An-Najah National University

Faculty of Graduate Studies

Using Maghemite Nanosorbcats for Adsorptive Removal of Alizarin Dye from Aqueous Solution for Wastewater Treatment and Catalyst Regeneration

By

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Dedication

I dedicate this thesis to my wonderful parents for their love, unfailing support and continuous encouragement throughout my life. Also to my brothers and sister: Mohammad, Mothana, and Nouran, whom I am truly grateful for having in my life.

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First and foremost, I would like to thank God Almighty for giving me the strength and ability to persevere and complete this thesis.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحت عنوان:

Using Maghemite Nanosorbcats for Adsorptive Removal of Alizarin Dye from Aqueous Solution for Wastewater Treatment and Catalyst Regeneration

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.

Declaration

The work provided in this thesis, unless otherwise referenced is my own research work and has not been submitted elsewhere for any other degree or qualification

Student's name : **اسم الطالب:**

Signature : **التوقيع :**

Date **التاريخ:**

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List of Abbreviations

Symbol	**Abbreviations**
NP's	Nanoparticles
ALZ	Alizarin
AC	Activated Carbon
DW	Distilled Water
C_o	Initial concentration of adsorbate in the solution
C_e	Equilibrium 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
K_S	SIPS isotherm constant
R^2	Correlation coefficient
R	Ideal gas constant
$\Delta G°$	Standard Gibbs free energy
$\Delta H°$	Standard enthalpy
$\Delta S°$	Standard entropy
pzc	Point of zero charge

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Abstract

In this study, maghemite iron oxide (γ-Fe_2O_3) nanoparticles (NP's) were used as adsorbents for the removal of Alizarin (ALZ) dye from aqueous solution. Different experimental parameters such as effect of amount of adsorbent, solution pH, shaking-contact time and temperature have been studied. It was observed that adsorption was affected by the amount of maghemite NP's until the equilibrium level. The optimum pH value for ALZ adsorption was *ca.*11 and the equilibrium was established within the first hour. It was also evident that the adsorbed ALZ was decreasing as temperature was increased, suggesting an exothermic adsorption. Pseudo-order kinetic models were used to test the experimental data in order to elucidate the kinetic adsorption process. It was found that ALZ adsorption kinetics has followed pseudo-second-order. Experimental data were analyzed using three model equations: Langmuir, Freudlinch and SIPS isotherms at pH range 8-12 and it was found that the data fitted well with Langmuir isotherm model. The maximum sorption capacity at 298 K for ALZ dye was 28.5 mg g^{-1}. The thermodynamics of ALZ adsorption onto the NP’s was investigated and the thermodynamics parameters, such as standard Gibbs free energy ($\Delta G°$), standard enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) were calculated and indicated that the process is spontaneous, exothermic in nature and follows physisorption mechanism. This study shows that the γ-Fe_2O_3 NP's can be regenerated four cycles using HNO_3 without impacting its adsorption capacity. Catalytic properties of γ-Fe_2O_3 NP's were investigated by photocatalytic degradation under UV-light; the results showed that the removal efficiency of ALZ was increasing without affecting the γ-Fe_2O_3 NP’s magnetic properties with near complete removal of ALZ dye.

CHAPTER 1

Introduction

1.1 Background

Fresh water, the most vital element of life, is becoming depleted. Wastewater is one of most serious challenges facing the world in recent years.[1,2] Rapid increase in world population, industrialization, and modernization require higher demand of fresh water. In Palestine, wastewater represent one of the most serious challenges resulting from both population growth and rapid industrial development.[3] There are approximately 1700 factories producing textiles in Palestine.[4] Moreover, large amounts of wastewater are being produced daily from factories, farms and houses.[5] While clean water is an essential resource for humans and their environments throughout the world; various types of water pollution, including heavy metals,[6] dyes[7] and industries such as petroleum refining, petrochemical, pulp, paper, food and textile involve processes that generate a wide variety of effluents and their effects on the aquatic environment are investigated over the years.[8] Wastewater sourced from these types of effluents typically has high levels of colloidal suspension and dissolved organic pollutants.[3] Many researchers have been focused on finding a solution to these problems using several techniques and technologies including electrochemical technologies,[9] adsorption onto different adsorbents,[10,11,] and reverse osmosis processes,[12] and nanotechnology[13] typically in the form of nanoadsorbent.[14] But the main goal remains on finding a new, efficient, and cost-effective technique. So we should work on developing a cheap, simple, easy and widely applicable treatment technologies able to treat maximum amount of wastewater effectively.

1.2 Sources of water pollution

Water pollution can be defined as the contamination of streams, lakes, seas, underground water or oceans by substances which are harmful for living beings.[15] When these contamination reaches beyond certain allowed concentration, it is called pollution and the contaminants are called the pollutants which are capable of making any physical, chemical or biological change in the water body.[16] There are numerous sources of pollutants like human and animal sewage, fertilizers, pesticides and industrial effluents that generate natural and synthetic organic chemicals which are a major problem of water pollution.[8]

1.2.1 Dyes

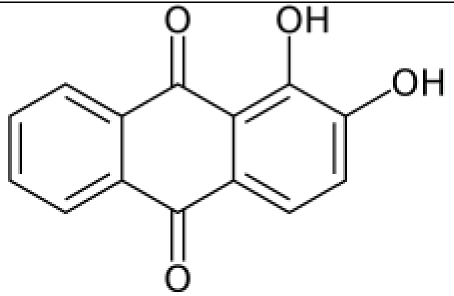
Dyes are an important class of synthetic organic compounds used in many industries like textile, rubber, plastic, leather, cosmetics, and medicine. However, textile industries are the main consumer of dyes,[8] which make them a significant source of a contamination responsible for the environmental pollution. Dyes can be easily identified by the human eye, aren’t easily biodegradable and many of them are toxic in nature, with suspected carcinogenic and mutagenic effects.[17] Dyes wastes represent one of the most problematic groups of pollutants. It is estimated that more than 100,000 commercially available dyes and pigments with over 700,000 tons produced annually in the world,[18] which is quite harmful to the environment. In Palestine, the textile and clothing industry is one of the important sectors in terms of production, investment, employment and exports. The Palestinian Investment Promotion Agency (PIPA) estimated that the highest concentration of textile factories in the West Bank is concentrated in the city of Nablus with 362 factories in business. There are 760 factories in Gaza with the rest of 578 factories distributed throughout the West Bank towns and cities. Israeli settlements are the main cause of environmental pollution, which results mainly from wastewater and sewage that flows from these settlements into Palestinian agricultural land nearby. This has destroyed crops and diffused diseases and epidemics in the area. Consequently, establishment of strategies to reduce their harmful effects is very important. The disposal of wastewater from different industries has received a great attention by environmental studies.[19] Furthermore, increasing manufacture and application of synthetic dyes taking into account their impact on the environment, needs an effective response in terms of modern and viable treatment processes.

A very common classification of the dyes is based on the source from which it is made, according to this classification, dyes could be natural and synthetic.[20] Dyes also may be classified according to the type of chromophores present in their structure including azo dyes, nitro and nitroso dyes, and anthraquinone dyes. Anthraquinone dyes are the second most important class of dyes after azo dyes, it is an important and widely used raw materials for the manufacture of vat dyes, which are a class of water-insoluble dyes.[21] A lot of dyes belong to anthraquinone including; purpurin, morindon, rubuadin, and alizarin dye.

1.2.2 Alizarin dye

Alizarin (ALZ) dye is the a well-known anthraquinone isolated from madder plant.[22] It is an orange crystalline compound, insoluble in water and acidic medium, and used in the manufacture of dyes and red pigments.[23] ALZ can be used as a pH indicator because it produces colored solution depending on pH of solution, and in biochemical assay (stain) to identify calcium in tissue section.[24] The chemical structure and general physical properties of ALZ are outlined in Table 1.1.

Table 1.1: Structure and properties of Alizarin dye.

Name	**Alizarin**
Chemical structure	
Synonym	1,2-Dihydroxyanthracene-9,10-dione
Molecular weight	240.21 g/mol
Chemical formula	$C_{14}H_8O_4$
Solubility in water	Insoluble at pH ≤ 7, soluble at pH ≥ 8
Color	Yellow below pH 7, purple at pH 7, orange between 8 and 9, red at pH higher than 9
Color index number	58000
λ_{max}	Depending on pH solution

Many types and structures, like Alizarin red S (ARS) and Alizarin Yellow R (AYR), are used in various fields and industries especially as a textile dyes. These dyes were not given a lot of attention from researchers over years. Despite the fact that some research was done to remove ALZ dye from wastewater, this research lacks deep investigation about thermodynamics, adsorption mechanism, and the catalyst regeneration. Also, such studies were performed in acidic solution;[25] were solubility of ALZ in that medium is very low.[23] Fayazi *et al.*[26] investigated the adsorption behavior of (ARS) from aqueous solution onto magnetic activated carbon nano-composite under various experimental conditions including pH, concentration of the dye, amount of adsorbents and contact time. Fu *et al.*[27] investigated the adsorption (ARS) on activated clay modified by iron oxide (Fe-clay) in a batch reactor. Gholivand *et al.*[28] used polypyrrole-coated Fe_3O_4 NP's for removal of ARS and ARY from aqueous solutions and several parameters such as pH, sorbent amount, and contact time were studied. Although many studies [29,25] have highlighted on the adsorptive removal of different types of Alizarin dyes from aqueous solutions, they did not focus on the ALZ dye itself which is the simplest anthraquinone and mimics many organic pollutants. Also, they did not attempt to develop a technique to treat this dye were its solubility in acidic solution is very low. Herein, a technique to treat ALZ with its low solubility was developed and ALZ was used as a model molecule of pollutants. The choice of ALZ for this study was based on its unique structure which mimics many hydrocarbon pollutants. These pollutants are not limited to the textile industry, but also exist in several industrial activities, especially in the oil industry.

1.3 Wastewater treatment technology

Dye waste treatments including biological treatment, catalytic oxidation, filtration, and sorption process have been developed over the past years. Choosing one or more of these processes depends on the nature of dyes and their classification. Sometimes. A single technology may not be sufficient for the treatment of polluted water. Dye pollutants, however, are often the most difficult substances to treat, and therefore, they have received a lot of attention over the last few decades.[13,30] The traditional treatment technologies like adsorption by activated carbon, oxidation, extraction and reverse osmosis membrane are somewhat effectively but they are often very expensive and are not able to address adequately the removal of toxic chemicals present in water. Biological treatment technology, for example, removes a significant amount of the organic content. The average removal efficiency of acid dyes using this method is between 80 and 90%, but it generates high amounts of sludge.[31,32] Similarly, activated carbon (AC), which was one of the first materials to be used in this field, shows a high removal of wide variety of dyes but the filters used for separation of the contaminated AC from treated solution have a lot of limitations including short service life, so it has to be replaced regularly. Because when the filter surfaces are saturated with adsorbed pollutants, no further purification occurs and this in turns makes the water treatment by AC very expensive.[33] Although ion exchange method has an advantage where no adsorbents are lost, but generally limited by high operational costs, selectivity and water acidity due to sodium ions into the softened water.[8] In shortly, traditional wastewater technologies become ineffective for wastewater treatment especially with increasing in sources of pollutants and demanding for water in parallel. So, we should work on finding effective techniques have the ability to remove such pollutants from water. In general, adsorption techniques have proved to be an effective process for removal of non-biodegradable dyes from wastewater; it is involved as one of the most effective physical processes for the treatment of textile wastewater. It is a simple, easy, efficient, and economical method for the removal of dyes which in turns made it a major part of many different processes through industrial field.

