Moroccan Journal of Chemistry

Removal of methylene blue from industrial wastewater in Palestine using polysiloxane surface modified with bipyrazolic tripodal receptor

S. Jodeh[1]*, J. Amarah[1], S. Radi[2], O. Hamed[1], I. Warad[1], R. Salghi[3], A. Chetouni[2], S. Samhan[4], R. Alkowni[5]

[1]*Department of Chemistry, An-Najah National University, P. O. Box 7, Nablus, Palestine.*
[2]*LCAE-URAC 18, Faculty of Science, University of Mohammed Premier, Po Box 717 60000 Oujda, Morocco.*
[3] *Laboratory of Materials and Environment, University Ibn Zohr, B.P. 8106, 80000, Agadir, Maroc*
[4]*Director of Research and Development Palestinian Water Authority, Ramallah, Palestine*
[5]*Department of Biology, An-Najah National University, P. O. Box 7, Nablus, Palestine.*

**Correspondence Author :E-mail:sjodeh@hotmail.com; Tel: +970599590498; Fax: +97092345982.*

Received 05 Nov 2015, Revised 25 Dec 2015, Accepted 05 Jan 2016

Abstract

Different pollutants from industries leach every day to soil and ground waters without treatment. The product N,N-bis (3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$) was successfully prepared. The FTIR results confirmed that the dimethylpyrazole units have been immobilized onto the surface of the modified silica gel. The adsorption experiments were conducted for a wide range of solution pH, adsorbent dosage, temperature, initial concentration and contact time. It was observed that the percentage removal of methylene blue dye decreased with an increase initial concentration and temperature while it increased with increase in solution pH, contact time and adsorbent dose. Over 82% removal efficiency of methylene blue dye was achieved after 180 min at solution pH around 10, 20°C temperature, 0.25 g weight of dose and initial concentration of 15 mg/L of 50mL MB dye solution.

Negative ΔG° values (-17.17 to -17.25 KJ/mol) indicate that the adsorption is favorable and spontaneous at these temperatures. The negative value of ΔH° (-16.66 KJ/mol) reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. The value of ΔH° was higher than those corresponding to physical adsorption. This would suggest that the adsorption process is chemical in nature. The small positive value of ΔS° (+1.78 J/mol.K) suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process. The results of the present study show that the prepared compound has a negative biological activity against Pseudomonas aeruginosa, Staphylococcus aurous, and Escherichia coli.

***Keywords**: adsorption, methylene blue, bipyrazolic tripodal receptor, kinetics, thermodynamics, wastewater.*

1. Introduction

Pollution is the process of making land, water, air or other parts of the environment dirty and unsafe or unsuitable to use. This can be done through the introduction of a contaminant into a natural environment. 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]. 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]: 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]. Methylene blue dye (MB) is a basic aniline dye 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. 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].

Methylene Blue is a heterocyclic aromatic chemical compound with molecular formula $C_{16}H_{18}N_3SCl$ as shown in **Fig**. 1, with IUPAC chemical name *3,7-bis (Dimethylamino)-phenazathionium chloride Tetramethylthionine 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 [7]. MB and leucomethylene blue exist as a redox couple in equilibrium and together form a reversible oxidation-reduction system or electron donor-acceptor couple [8]. 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 [9]. 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 and (vi) 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. In this study a silica gel material modified with N,N-bis(3,5-dimethylpyrazol-1-ylmethyl) amine (Si-$C_3H_6NPz_2$) will be synthesized and characterized. The obtained product exhibits good chemical and thermal stability [10]. The aim of this study is to remove methylene blue dye from wastewater, using this new prepared material as an adsorbent for the solid-phase extraction of MBD. 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 MBD 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.

2. Experimental Methods

2.1 Chemicals and Materials

All solvents and other chemical were of analytical grade and used without further purification. Silica gel (Sigma-Aldrich, purity ≥ 98.5%) with particle size in the range 40-63 µm, extent of labeling: ~1 mmol/g loading NH_2. The chelating agent 3,5-Dimethylpyrazole-1-methanol (Sigma-Aldrich, purity ≥ 99%) was used without purification. 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_3 (0.1M) and KOH (0.1M) were used for pH adjustment.

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 at a heating rate of 50°C/min and in N_2 gaseous atmosphere.

2.2 synthesis of N,N-bis (3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$)

A mixture of 3-aminopropyl-functionalized silica gel (Si-$C_3H_6NH_2$) (5 g, approximately 5.1 mmol-NH_2) and an excess of 3,5-Dimethylpyrazole-1-methanol (about 2.0 g, 15.9 mmol) in 50 mL of dry acetonitrile were stirred at room temperature for 7 days. NH_2-group onto the silica surface was capable to react with 3,5-Dimethylpyrazole-1-methanol under moderate conditions (at room temperature, atmospheric pressure, 4–7 d), using anhydrous acetonitrile as solvent. After being filtered, the solid product was washed with several portions of methanol and dichloromethane respectively. The product *N,N*-bis (3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$) was dried in a desiccators for 2 days then it was dried under vacuum at 70°C for 3 h. The synthesis procedure is shown in Scheme 1.

Scheme 1: The synthesis procedure of (Si-$C_3H_6NPz_2$)

2.3 Characterization of (Si-$C_3H_6NPz_2$)

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 confirmed by FT-IR analysis to show that the dimethylpyrazole units have been immobilized onto the surface of the modified silica gel. Thermal stability of polysiloxane derivatives (Si-$C_3H_6NH_2$) and (Si-$C_3H_6NPz_2$) have been determined by thermogravimetric analysis (TGA).

2.4 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.

2.5 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 the absorbance was determined at different wavelengths to obtain a plot representing the absorbance versus wave length. The wave length corresponding to maximum absorbance was obtained from this plot was 665 nm.

