An-Najah National University
Faculty of Graduate Studies

Phenylamine and Phenylamide -Functionalized Silica (SiBN and SiBCON) for the Removal of Carbamazepine from Wastewater

By
Israa Marwan Mahmod Aqel

Supervisor
Prof. Shehdeh Jodeh
Co- Supervisors
Prof. Raed Al Kowni

This Thesis is Submitted in Partial Fulfillment of the Requirements for the Master Degree of Chemistry, Faculty of Graduate Studies, An-Najah National University, Nablus-Palestine.

2021

Phenylamine and Phenylamide -Functionalized Silica (SiBN and SiBCON) for the Removal of Carbamazepine from Wastewater

By
Israa Marwan Mahmod Aqel

This thesis was defended successfully on 8/6/2021 and approved by:

Defense Committee Members	**Signature**
1. Prof. Shehdeh Jodeh/Supervisor	.....
2. Prof. Raed ALKowni/Co-Supervisor	.....
3. Dr. Subhi Samhan/External Examiner	.....
4. Dr. Nidal Zatar /Internal examiner	.....

Dedication

To my father and my mother who taught me how to give

To my beloved husband Ahmad

To dear children my Rakan and Ayla

To my brothers and sister

To all my friends who spared no effort to help

I dedicate this modest work

Acknowledgment

Foremost, praise to almighty God, lord of the worlds before and after, and blessings and peace be upon the most honorable prophets and messengers, our Prophet Muhammad.

At the outset, I extend my great thanks to Prof. Dr. Shehda Judeh and Dr. Raed Al-Koni for supervising this work for all the support and advice in my research work.

We thank Professor Ismail Radi and Dr. Said Taghdouini for preparing Phenyl Amine Silica (SiBN) in their laboratories at Mohamed Bremer University in Morocco.

Many thanks to MEDRC for funding me for my masters. I also thank the projects through the Palestinian Water Authority for their follow-up to the project.

I also extend my sincere thanks to my colleague Dr. Ghadeer Al-Hanbali, who helped and guided me during my work in preparing and analyzing samples.

I am also grateful to all my professors (a giant in the Department of Chemistry) at An-Najah National University.

Thanks are also due to all the technicians and workers in the Department of Chemistry at An-Najah National University, especially Mr. Omair Nabulsi and Mr. Nafez Dweikat for their assistance.

Finally, my thanks to everyone who has helped me in my endeavors throughout my work.

الإقرار

أنا الموقعة أدناه، مقدمة الرسالة التي تحمل العنوان:

Phenylamine and Phenylamide -Functionalized Silica (SiBN and SiBCON) for the Removal of Carbamazepine from Wastewater

سيليكا الفينيلامين والفينيلاميد الوظيفية (SiBN و SiBCON) لإزالة الكاربامازايبين من الصرف الصحي

أقر بأن ما اشتملت عليه هذه الرسالة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الإشارة إليه، حيث أن هذه الرسالة كاملة، أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمـــي أو بحث لدى أي 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 الطالبة: إسراء مروان محمود عقل

Signature: التوقيع: 

Date: التاريخ: ٨/٦/٢٠٢١م

Table of Contents

List of Tables

List of Figure

List of Abbreviation

Symbol	Abbreviation
CBZ	Carbamazepine
Ce	Metal concentration in the solution after treatment (mg / L)
Co	Metal concentration in the solution before treatment (mg / L)
FT-IR	Fourier Transform Infrared
GAC	Granular activated carbon
ΔG^{o}	Standard Gibbs free energy (J).
HPLC	High-Performance Liquid Chromatography
ΔH^{o}	Standard enthalpy change (J).
J	Joule
J/K	Joule per kelvin.
K	Kelvin.
KJ/mol	Kilo joule per mole.
KF	Freundlich Constant (mg/g).
KL	Langmuir constant isotherm (L/mg)
Kid	The intra-particle diffusion rate constant (mg/g.min-1/2).
K1	The rate constant of pseudo 1st-order (min-1).
K2	The rate constant of pseudo 2nd-order (mg/g.min-1).
Kd	The thermodynamic equilibrium constant (L/g).
L	Liter
L/g	Liter per gram.
µg/L	Microgram per liter.
Mg	Milligram.
Min	Minute
N	Dimensionless Freundlich constant indicating how favorable the adsorption process
NF	Nanofiltration
PAC	Powdered Activated Carbon
Qe	The amount of adsorbate per unit mass of adsorbent(mg/g).

Symbol	Abbreviation
Qt	The mass of adsorbate per unit mass of adsorbent at any time (mg/g)
R2	Correlation coefficient (regression coefficient)
RL	Dimensionless constant separation factor
R	Gas constant (8.314 J/mol K)
RO	Reverse osmosis
SiPr	3-aminopropylsilica
SiBN	Phenylamine-functionalized silica
SiBCON	Phenylamide - functionalized Silica
SEM	Scanning electron microscope
SiG	Silica gel
ΔS°	Standard entropy
T	The absolute temperature (K)
TGA	Thermal Gravimetric Analysis
V	Volume of solution
W	Mass of adsorbent (g).
WHO	World health organization

Phenylamine and Phenylamide -Functionalized Silica (SiBN and SiBCON) for the Removal of Carbamazepine from Wastewater

By
Israa Marwan Mahmod Aqel
Supervisor
Prof. Shehdeh Jodeh
Co- Supervisors
Prof. Raed Al Kowni

The study aims to remove Carbamazepine from aqueous solutions, through the use of functional silica phenylamine (SiBN), which is characterized by its excellent chemical stability and thermal stability. As silica aroused great interest, adsorbents based on it were prepared due to their unique large surface area, uniform pore structure, and well-modified surface properties. It was decided to prepare a new silica adsorbent with phenylamine with amide (SiBCON).

The adsorbent obtained were analyzed by various spectroscopy devices, including Fourier Transform Infrared Spectroscopy (FT-IR), Thermogravimetric Analysis (TGA), and Scanning Electron Microscopy (SEM). As a practical test application for prepared adsorbent.

Then analyzes were performed with High Performance Liquid Chromatography (HPLC) instrument to calculate the amount remaining in the solution after the adsorption process. The results obtained proved that the removal efficiency of Carbamazepine was very good. The maximum removal rates were 98.37% for SiBN and 98.22% for SiBCON.

The (SiBN) (SiBCON) adsorption efficiency of Carbamazepine was evaluated, and the adsorbents showed excellent removal efficacy of

Carbamazepine, with the optimum condition being found: (1) room temperature, (2) pH 9.0, (3) 10.0 ppm initial concentration and (4) contact time 15 min.

Isometric analysis showed that the adsorption of Carbamazepine on SiBN and SiBCON correlated with Langmuir uptake. But thermodynamic analysis showed that the uptake of Carbamazepine on SiBN and SiBCON is negative free energy.

Regeneration of SiBN and SiBCON can be done by treatment with 0.1N HCL so it can be used repeatedly.

In the end, I recommend providing water filters made of two adsorbent materials (SiBN and SiBCON) in different sizes and shapes at an affordable price to remove of carbamazepine for a percentage exceeding more than 9

Chapter One

Overview

Chapter One
Overview

1.1 Overview

Pharmaceutical waste contained in liquid waste has become an issue of global importance [1]. Excessive use of these products has increased their rate of accumulation in aquatic environments [2- 3]. CBZ is one of the antiepileptic drugs that is mainly indicated as a sedative for depressed patients and is widely consumed [4-6].

Previous studies reported that around 1.01 kilotons of CBZ are used annually globally. This has led to this great pollution of various water sources such as ground water, sewage treatment plants, and even drinking water. Therefore, various water resources are issues of global concern [7-14]. Consequently, CBZ has toxic effects on aquatic life, including fish and others [15].

Moreover, the use of CBZ bearing water for irrigation leads to accumulation in the soil [16-18]. According to the Food and Drug Administration, an environmental assessment of CBZ concentration should be performed in an aqueous environment [16]. Hence, removing this contaminant from the aquatic environment is a required remediation strategy.

However, treatment processes carried out in wastewater treatment plants are able to remove only 30-33% of the impact of pollutants such as CBZ from wastewater [18-19]. The pharmaceutical waste-bearing liquid waste is

said to have been treated with conventional processes such as photo catalysis of exposure to ultraviolet rays, among others. However, conventional treatment processes are ineffective [20].

Recent studies have reported that the adsorption process is an effective process for treating persistent pollutants [21-23].

1.2 Problem Statement

Pollution of all kinds, especially water pollution, is one of the most prominent challenges facing the Palestinian people in the West Bank. As we know, in Palestine there are countless wells containing groundwater that can be used for irrigation purposes. Wastewater may seep into the aquifers.

The inflow of wastewater may harm the agricultural economy by restricting agricultural activities. Hence it harms in many aspects, particularly the environment, nature and people's well-being. Discharge raw Israeli wastewater into Palestinian lands and communities, without effective treatment, is one of the most brutal practices against Palestinians.

Moreover, there is a lack of information about CBZ. In terms of chemical changes in the water, as the percentage of CBZ in wastewater reached (17 - 25)mg This work was carried out to try to remove CBZ at a high concentration by preparing two new functional samples used as adsorbents.

1.3 Objectives

1. To determine the adsorption efficiency for removal of CBZ from water using SiBN and SiBCON.

2. To study the adsorptive behaviors (kinetics, thermodynamic, and isotherm) of CBZ.

3. Study the effect of contact time, pH, temperature, and concentration on the adsorption of CBZ.

1.4 Overview of the Dissertation

The research thesis is divided into five chapters. The first chapter identifies the problem data and introduces the research objectives. The second chapter consists of an introduction and review of previous work. The third chapter consists of the procedures used for the synthesis of adsorbents. The fourth chapter consists of the results of the data collected from the pilot study and their analysis, while the final chapter consists of conclusions and recommendations.

Chapter Two

Introduction

Chapter Two
Introduction

2.1 Groundwater

Water is the secret of life, as living things cannot live without it, and the water cycle in nature describes the presence and movement of water on the earth. The water cycle begins from the evaporation of water from water bodies to the stage of condensation as clouds in the sky to rain again, there are some impurities in small quantities that enter Water in the normal state is from a living or natural source and there is no problem, the main problem arises from an uncontrolled amount that seeps into the water at either stage of its cycle [24].

Groundwater is an important natural resource. It provides safe water for human consumption for more than 90% of the rural population [25]. It is the largest reservoir of liquid fresh water on earth, used for domestic and other purposes, and is the only source of fresh water for more than a billion people around the world [26].

We must not forget that after the 1967 occupation, Israel controlled more than 85% of the various water sources. In addition to Jordan River, which the Israelis control and use exclusively [27]. Therefore, Palestine suffers from an acute water crisis mainly caused by its inability to control the Palestinian water resources due to the restrictions imposed by the Israeli occupation [28].

2.2 Groundwater pollution

The groundwater is polluted by the pollutants released to the ground [29].Contamination can occur from sewage systems, landfills, effluents from sewage treatment plants, sewage leaks, gasoline filling stations or from the overuse of fertilizers in agriculture. The use of polluted groundwater creates a public health risk through poisoning or the spread of disease [30].

The classification of groundwater pollutants includes biological agents, such as bacteria, fungi, and viruses. Physical pollutants such as color, conductivity, and chemical pollutants such as pesticides and others [31].

Several parameters can be used to study groundwater pollution, such as pH, salinity, phosphates, heavy metals, nitrates, and others [32].

2.3 Water pollutants from pharmaceuticals

Due to the increasing prevalence of prescription drugs, the proportion of drugs in different water sources has increased. This has become dangerous, because the World Health Organization (WHO) has reported the effects of pharmaceutical products and many of them have low-level research [33].

One of the drugs that has been detected in water sources is CBZ. It is often prescribed to treat seizure disorders [34].

Also, CBZ does not degrade easily and it is the current conventional treatment; not sufficiently removed from the treated wastewater by various methods.

In addition, it has the potential to have adverse health effects in humans [35].

2.4 Carbamazepine

CBZ is sold under the brand name Tegretol and is a medication primarily used to treat epilepsy and mental seizures. It is used in schizophrenia with other drugs [36-38]. It is ineffective in cases of absence [36].

CBZ was discovered by Swiss chemist Walter Schindler in 1953 [39-40]. It was first marketed in 1962 [41]. It is available as a generic medicine [42]. It is on the WHO List of Essential Medicines [43]. It is the most popular drug in the United States, in 2017 [44-46].

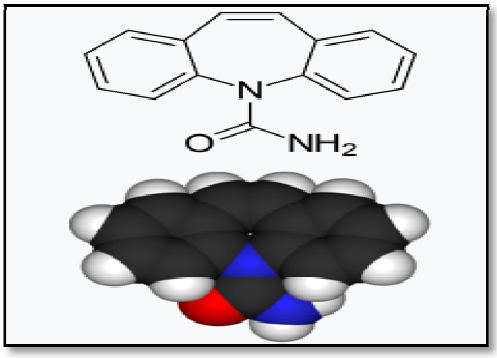


Figure (2.1): chemical structure of Carbamazepine three dimension.

2.4.1 Medical uses

CBZ is usually used to treat seizure disorders and epilepsy [36]. It is used as a second-class treatment in schizophrenia when treatment with other drugs has failed [36], [47]. However, evidence does not support this use [48]. It is not effective in absence seizures [36]. However, consideration should be given to choosing the right medication for patients, as more

research is needed to determine which medication is appropriate for people with severe epileptic seizures [38].

Figure (2.2): structure Tegretol medicine,when the as active ingredient.

2.4.2 Adverse effects

The CBZ label contains warnings about the following:

1. An imbalance in the body's production of various blood components [37].
2. Increased risk of suicide [49].
3. An increased risk of developing anemia [37], [50].
4. The risk of seizures, if a person suddenly stops taking the drug [37].
5. The risk of birth defects on the fetus during pregnancy [37], [51].

Common side effects may include dizziness, headache, nausea, constipation or vomiting. Drinking alcohol might worsen depression while taking CBZ [37],[52]. Also, rare cases of auditory side effects have been reported. Most people do not usually notice this unusual side effect, and it goes away after a person stops taking CBZ.

2.4.3 Environmental impact

Laboratory studies were conducted to understand the accumulation of CBZ in soil-grown food plants, after it was detected in water treatment plants [53]. Among these studies was a 2014 study that reported that the accumulation of CBZ in cultivated soils posed a risk to human health [54].

2.4.4 Methods for water purification from Carbamazepine

One method that has shown good results in removing CBZ compared to conventional methods. Methods for treating water are adsorption. Whereas, adsorbents have a limited adsorption capacity based on the particle surface area [55].

2.4.4.1 Ultraviolet (UV)

Since conventional biological processes for ultraviolet (UV) rays are not effective in removing CBZ, a new treatment step must be added. For example: UV / H_2O_2, UV / Cl_2, UV / TiO_2 [56].

2.4.4.2 Activated Carbon Adsorption

Activated carbon is a good adsorbent due to its low cost and high surface area, and several studies have been done to compare and adsorb CBZ over several adsorbents. Some adsorbents including Granular Activated Carbon **(**GAC), and Powdered Activated Carbon (PAC) [55].

GAC is one of the materials used in filters. These filters are readily available in various sizes and are inexpensive.

PAC is similar to GAC in that it is active carbon, but the particle size is smaller and should be used with a different technique. The longer the PAC is in contact with water, the adsorption will continue. ; However, this is time consuming and will not work for the "on demand" water treatment method for the home. This poses an additional problem for the homeowner [55].

The water must then be filtered to remove residual PAC. Although PAC has the greatest uptake capacity to remove CBZ than GAC, it introduces more steps, making this method less economically convenient [57].

