An-Najah National University Faculty of Graduate Studies

Functionalized C,N-Bipyrazole Receptor Grafted Onto Silica Surface for Arsenic (As) Adsorption and its Antibacterial Activity

By

Nagham Tahseen Mohammed Taha

Supervisor

Dr. Ahmad Abu Obaid

Co-supervisor

Dr. Motasem Al-Masri

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

Functionalized C,N-Bipyrazole Receptor Grafted Onto Silica Surface for Arsenic (As) Adsorption and its **Antibacterial Activity**

By

Nagham Tahseen Mohammed Taha

This thesis was defended successfully on 01 /02 / 2017 and approved by:

Defense committee members

-Dr. Ahmed Abu Obaid / Supervisor

-Dr. Motasem Al-Masri / Co-Supervisor

-Dr. Abdalhadi Dheghles / External Examiner

-Dr. Raed Alkowni / Internal Examiner

signature

Poll Alkour

Dedication.

First of all, my greatest gratitude to Allah,
To my family, especially my father and mother...
To my country "Palestine "...
To my teachers and partners...
To all who helped and encouraged me in any way....

Thank you all

Acknowledgements

First of all, I am so grateful to Allah, who gave me the patience to finish my thesis.

Special thanks and appreciation to my supervisors, Dr. Ahmed Abu Obaid and Dr. Motasem Al-Masri, for their supervision, suggestions, time they spent to help me and their guidance to the last stage.

My thanks to all technical staff of the department of chemistry at An Najah University, especially Mr. Nafeth Dwikat for his help.

My thanks and gratitude to my lovely family, sister and brothers for their continuous encouragement.

Endless thanks and regards to all who help me in any way, to all my dear friends ...

∨ الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل عنوان

Functionalized C,N-Bipyrazole Receptor Grafted onto Silica for Arsenic (As) adsorption and its antibacterial activity

أقر بأن ما شملت عليه الرسالة هو نتاج جهدي الخاص, باستثناء ما تمت الإشارة إليه حيثما ورد, وان هذه الرسالة ككل أو أي جزء منها لم يقدم من قبل لنيل أي درجة أو لقب علمي أو بحثي لدى أي مؤسسة علمية أو بحثية .

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 qualifications.

Student's name :

اسم الطالب: فلم كم سين محدث

التوقيع: نجم تحسين

Signature:

التاريخ: ١ / ٢ / ١٧. ٢ ٩

Date:

Table of contents

No.	Contents	Page
	Dedication	III
	Acknowledgment	IV
	Declaration	V
	Table of contents	VI
	List of tables	VIII
	List of figures	IX
	List of abbreviation	Χ
	Abstract	XI
	Chapter One: Introduction	1
1.1	Heavy metals	4
1.1.1	Arsenic	4
1.2	Traditional techniques	5
1.3	Adsorption	6
1.4	Antibacterial resistance	7
1.5	Novelty	8
1.6	Hypothesis	8
1.7	Objectives	9
1.8	Previous studies	9
	Chapter two: Methodology	11
2.1	Chemistry part	12
2.1.1	Preparation of arsenic (III) solutions	12
2.1.2	Preparation of calibration curves	12
2.1.3	Metal quantification	13
2.1.4	Instrumentation	14
2.1.5	Studied parameter	14
2.1.5.1	Effect of temperature	14
2.1.5.2	Effect of pH	14
2.1.5.3	Effect of initial metal ion concentration	15
2.1.5.4	Effect of adsorbent dose	15
2.1.5.5	Optimization of contact time	15

2.2	Biological part	16				
2.2.1	Media preparation	16				
2.2.2	Adsorbent substance SG2P solution preparation					
2.2.3	Bacterial suspension preparation	17				
2.2.4	Minimum inhibitory concentration procedure	17				
	Chapter Three: Results and discussion	18				
3.1	Effect of pH on As(III) adsorption	19				
3.2	Effect of temperature on As(III) adsorption	20				
3.3	Effect of initial As(III) concentration	21				
3.4	Effects of time contact on As(III) adsorption	23				
3.5	Effects of adsorbent dosage on As(III) adsorption	24				
3.6	Adsorption isotherm of As(III)	25				
3.6.1	Freundlich adsorption isotherm	25				
3.6.2	Langmuir adsorption isotherm	28				
3.7	Rate order of the adsorption process	29				
3.8	Adsorption thermodynamics	32				
3.9	Antibacterial activity of SG2P	34				
	conclusion	36				
	References	37				
	الملخص	ب				

VIII

List of Tables

No	Table	Page
Table 1	Parameters and correlation coefficient of Freundlich	26
	isotherm model for adsorption of As(III) onto SG2P	20
Table 2	Parameters and correlation coefficient of Langmuir	20
	isotherm model for adsorption of As(III) onto SG2P	28
Table 3	Pseudo first- order parameters for As(III) adsorption	20
	onto SG2P at 25°C	50
Table 4	Pseudo second - order parameters for As(III)	21
	adsorption onto SG2P at 25°C	51
Table 5	The values of the thermodynamic of As(III)	22
	adsorption atvarious temperatures	33
Table 6	Demonstration of bacterial growth and inhibition by	24
	SG2P	54

List of Figures

No	Figure	Page
figure 1	Linear calibration curve of absorbance vs. concentration	12
	for As(III) concentrations	15
figure 2	pH effect on As(III) adsorption	20
figure 3	Effect of temperature on As(III) adsorption	21
figure 4	Effect of As(III) concentration on adsorption	22
figure 5	Effects of contact time on As(III) adsorption	23
figure 6	Effect of dosage of adsorbent on the removal of As(III)	24
figure 7	Freundlich plot for As(III) adsorption on SG2P	26
figure 8	Langmuir plot for As(III) adsorption on SG2P	28
figure 9	Pseudo first- order adsorption kinetics of As(III) onto	30
	SG2P	50
figure 10	Pseudo second order adsorption kinetics of As(III) onto	31
	SG2P	51
figure 11	Van't Hoff plot . graph of lnKd vs. 1/T for As(III)	33
	adsorption on SG2P	55
figure 12	Antibacterial activity of SG2P	34

List of Abbreviation

Symbol	Abbreviation
Co	Concentration of As(III) in the sample solution before
	treatment ($\mu g/L$)
Ce	Concentration of As(III)in the sample solution after
	treatment (μ g/L) at equilibrium
Ci	Initial concentration of As(III) in the sample solution (μ g/L)
SG2P	Silica glycidoxypropyl polymer
FT-IR	Fourier Transform Infrared
K 1	The Lagergren's first order rate constant
K2	The pseudo second order rate constant
Kd	The distribution coefficient
KF	Freundlich constant which is an approximate indicator of
	adsorption capacity of the sorbent $(mg/g (L/mg)_{1/n})$
KL	Langmuir isotherm constant (L/mg)
LD50	Lethal Dose which causes the death of 50% (one half) of a
	group of test
Msed	Mass of adsorbent dose
n	Dimensionless Freundlich constant giving an indication of
	how favorable the adsorption process
Qe	The amount of As(III) adsorbed per gram of the adsorbent
	(mg/g)
Qm	Maximum monolayer coverage capacity (mg/g)
Qt	Amount of adsorbate per unit mass of adsorbent at time t
	(min)
R	The gas constant (8.314 J/mol. K)
R ²	regression coefficient
RL	Dimensionless constant separation factor
SPE	Solid Phase Extraction
t	Time
Т	The absolute temperature (°K)
TGA	Thermal gravimetric analysis
V	Volume of solution
ΔG°	Standard free Gibbs energy
ΔH°	Standard enthalpy
ΔS°	Standard entropy
RfC	Reference Concentration
RfD	Reference Dose
MIC	Minimum inhibitory concentration

