An-Najah National University

Faculty of Graduate Studies

Removal of Acetylsalicylic Acid from Water Using N-Pyrazole Modified Silica Gel

By
Haya Basem Akkad

Supervisor

Dr. Ibrahim Abu Shqair

Co- Supervisor

Prof. Shehdeh Jodeh

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This Thesis was Defended Successfully on 23/6/2020, and approved by:

<u>Defense Committee Members</u>	<u>Signature</u>
– **Dr. Ibrahim Abu Shqair / Supervisor**	....
– **Prof. Shehdeh Jodeh / Co. Supervisor**	....
– **Dr. Subhi Samhan / External Examiner**	....
– **Dr. Nidal Zatar / Internal Examiner**	....

III

Dedication

First of all, my greatest gratitude to Allah,

To my great parents, who never stop giving of themselves

in countless ways,

To my beloved sisters and brothers, who stands by me

when things look bleak,

To my homeland Palestine, the warmest womb,

To my teachers, who taught us the purpose of life,

To my friends, who encourage and support me,

To all who help and encourage me in any way,

I dedicate this research.

Acknowledgement

V

الإقرار

أنا الموقعة أدناه مقدمة الرسالة التي تحت عنوان:

Removal of Acetylsalicylic Acid From Water Using N-Pyrazole Modified Silica Gel

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

<u>Declaration</u>

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

Student's Name: اسم الطالبة: هيا باسم عقاد

Signature: التوقيع:

Date: التاريخ: 2020/6/23

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List of Abbreviations

ASA	Acetylsalicylic Acid
SiPz	N-Pyrazole Modified Silica Gel
C_o	Initial concentration of adsorbate in the solution
C_e	CEquilibrium concentration of adsorbate in the solution
C_t	Concentration of adsorbate in the solution at time t
q_e	Amount of adsorbate per unit of adsorbent
q_m	Maximum equilibrium adsorption capacity of adsorbate
m	Mass of adsorbent
V	Volume of aqueous solution
K	Adsorption equilibrium constant
K_f	Freundlich isotherm constant
K_L	Langmuir isotherm constant
R^2	Correlation coefficient
n	The adsorption intensity
q_{eq}	The amount of adsorption (mg/g) at equilibrium.
q_t	The amount of adsorption (mg/g) at contact time t (min).
$K_{1,ad}$	The pseudo first order rate constant (L/min).
$K_{2,ad}$	The pseudo second order rate constant (g/mg.min).

Removal of Acetylsalicylic Acid from Polluted Water Using N-Pyrazole Modified Silica Gel
By
Haya Basem Akkad
Supervisor
Dr. Ibrahim Abu Shqair
Co- Supervisor
Dr. Shehdeh Jodeh

Abstract

Water pollution is one of the most serious ecological threats we face today. The pharmaceutical drugs are emerging pollutants, which may cause serious hazards on human beings and on the environment. Therefore, from last two decades, plenty of studies were conducted on the occurrence, impact, and removal of pharmaceutical residues from the environment.

Many technologies including physical, biological and chemical processes have been extensively investigated for the removal of pharmaceutical compounds from water. This work is focused on the applications of new N-pyrazole-functionalized silica for selective extraction and elimination of ASA from water.

The adsorption potential of Silica gel supported N-pyrazole ligand (SiPz) to remove Acetylsalicylic Acid from water was studied. The effect of various parameters on the removal process was investigated. Such parameters included; pH, initial concentration of Acetylsalicylic Acid, Temperature, adsorbent dosage and contact time. Moreover, the adsorption isotherms were investigated and the reaction order was determined. Results revealed that the maximum percent removal of Acetylsalicylic Acid by SiPz was 65% after 20 min of shacking at solution conditions of 20ºC, 10 mg of

adsorbent dose at pH 7.0 and 50 mg/L of Acetylsalicylic Acid solution. The equilibrium concentration of Acetylsalicylic Acid in the supernatant was measured by UV-vis spectrophotometer.

The results showed that the adsorption followed Freundlich isotherm and the adsorption kinetics followed pseudo-second order kinetic adsorption model.

Chapter one

Introduction

Water pollution is one of the most serious ecological threats we face today. Contamination of water by chemicals or microorganisms will decrease its quality and turn it into a toxic substance to humans and the whole surrounding environment (Water pollution, Wikipedia).

Pharmaceuticals found in wastewater are very hazardous and toxic not only to humans but also to environmental life.

Recently, pharmaceutical products have attracted much attention because of their necessity in everyday life and the huge production and consumption all over the world. These substances may often remain in the environment even they have been consumed completely. Therefore, from last two decades, plenty of studies were conducted on the occurrence, impact, and removal of pharmaceutical residues from the environment. (Tiwari B. et al., 2017).

Many technologies including physical, biological and chemical processes have been extensively investigated for the removal of pharmaceutical compounds from wastewater. This work is focused on the applications of new N-pyrazole-functionalized silica for selective extraction and elimination of Aspirin from polluted water.

In recent years, great interest has been devoted to the preparation and study of organo-functionalized silica gel due to their multiple uses, in particular, in concentration and separation processes (Filho N. et al., 2006).

Due to human excretion of the drug and its metabolites, persistent environmental contamination of Acetylsalicylic Acid (ASA) occurs. This requires highly efficient sorbents which permit the isolation of such pharmaceuticals from wastewater (Meischl F. et al., 2016).

Many conventional and advanced methods were developed and used for water treatment, but adsorption is currently considerable to be very suitable method because of its simplicity and cost effectiveness (Kurniawan T. et al., 2006).

The proposed project is expected to answer the following questions:

- Can SiPz effectively remove Aspirin from aqueous solution?

- How to optimize the adsorption conditions(e.g., pH, contact time, and initial drug concentration,etc.)?

Chapter Two

Background and Literature Review

2.1 Water pollution Sources

Water pollution refers to contamination of any body of water (Savedge J., 2019). There are two types of contaminants: Organic pollutants, which include; herbicides insecticide, detergents, Chlorinated solvents, pharmaceutical pollutions and organic compounds such as industrial volatile solvents. Inorganic pollutants which include; Fertilizers, heavy metals, wastes of food industry like ammonia, Industrial discharges products like acids and overall industrial factories by-products. (Water pollution, Wikipedia).

2.2 Pharmaceuticals

In the last decades, the pharmaceutical drugs are emerging pollutants and posed serious global concerns, which may cause serious hazards on human beings and on the environment. These pollutants are becoming prevalent in the environment because the conventional wastewater treatment plants cannot effectively remove them. Due to their toxicity in addition to their resistant performance, attention have been increased toward pharmaceutical industry in the recent years. There are big concerns about drugs synthesis, products fate and their environmental risks (Wang J. et al., 2016).

Many recent reviews had discussed the causes of presence and the fate of pharmaceutical drugs in the aqueous environment. Many pharmaceutical

drugs had been found in different environmental samples such as; bisoprolol, biphenylol, carazolol, acetaminophen, bezafibrate, chlorophene, betaxol, carbamazepine, and acetylsalicylic acid (Ayyash F. et al., 2015).

