An-Najah National University Faculty of Graduate Studies

# Removal of Methylene Blue from Industrial Wastewater in Palestine Using Polysiloxane Surface Modified with Bipyrazolic Tripodal Receptor

By

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## Dedication

Every challenging work needs self-efforts as well as encouragements of others especially those who are very close to our heart.

To my father, Brother Mohammed and my dear family whose love and encouragement make me able to get success and honor. My great mother (Allah mercy her soul) who sacrificed for our sake.

To all of them I dedicate my modest efforts.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

# Removal of Methylene Blue from Industrial Wastewater in Palestine Using Polysiloxane Surface Modified with Bipyrazolic Tripodal Receptor

أقر بأن ما اشتملت عليه هذه الرسالة إنما هي نتاج جهدي الخاص, باستثناء ما تمت الإشارة إليه حيثما ورد, وأن هذه الرسالة ككل, أو أي جزء منها لم يُقدم لنيل أية درجة أو لقب علمي أو بحثى 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.

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## List of Abbreviation

Symbol	Abbreviation	
А	the Temkin isotherm constant (L/g)	
A°	Angstrom = $1.0 \times 10^{-10}$ meters	
A <sub>o</sub>	absorbance of methylene blue in the sample solution before treatment	
Abs.	Absorbance	
A <sub>e</sub>	Absorbance of methylene blue in the sample solution after treatment	
ARIJ	Applied Research Institute Jerusalem	
В	Dimensionless Temkin constant	
b	Temkin constant related to heat of sorption (J/mol)	
BOD	Biological Oxygen Demand	
COD	Chemical oxygen demand	
Co	Concentration of methylene blue in the sample solution before treatment (mg/L)	
C <sub>e</sub>	Concentration of methylene blue in the sample solution after treatment (mg/L) at equilibrium	
C <sub>i</sub>	Initial concentration of methylene blue in the sample solution (mg/L)	
DMSO	Dimethylsulfoxide	
DSC	Differential scanning calorimetry	
ε	Absorptivity (extinction coefficient)	
EQA	European Quality Assurance	
FT-IR	Fourier Transform Infrared	
G <sup>(-)</sup>	Gram-negative bacteria	
G <sup>(+)</sup>	Gram-positive bacteria	
IQ	Intelligence Quotient	
K <sub>1</sub>	The Lagergren's first order rate constant	
K <sub>2</sub>	The pseudo second order rate constant	
K <sub>d</sub>	The distribution coefficient	
K <sub>F</sub>	Freundlich constant which is an approximate indicator of adsorption capacity of the sorbent $(mg/g (L/mg)^{1/n})$	
K <sub>L</sub>	Langmuir isotherm constant (L/mg)	

MAC	Minimum alveolar concentration	
LD50	Lethal Dose which causes the death of 50% (one half	
LD30	of a group of test.	
MAO-A	Monoamine oxidase A	
MAOI	Monoamine oxidase inhibitors	
MB	Methylene Blue	
m <sub>sed</sub>	Mass of adsorbent dose	
n	Dimensionless Freundlich constant giving an indication of how favorable the adsorption process	
OPT	Occupied Palestinian territories	
PCBS	Palestinian Central Bureau of Statistics	
Qe	The amount of MB dye adsorbed per gram of the adsorbent $(mg/g)$	
$Q_{m}$	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)	
$\mathbb{R}^2$	Correlation coefficient (regression coefficient)	
$R_{\rm L}$	Dimensionless constant separation factor	
SEM	Scanning Electron Microscope	
Si-C <sub>3</sub> H <sub>6</sub> NH <sub>2</sub>	3-aminopropyl-functionlized silica gel	
Si-C <sub>3</sub> H <sub>6</sub> NPz <sub>2</sub>	N,N-bis (3,5-Dimethylpyrazol-1-yl methyl)-3- aminopropyl Polysiloxane	
SPE	Solid Phase Extraction	
Si(OEt)4	Tetraethoxysilane	
SVR	Systemic Vascular Resistance	
t	Time	
Т	The absolute temperature (°K)	
TGA	Thermal gravimetric analysis	
V	Volume of solution	
$\Delta { m G}^{\circ}$	Standard free Gibbs energy	
$\Delta \mathrm{H}^{\circ}$	Standard enthalpy	
$\Delta S^{\circ}$	Standard entropy	

#### Removal of Methylene Blue from Industrial Wastewater in Palestine Using Polysiloxane Surface Modified with Bipyrazolic Tripodal Receptor By Jamal Omar Mohamad Amarah Supervisor Prof. Shehdeh Jodeh

#### Abstract

Different pollutants from industries leach every day to soil and ground waters without treatment. This will lead to different health problems to both human beings and animals. The major problem here is to detect the concentration of one of the pollutants like methylene blue and try to remove it by adsorption.

The product N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-3-aminopropyl Polysiloxane (Si- $C_3H_6NPz_2$ ) was successfully prepared. Fourier Transform Infrared (FT-IR) results confirmed that the Dimethylpyrazole units have been immobilized onto the surface of the modified silica gel. Scanning Electron Microscope (SEM) images of the Modified Polysiloxane surface showed rough and porous nature, indicating that the materials present good characteristics to use as an adsorbent. The adsorption experiments were conducted for a wide range of pH, adsorbent dosage, temperature, initial concentration and contact time. It was observed that the percentage removal of Methylene blue (MB) dye decreased with an increase initial concentration and temperature while it increased with increase in solution pH, contact time and adsorbent dose. Over 70% removal efficiency of MB

dye was achieved after 180 min, at solution pH around 10 and 20°C temperature using 0.25 g weight of dose and initial concentration of 15 mg/L of 50 mL MB dye solution.

The sorption of MB dye on the  $(Si-C_3H_6NPz_2)$  was optimized under alkaline conditions and temperatures around room temperature. MB sorption using  $(Si-C_3H_6NPz_2)$  can be described using pseudo second order and Temkin isotherm model. Based on the results, the  $(Si-C_3H_6NPz_2)$  is able to remove MB rapidly within 15 min with high removal efficiency.

The values amount of MB dye adsorbed per unit mass of (Si- $C_3H_6NPz_2$ ) that obtained by Lagergren pseudo second order model,  $Q_e(calc.)$  was in consistent with the experimental value,  $Q_e(exp.)$  indicates that the chemisorption might be the rate limiting step where valence forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate. Adsorption behavior of Si- $C_3H_6NPz_2$  is described by Temkin isotherm, and the results indicate monolayer type exothermic adsorption process involved in the system.

The Langmuir maximum adsorption capacity  $Q_m$  is 11.09 mg/g, at 15°C, and pH 11.83 and 0.04 weight of adsorbent dose. The  $R_L$  value (0.138 at 15 °C) indicates that the adsorption of MB dye on (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favorable. From Freundlich isotherm model parameters, value of 1/n = 0.6041 while n=1.66 indicating that the sorption of MB dye on (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favorable.

The negative  $\Delta G^{\circ}$  values (-17.17 to -17.25 KJ/mol) indicate that the adsorption is favorable and spontaneous at these temperatures. The negative value of  $\Delta H^{\circ}$  (-16.66 KJ/mol) reflects an exothermic adsorption and indicates that the adsorption is favored at temperature 15°C. The value of  $\Delta H^{\circ}$  was higher than those corresponding to physical adsorption. This would suggest that the adsorption process is chemical in nature. The small positive value of  $\Delta S^{\circ}$  (+1.78 J/mol.K) suggests that some structural changes occur on the adsorption and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process.

## **Chapter One**

### Introduction

#### **1.1 Overview**

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 pollutants 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 [1].

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 [2].

Industrial effluents are one of the major causes of environmental pollution because effluents discharged from dyeing industries are highly colored with a large amount of suspended organic solid. Untreated disposal of this colored water into the receiving water body either causes damage to aquatic life or to human beings by mutagenic and carcinogenic effect. As a matter of fact, the discharge of such effluents is worrying for both toxicological and environmental reasons. Conventional wastewater treatment methods for removing dyes including physicochemical, chemical and biological methods, such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques, and fungal decolorization. Among these methods adsorption has gained favor in recent years due to proven efficiency in the removal of pollutants from effluents to stable forms for the above treatment methods [3].

Water pollution due to color dyestuff industrial waste becomes a major concern worldwide. Many industries including leather and textile industries use dyes extensively in different unit operation. There are more than 100,000 commercially available dye and more than  $7x10^5$  tons per year are produced annually. Wastewater containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to biological degradation and are stable to light. There are different methods for the removal of textile effluents [4].

Many dyes are widely used in different industries, such as textile, paper, rubber, plastics, leather, food and pharmaceutical. These industries release colored wastewater which may present an ecotoxic hazard and introduce the potential danger of bioaccumulation, which affect the human food chain. Wastewater containing small amounts of dyes can affect the aquatic life because of its toxicity and resistance to breakdown with time. Most of the dyes are toxic and carcinogenic, causing allergy, skin irritation. Chemical, physical and biological methods were used for removing dyes from wastewater. Adsorption is an effective and low-cost physical and chemical method for removing dyes from wastewater [5].

The wastewaters discharged from dying processes exhibit high Biological Oxygen Demand (BOD), high Chemical Oxygen Demand (COD) are highly colored, hot, alkaline and contain high amounts of dissolved solids. The disposal of colored wastes such as dyes and pigments into receiving waters damages the environment, as they are carcinogenic and toxic to humans and aquatic life. Besides the matters of color, some dye imparts non-visibility and can be modified biologically to toxic or carcinogenic compounds. Nowadays concern has increased about the longterm toxic effect of water bodies containing these dissolved pollutants. The wastewaters discharge from textile industries includes residual dyes; these dyes are not bio-degradable therefore they may cause water pollution and serious threat to the environment. Methylene blue dye is a basic aniline dye,  $C_{16}H_{18}N_3SCl$  that forms a deep blue solution when dissolved in water. Methylene blue is utilized in coloring paper, temporary hair coloring, dyeing cotton and wools, and coloring of paper stocks. Methylene blue is a dark green powder or crystalline solid. It is widely used as a stain and has a number of biological uses. It dissociates in aqueous solution in the same way that electrolytes dissociate into methylene blue cation and the chloride

ion. The removal of methylene blue from any wastewater is of utmost importance due to the serious environmental damage that can occur as a result of contact with it, particularly in the case of people [6].

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. Adsorption is integral to 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 [7].

