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Study the Adsorption of Phenol and p-Chlorophenol from Aqueous Solutions by using some Novel Polymer Attapulgite-Urea-Formaldehyde.

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بسم الله الرحمن الرحيم

((اللهُ لا اله ألا هو الحيّ
القَيّوم لا تأخذه سِنةٌ ولا نَوْمُ لَهُ
مَا في السموات وَ ما في
الأرض مَنْ ذا الذي يشْفَعُ
عِنْدَهُ إلا بإذنه يَعْلَمُ ما بينَ
أيديهم وما خلْفَهُم ولا يحيطُونَ
بشيء مِنْ عِلمِهِ إلا بِما شآءَ
وِسِع كُرسيّهُ السمواتِ
والأرض ولا يؤده حِفْظُهُما
وهُو العلي العظيمُ))

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AYAD

Abstract

This work includes the synthesis and characterization of new adsorbents of attapulgite-urea complex (AUC), and attapulgite-urea-formaldehyde polymer (AUFP). The Chemical structural formula of these tow adsorbents were confirmed by FTIR spectroscopy and XRD diffraction technique. The results showed that the urea was linked to attapulgite by hydrogen bonds through the NH_2 moieties. The disappearance of NH_2 stretching band from the IR spectrum of the complex during polymerization with formaldehyde gave good indication of polymer formation. The adsorption ability of AUC and AUFP in addition to attapulgite clay (A) and Urea-Formaldehyde resin (UFR) toward phenol and chlorophenol has been studied using UV-Visible spectrophotometry. This technique has been utilized to construct the relation between the amount of the adsorbate (phenol or chlorophenol) and the equilibrium concentration (isotherms).

The shape of the isotherm obtained from the adsorption of phenol or chlorophenol on the attapulgite, AUC, AUFP and UFR were found to be comparable in all cases to the Freundlich equation and were similar to S-curve type according to Gilles's classification.

Ability of the adsorbents to adsorb the phenol and chlorophenol is in the following order

AUFP > AUC > A > UFR

The adsorption phenomena on these adsorbents were studied at different temperatures 298, 308 and 318 K. The above sequence in activity of the adsorbents surfaces remained unchanged as the temperature changed.

The extent of the adsorption found to decrease as the temperature increased, i.e., exothermic adsorption. The thermodynamic functions ΔH,

ΔG and ΔS were calculated and were explained in the mean of the chemical structure of the adsorbate. Kinetic of adsorption was studied using Lagergren's equation and the adsorption rate constant K_{ad} was calculated. The kinetic results indicated that the adsorption was pseudo first order and the rate determining step was demonstrated.

Activation energy was calculated using Arrhenius equation and was found to be dependent on the nature of the adsorbents surfaces.

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Chapter One

Introduction

1.1 Water Pollution

Water quality can be affected by different form of pollution, chemical, biological and physical [1]. These polluting factors can influence natural and human environment directly by creating conditions that limit water utilization for specific purpose. Where possible, states identify the pollutants that degrade water quality and indicators that document impacts of water quality degradation.

Indicators of water quality degradation include physical, chemical and biological parameters. Examples of biological parameters include species diversity and abundance. Examples of physical and chemical parameters include pH, turbidity and temperature.

1.2 The Main Types of Pollution

1.2.1 Chemical Pollution

Chemical pollutants can be divided into non-persistent pollution, degradable and persistent, degrade slowly. Persistent pollution is the most rapidly growing type of pollution and includes substances that degrades very slowly or cannot be broken down at all; they may remain in the aquatic environment for years or longer periods of time. Which include some pesticides (e.g. DDT deil drain), some leachate components from landfill sites, petroleum and ploy aromatic hydrocarbons. The damage they cause is either irreversible or reversible only over decades or centuries. Non persistent pollutants include domestic sewage, fertilizers, and some industrial wastes. These compounds can be broken down by chemical reactions or by natural bacteria into sample [2].

1.2.2 Physical Pollution

Physical pollution includes warm water from cooling towers (thermal pollution), floating debris, garbage and foam. In power plants that generate electricity is certainly the most important type of physical pollution. Power plants need cool water to start with and they generally release warmer water back to the environment. The temperature of the released water can affect downstream habitats. Temperature also can be affect on the ability of organisms to resist certain pollutants.

1.3 Advanced Methods of Water Treatment

The main aim from this treatment is to improve water. There are many methods for this aim such as using oxidation chemicals for water pollution treatment by using strong oxidizing agent as the ozone [6], molecular oxygen [7], and hydrogen peroxide [8]. Ditto the industrial resins can be used as an ion exchanger [9], or used the natural substances for the same purpose such as (zoelite)[10]. But when it found high concentration from the pollutants in water can use (chemical extraction method)[11] . Adsorption method on the surface of activated carbon, silica gel and porous clay can be used when the concentration of the polluted substances become very low, and can not be removed by methods used previously. [12.13].

1.5 Adsorption

Adsorption process can be defined as the attachment of particles to a surface [14, 15], or is the collection of a substance on to the surface of adsorbent solids [16]. It occur on the surface of the solid and results from valence forces or molecules in the outer – most layer of the solid which are not so fully utilized as in the interior of the solid. The extent of adsorption depends also on the

concentration or pressure and on the temperature [17]. There are two types of adsorption:

1.5.1 physical adsorption (physisorption)

There is a Van der Waals interaction, for example, a dispersion or dipolar interaction between the adsorbate and the substrate. Van der Waals interactions have a long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation. The enthalpy of physisorption can be measured by the monitoring the rise in temperature of sample of known heat capacity, and typical value is in the region of (20 kJ/mole). This small change is insufficient to lead to bond breaking [18]. So a physisorbed molecule retains its identity, although it might be distorted by the presence of the surface.

1.5.2 Chemical adsorption (Chemisorption)

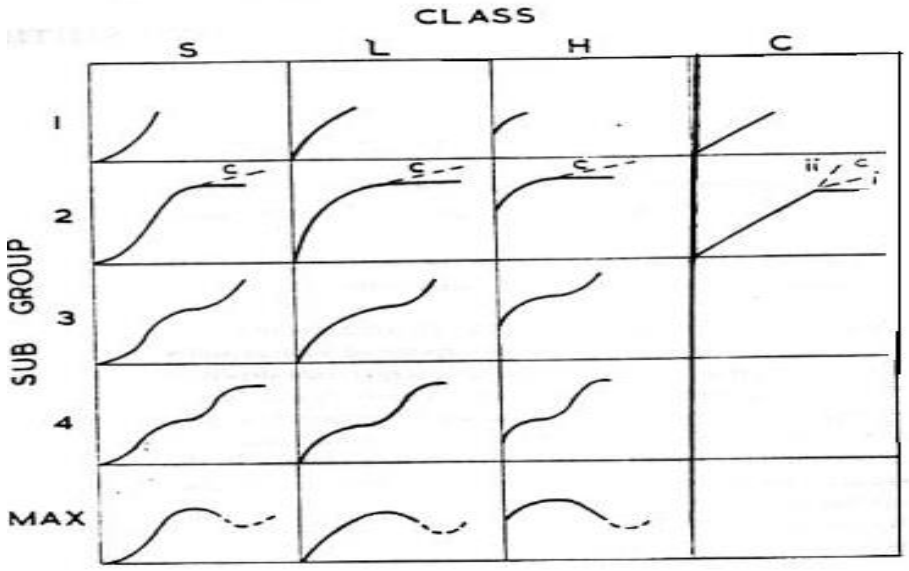
In chemisorption the molecules or atoms stick to the surface by forming a chemical "usually covalent " bond, and tend to find sites that maximized their coordination number with substrate, the enthalpy of chemisorption very much greater than for physisorption; and typical values are in the region of (200kJ/mole). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption [15] The theoretical treatment of adsorption from solution, however is generally more complicated than that of gas adsorption, since adsorption from solution always involves competition between solute and solvent or, between the component of a liquid mixture for the adsorption site. Adsorption from solution behavior can often be predicted qualitatively in terms of the polar /non-polar, nature of their solid of the solution component. In solution, physical adsorption is far more common than chemisorption [19].

1.6 Adsorption Isotherm

The variation of amount of solute adsorbed by a given amount of adsorbent (Q_e) with pressure or concentration at chosen temperature is called the adsorption isotherm [15]. It is standard method for characterizing the adsorption capacity of adsorbents and is constructed for equilibrium adsorption of individual components over arranges of concentration [20]. Graphic representation of the adsorption isotherm obtained by plotting Q_e against the equilibrium concentration of solute in the liquid phase after it attains equilibrium.

Classification of isotherm is a stated necessary to their theoretical treatment and interpretation. A classification system of solid solute adsorption (SSA) isotherms has been described by Gilles and co-workers [21] as represented in Figure 1.1. They divided them all by their initial slope into four main classes, termed for convenience, the S-curve, slope at first increases with concentration because in cooperative adsorption, sites capable of retaining a solute molecule increase, i.e., The S-curve formation by competition of an adsorbed impurity and refers to highly polar adsorption. S-curve is usually taken to mean an end – on orientation provided the possibility of the competitive effects[22] . L, Langmuir, L-curve, there are relatively strong attractive forces between solute molecules and substrate but very week forces between solute molecules themselves, H (high affinity), H -curve can be happen if the cooperating molecules move as a large unit from solvent to substrate and C (constant Partition) classes in all other C -curve systems so far discovered, there is good reason to believe that the solute initiates the adsorption by penetrating into the structure of the substrate, and farther into several sub groups (1, 2, 3, etc) or max by subsequent variation as shown in Figure 1.1. Curves in subgroup 1 represent systems in which the adsorbate monolayer has not been completed. In subgroup 2 and higher we confidently the plateau.

Equilibrium Concentration of Solute in Substrate.



Equilibrium Concentration of Solute in Bath.

Figure 1.1. Gilles classification of adsorption isotherm.

1.6.1 Langmuir Equation:

The adsorption process can be written as:

N_2 (solute in solution) + N_1^S (adsorbed solvent) = N_2^S (adsorbed solute) +

N_1 (solvent in solution) (1.1)

The equilibrium constant K for this process is

$$K=(N_2^S a_1 / N_1^S a_2) \quad (1.2)$$

Where a_1 and a_2 are the solvent and solute activities in solution, the activities in the adsorbed layer are given by the respective mole fractions N_2^S and N_1^S.

Since the treatment is restricted to dilute solutions, a_1 is constant, and we can write $b=K/a_1$; also $N_1^S + N_2^S = 1$, so that equation 1.2 becomes

$$N_2^s = \frac{n_2^s}{n^s} = \theta = \frac{ba_2}{1+ba_2} \quad (1.3)$$

Where θ is the fraction of surface occupied by solute and $n_2^S = n^S N_2^S$, where n^S is the number of moles of adsorption sites per gram. In sufficiently dilute solutions, the activity coefficient, a_2 can be replaced by C_2.

$$N_2^s = \frac{n_2^s}{n^s} = \theta = \frac{bC_2}{1+bC_2} \quad (1.4)$$

At sufficiently high concentrations, n_2^S approaches the limiting value n^S. Thus n^S is a measure of the capacity of the adsorbent and b of the intensity of the adsorption .the two constant n^S and b are conveniently evaluated by putting equation 1.4 in the form

$$\frac{C_2}{n_2^s} = \frac{1}{bn^s} + \frac{C_2}{n^s} \quad (1.5)$$

that is, a plot of C_2 / n_2^S versus C_2 should give straight line of slope $(1/n^s)$ and intercept $(1/bn_s)$ [23]. Equation 1.5 represents the Langmuir equation for adsorption in solution. Also, we can write the linear form of this equation as:

$C_e /x/m = 1/kv_m + C_e /v_m$ (1.6)

Where C_e is the equilibrium concentration; x is the amount adsorbed per a unit weight m of clay; k and v_m are constants, the latter being identifiable with the monolayer capacity of the adsorbent. Conformity of data to equation 1.5 is indicated by the straight line observed when (C_e/x/m) is plotted against C_e. Plotting, C_e/x/m (C_e /Q_e) viruses C_e gives straight line of slope $1/v_m$ and intercept $1/kv_m$ as shown in figure 1.2 However, this in itself does not provide information on the mechanisms of adsorption [24].

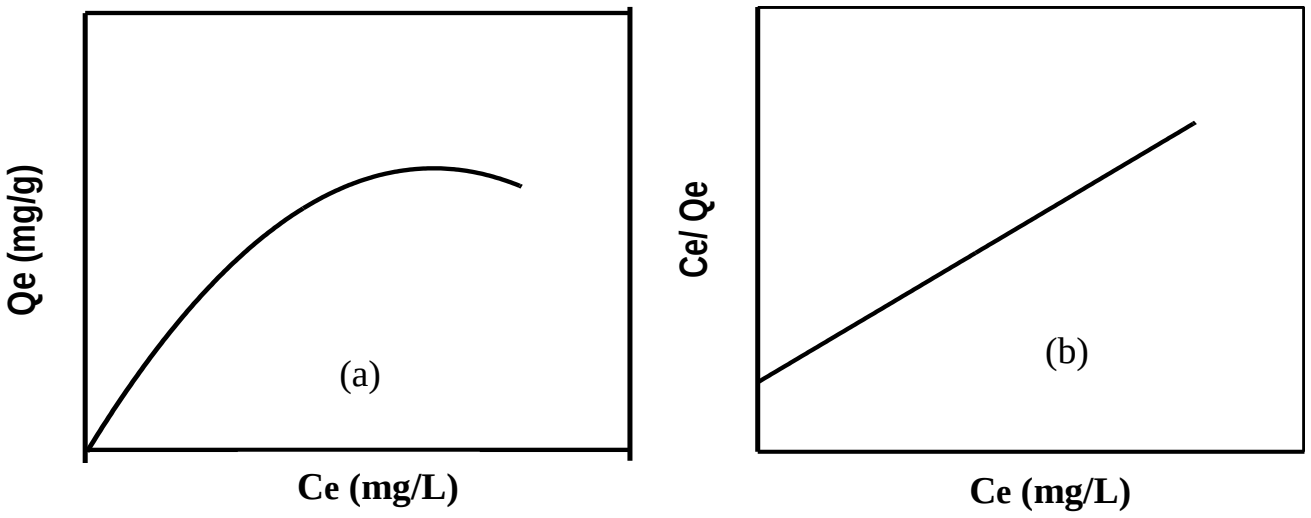


Figure 1.2 (a) Langmiur isotherm, (b) The linear form of Langmuir isotherm.

1.6.2 The Freundlich Equation

The Freundlich equation is an empirical expression used to describe adsorption isotherms. The equilibrium adsorption data could be described satisfactorily by the Freundlich isotherm:

$X/m = k. C^{(1/n)}$ (1.7)

Where X is the amount adsorbed per a unit of adsorbent (m); C is the equilibrium concentration of the adsorbate in the liquid phase [25]. The constant K and n in

equation (1.8) are determined by measuring (X/m) as a function of C. as shown in figure (1.3a), and when plotting log (C) on the abscissa and log (x /m) on the ordinate, and finding the slope (equal to 1/n) and ordinate intercept equal to log (K) of the best fit line through the experimental point as shown in equation below:

$$\log (Q_e) = \log K + 1/n \log C_e \qquad (1.8)$$

The constant K, partition coefficient in equilibrium is positively related to the extent or degree of adsorption or adsorbent capacity. While the constant (n) provides a rough estimation of the intensity of adsorption [26] .The Freundlich equation is especially useful, where the actual identity of the adsorbate is not known .The disadvantage of using the Freundlich plot is that, it is only useful for limited adsorbate concentration ranges and it has limited predictive ability with regard to adsorption isotherms for similar adsorbate.[20]

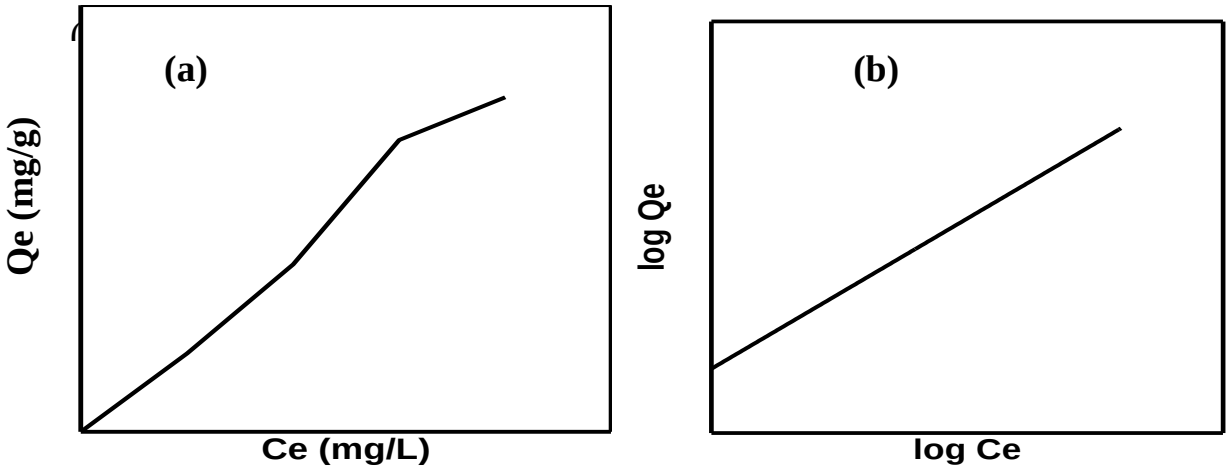


Figure 1.3. (a) The Freundlich isotherm,(b) The Freundlich linear isotherm.

