column experiment. It is obvious that the breakthrough bed volumes decreased as the flowrate increased but no significant changes occurred from 4 ml/min to 6 ml/min. However, a significant decrease (almost 50%) was observed from the flowrate 3 ml/min to 4ml/min and 6 ml/min. Moreover, the surface concentration at breakthrough decreased significantly from 3 ml/min to 4ml/min and 6 ml/min from 4.13 mg/g to 2.18 mg/g and 2.186 mg/g, respectively.

4.3.1. Different Bed Heights

In these set of experiments, different bed heights of activated carbon were used by adding different weights of activated carbon starting. Activated carbon weights used for these experiments were 1, 1.5, and 1.7 grams. Effluent concentration should also be compared to bed volume, not run time as in experiments at different flow rates.

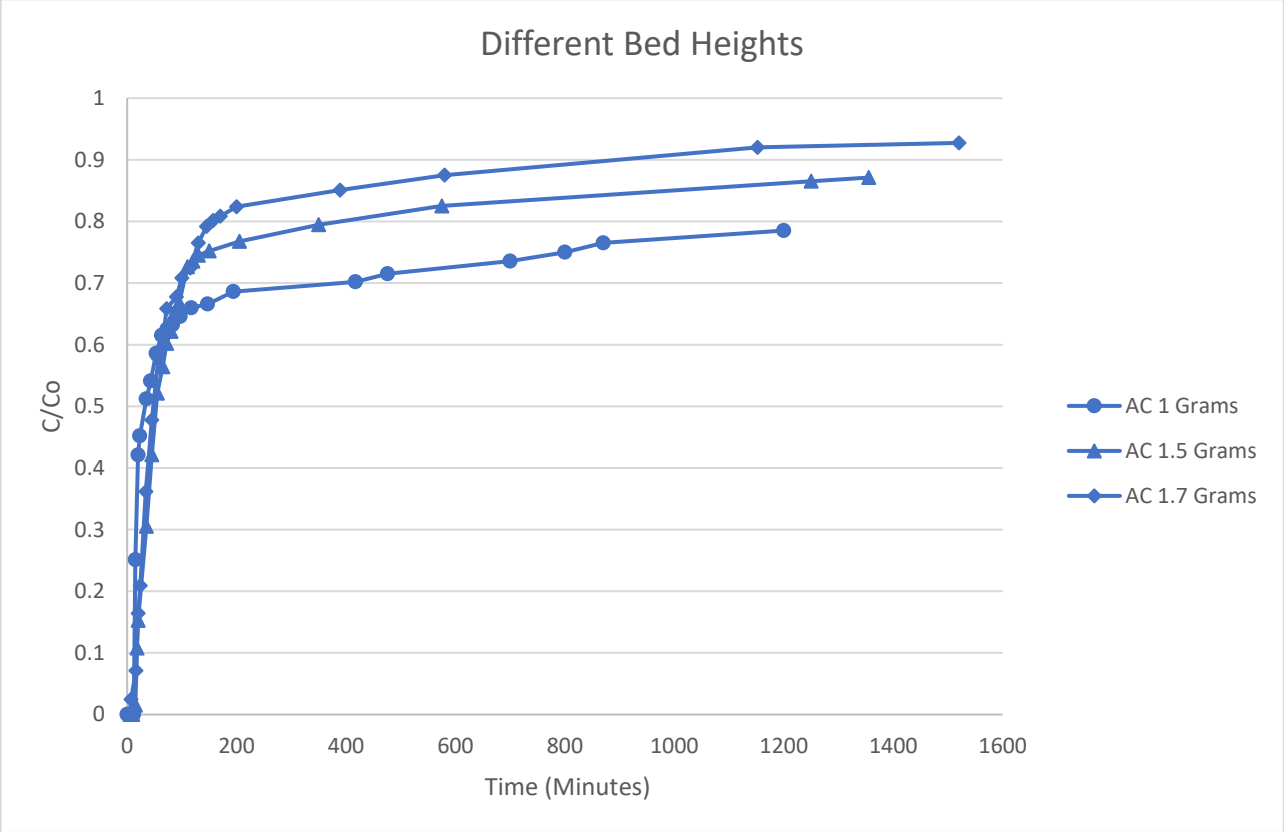

Figure 4-23: Breakthrough Curves using Different Bed Heights

Different bed heights from 3.3 cm to 7.5 cm were used in the change in bed heights experiments, to study the activated carbon adsorption behavior. Figure 4-23 depicts the breakthrough curves of different bed heights of activated carbon used (1, 1.5 & 1.7 grams). Same Flow rate (3 ml/min) and initial diclofenac concentration (10 mg/l) were used in the three experiments.

The results of the first experiment are shown in Figure 4-17 and Figure 4-18 above, and the results are summarized in Table 4-11.

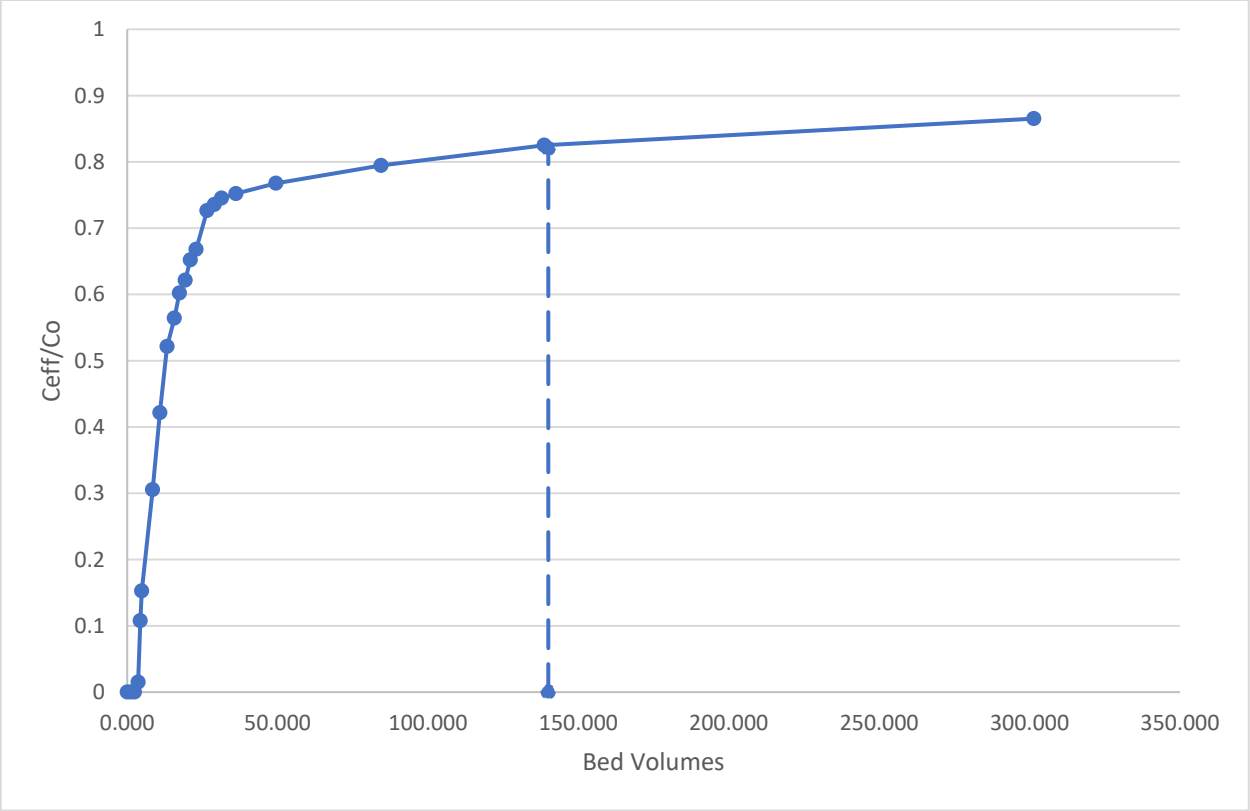

Figure 4-24: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 10 mg/l, Activated carbon = 1.5 grams, and flow rate = 3 ml/min)

Both Figure 4-24 and Figure 4-25 both depict the breakthrough of sodium diclofenac in relation to time and bed volumes. The bed height for this experiment was 5.5 cm. It is demonstrated that after almost 10 hours, the effluent concentration has reached more than 82% of its initial value. It also reached equilibrium 3 hours after the bed height of 3.3 cm where only 1 gram of activated carbon was used. Also, the bed volumes at breakthrough decreased from 3.3 cm 5.5 cm, therefore, the higher the layer height, the longer it takes to reach breakthrough and the less layer volume is required.

