An-Najah National University

Faculty of Graduate Studies

Amine Modif ied Silica for Water Purification from Ibuprofen and Naproxen

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Dedication

To my hero, my father, to my paradise, my mother, thanks for always being there for me, may Allah bless and keep you in my life.

To my stars, my sisters and my brother Mohammad

To my dear husband, who always tells me that everything will be okay

To my teachers who taught me in my life

To my friends

To everyone who helped and supported me

With love and respect

Acknowledgment

The first and greatest thank is to Allah, the lord of the worlds, who always gave me the strength and the ability to achieve my aims and goals.

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الاقرار

أنا الموقعة أدناه، مقدّمة الرسالة التي تحمل العنوان:

Amine Modified Silica for water Purification from Ibuprofen and Naproxen

أقر بأن ما اشتملت عليه هذه الأطروحة إنما هو نتاج جهدي الخاص، باستثناء ما تمت الاشارة إليه حيثما ورد. وأن هذه الرسالة كاملة، أو اي جزء منها لم يقدم من قبل لنيل اي درجة او لقب علمي او بحثي 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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Date: **التاريخ:** ١/٣/٢٠٢١ م

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List of Abbreviation

NSAID	Non- steroidal anti- inflammatory drugs
COX	Cyclooxygenase Enzyme
COX1	Nonselective cyclooxygenase inhibitor
COX2	Selective cyclooxygenase inhibitor
IBP	Ibuprofen
Nap	Naproxen
ΔG^o	Gipps free energy change
ΔH^o	Enthalpy change
ΔS^o	Entropy change

Amine Modified Silica for water Purification from Ibuprofen and Naproxen

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Abstract

Adsorption of ibuprofen and naproxen on amine modified silica was carried out, Concentrations of the drugs before and after equilibrium were measured using UV-visible spectrophotometry at 220, and 230 nm for ibuprofen and naproxen respectively, and then the percent's of adsorption were calculated.

The effect of contact time, drug concentration, adsorbent amount, pH, and temperature on adsorption were studied.

The equilibrium time was 15 min for the adsorption of ibuprofen, and 5 min for naproxen adsorption.

For both drugs, the adsorption percentages decreased with increasing the drug concentration, where it increased with increasing the amount of the adsorbent.

Adsorption was found to be affected by pH, and temperature. The optimum pH was 3 for both drugs, and the percentages of adsorption were decreased with increasing temperature.

Freundlich and Langmuir isotherms were applied for equilibrium studies. Adsorption of ibuprofen and naproxen on amine modified silica fitted the Freundlich isotherm.

The thermodynamic parameters ΔG^o, ΔH^o, and ΔS^o were calculated at 25^oC. The results showed that the adsorption of both drugs was exothermic and spontaneous, where ΔG^o, ΔH^o were negative, and ΔS^o had a positive value.

Chapter One
Introduction

1. Introduction

1.1 Background

Presence of pharmaceutical compounds in the environment, and there effect have become an issue of many environmental and health organizations worldwide (1).

These compounds are used in huge amounts for the treatment and protection from different diseases. Somehow, these pharmaceutical compounds can find their way into the environment from many sources (2), such as, hospitals waste, excretion by human, improper disposal of pharmaceutical wastes, and from the sewage of the health facilities (3,4).

Many studies show that the pharmaceutical compounds that derived from antibiotics, antidepressant and anti-inflammatory drugs appear in surface and ground water, in concentrations ranging from ppb to ppt (4). These pharmaceutical products have significant adverse effect on living organisms, and human health even at low concentrations (5,6).

Water treatment and removing pharmaceutical products from water, was studied by many researchers using different methods (7).

Recently, researchers have been directed toward using adsorption, by using many adsorbent materials such as carbonaceous, carbon nano-tubes, cellulose, clay, silica…etc (8).

1.2 Non-steroidal anti-inflammatory drugs (NSAIDs)

Non-steroidal anti-inflammatory drugs (NSAIDs), are one of the most used drugs around the world (9), that belong to a class of drugs that are used for lowering pain, fever, and preventing blood clots (10) . They also have anti-inflammatory effect in higher doses (11).

NSAIDs act by inhibiting the activity of cyclooxygenase enzymes, (COX1 and COX2), which are the enzymes of prostaglandin formation (12).

According to the inhibition action, NSAIDs can be classified into two categories, non-selective COX inhibitors, and COX2 selective inhibitors.

Non selective inhibitor works by inhibiting the action of both COX1 and COX2 enzymes, where COX2 selective inhibitor acts by inhibiting the COX2 enzyme only (13,14).

Non-steroidal anti-inflammatory drugs are classified also according to their structures into two types, carboxylic acid NSAIDs and phenyl butazone NSAIDs (9).

Carboxylic acid non steroidalanti-inflammatory drugs including salysilate derivatives, such as; aspirin, propanoic acid derivatives, such as naproxen and ibuprofen, and phenyl acetic acid derivatives, such as declofenac (9).

Non steroidalanti-inflammatory drugs are one of the most used drugs (15), especially ibuprofen and naproxen that are used massively in the world (14).

1.3 Ibuprofen

1.3.1 Definition

Ibuprofen is 2-4 isobutyl phenyl propanoic acid (17), with a molecular weight of 206.281 g/mole (1). It is one of the most commonly used non-steroidal anti-inflammatory drugs, that belong to the propanoic acid derivatives (18, 19), which was made on 1969 (20), Fig1.3.1 shows the chemical structure of ibuprofen (16).

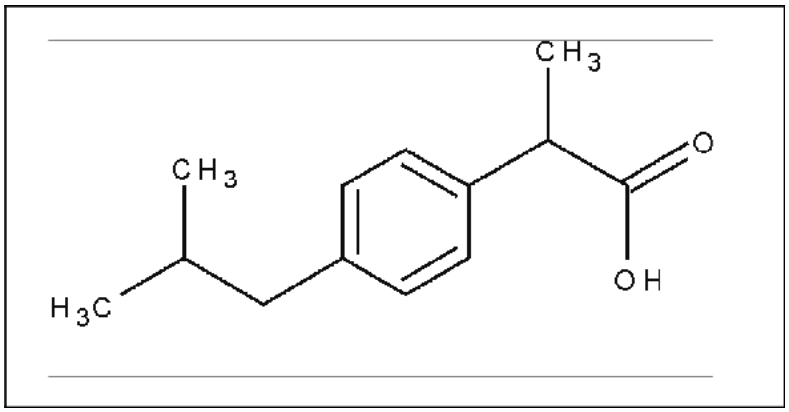

Fig 1.3.1 : the chemical structure of ibuprofen.

1.3.2 Mode of action

Ibuprofen is a nonselective cyclooxygnase enzyme inhibitor, it works by inhibiting the activity of both COX1 and COX2 enzymes (9).

1.3.3 Uses and effects

Ibuprofen is good for fever and moderate pain treatments, such as dental pains, kidney stone pains, back and muscles aches (19).

Despite of its benefits in pain treatment, ibuprofen has a few adverse effects, These include effects on kidney, gastrointestinal tract and coagulation system. It also can cause rach and dizziness (19).

Ibuprofen does not metabolize completely in the body, it can enter the aquatic environment by urine and feces, causing pollution (21).

1.4 Naproxen

1.4.1 Definition

Naproxen is 2-6-methoxy-naphthyl propanoic acid (22), with a molecular weight of 230.27 g/mole (1). Naproxen is one of the non steroidal anti-inflammatory drugs that are used in huge amounts around the world (23-25), Fig1.4.1 shows the chemical structure of naproxen (7).

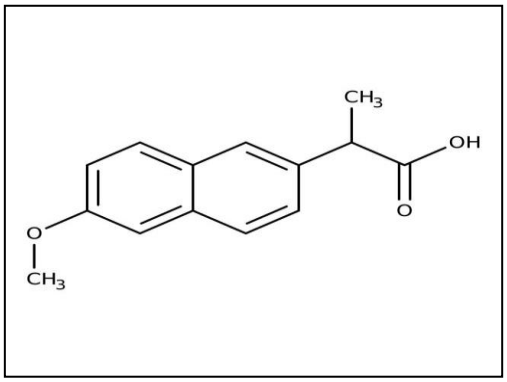

Fig 1.4.1 : the chemical structure of naproxen.

1.4.2 Mode of action

Naproxen acts by inhibiting the activity of both COX1, and COX2 enzymes (9).

1.4.3 Uses and effects

Naproxen is used for mild pain treatment, it also has anti-inflammatory, antipyretic, and analgesic effect (23).

Although of its benefits, it has many adverse effects, including gastric erosion, bleeding in the mucosa, antralulceration, and the long term use of naproxen may cause heart disease and toxic effect on the lung (26).

Naproxen was observed in aquatic environment in ng/L levels (23).

1.5 Adsorption

Adsorption refers to the accumulation of a gas or liquid solute on the surface of a solid or liquid, with or without chemical reaction, resulting in a chemical or physical adsorption (27, 28).

Adsorption percent can be calculated by using the relation

%Adsorption= $(Co - Ce)/Ce * 100\%$ (29).

Where Co and Ce are the initial and equilibrium concentrations, respectively.

Substance accumulates on the surface is called adsorbate, where the material that adsorption take place on its surface is called adsorbent (30).

1.6 Adsorption isotherm

Adsorption isotherm is a function obtained at constant temperature for quantitative evaluation of the adsorbent capacity (31).

The most frequently used are Langmuir isotherm and Freundlich isotherm, both of them give relationship between the amount of the adsorbed material and the equilibrium concentration in exponential form (30).

1.6.1 Langmuir model

Langmuir model assumption:

Langmuir assumes a monolayer adsorption, where each site of adsorbent surface can be occupied with just one adsorbate molecule, no more (32).

All surface sites are identical with the same energy (uniform adsorption surface) (33).

Adsorption is localized; adsorption of an adsorbate molecule on a specific adsorbent site is not affected by other neighboring sites (30).

Langmuir equation:

$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{ce}{Qo}$(31).

The equation can be rearranged to this form for linearization

$\frac{1}{qe} = \frac{1}{Qo} + \frac{1}{bQo} * \frac{1}{Co}$(31)

Ce: equilibrium concentration of adsorbate(mg/L).

Qo constant that indicates the monolayer adsorption capacity (mg/g).

b: Langmuir constant.

qe: amount of adsorbed material (mg/g).

Using the experimental data, plotting of 1/qe versus 1/Ce gives a straight line of a slope equals to 1/bQo, and y-intercept equals to Qo.