Recently Solid Phase Extraction (SPE) technique using organic modified Polysiloxane has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes. The SPE has several major advantages that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) the ability to combine with different modern detection techniques. Chemically modified Polysiloxane is one of the most successful adsorbents, because this inorganic polymer support does not swell or shrink like the organic polymeric resin. The modified Polysiloxane may be employed in aqueous and organic solvents media; they present good thermal stability and appropriate accessibility of ions to the adsorbent groups; in addition the organofunctionalized Polysiloxane exhibits higher sorption capacities than polymeric resins, because the number of organic molecules immobilized on the support surface is large, allowing thus more removal of ions from aqueous solution. These systems can be operated indefinitely without loss of the expensive organic molecules. Their potential applications are due essentially to the nature of the grafted ligands. A new silica gel compound modified N,N-bis(3,5-dimethylpyrazol-1-ylmethyl) amine (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) will be synthesized and characterized. The new product exhibits good chemical and thermal stability [8].

The aim of this study is to remove methylene blue dye from wastewater, using this new prepared material as an adsorbent for the solidphase extraction of MB. The adsorption behaviors of the new surface with methylene blue dye will be studied. The effect of pH, temperature, and amount of adsorbent, concentration and the contact time on the adsorption of MB will be studied. The adsorption capacity will be investigated using kinetics and pH effects. Equilibrium Isotherm studies will be done by varying the following three parameters: initial concentration of Methylene blue dye solution, volume of the dye solution, and adsorbent dose on the uptake of dye from the solution.

#### **1.2 Objectives of this work**

#### **1.2.1 General Objectives**

- 1. To remove methylene blue dye from industrial wastewater, using this new prepared material as an adsorbent for the solid-phase extraction of MB.
- 2. To identify the optimal conditions for the adsorption.

#### **1.2.2 Specific objectives**

- 1. To study the adsorption behaviors of the new surface with methylene blue dye.
- 2. To determine if (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) can be used to clean up MB polluted wastewater.
- 3. To determine the extent that new silica gel compound modified can tolerate and adsorb MB.
- 4. To specify the margin of methylene blue dye that exists in industrial wastewater in Palestine.
- 5. To study the effect of pH, temperature, amount of adsorbent, concentration and contact time on the adsorption of MB.

Beside the major objective of removal methylene blue from industrial wastewater; other objectives will be like screening the wastewater of other pollutants and this will give an idea to different ministries in Palestine like ministries of health, agriculture and water to put some guidelines and restrictions on those industries.

#### 1.2.3 Research question and identified problems

The main questions addressed in this thesis are:

- 1. Can  $(Si-C_3H_6NPz_2)$  be used to clean up MB polluted wastewater?
- 2. To which extent that  $(Si-C_3H_6NPz_2)$  can tolerate and adsorb MB?
- 3. What are the optimum condition of pH, temperature, amount of adsorbent, concentration, and contact time for (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) to adsorb MB efficiently?

## **Chapter Two**

### **Background and Literature review**

### 2.1 Methylene Blue Dye

#### 2.1.1 Structure and Properties

Methylene Blue is a heterocyclic aromatic compound with molecular formula  $C_{16}H_{18}CIN_3S$  as shown in Figure 2.1, with IUPAC name **3**,7*bis(Dimethylamino)-phenothiazin-5-ium chloride*. Methylene blue (MB) is a cationic thiazine dye that is deep blue in the oxidized state while it is colorless in its reduced form leucomethylene blue [9]. MB and leucomethylene blue exist as a redox couple in equilibrium and together form a reversible oxidation-reduction system or electron donor-acceptor couple as shown in Figure 2.2 [10].



Figure 2.1: Molecular structure scheme of the methylene blue.

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Leucomethylene blue

Figure 2.2: A reversible oxidation-reduction system of methylene blue and leucomethylene blue.

Chemical and Physical Properties of Methylene Blue is summarized in

Table 2.1 [11].

 Table 2.1: Physical and chemical properties of MB dye

Physical and chemical properties	Values
Melting temperature	180°C
Boiling temperature	No data (Decomposes)
Solubility in water	35.5 g/L
pH value	3 (10 g/L H <sub>2</sub> O)
Molecular weight	319.09 g/mol
Color	Dark blue-green in oxidized
	form, colorless in reduced form
	(Leucomethylene blue)
Chemical formula	$C_{16}H_{18}N_3ClS$

#### 2.1.2 Uses of methylene blue

#### 2.1.2.1 Industrial uses of methylene blue

Various types of dye, various cationic dyes, including methylene blue, are used in dye, paint production and wool dyeing. Methylene blue is also used in microbiology, surgery, and diagnostic and as a sensitizer in photo-oxidation of organic pollutants [12]. Many dyes are widely used in different industries, such as textile, paper, rubber, plastics, leather, food and pharmaceutical [5][6].

#### 2.1.2.2 Medical uses of methylene blue

Methylene blue finds its major utilization in toxicology in the treatment of methemoglobinemia at a dose of 1 to 2 mg/kg intravenously. Methylene blue has several notable uses in clinical medicine. Examples include use as a bacteriostatic genitourinary antiseptic, herpes simplex, use in combination with vitamin C for the management of chronic urolithiasis, and use as an indicator dye. Methylene blue is also used to increase vascular tone and myocardial function in patients with septic or anaphylactic shock. It is as the antidote of choice in the treatment of symptomatic methemoglobinemia, however, that methylene blue's use is most prominent in the critical care setting. Methylene blue is a generally safe drug with dose-related hemolytic effects [13].

#### 2.1.3 Toxicity of methylene blue

Methylene blue is a biologically active substance, and if administered inappropriately, it can lead to a number of health complications, including gastrointestinal disturbances and dysuria [14]. Large doses of methylene blue can produce methemoglobinemia, chest pain, dyspnea, restlessness, apprehension, tremors, a sense of oppression, urinary tract irritation, as well as a mild hemolysis with moderate hyperbilirubinemia, reticulosis, and slight anemia [15].

Methylene Blue is an extremely potent monoamine oxidase inhibitor (MAOI) in vitro and that in human it causes potentially fatal serotonin toxicity. There have been a number of deaths in humans due to serotonin toxicity. Various evidences suggest MB helps memory and neuronal degeneration. It may also have acetylcholinesterase antagonist activity. Also MB dissolves Tau polymers isolated from Alzheimer disease brains, and prevents Tau aggregation in cell models in the high nanomolar concentration range (150 - 580 nM) and also reverses Tau pathology in the brain. MAO-A inhibition probably occurs at a lower concentration than Tau inhibition. At > 0.5 - 1 mg per kg intravenously it will be active as an MAOI [16].

Methylene blue toxicity is nearly always associated with its administration to patients treated with psychotropic medications, particularly those affecting central nervous system serotonin levels. Methylene blue should be administered with caution to these patients. No safe dosage regimen has been established. No recommendations can currently be made regarding the safety of methylene blue administration if or when antidepressant medications are discontinued. Methylene blue toxicity has occurred at a wide range of doses [17]. Dose-related toxicity of MB is summarized in Table 2.2 [11].

Animal studies	Toxic doses (mg/kg)	Manifestation
Rat	5-50	Neuronal apoptosis, reduced MAC
		isoflurane
	1250 (LD50)	
Mouse	3500	
Sheep	40	
Dog	10-20	Hypotension, decreased SVR, renal
		blood flow, pulmonary hypertension
	Dece	
Human studies	(mg/kg)	Toxic manifestations
Human studies	(mg/kg) 2-4	Toxic manifestationsHemolytic anemia,
Human studies	(mg/kg) 2-4	<b>Toxic manifestations</b> Hemolytic anemia, skin desquamation in infants
Human studies	(mg/kg) 2-4 7	Toxic manifestationsHemolytic anemia, skin desquamation in infantsNausea, vomiting, abdominal pain,
Human studies	Dose       (mg/kg)       2-4       7	Toxic manifestationsHemolytic anemia, skin desquamation in infantsNausea, vomiting, abdominal pain, chest pain, fever, hemolysis
Human studies	Dose       (mg/kg)       2-4       7       7.5	Toxic manifestationsHemolytic anemia, skin desquamation in infantsNausea, vomiting, abdominal pain, chest pain, fever, hemolysisHyperpyrexia, confusion
Human studies	Dose       (mg/kg)       2-4       7       7.5       20	Toxic manifestationsHemolytic anemia, skin desquamation in infantsNausea, vomiting, abdominal pain, chest pain, fever, hemolysisHyperpyrexia, confusionHypotension
Human studies	Dose       (mg/kg)       2-4       7       7.5       20       80	Toxic manifestationsHemolytic anemia, skin desquamation in infantsNausea, vomiting, abdominal pain, chest pain, fever, hemolysisHyperpyrexia, confusionHypotensionBluish discoloration of skin (similar

Table 2.2: Dose-related toxicity of MB dye

## 2.2 Dyes and MB dye in industrial effluents

Over 70,000 tons of approximately 10,000 types of dyes and pigments are produced annually world wide of which about 20 - 30% are wasted in industrial effluents during the textile dyeing and finishing processes.

Methylene blue has long been used as a model for the adsorption of organic dye from aqueous solution. Methylene blue is one of the most commonly used thiazine dyes and various adsorbents have been reported for its removal from aqueous solutions [18].

Dyes are widely use in textile, paper, plastic, food and cosmetic industries. The wastes coming from these industries can effect on our atmosphere causing pollution. The level of pollutants even in very low concentration is highly visible and will affect aquatic life as well as food web. Many dyes are difficult to degrade. They are generally stable to light, oxidizing agents and are resistant to aerobic digestion (McKay and Sweeney, 1980). Hence, pollution due to dyes poses not only a severe public health concern, but also many serious environmental problems because of their persistence in nature and non-biodegradable characteristics [19].

About 15% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of those colored waste waters in the ecosystem is a dramatic source of non-aesthetic pollution, eutrophication and perturbations in the aquatic life [20].

The discharge of dyes in the environment is worrying for both toxicological and esthetical reasons. Industries such as textile, leather, paper, plastics, etc., are some of the sources for dye effluents. It is estimated that more than 100,000 commercially available dyes with over  $7 \times 10^5$  tons of dyestuff produced annually. Although MB is used in some

medical treatments, and in dying textile, it can cause eye injury for both human and animals. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, diarrhea, gastritis, mental confusion and methemoglobinemia. Thus, the removal of MB from industrial effluents has become one of the major environmental concerns [21].