Functionalized C,N-bipyrazole receptor grafted onto silica surface for Arsenic (As) adsorption and its anti bacterial activity

By Nagham Tahseen Mohammed Taha Supervisor Dr. Ahmad Abu Obaid Co-supervisor Dr. Motasem Al-Masri

Abstract

The ability of C,N- bipyrazole receptor grafted onto silica surface (SG2P) of adsorption arsenic (As) from aqueous solutions was studied. The effect of various parameter on the adsorption process was investigated. Such parameters included; PH, contact time, concentration of initial ions of arsenic in solution and dosage of adsorbent.

The results obtained indicated the percentage removal of arsenic decreased with the increase of As concentration and pH, while the percentage removal increased with the increase of contact time, adsorbent dose and temperature. The removal efficiency for As(III) adsorption could reach 60% after 24hour was achieved at pH around 3, and temperature 25°C, using 0.02g weight of dose, at initial concentration 10ppb for 10mL As(III) solution.

The studied parameter result on adsorption showed the optimal conditions for arsenic adsorption process were pH around 3 (acidic solution), 45° C, initial concentration of arsenic ions was at 10 ppb, the optimal time interval was 20 minutes, and the dosage of adsorbent had maximum adsorption capacity at 0.15g.

Two kinetics models were applied the adsorption process: pseudo-first order kinetic model and pseudo second order kinetic model. The results that adsorption process of arsenic harmonized pseudo second order model.

The adsorption capacity of SG2P was studied using Freundlich and Langmiur models at equilibrium to determine the behavior of adsorption process, both models result showed favorable adsorption process.

Thermodynamics parameters such standard enthalpy, standard entropy and standard free energy were calculated for SG2p adsorbent. The negative $\triangle G^{\circ}$ values indicate that the adsorption is spontaneous at these temperatures. The negative value of $\triangle H^{\circ}$ reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. In the other hand, the positive value of $\triangle S^{\circ}$ suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process.

The antibacterial activity of SG2P was determined against two bacterial references strains using micro- broth dilution method. The references strains were *Escherichia coli* (ATCC25922) and Staphylococcus *aureus* (ATCC25932). The SG2P possessed limited antibacterial activity, where it was able to inhibit growth only at high concentration (MIC =1.5625 mg per ml).

Chapter One

Introduction

Chapter One

Introduction

More than two thirds of earth's surface is covered by water; less than a third is taken up by land. As earth's population continues to increase, people are causing high pressure on the planet's water resources, also as we know that pollution is a human problem because it is a relatively recent development in the planet. As industrialization has spread around the globe, so the problem of pollution has spread with it. When Earth's population was much smaller, no one believed pollution would ever present a serious problem. It was once popularly believed that the oceans were far too big to pollute. Today, with around 7 billion people on the planet, it has become apparent that there are limits. Pollution is one of the signs that humans have exceeded those limits. seriousness of the problem can environmental organization appear according the campaign to WWF: "Pollution from toxic chemicals threatens life on this planet. Every ocean and every continent, from the tropics to the once-pristine polar regions, is contaminated [1].

Pollution is the process of making land, water, air or other parts of the environment dirty and unsafe or unsuitable to use. This can be done through the introduction of a contaminant into a natural environment. Toxic pollution affects more than 200 million people worldwide, according to Pure Earth, a non-profit environmental organization. In some of the world's worst polluted places, babies are born with birth defects, children have lost 30 to 40 IQ points, and life expectancy may be as low as 45 years because

of cancers and other diseases. Water pollution happens when chemicals or dangerous foreign substances are introduced to water, including chemicals, sewage, pesticides and fertilizers from agricultural runoff, or metals like lead or mercury [2].

The need to maintain a cleaner environment for the survival of both aquatic and terrestrial lives including human beings is very crucial and is a subject of increasing concern to the environmentalist. Pollution caused by agents such as heavy metals and dyes are amongst the list which rendered the environment unwholesome and posed serious health concern to the populace [3].

The environment is not something distant and separate from our lives. The environment is everything that surrounds us that gives us life and health. Destroying the environment ultimately reduces the quality of our own lives. As a result of that attention in the world is growing with respect to the idea of accumulation of heavy metals in the environment. Theses metals are considered as a threat to both human health and environment, especially when their tolerant levels are exceeded. This results from the fact that the heavy metals are not biodegradable over time, and accumulate in the environment. So there is an argent need for stopping heavy metals releasing in the environment. Heavy metals such as manganese, arsenic, lead and nickel can reach water mainly through industrial waste and landfill runoff.

1.1. Heavy metals

Heavy metals are naturally occurring elements that have a density at least 5 times greater than that of water[4].

Heavy metals enter the water system from various sources, as agriculture sources due to use of fertilizers and pesticides that reach the water bodies through runoff as well as to sewage effluent. Heavy metals are the most toxicological species found in industrial effluents due to painting ,constructing, etc... that leads to accumulate in living tissues by food chains, doubling the danger.

In this study arsenic (III) adsorption from contaminated water by SG2P as a novel adsorbent was investigated.

1.1.1. Arsenic

Arsenic (As) is naturally present at high levels in the groundwater of a number of countries. Arsenic is highly toxic in its inorganic form. Contaminated water used for drinking, food preparation and irrigation of food crops poses the greatest threat to public health from arsenic. Long-term exposure to arsenic from drinking-water and food can cause cancer and skin lesions. It has also been associated with developmental effects, cardiovascular disease neurotoxicity and diabetes [5]. The two forms of inorganic arsenic, arsenate As (V) and arsenite As(III), are easily taken up by the cells of the plant root. Once in the cell, As (V) and As(III) both disrupt plant metabolism, but through distinct mechanisms, in addition

to its effects on plants and living creatures in water, and as arsenic inorganic is the common form in the water. There is an argent need to try to reduce the arsenic in water to a normal levels. Arsenic is one of WHO's 10 chemicals of major public health concern. WHO's work to reduce arsenic exposure includes setting guideline values, the current recommended limit of arsenic in drinking-water is 10 μ g /litre, although this guideline value is designated as provisional because of measurement difficulties and the practical difficulties in removing arsenic from drinkingwater. Where it is difficult to achieve the guideline value, Member States may set higher values as standards taking into account local circumstances, resources and risks from low arsenic sources that are contaminated microbiologically [6].

1.2. Traditional techniques to remove heavy metals:

As heavy metal pollution has become one of the most serious environmental problems today. The treatment of heavy metals is of special concern due to their recalcitrance and persistence in the environment so many methods of treatment of heavy metals were extensively studied. These technologies include chemical precipitation, filtration, ion-exchange, flocculation and adsorption [7].