The effect of isotherm

In Langmuir equation, extra analysis can be made by using the separation factor (Rl), to find out if the adsorption is preferred or not (34).

$$Rl = \frac{1}{1 + bCo}$$

Co: initial concentration of adsorbate in solution (g/L).

b: Langmuir constant.

The separation factor (RI) value illustrates the type of adsorption as shown in the following table.

Table 1.6.1: Adsorption type according to RL value (34)

RL value	adsorption type
0 <RL< 1	Favorable adsorption
RL> 1	unfavorable adsorption
RL = 1	Linear
RL= 0	Irreversible

1.6.2 Freundlich Isotherm

Freundlich Isotherm model assumes that the adsorbent surface is not uniform, it is heterogeneous, and the adsorption is multilayer (35).

Freundlich equation:

$Log\ qe\ = \log Kf + \frac{1}{n} \log Ce$(31).

Kf: constant related to the adsorption capacity (mg/g).

1/n: constant related to the intensity of adsorption.

qe: amount of adsorbed material (mg/g).

Ce: equilibrium concentration of adsorbate (mg/L)

Plotting log qe versus log Ce, give straight line with slope equals to 1/n, and y-intercept equals to log Kf.

1.7 Kinetic Study

Because of the dependence of adsorption on time, the rate of adsorption is very important in the evaluation of the adsorption of the adsorbate on the adsorbent.

There are two general types of kinetics, which are Pseudo first order and pseudo second order models (36, 37).

1.7.1 Pseudo first order model

Pseudo first order rate equation was introduced in this form:

$$Log\ (ye - yt) = Log\ ye - \frac{[k1t]}{2.303} (37)$$

Ye: The adsorbed amount at equilibrium (mg/g).

Yt: The adsorbed amount at time t (mg/g).

K_1: Rate constant for pseudo first order model $(min)^{-1}$.

A plot of Log (Ye-Yt) versus t gives a straight line with slope of $K_1/2.303$ and intercept of Log ye.

1.7.2 Pseudo second order model

Pseudo second order model was proposed in this form.

$$t/yt = 1/[k_2 ye^2] + [1/ye]\ t (37)$$

Ye: The adsorbed amount at equilibrium (mg/g).

Yt: The adsorbed amount at time t (mg/g).

K_2: Rate constant for pseudo second order model $(min)^{-1}$.

Plotting of t/Yt versus t will give a straight line of a slope equals to [1/Ye] and an intercept equals to $1/ [K_2 Ye^2]$.

1.8 Adsorbent

Adsorbent is the material where on its surface adsorption occurs (30).

1.8.1 Requirements of Adsorbents

Adsorbent must have abrasion resistance, high thermal stability, small diameters, high surface area, and high adsorption capacity (30).

1.8.2 Silica gel

Silica gel is a porous granular form of silica that is synthesized from the reaction of sodium silicate and acetic acid, it has small particle size (2-5nm), large surface to volume area $2x10^{9}$ m^{-1}, and a high specific area of $900m^{2}/g$ (8, 38).

1.8.3Amine modified silica

Amine modified silica is a modified form of silica with rough and porous nature more than silica itself. It is thermally and chemically stable in acidic media, these prosperities make it good for adsorption (39).

Preparation of amine modified silica:

Amine modified silica can be prepared by the reaction of porous silica with phenyl amine, and phenyl diamine using the homogeneous route, which involve the reaction of carbaldehyde derivatives with 3-amine propyl trimethoxysilane (39).

1.9 Literature Review

Several researchers studied the interaction between pharmaceutical compounds and different adsorbents. These are some studies that focus on the removal of ibuprofen and naproxen from water by adsorption process.

Adsorption of ibuprofen and naproxen on natural clay was studied by spectrophotometry, the maximum percentages of removal were obtained after 180 and 240 min for ibuprofen and naproxen, respectively.

Results showed that the adsorption follow pseudo second order kinetics, and the results agreed with Freundlich isotherm (1).

High surface area nanographene was also used as an adsorbent for ibuprofen and naproxen. It was shown that ibuprofen and naproxen could be removed within few minutes by using 10mg of the adsorbent; the adsorption capacity was 11.9mg/g and 19.8 mg/g for ibuprofen and naproxen, respectively (40).

Several researchers worked on the synthesis of modified silica, and used it as an adsorbent for many materials.

Silica with (3-trimethoxy silylpropyl) diethelenetriamine was used for CO_2 adsorption, the adsorption capacity was 3.8 mmol/g at 60^oC (41).

Silica with 4-aminobenzaldehyde was used for removing copper from water, the results showed that after 15min 63% of copper was removed (39).

1.10 Objectives

This research is aiming to understand the adsorptive behavior of amine modified silica for the removal of naproxen and ibuprofen from water.

The effect of the following parameters on the adsorption will be studied.

- Drug concentration
- Contact time
- Adsorbent amount
- pH of the solution
- Temperature
- Kinetics and adsorption isotherms will also be investigated

Chapter Two
Materials and Methods

2. Materials and methods

2.1 Nonsteroidal anti-inflammatory drugs (adsorbate)

Ibuprofen and naproxen were obtained from Sigma Aldrich (USA).

2.2 Adsorbent

Amine modified silica was prepared by prof. Smail Radi at mohammed premier university in Oujda, Morocco.

2.3 Instrumentation

- For spectral measurements, dual beam UV-Visible-NIR scanning spectrophotometer (UV-1800, SHIMADZU) with 1 cm quartz cell was used.

- pH meter (Jenway 3510, England).

- Burrell Wrist-Action Shaker was used for mixing samples.

2.4 Preparation of standard stock solutions

Ibuprofen stock solution of 20 ppm was prepared by dissolving 0.0100± 0.0001g of ibuprofen powder (M.Wt= 206.281) in a 500-mL volumetric flask, then, It was filled to the mark by distilled water.

Naproxen stock solution of 6 ppm was prepared by dissolving 0.0030± 0.0001 g of naproxen powder (M.Wt= 230.27) in a 500-mL volumetric flask, then it was filled by distilled water to the mark.

Stability of stock solutions with time was studied by measuring the absorbance of control solution before each experiment.

2.5 Absorption spectrum of ibuprofen and naproxen

Ibuprofen and naproxen solutions were prepared in distilled water, and spectrophotometrically analyzed by scanning in the range200-400nm, against a blank, to determine the absorption spectrum for the two drugs.

2.6 Preparation of standard solutions

2.6.1 Preparation of ibuprofen standard solutions

0, 5, 10, and 15 ppm ibuprofen standard solutions were prepared in 100-mL volumetric flasks, by taking 0, 25, 50, 75 ml from the 20 ppm ibuprofen stock solution respectively, then diluting with distilled water to the mark.

2.6.2 Preparation of naproxen standard solutions

0, 0.9, 1.2, 3 ppm standard solutions of naproxen were prepared in 100-mL volumetric flasks.

2.7 Construction of calibration curves

The absorbance of each standard solution was measured at the maximum wavelength; 220 and 230 nm for ibuprofen and naproxen, respectively against the blank.

The calibration curves of ibuprofen and naproxen were obtained by plotting the absorbance versus drug concentrations.

2.8 Adsorption study

2.8.1 Equilibrium study

For equilibrium calculations, constant initial amount of amine modified silica was added to different initial concentrations of 10 mL drug solutions with specific pH. The samples were placed on a thermo-stated shaker at constant temperature for different time intervals to determine the equilibrium time.

The effect of drug concentration, adsorbent amount, pH and temperature on adsorption process was studied, Each parameter was repeated two times.

Samples were filtered, and the supernatants were analyzed using a spectrophotometer against the blank.

The blank was prepared by dissolving the same amount of adsorbent in 10 ml of distilled water, without a drug, and it was treated as the sample

treatment by putting it in the shaker for the same time, and at the same temperature.

2.8.2 Effect of contact time on adsorption (kinetic study)

The kinetic experiment was implemented by adding a constant amount of the adsorbent into 10 ml of the drug standard solution with a constant initial concentration.

0.0040±0.0001 g amine modified silica were added to 10 ml sample of 15 ppm ibuprofen, then it was fixed in the thermostated shaker at a constant temperature of 25^{o}C for a specific time interval (5, 15, 30, 40, and 50 min). Then, the samples were filtered and the supernatants analyzed at the maximum wavelength (220 nm). The equilibrium time was then obtained.

The same procedure was followed for naproxen solution of 3 ppm, but the analysis was carried out at wavelength of 230nm.

2.8.3 Effect of drug Concentration on Adsorption

This parameter was studied by mixing constant amount of the adsorbent with 10 ml drug samples of different concentrations. The mixtures were put on the thermostated shaker for equilibrium time. After filtration, spectral analysis at maximum wavelength was made for the supernatants.

Ibuprofen samples of (5, 10, 15, and 20 ppm) were mixed with 0.004±0.0001g amine modified silica for 15 min in a thermostated shaker. The samples were then filtered and the absorbance at 220nm was measured.

The same procedure was followed for (0.9, 1.2, 3, and 6ppm) naproxen sample, the shaking was for 5 min, and the analysis was carried out at 230 nm.

2.8.4 Effect of the adsorbent amount on the adsorption

Drug samples of the same initial concentrations were mixed with different amounts of the adsorbent. Then, samples were shaken at constant temperature, After equilibrium, the samples were filtered and analyzed using UV-Visible spectrophotometer device.

Ibuprofen samples of 15 ppm were mixed in the thermostated shaker at 25^{o}C, with different amounts of amine modified silica (2, 4, 8, and 10 mg). After 15 min, samples were filtered and the supernatant analyzed.

The same procedure was followed for mixing 3ppm naproxen samples with (2, 4, 6, and 8 mg) amine modified silica for 5 min.

2.8.5 Effect of pH on adsorption

Drug sample of specific concentration, and specific pH was mixed on the thermostated shaker with specific amount of amine modified silica. When the equilibrium time was reached, samples were filtered, and analysis was done.

The same experiment was repeated with different pH values, pH was adjusted by using 0.1M HCl and 0.1M NaOH solutions.

Ibuprofen samples of 15 ppm with pH of (3, 4.5, and 7) were prepared, and then mixed with 0.0040±0.0001 gof amine modified silica for 15 min. After that, samples were filtered and analyzed at 220 nm.

Naproxen samples of 3 ppm with pH values of (3, 4, and 6) were prepared, and then mixed with 0.0040±0.0001 g of amine modified silica for 5 min. After that, the samples were filtered and analyzed spectrophotometrically at 230 nm.