1.4 Adsorption process

Adsorption is a phase transfer process that is widely used in practice to remove substances from fluid phases (gases or liquids).[34] It can also be observed as natural process in different environmental compartments. The most general definition describe adsorption as an enrichment of chemical species from a fluid phase on the surface of a liquid or a solid. In water treatment, adsorption has been proved as an efficient removal process for a multiplicity of solutes. Here, molecules or ions are removed from the aqueous solution by adsorption onto solid surfaces. The solid material that provides the surface for adsorption is referred to as adsorbent. the species that will be adsorbed are called adsorbate.[10] While understanding the adsorption process cannot be considered separately from properties of the solid surface, i.e. adsorbent surface because these adsorbents take a wide range according to their chemical and physical properties. During the last few decades, there is growing interest and an obvious tendency for the use of nanoadsorbents which offer significant improvement with their distinctive properties in different fields.

Nanotechnology has emerged in recent years with a wide range of applications. Over 50,000 nanotechnology articles have been published annually worldwide in recent years with applications in several scientific and research field, such as information and communication technology, electronics, energy, biology, and medical technology.[35] Nanotechnology can offer important applications such as catalytic membranes, nanosorbents, bioactive NP’s and metal NP’s such as iron, silver, titanium oxides and many others. During the last few decades, there is growing interest for the use of NP’s in water and wastewater treatment technology as a nanoadsorbents which offer a significant improvement with their extremely high specific area and associated sorption sites.[36] In the last few years, there was a rapid progress in the fabrication and processing of magnetic nanosorbents that helps treating wastewater and proved very interesting tool especially for organic contaminants removal. Since most of the contaminants are not of magnetic nature and separation of contaminated NP’s is necessary, the adsorption process followed by magnetic separation benefited from NP’s magnetic properties which make the method easy and effective method.

Numerous types of NP's have been used as magnetic adsorbents for treating water from different types of contaminants and many researchers have been focusing their efforts on utilizing of iron oxide nanomaterials due to their unique properties, such as high surface area to volume ratio, chemical inertness, surface modifiability, excellent magnetic properties, catalytic oxidizing capabilities, cost-effective, and ability to penetrate through porous media.[39] Additionally, due to their low toxicity, iron oxide NP's are environmentally friendly.

For adsorption technologies, especially if the pollutants are toxic, the actual process is achieved by the accumulation and transfer of pollutants from aqueous solution to the adsorbent phase. So, the pollutants will not eliminate but simply transfer from wastewater to adsorbent surface. While using NP’s which has distinctive properties like iron oxide will solve the problem of contaminated NP's themselves.

Iron oxides exist in numerous forms in nature; magnetite (Fe_3O_4), maghemite (γ-Fe_2O_3), and hematite (α-Fe_2O_3) are the most common because of their high adsorption capacity and short adsorption equilibrium time, which provides the opportunity to remove high amount of pollutant in shorter time.[37]

There are various studies applied magnetic iron oxide NP's as adsorbent to remove different contaminants and pollutants from aqueous solutions. El-Qanni *et al.*[38] investigated the adsorption subsequent catalytic thermo-oxidative decomposition for methylene blue on surface of maghemite (γ-Fe_2O_3) NP's. Nassar[39] studied the adsorption of acid red dye 27 onto (γ-Fe_2O_3) nanoadsorbents for the removal of red dye from aqueous solutions by the batch-adsorption technique. Mak *et al.*[40] have studied the adsorption of methylene blue from an aqueous solution by polyacrylic acid-bound iron oxide magnetic NP's. Iram *et al.*[41] have removed natural dye from an aqueous solution using magnetite hollow nanospheres. Xu *et al.*[42] have used iron oxide magnetic NP's and Ca-alginate immobilized Phanerochaetechry-sosporium was prepared for removal of Pb(II) ions. Although previous research has studied the ability of iron oxide NP's for metal ion and dyes adsorption, few dyes were actually tested. Moreover, many studies focused into percentage removal of contaminates from water by adsorption methods using NP's without deep investigation onto the adsorption mechanism and thermodynamics parameters.[40,43] These studies did not attempt to solve the problem of contaminated NP's themselves or regenerating the NP's catalyst.

Catalysis, are closely connected with adsorption and plays an important role in environmental protection and everyday life. The term catalyst denotes a body or a material which accelerates a chemical equation but does not appear either in the reactants or products of chemical equation of this reaction. It enhances the rate of the reaction, and is finally regenerated as its end. [44]

At recent years, the adsorption and catalytic processes were integrated as an effective technique for removing organic contaminants from wastewater and benefit from catalytic behavior for regeneration by using a nanosorbcats; which is a new acronym introduced to the world of adsorption and catalysis by Dr. Nassar Group for Nanotechnology Research at the University of Calgary, Alberta, Canada. The development and employment of nanosorbcats in adsorption process as an adsorbent can be considered as the best choice to provide a very effective process for wastewater treatment.[38, 45]

Herein, γ-Fe_2O_3 NP's were used as nanosorbcats for adsorptive removal of ALZ dye from aqueous solution and catalyst regeneration.

1.5 Adsorption isotherm

Adsorption isotherm is an invaluable tool for the theoretical evaluation and interpretation of experimental data obtained from adsorption process at equilibrium under optimum conditions with constant pH and temperature. Experimental data obtained by batch adsorption tests is processed using several equations and relations to obtain adsorption isotherm relation between the amount of adsorbate per unit of adsorbent (q_e) and the equilibrium concentration of solution after adsorption (C_e). Adsorption isotherm is a good method for determining the performance of an adsorbent and the efficiency of adsorption process but lonely, without any interpretation or modeling of data, it does not provide any information especially about the adsorption mechanism. So, modeling of adsorption isotherm data is a necessary way for predicting the mechanism of adsorption. Several isotherm models were developed over the years. There are three common models for isotherms including, Langmuir, Freundlich, and SIPS isotherms. These isotherms relate adsorbate uptake per unit mass of adsorbent, q_e, to the equilibrium adsorbate concentration in solution after adsorption, C_e by the following equations:[46,34]

$$q_e = \frac{C_o - C_e}{W} V \tag{1}$$

$$q_t = \frac{C_o - C_t}{W} V \tag{2}$$

where C_o, C_t, and C_e (mg/ L) are adsorbate concentration of initialization, time t, and equilibrium and V (L) and W (g) are solution volume and adsorbent dosage, respectively.

Each model based on a set of assumptions that are mainly give an idea about the adsorption mechanism. In order to determine the best fit isotherm model, the correlation coefficient (R^2) was used. In this study, the experimental data were analyzed by three well-known Langmuir, Freundlich, and SIPS isotherm models.

The Langmuir isotherm is generally considered as the simplest models which is widely used for modelling equilibrium data. Langmuir isotherm assumes that the surface of an adsorbent is homogenous, which means that all sorption sites on the surface are identical and they all bind with the same strength for one type of sorbate. Another important assumption is that the adsorption involves the attachment of only one layer of molecules to the surface, i.e: monolayer adsorption.[47] Based upon these assumptions, Langmuir represents the following equation:-

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{1}{q_m} C_e \qquad (3)$$

Langmuir adsorption parameters are usually determined by transforming the Langmuir equation into linear form:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m} K_L C_e \qquad (4)$$

where:

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

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

q_m = maximum monolayer coverage capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg).

Freundlich isotherm

The Freundlich isotherm was derived by modifying the Langmuir model to allow for several kinds of adsorption sites on the solid, each kind having a different heat of adsorption.[48] The Freundlich isotherm is not valid at very high pressures, but it is frequently more accurate than the Langmuir isotherm for intermediate pressures. The main Freundlich equation is given by:[49]

$$q_e = K_f \, {C_e}^{1/n} \qquad (5)$$

Where K_F (L/mg) and $1/n$ are the Freundlich adsorption constants. eq.(5) can be rearranged to:

$$log\, q_e = \; log\, k_f + \frac{1}{n} log\, C_e \tag{6}$$

Hence a plot of log q_e vs. LogC_e gives a slope of 1/n and an intercept = log K_F.

SIPS Isotherm

The SIPS isotherm is combined formula of the Langmuir and Freundlich isotherm models deduced for predicting the heterogeneous adsorption systems. At low adsorbate concentration, it reduces to Freundlich isotherm, while at high concentration, it predicts a monolayer adsorption which is characteristic of the Langmuir isotherm. The general form of the SIPS isotherm model is: [50]

$$q_e = q_m K_s\, {C_e}^{1/n} / (1 + \; K_s {C_e}^{1/n}) \tag{7}$$

where C_e is the equilibrium concentration of the analytes in the solution(mg/L), q_e is the amount of analytes adsorbed per unit mass of adsorbent (mg/g), K_S is the SIPS constant and q_m shows the maximum adsorption capacity (mg/g), which depends on the number of adsorption sites.

1.6 Aims of the study

The main purpose of this study is to develop an efficient, and cost-effective technique for adsorptive removal of ALZ dye from aqueous solution using maghemite (γ-Fe_2O_3) NP's. In addition, this work aims to investigate the possibility of regenerate NP’s without affecting its adsorption capacity and magnetic properties. At our knowledge, it is the first study reporting the use of γ-Fe_2O_3 NP’s for treating wastewater from ALZ dye, regenerate the γ-Fe_2O_3 NP’s and benefiting from their catalytic properties while keeping their magnetic properties.

The framework of this work is based on studying the effect of different parameters such as amount of adsorbent, solution pH, shaking-contact time and temperature on the adsorptive removal of ALZ on γ-Fe_2O_3 NP's. In each set all variables were fixed and only one variable was changed. Batch adsorption experiments were carried out by using 25 mL vials each containing 10 mL ALZ solution with initial concentration ranging from 0 to 96.08 mg/L and at different pH ranging from 8-12, with specified amount of NP's. The vials were tightly sealed and shaken at 130 rpm at 25 °C for 4 h. In all experiments, the contaminated NP’s were separated from treated solution using small magnet bar. After that, the supernatant was decanted and its concentration was measured by UV-Spectrophotomerty (UV-vis).The separated contaminated NP’s were regenerated by washing with distilled water (DW) and HNO_3 and reused for four cycles without loss their adsorption capacity. The catalytic properties for NP’s were investigated by photocatalytic degradation under UV-light irradiation without affecting their magnetic properties.

CHAPTER 2

Experimental

Instruments and Materials

All chemicals including γ-Fe_2O_3 NP's, ALZ dye, Borax, NaOH, HCl, KH_2PO_4, KHP and acetic acid were purchased from Aldrich Chemical Company, and were used as received without further purifications. MRC analytical balance ASB-310-C2-V2 was used for weighting in all experiments. ALZ dye was selected as a source of organic pollutant for this study. Batch adsorption experiments were carried out using 25 ml plastic vials. The vials, containing 10 ml of an aqueous solution and specified amount of NP's, were tightly sealed and shaken using Lab Tech® shaker (DaihanLabtech). The pH was adjusted and measured using JENWAY 3510 pH meter at the laboratory ambient temperature. In all experiments, the contaminated NP's were separated from treated media by magnetic separation using small magnet bar, and the supernatant was decanted. No filtration was performed to avoid any side adsorption by filter papers. The concentration of ALZ in the supernatant was measured by UV-vis spectrophotometer (UV-vis. SHIMADZU UV-1800). Fourier transform infrared (FTIR) spectroscopy in the range (4000- 400 cm^{-1}) were used for characterization of ALZ and identify the changes on NP's before and after adsorption. Spectra were recorded using Thermo Scientific Nicolet Is5FTIR spectrophotometer. The apparatus employed in the photocatalytic experiments consist of the light source and the photoreactor. The UV chamber equipped with a UV lamp, fitted on the top of the chamber. To stabilize the temperature inside the chamber, a fan was fitted on the sidewall of the chamber.