#### **2.3 Industrial Wastewater in the Palestinian Territories**

An essential tool in the management of hazardous waste is an inventory of national hazardous waste substances. No such inventory exists in the Occupied Palestinian Territories (OPT), and its absence makes it difficult to determine what types of waste are being generated, and where they are being disposed of. OPT has inadequate facilities for sewage and wastewater treatment and disposal. There are very few estimates of the amounts of hazardous waste generated in the OPT. In the West Bank, the amount has been estimated at 2,500 tons per year. The true amount is likely to be much higher. There are 71 textile-dyeing facilities in the West Bank producing both printed and dyed fabrics. Effluent from these industries contains high concentrations of ionic substances, organic color and reactive dyestuffs. Heavy metals, which are used for fixing colors in the dye, are also present. Estimates of annual solid and liquid hazardous waste are 290 and 600 tons respectively. Tanneries consume large quantities of scarce freshwater, and generate and release corresponding amounts of wastewater

with significant pollution loads, and sometimes with extreme pH values. The disposal of wastewater containing untreated tannery effluent presents a high risk of groundwater pollution, as wastewater infiltrates through the limestone into the aquifer. The paint manufacturing process involves the mixing of different agents such as pigments and solvents. A range of hazardous substances are used in the processes such as ethylbenzene and similar organic compounds, various acids, metals, acrylates, hazardous isomers, and alcohols. Estimates of annual solid and liquid hazardous waste generation are 8 and 201 tons respectively. About 2,500 million m<sup>3</sup> of used mineral oil are released annually in the OPT without any collection systems or adequate treatment. The mini steel mills in the OPT use a range of hazardous substances, such as heavy metals, phenol (and its salts), dioxins, furans, cyanides, and several dangerous halogenated hydrocarbons. Estimates of annual solid and liquid hazardous waste generation are 1,016 and 1,200 tons respectively. Medical waste covers several categories: infectious waste, pathological waste, pharmaceutical waste, genotoxic waste, chemical waste, wastes with high heavy metal content, pressurized containers, and radioactive waste. In the West Bank, 330 tons of contagious waste, 65 tons of biological waste and 2 tons of sharp objects are generated each year. The quantity for Gaza has been estimated at only 0.2 tons. The low value of this figure is that it refers to amounts that are collected, rather than total amounts including the waste that enters the domestic waste stream. Israeli colonies are also reported to release quantities of hazardous waste without treatment, such as Bargan industrial zone are release 810,000 cubic meters of industrial wastewater per year, including hazardous waste [22][23].

### 2.4 Adsorption

Adsorption is an important physical phenomenon, which provides bases for understanding such processes as heterogeneous catalysis, chromatographic analyses and dyeing of textiles. After the discovery of adsorption, a large number of scientists have been working either on adsorption of gases or liquids on different adsorbents. The property possessed by charcoal of removing coloring matter from solutions has been reported and many observations have since been made showing that these finely divided powders are able to take up dyestuff and other substances from solution [24].

#### 2.4.1 Adsorption phenomenon

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid surface. The solute retained on the solid surface in adsorption processes is called adsorbate, whereas, the solid on which it is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption. This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology [25].

Other definition of adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions. Large surface area leads to high adsorption capacity and surface reactivity [26].

Adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements (be they ionic, covalent, or metallic) of the constituent atoms of the material are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbate. The exact nature of the bonding depends on the details of the species involved, but generally the adsorption process is classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction [27].

#### 2.4.2 Adsorption Isotherms Models

The modeled adsorption isotherm is an invaluable non-linear curve describing the adsorption phenomenon at a constant temperature and pH; and the mathematical correlation which is depicted by the modeling analysis is important for operational design and applicable practice of the adsorption systems [28]. Adsorption isotherm models are described in many mathematical forms, some of which are based on a simplified physical description of adsorption and desorption, while others are purely empirical and intended to correlate experimental data [29]. Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration [30]. Adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal [31]. The mathematical correlation, which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration [32]. The physicochemical parameters together with the underlying thermodynamic assumptions of an isotherm provide insight into the adsorption mechanism, surface properties and the degree of affinity of the adsorbents which are fundamentals in the characterization of adsorption process [33].

A wide variety of equilibrium isotherm models; Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich– Peterson, Dubinin– Radushkevich, Temkin, Toth, Koble–Corrigan, Sips, Khan, Hill, Flory– Huggins and Radke–Prausnitz isotherm, have been formulated in terms of three fundamental approaches [34]. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined being a state of dynamic equilibrium, with both adsorption and desorption rates are equal. Whereas, thermodynamics, being a base of the second approach, can provide a framework of deriving numerous forms of adsorption isotherm models, and potential theory, as the third approach, usually conveys the main idea in the generation of characteristic curve. However, an interesting trend in the isotherm modeling is the derivation in more than one approach, thus directing to the difference in the physical interpretation of the model parameters [35].

#### 2.4.2.1 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 [36]-[45]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \tag{2.1}$$

Where:

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

 $Q_e$ = the amount of MB dye adsorbed per gram of adsorbent (mg/g)

Q<sub>m</sub>= Maximum capacity of monolayer coverage (mg/g)

 $K_L$  = Langmuir isotherm constant (L/mg)

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 [38][41]-[45]:

$$R_L = \frac{1}{(1 + K_L C_0)}$$
(2.2)

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

The  $R_L$  value indicates the shape of the isotherm to be either unfavorable if ( $R_L > 1$ ), Linear if ( $R_L = 1$ ), favorable if ( $0 < R_L < 1$ ), or irreversible if ( $R_L = 0$ ).

#### 2.4.2.2 Freundlich model Isotherm

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems. This model is defined by the following equation [36]-[45]:

$$Q_e = K_F C_e^{1/n} \tag{2.3}$$

The linear form of this equation can be written as [36]-[45]:

$$\ln Q_e = \frac{1}{n} \ln C_e + \ln K_F \tag{2.4}$$

 $K_F$  and n are Freundlich constants.  $K_F$  is a rough indicator of the adsorption capacity of the sorbent and n giving an indication of the favorable way of the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the adsorption favorability. If the value of 1 / n is less than one this indicates a normal adsorption. If n is between one and ten, it indicates a favorable sorption process [36][40].
As the temperature increases, the constants K and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface [36].

#### 2.4.2.3 Temkin model Isotherm

This isotherm contains a factor reflecting the adsorbent-adsorbate interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer decrease linearly with the coverage [41]. The model is given by the following equation [40][44]:

$$Q_e = BlnC_e + BlnA \tag{2.5}$$

Where  $\mathbf{B} = \mathbf{RT/b}$ , b is the Temkin constant related to heat of sorption (J/mol); A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol K) and T the absolute temperature (<sup>o</sup>K).

#### 2.4.3 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  $\Delta G$  (Gibbs free energy change), which can be calculated by the following equation [29][42]:

$$\Delta G = -RT ln K_d \tag{2.6}$$

Where  $K_d$  is the thermodynamic equilibrium constant (L g<sup>-1</sup>).

According to thermodynamics, Gibbs free energy ( $\Delta G$ ) is the difference between the adsorption enthalpy ( $\Delta H$ ) and adsorption entropy ( $\Delta S$ ) multiplied by the temperature. In this way, by applying this concept to the equation (4.8),  $\Delta H$  and  $\Delta S$  can be determined using the Van't Hoff plot (Figure 4.14), according to equation (4.9) [29][42]:

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{2.7}$$

## 2.4.4 Adsorption kinetics

The study of the adsorption kinetics is important because it provides valuable insights into the reaction path and the mechanism of the reactions. The adsorption rate was followed by the study of the contact time up to 6 hours and compared to theoretical models. Pseudo first-order and second-order kinetic models were tested in this study where experimental data obtained for the different contact times were used.

The rate constant for the adsorption of adsorbate from the effluent on adsorbent is determined using the pseudo first-order equation (Lagergren equation) [40][43][45]:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{\kappa_1}{2.303}\right)t$$
(2.8)

Where  $Q_e$  is the adsorption capacity of the adsorbent at equilibrium (mg/g),  $Q_t$  is the amount of dye adsorbed at time t (mg/g) and  $K_1$  is the pseudo first order rate constant (min<sup>-1</sup>).

The pseudo second order kinetics can be expressed in a linear form as integrated second order rate law [38][45][56]:

$$\frac{t}{q_t} = \frac{1}{q_e}t + \frac{1}{K_2 q_e^2}$$
(2.9)

Where  $K_2$  is the pseudo second order rate constant (g mg<sup>-1</sup> min<sup>-1</sup>).

A pseudo second order suggests that this adsorption depends on the adsorbate and the adsorbent and involves chemisorption process in addition to physisorption. The chemisorption might be the rate limiting step where valence forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate [38][43].

#### 2.4.5 Types of adsorbents

Different types of adsorbents are classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, clay minerals, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, house hold wastes, Industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, scrap tires, bark and other tannin-rich materials, sawdust, rice husk, petroleum wastes, fertilizer wastes, fly ash, sugar industry wastes blast furnace slag, chitosan and seafood processing wastes, seaweed and algae, peat moss, clays, red mud, zeolites, sediment and soil, ore minerals etc. [25].

## 2.4.6 Adsorption as an effective method for removing dyes from wastewater

Many treatment methods have been used to remove the dyes from wastewater. These can be divided into physical, chemical, and biological methods. Among the various methods, adsorption is an effective separation process for a wide variety of applications. It is now recognized as an effective and economical method for the removal of both organic and inorganic pollutants from wastewaters [46]. Adsorption is a common technique used for dye removal from aqueous solution, mainly because it is relatively low in cost, robust, environmentally friendly and simple. A starting point in the development of an adsorption unit is the choice of an adsorbent among the various adsorbents [47].

Due to low biodegradation of dyes, a conventional biological treatment process is not very effective in treating a dyes wastewater. It is usually treated with either by physical or chemical processes. However, these processes are very costly and cannot effectively be used to treat the wide range. The adsorption process is one of the effective methods for removal dyes from the waste sewage. The process of adsorption has an advantage over the other methods due to its sludge free clean operation and completely removed dyes, even from the diluted solution [48]. A synthetic dye in wastewater cannot be efficiently decolorized by traditional methods. This is because of the high cost and disposal problems for treating dye wastewater at large scale industries. Adsorption is a well-known

equilibrium separation process for water decontamination applications. Adsorption has been found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design and ease of operation [4].

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. Adsorption is integral to 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. Applications of adsorption for chemical processing air pollution control and water treatment are well known, applications in wastewater treatment and water pollution control are generally not as well recognized, nor as well understood. The process has been demonstrated to be widely effective for removing dissolved organic substances from wastewaters, but it should not be viewed as a catholicon for waste treatment, nor should its application be made in an empirical fashion [7].

