An-Najah National University

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Continuous Flow Adsorption Removal of Glimepiride Using Multi-Walled Carbon Nanotubes from Water Resources

By

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Dedication

I dedicate this project to Allah Almighty my creator, my strong pillar, my source of inspiration, wisdom, knowledge and understanding. He has been the source of my strength throughout my life. I also dedicate this work to my family for their unlimited love and encouragement, especially my wonderful mother and father who created me a good upbringing; they were literally willing to do anything for us in the most difficult circumstances, to my dear wife "Zaina", my first love, who has always been my source of strength, to my brothers and sister for their unfailing support.

I also dedicate this thesis with many thanks to all my professors and faculty members in the Chemistry Department who never hesitated to help me. Also I would like to extend my gratitude to all my colleague and friends who always stand beside me firmly in critical moments, it's difficult to list all the names here, but you are always on my mind.

Words would never say how grateful I am to all of you, so I hope my actions will express that on this day. Finally, we will never finish the work, and these are just stations in our life while the sky will be the limit.

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“When you arrive, do not forget who paved the way for you”

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Last but not the least; I would like to thank my family: my parents, my brothers and sister for supporting me spiritually throughout writing this thesis and my life in general.

الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Continuous Flow Adsorption Removal of Glimepiride Using Multi-Walled Carbon Nanotubes from Water Resources

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه حيثما ورد، وأن هذه الرسالة ككل، أو أي جزء منها لم يقدم لنيل أية درجة أو لقب علمي أو بحثي لدى أية مؤسسة تعليمية أو بحثية أخرى.

Declaration

The work provided in this thesis, unless otherwise referenced, is the researcher's own work, and has not been submitted elsewhere for any other degree or qualification.

Student's Name: **اسم الطالب :**

Signature: **التوقيع :**

Date: **التاريخ :**

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List of Abbreviations

Symbol	Abbreviation
ACWA	Advancing Canadian Wastewater Assets
BTC	Breakthrough curve
CNT	Carbon nanotubes
C_e	Concentration of adsorbate at equilibrium (mg/L)
C_o	Concentration of adsorbate at initial time (mg/L)
C_t	Concentration of adsorbate at time t (mg/L)
F	Cross-sectional flow rate (cm.min-1)
GPD	Glimepiride
k_{AB}	Adams-Bohart rate constant (mL mg^{-1} min^{-1})
K_d	The thermodynamic equilibrium constant (L/g)
K_{TH}	Thomas rate constant (mL mg^{-1} min^{-1})
MTZ	Mass-transfer zone
MWCNT	Multi-walled carbon nanotubes
N_{AB}	Saturation concentration (mg.L-1)
PPCPs	Pharmaceuticals and personal care products
q_e	Amount of adsorbate per unit of adsorbent
q_o	Total adsorption capacity ($mg.g^{-1}$)
SWCNT	Single-walled carbon nanotubes
T_b	Breakthrough point
t_b^{id}	Ideal break point time
UV-Vis	Ultraviolet visible spectroscopy

V	Volume
ν	Flow rate (mL/min)
W	Adsorbent dosage
WTPs	Wastewater treatment plants
x	Mass (g)
Z	Bed height (cm)
λ_{max}	Maximum wavelength

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Abstract

In this study, Multi-walled carbon nanotubes (MWCNT) were used as adsorbent for the removal of Glimepiride (GPD) drug from aqueous solution. This research has been performed in two stages. First, it was done in batch mode to ensure that the adsorption process occurs naturally by using a stock solution of glimepiride and different weights of MWCNT. The UV-Vis absorbance of GPD was observed to decrease after mixing with MWCNT and the GPD removal was increased when the amount of MWCNT increased. Secondly, a continuous process was applied by which the effects of different parameters were studied. This study showed that carbon nanotubes are effective adsorbents to remove GPD from water in short time with near complete removal. The results also showed that the adsorption process was dependent on the amount of adsorbent, column height, pH, and flow rate. The adsorption efficiency had increased as the amount of adsorbent increased. The adsorption was highly pH dependent and maximum removal was obtained at pH=3. The adsorption efficiency was increasing as the column height increased. In addition, the adsorption

efficiency was increasing as the flow rate decreased. The continuous adsorption of GPD was described by Thomas and Adams-Bohart models and found to fit the Thomas model. The regeneration study was carried out and it was found that flushing the column with diluted NaOH was successful in regenerating the fixed-bed column and MWCNT can be reused. In conclusion, this study confirmed that the adsorption process using MWCNT is efficient, simple, and cost-effective which enable it to upgrade from laboratory to industrial scale.

CHAPTER 1

INTRODUCTION

1.1 Background

Fresh water, most necessary for life, is becoming lacked. Wastewater is one of the most dangerous challenges facing the world in recent years.(Schultze, 1975; Vörösmarty, Green, Salisbury, & Lammers, 2000) Huge amounts of wastewater are being produced daily from manufactories, farms and houses. At the same time, the world is suffering from the exhaustion in fresh water.(Einschlag & Carlos, 2013; Vörösmarty et al., 2000) There is a huge demand for fresh water due to the large increase in population, industrialization and modernization. In Palestine, population growth and rapid industrial development leading to produce large amount of wastewater which is one of the most dangerous challenges facing this area.(Al-Saed, 2007) Moreover, factories, farms and houses are producing huge amounts of wastewater daily.(Bowen, 1979) There are different types of water contaminations, including heavy metals, Pharmaceuticals and industries like petrochemical, petroleum refining, paper, food and texture include processes that produce wide types of liquid waste and their effects on the watery environment over the years.(Robinson, McMullan, Marchant, & Nigam, 2001) Wastewater consist of these kinds of liquid waste usually has high levels of colloidal suspensions and dissolved organic pollutants.(Al-Saed, 2007) Many researchers have focused on solving these problems using various techniques and methods such as adsorption onto

different adsorbents,(C.-H. Wu, 2007; Yang, 2003) reverse osmosis processes,(Carlos, Einschlag, González, & Mártire, 2013) electrochemical technologies(Feng, Yang, Liu, & Logan, 2016) and nanotechnology,(Nassar, 2013) usually in the form of nano adsorbent.(Tiwari, Behari, & Sen, 2008) But the main goal remains to find a new technology that is effective, selective. Therefore, we must work to develop simple, easy, cheap and applicable technologies on a larger scale and therefore to treat the largest possible amount of wastewater.

1.2 Sources of water pollution

Water pollution can be defined as the entry of harmful substances for living creatures into groundwater, lakes, rivers, seas and oceans.(Goel, 2006) Pollutants are caused pollution when this pollution exceeds the permissible concentration, and if it causes a chemical, physical, or biological change in the body of water.(Novotny, 1994) There are many sources of pollutants such as pesticides, fertilizers, human, animal sewage and industrial effluents that produce natural and synthetic organic chemicals which are a large contributor to water pollution.(Robinson et al., 2001)

1.2.1 Pharmaceuticals pollution

One of the main organic pollutants in water bodies is pharmaceuticals. Ecological contamination by pharmaceuticals and personal care products (PPCPs) has recently gained wide public attention.(Suntisukaseam, Weschayanwiwat, & Sabatini, 2007) PPCPs are

important and necessary elements of modern life.(Mestre, Pires, Nogueira, & Carvalho, 2007) To date, more than 70 distinct PPCP compounds such as prescription and over-the-counter drugs have been detected in surface water and groundwater in the United States.(Heberer, 2002; Jim, Bouwer, & Coelhan, 2006) PPCPs are stable and are not fully metabolized in the human body and animal during use, but are partially metabolized and some are excreted in the urine, so wastewater can enter the treatment plant or the aquatic environment.(Badran, Hassan, Manasrah, & Nassar, 2019; Yan et al., 2017) In fact, in wastewater treatment plants (WTPs), surface water, groundwater, and even in drinking water, a number of PPCPs have been detected.(Badran, Manasrah, & Nassar, 2019; Badran, Qut, Manasrah, & Abualhasan, 2020; Masoud et al., 2017; Yidong et al., 2017) Wastewater treatment plants (WTPs) are considering as hotspots for Pharmaceuticals contamination sources.(Thiebault et al., 2016) There are an increasing number of studies showing the presence of PPCPs from leakage of WTPs to water resources.(Blair, Nikolaus, Hedman, Klaper, & Grundl, 2015; Challis, Hanson, Friesen, & Wong, 2014; De la Cruz et al., 2013; Oosterhuis, Sacher, & ter Laak, 2013; Sarkar, Das, Choi, & Bhattacharjee, 2014) Therefore, the presence of these wastes in water requires serious attention to water treatment and to stop the leakage of PPCPs from WTPs. Pharmaceuticals have low susceptibility to biodegradation,(Badran, Manasrah, et al., 2019) high persistence and easy bioaccumulation, and therefore have high potential environmental hazards.(Zhang et al., 2016) These compounds include different types, such as antibiotics, anti-diabetic