This experimental section is divided into two parts. (1) Adsorption process. (2) Regeneration of the adsorbent. The first part include studying the effect of various parameters such as amount of adsorbent, shaking-contact time, solution pH, effect of temperature, and UV-light irradiation on adsorption process and removal efficiency. In the second part, the contaminated adsorbent was regenerated and reused several times to test its reusability.

2.1 Sample preparation and calibration curve.

2.1.1 Preparation of stock solution

For the preparation of 1.00×10^{-4} and 4.00×10^{-4} M ALZ stock solutions, 24.021 and 96.08 mg ALZ (240.21g/mol), respectively were accurately weighed and dissolved in 500 mL buffer solutions in 1000 mL volumetric flasks and then adjusted to 1000 mL with buffer solutions.

In this work, the adsorption was studied at different pH. So that, stock solutions were prepared for each experiment using suitable buffers to adjust solution pH. Stock solutions were scanned in the range of 300-800 nm to determine the wavelength of maximum absorption (λ_{max}).

2.1.2 Preparation of standard solutions

Standard solutions in the range 0.12, 0.48, 4.80, 12.01, 19.22, and 24.02 mg/L were prepared by dissolving 0.05, 0.2, 2, 5, 8, and 10 mL, respectively from 1.00×10^{-4} M stock solution with DW in 10 mL volumetric flask. And standard solutions in the range 0.48, 1.90, 19.21, 48.04, 76.86, and 96.08 mg/L were prepared by dissolving 0.05, 0.2, 2, 5, 8, and 10 mL, respectively from 4.00×10^{-4}M stock solution with DW in 10 mL volumetric flask.

2.1.3 Construction of a calibration curve

Calibration curve is the relation between the concentration of prepared standard solutions and there absorbance at λ_{max} of stock solution. In this work, calibration curve were established for each experiment and the concentration of ALZ in each treated sample was determined based on the equation derived from the calibration curve.

2.2 Changing amount of adsorbent.

2.2.1 Sample Preparation

1.00×10^{-4}M ALZ stock solution was prepared by dissolving 24.021 mg ALZ (240.21g/mol) in 1000 mL distilled water at pH of 11.00. Twelve samples were prepared by adding different amount of NP's ranging from (1 mg - 45 mg) to 10 mL vials each containing 10 mL stock solution. The vials were sealed and shaken at 130 rpm at room temperature for 4 hrs. After that, the samples were allowed to settle then the maghemite NP's were separated from the mixture by a small magnet and the supernatant was decanted.

2.2.2 Effect of amount of adsorbent

The absorbance of the supernatant was measured using UV-Spectrophotometer at λ_{max}= 498 nm at pH=11. As discussed in section 2.1, standard solutions from 1.00×10^{-4}M ALZ stock solution were prepared by adding a specified volume from stock solution to DW in 10mL volumetric flask. Accordingly, a calibration curve was constructed.

2.3 Effect of shaking-contact time

The adsorption of ALZ onto maghemite NP's was studied at different shaking-contact time ranging from 1 to 240 min. The initial ALZ concentration was 24.02 mg/L, the pH value of solution was 11.00 at room temperature and 15 mg maghemite NP's. When testing the effect of time, the effect of shaking and contact time must be considered. In other words, the instantaneous time for separating maghemite NP's from solution using small magnet could not be neglected. So, 60 min means; 55 min shaking and 5 min for settling and separating NP's, and so on.

2.4 Effect of pH

pH is one of the most important factors which affect the adsorption process, especially if the properties of adsorbate is affected by changing solution pH. Herein, the color of ALZ and its solubility are affected by solution pH. That is, ALZ color changes depending on the pH of the solution. ALZ is yellow in acidic medium and red in basic medium. Also, the solubility of ALZ depends on the pH; ALZ is insoluble in acidic medium but soluble in aqueous alkaline solution in the pH range 8.00-12.00

In this work, the effect of pH on the adsorption process was carried out under solution pH ranging from 3.00-12.00 by using suitable buffers, and the adsorption isotherm was studied for each case by changing the initial concentration of ALZ at each pH experiment.1×10^{-4} M and 4×10^{-4} M stock solutions were prepared for studying the adsorption isotherm.

2.4.1 pH measurement

The effect of pH on adsorption process was studied under acidic, neutral and basic medium. In each case, ALZ stock solution was prepared by dissolving a specified amount of ALZ in 500mL buffer solution. The conditions for preparation of buffer solution are illustrated in Table 2.1. In adjusting pH, care was taken not to change the pH solution when adding ALZ, NP’s or DW.

Table 2.1: preparation of buffer solutions

Solution pH	Buffer solution		Initial concentration range, C_0 (ppm)	[ALZ] stock solution (ppm)	λ_{max} (nm)
3.00	0.10 M KHP	0.10 M NaOH	0.48-4.80	0.20	428.00
5.00	0.10 M CH_3COOH	0.10 M NaOH	0.48-4.80	0.20	428.00
7.00	0.10 M KH_2PO_4	0.10 M HCl	0.48-4.80	0.20	388.00
9.00	0.10 M Borax	0.10 M HCl	2.40 – 96.08	100 & 400	451.50
10.00	0.10 M Borax	0.10 M NaOH	2.40 – 96.08	100 & 400	454.00
11.00	0.10 M Borax	0.10 M NaOH	2.40 – 96.08	100 & 400	515.50
12.00	0.10 M Borax	0.10 M NaOH	2.40 – 96.08	100 & 500	566.00

For acidic and neutral medium, the least possible amount of ALZ was tried to dissolve in DW and different buffers for the same pH. However, the solubility of ALZ in acidic and neutral medium was still very low.

2.4.2 Adsorption process of ALZ dye on maghemite NP's

To study the effect of important parameters like the pH, batch experiments were performed by adding 15 mg of NP's into a 10 mL vial. Then, 10 mL of ALZ aqueous solution with known initial concentration ranging from 2.40 mg/L - 96.08 mg/L was added to each vial. The vials were sealed tightly and shaken at 130 rpm at room temperature for 4 hrs. The contaminated NP's were separated using small magnet and the supernatant was decanted. The absorbance of supernatant solution was measured using UV-spectrophotometer at λ_{max} depending on pH of ALZ stock solution. λ_{max} typically varies due to changing the color of ALZ stock solution from acidic to basic medium.

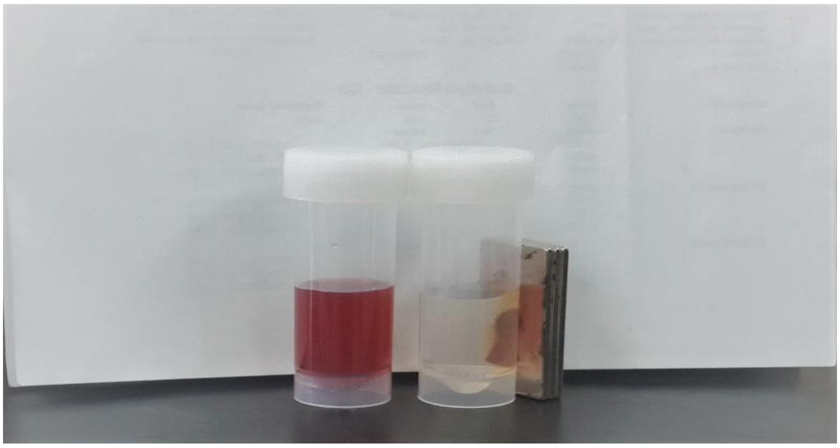


Figure 2.1. Photographs of a sample that was kept shaking for 4 hrs. . Conditions: 10 mL of the dye solution (24.02mg/L), solution's pH= 11, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^{0}C.

Standard solutions containing ALZ were prepared by adding a specified volume from ALZ stock solutions to D.W in 10 mL volumetric flask. Accordingly, a calibration curves were constructed and the concentration of ALZ in the supernatant solution was determined.

2.5 Effect of initial dye concentration

To study the adsorption isotherm for this process, batch experiments were performed by adding 15 mg of NP's into a 25 mL vial. For each pH, 10.0 mL of ALZ aqueous solution with known initial concentration, C_0 (mg/L), ranging from 0.48 to 96.08 mg/L was added to each vial, as presented in Table 2.1. The vials were sealed tightly and were shaken at 130 rpm at room temperature for 4 hrs. The contaminated NP's were separated using small magnet and the supernatant was decanted. The absorbance of supernatant solution was measured using UV-spectrophotometer at λ_{max} which is typically varies due to changing the color of ALZ with changing solution pH.

Standard solutions containing ALZ stock solution were prepared by adding a specified volume from stock solutions to DW in 10 mL volumetric flask. Accordingly, calibration curves were constructed for each pH and the concentration of ALZ in the supernatant solutions were determined.

2.6 Effect of temperature

Temperature is an important parameter that affects the adsorption process. Hence, a study of the temperature-adsorption processes provides valuable information about the adsorption capacity of adsorbent. For instance, the adsorption is an exothermic reaction, and the adsorption capacity decrease upon increasing the temperature, while it is an endothermic when the capacity increase.

In this work, the adsorption of ALZ on NP’s was studied at different temperatures of 298, 313, and 328 K. In each experiment, 10 mL of 1.00×10^{-4}M ALZ stock solution at pH of 11.0. Then, 15 mg NP’s each were added into 10 mL vials separately, two vials were put in water bath for 15 min until thermal equilibrium reached. After checking the thermal equilibrium, ALZ stock solution was added into vial containing NP’s, the vial sealed tightly to prevent any evaporation or entrance of water during water bath while shaking speed was 130 rpm for 4 hrs. The contaminated NP's were separated using small magnet and the supernatant was decanted. The absorbance of supernatant solution was measured using UV-spectrophotometer at λ_{max}. The concentration of supernatant was determined based on a calibration as discussed in section 2.1.

2.7 Effect of UV-light

Wastewater treatment from organic pollutants under UV-light has appeared as one of the most promising techniques to degrade organic pollutants.[51] This process is called photocatalytic degradation. It depends on using suitable substance called photocatalyst, which is activated to degrade organic pollutants by absorbing a photon and is capable of accelerating the degradation of organic pollutants without being consumed.[52]

By using UV-light, it was expected that removal efficiency of ALZ dye will increase, while γ-Fe_2O_3 nanosorbcats act as adsorbent and catalyst. These catalytic properties activated the degradation of organic pollutants under UV-light.

In this work, three experiments were carried out under dark, indirect sunlight, UV-light conditions. In each experiment, 150 mg NP's and 100 mL of 1.00×10^{-4} stock solution were added into 250 mL beaker. For UV-light conditions, The UV chamber equipped with a UV lamp, fitted on the top of the chamber. A fan was fitted on the sidewall of the chamber to stabilize the temperature inside it. The beakers for three experiments were placed on the stirrer for 2 hrs. After that, NP's were separated by small magnet and the absorbance was measured for the supernatant using UV-spectrophotometer at λ_{max}= 498 nm.

2.8 Regeneration of adsorbents

To test the reusability of the NP’s, 15 mg NP’s were added to 10 ml dye solution (24.02 mg/L) and the mixture was shacked at 25°C for 4 hrs. After the magnetic separation, the supernatant was decanted and the contaminated NP’s were collected by a magnet and washed with HNO_3. After that, the adsorbent was washed with DW and reused for adsorption again. The supernatant solutions were analyzed by UV–vis spectrophotometer. The cycles of adsorption–desorption processes were successively conducted four times.