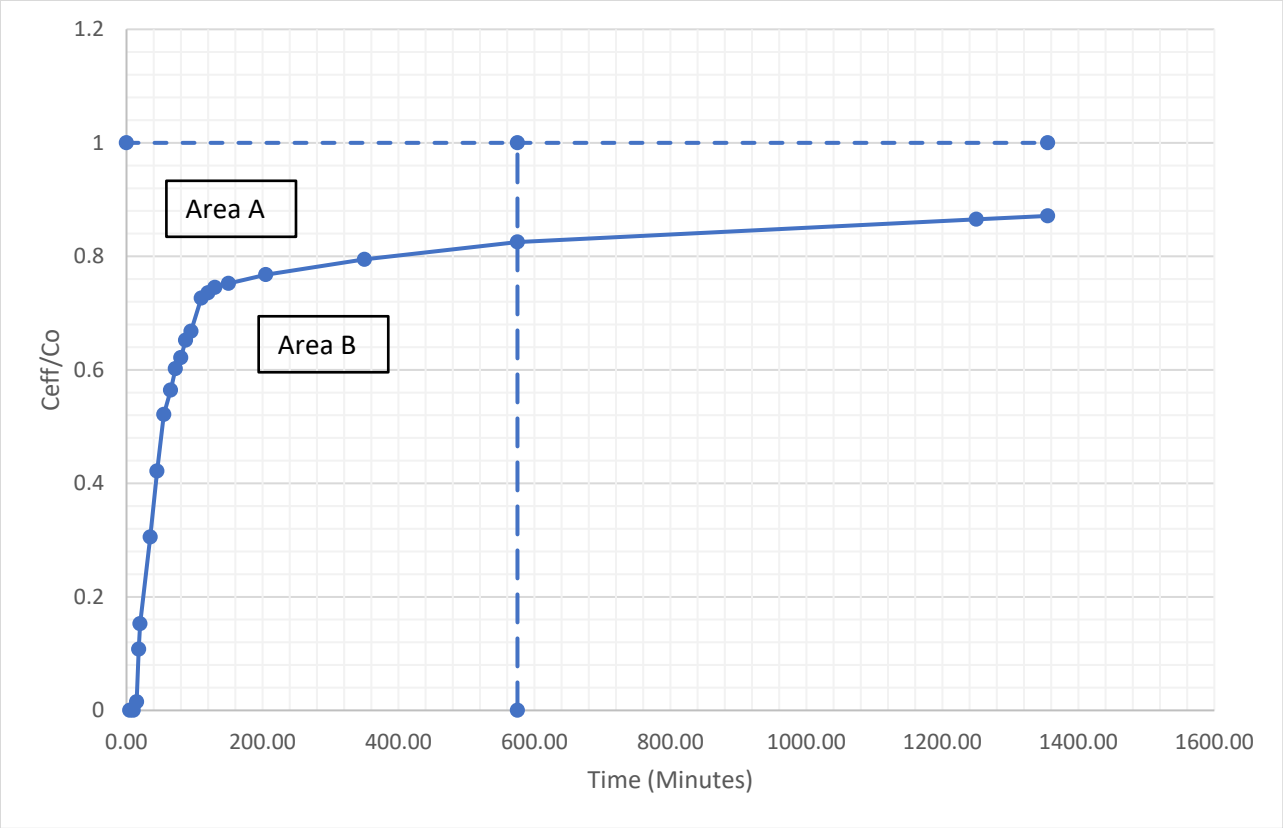

Figure 4-25: Effluent diclofenac Concentration versus Time (Initial concentration = 10 mg/l, Activated carbon = 1.5 grams, and flow rate = 3 ml/min)

Surface concentration calculations were performed as previously described in different flow rates experiments. Figure 4-25 summarizes the results of adsorbing diclofenac by the activated carbon material in a higher Bed height (Bed height = 5.5 cm). Table 4-14 summarizes the design-related calculations.

$$M\ Passing\ = (F\ \times tf \times Co) = 0.0026\ \times 575 \times 10\ = 14.96\ mg$$

$$\frac{M\ ads}{M\ passing} = \frac{A}{A+B} = \frac{97}{97+181} = 0.349$$

$$M\ ads\ = \frac{A}{A+B} \times M\ passsing\ = 5.22\ mg$$

Surface concentration at exhaustion $= \frac{M\ ads}{Mass\ of\ Activated\ carbon\ in\ column} = \frac{5.22}{1.5}$

$= 3.48\ mg/g$

$$EBCT = \frac{V}{Q} = \frac{Lbed}{\frac{Q}{A}} = {}^{6.22}/_{2.6} = 2.39\ minutes$$

Where the Volume= the column area x the packed activated carbon length in the column=

$$\pi\ r^2\ x\ L = \pi\left(\frac{1.2}{2}\right)^2 (5.5) = 6.22 cm^3$$

$$HLR = \frac{2.6}{\pi \times \frac{1.2^2}{2}} = 2.3\ cm/min$$

Table 4-14: Analysis of the Column Experiment for Initial Concentration 10 mg/l, flowrate 3 ml/min, and Activated Carbon used = 1.5 gram

Parameter	Value
Breakthrough Bed Volumes	140
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	3.48
Hydraulic Loading rate (HLR) (cm/min)	2.30
Empty Bed Contact Time (EBCT) (minutes)	2.39

It is obviously shown from the previous table that the EBCT also increases as bed height increases from 1.43 minutes at bed height 3.3 cm to 2.38 minutes at bed height 5.5 cm.

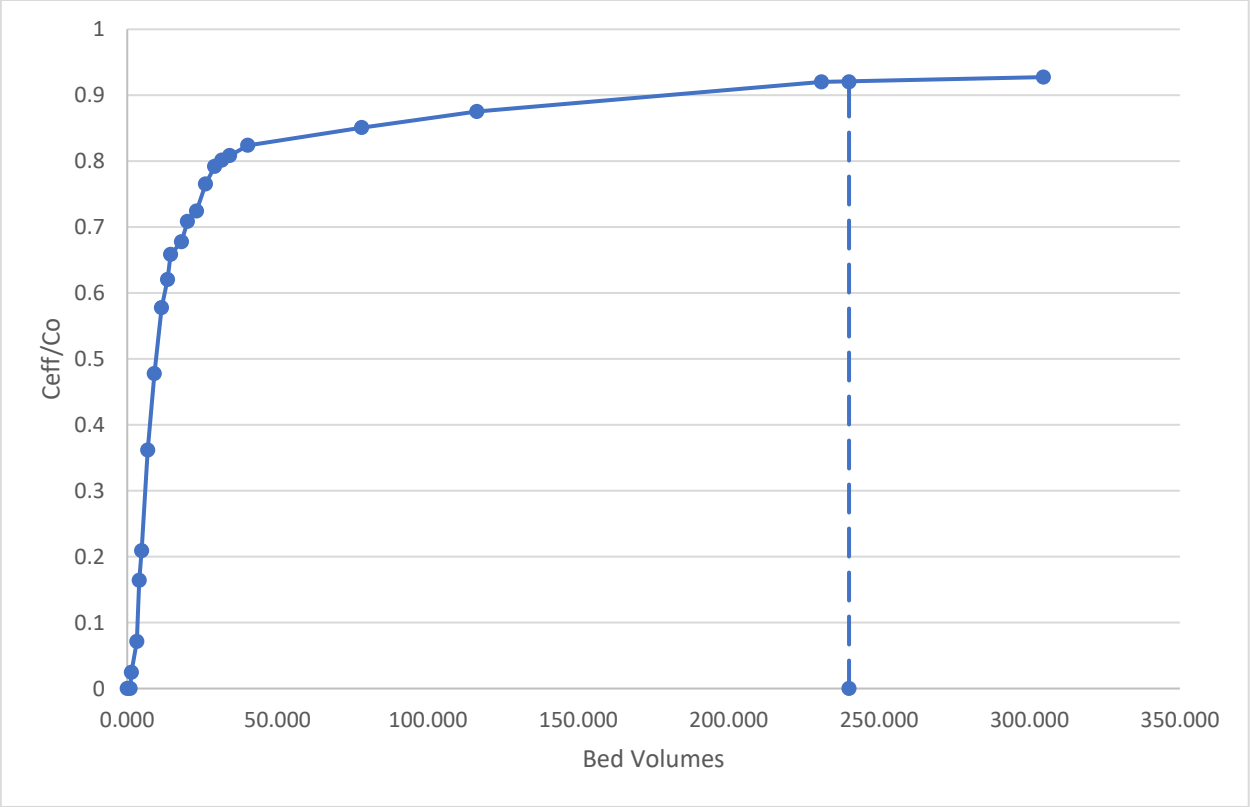

Figure 4-26: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 10 mg/l, Activated carbon = 1.7 grams, and flow rate = 3 ml/min)

Both Figure 4-26 and Figure 4-27 both depict the breakthrough of sodium diclofenac in relation to time and bed volumes. The bed height for this experiment was 7.5 cm. It is demonstrated that after almost 20 hours, the effluent concentration has reached more than 90% of its initial value.

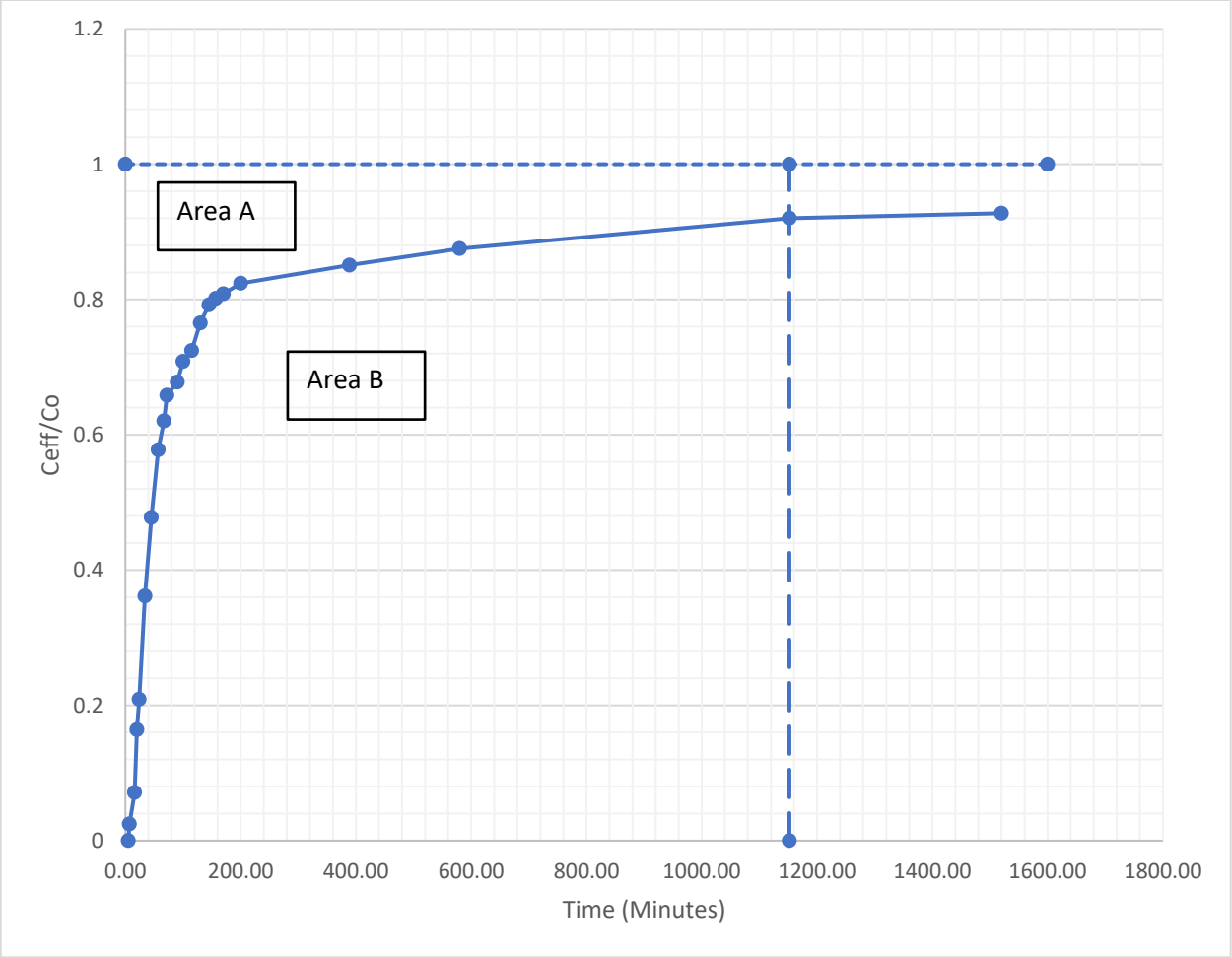

Figure 4-27: Effluent diclofenac Concentration versus Time (Initial concentration = 10 mg/l, Activated carbon = 1.7 grams, and flow rate = 3 ml/min)