2.4.4.3 Ozone oxidation

Ozone oxidation is widely used in drinking water applications and in some plants for wastewater. Ozone can oxidize and break large molecules into smaller molecules. This method is used to improve taste, color and aroma [58].

2.4.4.4 Nanofiltration and reverse osmosis

Nanofiltration (NF) and Reverse osmosis (RO) are two good methods for removing CBZ from drinking water. As the study conducted in South Korea showed. However, it is more expensive because contamination is continuous, and the membranes are easily perishable, resulting in a concentrated waste stream [59-61].

Table (2.1) Describing previous studies on removing CBZ from water

Method	Optimum Condition	capacity (q_m) or Percentage removal	Reference
1. **Ultraviolet (uv)**			
1.1 UV alone	UV Wavelength = 202–278 nm Irradiation time = NA	6%	[62]
1.2 UV/H_2O_2	UV Wavelength = 255 nm H_2O_2 dose = 6 mg/L Irradiation time = 20 min	59%	[63]
1.3 UV/Cl_2	UV Wavelength = 256 nm Cl_2 dose = 1.3 mg/L Irradiation time = 25 min	54%	[64]
1.4 UV/TiO_2	UV Wavelength = 255 nm TiO_2 dose = 25–500 mg/L Irradiation time = 35 min	77%	[65]
2. Carbon Loading Experiment			
2.1 granular activated carbon (GAC)	2.3g of GAC, For this experiment, 1 L solutions of 1 ppm CBZ, the solution contained 20 ppm sucrose.	90.43%	[55],[57] .
2.2 Powdered Activated Carbon (PAC)	2.3g of PAC, For this experiment, 1 L solutions of 1 ppm CBZ, the solution contained 20 ppm sucrose.	91.9%	[55],[57]
3.Ozone Oxidation			
3.1 First Experiment	the concentration of ozone soluble in water (8.50µmol O_3/L water), the concentration of CBZ 1 ppm, contact time of 45 min, temperature (23-25°C)	95.8%	[58]
3.2 second experiment	the concentration of ozone soluble in water (8.50µmol O_3/L water),, the concentration of CBZ 1 ppm and20 ppm sucrose, contact time of 7 min temperature (23-25°C)	94.5%	[58]
4. Nanofiltration (NF) and reverse osmosis (RO)	They use semi-permeable membranes.	95%	[59-61]

2.5 Phenylamine-functionalized silica (SiBN)

In the past period, silica and the preparation of adsorbents on which it depends has aroused great interest due to its regular pore structure, well-modified surface properties, and large surface area [66-68]. In addition, it can also be regenerated multiple times after the adsorbent is saturated [67].

2.6 DCC Coupling – Amides from Amines and Carboxylic Acids

2.6.1 Phenylamide - functionalized Silica (SiBCON)

The direct conversion of a carboxylic acid to an amide is difficult because amines are basic and tend to convert carboxylic acids to their highly unreactive carboxylates. In this reaction the carboxylic acid adds to the Dicyclohexylcarbodiimide molecule to form a good leaving group which can then be displaced by an amine during nucleophilic substitution. DCC induced coupling to form an amide linkage is an important reaction in the synthesis of peptides.

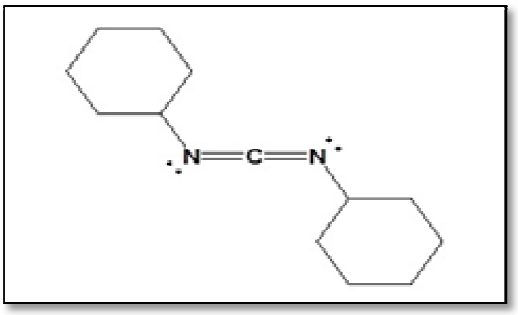
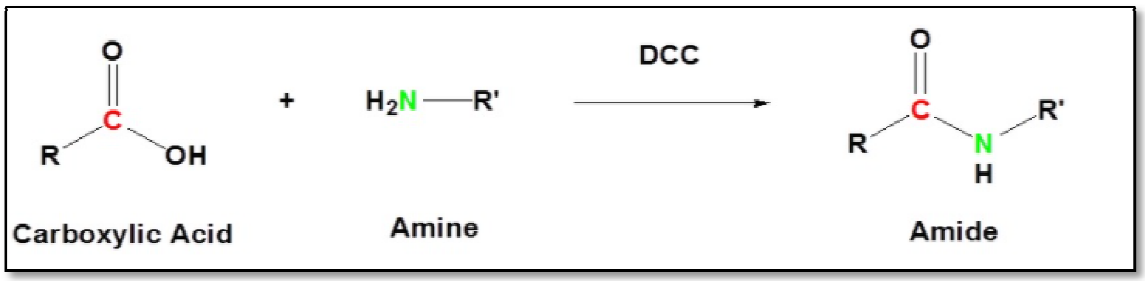
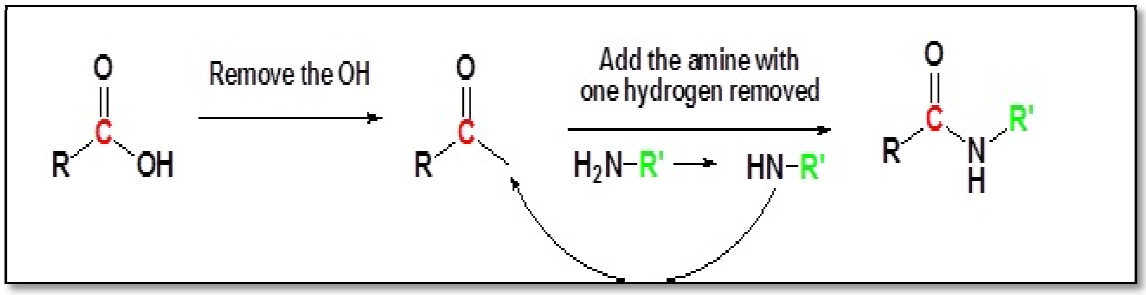


Figure (2.3) chemical structure of Dicyclohexylcarbodiimide in active site for reaction

Basic reaction

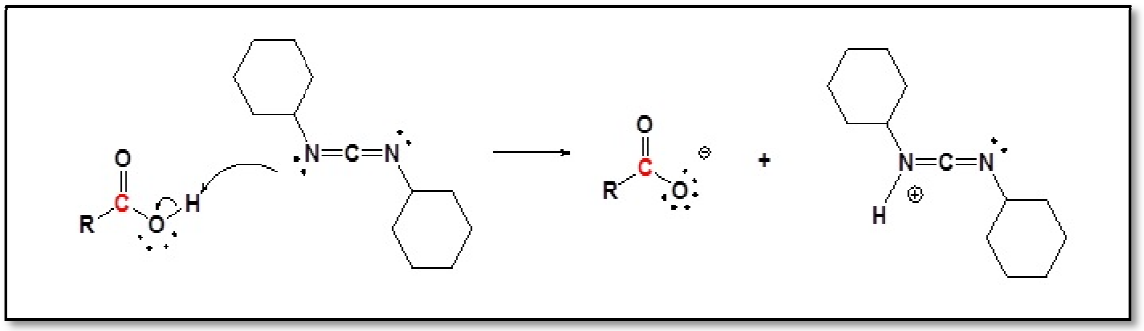


Going from reactants to products simplified

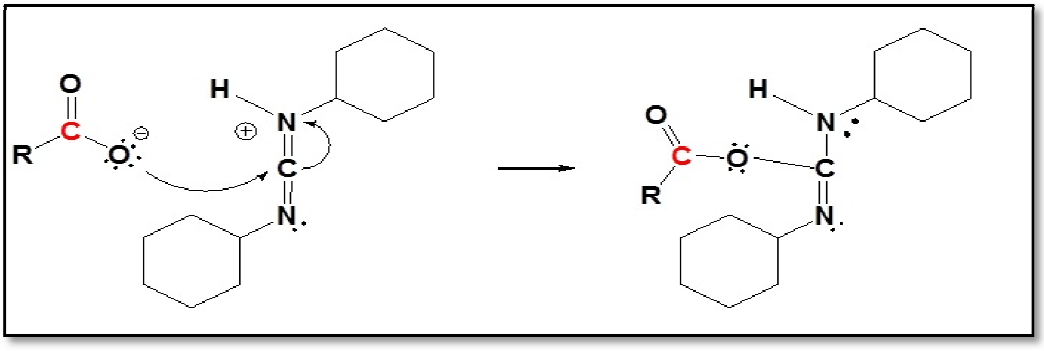


Mechanism

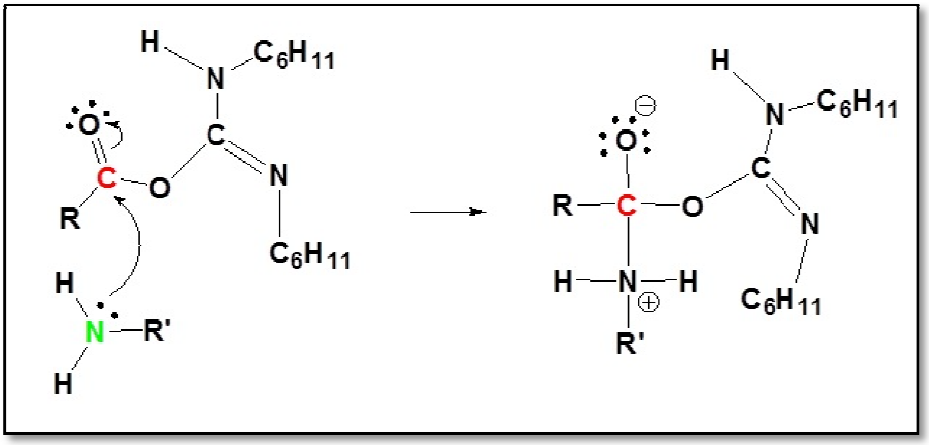
1) Deprotonation



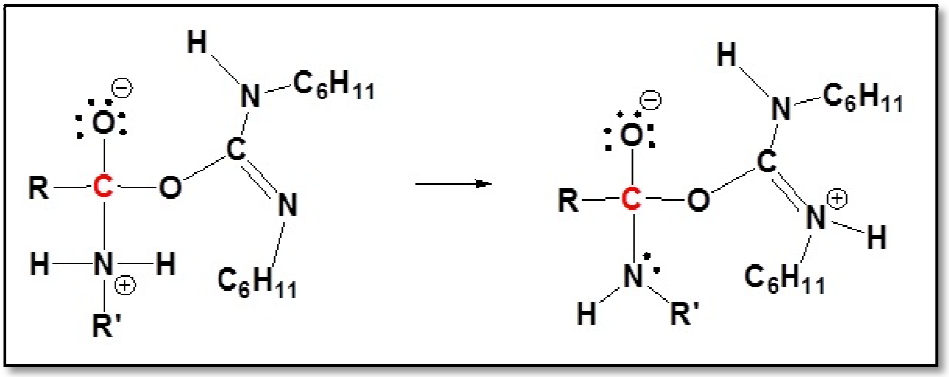
2) Nucleophilic attack by the carboxylate



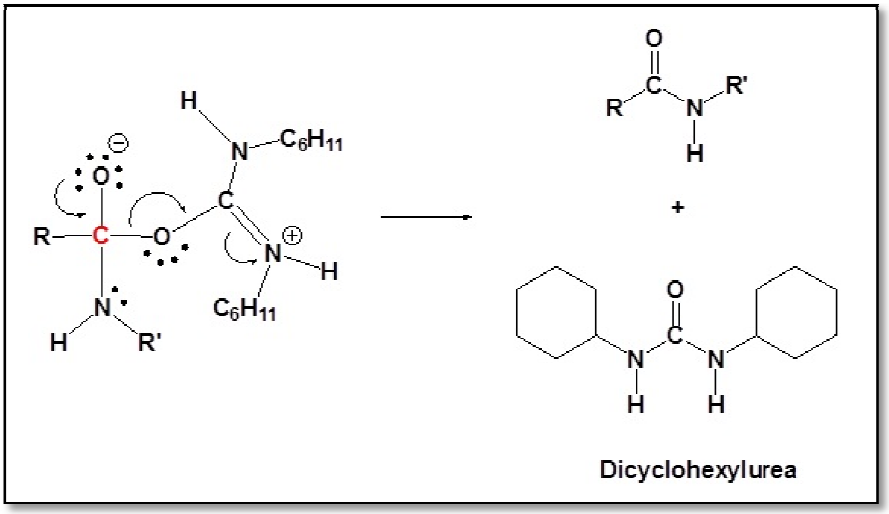
3) Nucleophilic attack by the amine



4) Proton transfer



5) Leaving group removal



2.7 Adsorption: Definition and Types

2.7.1 Adsorption definition

Adsorption is a surface phenomenon in which atoms, molecules, or ions of a substance stick, regardless of the state of the substance on the surface [69]. As this process differs from absorption. [70-71].

There is a set of factors influencing the adsorption process: they are temperature, pH, contact time, initial concentration of the adsorbate etc [72].

2.7.2 Types of adsorbents

Adsorbents are classified into natural or synthetic materials. Examples of natural adsorbents are charcoal and zeolite. These natural materials are in many cases inexpensive and available. Synthetic adsorbents are prepared from agricultural products, domestic and industrial waste, and wastewater. Each adsorbent material has its own characteristics such as the nature of adsorbent surfaces, pores and pore structure [73- 74].

2.7.3 Adsorption isotherms models

The isotropic models are important because they illustrate the interaction mechanism between adsorbents and adsorbate. Various models are available for this purpose, the two most popular being the Langmuir and Freundlich [75].

2.7.3.1 Langmuir Adsorption Isotherm

The Langmuir model adopts the advent of a monolayer of adsorbate on a homogeneous surface of an adsorbent and expressed as:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_e K_L C_e} \quad \text{Eq. 2.1}$$

Whereas:

C_e = adsorbate concentration at equilibrium (mg/L)

q_0 = maximum capacity of monolayer coverage (mg/g)

K_L = Langmuir isotherm constant (L/mg).

The q_e value (amount of adsorption per unit mass of adsorbed) (mg / g) can be calculated by the following relationship:

$$q_e = (C_o - C_e)\frac{V}{m} \quad \text{Eq. 2.2}$$

Whereas:

C_o is the initial adsorbate concentration in (mg/L).

V is the solution volume in (L).

m is the adsorbent mass in (g).

(C_o - C_e) represents the amount adsorbed (ppm). We can understand the Langmuir parameters by plotting the (C_e / q_e) values on the Y axis and the C_e values on the X axis, the slope of this graph represents (1 / q_0), while the y-intercept represents (1 / $K_L q_0$) [76].

The Dimensionless constant separation factor (R_L) which is given by the following equation can be expressed:

$$R_L = \frac{1}{1 + K_L C_0} \quad \text{Eq. 2.3}$$

Whereas:

C_0 = initial concentration.

K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the isotherm shape to be unfavorable if (R_L >1) Linear if (R_L = 1), favorable if (0 <R_L <1), or irreversible if (RL = 0).

2.7.3.2 Freundlich Adsorption Isotherm

The Freundlich isotherm explains the adsorption on a heterogeneous surface. The Freundlich equation is expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad \text{Eq. 2.4}$$

Whereas:

KF is a constant indicating the capacity of the adsorbent (mg / g).

N is a coefficient that gives an indication of the preferred method of the adsorption process (g / L) m. and 1/n is an indicator of favorability of the adsorption process.If 1 / n is less than 1, the adsorption is normal. If (10 > n> 0) this donates a favorable adsorption process [77- 79].