Recently solid-phase extraction (SPE) technique using organic modified Polysiloxane has become known as a powerful tool for separation and enrichment of various inorganic and organic analytes. The SPE has several major advantages that include (i) higher enrichment factor, (ii) simple operation, (iii) safety with respect to hazardous samples, (iv) high selectivity, (v) lower cost and less time, (vi) the ability to combine with different modern detection techniques. Chemically modified Polysiloxane is one of the most successful adsorbents, because this inorganic polymer support does not swell or shrink like the organic polymeric resin. The modified Polysiloxane may be employed in aqueous and organic solvents media; they present good thermal stability and appropriate accessibility of ions to the adsorbent groups; in addition the organofunctionalized Polysiloxane exhibits higher sorption capacities than polymeric resins, because the number of organic molecules immobilized on the support surface is large, allowing thus more removal of ions from aqueous solution. These systems can be operated indefinitely without loss of the expensive organic molecules. Their potential applications are due essentially to the nature of the grafted ligands [8].

## 2.5 Polysiloxane and functionalized Polysiloxane

There is a growing interest in synthesis of inorganic Polysiloxane supports bearing organofunctionalized groups. Chemisorbents based on incorporation of chelating ligands at high intensity on to the inorganic polymeric matrix are of particular interest. There are two common methods used to prepare these functionalize ligand systems. The first method is the sol-gel process which involves hydrolysis and condensation of Si(OEt)<sub>4</sub> with the appropriate silane coupling agent (RO)<sub>3</sub>SiX where X represents an organofunctionalized ligand. The second approach is the chemical modification of the pre-prepared functionalized Polysiloxane. The second method appears as an interesting alternative mainly on account of substitution of organofunctionalized groups when appropriate chelating silane agents are difficult to prepare. The main advantages of these functionalized inorganic supports are their high thermal, hydrolytic and mechanical stability in addition to lack of swelling in solvents. These functionalized systems have been used in many important applications such as; chemisorption, recovery and separation of metal cations from organic solvents and aqueous solutions. In addition they were used widely as stationary phases in chromatography and as heterogeneous catalysts [49].

The most commonly attached chelate ability for this purpose is devoted for donor atoms, such as oxygen, nitrogen and sulfur which have a large capability in forming complexes with a series of metal ions, forcing in some cases, a distinguishable selective extraction property [8].

# 2.6 Polysiloxane surface modified with bipyrazolic tripodal receptor

The ability of pyrazole and its derivatives to act as ligands with sp<sup>2</sup> hybrid nitrogen donors is evident from the large number of articles, several of them being reviews. A series of acyclic pyrazole compounds containing one, two, three or four pyrazole rings were prepared and demonstrated to extract only bivalent metal cations whereas macrocyclic pyrazolic compounds are expected to also form stable complexes with alkali metals.

The chemistry of the pyrazole compounds bonded to polysiloxane has not yet been sufficiently developed [8].

# 2.7 Methodology of preparing Polysiloxane surface modified with bipyrazolic tripodal receptor

- I. synthesis of 3-aminopropylsilica (Si-NH<sub>2</sub>)
  - Silica gel with particle size in the range 70-230 mesh and median pore diameter 60 Å, was activated before use by heating it at 160°C during 24 h.
  - Silica gel SiO<sub>2</sub> (25 g) suspended in 150 mL of dried toluene will be refluxed and mechanically stirred under nitrogen atmosphere for 2 h.
  - 3) 10 mL of aminopropyltrimethoxysilane will be added dropwise and the mixture will be kept under reflux for 24 h.
- II. synthesis of Synthesis of N,N-bipyrazole-substituted silica (Si-NPz<sub>2</sub>)
- A mixture of 3-aminopropylsilica (SiNH<sub>2</sub>) (10 g, approximately 10.2 mmol-NH<sub>2</sub>) and an excess of 3.0 equiv. of N-hydroxymethyl-3,5-dimethylpyrazole (3.85 g, 30.6 mmol) in 100 mL of dry acetonitrile will be stirred at room temperature for 6 days.
- NH-group onto the silica surface is capable to react with Nhydroxymethylpyrazoles under gentle conditions (room temperature,

atmospheric pressure, 4–7 d), using anhydrous acetonitrile as solvent.

- 3) After being filtered, the solid product was transferred to the Soxhlet extraction apparatus for reflux-extraction in acetonitrile, methanol and dichloromethane for 12 h respectively.
- 4) The product Si-NP<sub>2</sub> was dried under vacuum at 70°C over 24 h.

NH<sub>2</sub>-group onto the silica surface is capable to react with 3,5-Dimethylpyrazole-1-methanol under gentle conditions (room temperature, atmospheric pressure, 4–7 d), using anhydrous acetonitrile as solvent (Figure 2.1). The reaction is very slow but selective at room temperature [8][50].



Figure 2.3: The synthesis route of modified polysiloxane [8].

This work is focused on the synthesis, characterization and applications of a new N,N-bis (3,5-Dimethylpyrazol-1-yl methyl)-3aminopropyl Polysiloxane (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) by the chemical modification of the pre-prepared functionalized silica gel for quantitative extraction and elimination of methylene blue (MB) from industrial wastewater. This new product (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) can be synthesized by mixing and stirring for 7 days of the pre-prepared functionalized silica gel with an excess of 3,5-Dimethylpyrazole-1-methanol under mild conditions ( room temperature and atmospheric pressure) using anhydrous acetonitrile as a solvent.

## **Chapter Three**

## **Experimental Work**

## **3.1 Chemicals and Materials**

All solvents and chemicals were of analytical scale and used without additional purification. 3-aminopropyl-functionalized silica gel (Sigma-Aldrich, purity  $\geq$  98.5%) having a particle size between 40-63 µm, extent of labeling: ~1 mmol/g loading NH<sub>2</sub> [59]. The chelating agent 3,5-Dimethylpyrazole-1-methanol (Sigma-Aldrich, purity  $\geq$  99%) was used without purification [60]. Dry acetonitrile was used as a solvent, methanol and dichloromethane were used for reflux extraction. Analytical grade Methylene blue Dye was used as adsorbent. Distilled water was used to prepare stock solution. HNO<sub>3</sub> (0.1M) and KOH (0.1M) for pH adjustment were used.

The required materials and apparatus are: glassware, scale, UV-visible spectrophotometer (model: UV-1601, SHIMADZU), pH meter (model: 3510, JENWAY), FT-IR Spectrometer (Nicolet iS5, iD3 ATR, Thermo Scientific), centrifuge (model:1020 DE, Centurion Scientific), Shaking Water Bath (Daihan Labtech, 20 to 250 rpm Digital Speed Control), TGA Q50 V20.10 Build 36 instrument with heating rate of 50°C/min and in N<sub>2</sub> gaseous atmosphere, Differential Scanning Calorimeter (DSC) Q200, TA Instruments, desiccator.

## 3.2 synthesis of N,N-bis(3,5-Dimethylpyrazol-1-yl methyl)-3aminopropyl Polysiloxane (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>)

A mixture of **3-aminopropyl-functionalized silica gel** (Si-C<sub>3</sub>H<sub>6</sub>NH<sub>2</sub>) (5 approximately 5.1  $mmol-NH_2$ ) and an excess of **3.5**g, **Dimethylpyrazole-1-methanol** (about 2.0 g, 15.9 mmol) in 50 mL of dry acetonitrile will be stirred at room temperature for 7 days. NH-group on the silica surface is adequate for reacting with 3,5-Dimethylpyrazole-1methanol under moderate conditions ( atmospheric pressure, room temperature, 4–7 d), using anhydrous acetonitrile as solvent. After being filtered, the solid product was washed respectively with several portions of methanol and dichloromethane. The product N,N-bis(3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) was dried in a desiccator for 2 days then it was dried under vacuum at 70°C for 3 h [8]. The synthesis procedure is shown in Figure 3.1.



**Figure 3.1**: The synthesis procedure of (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>)

## **3.3** Characterization of (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>)

A SEM study was carried out to provide information about the physical morphology of Polysiloxane surface modified with bipyrazolic tripodal receptor. The modified silica gel was corroborated by FTIR analysis to show that Dimethylpyrazole units have been immobilized onto the surface of the modified silica gel. Thermal stability of polysiloxane derivatives (Si-C<sub>3</sub>H<sub>6</sub>NH<sub>2</sub>) and (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) have been determined by thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) [8][53].

## 3.4 Preparation of methylene blue solutions

About 0.5 g of methylene Blue was taken in a 500 mL volumetric flask and diluted up to the mark by addition of deionized water. Different concentration; 5, 10, 15, 20, 25, 30, 40 and 50 mg/L were prepared by dilution [4][6].

## **3.5 Calibration Curve**

The concentration of MB was analyzed by UV-visible Spectrophotometer (UV-1601 SHIMADZU). A standard MB solution of 1000 mg/L was prepared and absorbance was determined at various wavelengths to obtain a representative plot of absorbance versus wavelength (Figure 3.2). The wavelength related to the maximum absorbance which determined from this plot was 665 nm.



Figure 3.2: A representative plot of absorbance versus wavelength for a standard MB solution

At high concentrations of MB, Beer-Lambert relation deviates from linearity and gives a non-linear relationship, as shown in Figure 3.3, so our work was restricted at concentration up to 25 mg/L. At higher concentrations, the individual particles of analyte will not behave independently of each other. The interaction between the particles resulting from the analyte can change the value of  $\varepsilon$ . Also the absorption capacity (a) and molar absorptivity ( $\varepsilon$ ) depend on the sample refractive index. Since the refractive index varies with the concentration of the analyte, the values of a and  $\varepsilon$  change. At enough low concentrations of analyte, the refractive index remains constant, and the calibration curve is linear [41]. Few large ions or molecules deviate from Beer-Lambert law even at low concentrations, for example, methylene blue which has absorbance at 436 nm fails to obey Beer-Lambert law even at concentrations as low as 10 $\mu$ M. [52].



Figure 3.3: A representative plot of the absorbance versus concentration of MB solution.

Linear calibration curve between the absorbance and the concentration was obtained with MB concentrations in the range 5-20 mg/L ( $R^2 = 0.9998$ ) as shown in Figure 3.4.



**Figure 3.4**: Linear calibration curve of absorbance vs. concentration for MB concentrations in the range 5-20 mg/L

## **3.6 Adsorption Experiments**

The maximum absorbance ( $\lambda_{max}$ = 665 nm) as determined from the plot was used for measuring the absorbance of residual concentration of MB. The pH of solutions was adjusted using roughly concentrations of 0.1M HNO<sub>3</sub> and 0.1M KOH. By conducting batch mode experimental studies the efficiency of the adsorbent was evaluated. The adsorption behavior of the new surface with MB dye was studied. The effect of pH, temperature, dose of adsorbent, concentration of MB solution and the contact time on the adsorption of MB dye was studied. The adsorption capacity was investigated using kinetics and pH effects. Equilibrium isotherm studies were conducted by varying the following parameters: initial concentration of MB dye solution, temperature, and adsorbent dose on dye adsorption from the solution. At the end of time terms, the adsorbent was removed by centrifuging at 600 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

The proportion of dye removal (% Removal) is recognized as the ratio of disparity of the dye concentration before and after adsorption to the initial concentration of dye in the aqueous solution and was calculated by the following equation [4][12]:

Removal efficiency (%) = 
$$\left[\frac{(C_o - C_e)}{C_o}\right] \times 100$$
 (3.1)

Where,  $C_o$  is the Initial dye concentration (mg/L) in the sample and  $C_e$  is the final dye concentration in the sample solution after treatment.