Surface concentration calculations were performed as previously described in different flow rates experiments. Figure 4-27 summarizes the results of adsorbing diclofenac by the activated carbon material in a higher Bed height (Bed height = 7.5 cm). summarizes the design-related calculations.

Table 4-15: Analysis of the Column Experiment for initial concentration 10 mg/l, flowrate 3 ml/min, and activated carbon used = 1.7 gram

Parameter	Value
Breakthrough Bed Volumes	240
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	3.086
Hydraulic Loading rate (HLR) (cm/min)	2.30
Empty Bed Contact Time (EBCT) (minutes)	3.26

As expected, it is obviously shown in the previous table the Surface Concentration at breakthrough decreased as the bed height increased and the EBCT increased as bed height increase for these set of column experiments.

It is conducted that the removal efficiency of the diclofenac increases as the weight of activated carbon increases or as the bed height increases. For example, at time 400 minutes (more than 6.5 hours) the removal efficiency of 1 grams of activated carbon (bed height = 3.3 cm) was approximately 70% while the removal efficiency at the same time for 1.5 grams of activated carbon (bed height = 5.5 cm) was approximately 80%. At 1.7 grams of activated carbon (bed height = 7.5 cm) the removal efficiency at the same time was approximately 85%.

4.3.2. Different Diclofenac initial Concentrations

Different initial diclofenac concentrations were examined to determine the behavior of activated carbon adsorption with different diclofenac concentrations. Concentrations of diclofenac from 3 mg/l to 20 mg/l were used in the different diclofenac initial concentrations experiments. The following figure (Figure 4-28) shows the breakthrough curves of different initial diclofenac concentrations. The same bed height (3.3 cm) and flow rate (3 ml/min) were used in these set of experiments.

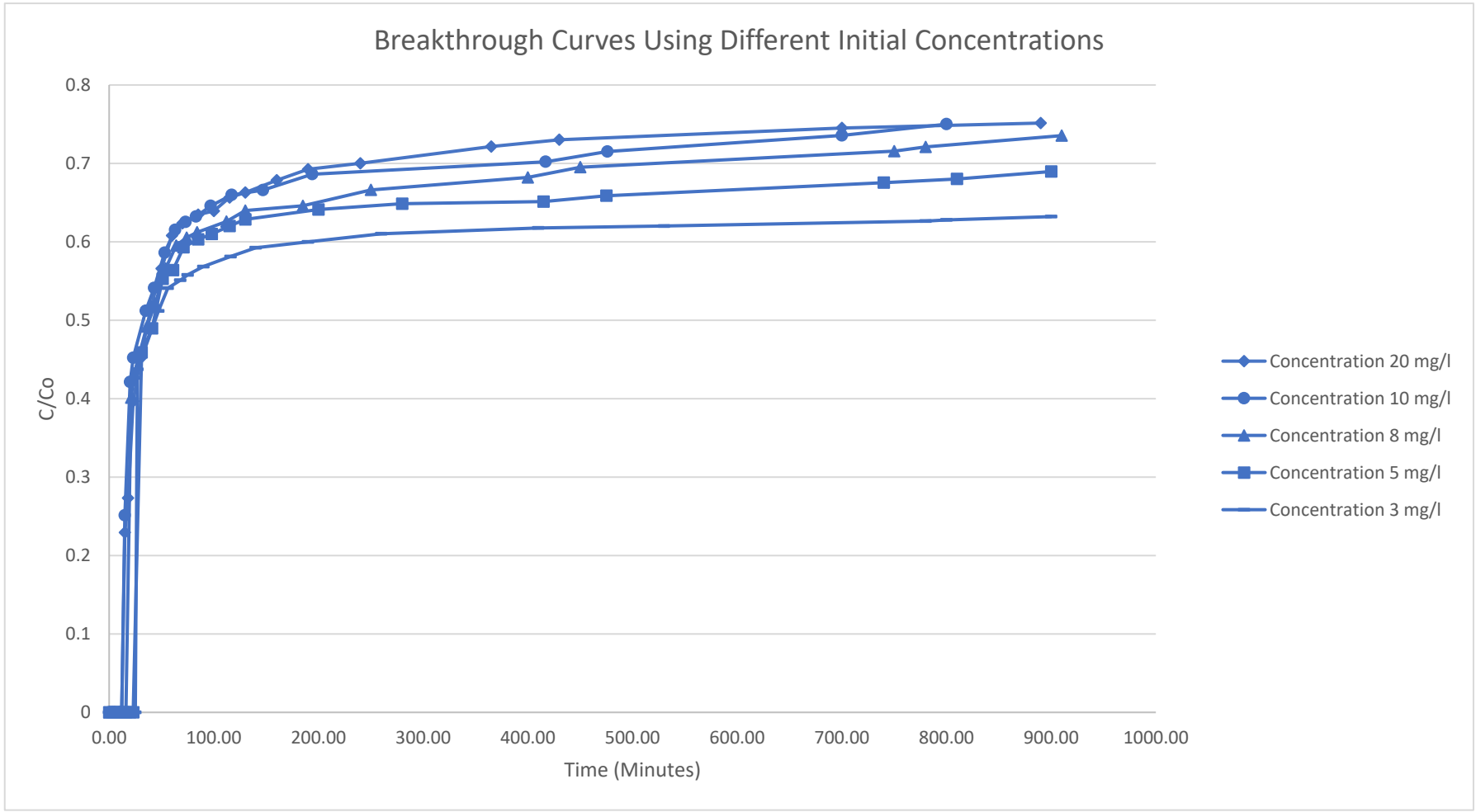

Figure 4-28: Breakthrough Curves using Different Initial Diclofenac Concentrations.

Table 4-16: Analysis of the Column Experiments for different initial concentrations with fixed flowrate = 3 ml/min, and activated carbon used = 1 gram

Parameter	Concentration 3 mg/l	Concentration 5 mg/l	Concentration 8 mg/l	Concentration 10 mg/l	Concentration 20 mg/l
Breakthrough Bed Volumes	630	560	455	300	255
Total time of the column run until exhaustion. (minutes)	900	810	650	417	365
Surface Concentration at breakthrough (mg Diclofenac/ g activated carbon)	2.98	3.95	4.84	4.133	7.186
Hydraulic Loading rate (HLR) (cm/min)	2.30	2.30	2.30	2.30	2.30
Empty Bed Contact Time (EBCT) (minutes)	1.434	1.434	1.434	1.434	1.434

Analyses for different concentrations were calculated as mentioned before in different flow rates experiments. Figure 4-28 summarizes the results of adsorbing diclofenac by the activated carbon material indifferent diclofenac initial concentrations. Table 4-16 summarizes the design-related calculations. Further figures for each concentration are provided below for more detailed data.