To study the effect of HNO_3 and NaOH on regeneration, different experiments were carried out and the performance of NP’s at different operations parameters and a comparison was investigated between the results each washing process using NaOH or HNO_3 at different concentration. Then, the washed adsorbents were used for the subsequent adsorption cycles.

CHAPTER 3

Results and Discussion

In this chapter, the effect of different parameters such as amount of adsorbent, shaking-contact time, solution pH, UV-light and temperature were discussed. All the results obtained from the UV-spectrophotometer were analyzed using OriginPro 8.5 software to study the adsorption isotherms, thermodynamics, and kinetics for the adsorption process, which in turn provided deeply understanding the mechanism and nature of adsorbent/adsorbate system. Realizing the mechanism and nature of adsorption process helped to improve the removal efficiency of adsorption process and to investigate other possibility for adsorbent regeneration. FTIR characterization was also recorded for the adsorbent NP’s before and after adsorption to understand the changes on the surface of the NP’s and to obtain complementary evidence for the adsorption of ALZ onto NP’s.

3.1 Construction of calibration curves

Calibration curve is a quality control method for determining the concentration of a substance in an unknown sample by comparing the unknown to a set of standard solution with known concentration.[53] It is a relation between the concentration of prepared standard solutions and their absorbance at λ_{max}. Fig.3.1 shows a calibration curve for 1.00×10^{-4} M ALZ stock solution at $\lambda_{max} = 498$ nm.

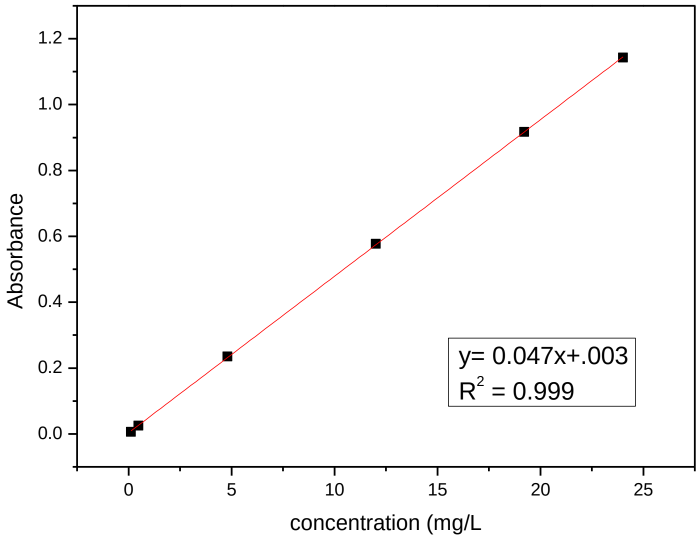


Figure 3.2: Calibration curve with ALZ standard solution. Conditions, 1.00 × 10^{-4}M ALZ stock solution at pH= 11.

Many calibration curves are linear and can be fit with the basic equation. The linearity of the calibration curve was determined by the correlation coefficient (R^2) with the best fit when $R^2 = 1$. The linear equation derived from the calibration curve was then used to determine the concentration of ALZ in treated aqueous solution.

3.2 Effect of amount of Adsorbent

The effect of amount of adsorbent for adsorption of ALZ onto NP's was investigated by changing the amount of adsorbent from 1 to 45 mg. As explained in Section 2.4, changing the amount of adsorbent at pH around 5 introduced uncertainty into the results, because ALZ dye does not dissolve in acidic medium except at very low ALZ concentration (4.8 mg/L), so the effect of amount of adsorbent in acidic medium could not be studied.

Fig.3.2 shows the effect of amount of adsorbent by changing the amount of adsorbent from 1 to 45 mg with dye concentration (24.02 mg/L) at pH of 11. The dye removal percentage calculated as follows:

$$\% \, of \; dye \; removal = \frac{C_o - C_e}{C_o} * 100 \qquad (8)$$

Where C_o and C_e (mg/L) are the initial and equilibrium concentration of the dye in solution.

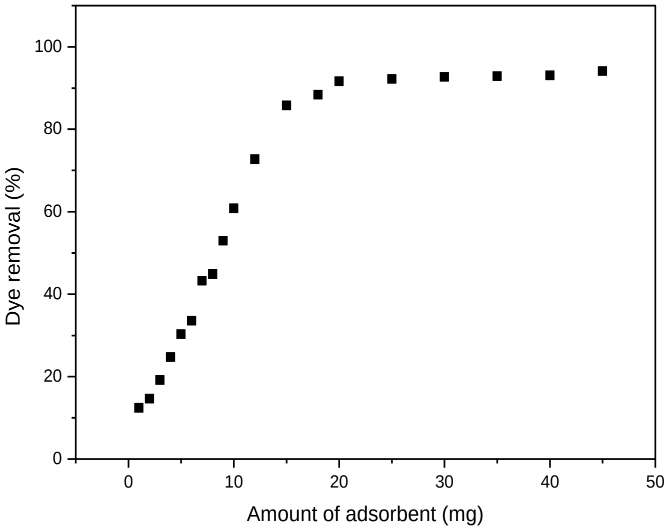


Figure 3.2: Effect of adsorbent amounts (mg) on removal efficiency of the dye. Conditions: 10 mL of the dye solution (24.02mg/L), solution’s pH= 11, shaking time = 4hrs, shaking speed 130 rpm, 25^0C.

Fig.3.2 shows that the removal efficiency did not increase linearly with the increase in the amount of adsorbent. As seen above, the increase in adsorbent amount cause increasing in dye removal percentage up to 90% at 20 mg for the 24.02mg/L dye solution. Consequently, further increase of the adsorbent dosage did not show significant affect on the removal of dye. This is due to the fact that the active sorption sites in adsorbent increases as the amount of adsorbent increases, which leads to an increase the removal of adsorbate.[54] However, increasing in the amount of adsorbate to more than 20 mg did not increase the number of active sites. This phenomenon may be explained by aggregation of adsorbent particles causing the number of active sites been the same or increasing slightly.

3.3 Effect of shaking-contact time

The effect of time on adsorption of ALZ dye on NP's was studied at pH of 11. Fig.3.3 illustrates the adsorption of ALZ onto maghemite NP's at different shaking-contact time. As seen, the adsorption of ALZ increases fast in the first 60 min, and then slowed down until the adsorption process achieves equilibrium.

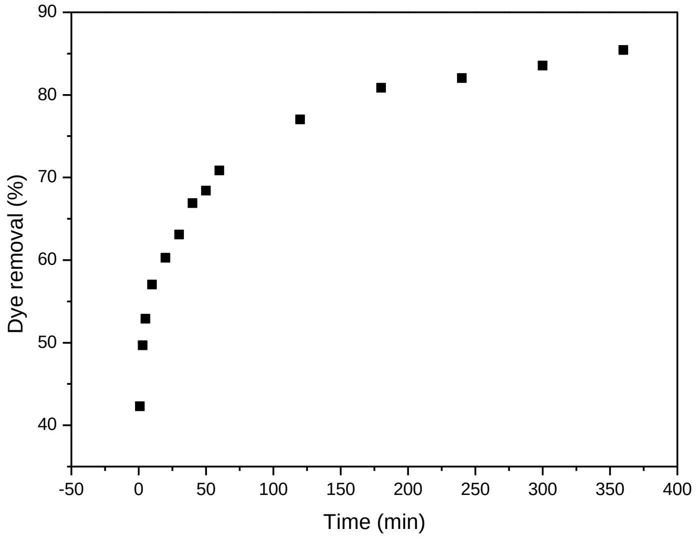


Figure 3.3: Effect of shaking-contact time (min) on removal efficiency of the dye. Conditions: 10 mL of the dye solution(24.02mg/L), solution's pH= 11, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^{0}C.

Herein, it is worth noting that the fast removal rate during the first hour may be attributed to the rapid diffusion of ALZ from the solution to the external surfaces of γ-Fe_2O_3 NP's. The short equilibrium time is in agreement with that reported by other studies. Nassar[37] investigated the rapid removal of Pb(II) onto iron oxide NP's. It was reported that the rapid removal by iron oxide NP's is due to their small size which was favorable for the diffusion of adsorbate from bulk solution onto the active sites of the solid surface.[37,55] Meanwhile, as the sites being gradually occupied, the adsorbed ALZ tend to be transported slowly from the bulk solution to the actual occupied sorption sites. Such slow diffusion will decrease the adsorption rate of ALZ at later hours.

As seen in Fig.3.3, the removal process is fast during the first hour. Despite this result, all experiments were done for 4 hrs to ensure attaining adsorption equilibrium.

3.4 Effect of pH on Adsorption

It is well known that pH is an important parameter which affect the adsorption process. As seen in section 2.4, several experiments were performed in this work for investigation the effect of solution pH in acidic, neutral, and basic medium. The results showed that the effect of pH could not be investigated in the acidic medium. As discussed in section 3.2, the initial concentrations of stock solutions differ between acidic and basic medium due to very low solubility of ALZ in acidic medium. When the initial concentration differs between stock solutions at different pH, another parameter must be considered. That is, in the more concentrated solution, ALZ tends to be transported from bulk phase to the adsorbent's surface. So, as the concentration of stock solution increase the adsorption will increase. Which in turn introduce uncertainty into the comparison between the adsorption capacity in acidic and basic medium.

Thus, the effect of pH was only investigated in basic medium range 8-12. Fig.3.4 presents the effect of pH on the adsorption of ALZ onto NP's. As seen, the removal of ALZ is clearly pH dependent and increasing with increasing pH.

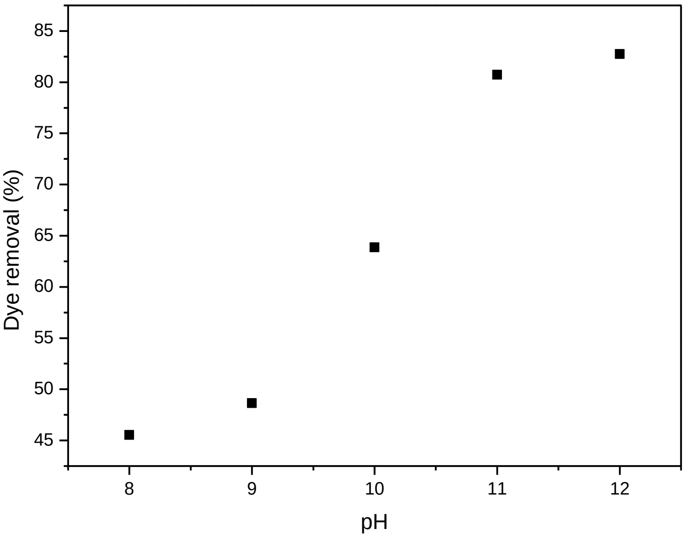


Figure 3.4: Effect of pH on removal efficiency of the dye. Conditions: 10 mL of the dye solution(24.02mg/L), shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^{0}C.