Pharmaceutical industry is one of the most important industries worldwide. The big demand on drugs and their necessity in everyday life had highly increased their production and consumption around the world (Seo P. et al., 2016).

Pharmaceutical drugs and the metabolites produced can come into the environment by two main pathways; First pathway is from the wastewater of pharmaceutical industries. Second pathway is from medicines and the expired medications disposal in the sink/toilet or in household waste, which subsequently are taken to landfill sites. (Bound J. and Voulvoulis N., 2005).

The metabolism of pharmaceutical compounds in the body does not occur completely, they are excreted in wastewater. These unchanged drugs residuals that remains in treated water are considered as micro pollutants, which can enter the environment by discharge of the treated water. (Tiwari B. et al., 2017).

A lot of Pharmaceutical compounds remain on the water's surface or settle in the ground water. This has increased concern regarding their environmental toxicity. Many previous studies were conducted to study the occurrence, impact and elimination of pharmaceutical remnants because of their negative impact on water which can cause toxicity to many living organisms (Tiwari B. et al., 2017).

Many pharmaceuticals enter the environment by wastewater treatment plants, which are considered as the most significant sources of pharmaceutical pollutants. Therefore, there is a need for more efficient and novel technologies for wastewater treatment in order to produce a safe reclaimed wastewater (Gadipelly C. et al., 2014). Many methods are used for pharmaceuticals elimination from wastewater such as: biodegradation, deconjugation, partitioning and photo degradation.

2.3 Acetylsalicylic acid (ASA)

ASA is the prototypical analgesic used to reduce fever and pain, it belongs to nonsteroidal anti-inflammatory drugs (NASIDs) which possess their anti-inflammatory activity by inhibition of cyclooxygenase enzyme. ASA also has an anti-coagulant effect, thus it is used for prevention of heart attack and blood clotting events (Meek I. et al., 2010).

Even though ASA is widely consumed as a common over-the-counter drug in Palestine, attention toward it has not been given sufficiently up to date.

As we mentioned before, human body cannot metabolize all drugs completely. Acetylsalicylate is not a completely metabolized drug and it has a 2-3 hr elimination half-life time from the body (Acetylsalicylic acid, drug bank website). Therefore, it has a big chance to reach the environment and it is very important to find a way to remove it from the environment.

NSAIDs cause the toxicity into the environment even at very low concentration ng/L to μg/L as well other pharmaceuticals. The occurrence of NSAIDs in the environment has become the issue of major concern due

to their potential ecotoxicity into the environment as they severely affect the aquatic and terrestrial organisms at different trophic levels. (Sharma k. and Kaushik G.,2017)

The available studies that discussed the elimination of ASA from wastewater in the environment were focused on advanced oxidation process, micro algal-bacterial system and decomposition of the compound through photo degradation.

Many applications have been explored by researchers regarding ASA environmental elimination. Nanotechnology had gained much attention in which applications like; graphene nanoplatelets, size-tunable molecularly imprinted polymer, nanocomposites and commercial activated carbons as adsorbents were examined for ASA removal from water (Wong S. et al., 2017).
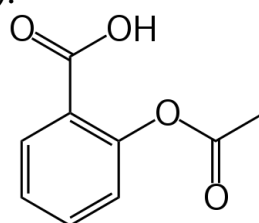
Figure 1: Acetylsalicylic acid chemical structure

2.4 Adsorption process

Many conventional and advanced methods were developed and used for water treatment, but adsorption is currently considered to be a very suitable method due to its simplicity and cost effectiveness. (Singh N. et al. 2018).

Several advanced methods have been applied for water treatment such as ozonation, advanced oxidation technology, and reverse osmosis, --- etc.

These methods are effective, but they are expensive, consume high energy, and form residual products. So, recently researches have been directed toward using low cost, environment friendly substances and methods such as adsorption. (Gisi S. et al. 2016).

Adsorption is one of the available methods in wastewater treatment. It is a physico-chemical process for producing highly safe and reusable effluents after treatment process. Many studies had proved its effectiveness, which make it an attractive method for this issue. Investigation to find various low cost material has been made and many materials were examined such as: activated carbon, ash cinder, biogases pith, coconut husk and fuller's earth. They showed varying degrees of success (Gaikwad R.W. and Misal S.A., 2010).

2.5 Silica gel

Organo-functionalized silica gel preparations have gained a great interest recently due to their feasible and multiple uses in many processes, particularly in concentration and separation processes (Radi S. et al., 2008).

Silica gel was used for the removal of cationic surfactants from industrial wastewater, removal of 2,4-D Pesticide from agricultural wastewater (Koner S. et al., 2012) and also for sorption of methylene blue.(Gaikwad R.W. and Misal S.A., 2010).

Silica gel is a material, which is known for its high chemical and thermal stability, swelling resistance, good selectivity, possibility of repeated use and economic viability (Koner S. et al., 2012).

Silica gel is a porous, granular, vitreous form of silicon dioxide made from sodium silicate. It contains a nano porous silica micro-structure, suspended in a liquid. It has a high specific surface area (around 800 m2/g), that allows it to be a good adsorbent for many materials. The surface of silica contains hydroxy groups. These groups can be functionalized to afford specialty to the silica gel, then it can be used for many applications (Silica gel, Wikipedia).

The polar organic molecule N-(2-hydroxyethyl)-3,5-dimethyl-pyrazole was made to react with a 3-glycidoxypropyl-trimethoxysilane agent, previously anchored on a silica surface in a heterogeneous way to yield the product SiPz (Pyrazole-substituted silica) as shown in Figure 2 (Radi S. et al., 2008).
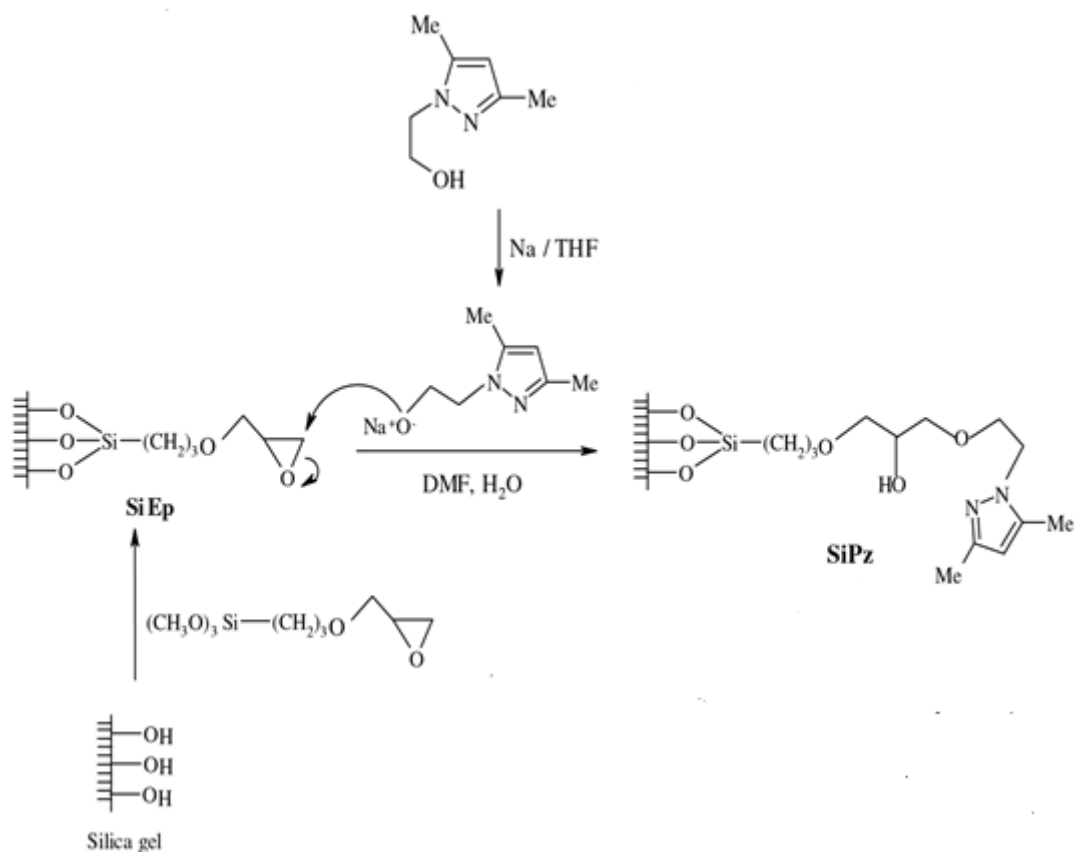
Figure 2: Synthesis of pyrazole-substituted silica (SiPz)