1.7 Factor Influencing Adsorption Process

1.7.1 Concentration of Adsorbate

In general when the concentration of adsorbed increases the capacity of adsorption increases [27], but in some cases, adsorption may be confined to only one layer of adsorbed molecules. Further increase of concentration of adsorbate can produce no further adsorption because the surface of the crystal lattice of adsorbent is covered.

1.7.2 Surface Area of Adsorbent

The dominate factor of adsorption for substance is the specific surface area and pore volume [28], therefore when the surface area increases it refers to high active sites that cause increase in the capacity of adsorption [29].

1.7.3 Temperature

The important factor of adsorption is the temperature, when increases, the effective layers thickness for adsorption decreases. That means The adsorption process in general (exothermic) [15].

1.7.4 Effect of pH

pH plays a major role in the phenomena of adsorption, the ability of adsorption may increase, decrease, or remain unchanged as a result of changing pH.Many variables can take part in this process, such as, the nature or chemical state of the adsorbent, adsorbate and solute .The adsorption of the adsorbent presents an optimum for a pH understood the capacity of adsorption change with the pH [30].

1.7.5 Ionic Strength

The solubility of ionic salts is effected in adsorption process, because when the ionic salts having solubility are better than the adsorbent substances caused increased in adsorption [31], or decrease because the ionic salts caused interference

on the surface adsorption [32].

1.7.6 Effect of Agitation Velocity

The increase of the agitation velocity acts favorably on the adsorption. It is obvious that the effect of agitation speed cannot be indefinite and quantities adsorbed at equilibrium (Q_e) seem tender toward the values constant for greater speed. Indeed, after certain speed limits, the effect must become constant when the phenomena of mass transfer is not limited by diffusion [30].

1.8 The Clay

Clays are composed mainly of silica, alumina, and water; frequently with appreciable quantities of iron, alkalis, and alkali earth [33] .Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen or hydroxyls in which alumina, iron or magnesium atoms are embedded in one octahedral combination, so that they are equidistant from six oxygen's or hydroxyls. The second unit is built of silica tetrahedrons. Which are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition $SiO_6(OH)_4$ [33]. The surface oxygen in layer silicates, however, is a weak electron donor. The (Si - O) bond, of prime important, is marked by a considerable degree of polarity [34]. Every silicon atoms is a tetrahedral arrangement, the second valence of the oxygen atoms, as a rule, links them either to another atom of silicon or to on atom of a metal such as aluminum. In the latter case the oxygen atoms become monovalent negative ions. In more complex cases the silicate groups are linked up forming planner networks or three–dimensional structures that comprise the framework of the crystal [35].

1.9 Classification of Clay Mineral

The most common clay minerals can be classified into five groups:

A –Sepolite (sepolite, and palygorskite "attapulgite").

B – Illite (illite, and glauconite).

C-Smectite (montmorillonite, beidellite, and nontronite).

D – Kaolinite (kaolinite, halloysite, and others).

E – Chlorite (chlorite and others). [36].

1.9.1 Attapulgite Clay

Attapulgite structure is commonly called a chain layer. It is unique mineral structure that manifests ribbons of alumino–silicate layers to be joined at their edges. Attapulgite crystals are needles shaped (circular) rather than flat or flake – like [37], which have high surface area [38]. Attapulgite is superior kaolinite, because it is an open structure enclosing channels into which organic compound [39,40]. It is composed of arimorphic layer arranged in chain (bands) which are joined through oxygen. It has smaller trimorphic unit, intermediate between di – and trioctahedral in character. These minerals have been considered to belong to the category of (chain –lattice silicates). However; since they bear a closer relationship to the phyllosilicates than to the chain silicates [24].

Phyllosilicates are essentially made up of layers formed by condensation of sheets of linked $Si(O,OH)_4$ tetrahedral with those of linked $M_2(OH)_6$ octahedral, where M is divalent cation [24]. The attapulgite is a kind of crystalloid hydrous magnesium aluminum silicate mineral having a special laminated chain structure in which there [41], the chemical structure of one layer of attapulgite can be written in the form

$2[(OH_2)_4(Mg,Al,Fe)_5(OH)_2Si_8O_{20}]4H_2O$ see Figures 1.4 and 1.5, Table 1.1 lists

the main oxides content in the attapulgite clay .

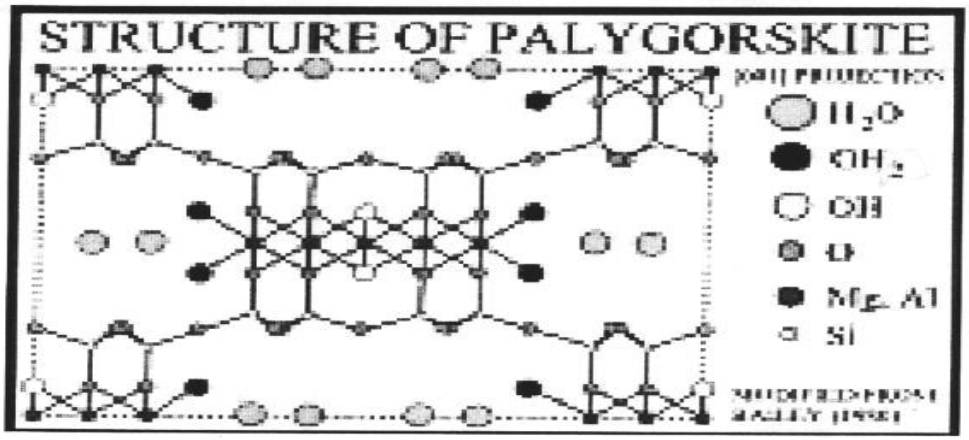


Figure (1.4): Stereo structure of attapulgite clay

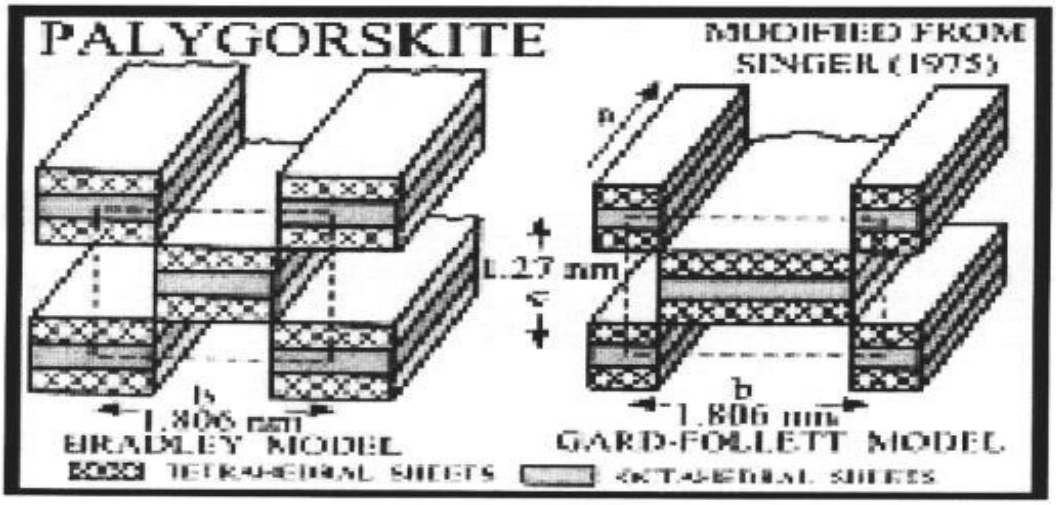


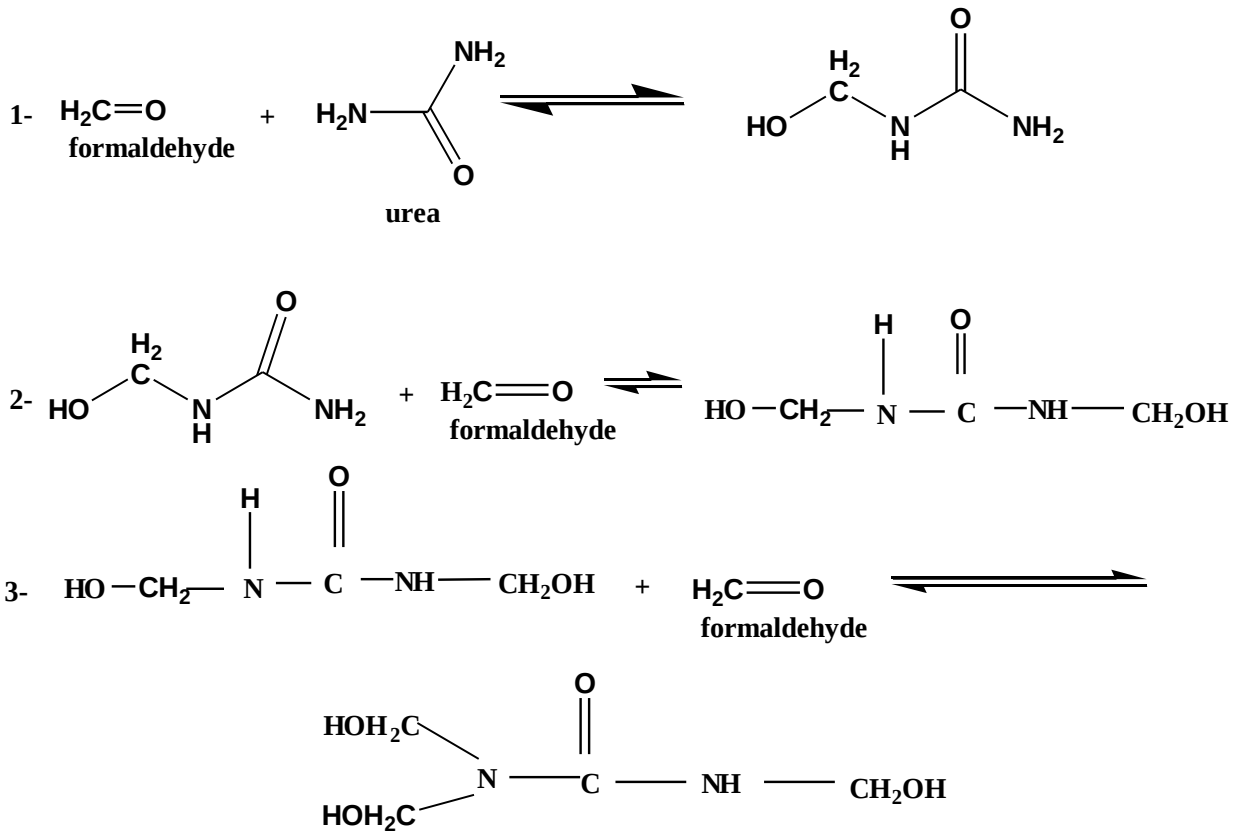
Figure 1.5: Pore Volume of Attapulgite Clay.

Table (1.1) the main oxides content in the attapulgite clay [42].

Oxides	%
SiO_2	55.6-60.5
Al_2O_3	9-10.1
Fe_2O_3	5.7-6.7
Na_2O	0.03- 0.11
K_2O	0.28-1.3
CaO	0.22-1.95
MgO	10.7-11.35
MnO	0.61
TiO_2	0.32- 0.63
L.of I.	10.53-11.8

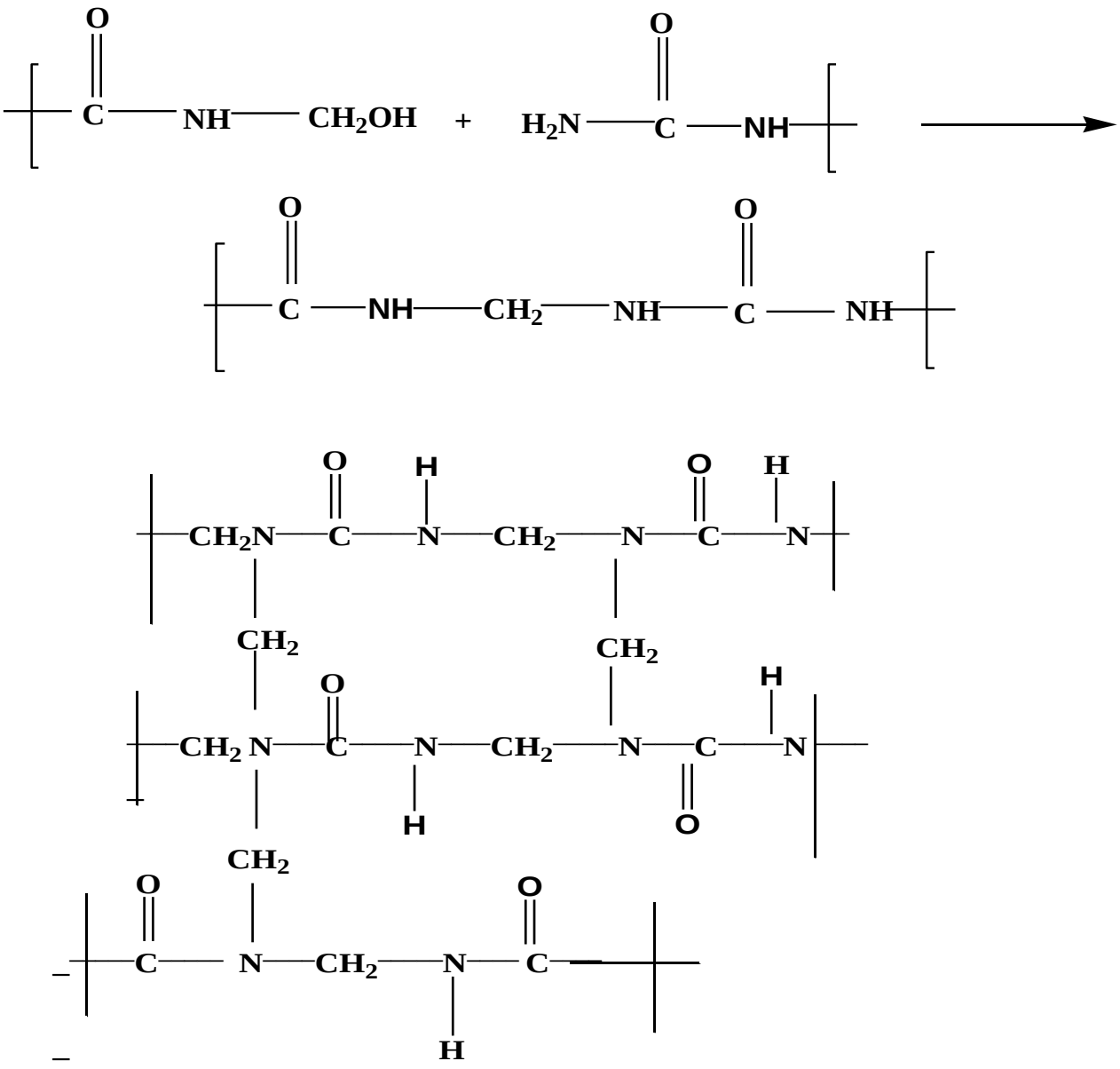
1.10 Condensation of Urea with Formaldehyde

Urea and poly functional amides condense with formaldehyde to form important class resins that are thermosetting materials [43]. The reactants condense to form linear polymer, which form infinite networks on heating. Plastics are called thermosetting, since the fluid material is heated in a mold to form an infusible product. [44]. The obtained product does not contain hydroxyl groups,but has very large macromolecules, and is insoluble in water [45]**.** The character and rate of the reaction between urea and formaldehyde in an aqueous solution depend on the reaction conditions. The preparation of polymer urea-formaldehyde is depens on the main step [42] described in scheme 1.1



Scheme 1.1

The reaction (1) happens by using alkaline agent or acidic agent. It becomes reversible reaction when using acidic agent, and the reaction (1) capable to formation condensation reaction therefore is very fast. In the formaldehyde –urea resins the long chains are tied together with many methylene cross-links as indicated in scheme 1.2



Scheme 1.2

1.11 X-ray Diffraction Analysis

The x-ray diffraction method is a powerful tool for investigating orderly arrangements of atoms or molecules through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wavelength of the radiation. If the structures are arranged in an orderly array or

lattice. The interference is sharpened so that the radiation is scattered or diffracted only under specific experimental conditions. Knowledge of these conditions gives information regarding the geometry of the scattering structure. The wavelengths of X-rays are comparable to inter atomic distances in crystals; the information obtained from scattering at wide angles describes the spatial arrangements of the atom [46, 47].

1.12 Literature survey

There are many studies of adsorption in different fields such as, pollution, medicine, and chromatography. The adsorption of phenol and chlorophenol on different adsorbents has been studied extensively.

White, and Ledox [48] are studied the (IR) and hydrogenic bond between the kaolin surface and formaldehyde and hydrazine, they found the interaction of hydrazine with kaolin increase the stretching in-group (NH_2) from 2738$cm^{-1}$to 2765 cm^{-1} in complex.

Ratanuman et.al,[49] are studied the adsorption of phenolic compounds from water by surfactant modified pillared clays and they found that the presence of the Hexa Decayl Tri Methyl Ammonium (HDTMA) enhanced the adsorption ability of the clays towards phenolic compounds from aqueous systems. And they proved the adsorption affinity decreasing in following sequence: 3,4 dichlorophenol > 3-monochlorophenol > phenol.

Al –Hayali [50] studied the adsorption from solution of two widely used antibiotic drugs, the adsorption of the drugs on kaolin and bentonite surfaces was found to be an endothermic reactions while the adsorption process on attapulgite surface was exothermic.