It is noteworthy to consider the role of point of zero charge (pzc) in the effect of pH on the adsorption process. The pH_{pzc} of γ-Fe_2O_3 NP's was found to be 6.5.[56] At this value, the total positive charges on the surface of γ-Fe_2O_3 are equal to the total negative charges. In general, the adsorbent surface is positively charged when $pH < pH_{pzc}$ because the acidic solution donates more protons than hydroxide groups. In contrast, when $pH > pH_{pzc}$ the surface is negatively charged. But as known, the solubility of ALZ in acidic medium is very low and increases with increasing pH in basic medium. In other words, as pH increases, the deprotonation of ALZ increases and the protonation of γ-Fe_2O_3 NP's surface increase which leads to increase the positive sites on NP's surface and negative ones on ALZ which enhances electrostatic forces between adsorbent's surface and ALZ molecules. This explained the reason for increasing the adsorption capacity and dye removal as solution pH increases in basic medium as shown in Fig.3.4. Different observations have been discussed by other researchers. Nassar [39] found that the adsorptive removal of acid red dye using γ-Fe_2O_3 NP's was decreasing with increasing pH. Also, Fayazi *et al.*[26] found that the removal efficiency of ALZ red S using AC/γ-Fe_2O_3 nano-composite was also decreasing with increasing pH. Herein, It is noteworthy to highlight the influence of the functional groups on the effect of pH. The dyes used in these two studies have a sulfonate groups which in turn make them an anionic dyes that are negatively charged in aqueous solution. So that, the positive sites on the surface of NP's was increasing with decreasing pH. Which in turn enhances the interactions between the anionic dyes and positive active sites on the NP's. In this study, the structure of ALZ and its deprotonation in basic medium increased the adsorptive removal with increasing pH, as discussed previously. From these different observations, the effect of pH depends not only on the pH_{pzc} of the NP's, but also on the structure of dyes and their functional groups.

3.5 Adsorption kinetic

It is very important to study the kinetics of adsorption. This involves studying the adsorption rate to investigate the kinetic mechanism that controls the adsorption process. Two of the most widely kinetic models were used to study the adsorption kinetic behavior of ALZ onto NP's are the Lagergren pseudo-first-order [57] and pseudo-second-order.[58] Fig.3.5 shows the effect of shaking time on the adsorbed amount of ALZ.

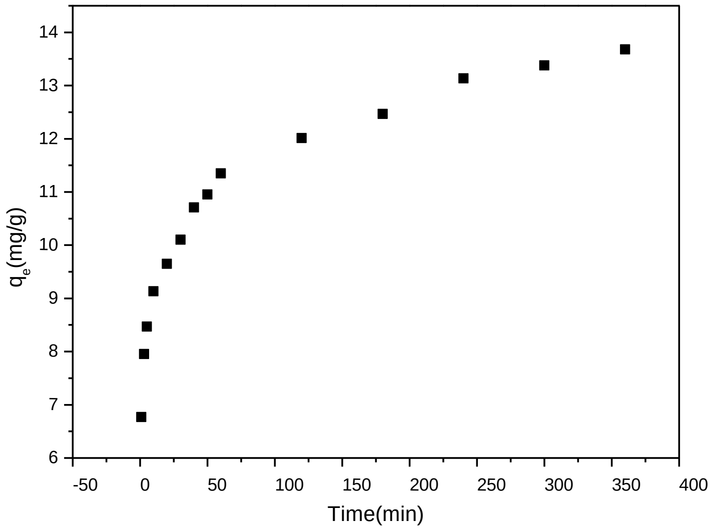


Figure 3.5: Effect of shaking-contact time (min) on the adsorbed amount of ALZ. Conditions: 10 mL of the dye solution(24.02mg/L), solution's pH= 11, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^0C.

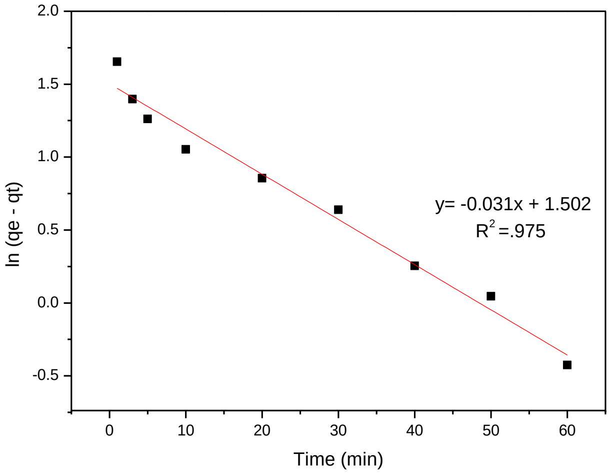
The experimental data obtained from Fig.3.5 were analyzed using pseudo-first-order and pseudo-second-order models.

The pseudo-first-order kinetic model can be expressed as:

$$ln(q_e - q_t) = ln\, q_e - k_1 t \tag{9}$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively, and k_1 is the rate constant of the pseudo-first-order adsorption (min). By plotting $\ln(q_e - q_t)$ versus time from Fig.3.6, one can obtain the values of k_1 from the slope and q_e from the intercept. The kinetics parameters obtained from the pseudo first-order models are summarized in Table 3.1.

(a)



(b)

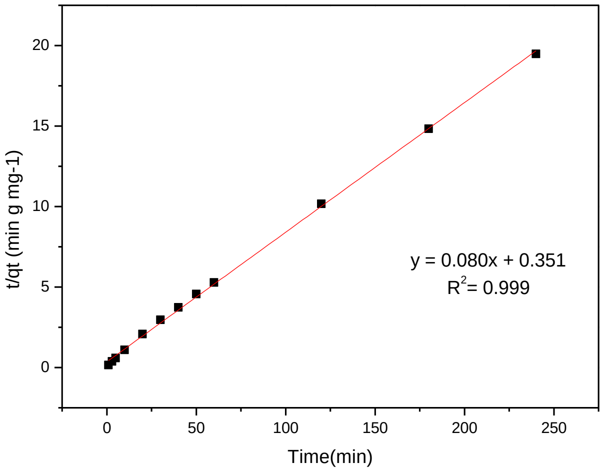


Figure 3.6: (a) Pseudo-first-order kinetics (b) and pseudo-second-order of ALZ adsorption on the NP's.

Table 3.1: Kinetic parameters for ALZ adsorption on the NP's.

Pseudo-first-order				Pseudo-second-order		
$q_{e,cal}$ (mg/g)	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g /mg min)	R^2
4.481	12.3	0.031	0.975	12.5	0.018	0.999

As Fig.3.6(a) shows, it was found that the correlation coefficient (R^2) has a value 0.975 and a very large difference exists between $q_{e,exp}$ (which is determined experimentally from the results obtained in Fig.3.5) and $q_{e,cal}$(which is calculated from a linear equation of straight line) indicating a poor pseudo-first-order fit to the experimental data. Therefore, it is necessary to fit the experimental data to another model.[26] The adsorption may be describe by pseudo-second-order kinetic model as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} \qquad (10)$$

where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and time t, respectively, and k_2 is the rate constant of the pseudo-second-order adsorption (g/ mg min). The slope and intercept obtained by plotting t/q_t versus time were used to calculate the second order rate constant k_2. For Fig.3.6.(b) It was found that the correlation coefficient (R^2) has a value 0.999 and a $q_{e,cal}$ was obtained as 12.5 mg/g which very closely to the value of $q_{e,exp}$ indicating that the best fit is pseudo-second-order with the correlation coefficient values, R^2=0.999. The kinetics parameters obtained from the pseudo second-order models are outlined in Table 3.1.

3.6 Adsorption isotherms

Adsorption isotherms are the relationship between capacity of adsorption at equilibrium (q_e) and the equilibrium concentration of ALZ solution (C_e). The adsorption isotherms of ALZ on the maghemite NP's at different pH values and initial concentration ranging from 2.40 to 96.08 mg/L are given in Fig. 3.7.

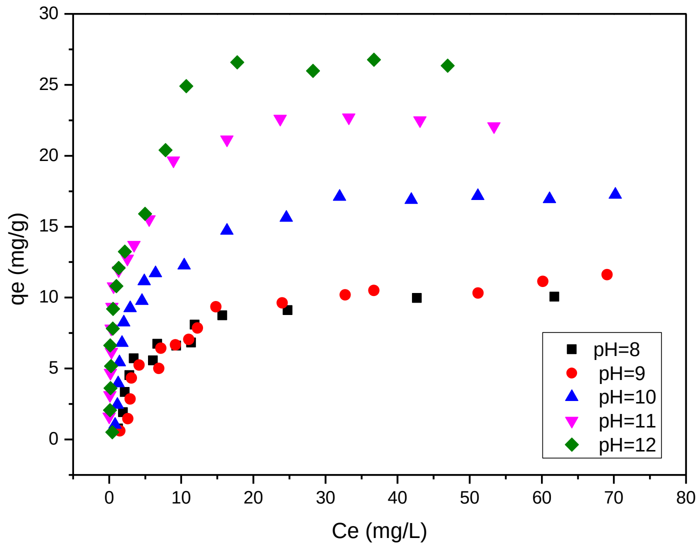


Figure 3.7. Adsorption isotherms of ALZ onto NP's at different pH values. Conditions: shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^{0}C.

The adsorbed amount of ALZ at equilibrium, q_e (mg/g) was calculated using the equation:

$$q_e = \frac{C_i - C_e}{m} V \qquad (11)$$

Where C_i and C_e (mg/L) are the initial and equilibrium concentrations of ALZ solution, respectively, V is the volume of the solution used (L), and m is the mass of the dry adsorbent (nanoparticles) (g). The Langmuir, Freundlich, and SIPS isotherms were used to analyze the equilibrium data, and the equilibrium adsorption data were fitted by these isotherm models.

3.6.1 Langmuir isotherm

The Langmuir isotherm assumes that all of the adsorption sites are equivalent and the monolayer adsorption occur at binding sites with homogenous energy levels and there is no phase transition, *i.e.* no transmigration of adsorbed molecules on the adsorption surface. Also, Langmuir assumes that there are no interactions between adsorbed molecules. [47] The Langmuir equations can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{12}$$

Or

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{13}$$

where C_e is the equilibrium concentration of the ALZ solution (mg/L), q_e is the adsorption capacity at equilibrium (mg/g), K_L is the constant related to free energy of adsorption (L/mg), and q_m(mg/g) is the maximum adsorption capacity, representing the maximum amount of ALZ adsorbed per unit weight of nanoadsorbents for complete monolayer coverage.

By plotting the linear graph of C_e against C_e/q_e, the values of K_L and q_m can be determined from the intercept and slope of the plot, where the parameter q_m (mg/g) is the maximum adsorption capacity of dye per unit mass of sorbent to form a complete monolayer on the surface bound at high C_e and

K_L (L/mg) is the Langmuir energy constant which is related to the heat of adsorption. The Langmuir linear plots are shown in Fig.3.8.

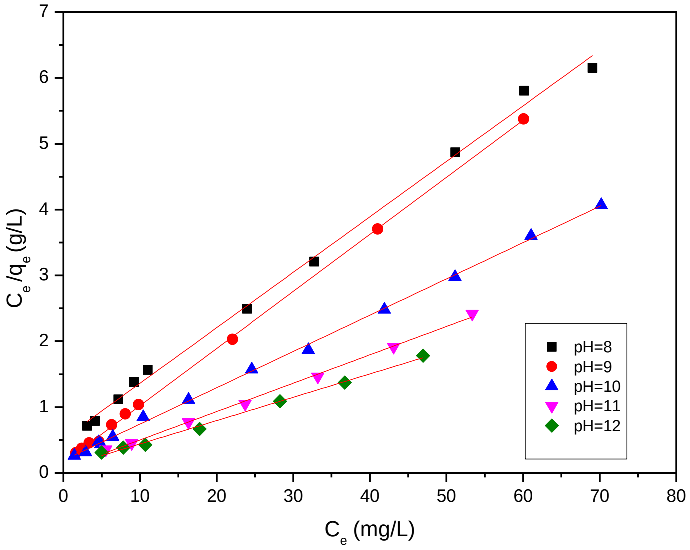


Figure 3.8.: Langmuir isotherms of ALZ onto NP's at different pH values. Conditions: shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25 °C.