At high concentrations of MB the Beer Lambert relationship breaks down and gives a non-linear relationship, so our work was restricted at concentration up to 25 mg/L. At higher concentrations the individual particles of analyte no longer behave independently of one another. A reason for that is the absorptivity, a, and molar absorptivity, ε, depend on the sample's refractive index. Since the refractive index varies with the analyst's concentration, the values of a and ε will change. For sufficiently low concentrations of analyte, the refractive index remains essentially constant, and the calibration curve is linear [11]. Some large ions or molecules show deviations even at very low concentrations, for e.g. methylene blue absorptivity at 436 nm fails to observe Beer Lambert law even at concentrations as low as 10μM [12].

2.6 Adsorption Experiments

The maximum absorbance (λ_{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_3 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 effects of pH, temperature, dose of adsorbent, concentration of MB solution and the contact time on the adsorption of MB dye were studied. The adsorption capacity was investigated using kinetics and pH effects. Equilibrium Isotherm studies were done by varying the following parameters: initial concentration of MB dye solution, temperature, and adsorbent dose on the uptake of dye from the solution. At the end of time intervals, adsorbent was removed by centrifugation at 600 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

The percentage removal dye is defined as the ratio of difference in dye concentration before and after adsorption (C_i-C_f) to the initial concentration of dye in the aqueous solution (C_i) and was calculated according to the following equation. Eq. 1 [4, 13]:

$$\% \, Removal = \frac{(C_i - C_f)}{C_i} \times 100\% \quad (1)$$

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

2.6.1 Effect of temperature

For studying the effect of temperature 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 time intervals, adsorbent was removed by centrifugation at 600 rpm and supernatant was analyzed by UV-visible spectrophotometer (UV-1601, SHIMADZU) for the residual concentration of MB, at 665 nm wavelength.

2.6.2 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_3 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 time intervals, adsorbent was removed by centrifugation at 600 rpm and supernatant was analyzed by UV-visible spectrophotometer for the residual concentration of MB, at 665 nm wavelength.

2.6.3 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^oC) and pH 10 for 30 min. The absorbance of supernatant was measured by using UV-spectrophotometer.

2.6.4 Effect of adsorbent dose

The effect of amount of adsorbent 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 supernatant was measured by UV-visible for the residual concentration of MB dye.

2.6.5 Optimization of contact time

The adsorption of MB dye on the adsorbent was studied as a function of shaking time at 20^oC. 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 Spectrophotometer at wavelength 665 nm.

2.7 Thermodynamics and Kinetics of Adsorption

The removal of methylene blue dye was studied by adsorption technique using the prepared adsorbent (Si-$C_3H_6NPz_2$). The batch technique was adopted under the optimize condition of dose of adsorbent, contact time, concentration, temperature and pH. By using UV-spectrophotometer, concentration of dye was measured before and after adsorption. The removal data were fitted into the Langmuir, Freundlich and Temkin adsorption isotherm equations. The values of their corresponding parameters were determined. Thermodynamic parameters like free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the systems were calculated by using Van't Hoff's plot. The values of % removal and K_d for dye systems were calculated at different temperatures ranging (15 – 55°C) with intervals of 10°C.

A 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 adsorption rate was monitored by studying the contact time up to 6 h and compared to theoretical models. Pseudo first order and pseudo second order kinetic models were tested in this study where the experimental data obtained for various contact time were used. Pseudo first order and pseudo second order kinetic model parameters (K, Q_e and R^2) for MB dye adsorption on Si-$C_3H_6NPz_2$ were determined. The values of the calculated and experimental Q_e were compared.

3. Results and Discussion

3.1 Modified Polysiloxane (Si-$C_3H_6NPz_2$) Characterization

3.1.1 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 (**Fig**. 1) of the Modified Polysiloxane surface show rough and porous nature, indicating that the materials present good characteristics to be employed as an adsorbent.

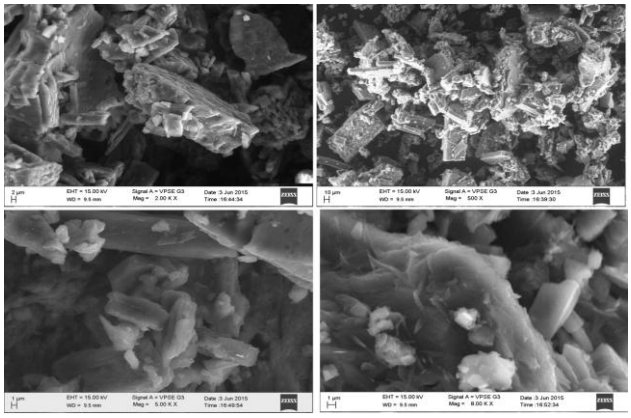


Fig. 1: SEM micrographs of the modified Polysiloxane surface (Si-$C_3H_6NPz_2$)

3.1.2 FT-IR Characterization

The modified silica gel was confirmed by FT-IR analysis. As shown in **Fig**. 2, the sharp band around 1060 cm^{-1} corresponds to Si-O-Si anti-symmetric stretching vibrations. The characteristic absorption band of the 3-aminopropyl-functionlized silica gel (Si-$C_3H_6NH_2$) for N-H bond was observed at 1590 cm^{-1}. On the spectrum of the final material (Si-$C_3H_6NPz_2$), it was noticed the disappearance of the absorption band at 1590 cm^{-1} which gives evidence at the reactivity of the primary amine (–NH_2) and the appearance of new

characteristic weak bands around 1500 cm^{-1} and 1600 cm^{-1} resulted from C=C stretching vibrations in ring and another band around 1700 cm^{-1} corresponds
to C=N stretching vibration. This confirms that the dimethylpyrazole units have been immobilized onto the surface of the modified silica gel [10].