2.7.4 Adsorption kinetics

Several adsorption kinetic models have been used to determine the kinetics and rate determination steps. These models provide evidence of the performance of the adsorption system and the rate of elimination of a specific component through the use of a specific adsorbent. In addition, it determines whether the adsorption process is actually chemical in nature and what is the step that determines the rate. A common example of a kinematic model of adsorption is: a pseudo-kinetic 1^{st} / 2^{nd} model, etc [80].

2.7.4.1 Pseudo 1^{st} Order Kinetics

This was the first model placed to describe kinetics energy for the adsorption reaction.

the pseudo-first-degree equation:

$$\log(qe - qt) = \log qe - (K1/2.303)t \text{ Eq. } 2.5$$

Whereas:

q_e and qt are amounts of the target analyte absorbed (mg / g).

k_1 is the pseudo-first-order rate constant for adsorption (min^{-1}).

The rate constant K_1 can be calculated by plotting the values of Log (q_e - q_t) as the y-axis versus values of t as the x-axis.

2.7.4.2 Pseudo 2nd Order Kinetics

This type of kinetic assumes that the chemical adsorption is represent the rate determining step, which involves valence attraction between the adsorbate and the adsorbent by (exchange / sharing)of electrons.

The equation for this model type of kinetic is:

$$\frac{t}{q_t} = \frac{1}{K_{2q_e^2}} = \frac{t}{q_e} \text{ Eq. 2.6}$$

Here;

K_2: rate constant for adsorption pseudo-2nd-order ($g.mg^{-1}.min^{-1}$). By plotting a linear relation between the values of t/qt as y-axis versus values of t as x-axis, we can drive ($1/ K_2 q_e^2$) from y-intercept and ($1 /q_e$) that equals the slope of the graph.

2.7.4.3 IPD Kinetic Model

The equation of adsorption kinetic model:

$$q_t = K_{id} t^{1/2} + Z \text{ Eq. 2.7}$$

Whereas;

K_{id}: rate constant for IPD ($mg/g.min^{1/2}$).

Z: A constant that provides information about the layer thickness (mg/g).

By plotting a linear relation between the values of qt as y-axis versus the values of $t^{1/2}$ as x-axis, we can drive the values of Z that equals a y-intercept and K_{id} that equal a slope of the graph.

2.7.5 Adsorption thermodynamics

The thermodynamic study is performed by studying enthalpy, free energy, and entropy.

To decide the process is spontaneous or not, thermodynamic parameters are necessary. Gibb's free energy change, ΔG, is an example of a chemical reaction's spontaneity. Enthalpy (ΔH) and entropy (ΔS) factors must both be considered to determine Gibb's free energy of the process.

The general relation which connects between the adsorption parameters will be written as [81]:

$\Delta G = \Delta H - T \Delta S$ Eq. 2.8

ΔG can be calculated by the following equation:

$\Delta G = -R\ T \ln K_d$ Eq. 2.9

Whereas:

R: The Universal gas constant (8.314) $J.mol^{-1}.K^{-1}$.

K_d: Constant for thermodynamic equilibrium which equals (q_e/C_e) and has a unit of mole or (L/g).

When the two previously mentioned equations are equal, the following equation will be produced:

$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$ Eq. 2.10

By plotting a Van't Hoff linear relationship, a plot between the Ln K_d values as the y-axis versus the (1 / T) values as the x-axis, we can drive the (ΔS / R) values equal to the y-intercept and (-H / R) that equals the slope of the plot Graphic.

2.8 Analytical techniques

The analytical method should generally be suitable for target analysis so that it can be transferred to its concentration with a different value. Each step was performed by HPLC by a special analytical method, and the adsorbed concentration qe (mg / g), as in the following equation:

equation: $$q_e = \frac{C_0 - C_e}{W} V$$ Eq. 2.11

Here:

C_0 (mg / L): Metal concentration in the solution before treatment

C_e(mg / L): Metal concentration in the solution after treatment

V (L):the volume of solution.

W (g): the dose of adsorbent.

The removal efficiency of CBZ was calculated using:

$$\%\text{Removal} = \frac{C(o) - C(e)}{C(o)} * 100$$ Eq. 2.12

Chapter Three

Methodology

Chapter Three
Methodology

3.1 Chemicals and materials

All chemicals used in this study were purchased from Sigma-Aldrich. They were all of analytical grade and used as received.The chemicals include hydrochloric acid (HCl), Dicyclohexylcarbodiimide (DCC), Methanol (CH_3OH), Acetic acid(CH_3COOH), Magnesium Sulfate($MgSO_4$),sodium hydroxide (NaOH), tetrahydrofuran(THF), Ethyl acetate (EtOAc),Sodium bicarbonate($NaHCO_3$),sodium chloride (NaCl), phenylamine-functionalized silica (SiBN), Carbamazepine(CBZ) standard was of (purity $\geq$ 99%) and was obtained from Jerusalem Pharmaceuticals Company, Palestine.

3.2 Analytical method and instrumentation

Instrumentation used in this work include: a water bath equipped with a shaker (Daihan Labtech, Korea) with 20 to 250 rpm digital speed control, pH meter (model: 3510, JENWAY, USA), Fourier Transform Infrared Spectroscopy (FTIR-SHIMADZU, Japan, Model: FTIR-8700). FT-Raman spectrometer (RFS 100/S –Bruker Inc., Karlsruhe, Germany) with a liquid-nitrogen-cooled germanium diode detector and an ND:YAG laser providing an impressive NIR line at 1064 nm was used for characterization.

The spectra were recorded in a spectral area of 400 cm^{-1} to 4000 cm^{1-} at a spectral resolution of 4.0 cm^{-1} with 800 samples at approximately 30 mW laser power. Scanning Electron Microscopy (SU8000 Hitachi, Japan).

thermogravimetric analysis (TGA Instruments, New Castle, DE, USA) from 20 to 700^0C, Vibrating Sample Magnetometer (VSM-LAKESHORE 7404, Boston, MA, USA). High Performance Liquid Chromatography (HPLC) - shimadzu SCL-10A VP, version 5.22 high performance liquid chromatography equipped with a variable length UV/visible detector (SPD 10A VP) using a SUPELCO Discovery reversed phase C18 column, (25 cm x 4.6 mm i.d., particle size 5 μm). The samples were injected manually through a Rheodyne injector. HPLC working conditions were, gradient mobile phase using a previously prepared solvent which was(methanol – water 50:50) with 1ml/min flow rate and injection volume (loop size) 20 μL. The wavelength of the UV/visible detector was fixed at 285 nm.

3.3 Preparation of phenylamine-functionalized silica (SiBN)

The preparation of the SiBN adsorbent can be summarized in Figure 3.4 The preparation involves the reaction of an activated silica gel (SiG) (2g) with 3-aminopropylsilica (SiPr) (0.83g). The solid was filtered and washed with toluene to form silica surface (SiG) amino groups. The NH_2 groups present on the silica surface were then reacted with 4-aminobenzaldehyde (0.25g) under gentle conditions (stirring for 12 h) at room temperature, using anhydrous diethyl ether (100 mL) as the solvent to form a new SiBN adsorbent [82].

Note: The SiBN adsorbent was prepared by Professor Smaail Radi and Dr. Said Tighadouini in Morocco, with all thanks, respect and appreciation to them[83].

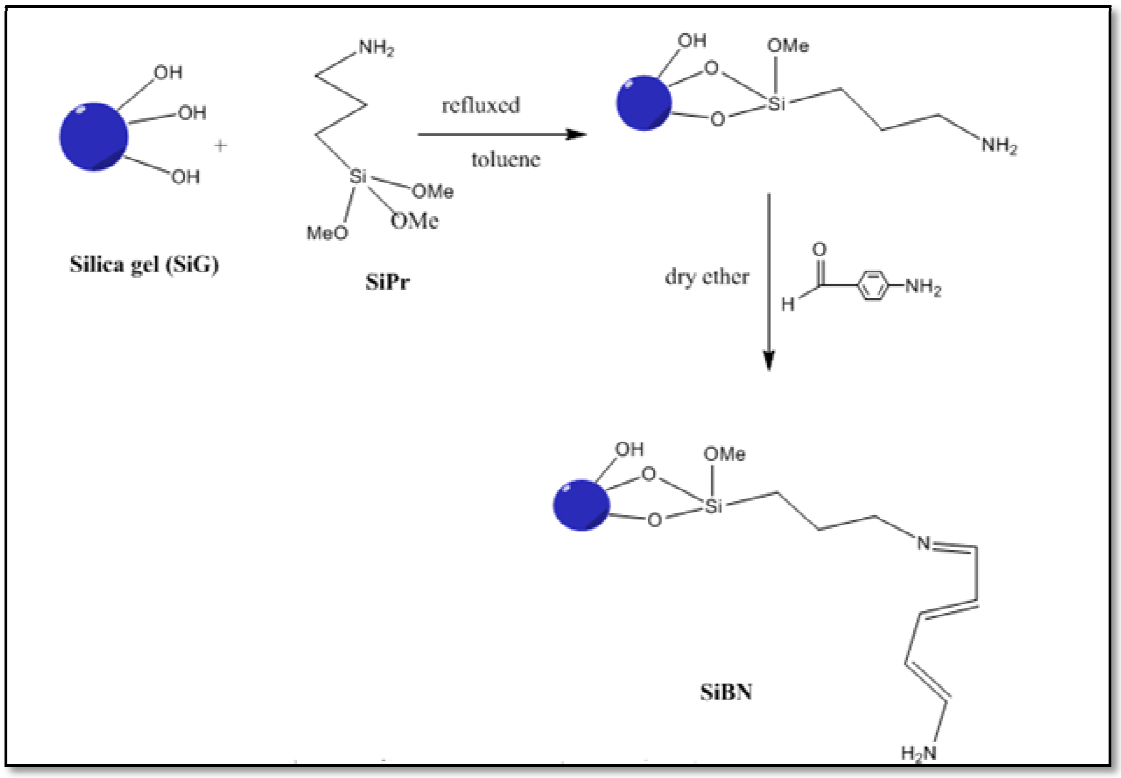


Figure (3.4): The synthesis Phenylamine- functionalized Silica.

3.4 Preparation of Phenylamide - functionalized Silica (SiBCON)

SiBCON adsorbent was prepared as shown in Scheme 3.5. Amine (SiBN) (0.09 g) and acid (acetic acid) (0.09 ml) were added in to THF (9 ml) at 0°C (Because it's volatile) and then DCC (0.18 g) was added. Leave to stir for 48 hours at room temperature. Then the product is taken after two days and washed with a small amount of the following substances EtOAc, $NaHCO_3$, HCl and brine(0.9%). The organic layer was dried with $MgSO_4$ [84].

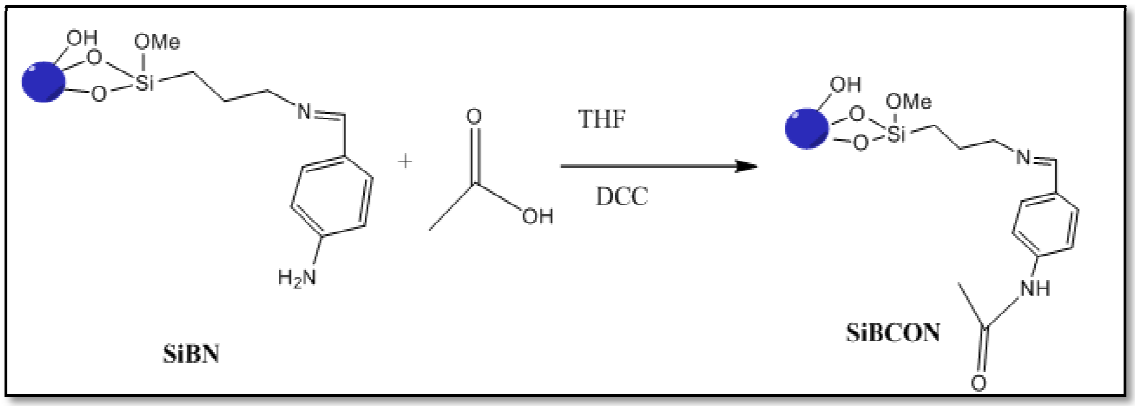


Figure (3.5): The synthesis Phenylamide - functionalized Silica.

3.5 Preparation of standard solutions (CBZ)

Standard solutions of CBZ at a concentration of 1000 ppm was prepared by dissolving 1 g CBZ in 1 L methanol. Dilute solutions were prepared at concentrations (0.1 to 30.0 ppm) from the stock solution and used then in our batch experiments to study the effect of different parameters that affecting adsorption process such as time, pH, and temperature and hence to predict the optimum conditions for efficient adsorption reaction for CBZ with SiBN and SiBCON. The adsorbent of filtrate was determined using HPLC at 285 nm wavelength. The mobile phase (50% methanol and 50% of water) with flow rate of 1 mL min^{-1}. The column used for separation was a C18 HPLC - shimadzu SCL-10A VP.

3.6 Calibration curves

Stock solution was diluted to prepare a series of several standard solutions of CBZ by using the following relation for dilution calculations ($M_1*V_1 = M_2*V_2$) with 0.1, 0.2, 0.5, 1, 5, 10, 20, and 30 ppm concentrations were prepared. The solutions were used to develop a calibration curves. Calibration curve is shown in Fig. 3.6.

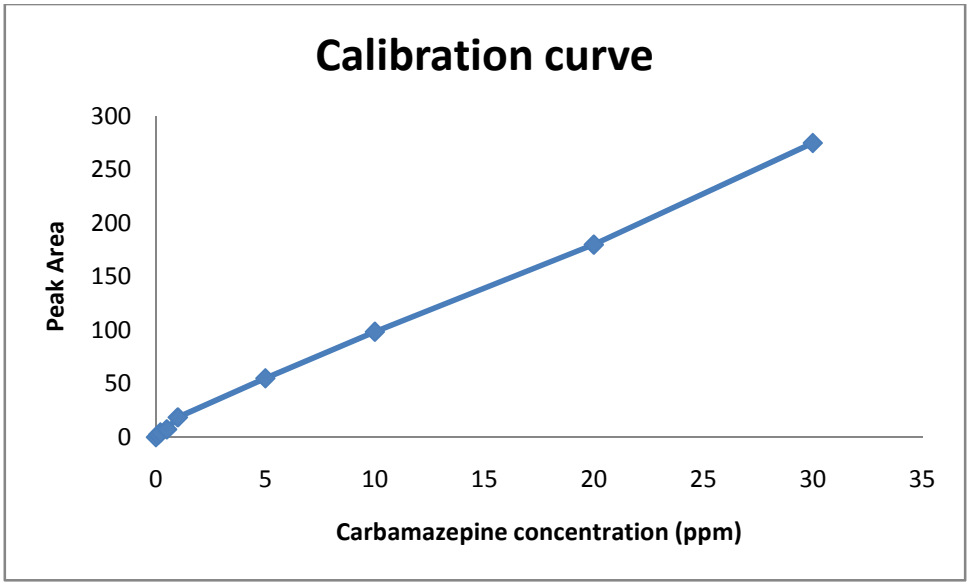


Figure (3.6): Calibration curve for CBZ using HPLC instrument.

3.7 Adsorption experiments

All adsorption processes were carried out in plastic bottles (50 ml) which were placed in a water bath equipped with a thermostat and a shaker. The effect of various variables such as initial concentration, pH values, adsorption time and temperature on adsorption efficiency was studied. Adsorption experiments were performed on the adsorbents. After each adsorption process, the adsorbent was separated to determine the residual concentration of CBZ. All adsorption experiments were performed and the adsorption efficiency was calculated.

3.7.1 Optimization of contact time

It is extremely important to predict the optimal time required to reach reaction equilibrium. The amount of adsorbed CBZ was studied on each adsorbent (SiBN and SiBCON) to determine the optimal time for the adsorption process. The experiments were performed at 25°C, during the

time period (1 to 120 min) the residual CBZ concentration was measured with HPLC.