The resulting modified silica gel has a rough and porous nature more than the original silica gel, so it can be used as a good adsorbent.

2.6 Previous Studies

- One study investigated the adsorption potential of graphitic carbon nitride nanosheet for the removal of Aspirin from aqueous solutions. The highest percent removal of 100 mg adsorbent was 52% at pH 7.0 and contact time of 24 hours (Chegeni M. et al., 2019).
- Another study discussed the adsorption of Aspirin by Carbonaceous material prepared by ultrasonic assisted pyrolysis from algae (Bifurcaria bifurcata). The highest percent removal was 98% (Ouasfi et al., 2019).

- A study determined the percent removal of Aspirin from aqueous solutions by using spent tea leaves. The percent removal was up to 94.28% (Wong. et al., 2018).

- A study determined the potential of hydrothermally synthesized iron oxide-mesoporous silica MCM-41 composites to adsorb acetylsalicylic acid (Ting et al., 2016).

- One of the studies discussed the adsorption and desorption of acetylsalicylic acid onto activated carbon of babassu coconut mesocarp. The highest percent removal were 80% for adsorption, and 25% for desorption (Hoppen et al., 2019).

2.7 Novelty

In this work, the adsorption of ASA using silica gel supported N-pyrazole ligand from water was investigated for the first time. This study has not been performed, to our knowledge, before.

2.8 Objectives of the study

- The objective of this research is to study the use of less expensive adsorbents for the elimination of pharmaceutical substances from water. Silica gel supported N-pyrazole ligand will be used for the elimination of ASA from water.

- Determine the adsorption potential of the N-pyrazole silica gel to remove ASA from water.

- Investigate the optimum conditions for adsorption e.g., pH, Temperature, adsorption time, concentration of drug…etc.

- Study the kinetics and mechanisms of the adsorption process and the adsorption isotherms.

Chapter Three

Methodology

3.1 Materials and methods:

Acetylsalicylic acid was purchased from Aldrich Chemical Company, and was used as received without further purifications. Pyrazole-substituted silica (SiPz) that used in this work was prepared previously (Radi, et al., 2008).

The instrumentation used for this research include shaking water bath (Daihan Labtech), pH meter (3510, JENWAY), UV spectrophotometer (UV-1800, SHIMADZU).

3.2 Preparation of stock solution of ASA

An ASA stock solution of 1000 mg/L was prepared by dissolving 100 mg of aspirin in 100 mL DW in a 0.1 L volumetric flask. The stock solution was used to prepare standard solutions with different ASA concentrations (50, 75, 100 and 150 mg/L).

3.3 Preparation of calibration curve

The absorbance of the prepared solutions in section 3.2 was measured by UV-visible Spectrophotometer at 273 nm.

3.4 Drug quantification

The percent removal of drug by pyrazole-substituted silica (SiPz) and the amount of ASA adsorbed were calculated by applying equations 1 and 2 respectively:

$$\%Removal = \frac{C_0 - C_f}{C_0} . 100 \qquad (1)$$

$$q = \frac{C_0 - C_F}{m} . V \qquad (2)$$

Where:

q =the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g).

C_0 =the initial concentration of the adsorbate in solution (mg/L).

C_F = the final concentration of the adsorbate in solution (mg/L).

V = the volume of the solution (L).

m = the mass of the adsorbent in solution (g).

3.5 Batch Experiments

5.0 mg of SiPz adsorbent was added to a 10.0 mL of standard solution of ASA. The effect of various parameters such as amount of adsorbent, contact time, pH value, effect of Temperature, and concentration of Aspirin on adsorption process were studied.

 The UV-Spectrophotometer was set at 273 nm (the characteristic wavelength for ASA) for absorbance measurement.

3.5.1 Effect of pH

Studying the initial pH value on the adsorption behaviour was performed at pH range 3.0 – 9.0. The pH of each solution was adjusted by either 0.1M NaOH or 0.1M HCl solutions. A 5.0-mg quantity of SiPz was added to 10.0 mL of ASA solution with a concentration of 50 mg/L. All samples were stirred at a temperature of 25℃ for 20 minutes at an agitation speed of 120 rpm.

3.5.2 Effect of temperature

The adsorption of ASA was studied at different temperatures ranging from 15 to 40℃. For each temperature, 10.0 mg of SiPz were added into 10.0 mL of 50 mg/L ASA solution with pH 7. All samples were stirred at the appropriate temperature for 20 minutes at an agitation speed of 120 rpm.

3.5.3 Effect of initial concentration of ASA

To determine the effect of the concentration of ASA on the adsorption process, 10.0 mg of SiPz were added to four flasks each contains 10.0 mL of ASA solution with a different concentration (50, 75, 100 and 150 mg/L). The samples were stirred at 20℃ for 20 min at agitation speed of 120 rpm. After that, the solutions were filtered and the absorbance of the supernatant solution was measured using UV-spectrophotometer at 273 nm.

3.5.4 Effect of contact time

The adsorption of ASA onto SiPz was studied at different contact time intervals (5, 20, 35, 45 and 60 min). The concentration of ASA was 50 mg/L (adjusted to pH 7) with 10 mg of the polymer at 25℃ at an agitation speed of 120 rpm. The solution was filtered and the absorbance of supernatant solution was measured at 273 nm.