3.6.2 Freundlich isotherm

The Freundlich isotherm is an empirical relationship describes the multilayer adsorption of heterogeneous systems and assumes that different sites have several adsorption energies involved.[59] The corresponding equations are commonly represented by this equation:

$$q_e = k_f \, C^{1/n}{}_e \qquad (14)$$

Or

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \qquad (15)$$

Where K_f and n are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively.

If the value of 1/n is lower than 1, it indicates a normal Langmuir isotherm. The values of parameters K_f and n can be determined from the intercept and slope of the plot log C_e against log q_e, where K_F (1/g) is the Freundlich adsorption capacity constant and $1/n$ is related to the adsorption intensity constant that varies with the heterogeneity of the adsorbate. The Freundlich linear plots are presented in Fig.3.8.

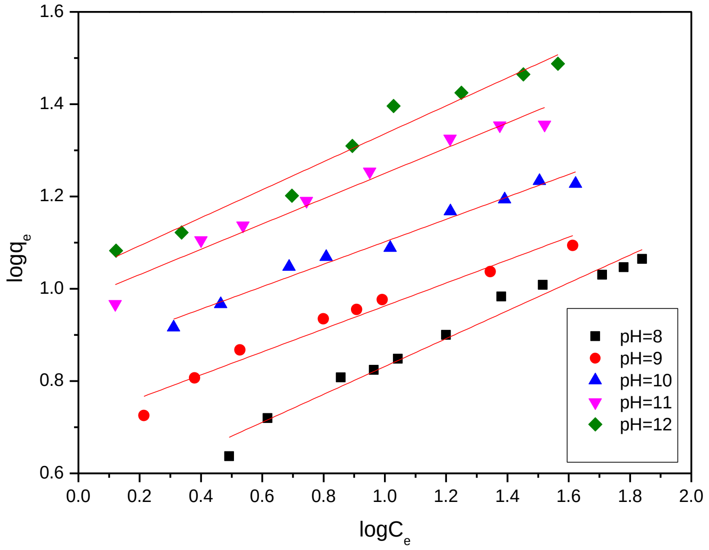


Figure 3.9: Freundlich isotherms of ALZ onto NP's at different pH values. Conditions: shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm, 250C**.**

The isotherm parameters from Langmuir and Freundlich models are listed in Table 3.2.

Table 3.2: Parameters for the Langmuir and Freundlich models at different pH

pH	Langmuir constants			Freundlich constants		
	K_L	q_m	R^2	K_F	1/n	R^2
8.00	0.161	11.904	0.995	3.380	0.301	0.972
9.00	0.547	11.905	0.995	5.164	0.248	0.956
10.00	0.286	18.181	0.997	7.211	0.243	0.978
11.00	0.614	23.255	0.998	9.462	0.274	0.961
12.00	0.406	28.571	0.991	10.764	0.303	0.963

As seen from Table 3.2, the adsorption of ALZ was fitted well with the Langmuir isotherm model with the higher R^2 (0.998). This indicated that the adsorption took place at specific homogeneous sites within the adsorbent forming monolayer coverage of ALZ at the surface of the absorbent. In addition, the Freundlich constant 1/n was smaller than 1, indicating a normal Langmuir isotherm.[60] These observations confirmed that the adsorption process in this study follows Langmuir isotherm model.

3.6.3 SIPS isotherm

To further understand the adsorption behavior, the experimental data were fitted to the SIPS isotherm. The SIPS isotherm is combined form of Langmuir and Freundlich isotherms. The model is valid for localized adsorption without adsorbate- adsorbate interactions.[61] When adsorbate concentrations C_e is low, it reduces to Freundlich isotherm; while at high concentrations, it predicts a monolayer adsorption capacity characteristic of the Langmuir isotherm. The general form of the SIPS isotherm is[61]

$$q_e = q_m K_s\, C_e{}^{1/n}/(1 + K_s C_e{}^{1/n}) \qquad (16)$$

where K_s (1/mg) and q_{max}(mg/g) are the SIPS equilibrium constant and maximum adsorption capacity values. The SIPS isotherm equation is characterized by the dimensionless heterogeneity factor, n, which can also be employed to describe the system's heterogeneity when n is between 0 and 1.[62] The isotherm parameters from SIPS models are listed in Table 3.3. All of the SIPS model parameters were performed by non-linear fitting of equation (16) to the experimental data using OriginPro 8.5, as shown in Fig.3.10.

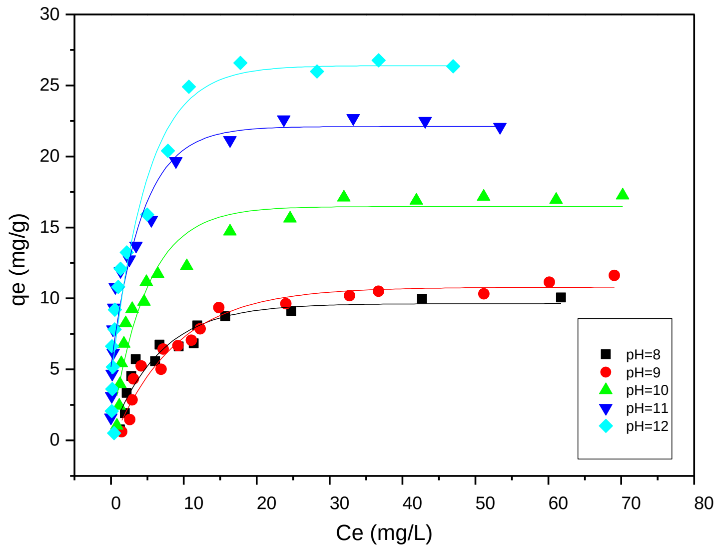


Figure 3.10: Non-linear fitting for SIPS isotherms of ALZ onto NP's at different pH values. Conditions: shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm, 25^{0}C.

Table 3.3: Parameters for the SIPS model at different pH

pH	SIPS constants				
	K_s	1/n	n	q_m	R^2
8.00	2.647	0.925	1.081	10.313	0.970
9.00	2.112	0.935	1.069	11.359	0.968
10.00	1.780	0.975	1.025	17.108	0.980
11.00	1.306	0.932	1.072	23.325	0.990
12.00	0.807	0.948	1.054	28.563	0.994

As seen from Table 3.3, q_m values indicated that adsorption capacity increased with increasing solution pH, confirming the effect of pH on adsorption process as discussed in section 3.3. The value n in SIPS isotherm gives information about the system's heterogeneity when n is between 0 and 1, and when n is unity it implies a homogeneous adsorption process indicating Langmuir isotherm.[62]

In this study, n values suggest a homogeneous adsorption process while it is unity. Confirming the adsorption in this study follows Langmuir isotherm.

3.7 Effect of temperature

Temperature has been recognized as an important parameter governing the adsorption process.[63] It is important to understand how temperature may affect the adsorption process, not only to understand the mechanism of adsorption but also because useful thermodynamic information can be investigated.[64] Hence, studying the temperature-dependent adsorption processes provides valuable information about the standard Gibbs free energy, enthalpy and entropy changes accompanying adsorption.

Changing the temperature may affect the equilibrium adsorption capacity of the adsorbent. For instance, the adsorption capacity will decrease upon increasing the temperature for an exothermic reaction; while it will increase for an endothermic one.[37]

In this study, the adsorption of ALZ dye on NP’s was studied at temperatures of 298, 313, 328 K, with these adsorption isotherms being shown in Fig.3.11.

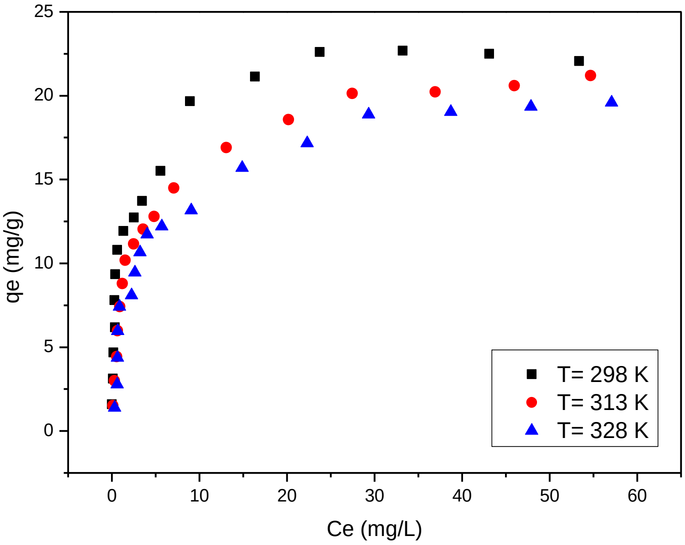


Figure 3.11: Adsorption isotherms of ALZ onto NP’s at different temperature. Conditions: shaking time= 4hrs, amount of adsorbent = 15 mg, shaking speed 130 rpm.

As seen, the amount of ALZ adsorbed decreases as the temperature increases. This decrease in ALZ removal suggests that the adsorption of ALZ onto the NP’s surface is an exothermic process. Decreasing the ALZ adsorption as temperature increase is due to the fact discussed by several studies. Alkan *et al.*[65] reported that decreasing the adsorption with increasing temperature is mainly due to the weakening of adsorptive forces between the active sites of adsorbent and adsorbate species. This means that as temperature increases the desorption process is dominant due to the weakening interaction between adsorbent/adsorbate system. So that, the adsorption of ALZ onto γ-Fe_2O_3 NP's decreases which in turn affect the removal efficiency of ALZ from wastewater negatively. Similar observations have been discussed by other researches for the reason of decreasing adsorption as temperature increases.[66,39] They found that exothermic nature of adsorption process is due to the weakening of adsorptive forces between adsorbent and adsorbate with increasing temperature.

3.8 Thermodynamic parameters

The experimental data obtained as a function of different temperature from Fig.3.11 in the previous section, were analyzed to determine the thermodynamic parameters, such as changes in standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy (ΔS°) using different equations. Generally, determining these parameters provides valuable information not only on the type of process but also it provides knowledge about the adsorption mechanism.

The thermodynamic parameters were calculated by the following equations:

$$\Delta G° = \Delta H° - \mathrm{T}\Delta S° \qquad (17)$$

$$\Delta G° = -RT\ lnK \qquad (18)$$

$$ln\,K = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R} \qquad (19)$$

where T is the temperature in Kelvin, R is the ideal gas constant (R= 8.314 J/mol K), K is the equilibrium constant (dimensionless). K can be expressed as $K_L \times C_s$, where K_L is the equilibrium Langmuir constant (L/mmol) and C_s is the solvent molar concentration (mM), which can be calculated from the density and molecular weight of water at given temperature as presented in table.[67]

The values of ΔS° and ΔH° can be determined by plotting lnK versus 1/T as presented in Fig.3.12. From the slope and intercept in Fig.3.12, ΔH° and ΔS° were calculated using Eq.(19). The thermodynamic parameters at the studied temperature are presented in Table 3.5.