agents, analgesics, anti-inflammatory agents, and steroid hormones.(Peltzer et al., 2017; Sun, Luo, Wang, & Wang, 2015) In recent times, concerns related to the adverse effects on human health and on environment have increased, resulting from the production, consumption and disposal of many organic compounds that provide improvements in medical treatment, industry, agriculture and common household amenities.(Kolpin et al., 2002) These can include toxic human effects and endocrine disorder.(Kolpin et al., 2002) The main sources of contamination with pharmaceuticals or organic compounds in general are factories, hospitals and agricultural fields.(Nazari, Abolghasemi, & Esmaieli, 2016) Surface water contaminated with these compounds can enter into drinking water sources and accumulate in the form of human pollutants,(S. Wu, Zhang, & Chen, 2012) although these compounds are present in traces of ng L^{-1} levels to μg L^{-1} levels.(Cai et al., 2018) Consequently, the continuous release of these pollutants into the water environment has negatively effects on humans and environment.(Ma et al., 2016) According to the Advancing Canadian Wastewater Assets (ACWA) located at the Pine Creek WTPs in Calgary, several pharmaceutical compounds have been observed at the post-treatment stages. Among these compounds, analgesic, anti-inflammatory and anti-diabetic drugs are ubiquitous in Calgary's water.(Alnajjar, 2018) A lot of drugs belong to anti-diabetic including; Glimepiride.

1.2.2 Glimepiride (GPD)

Glimepiride (GPD is a white powder, odorless, with molecular weight 490.617 g/mol. GPD has the chemical formula $C_{24}H_{34}N_4O_5S$ and pKa value 6. Its solubility in water is less than 4 mg/L. As pH increase, the solubility of GPD increases. GPD is soluble in dimethylformamide, acetonitrile, slightly soluble in methylene chloride and very slightly soluble in methanol. GPD is colorless but absorbs in the UV region (λ_{max} 229 nm). Figure 1.1 shows the molecular structure of Glimepiride (GPD).

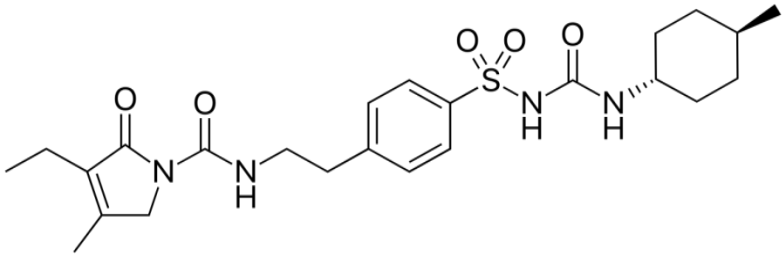

Figure 1.1: Molecular structure of Glimepiride (GPD)

Glimepiride drug is among the sulfonylureas used in diabetes treatment. (Badran, Manasrah, et al., 2019; Badran et al., 2020; Papich, 2007) This drug is excreted by the human body as metabolites (hydroxyl or carboxyl derivatives),(Takla, 1981) which supports their solubility in the environment and thus access to water sources.(Mrozik & Stefańska, 2014)

1.3 Wastewater treatment technology

The spread of pharmaceuticals in water indicates the ineffectiveness of traditional water treatment methods, so new methods must be developed to remove these pollutants from water bodies.(Badran, Manasrah, et al., 2019; Badran et al., 2020; Weigel, Kuhlmann, & Hühnerfuss, 2002) During the past years, many techniques used in the treatment of polluted water

have been developed such as filtration, catalytic oxidation and adsorption. Among these methods, adsorption is one of the most versatile technologies due to the flexibility of its design and application, it is easy to retrofit the treatment process, it is considered environmentally safe, high efficiency and it can be taken out from the laboratory scale to the pilot scale.

1.4 Adsorption process

Adsorption is the process by which molecules of a substance from a gas mixture or liquid solution became attached to a solid or liquid surface. As the solid that provides the surface is called adsorbent and the materials that will be absorbed are called adsorbate.(Yang, 2003) Thus, a layer of adsorbate is located on the adsorbent surface. Water treatment has proven that adsorption is an effective process in removing dissolved materials. Understanding the adsorption process cannot separated from comprehending the properties of the solid surface, i.e. adsorbent surface, because these adsorbents take a wide range according to their chemical and physical properties. During the last few decades, there is an increasing in interest and clear tendency for the use of nano adsorbents which show significant advancement with their special properties in several fields.

Carbon nanotubes (CNT) contain one single-walled (SWCNT) or multiwalled (MWCNT) graphene sheets tumbled down into a long, thin, hollow cylinder with a nanoscale outer diameter, typically in the range of 1-30 nm.(Badran, Manasrah, et al., 2019; Badran et al., 2020; Iijima, 1991) Commercially manufactured CNTs have possible environmental relevance

as both fixed-phase sorbents,(Majumder, Chopra, & Hinds, 2005; Majumder, Zhan, Andrews, & Hinds, 2007) and dispersed-phase sorbents, which can facilitate the transport of contaminants.(Cho, Smith, Wnuk, Fairbrother, & Ball, 2008; Cho et al., 2010) Because of their desirable combination of physical and chemical properties, both SWCNTs and MWCNTs are being manufactured at increasing averages and are among the most vastly used sorts of engineered nanomaterials.(Mauter & Elimelech, 2008; Templeton, Ferguson, Washburn, Scrivens, & Chandler, 2006)

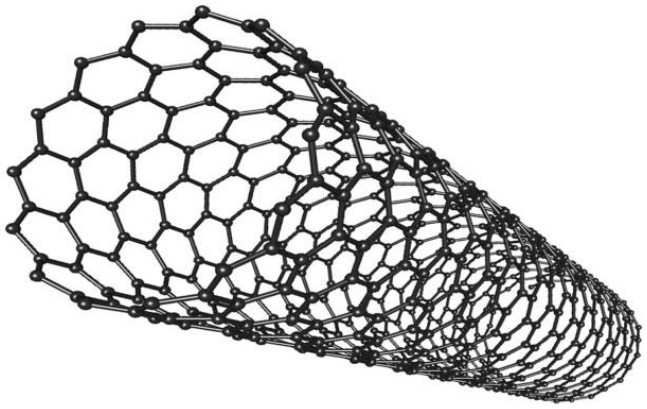

Figure 1.2: A model of carbon nanotube molecule.

1.5 Adsorption isotherms

Adsorption isotherm is a tool used to interpret the data obtained from the adsorption process under optimal conditions. Equations are used to get adsorption isotherm relation between the amount of adsorbate per unit of adsorbent (q_e) and the equilibrium concentration of solution after adsorption (C_e). Adsorption isotherm is a kindly method for defining the performance of an adsorbent and the adequacy of adsorption process but

alone, without any modeling of data, it does not supply any information particularly about the adsorption mechanism. To date, fifteen different isotherm models were developed. There are five common models for isotherms including Linear isotherm, Langmuir, Brunauer, Emmett, and Teller (BET), Freundlich and Temkin isotherms. These isotherms relate adsorbate uptake per unit mass of adsorbent, q_e, to the equilibrium adsorbate concentration in solution after adsorption, C_e, by the following equations:(Limousin et al., 2007; Worch, 2012)

$$q_e = \frac{C_o - C_e}{W} V \qquad (1.1)$$

$$q_t = \frac{C_o - C_t}{W} V \qquad (1.2)$$

where C_o, C_t, and C_e (mg/ L) are adsorbate concentration of initialization, time t, and equilibrium and V (L) and W (g) are solution volume and adsorbent dosage, respectively.

1.5.1 Langmuir isotherm

Langmuir isotherm assumes that the surface of an adsorbent is homogenous, which means that the surface containing the adsorbing sites is a perfectly flat plane with no folds and all sorption sites bind are equivalent. Another significant postulate is that each site can hold at most one molecule of adsorbent (mono-layer coverage only). There are not any interactions between adsorbate molecules on adjacent sites. Adsorbates molecules have tendency to get adsorb and desorb from surface. So, dynamic equilibrium exits between the adsorbed molecules and free

molecules. Based upon these assumptions, Langmuir represents the following equation:(Limousin et al., 2007; Worch, 2012)

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \quad (1.3)$$

where:

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

q_m = maximum monolayer coverage capacity (mg/g).

C_e = the equilibrium concentration of adsorbate (mg/L).

K_L = Langmuir isotherm constant (L/mg).