3.5.5 Effect of adsorbent dose

To study the effect of the dose of the adsorbent on the removal of ASA, different doses of adsorbent ranging between 5.0 – 25.0 mg were tested. The Aspirin concentration used was 50 mg/L at pH 7. All samples were stirred at temperature of 25℃ for 20 minutes at an agitation speed of 120 rpm. The absorbance of supernatant was measured by UV-visible for the residual concentration of the solution.

Chapter Four

Results and Discussion

4.1 Absorption spectra of ASA

The Absorbance spectra of the ASA is presented at Figure 3
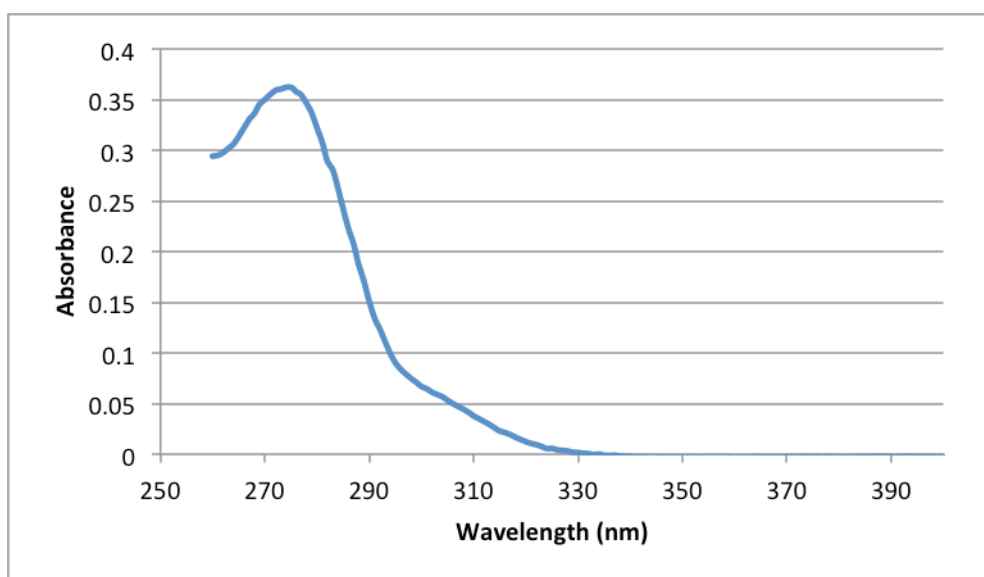
Figure 3: Absorption Spectra of ASA

As shown in Figure 3 the maximum wavelength of ASA is at 273 nm. Therefore, the UV- Spectrophotometer was set up at 273 nm for absorbance measurement.

4.2 Calibration Curve and range of linearity

The absorbance was plotted versus concentration. A linear plot was obtained with ASA concentrations in the range 50-150mg/L as shown in Figure 4.
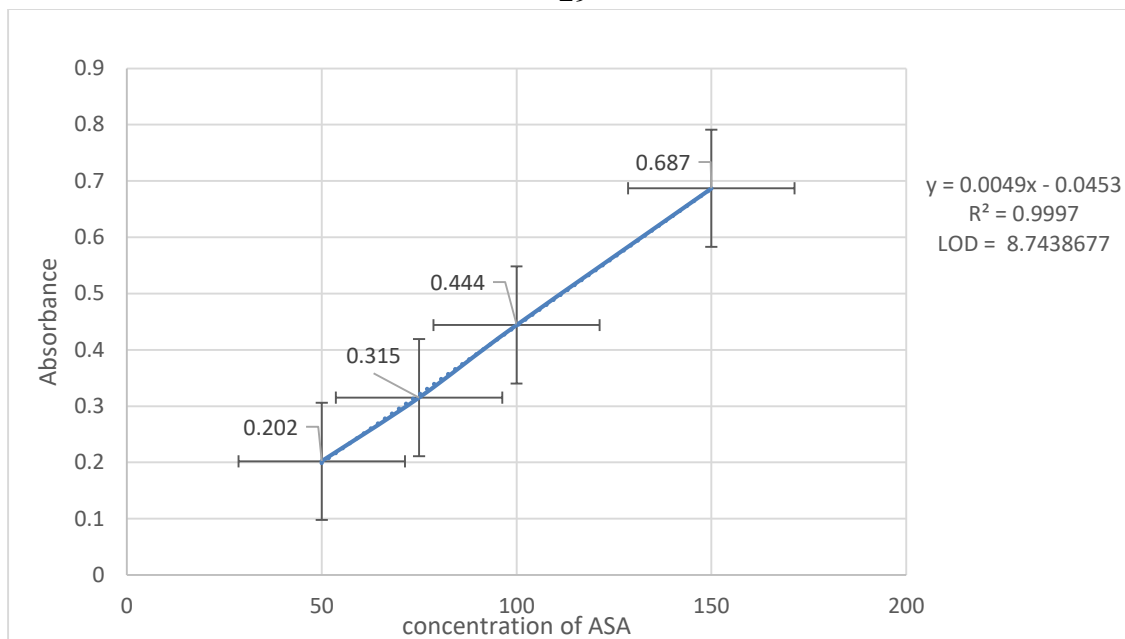
Figure 4: Calibration curve of Acetylsalicylic Acid

Table 4.1: Regression Statistics

Standard Error (SE) of intercept	0.006462135
Standard Deviation (SD) of intercept	0.012924269
Limit of detection (LOD)	8.743867702

4.3 ASA adsorption on SiPz

The optimum conditions for ASA adsorption process on SiPz adsorbent were determined. The absorbance of the supernatant was measured using UV- Spectrophotometer at 273 nm.

4.3.1 Effect of pH

Figure 5 illustrates the effect of pH on the adsorption of ASA. The percent removal was small in acidic medium, while in neutral to basic medium at a

pH of 7.0 – 9.0, the average percent removal of ASA was the highest. Therefore, for environmental and economical considerations; pH 7.0 is the optimum value in which the percent removal of ASA was 42% when using 5.0 mg of adsorbent, shaking for 20 minute at 25 °C.
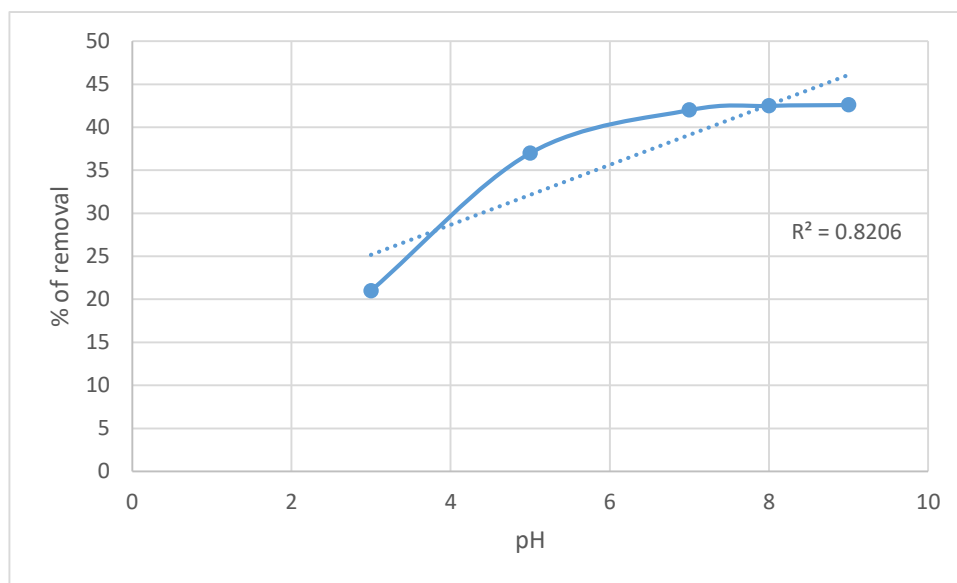
Figure 5: Effect of pH on the % removal of ASA by SiPz