Although precipitation is the most common one, but it only reduces the dissolved metals concentration to solubility product level with for many exceed the discharge permit standards and thus leads to extra cleaning stages [8].

Ion exchange is another method used successfully in the industry for the removal of heavy metals from effluent. An ion exchanger is a solid capable of exchanging either cations or anions from the surrounding materials. Commonly used matrix for ion exchange are synthetic organic ion exchange resins. The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover, ion exchange is nonselective and is highly sensitive to the pH of the solution [9]. Flocculation techniques are dependent basically on the use of flocculants to clean wastewater, but they are expensive and produce sludge and saline effluent [10]. Filtration technique depends on the material of filtrate, the most common one is the charcoal that is used to remove organic contaminants from aqueous solution, the extensive use of it for metal removal from industrial effluents is expensive [11]. The last technique and the applicable one in this research is adsorption.

1.3. Adsorption

Adsorption (in language), is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption is a surfacebased process [12]. Adsorption is a fundamental process in the physicochemical treatment of municipal wastewaters, a treatment which can economically meet today's higher effluent standards and water reuse requirements. Also it considered as a broad spectrum of physical, biological, and chemical processes and operations in the environmental field. Purification of gases by adsorption has played a major role in air pollution control, and adsorption of dissolved impurities from solution has been widely employed for water purification. Adsorption is now viewed as a superior method for wastewater treatment and water reclamation [13]. In this research adsorption on new chemical adsorbent (C,N-bipyrazole with a 3-glycidoxyprpoyl-trimethoxyilane silylant agent) onto a silica surface in short(SG2P) was used.

1.4. Antibaterial resistance

Nowadays, antimicrobial resistance threatens the effective prevention and treatment of an ever-increasing range of infections caused by bacteria, parasites, viruses and fungi. Antimicrobial resistance is an increasingly serious threat to global public health that requires action across all government sectors and society. Without effective antibiotics, the success of major surgery and cancer chemotherapy would be compromised. The cost of health care for patients with resistant infections is higher than care for patients with non-resistant infections due to longer duration of illness, additional tests and use of more expensive drugs [14].

The continuous increase in antimicrobial resistance led to urgent need to find alternative materials possessing antibacterial activity to help in reducing the resistance of bacterial activity.

Micro Dilution methods are used to determine the minimum inhibitory concentrations (MICs) of antimicrobial agents and are the reference methods for antimicrobial susceptibility testing. In micro dilution tests, microorganisms are tested for their ability to produce visible growth in micro titration plate wells of broth (broth micro dilution) containing serial dilutions of the antimicrobial agents. The MIC is defined as the lowest concentration of an antimicrobial agent that inhibits the growth of a microorganism [15].

1.5. Novelty

A number of studies have indicated that various complexes are formed in the adsorption of arsenic. No previous studies worked at adsorption of arsenic by SG2P. Although the antibacterial activity of numerous materials against *Escherichia coli* (ATCC25922) and *Staphylococcus aureus* (ATCC25932) was studied ,there is no previous research about the antibacterial activity of SG2P in both mentioned bacteria.

This research studies the adsorption of arsenic by SG2P in various standards and the antimicrobial activity of SG2P.

1.6. Hypothesis

This study was related to the hypothesis that the silica surface containing functionalized groups (SG2P as the example) that able to adsorb certain amounts of the heavy metal from aqueous solutions and that any new chemical may have antibacterial activity.

1.7. Objectives

The objective of this research was to determine the ability of SG2P to remove arsenic from aqueous solution. This includes investigating the optimum conditions of SG2P such as pH, temperature, adsorption time, binding capacity, concentration of metal ions, and effect of other competing ions. The kinetics of the adsorption process, as well as, the adsorption isotherms that would be explored.

In the biological part, the objective was to find out if the studied SG2P material had any antibacterial activity against *Escherichia coli* (ATCC25922) and *Staphylococcus aureus* (ATCC25932).

1.8. Previous study

One study investigated the functionalized SIO₂ in adsorption of Hg⁺², Pb²⁺, Cu²⁺ and Zn²⁺ from aqueous solution. The results showed the maximum adsorption capacity of 25.07mg/g was assigned to Hg⁺², with the optimal contact time about 5 minute, whereas other metal ions are less well extracted (Pb²⁺ and Cu²⁺) or not extracted (Zn²⁺) [16].

Another study showed that various complexes are formed in the adsorption of As(V) on ferrihydrite, the result showed that the arsenic(V) is adsorbed to ferrihydrite as a strongly bonded inner-sphere complex with either monodentate or bidentate attachment. It has also been reported that monodentate attachment predominates near the optimal pH of 4 to 5 for adsorption [17]. One of the studies investigated the adsorption of arsenic (III) on ferrihydritehas at the optimal pH. In this case, adsorption occurs at pH of 8 to 9 [18].

Another study determined the adsorption of As (V), from aqueous solutions. The study was carried out on the adsorption of As (V) as a function of pH, contact time, initial concentration, and ionic strength. Maximum adsorption occurred at pH 3.0. The adsorption capacity did not change significantly with increasing ionic strength. A kinetics study revealed that adsorption of As (V) by the goethite/silica nano-composite was rapid: Equilibrium was reached within 120 min. Adsorption kinetics followed a pseudo-second-order kinetic model. The adsorption data were analyzed by both the Langmuir and Freundlich isotherm models. The maximum adsorption capacity of goethite/silica nanocomposite for As (V) from the Langmuir isotherm was 17.64 mg per ml [19].

In one of the previous studies, the paper investigated the antimicrobial properties of a novel silver-silica nanocomposite material, the results showed that the MICs of silver nitrate varied from 3.9 to 31.2 μ g/ml (corresponding to 2.4 to 19.8 μ g Ag/ml), and the MICs of silver zeolite ranged from 3.9 to 31.2 μ g/ml (corresponding to 2 to 12 μ g Ag/ml) [20].

Chapter Two

Methodology

Chapter Two

Methodology

2.1. Chemistry part

2.1.1. Preparation of arsenic(III)solution

 As_2O_3 (arsenic oxide: 197.841 g/mol) was used to prepare 1000ppm arsenic solution: about 0.222g of As_2O_3 was weighted and HCL drops were added until the amount was dissolved, then the solution was transfer to a 1000 ml flask. In separate flasks, concentrations were prepared, which where 10 ppb, 20ppb, 30ppb,40ppb and 60ppb.

2.1.2. Preparation of calibration curves

A fresh 50 ppm metal ion solution was prepared daily by successive dilution of the stock 1000 ppm solution. Then 10, 20, 30, 40 and 60 ppb solutions were prepared by diluting 3, 6, 9 and 12 mL, respectively from the 50 ppm standard solution into 100 mL volumetric flasks. Volumetric flasks were soaking in 0.1 M HNO₃ before used. The concentration of the metal ion was followed by measuring the absorbance of the solution by flame atomic absorption spectrometry (FAAS). A calibration curve of absorbance versus concentration was constructed at the time of analysis. Calibration coefficient (\mathbb{R}^2) was at least 0.983 for all analyses. Deionized water was aspirated into the instrument before and after the analysis of each sample to prevent interferences.