3.7.2 Effect of pH

The adsorption process is strongly affected by the amount of H^+ and OH^- ion in the solution, which means that the effect of the pH value is a very important factor for study and control, as these ions can be linked to the adsorption surface site of the adsorbent and change their behavior and their attractiveness towards the target analyte either by decreasing or increasing the quantity. Therefore, samples with a pH ranging from (2 - 11) were prepared in order to predict the value at which the adsorption reaction would be most efficient. The initial pH of the CBZ solutions before any adjustment was 6 and prepared solutions of 0.1 M HCL and 0.1 M NaOH were used to control the pH value of the CBZ solutions before adding the adsorbent.

The adsorbent (0.02 g of each) was added to 10 ml of 10 ppm CBZ standard solution. The mixture was placed in shaking water bath at room temperature for a period of optimum contact time that is already measured for each previous adsorption process.

3.7.3 Effect of temperature

The direction of heat flow between the system and its surroundings is important to predict the type of our interactions or processes if it is an endothermic process in order to prepare good thermal conditions to obtain a

good percentage of removal for analysis, as well as the data obtained can be used to compute van 't Hoff coefficients to understand the nature of the spontaneous reaction the energy required or emitted.

So that to study the effect of solutions temperature on the adsorption process, 10 ml of 10 ppm standard solution of CBZ was transferred into vials with adjusting its pH to the optimum value that was predicted previously for each one.

The solutions were placed in shaking water bath at desired temperature (the range was 4°C to 45°C), then the adsorbent (0.02 g) was added to it for optimum contact time. After the time is over the samples were filtered and the residual concentration of CBZ was determined by HPLC instrument,and the data obtained was a percent removal of CBZ and plotted as a function of temperature.

3.7.4 Initial concentrations

To find the effect of initial concentration of CBZ, the adsorbent (0.02 g), was added to a number of vials that contain 10 ml of a series of different concentrations (0.1, 0.2, 0.5,1, 5,10, 20, and 30 ppm) of CBZ, with adjusting its pH and optimum temperature to the optimum value were predicted previously for each one. The solutions were placed in shaking water bath at optimum contact time. After the time is over the samples were filtered and the residual concentration of CBZ was determined by HPLC instrument, the data obtained was a percent removal of CBZ and plotted as a function of Initial concentrations.

3.8 Thermodynamics and kinetics of adsorption

Parameters for pseudo-(first /second)-order kinetic model for adsorption of CBZ have been determined for two adsorbent.

Thermodynamic parameters like (ΔS), (ΔH), and (ΔG) were evaluated employing Van't Hoff's equation. At different temperatures ranging (4 °C–45 °C).

3.9 Adsorption isotherm

The isothermal experiments were by shaking a mixture of 10 ml of different concentration (0.1, 0.2, 0.5, 1.0, 5, 10, 20, 30 ppm) with 0.02 g of the adsorbent at the specified contact time. CBZ concentration was analyzed at the end of each steady period. Langmuir, Freundlich model parameters for CBZ adsorption in two different adsorbents.

3.10 Adsorbent regeneration

After reaching the saturation state for the adsorbent that presented by the equilibrium, a reverse process is the desorption, in such case adsorbate taken off from the adsorbent site were linked in, despite the lower in efficiency of removal it can used for another adsorption process for another times, a mixture of 0.02g adsorbent (SiBN) and 10 ml of 10 ppm adsorbate at pH=9 was shaken in a water bath for 15 min at 35°C, then HPLC measurements for the filtrate were determined, in the same way for SiBCON 0.02g considering all Other optimal parameters..

The adsorbent after each adsorption process is washed with(0.1 M HCl or 0.1 M NaOH)solution then with distilled water. After that, each regenerated adsorbent left to dry for 24 hours before second using. The same recovery technique is then used for each regenerative adsorbent to demonstrate that SiBN and SiBCON can be used multiple times with virtually no effect on the percentage of CBZ removal.

Chapter Four

Result and Discussion

Chapter Four
Result and Discussion

4.1 Characterization of adsorbents

4.1.1 FT-IR characterization

Modified silica (SiBN) was confirmed by FT-IR analysis. As shown in Fig.4.7, the 3-aminopropylsilica (SiPr) characteristic in comparison with native silica (SiG) has an appearance (NH_2) of about 1580 cm^{-1} and weak bands CH at 2700 cm^{-1} corresponding to the carbon chain. The SiBN final materials show and reveal the emergence of new characteristic bands around 1500 cm^{-1} corresponding to the C = N and C = C vibrations[85].

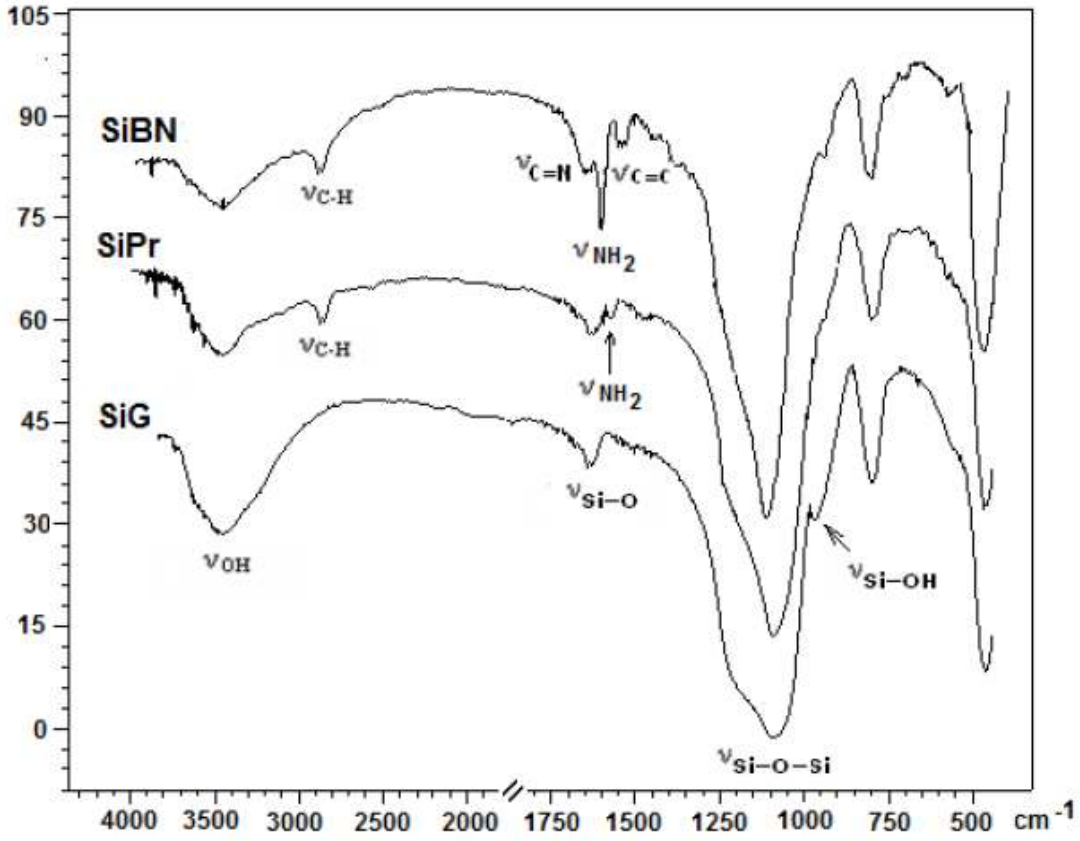


Figure (4.7): FT-IR spectra of SiG, SiPr and SiBN.

FT-IR measurements were performed to provide further evidence for SiBN, SiBCON, and acetic acid attachments.The figure below(4.8a, 4.8b and 4.8c) also shows the FT-IR spectra of SiBN at about 1500 cm^{-1} corresponding to the vibrations of C = N and C = C. SiBCON was about 1640 cm^{-1} with C = O vibrations, but the acetic acid exhibited the carbon dioxide characteristic at 1755 cm^{-1} and 1703 cm^{-1} and the asymmetric deformation of CH_3 at 1,400 cm^{-1} were also present in acetic acid.

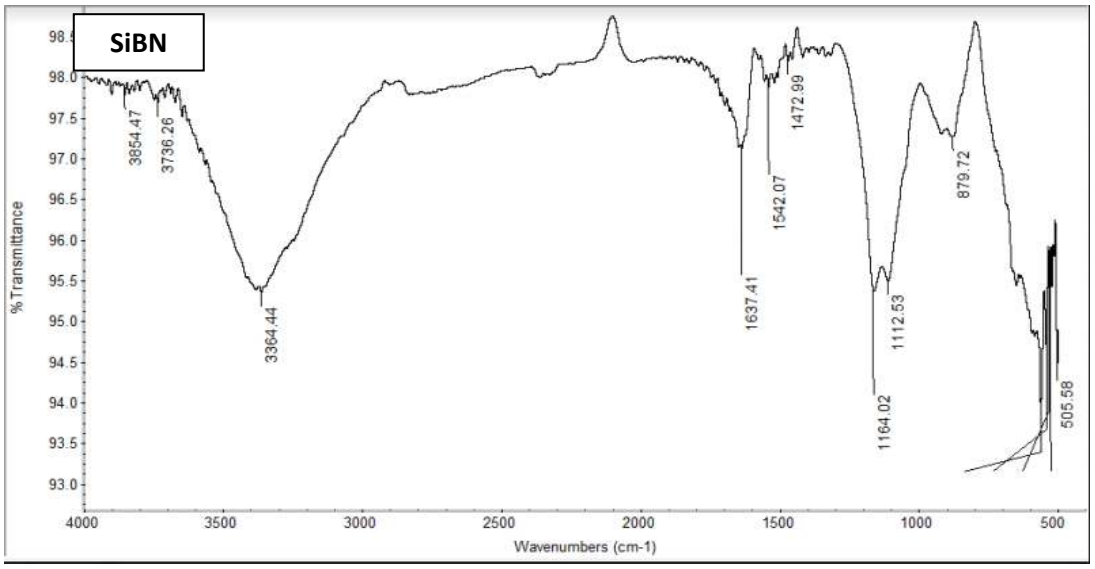


Figure (4.8a)

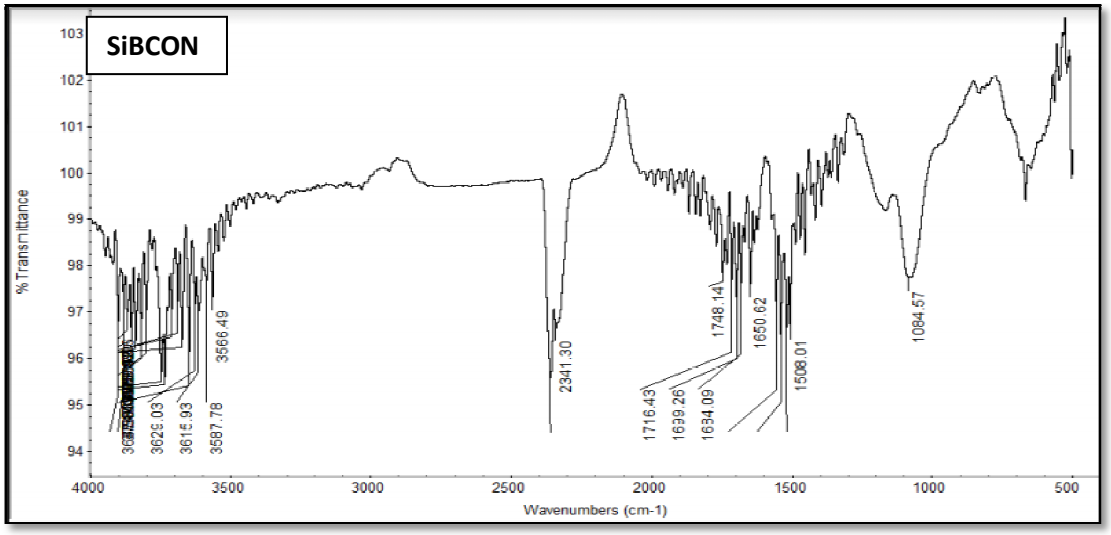


Figure (4.8b)

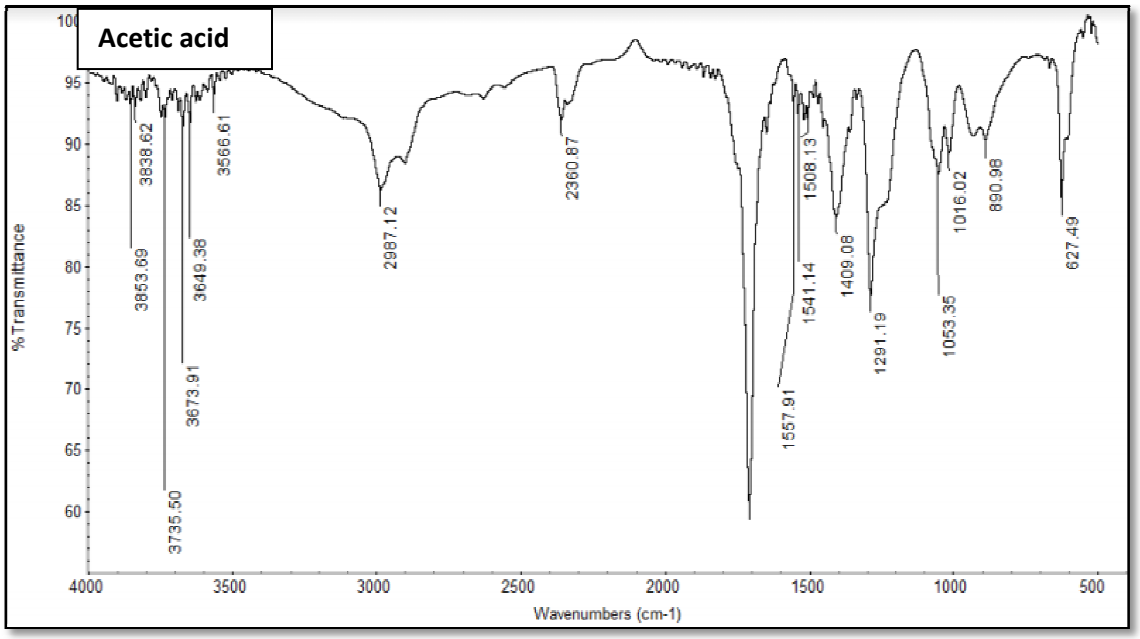
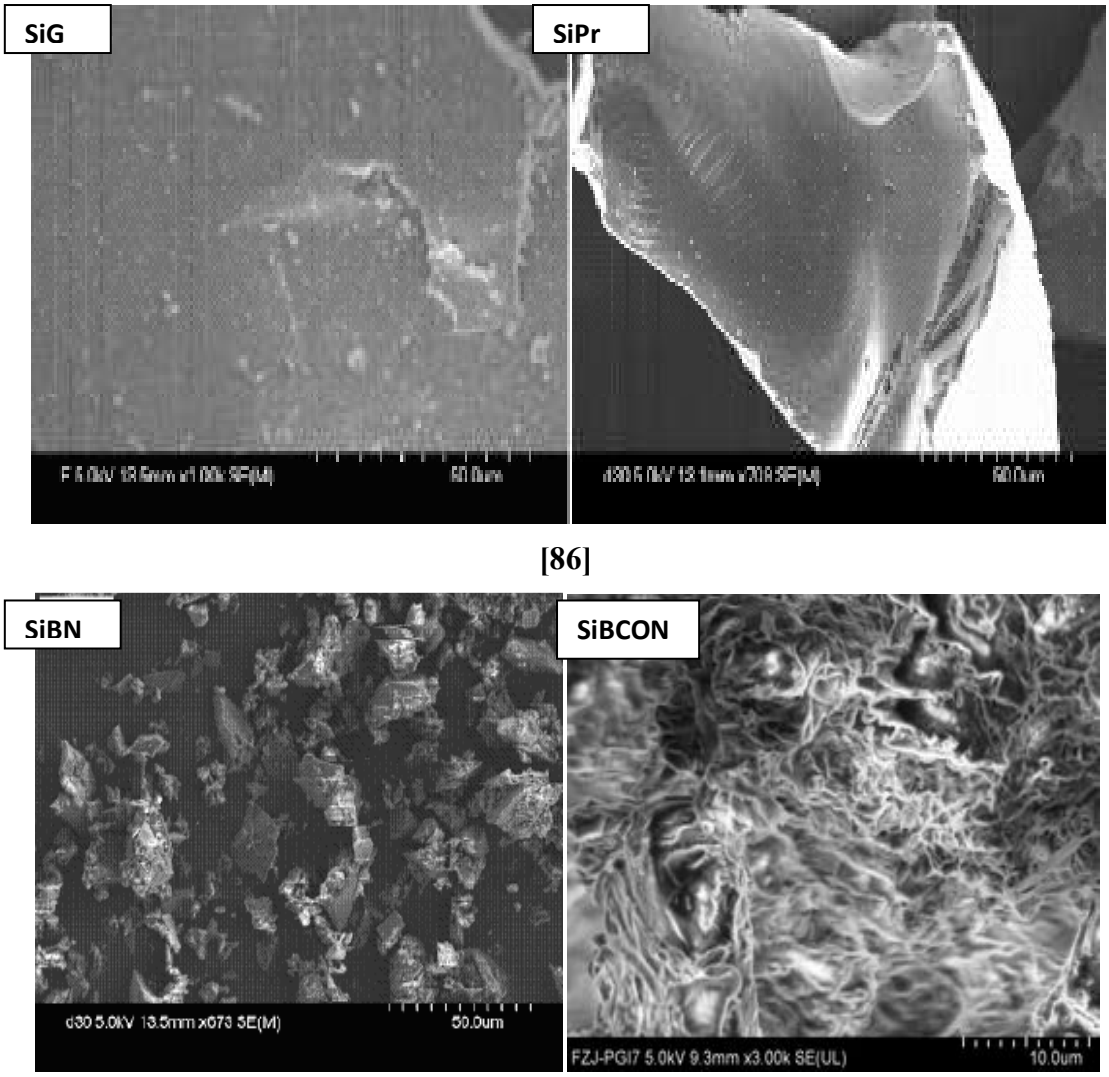