Al-Timmimi [51] investigates the activity of kaolin, bentonite, and attapulgite as antidotes in treatment of poisoning, and was found that the bentonite surface

possesses the highest activity for adsorption of these drugs.

El-bahrani and Martin [52] studied some types of phenols on carbon by using (GLC) technique. They found the adsorption is obeyed to langmuire and freundlich equations and they found the group which are capable to formation hydrogenic bond such as (OH, NH_2) caused decrease in adsorption process.

Mattson et. al., [53] studied adsorption of phenol and paranitro phenol on activated carbon. They found the adsorption process was found to depend on the charge transfer between of these compounds and the surface of carbon.

Brown et. al.,[54] studied the ability of attapulgite, bentonite, and kaolin to adsorption of tetracycline and found the adsorption process is depending on the ion exchange between the surface and the drug.

Mckay et. al.,[55] studied the adsorption of phenol and para chlorophenol from aqueous solution by activated carbon have been studied by system were found obeyed to Langmuire and Freundlich equation.

Statendra et. al.,[56] studied the adsorption of phenol, cresol and the mixture of these compounds on fly ash. They found that the adsorption obeyed to Freundlich equation.

Al-Ameene [57] studied the adsorption of some phenol compounds from aqueous solution by carbon and asphalt surface .He found that the adsorption process on carbon surface obeyed the Freundlich equation and also found the substituted group on the ortho and para position, the adsorption when the substitution groups has been electron withdrawing groups.

Albanis et. al.,[58] used the flash ash and soil for the removal of dyes from aqueous solutions. They found that the logarithmic form of Freundlich equation gave high linearity and the constant (K) are increasing with increase of fly ash content in adsorbent mixture and the affinity between the adsorbent surface and

adsorbent solute.

Zawadzki [59] using FTIR technique to study the adsorption of phenol on clay, showed exactly the opposite effect, concluded that phenol creates hydrogen bond with surface oxides, and the adsorption of water on active site can be neglected. Thus it can be seem that the process of hydrogen bonding and the competition between the solute and solvent are important and can not be neglected.

Terzyk [60] studied the adsorption of biological active compounds from aqueous solutions on two unmodified activated carbons. He found that the rate of adsorption for unmodified carbon increased with temperature.

Jordanian zeolitic tuffs and their admixtures with urea and thiourea studied by Rushed et. al., [61], the chemical and structure properties from point of with urea and thiourea and they used as potential scavengers for phenolics in aqueous medium. They found that the time and temperature dependence adsorption experiments both indicated that (zeolitic-urea). Which displayed the largest surface area and they also found that showed the greatest ability to remove phenolic compounds from water.

Reinik et. al.,[62] studied the adsorption of (2,4-xylidien) on granulated activated carbon (GAC), they found that the adsorption isotherm by using Freundlich equation on (GAC) better than the Langmuir isotherm.

The effects of temperature on the adsorption have been studied by Mattson et. al.,[63] they found that the temperature dependence of adsorption is mainly due to decrease in the number of electrostatically interacting molecules with surface groups.

Nakamura et. al.,[64] studied the decolorization of acidic dye by charcoal from coffee grounds and they found also that the dominate factor of adsorption for organic pollutants is the specific surface area and pore volume.

The adsorption of phenol on titanium oxides (TiO_2) has been investigated by the Bekkouche et. al.,[30]. They found that the equilibrium of adsorption was reached after 1h, and they found also the kinetics of adsorption were slow and obeyed the Lagergreen model.

1-13 Aim of The Study

The project includes synthesis of the complex AUC and AUFP by the treatment of the clay attapulgite with urea then by the polymerization of the complex AUC with formaldehyde to obtained attapulgite urea formaldehyde polymer by the interaction the polymer urea – formaldehyde with holes of the clay. Then it studies the ability of clay A, AUC, AUFP and UFR as the adsorbent surfaces of phenol and chlorophenol from its aqueous solution and studies the effect of temperature on adsorption of all adsorbent surfaces.

Chapter Two

Experimental Part

2.1 Chemicals

The chemicals used for this work are listed in Table (2.1) together with the purity and sources. All chemicals were used without further purification.

Table 2.1. Chemical and their purity and manufacture used in this study.

Chemical	Source	Purity %
Phenol	BDH	99
2,3 Dichlorophenol	BDH	98
Urea	Aldrich	99
Formaldehyde	Aldrich	98
Hydrochloric Acid	BDH	37

2.2 Instruments

The flowing instruments were used in this study

1. Uv-Visible Spectrometer, Cintra (5) GBC Scientific Equipment (England).
2. Digital pH-Meter **,**Knick (England) **.**
3. Digital balance, Sartoris **,**BP 3015 (Germany).
4. Oven, Heracus (D-6450), Hanau, (England).
5. Centrifuge machine, Hettich: EDA. 35 (Japan).
6. Shaker Bath, SB-16-Te, Tecam, Temperor, England **.**
7. FT.IR **8300–** Schimadzu, single beam bath Laser, Japan.
8. X-Ray diffractometry Philips.

2.3 The Clay

Attapulgite clay used in this study was obtained from the general company

for geological survey and mining, Baghdad, Iraq. It was obtained from Akashatt area in Iraqi western desert. It was collected from an opened mine. It is a buff material, yellow-light orange powder and is practically insoluble in water, organic and inorganic acids and in solutions of the alkali hydroxides. The chemical analysis of attapulgite is listed in Table (2.2).

Table 2.2. The chemical analysis of attapulgite[41]

Chemical	Wt% .
SiO_2	44.66
Al_2O_3	13.36
CaO	13.71
Fe_2O_3	4.2
MgO	3.2
SO_3	0.23
Loss on ignition	17.97
Total	97.33

2.3.1 Preparation of Clay Powder

Attapulgite clay was supplied in the powder form. It was suspended in HCl solution of pH=3 to remove carbonate and it was washed with an excess amount of distilled water to remove the soluble materials. Then it was dried in the oven at

388 K for twenty-four hours then kept in airtight containers. Using the available sieve (200 mesh) the maximum particle size obtained was (75μm). Which was used in all experiments through out this work.

2.3.2 Preparation of Attapulgite -Urea Complex.

Sample of 5g of attapulgite clay was placed in (100 ml) stoppered Erlenmyer flask, and 50 ml of saturated solution of urea was added to it. The urea solution was prepared by dissolving the required amount in distilled water to produce nearly saturated solution of 16.7 M of urea, and the mixture was kept at room temperature for time extending from 2-16 days. After decantation of the supernatant solution, the wet sample was washed with distilled water, then dried in an oven at **378** K , and then kept in desecator; the urea-attapulgite complex obtained was labeled AUC.

2.3.3 Preparation of Attapulgite– Urea Formaldehyde Polymer

Sample of 5g of AUC was placed in (25 ml) conical flask, and (5ml) formaldehyde was added to the mixture, about 5 minute, the reaction is happened at acidic media. The mixing process continued about half an hour then the mixture was put in water bath at 298 K for two hours to complete the cross linkage between the AUC and formaldehyde, and putting in closed container for one week.

2.3.4 Preparation of Urea – Formaldehyde Resin

Sample of 20g of urea was placed in (100ml) stoppered Erlenmyer flask, 20 ml of formaldehyde added to it, and the mixture was treated with a small amount of HCl, then dried in an oven at 358 K, and then washed by ethanol and kept in a desecator. The urea–formaldehyde resin obtained was labeled UFR.

2.3.5 Determination of Maximum Absorption λ_{max}

UV/Visible scanning spectrum of each phenol or 2,3 Dichlorophenol has been recorded and shown in Figures 2.1 and 2.2. Wavelength values corresponding to the maximum absorbency λ_{max} for phenol and chlorophenol was found to be 269 nm and 283 nm respectively. These values were utilized for the measurements of quantitative estimations throughout the course of this work.

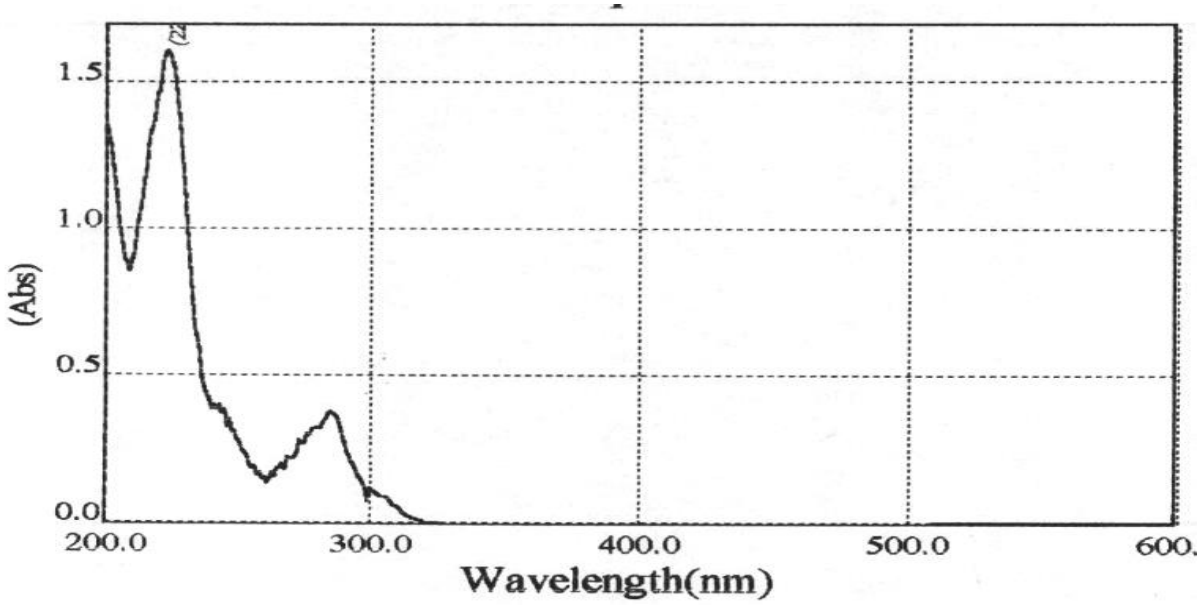


Figure 2.1. U.V spectrum of phenol

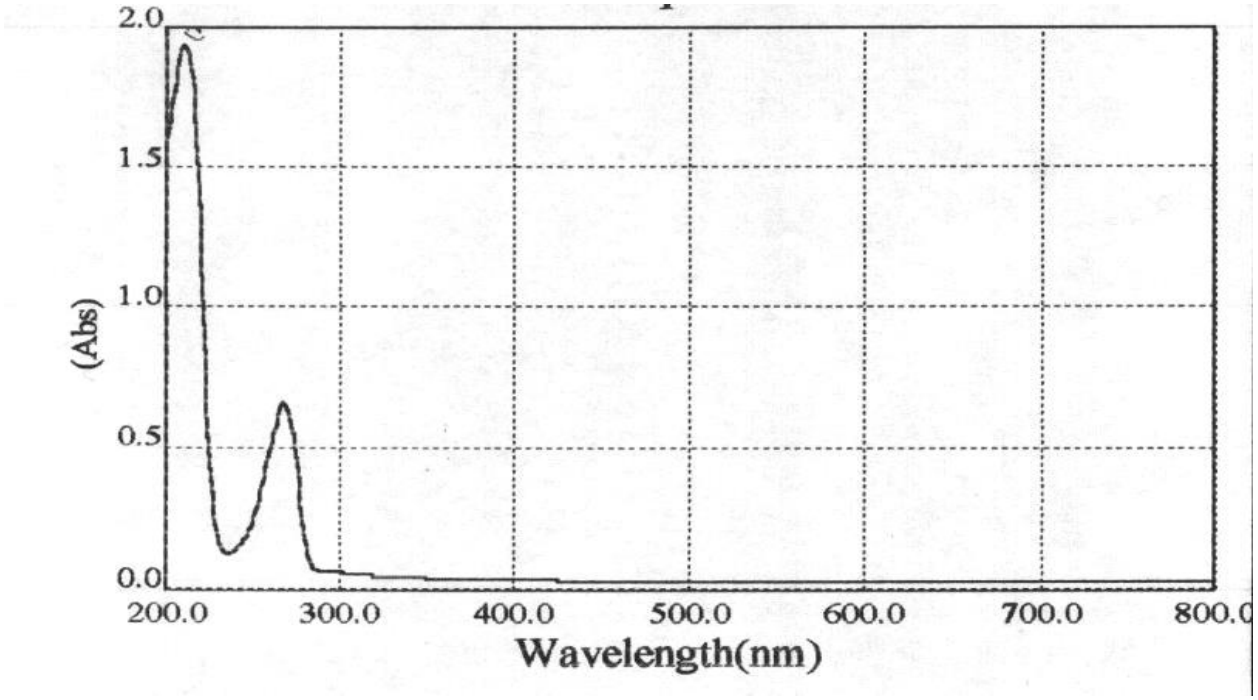


Figure 2.2. U.V spectrum of chlorophenol.

2.3.6 Calibration Curves

Solutions of different concentrations were prepared by serial dilutions for each phenol and chlorophenol. Absorbency values of these solutions were measured at the specified λ_{max} values for each phenol and chlorophenol and plotted versus the concentration range from 5-30 ppm, that fell in the region applicability of Beer- Lambert's law were then used in subsequent quantitative estimation. Figures 2.3 and 2.4 show the calibration curves of phenol and chlorophenol.

2.4 Equilibrium time of adsorption systems

To determine the equilibrium time that is needed for the adsorption system to reach equilibrium at a given temperature, the following procedure was carried out: A concentration of (20 ppm) for each phenol or chlorophenol that putting in 10 ml glass bottles was shaken with (0.02g) from the adsorbent attapulgite (A), attapulgite-urea complex (AUC), attapulgite–urea-formaldehyde polymer (AUFP) and urea-formaldehyde polymer (UFR). Then the concentration of adsorbate solutions were determined spectrophotometrically at different intervals 15, 30, 45, 60, 75, 90, 105, 120, 150, and 185 minutes, until reaching equilibrium. Equilibrium times of adsorption systems studied are listed in Table 2.3.

Table 2.3 Equilibrium time for each pair adsorbent –adsorbate system.

Adsorbate	Adsorbent	Equilibrium time /(min)
Phenol	A	120
	AUC	120
	AUFP	120
	UFR	105
Chlorophenol	A	120
	AUC	120
	AUFP	120
	UFR	105

2.5 Adsorption Isotherm

To determine the adsorption isotherm for each phenol or chlorophenol on the adsorbent A, AUC, AUFP, and UFR the following procedure was carried out: A volume of (10ml) from each of the six different concentration of each phenol and chlorophenol solution the ranging used from 5 - 30 ppm at a certain pH and temperature was shaken with 0.02 g of the adsorbents, by using thermostat shaker bath at speed 70 cycles per minute. After the period of equilibrium time, the mixture was allowed to settle and the clear liquid was centrifuged at (3000rpm) for (10 minutes). The equilibrium concentrations were obtained by usual manner of comparing the experimental data with calibration curves .

2.6 Effect of temperature

The study the effect of temperature were obtained by agitating the solution of (10 ml) of phenol or chlorophenol concentration ranges from 5 to30 ppm with a 0.02 g of adsorbents A, AUC, AUFP or UFP in (25 ml) glass bottles. These bottles were sealed and agitating in a constant temperature 298.15, 308.15, and 318.15 K until the equilibrium time for each adsorbents are attend and the solution were separated by a combination of centrifugation and filtered. The clear solution was analyzed by U.V spectrophotometer.

2.7 Kinetics Study

Kinetic study was obtained by agitating the solution of (10 ml) of phenol or chlorophenol at different concentration from 5 -30 ppm and composition with a (0.02 g) of adsorbents A, AUC, AUFP and UFR in (25 ml) glass bottles. These bottles were sealed and agitating in a constant temperature thermostat 298.15, 308.15, and 318.15 K at different time 15, 30, 45, 60, 75, 90, 105, 120, 135, 150, and 180 minutes. For each adsorbent the solution were separated by a combination of centrifugation and filtered. The clear solution was analyzed by U.V spectrophotometer.

Chapter Three

Results and Discussion

3.1 Characterization of Adsorbents

The synthesized compounds, attapulgite (A), attapulgite– urea complex (AUC), attapulgite -urea -formaldehyde polymer (AUFP) and urea–formaldehyde resin (UFR) were characterized by FTIR spectroscopy and X-ray diffraction technique.

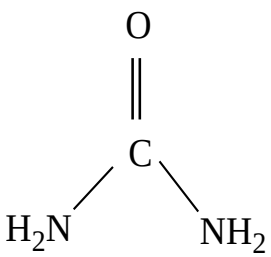
The characteristic FTIR absorption bands of urea (U), A, AUC, AUFP and UFR are given in Tables 3.1-3.5 and are illustrated in Figures 3.1- 3.5. The bands 3421-3820 cm^{-1} in attapulgite spectrum could be attributed to ν_{O-H} vibration in different environments, i.e., terminal silanol –OH, bridge Si– O – Si (Al) and the hydrogen bonded Si (Al) OH [65-,67]. The bonded water absorption broad bands are found at 3421 cm^{-1} and the bending vibration of H_2O is found at 1645 cm^{-1}. The latter has as expected suffered shift to higher frequency as compared to molecular water [72]. The spectrum also clearly shows the characteristic asymmetric stretching vibrations, which appear as strong band at 1036 cm^{-1} and a prominent shoulder at 920cm^{-1} due to different phillipsite.