4.3.2 Effect of temperature

The effect of temperature on the adsorption of ASA by SiPz was studied at different temperatures (15 – 40°C), as shown in Figure 6. The optimum conditions of drug concentration, contact time, adsorbent dose and pH were taken in consideration.
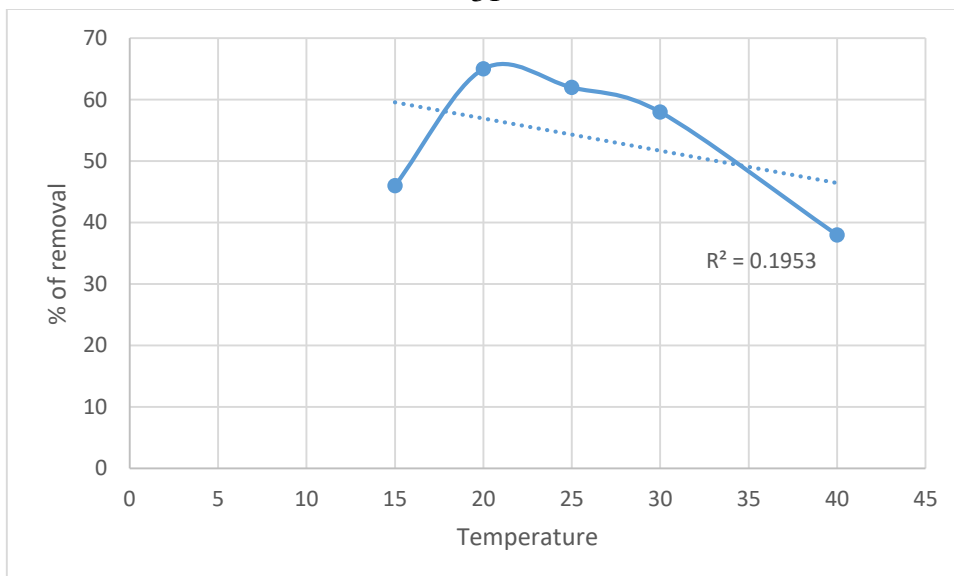
Figure 6: Effect of temperature on the % removal of ASA by SiPz

As shown in Figure 6, the adsorption of ASA increases with increasing the temperature then reaches a maximum at 20ºC, after that the efficiency of removal decreases with increasing the temperature above 20ºC. The percent of removal at 20ºC was found to be 65%. Low temperatures enhance the complexation ability between SiPz and ASA and hence increase the adsorption efficiency.

4.3.3 Effect of drug initial concentration

Figure 7 illustrates the effect of initial drug concentration on the adsorption process at the optimum conditions. As can be seen, increasing the initial concentration of the drug decreases the efficiency of removal. The maximum percentage removal was 65% using a drug concentration of 50 mg/L. Higher concentrations of ASA result in smaller number of the vacant sites available for adsorption process.
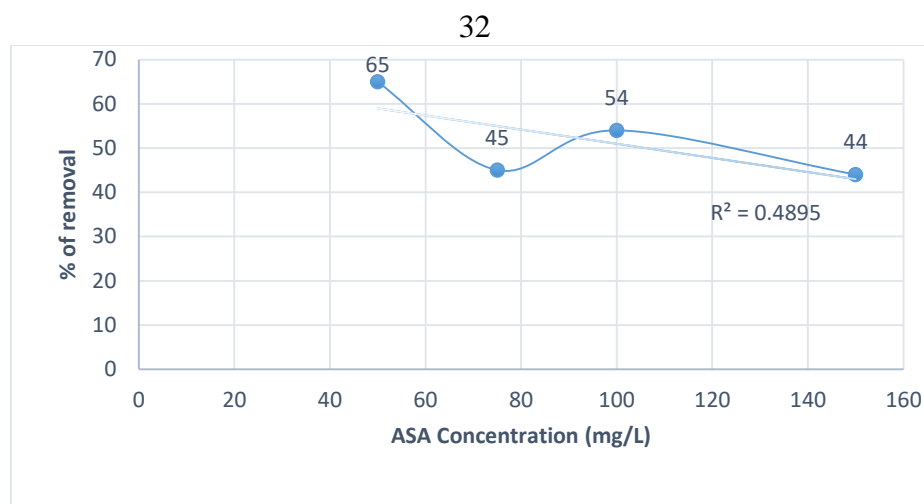
Figure 7: Effect of drug initial concentration on the % removal of ASA by SiPz

4.3.4 Effect of contact time

Contact time is one of the most important parameters that must be taken into account for water treatment. The optimum conditions of drug concentration and pH were used to study the effect of contact time on ASA adsorption. Figure 8 illustrates the adsorption of ASA onto SiPz at different contact times.
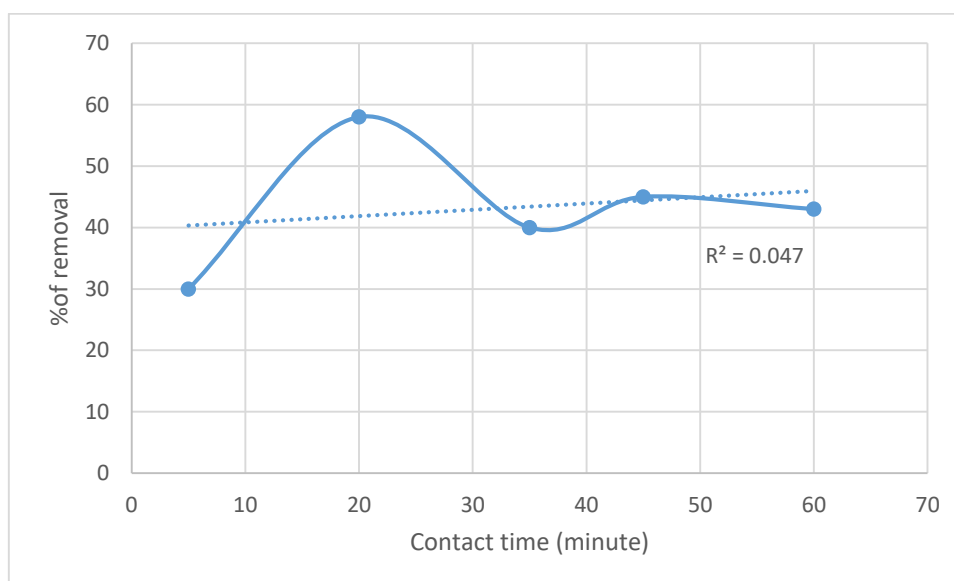
Figure 8: Effect of contact time on the % removal of ASA by SiPz

Herein, the highest percent of ASA removal equals 58% after 20 minutes of shaking as optimum contact time. As time progress, the remaining vacant sites on the adsorbent surface decreased, resulting in the observed reduction of adsorption rate. This is due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase (Wong S. et al., 2017).