#### **3.6.1 Experiment (1) - The temperature effect**

For studying the temperature effect on adsorption, 0.10 g adsorbent samples were added to 50 mL of methylene blue dye solutions with concentration 20 mg/L at pH 7. Each mixture was placed in Shaking Water Bath (Daihan Labtech) at desired temperature (the range was 15-55°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 UV-visible spectrophotometer (UV-1601, SHIMADZU) for the residual concentration of MB, at 665 nm wavelength.

## **3.6.2 Experiment (2) - Effect of pH**

Effect of initial pH on adsorption was investigated in the pH range 2.5-12. The pH was adjusted using roughly concentrations of 0.1M HNO<sub>3</sub> and 0.1M KOH. 0.05 g adsorbent samples were added to 20 mL of MB dye solutions with concentration 20 mg/L. The mixtures were placed in Shaking Water Bath at constant 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 analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

#### **3.6.3 Experiment (3) - Effect of initial concentration of MB dye**

In order to find out the optimum concentration, 0.041 g of adsorbent was added to a number of vials contains 20 mL of different concentrations of MB dye solution (5-25 mg/L), under optimized temperature (15°C) and

pH 10 for 30 min. The absorbance of the solution above the solid residue was measured by UV-spectrophotometer.

#### **3.6.4 Experiment (4) - Effect of adsorbent dose**

The effect of adsorbent dosage on the adsorption of methylene blue dye system was studied. In order to find out the optimum adsorbent dose, 0.015, 0.05, 0.10, 0.15 and 0.20 g of adsorbent were added to five vials contains 20 mL of 15mg/L MB dye solution at pH 11.4 . The mixtures were placed in Shaking Water Bath at constant temperature (15°C) for 30 min. The absorbance of the solution above the solid residue was measured by UV-visible for the residual concentration of MB dye.

## **3.6.5 Experiment (5) - Optimization of contact time**

The adsorption of MB dye on the adsorbent was studied as a function of shaking time at  $20^{\circ}$ C. A sample of 50 mL of dye (15 mg/L) solution at pH 10.7 was taken in a volumetric flask and shaken with 0.25g of adsorbent. Aliquots of the clear solution were drawn out by a small slim pipette at different time intervals until equilibrium was achieved. Each aliquot was taken and centrifuged for 5 minutes at 600 rpm. The supernatant was carefully removed by a thin plastic dropper and absorbance was measured by UV-visible at 665 nm wavelength.

## 3.7 Thermodynamics and Kinetics of Adsorption

The removal of MB dye was studied by adsorption technique using the prepared adsorbent (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>). The method was arranged under the optimized case of adsorbent dose, contact time, concentration, temperature and pH. Using a UV-spectrophotometer, the concentration of dye was determined before and after adsorption. The data were provided into Langmuir, Freundlich and Temkin adsorption isotherm equations. The values of their relevant parameters were determined. Thermodynamic parameters like free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of the systems were calculated by using Van't Hoff's plot. Removal proportions and Kd values for dye systems were calculated at different temperatures between (15 – 55°C) with intervals of 10°C.

0.25 g of adsorbent was added to 50 mL of 15 mg/L of MB dye solution at pH 10.7. The mixture was placed in Shaking Water Bath at constant temperature (20°C). The rate of adsorption was observed by studying the contact time up to 6 hours and matched to theoretical models. Pseudo first-order and second-order kinetic models were examined in this study using experimental data obtained for different periods of contact time. Parameters of Pseudo first and second order kinetic models, (K, Q<sub>e</sub> and R<sup>2</sup>) for MB dye adsorption on Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> were determined. The values of the calculated and experimental Q<sub>e</sub> were compared.

## **Chapter Four**

## **Results and Discussion**

## 4.1 Modified Polysiloxane (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) Characterization

## 4.1.1 SEM Analysis of the Modified Polysiloxane

A SEM study was carried out to provide information about the physical morphology of Polysiloxane surface modified with bipyrazolic tripodal receptor. SEM images (Figure 4.1) of the Modified Polysiloxane surface exhibit coarse and pored nature, showing that the material exhibit good features for use as an adsorbent.



Figure 4.1: SEM micrographs of the modified Polysiloxane surface (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>)

#### 4.1.2 FT-IR Characterization

The new modified silica gel was checked up on by FT-IR analysis. As presented in Figure 4.2, the sharp band around 1060 cm<sup>-1</sup> corresponds to Si-O-Si anti-symmetric stretching vibrations. Characteristic absorption band of the 3-aminopropyl-functionlized silica gel (Si-C<sub>3</sub>H<sub>6</sub>NH<sub>2</sub>) for N-H bond was observed at 1590 cm<sup>-1</sup>. On the spectrum of the final product (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>), it was noticed the disappearance of the absorption band at 1590 cm<sup>-1</sup> giving evidence at the reactivity of the primary amine (–NH<sub>2</sub>) and the appearance of new characteristic weak bands around 1500 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> resulted from C=C stretching vibrations in ring and another band around 1660 cm<sup>-1</sup> corresponds to C=N stretching vibration. This confirms that the Dimethylpyrazole units have been immobilized onto the surface of the modified silica gel [8].



**Figure 4.2**: FT-IR spectra of (a) 3-aminopropyl-functionalized silica gel  $(Si-C_3H_6NH_2)$ (b) and the modified Polysiloxane surface  $(Si-C_3H_6NPz_2)$ 

#### 4.1.3 TGA Analysis and Thermal Stability

The thermal stability of polysiloxane derivatives  $(Si-C_3H_6NH_2)$ , and  $(Si-C_3H_6NPz_2)$ determined thermogravimetric were by analysis. Thermogravimetric curves indicate the thermal stability of this new product. The amount broken down in each phase sets the amount of the grafted compounds. It can be seen in Figure 4.3a, 3-aminopropyl-silica (Si- $C_{3}H_{6}NH_{2}$ ) a weight loss after removal of the physically adsorbed water, mainly referred to the organic offshoot. The final product  $(Si-C_3H_6NPz_2)$ also exhibited an increase in weight loss attributed to decomposition of the pyrazolic portion grafted on the surface of silica gel, as shown in Figure 4.3b. The evident increase of the weight loss indicates the break of organic groups which were grafted on the surface of this silica gel. [8] [50] [53].



**Figure 4.3a**: Thermogravimetric curves of 3-aminopropyl-functionalized silica gel (Si- $C_3H_6NH_2$ )



Figure 4.3b: Thermogravimetric curves of the modified Polysiloxane surface (Si- $C_3H_6NPz_2$ )

Figure shows a process of degradation between 150-750°C, which underlines the high thermal stability for the prepared material [54].

## **4.2 Investigation of adsorption parameters**

## 4.2.1 Effect of pH on Methylene Blue dye adsorption

The pH of a solution is an important factor that influences the adsorption capability of the adsorbent, particularly those having functional groups such as amino groups, which may be protonated or deprotonated easily to form various surface charges in solutions at varied pH [8][50]. Decrease adsorption of MB dye at low pH is a consequence of the existence of hydrogen ions which compete with cationic groups on MB for adsorption spots, thereby blocking the absorption of dye [4]. In addition,

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under acidic condition (low pH) the basic dye is protonated and the intensity of the positive charge is localized more on dye molecules causes a decrease in adsorption [8].

To estimate the pH effect on the adsorption capability of the modified Polysiloxane surface (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>), the adsorption experiments were done in solutions with different pH values. Figure 4.4 presents the pH effect on the uptake of MB dye from its aqueous solution by (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>). Results demonstrate an increase of MB dye uptake as the pH increased. The uptake attained its extreme at pH 10. Low absorption capability happens at lower pH, which may be due to protonation of the ligand nitrogen atoms. At low pH, the detention of MB dye by the (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is not considerable since the ligand is fully in its protonated state.



**Figure 4.4**: pH effect on MB dye adsorption. ( $C_0$ = 20 mg/L, time= 30 min., T=25<sup>o</sup>C, adsorbent dose= 0.05 g, sol. Volume= 20 mL)

#### 4.2.2 Temperature effect on MB dye adsorption

The effect of temperature on the uptake % of MB dye by (Si- $C_3H_6NPz_2$ ) was studied at (15-55°C) as represented in Figure 4.5. The figure presents that in general the % removal of MB dye decreases with increasing the temperature to some extent. Increasing the temperature above the room temperature has slightly effect on decreasing the adsorption capability of the new modified surface. The maximum adsorption (78%) was achieved at 15°C. This indicates that the adsorption of MB dye on (Si- $C_3H_6NPz_2$ ) follows exothermic process.



Figure 4.5: Effect of temperature on MB dye adsorption. ( $c_0 = 20 \text{ mg/L}$ , time= 30 min., adsorbent dose= 0.1 g, sol. Volume= 50 mL)

#### 4.2.3 Effect of MB dye concentration

The effect of initial concentration on the removal efficiency of  $(Si-C_3H_6NPz_2)$  was investigated over wide range of MB dye concentration keeping other conditions as adsorbent dose, volume of solution and

solution pH as constant. The results are presented in Figure 4.6 and Figure 4.7. It can be noticed from these figures that uptake of MB dye was rapid at lower concentration (5-10 mg/L) and as concentration increase the amount of MB dye adsorbed was decreased. At lower concentration, the ratio of the initial number of MB dye molecules to the available surface area is low and the available sites are high, but at high concentrations of dye, the available sites are fewer [4] [5]. Proportion removal of MB dye lowered from 80% to 62%. Amount of MB dye adsorbed per unit mass of adsorbent increased from 1.93 to 7.53 mg/g with increasing MB dye concentration from 5 to 25 mg/L. When all sites are occupied, the adsorption becomes nearly constant whatsoever concentration of dye is increased. This suggests forming a monolayer on the modified Polysiloxane surface [4].