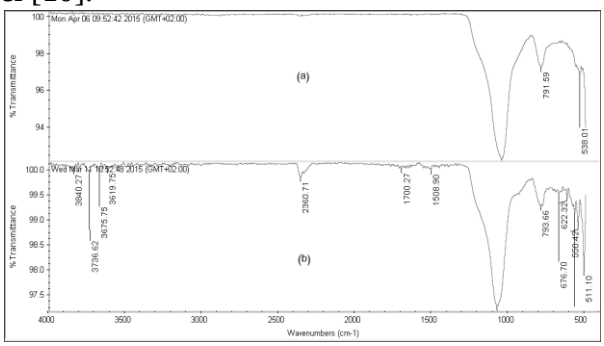


Fig. 2: FT-IR spectra of (a) 3-aminopropyl-functionalized silica gel (Si-$C_3H_6NH_2$) (b) and the modified Polysiloxane surface (Si-$C_3H_6NPz_2$)

3.1.3 TGA Analysis and Thermal Stability

Thermal stability of polysiloxane derivatives (Si-$C_3H_6NH_2$) and (Si-$C_3H_6NPz_2$) have been determined by thermogravimetric analysis. The thermogravimetric curves reflect the thermal stability of this new product. The quantity decomposed in each stage confirms the amount of the compounds grafted. As can be seen from **Fig**. 3a, the 3-aminopropyl-silica (Si-$C_3H_6NH_2$) presents a weight loss, after the drainage of physically adsorbed water, mainly attributed to the organic arm. The final material (Si-$C_3H_6NPz_2$) showed also an increase of mass loss allotted to the decomposition of the pyrazolic fraction immobilized on the surface of silica gel, as shown in **Fig**. 3b. The pronounced increase in mass loss reflects the higher amount of the anchored organic groups [8, 14, 16]. The profile indicates a degradation process between 170 and 800 °C which confirms the high thermal stability for the prepared material [15].

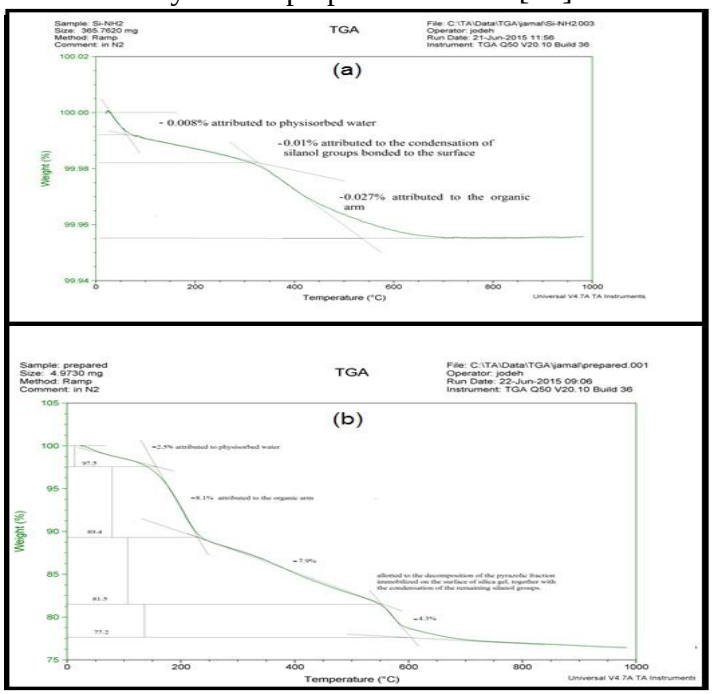
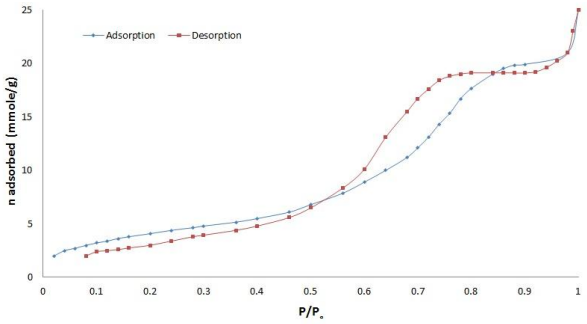


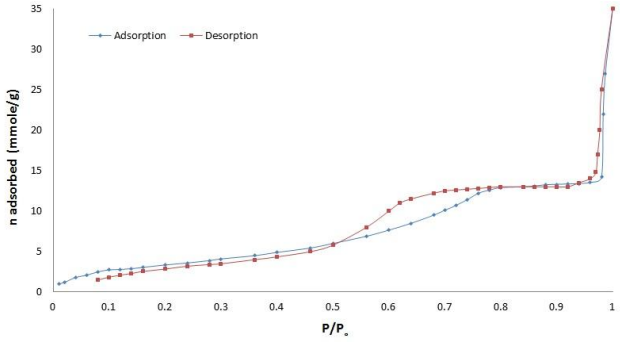
Fig. 3: Thermogravimetric curves of (a) 3-aminopropyl-functionalized silica gel (Si-$C_3H_6NH_2$) (b) modified Polysiloxane surface (Si-$C_3H_6NPz_2$).

3.1.4 Surface properties

The surface area S_{BET} (Brunauer–Emmett–Teller), pore volumes, and pore diameters of both porous silica and its derivatives were measured with nitrogen adsorption–desorption isotherms and Barrett–Joyner–Halenda (BJH) pore diameters methods [16,17]. The density of the groups covalently attached to the inorganic silica changes the characteristics of the surface. Thus, the initial specific surface area (S_{BET}) of 550 m^2 g^{-1} decreases as the immobilization takes place to give 332.1 m^2 g^{-1} determined through the BET equation (**Fig**. 4a). A decrease in S_{BET} is mainly due to the presence of the organic moieties that can block the access nitrogen to the silica base.



(a)



(b)

Fig.4: Nitrogen adsorption–desorption isotherm plots of 3-aminopropyl-functionalized silica gel ($SiC_3H_6NH_2$) (a) and N,N-bis(3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$)(b).

On the other hand, we observed that Si-$C_3H_6NPz_2$ has a further decrease BET surface area (**Fig**. 4b) as additional groups were grafted to give 312.8 m^2/g. The modified polysiloxane has a smaller surface area compared with the untreated polysiloxane; its adsorption capacity is higher than that for the untreated one which likely arises from its amino groups. This would suggest that the adsorption process is chemical in nature, where valence forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate. The unpaired electrons of nitrogen of amino groups are responsible for this adsorption which works for complex properties [18].