4.3.5 Effect of adsorbent dose

The effect of adsorbent dose on the efficiency of ASA removal by using optimum concentration of ASA (50 mg/L) is shown in Figure 9 over the range 5 mg to 20 mg, at 25 °C for 20 minutes and pH 7.0.
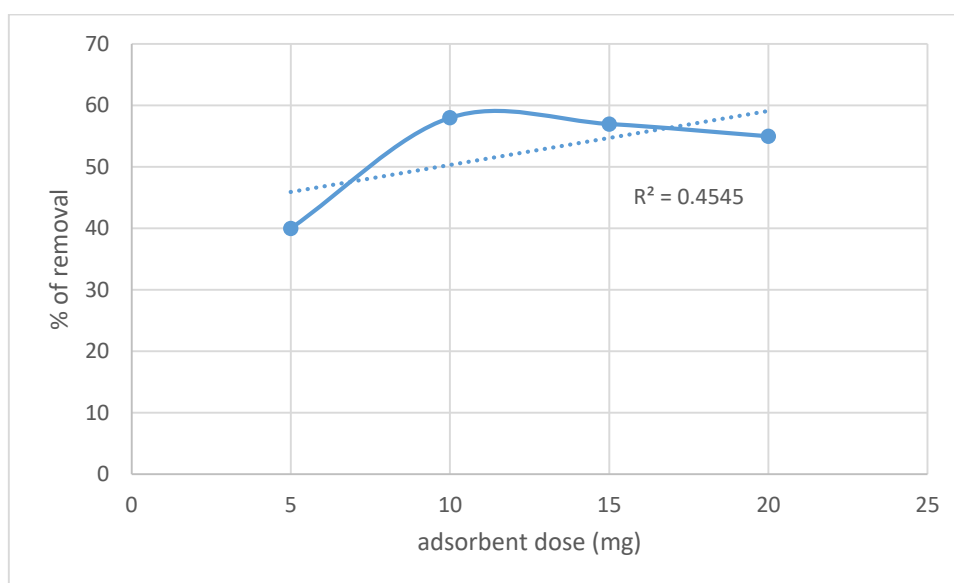
Figure 9: Effect of adsorbent dose on the % removal of ASA by SiPz

From the Figure 9, it was observed that the maximum percentage of adsorbed ASA is 58%. With increasing the adsorbent dosage from 5 to 20

mg. Above 10 mg of adsorbent, adsorption of ASA reached equilibrium, so extraction percentage remains constant.

The results of removing ASA from water by SiPz adsorbent is represented in table 4.2

Table 4.2: the adsorption results for removing ASA using SiPz.

Adsorption of ASA	
Optimum condition and % of ASA Removal	SiPz
Drug concentration (mg/L) % of ASA Removal	50 61%
pH value % of ASA Removal	7 42%
Contact time (min) % of ASA Removal	20 58%
Adsorbent dose (mg) % of ASA Removal	10 58%
Temperature (^{o}C) % of Aspirin Removal	20 65%

4.4 Adsorption isotherms

Adsorption isotherms can indicate the qualitative interaction between the adsorbent and the adsorbate.

Adsorption isotherms models, namely Freundlich and Langmuir, were used to determine the adsorption isotherm for ASA adsorption onto SiPz. These models might determine some kinetics and thermodynamic parameters.

The quantity of ASA adsorbed was then determined from the difference between the initial (C_i) and residual (C_e) concentrations.

Relationship between C_e and C_e/q_e describes Langmuir isotherm model; Langmuir isotherm suggests that adsorption is monolayer, occurred on a homogeneous surface with energetically equivalent for all binding site and there is no interaction between adjacent adsorbed molecules.

The linear form of the Langmuir isotherm is given by Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \tag{3}$$

Where:

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

q_m = maximum monolayer coverage of adsorbent with adsorbate (mg/g).

K_L = Langmuir coefficient related to surface adsorption energy (L/mg).

q_e = the amount of adsorbate per unit mass of adsorbent at equilibrium (mg/g), and it can be calculated using the following relation:

$$q_e = (C_o - C_e) \frac{V}{m}$$

Where:

C_o = the initial concentration of the adsorbate in solution (mg/L).

V = the volume of the solution (L).

m = the mass of the adsorbent in solution (g).

Therefore, a plot of $\frac{C_e}{q_e}$ versus C_e gives a straight line of a slope $\frac{1}{q_m}$ and an intercept equals $\frac{1}{q_m k_L}$.

Whereas, Freundlich isotherm model describes multilayer adsorption on heterogeneous surface with interactions between adsorbed molecules.

The linear form of the Freundlich isotherm is given by Eq.4:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \tag{4}$$

Where:

q_e = the quantity of adsorbate uptake per unit mass of adsorbent at equilibrium (mg/l)

k_f = the Freundlich constant, which indicates the adsorption capacity of the sorbent (mg/g).

n = the adsorption intensity (g/L).

C_e = the equilibrium concentration of adsorbate in solution (mg/l).

Therefore, a plot of $\ln q_e$ versus $\ln C_e$ gives a straight line of a slope $\frac{1}{n}$ and an intercept equals to $\ln k_F$.

