

An-Najah National University

Faculty of Graduate Studies

**Studies Toward Removal of Phenol From Olive Industry Liquid Waste
Using Poly Itaconic Acid**

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Dedication

To my father, to my beloved mother, who raised me to be who I am today...

To my brothers, my sister and their families who have supported me

To the memory of my dearest friends.

I dedicate this work.

Acknowledgement

First of all, I would like to express my gratitude to ALLAH for helping me to complete my graduate study.

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الإقرار

أنا الموقع أدناه مقدم الرسالة التي تحمل العنوان:

Studies Toward Removal of Phenol From Olive Industry Liquid Waste Using Poly Itaconic Acid.

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التاريخ

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Lists of Abbreviation

Symbol	Abbreviation
ABS	Absorbance
A	Intra-particle diffusion constant gives an idea about the thickness of the boundary layer
P.I.A	Polyitaconic acid
OMWW	Olive mill wastewater
B	Langmuir constant related to the rate of adsorption
C_e	Concentration of phenol at equilibrium
C_i	Initial liquid-phase concentration of adsorbate
C_t	Adsorbate concentration in the fluid phase at time t
K₁	Equilibrium rate constant of pseudo-first-order kinetic model
K₂	Equilibrium rate constant of pseudo-second-order kinetic model
K_f	Freundlich constant represents the quantity of adsorbate into adsorbent per a unit equilibrium concentration
K_b	Rate constant of intra-particle diffusion (mg\g min ^{1/2})
N	Freundlich constant
PR	Percentage removal (%)
q_e	Amount of adsorbate per unit mass of adsorbent at equilibrium (min)
q_m	Maximum amount of phenol adsorbed per unit mass of adsorbent (mg\g)
q_t	Amount of adsorbate per unit mass of adsorbent at time t (min)
R²	Correlation coefficient
R_L	Separation factor
R	Universal gas constant (8.314 J / mol.K)
SEM	Scanning Electron Microscopy
V	Volume of the solution
W	Mass of dry adsorbent
T	Absolute solution temperature
ΔH^o	Standard enthalpy
ΔS^o	Standard entropy
ΔG^o	Standard free energy

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Abstract

This study focuses on preparing and studying the properties of poly itaconic acid (P.I.A) and the mechanism and effectiveness of this polymer on adsorption of phenol from the aqueous solution.

The adsorption properties of the prepared P.I.A were investigated in terms of adsorbent dosage, pH, temperature, contact time, and contaminant concentration. The adsorption capacity of P.I.A was studied using Freundlich and Langmuir models at equilibrium to determine the behavior of adsorption process, if it is chemical or physical adsorption.

Three kinetics models were applied to describe the adsorption process: pseudo-first-order kinetic model, pseudo-second-order kinetic model and Intra-particle diffusion model. The surface area of the polymer was determined by iodine number and BET and showed 262.5 m²/g and 355 m²/g, respectively.

Results show that the optimum percent of phenol removal reached 12.2 mg/g when adsorbent dosage was 0.1g of P.I.A with a phenol concentration of 50 mg/g. When increasing pH from 4 to 12, it was found that phenol adsorbent increases slightly. The results indicate that the temperature effect is a reversible process on the P.I.A adsorption like when the temperature

increases the phenol percentage of adsorption decreases. The results of the contact time studies showed that the equilibrium time for phenol adsorption process is 130 min. The percentage removal of phenol increases when the concentration of phenol increases.

The results also showed that the adsorption model followed Langmuir with B equal 0.031 which indicate that adsorption is favorable. This means that a monolayer and uniform energies adsorption.

The pseudo-second-order model was the best for describing the kinetic adsorption of phenol with correlation coefficient valued (R^2) is 0.9975 and K_2 , q_e of 0.0118, 11.933 respectively. This validated that the adsorption process was chemical adsorption.

Thermodynamic parameters such as standard enthalpy ΔH° , standard entropy change ΔS° and standard free energy ΔG° were calculated for P.I.A adsorbent of phenol. The negative values of both enthalpy and entropy indicated that the adsorption is exothermic process and the adsorption is more favorable at lower temperature, while the positive values of Gibbs free energy at various temperatures indicate that the adsorption process is feasible but not spontaneous.

Chapter one

Introduction

1.1 General Overview

The widespread contamination of wastewater by phenol and their derivatives and other organic chemicals compounds has become a major problem in recent years. So that the removal of pollutants from wastewater become the subject of many study of research in recent years [1].

The olive oil production is an important industry and related to the culture, since ancient time, especially, in the region and among the countries of the Mediterranean. Recent researches revealed the fact that there is some contamination occurs through olive oil production process. The worldwide olive oil production for the years 2002 - 2009 is reported to be 2,775,800 tons [2]. Olive mills wastewater OMWW (*Alzibar*), is found to be the highest source of environmental pollution in the countries of Mediterranean region [3, 4].

In many countries such as Palestine, Spain, Syria, and Tunisia the extraction of olive oil is performed by pressing or centrifuging processes. All the methods, currently used for the extraction of olive oil, result different wastes and pollutants. The olive industry liquid waste has produces a large amount of pollutants, especially, the phenolic compounds. Other important resources of phenolic compounds in wastewater are gasoline, coal, petroleum, petrochemical and pharmaceuticals [5].

There are several disadvantages of throwing the storage of olive extracts on soil. This will reach out to the groundwater or to the surface water and will be dissolved in the water and therefore increases the amount of organic matter in it. Over time, this phenomenon leads to reduce the amount of fish in the sea water and limit their reproduction [6,7]. As a result, many modern technologies and treatment procedures including physical, chemical, and biological were developed to reduce the severity of wastewater contamination from olive presses. All traditional methods used until now to remove these contaminants and harmful compounds from OMWW did not work efficiently. For this reason researchers developed new methods to deal with this OMWW resulting from the extraction of olive oil [8, 9]. The severity of OMWW on intoxication of the plants and other organisms is due to the organic matter found in high concentration and thus inhibit growth of organism [10 - 13]. There are several methods used to remove phenol and other phenolic compounds from wastewater, biological treatment, procedures using a filtration membrane, electrochemical methods and adsorption processes is the base of many methods due to low cost of processing and no need for large facilities [14].

Phenol is found with a moderate concentration in most of the natural waters. It occurs naturally due to the industrial and agricultural activities. One of the major pollution sources is OMWW, generated from olive oil extraction processes. It discharged to valleys without pre-treatment, and may contaminate ground water resources, mainly due to its high phenolic content, so that phenol compounds are present in OMWW at concentration

in the range from 0.5 to 24 g/L, in addition to that the amount of organic compounds up to approximately 25-45 g/L, and content of polyphenols (5-24g/L) [15]. The dark brown color of OMWW is due to the polymerization process occurs for a few phenolic compounds which has lower molecular weight [16, 17].

In general, water Phenol has low toxicity, but may be converted to very toxic compounds via substituted with chlorine atoms and formation of organic radicals in a very short time, which makes it dangerous on all living organism at low concentration [18].

Marvel and Shepherd have been prepared of P.I.A by various methods in the presence of various initiators to form a polymerization processes in water medium, or by poly (itaconic anhydride) hydrolysis [19]. The main purpose was to synthesize of adsorbent has large surface area for interaction with adsorbate, micro-porous properties, capacity of adsorption and easy to use [20].

1.2 Aspect of this work.

This research is based on the hypothesis that itaconic acid (I.A) is used for developing (P.I.A) with high capacity of adsorption of phenol from wastewater. Phenol contamination of surface and ground water become an important problem in many countries.

To understand and perform adsorption of phenols using the polymer, we did several experiments including the analysis of the isotherm parameters of both Langmuir and Freundlich models, free energy of adsorption, thermodynamic parameters (ΔG° , ΔH° , ΔS°), kinetic and intra-particle diffusion parameters.

1.3 Objectives of this study.

In Palestine, phenolic compounds contamination, due to OMWW which contaminates the soil, surface and ground water, is becoming a major source of pollution. Therefore, the overall goal of this study was to discover the way to reduce phenolic compounds concentration in water by using adsorbent (P.I.A) in the laboratory. To achieve this study, the following experimental objectives will be studied and applied.

- Synthesize and analyze crosslinked polymer (P.I.A) in the Lab and then use it as adsorbent for phenolic compounds.
- Study the adsorption process of the contaminant in the influence of several variables such as concentration of phenol, pH, polyitaconic acid dosage, contact time and temperature.
- Study the adsorption isotherm models, kinetics and thermodynamics of phenolic compounds which adsorbed by the prepared polymer (P.I.A).

1.4 Previous studies.

The use of carbon for adsorption of phenolic compounds from wastewater extends far back into history. *Bassalat* used activated carbon from cypress fruit to adsorb of p-nitro phenol (PNP) from the wastewater [21].

Results indicated that the optimum percent of PNP removal was 90.9% when adsorbent dosage was 0.3g. Percentage removal of PNP increases when the concentration of PNP decreases. When lowering pH from 6 to 2, he found that PNP adsorbent increases, but the PNP adsorbent decreases when increasing pH from 6 to 12. The equilibrium of adsorption was reached in the range of 15-45 °C and 150 min.

Aladham studied the removal of polyphenols from OMWW by using activated olive stones [22].

The activated carbon is chemically prepared from olive stones using potassium hydroxide (KOH) as an activating agent; this led to the produce of a highly micro porous activated carbon with 368.3 m²/g surface area.

Adsorption capacity is represented by Langmuir isotherm model ($q_{\max} = 333.3$ mg/g). The kinetics adsorption of phenol supports pseudo-second order model and Dumwald-Wagner (intra-particle) diffusion model.

Ayad et al., used new adsorbent of attapulgite – urea – formaldehyde polymer (AUFPP) to study the kinetics adsorption of phenol [23].

The Freundlich equation describes very well the adsorption process, and the adsorption on these adsorbent were studied at different temperature 298, 308 and 318 K. They noted that the adsorption was decreased as the temperature increased. Kinetic of adsorption was obeyed the pseudo-first order equation of Lagergren equation and the adsorption rate constant K_{ad} was calculated. The kinetics adsorption supports pseudo-first order model.

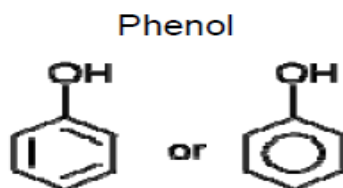
Chapter Two

Background

2.1 Phenol Compounds of OMWW.

2.1.1 Phenol Definition

The phenol compounds are a class of aromatics compounds consisting of one or more hydroxyl groups bonded to an aromatic hydrocarbon group. Its chemical formula is C_6H_5OH and a colorless solid when pure, dissolves in water very strong and flammable [24]. Its structure is that of a hydroxyl group (-OH) attached to a phenyl ring as show in below.



As a result phenol is naturally presents in most foods, and it is produced naturally as atmospheric degradation of benzene in the presence of light, formed during forest fires. Phenols compounds are, also, produced through industrial methods and mainly from the olive oil extraction process, especially in Palestine, so a phenolic compounds in OMWW are resistant to a bio-degradable however they cause many dangerous for the living environment [25].

Phenol compounds are produced in very high quantities in the world and enormous amounts are disbursed annually for the production of phenol. It's

estimated that the United States disbursed annually about 3-billion pounds while other 6-billion pounds disbursed from worldwide.

The major uses of phenol are as chemical intermediate to produce phenolic resins, and biphenol is used primarily in the production of polycarbonate plastics [26].

Table 2.1: The main physical properties of phenol compound

Values	Properties
C_6H_5OH	Molecular formula
94.11 g/mol	Molar mass
Sweet and tarry	Odor
1.07 g/cm^3	Liquid density
$40.5 \text{ }^\circ\text{C}$	Melting point
$182 \text{ }^\circ\text{C}$	Boiling point
8.3 g/100 ml ($20 \text{ }^\circ\text{C}$)	Solubility in water
270.5 nm	Maximum Wavelength
1.7 D	Dipole moment
9.90	Acidity constant, Pka
6	pH of aqueous solution

Phenol compound is used in the manufacture of some types of wood, construction and automotive industry, some devices and enters in the production of nylon. Phenol compound could become a disinfectant and sometimes added in the manufacture of certain types of drugs [27].

2.1.2 Phenols in the Environment

The widespread use of phenol compound in many industries worldwide, in the production of slimicide, disinfectant, medicinal preparation for sore throat, olive oil extraction etc. Due to their many application, phenolic compounds become a more contaminant in aqueous streams. Phenol compounds are toxic to all living organisms even at low concentration [28].