1.5.2 Freundlich isotherm

Freundlich isotherm is an empirical expression that accounts for surface heterogeneity**.** This isotherm was an empirical expression that accounts for surface heterogeneity by multilayer adsorption, exponential distribution of active sites of adsorbent and their energies towards adsorbate. The Freundlich isotherm is not good at very high pressures, but it is more accurate than the Langmuir isotherm for medium pressures. The main Freundlich equation is given by**:**(Nassar, 2013; Worch, 2012; Yang, 2003)

$$q_e = K_F\, C_e^{\frac{1}{n}} \quad (1.4)$$

Where K_F (L/mg) and 1/*n* are the Freundlich adsorption constants.

1.5.3 Sips Isotherm

The Sips isotherm is joint formula of the Freundlich and Langmuir isotherm models concluded for predicting the heterogeneous adsorption systems. At high concentration, it predicts a monolayer adsorption which is feature of the Langmuir isotherm, while at low concentration, it leads to Freundlich isotherm. The common form of the Sips isotherm model is: (Foo & Hameed, 2010)

$$q_e = q_m K_s {C_e}^{1/n} / (1 + K_s {C_e}^{1/n}) \qquad (1.5)$$

Where:

C_e = the equilibrium concentration of the analytes in the solution (mg/L).

q_e = the amount of analytes adsorbed per unit mass of adsorbent (mg/g).

K_S = the Sips constant.

q_m = the maximum adsorption capacity (mg/g), which depends on the number of adsorption sites.

The Sips isotherm equation is described by the dimensionless heterogeneity factor, *n*, which used to describe the system's heterogeneity as *n* varies between 0 and 1.55 when n, is unity; it hints a homogeneous adsorption process close to a Langmuir behavior. Otherwise, it looks like a Freundlich behavior.

1.5.4 Continuous adsorption and Breakthrough Curves

Despite the advantages of adsorption in removing water pollutants, most studies focus on batch experiments. This study is different in terms of

applying a continuous approach in order to provide a practical methodology to remove GPD from water. Since this study is carried out using a continuous-flow setup, a breakthrough curve is required to follow the adsorption process. Such curve is constructed by following the effluent adsorption concentration at the outlet of a fixed bed adsorber. Breakthrough curves are important for adsorptive separation technologies and for the characterization of porous materials.(Samarghandi, Hadi, & McKay, 2014) Details on the BTC and the mathematical models used to describe it are discussed in Chapter 2 of this thesis.

1.6 Aims of the study

This work aims to develop a new method to remove GPD from water resources using multi-walled carbon nanotubes (MWCNT). The study investigated the different parameters affecting the adsorption, such as, concentration of the carbon nanotubes, concentration of drugs, pH, flow rate, and column height. In addition, this work aims at the possibility of regeneration MWCNT without affecting its adsorption capacity.

The specific objectives of this research are sorted as follows:

1. A preliminary batch experiments will be carried out to prove the concept through adsorbing drug from aqueous solution using MWCNT as adsorbates, followed concentration determination after adsorption by UV.
2. Performing the adsorption study using the continuous-flow setup

3. Study the effect of solution pH, column height, flow rate and adsorbent amount, on the adsorption efficiency, in order to optimize the adsorption process conditions.
4. Construct a breakthrough curve based on the best parameters from the previous step
5. Attempt to regenerate the MWCNT adsorbent by rinsing it with NaOH and distilled water.

CHAPTER 2

EXPERIMENTAL AND METHODS

2.1 Instruments and Materials

Glimepiride (99.0%, M.Wt. 490.62 g/mol) was obtained from Alfa Aesar (Tewksbury, MA, USA) Commercial multi-walled carbon nanotubes (MWCNT, 95%) was purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, Sichuan, China). Acetonitrile (99.8 %), white silica (mesoporous, 99.9%) and other reagents used to prepare the pH-regulating including borax, sodium hydroxide (NaOH), hydrochloric acid (HCl), potassium dihydrogen phosphate (KH_2PO_4), potassium hydrogen phthalate (KHP) and acetic acid (CH_3COOH)were of high purities and were obtained from Sigma-Aldrich Chemical Company (Milwaukee, Wisconsin, USA). The pH of the solutions was measured using a Jenway 3510 pH meter (Jenway, Staffordshire, UK). A Lab Tech shaker (Daihan Labtech, Korea) was used to sonicate the samples as required. A UV-Vis spectrophotometer (UV-1800, Shimadzu, Canby, OR, USA) coupled to a temperature controller (Fried electric device WBH-060N) was used to obtain the spectra of the drugs and follow the adsorption process. Sample weighing was done using an analytical balance (ASB-310-C2-V2, MRC Lab Equipment. Essex, UK). The peristaltic pump (model PP-F-380, with head model LEAD-15-44, Longer Precision Pump Co., Ltd, Baoding, Hebei, China) that is used in this work is an 8-channel, 4 rollers with a flow rate between

1-380 mL/min. The pump was supplied by Biotech Medical Supplies, Ramallah, Palestine.

2.2 Preparation of the stock solution

A standard solution of glimepiride (GPD) was prepared by dissolving 25.00 mg of GPD powder in 1.0-L of 50:50 acetonitrile/distilled water mixtures. The solution was sealed to bottle and covered with aluminum foil for no longer than three days.

2.3 Preparation of standard solutions

Standard solutions with the following concentration 1, 5, 10, 15, and 20 mg/L were prepared by diluting 0.4, 2, 4, 6, and 8 mL, respectively from 25 ppm stock solution of Glimepiride (GPD) with acetonitrile/DW mixture.

2.4 Preparation of pH-regulating solutions

In this work, the solvent used to dissolve GPD was a mixture of 1:1 distilled water and acetonitrile. For the effect of pH study, this mixture was replaced with a buffer (or pH-regulating) solution. Table 2.1 lists the different mixtures used to prepare pH-regulating solutions that were used for the pH study. For instance, to prepare the solution of pH = 1, equal volumes of 0.2 M KCl and 0.2 M HCl were mixed, and the final pH was adjusted by adding diluted solutions of NaOH or HCl.

Table 2.1: Preparation of pH-regulating solutions.

Solution pH	Solutions	
1.0	0.20 M KCl	0.20 M HCl
3.0	0.10 M KHP	0.10 M NaOH
5.0	0.10 M CH_3COOH	0.10 M NaOH
7.0	0.10 M KH_2PO_4	0.10 M HCl
9.0	0.10 M Borax	0.10 M HCl
12.0	0.10 M Borax	0.10 M NaOH

2.5 Construction of a calibration curve

A calibration curve was constructed by reading the absorbance for 1.0 mL of each standard solution prepared above and plotting the absorbance vs. concentration for each concentration. The measurements were recorded at the maximum wavelength of GPD which was 229 nm. The calibration curve was repeated three times, and the average of the three readings was calculated. In addition, the error bars were obtained from the standard deviation which was calculated according to the following equation:

$$SD = \sqrt{\frac{\sum|x-\bar{x}|^2}{N}} \qquad (2.1)$$

where $\sum$ means "sum of", x is a value in the data set, $\bar{x}$ is the mean of the data set, and N is the number of data points.

2.6 The experimental setup

The experimental setup used in this study is shown in Figure 2.1. The setup is constructed by connecting the container of the drug stock solution of GPD, to the adsorption column through a peristaltic pump. The column was filled by a mixture of MWCNT and white silica. Samples were

withdrawn from the adsorption column into a collection container, to be analyzed by UV-Vis spectrophotometry.

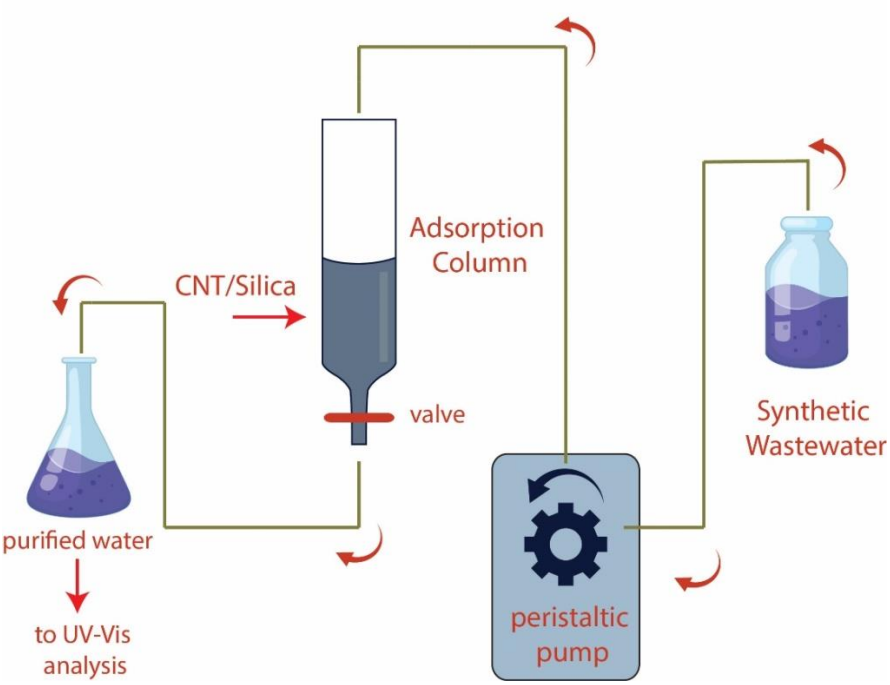

Figure 2.1: Experimental setup for the continuous adsorption

2.7 Adsorption experiments

The adsorption experiments were performed by first filling the adsorption column by a known mixture of MWCNT/white silica, the top and bottom of the column were covered by a layer of glass wool and cotton to avoid the loss of adsorbent and ensure a closely packed arrangement. Then, the peristaltic pump was connected to the sample container and the adsorption column and turned on; the system was checked against any leaks. Then, the flow was started by pulling the liquid from the sample container through the pump into the adsorption column at a constant flow

rate. Samples were then taken at constant time intervals in small vials for UV-Vis. analysis. The analysis was done immediately.