Figure 4.8c

Figure 4.8 (a-c): FT-IR spectrum of SiBN, SiBCON, acetic acid.

4.1.2 Scanning Electron Micrographs

Some of the micrographs show SEM analysis of modified silica as shown in the figure below and display a rough and increased porous nature, indicating that the material offers the potential for excellent use of CBZ.



[86]

Figure (4.9): SEM photographs of SiG, SiPr, SiBN, and SiBCON.

4.1.3 TGA analysis and thermal stability

Thermogravimetric analysis (TGA) was performed with nitrogen at a heating rate of 10°C / min throughout the entire analysis. The results of the analysis are illustrated in Fig.4.10. The analysis results show that the SiBN is stable and shows no weight loss at a temperature below 600°C while SiBCON shows some weight loss at around 170 °C. This is another indication of the occurrence of the functional group.

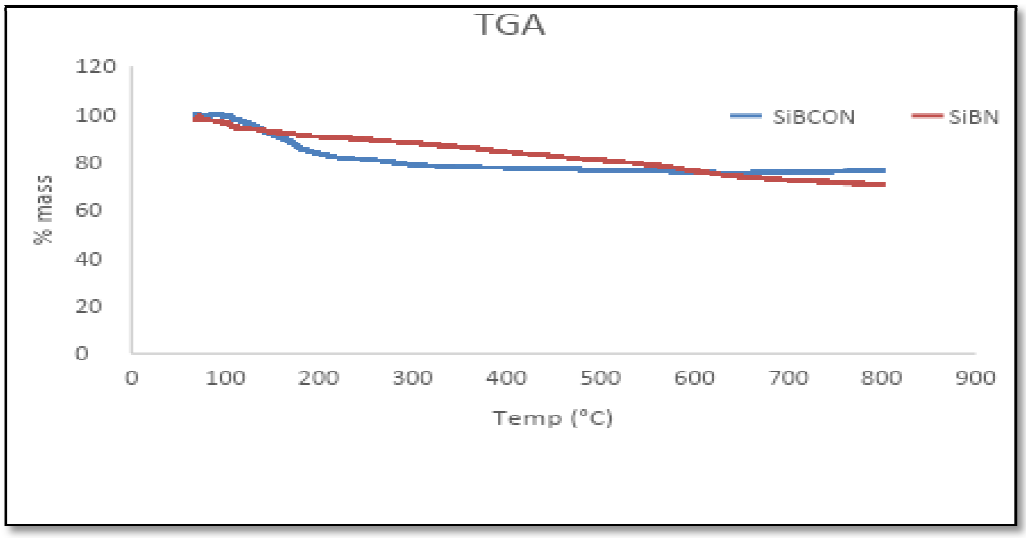


Figure (4.10): Thermogravimetric Analysis (TGA) for SiBN, SiBCON.

4.2 Results of Adsorption

This work aims to prepare adsorbents for removing CBZ from water. These adsorbents, namely SiBN and SiBCON, were evaluated by studying the properties of each by FT-IR, SEM and TGA analysis.As a practical test application for prepared adsorbents.

Then, to make a comparison for the adsorption efficiency and other isothermal and kinetic parameters for these processes, this was done by predicting the remaining concentration amounts at equilibrium, the percentage removal for each adsorption process then was determined. This value meaning the ratio of difference in the adsorbate amounts before and after adsorptions ($C_0 - C_e$), to the initial amount of the target analyte which is CBZ in the aqueous solution (C_0), as shown in the following equation:

$$\text{Percentage removal} = \%\text{Removal} = (C_o - C_e)/(C_o)*100 \quad \text{Eq. 2.12}$$

4.2.1 Adsorption of Carbamazepine using phenylamine (SiBN) and Phenylamide (SiBCON).

Our goal in this section of the research is to compare two SiBN and SiBCON functional silica adsorbents to determine which has the best CBZ adsorption capacity from aqueous solutions.

4.2.1.1 Effect of contact time

The contact time required between adsorbent and adsorbate to allow the direct and dynamic contact for saturation state was studied.

It's important to predict the time of contact that required for achieving optimum removal of CBZ, that give us an information about the kinetic of the adsorption reaction occur and how fast the process. It was done by dissolving 0.02 g of adsorbent in 10 ml of 10 ppm initial concentration of CBZ solution with no pH modifying at room temperature then taking a sample to analyzed each period of time (5, 10, 15, 20, 25, 30) min. The measurement was made on HPLC instrument, the following figure shows the effect of contact time on CBZ removal.

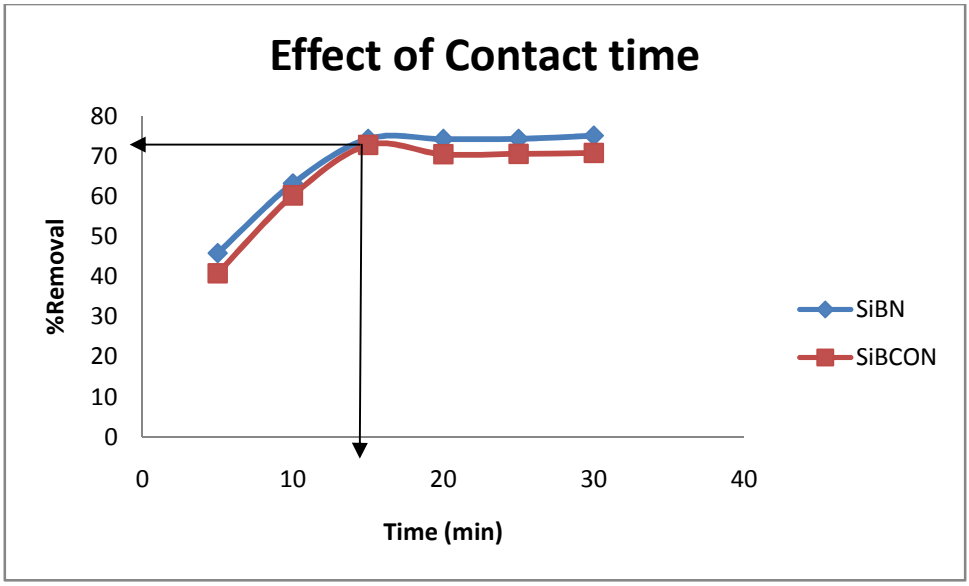


Figure (4.11): Effect of contact time on the removal of CBZ using SiBN, SiBCON.

As shown in the graph, we observed that 15 minutes is the ideal time for CBZ removal using SiBN and SiBCON, and the adsorption increases from (45.88% to 74.36%) and from (40.85% to 72.86%), respectively,and then no more high effect appears on the concentration of CBZ with extra contact time. So this 15 minutes is the optimal contact time for the two adsorbents.

4.2.1.2 Effect of pH

The pH of the solution highly effected the adsorption process, so it was an important parameter to study, that was done by plotting a %removal of CBZ as a function of pH to find at which pH value, the maximum adsorption occur. The following figure (4.12) shows the effect of pH of the soultion on the removal of CBZ.

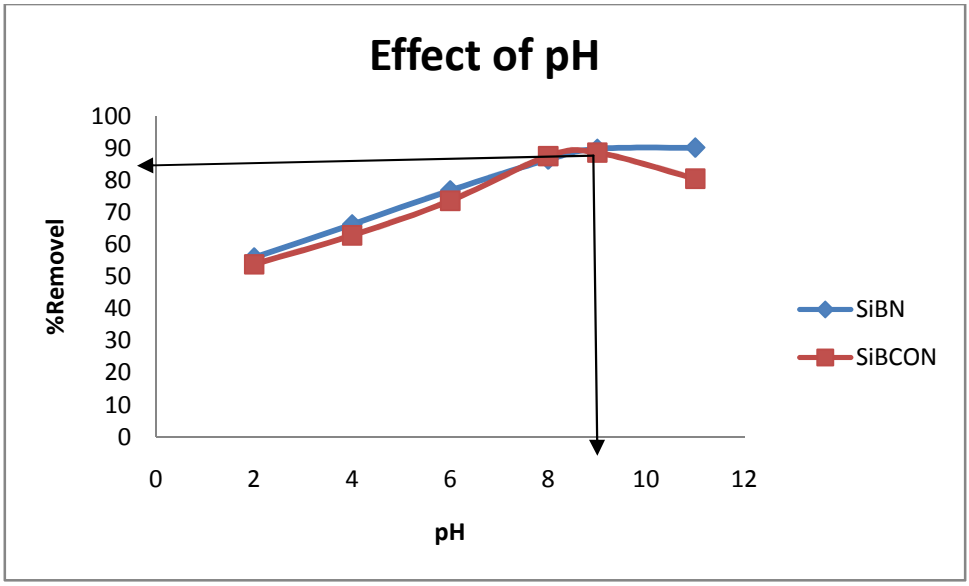


Figure (4.12): Effect of pH modification on the removal of CBZ using SiBN, SiBCON.

The adsorption was studied over a wide range of pH (2 - 11), by taking 0.02g of adsorbent with 10 ml of 10 ppm of adsorbate initial concentration at room temperature, taking in account the optimum time required. It was clear that the reaction favored the alkaline medium at a high pH value of both adsorbents (SiBN, SiBCON) and the removal ratio increased sharply between 4 and 8, then increased further until it reached pH = 9, then there was no longer increase in adsorption. This adsorption favored the alkaline medium as the removal was raised from (55.96%),(53.87) at pH = 2 to(89.84%),(88.89%) at pH = 9 respectively, so pH = 9 was taken into account as optimum in subsequent experiments.

4.2.1.3 Effect of temperature

To study the effect of temperature on the removal efficiency of CBZ using the two adsorbents (SiBN and SiBCON), the optimum conditions for other parameters was taken in consideration. In general the, the adsorption efficiency becomes higher when increasing temperature values.

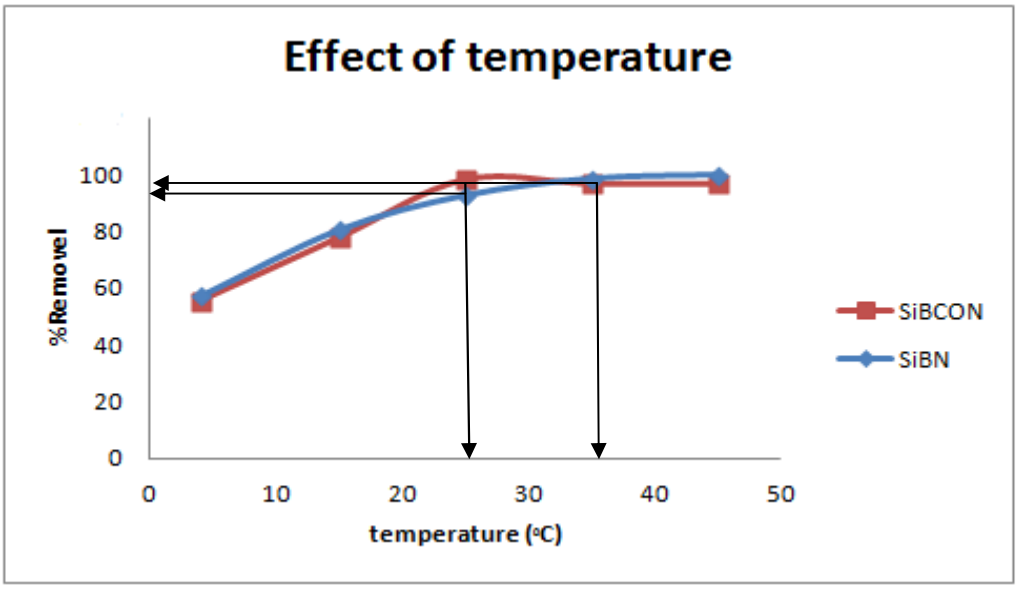


Figure (4.13): Effect of temperature on the removal of CBZ using SiBN and SiBCON.

As shown in figure 4.13 the adsorption of CBZ when use the two adsorbents (SiBN, SiBCON) increased as temperatures rose from(4°C to 35°C) and (4°C to 25°C) respectively, then the efficiency of removal stay constant with farther increasing in temperature, such that the percentage removal of CBZ at the optimum temperature was 98.37% in SiBN and 97.98% in SiBCON, then still to be nearly constant, the high temperature value of the solutions increasing the adsorption efficiency, that indicating endothermic process. 35°C for SiBN and 25°C for SiBCON were taken as optimum temperature in further test for adsorption of CBZ.

4.2.1.4 Effect of initial concentration

The adsorbent has a maximum adsorption capacity for the analyte or adsorbate due to its limited adsorption sites on its surface, there is a suitable initial concentration to start with, to achieve the optimum removal as a high % of removal by plotting it as a function of initial concentration

of CBZ. This was done by taking 10 ml of 5 different initial concentrations of CBZ standard solution (1, 5, 10, 20, 30) ppm treated with a constant adsorbent dose of 0.02g for 15 min, at (35°C 25°C), (pH for the solution is 9).