Phenolic compounds, in general, polymerize if they exposed to long-term storage and they change to polymer of high molecular weight that are difficult to decompose. For the time being, farmers in Palestine get rid of phenols from OMWW by exposing the wastewater, which is placed in large and open pools, to evaporate. Unfortunately, this method is unusual because it does not get rid entirely from phenols compounds [29].

The phenol compounds are very toxic compounds on natural water sources, it comes from multiple sources such as cool refineries, pharmaceuticals manufacturing, paints industries, petrochemical, textile wood, oil refineries, phenolic resin industries [30,31,32], Therefore, the phenolic compounds represent a real threat to human life and living organism [33].

When payment is made with a phenol compound to nature, it causes a series of problems on the environment by contaminating natural water, so that these compounds find their way into the environment as water pollution, water analysis process to determine the concentration and ratio of

phenols and its derivatives are very important due to the toxicity of these compounds to normal life [34].

In general, empirical studies showed that the phenolic compound is more toxic when it enters the human body directly than enters the waters [35].

Phenolic compounds are known for its rapidly degrade in soil under both aerobic and an aerobic condition [36, 37].

The best condition for the degradation of soil phenolic compounds is not always available. The scientists observed that the impact of the toxicity of phenol compound on soil microbial activity depends mainly on the type of soil and mineral composition, organic content and pH [38]. *Mrozik* observed that phenols, which decaying in soil, are more toxic in soil with low organic matter content [39]. In contrast, he observed that in lower decomposition of phenol in soil be a return to the increased absorption that occurs for phenolic compounds [40].

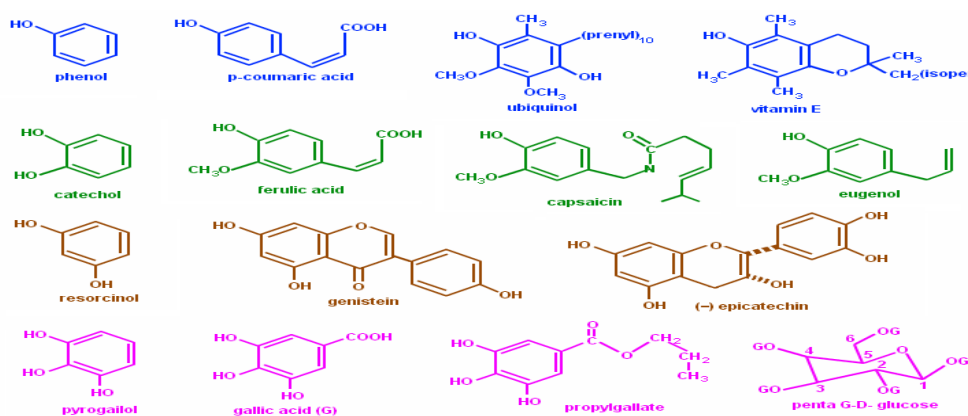


Figure 2.1: Most important phenolic compounds derivatives in wastewater(OMWW).

2.1.3 Phenols in Drinking Water.

With the increasing pollutants in drinking water and the resulting diseases over various countries in the world, this issue pushes states to pay attention to study the proper way to remove these contaminants from various water sources. Phenol and phenols substituent the most important compounds that cause pollution to water, which is one of the toxic and hazardous substances to environmental life [41].

The phenol compounds affected negatively portable water so when the phenol compounds mixed with water for a long time; it adds an unpleasant odor and flavor. These negative effects of phenol to portable water occur in very low phenol concentration as 5mg/L [42, 43].

The World Health Organization (WHO) decides that the maximum allowed concentration of phenol in drinking water is 1mg/L, in palestine phenol presents in drinking water at concentration as low as 0.1mg/L [44]. The increasing of pollutants in portable water, especially phenol, in the recent years encouraged scientists to increase their efforts on removing these pollutants from wastewater. Phenol is considered to be one of the most serious water pollution in the world [45], The seriousness of the presence of phenol that even low concentration have a water interaction and overlap with a lot of vital processes in nature and all organisms, therefore phenol compounds causes a lot of diseases and impede the use of wastewater [46]. The phenol content in drinking water must not exceed 0.002 mg\L.

The danger of toxic phenol increases when phenol compounds exist in water for long time and interact with other elements with produce many substituted phenolic compounds as, halogenated (e.g. chlorophenol), nitrated(e.g,2- nitrophenol),alkylated(e.g,2,4dimethylphenol). Many of phenolic compounds, especially the chlorophenol, are known for their toxicity, carcinogen [47].

Many phenol compounds derivatives are now in the world. The U.S determined the eleven most dangerous and toxic of phenolic compounds but European Union determine more than eleven of dangerous and toxic phenolic compounds in wastewater [48]. The researchers use a High Performance Liquid Chromatography (HPLC) for determination of phenolic compounds in water.

2.1.4 Phenols Health Effect to Human Body

The phenols is well absorbed from body of plants, animals, humans in different ways, after so many disease causes to these organisms, the most important diseases caused by phenol compound to human is associated with headache, fainting, vertigo, and mental disturbances [49].

The people whom their skin is exposed to high amount of phenol have skin burns, liver damage, darks urine, irregular heart beat and some even dies. In addition to the health damage to phenol compound on living organisms, the phenol owns property corrosion and may also be a skin irritant, especially to human [50].

The phenol compounds have serious implications and chronic effects on human health in the long run, especially, through inhalation as volatile or skin contact. Skin exposure to the phenol compounds is serious and can cause damage to the skin, eyes and trachea mucous. Other negative health effects resulting from exposure to phenol are: headache, dizziness, fatigue, fainting, weakness, nausea, vomiting and loss of appetite. The chronic exposure to phenol in humans leads to gastrointestinal irritation, change in blood pressure and cause damage to the nervous system [51].

Doctor *Ahzaw* pointed that poisoning of phenols will more significant among children, so young people are more sensitive and impact damage than adult people [52].

2.2 Polymer of Polyitaconic Acid.

2.2.1 Polyitaconic Acid Properties.

The cross-Linked polyitaconic acid could be prepared by polymerizing itaconic acid with free radical initiator sodium or Potassium Persulfate in the presence of cross-Linking agent 1,4-Butanedioldiglycidyl Ether as shown in Figure 2.2.

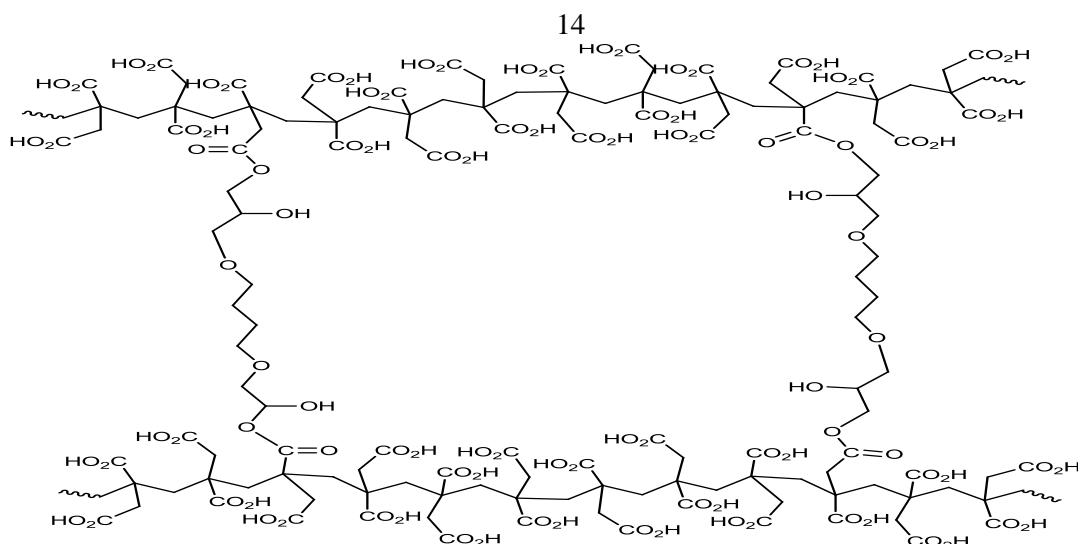


Figure 2.2: Possible Structure of cross-linking polymer will be prepared and used in extraction of phenol.

Cross-Linked polyitaconic acid being rigid, and insoluble in common organic solvents or water [53]. Compared with the adsorbent traditionally used in previous studies and researches, especially like carbon activated, this polymer is more efficient, because it is form adsorption to organic compounds such as phenol, without the use of any factors that help (catalysts) or activate to adsorption, so the high efficiency in adsorption to phenol compound at this polymer due to the controllable pore Structure and surface characteristics, and presence of OH- group on the surface, so that this polymer could be become widely used in the adsorption of various organic compounds, especially phenolic compounds from wastewater [54,55].

In addition to that, the adsorption process for phenol depends on the nature of the surface of the material adsorbed in terms of porosity of the surface. So there is a lot of adsorbent, due to large surface area, which

contain a lot of pores dense that has been developed to operate as adsorbent more effectively. Scientifically was proven that the presence of pores frequent on the adsorbent surface encourages the adsorption to occurs and affects the adsorption kinetics. For any good adsorbent material, it must featuring large surface area, it proximity to many pores and need a little time to achieve the equilibrium balance in process of adsorption [56].

2.2.2 Historical adsorption of phenols.

Phenol compounds and its derivatives is one of the very dangerous substances on human health, even if existed in water at very low concentrations, may reach concentrations of phenolic compounds in the water to 400 g / L. For this reason, it is necessary to remove these compounds and their derivatives from industrial water immediately prior to its disposal to stream surface or ground water sources [57].

The majority of industrial wastes contain phenolic compounds are difficult or impossible to remove by conventional biological treatment processes [58].

Phenols as a class of organic that is similar in structure to the more common herbicides and insecticide in that they are resistant to biodegradation [59].

The knowledge of both adsorption equilibrium and heat of adsorption is fundamental for adequate description of any adsorption process. On the other hands, the adsorbent and the solution are brought into contact for a limited period of time in the industrial process of wastewater purification [60, 61].

There are lots of adsorbents that have been studied previously for purification and removal of phenolic compounds and derivatives from wastewater.

2.3 Adsorption.

2.3.1 Adsorption Definition.

There are many methods, previously used, to purify wastewater from phenolic compounds such as oxidation [62, 63], precipitation [64], ion exchange [65], solvent extraction [66], but finally proved that the most successful method to extract and remove phenolic compounds from wastewater is adsorption method [67, 68, 69, 70].

The choice of suitable and effective treatment technique depends on economic factors and special wastewater characteristics. The commonly used treatment method, will be used frequently, is the adsorption method.

Adsorption method is the most important method used in large quantity to many countries in the world and this related to many characteristic of adsorption method. It is economical, more effective, and simple to use.

However the adsorption method to be affected by the nature of adsorbate and its functional group, then relationship between functional group of adsorbent and adsorbate because this phenomenon plays an important role in the capacity and efficiency and mechanism of adsorption to adsorbate molecules [71, 72].

The material which used as adsorbent have too many different characteristics from each other and the famous adsorbent has been widely used so far is activated carbon [73].

The adsorption is different from absorption. Adsorption process is the adhesion of molecules such as a gas or liquid to a surface of the material which used in adsorption process while in the absorption is defined as the process when one thing become part of another thing, the molecules of substance to be absorbed interference within a material used and penetrate walls. The adsorption technique is the best method newly used to treat wastewater [74, 75, 76]. This adsorption property has encouraged scientists to research and study for cheaper and efficient adsorbent technique as bottom ash, brick kiln ash, fly ash peat, soil, rice husk, wood and others substances [77,78,79]. Adsorption process is proved to be one of the most effective and efficient methods for purification and treatment of pollutants from wastewater [80, 81, 82].

In addition to that the adsorption method technique characterize from other techniques used to remove contaminants from water sources that are more flexible and simple to use and ease of operation and does not result a toxic pollutants to the environment.

2.3.2 Adsorption Features

The physical adsorption (physisorption) is defined as an operation of weak forces between molecules. In this state the adsorbate molecules does not remain fixed on affixed location at the surface of adsorbent, but it will be free to move from one place to another on the surface of adsorbent [83]. Physical adsorption interpretation based on that a physical interaction between molecules as electrostatic force, dipole-dipole interaction, dispersion interaction and Hydrogen bonding.