2.8.6 Effect of temperature on the adsorption

Drug sample of constant concentration was mixed on the thermostated shaker at specific temperature with specific amount of amine-modified silica. When the equilibrium time was reached, filtration and analysis were done.

The same experiment was repeated at different temperatures to obtain the effect of temperature on the adsorption process.

Ibuprofen sample of 15 ppm was mixed with 0.0040±0.0001g amine modified silica in the thermostated shaker at 25 ^{o}C, after 15 min filtration and analysis were performed. The same experiment was repeated at 15, 35, and 45^{o}C.

Chapter Three

Results and Discussions

3. Results and discussion

3.1 Absorption Spectra

Ibuprofen and naproxen solutions were spectrophotometrically analyzed by scanning in the range 200-400 nm.

3.1.1 Absorption Spectrum of ibuprofen

The absorption spectrum for ibuprofen is shown below.

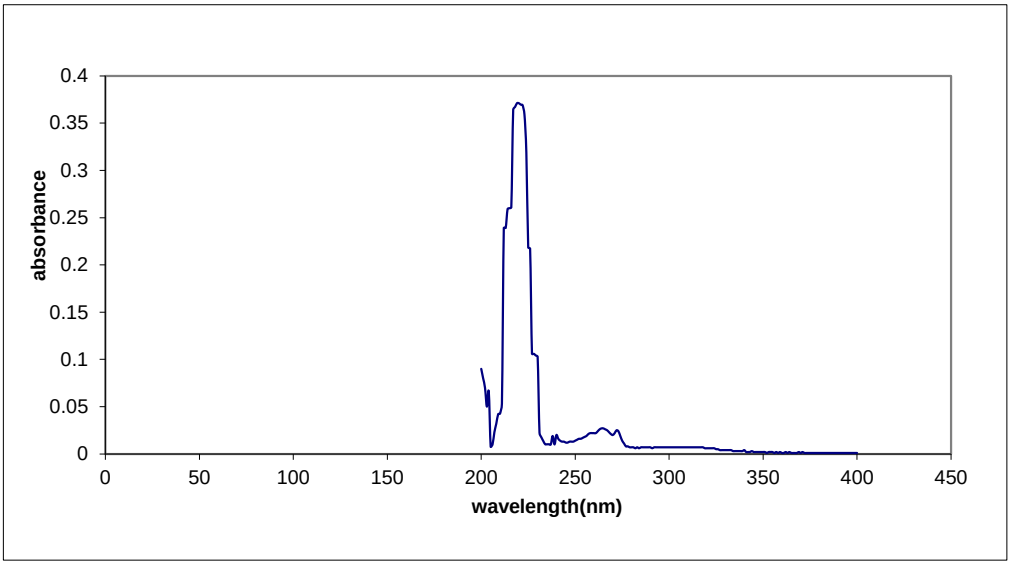

Fig 3.1.1: absorption spectrum for ibuprofen.

Maximum wavelength (λ_{max}) was found to be at 220nm.

3.1.2 Absorption Spectrum of naproxen

The absorption spectrum for naproxen.

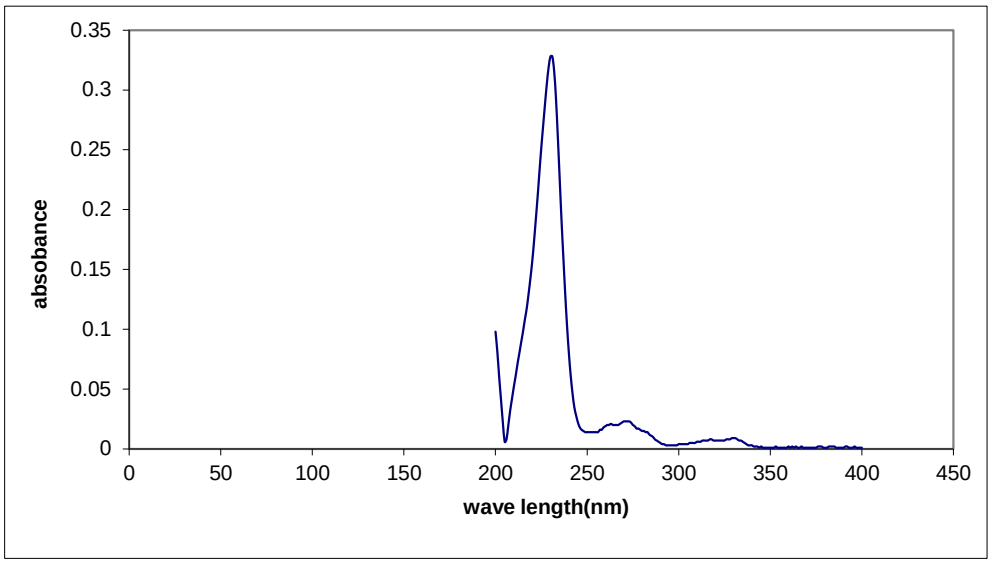

Fig3.1.2: absorption spectrum for naproxen

Maximum wavelength (λ_{max}) was found to be at 230nm.

3.2 Calibration curves

3.2.1 Calibration curve of ibuprofen

From the calibration curve (Fig.3.2.1) the detection limit (LOD) was found to be 0.933 ppm.

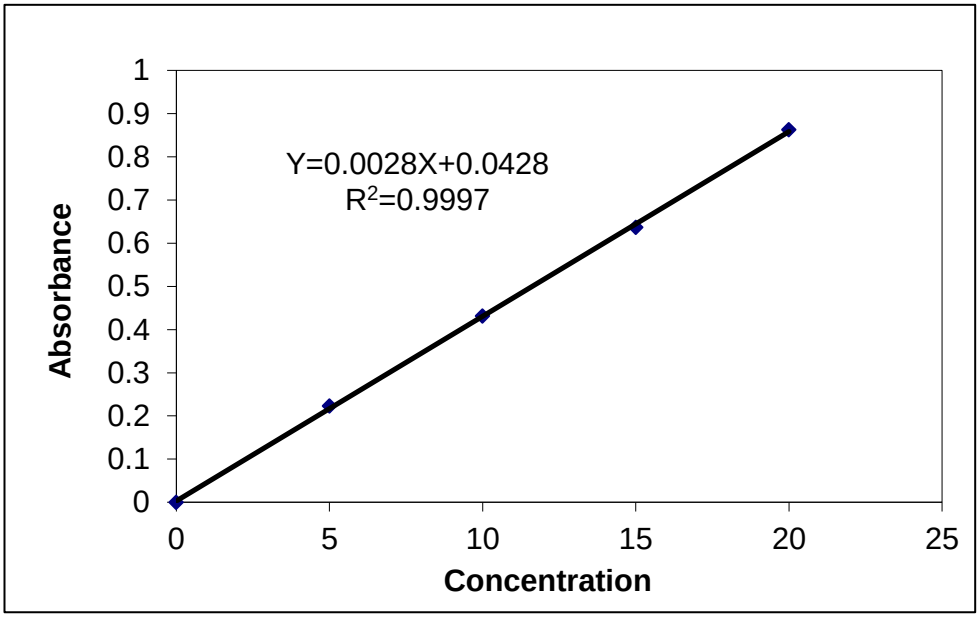

Fig 3.2.1: Calibration curve for estimation of ibuprofen concentration

3.2.2 Calibration curve of naproxen

From the calibration curve (Fig.3.2.2) the detection limit (LOD) was found to be 0.170 ppm.

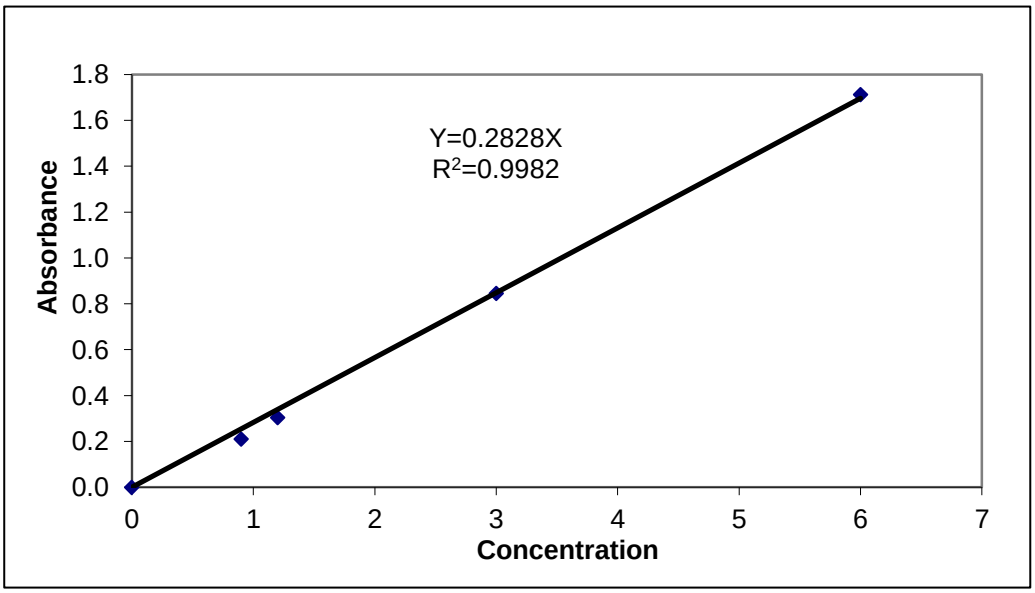

Fig 3.2.2: Calibration curve for estimation of naproxen concentration

3.3 Adsorption of ibuprofen on amine modified silica

3.3.1 Effect of ibuprofen concentration on adsorption

The equilibrium concentration (Ce), and %removal of ibuprofen were calculated from different initial concentrations of ibuprofen (Co).