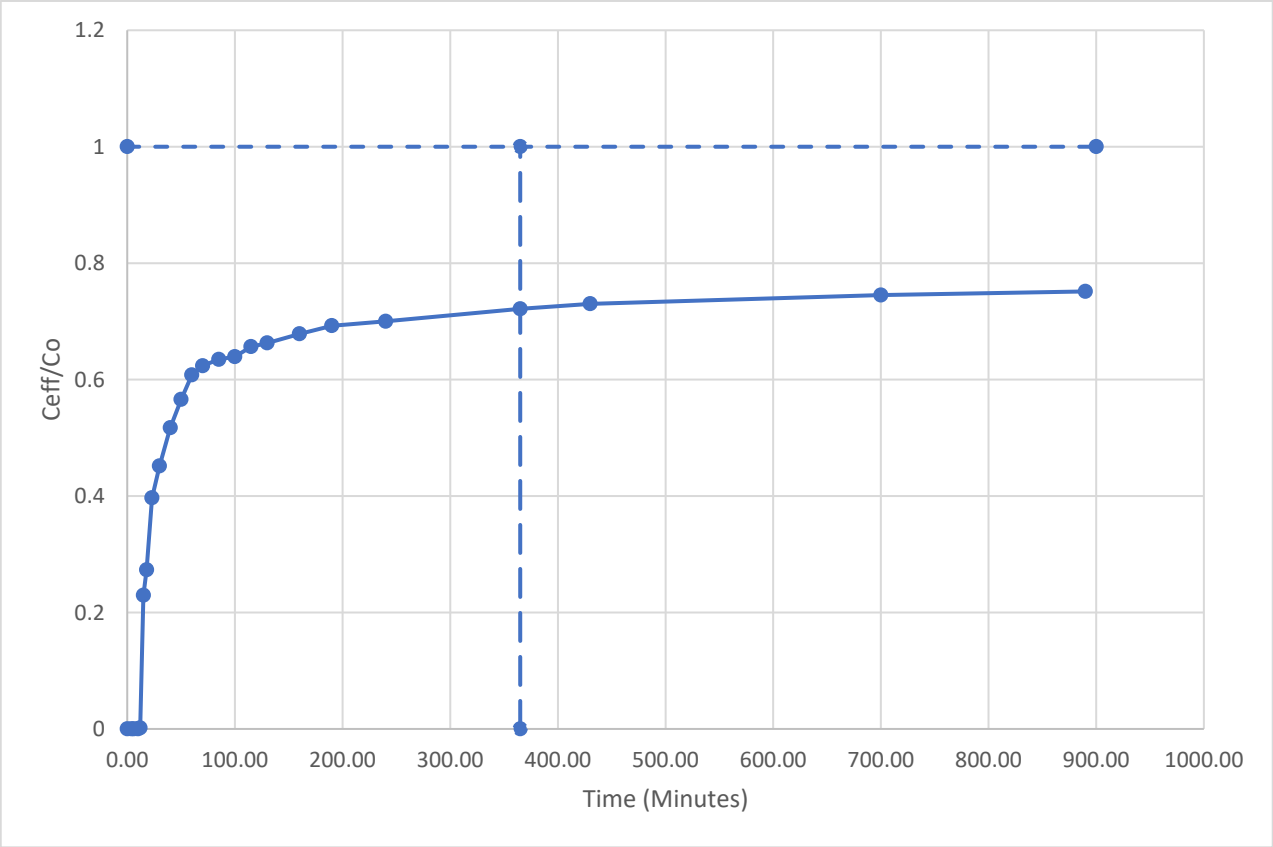

Figure 4-29: Effluent diclofenac Concentration versus Time (Initial concentration = 20 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

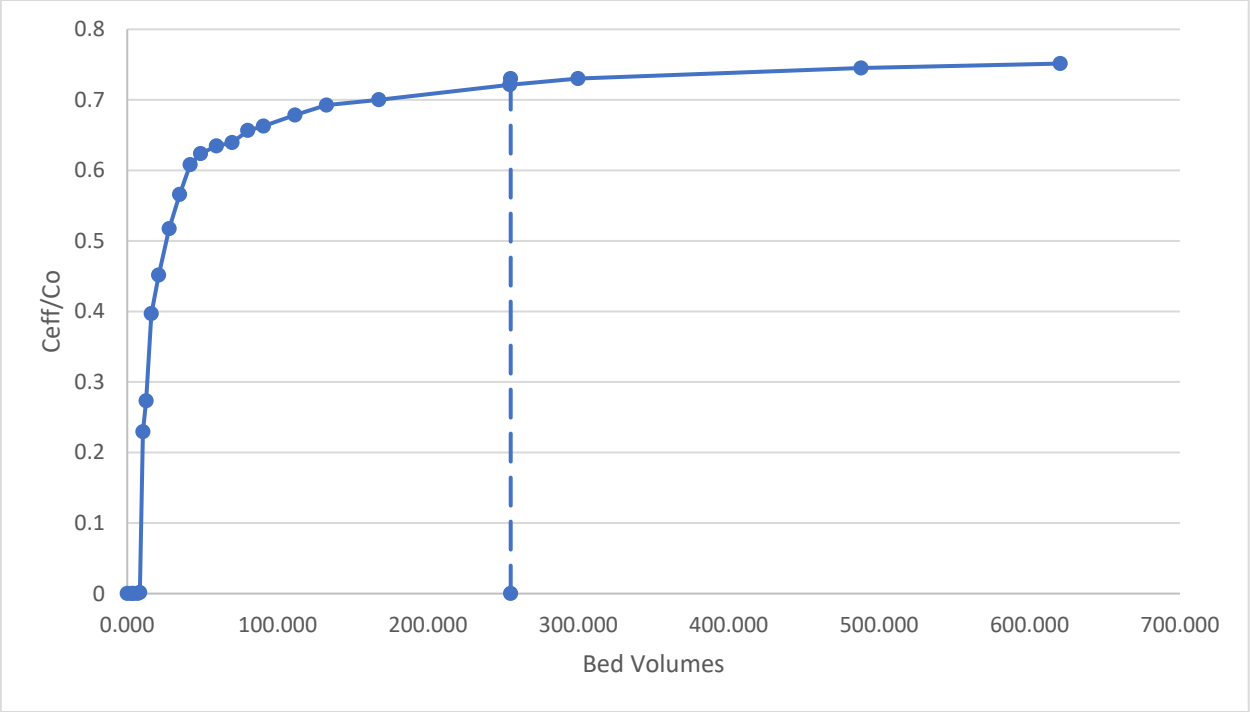

Figure 4-30: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 20 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

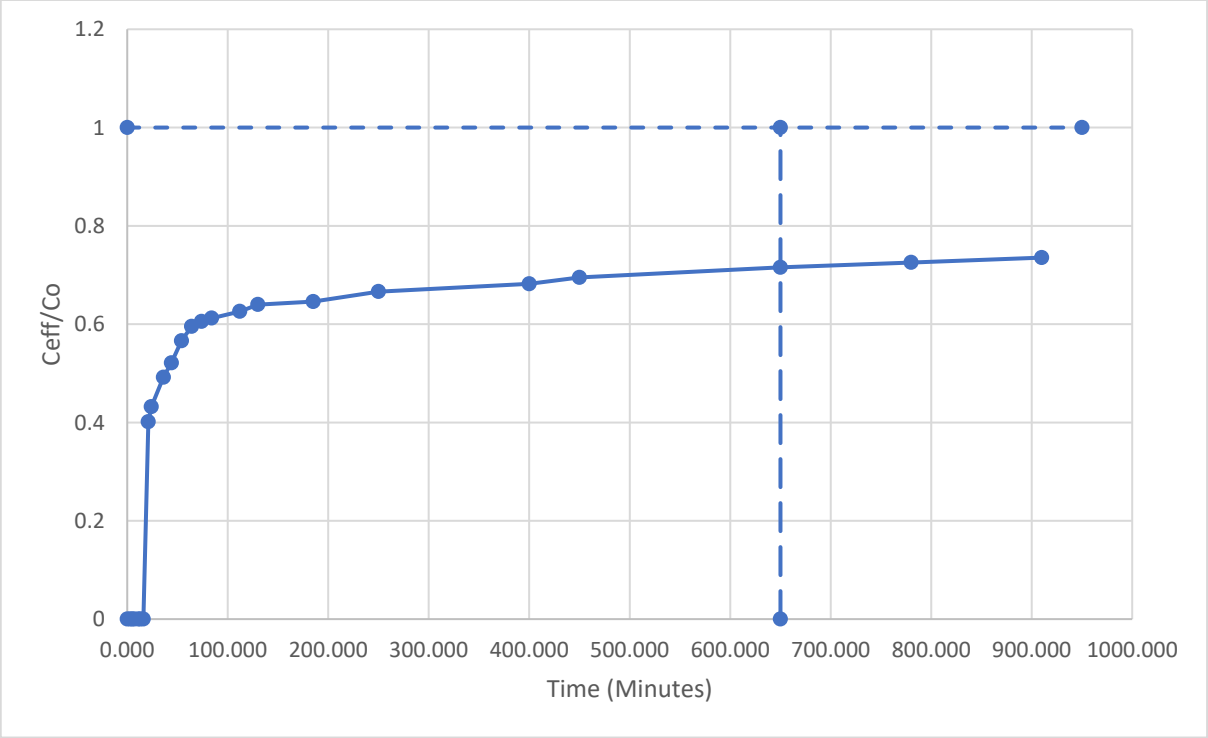

Figure 4-31: Effluent diclofenac Concentration versus Time (Initial concentration = 8 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

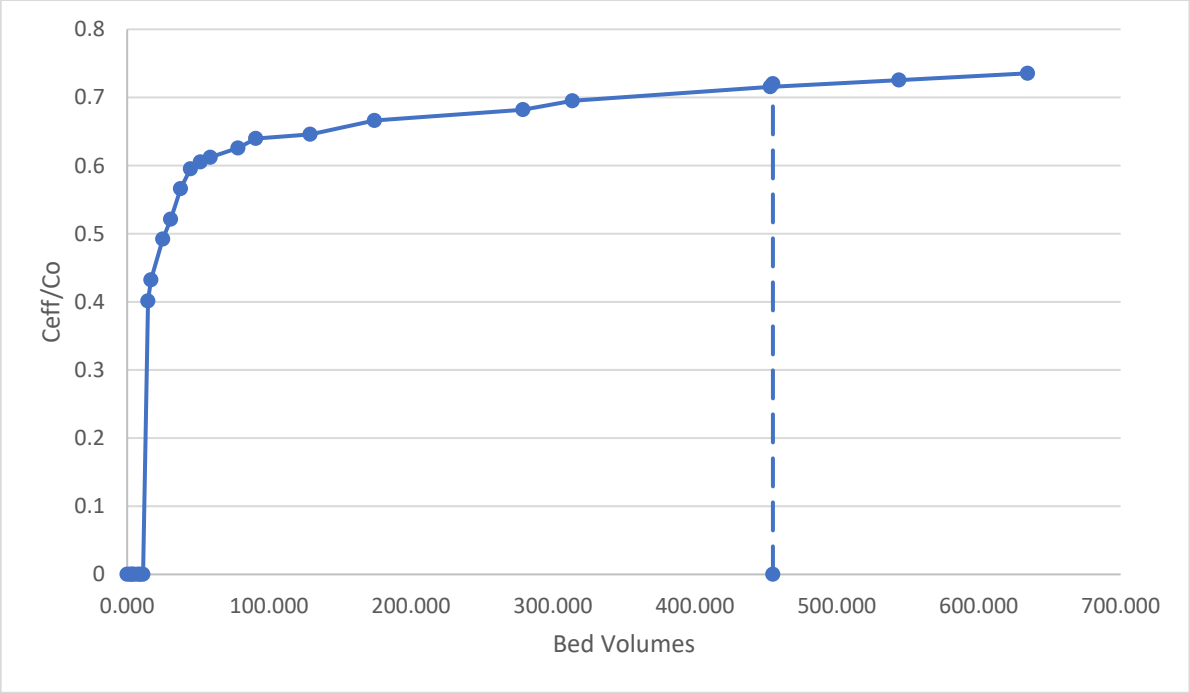

Figure 4-32: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 8 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