Figure 1: Linear calibration curve of absorbance vs. concentration for As (III) concentrations in the range 10-60 μ g/L.

2.1.3. Metal quantification

The amount of metal ions that was sorbed and the percent removal of metal ion by adsorbent were calculated by applying equations 1 and 2, respectively:

 $q = (Co - Cf) \div m . V (1)$

% $Removal = (Co - Cf) \div Co .100 (2)$

Where q is the amount of metal ion sorbed by the adsorbent (mg/g); C0 is the initial metal ion concentration; (mg/L), Cf is the final ion concentration (mg/L) after the chemo-sorption occurred, V is the volume of aqueous solution (L) in contact with the adsorbent, and m is the mass (g) of adsorbent.

13

2.1.4. Instrumentation

- 1. (ICE 3000 SERIES, Thermo Scientific) Flame atomic absorption spectrometer with acetylene-air flame was used for absorption measurements.
- 2. JENWAY (3510) pH Meter was used to measure pH.
- 3. (Centurion, Scientific Ltd) Centrifuge was used for separation.
- 4. Shaking water bath. Incubator (EN500, nüve).

2.1.5. Studied parameters

2.1.5.1. The temperature effect

The effect of temperature was investigated at different degrees, 25, 35, 45 and 55 °C. For each temperature, a 0.02 g adsorbent (SG2P) samples was added to 10 mL of As(III) solutions with concentration of 10 μ g/L at pH around 6. Each mixture was placed in shaking water bath (JLabtech) for 30 min. After that the adsorbent was separated by centrifuging at 600 rpm and supernatant was tested by flame atomic absorption for the residual concentration of As(III) at 193.7 nm wavelength.

2.1.5.2. Experiment (2) Effect of pH

Effect of initial pH on adsorption of As (III) onto SG2P was investigated in the pH range 1-12. The pH ranges were adjusted by either adding 0.1 M HCl or 0.1 M NaOH. For each test tube 0.02 g adsorbent samples were added to 10 mL of As(III) solutions with concentration of 10 μ g/L. The mixtures were placed in shaking water bath at constant temperature (25°C) for 30 min. At the end of time interval, the adsorbent was separated by centrifuging at 600 rpm and supernatant was analyzed by flame atomic absorption for the residual concentration of As (III) at 193.7 nm wavelength.

2.1.5.3. Experiment (3) Effect of initial concentration of As (III)

Solutions with concentrations of 10, 20, 30, 40 and 60 ppb were prepared from the stock solution to find out the optimum concentration. A weight of 0.02 g of adsorbent(SG2P) was added to a number of tubes contains 10 mL of the previous concentrations of As(III) solutions under optimized temperature (25°C) and pH 6 for 30 min, the absorbance of the solution above the solid residue was measured by flame atomic absorption at 193.7 nm.

2.1.5.4. Experiment (4) Effect of adsorbent dose

In order to find out the optimum adsorbent dose, 0.020, 0.040, 0.10, 0.15 g and of adsorbent(SG2P) were added to five tubes contains 10 mL of $10\mu g/L$ As(III) solution at pH 6. The mixtures were placed in shaking water bath at constant temperature (25°C) for 30 min. The absorbance of the solution above the solid residue was measured by flame atomic absorption at 193.7 nm for the residual concentration of As (III).

2.1.5.5. Experiment (5) Optimization of contact time

The binding time intervals studied were 5,15,40 and 180 minutes, for studying the time effect on adsorption, 0.02 g adsorbent (SG2P) samples

were added to 10 mL of As (III) solutions with concentration of 10 μ g/L at pH around 6. Each mixture was placed in Shaking Water Bath (JLabtech) at room temperature (25°C) for 30 min. At the end of each time interval, the adsorbent was separated by centrifuging at 600 rpm and supernatant was tested by Flame Atomic Absorption for the residual concentration of As (III) at 193.7 nm wavelength.

2.2. Biological part (antibacterial activity)

Micro-broth dilution method was used to determine antibacterial activity and minimum inhibitory concentrations (MIC) of SG2P against two bacterial reference strains. The reference bacterial stains were *Escherichia coli* (ATCC25922) and *Staphylococcus aureus* (ATCC25932). The included bacterial reference strains were obtained from American Type Culture Collection (ATCC).

2.2.1 Media preparation

A weight of 4.4g of Mueller Hinton II Broth (USA) was added to 200 ml of distilled water. The mixture was heated until the media was dissolved completely. Broth was pipetted in tubes, which were covered with cotton plugs and sterilized by an autoclave.

2.2.2 Adsorbent substance (SG2P) solution preparation

A 50% DMSO solution was prepared with distilled water. Adsorbent powder (0.01g) was dissolved in a 50% DMSO.

2.2.3 Bacterial suspension preparation

With a sterile loop fresh bacterial isolate (*Escherichia coli* or *Staphylococcus aureus*) was sub cultured into 5 ml Mueller Hinton II broth (MHB). The turbidity of bacterial suspension in MHB was adjusted to be equivalent to 0.5 McFarland standards (bacterial concentration is 1.5×10^8 CFU/ml). The solution was then diluted 1:3 with MHB to have 5×10^7 CFU/ml bacterial concentration.

2.2.4. Minimum inhibitory concentration procedure

Using a micropipette, 100 µl of Mueller Hinton broth (MHB) was pipetted into each well in a micro titer plate. Then 100 µl of adsorbent substances was transferred to first well and the contents were mixed. A volume of 100 µl of mixture was transferred to following well and mixed before transferring 100 µl to next well. This dilution was repeated until well number 11, from which 100 µl was discharged after mixing. Well number 11 was considered the negative control of bacterial growth, where as well number 12 contained only MHB and was considered as positive control of bacterial growth. This procedure was applied in the first four rows (A, B, C, D). In the other hand in the remains four rows (E, F, G, H), a serial dilution of 50% DMSO was prepared in parallel to detect antibacterial activity of DMSO. Then 1 μ l of bacterial suspension (5×10⁷ CFU/ ml) was transferred to each well except well number 11 (negative control of bacterial growth). Inoculated plates were incubated at 35 °C for 18 hours. Each substance was examined in duplicate. The lowest concentration of examined substance that inhibited visible bacterial growth was considered the MIC.

Chapter Three

Results and Discussion

Chapter Three

Results and Discussion

3.1. Effect of pH on arsenic (III) adsorption

The study of pH effects in the arsenic (III) adsorption is a significant parameter as it affects the charge of adsorbent surface, degree of ionization of metals ions and extent of dissociation of functional groups present on the active site of adsorbent [21]. At low pH the acidic solution (pH: 3 to 5) the adsorption showed the maximum adsorption at pH: 3 as the solutions contains protons that bind with electrons from oxygen, so the negative charge on the surface attract the positive ions of As, where at high pH in alkaline conditions the result showed is not favorable for arsenic sorption because carboxyl, hydroxyl, and amide groups of the adsorbent become negatively charged and a high density of OH- at alkaline conditions would compete with all anionic species of As(III) [22].

Different solutions of As (III) with different pH were used to study the effect of pH on the adsorption, the results shown in figure 2.



Figure 2: pH effect on As (III) adsorption ($C_o=10\mu g / L$, T=25°C, adsorbent dose= 0.02g).