For adsorption of ASA on SiPz, the experimental data were better fitted to the Freundlich equation ($R^2 = 0.711$) than Langmiur equation ($R^2 = 0.6109$) as seen in Figures 10 and 11, (Tables 6 and 7). The parameters are shown in Table (4.3).
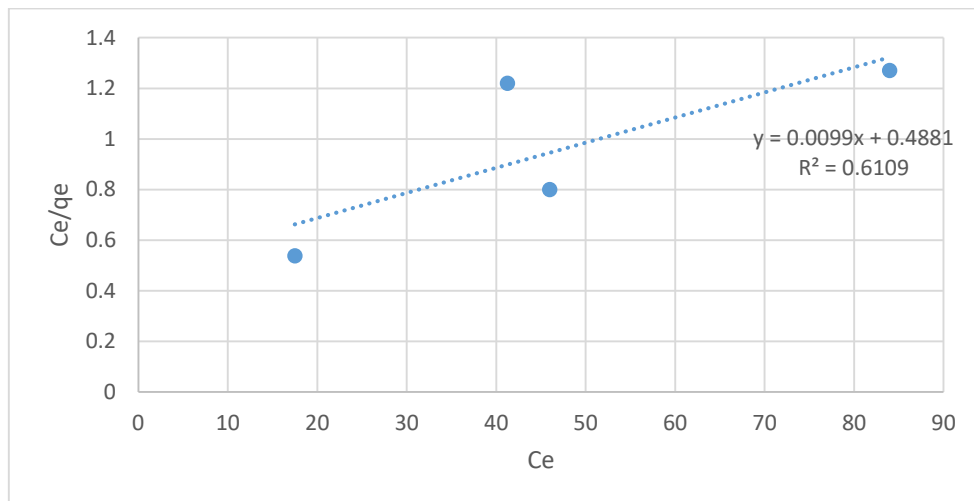
Figure 10: Application of Langmiur adsorption isotherm on % removal of ASA by SiPz
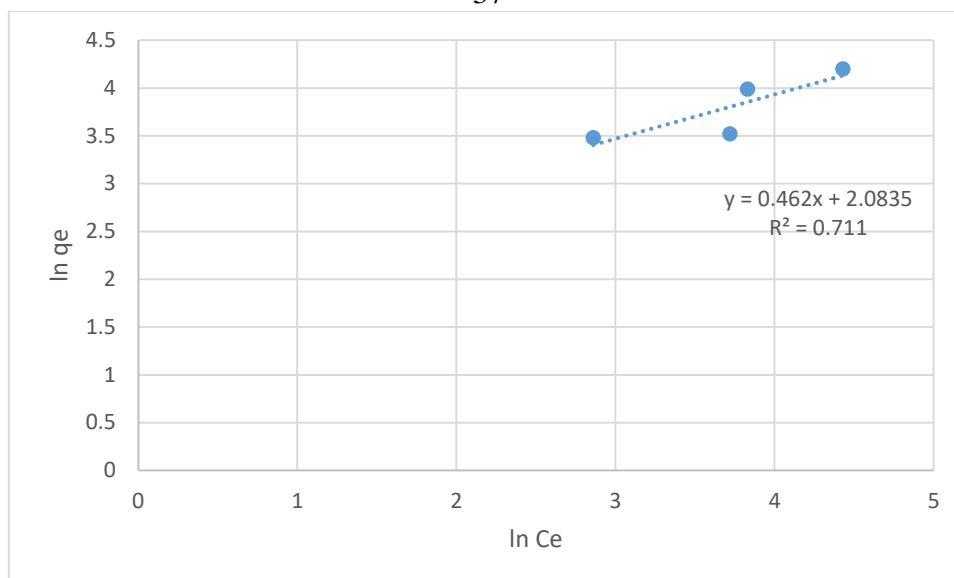
Figure 11: Application of Freundlich adsorption isotherm on % removal of ASA by SiPz

Table 4.3: Parameters from the Adsorption isotherms

Langmuir constants			Freundlich Constants		
K_L	q_m	R^2	K_F	n	R^2
0.02	102	0.6109	8.03	2.16	0.711

4.5 Adsorption kinetics

Kinetic models can be used to determine the adsorption rate of contaminants and the time needed for the process to reach equilibrium. The experimental kinetic data for ASA adsorption were applied to pseudo - second order, and pseudo-first order models, to determine the mechanism of the adsorption process.

The pseudo first order rate equation can be expressed as:

$$\log(q_{eq} - q_t) = \log q_e - \frac{K_{1,ad}}{2.303} t \qquad (5)$$

Where:

q_t = the amount of adsorption (mg/g) at contact time t (min).

q_{eq} = the amount of adsorption (mg/g) at equilibrium.

$K_{1,ad}$ = the pseudo first order rate constant (L/min).

Therefore, If the previous equation is applicable, a plot of $\log \left(q_{eq} - q_t \right)$ versus t should give a straight line with a slope of $\dfrac{K_{1,ad}}{2.303}$ and an intercept equals to $\log q_e$.

Pseudo-first order model for the adsorption of ASA onto SiPz is shown in Figure 12 and the data are shown in Table 9.
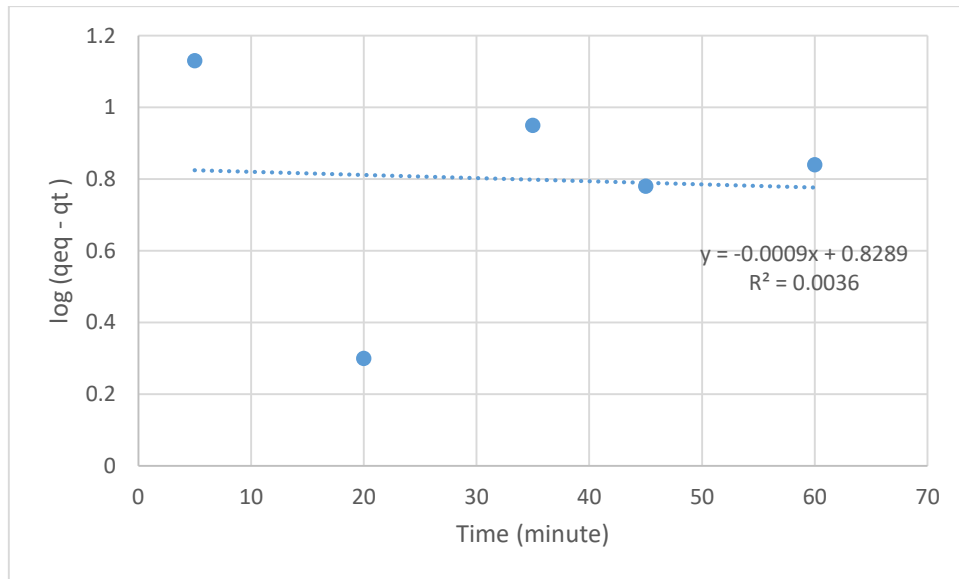
Figure 12: Applying first order equation on the % removal of ASA by SiPz

The pseudo second order rate equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_{2,ad}q_{eq}^2} + \frac{1}{q_{eq}}t \qquad (6)$$

Where:

q_t = the amount of adsorption (mg/g) at contact time t (min).

q_{eq} = the amount of adsorption (mg/g) at equilibrium.

$K_{2,ad}$ = the pseudo second order rate constant (g/mg.min).

Therefore, if the previous equation is applicable, then a plot of $\dfrac{t}{q_t}$ versus t should give a straight line with a slope of $\dfrac{1}{q_{eq}}$ and an intercept equals to $\dfrac{1}{K_{2,ad}q_{eq}^2}$.