The chemical adsorption (chemisorption), the particles attached to the surface by forming covalent bond. The enthalpy of chemisorption is very much greater than physisorption [84]. Figure 2.3 and Table 2.2 summarizes the main differences between both processes.

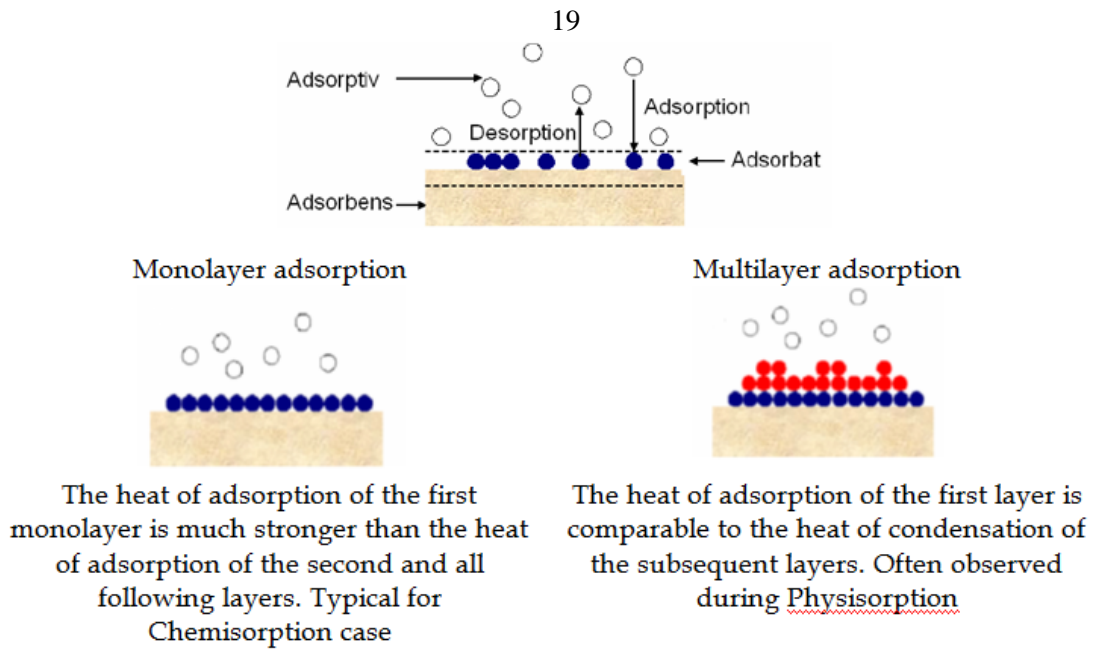


Figure 2.3: comparison between the chemical and physical adsorption in drawing [85].

Table 2.2: Comparison between Physisorption and Chemisorption properties [86].

Chemisorption	Physisorption	Face Comparison
Approximately 200 KJ/mol	Approximately 20 KJ/mol	Adsorption enthalpy (ΔH°)
Donor – Acceptor	Dipolar interaction	Bonding
Impossible	Possible	Adsorbate recovery

The adsorption of multi-component solvent is in truth a very complex and difficult process, because in this case we will separate a one component among many of a component which dissolve and suspended in the liquid [87].

The OMWW is an example of a multi-component solvent and we have to separate only a phenol compound from it. The adsorption process of a substance depends strongly on the property of physicochemical. An example of this is when the molecular weight of adsorbate increases the amount of adsorption increasing. On the contrary for the polarity property is opposite of that where if adsorbate are not polar be adsorbed and separate in easier process, while if the adsorbate is polar they will form strong bonds with water, particularly hydrogen bonds, therefore non-polar organic materials are easier to separate from the water and this thing known in the hydrophobic bond, such as phenol compounds forming H-bonding with each other molecules and with water molecules, therefore be separated and adsorbed become difficult and complex [88,89].

In addition, the organic compounds containing chains of long length are less solubility in the water, so that increase the adsorption by using non polar adsorbent [90].

To describe the mechanism of adsorption process for phenol compounds, several equations was used. This kind of equation has been proposed to describe the adsorption on heterogeneous surface of adsorbent as Freundlich equation and other equation proposed to describe the adsorption on a homogeneous surface of adsorbent as Langmuir equation, and some equation used to describe the kinetic and thermodynamic of adsorption [91,92].

The process of adsorption of phenol compounds from olive oil wastewater will be useful and feasible from both sides must Firstly in this process a toxic compound of phenols are adsorbed from wastewater and thus reduce the contamination of water and seriousness in future.

In this study, adsorption process of phenolic compounds will be performed via adsorbent which prepared in our lab (cross-linked of polyitaconic acid). More over Kinetics and Mechanisms of the adsorption process will be investigated.

OMWW represent an important environmental problem especially in the Mediterranean areas where they are generated in large amounts at very short time and annually [93].

2.3.3 Adsorption Theory

2.3.3.1 Mechanism of Adsorption.

Adsorption of the substances involves accumulation the adsorbate at the surface of the adsorbent to creates a film, the molecules that adsorbs at the surface called an adsorbate and the substance on which adsorption occurs called an adsorbent.

2.3.3.2 Adsorption Isotherm.

The study of Adsorption isotherm tells us in the knowledge of the relationship between the concentration of the adsorbate when soluble in liquid before adsorption and concentration of the same adsorbate after

adsorption on the surface of the adsorbent at a given temperature. Isotherm adsorption is the constant – temperature equilibrium relationship between the quantity of adsorbate per unit mass of adsorbent q_e and its equilibrium solution concentration C_e , the most common equation describing this relationship between adsorbate and adsorbent vs. equilibrium concentration is the Langmuir and Freundlich equation [94].

The Langmuir equation form (2.1) is given as follows:

$$C_e/q_e = 1/bq_{\max} + C_e/q_{\max} \quad (2.1)$$

Where q_e is the amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g) at equilibrium, q_{\max} is the maximum amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g), c_e is the equilibrium concentration of the adsorbate (mg/L), and b is the Langmuir constant (L/mg) [95].

The Freundlich equation (2.2) has form as this:

$$q_e = K C_e^{1/n} \quad (2.2)$$

And this equation can be linearized as follows:

$$\text{Log } q_e = \text{Log } K + 1/n \text{ Log } C_e$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K_f and $1/n$ are Freundlich constant, $1/n$ is unitless, and the unit of K is determined by the unit of q_e and C_e [96].

2.3.3.3 Kinetics Adsorption.

The study and discussion of the result of the research, especially the result of kinetic adsorption, are very important study because it shows that the adsorption process occurs at a specific interval of time [97].

The kinetics of adsorption is defined as process of adsorbates must be transported from bulk solution to the boundary layer of water surrounding the adsorbent particle by molecular diffusion through the stationary layer of water, after that transport to an available site, an adsorption bond is formed between the adsorbate and adsorbent [98].

The process of adsorption of phenol compound by polymer occurs in sequential steps Firstly the molecules of phenol transport to the outer surface of the adsorbent then begin to move from their location to stabilizes on an active site in the surface of adsorbent by the property spread after that the adsorption process occurs to molecules of adsorbates at the active sites then penetrate the outer surface and the intervention of the inside through pores [99].

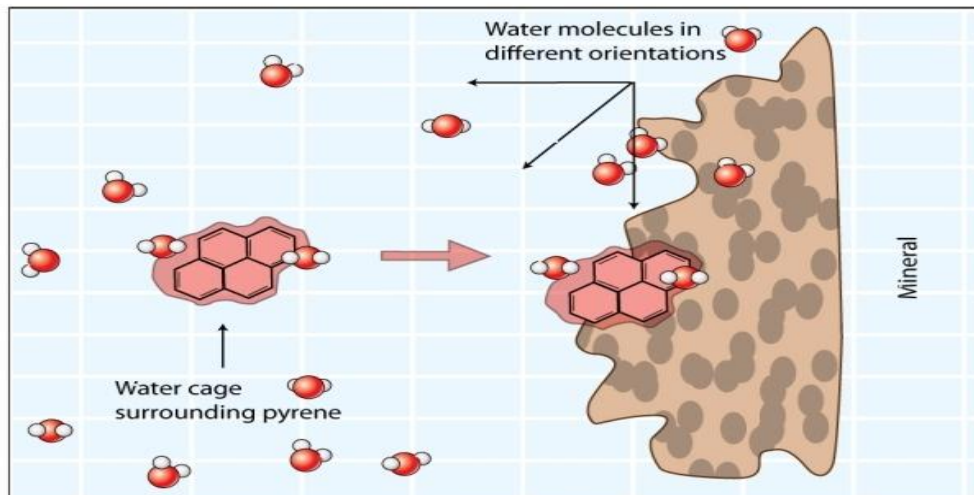


Figure 2.4: Illustration explain the mechanism to adsorption process of phenol compounds on a surface of polymer which used as adsorbent [100].

The knowledge of kinetic feature is indispensable to provide the principle information required for the design and operation of adsorption equipment used for removal phenol from olive oil wastewater (*zibar*). To correlate the kinetic data of the studied system, the theoretical expression developed from statistical rate theory (SRT) of interfacial transport [101,102]. There are growing interests of using polymers for treatment wastewater in the last decade.

The mechanism of adsorption have been studied using the following model:

1) Pseudo first order kinetic models.

Consider this is the equation of firstly equations have been developing to study the kinetic of adsorption. The latest model, which recently reached by the researchers of this relationship is as follows:

$$\text{Log } (q_e - q_t) = \text{log } q_e - K_1 t / 2.303 \quad (2.3)$$

Where q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, q_t is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at time t (min), K_1 (min^{-1}) is the pseudo-first order rate constant [103].

2) Pseudo second order models.

This type of equation was used to describe the adsorption process that occurs to the ions and compound which containing of polar functional group as ketones, aldehyde, carboxylic acid, phenolic compounds, as well as. The famous relationship is used to describe this equation as follows:

$$t/q_t = 1/K_2 q_e^2 + 1(t)/q_e \quad (2.4)$$

Where q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, and q_t is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at time t (min), K_2 is the rate of pseudo-second order constant [104].

3) Internal-particle diffusion model.

Weber and Morris were discovered the theory to explanation the mechanism or system of adsorption material from the media center by using a solid material as adsorbent. The relationship was clarified by the following equation:

$$q_t = K_b (t)^{1/2} + A \quad (2.5)$$

Where q_t is the amount of adsorbate which adsorbed (mg/g) at time t (min), k_b (mg/g min^{1/2}) is the rate constant of intra-particle diffusion and A is express about of the thickness to surface of adsorption.

The value of k_b and A will be calculated from the slope and intercept of plotting q_t v.s $t^{1/2}$ [105].

Chapter Three

Experimental Work

3.1 Chemicals and Reagents.

All chemicals used in this study were very high purity and supplied from source company. The chemical that used in our study are sodium hydroxide, hydrochloric acid, Itaconic acid, crosslinking agent, 1,4- butane diglycidyl ether, distilled water, solution of $K_2S_2O_8$.

3.2 Equipment and Devices.

The following glassware used during the study; funnels, beaker (50ml, 100ml), glass spoon, volumetric flask (100ml, 500ml), glass bottles, para film, pipet, filter papers, and dropper.

The three instruments used in the study are a Nicolet iS5 FTIR Spectrometer used for the detection of functional groups in the prepared polymers and when they mixed with phenol samples. The second one was UV-visible spectrophotometer Shimadzu- Model No: UV-1601, double beam spectrophotometer wave length range 190-1100 nm, accuracy ± 0.004 . UV-Visible spectrophotometer and pH-meter.

3.3 Preparation and Characterization of adsorbent.

3.3.1 Preparation of the polymer(P.I.A) as adsorbent.

The polymer (polyitaconic acid), which is used as adsorbent in this study, was prepared in the laboratory using the following procedure. In the first one, reaction used only 10% of crosslinking agent (1,4-butane diglycidyl ether), and in the second one, reaction used 20 % of these crosslinking agent, then for each reactions 50 g of itaconic acid was used as follows:

To a 500 ml- beaker a 50 g of itaconic acid were added then added a crosslinking agent with a specific amount of 10% and 20% to the two methods of preparation, respectively. Then 50 mL of distilled water was added. Finally a solution of $K_2S_2O_8$ (initiator) (10 mL- water containing 0.5g initiator) was added. All the materials have been added mix at 60 °C until polymer forms [106].