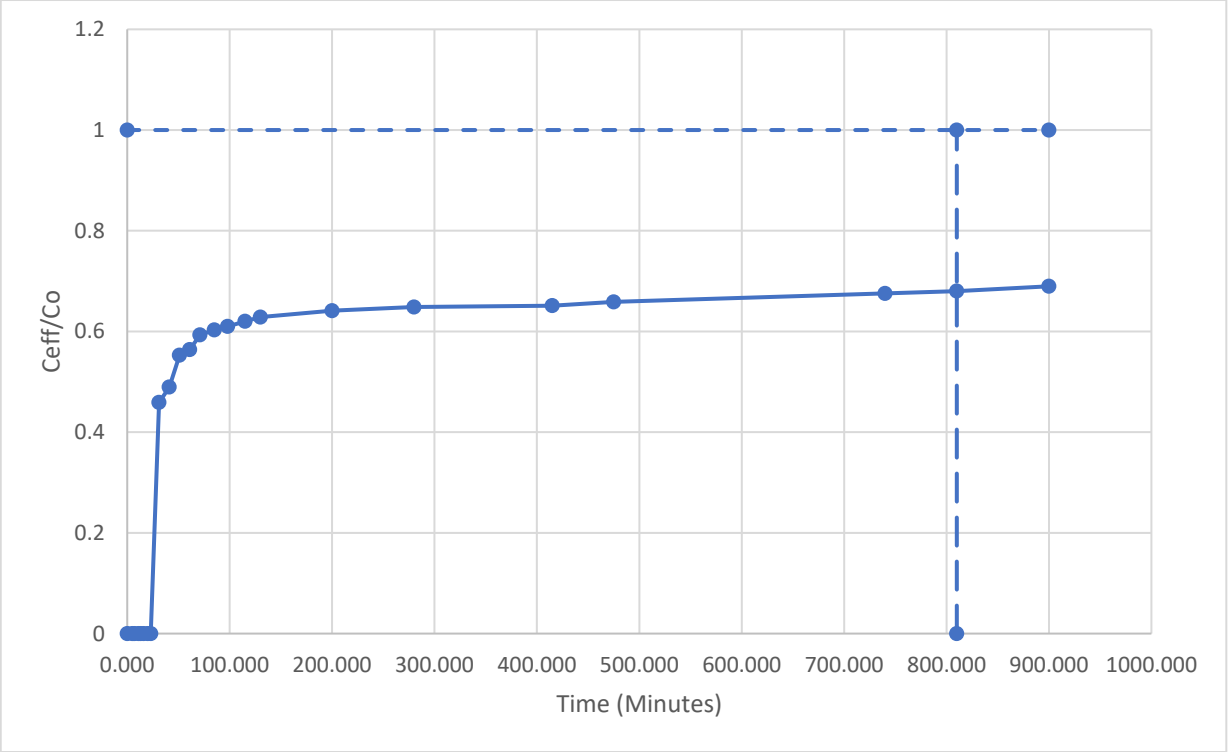

Figure 4-33: Effluent diclofenac Concentration versus Time (Initial concentration = 5 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

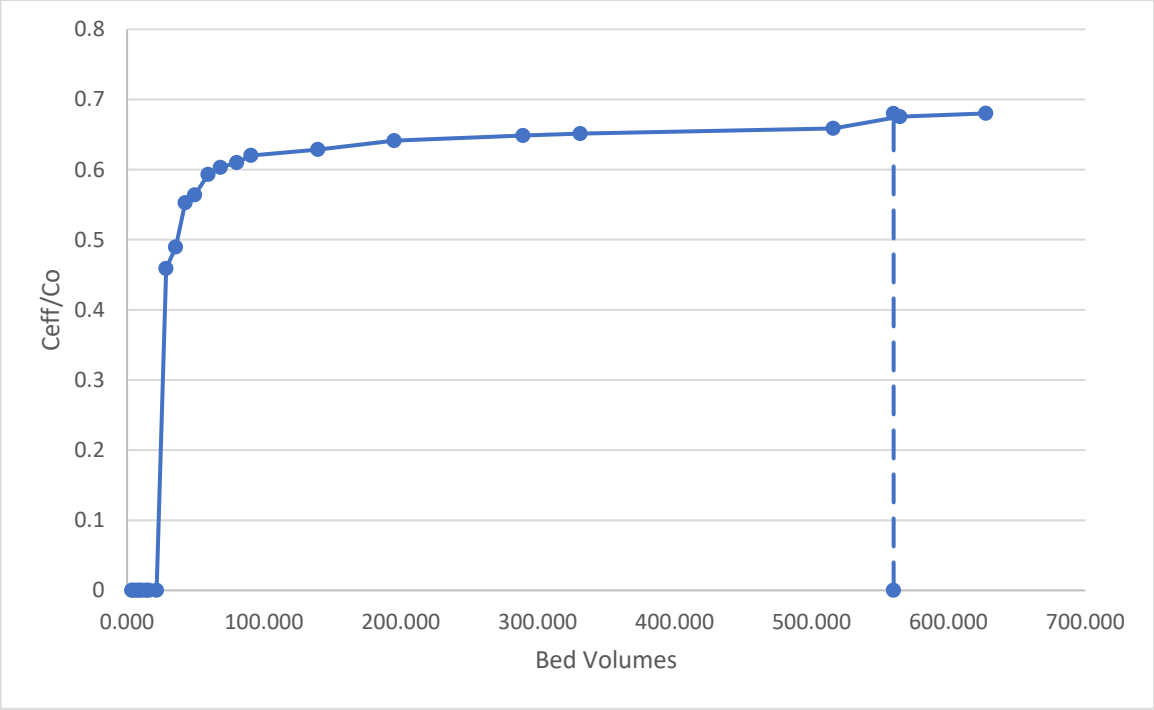

Figure 4-34: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 5 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

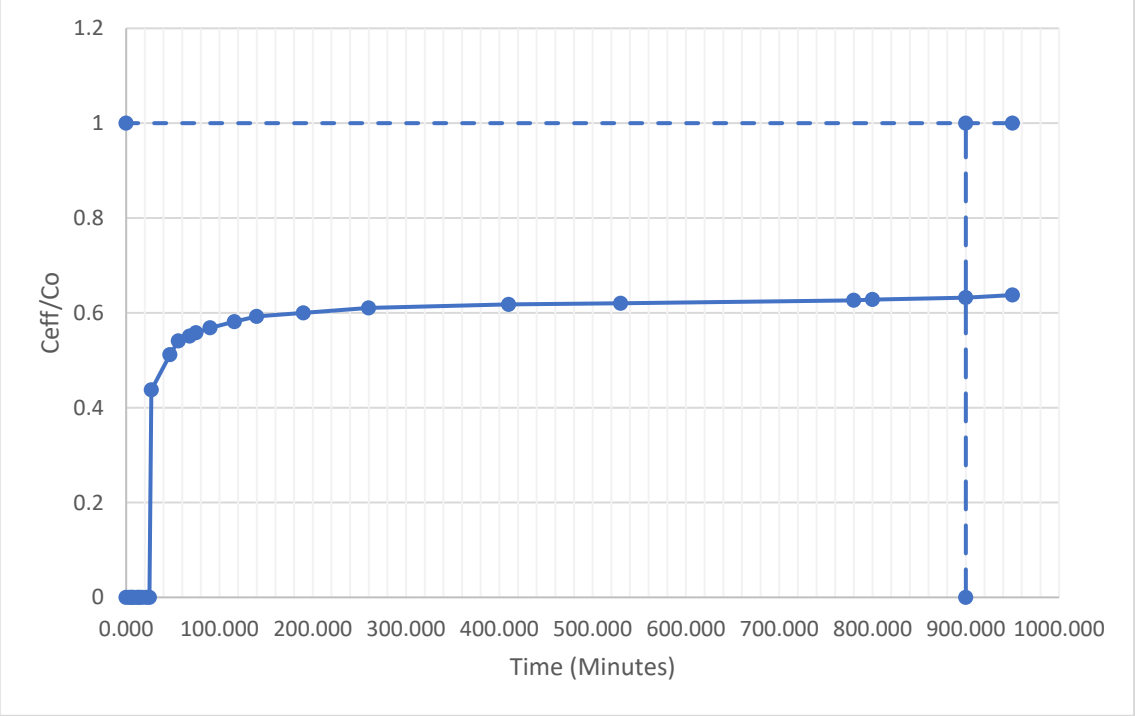

Figure 4-35: Effluent diclofenac Concentration versus Time (Initial concentration = 3 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

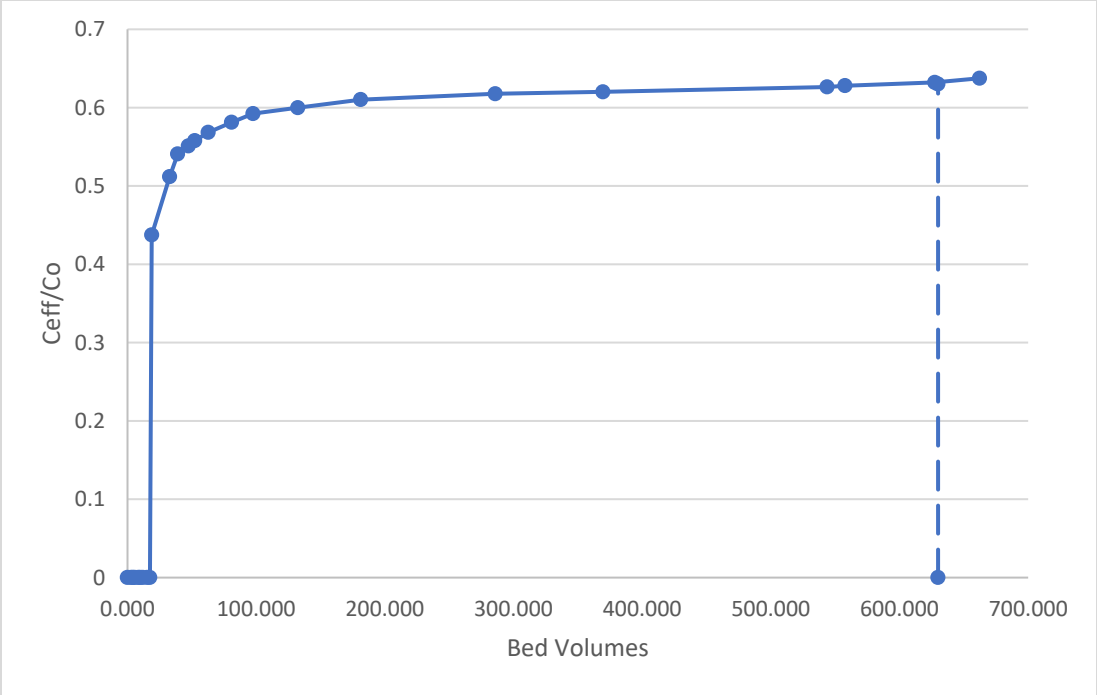

Figure 4-36: Effluent diclofenac Concentration versus Bed volumes (Initial concentration = 3 mg/l, Activated carbon = 1 grams, and flow rate = 3 ml/min)