As the initial concentration of ibuprofen increases % removal of ibuprofen decrease as shown in Figure 3.3.1

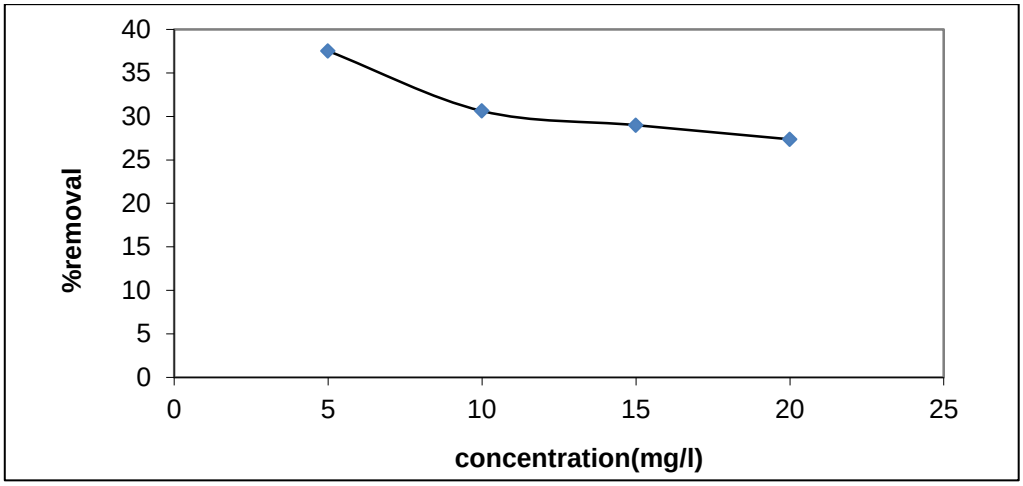

Fig 3.3.1: %Removal of ibuprofen adsorbed vs. different Co

3.3.2Effect of contact time on the adsorption of ibuprofen

The results show that the concentration of remainig ibuprofen in the solution start to decrease with time, then after 15 min, the remaining concentration is increasing with time, the lowest concentrtion of remainig ibuprofen appear at 15min, which is the equilibirium time, after that the changes in concentrations become insiginificant, figgure 3.3.2 show the efecct of contact time on adsorption.

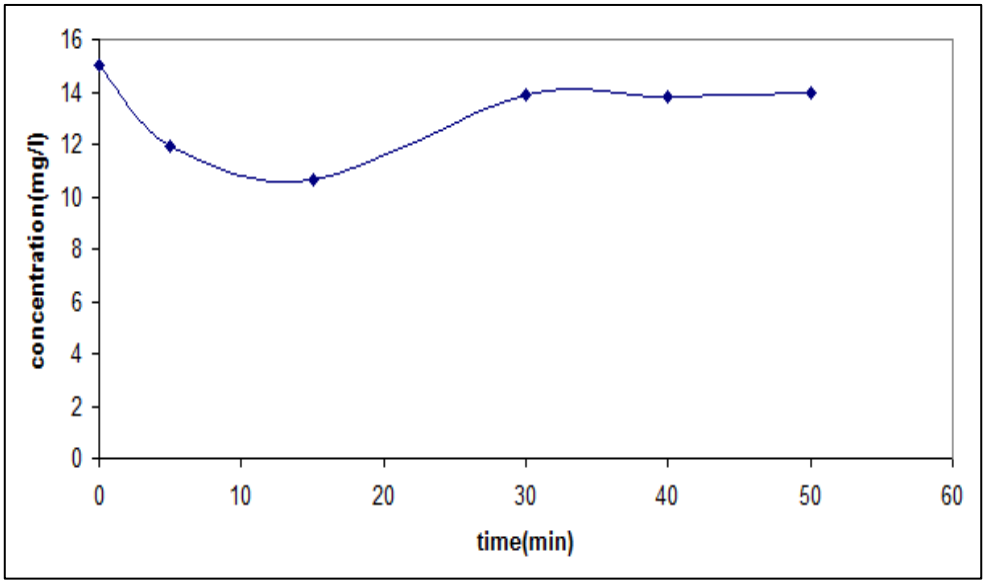

Fig3.3.2: concentration of ibuprofen remaining vs. time with amine modified silica.

3.3.3 Effect of amine modified silica amount on adsorption of ibuprofen.

%Removal of ibuprofen with constant initial concentration of 15 ppm (Co) versus different amounts of amine modified silica (M) was calculated at the equilibrium time.

%Removal of ibuprofen increases as the amount of amine modified silica increases as shown in Fig3.3.3. This means that the amount of adsorbed ibuprofen increases with increasing the mass of the adsorbent. This can be attributed to the greater surface area and the availability of more adsorption sites on the surface of adsorbent.

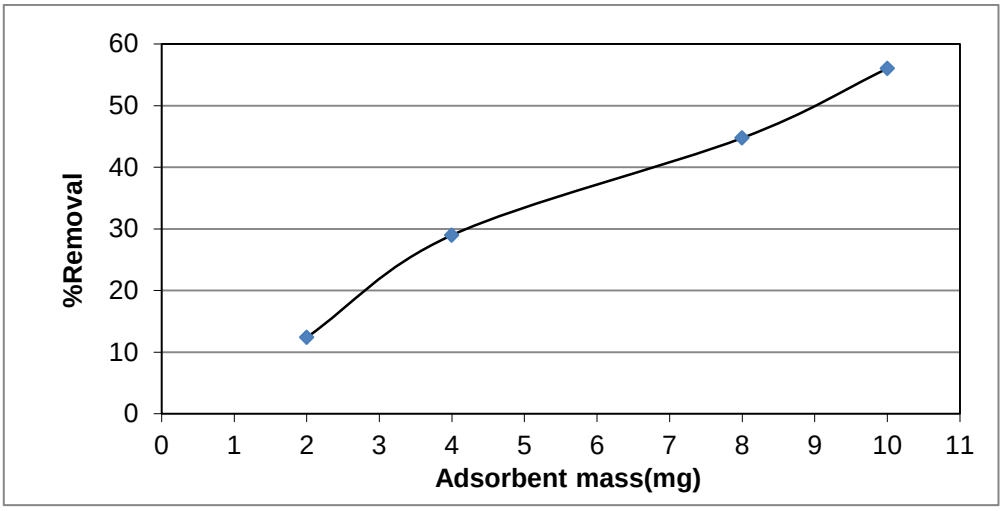

Fig 3.3.3: %Removal of ibuprofen vs. the amount of amine modified silica

3.3.4 Effect of pH on Adsorption of ibuprofen

Equilibrium concentrations (Ce), and % removal of ibuprofen of constant initial concentration of 15 ppm (Co) versus different pH values were calculated at the equilibrium time as shown in Fig 3.3.4

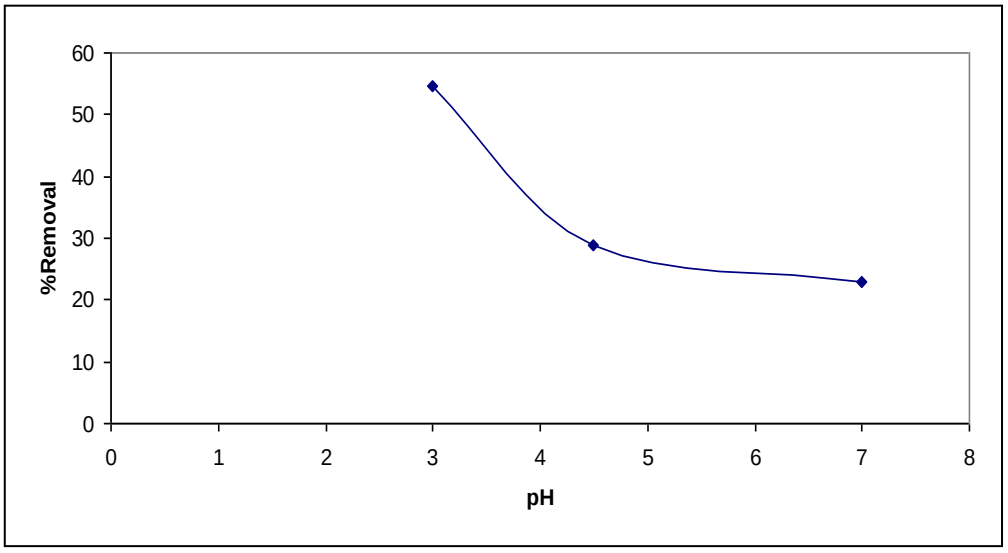

Fig 3.3.4: % Removal of ibuprofen vs pH

It appears from the figure that %removal of ibuprofen increases with decreasing the pH value.

Only acidic media was used in this study because amine modified silica is not stable in basic media, in basic media amine group is protonated and goes into the aqueous solution.

3.3.5 Effect of temperature on the adsorption of ibuprofen

Amount of adsorbed ibuprofen by 0.004 g amine modified silica was studied versus temperature at the equilibrium time, by using constant initial concentration of 15 ppm, results are found in Fig3.3.5

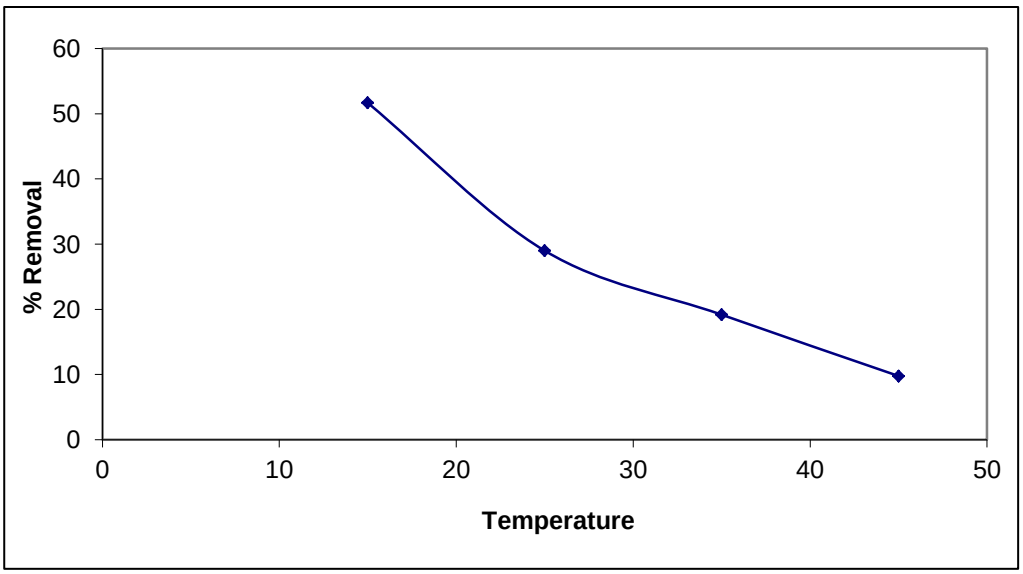

Figure 3.3.5: Amount of adsorbed ibuprofen on amine modified silica versus temperature.

As we see the amount of ibuprofen adsorbed on amine modified silica decreased with increasing temperature, this is because that the hydrogen bond between amine modified silica and ibuprofen become weaker with increasing temperature.