After that, the result compound dried by exposing to atmosphere for a whole week while shaking it every 3 days. The compound was placed in the furnace at 80 °C to a period of 3 hour, or till to make sure that a polymer had dried completely from water. Then its placed in the two tightly closed and dried plastic cups.

The polymer prepared by the first method was used as adsorbent in this studies.

3.3.2 Characterization of Adsorbent (P.I.A).

The characteristics and qualities of any substance used in the adsorption process were studied before being used for the purpose of this study.

The study of the surface properties (surface area and SEM) of the adsorbent material is very important to confirm its ability to adsorption process because the adsorption process always occur on the surface of the adsorbent material [107].

So that always characteristics of adsorbed material linked to the surface of its, usually measure the spaces on the surface of the adsorbent and the surface roughness and the size of the pores scattered on the surface.

The polyitaconic acid adsorption is influenced by two important factors: the surface area and porous structure. Therefore, it is important to explain the properties of this prepared polymer based on these two factors.

3.3.2.1 Iodine number.

The Iodine number is defined as the amount of Iodine which adsorbed by an adsorbent (P.I.A). The Iodine number is useful to measure of the microspore content and surface area to adsorbent by adsorption of Iodine from prepared solution. In general, the iodine number of prepared polymer which used as adsorbent was determined as follows: 10 ml- of 0.1N Iodine solution in a conical flask is titrated with 0.05N sodium thiosulfate solution in the presence of 2 drops of 1 wt % starch solution as indicator, till it

becomes colorless. The burette reading is corresponding to V_b . Then weight very accurately 0.2g of P.I.A and add it to conical flask containing 40ml of 0.1N Iodine solution, shake it very well for 4 min and filter it, then titrate 10 ml of filtrate with standard sodium thiosulfate solution using 2 drops of starch solution as indicator, the burette reading is corresponding to V_s . The Iodine number was then calculated by using the following equation [108].

$$IN = \frac{(V_b - V_s) \cdot N \cdot (126.9) \cdot (15/10)}{M} \quad (3.1)$$

Where IN is Iodine number (mg/g), V_b and V_s are the volume of sodium thiosulfate solution required for blank and sample titration (mL), respectively. N is the normality of sodium thiosulfate solution (mol/L), 126.9 is atomic weight of Iodine, and M is the mass of P.I.A used (g).

The surface area of the prepared polymer of P.I.A which used as adsorbent was determined through a calibration curve which has a correlation coefficient of 0.997 between the Iodine number and BET surface area of some established activated carbons which used as adsorbent in the literature [109].

3.3.2.2 Scanning Electron Microscopy (SEM).

The analysis of the SEM is usually used to study the density and morphology of the surface of the P.I.A used for the adsorption so this

method give us high-resolution images from the surface of the article clearly on the three dimensions.

So by use the a field emission-scanning electron microscopy (FE-SEM, JEOL JSM-6700F) with an energy dispersive x-ray spectrometer (EDS), we can study the surface shape of the materials which used in adsorption process.

3.4 Adsorption Experiments.

The adsorption of phenol compounds has been studied in sequential steps. In all steps used, equipment were cleaned with distilled water, then dried by exposing them to air or put it a period of time in the oven.

After that, at each addition of phenol compound to polymer, pH has been installed to solution in arrange of 12-13, and the glass bottles were shaken at 130 rpm and determine the temperature of water bath with shaken machine.

Each glass bottles are moved to a specified period of time under the influence of a certain temperature. The pH of phenol solution was changed and determine with the desired values by adding a few drops of dilute solution of sodium hydroxide and Hydrochloric acid. The values of pH were identified by the use of pH-Meter.

3.4.1 Phenol Adsorption Experiments.

A solution of phenol (500 mg/L) was prepared by dissolving 0.25g phenol with a high concentration in 100 mL distilled water then diluted to 500 mL in volumetric flask. From this solution of phenol, samples were prepared for study to get the concentration 50mg/L of phenol by dilution. In each phenol adsorption study was used only (50 mL) of these solution, The adsorption of phenol was analyzed using the UV-visible.

3.4.2 Effect of Adsorption Dosage.

Different amount of polyitaconic acid, prepared in laboratory (0.1g, 0.3g, 0.4g, 0.7g, 1g), were added into each glass bottle, then (50ml of 50mg/L) of phenol were added to each glass bottle and pH was adjusted at range (12-13). All samples were left to shaking for the 130 min at 25 °C.

3.4.3 Effect of Initial pH.

The effect of initial pH to the adsorption of phenol compound by using polymer was studied with pH range (3-13).

The values of pH in solution of phenol was changed by adding a few drops of sodium hydroxide (NaOH) to increase the value of pH, and adding a few drops of hydrochloric acid (HCl) to lowering the value of it, so phenol solution (50ml, 50mg/L), to each samples were added 0.1g of adsorbent. All samples were shaken for a 130 min at 25 °C.

3.4.4 Effect of Temperature.

The influence of change temperature to adsorption of phenol compound by using this of new polymer was studied. Phenol solution (50ml, 50mg/L to each) were added to adsorbent of (0.1g) and pH determined in range from (12-13).

All samples were shaken for 130 min at different values of temperature that range 15-45 °C.

3.4.5 Effect of contact Time (kinetic study).

The effect of contact times on adsorption of phenol was studied at different of contact times. Phenol solution (50ml, 50mg/L to each) was added adsorbent at fixed amount (0.1g) and pH determined in range from (12-13). All samples were shaken at 25°C, and then each sample was taken at different time until equilibrium adsorption was reached after 130 min.

3.4.6 Effect of phenol concentration.

In each glass bottles, phenol compound, which dilute in distilled water of concentration ranging from (10-50 mg/L, 50ml), were added to 0.1g of adsorbent , at initial pH range from (12-13). Each glass bottle left to shake at 25 °C for 130 min.

The initial and final concentration of phenol compound was measured by using a calibration curve to phenol compound, and the removal percentage of phenol was calculated by using the following equation:

$$\text{PR (\%)} = \frac{C_o - C_e}{C_o} \times 100 \quad (3.1)$$

Where PR is the percentage removal (%) to phenol, C_o and C_e are initial and equilibrium concentration of phenol in a solution, respectively.

The amount of phenol which adsorbed at equilibrium, q_e (mg/g), was measured by using a following equation:

$$q_e = \frac{(C_o - C_e) V}{W} \quad (3.2)$$

Where C_o and C_e (mg/L) are the concentration of phenol at initial and equilibrium, respectively, v is a volume of the solution (L) and W is the weight of adsorbent (g).

The whole data were fitted to Langmuir and Freundlich equation (2.1), (2.2), respectively, to describe the isotherm adsorption.

Chapter Four

Results and discussion

4.1 Characterization of the adsorbent.

4.1.1 Surface Area of P.I.A.

Surface area were measured using the iodine number method. The results show that the iodine number equal 272.26 mg/g by using equation.3.1.

Using standard calibration curve for iodine number shown in Figure 4.1. The surface area of P.I.A was calculated and found to be equal to $262.5\text{m}^2/\text{g}$.

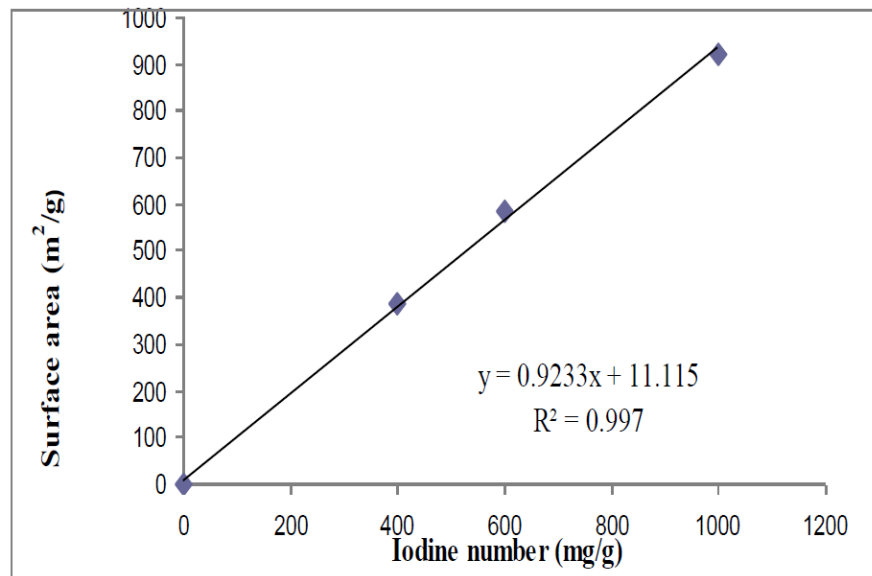


Figure 4.1: standard calibration curve for iodine number [110].

4.1.2. SEM Analysis of the Adsorbent.

The Morphology of adsorbent was studied using SEM (Scanning Electron Microscopy) technique was used to observe the surface physical morphology of the (P.I.A) which used as adsorbent in this study. Figure 4.2, shows the SEM micrographs of (P.I.A).

The SEM micrographs of P.I.A show that the external surface of this polymer is rich with cavities and porous, as shown in Figure 4.2, After phenol adsorption occur the majority of these scattered cavities and porous on surface have been filled and covered, indicating an adsorption process for phenol compounds.

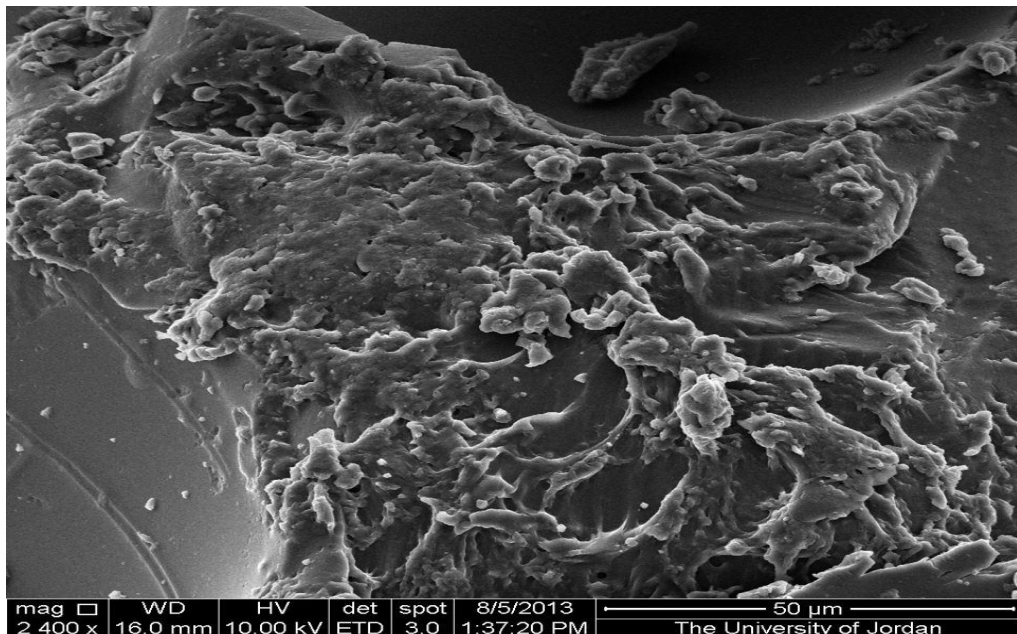


Figure 4.2: SEM of P.I.A before the adsorption process occurs to phenol.