The spectra of A, AUC, AUFP, UFR and U are displayed in Figures 3.1-3.5. The ν_{O-H} bands of attapulgite, as detected in samples A and are observed in the AUC, AUFP. The medium strong vibration of the bounded OH appearing at 3542 cm^{-1} has shifted to 3554cm^{-1} and 3561cm^{-1} in AUC and AUFP respectively. The band at 3421 cm^{-1} in attapulgite shows a shift to higher frequency appearing at 3452cm^{-1} in AUC. It was appeared in AUC distinct shoulders at 2960 cm^{-1}, 2902cm^{-1} and 2690cm^{-1}. These bands, which appear shifted to lower frequencies, could be attributed to water acting as bridge between attapulgite and urea through hydrogen bonding. Furthermore,

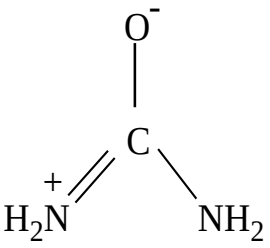
the water bending vibration appearing at 1645cm^{-1} in attapulgite has shifted to a higher frequency of 1627 cm^{-1} in AUC.

When considering the– NH_2 vibrations, it is observed that in spectra of urea, the ν_{asy} (NH_2) appears to have given rise to strong bands 3439cm^{-1} for urea where the spectra are measured in KBr matrix.

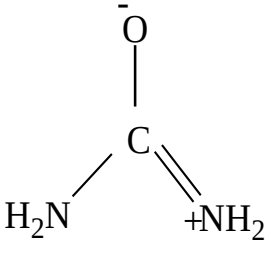
In AUC and AUFP, these appear as medium strong and medium bands at 3348cm-1 and 3354cm^{-1} respectively. The ν_{sym} (NH_2) which appears at 3345cm^{-1} in urea has correspondingly observed band in AUC and AUFP. The bonded -NH_2, which gives a band at 3259 cm^{-1} in urea, has suffered significant shift to 3275 cm^{-1} in AUC. The changes observed in the bending NH2 and ν_{asy} NCN bands are of special interest. The ν_{asy} (NCN) appearing as strong bands at 1466 cm^{-1} in urea ,has showed marked lower frequency shifts to 1385cm^{-1}. On the other hand, the bending NH_2 bands that appear at 1680 cm^{-1} in urea have suffered high frequency shifts in AUC. This behavior indicates that of the two tautomeric structures, structure I seems to predominate over structures II in the AUC admixture. Furthermore, the band at 1606 cm^{-1} in urea, which is usually attributed to ν(CO) with a contribution from bending NH_2, has in AUC and AUFP showed a considerable shift to 1627 cm^{-1} and 1645 cm^{-1} respectively, thus supporting the views of the predominance of structure II.



I



IIa



IIb

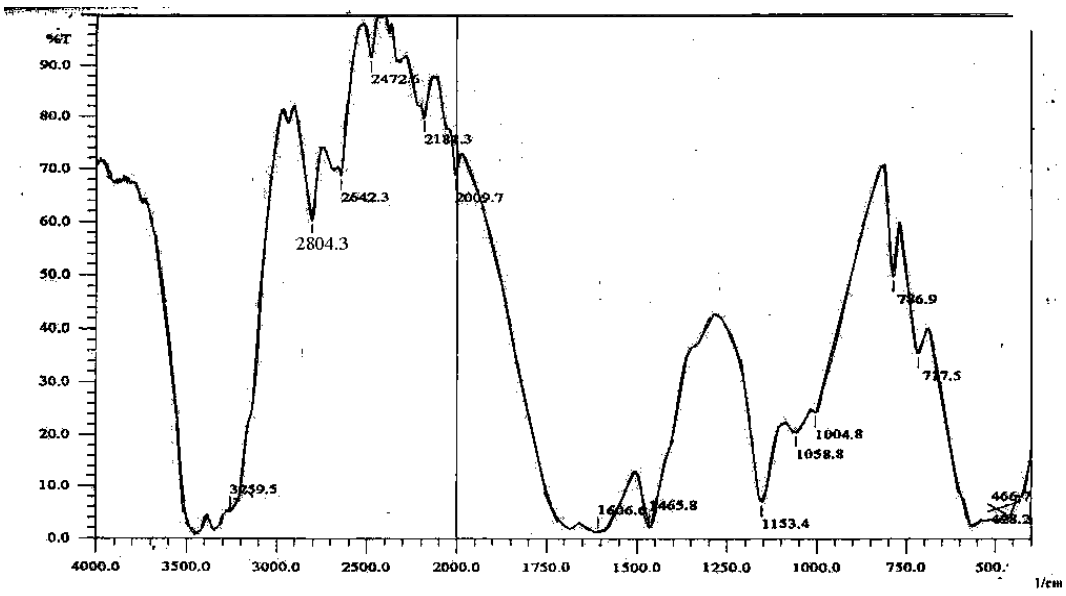


Figure 3.5. IR Spectrum of urea.

The characteristic attapulgite bands in the region 1200- 400 cm^{-1} seem to have hardly been effected by the presence of urea as shown in Figure 3.2. Taken together with the observed shifts in ν_{NH2}, it seems that the interaction is among urea molecules and with the matrix is mainly through the hydrogen bonding with $–NH_2$ moiety, the shift in those band are listed in Table 3.6.

Table 3.6. The shift in characteristic IR. band of U, A, AUC and AUFP.

Vibration	Urea	AUC	Δ	AUFP	Δ
ν_{NH2}	3439	3348	-91	3354	-85
ν_{CO}	1606	1627	+21	1645	+39
ν_{NCN}	1466	1385	+81	1384	-82

All adsorbent are also characterized by X-ray diffraction patterns, the lattice distances obtained for the original attapulgite, AUC, AUFP and UFR samples, along with their intensities ,are listed in Table 3.7 and illustrated in Figure (3.6 -3.9).

Table 3.7. The X-ray diffraction spacing d and angle 2θ of A, AUC, AUFP and UFR.

Compound	2θ	d/A^o	Intensity %
A	20.9	4.242	75.48
	26.7	3.329	98.7
AUC	20.8	4.264	52.2
	26.5	3.352	60.6
AUFP	20.7	4.272	69.7
	26.4	3.365	97.26
UFR	**Amorphous**		

The diffraction pattern of A as shown in Figure 3.6 shows that A has many diffraction peaks, as is typical of high degree of crystallinity with characteristic attapulgite diffraction spacing 4.242 and 3.329 A^0 with intensity 75.5% and 98.7% respectively. When attapulgite treated with urea form AUC, degree of crystallinity decrease and those two peaks almost remain at the same location but with the intensity of 52.3 and 60.7 respectively. The lowers in intensity of those two peaks could be attributed to the fact that urea interact with attapulgite hydrogen bonding forces leads to broadening of the attapulgite tunnels. It seems also that the accommodation of urea molecules inside attapulgite tunnels occurred easily.

The treated of AUC with formaldehyde seems as shown in figure 3.7 to have no effect on diffraction pattern of the original sample. The two distinguished peaks occur at 4.272 and 3.365 A^0 with almost the same intensity of the attapulgite samples.

This could be interpreted by the fact that formaldehyde releases urea and polymerized with active group forming urea –formaldehyde polymer. The polymer formed interacts with attapulgite at the surface through the hydrogen bond forces. On the other hand, the formaldehyde molecules interpenetration the attapulgite retain its crystalline lattice structure with the same spacing and intensity as shown in figure 3.8.

Figure 3.9 shows the X-ray diffraction pattern of urea– formaldehyde resin. This pattern indicates that there is no crystallinity present. There is a very strong diffuse halo with an observable maximum at about 4.049 A^0.

3.2 Adsorption Isotherms

Adsorption at equilibrium conditions was determined for phenol and chlorophenol on A, AUC, AUFP and UFR adsorbents. The adsorbed quantities at equilibrium concentrations were calculated by using the following equation:

$$Q_e = \frac{V\,(C_o - Ce)}{m} \qquad 3.1$$

Where Q_e is the amount adsorbed per unit mass of adsorbent, C_o and C_e (mg/L) are the initial and equilibrium concentration respectively, m(g) is the weight of adsorbates and V(L) is the volume of solution.

Plots of the Q_e ($mg.g^{-1}$) against equilibrium concentration C_e(mg/L) for phenol and 2,3 dichlorophenol onto A, AUC, AUFP and UFR, Figures 3.10 and 3.11 respectively showed multilayer adsorption at relatively high concentration concerning the heterogeneity of the surface S type of Gilles classification which is conform of the Freundlich adsorption model[73]. These plots are obtained by using the average values obtained from three replicates. The data are listed in Tables 3.3 and 3.4, for adsorption of phenol and 2,3 dichlorophenol respectively.

Table 3.8. Adsorption isotherms values of phenol on the A, AUC, AUFP and UFR at 25 ^{0}C.

C_o mg/L	C_e mg/L	Q_e mg/g	ln C_e	ln Q_e	C_e mg/L	Q_e mg/g	ln C_e	ln Q_e
	Attapulgite				AUC			
5	1.77	1.62	0.25	0.21	1.68	1.66	0.22	0.22
10	4.50	2.75	0.65	0.44	4.17	2.92	0.62	0.47
15	7.23	3.89	0.85	0.59	6.57	4.22	0.82	0.63
20	10.02	4.99	1.00	0.70	9.31	5.34	0.97	0.73
25	12.70	6.15	1.10	0.79	11.66	6.66	1.07	0.82
30	14.20	7.90	1.15	0.89	13.82	8.09	1.14	0.91
C_o	AUFP				UFR			
5	1.43	1.79	0.15	0.25	2.46	1.27	0.39	0.10
10	3.40	3.30	0.53	0.51	5.32	2.34	0.73	0.37
15	5.75	4.63	0.76	0.66	7.99	3.51	0.90	0.54
20	8.10	5.95	0.90	0.77	11.15	4.43	1.05	0.65
25	10.30	7.45	1.01	0.87	12.97	6.02	1.11	0.78
30	11.65	9.02	1.07	0.95	15.00	7.50	1.18	0.88

Table 3.9. Adsorption isotherms values of chlorophenol on the A, AUC, AUFP and UFR at 25^0 C.

Co	C_e mg/L	Qe mg/g	ln C_e	ln Qe	Ce mg/L	Qe mg/g	ln Ce	ln Qe
mg/L	Attapulgite				AUC			
5	2.47	1.26	0.39	0.10	2.80	1.09	0.45	0.03
10	6.74	1.63	0.83	0.21	6.00	2.23	0.78	0.30
15	10.46	2.27	1.02	0.36	8.80	3.10	0.94	0.49
20	14.34	2.83	1.16	0.45	11.60	4.20	1.06	0.62
25	16.94	4.03	1.23	0.61	15.10	4.95	1.18	0.69
30	20.94	4.53	1.32	0.66	18.30	5.85	1.26	0.77
C_o	AUFP				UFR			
5	2.25	1.38	0.35	0.14	2.73	1.14	0.44	0.06
10	5.50	2.25	0.74	0.35	7.00	1.50	0.85	0.18
15	7.80	3.60	0.89	0.57	10.71	2.15	1.03	0.33
20	10.66	4.67	1.03	0.66	14.70	2.65	1.17	0.42
25	13.10	5.95	1.12	0.77	17.70	3.65	1.25	0.56
30	14.90	7.550	1.173	0.878	21.80	4.100	1.338	0.613

In Figures 3.12 and 3.13 a linear form of Freundlich isotherm with correlation factor more than 98 are presented by plotting $\ln Q_e$ as a function of $\ln C_e$ of phenol and chlorophenol adsorbed on A, AUC, AUFP and UFR. The value of 1/n was calculated from the slop of the straight line which gives an indicator for the intensity of adsorption, while the intercept with y-axis gives K Freundlich constant which is the measure of the adsorption capacity. Freundlich constants are listed in Table 3.10 of phenol and para-chlorophenol.

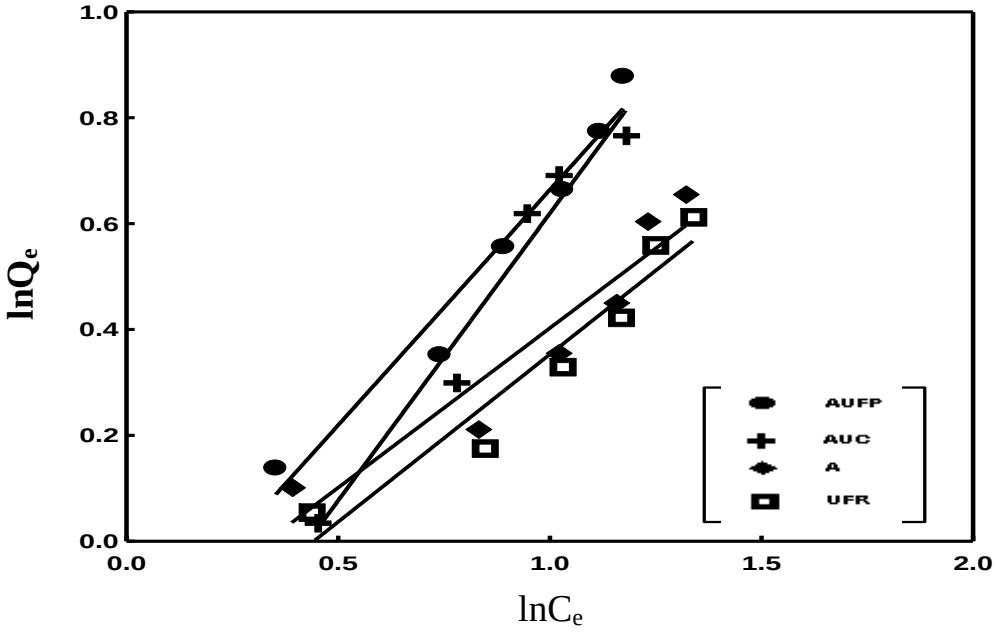


Figure 3.12. Linearized Freundlich plot for phenol on A, AUC, AUFP and UFR.

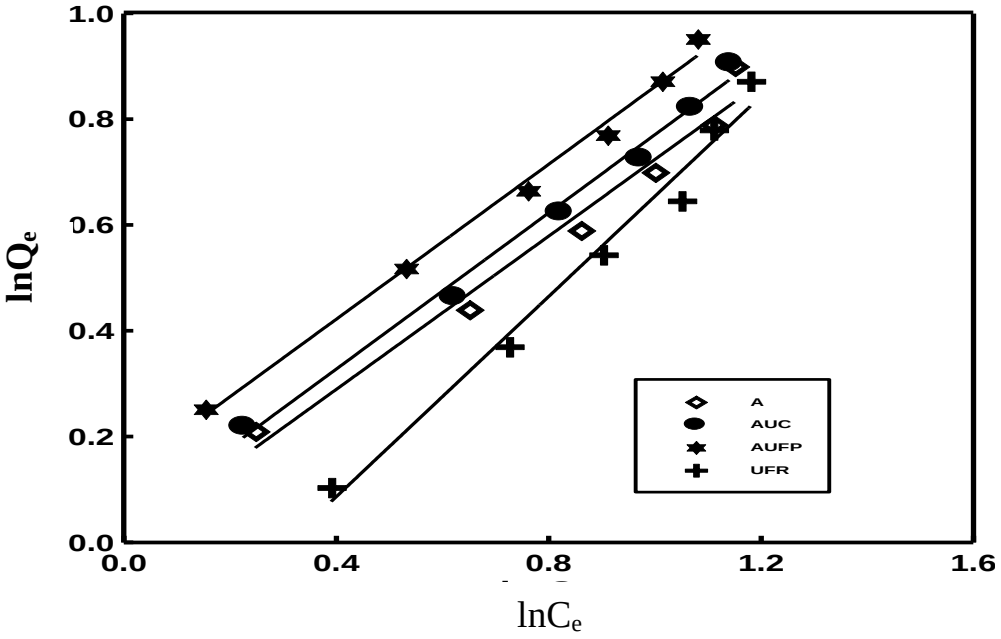


Figure 3.13. Linearized Freundlich plot of 2, 3 dichlorophenol on A, AUC, AUFP and UFR.

Table 3.10. Freundlich constants of phenol and 2, 3 dichlorophenol on the A, AUC, AUFP and UFR at 25^0C

Adsorbent Surface	A	AUC	AUFP	UFR
Freundlich constants of phenol				
1/n	0.724	0.739	0.735	0.948
K (mg/g)	0.997	1.077	1.339	0.509
Freundlich constants of 2, 3 dichlorophenol				
1/n	0.605	0.923	0.887	0.632
K (mg/g)	0.628	0.408	0.598	0.526

Attapulgite surface is heterogeneous and this feature could be attributed by the different properties of the unsaturated adsorption sites which lead to different characters of these sites [(74)]. Also AUC, AUFP and UFR all of their were precipitated as crud powder during the synthesis procedure. So, all of these adsorbents are with different imperfection and orientation of their crystal lattice. Surface imperfection and the presence of impurities can also play an important role in this respect.

The adsorption on different active sites occurs throughout different types of forces leading to the formation of clusters or packed line of the adsorbed molecules on the surface [(73)]. The maximum quantities adsorbated of phenol and chlorophenol on four adsorbents follow the order AUFP >AUC>A>UFR.