3.4 Adsorption of naproxen on amine modified silica

3.4.1 Effect of naproxen concentration on adsorption

The equilibrium concentration (Ce), and % removal of naproxen were calculated from different initial concentrations of naproxen (Co). As the initial concentration of naproxen increases, the %removal of naproxen also decreases as shown in Fig3.4.1.

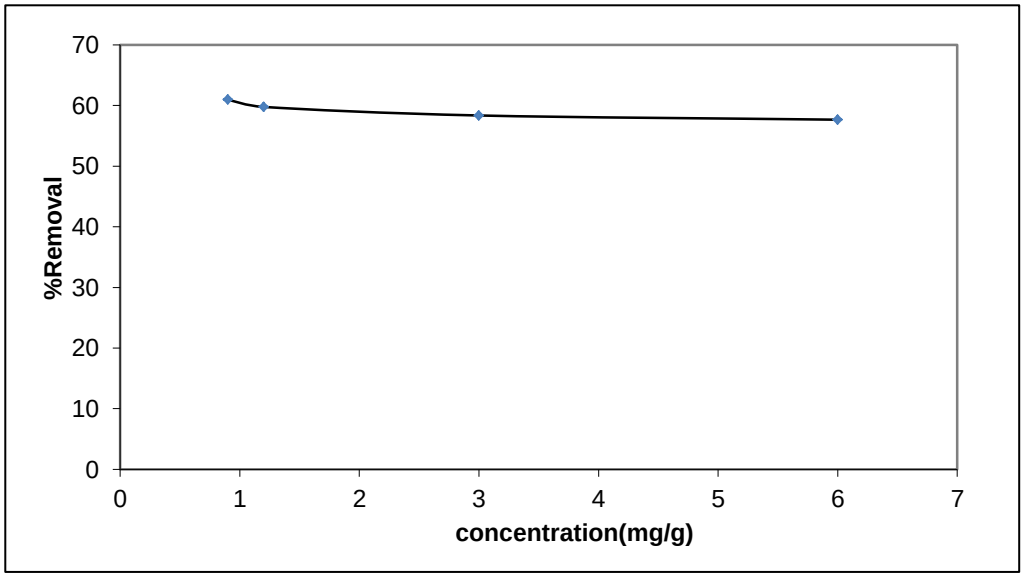

Fig 3.4.1: % Removal of naproxen versus initial concentration of ibuprofen.

3.4.2 Effect of contact time on the adsorption of naproxen

The results show that the remaining concentration of naproxen in solution has lowest value at 5 min, after that it incraese in insignificants amount as shown in Fig3.4.2.

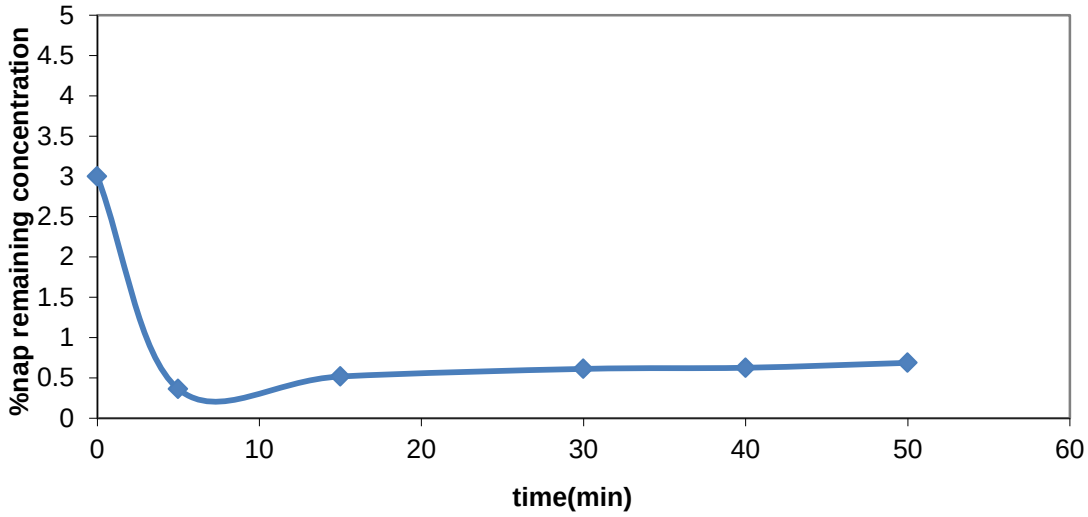

Fig 3.4.2: Concentration of ibuprofen vs. time

3.4.3 Effect of amount of amine modified silica on adsorption of naproxen.

Equilibrium concentrations (Ce), and % removal of naproxen at a constant initial concentration of 3 ppm (Co) versus different amounts of amine modified silica (M) were calculated at the equilibrium time.

% Removal of naproxen increases as the amount of amine modified silica increases as shown in Fig3.4.3.

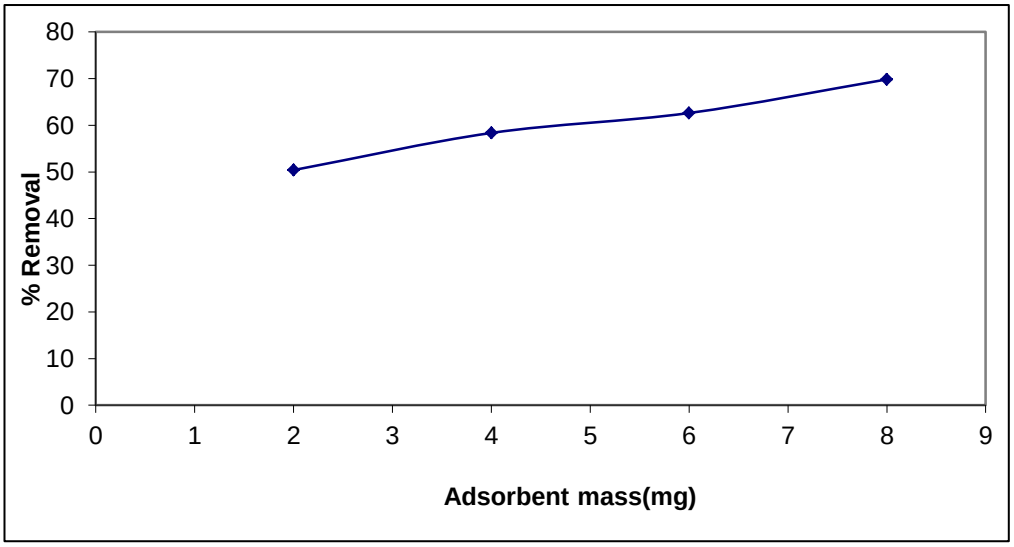

Fig3.4.3: % Removal of naproxen vs. amount of amine modified silica.

3.4.4 Effect of pH on Adsorption of naproxen

Equilibrium concentrations (Ce), and % removal of naproxen at constant initial concentration of 3 ppm (Co) versus different pH values were calculated at the equilibrium time, as shown in figure 3.4.4.

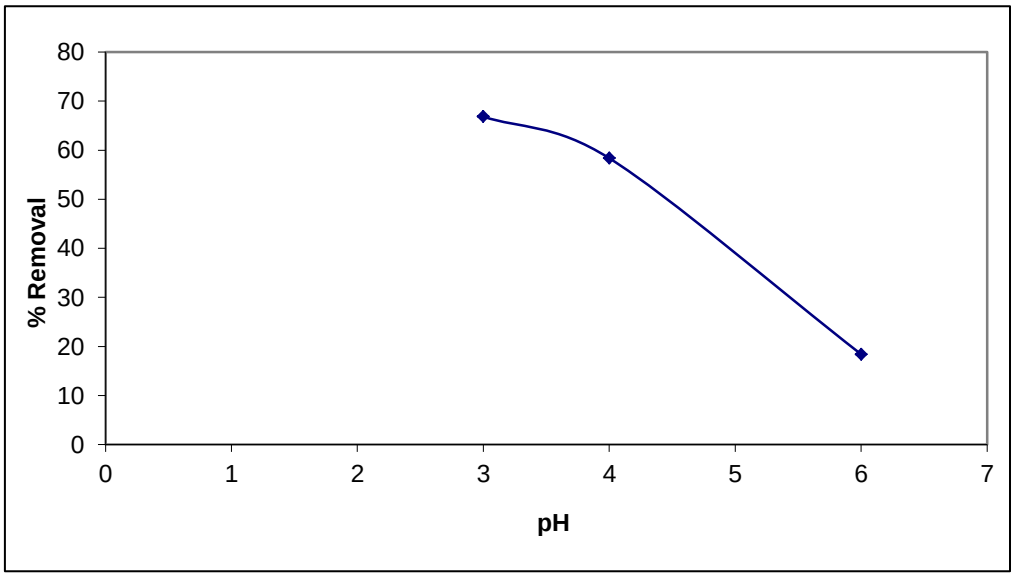

Fig 3.4.4: % Removal of naproxen vs. pH

It appears that as the value of pH decreases, the percent of removal of naproxen increases.

3.4.5 Effect of Temperature on the adsorption of naproxen

The amount of adsorbed naproxen by 0.004g of amine modified silica was studied versus temperature at equilibrium time, by using constant initial concentration of 3 ppm.

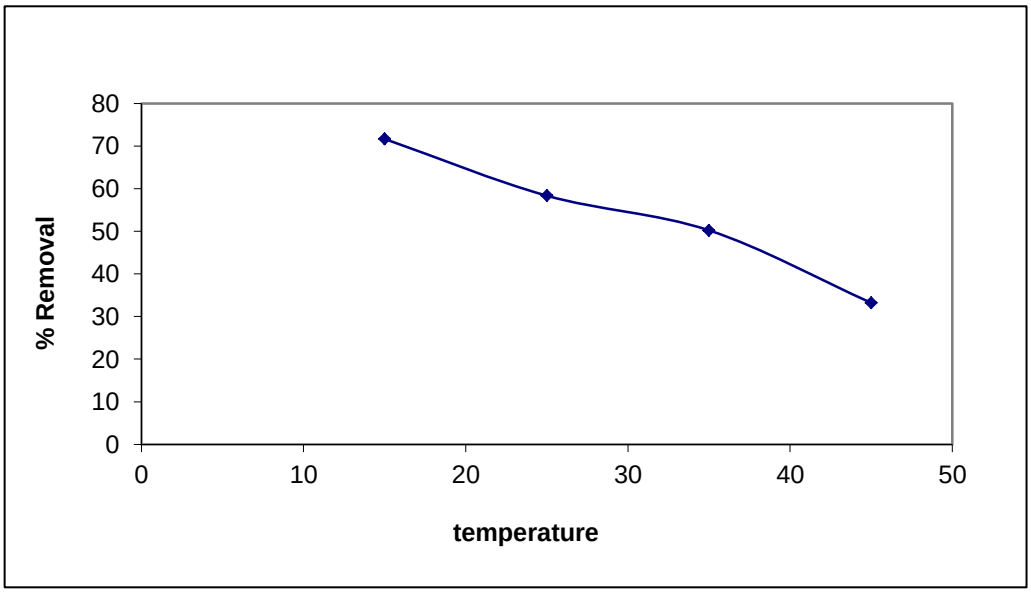

Fig 3.4.5: % Removal of naproxen vs. temperature

The figure show that the amount of naproxen adsorbed in amine modified silica decrease as the temperature increase, this is because that the increasing of temperature making the hydrogen bonds weaker.