3.2 Investigation of adsorption parameters

3.2.1 Effect of pH on MB dye adsorption

The pH of a solution is an important factor affecting the adsorption capacities of adsorbents, especially those containing functional groups like amino groups, which can be easily protonated or deprotonated to form different surface charges in solutions at different pH [13, 19]. Lower adsorption of Methylene blue at low pH is probably due to the presence of H^+ ions competing with the cations groups on the MB dye for adsorption sites, there by inhibiting the adsorption of dye [4]. In addition, the basic dye will become protonated in the acidic medium and the positive charge density would be located more on the dye molecules at low pH results the lower uptake [13]. To evaluate the effect of pH on the adsorption capacity of the modified Polysiloxane surface (Si-$C_3H_6NPz_2$), the adsorption experiments were carried out in solutions having different pH values. **Fig**. 5a shows the effect of the pH value on the uptake of MB dye from its

aqueous solution by (Si-$C_3H_6NPz_2$). The results show an increase of MB dye uptake as the pH value is increased. The uptake reached its maximum at pH 10. Low uptake capacity occurs at lower pH values, this is probably due to protonation of ligand nitrogen atoms. At low pH, the retention of MB dye by the (Si-$C_3H_6NPz_2$) is not significant since the ligand is entirely in its protonated form.

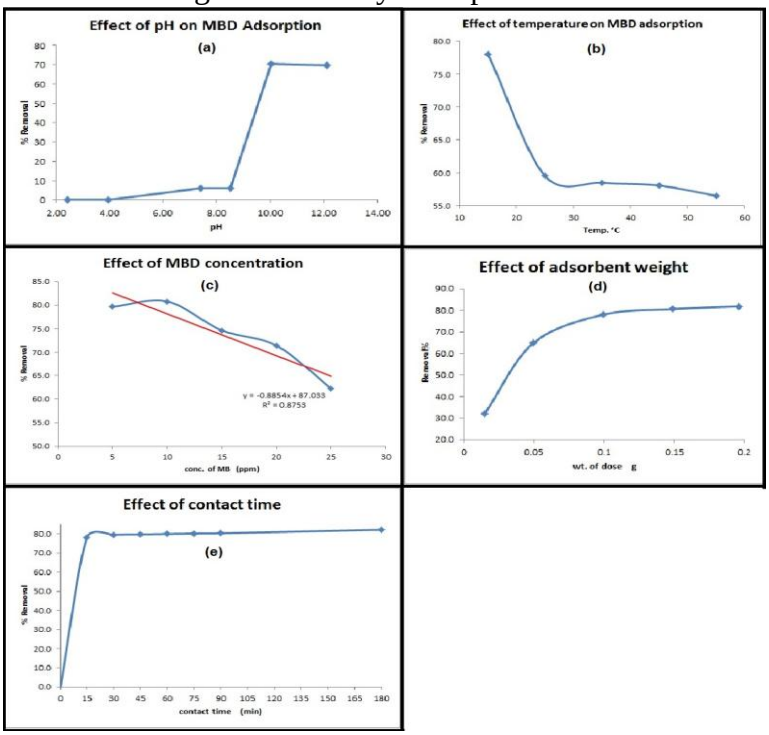


Fig. 5: The percentage removal of Methylene blue dye under different conditions. The adsorption experiments were conducted for a wide range of (a) pH (b) temperature (c) MB dye concentration (d) adsorbent weight and (e) contact time.

3.2.2 Effect of temperature 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^oC) as shown in **Fig**. 5b. This **Fig**ure shows 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 influence on decreasing the adsorption capacity of the new modified surface. The maximum adsorption (78%) was achieved at 15^oC. This indicates that the adsorption of MB dye on (Si-$C_3H_6NPz_2$) follows exothermic process.

3.2.3 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 such as adsorbent dose, volume of solution, adsorbent size, and solution pH as constant. The results are presented in **Fig**s 5c and 6d. It can be noticed from these **Fig**ures 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. That is because, 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]. Percentage removal of MB dye decreased from 80% to 62%. The 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 ppm. When

all sites are occupied, the adsorption becomes nearly constant whatsoever concentration of dye is increased. This suggests formation of monolayer on the modified Polysiloxane surface [4].

3.2.4 Effect of amount of adsorbent

The effect of the amount of adsorbents on the removal of methylene blue was investigated. Initial concentration of methylene blue solution was kept constant at 15 mg/L, initial volume was 20 mL, pH was 11.42 and temperature was 15^{o}C. The results were represented in **Fig**. 6 shows that removal efficiency was increased sharply with increasing amount of adsorbent up to 0.1 g. Then removal efficiencies were not changed significantly with increasing amount of adsorbent. It shows that removal efficiency was 78% when the amount was 0.1 g. For 0.15 g, it was 80.5% and 81.8% for 0.2 g. That is adsorption efficiency increased due to the increased number of adsorption sites [13]. Therefore, removal efficiency reached in equilibrium with the amount of 0.1 g of adsorbent.

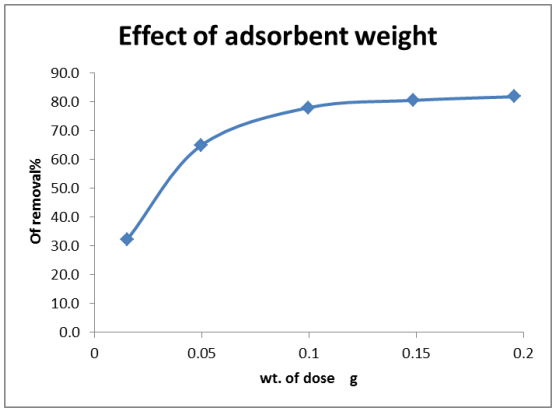


Fig. 6: Effect of amount of adsorbent on the removal of MB dye. (Temp.= 15^{o}C, time= 30 min., pH= 11.42, conc. Of MB dye= 15 mg/L, sol. Volume= 20 mL)