4.4 Surface Titration Experiments

Surface titration experiments were performed on both activated carbon and diclofenac sodium powder. Experiments were performed at different ion backgrounds of 0.01M and 0.001M. Experiments have shown that activated carbon behaves consistently when titrated with NaOH. The activated carbon did not show regular behavior in HNO_3 titration. This implies that activated carbon is resistant to pH changes when acid is added. This is believed to be due to the affinity of HNO_3 to absorb H+ ions through the naturally alkaline surface of the activated carbon when HNO_3 is added. Figure 4-37 shows surface titration data for activated carbon at various ionic background intensities.

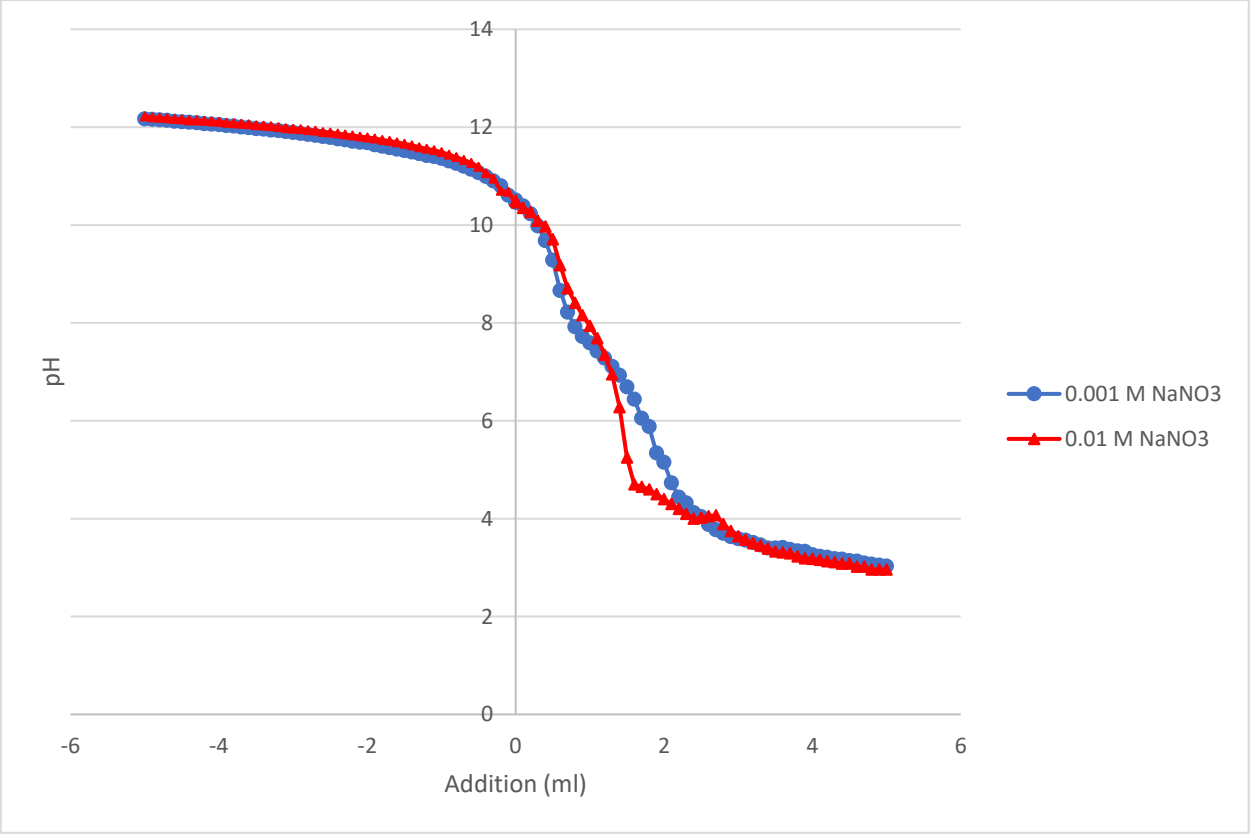

Figure 4-37: Surface Titration Data of activated carbon at Two Different Ionic Strengths

Figure 4-37 shows the acid-base titration curve of the activated carbon aqueous solution. It features a weakly acidic system with varying ionic background intensities. Both curves intersects at approximately pH 10.5. This means that the system will thermodynamically tend to drive toward this point. The pH Point of Zero Charge (PZC) for the activated carbon was 10.5 which means that the net surface charge becomes zero or neutral at pH 10.5. ZPC is the pH where the charge on the surface of the particles is zero (neutral), and it is expressed as pH ZPC (M. Jang, et. al, 2022). On the other hand, the surface titration curve from diclofenac sodium powder was conducted as shown in Figure 4-38.

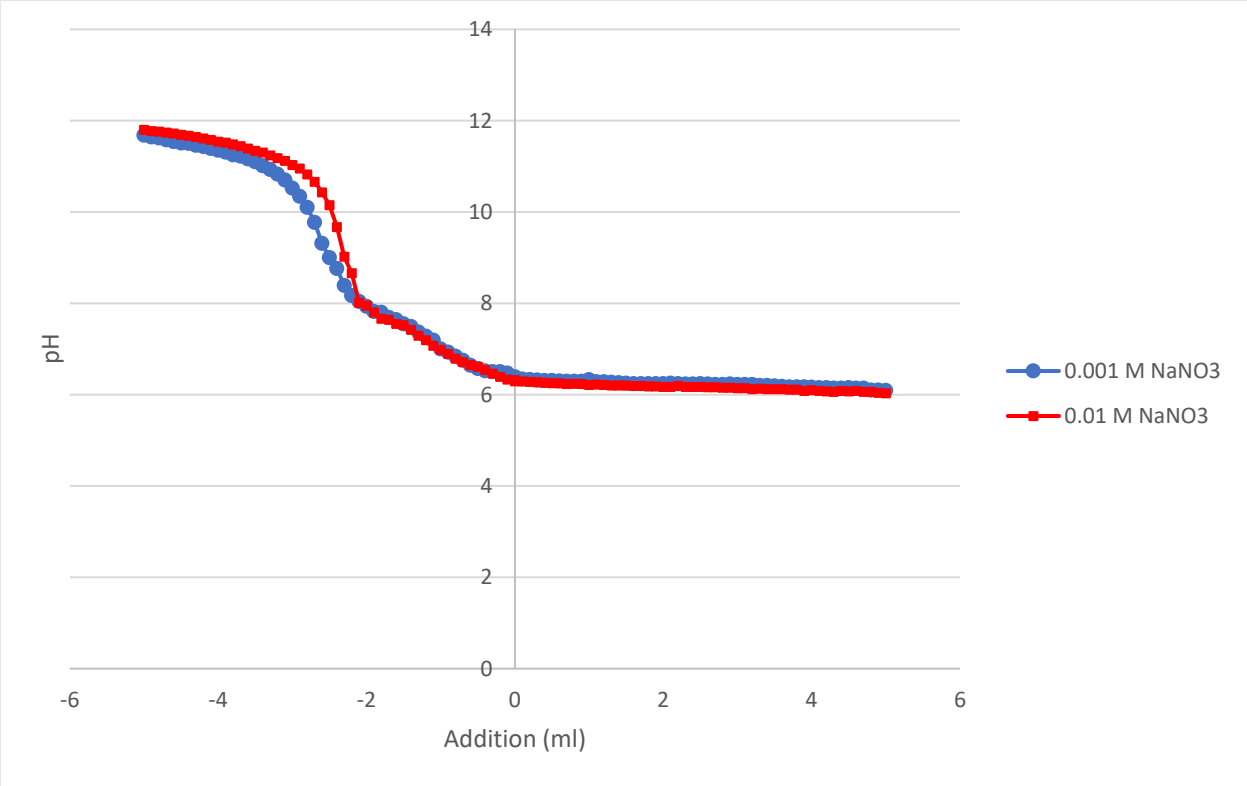

Figure 4-38: Surface Titration Data of Diclofenac Sodium Powder at Two Different Ionic Strengths

Figure 4-38 shows the acid-base titration curve of the diclofenac sodium powder aqueous solution. It is characterized by an acid system with different ionic background strengths. Both curves intersect at ≈ pH 6.3. This means that the system will thermodynamically tend to drive toward this point. The pH PZC for the diclofenac recorded 6.3 which means that the net surface charge becomes zero at pH 6.3. From Figure 4-37 and Figure 4-38 we can conclude that the commercial purchased granular activated carbon has a different thermodynamically drive than the diclofenac sodium which can verify the absorption of diclofenac on the activated carbon surface.