3.5 Adsorption isotherms

To study the adsorption behavior of ibuprofen and naproxen on amine modified silica, two adsorption isotherm were used; Langmuir and Freundlich isotherms.

3.5.1Adsorption isotherms for adsorption of ibuprofen

Table 3.5.1:Adsorption isotherm of ibuprofen into amine modified silica.

Co	Ce	Ye	1/Ce	1/Ye	LogCe	Log(Ye –Yt)
5	3.124	4.690	0.320	0.213	0.495	0.671
10	6.938	7.655	0.144	0.131	0.841	0.884
15	10.651	10.872	0.094	0.092	1.027	1.036
20	14.527	13.682	0.069	0.073	1.162	1.136

Langmuir isotherm was obtained by plotting 1/Ye vs. 1/Ce as shown in (Fig.3.5.1.1).

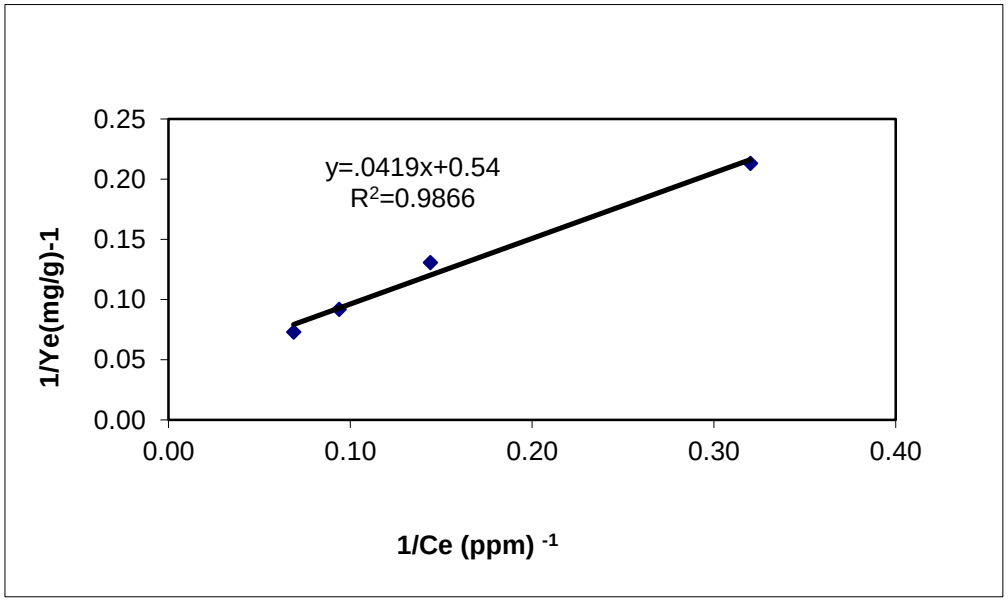

Fig 3.5.1.1: Langmuir isotherm for adsorption of ibuprofen onto amine modified silica.

From the relation between Log Ye versus Log Ce, Freundlich isotherm was obtained as shown in Fig 3.5.1.2

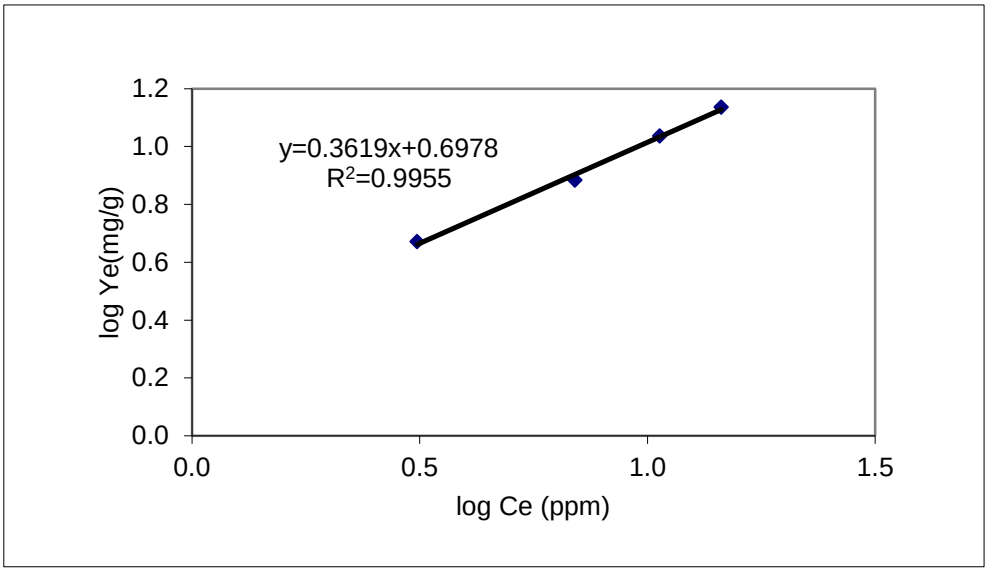

Fig 3.5.1.2: frendlich isotherm for adsorption of ibuprofen onto amine modified silica.

Langmuir and Freundlich figures show that the adsorption of ibuprofen on amine modified silica follows the Freundlich adsorption isotherm because its correlation coefficient is closer to unity.

From Freundlich isotherm equation: y= 0.697x +0.316

Freundlich constant (Kf) = 2.07 mg/g.

3.5.2 Adsorption isotherm of naproxen into amine modified silica.

Table 3.5.2: Adsorption isotherm of naproxen into amine modified silica

Co	Ce	Ye	1/Ce	1/Ye	LogCe	Log(Ye – Yt)
0.9	0.351	1.996	2.847	0.501	-0.454	0.300
1.2	0.483	2.651	2.072	0.377	-0.316	0.423
3	1.249	6.598	0.801	0.152	0.097	0.819
6	2.540	13.165	0.394	0.076	0.405	1.119

Langmuir isotherm was obtained from the relation of 1/Ye vs. 1/Ce as shown in Fig 3.5.2.1

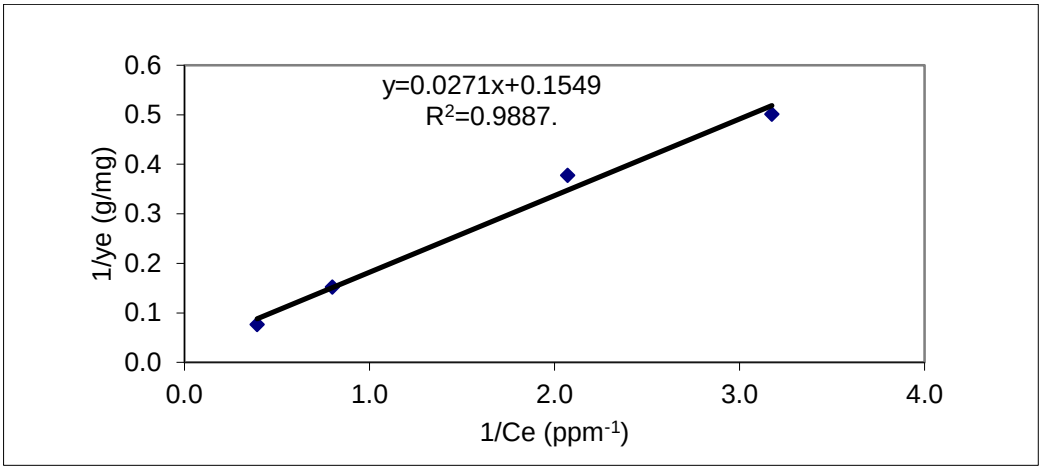

Fig 3.5.2.1: Langmuir isotherm for adsorption of naproxen onto amine modified silica

Freundlich isotherm was obtained by plotting log Ye vs. log Ce as shown in Fig 3.5.2.2

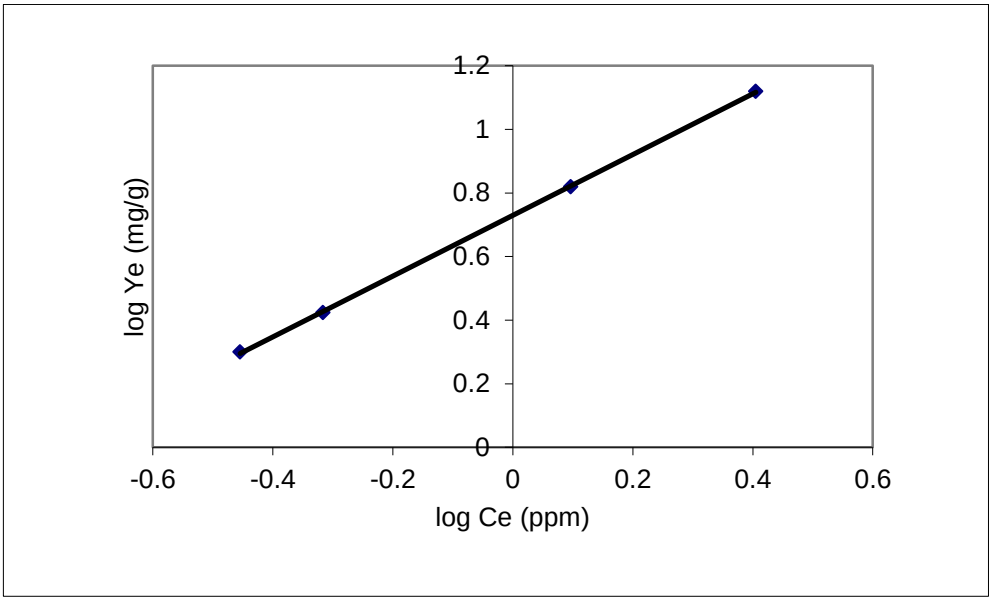

Fig 3.5.2.2: Freundlich isotherm for adsorption of naproxen onto amine modified silica

The adsorption followed Freundlich isotherm (R^2 = 0.999) better than Langmuir isotherm (R^2 = 0.988).