**Figure 4.6**: Effect of MB dye concentration on adsorption. (Temp.=  $15^{\circ}$ C, time= 30 min., pH= 10, adsorbent dose= 0.04 g, sol. Volume= 20 mL)



Figure 4.7: Effect of MB dye conc. on adsorption capacity. (Temp.= 15°C, time= 30 min., pH= 10, adsorbent dose= 0.04 g, sol. Volume= 20 mL)

The distribution coefficient  $K_d$  was calculated from equation (4.2) [5][55]:

$$K_d = \frac{amount \ of \ dye \ in \ adsorbent * Volume \ of \ solution \ (mL)}{amount \ of \ dye \ in \ solution * mass \ of \ adsorbent \ dose \ (g)}$$
(4.1)

K<sub>d</sub> term is measured directly in the laboratory. Thus,

$$K_d = \frac{V_w(C_o - C_e)}{m_{sed} \times C_e} \tag{4.2}$$

Figure 4.8 shows that the distribution ratio (K<sub>d</sub>) as a function of concentrations. The  $K_{\rm d}$  values decrease with the increase in dye concentration.



**Figure 4.8**: Effect of MB dye conc. On the Distribution Ratio (K<sub>d</sub>). (Temp.=  $15^{\circ}$ C, time= 30 min., pH= 10, adsorbent dose= 0.04 g, sol. Volume= 20 mL)

### 4.2.4 Effect of amount of adsorbent

The effect of the dosage of adsorbents on the removal of methylene blue was studied. Initial concentration of methylene blue solution was preserved at 15 mg/L, initial volume was 20 mL, pH was around 10 and temperature was  $15^{\circ}$ C. The results were represented in Figure 4.9 demonstrates that removal efficiency was greatly increased with increasing the dose of adsorbent up to 0.1 g. Then removal efficiency did not change significantly with increasing dose of adsorbent. It shows that removal efficiency was 78% when the dose was 0.1 g. For 0.15 g, it was 80.5% and 81.8% for 0.2 g. The increment in adsorption effectiveness was a result of the increased number of adsorption sites [5]. Therefore, removal efficiency became in equilibrium with the amount of 0.1 g of adsorbent within the specified parameters.



**Figure 4.9**: Effect of dosage of adsorbent on the removal of MB dye. (Temp.= 15°C, time= 30 min., pH= 10, conc. of MB dye= 15 mg/L, sol. Volume= 20 mL)

## **4.2.5 Effect of contact time**

To determine the time of maximum adsorption, the adsorption of MB dye on  $(Si-C_3H_6NPz_2)$  was studied as a function of contact time as shown in Figure 4.10.

The MB dye showed a rapid rate of adsorption for the first 15 minutes and the adsorption rate becomes almost insignificant after that, because of use of the adsorption sites. The adsorption capacity rate is high at the beginning due to large surface area of adsorbent available for adsorption of methylene blue dye. At the beginning of the adsorption process all reaction sites are vacant and therefore the degree of removal is high. After the initial rapid absorption, the absorption rate was very slow almost reaching a constant value [37] [38].



**Figure 4.10**: Effect of contact time to determine the time of maximum adsorption of MB dye. (Temp.=  $20^{\circ}$ C, pH= 10, conc. Of MB dye= 15 mg/L, sol. Volume= 50 mL, adsorbent dose= 0.2504 g)

## 4.3 Adsorption isotherm of MB dye

Adsorption study at equilibrium gives input about capability of the adsorbent. An adsorption isotherm is described by specific values, which articulate the surface properties and affinity of the adsorbent and also be used to find the maximum adsorption capacity. Equilibrium data can be tested using commonly known adsorption methods. Several mathematical models can be used to describe the experimental data of adsorption isotherms. Models Freundlich, Langmuir and Temkin are used in the data analysis of the adsorption isotherm experiment [39].

## 4.3.1 Langmuir Adsorption Isotherm

According to equation (2.1), the values of  $Q_m$  and  $K_L$  were calculated from the slope and the y-intercept of the Langmuir plot of  $C_e/Q_e$  versus  $C_e$ . From Langmuir plots which is shown in Figure 4.11 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 4.1.



**Figure 4.11**: Langmuir plot for MB dye adsorption on  $(Si-C_3H_6NPz_2)$ . (Temp.=  $15^{\circ}C$ , pH= 10, time= 30 min., sol. Volume= 20 mL, adsorbent dose= 0.0413 g)

Table 4.1: Parameters and correlation coefficient of Langmuir isotherm model for adsorption of MB dye onto  $(Si-C_3H_6NPz_2)$ .

Langmuir isotherm model parameters					
Adsorbate	Parameters				
	$Q_m (mg/g)$	$K_L = (L/mg)$	R <sub>L</sub>	$\mathbf{R}^2$	
$(Si-C_3H_6NPz_2)$	11.09	0.25	0.138	0.9694	

The  $R_L$  value in this investigation was calculated according to equation (2.2). It was found to be equal 0.138 at 15 °C which is between 0 and 1 indicating that the MB dye adsorption on (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favorable [38] [44].

## 4.3.2 Freundlich Adsorption Isotherm

The constants  $K_F$  and n were determined by using equation (2.4) which can be used to make a graph of  $ln(Q_e)$  vs.  $ln(C_e)$  as shown in Figure 4.12:



**Figure 4.12**: Freundlich plot for MB dye adsorption on  $(Si-C_3H_6NPz_2)$ . (Temp.=  $15^{\circ}C$ , pH= 10, time= 30 min., sol. Volume= 20 mL, adsorbent dose= 0.0413 g)

Freundlich constants  $K_F$  and n and regression constant ( $R^2$ ) were determined and values are shown in Table 4.2:

Table 4.2: Parameters and correlation coefficient of Freundlich isotherm model for adsorption of MB dye onto (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>).

Freundlich isotherm model parameters					
	Parameters				
Adsorbate	1/n n K <sub>F</sub> =		$\mathbf{K}_{\mathbf{F}} = (mg/g$	$\mathbf{R}^2$	
			$(L/mg)^{1/n})$		
$(Si-C_3H_6NPz_2)$	0.602	1.66	2.25	0.9307	

From the data in Table 4.2, that value of 1/n = 0.6041 while n=1.66 indicating that the sorption of MB dye on (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favorable and the R<sup>2</sup> value is 0.9307.

## 4.3.3 Temkin Adsorption Isotherm

According to equation (2.5) a graph of  $Q_e$  vs. (ln  $C_e$ ) can be plotted as shown in Figure 4.13. The constants A, B and b were calculated. All parameters and correlation coefficient are listed in Table 4.3.



**Figure 4.13**: Temkin plot for MB dye adsorption on  $(Si-C_3H_6NPz_2)$ . (Temp.=  $15^{\circ}C$ , pH= 10, time= 30 min., sol. Volume= 20 mL, adsorbent dose= 0.0413 g)

## Table 4.3: Temkin isotherm model parameters and correlation coefficient for adsorption of MB dye on $(Si-C_3H_6NPz_2)$ .

Temkin isotherm model parameters					
Adsorbate	Parameters				
	<b>A</b> (L/g)	<b>b</b> (J/mol)	В	$\mathbf{R}^2$	
(Si-C <sub>3</sub> H <sub>6</sub> NPz <sub>2</sub> )	0.1326	6242	0.3838	0.9856	

The graphically calculated  $Q_m$ ,  $K_L$ ,  $R_L$  and  $R^2$  (Langmuir isotherm), 1/n, n,  $K_F$ , and  $R^2$  (Freundlich isotherm), A, b, B, and  $R^2$  (Temkin isotherm) are rearranged in Table 4.4.

Langmuir isotherm model parameters					
	Parameters				
Adsorbate	$Q_m (mg/g)$	$K_{L} = (L/mg)$	R <sub>L</sub>	$\mathbf{R}^2$	
$(Si-C_3H_6NPz_2)$	11.09	0.25 0.138 0		0.9694	
Freundlich isotherm model parameters					
	Parameters				
Adsorbate	1/n	n	$\frac{\mathbf{K_F}}{(\text{mg/g} (\text{L/mg})^{1/n})}$	$\mathbf{R}^2$	
(Si-C <sub>3</sub> H <sub>6</sub> NPz <sub>2</sub> )	0.602	1.66	2.25	0.9307	
Temkin isotherm model parameters					
	Parameters				
Adsorbate	<b>A</b> (L/g)	b (J/mol)	В	$\mathbf{R}^2$	
$(Si-C_3H_6NPz_2)$	0.1326	6242	0.3838	0.9856	

Table 4.4: Parameters and correlation coefficient of Langmuir, Freundlich and Temkin for adsorption of MB dye on  $(Si-C_3H_6NPz_2)$ .

Three adsorption isotherm models were examined. The adsorption data appropriated to Langmuir, Freundlich, and Temkin. From Langmuir isotherm data in Table 4.4 the value of  $R_L$  in this investigation was found to be 0.138 at 15 °C indicating that the adsorption of MB dye on (Si- $C_3H_6NPz_2$ ) is favorable and  $R^2$  value is 0.9694. From Freundlich isotherm data in Table 4.4, that value of 1/n = 0.6041 while n=1.66 pointing that the adsorption of MB dye on (Si-comparison dye)) is favorable and the R<sup>2</sup> value is

0.9307. Larger value of n which means smaller value of 1/n involves stronger interaction among adsorbent and adsorbate [41][42]. 1 / n between 0 and 1 is a measurement of the adsorption density and heterogeneity of the surface, which can become more heterogeneous when 1 / n becomes close to zero [38]. Adsorption data equipped in Langmuir, Freundlich, Temkin and from which Temkin adsorption model has the greatest value of regression and therefore the most convenient. This isotherm contains a factor that includes adsorbent-adsorbate interactions which indicates the presence of this interaction.

## 4.4 Adsorption Thermodynamics

 $\Delta$ H and  $\Delta$ S can be determined using the Van't Hoff plot (Figure 4.14), according to equation (4.9):



**Figure 4.14**: A graph of  $lnK_d$  vs. 1/T for MB dye adsorption on (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>). (Temp.= 15°C, pH= 10, time= 30 min., adsorbent dose= 0.0413 g, sol. Volume= 20 mL)

 $\triangle H^{\circ}$  and  $\triangle S^{\circ}$  were computed from the slope and y-intercept of a linear plot for  $\ln K_d$  versus 1/T. The results present that enthalpy of adsorption  $\triangle H^{\circ}$  was -16.66 kJ mol<sup>-1</sup> and  $\triangle S^{\circ}$  was 1.78 J mol<sup>-1</sup> K<sup>-1</sup>.  $\triangle G^{\circ}$  was calculated at different temperatures from the following equation [56]:

$$\Delta G^o = \Delta H^o - T \Delta S^o \tag{4.1}$$

The computed thermodynamic values are listed in Table 4.5.

Table 4.5: The values of the thermodynamic of MB dye adsorption atvarious temperatures.