Pseudo-second order model for the adsorption of ASA onto SiPz is shown in Figure 13 and the data are shown in Table 10.
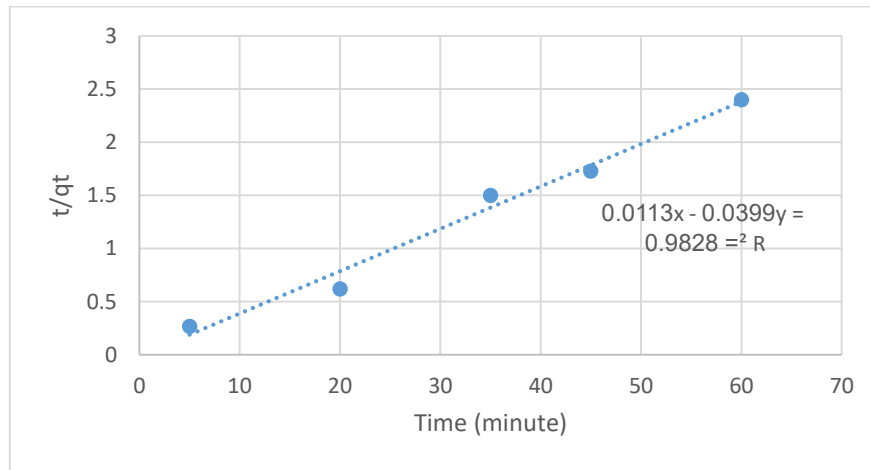
Figure 13: Applying second order equation on the % removal of ASA by SiPz

According to R^2 values from the two figures, adsorption of ASA onto SiPz follows pseudo- second order model.

Parameters of first and second order reactions for ASA are shown in Table 4.4.

Table 4.4: Parameters of first and second order reactions for Aspirin adsorption.

Pseudo first order			Pseudo second order		
$K_{1,ad}$	q_{eq}	R^2	$K_{2,ad}$	q_{eq}	R^2
0.002	6.74	0.0036	0.14	25	0.9828

Conclusion

The optimal percent removal of ASA by SiPz was 65%. The suitable conditions for adsorption were at pH 7.0, an initial concentration of ASA of 50 mg/L, a temperature of 20 C°, a 10 mg of adsorbent dose, and a contact time of 20 minutes.

The results showed that the adsorption of ASA followed Freundlich adsorption isotherm and the mechanism of this process followed pseudo-second order kinetics.

Using Silica Gel Supported N-Pyrazole Ligand as an adsorbent, showed a good efficiency in removal of ASA from water.

The studied parameters such as pH, initial concentration of drug, Temperature, adsorbent dosage and contact time have an effect on the removal of Aspirin by SiPz.

Recommendations:

- Synthesis and preparation of the adsorbent (Silica Gel Supported N-Pyrazole Ligand) in Palestine

- Studying the adsorption potential of SiPz on other drugs.

- Studying the Adsorption potential of SiPz on a sample of wastewater.

- Create a comparative study of the absorption capacity between Silica gel and SiPz.

Tables

Table (1): Effect of drug initial concentration on the % removal of ASA by SiPz. (10mg/mL adsorbent, pH 7.0, 20 min., 20℃, 120 rpm).

Initial concentration (mg/L)	% Removal of ASA
50	65
75	45
100	54
150	44

Table (2): Effect of pH on the % removal of ASA by SiPz. (5 mg/mL adsorbent, 50 mg/L drug, 20 min., 25℃, 120 rpm).

pH	% Removal of ASA
3	21
5	37
7	42
8	42.5
9	42.6

Table (3): Effect of contact time on on the % removal of ASA by SiPz. (10 mg/mL adsorbent, 50 mg/L drug, pH 7.0, 25℃, 120 rpm).

Time (minute)	% Removal of ASA
5	30
20	58
35	40
45	45
60	43

Table (4): Effect of adsorbent dose on the % removal of ASA by SiPz.

(50 mg/L drug, pH 7.0, 25℃, 20 min, 120 rpm).

Adsorbent dose (mg)	% Removal of ASA
5	40
10	58
15	57
20	55

Table (5): Effect of temperature on the % removal of ASA by SiPz.

(10mg adsorbent, 50 mg/L drug, pH 7.0, 20 min, 120 rpm).

Temperature (℃)	% Removal of ASA
15	46
20	65
25	62
30	58
40	38
45	35

Table (6): Application of Langmiur adsorption isotherm on % removal of ASA by SiPz.

$/q_e C_e$	C_e
0.538	17.5
1.22	41.25
0.8	46
1.27	84

Table (7): Application of Freundlich adsorption isotherm on % removal of ASA by SiPz.

$ln\ q_e$	$ln\ C_e$
3.48	2.86
3.52	3.72
3.99	3.83
4.2	4.43

Table (8): Concentration of 50 mg/L ASA by SiPz with time.

Time (minute)	C_e	q_t
5	31.5	18.5
20	17.5	32.5
35	26.5	32.5
45	24	26
60	25	25

Table (9): Applying first order equation on the % removal of ASA by SiPz.

Time (minute)	$log(q_e - q_t)$
5	1.16
20	-0.3
35	1
45	0.84
60	0.9

Table (10): Applying second order equation on the % removal of ASA by SiPz.

Time (minute)	(mg/g)q_t	$\dfrac{t}{q_t}$
5	18.5	0.27
20	32.5	0.62
35	23.5	1.5
45	26	1.73
60	25	2.4

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جامعة النجاح الوطنية

كلية الدراسات العليا

استخدام السليكا جل المعدل بالبايرازول لإزالة حمض الاستيل سلسليك من المياه

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الملخص

تلوث المياه هو واحد من أخطر التهديدات البيئية التي نواجهها اليوم. المواد الكيميائية أو الكائنات الحية الدقيقة تلوث المياه، تدهور جودتها وتجعلها سامة للإنسان والبيئة.

تشكل الأدوية الصيدلانية مخاوف عالمية خطيرة، والتي قد تشكل مخاطر محتملة على البيئة والبشر. أصبحت هذه الملوثات سائدة في البيئة لأن محطات معالجة مياه الصرف التقليدية لا يمكنها إزالتها بشكل فعال بسبب أداؤها السام والمقاوم.

في بحثنا هذا تم دراسة قدرة جل السليكا المعدل(Silica N-pyrzole ligand (SiPz)) على التخلص من حمض الاستيل سلسليك من المياه.

تم دراسة تأثير بعض العوامل المختلفة على عملية الامتزاز مثل: تركيزحمض الاستيل سلسليك الابتدائي، درجة الحرارة، أثر كمية الممتز، درجة الحموضة والوقت اللازم. كذلك تم التحري عن منحنيات الامتزاز (Adsorption isotherms) ورتبة التفاعل (Adsorption kinetic models). خلصت الدراسة الى أن ل SiPz قدرة على إزالة حمض الاستيل سلسليك من المياه بنسبة أقصاها 65%. كما ان لزيادة درجة الحموضة أثرا واضحا حيث بلغت نسبة الازالة قيمتها القصوى عند درجة حموضة 7.0 لحمض الاستيل سلسليك، وكان التركيزالاولي لحمض الاستيل سلسليك 50ملغرام/لتر، 10ملغرام من الممتز، درجة الحرارة 20 درجة مئوية والوقت اللازم 20 دقيقة.

تم تفسير نتائج عملية الامتزاز التي تم الحصول عليها عند الاتزان باستخدام معادلة لنغمير (Langmiur adsorption isotherm) وفرندليش (Fruendlich adsorption isotherm). حيث كان نموذج فرندليش أنسب لتفسير امتزاز ASA على SiPz. كما تم تقدير رتبة التفاعل من الدرجة الثانية.