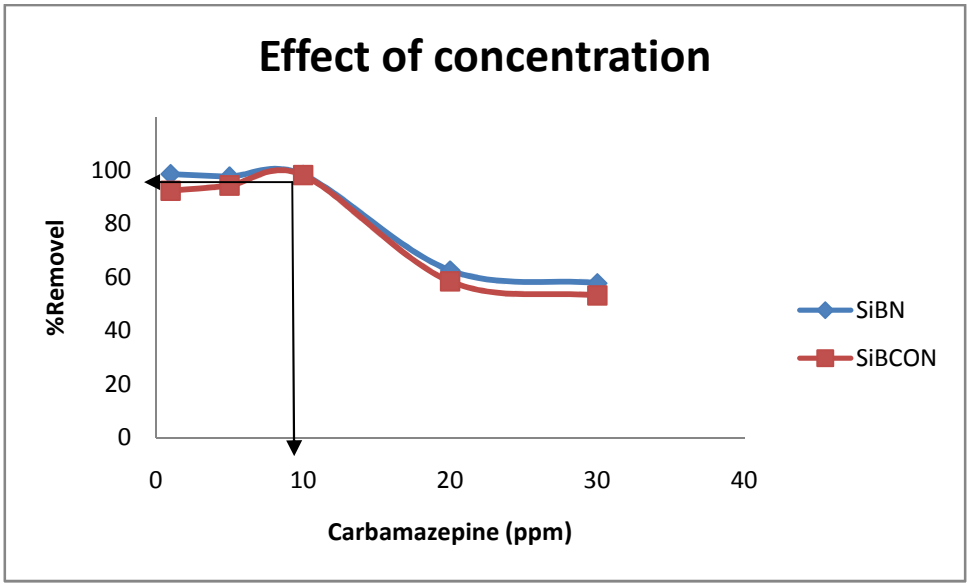


Figure (4.14): Effect of adsorbate initial concentration dose on the removal of CBZ using SiBN, SiBCON.

As the initial concentration increased from 2 ppm to 10 ppm the % removal was decreased, strongly when the concentration was higher than 10 ppm in the two adsorbents.

The maximum removal was taken as 98.37% for SiBN and 98.22% for SiBCON at the initial concentration of 10 ppm even it was still constant for the lower one concentrations (1 ppm and 5 ppm), while it was just 57.84% for SiBN and 53.21% for SiBCON in 30 ppm solution.

4.3 Summary

The adsorption maximum for each variable affecting the adsorption of CBZ on SiBN or SiBCON was studied, so as to use optimal conditions in other determinations of isotherm, kinetic and thermodynamic study.

We also observed the maximum removal of CBZ by SiBN and SiBCON was 10 ppm with the maximum clearance (98.37%) and (98.22%) respectively, for the pH value, to remove the CBZ by SiBN was the pH exponent at 9 and the maximum removal was About (89.84%). As for SiBCON the pH was 9 and the maximum removal was about (88.69%). The vibration time required to reach the maximum CBZ adsorption varies, with the required contact time being a sign of the adsorption velocity, and the fastest when the contact time getting shorter, however it took 15 minutes to reach the optimum elimination of CBZ adsorption in both SiBN and SiBCON adsorbents and the limit was maximum expulsion (74.36%) and (72.86%) respectively.

The temperature of the solution as CBZ is adsorbed into SiBN and SiBCON at an ideal temperature of (35 °C) and (25 °C) and the maximum removal is about (98.37%) and (97.98%) respectively, this is important for the prediction of the thermodynamic parameters. The main one that helps to understand the spontaneity of reactions and the energy associated with them to classify them as either an endothermic reaction or an exothermic reaction, along with our knowledge of the randomness of the process.

4.4 Regeneration of adsorbent

The adsorbent after each adsorption process is washed with 0.1 M HCl solution then with distilled water(from the figure 4.12 Effect of the pH it was found that as pH increases adsorption increases). After that, each regenerated adsorbent left to dry for 24 hours before second using. The same recovery technique is then used for each regenerative adsorbent to demonstrate that SiBN and SiBCON can be used multiple times with virtually no effect on the percentage of CBZ removal.

The effect of regeneration of adsorbent on the adsorption of CBZ on SiBN and SiBCON, showed that the difference in the percentage of removal between the first and second use of SiBN to remove CBZ was very small, the loss of 1.86% efficiency, also decreased by 0.75% for the third use.

Regarding the SiBCON removal adsorbent for CBZ was also small, it also decreased 1.90% efficiency, also decreased by 0.83% for the third use, as shown in Figure 4.15:

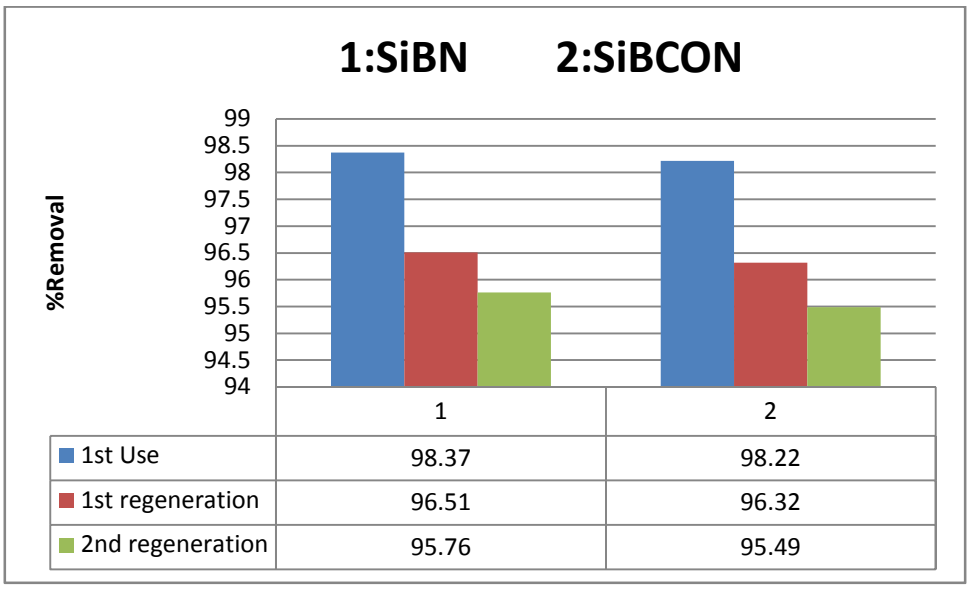


Figure (4.15): Regeneration of adsorbent (SiBN, SiBCON) for the removal of CBZ.

4.5 Equilibrium Isotherm Models

To determine the appropriate adsorption temperature for CBZ on SiBN and SiBCON, a suitable isothermal model for this adsorption process can be predicted by choosing the higher correlation coefficient near 1 as shown in the following figures (4.16,4.17):

4.5.1 Langmuir adsorption isotherm

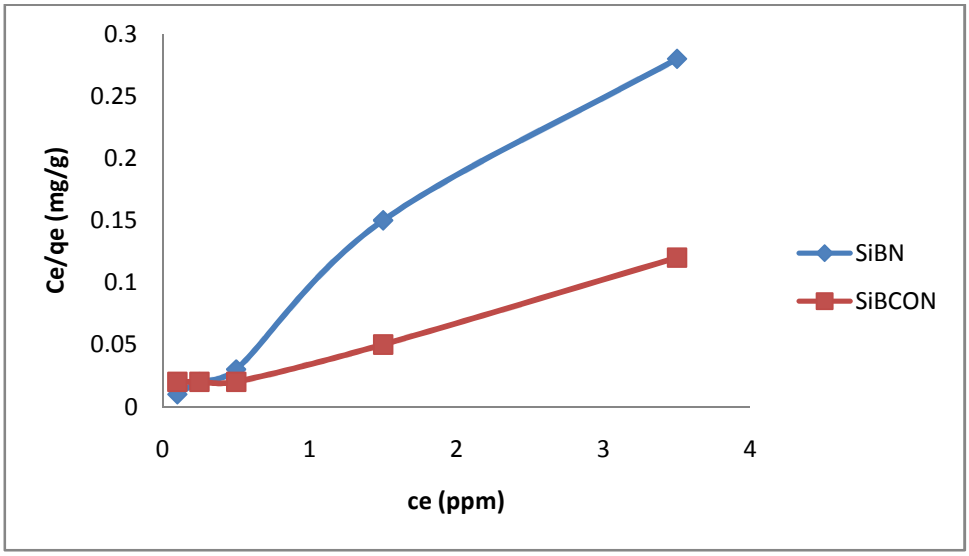


Figure (4.16): Langmuir adsorption of CBZ on SiBN, SiBCON.

4.5.2 Freundlich adsorption isotherm

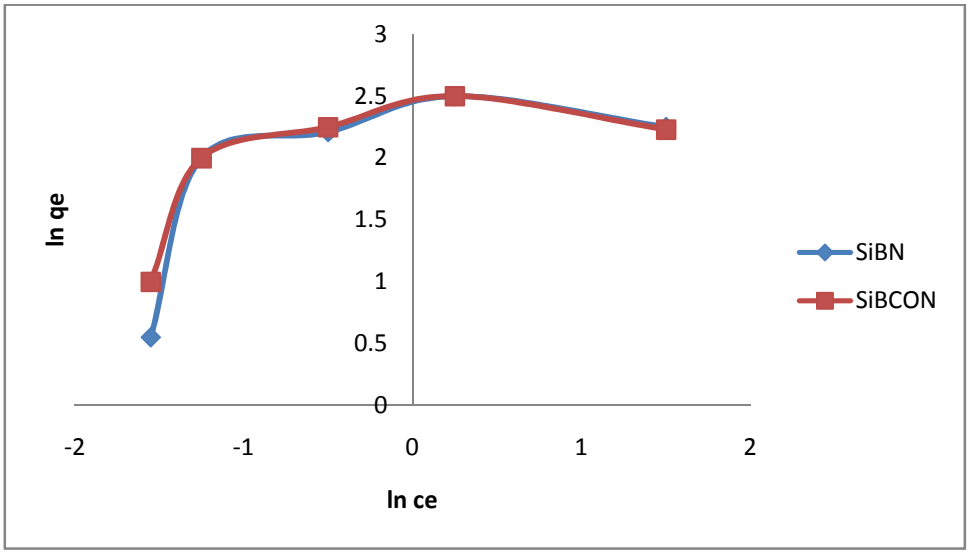


Figure (4.17): Freundlich adsorption of CBZ on SiBN, SiBCON.

R^2 has affinity values of 1 when synthesized as a Langmuir model indicating that the adsorption of CBZ on SiBN and SiBCON is with respect to the adsorption of Langmuir. Moreover, the R_L values in all cases for the Langmuir uptake isotherm were less than one and more than zero, indicating that the process was favorable. The following table represents the values of the Langmuir and Freundlich isothermal parameters for CBZ adsorption on SiBN and SiBCON:

Table (4.2): The parameters of Langmuir and Freundlich isotherms for the adsorption of CBZ on SiBN, SiBCON.

Adsorbents	Equilibrium Isotherm Models							
	Langmuir Isotherm				Freundlich Isotherm			
	Qo (mg/g)	K_L (L/mg)	R^2	R_L	K_F (mg/g)	1/n (L/g)	n (g/L)	R^2
SiBN	12.78	12.22	0.993	0.4	8.414	0.340	2.93	0.528
SiBCON	18.45	4.9	0.986	0.6	8.302	0.338	2.952	0.520

4.6 Adsorption kinetic models

The experimental kinetic data for CBZ adsorptions on predicted adsorbents were plotted following pseudo-($1^{st}/2^{nd}$) -order kinetic models and also as IPD model. The R^2 can tell how this process is suitable and follow that type of kinetic and its mechanism. The correlation coefficients and also kinetics parameters can be found from the linear relation for each type that mentioned previously as shown in the next figures (4.18 – 4.20):

4.6.1 Pseudo-1st-order kinetic model

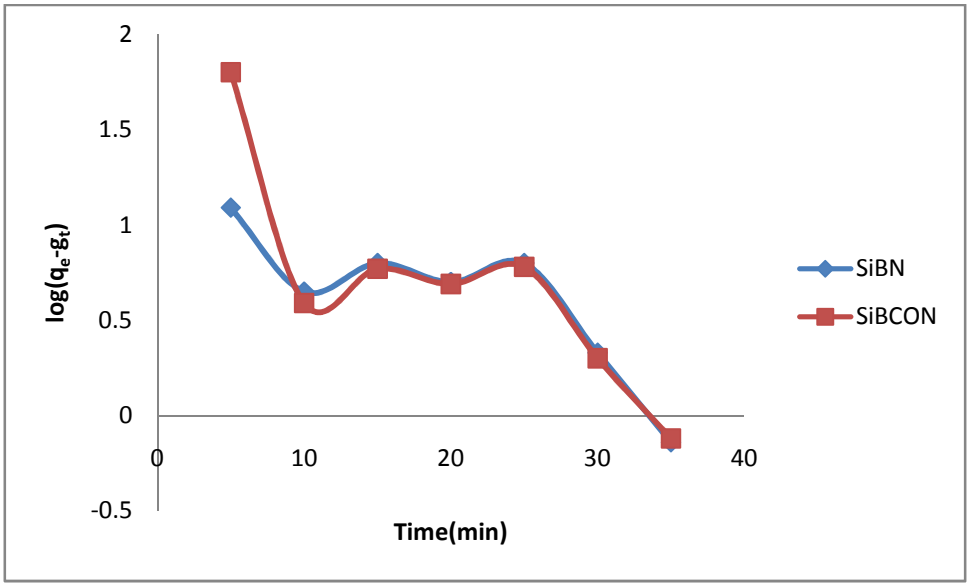


Figure (4.18): The pseudo 1st-order kinetic model for the adsorption of CBZ on SiBN, SiBCON.

4.6.2 Pseudo-2nd-order kinetic model

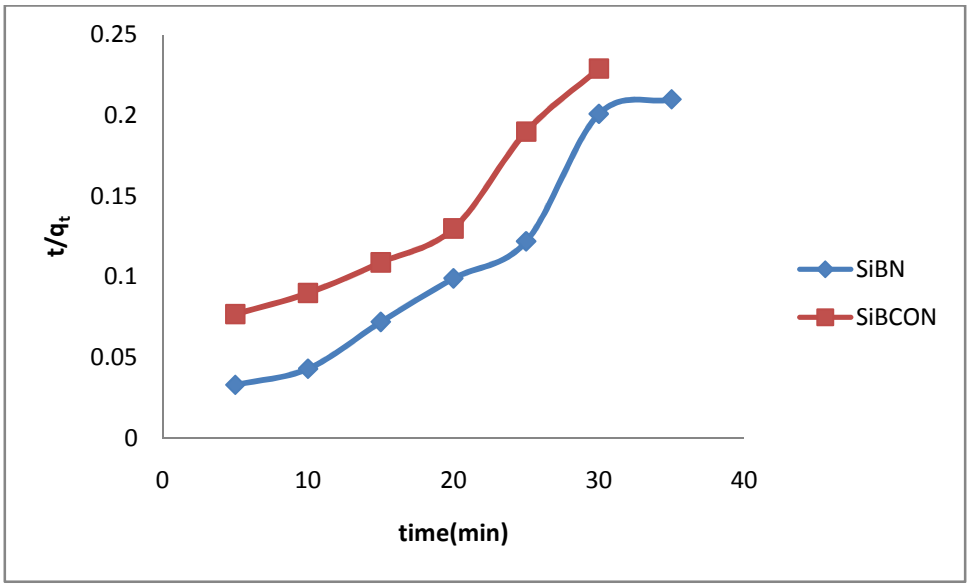


Figure (4.19): The pseudo-2nd-order kinetic model for the adsorption of CBZ on SiBN, SiBCON.