These differences in adsorbents ability of adsorption could be attributed to the differences in the surface morphology. Structurally, AUFP is described as composed of attapulgite stuck with urea- formaldehyde polymer in which each attapulgite surface is shared between two adjacent polymer. This is comparable with one layer surface of AUC, in which urea is accommodate through the tunnels of attapulgite. Thus, AUFP showed be capable of adsorption layer amount of phenol and chlorophenol. This is supported by the large adsorptive capacity of AUFP as demonstrated by the present results. The influence of isotherm shape on weather adsorption is favorable or unfavorable has been consider by Weber and Chakravorti [(70)]. For the Freundlich-type adsorption process the isotherm shaped can be classified by a term K a Freundlich constant adsorption and 1/n intensity of adsorption capacity. Values of 1/n < 1 represent favorable adsorption and values 1/n> 1 represent unfavorable adsorption. The results for phenol and chlorophenol adsorption systems of this study are favorable. Adsorption capacity of phenol is greater than that of chlorophenol. Phenol adsorption capacity is 0.997, 1.077, 1.339 and 0.509 mg/g on the A, AUC, AUFP and UFP adsorbents respectively, whereas these capacities for chlorophenol around 0.628, 0.408, 0.598 and 0.526 mg/g on the A, AUC, AUFP and UFR adsorbents respectively. Since the

polarity of chlorophenol greater than phenol. The difference in adsorption capacities must therefore be linked to the solute acidity. The presence of chlorine atom increase the acidity make phenol less acidic character and enhanced its affinity for adsorption at the adsorbent surface.

3.3 Temperature Dependence of the Adsorption

The effect of temperature variation on the adsorption extent of phenol or chlorophenol on the four adsorbents surface A, AUC, AUFP, or UFR has been studied at neutral media pH= 7. Tables 3.11-3.14 and Figures 3.14-3.21 illustrates the general shapes of phenol and chlorophenol adsorption isotherm at 298, 308 and 318 K. it can be seen that as the temperature increased, the adsorption quantity decreased.

Table 3.11.Adsorption quantities of phenol and 2,3 dichlorophenol on the Attapulgite surface at different temperature.

Phenol						
C_o	298K		308K		318K	
	C_e mg/L	**Q_e mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Q_e mg/g**
5	1.77	1.62	2.33	1.34	2.72	1.14
10	4.50	2.75	5.00	2.50	5.42	2.29
15	7.23	3.89	7.74	3.63	8.18	3.41
20	10.03	4.99	10.44	4.78	10.93	4.54
25	12.70	6.15	13.21	5.89	13.61	5.69
30	14.20	7.90	14.76	7.62	15.15	7.43
Chlorophenol						
C_o	298K		308K		318K	
	C_e mg/L	**Q_e mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Q_e mg/g**
5	2.47	1.27	3.15	0.92	3.57	0.72
10	6.74	1.63	7.26	1.37	7.61	1.19
15	10.46	2.27	11.09	1.96	11.48	1.76
20	14.34	2.83	15.10	2.45	15.59	2.21
25	16.94	4.03	17.53	3.74	18.25	3.38
30	20.90	4.53	21.91	4.05	22.59	3.71

Table 3.12. Adsorption quantities of phenol and 2,3 dichlorophenol on the AUC surface at different temperature.

Phenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	1.678	1.661	2.13	1.435	2.498	1.251
10	4.167	2.9165	4.65	2.675	5.082	2.459
15	6.566	4.217	7.131	3.935	7.58	3.71
20	9.317	5.34	9.877	5.06	10.325	4.837
25	11.667	6.66	12.18	6.41	12.63	6.1852
30	13.82	8.09	14.32	7.84	14.778	7.611
2,3 dichlorophenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	2.83	1.085	3.29	0.855	3.63	0.685
10	6	2.2	6.43	1.785	6.83	1.585
15	8.8	3.1	9.25	2.875	10	2.5
20	11.6	4.2	12.07	3.965	12.5	3.75
25	15.1	4.95	15.71	4.645	16.29	4.355
30	18.3	5.85	18.93	5.535	19.41	5.295

Table 3.13 .Adsorption quantities of phenol and chlorophenol on the AUFP surface at different temperature.

Phenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	1.425	1.788	1.565	1.718	1.7	1.65
10	3.4	3.3	3.81	3.095	4.25	2.875
15	5.75	4.625	6.16	4.42	6.6	4.2
20	8.1	5.95	8.52	5.738	8.92	5.54
25	10.3	7.45	10.52	7.24	10.88	7.06
30	11.965	9.0175	12.47	8.765	12.9	8.55
2,3 dichlorophenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	2.25	1.375	2.61	1.195	2.97	1.015
10	5.5	2.25	6.01	1.995	6.45	1.775
15	7.8	3.6	8.21	3.395	8.59	3.205
20	10.76	4.62	11.54	4.23	12.02	3.99
25	13.1	5.95	13.53	5.735	13.902	5.549
30	14.9	7.55	15.29	7.355	15.65	7.175

Table 3.14 .Adsorption quantities of phenol and chlorophenol on

the UFR surface at different temperature.

Phenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	2.455	1.272	2.965	1.017	3.44	0.78
10	5.315	2.3425	5.87	2.064	6.42	1.79
15	7.99	3.505	8.55	3.23	9.087	2.95
20	11.15	4.425	11.62	4.19	12.06	3.97
25	12.97	6.015	13.5	5.75	14.08	5.46
30	15.0	7.5	15.51	7.25	16.05	6.975
2,3 dichlorophenol						
C_o	298K		308K		318K	
	C_e mg/L	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**	**C_e mg/L**	**Qe mg/g**
5	2.73	1.135	3.066	0.967	3.408	0.796
10	7	1.5	7.36	1.32	7.72	1.14
15	10.71	2.145	11.12	1.94	11.5	1.75
20	14.5	2.65	15.08	2.46	15.41	2.295
25	17.7	3.65	18.12	3.44	18.53	3.35
30	21.8	4.1	22.24	3.88	22.65	3.675

The study of the temperature effect on adsorption will also help in calcuation the basic thermodynamic functions Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) of the adsorption process.

The equilibrium constant (K_e) of the adsorption process at each

$$K_e = \frac{(Q_e)\ (0.02\ g)}{(C_e)\ (0.01L)} \qquad 3.2$$

temperature, is calculated from the equation

Where Q_e is the amount adsorbed in milligram per one gram adsorbent, C_e is the equilibrium concentration of the adsorbent expressed in mg/L, 0.02g represents the weight of the adsorbate that has been used, and 0.01L represents the volume of the phenol or chlorophenol solution used in the adsorption process. The change in the free energy could be determined from the equation:

$$\Delta G = -RT\ln K_e \qquad 3.3$$

Where R, is the gas constant (8.314 $J.K^{-1}.mole^{-1}$), T is the absolute temperature in Kelvin.

The enthalpy of adsorption may be obtained from the Clausis-Clapeyron equation[69]:

$$\ln X_m = -\Delta H/RT + \text{constant} \qquad 3.4$$

When X_m is the maximum value of adsorption at a certain value of equilibrium concentration (C_e). Tables 3.15 and 3.16 give X_m values at different temperatures for phenol, and 2,3 dichlorophenol.

Plotting $\ln X_m$ versus (1/T) should produce a straight line with a slope $-\Delta H/R$ as shown in Figures 3.22 and 3.23.

Table 3.15. Maximum adsorption quantity Xm values of phenol and Para-chlorophenol on the A and AUC surfaces at different temperature.

Attapulgite	
Phenol	Chlorophenol

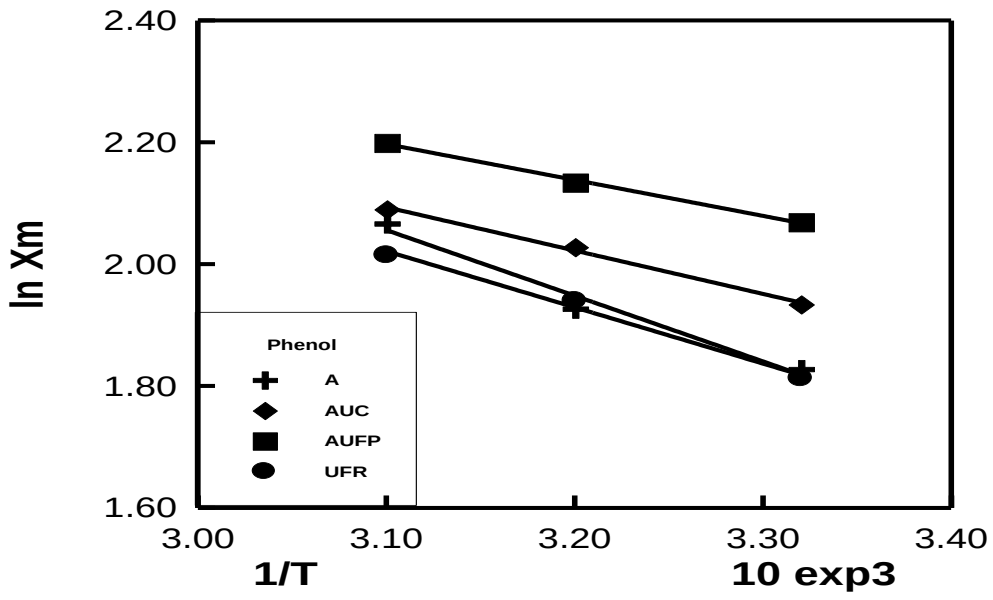
T/(K)	When Ce=14.2 mg/L	lnX_m	T/(K)	When Ce=20.9 mg/L	lnX_m
298	7.9	2.067	298	4.53	1.51
308	6.87	1.927	308	4.01	1.388
318	6.1	1.828	318	3.72	1.313
Attapulgite -Urea Complex (AUC)					
Phenol			Chlorophenol		
T/(K)	When Ce=13.8 mg/L	lnX_m	T/(K)	When Ce=18.3 mg/L	lnX_m
298	8.09	2.09	298	5.85	1.766
308	7.6	2.028	308	5.37	1.68
318	6.92	1.934	318	4.77	1.562

Table 3.16. Maximum adsorption quantity X_m values of phenol and Para-chlorophenol on the AUFP and UFR surfaces at different temperature.

	Phenol			Chlorophenol	
T/(K)	When C_e=11.9mg/L	$\ln X_m$	T/(K)	When C_e=14.9 mg/L	$\ln X_m$
298	9.0175	2.199	298	7.55	2.02
308	8.45	2.134	308	6.97	1.94
318	7.92	2.069	318	7.92	1.826

Urea -Formaldehyde Polymer (UFP)

	Phenol			Chlorophenol	
T/(K)	When C_e=15 mg/L	$\ln X_m$	T/(K)	When C_e=21.8 mg/L	$\ln X_m$
298	7.5	2.015	298	4.1	1.41
308	6.98	1.94	308	3.72	1.313
318	6.13	1.813	318	3.42	1.23



1/T X 10^3 K^{-1}

Figure 3.22. Plot of ln X_m versus 1/T of phenol on the adsorbent surface for each A, AUC, AUFP and UFR.

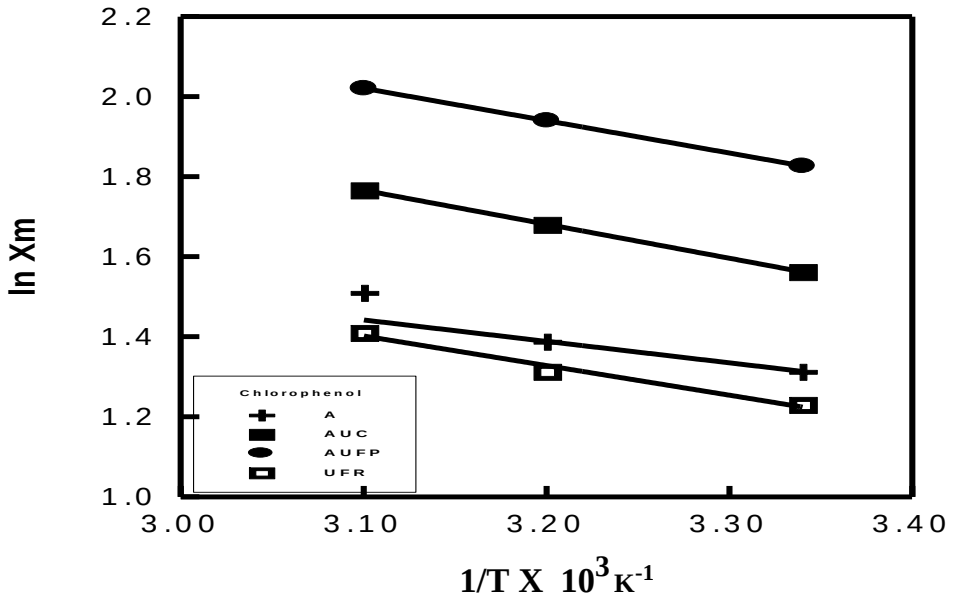


Figure 3.23. Plot of ln X_m versus 1/T of 2, 3 dichlorophenol on the adsorbent surface for each A, AUC, AUFP and UFR.

The change in entropy (ΔS) was calculated from Gibbs-Helmholtz equation:[69]

$$\Delta G=\Delta H - T\Delta S \qquad (3.5)$$

Table (3.17) gives the quantitative thermodynamic data of phenol and chlorophenol on the adsorbent surfaces A, AUC, AUFP, and UFP. Table 3.17 shows that ΔH values of phenol and chlorophenol is negative indicating that the adsorption process is exothermic reaction [70]. All process of adsorption

consider spontaneous from the negative value of ΔG. While, ΔS have positive value for each phenol and chlorophenol that refer the interaction of molecules caused random of the total system.

Table 3.17. Thermodynamic function ΔG, ΔS and, ΔH of phenol and 2,3 dichlorophenol on the adsorbent surfaces A, AUC, AUFP and UFR.

Phenol			
Adsorbent	ΔG / (kJ/mole)	ΔS/ (J/mole.K)	ΔH / (kJ/mole)
AUFP	- 18.131	43.65	-5.121
AUC	- 17.505	38.12	-6.145
Attapulgite	-17.378	24.077	-10.202
UFP	-17.114	30.46	-8.036
2,3 dichlorophenol			
Adsorbent	ΔG /(kJ/mole)	ΔS / (J/mole.K)	ΔH / (kJ/mole)
AUFP	- 17.147	31.1	-7.878
AUC	-16.006	26.6	-8.075
Attapulgite	-15.038	24.02	-7.878
UFP	- 14.692	25.242	-7.169

3.4 Contact Time Curves

The results of the time adsorption dependence under a constantly stirred condition of phenol or chlorophenol on sample surfaces A, AUC, AUFP, and UFP, are illustrated in Figures 3.24-3.27.

The results of the plotting of C_o-C_t / C_o against time indicate that the adsorption increases with longer contact time for all samples.

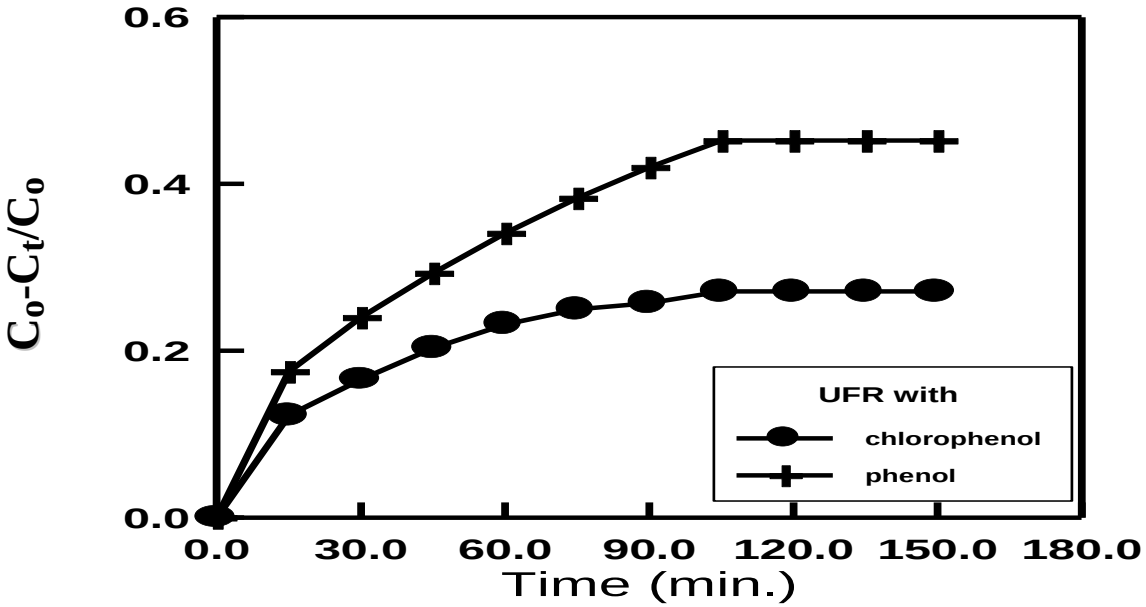


Figure 3.24. The uptake quantity of contact time of phenol and chlorophenol on the UFR surface at 298 K.