Adsorbent	$\triangle H^{o}$	$\Delta H^{o}$ $\Delta S^{o}$		∆G° (KJ/mol)				
	(KJ/mol)	(J/mol.K)	288 K	298 K	308 K	318 K	328 K	
Si-C <sub>3</sub> H <sub>6</sub> NPz <sub>2</sub>	-16.66	1.78	-17.17	-17.19	- 17.21	- 17.23	-17.25	

Negative values of  $\Delta G$  point that adsorption is spontaneous at these temperatures. The negative  $\Delta H^{\circ}$  denotes that this adsorption is an exothermic process, declaring that this adsorption is promoted at low temperature. In general enthalpy change value  $\Delta H$  for physical adsorption is lower than that of the chemical adsorption. Generally,  $\Delta H$  for physical adsorption reaches up to 40 KJ/mol which is much less than that of chemical adsorption which varies from 40 to 800 KJ / mol.  $\Delta H$  value was higher than that corresponding to the physical adsorption. This suggests that the nature of adsorption is a chemical process which may be provided as shown in Figure 4.15. The small positive value of  $\Delta S^{\circ}$  indicates that some structural changes take place on the adsorbent and the entropy at the
solid / liquid interface in the adsorption system increases through adsorption process [29].



**Figure 4.15:** The suggested interaction between MB dye and Modified SiO<sub>2</sub> with bipyrazolic tripodal receptor

## 4.5 Adsorption kinetics of methylene blue dye

Rate constant for the adsorption of methylene blue from the dyeing effluent on adsorbent (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) was specified depending on the pseudo first-order equation (equation 2.6). A linear graph of  $\log(Q_e - Q_t)$ vs. time as shown in Figure 4.16 was plotted to obtain the pseudo first order rate constant. If the plot was linear with high correlation coefficient, this indicated that Lagergren equation is proper to MB dye adsorption on Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>, so the adsorption process is a pseudo first order. The Lagergren first order rate constant (K<sub>1</sub>) and Q<sub>e</sub> specified from this model are presented in Table 4.6 with the corresponding correlation coefficient.



**Figure 4.16**: Pseudo first order sorption kinetics of MB dye on  $(Si-C_3H_6NPz_2)$ . (Temp.= 20°C, pH= 10, sol. Volume= 50 mL, adsorbent dose= 0.2504 g)

The calculated  $Q_e$  value does not match with the experimental  $Q_e$  value (Table 4.6). This pointed that the adsorption of MB dye does not obey the first-order kinetics so that the pseudo first order model is not the appropriate one [40].

The results confirm that the pseudo second order kinetic model perfect fit the experimental data with linear regression coefficient which equals 0.9999 (Figure 4.17) [56].

 $Q_e$  experimental and  $Q_e$  calculated values for the pseudo second order model are illustrated in Table 4.6. It can be observed from this table that there is an agreement between  $Q_e$  experimental and  $Q_e$  calculated values for the pseudo second order model. Also  $K_2$  is much greater than  $K_1$ . Hence, the pseudo second order model well represented the adsorption kinetics.



**Figure 4.17**: Pseudo second order adsorption kinetics of MB dye on  $(Si-C_3H_6NPz_2)$ . (Temp.= 20°C, pH= 10, sol. Volume= 50 mL, adsorbent dose= 0.2504 g)

Table 4.6: Pseudo first order and pseudo second order parameters for MB dye adsorption onto Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> at 20°C.

Adsorbont	Qe (exp)	Pseud	o first o	order	Pseudo second order			
Ausorbent	(mg/g)	$\frac{\mathbf{K_1}}{(\min^{-1})}$	$\mathbf{Q}_{e (calc)}$ (mg/g)	$\mathbf{R}^2$	K <sub>2</sub> (g/mg min)	${f Q_e}_{(calc)} \ (mg/g)$	$\mathbf{R}^2$	
Si-C <sub>3</sub> H <sub>6</sub> NPz <sub>2</sub>	2.53	5.07×10 <sup>-3</sup>	0.203	0.9567	406.01×10 <sup>-3</sup>	2.46	0.9999	

#### 4.6 Recovery and reusability of Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> adsorbent

Recovering MB dye from Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> was carried out at 20 °C. The adsorbent was recovered by filtration, washed with portions of 6N HCl and then washed with deionized water and allowed to dry at room temperature for two days. The adsorption capability of regenerated Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> was tested under similar conditions and compared to the first use. 0.1 g of regenerated adsorbent was added to a 20 mL of 15 mg/L MB dye solution at pH 10. Comparing the adsorption capacity of the regenerated adsorbent with a fresh one (Figure 4.18) showed good adsorption capacity and has good stability and can be used again and again without reducing its capability [55].



**Figure 4.18**: Percentage of MB dye removal by the regenerated adsorbent compared with a fresh one at (Temp.=  $15^{\circ}$ C, pH= 10, adsorbent dose= 0.1002 g, sol. Volume= 20 mL, contact time= 30 min)

#### 4.7 Studying the Antimicrobial Activity of Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>

N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-3-aminopropyl

Polysiloxane (Si- $C_3H_6NPz_2$ ) and Si- $C_3H_6NPz_2$  with adsorbed cupper had been tested for their antimicrobial activity. The compounds were dissolved with Dimethyl sulfoxide (DMSO) Positive control (using and sensitive media) especially against pseudomonas aeruginosa, Staphylococcus aurous, and Escherichia coli. The result was negative; MacConkey Agar media, Mannitol Salt Agar, and Eosin Methylene Blue Agar were prepared for detection of antimicrobial activity of the isolates Pseudomonas aeruginosa, Staphylococcus aurous, and Escherichia coli respectively. 10 mg of Si- $C_3H_6NPz_2$  were dissolved in 1 ml of 10% Dimethyl sulfoxide (DMSO). After agar plate was fertilized by staining with bacterial-inoculated wipe over the whole antiseptic agar surface to ensure an even distribution of inoculums; wells were made by sterile tips. 100µl of Si- $C_3H_6NPz_2$  was added; in one well where the other wells 100µl of DMSO was added and third well with positive control (some cases an Antibiotic disk was added as positive control). Then the plates were incubated at 37°C for 16 hrs. All plates (including the three types of bacteria) were showed negative results for Si- $C_3H_6NPz_2$  and the formula+Cu (figure 4.19) [57][58].



**Figure 4.19**: Antimicrobial Activity of Si- $C_3H_6NPz_2$ , all plates were showed negative results for Si- $C_3H_6NPz_2$  and the formula+Cu.

#### Conclusions

In this study,  $(Si-C_3H_6NPz_2)$  was applied successfully for the removal of MB dye from aqueous solution. Depending on the results,  $(Si-C_3H_6NPz_2)$  was able to remove MB rapidly within 15 min with high removal efficiency at pH around 10, 20°C temperature, 0.25 g weight of dose and initial concentration of 15 mg/L of 50mL MB dye solution. Around 80% removal efficiency of MB dye was achieved after 180 min. at the same condition.

Following conclusions can be made based on experimental data: It was found that adsorption of methylene blue using  $(Si-C_3H_6NPz_2)$  was explained well by Temkin model. Temkin adsorption model has the highest value of regression (0.9856) and thus the best fit. This model includes a factor of adsorbent-adsorbate interactions which points out the existence of this interaction and the results indicate monolayer type exothermic adsorption process involved in the system.

The Langmuir maximum adsorption capacity  $Q_m$  and the  $R_L$  value indicate that adsorption of MB dye onto (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favor. Freundlich model parameters, value of 1/n and n showing that the adsorption of MB dye onto (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) is favorable.

The amount of MB dye adsorbed per unit mass of  $(Si-C_3H_6NPz_2)$  obtained by Lagergren pseudo second order model,  $Q_e(calc.)$  was in agreement with the experimental value,  $Q_e(exp.)$  indicates that the chemisorption may be the rate limiting step where the valence forces are

involved by electrons sharing or exchange between the adsorbent and the adsorbate.

The negative  $\triangle G^{\circ}$  values show that the adsorption is favorable and spontaneous at these temperatures. The negative  $\triangle H^{\circ}$  indicates that the adsorption is an exothermic process and points out that the adsorption is preferable at low temperature.  $\triangle H$  value was higher than those corresponding to physical adsorption. This would suggest that this adsorption is a chemical process. Small positive value of  $\Delta S^{\circ}$  indicates that some structural changes take place on the adsorbent and the entropy at the solid / liquid interface in the adsorption system increases through adsorption process.

Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> is a good effective adsorbent for the removal of MB dye from the wastewater. Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> has lower adsorption capacity compared to many other non-conventional adsorbents. Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub> can provide a convenient way for effective treatment of industrial wastewater polluted with methylene blue under alkaline, low concentration of MB dye at temperature around 20<sup>o</sup>C for removal over 70%.

#### **Suggestions for Future Work:**

- Further investigation is needed to study the mechanism of removing methylene blue using this adsorbent.
- More study on the economic feasibility of the modified silica gel.
- Studying the effect of presence of metal ions in the aqueous medium on MB dye adsorption.

## **Recommendations:**

This new organic-inorganic material can be investigated in various applications. Among these applications is the biological activity of some new amine-modified silica gel against some G(+) and G(-) Bacteria. Another attractive application of such these materials is that may be tested in solar cells.