2.7.1 Batch experiments

This part follows batch experiment procedure that each step done alone in vials without flowing of analyte or polluted water throwing a constant adsorbent column. The batch experiments were done by filling 10-mL of the standard 25.0 ppm solution of GPD in small plastic vials, followed by an addition of different masses of MWCNT in the range of 2-100 mg. The solutions were shaken for 30 minutes at room temperature and then allowed to settle for 4 hours and it has been filtered. Samples from the aliquots were taken for UV-vis.

2.8 Studying the parameters affecting the adsorption

Various environmental parameters have been studied to achieve the greatest possible drug adsorption. First, the effect of column height was studied by setting a fixed ratio between the amount of MWCNT and the amount of white silica (1:40). Table 2.2 shows quantities of MWCNT and white silica that were used. This part was carried out under the flow rate of 4 mL / min. and a specific concentration for drug; 25 ppm. The second parameter studied was the effect of the amount of adsorbent by changing the amount of MWCNT used. And the quantities were as follows 50, 100, 150, 200, 300 and 400 mg MWCNT, with a fixed column height of 3 g and a constant flow rate of 4 mL / min. Therefore, the best amount of adsorbent was 400 mg. In order to achieve the best adsorption efficiency, the effect

flow rate was studied by fixing all other parameters. The measured flow rates were 2 mL / min, 4 mL / min and 6 mL / min. The next factor studied was the pH, which is considered one of the most important parameters affecting the adsorption process. The adsorption of drugs on MWCNT was studied in acidic, neutral, and basic media.

Table 2.2:Quantities of MWCNT and white silica for study effect of column height.

White silica (g)	MWCNT (mg)
1	40
2	80
3	120
4	160

2.9 Data analysis and continuous adsorption models

A typical breakthrough curve is shown in Figure 2.2. The adsorption is initiated by introducing the sample through the fixed bed with the help of a peristaltic pump. The bed is packed with an adsorbent, which consists in our case with MWCNT supported on silica. The sample concentration is then measured at the outlet of the fixed bed.

At the beginning of the adsorption process, a rapid drop in the sample concentration is observed as shown in Figure 2.2. As time elapsed, the adsorption became weaker due to coverage of the active sites of the adsorbent. A sudden increased in the sample concentration was observed,

and a breakthrough point (T_b) was determined. The performance of the adsorbent is based on the T_b. A delay in T_b indicates a better adsorbent.

In a fixed-bed adsorption, the process takes place within a narrow region called the mass-transfer zone (MTZ) or adsorption zone, as shown in Figure 2.2. As time elapsed, this region moves down, until the adsorbent was fully exhausted.(Hethnawi et al., 2020; Hethnawi, Nassar, Manasrah, & Vitale, 2017; Tian et al., 2013)

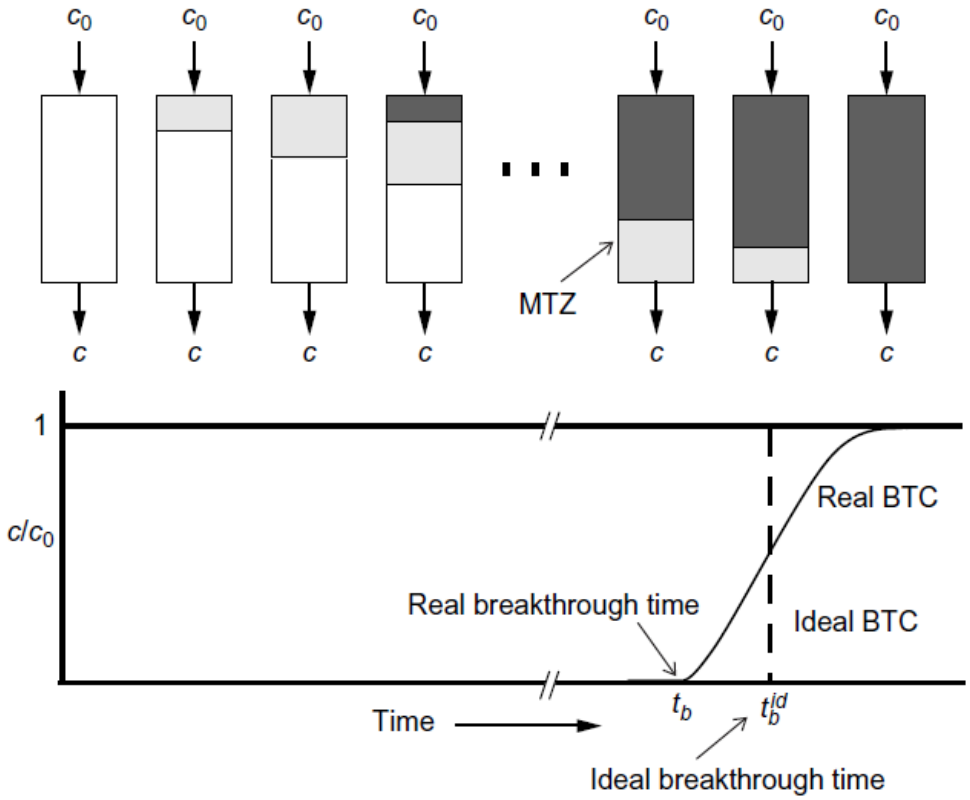

Figure 2.2: Traveling of the mass transfer zone (MTZ) through the adsorber bed and development of the breakthrough curve (BTC). (Taken from Ref.51)

Based on these concepts, different mathematical models were developed to describe the continuous adsorption and the breakthrough curve. A commonly used model is the one proposed by Thomas. In this

model, the mass transfer is proportional to axial dispersion and thickness liquid film on the particle surface, as per the equation:(Thomas, 1944)

$$\frac{C}{C_0} = \frac{1}{1+e^{(k_{TH}q_0\frac{x}{v}-k_{TH}c_0t)}} \quad (2.2)$$

Where C is the adsorbate concentration (mg L^{-1}) at time t (min), C_0 is the initial sample concentration, q_0 is the total adsorption capacity (mg g^{-1}), v is the flow rate (mL/min), k_{TH} is the Thomas rate constant (mL mg^{-1} min^{-1}), and x is the mass (g) of the material in the column. Thus, a nonlinear curve fitting can be done using eq. 3 to obtain the unknown paramours, k_{TH} and q_0. In this work, the fitting was done in Originlab(OriginLab Corporation, 2019) according to the following mathematical equation:

$$y = \frac{1}{1+e^{(ab-cx)}} \quad (2.3)$$

Therefore, we can obtain the ideal break point time ($t_b^{id)}$ (see Fig. 2.2) as its equal the ratio of ab/c.

Another model is the one proposed by Adams and Bohart.(Bohart & Adams, 1920) This model assumes that the rate of adsorption is proportional to the residual adsorbent and adsorbate concentration. This model was originally proposed for gas-solid adsorption, but it is now extended to other systems:

$$\frac{C}{C_0} = \exp(k_{AB}C_0t - k_{AB}N_{AB}\frac{Z}{F}) \quad (2.4)$$

Where C and C_0 are defined as before. N_{AB} is the saturation concentration (mg L^{-1}). F is the cross-sectional flow rate ($cm.min^{-1}$), k_{AB} is the Adams-Bohart rate constant (mL mg^{-1} min^{-1}), and Z of the bed height

(cm). Using nonlinear fitting, the unknown parameters N_{AB} and k_{AB} can be obtained. In this work, the fitting was done in Originlab(OriginLab Corporation, 2019) according to the following mathematical equation:

$$y = \exp(abx - ac) \qquad (2.5)$$

CHAPTER 3

RESULTS AND DISCUSSION

The adsorption of GPD on the MWCNT surface was investigated as per the procedure in the previous chapter. Prior to the continuous adsorption experiments, batch experiments using a stock solution of GPD and different weights of MWCNT were used to prove that the adsorption is working. The results of the batch experiments were successful. The absorbance of GPD was observed to decrease upon mixing with the MWCNT, and the removal of the drug was increasing with the amount of the MWCNT. Therefore, the continuous experiments continued.