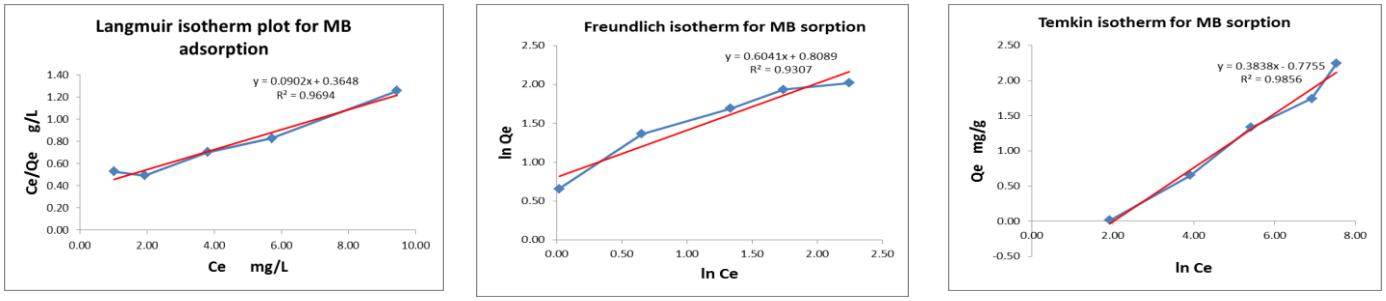
3.2.5 Effect of contact time

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 **Fig**. 5e.

The MB dye showed a fast rate of adsorption during the first 15 min, and then the rate of adsorption becomes almost insignificant after that due to consuming of the adsorbing sites. The rate of adsorption capacity is high in the beginning due to large surface area of the adsorbents available for the adsorption of MB dye. At the beginning of the adsorption process all the reacting sites are vacant and hence the extent of removal is high. After the rapid initial uptake, the rate of uptake was very slow reaching almost a constant value [21, 22].

3.3 Adsorption isotherm of MB dye

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to find the maximum adsorption capacity. Equilibrium data can be analyzed using commonly known adsorption systems. Several mathematical models can be used to describe experimental data of adsorption isotherms. The Freundlich, Langmuir and Temkin models are employed to analysis adsorption occurred in the experiment data of adsorption isotherms [23].



(a) (b) (c)

Fig. 7: Adsorption isotherm plots of MB dye (a) Langmuir (b) Freundlich and (c) Temkin. (Temp.= 15oC, pH= 11.8, time= 30 min., sol. Volume= 20 mL, adsorbent dose= 0.0413 g)

3.3.1 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. Eq. 2 [20-32]:

$$\frac{C_e}{Q_e} = \frac{1}{Q_m} C_e + \frac{1}{Q_m K_L} \quad (2)$$

Where:

C_e= the equilibrium concentration of adsorbate (mg/L); Q_e= the amount of MB dye adsorbed per gram of the adsorbent (mg/g); Q_m= maximum monolayer coverage capacity (mg/g); K_L= Langmuir isotherm constant (L/mg).

The values of Q_m and K_L were computed from the slope and intercept of the Langmuir plot of C_e/Q_e versus C_e. From Langmuir plots which is shown in **Fig**. 7a 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 1.

Table. 1: Parameters and correlation coefficient of Langmuir, Freundlich and Temkin for adsorption of MB dye on (Si-$C_3H_6NPz_2$).

Langmuir isotherm model parameters				
Adsorbate	Parameters			
	Q_m (mg/g)	**K_L= (L/mg)**	**R_L**	**R^2**
(Si-$C_3H_6NPz_2$)	11.09	0.25	0.138	0.9694
Freundlich isotherm model parameters				
Adsorbate	Parameters			
	1/n	**n**	**K_F** (mg/g (L/mg)$^{1/n}$)	**R^2**
(Si-$C_3H_6NPz_2$)	0.602	1.66	2.25	0.9307
Temkin isotherm model parameters				
Adsorbate	Parameters			
	A (L/g)	**b** (J/mol)	**B**	**R^2**
(Si-$C_3H_6NPz_2$)	0.1326	6242	0.3838	0.9856

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given by Eq. 3 [12, 25-29]:

$$R_L = \frac{1}{(1+K_L C_o)} \quad (3)$$

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

The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The R_L values between 0 and 1 indicate favorable adsorption. The value of R_L in the present investigation was found to be 0.138 at 15 °C indicating that the adsorption of MB dye on (Si-$C_3H_6NPz_2$) is favorable [12, 28].

3.3.2 Freundlich model Isotherm

The Freundlich isotherm is an empirical equation employed to describe heterogeneous systems. This model is specified with Eq. 4 [20-32]:

$$Q_e = K_F C_e^{1/n} \quad (4)$$

The linear form of this equation can be written as Eq. 5[20-32]:

$$\ln Q_e = \frac{1}{n} ln\, C_e + lnK_F \quad (5)$$

Where K_F and n are Freundlich constants with K_F is an approximate indicator of adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent, 1/n, gives an indication of the favorability of adsorption. If value of 1/n is below one it indicates a normal adsorption. If n lies between one and ten, this indicates a favorable sorption process [20, 24]. To determine the constants K_F and n, the linear form of the equation may be used to produce a graph of ln(Q_e) against ln(C_e) as shown in **Fig**. 7b. Freundlich constants K_F and n and regression constant (R^2) were determined and values are shown in Table 1:

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 [20]. From the data in Table 1, that value of 1/n = 0.6041 while n=1.66 indicating that the sorption of MB dye on (Si-$C_3H_6NPz_2$) is favorable and the R^2 value is 0.9307.

3.3.3 Temkin model Isotherm

This isotherm contains a factor that taking into the account of adsorbent–adsorbate interactions and suggested that because of these interactions the heat of adsorption of all the molecules in the layer would decrease linearly with coverage [20]. The model is given by the following equation [21, 25]:

$$Q_e = BlnC_e + BlnA \quad (6)$$

where B = 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 (°K). By plotting Q_e versus (ln C_e) as shown in **Fig**. 8c the constants A and b can be calculated. The constants A and B are listed in Table 1. 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. 1.