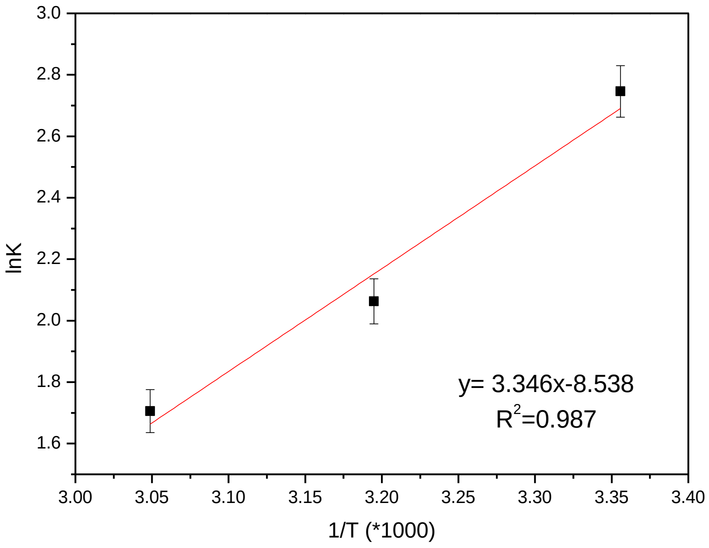


Figure 3.12: Determination of thermodynamic parameters for the adsorption of ALZ onto Fe_2O_3 NP's**.**

Table 3.4: Adsorption equilibrium constant at different temperature.

Tempe-rapture(K)	Density water (g/mol)	Molecular weight (g/mol)	C_s (mM)	K_L (L/mmol)	K	lnK	(1/T) *1000 1/K
298	0.998	18.015	18.034	0.864	15.5	2.74	3.355
313	0.989	18.015	18.209	0.430	7.8	2.06	3.194
328	0.979	18.015	18.394	0.299	5.4	1.70	3.048

Table 3.5: Thermodynamic parameters for the adsorption of ALZ onto NP's at different temperature.

Temperature(K)	ΔG°(kJ/mol)	ΔH°(kJ/mol)	ΔS°(J/mol)	R^2
298	-6.788	-27.818	-70.984	0.987
313	-5.360			
328	-4.635			

Each magnitude presented in Table.3.4 indicating specific information about the adsorbent/adsorbate system which helped us to understand deeply the mechanism and nature of adsorption process. Many researchers reported the indications of these parameters. Xu *et al.*[42] said that negative values of ΔG° indicate that the adsorption took place spontaneously, and the increasing of ΔG° as temperature rises indicated that the adsorption was more favorable at low temperatures. Also, they found that negative values of ΔH° confirmed that the adsorption is an exothermic process and the negative value of ΔS° indicates that the randomness decreases at the interface between solid and solution during the sorption process. The ΔH° and ΔS° magnitudes obtained in this study were found to be -27.818 kJ/mol and-70.984 J/mol, respectively. These values confirmed that the adsorption process is exothermic and spontaneous in nature.

Generally, the small magnitudes of ΔG° indicate a weak adsorptive forces between the active sites of adsorbent and ALZ. Yu *et al.*[68] found that when ΔG° values between −20 and 0 kJ/mol, the adsorption process corresponds to physical adsorption while that with values between −80 and −400 kJ/mol corresponds to chemisorption process. This is also supported by the fact that the absolute magnitude of the change in Gibbs free energy for physical adsorption is smaller than that in chemisorptions. The ΔG° values obtained in this study were found to be -6.788, -5.360, -4.635 kJ/mol, indicating a physisorption process.

Similar studies discussed a relation between ΔH° and the nature of adsorption process, Bride *et al.*[69] said that when ΔH° < 40 kJ/mol the adsorption process corresponds to spontaneous physical process. The ΔH° value obtained in this study was found to be -27.818 kJ/mol, confirmed that the adsorption process between γ-Fe_2O_3 and ALZ corresponds to physical adsorption process.

3.9 Regeneration of adsorbent

Adsorption is a promising process for removal of ALZ dye from wastewater. As explained in previous sections, low cost of γ-Fe_2O_3 adsorbent, high removal efficiency and simplicity are the most important properties of the adsorption process. In order to make this process more environmentally friendly; regeneration of adsorbent is very important aspect. Regeneration is an important factor which determines the cost effectiveness and possibility of reuse of NP's. It mainly has two advantages, namely valuable ALZ can be recovered and nanoadsorbents can be reused for another cycle.[70]

Results obtained from thermodynamics study showed that the adsorption between γ-Fe_2O_3 NP's and ALZ is govern by physisorption, indicating a weak adsorptive forces between adsorbent and adsorbate. This means that the regeneration of the adsorbent is feasible.

Also, from the results of the effect of pH observed in this study, it has been found that adsorption of ALZ is highly dependent on pH and the removal efficiency increased as pH increased in basic medium. Consequently, the desorption of ALZ can be carried out by decreasing the pH of the solution. This suggests that washing the contaminated NP's with acidic solution is more efficient than that with basic for regeneration. Fig. 3.13 shows the removal efficiency of NP's after regeneration using different concentrations of NaOH and HNO_3. As seen, the removal efficiency of NP's after regeneration using $HNO_3$is higher than in the case of using NaOH. Also, the efficiency of regenerated NP's increased with the decrease in HNO_3 concentration. This reasonable result is due to the fact that the entropy is usually occur from bulk solution, i.e. from adsorbent's pores to more dilute HNO_3 solution, i.e as the concentration of HNO_3 decreased the entropy is increased. This suggest that adsorption of ALZ onto γ-Fe_2O_3 is reversible, and the bonding between the active sites on γ-Fe_2O_3 and the adsorbed ALZ is not strong. The results also suggest that the ALZ adsorbed on NP's can be easily desorbed using a very low concentration of HNO_3, and γ-Fe_2O_3

nanoadsorbents has the potential to be used as an adsorbent for the removal and recovery of ALZ dye from wastewater.

Also, the cycles of adsorption-desorption experiments were investigated, as shown in Fig.3.14, the NP's can be regenerated by 10mM HNO_3 and reused for at least four successive removal processes with efficiency higher than 80%. Meanwhile, after four cycles of adsorption the efficiency of regenerated NP's decreased to 40%.

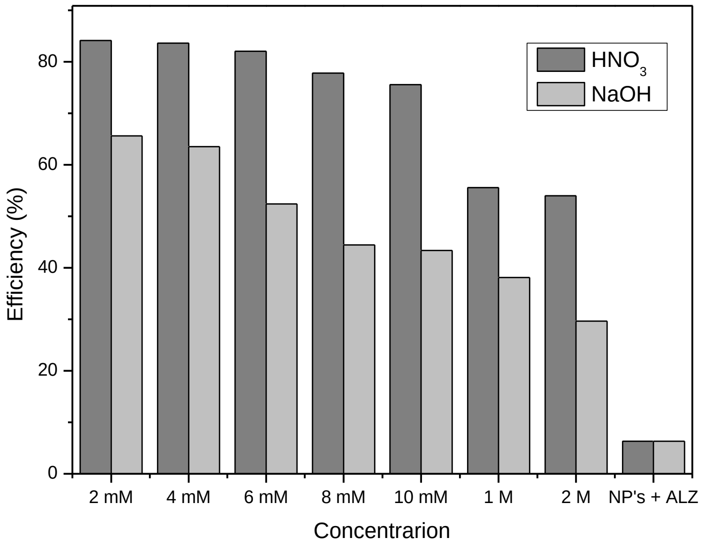


Figure 3.13: Removal efficiency of NP's after regeneration using different concentration of NaOH and HNO_3 solutions at fixed initial concentration of ALZ: 12 mg/L, pH=11, shaking rate: 130 rpm, shaking-contact time: 4h, T = 298 K.

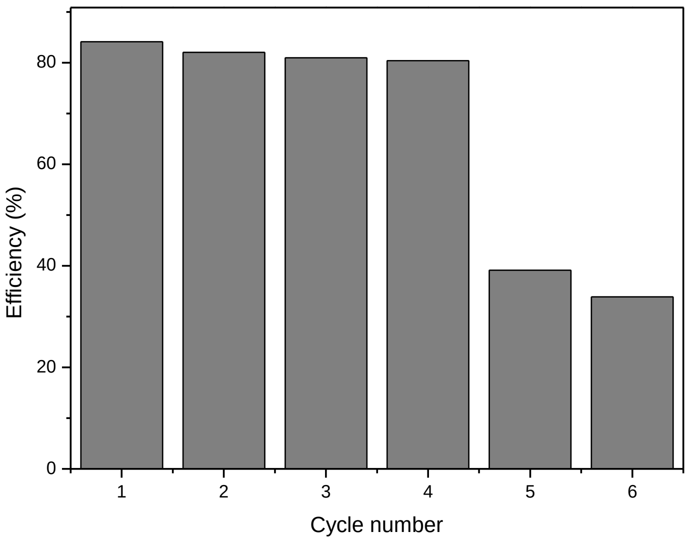


Figure 3.14: Reusability of Fe_2O_3 NP's for adsorption/desorption of ALZ during six cycles. Adsorption: initial concentration of ALZ: 12 mg/L, amount of adsorbent:15 mg, pH=11, shaking rate: 130 rpm, shaking-contact time: 4 h, T = 298 K.

3.10 Effect of UV-light

Fig. 3.15 shows the removal efficiency of γ-Fe_2O_3 NP's under dark, indirect sunlight, and UV-light for 2hrs. As seen, the efficiency of γ-Fe_2O_3 NP's under UV-light is the highest. This is due to the fact that γ-Fe_2O_3 act as a photocatalyst under UV for enhancing the degradation of ALZ, [71] as explained in section 2.7.

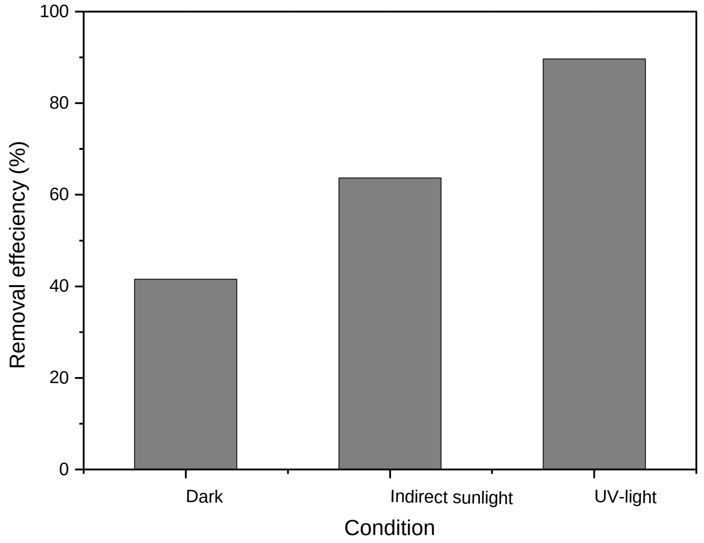


Figure 3.15: Effect of UV-light on adsorptive removal of ALZ onto γ-Fe_2O_3 NP's : initial concentration of ALZ: 24 mg/L, amount of adsorbent:15 mg, pH=11, stirring time: 2 h, T = 298 K.

Generally, catalytic properties for γ-Fe_2O_3 NP's can be enhanced in different ways including, thermogravemetric analysis for contaminated NP's. elqanni *et al.*[38] studied the thermogravimetric analysis for contaminated γ-Fe_2O_3 NP's for catalytic oxidation of adsorbed Methylene Blue (MB)dye molecules. The experiment showed a good results for the catalytic effect γ-Fe_2O_3 NP's on thermo oxidative decomposition of adsorbed MB. However, a very high temperature in TGA analysis leaded to loss the magnetic properties of γ-Fe_2O_3 NP's.

Herein, it is very important to highlight the unique magnetic behaviors for γ-Fe_2O_3, and maintaining this property during wastewater treatment process is very important. Magnetic behaviors for γ-Fe_2O_3 NP' help us to separate them from treated media, this property made γ-Fe_2O_3 favorable than other adsorbents like charcoal and preserve magnetic properties is needed. In our work, catalytic properties of γ-Fe_2O_3 NP's were enhanced by UV-light irradiation without affect their magnetic properties.