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# Appendix



A.1: SEM micrographs for the Modified Polysiloxane



A.2: SEM micrographs for the Modified Polysiloxane with Methylene blue

A.3: Thermogravimetric curves of 3-aminopropyl-functionalized silica gel (Si-C<sub>3</sub>H<sub>6</sub>NH<sub>2</sub>)





A.4: Thermogravimetric curves of the modified Polysiloxane surface (Si-



A.5: FT-IR spectra of 3-aminopropyl-functionalized silica gel (Si- $C_3H_6NH_2$ )



A.6: FT-IR spectra of the modified Polysiloxane surface (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>)





## A.7: Data Tables of Experiments

volume = 50mL											
conc.= 20 ppm		т			1 500	( CT					
time = 30 min.			Jata of e	xperimer	nt I: Effe	ect of Te	mperatur	e			
λ = 665 nm											
Abs_before= 2.4	729										
Temp. *C	Temp. *K	wt. of adsorbant (g)	Abs.	% Removal	Ci (mg/L)	Kd (mL/g)	InKa	1/T ( 1/°K)	∆H (J/mol)	∆ S (J/mol K)	∆G (J/mol)
15	288.15	0.1001	0.5443	78.0	4.40	1771.63	7.48	0.00347	-16661.25	1.78	-17174.157
25	298.15	0.1004	1.0008	59.5	8.09	735.46	6.60	0.00335	-16661.25	1.78	-17191.957
35	308.15	0.1004	1.0264	58.5	8.30	704.65	6.56	0.00325	-16661.25	1.78	-17209.757
45	318.15	0.1003	1.0368	58.1	8.39	692.56	6.54	0.00314	-16661.25	1.78	-17227.557
				50.5	9.70	640.76	6.49	0.00205	10001.00	1 70	17046 367

volume = 20mL				
conc.= 20 ppm	Data of E	periment 2: ]	Effect of pH	I
time = 30 min.			_	
<b>λ</b> = 665 nm				
Temp. 25 °C				
sample	pН	wt. of adsorbant (g)	Abs.	% Removal
1	2.44	0.0508	2.8341	0
2	3.96	0.0497	2.8341	0
3	7.40	0.0495	2.6668	5.9
4	8.51	0.0505	2.6587	6.2
5	10.03	0.0501	0.8431	70.3
6	12.11	0.0505	0.8563	69.8
average		0.0502		
volumo – 20ml				

volume = 20mL						
Temp. = 15 oC	Data o	of Experime	ent 3: Effe	ct of MB c	oncentratio	on
time = 30 min.						
λ = 665 nm						
conc. Of MB (ppm)	wt. of adsorbant (g)	рН	Abs.Before	Abs.After	% of removal	Kd (mL/g)
5	0.0418	10.00	0.6601	0.1342	79.7	1897.71
10	0.0408	10.05	1.2756	0.2451	80.8	2036.03
15	0.0417	10.03	1.8711	0.4741	74.7	1426.94
20	0.0410	10.01	2.5710	0.7344	71.4	1211.05
25	0.0411	10.04	2.6592	1.0049	62.2	797.21
	0.0413	10.03			73.8	

volume =	20mL		
Temp. = 1	5 oC	Data o	of Exp.4:
time = 30	min.	Effect	of Dose
<b>λ</b> = 665 nr	n	211000	01 2 000
Abs.= 1.8	791		
pH = 10.0	2		
conc. of N	1B = 15 pp	m	
	wt. of	۸۵۰ ۸	% of
sample	dose (g)	ADS.A	removal
1	0.0151	1.2744	32.2
2	0.0405	0.0045	04.0
<u> </u>	0.0495	0.6615	64.8
3	0.0495	0.6615	64.8 78.0
2 3 4	0.0495 0.0997 0.1486	0.6615 0.4136 0.3656	64.8 78.0 80.5

volume	= 50mL		
Temp. =	20°C	Data o	of exp.5:
λ = 665	nm	Conta	ct Time
pH = 10	.04		
conc. of	MB = 15 p	opm	
wt. of ac	lsorbant =	0.2504 g	
	time		% of
sample	(min.)	ADS.A	removal
0	0	1.8413	0.0
1	15	0.4036	78.1
2	30	0.3770	79.5
3	45	0.3728	79.8
4	60	0.3683	80.0
5	75	0.3648	80.2
6	90	0.362	80.3
7	180	0.329	82.1

volume = 20mL		wt. of adsor	bant (g)= 0.0	413							
Temp. = 15 °C		pH= 10.03				Adsor	ption iso	therm o	f MBD		
time = 30 min.											
λ = 665 nm											
conc. Of MB (ppm)	Abs.Before	Abs.After	% of removal	Ce (MB)	The amount of dye adsorbed per gram of adsorbent (Qe)	Ce/Qe	log Ce	log Qe	In Ce	In Qe	Kd (mL/g)
5	0.6601	0.1342	79.7	1.02	1.93	0.53	0.01	0.29	0.02	0.66	1897.71
10	1.2756	0.2451	80.8	1.92	3.91	0.49	0.28	0.59	0.65	1.36	2036.03
15	1.8711	0.4741	74.7	3.80	5.42	0.70	0.58	0.73	1.34	1.69	1426.94
20	2.5710	0.7344	71.4	5.71	6.92	0.83	0.76	0.84	1.74	1.93	1211.05
25	2.6592	1.0049	62.2	9.45	7.53	1.25	0.98	0.88	2.25	2.02	797.21
average			73.8								

volume = 50mL	0.05	L	Abs.	1.7912			
Temp. = 20°C	293.15	k				kinetics of M	IBD
λ = 665 nm							
pH = 10.04							
conc. of MB = 15 ppm	15	mg/L					
wt. of adsorbant = 0.2504 g	0.2504	g					
sample	time (min.)	Abs.A	Ct	Qt	Qe-Qt	log(Qe-Qt)	t/Qt
0	0	1.7912	15	0.00			
1	15	0.4036	3.38	2.32	0.21	-0.69	6.46
2	30	0.3770	3.16	2.36	0.16	-0.79	12.69
3	45	0.3728	3.12	2.37	0.15	-0.81	18.97
4	60	0.3683	3.08	2.38	0.15	-0.83	25.22
5	75	0.3648	3.05	2.39	0.14	-0.85	31.44
6	90	0.3622	3.03	2.39	0.14	-0.86	37.66
7	180	0.3293	2.76	2.44	0.08	-1.09	73.63
8	360	0.2803	2.35	2.32			
Ce	Qe						

	volume = 20mL		wt. of dose (g)=	0.1002 g
	conc.= 15 ppm		pH=	10.03
	time = 30 min.			
	λ = 665 nm		Recovery of MB	D
	Temp. 15 °C			
sample	Abs.before	Abs.after	% Removal	
1	1.8604	0.4117	77.9	Fresh
2	1.8604	0.4230	77.3	regenerated
3	1.8604	0.4406	76.3	regenerated
average			77.2	

جامعة النجاح الوطنية

كلية الدراسات العليا

# إزالة الميثيلين الأزرق من المياه العادمة الصناعية في فلسطين عن طريق سطح البوليسيلوكسين المعدل مع بايباير ازوليك ثلاثي المستقبلات

إعداد جمال عمر محمد عمارة

## إشراف

أ.د.شحدة جودة

قَدّمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء من كلية الدراسات العليا في جامعة النجاح الوطنية, نابلس فلسطين 2015

إزالة الميثيلين الأزرق من المياه العادمة الصناعية في فلسطين عن طريق سطح البوليسيلوكسين المعدل مع بايباير ازوليك ثلاثي المستقبلات إعداد جمال عمر محمد عمارة إشراف أ.د.شحدة جودة

#### الملخص

تصب العديد من المراكز الصناعية حول العالم الكثير من الملوثات الصناعية كل يوم إلى التربة والمياه السطحية دون معالجة, مما يحمل في طياته خطر تسربها إلى المياه الجوفية, ويؤدي هذا إلى حدوث مشاكل صحية خطيرة على الانسان والكائنات الحية الأخرى.

المشكلة الرئيسية هنا هو الكشف عن تركيز أحد هذه الملوثات مثل المثيلين الأزرق ومحاولة إزالته والتخلص منه عن طريق الامتزاز.

يركز هذا البحث على تعديل سطح البوليسيلوكسين كيميائيا لزيادة قدرته على الامتزاز, وكذلك تشخيص طبيعة سطح البوليسيلوكسين المعدّل واستخدامه في امتزاز المثيلين الأزرق من مياه الصرف الصناعية.

لقد تم تحضير البوليسيلوكسين المعدّل (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) , وقد أجريت عليه جميع الفحوصات المتاحة لتشخيصه والتعرف على خصائص سطحه, حيث أكدت نتائج تحليل FT-IR أن وحدات Dimethylpyrazole قد تم تثبيتها بنجاح على سطح البوليسيلوكسين, كما أظهرت صور المسح الإلكتروني (SEM) أن السطح المعدّل الجديد يتميز بخصائص تجعله قادرا على الامتزاز.

أجريت تجارب عديدة تحت ظروف ومتغيرات مختلفة مثل: درجة الحرارة, درجة الحموضة, تركيز المثيلين الأزرق, كمية المادة المازة ومدة الاتصال, لتحديد الظروف المثلى لأفضل نسبة امتزاز للمثلين الأزرق. وقد لوحظ من خلال هذه التجارب أن نسبة ازالة المثلين الأزرق من المحاليل المائية قد ازدادت مع زيادة درجة الحموضة, كمية المادة المازة ومدة الاتصال, بينما انخفضت هذه النسبة بزيادة تركيز المثلين الأزرق وزيادة درجة الحرارة.

أجريت تجربة على 50 ملليتر من محلول المثلين الأزرق بتركيز 15 ملغم/لتر, حيث تم إزالة أكثر من 70% منه خلال 15 دقيقة الأولى باستخدام سطح البوليسيلوكسين المعدل بينما ارتفعت إلى حوالي 80% بعد مرور 180 دقيقة من زمن الاتصال.

Si- كميات المثلين الأزرق التي تم امتزازها لكل وحدة كتلة من المادة المازة (Si- Si- Q<sub>e</sub>) و  $Q_e$  تم حسابها باستخدام نموذج Lagergren للتفاعلات من الدرجة الثانية, قيمة Q<sub>e</sub>) (2.46) المحسوبة قد توافقت مع قيمة Q<sub>e</sub> (2.53) التجريبية, كما أن عملية الامتزاز يمكن وصفها وفقا لنموذج Temkin حيث (R<sup>2</sup>= 0.99) لهذا النموذج مما يدلل على أن عملية الامتزاز تتضمن قوى تبادل الكتروني تتم من خلاله مشاركة أو تبادل الالكترونات بين المادة المازة والمادة الممتزة. وتشير النتائج كذلك بأن عملية الامتزاز هي من نوع أحادي الطبقة الطارد للحرارة.

قيم  $\Delta G^{\circ}$  السالبة تشير إلى أن عملية الامتزاز موائمة وتلقائية على درجات الحرارة المحددة, كما ان القيمة السالبة لـ  $\Delta H^{\circ}$  تشير إلى أن عملية الامتزاز طاردة للحرارة ومحبذة على درجات حرارة منخفضة لا تتجاوز كثيرا حرارة الغرفة, وكذلك قيمة  $\Delta H^{\circ}$  أعلى بكثير من تلك المصاحبة للامتزاز الفيزيائي مما يؤكد الطبيعة الكيميائية لعملية الامتزاز. القيمة القليلة جدا الموجبة لـ  $\Delta S^{\circ}$  تشير إلى حصول تغيرات هيكلية على سطح المادة المازة, وان الفوضى قد ازدادت بالقرب من سطح الامتزاز أثناء عملة الامتزاز.

تعتبر (Si-C<sub>3</sub>H<sub>6</sub>NPz<sub>2</sub>) مادة فعّالة في إزالة المثيلين الأزرق من مياه الصرف الصناعية بالرغم من انخفاض سعة الامتزاز لها بالمقارنة مع بعض المواد المازة غير التقليدية الأخرى.

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