Figure 3.1 shows the room-temperature UV-Vis spectrum of the stock solution of GPD (25 ppm). Visually, the GPD solution was colorless. This was reflected by the absence of any absorption in the visible region. However, the drug absorbs strongly in the UV region, and the maximum wavelength, λ_{max}, was determined to be 229 nm. Therefore, all future spectra are recorded at this wavelength.

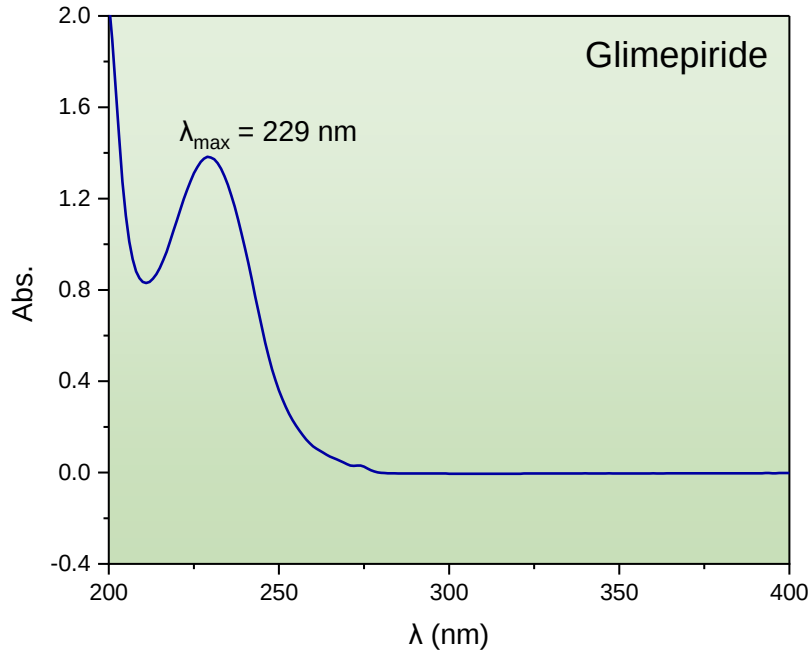

Figure 3.1: Room-temperature UV-Vis spectrum of 25 ppm Glimepiride.

3.1 Calibration curve of GPD

A calibration curve is a public method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard samples with known concentration.(Thévenot, Toth, Durst, & Wilson, 2001) The calibration curve was used to calculate the concentrations of the effluent samples during the adsorption experiments. The calibration curve was constructed by preparation a standard solution with known concentrations from 25 ppm GPD stock solution at λ_{max}. Figure 3.2 shows a calibration curve for GPD standard solutions at λ_{max} = 229 nm. The points represent the average of three replicates, and the error bars represent the standard deviation of the three readings.

The concentrations of the analyte and the instrument response for each standard can be fit to a straight line. This yields a model described by the equation y = mx + b. Where m is a slope, *x* is a concentration of analyte of unknown sample and b is a y-intercept. Linearity of the calibration curve is generally determined through the correlation coefficient (R^2). A correlation coefficient close to unity (R^2 = 1) is considered an adequate evidence to conclude that the calibration curve is linear.(Moosavi & Ghassabian, 2018) The linear equation derived from the calibration curve was then used to determine the concentration of GPD in treated aquatic solution.

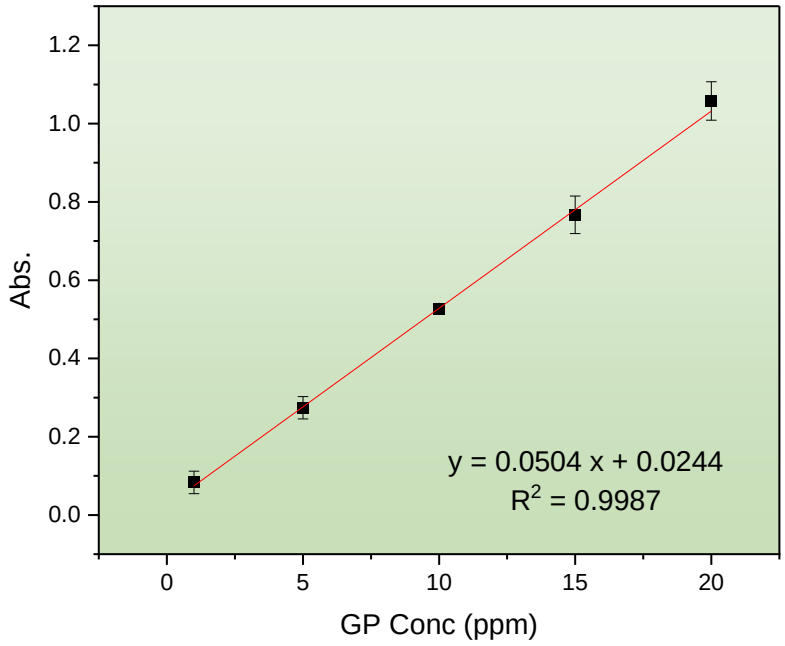

Figure 3.2: Calibration curve for GPD standard solutions at 25°C, and pH ≈ 7.

3.2 Batch experiments and adsorption isotherms

Before performing any continues adsorption experiments on GPD, batch experiments were done to explore its adsorption behavior and determine the isotherm model. The adsorption isotherms used in this study were discussed in the introduction.

The experimental data for the batch adsorption experiments were fitted to the models of Langmuir, Freundlich and Sips. Figure 3.3 shows the nonlinear fitting of the data according to the Langmuir model. The R^2 value was 0.9593. The 3.4 shows Freundlich fitting with an R^2= 0.9583. Therefore, these results are not inclusive. So, the data were fitted to a Sips model (equation 1.5) as shown in Figure 3.5. The R^2 value was 0.9586. The fitting parameters were found in Table 3.1. Since the exponent *n* in the Sips isotherm is < 1, the adsorption of GPD can be described by Freundlich behavior.

Table 3.1: Fitting parameters for the batch adsorption of GPD

Freundlich				**Sips**			
n	K_F	R^2		n	K_S	q_m	R^2
1.0512	0.6083	0.9583		0.7983	0.0131	29.58	0.9586

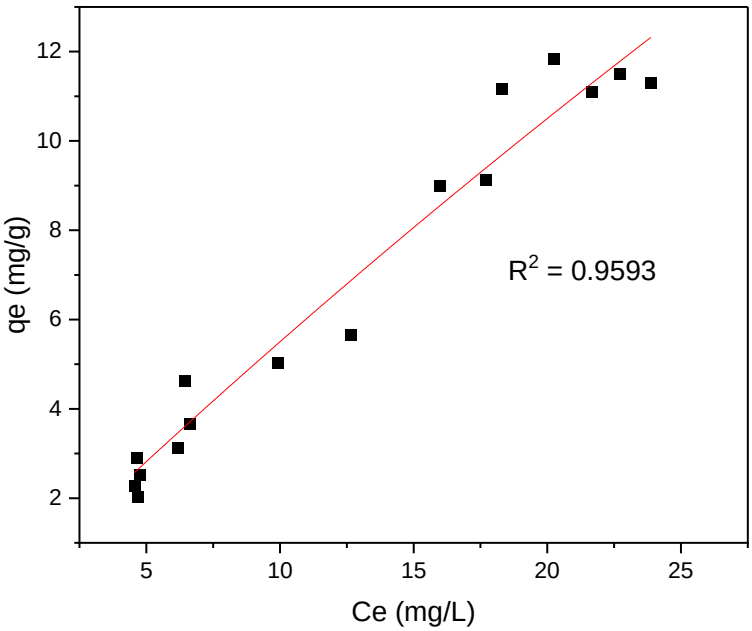

Figure 3.3: Nonlinear fitting for the adsorption of 25 ppm GPD on MWCNT at room temperature based on the Langmuir model. Temp. = 25°C, pH ≈ 7.