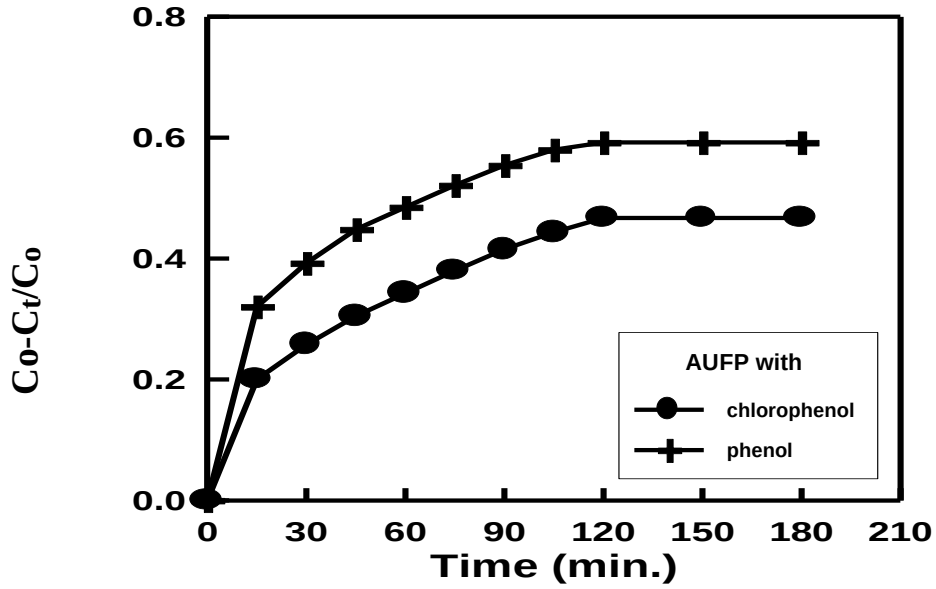


Figure 3.27. The uptake quantity of contact time of phenol and Para-Chlorophenol on the AUFP surface at 298 K.

3.5 Temperature Dependence of Contact Time

The temperature effect on contact time for all experiments of adsorption on the adsorbent surfaces A, AUC, AUFP, and UFP to remove the phenol or chlorophenol from aqueous solutions are studied. The effective of temperature on contact time according to adsorbent surfaces are shown in Figures 3.28-3.35

with initial concentrations 20 ppm for each phenol or chlorophenol, and the weight of adsorbent substances for the four adsorbent surfaces are (0.02 g) of particle sizes less than 320 ɥm. The experiments are carried out at temperature 25, 35 and 45ºC. From the results that are shown in the Figures 3.28-3.35 indicate that ability of adsorption and capacity of it usually decreases with temperature increases. Increasing temperature tends the adsorbate molecules to leave the surface and caused decreasing in adsorption capacity [71].

Figures 3.28-3.35 also show that the increases of temperature affect the adsorption capacity without affecting equilibrium. The amount of adsorbent dissolved substance, as a rule, decrease with growth in temperature. Hence, in accordance with Le Chatelier's principle "any change in the parameters that determine the state of a system in equilibrium causes a shift in the position of equilibrium in direction that tends to counteract the change produced [30]. Thus, the adsorption process is accompanied by the evolution of heat.

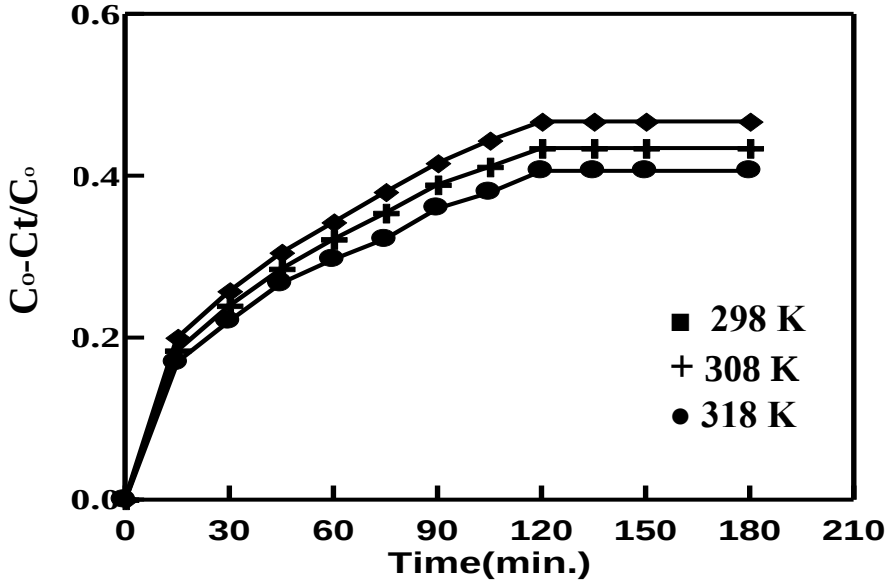


Figure 3.28. Temperature dependence of the contact time of Adsorption of para-chlorophenol on the AUFP surface.

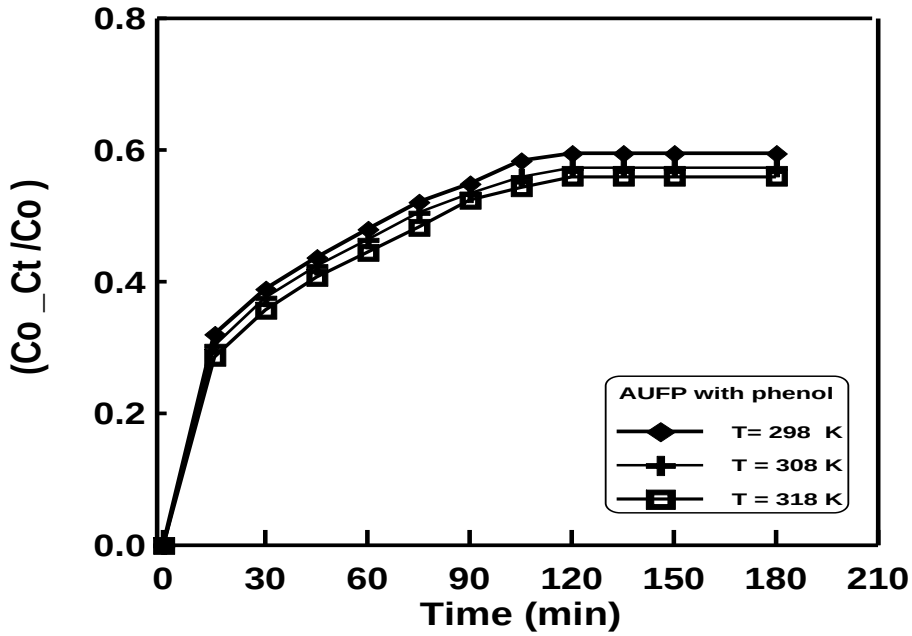


Figure 3.35. Temperature dependence of the contact time of adsorption of phenol on the AUFP surface.

3.6 Adsorption Kinetics

The kinetics of solute adsorbed from solution (solvent-solute)phase to the surfaces of adsorbent particles is controlled either by the film or external diffusion, pore surface diffusion and adsorption on the pore surface or the combined effect of more than one of these [72]. The film or surface mass transfer is an important rate –controlling step and is a function of particle size, hydrodynamic conditions, system physical properties, etc. The contact time data can be effectively used to test if the adsorption or sorption process is a rate – controlling step. Figures 3.36-3.43 show the plots of ln Q_e-Q_t against contact time. All plots give straight line, indicated that the adsorption of phenol

and chlorophenol have obeyed the pseudo-first order equation of Lagergren equation [68] which is generally expressed as follow:

$dq_t/dt = k1(Qe-Qt)$ (3.6)

Where Qe and Qt (mg/g) are the sorption capacity at equilibrium and at time t, respectively and k_1 is the rate constant of pseudo-first order sorption (min^{-1}). After integration and applying boundary conditions t=0 to t=t and Q_e=0 to Q_t=Q_t, the integrated form of equation (3.5)becomes:

$\ln(Q_e-Q_t) = -k_1t + \ln Q_e$ (3.7)

The equation applicable to experimental results that generally differs from a true first order equation in two ways

1-The parameter $K_1(Q_e-Q_t)$ doesn't represent the number of an available site.

2-The parameter ln(Qe) is an adjustable parameter and often it is found not equal to the intercept of a plot of ln(Qe-Qt) against time, whereas in a true first order $\ln(Q_e)$ should be equal to the intercept of a plot of $\ln (Q_e-Q_t)$ against time.

This kinetic indicate that system variables, should be more extensively tested and that several kinetic models and correlation coefficients should be used to test experimental sorption data if a mechanism cannot be confirmed. The variables should include agitation speed, sorbent diameter, solute concentration, sorbent mass and solute temperature. Our experiments data carry out by depending on the Lagergreen equation.

3.7 Temperature Dependence of the rate of Adsorption

Temperature effect on adsorption process normally achieved by measuring the activation energy and adsorption rate constant

$$K_{ad} = Ae^{-Ea./RT} \quad 3.8$$

According to Arrehniuse equation the dependency of rate constant of adsorption K_{ad} on temperature are limited over a narrow range of temperature. Where K_{ad} the adsorption rate constant, A is the pre-exponential factor, Ea is activation energy and R and T have the usual physical meaning.

The pre - exponential factor A has the same units as the adsorption rate constant, equation3.8 can be written in logarithmic form:

$$\ln K_{ad} = \ln A - Ea/RT \quad 3.9$$

According to this equation a straight line should be obtained when $\ln K_{ad}$ is plotted against the reciprocal of the absolute temperature (1/T) The parameter A, which is given by the intercept of the straight line at 1/T =0, and Ea, which is obtained from the slope of the straight line (-Ea/R), collectively the two quantities are called the Arrehenius parameters.

Activation energy Ea of adsorption of phenol and chlorophenol on the adsorbent surfaces at temperature rang 298- 318 K are calculated. Ea values are listed in Tables 3.23. Values of K_{ad} are calculated from Figures 3.44-3.53 and listed in Tables 3.22. These values are found to be increased for some adsorbent and decreased for the other with increases of temperature. Increasing behavior could be attributed to the possibility of diffusion rate of the adsorbent more than desorption rate for the adsorption process. While the decreases of K_{ad} values with increase of temperature could be interpretated in term of that

the gained thermal energy from the adsorbate molecules decreases from their bounded energy to the adsorbent surfaces, leading to increase the desorption rate of intra – molecules from intralayer lattice surfaces of adsorbent.

Table 3.18. Kinetics adsorption of phenol on the adsorbent surfaces for each (Attapulgit, and AUC) at different temperature.

Attapulgite

Time	**ln (Qe-Qt)**		
(min)	**298 K**	**308 K**	**318 K**
15	1.045	1.028	1.027
30	0.746	0.722	0.717
45	0.366	0.359	0.354
60	-0.015	-0.127	-0.108
75	-0.462	-0.575	-0.382
90	-1.093	-0.935	-0.787
105	-2.207	-2.079	-2.353

AUC

Time	**ln (Qe-Qt)**		
(min)	**298 K**	**308 K**	**318 K**
15	0.502	0.471	0.457
30	0.433	0.401	0.339
45	0.327	0.298	0.241
60	0.176	0.140	0.161
75	0.031	-0.004	0.0096
90	-0.174	-0.216	-0.16
105	-0.486	-0.827	-0.429

Table 3.19. Kinetics adsorption of phenol on the adsorbent surfaces for each (AUFP, and UFR) at different temperature.

	AUFP		
Time (min)	**ln (Q_e-Q_t)**		
	298 K	**308 K**	**318 K**
15	1.009	0.993	1.006
30	0.720	0.720	0.701
45	0.454	0.454	0.4
60	0.139	0.139	0.131
75	-0.305	-0.310	-0.283
90	-0.787	-0.787	-1.05
105	-2.079	-2.079	-1.832
	UFR		
Time (min)	**ln (Q_e-Q_t)**		
	298 K	**308 K**	**318 K**
15	1.019	0.967	0.924
30	0.752	0.694	0.662
45	0.46	0.392	0.332
60	0.099	0.066	0.025
75	-0.366	-0.390	-0.483
90	-1.161	-1.250	-1.337

Table 3.20. Kinetics adsorption of chlorophenol on the adsorbent

surfaces for each (Attapulgite and AUC) at different temperature.

Attapulgite clay			
Time (min)	ln (Q_e-Q_t)		
	298 K	308 K	318 K
15	0.741	0.700	0.680
30	0.422	0.398	0.402
45	0.095	0.063	0.095
60	-0.193	-0.168	-0.051
75	-0.693	-0.446	-0.248
90	-1.291	-0.821	-0.520
105	-2.120	-1.187	-1.008
AUC			
Time (min)	ln (Q_e-Q_t)		
	298 K	308 K	318 K
15	1.073	1.039	0.980
30	0.788	0.725	0.673
45	0.485	0.385	0.307
60	0.182	0.039	-0.056
75	-0.075	-0.210	-0.294
90	-0.590	-0.690	-0.776
105	-1.290	-1.366	-1.490

Table 3.21. Kinetics adsorption of chlorophenol on the adsorbent surfaces for each (AUFP and UFR) at different temperature

	AUFP		
Time (min)	ln (Q_e-Q_t)		
	298 K	308 K	318 K
15	0.982	0.916	0.860
30	0.739	0.665	0.620
45	0.482	0.305	0.329
60	0.219	0.118	0.095
75	-0.140	-0.223	-0.168
90	-0.663	-0.813	-0.755
105	-1.448	-1.469	-1.291

	UFR		
Time (min)	ln (Q_e-Q_t)		
	298 K	308 K	318 K
15	0.203	0.381	0.367
30	0.054	0.082	0.081
45	-0.385	-0.371	-0.503
60	-0.928	-0.832	-0.88
75	-1.537	-1.328	-1.311
90	-1.966	-1.714	-1.867

Table 3.22. A comparison of rate constant of the p6seudo -first order Kinetic for each phenol and chlorophenol at different temperature.

Phenol			
Temperature / **Adsorbent**	**K_{ad} /(min.$^{-1}$)**		
	298 K	308 K	318 K
Attapulgite	0.0268	0.0288	0.0244
AUC	0.0089	0.0093	0.00732
AUFP	0.0227	0.0174	0.0218
UFP	0.0245	0.024	0.0244

Chlorophenol			
Temperature / **Adsorbent**	**K_{ad}/(min.$^{-1}$)**		
	298 K	308 K	318 K
Attapulgite	0.0247	0.0187	0.0144
AUC	0.0192	0.0207	0.0214
AUFP	0.0184	0.0198	0.0175
UFP	0.0327	0.0304	0.0331

Table 3.23. Activation energy values for each phenol and Chlorophenol.

Adsorbent / Compound	Activation energy (kJ/mole)			
	Attapulgit	AUC	AUFP	UFP
Phenol	5.492	3.354	18.35	4.616
Chlorophenol	19.939	4.273	5.592	6.928

Figure 3.1. IR Spectrum of UFR.

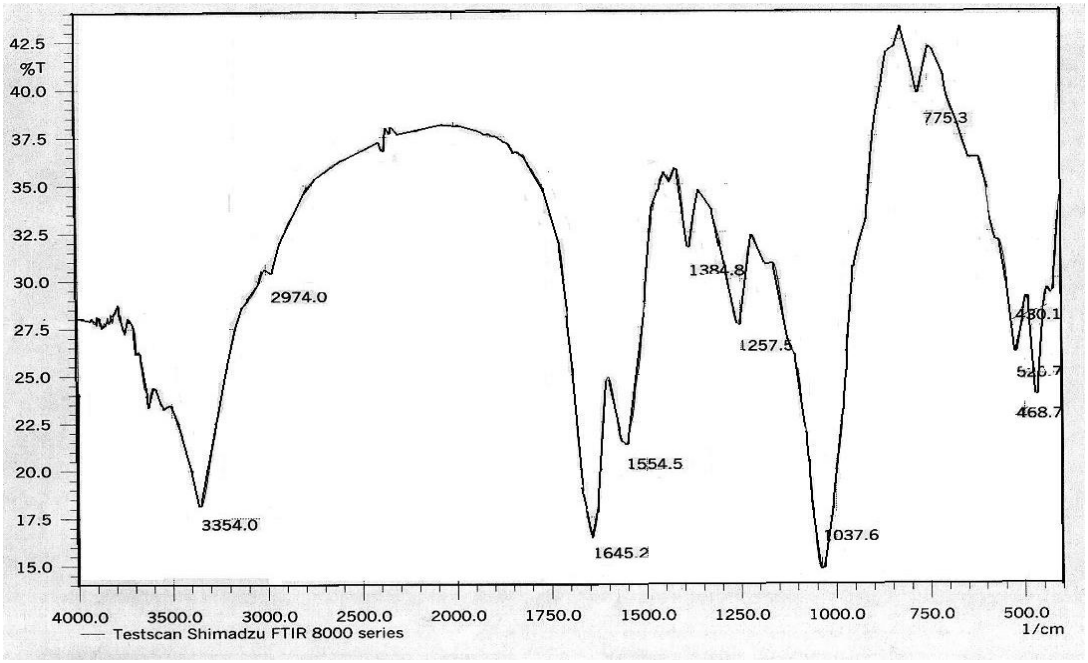
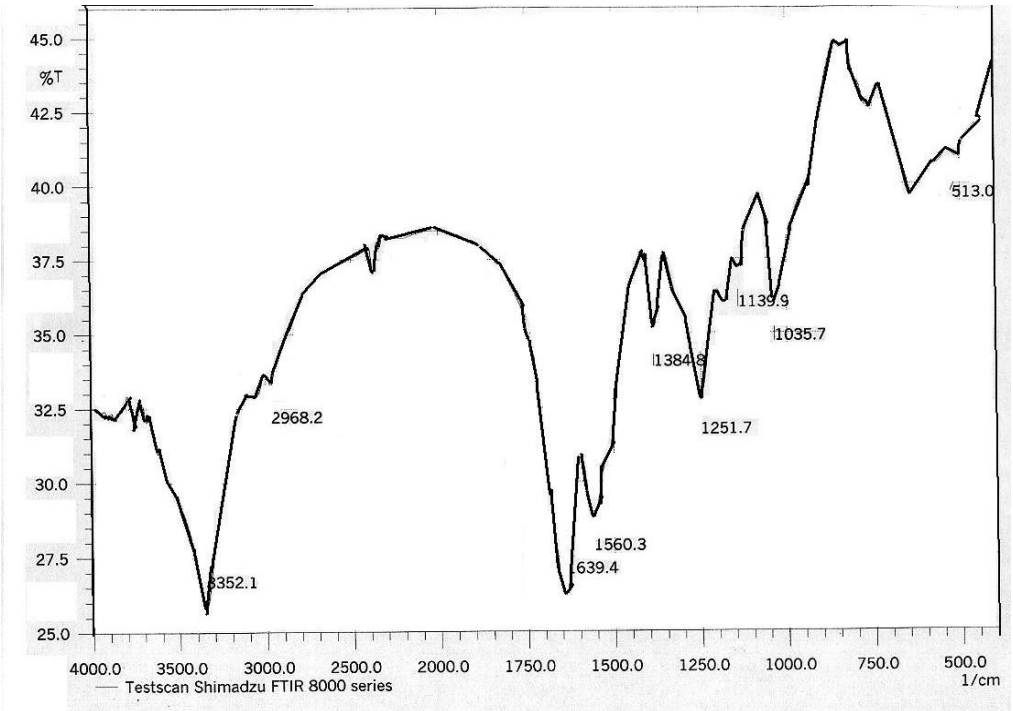


Figure 3.3. IR Spectrum of AUFP.