4.6.3 IPD kinetic model

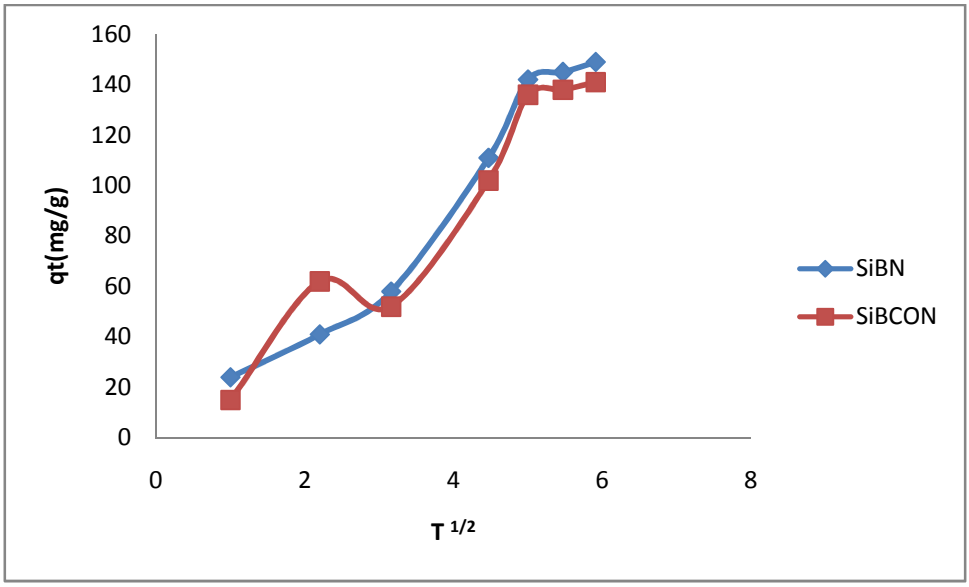


Figure (4.20): The IPD kinetic model for the adsorption of CBZ on SiBN, SiBCON.

Regarding the values of the correlation coefficient in the data of previous kinematic models, it was shown that the adsorption of CBZ on SiBN, SiBCON. The mechanism of the second-order pseudo-kinetic model was followed, since the R^2 values in this kinematic model are approximately 1. The following table shows the kinematic parameters of the pseudo-first- and second-order kinematic models and the IPD of the kinematic models of CBZ adsorption on SiBN, SiBCON.

Table (4.3): the parameters of pseudo-1st-order, pseudo-2nd-order, and IPD kinetic models for the adsorption of CBZ on SiBN, SiBCON.

Adsorbents	Adsorption kinetic models									
		Pseudo 1st order			Pseudo 2nd order			IPD		
	qe EXP.	qe (mg/g)	K1 ($mg.g^{-1}.min^{-0.5}$)	R^2	qe (mg/g)	K2 ($mg.g^{-1}.min^{-1}$)	R^2	Z (mg/g)	Kid ($mg.g^{-1}.min^{-0.5}$)	R^2
SiBN	148	78	0.14	0.70	148	1.86	0.99	9.717	0.29	0.95
SiBCON	141	98	0.12	0.69	143	1.52	0.99	8.765	0.217	0.93

The experimental values of q_e are closer to calculated one in pseudo- 2nd -order adsorption model, that's sign this adsorption follow the 2nd -order model mechanism.

4.7 Adsorption thermodynamic

Van't Hoff equation was used to study adsorption thermodynamic; the thermodynamic parameters (ΔH, ΔS, and ΔG) for the adsorption of CBZ on SiBN, SiBCON can be calculated from the slope and y-intercept of the graph of ln K_d versus 1/T(k^{-1}), as shown in the following figure 4.21:

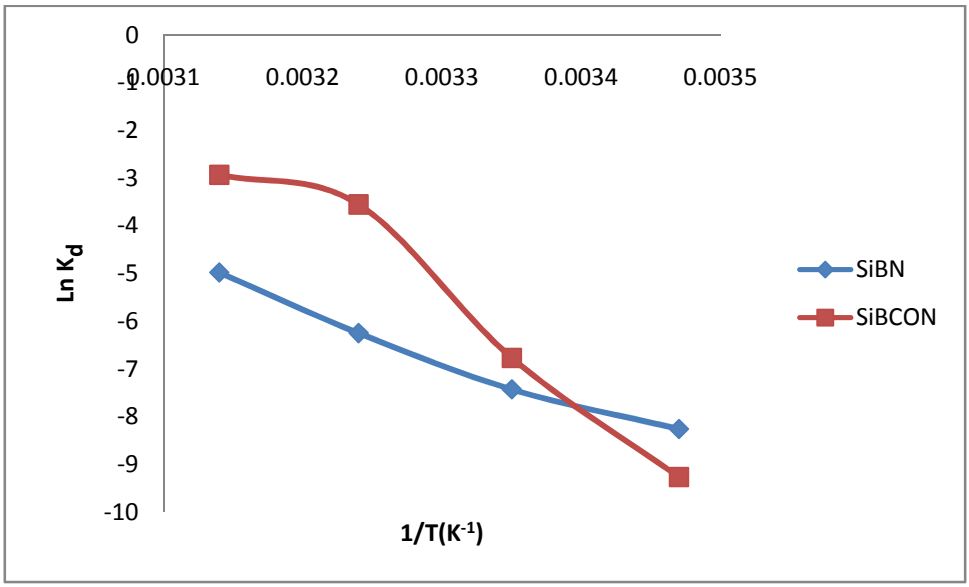


Figure (4.21): Van't Hoff plot for the adsorption of CBZ on SiBN, SiBCON.

The following table represents the values of the thermodynamic parameters (ΔH, ΔS, and ΔG) for the adsorption of CBZ on SiBN, SiBCON.

Table (4.4): the thermodynamic parameters for the adsorption CBZ on SiBN, SiBCON.

Adsorbents	Adsorption thermodynamic		
	ΔH (KJ)	ΔS (J/K)	ΔG (25°C) (KJ)
SiBN	82.85	217.46	-18.18
SiBCON	169.10	511.24	-16.82

As shown in this table, the adsorption of CBZ on SiBN and SiBCON is an endothermic process ($\Delta H > 0$) which gives a high percentage of removal with increasing temperature, as well as spontaneously ($\Delta G < 0$); Moreover, both processes tend towards more chaos because the entropy coefficient has positive values ($\Delta S > 0$).

Chapter Five

Conclusion and Recommendations

Chapter Five
Conclusion and Recommendations

5.1 Conclusion

In recent years, the preparation of silica-based adsorbents has aroused great interest due to its unique large surface area, uniform pore structure and well-modified surface properties. Moreover, it can also be recreated many times after the adsorption is saturated.

Functional silica with SiBN and SiBCON reversed that the result for the adsorption of CBZ were highly efficiency, as both have good adsorption capacity, and the rate of removal was increased under optimum conditions: (1) room temperature, (2) pH 9.0, (3) 10.0 ppm initial concentration and (4) contact time 15 min. Thus it can be used as an ideal adsorbent of CBZ from wastewater.

The results showed that all adsorption processes followed Langmuir temperature, and all were favorable ($1 > R_L > 0$). The mechanism of all interactions followed the pseudo-kinetic adsorption class II model. Regarding thermodynamics, the parameters showed that all processes are endothermic ($\Delta H > 0$),), favorable and spontaneous ($\Delta G < 0$), and the processes reveal a random increase ($\Delta S > 0$), in the solid and liquid surface, indicating an accumulation of CBZ.

5.2 Recommendations

This work aims to use SiBN and SiBCON modified silica to remove CBZ from aqueous solutions.

1. Study the possibilities of applying these materials in scientific applications.
2. Try to design specialized and commercially available materials using these materials.
3. Use other adsorbents or other effective techniques to remove CBZ.

References

1. Daghrir, R., Drogui, P., Dimboukou-Mpira, A., & El Khakani, M. A. (2013). Photoelectrocatalytic degradation of carbamazepine using Ti/TiO2 nanostructured electrodes deposited by means of a pulsed laser deposition process. *Chemosphere*, *93*(11), 2756-2766.

2. Martin-Diaz, L., Franzellitti, S., Buratti, S., Valbonesi, P., Capuzzo, A., & Fabbri, E. (2009). Effects of environmental concentrations of the antiepilectic drug carbamazepine on biomarkers and cAMP-mediated cell signaling in the mussel Mytilus galloprovincialis. *Aquatic Toxicology*, *94*(3), 177-185.

3. Mohapatra, D. P., Brar, S. K., Daghrir, R., Tyagi, R. D., Picard, P., Surampalli, R. Y., & Drogui, P. (2014). Photocatalytic degradation of carbamazepine in wastewater by using a new class of whey-stabilized nanocrystalline TiO2 and ZnO. *Science of the total environment*, *485*, 263-269.

4. Scheytt, T., Mersmann, P., Lindstädt, R., & Heberer, T. (2005). 1-Octanol/water partition coefficients of 5 pharmaceuticals from human medical care: carbamazepine, clofibric acid, diclofenac, ibuprofen, and propyphenazone. *Water, Air, and Soil Pollution*, *165*(1), 3-11.

5. Chong, M. N., & Jin, B. (2012). Photocatalytic treatment of high concentration carbamazepine in synthetic hospital wastewater. *Journal of Hazardous Materials*, *199*, 135-142.

6. Miao, X. S., & Metcalfe, C. D. (2003). Determination of carbamazepine and its metabolites in aqueous samples using liquid chromatography− electrospray tandem mass spectrometry. *Analytical chemistry*, *75*(15), 3731-3738.

7. Zhang, Y., Geißen, S. U., & Gal, C. (2008). Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. *Chemosphere*, *73*(8), 1151-1161.

8. Calisto, V., Domingues, M. R. M., Erny, G. L., & Esteves, V. I. (2011). Direct photodegradation of carbamazepine followed by micellar electrokinetic chromatography and mass spectrometry. *Water research*, *45*(3), 1095-1104.

9. Metcalfe, C. D., Koenig, B. G., Bennie, D. T., Servos, M., Ternes, T. A., & Hirsch, R. (2003). Occurrence of neutral and acidic drugs in the effluents of Canadian sewage treatment plants. *Environmental Toxicology and Chemistry: An International Journal*, *22*(12), 2872-2880.

10. Focazio, M. J., Kolpin, D. W., Barnes, K. K., Furlong, E. T., Meyer, M. T., Zaugg, S. D.,... & Thurman, M. E. (2008). A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States—II) Untreated drinking water sources. *Science of the total Environment*, *402*(2-3), 201-216.

11. Lapworth, D. J., Baran, N., Stuart, M. E., & Ward, R. S. (2012). Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. *Environmental pollution*, *163*, 287-303.

12. Hummel, D., Löffler, D., Fink, G., & Ternes, T. A. (2006). Simultaneous determination of psychoactive drugs and their metabolites in aqueous matrices by liquid chromatography mass spectrometry. *Environmental science & technology*, *40*(23), 7321-7328.

13. Bahlmann, A., Weller, M. G., Panne, U., & Schneider, R. J. (2009). Monitoring carbamazepine in surface and wastewaters by an immunoassay based on a monoclonal antibody. *Analytical and bioanalytical chemistry*, *395*(6), 1809-1820.

14. Heberer, T., Reddersen, K., & Mechlinski, A. (2002). From municipal sewage to drinking water: fate and removal of pharmaceutical residues in the aquatic environment in urban areas. *Water Science and Technology*, *46*(3), 81-88.

15. Ferrari, B., Paxéus, N., Giudice, R. L., Pollio, A., & Garric, J. (2003). Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac. *Ecotoxicology and environmental safety*, *55*(3), 359-370.

16. Hai, F. I., Yang, S., Asif, M. B., Sencadas, V., Shawkat, S., Sanderson-Smith, M.,... & Yamamoto, K. (2018). Carbamazepine as a possible anthropogenic marker in water: occurrences, toxicological effects,

regulations and removal by wastewater treatment technologies. *Water*, *10*(2), 107.

17. Kinney, C. A., Furlong, E. T., Zaugg, S. D., Burkhardt, M. R., Werner, S. L., Cahill, J. D., & Jorgensen, G. R. (2006). Survey of organic wastewater contaminants in biosolids destined for land application. *Environmental science & technology*, *40*(23), 7207-7215.

18. Chen, F., Ying, G. G., Kong, L. X., Wang, L., Zhao, J. L., Zhou, L. J., & Zhang, L. J. (2011). Distribution and accumulation of endocrine-disrupting chemicals and pharmaceuticals in wastewater irrigated soils in Hebei, China. *Environmental Pollution*, *159*(6), 1490-1498.

19. Fernández-López, C., Guillén-Navarro, J. M., Padilla, J. J., & Parsons, J. R. (2016). Comparison of the removal efficiencies of selected pharmaceuticals in wastewater treatment plants in the region of Murcia, Spain. *Ecological Engineering*, *95*, 811-816.

20. Banerjee, P., kumar Dey, T., Sarkar, S., Swarnakar, S., Mukhopadhyay, A., & Ghosh, S. (2016). Treatment of cosmetic effluent in different configurations of ceramic UF membrane based bioreactor: Toxicity evaluation of the untreated and treated wastewater using catfish (Heteropneustes fossilis). *Chemosphere*, *146*, 133-144.

21. Liu, L., Li, C., Bao, C., Jia, Q., Xiao, P., Liu, X., & Zhang, Q. (2012). Preparation and characterization of chitosan/graphene oxide composites for the adsorption of Au (III) and Pd (II). *Talanta*, *93*, 350-357.

22. Banerjee, P., Sau, S., Das, P., & Mukhopadhayay, A. (2015). Optimization and modelling of synthetic azo dye wastewater treatment using graphene oxide nanoplatelets: characterization toxicity evaluation and optimization using artificial neural network. *Ecotoxicology and environmental safety*, *119*, 47-57.

23. Banerjee, P., Das, P., Zaman, A., & Das, P. (2016). Application of graphene oxide nanoplatelets for adsorption of ibuprofen from aqueous solutions: evaluation of process kinetics and thermodynamics. *Process Safety and Environmental Protection*, *101*, 45-53.

24. Schilling, K. E. (2009). Investigating local variation in groundwater recharge along a topographic gradient, Walnut Creek, Iowa, USA. *Hydrogeology Journal*, *17*(2), 397-407.

25. PANDIT, G. L. (2004). Blue Gold: The Battle against Corporate Theft of the World's Water.

26. Adams, H. E., Crump, B. C., & Kling, G. W. (2014). Metacommunity dynamics of bacteria in an arctic lake: the impact of species sorting and mass effects on bacterial production and biogeography. *Frontiers in Microbiology*, *5*, 82.

27. Messerschmid, C. (2012). Nothing new in the Middle East–reality and discourses of climate change in the Israeli-Palestinian conflict. In *Climate Change, Human Security and Violent Conflict* (pp. 423-459). Springer, Berlin, Heidelberg.

28. Zahra, B. A. A. A. (2001). Water crisis in Palestine. *Desalination*, *136*(1-3), 93-99.

29. Cosgrove, W. J., Rijsberman, F. R., & Rijsberman, F. (2000). *World water vision: making water everybody's business*. Earthscan.

30. Abdelmadjid, B., & Omar, S. (2013). Assessment of groundwater pollution by nitrates using intrinsic vulnerability methods: A case study of the Nil valley groundwater (Jijel, North-East Algeria). *African Journal of Environmental Science and Technology*, *7*(10), 949-960.

31. Hailin, Y., Ligang, X., Chang, Y., & Jiaxing, X. (2011). Evaluation of groundwater vulnerability with improved DRASTIC method. *Procedia Environmental Sciences*, *10*, 2690-2695.