3.2. Effect of temperature on As (III) adsorption

Temperature effect on As (III) adsorption was studied, at temperature 25°C-55°C the % of removal and temperature results are represented in figure 3.2, the % of removal of As(III) increases with increasing the temperature above the room temperature to a limit value, at 45°C the maximum adsorption 50% was achieved at the surface of modified silica compound (SG2P).



Figure 3: Effect of temperature on As(III) adsorption ($C_0=10$ mg / L, time=60min, adsorbent dose=0.02gm).

As expected, increasing temperature will results in increase in mobility of large metal ions, which indicates that the adsorption process is endothermic, leads to swelling effect within the internal structure of adsorbent that in turn, encourages the metal ions to penetrate further and increase in the kinetic energy of adsorbent particles that increase the collision between adsorbent and adsorbate molecules results in enhancing the removal of metals from adsorbent surface [23].

3.3. Effect of As (III) concentration

Figure (4) illustrates the effect of initial metal ions concentration on their removal by SG2P adsorbent. As can be seen, increasing the initial metal ion concentration decreases the percent of removal of the metal ions by SG2P adsorbent. At low concentration, most metal ions will occupy the available sites of adsorbent. As concentration of these ions increases, the sites will be filled until saturation, more ions have no empty sites to be occupied (removal is decreased).



Figure 4. Effect of As(III) concentration on adsorption .

This figure shows that at lower concentration the adsorption of As(III) was rapid, and as the concentration of As(III) the adsorption of its ions was decreased. This decrease in adsorption may be related to the increase of As(III) ions for affixed amount of (SG2P). At the beginning the removal of As(III) ions is high due to large surface area of adsorbent and when the saturation point is reached, at equilibrium the capacity of the (SG2P) to adsorb As(III) ions is controlled and the ions transported from the exterior to the interior sites of the (SG2P) particles [24].

By increasing the As(III) concentration from 10 ppb to 20 ppb all sites of the adsorbed occupied, then the adsorption becomes constant whatever the concentration increase in order to study the effect of As(III) concentration on the adsorption capacity [25].

3.4. Effect of contact time

Contact time is one of the most important parameters that must be taken into account for waste water treatment applications. The determination of the contact time of maximum adsorption of the As(III) on SG2P was made and the results shown in figure 5.



Figure 5: Effect of contact time to determine the time of maximum adsorption of As (III).

The rate of adsorption of As (III) on SG2P at the first 20 minutes was rapid and become insignificant after that, the increase in contact time has negligible effect on percentage removal of As(III), it may be due rapid accumulation of chromium ions at the surface of As(III) [26].

At the first few minutes the contact of As(III) ions and solid particles of the adsorbent is high, and the transfer onto the SG2P particle surface is faster, after 20 minutes the As(III) ions take more time to transfer to the internal adsorption sites through the pores. So the optimum time for the adsorption of As(III) on SG2P is 20 minutes.

3.5. Effect of the adsorbent dose

The effect of the dosage of adsorbent SG2P on the removal of As(III) was studied. Various doses (0.20 g to 0.15 g) were mixed with metal ion solutions, while keeping the temperature 25°C, pH=6, initial volume=10ml, and As(III) concentration= 10ppm for 24 hour on the shaker.

The results were represented as in Figure 6. The removal efficiency on As(III) increases with the increase of weight of adsorbent dose of SG2P up to 0.15 g, then removal efficiency showed a constant percent, this due to that all ions of arsenic attached on adsorbent surface at 0.15 g, so any more dose doesn't affect in removal.



Figure 6. Effect of dosage of adsorbent on the removal of As(III).

From the figure the removal efficiency at 0.15 g dose is high, this may be due to the greater availability of the exchange of the sites of the adsorbent. The optimum value of adsorption at 10 ppb of As(III) at pH=6, solution volume =10ml, is at 0.15 g SG2P.

3.6. Adsorption isotherm of As(III)

The process of removal of heavy metals from polluted aqueous solutions using chemical adsobents is a physic-chemical process with uncontrolled metabolic mechanism(s). Adsorption isotherms are used to explain the equilibrium of metal ions that occurs between the solid phase of adsorbent and the aqueous solution. These models might determine some kinetic and thermodynamic parameters that can give a clearer image about the binding mechanism. The more known non- linear models are Langmiur and Freundlich isotherms.

Langmiur model suggests that the uptake of metal ion is monolayer occurred on homogeneous surface with no different energies for all binding sites and no interactions between adsorbed molecules [27].

In the other hand Freundlich model also suggests a monolayer uptake of metal ion on a adsorbent. It differs from Langmiur in that it assumes that the distribution of energy of the active binding sites the affinities of binding sites of adsorbent to vary with these interactions; those with stronger affinities are occupied first [28].

3.6.1. Freundlich Adsorption Isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. This model is specified with the following equation [29]-[30]:

$$Q_e = K_F C_e^{1/n} \tag{3}$$

The linear form of this equation can be written as [31]-[32]:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{4}$$

Where K_F and nare Freundlich constants with K_F is an approximate indicator of adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption. If value of 1/n is below one it indicates a normal adsorption. If n lies between one and ten, this indicates a favorable sorption process [32] [33]. To determine the constants K_F and n, the linear form of the equation may be used to produce a graph of $\ln(Q_e)$ against $\ln(C_e)$ as shown in Figure 7:



Figure 7: Freundlich plot for As(III) adsorption on (SG2P).

Table 1: Parameters and correlation coefficient of Freundlich

Freundlich isotherm model Parameters					
Adsorbate	Parameters				
	$\frac{1}{n} \qquad n \qquad K_F = (mg/g) \qquad R^2$				
SG2P	0.59	1.6949	2.1	0.911	

isotherm model for adsorption of As(III) onto SG2P

From table 1 the values of n=1.6949 and 1 / n=0.59, as Freundlich isotherm model these values indicate that, the sorption of As(III) on SG2P is favorable and the R² value is 0.911.

3.6.2. Langmuir adsorption isotherm

This describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of MB dye between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation [33]-[34]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \tag{5}$$

Where:

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

 Q_e = the amount of As(III) adsorbed per gram of the adsorbent (mg/g)

 Q_m = maximum monolayer coverage capacity (mg/g)

 K_L = Langmuir isotherm constant (L/mg)

The values of Q_m and K_L were computed from the slope and intercept of the Langmuir plot of C_e/Q_e versus C_e . From Langmuir plots which is shown in Figure 8 amount adsorbed for monolayer formation (Q_m), Langmuir

adsorption-desorption equilibrium constant (K_L) and regression constant (R^2) were determined and values are shown in Table

The adsorption capacity of SG2P was estimated by applying Langmuir represented in the figure below:



Figure 8: Langmuir plot for As(III) adsorption on (SG2P).

Table	2:	Parameters	and	correlation	coefficient	of	Langmuir
-------	----	------------	-----	-------------	-------------	----	----------

Langmuir isotherm model parameters								
Adsorbate	Adsorbate Parameters							
	Qm(mg/g)	$Q_m(mg/g)$ $K_L=(L/mg)$ R_L R^2						
SG2P	SG2P 4.61 0.578 0.166 0.958							

isotherm model for adsorption of As(III) onto (SG2P)

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by the following equation [35]:

$$R_L = \frac{1}{(1+K_L C_o)} \tag{6}$$

Where C_o is the highest initial concentration of adsorbate (mg/L).