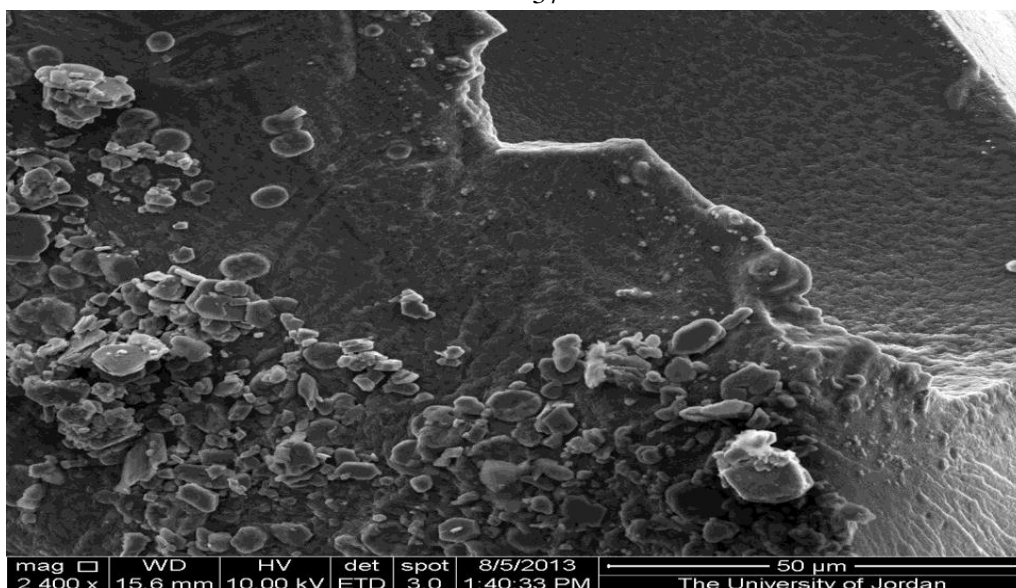


Figure 4.3: SEM of P.I.A after the adsorption process occurs to phenol.

4.1.3. FTIR analysis of adsorbent materials.00

In these below Figure 4.4. FTIR analysis show the functional groups which present on the surface of adsorbent before the adsorption process occurs, where the knowledge the type of these functional helps us to explain the mechanism of the adsorption process.

FTIR spectra in the Figure 4.4 interpreted each functional groups existence on the surface of adsorbent. The bands at 3329.85 cm^{-1} (O---H stretch an carboxylic acid) and 2941.66 cm^{-1} (C----H stretch an alkanes). The bands around 2365.49 cm^{-1} show the existence of (O----H stretch an carboxylic acid), the 1699.43 cm^{-1} band, indicated the presence of an (C=O of ester & carboxylic acid). The band observed at 1548.24 cm^{-1} , which is indicates the existence (CH_2 ----bend), the band at 1392.96 cm^{-1} indicate the presence of (C---O stretch of an carboxylic acid), 1155.96 cm^{-1} indicate the presence of (C---C---(O)---C stretch to all others).

The Figure 4.5 show the FTIR analysis for adsorbent prepared (P.I.A) after adsorption occurs to phenol, from this analysis we note the appearance of broad band at 3297cm^{-1} and this indicated the presence of phenol molecules on (P.I.A) surface.

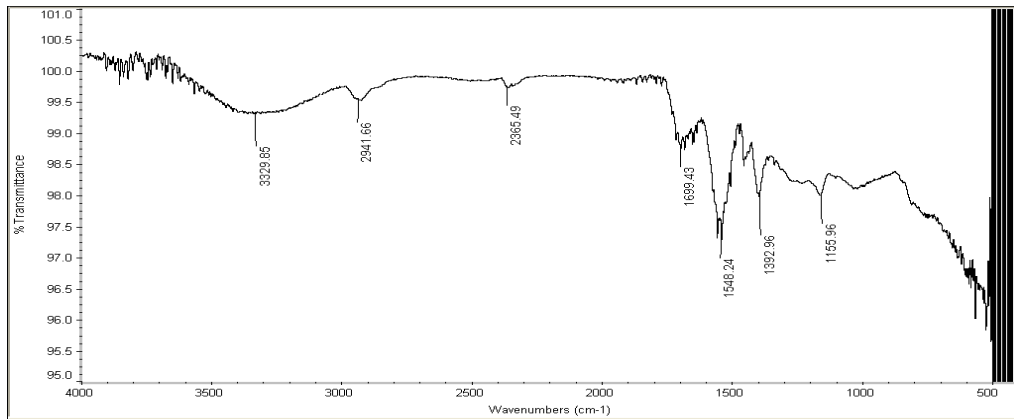


Figure 4.4: FT-IR analysis for adsorbent prepared (P.I.A) before adsorption occurs to phenol.

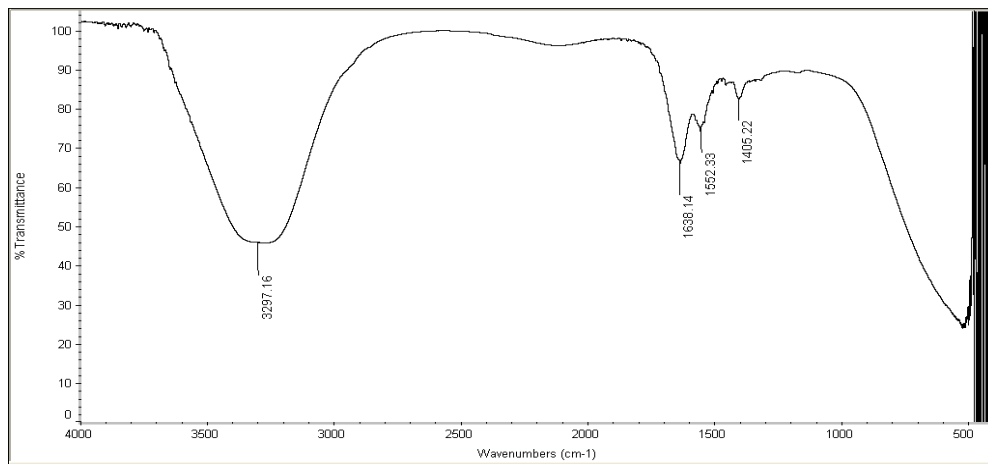


Figure 4.5: FT- IR analysis for adsorbent prepared (P.I.A) after adsorption occurs to phenol.

Table 4.1: Functional groups of P.I.A by FT-IR analysis.

Functional groups	Wave number (cm ⁻¹)
O---H stretch alcohol	3329.85
C----H stretch alkanes	2941.66
O----H stretch carboxylic acid	2365.49
C=O of easter and carboxylic acid	1699.43
CH ₂ ----bend	1548.24
C----O stretch of an carboxylic acid	1392.96
C---C---(O)---C stretch to all others	1155.96

4.2 Characterization of Phenol using UV-VIS.

The Ultraviolet-Visible spectroscopy (UV-Vis), in this work used to verify the existence of some metal ions or organic compound. The UV – Vis is a powerful technique used in most laboratories, due to its low pollution effects, simplicity and speedy to use. Typical calibration curve for phenol analysis is shown in Figure 4.6, the line appear for calibration curve in Figure 4.6 should pass through against (0,0) point, but distilled water has some contamination and doesn't start from point (0,0).

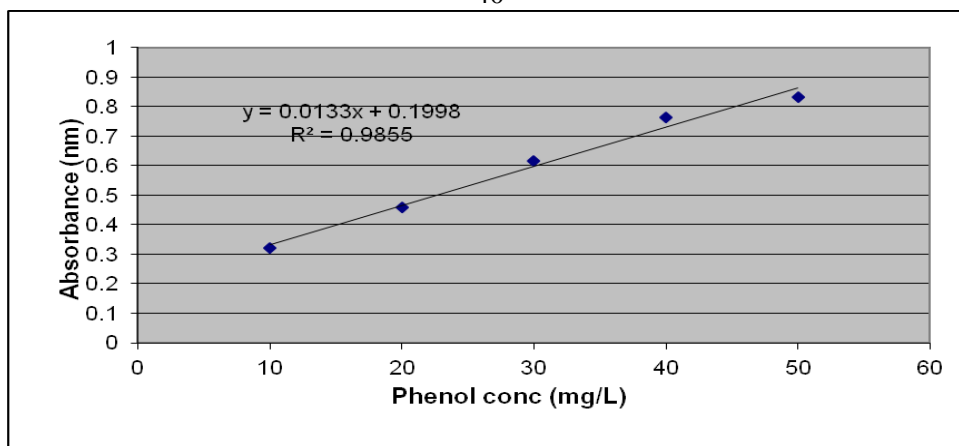


Figure 4.6: A typical calibration curve for phenol using UV-VIS spectrometric method

4.3 Phenol Adsorption Experiments.

4.3.1 Effect of Adsorbent Dosage.

The effect of P.I.A amount on the adsorption of phenol was studied using different P.I.A amount from 0.1 to 1.0 g and initial phenol concentration of phenol 50 mg/L, temperature of 25°C was kept constant, the volume of phenol solution (50mL) was kept constant, pH 13 and for 130 min. The result of adsorption of phenol compound by using a different amount of adsorbent is illustrated in below Figure 4.7.

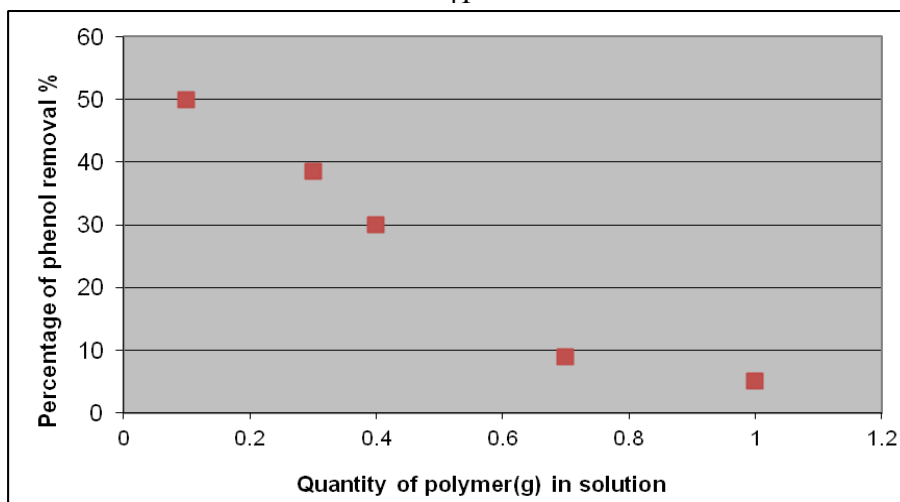


Figure 4.7: Effect of adsorbent dosage on phenol removal by at (initial conc: 50 mg/L, initial pH: 13, temperature: 25 °C and contact time: 130 min).

The amount of phenol was adsorbed decreased with increasing the amount of polymer (P.I.A), so the adsorption increase up to 50% with adsorbent dosage of (0.1 g\50mL). The explanation to this phenomenon is occurrence of split in flux, concentration of phenol compound become as neutrally between un adsorbed phenol in the solution and the adsorbed phenol on the surface of the adsorbent [111].

4.3.2 Effect of pH

The influence pH on the adsorption of phenol compound was studied in the pH range (3-13). The increase in the value of pH was obtained by adding a few drops of sodium hydroxide (NaOH), and the decrease in the value was obtained by adding a few drops of Hydrochloric acid (HCl). The impact of pH change on the adsorption of phenol compounds was studied at adsorption time of 130 min to reach the equilibrium adsorption and at initial concentration which was kept constant to all samples at 50 mg/L,

volume of solution (50ml) and temperature 25°C. Figure 4.8 shows the effect of pH value on the adsorption of phenol compounds:

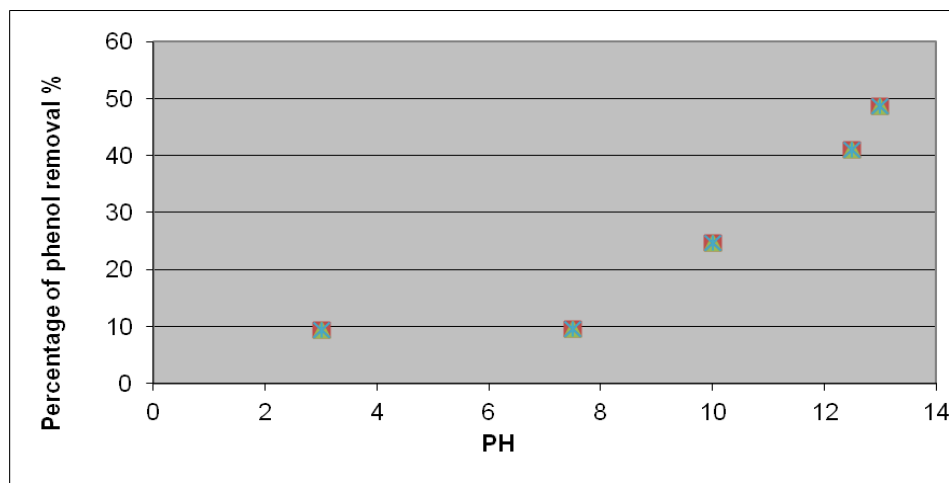


Figure 4.8: Effect of pH on phenol removal by (P.I.A) at (initial conc: 50 mg/L, temperature: 25 °C, contact time: 130 min)

The Figure 4.8 shows that amount of phenol adsorbed increases with increasing the pH value. This behavior is due to the excess of hydroxide ions at higher pH value. This increase the amount of negatively charge on adsorbent surface, P.I.A which used as adsorbent is very rich with $-\text{COOH}$ group on the surface as is clear to us from the Figure 4.8, therefore increasing occurrence of H- bonding bonds between the phenol molecules and the OH groups which are attached on the surface of adsorbent.