From Freundlich isotherm equation: y= 0.955x +0.73

Freundlich constant (kf) = 5.3 mg/g.

3.6 Kinetic study

3.6.1 Kinetic study for ibuprofen

3.6.1.1 Pseudo-first order model for the adsorption of ibuprofen on amine modified silica

Table 3.6.1.1 pseudo-first order model for the adsorption of ibuprofen on amine modified silica

Time(min)	Yt	Ye-Yt	Log(Ye-Yt)
5	7.636	0.510	3.236
30	2.713	0.912	8.159
40	2.907	0.901	7.965
50	2.636	0.916	8.236

The pseudo first order rate expression can be obtained by Plotting of Log (Ye-Yt) versus time as shown in Fig 3.6.1.1

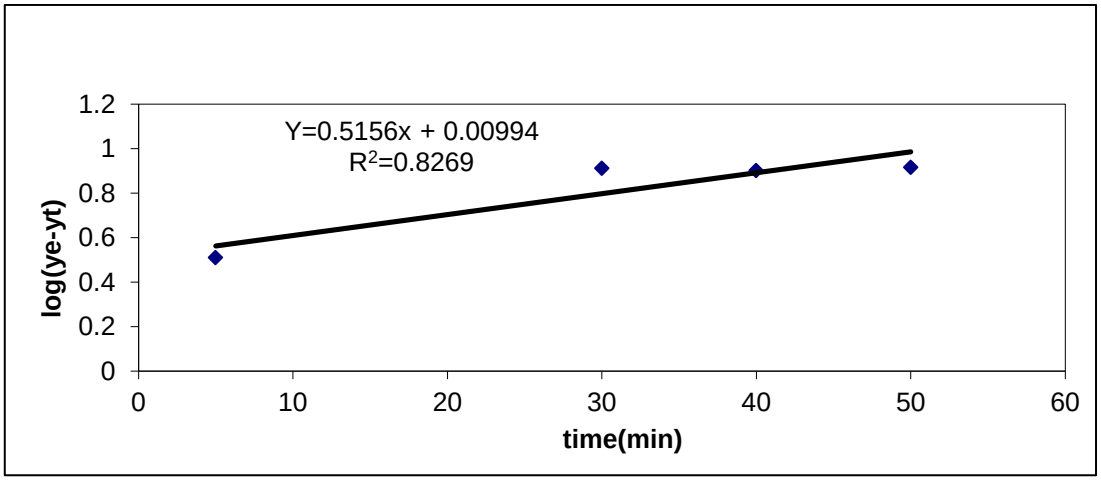

Fig 3.6.1.1: The pseudo first order rate expression for adsorption of ibuprofen on amine modified silica.

3.6.1.2 Pseudo-second order model for the adsorption of ibuprofen on amine modified silica.

Table 3.6.1.2 pseudo-second order model for the adsorption of ibuprofen on amine modified silica.

Time(min)	Yt	t/Yt
5	7.636	0.655
15	10.872	1.380
30	2.713	11.057
40	2.907	13.760
50	2.636	18.971

Plotting of t/Yt versus t give the expression of the pseudo second order adsorption as shown in Fig 3.6.1.2

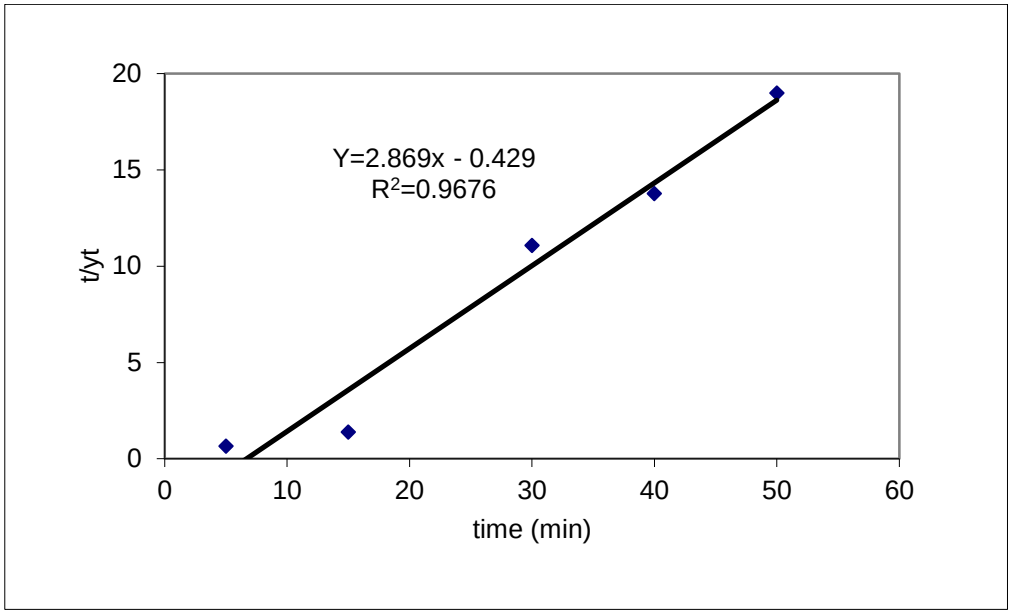

Fig 3.6.1.2: expression of the pseudo second order of adsorption of ibuprofen on amine modified silica.

The previous plots show that the correlation coefficient in the pseudo-second order model is closer to unity than in the pseudo-first order model, this mean that the adsorption of ibuprofen on amine modified silica follows the pseudo second order model.

From the slope and the intercept, the adsorption can be described with Ye=2.327mg/g, and K_2 = 0.064 g $mg^{-1}min^{-1}$.

3.6.2 Kinetic study for naproxen

3.6.2.1 Pseudo-first order model for the adsorption of naproxen on amine modified silica.

Table 3.6.2.1: Pseudo-first order model for the adsorption of naproxen on amine modified silica.

Time(min)	Yt	Ye-Yt	Log(Ye-Yt)
15	3.032	1.345	0.129
30	2.215	2.162	0.335
40	2.098	2.279	0.358
50	1.570	2.807	0.448

The expression of pseudo first order reaction can be obtained by plotting Log (Ye-Yt) versus time as shown in Fig 3.6.2.1

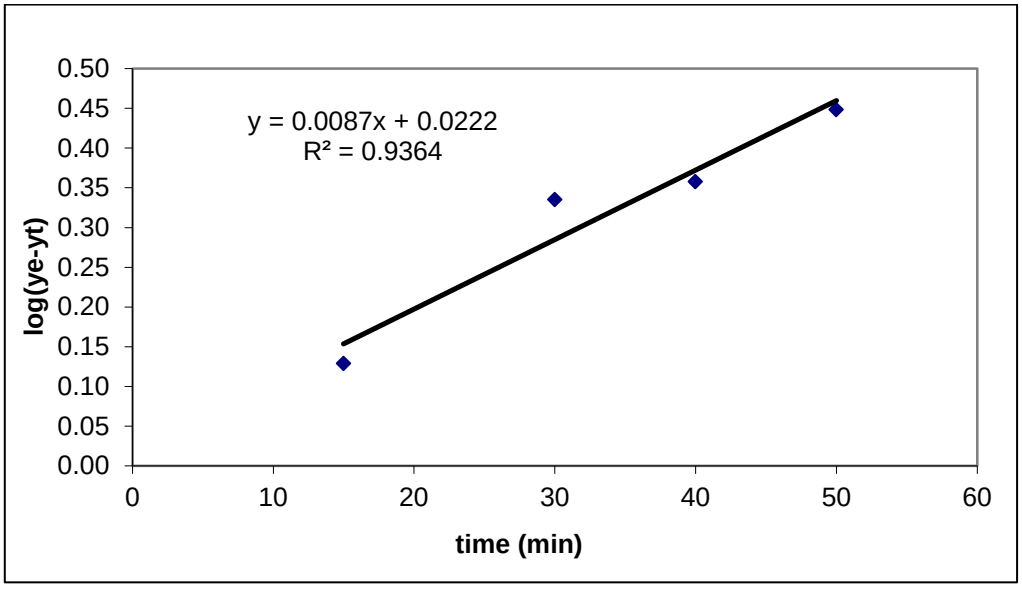

Fig 3.6.2.1: Pseudo-first order model for the adsorption of naproxen on amine modified silica.

3.6.2.2 Pseudo-second order model for the adsorption of naproxen on amine modified silica.

Table 3.6.2.2: pseudo-second order model for the adsorption of naproxen on amine-modified silica

Time(min)	Yt	t/Yt
5	1.142	4.377
15	4.947	3.032
30	13.547	2.215
40	19.068	2.098
50	31.846	1.570

Plotting oft/Yt versus t give the straight line of the pseudo second order adsorption as shown in the Fig 3.6.2.2

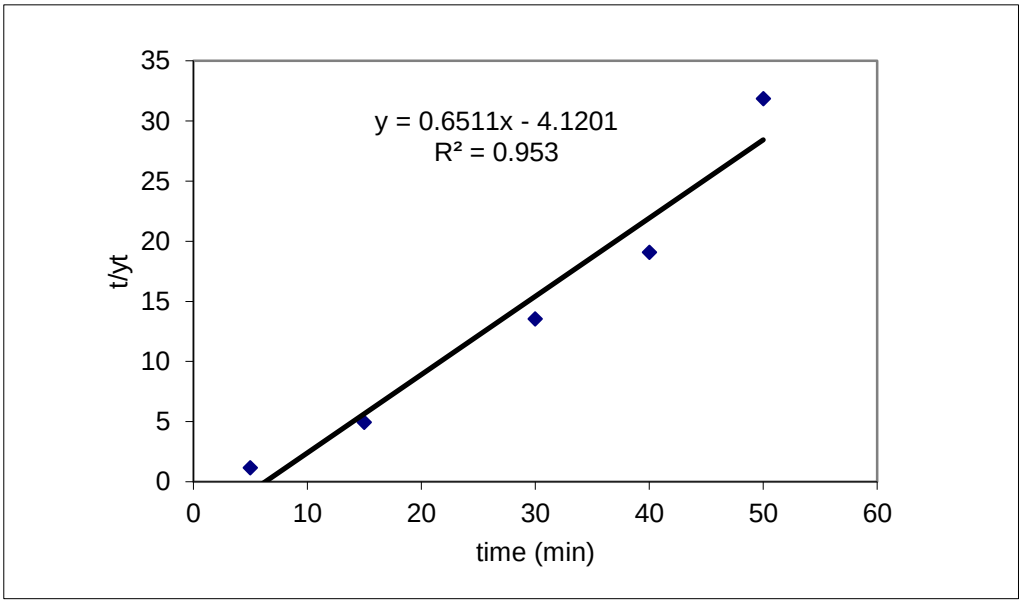

Fig3.6.2.2: pseudo-second order expression for the adsorption of naproxen on amine-modified silica.