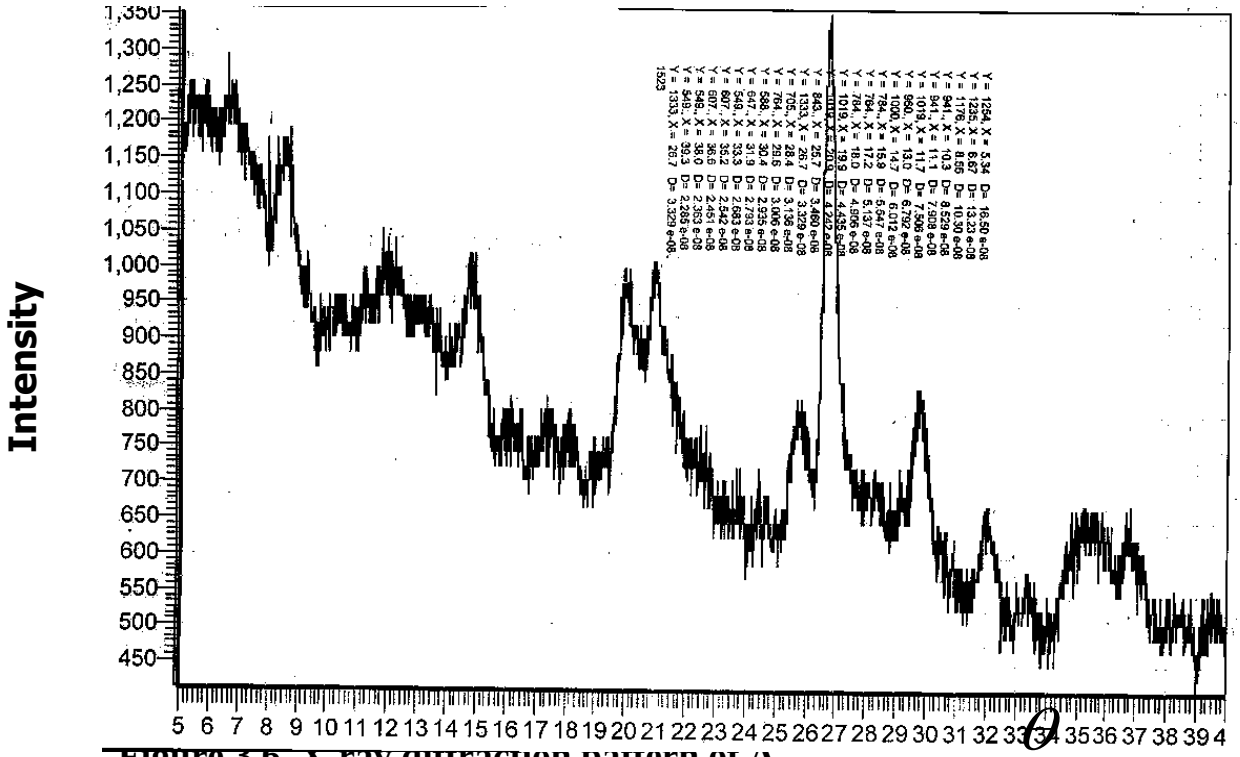


Figure 3.6. X-ray diffraction pattern of A.

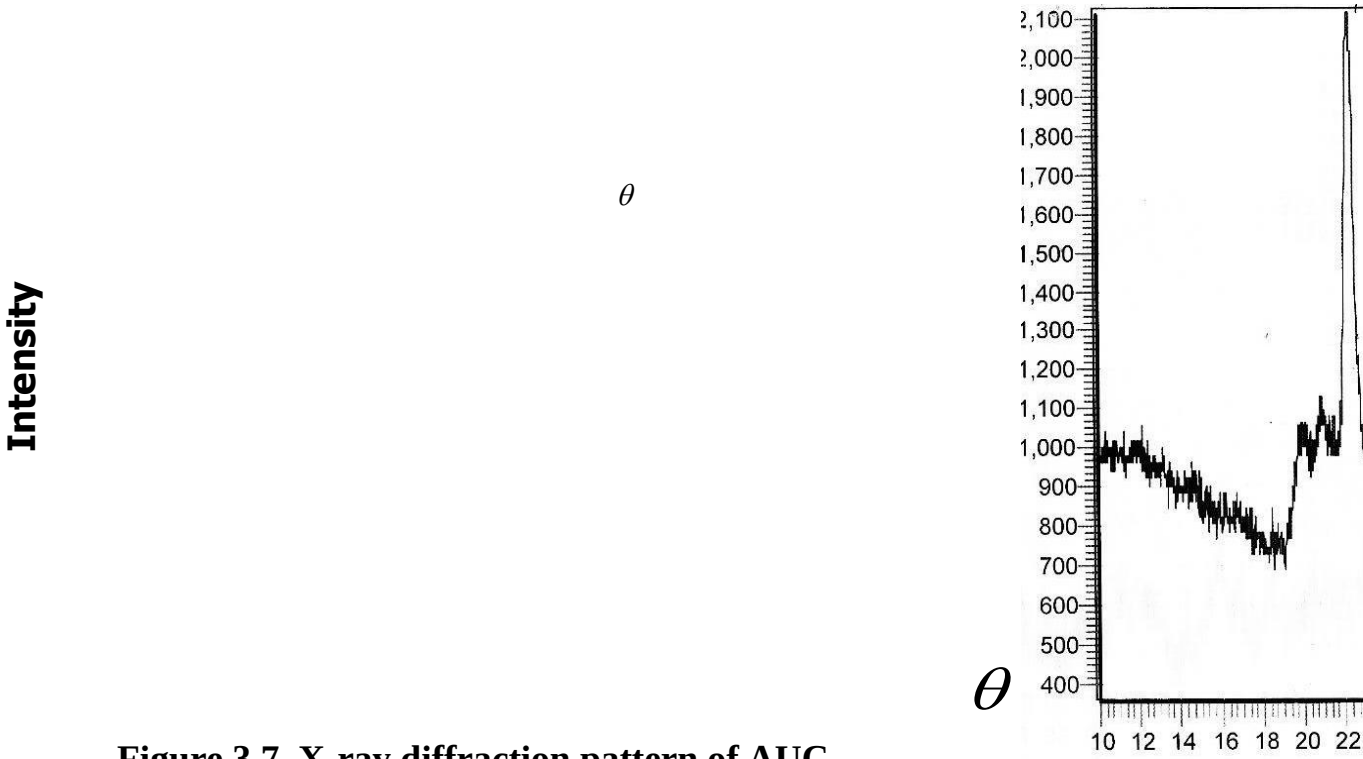


Figure 3.7. X-ray diffraction pattern of AUC.

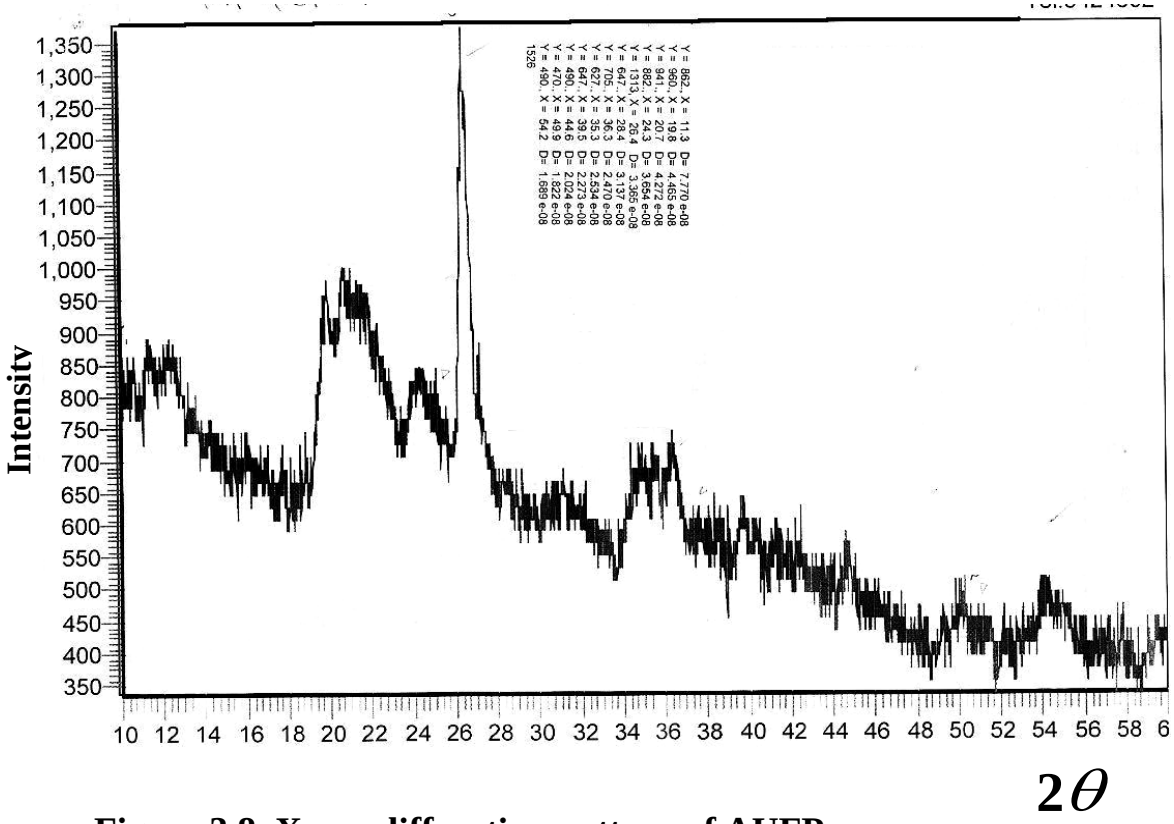


Figure 3.8. X-ray diffraction pattern of AUFP.

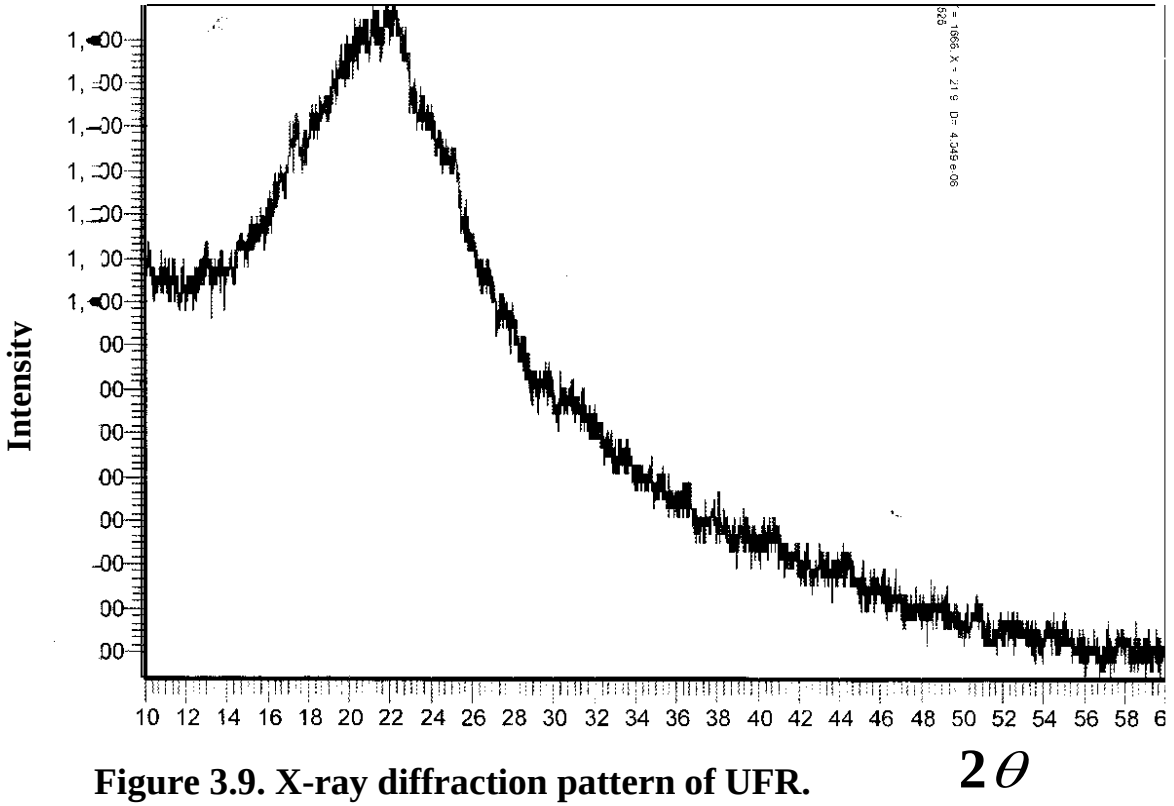


Figure 3.9. X-ray diffraction pattern of UFR.

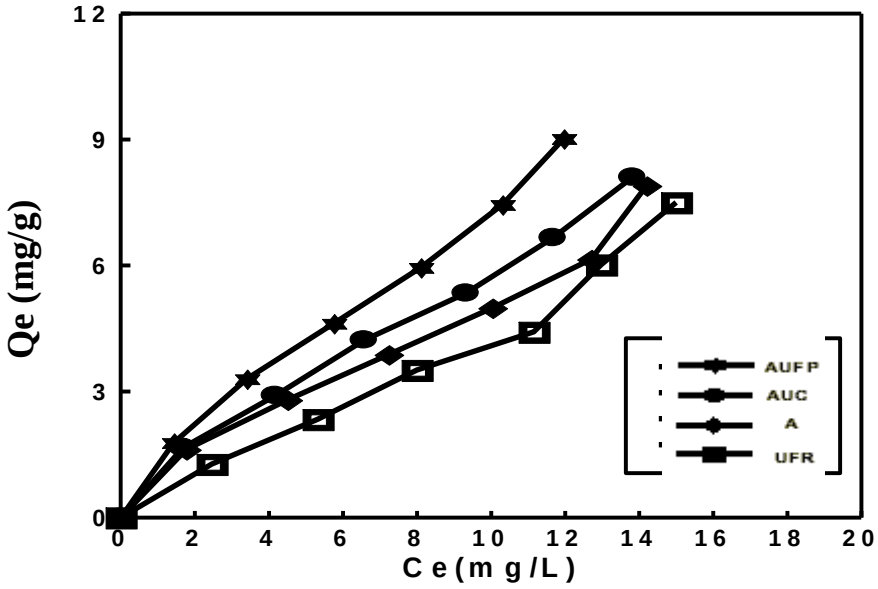


Figure 3.10. Adsorption isotherm of phenol on A, AUC, AUFP and UFR at 25 ^{0}C.

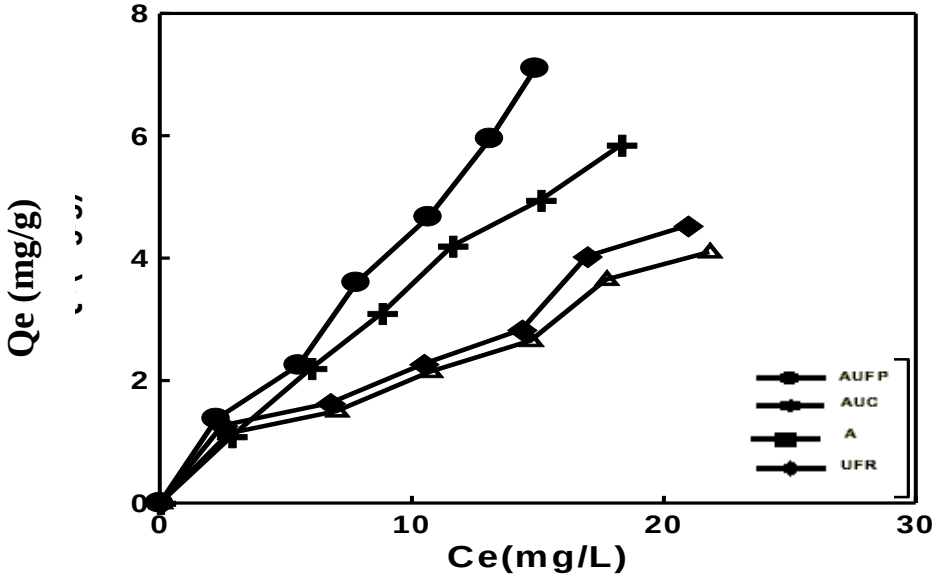


Figure 3.11. Adsorption isotherm of 2,3 dichlorophenol on A, AUC, AUFP and UFR at 25 ^{0}C.