3.11 FTIR characterization

In order to obtain complementary evidence for the adsorption of ALZ onto NP's; FTIR characterization were investigated for ALZ, pure and contaminated γ-Fe_2O_3 NP's. Fig.3.16 shows the changes on the surface of the NP's before and after adsorption of ALZ as obtained from the FTIR spectrophotometer. Fig.3.16(a) presents the FTIR spectra for pure γ-Fe_2O_3 NP's. As seen, there are no peaks in the range (1000-4000 cm^{-1}); while the ALZ peaks appear in the range (1000-4000 cm^{-1}) as shown in Fig.3.16(b). This indicates that no organic compounds existed on the pure γ-Fe_2O_3 surface. After adsorption occur, the FTIR spectra for contaminated NP's were recorded as shown in Fig.3.16(c). Clearly, the differences between the spectra for NP's before and after adsorption process were obvious. As seen, Fig.3.16(c) is sum of the pure spectrum of ALZ with the pure spectrum of γ-Fe_2O_3 NP's. The peak around 1630 $cm^{-1}$is assigned to aromatic C=C stretching vibration.[72] The peak around 1660 corresponds to carbonyl group –C=O bond stretching vibration,[73] the peak at 3373.09 is assigned for hydroxyl group on aromatic ring of ALZ molecules. As seen in Fig.3.16(c), the spectrum shows that there are modifications of the γ-Fe_2O_3 NP's by comparing with Fig.3.16 (a) confirming in this way the interaction between ALZ and γ-Fe_2O_3 NP's by adsorption process.

As discussed in section 3.4, adsorbate may have functional groups that can be protonated and deprotonated to produce different surface charges, resulting the electrostatic interactions between adsorbate molecules and adsorbents. Fig. 3.16(b) shows peak at 3373.09 for hydroxyl group presenting as a functional group of ALZ and responsible for electrostatic attraction between negative charged adsorbate molecules and positive charged adsorbent active sites.

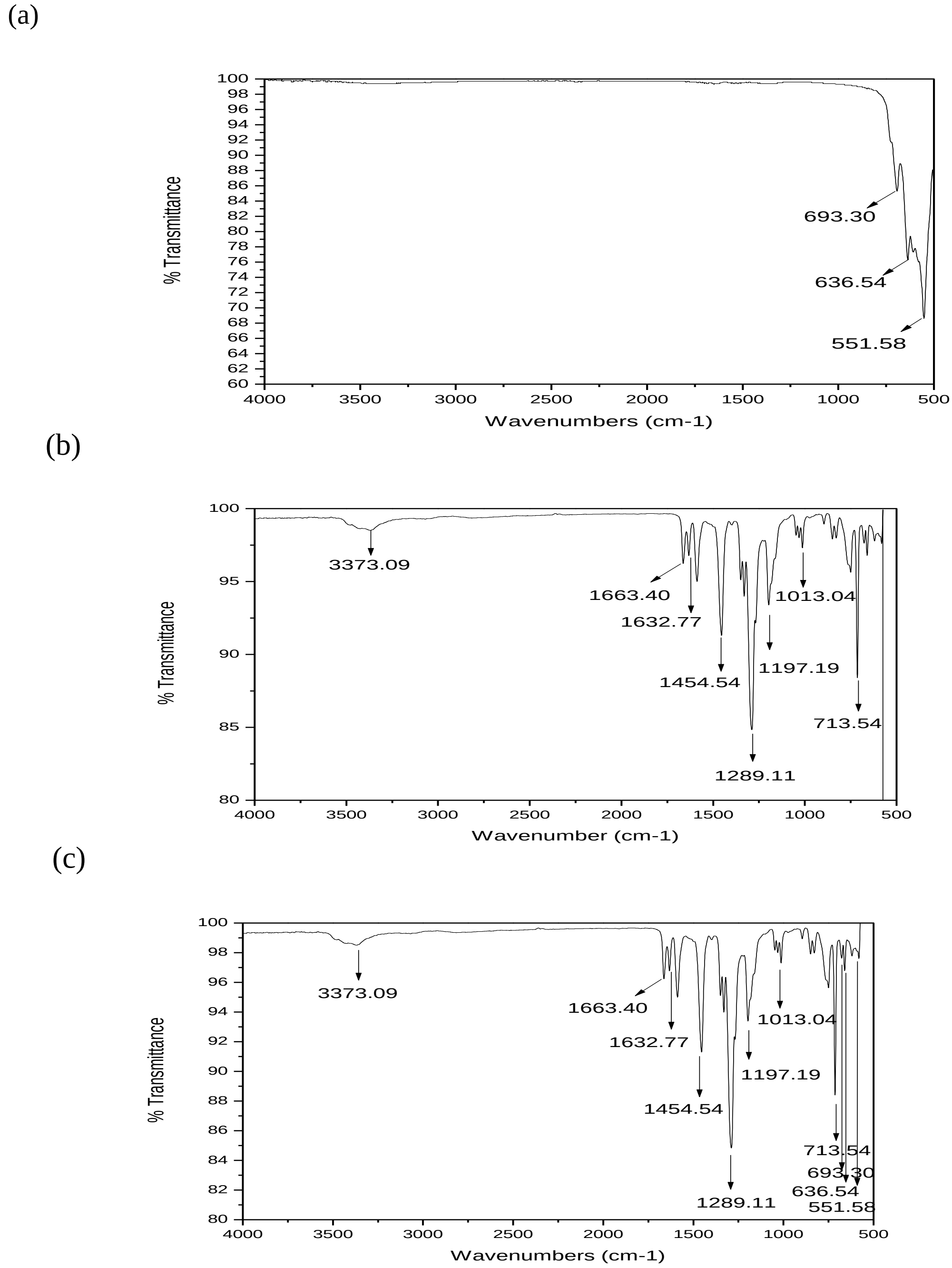


Figure 3.16: FTIR spectra for ALZ adsorption onto NP's: (a) pure NP's, (b)ALZ (c)ALZ-adsorbed on NP's.

Conclusion

This study showed that γ-Fe_2O_3 NP's could be used as nanoadsorbents and catalysts (nanosorbcats) which is a new acronym introduced to the world of adsorption and catalysis for the adsorptive removal of ALZ dye from an aqueous solution in short time with near complete removal. The effect of various paremeters were investigated and the results shown that the adsorption process was dependent on the amount of γ-Fe_2O_3 NP's, time, pH, UV-light and temperature. Adsorption increased as the amount of adsorbent and time increased and as temperature decreased. Maximum removal was obtained at pH=11. UV-light irradiation increased the adsorptive removal without affecting the magnetic properties and adsorption capacity of γ-Fe_2O_3. This result confirmed the catalytic properties for γ-Fe_2O_3. The adsorption isotherms were also investigated and were described by Freundlich, Langmuir, and SIPS model and fitted well the Langmuir isotherm indicated that the adsorption was monolayer and homogenous. A comparison of kinetic models on the overall adsorption rate showed that ALZ dye/ γ-Fe_2O_3 adsorbent system was best described by the pseudo-second-order rate model. The thermodynamic study of ALZ adsorption onto the γ-Fe_2O_3 indicated that the process is exothermic, spontaneous, and physisorption nature of the adsorption process. Physisorption nature indicated that there are weak interactions between adsorbent and adsorbate and the desorption and regeneration process could be done. So that the regeneration studies were carried out using HNO_3 confirmed that the γ-Fe_2O_3 can be reused four cycles. In conclusion, γ-Fe_2O_3 NP's are effective and inexpensive adsorbent and its regeneration is simple. These results confirmed that the adsorption process using γ-Fe_2O_3 nanosorbcats is efficient, simple, and cost-effective which made it suitable to convert from batch experiments to large scale industry.

Future work

Our future efforts will be focusing on developing batch experiments to continuous adsorption process using fixed bed column for treating wastewater from ALZ dye. After that, the contaminated adsorbent can be regenerated or re-used for treating wastewater from another organic pollutant which can make chemical interaction with ALZ molecules adsorbed on the surface of adsorbent.

In addition, there are some ideas that we would have like to try in the future. This thesis has been mainly focused on using γ-Fe_2O_3 as nanosorbcats without any modifications on γ-Fe_2O_3 NP's or on the adsorption process itself. The following ideas could be tested:

(1) By benefiting from the magnetic properties for γ-Fe_2O_3 nanosorbcats; it can be used for enhancing the properties of another adsorbents as activated carbon to have magnetically separable and efficient adsorbent for ALZ dye removal from water.

(2) Using γ-Fe_2O_3 as a semiconductor with energy band gap (~2.2 eV) for investigating the photocatalytic degradation of ALZ dye under UV or visible light irradiation.[74] In this process, ALZ dye could be converted onto final relatively nontoxic compounds such as H_2O and CO_2. These

simple compounds are generated by the reaction between organic pollutants and radicals which generated due to transfer of electrons after absorbing energy equal or higher than the energy of band gap.[51]

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كلية الدراسات العليا

استخدام دقائق أكسيد الحديد المغناطيسية كحفاز وماص لتنقية المياه الملوثة بصبغة الأليزارين وإعادة استخدام الحفاز

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إشراف

د.إسماعيل بدران

قدمت هذه الأطروحة استكمالا لمتطلبات الحصول على درجة الماجستير في الكيمياء بكلية الدراسات العليا في جامعة النجاح الوطنية، نابلس- فلسطين.

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الملخص

في هذه الدراسة، تم استخدام دقائق أكسيد الحديد المغناطيسية كحفاز و ماص لتنقية المياه الملوثة بصبغة الأليزارين. وحيث أن هذه تقنية جديدة تعتمد على الاستفادة من خصائص دقائق أكسيد الحديد كماص لتنقية المياه من الملوث وكحفاز يمكن إعادة استخدامه عدة مرات. تم دراسة عدة عوامل تؤثر على عملية التنقية ومنها: الوقت اللازم للتنقية، كمية الماص، درجة الحموضة للوسط، درجة الحرارة. ولقد وجد أن عملية الاضمصاص تتأثر بكمية الماص حتى وصول الاتزان. و درجة الحموضة المناسبة كانت 11 والوقت اللازم للوصول لحالة الاتزان ساعة واحدة. ومن دراسة تأثير درجة الحرارة تبين أن كفاءة عملية الاضمصاص تقل مع زيادة درجة الحرارة وهذا يدل أنها طاردة للحرارة. ووجد أن العملية تتبع Pseudo-second-order.

وتم دراسة وتحليل النتائج على درجة حموضة من 8-12 باستخدام نموذج لانغمير وفرينلدخ وسيبس وتبين أن عملية الاضمصاص تتوافق جيدا مع نموذج لانغمير. قدرة الماص العليا لاضمصاص صبغة الأليزارين كانت 28.5 ملغم صبغة لكل غم من الماص. بالإضافة إلى ذلك تم دراسة ديناميكية عملية الاضمصاص وفهم طبيعته من خلال حساب العوامل الآتية: Gibbs free energy (ΔG°) و standard enthalpy (ΔH°) و standard entropy (ΔS°). وأشارت هذه العوامل أن عملية الاضمصاص طاردة للحرارة و تلقائية وأنها عملية فيزيائية ذات طاقة تنشيط منخفضة.

ومن تجارب إعادة استخدام الحفاز تبين أنه يمكن إعادة استخدامه أربع مرات. ولقد تم التأكد من الخاصية الحفزية للماص من خلال استخدامه لتنقية المياه الملوثة بصبغة الأليزارين وتعريضه للأشعة فوق البنفسجية. وتبين أن هذه الأشعة تحسن من كفاءة الماص دون التأثير على خواصه الحفزية والمغناطيسية.