4.3.3. Effect of Temperature on Adsorption.

The effect of temperature on the adsorption of phenol by (P.I.A) was investigated in a temperature range (15 – 45 °C). This study has occurred at initial concentration 50 mg/L of phenol, constant volume solution of 50 ml to all samples, pH (13), for 130 min to reach the equilibrium adsorption to

all samples, The influence of temperature change are shown in below Figure 4.9.

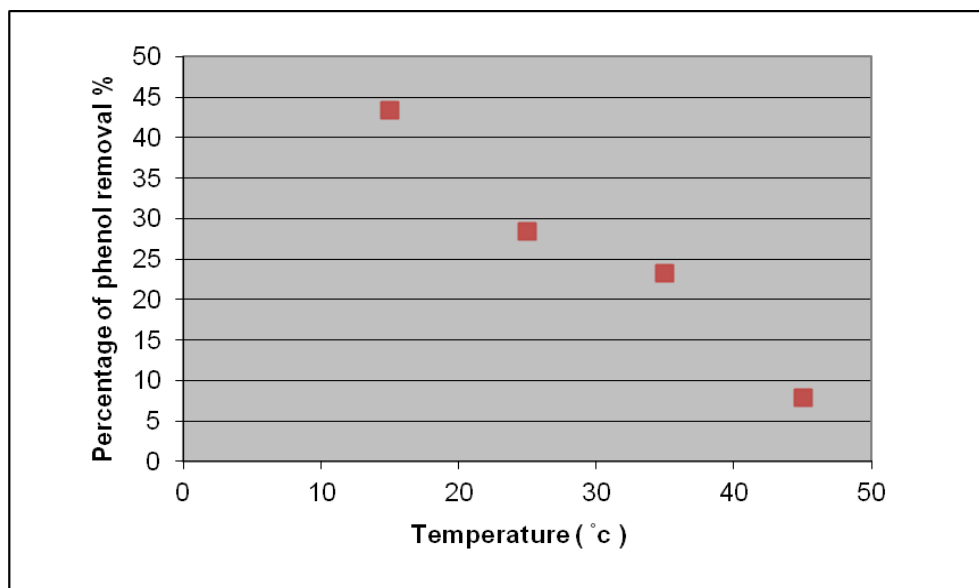


Figure 4.9: Effect of temperature on phenol removal by (P.I.A) at (initial conc: 50 mg/L, initial pH: 13, contact time: 130 min).

The results shows in Figure 4.9 indicate that the adsorption of phenol compound decreased with increased temperature, because when temperature increases the solubility and ionize of phenol in water is increasing, so that if solubility of phenol increase in water with increasing temperature the probability occurred of H-bonding between phenol and water molecules become stronger than the occurring H- bonding between phenol and OH groups which Its attached on adsorbent surface, and water is known as an excellent solvent in the nature due to it is polarity, high dielectric constant and small size, and this character are suitable for polar and ionic, compounds to dissolve in water [112,113]. Water ionizes and allow the proton to exchange in easy way between molecules, the highest amount of phenol are adsorbed at 15°C which reach to ~ 45% [114].

4.3.4 Effect of Contact Time.

The effect of contact time on adsorbed amount is shown in Figure 4.10.

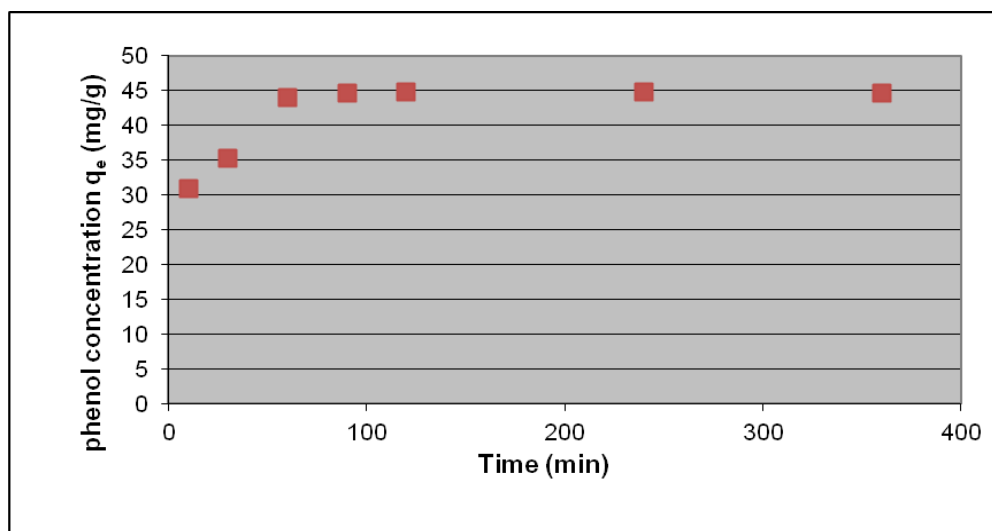


Figure 4.10: Effect of contact time on the removal of phenol by (P.I.A) at (initial conc: 50 mg/L, initial pH:13, temperature: 25 °C).

The maximum amount of phenol removal was ~ 45% after 130 min. The study began at initial concentration 50 mg/L of phenol, constant volume solution of 50 mL, pH (13), and constant temperature to all samples at 25°C.

The adsorption of the phenol compound was increased with the increasing the contact time, as shown in Figure 4.10, and the equilibrium adsorption of phenol was reached at ~ 130 min.

At the beginning (10 – 30min), the adsorption of phenol increased rapidly. The higher adsorption of phenol at the initial period of contact time is due to the higher availability of vacant sites on the external surface of adsorbent [115].

4.3.5 Effect of Phenol Concentration.

The effect of initial concentration of phenol on the adsorption capacity was studied and the results are shown in Figure 4.11.

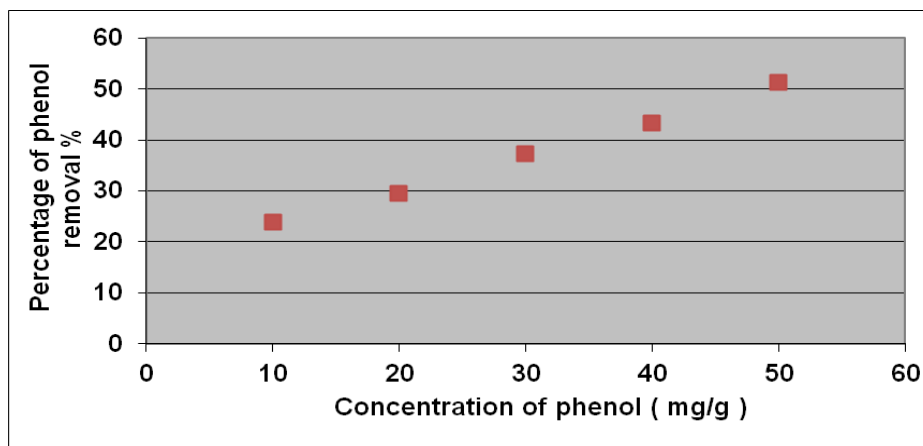


Figure 4.11: Effect of phenol concentration on % removal by (P.I.A) at (initial adsorbent dose: 0.1 g, initial pH:13, contact time: 130 min, Temperature 25 °C).

Figure 4.11 shows the effect of initial phenol concentration on percentage removal of phenol at equilibrium. This figure shows that the increase of concentration increased the percentage of phenol removal.

As phenol concentration increases from 10mg/L to 50mg/L, the percentage removal was increased from 24% to 56%, because when the concentration of phenol increased that leads to increasing the mass of phenol molecules after that increase in driving force to these molecules and therefore acceleration the rate of mobility from solution to a surface of adsorbent [116].

4.3.6 Adsorption Isotherms.

In this research, the adsorption isotherms equation was used to describe the relationship between the amount of phenol adsorbed by (P.I.A) at equilibrium at 25°C, pH 13, solid\liquid ratio 0.1g/50mL is shown in below Figure 4.12.

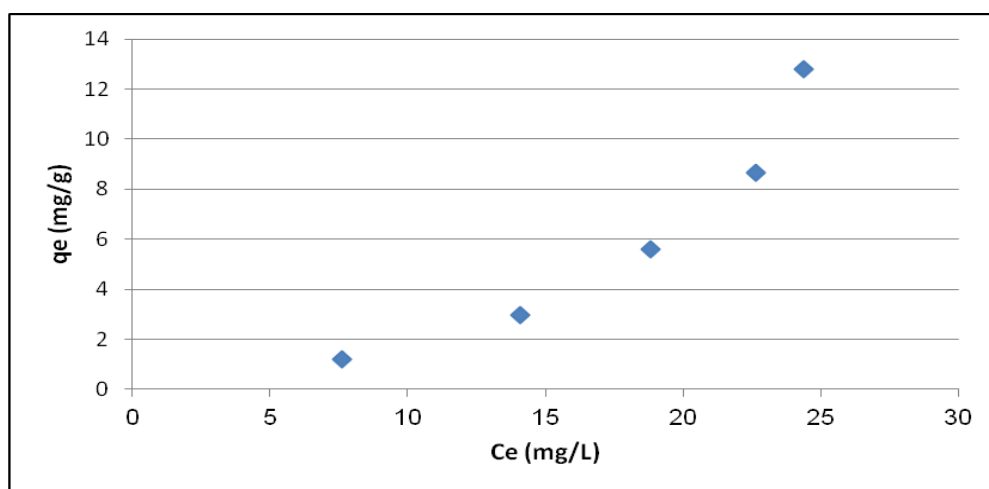


Figure 4.12: Equilibrium adsorption isotherm of phenol into (P.I.A) at (temperature: 25 °C, initial pH:13 and solid/liquid ratio 0.1 g/50 mL).

The equilibrium adsorption isotherm has an important role to describe the any adsorption system [117].

The Langmuir, Freundlich and Intra-Particle diffusion, which are very important to determine the adsorption capacity of adsorbent to remove a phenol compound, is used to describe the equilibrium phenomenon between adsorbed phenol on the surface of adsorbent and unadsorbed phenol in solution [118,119]. The value of Langmuir, Freundlich data are obtained by plotting C_e/q_e versus C_e which shows in Figure 4.13, and $\text{Log } q_e$ versus $\text{Log } C_e$ Figure 4.14, respectively.

The adsorption isotherm data are calculated from the slope and intercept of the linear plots used the Langmuir equation (2.1), and Freundlich equation (4.2), together with R^2 value to both equation are given in Table 4.2.

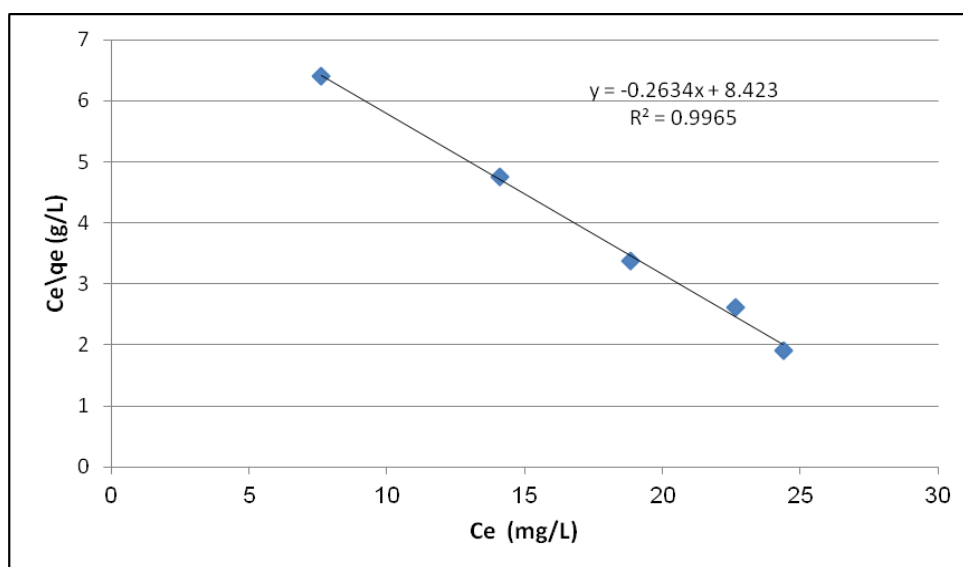


Figure 4.13: Langmuir plot for phenol adsorption into P.I.A at (Temperature; 25 °C, initial pH:13 and solid/liquid ratio 0.1 g/50 mL).