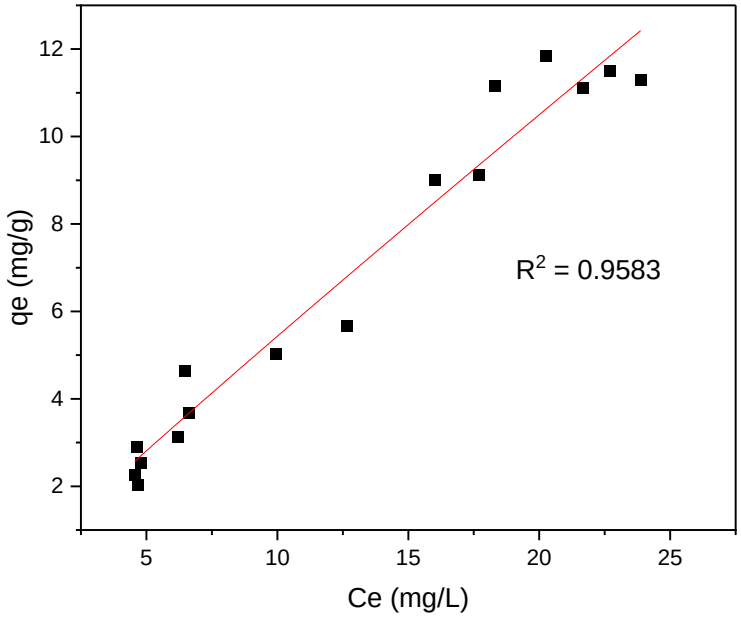

Figure 3.4: Nonlinear fitting for the adsorption of 25 ppm GPD on MWCNT at room temperature based on the Freundlich model. Temp. = 25°C, pH ≈ 7.

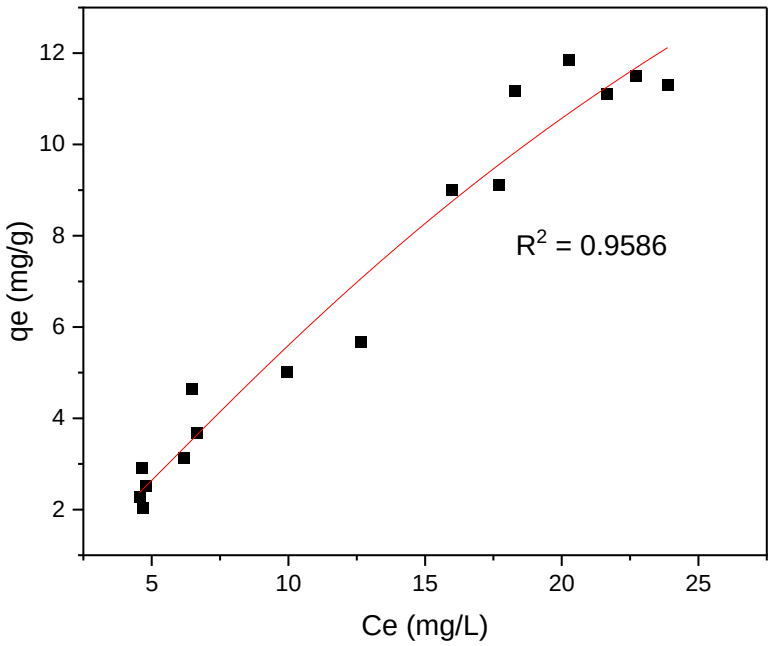

Figure 3.5: Nonlinear fitting for the adsorption of 25 ppm GPD on MWCNT at room temperature based on the Sips model. Temp. = 25°C, pH ≈ 7.

3.3 Effect of column height

The effect of column height was investigated by setting a constant ratio between the amount of MWCNT and the amount of white silica. Quantities were used are shown in Table 2.2. The top and bottom of the bed were covered by a layer of glass wool and cotton in order to avoid the loss of adsorbent and ensure a closely packed arrangement.(Afroze, Sen, & Ang, 2016) This part was carried out under the flow rate of 4 mL/min. and a 25 ppm GPD stock solution. Figure 3.6 shows the effect of bed-height on the adsorption on 25 ppm GPD adsorption.

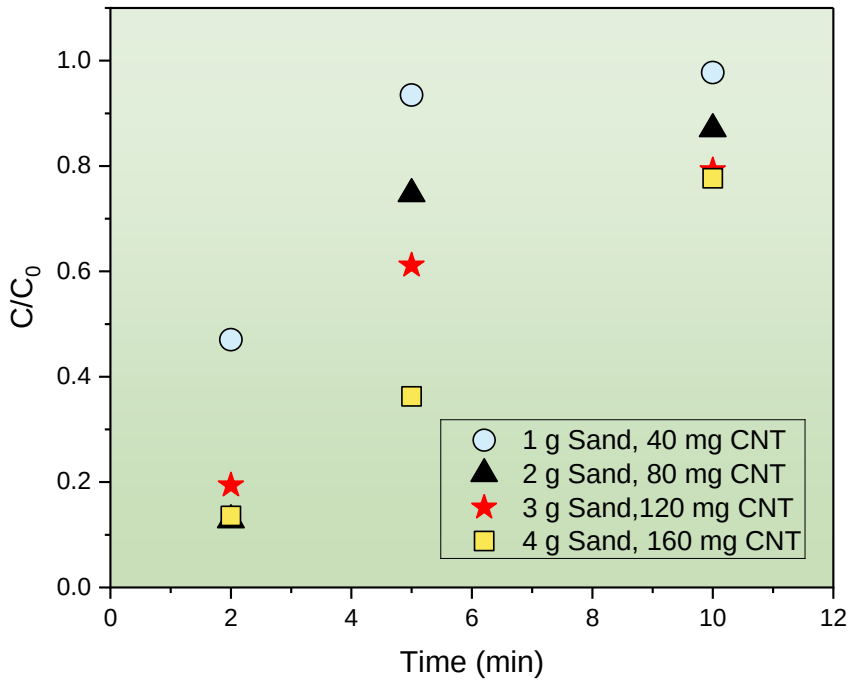

Figure 3.6: Effect of bed-height on the adsorption on 25 ppm GPD adsorption, using constant ratio of silica to MWCNT at 25°C, and pH ≈ 7.

Figure 3.6 shows that the removal efficiency increases when the column height increase. As the bed height increased, the contact time of GPD solution inside the column increased, allowing the GPD molecules to spread deeper into the silica supported MWCNT and resulting in higher GPD removal efficiency. The efficiency is close at 120 mg MWCNT: 3 g silica and 160 mg MWCNT: 4 g silica. At 3 and 4 grams of silica, the removal efficacy is close to each other. Therefore, based on the results, the best study height is 3 grams of silica.

3.4 Effect of flow rate

The flow rate greatly affects the column performance and the adsorption efficacy in continuous process, as the flow rate is an important parameter to assess the adsorption efficiency in the continuous process on the pilot or industrial scale. The effect of the flow rate on the adsorption of the GPD was investigated by changing the flow rate (2, 4 and 6 mL / min) with a fixed bed height and 25 ppm GPD stock solution. In this effort, the flow rate was changed to achieve the maximum removal of GPD adsorbate, and it was found that the maximum uptake was achieved at a flow rate of 2 mL/min. Figure 3.7 shows the effect of flow rate on the continuous adsorption of 25 ppm GPD.

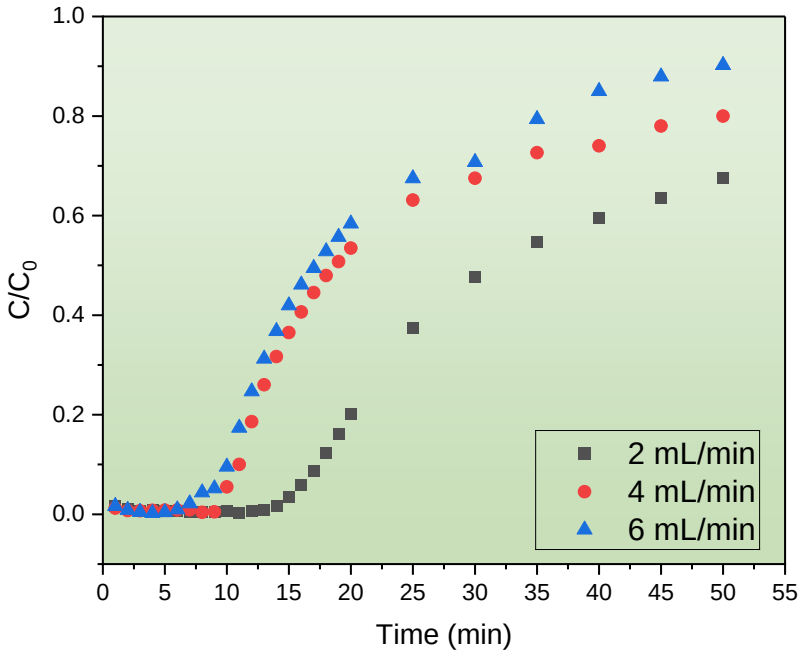

Figure 3.7 : Effect of flow rate on the continuous adsorption of 25 ppm GPD at 25°C, and pH ≈ 7, MWCNT concentration = 400 mg, bed-height = 3 cm.