Three adsorption isotherm models were studied. The sorption data fitted into Langmuir, Freundlich, and Temkin. From Langmuir isotherm data in Table 4, the value of R_L in the present 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. 1, that value of 1/n = 0.6041 while n=1.66 indicating that

the sorption of MB dye on (Si-$C_3H_6NPz_2$) is favorable and the R^2 value is 0.9307. Larger value of n (smaller value of 1/n) implies stronger interaction between the adsorbent and the adsorbate [25-26]. 1/n ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, which may become more heterogeneous when 1/n gets close to zero [22]. The sorption data fitted into Langmuir, Freundlich, and Temkin out of which Temkin adsorption model was found to have the highest regression value and hence the best fit. This isotherm contains a factor that taking into the account of adsorbent–adsorbate interactions which indicates the presence this interaction.

3.4 Adsorption Thermodynamics

Adsorption thermodynamics were determined using the thermodynamic equilibrium coefficients obtained at different temperatures and concentrations in order to verify possible adsorption mechanisms. The adsorption characteristics of a material can be expressed in terms of thermodynamic parameters such as ΔG (Gibbs free energy change), which can be calculated by Eq. 7 [26]:

$$\Delta G = -RTlnK_d \quad (7)$$

Where K_d is the thermodynamic equilibrium constant (L g^{-1}).

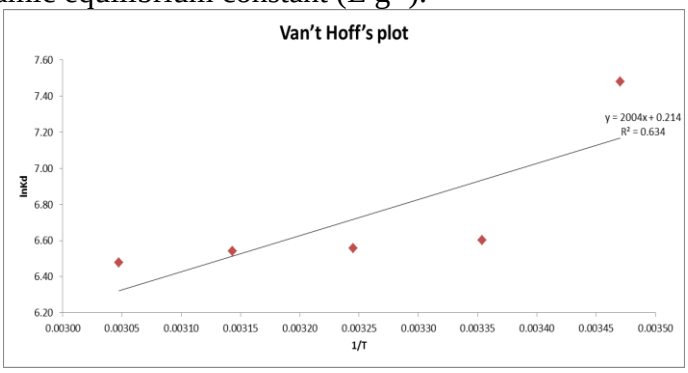


Fig. 8: Plot of lnK_d versus 1/T for MB dye adsorption on (Si-$C_3H_6NPz_2$). (Temp.= 15°C, pH= 11.8, time= 30 min., sol. Volume= 20 mL, adsorbent dose= 0.0413 g)

According to thermodynamics, the Gibbs free energy is the difference between the adsorption enthalpy (ΔH) and adsorption entropy (ΔS) multiplied by the temperature. In this manner, by applying this concept to Equation (7), the thermochemical parameters ΔH and ΔS can be determined using Van't Hoff's plot (**Fig**. 8) , according to Eq. 8 [26]:

$$lnK_d = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

$\triangle H^\circ$ and $\triangle S^\circ$ were calculated from the slope and intercept of the linear plot of lnK_d versus 1/T respectively. The results show that the enthalpy of adsorption $\triangle H^\circ$ was −16.66 kJ mol^{-1} and $\triangle S^\circ$ was 1.78 J mol^{-1} K^{-1}. $\triangle G^\circ$ was calculated at different temperatures from the following Eq.9 [30]. The obtained thermodynamic values are given in Table. 2.

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (9)$$

Table . 2: The values of the thermodynamic of MB dye adsorption at various temperatures.

Adsorbent	**$\triangle H^o$(KJ/mol)**	**$\triangle S^o$ (J/mol.K)**	**$\triangle G^o$ (KJ/mol)**				
			288 K	298 K	308 K	318 K	328 K
Si-$C_3H_6NPz_2$	-16.66	1.78	-17.17	-17.19	-17.21	-17.23	-17.25

The negative $\triangle G^o$ values indicate that the adsorption is spontaneous at these temperatures. The negative value of $\triangle H^o$ reflects an exothermic adsorption and indicates that the adsorption is favored at low temperature. The enthalpy change value ΔH for physical adsorption is generally smaller than that of chemical adsorption. Typically, ΔH for physical adsorption ranges from 0-40 KJ/mol compared to that of chemical adsorption ranging from 40-800 KJ/mol. The value of ΔH was higher than those corresponding to physical adsorption. This would suggest that the adsorption process is chemical in nature. The small positive value of ΔS° suggests that some structural changes occur on the adsorbent and the randomness at the solid/liquid interface in the adsorption system increases during the adsorption process [30].

3.5 Adsorption kinetics of MB dye

The study of adsorption kinetics is significant as it provides valuable insights into the reaction path ways and into the mechanism of the reactions. The adsorption rate was monitored by studying the contact time up to 6 h and compared to theoretical models. Pseudo first order and pseudo second order kinetic models were tested in this study where the experimental data obtained for various contact time were used.

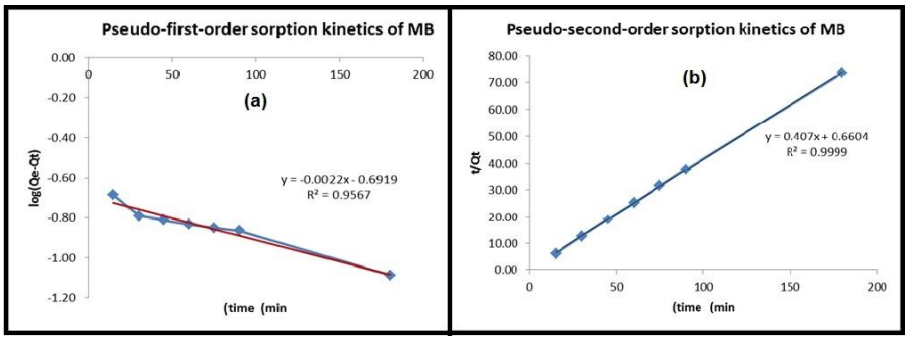


Fig. 9: (a) Pseudo first order (b) Pseudo second order adsorption kinetics of MB dye on (Si-$C_3H_6NPz_2$). (Temp.= 20°C, pH= 10.7, sol. Volume= 50 mL, adsorbent dose= 0.2504 g).