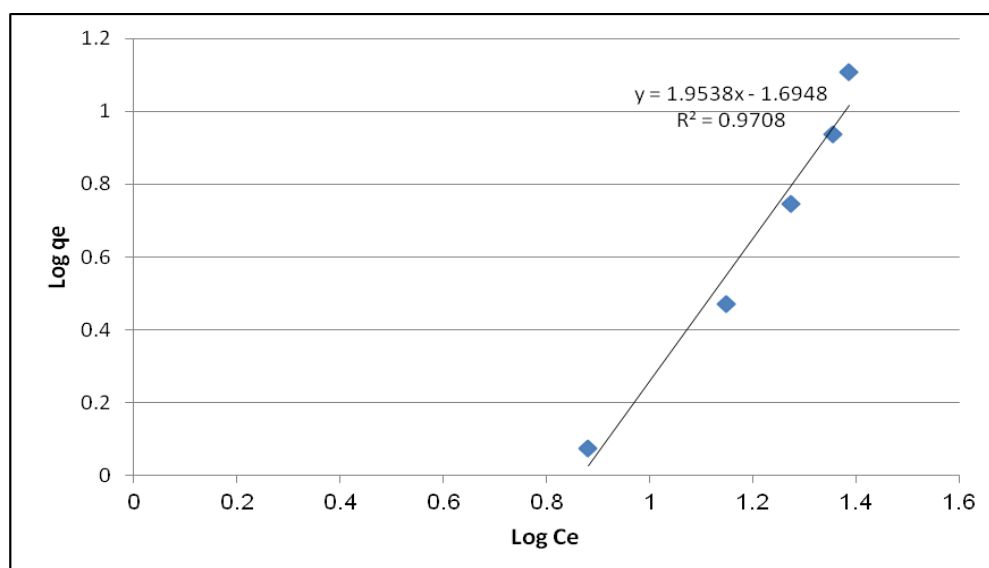


Figure 4.14: Freundlich plot for phenol adsorption into P.I.A at (temperature: 25 °C, initial pH:13 and solid/liquid ratio: 0.1 g/50 mL).

Table 4.2: Isotherms constants for phenol Adsorption into P.I.A

Langmuir Isotherm			Freundlich Isotherm		
R^2	b (L/mg)	$q_{(max)}$ (mg/g)	R^2	K_F $((mg/g)(L/mg)^{1/n})$	n
0.9965	0.031	3.796	0.9708	49.52	0.511

It is clear from Table 4.2 the R^2 values that both Langmuir and Freundlich isotherm describe the experimental data, but Langmuir isotherm model describe data better than Freundlich.

The Langmuir isotherm model shows that the adsorption increases with increasing in phenol concentration until it reaches the saturation point.

This describes the adsorption process which occurs by formation monolayer to phenol molecules on the surface of the adsorbent, and after that no further adsorption will be occurred [120]. All sites on surface of adsorbent are occupied by phenol molecules so any further increase in concentration of phenol compound in the solution will not increase the amount of adsorbed phenol.

We assumes, from the study and analysis of isotherm data, that adsorption of phenol occurs on surface of adsorbent as uniform energies and no transportation occurs to phenol molecules on the plane of surface of adsorbent.

A favorable adsorption does not tend to have Freundlich, constant (n) not between 1 and 10. Smaller value of n (Larger value of $1/n$), indicates that it does not cause strong interaction between the phenol molecules and adsorbent [121]. Table 4.2, shows that (n) value was not between 1 and 10, therefore we are sure that the assumption of monolayer chemical adsorption between adsorbate and adsorbent which used in this research was achieved completely, on the contrary the multilayer physical adsorption was not achieved.

4.3.7 Kinetics of phenol Adsorption.

The mechanism of adsorption have been studied using the following models, pseudo-first-order kinetic model, pseudo-second-order kinetic model and the intra particle diffusion model were all used to test the experimental data [122,123].

The results of these all kinetic models are shown in Figures 4.15, 4.16 and 4.17, respectively.

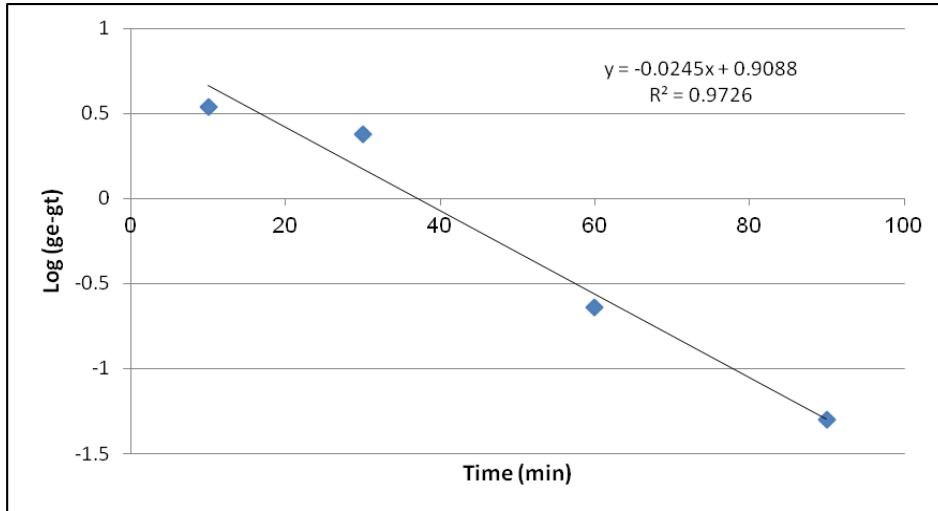


Figure 4.15: Pseudo-first order kinetic modeling of phenol adsorption into P.I.A

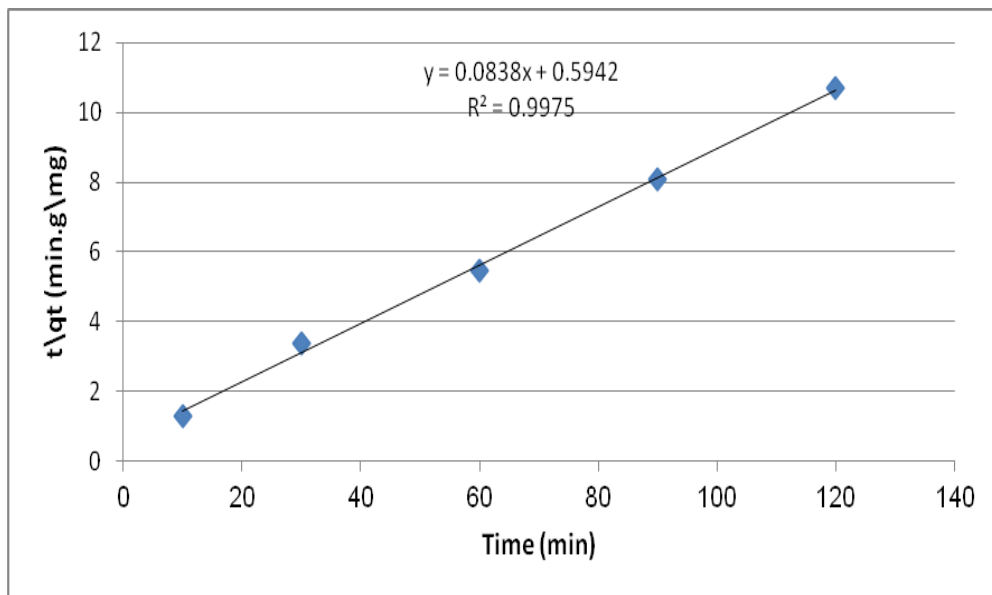


Figure 4.16: Pseudo-second order kinetics modeling of phenol adsorption into P.I.A

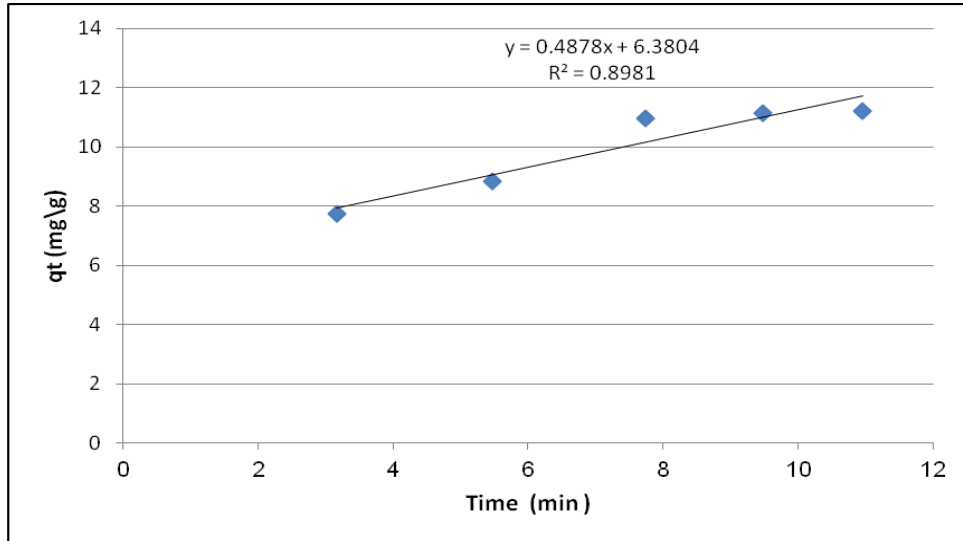


Figure 4.17: Intra-particle diffusion (Weber-Morris) modeling of phenol adsorption into P.I.A.

Kinetic adsorption models parameters of phenol adsorption into P.I.A are summarized in Table 4.3 and 4.4.

Table 4.3: Pseudo-first-order and pseudo-second-order kinetic model parameters for phenol Adsorption into P.I.A at 25 °C

Pseudo-First Order		
K_1	q_e	R^2
min^{-1}	(mg/g)	
0.0564	8.105	0.9726
Pseudo-Second Order		
K_2	q_e	R^2
(mg/(g.min))	(mg/g)	
0.0118	11.933	0.9975

Table 4.4: Intra-particle diffusion kinetic (Weber – Morris) model parameters for phenol adsorption into P.I.A at 25 °C

Weber-Morris	
K_b (mg/g.min^{-0.5})	R^2
0.4878	0.8981

Table 4.3 shows that the correlation coefficient values (R^2) of the pseudo-second-order model for adsorbent are greater than those obtained for the pseudo-first-order model. On the other hand, Table 4.3 shows that the values of the equilibrium of adsorption (q_e), that have been calculated to the pseudo-second-order model, are very close to the (q_e) of experimental value.

As a result, it can be concluded that the higher correlation coefficient of pseudo-second-order model and the close the $q_e(\text{calc})$ values to the q_e of experimental value, the more appropriate the pseudo-second-order kinetic model to describe the mechanical and kinetic process occurs in adsorption of phenol molecules into a surface of P.I.A adsorbent. The chemisorption processes between the adsorbent surface of P.I.A and phenol adsorbate can explain the adsorption process for phenol [124].

Through the study, which used the intra-particle diffusion model, the values obtained as the correlation coefficient R^2 and K_b constant, which obtained from the linear plots of q_t versus $t^{1/2}$, given in Figure 4.17, are

summarized in Table 4.4. Figure 4.17 implies that the rate of phenol adsorption into P.I.A is not limited by mass transfer across the boundary layer on adsorbent.

4.3.8 Adsorption Thermodynamics.

In order to describe the thermodynamic adsorption of phenol molecules under the influence of thermal effect by change temperature, the Gibbs free energy (ΔG°), the entropy (ΔS°), and the enthalpy (ΔH°) will be found, so that, The spontaneity of adsorption process can be interpreted by thermodynamic parameters such as enthalpy change (ΔH°) [125].