Figure 3.7 shows that at a flow rate of 6 mL/min., breakthrough curve became steeper and the breakthrough time and GPD concentration decreased, because the contact time of GPD adsorbate in column not enough to reach the adsorption equilibrium at this flow rate, the front of the adsorption area reached very fast to the bottom of the column, which column going early saturated, thus the GPD solution left the column before equilibrium occurred,(Ghorai & Pant, 2005; Singh & Pant, 2006) so the contact time between GPD solution and silica supported MWCNT was very short at high flow rate, which caused a decrease in the removal efficiency. At flow rate 4 mL/min., GPD solution had more time to contact with silica supported MWCNT, breakthrough curve became less steep and the breakthrough time increased, resulting higher removal GPD molecules in column. So, the time of column saturation arrival was slower. When at flow rate 2 mL/min., GPD had most time to contact the silica supported MWCNT, so the breakthrough time increased and highest removal of GPD molecules in column. Therefore, it was observed that the GPD removal percentage of column increases with decrease in flow rate. The variation in the slope of the breakthrough curve and adsorption capability may also be explained on the basis of mass transfer fundamentals. At higher flow rate, the rate of mass transfer increases, i.e., the amount of GPD adsorbed onto the unit bed height increases with increasing flow rate, causing faster saturation at a higher flow rate.

3.5 Effect of pH

The solution pH is one of the most important parameters that affect the adsorption process. The effect of solution pH on the adsorption of GPD was studied in the pH range of 1-12. GPD solutions with different pH values were prepared using the pH-regulating described in section 2.4. The effect of pH was studied in batch mode rather than in continuous-flow mode to avoid the influence of other parameters. Figure 3.8 shows the results of the effect of pH on the GPD % removal when MWCNT was used as adsorbent. As the figure shows, the removal efficiency increases as the solution becomes more acidic. The best removal efficiency was obtained at pH = 3 and reaches values < 95%. Interestingly, this observation is in disagreement with the adsorption of glimepiride on activated carbon, for mercury (II) adsorption over MWCNT/silica,(Saleh, 2015) and for the adsorption of alizarine dye on maghemite surface.(Badran & Khalaf, 2019) The effect of pH on adsorption can be explained by understanding the electrostatic attractions between the functional groups of the adsorbate and the adsorbent surface. Glimepiride has -NH groups so it behaves as a week base in aqueous solutions. In acidic medium, the -NH groups are protonated forming a GPD cation (GPD+). The reported pKa of GPD is 8.1 (corrected from a previous value of ca. 5-6).(Grbic, Parojcic, Malenovic, Djuric, & Maksimovic, 2010; Sanofi-Aventis Canada Inc., 2016) Also The reported zero-point charge (ZPC) of native MWCNT is 5.3.(Q. Wu & Xiong, 2015; Zha et al., 2018) As a result, the adsorbent would have a net positive charge below pH 5.3, and a net negative charge above that value.

Under these conditions, there should be an electrostatic repulsion between the MWCNT surface and the GPD cation (GPD+), which hinder the adsorption at lower pH, in contraction to the experimental results. Therefore, the adsorption enhancement at lower pH in this work should be attributed to other factors. As the pH decreases, the GPD^{+} ion concentration increases in water leading to increasing the drug mobility. Since MWCNT has two adsorption mechanisms; on the surface and within the tubes, the increase in the drug's mobility will increase the contact time and facilitate the adsorption inside the tubes. This is supported by the fact that adsorption followed Freundlich (physical) behavior, rather than chemical.

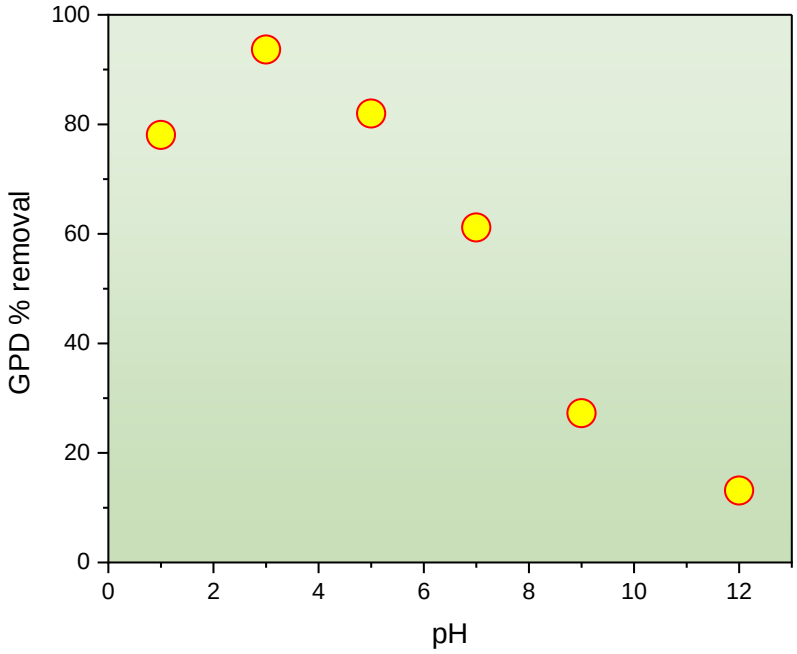

Figure 3.8: Effect of solution pH on the batch adsorption of 25 ppm GPD at 25°C. MWCNT concentration = 50 mg, bed-height= 3 cm.

3.6 Effect of amount of adsorbent

The effect of the amount of MWCNT on the adsorption of GPD was studied in order to optimize the adoption process. As discussed in the introduction, this effect can be best described by a breakthrough curve (BTC). Figure 3.9 shows the BTC's obtained by continuous-flow adsorption of 25 ppm of GPD on different amount of MWCNT supported on silica. As the figure illustrates, the adsorption capacity of the MWCNT increases with increasing the amount of adsorbent, which results in a delay to obtain the breakthrough time (T_b) from 1.6 to almost 14.7 minutes, when the amount of MWCNT increased from 100 to 400 mg. This can be explained by the increase in the active sites available for adsorption as the amount of adsorbent increases.

As mentioned in the chapter 2 (section 2.8), nonlinear curve fitting was used to fit the data obtained for the amount of adsorbent. Both the Adams–Bohart and Thomas models were also applied to the breakthrough curves. The Adams–Bohart model has failed to describe the adsorption data as shown in Figure 3.9. On the other hand, the Thomas model has succeeded to predict the breakthrough curves to a high extent as seen in Figure 3.10 The fitting parameters for both models are tabulated in **Table 3.2**. The maximum adsorption capacity, q_0, obtained by the Thomas model ranges between 48.8 and 275.3 mg/g. The maximum value is obtained with 400 mg of MWCNT. This indicates the high adsorption capacity of the

MWCNT to absorb pharmaceuticals such as GPD. Also, Figure 3.10 also shows that removal efficiency is >95%.

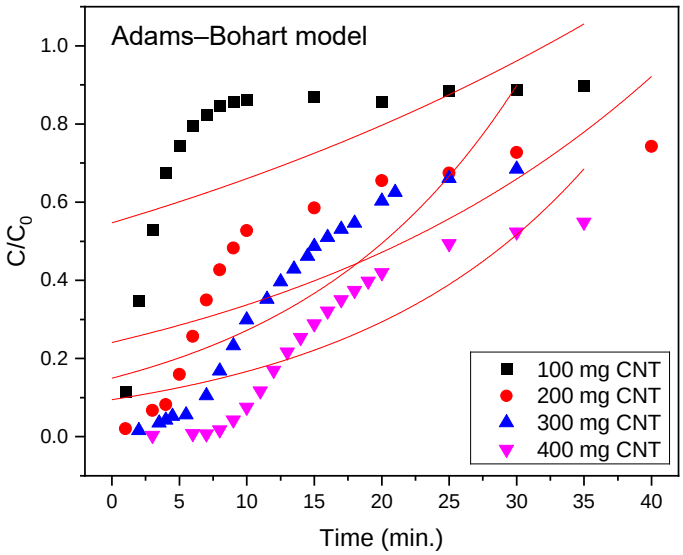

Figure 3.9: Non-linear curve fitting according to the Adams–Bohart model for 25 ppm GPD adsorption at 25°C. pH ≈ 7, bed-height= 3 cm.