Using the titration data, we calculated the surface charges of activated carbon and diclofenac sodium using the following equations: (J. Lützenkirchen, et. al, 2012; M. El Zayat, et. al, 2010):

$$\sigma = \frac{F}{AS} \times [\, C_A - C_B - (H^+) + (\, OH^-)] \qquad \text{Equation 4.2: Surface Titration Charge Equation}$$

Where;

F: Faraday Constant = 96485.339 Coulomb/mole

S: Sorbent concentration = 10 g/l according to this study

A: Surface area of sorbent = 875 m^2/g for activated carbon; and 11 m^2/g for diclofenac sodium

H+: 10 (pH value)

OH-: 10 (14-pH value)

C_A: Added acid (moles/L)

C_B: Base added (moles/L)

σ: The surface charge density

As shown in Figure 4-39 the activated carbon at the 0.01 M ionic background illustrates that the activated carbon surface was negatively charged at pH more than≈ 7.0 and negatively charged above pH≈ 7.0. The activated carbon has weak positive charges from pH< 10.0 to pH> 4.0, while it has strong negative charge at the alkaline conditions for pH >10. Figure 4-40 for the 0.001 M ionic background cases, it is obvious that the activated carbon surface was negatively charged at pH more than ≈ 7.0 and negatively charged above pH= 7.0. Activated carbon has a weak positive charge from pH< 10.0 to > 4.0, but a strong negative charge from pH values >10 under alkaline conditions.

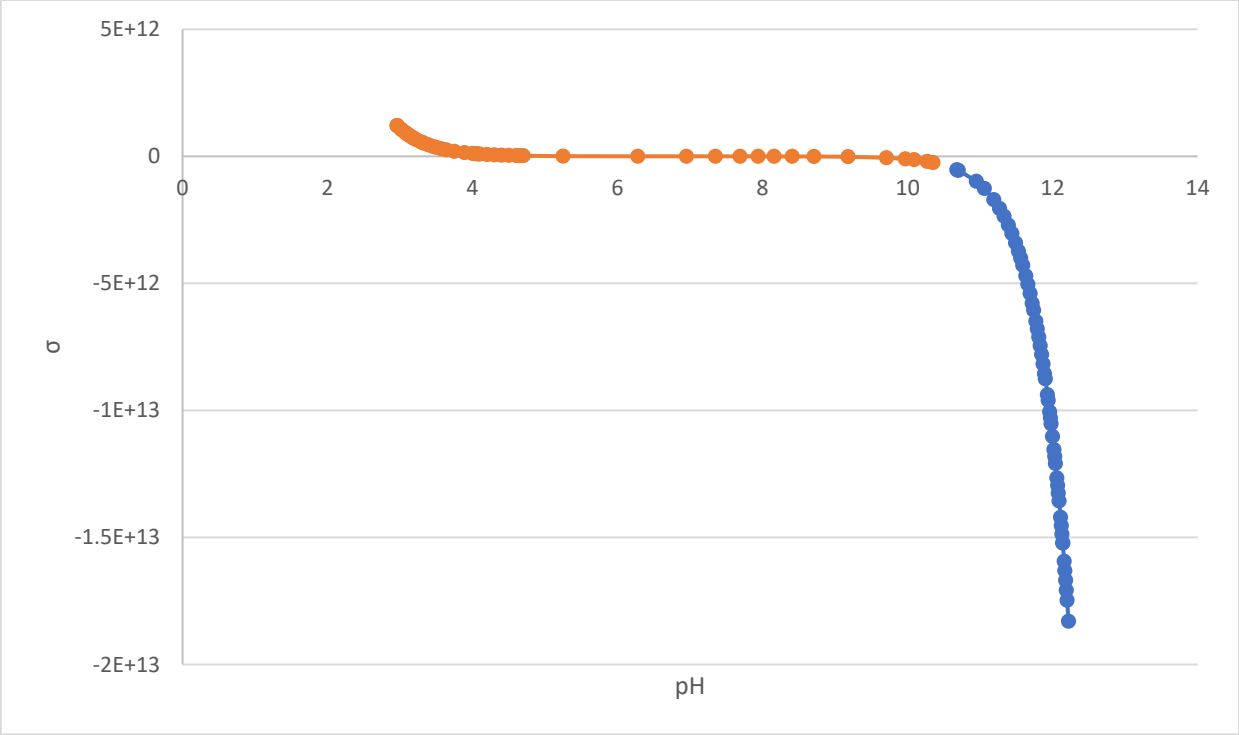

Figure 4-39: Activated Carbon Surface Charge at different pH values at Ionic Background of 0.01 M

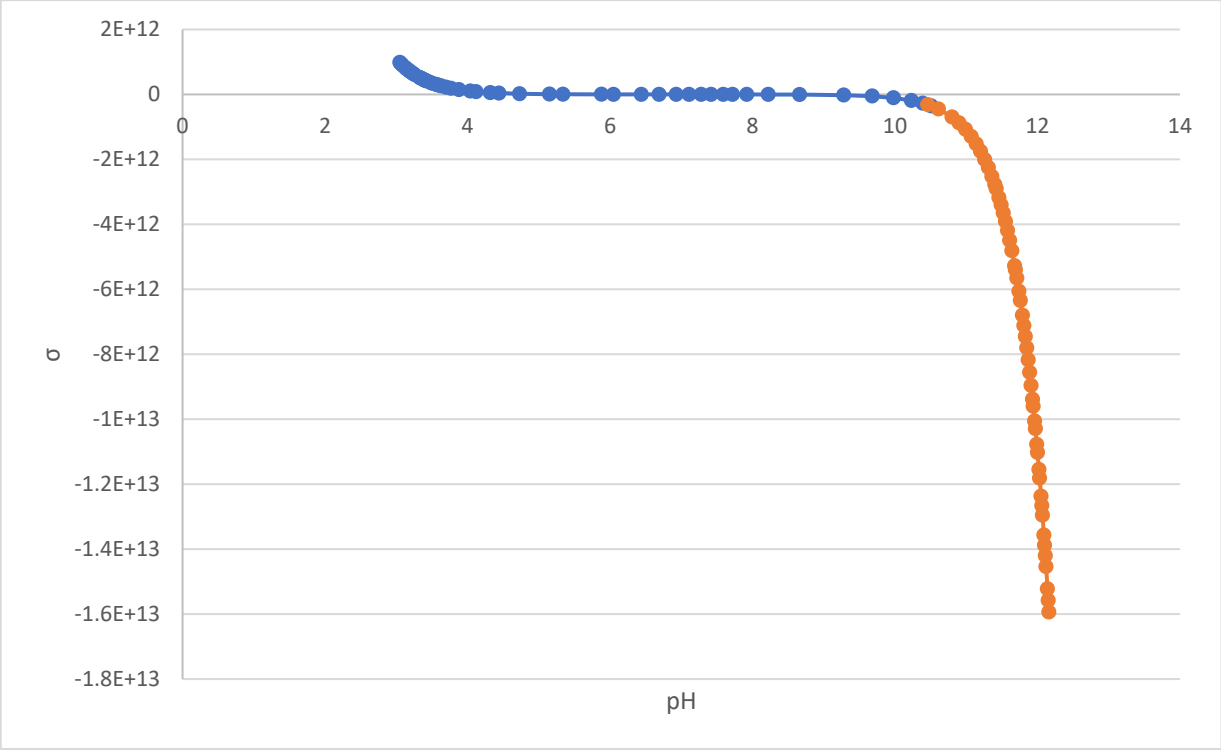

Figure 4-40: Activated Carbon Surface Charge at different pH values at Ionic Background of 0.001 M

As shown in Figure 4-41 the activated carbon at the 0.01 M ionic background illustrates that the diclofenac sodium solution was negatively charged at pH more than≈ 7.0 and negatively charged above pH≈ 7.0. The diclofenac sodium solution has weak positive charges from pH< 9.77 to pH> 6.1, while it has strong negative charge at the alkaline conditions for pH > 9.77. Figure 4-42 for the 0.001 M ionic background cases, it is obvious that the diclofenac sodium solution was negatively charged at pH more than ≈ 7.0 and negatively charged above pH= 7.0 which indicates its high resistance to acid. The diclofenac sodium has weak positive charges from pH< 9.67 to pH> 6.03, while it has strong negative charge at the alkaline conditions for pH >9.67. The pH PZC for the diclofenac was 7 which means that the net surface charge becomes zero at pH 7.