The figures of the pseudo first and pseudo second order show that the adsorption of naproxen on amine modified silica follow the pseudo second order adsorption because its correlation coefficient is closer to unity.

From the slope and the intercept ye and k_2 can be calculated, which equal 1.535mg/g, and 0.103g mg $^{-1}$min^{-1} respectively.

3.7 Thermodynamic study

Different thermodynamic parameters were studied to decide if the adsorption of ibuprofen and naproxen on amine modified silica is spontaneous or not. These parameters are enthalpy change ΔH, entropy change ΔS, and Gibbs free energy change ΔG.

These parameters were calculated from the difference of the thermodynamic distribution coefficient D with the temperature change, according to these equations:

$$D = qe/Ce$$

$$ln\, D = (\Delta So/R) - (\Delta Ho/RT)$$

qe is the amount of ibuprofen, naproxen, adsorbed on amine modified silica(mg/g) at equilibrium.

Ce is the equilibrium concentration of ibuprofen and naproxen.

3.7.1 Thermodynamic calculations of the adsorption of ibuprofen onto amine modified silica

Table 3.7.1: Thermodynamic calculations of the adsorption of ibuprofen onto amine modified silica.

T(k)	1/T(k)	Ceppm	Qe(mg/g)	D(l/g)	LnD(l/g)
288	0.0035	7.249	19.378	1.819	0.598
298	0.0034	10.651	10.872	1.021	0.021
308	0.0032	12.124	7.190	0.675	-0.393
318	0.0031	13.535	3.663	0.344	-1.067

Plotting lnD vs. 1/T gives a straight-line, enthalpy change and entropy change were calculated from the slope and the intercept.

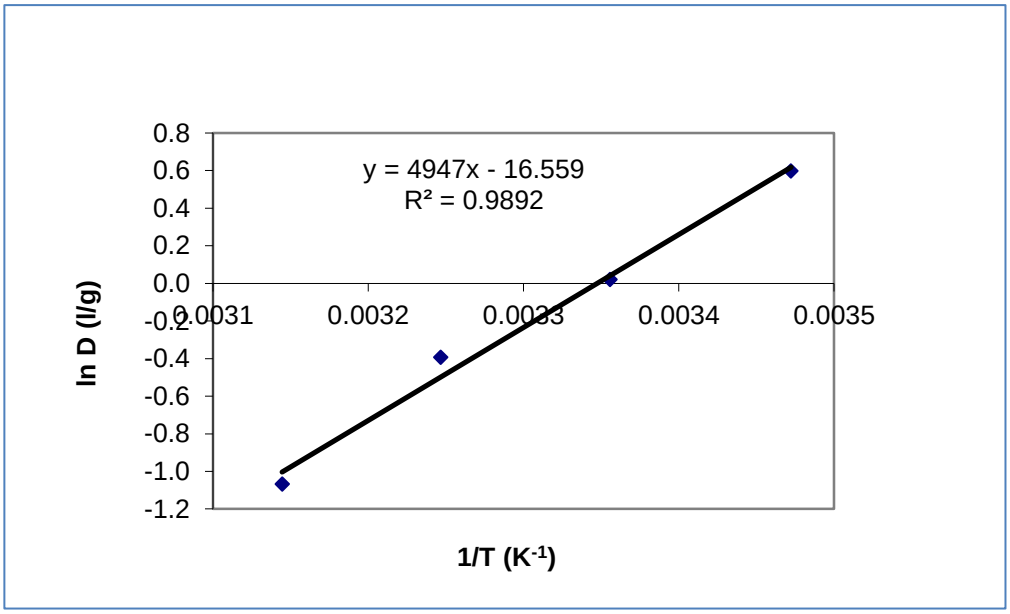

Fig 3.7.1: Thermodynamic study of the adsorption of ibuprofen on amine modified silica.

From the slope and the y intercept, the enthalpy change= -1.49 KJ, and the entropy change= 0.054KJ.

ΔG was calculated from the equation; ΔG= ΔH-TΔS and was found to be -17.582 KJ.

The negative values of the enthalpy change and Gibbs free energy change indicate that the adsorption of ibuprofen on amine-modified silica is exothermic and spontaneous respectively.

3.7.2 Thermodynamic studies of the adsorption of naproxen onto amine modified silica.

Table 3.7.2: Thermodynamic calculations of the adsorption of naproxen onto amine modified silica.

T(k)	1/T(k)	Ce(ppm)	Qe(mg/g)	D(l/g)	LnD(l/g)
288	0.0035	0.849	5.377	4.304	1.460
298	0.0034	1.249	4.38	3.505	1.254
308	0.0032	1.493	3.767	3.016	1.104
318	0.0031	2.003	2.491	1.995	0.690

Plotting of lnD vs. 1/T gave a straight-line; enthalpy change and entropy change were calculated from the slope and the intercept.

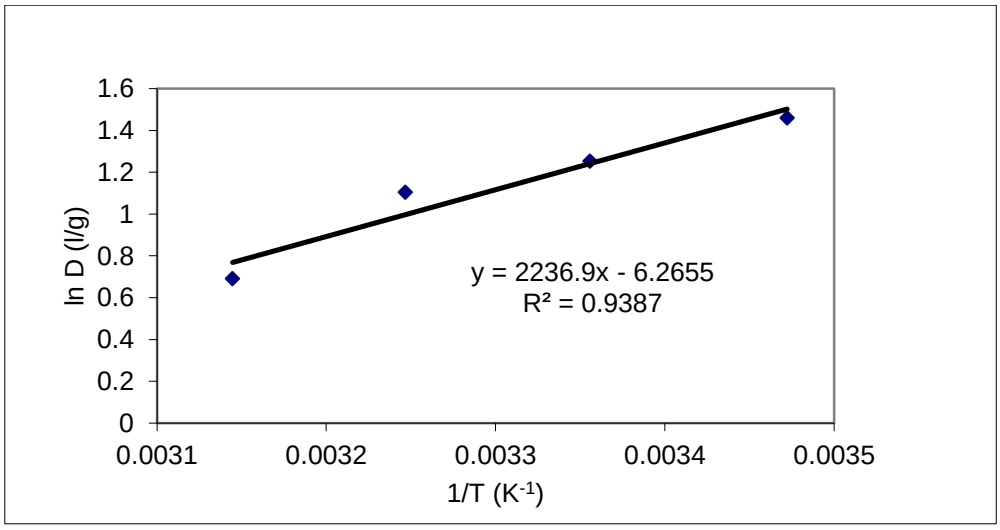

Fig 3.7.2: Thermodynamic study of the adsorption of naproxen on amine modified silica.

The slope and the y intercept gave that the enthalpy change= -0.675 KJ, and the entropy change= 0.021 KJ.

The equation; $\Delta G= \Delta H-T\Delta S$ gave that $\Delta G= -6.933$ KJ.

The enthalpy change and Gibbs free energy change were negative, which means that the adsorption of naproxen on amine modified silica is exothermic and spontaneous.

Conclusion

The results show that the adsorption of ibuprofen and naproxen on amine modified silica is good.

Adsorption of ibuprofen and naproxen on amine modified silica was affected by many factors, which are time, drug concentration, adsorbent amount, pH, and temperature.

The best adsorbed amount of ibuprofen on amine modified silica was obtained after 15 minute shaking, where it was after 5 minute shaking for naproxen.

The adsorbed amount of ibuprofen and naproxen increased with increasing the amine modified silica amount, where it decrease with increasing drug concentrations, pH, and temperature**.**

The results show that the adsorption of ibuprofen and naproxen followed Frendulich isotherm, it's also showed that the mechanism of the adsorption of both drugs followed thepseudo-second order kinetic adsorption model.

Gibbs free energy of the adsorption of ibuprofen and naproxen had negative values, which mean that the adsorption was spontaneous and exothermic.

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جامعة النجاح الوطنية

كلية الدراسات العليا

تنقية المياه من الايبوبروفين والنابروكسين باستخدام السيليكا المعدل بالأمين

إعداد

غدير إياد محمد سباعنة

إشراف

د. إبراهيم أبو شقير

أ. د. شحدة جودة

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

2021

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الملخص

يهدف هذا البحث إلى تنقية المياه من بعض العقاقير الطبية مثل الايبوبروفين والنابروكسين حيث تم استخدام السيليكا المعدل بالأمين كمادة مازة للتخلص منهما بالاعتماد على خاصية الادمصاص من خلال تحضير محاليل معيارية معروفة التركيز من الايبوبروفينو النابروكسين ومن ثم معاملتها مع السيليكا المعدل بالأمين وقياس تركيز الدواء قبل وبعد المعاملة باستخدام جهاز مطياف الأشعة المرئية وفوق البنفسجية على طول موجة 220 للايبوبروفين و230 للنابروكسين.

تمت دراسة اثر بعض العوامل على عملية الادمصاص، وهي كمية المادة المازة، وتركيز الدواء، ودرجة الحموضة، ودرجة الحرارة، وكذلك زمن اتصال العقار الطبي مع السيليكا المعدل بالامين.

أظهرت النتائج ان الوقت الأمثل لادمصاص الايبوبروفين هو 15 دقيقة، بينما هو 5 دقائق للنابروكسين.

كما تبين ايضا ان عملية الادمصاص لكلا العقارين تتأثر بكمية المادة المازة، وتركيز الدواء، ودرجة الحموضة، ودرجة الحرارة، حيث ان نسبة الادمصاص تزداد مع ازدياد الكمية المستخدمة من السيليكا المعدل بالامين, بينما تقل بازدياد تركيز العقار ودرجة الحرارة, وتبين ان افضل نسبة ادمصاص تكون عند درجة حموضة = 3.

تم وصف منحنيات الادمصاص من خلال تطبيق معادلتي لانجميروفرندلش، كما وتم دراسة وحساب بعض المتغيرات الثيرموديناميكية.