The thermodynamic values are calculated by using the following equations:

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT \quad (4.1)$$

Where, R is the universal gas constant (8.314 J/mol.K), T is the temperature in Kelvin, and K_d is the distribution coefficient which can be calculated from this below equation:

$$K_d = C_{Ae} / C_e \quad (4.2)$$

where C_{Ae} (mg) is the amount of phenol adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration of phenol.

Gibbs free energy (ΔG°) can be calculated by the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (4.3)$$

After that, the values of ΔH° and ΔS° are calculated from the slope and intercepts of the linear equation which results from the plotting of $\ln K_d$ versus $1/T$ in Figure 4.18 [126], then the all thermodynamics parameter values are summarized in Table 4.5, as follows:

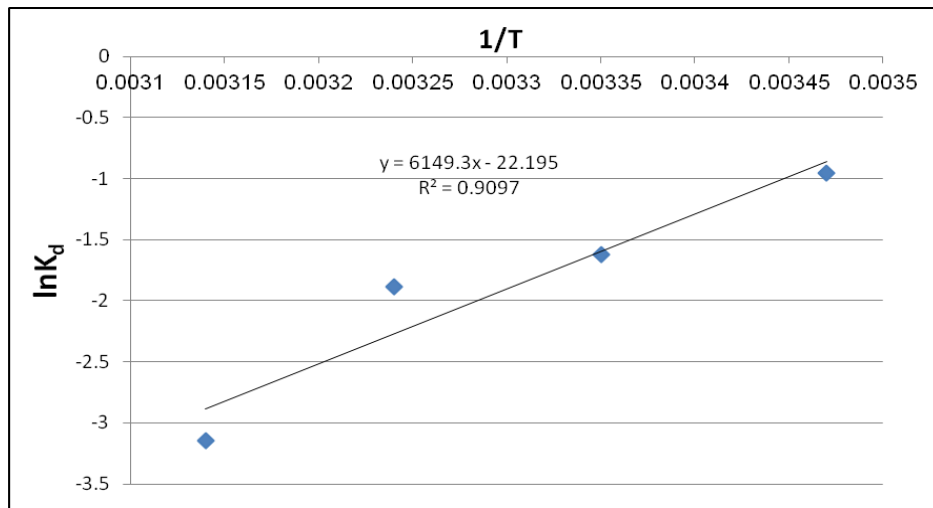


Figure 4.18: Thermodynamic adsorption plot of Ln K versus 1/T for 50mg/L of phenol Concentration.

Table 4.5: Thermodynamic parameters for phenol adsorption into P.I.A at different temperatures with initial concentration of phenol of 50 mg /L.

T (K)	K_d	ΔH° (Kj/mole)	ΔG° (Kj/mole)	ΔS° (j /mole.k)
288	0.383	-51	2.29	-184.5
298	0.197		4.02	
308	0.151		4.84	
318	0.043		8.31	

The positive value of Gibbs free energy (ΔG°) at various temperatures indicates that the adsorption process which occurs to phenol by this adsorbent P.I.A is feasible but not spontaneous [127]. The increase in the value of ΔG° with rise in temperature shows that the adsorption is more favorable at lower temperature.

The negative value of the enthalpy (ΔH°) indicates that the adsorption is exothermic process [128,129].

Furthermore, the negative value of entropy (ΔS°) indicates the affinity of adsorbent material for phenol.

Conclusion:

This work has given good results and a lot of areas that can be achieved in the future and the most important goals that have been achieved through this research are as follows:

- 1) The P.I.A polymer, in basic medium, was effective for phenol adsorption from OMWW more than in Neutral medium.
- 2) The higher percent of phenol removal ~ 50% occurs when the amount of dosage is 0.1g and phenol concentration is 50mg/L.
- 3) The data shows that the adsorption of phenol by P.I.A increases with increasing of pH values in solution.
- 4) Removal percentage of phenol increases when the concentration of phenol increases.
- 5) The experimental results show that the equilibrium time to reach the optimum adsorption of phenol is 130 min.
- 6) Phenol adsorption decreases when temperature increases, as a result of phenol dissolving in water which leads to lowering an adsorption of phenol from water.
- 7) The pseudo-second-order model is more suitable to describe the kinetics adsorption more than pseudo-first-order model.
- 8) The description of phenol equilibrium adsorption followed Langmuir isotherm more efficiently than Freundlich model.

- 9) The value of the intra-particle diffusion model indicates that the phenol adsorption into P.I.A occurs by mass transfer across the boundary layer.
- 10) The values of thermodynamic parameters show that the adsorption process of phenol, by adsorbent P.I.A, is feasible but not spontaneous and exothermic.
- 11) OMWW is the most waste materials in the Mediterranean region. However it is possible to treatment this contaminated water through economic and easy methods.

Suggestion for future works:

The current research achieved its objectives and goals and at the same time it opens the door for further investigations, including the following:

- 1) Study the adsorption of P.I.A adsorbent on removing other serious pollutants from wastewater, as heavy metals.
- 2) Study the effect of other pollutants, especially organic compounds, in the aqueous medium on phenol over time.
- 3) Work on changes and amendments on P.I.A polymer to increase its efficiency in the process of adsorption of phenol compound from wastewater.
- 4) Undergo more experiments to investigate the possibility of using the phenol compound to adsorb by-products in other industries.
- 5) Study other efficient economic methods for the treatment of OMWW from all pollutants in one step.

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Appendix

1) Appendix for calculation of PR (%), q_e .

$$\text{PR (\%)} = \frac{C_o - C_e}{C_o} \times 100$$

Where PR is the percentage removal (%) to phenol, C_o and C_e are initial and equilibrium concentration of phenol in a solution, respectively.

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

Where C_o and C_e (mg/L) are the initial concentration of phenol and at equilibrium, v is a volume of the solution (L) and W is the weight of adsorbent (g).

2) Appendix for calculation of Adsorption Isotherm data.

2.1) Langmuir equation.

The Langmuir equation form is given as follows:

$$C_e/q_e = 1/bq_{\max} + C_e/q_{\max}$$

Where q_e is the amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g) at equilibrium, q_{\max} is the maximum amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g), c_e is the equilibrium concentration of the adsorbate (mg/L), and b is the Langmuir constant (L/mg).

The adsorption isotherm data (Q_{\max} , B) are calculated from the slope and intercept of the linear plots $C_e q_e$ versus C_e for the Langmuir equation.

2.2) Freundlich equation.

The Freundlich equation has form as this:

$$q_e = K C_e^{1/n}$$

And this equation can be linearized as follows:

$$\text{Log } q_e = \text{Log } K + 1/n \text{ Log } C_e$$

Where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, K_f and $1/n$ are Freundlich constant, $1/n$ is unit less, and the unit of K is determined by the unit of q_e and C_e .

The adsorption isotherm data (n , K_F) are calculated from the slope and intercept of the linear plots $\text{Log } q_e$ versus $\text{Log } C_e$ for the Freundlich equation.

3) Appendix for calculation of kinetics adsorption.

3.1) Pseudo first order kinetic models.

$$\text{Log } (q_e - q_t) = \text{log } q_e - K_1 t / 2.303$$

Where q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, q_t is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at time t (min), K_1 (min^{-1}) is the pseudo-first order rate constant.

The kinetics adsorption data (K_1 , q_e) are calculated from the slope and intercept of the linear plots $\text{Log}(q_e - q_t)$ versus Time (min).

3.2) Pseudo second order kinetic models.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where q_e is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium, and q_t is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at time t (min), K_2 is the rate of pseudo-second order constant.

The kinetics adsorption data (q_e , K_2) are calculated from the slope and intercept of the linear plots t/q_t versus Time (min).

3.3) *Internal-Particle diffusion model.*

$$q_t = k_b t^{1/2} + A$$

Where q_t is the amount of adsorbate which adsorbed (mg/g) at time t (min), k_b ($\text{mg/g min}^{1/2}$) is the rate constant of intra-particle diffusion and (A) is express about of the thickness to surface of adsorption.

The value of kb and A will be calculated from the slope and intercept of plotting qt v.s $t^{1/2}$.

4) Appendix for calculation of adsorption thermodynamics data.

The thermodynamic values are calculated by using the following equations:

$$\ln K_d = \Delta S^\circ / R - \Delta H^\circ / RT$$

Where, R is the universal gas constant (8.314 J/mol.K), T is the temperature in Kelvin, and K_d is the distribution coefficient which can be calculated from this below equation:

$$K_d = C_{Ae} / C_e$$

where C_{Ae} (mg) is the amount of phenol adsorbed on solid at equilibrium and C_e (mg/L) is the equilibrium concentration of phenol.

After that, the values of ΔH° and ΔS° are calculated from the slope and intercepts of the linear equation which results from the plotting of $\ln K_d$ versus $1/T$.

Gibbs free energy (ΔG°) can be calculated by the following equation:

$$\Delta G^\circ = -RT \ln K_d .$$

جامعة النجاح الوطنية

كلية الدراسات العليا

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الاتياكونيك الحمضية

إعداد

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2013

ب

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الملخص

لقد تم عمل هذا البحث العلمي بهدف إزالة مادة الفينول من المياه العادمة وخاصة المياه الناتجة عن معاصر الزيتون في منطقة حوض البحر الابيض المتوسط. وتعتبر مادة الفينول من أخطر المركبات على الحياة بشكل عام وخصوصا الانسان حيث أن وجود مركبات الفينول في مياه الشرب تسبب الكثير من الامراض للانسان حتى وأن كانت بتركيز قليلة جدا، لذلك حاولنا استخدام طريقة اقتصادية وبسيطة لاستخلاص مركب الفينول من المياه العادمة بواسطة أعداد وتحضير في المختبر لادمصاص مادة الفينول الموجودة في المياه.P.I.A.

تم التحقق من خصائص عملية الادمصاص بواسطة هذه المادة المحضرة في المختبر وذلك من خلال دراسة أثر كمية هذه المادة ودرجة الحموضة ودرجة الحرارة وزمن التعريض وتركيز الملوثات. تشير النتائج من البحث أن فعالية الادمصاص لمادة الفينول قد زادت عند رفع الرقم الهيدروجيني.

وقد أشارت النتائج الى أن أفضل أستخلاص للفينول كانت 51% عندما كانت كمية المادة الممتزة 0.1غم وتركيز الفينول 50ملغم/لتر.

أما فيما يتعلق بتأثير تركيز الفينول فكانت أفضل نسبة ادمصاص له 55% عندما كان تركيز الفينول 50ملغم/لتر، وكتلة المادة الممتزة 0.1غم . وفيما يخص تأثير درجة الحرارة على الامتزاز فقد تم دراسة ذلك على درجات حرارة ما بين 15-45 درجة مئوية. حيث تشير النتائج

ج

الى أن درجة الحرارة تؤثر بشكل كبير على فعالية الادمصاص حيث تقل كمية الادمصاص عند ارتفاع في درجة الحرارة .

ولقد تم تفسير نتائج عملية الادمصاص التي تم الحصول عليها عند الاتزان باستخدام معادلة لانجموير وفرندليش لتفسير حدوث عملية الادمصاص لمادة الفينول عند درجة حرارة 25 درجة مئوية.

من أجل التحقق من اليات الادمصاص للفينول، تم تطبيق النتائج على ثلاثة نماذج مبسطة للحركة هي : نموذج الاعتماد من الدرجة الاولى ظاهريا ونموذج الاعتماد من الدرجة الثانية ظاهريا ونموذج تدفق الجزيئات الى داخل الجسيمات. هذا وقد دلت كل النتائج التي تم الحصول عليها لادمصاص الفينول مع نموذج الاعتماد من الدرجة الثانية فمن النتائج التي حصلنا عليها ومن الثوابت التي تم حسابها تبين أن عملية انتقال الجزيئات لمركب الفينول محدودة وأن عملية الادمصاص تتم على حدود الطبقات وعلى السطح الخارجي فقط، وتم أيضا حساب بعض ثوابت الثيرموديناميك لادمصاص الفينول ، وذلك مثل المحتوى الحراري للحرارة وطاقة غيبس والتغير في ΔS° و ΔG° و ΔH° الاعتلاج .

وفي الختام، نسأل الله تعالى التوفيق والسداد في الدارين، والحمد لله رب العالمين .