The value of R_L indicates the shape of the isotherm to be either unfavorable $(R_L > 1)$, linear $(R_L = 1)$, favorable $(0 < R_L < 1)$, or irreversible $(R_L = 0)$. The R_L values between 0 and 1 indicate favorable adsorption. The value of R_L in the present investigation was found to be 0.166 at 25 °C indicating that the adsorption of As(III) dye on (SG2P) is favorable [35] [36].

3.7. Rate order of the adsorption process

Uptake of each metal ion from different initial concentrations of the metal can be used to study the dependency of the rate of adsorption on the concentration of metal ion left in solution. Thus, the reaction order of the adsorption process can be determined.

Pseudo first- order equation was applied for evaluation the adsorption kinetics for As(III) onto SG2P, the rate constant for the adsorption K1was evaluated .

The pseudo first- order equation expressed as equation 4 :

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right)t$$
 (7)

Where Q_e is the adsorption capacity of the SG2P at equilibrium (mg/g), Q_t is the amount of As(III) adsorbed at time t (mg/g) and K₁ is the pseudo first order rate constant (min⁻¹).

A linear plot of $log(Q_e - Q_t)$ against time allows to obtain the rate constant (Figure: 9). If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to As(III) sorption on SG2P so the adsorption process is a pseudo first order process. The Lagergren's first order rate constant (K₁) and Q_e determined from the

model are presented in Table 3 along with the corresponding correlation coefficients. It was observed that the pseudo first order model did not fit well. It was found that the calculated Q_e values do not agree with the experimental Q_e value This suggests that the adsorption of As(III) does not follow first-order kinetics



Figure 9: Pseudo first- order adsorption kinetics of As(III) onto (SG2P).

From Figure 9, the R² value shows that the adsorption As(III) onto SG2P does not obey the pseudo first- order kinetics, and the pseudo first- order model is not appropriate for the adsorption.

The Lagergren pseudo first- order rate constant (K_1) and (q_e) values are

Table.	3:	Pseudo	first-	order	parameters	for	As(III)	adsorption
onto S	G2P	at 25°C						

Adsorbent	qe(exp)	pseudo first- order		
	(mg/g)	K1 qe (calculated)		R ²
		min^{-1}	(mg/g)	
SG2P	2.3	4.6×10 ⁻³	0.51	0.408

The pseudo second order kinetics may be expressed in a linear form as integrated second order rate law [34][37][38]:

$$\frac{t}{Q_t} = \frac{1}{Q_e} t + \frac{1}{K_2 Q_e^2}$$
(8)

Where K_2 is the pseudo second order rate constant (g mg⁻¹min⁻¹).

Pseudo second - order adsorption model for As(III) adsorption onto SG2P was applied and the rate constant for the adsorption K2 was evaluated as shown in figure 10.



Figure 10. Pseudo second order adsorption kinetics of As(III) onto (SG2P).

The results obtained shows that the value of linear regression coefficient R^2 is 0.999, the values of qe experimental, K2, R²and qe calculated as shown in Table 4.

Table 4: Pseudo second	- order parameters for	As(III) adsorption	onto
SCOD at 25°C			

SG2P at 25°C.

Adsorbent	qe (exp)	pseudo second – order				
	(mg/g)	K2 (min ⁻¹)	qe (calculated) (mg/g)	R²		
SG2P	2.3	171.1×10 ⁻³	2.1	0.999		

The results shows that the Pseudo second – order kinetic model perfect fit with experimental data and the value of R^2 = 0.999, by comparing (q_e) experimental and (q_e) calculated values from Table 4, there is agreement between experimental and calculated values for pseudo second order model, and K_2 value greater than K_1 value, so the pseudo second order model is favorable model for As(III) adsorption onto SG2P.

3.8. Adsorption Thermodynamics:

Adsorption thermodynamics were determined using the thermodynamic equilibrium coefficients obtained at different temperatures and concentrations in order to verify possible adsorption mechanisms. The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters such as ΔG (Gibbs free energy change), which can be calculated by Equation[33][37]:

$$\Delta G = -RT ln K_d \tag{9}$$

Where K_d is the thermodynamic equilibrium constant (L g⁻¹).

According to thermodynamics, the Gibbs free energy is the difference between the adsorption enthalpy (Δ H) and adsorption entropy (Δ S) multiplied by the temperature. In this manner, by applying this concept to Equation (9), the thermo chemical parameters Δ H and Δ S can be determined using Van't Hoff's plot (Figure 11), according to Equation (10)[39]:

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{10}$$



Figure11: Plot of lnK_d versus 1/T for As(III) adsorption on (SG2P).

 $\triangle H^{\circ}$ and $\triangle S^{\circ}$ were calculated from the slope and intercept of the linear plot of lnK_d versus 1/T respectively. The results show that the enthalpy of adsorption $\triangle H^{\circ}$ was -3.7886 kJ mol⁻¹ and $\triangle S^{\circ}$ was 9.9 J mol⁻¹ K⁻¹. $\triangle G^{\circ}$ was calculated at different temperatures from the following equation [40]:

$$\Delta G^o = \Delta H^o - T \Delta S^o$$

The obtained thermodynamic values are given in Table 5.

 Table 5: The values of the thermodynamic of As(III) adsorption at

 various temperatures.

Adsorbent	ΔH^{o} (KJ/mol)	∆S° (J/mol.K)	△G ^o (KJ/mol)						
			289 K	308 K	318 K	328 K			
SG2P	-3.7886	9.9	-6.6	-6.8	-6.9	-7.0			

The negative $\triangle G^{\circ}$ values indicate that the adsorption is spontaneous at these temperatures. The negative value of $\triangle H^{\circ}$ reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. In the other hand, the positive value of ΔS° suggests that some structural

33

changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process.

3.9. Antibacterial activity of SG2P

The results of the minimum inhibitory concentration of micro dilution tray of the examined microorganism is shown in the Figure 12 and table 6 below.



Figure 12: The inhibitory activity of SG2P against *E. coli* and *S. aureus*.

A: Bacterial growth inhibition in broth micro dilution tray.

Table 6: Demonstration of bacterial growth and inhibition of growth

by SG2P in each well. (Abbreviation: -, no visible bacterial growth; +,

substance		1	2	3	4	5	6	7	8	9	10	11	12
<i>S.aureus</i> +25mg/	А	-	-	-	-	+	+	+	+	+	+	-	+
ml of SG2P													
<i>S.aureus</i> +25mg/	В	-	-	-	-	+	+	+	+	+	+	-	+
ml of SG2P													
<i>E.coli</i> +25mg/ml	С	-	-	-	-	+	+	+	+	+	+	-	+
of SG2P													
<i>E.coli</i> +25mg/ml	D	-	-	-	-	+	+	+	+	+	+	-	+
of SG2P													
S.aureus	E	-	-	+	+	+	+	+	+	+	+	-	+
S.aureus	F	-	-	+	+	+	+	+	+	+	+	-	+
E.coli	G	-	-	+	+	+	+	+	+	+	+	-	+
E.coli	Н	-	_	+	+	+	+	+	+	+	+	-	+

visible bacterial growth).