The rate constant for the adsorption of methylene blue from dyeing effluents onto adsorbent (Si-$C_3H_6NPz_2$) was determined using the pseudo first order equation (Lagergren equation) Eq. 10 [24, 27, 29]:

$$\log(Q_e - Q_t) = \log Q_e - \left(\frac{K_1}{2.303}\right) t \qquad (10)$$

Where Q_e is the adsorption capacity of the Si-$C_3H_6NPz_2$ 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^{-1}).

Table. 3: Pseudo first order and pseudo second order kinetic model parameters for MB dye adsorption on Si-$C_3H_6NPz_2$ at 20°C.

Adsorbent	**$Q_{e\ (exp)}$** (mg/g)	**Pseudo first order**			**Pseudo second order**		
		K_1 (min^{-1})	**$Q_{e\ (calc)}$** (mg/g)	**R^2**	**K_2** (g/mg min)	**$Q_{e\ (calc)}$** (mg/g)	**R^2**
Si-$C_3H_6NPz_2$	2.53	5.07×10^{-3}	0.203	0.9567	406.01×10^{-3}	2.46	0.9999

A linear plot of $\log(Q_e - Q_t)$ against time allows to obtain the rate constant (**Fig**. 9a). If the plot was found to be linear with good correlation coefficient, indicating that Lagergren's equation is appropriate to MB dye

sorption on Si-$C_3H_6NPz_2$ so the adsorption process is a pseudo first order process. The Lagergren's first order rate constant (K_1) and Q_e determined from the model are presented in Table. 3 along with the corresponding correlation coefficients. It was observed that the pseudo first order model did not fit well. It was found that the calculated Q_e values do not agree with the experimental Q_e value (Table. 3). This suggests that the adsorption of MB dye does not follow first-order kinetics [24]. The pseudo second order kinetics may be expressed in a linear form as integrated second order rate law. Eq. 11 [22, 29-30]:

$$\frac{t}{Q_t} = \frac{1}{Q_e}t + \frac{1}{K_2 Q_e^2} \qquad (11)$$

Where K_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}). The results show that the pseudo second order kinetic model fits perfectly the experimental data with linear regression coefficients 0.9999 (**Fig**. 9b) [30]. A pseudo second order suggests that this adsorption depends on the adsorbate as well as the adsorbent and involves chemisorption process in addition to physicsorption. The chemisorption might be the rate limiting step where valence forces are involved via electrons sharing or exchange between the adsorbent and the adsorbate [22, 27]. The values of the calculated and experimental Q_e are represented in Table 3. It can be seen from Table 6 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 better represented the adsorption kinetics.

3.6 Recovery of MB dye and reusability of the adsorbent

The recovery of the dye from the Si-$C_3H_6NPz_2$ was carried out at 20 ˚C. The adsorbent was collected by filtration, washed with portions of 6N HCl then washed with deionized water, and left to dry at room temperature for two days. The adsorption capacity of the regenerated Si-$C_3H_6NPz_2$ was tested under similar conditions and compared to the first use. A 0.1 g of the regenerated adsorbent was added to a 20 mL of 15 ppm MB dye solution at pH 11. The comparison of the uptake capacity of the recycled adsorbent (**Fig**. 10) showed an excellent adsorption ability and has a good stability and can be reused many times without decreasing its extraction percentage [33]. MB dye desorption experiments were studied for the purpose of recovering and reusing the adsorbent.

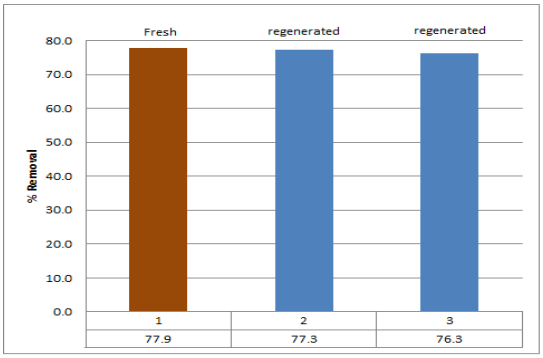


Fig. 10: Percentage of MB dye removal by the regenerated adsorbent compared with a fresh one at (Temp.= 15°C, pH= 11.03, sol. Volume= 20 mL, adsorbent dose= 0.1002 g, contact time= 30 min)

3.7 Studying the Antimicrobial Activity of Si-$C_3H_6NPz_2$

N,N-bis(3,5-Dimethylpyrazol-1-ylmethyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$) and Si-$C_3H_6NPz_2$ with adsorbed copper 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. A 10 mg of Si-$C_3H_6NPz_2$ were dissolved in 1 ml of 10% Dimethyl sulfoxide (DMSO). After agar plate was inoculated by streaking with bacteria-inoculated swab over the entire sterile 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 (**Fig**. 11) [31, 32].

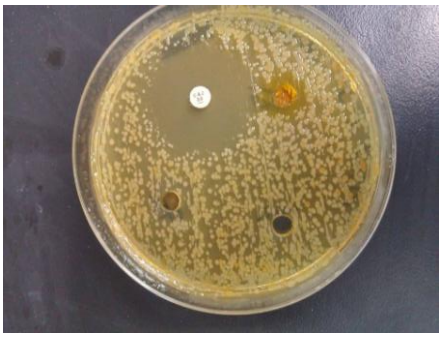


Fig. 11: Antimicrobial Activity of Si-$C_3H_6NPz_2$, all plates were showed negative results for Si-$C_3H_6NPz_2$ and the formula+Cu.