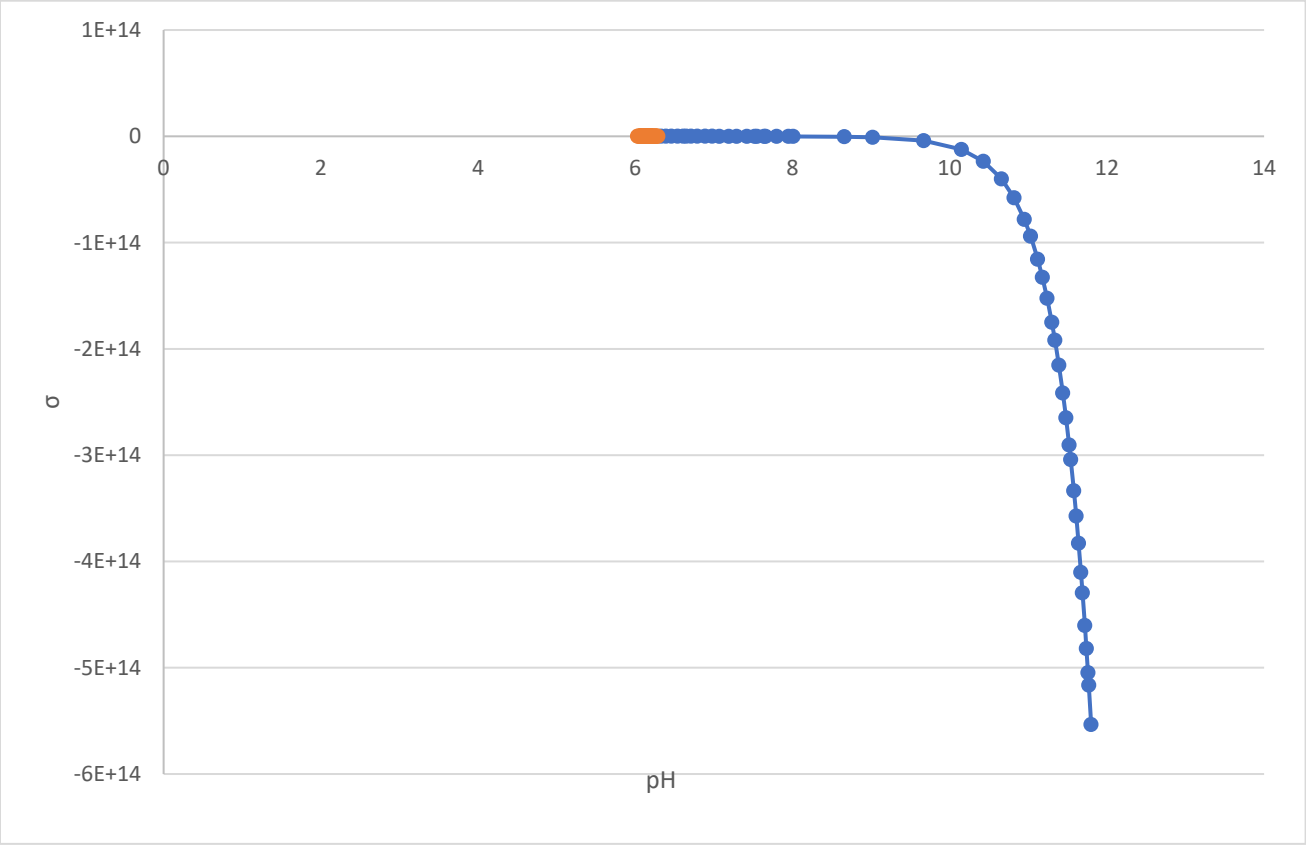

Figure 4-41: Diclofenac Sodium Surface Charge at different pH values at Ionic Background of 0.01 M

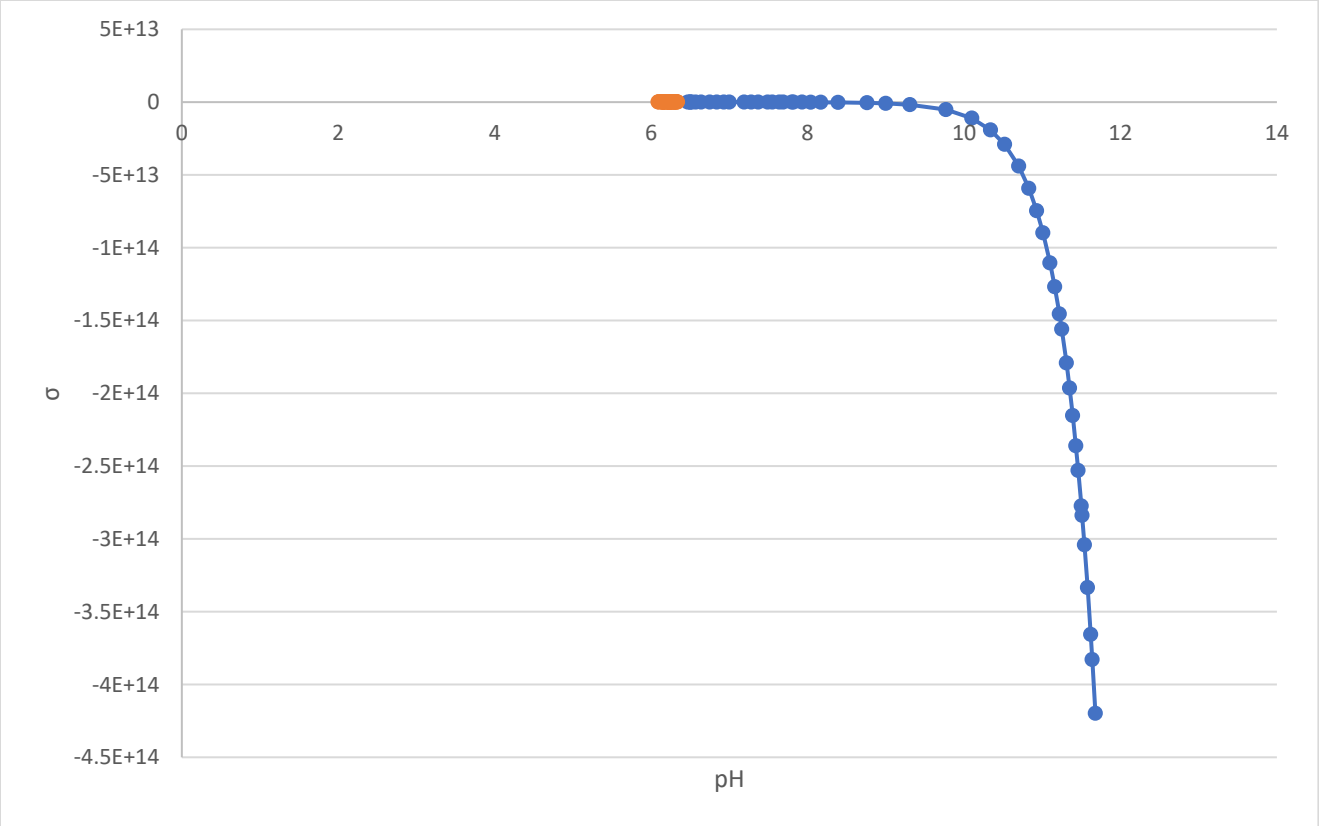

Figure 4-42: Diclofenac Sodium Surface Charge at different pH values at Ionic Background of 0.001 M

The experiment showed that the diclofenac sodium compound is negatively charged in water. The diclofenac molecule contains a carboxyl group, which means that the diclofenac molecule is negatively charged in water. Therefore, electrostatic interactions may occur between diclofenac molecules and other positively charged absorbers (M. Liu, et. al, 2021). It is assumed that the main forces responsible for diclofenac adsorption on activated carbon surface are electrostatic interactions between diclofenac and activated carbon surface. In addition to van der Waals forces, and hydrophobic effect that play an important role in diclofenac adsorption on activated carbon surface (A. P. Ramasamy, et. al, 2022).

Chapter 5. **Conclusion and Recommendations**

5.1 Conclusion

Unfortunately, diclofenac is found in wastewater treatment plant's effluent around the world. It is shown that most of the conventional wastewater treatment process cannot efficiently remove it from wastewater causing the return of diclofenac compound back to the environment (M. Rosset, et al, 2019). Diclofenac has numerous harmful effects on the aquatic life, animals, and plants which urges the need to search for different methods for point source treatment for the diclofenac compound before reaching the environment.

In the present work, the use of activated carbon for removal diclofenac sodium from treated wastewater is reported to study the adsorptive performance in the removal of diclofenac sodium from treated wastewater in both batch and column modes. The selected process for the removal of diclofenac sodium compound using granular activated carbon at the laboratory scale yielded high removal efficiency. The adsorption properties of activated carbon based on adsorption studies with diclofenac in wastewater and two types of applications in fully mixed batch reactors and continuous flow columns are summarized in the following points.

- The adsorption investigations indicated that the adsorption of diclofenac sodium depends on the initial concentration of diclofenac sodium compound, the quantity of adsorbent (activated carbon), and the time for mixing.
- In batch reactors, was added the higher the percentage removal achieved for the same amount of time at the more the activated carbon. For example, at initial concentration 8 mg/l of diclofenac sodium at time 3.3 hours the removal percentage using 5 gm/l activated carbon was 100% and decreases as the activated carbon dose decreases reaching approximately 22% with activated carbon dose of 0.5 gm/l
- In completely mixed batch reactors, as initial concentration increases the removal percentage of diclofenac sodium decreases, for example, with the same amount of carbon

at the same time the percentage of removal of diclofenac sodium decreases almost 20% when changing initial concentration from 8 mg/l to 10 mg/l.

- In the equilibrium study, after testing Freundlich and Langmuir isotherms, it was detected that the Langmuir model provided the best fit and this model agrees with a monolayer adsorption for the diclofenac sodium compound.
- Investigations in column experiments using granular activated carbon (GAC) confirmed high removal efficiencies.
- In continuous flow columns experiments, it was clearly detected that the higher the flow rate used the higher the bed volumes were starting from 557.7 at flow rate 3 ml/min to 1154.05 at flow rate 6 ml/min.
- In continuous flow columns experiments, the greater the bed height is in the column the higher the removal efficiency for the same flow rate and diclofenac concentration. For example, at time 10 hours the removal efficiency decreased approximately 16% from bed height 7.5 cm to 3.3 cm.
- In continuous flow columns experiments, it was concluded that the greater the initial diclofenac sodium concentration the total time of the column run until exhaustion the less the number of bed volumes.
- Surface titration experiments showed that the surface charge density of the produced activated carbon decreased with an increase in pH, similar to other activated carbons.

5.2 Recommendations

The process adopted for the removal of diclofenac sodium using activated carbon material is successful and achieves high removal efficiencies. There can be some potential enhancements that can be made to improve the process, the following are some recommendations.

- Recycling and reusing methods for the activated carbon after every use should be developed. This would minimize running costs and protect the environment.

- More studies should be conducted to measure the minimum concentration exposure for the diclofenac and limits for diclofenac compound in water and wastewater streams should be conducted and added in the Egyptian law.
- The activated carbon adsorption capacity for different pharmaceutical compounds should be investigated.
- Different types of activated carbon should be tested in the adsorption columns. This might help to handle and transport wastewater treatment plants.
- Pilot scale runs are needed for more promising results.
- Experimenting the reasons of adsorption whether it is based on electrostatic alteration, chemical reflexes, or more complex mechanism.
- Assessing the adsorption mechanism using more than one pharmaceutical compound to see the difference in removal efficiency and to study the competition between different pharmaceutical compounds.
- Experiment the Activated carbon before and after adsorption using SEM and FTIR.
- A complete cost analysis report should be deeply studied to assess the economic conditions for diseases treatment in Egypt, so it can be compared by the cost of modifying the treatment processes for the current water and wastewater treatment plants in Egypt.
- Assessing the cumulative impact and residual risk of not treating pharmaceutical compounds in general and diclofenac in particular is recommended.

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