As shown in Figure 12, wells in column number 1, 2, 11 and part of 3 and 4 possessed clear broth indicating absence of bacterial growth (growth inhibition) or inoculation (well 11). On the other hand, wells with turbid broth indicated growth of bacteria du considered as to absence of inhibition or SG2P as in positive control of bacterial growth (well 12).

To well number 1 in the first four rows (A, B, C, D), 100 μ l of 25 mg/ml adsorbent (SG2P) dissolved in 50% DMSO was add, thus this well contained 12.5% of adsorbent (SG2P). This was further serially diluted as described in materials and method section.

On the other hand, to the first well (number 1) in the remaining four rows (E, F, G, H) 100 μ l of 50% DMSO was added and a serial dilution of DMSO was prepared to detect antibacterial activity of DMSO and to ensure that the bacterial growth inhibition was due to SG2P and not DMSO.

The results shown in Figure 12, indicate that the inhibition of both of *E. coli* and *S. aureus* growth occurred in the first four wells containing SG2P concentrations of 12.5, 6.25, 3.125 and 1.5625 mg/ml), so the minimum inhibition concentration of SG2P was 1.5625 mg/ml. On the other hand, DMSO inhibited growth of *E. coli* and *S. aureus* in the first two wells (25% and 12.5%) and did not show any antibacterial activity in wells number 3 and 4 in which SG2P showed antibacterial activity. These results indicated that SG2P possessed antibacterial activity against examined bacteria.

Conclusions:

The adsorption of as (III) onto SG2P was successfully tested for removing as (III) from the aqueous solution. SG2P is considered as a good alternative in removal of heavy metals from contaminated solution, it is a promising method for waste management and environmental treatment.

Studied adsorption parameters as pH, initial concentration of metal ions, temperature and contact time have an effect on the removal of As(III) by SG2P.

The percent removal of as (III) ions by SG2P could reach 60% at specific conditions. The suitable conditions for adsorption were pH 3.0, initial concentration of 10 μ g/L, temperature of 45°C and contact time 20 minutes.

In the adsorption models that were applied Freundlich model parameters value 1/n and n, also Langmuir models parameter both were showing that the adsorption of As (III) onto SG2P is favorable.

In the other hand through studying kinetics models pseudo second order and pseudo first order, the results showed fitting with pseudo second order in adsorption process of arsenic by SG2P.

SG2P has a low antibacterial activity against both *Staphylococcus aureus*, *Escherichia coli*.

This study is suggest to use silica gel compound in arsenic adsorption in wastewater, more studies are needed to explain the adsorption of toxic heavy metals onto silica gel compounds, also further studies of antibacterial activity of this silica gel compound (SG2P) are needed.

References

- [1] Sathiadas, M.G., Mubarak, F.N and Arulmoli, S.K, Clinical manifestations and microbiology of Shigella diarrhoea in children. 2016; 6 (2):94-100.
- [2] Bradford, A., *Pollution Facts & Types of Pollution*, Live Science Contributor, 2015; 1-12.
- [3] Rashed, M., Low cost adsorbents for the removal of organic pollutants from wastewater. Journal of Environmental Management. 2012;113(5):170-183.
- [4] Graeme, K., Pollack C. *Heavy metal toxicity*, Part I: Lead and metal fume fever. Journal of Emergency Medicine. 1998; 16(2): 171-177.
- [5] Quansah R, Armah FA, Essumang DK, Luginaah I, Clarke E, Marfoh K, et al. WHO media centre. *Environ Health Perspect*. 2015;123(5):412-21.
- [6] Flanagan, SV., Johnston, RB., Zheng, Y., *Bull World Health Organ*.2012; 90(3):839-846.
- [7] Hu, J., Chen, C.L., Zhu, X.X., Wang, X.K., Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes. J. Hazard. Mater. 2009;162: 1542-1550.
- [8] Gardea-Torresdey, L., Rosa, G., and Peralta, J. R., Use of phytofiltration technologies in the removal of heavy metals: A review". Pure Appl. Chem;2004 76(4): 801–813.
- [9] Barakat, M., New trends in removing heavy metals from industrial wastewater. science direct. 2011; 4(4): 361–377.

- [10] Semerjian, L., Ayoub, G.M., Advances in Environmental Research, 2003; 7(2), 389-403.
- [11] Lima, I.M., Wartelle, L.H., Marshall, W.E., Preprints of Extended Abstracts presents at the ACS National Meeting, American Chemical Society, Division of Environmental Chemistry, 2002; 42(2):112-116.
- [12] Glossary of atmospheric chemistry terms. Pure and Applied Chemistry. 1990; 62(11): 2167-2219.
- [13] Walter J. and Weber JR, Adsorption Processes, The University of Michigan, College of Engineering, Ann Arbor, Michigan 48104, USA. 1974; 37(3):375-392.
- [14] Media centre. WHO. Antimicrobial resistance; 2016; available on: http://www.who.int/mediacentre/factsheets/fs194/en/.
- [15] James. H., Jorgensen, 1., Mary, J., *clinical infectious decease*, 2009;
 49(11):1749-1755.
- [16] Attinti, R., Sarkar, D., Barrett, K.R. et al. Int. J., Adsorption of arsenic(V) from aqueous solutions by goethite/silica nanocomposite, 2015, 12(12), 3905–3914.
- [17] Robert G. Robins. *Removal of Arsenic from Drinking Water by Precipitation, Adsorption or Cementation,* 1999; 47(4): 474-480.
- [18] Tiwari, S., Pandey, v., Removal of arsenic from drinking water by precipitation and adsorption or cementation: An environmental prospective, 2013, 5(5): 88-91.

- [19] Attinti, R., Sarkar, D., Barrett, K.R., Adsorption of arsenic(V) from aqueous solutions by goethite/silica nanocomposite, 2015, 12(12), 3905–3914.
- [20] Egger, S., Rainer, P., Lehmann, J., Martin, J., and Markus Schuppler., Antimicrobial Properties of a Novel Silver-Silica Nanocomposite Material, 2009 May; 75(9): 2973–2976.
- [21] Nandi, B.K., Goswami, A., Purkait, M.K., "adsorption characteristics of brilliant green dye on kaolin", Journal of Hazardous Materials, 2009; 161(1):387-395.
- [22] Khan, T., Chaudhry, S., Ali, I.," Mercapto functionalized silica entrapped polyacrylamide hydrogel: Arsenic adsorption behaviour from aqueous solution". 2015; 45(6):241-5.
- [23] Guo, S., Li, W., Zhang, L., Peng, J., Xia, H., Zhang, S. Kinetic and equilibrium adsorption study of lead (II) onto the low cost adsorbent-Eupatorium adenophorum spreng, Process Safety and Environmental Protection, 2009; 87 (5): 343-351.
- [24] Maher, FathiAqra, SafaShahin and AwniKhatib, *Monitoring chromium content in tannery waste water*, The Journal of the Argentine Chemical Society. 2009; 97 (2):77-87.
- [25] Mulani, J., Daniels, S., Rajdeo, K., Tambe, S., Chava, N., Adsorption of Chromium(VI) from Aqueous Solutions by Coffee Polyphenol-Formaldehyde/Acetaldehyde Resins, 2010; 43(3):106-116.
- [26] Kubilay, S., Gürkan, R., Savran, A., Sahan, T., Removal of Cu(II), Zn(II) and Co(II) ions from aqueous solutions by adsorption onto natural bentonite, 2007; 13: 41–51.