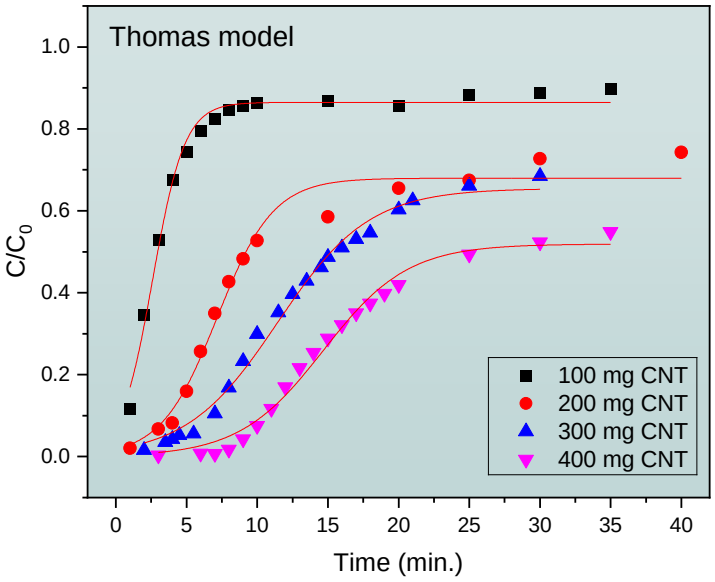

Figure 3.10: Non-linear curve fitting according to the Thomas model for 25 ppm GPD adsorption at 25°C. pH ≈ 7, bed-height= 3 cm.

Table 3.2: Fitting parameters obtained applying non-linear fitting according to the Adams–Bohart and Thomas models

Thomas Fitting		A	b	c	R^2	K_m (mL mg^{-1} min^{-1})	q_0 (mg/g)	T_b (min.)
	400 mg	0.519	0.647	7.618	0.9865	1.34×10^{-2}	275.3	14.7
	300 mg	0.655	0.473	7.489	0.9901	1.24×10^{-2}	214.5	11.4
	200 mg	0.680	0.741	4.872	0.9777	2.01×10^{-2}	134.4	7.2
	100 mg	0.865	1.022	2.252	0.9866	3.53×10^{-2}	48.8	2.6
		A	b	c	R^2			
Adams Fitting	400 mg	0.240	0.241	4.01	0.6977			
	300 mg	0.499	0.089	10.85	0.6276			
	200 mg	0.156	0.281	-1.53	0.5936			
	100 mg	0.731	0.019	7.81	0.2162			

3.7 Regeneration

High removal efficiency and simplicity are the most important properties in adsorption process, so adsorption is a favorable process for removal of drugs from water. To make this process environment friendly, we investigated the regeneration of adsorbent. Regeneration is significant factor which determines the effectiveness of cost and reuse of MWCNT. From the effect of the pH results, it was found that the adsorption of drugs is dependent on pH and when pH decreased, the removal efficiency increased in acidic medium. Thus, desorption of drugs can be carried out at neutral pH. This indicates that washing the contaminated MWCNT in neutral medium are more efficient than the acidic or basic medium for regeneration process. Figure 3.11 shows adsorption after regeneration process, using 0.1M NaOH and distilled water.

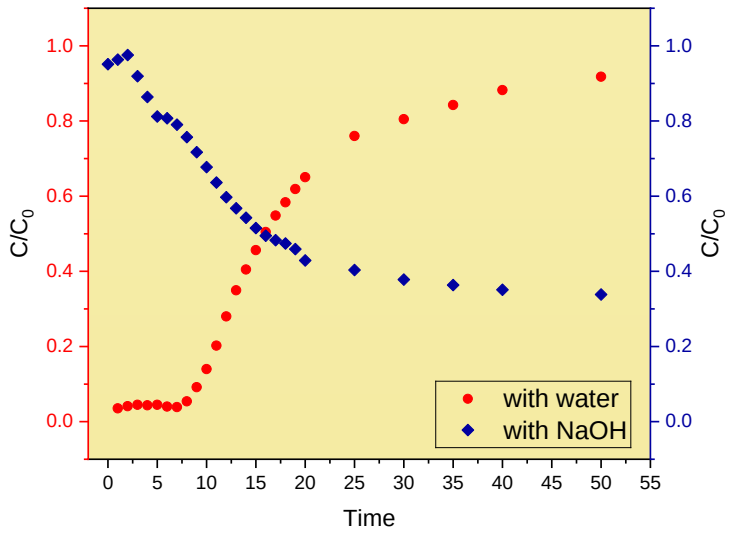

Figure 3.11: Effect of regeneration, flush with 0.1M NaOH, distilled water, flush time= 15 min.

As seen, when the column is flushed with water, the performance of the adsorption column pertained only for 5 min before the effluent concentration starts to increase. Yet, when the column was flushed with dilute NaOH, the column stayed functional for more than 50 min. Therefore, MWCNT can be reused in the column bed repeatedly to save costs.

CHAPTER 4

CONCLUSION AND FUTURE WORK

Conclusion

This study had been performed by two ways, the first way was batch process to ensure that the adsorption process occurs naturally by using a stock solution of Glimepiride and different weights of MWCNT, absorbance of GPD reduced after mixing with MWCNT and removal of GPD was increased when the amount of MWCNT increased. Second way was the continuous process by which the effects of the parameters were studied. This study showed that carbon nanotubes are an effective adsorbent to remove GPD from water in short time and near complete removal. The effects of different parameters were studied, and the results shown that the adsorption process was dependent on the amount of adsorbent, column height, pH, and flow rate. Adsorption efficiency increased as the amount of adsorbent increased. Maximum removal was obtained at pH=3. Adsorption efficiency increased as the column height increased. The adsorption efficiency increased as the flow rate decreased. Adsorption models were also investigated and were described by Thomas and Adams-Bohart model and fitted well the Thomas model. The regeneration studies were carried out using NaOH confirmed that the MWCNT can be reused. In conclusion, MWCNT are effective and selective adsorbent, and its regeneration is simple. These results confirmed that the adsorption process with MWCNT is efficient, simple, and cost-

effective which made it suitable to convert from laboratory scale to industrial scale.

Future work

Our future efforts will be focusing on regenerate the contaminated adsorbent and reused for treating water from another organic pollutant which can make chemical interaction with GPD molecules adsorbed on the surface of adsorbent.

There are many ideas that we would have like to attempt in the future. This thesis has been mainly focused on using MWCNT as adsorbent without any modifications on MWCNT or on the adsorption process itself. The following ideas could be tested:

(1) Develop this work and transfer from laboratory scale to industrial scale.

(2) Try to design a filter to use in everyday life that fixes on the tap to purify drinking water from organic pollutants.

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جامعة النجاح الوطنية

كلية الدراسات العليا

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إشراف

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قُدمت هذه الأطروحة إستكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية في نابلس ، فلسطين

2020

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الملخص

تم إجراء هذه الدراسة بطريقتين ، الطريقة الأولى كانت عملية الدُفعات للتأكد من أن عملية الإدمصاص تحدث بشكل طبيعي باستخدام محلول من دواء الجليمبرايد وأوزان مختلفة من أنابيب الكربون النانوية متعددة الجدران ، لوحظ أنه عند زيادة كمية أنابيب الكربون النانوية فإن كمية دواء الجليمبرايد المدمصة سوف تزداد. وتم دراسة وتحليل النتائج باستخدام نموذج لانغمير وفريندلخ وسيبس وتبين أن عملية الإدمصاص تتوافق جيدا مع نموذج فريندلخ.

الطريقة الثانية كانت العملية المستمرة التي تم من خلالها دراسة تأثيرات المتغيرات أظهرت هذه الدراسة أن الأنابيب النانوية الكربونية هي مادة ماصة فعالة لإزالة دواء الجليمبرايد من المياه في وقت قصير وإزالتها شبه كاملة. تمت دراسة تأثيرات المتغيرات المختلفة وأظهرت النتائج أن عملية الإدمصاص تعتمد على كمية المادة الماصة وارتفاع العمود ودرجة الحموضة ومعدل التدفق. زادت كفاءة الإدمصاص مع زيادة كمية أنابيب الكربون النانوية. تم الحصول على أقصى إزالة عند الرقم الهيدروجيني = 3. زادت كفاءة الإدمصاص مع زيادة ارتفاع العمود. أيضا ، زادت كفاءة الإدمصاص مع انخفاض معدل التدفق. أيضًا تم فحص نماذج الإدمصاص ووصفها حسب نموذج توماس و آدامز-بوهارت وتناسب مع نموذج توماس جيدًا. أجريت دراسات إعادة التدوير (الاستخدام) باستخدام قاعدة هيدروكسيد الصوديوم .أظهرت الدراسة أنه يمكن إعادة استخدام MWCNT. في الختام ، إن الأنابيب النانوية الكربونية هي مادة ماصة فعالة وغير سامة ، وتجديدها بسيط أكدت هذه النتائج أن عملية الإدمصاص بواسطة أنابيب الكربون النانوية تتسم بالكفاءة والبساطة والفعالية من حيث التكلفة مما يجعلها مناسبة للتحويل من النطاق المختبري إلى النطاق العملي .