Conclusions

The product N,N-bis (3,5-Dimethylpyrazol-1-yl methyl)-3-aminopropyl Polysiloxane (Si-$C_3H_6NPz_2$) was successfully prepared by reacting of 3-aminopropyl-functionalized silica gel (Si-$C_3H_6NH_2$) with excess of 3,5-Dimethylpyrazole-1-methanol by stirring for 7 days under moderate conditions; at room temperature and atmospheric pressure. The FTIR results confirmed that the Dimethylpyrazole units have been immobilized onto the surface of the modified silica gel. SEM images of the Modified Polysiloxane surface showed rough and porous nature, indicating that the materials present good characteristics to be employed as an adsorbent. The sorption of MB dye on the (Si-$C_3H_6NPz_2$) was optimized under alkaline conditions and low 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 adsorption experiments were conducted for a wide range of solution pH, adsorbent dosage, temperature, initial concentration and contact time. It was observed that the percentage removal of Methylene blue dye decreased with an increase initial concentration and temperature while it increased with increase in solution pH, contact time and adsorbent dose. Over 82% removal efficiency of Methylene blue dye was achieved after 180 min. at solution pH around 10, 20oC temperature, 0.25 g weight of dose and initial concentration of 15 mg/L of 50mL MB dye solution.

Acknowledgement

The authors would like to thank MEDREC and Palestinian Water Authority for supporting for my graduate student during his master thesis doing this study. We would like to thank the Arab Union Universities and the Palestinian Ministry of Higher Education for their financial support of this project.

References

[1] C. Schreiber, A. Rechenburg, E.Rind, T. Kistemann, Int. J. Hygiene and Environ. Health218(2015)181-187.
[2] I. Ali, M. Asim, T. A. Khan, J. Environ. Manage 30(2012) 170-183.
[3] R. Sivaraj, R. Venckatesh, A. Gowrl, G. Sangeethan, International Journal of Engineering Science and Technology, 2(2010) 2418-2427.
[4] M. Rahman, S. M. Amin, A. M. Alam, International Dhaka Univ. J. Sci 60(2012) 185-189.
[5] A. M. A. Shehata, International Journal of Emerging Technology and Advanced Engineering, 3(2013) 507-513.
[6] Y.C. Wong, M.S.R. Senan, N.A. Atiqah, Journal of Basic and Applied Sciences, 9(2013) 172-177.
[7] A, Miclescu, L. Wiklund, Romanian Journal of Anesthesiology and Intensive Therapy, 17(2010) 35-41.
[8] A. Tani, A. J. Thomson, J. N. Butt, Analyst, 126(2001) 1756-1759.
[9] J. Walter, J. R.Weber, ADSORPTION PROCESSES, The University of Michigan, College of Engineering, Ann Arbor, Michigan 48104, USA.
[10] S. Radi, S. Tighadouini, Y. Toubi, M. Bacquet, Journal of Hazardous Materials, 185 (2011) 494–501.
[11] O. N. Gadomsky, I. A. Shchukarev, Communication 348(2015) 38-42.
[12] Akul Mehta, Ultraviolet-Visible (UV-Vis) Spectroscopy – Limitations and Deviations of Beer-Lambert Law, Analytical Chemistry, Notes, May 14(2012), http://pharmaxchange.info
[13] J. Qi, X. Li, H. Zheng, P. Li, H. Wang, J. Hazardous. Materials, 293(2015) 105-111.
[14] S, Radi, N. Basbas, S. Tighadouini, M. Bacquet, Journal of Surface Engineered Materials and Advanced Technology, 4(2014) 21-28.
[15] S. Radi, S. Tighadouini, M. Bacquet, S. Degoutin, F. Cazier, M. Zaghrioui, Y. N. Mabkhot, Molecules 19(2014) 247-262.
[16] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60(1938)309–319.
[17] I. A. Banerjee, L. Yu, H. Matsui, Proc. Natl. Acad. Sci. U.S.A. 100(2003)14678–14682.
[18] S. Tascioglu, U. Koklu, Chim. Acta Turc. 14 (1986) 387–394.
[19] S. Radi, Y. Toubi, S. Tighadouini, M. Baequet, Indian Journal of Chemical Technology, 20(2013) 423-428.
[20] A. O. Dada, A. P. Olalekan, A. M. Olatunya, O. Dada, IOSR Journal of Applied Chemistry, 3(2012) 38-45.
[21] S. Shaibu, F. Adekola, H. Adegoke, O. Ayanda, Materials 7(2014) 4493-4507.
[22] H. Kamal, J. American. Sci 10(2014) 125-133.
[23] F. Gimbert, N. Morin-Crini, F. Renault, P. M. Badot, G. Grini, J. Hazardous Materials, 157(2008) 34-46.
[24] B.H. Hameed, D. K. Mahmoud, A. L. Ahmad, Journal of Hazardous Materials 158 (2008) 65–72.
[25] S. A. Umoren, U. J. Etim, A. U. Israel J. Mater. Environ. Sci. 4 (2013) 75-86.
[26] Z. Shahryari, A. Goharrizi, M. Azadi, International Journal of Water Resources and Environmental Engineering, .2 (2010) 16-28.
[27] S. Patil, S. Renukdas, N. Patel, International Journal of Environmental Sciences, 1(2011) 711-725.
[28] M.M. Abd El-Latif, A. Ibrahim, M. F. El Kady, Journal of American Science 6(2010) 267-283.
[29] J. Joseph, N. Xavier, Nature and Science J, 11(2013) 53-58.
[30] L. Abramian, H. El-Rassy, , Chemical Engineering Journal, 150 (2009) 403–410.
[31] D. L. Venton, E. Gudipati, , Biochim Biophys Acta. 1250(1995) 117-125.
[32] P. Zou, X. Yang, J. Wang, Y. Li, H. Yu, Y. Zhang, G.Liu, Food Chemistry, 190(2016) 1174-1181.
[33] S. Taha, M. Amer, A. Elmasrafy, M. Elkady,. J. Environ. Chem. Eng. 2(2014) 2013-2025.