- [27] Yao, Shuhua; Liu, Ziru; Shi, Zhongliang. Arsenic removal from aqueous solutions by adsorption onto iron oxide/activated carbon magnetic composite, 2014, 12(58), 1-7.
- [28] Amarah, J., Removal of Methylene Blue from Industrial Wastewater in Palestine Using Polysiloxane Surface Modified with Bipyrazolic Tripodal Receptor, An-Najah National University, Nablus Palestine. 2015; 1-103.
- [29] Solomon, G., Anagho, F., Equilibrium, kinetic and thermodynamic studies of phosphoric acidadsorption onto activated carbon, Pelagia Research Library, Der Chemica Sinica, 2013, 4(3):58-68.
- [30] Dada, A.O., Langmuir, Freundlich, Temkin and Dubinin– Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk, IOSR Journal of Applied Chemistry, 2012; 3(1):38-45.
- [31] Mehdi R., Mehdi V., Langmuir, Freundlich and Temkin Adsorption Isotherms of Propranolol on Multi-Wall CarbonNanotube, Journal of modern drug discovery and drug delivery research, 2014; 4(4): 933-937.
- [32] Ghiaci M., Abbaspur A., Kia R., Seyedeyn-Azad F., Equilibrium isotherm studies for the sorption of benzene, toluene, and phenol onto organo-zeolites and as-synthesized MCM-41, Separation and Purification Technology J., 2004; 40 (3): 217–229.
- [33] Hameed, B., Equilibrium modeling and kinetic studies on the adsorption of basic dye by a low-cost adsorbent: Coconut (Cocos

nucifera) *bunch waste*, Journal of Hazardous Materials 158 (2008) 65–72.

- [34] Umoren, S., Adsorption of methylene blue from industrial effluent using poly (vinyl alcohol), J. Mater. Environ. Sci. 4 (1) (2013) 75-86.
- [35] Shahryari, Z., Experimental study of methylene blue adsorption from aqueous solutions onto carbon nano tubes, International Journal of Water Resources and Environmental Engineering, 2010; 2 (2):016-028.
- [36] Patil,S., Removal of methylene blue, a basic dye from aqueous solutions by adsorption using teak tree (Tectona grandis) bark powder, International Journal of Environmental Sciences, 2011; 1(5): 711-726.
- [37] Abd El-Latif, M., Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite, Journal of American Science 2010; 6(6):267-283.
- [38] Antony, J., Xavier, N., Equilibrium and kinetic studies of Methylene blue onto activated carbon prepared form Crescentia cujete fruit shell, Nature and Science J, 2013;11(4):53-58.
- [39] Bolis, V., Busco, C., Ugliengo, P., Thermodynamic study of water adsorption in high-silica zeolites. J. Phys. Chem. B. 2006; 110(30), 14849–14859.

[40] Abramian, L., El-Rassy, H., Adsorption kinetics and thermodynamics of azo-dye Orange II onto highlyporous titania aerogel, Chemical Engineering Journal, 2009; 403–410.

جامعة النجاح الوطنية كلية الدراسات العليا

استخدام مستقبلات الكربون والنيتروجين المطعمة على سطح السيليكا في عملية إزالة الزرنيخ ونشاطها المضاد للبكتيريا

إعداد نغم تحسين محمد طه

إشراف د . احمد أبو عبيد د. معتصم المصري

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في العلوم البيئية من كلية الدراسات العليا في جامعة النجاح الوطنية – نابلس – فلسطين استخدام مستقبلات الكربون والنيتروجين المطعمة على سطح السيليكا في عملية إزالة الزرنيخ ونشاطها المضاد للبكتيريا إعداد نغم تحسين محمد طه إشراف د . احمد أبو عبيد د. معتصم المصري

الملخص

في هذا البحث تم دراسة إزالة عنصر الزرنيخ بواسطة قدرة مستقبلات الكربون والنيتروجين المطعمة على سطح السيليكا على نطاق واسع مع تأثير كل من درجة الحموضة، درجة الحرارة، التركيز البدائي للزرنيخ، وكمية المادة المستخدمة في الإزالة وفترة الاتصال بين المادة التي تقوم بالإزالة والمادة المراد إزالتها.

أظهرت النتائج أن نسبة الإزالة لايونات الزرنيخ تقل مع زيادة كل من تركيز الزرنيخ في المحلول ودرجة الحموضة، بينما تزداد النسبة مع زيادة فترة الاتصال، كمية المادة المستخدمة في الإزالة ودرجة الحرارة حيث أشارت النتائج إلى أن فعالية إزالة الزرنيخ الثلاثي وصلت 60%، وذلك على درجة حموضة منخفضة (3)، درجة حرارة 25 درجة حرارة مئوية، وتركيز 10 (جزء من البليون) لكمية 10 مل في حين كانت كمية المادة المستخدمة في الإزالة20. غرام. وعند دراسة الظروف الأمثل لعميلة الإزالة كانت على تركيز 10 (جزء من البليون)، ودرجة حموضة منخفضة (3)، وكمية المادة المستخدمة في الإزالة 20 دقيقة وعلى درجة حرارة مرتفعة 45 درجة مئوية.

لوصف معدل عملية الإزالة وعلاقتها بالتركيز تم دراسة نموذجين التفاعلات من الدرجة الأولى والتفاعلات من الدرجة الثانية، ومع مقارنة النتائج ظهر بان عملية الإزالة لزرنيخ الذي تبع تفاعلات الدرجة الثانية.

من جهة مدى القدرة على الإزالة لسطوح السيلكا المطعمة تم دراستها بإتباع كل من نماذج فرندلخ ولانجمير اللذان اظهرا عملية إزالة مفضلة على النموذجين المستخدمين. حسب معاملات الديناميكا الحرارية التي تم تطبيقها مثل المحتوى الحراري القياسي الطاقة الحرة القياسية والقصور الحراري. حيث الإشارة السالبة للطاقة الحرة الحرارية دلت على كون عملية الإزالة تلقائية، في حين دلت الإشارة السالبة للطاقة الحرة القياسية على أن التفاعل طارد للحرارة بالإضافة إلى أن تغييرات شكلية قد حدثت لجزئيات الممتص أثناء العملية ظهرت من خلال الإشارة الموجبة للقصور الحراري.

تم تحديد النشاط البكتيري لمركب السيلكا على نوعين من البكتيريا، نوعان البكتيريا التي تم دراستهما Escherichia coli (ATCC25922) and Staphylococcus aureus (ATCC25932) حيث اظهرت النتائج وجود اثر لهذه المادة من خلال قدرتها على تثبيط نمو الأنواع المدروسة، وكانت اقل كمية مثبطة لنمو البكتيريا 1.5625 مل غرام لكل مل لتر.