32. Adekunle, I. M., Adetunji, M. T., Gbadebo, A. M., & Banjoko, O. B. (2007). Assessment of groundwater quality in a typical rural settlement in Southwest Nigeria. *International journal of environmental research and public health*, *4*(4), 307-318.

33. Gadberry, J. A., Johnson, A., Rodriguez, J., Marrero-Rivera, P., Krumpolc, T., & Wiese, Z. (2018). Removal of Carbamazepine from Drinking Water.

34. Gadberry, J. A., Johnson, A., Rodriguez, J., Marrero-Rivera, P., Krumpolc, T., & Wiese, Z. (2018). Removal of Carbamazepine from Drinking Water.

35. Luo, Y., Guo, W., Ngo, H. H., Nghiem, L. D., Hai, F. I., Zhang, J.,... & Wang, X. C. (2014). A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment. *Science of the total environment*, *473*, 619-641.

36. Adams, E. N., Marks, A., & Lizer, M. H. (2009). Carbamazepine-induced hyperammonemia. *American Journal of Health-System Pharmacy*, *66*(16), 1468-1470.

37. Nevitt, S. J., Marson, A. G., Weston, J., & Smith, C. T. (2018). Sodium valproate versus phenytoin monotherapy for epilepsy: an individual participant data review. *Cochrane Database of Systematic Reviews*, (8).

38. Nevitt, S. J., Marson, A. G., & Smith, C. T. (2019). Carbamazepine versus phenytoin monotherapy for epilepsy: an individual participant data review. *Cochrane Database of Systematic Reviews*, (7).

39. Smith, H. S. (2009). *Current therapy in pain*. Elsevier Health Sciences.

40. Rbaa, M., Abousalem, A. S., Galai, M., Lgaz, H., Lakhrissi, B., Warad, I., & Zarrouk, A. (2020). New N-Heterocyclic Compounds Based on 8-Hydroxyquinoline as Efficient Corrosion Inhibition for Mild Steel in HCl Solution: Experimental and Theoretical Assessments. *Arabian Journal for Science and Engineering*, 1-18.

41. Shorvon, S., Perucca, E., & Engel Jr, J. (Eds.). (2015). *The treatment of epilepsy*. John Wiley & Sons.

42. Filipchuk, D. (2003). Classic trigeminal neuralgia: a surgical perspective. *Journal of Neuroscience Nursing*, *35*(2), 82.

43. World Health Organization. (2019). *World Health Organization model list of essential medicines: 21st list 2019* (No. WHO/MVP/EMP/IAU/2019.06). World Health Organization.

44. Pishnamazi, M., Zabihi, S., Jamshidian, S., Borousan, F., Hezave, A. Z., & Shirazian, S. (2020). Thermodynamic modelling and experimental validation of pharmaceutical solubility in supercritical solvent. *Journal of Molecular Liquids*, *319*, 114120.

45. Driver, L. R. The Mechanism and Management of Carbamazepine-Induced Hepatotoxicity.

46. Fortuna, A., Sousa, J., Alves, G., Falcão, A., & Soares-da-Silva, P. (2010). Development and validation of an HPLC-UV method for the simultaneous quantification of carbamazepine, oxcarbazepine, eslicarbazepine acetate and their main metabolites in human plasma. *Analytical and bioanalytical chemistry*, *397*(4), 1605-1615.

47. Ceron□Litvoc, D., Soares, B. G., Geddes, J., Litvoc, J., & Lima, M. S. D. (2009). Comparison of carbamazepine and lithium in treatment of bipolar disorder: a systematic review of randomized controlled trials. *Human Psychopharmacology: Clinical and Experimental*, *24*(1), 19-28.

48. Leucht, S., Helfer, B., Dold, M., Kissling, W., & McGrath, J. (2014). Carbamazepine for schizophrenia. *Cochrane Database of Systematic Reviews*, (5).

49. Lang, M., Kampf, J. W., & Matzger, A. J. (2002). Form IV of carbamazepine. *Journal of pharmaceutical sciences*, *91*(4), 1186-1190.

50. Gandelman, M. S. (1994). Review of carbamazepine-induced hyponatremia. *Progress in neuro-psychopharmacology and biological psychiatry*, *18*(2), 211-233.

51. Jentink, J., Dolk, H., Loane, M. A., Morris, J. K., Wellesley, D., Garne, E., & de Jong-van den Berg, L. (2010). Intrauterine exposure to carbamazepine and specific congenital malformations: systematic review and case-control study. *BmJ*, *341*.

52. Liu, L., Zheng, T., Morris, M. J., Wallengren, C., Clarke, A. L., Reid, C. A.,... & O'Brien, T. J. (2006). The mechanism of carbamazepine aggravation of absence seizures. *Journal of Pharmacology and Experimental Therapeutics*, *319*(2), 790-798.

53. Prosser, R. S., & Sibley, P. K. (2015). Human health risk assessment of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, and wastewater irrigation. *Environment international*, *75*, 223-233.

54. Posselt, M., Jaeger, A., Schaper, J. L., Radke, M., & Benskin, J. P. (2018). Determination of polar organic micropollutants in surface and

pore water by high-resolution sampling-direct injection-ultra high performance liquid chromatography-tandem mass spectrometry. *Environmental Science: Processes & Impacts*, *20*(12), 1716-1727.

55. Bahadur, R., & Samuels, W. B. (2011). Wastewater Critical Infrastructure Security and Protection. In *Handbook of Water and Wastewater Systems Protection* (pp. 87-102). Springer, New York, NY.

56. Hernández-Leal, L., Temmink, H., Zeeman, G., & Buisman, C. J. N. (2011). Removal of micropollutants from aerobically treated grey water via ozone and activated carbon. *Water research*, *45*(9), 2887-2896.

57. Suriyanon, N., Punyapalakul, P., & Ngamcharussrivichai, C. (2013). Mechanistic study of diclofenac and carbamazepine adsorption on functionalized silica-based porous materials. *Chemical Engineering Journal*, *214*, 208-218.

58. Mcdowell, D. C., Huber, M. M., Wagner, M., Von Gunten, U., & Ternes, T. A. (2005). Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products. *Environmental science & technology*, *39*(20), 8014-8022.

59. Kim, S. D., Cho, J., Kim, I. S., Vanderford, B. J., & Snyder, S. A. (2007). Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters. *Water research*, *41*(5), 1013-1021.

60. Radjenović, J., Petrović, M., Ventura, F., & Barceló, D. (2008). Rejection of pharmaceuticals in nanofiltration and reverse osmosis membrane drinking water treatment. *Water research*, *42*(14), 3601-3610.

61. Bellona, C., Drewes, J. E., Oelker, G., Luna, J., Filteau, G., & Amy, G. (2008). Comparing nanofiltration and reverse osmosis for drinking water augmentation. *Journal□American Water Works Association*, *100*(9), 102-116.

62. Gago, S., Fonseca, I. M., & Parola, A. J. (2013). Hybrid mesoporous silica grafted with photoisomerizable 2-hydroxychalcones. *Microporous and mesoporous materials*, *180*, 40-47.

63. Im, J. K., Cho, I. H., Kim, S. K., & Zoh, K. D. (2012). Optimization of carbamazepine removal in O3/UV/H2O2 system using a response surface methodology with central composite design. *Desalination*, *285*, 306-314.

64. Sichel, C., Garcia, C., & Andre, K. (2011). Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. *Water research*, *45*(19), 6371-6380.

65. Sichel, C., Garcia, C., & Andre, K. (2011). Feasibility studies: UV/chlorine advanced oxidation treatment for the removal of emerging contaminants. *Water research*, *45*(19), 6371-6380.

66. Shirazi, E., Torabian, A., & Nabi‐ Bidhendi, G. (2013). Carbamazepine removal from groundwater: effectiveness of the TiO2/UV, nanoparticulate zero‐ valent iron, and Fenton (NZVI/H2O2) processes. *CLEAN–Soil, Air, Water*, *41*(11), 1062-1072.

67. Alyoshina, N. A., & Parfenyuk, E. V. (2013). Functionalized mesoporous silica materials for molsidomine adsorption: Thermodynamic study. *Journal of Solid State Chemistry*, *205*, 211-216.

68. Vivero-Escoto, J. L., Carboni, M., Abney, C. W., deKrafft, K. E., & Lin, W. (2013). Organo-functionalized mesoporous silicas for efficient uranium extraction. *Microporous and Mesoporous Materials*, *180*, 22-31.

69. Lu, Y. K., & Yan, X. P. (2004). An imprinted organic− inorganic hybrid sorbent for selective separation of cadmium from aqueous solution. *Analytical chemistry*, *76*(2), 453-457.

70. Yount, K. R. (2003). What are brownfields? Finding a conceptual definition. *Environmental Practice*, *5*(1), 25-33.

71. Mahameed, A. (2017). *Comparative Study between Commercial Charcoal and Asphodelus ramosus Tuber Derived Activated Carbons for Adsorption of Heavy metals from Aqueous Solution* (Doctoral dissertation, An-Najah National University).

72. Atkins, P., & De Paula, J. (2013). *Elements of physical chemistry*. Oxford University Press, USA.

73. Dubey, S., Banerjee, S., Upadhyay, S. N., & Sharma, Y. C. (2017). Application of common nano-materials for removal of selected metallic species from water and wastewaters: A critical review. *Journal of molecular liquids*, *240*, 656-677.

74. Rashed, M. N. (2013). Adsorption technique for the removal of organic pollutants from water and wastewater. *Organic pollutants-monitoring, risk and treatment*, *7*, 167-194.

75. Weber Jr, W. J., & Van Vliet, B. M. (1981). Synthetic adsorbents and activated carbons for water treatment: overview and experimental comparisons. *Journal American Water Works Association*, *73*(8), 420-426.

76. Al-Khateeb, L. A., Hakami, W., & Salam, M. A. (2017). Removal of non-steroidal anti-inflammatory drugs from water using high surface area nanographene: kinetic and thermodynamic studies. *Journal of Molecular Liquids*, *241*, 733-741.

77. Dada, A. O., Olalekan, A. P., Olatunya, A. M., & Dada, O. J. I. J. C. (2012). Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn2+ unto phosphoric acid modified rice husk. *IOSR Journal of Applied Chemistry*, *3*(1), 38-45

78. Zhou, L., Pan, S., Chen, X., Zhao, Y., Zou, B., & Jin, M. (2014). Kinetics and thermodynamics studies of pentachlorophenol adsorption

on covalently functionalized Fe3O4@ SiO2–MWCNTs core–shell magnetic microspheres. *Chemical Engineering Journal*, *257*, 10-19.

79. Desta, M. B. (2013). Batch sorption experiments: Langmuir and Freundlich isotherm studies for the adsorption of textile metal ions onto teff straw (Eragrostis tef) agricultural waste. *Journal of thermodynamics*, *2013*.

80. Nethaji, S., Sivasamy, A., & Mandal, A. B. (2013). Adsorption isotherms, kinetics and mechanism for the adsorption of cationic and anionic dyes onto carbonaceous particles prepared from Juglans regia shell biomass. *International Journal of Environmental Science and Technology*, *10*(2), 231-242.

81. Dehghani, M. H., Mohammadi, M., Mohammadi, M. A., Mahvi, A. H., Yetilmezsoy, K., Bhatnagar, A.,... & McKay, G. (2016). Equilibrium and kinetic studies of trihalomethanes adsorption onto multi-walled carbon nanotubes. *Water, Air, & Soil Pollution*, *227*(9), 1-17.

82. Qu, R., Wang, M., Sun, C., Zhang, Y., Ji, C., Chen, H.,... & Yin, P. (2008). Chemical modification of silica-gel with hydroxyl-or amino-terminated polyamine for adsorption of Au (III). *Applied Surface Science*, *255*(5), 3361-3370.

83. Radi, S., Attayibat, A., Lekchiri, Y., Ramdani, A., & Bacquet, M. (2008). Synthesis and characterization of a new material based on porous silica—Chemically immobilized C, N-pyridylpyrazole for

heavy metals adsorption. *Materials Chemistry and Physics*, *111*(2-3), 296-300.

84 Ph. Eur. 9th Edition chapter 2.6. 12. (2018). Microbiological examination of non□sterile products: microbial enumeration tests.

85. Banerjee, I. A., Yu, L., & Matsui, H. (2003). Cu nanocrystal growth on peptide nanotubes by biomineralization: Size control of Cu nanocrystals by tuning peptide conformation. *Proceedings of the National Academy of Sciences*, *100*(25), 14678-14682.

86. Miao, J., Qian, J., Wang, X., Zhang, Y., Yang, H., & He, P. (2009). Synthesis and characterization of ordered mesoporous silica by using polystyrene microemulsion as templates. *Materials Letters*, *63*(12), 989-990.

جامعة النجاح الوطنية
كلية الدراسات العليا

سيليكا الفينيلامين والفينيلاميد الوظيفية (SiBN و SiBCON) لإزالة الكاربامازايبين من الصرف الصحي

إعداد
إسراء مروان محمود عقل

إشراف
أ. د. شحدة جودة
أ. د. رائد الكوني

قدمت هذه الأطروحة استكمالاً لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا، في جامعة النجاح الوطنية في نابلس، فلسطين.
2021

سيليكا الفينيلامين والفينيلاميد الوظيفية (SiBN و SiBCON)
لإزالة الكاربامازايبين من الصرف الصحي

إعداد

إسراء مروان محمود عقل

إشراف

أ. د. شحدة جودة

أ. د. رائد الكوني

الملخص

ركزت هذه الدراسة على إزالة الكاربامازابين من المحاليل المائية باستخدام السيليكا الوظيفية الفينيلامين، ولأن تحضير الممتزات القائمة على السيليكا قد أثار اهتمامًا كبيرًا نظرًا لمساحة سطحه الكبيرة الفريدة وبنية المسام المنتظمة وخصائص السطح المعدلة جيدًا. تقرر تحضير ماص سيليكا جديد هو فينيلاميد وقد تم تحليل المواد الماصة التي تم الحصول عليها من خلال تقنيات التحليل الطيفي المختلفة، بما في ذلك الفحص المجهري الإلكتروني،والتحليل الطيفي بالأشعة تحت الحمراء، و جهازالتحليل الوزني الحراري، كتطبيق اختبار عملي للمواد الماصة المعدة، حيث أظهرت الأجهزة نجاح النتائج للمجموعات الوظيفية.

تمت دراسة سلسلة من التجارب المجمعة لإجراء نماذج دراسة السلوك الحراري والتي تمت باستخدام نماذج فريندلخ ولانغمير، كما تم دراسة الديناميكا الحرارية والحركية باستخدام النموذج الحركي الزائف من الدرجة الاولى، والزائف الدرجة الثانية، تم إجراء مقارنة لهذين الممتزين من خلال تحديد الكمية الممتصة من الكاربامازابين (مبدأ المنافسة) ، كما تم دراسة تأثير العوامل المختلفة التي تؤثر على عملية الامتزاز، مثل درجة الحرارة وتركيز كل من المادة الممتزة والكاربامازابين وكذلك وقت التماس بينهما وذلك لأخذ ظروف الإزالة المثلى ، تم إجراء التحليلات باستخدام كروماتوغرافيا سائلة عالية الأداء لقياس الكمية المتبقية من المواد في المحلول بعد عملية الامتزاز، أظهرت النتائج التي تم الحصول عليها أن كفاءة إزالة الكاربامازابين كانت ملحوظة عند استخدام الممتزين و أن كل منهم يتبع نموذج لانغمير والزائف من الدرجة الثانية ,ومع ذلك ، لا يستغرق الأمر أكثر من 15 دقيقة لإزالة مستويات عالية من الكمية المذابة اعتمادًا على ظروف المختبر المثلى، كما أنه يمكن تجديد المواد الممتزة في الحالتين لإعادة استخدامها مرة اخرى.