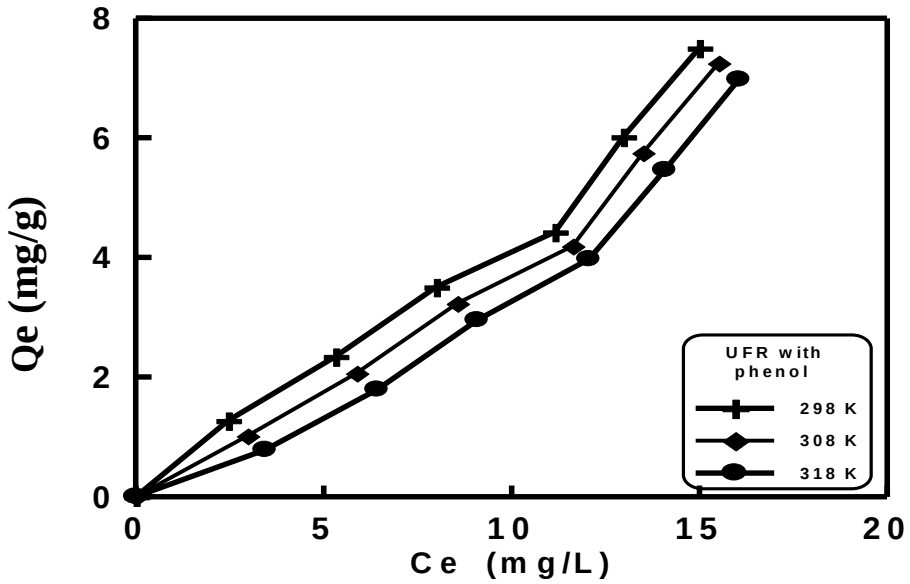


Figure 3.14. Temperature dependence of the adsorption of phenol on the UFR surface.

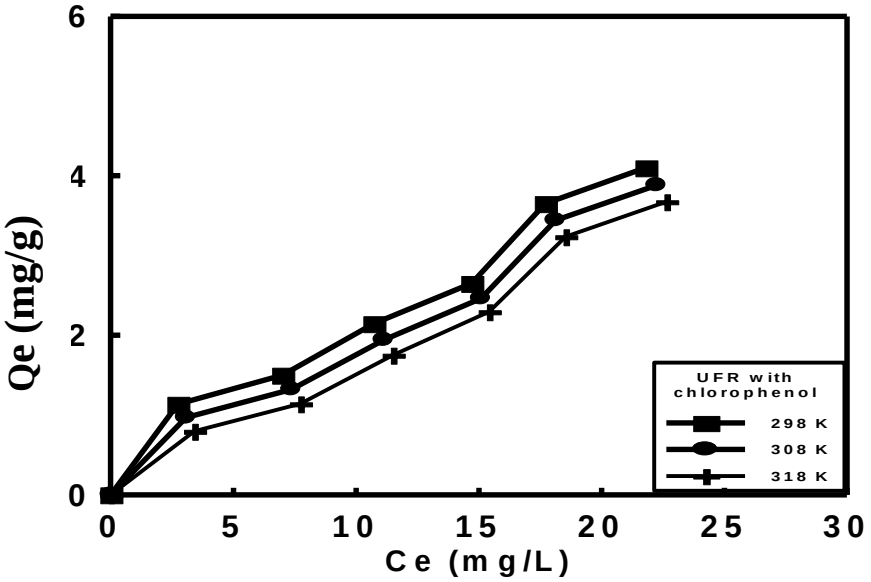


Figure 3.15. Temperature dependence of the adsorption of 2,3 dichlorophenol on the UFR surface.

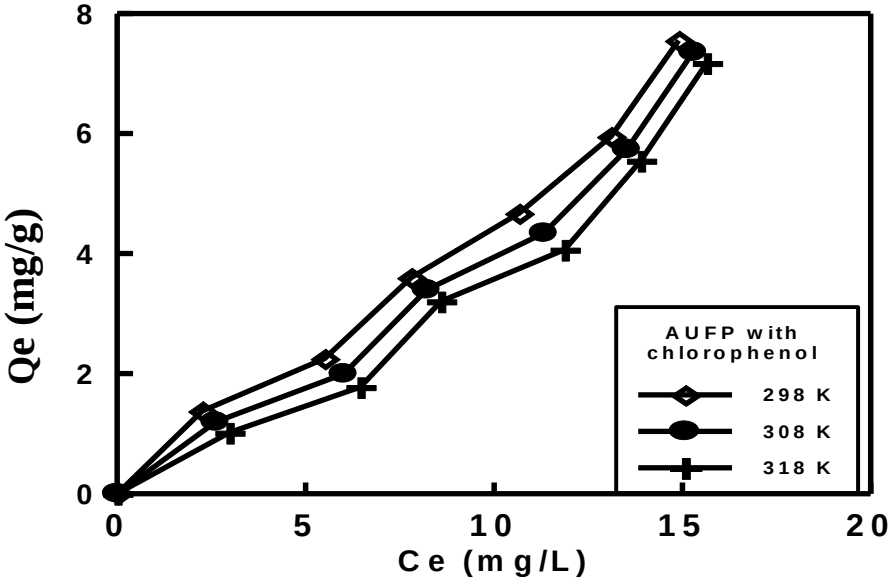


Figure 3.16. Temperature dependence of the adsorption of 2, 3 dichlorophenol on the AUFP surface.

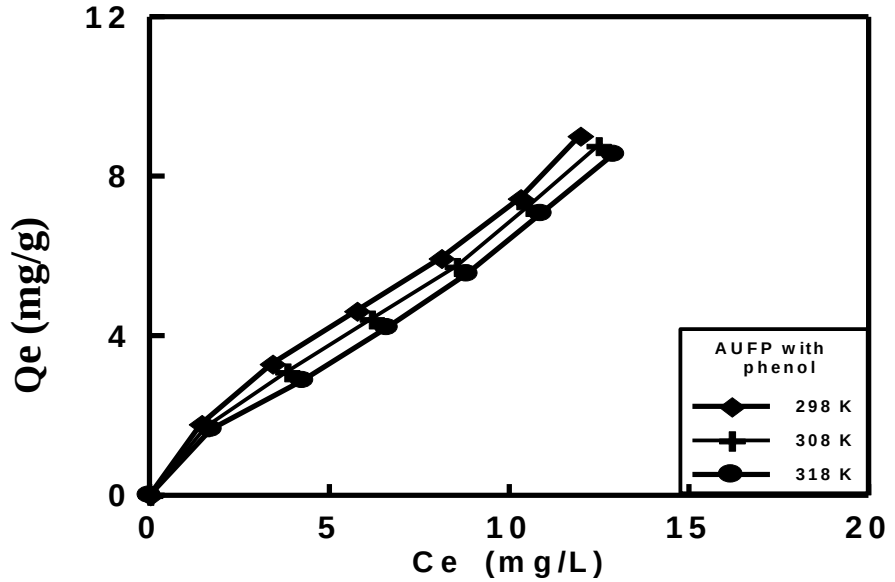


Figure 3.17. Temperature dependence of the adsorption of Phenol on the AUFP surface.

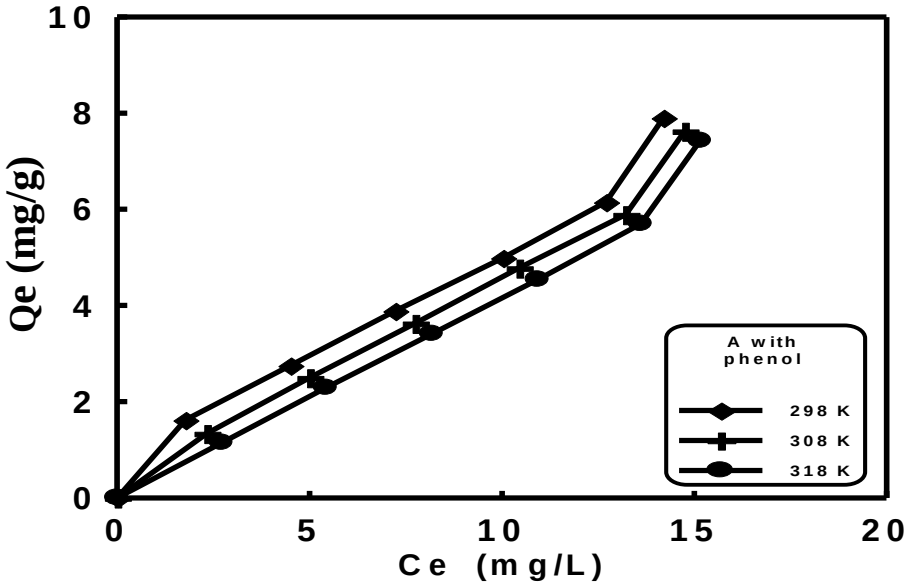


Figure 3.18. Temperature dependence of the adsorption of phenol on the A surface.

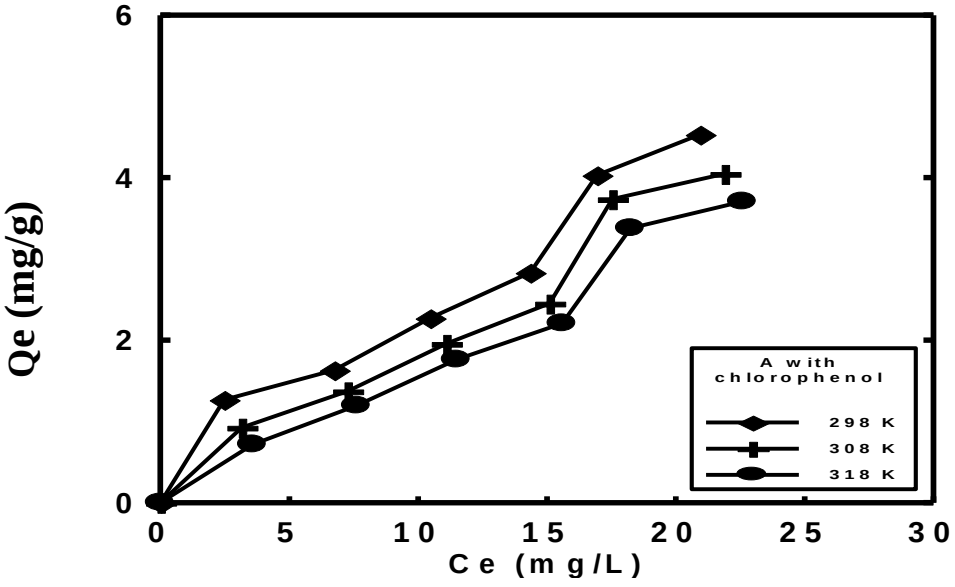


Figure 3.19. Temperature dependence of the adsorption of chlorophenol on the A surface.

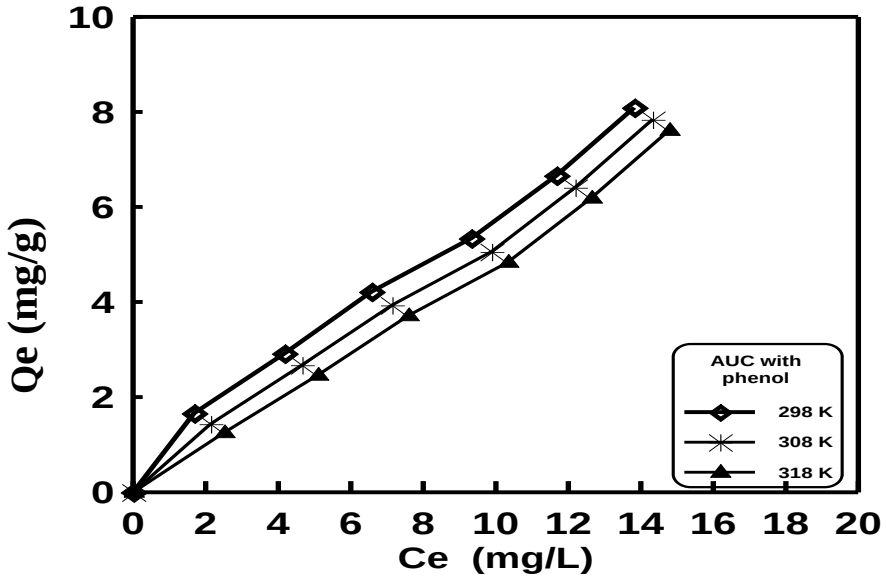


Figure 3.20. Temperature dependence of the adsorption of phenol on the AUC surface.

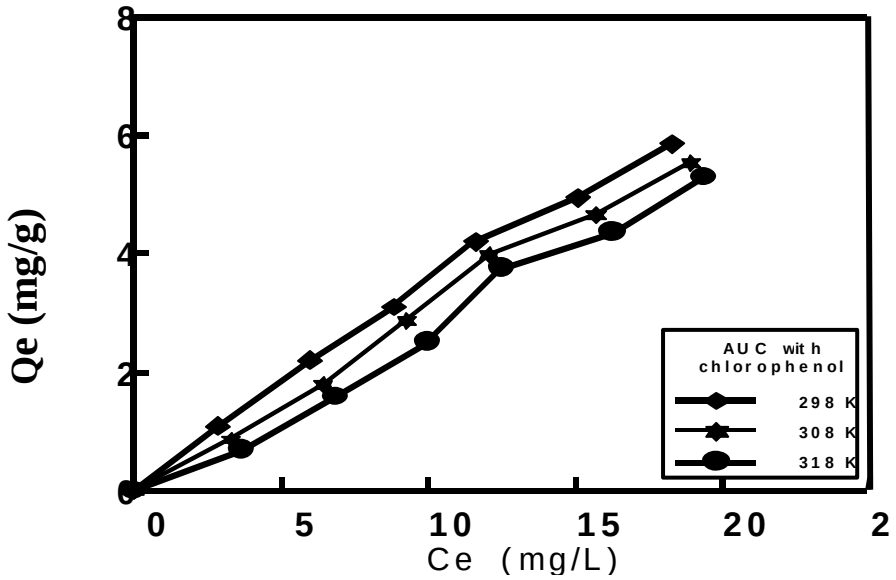


Figure 3.21. Temperature dependence of the adsorption of 2,3 dichlorophenol on the AUC surface.

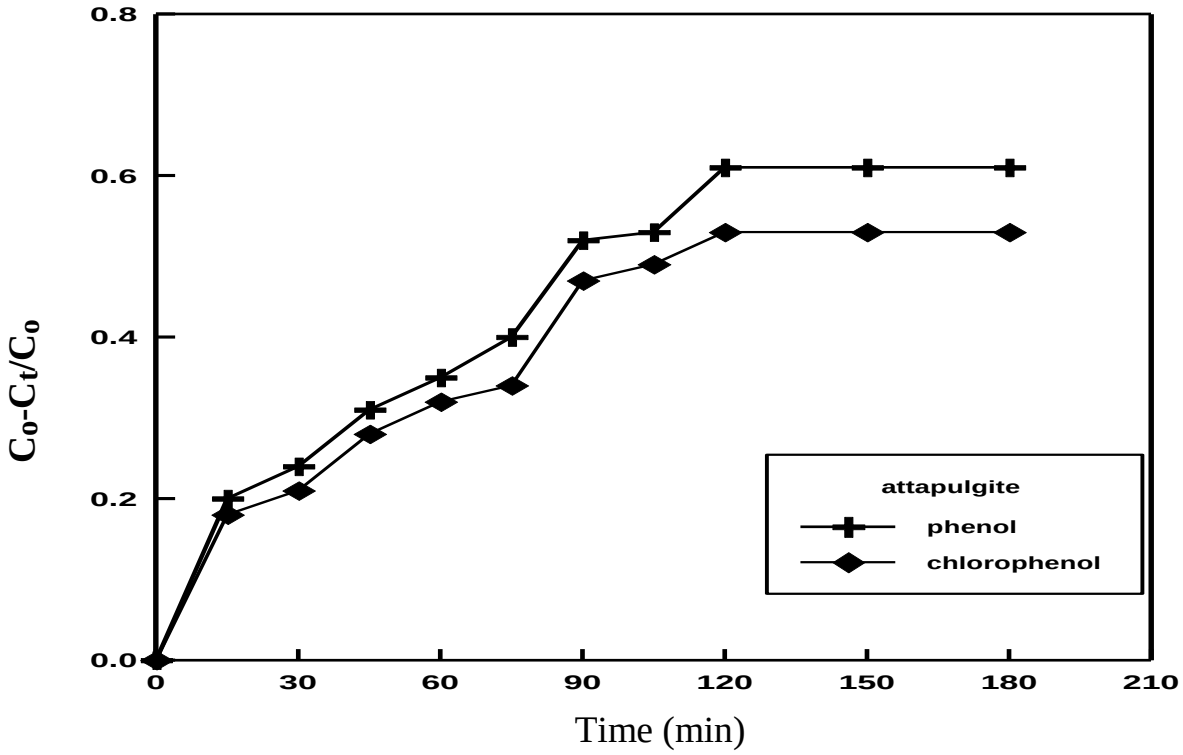


Figure 3.25. The uptake quantity of contact time of phenol and chlorophenol on the attapulgite surface at 298 K.

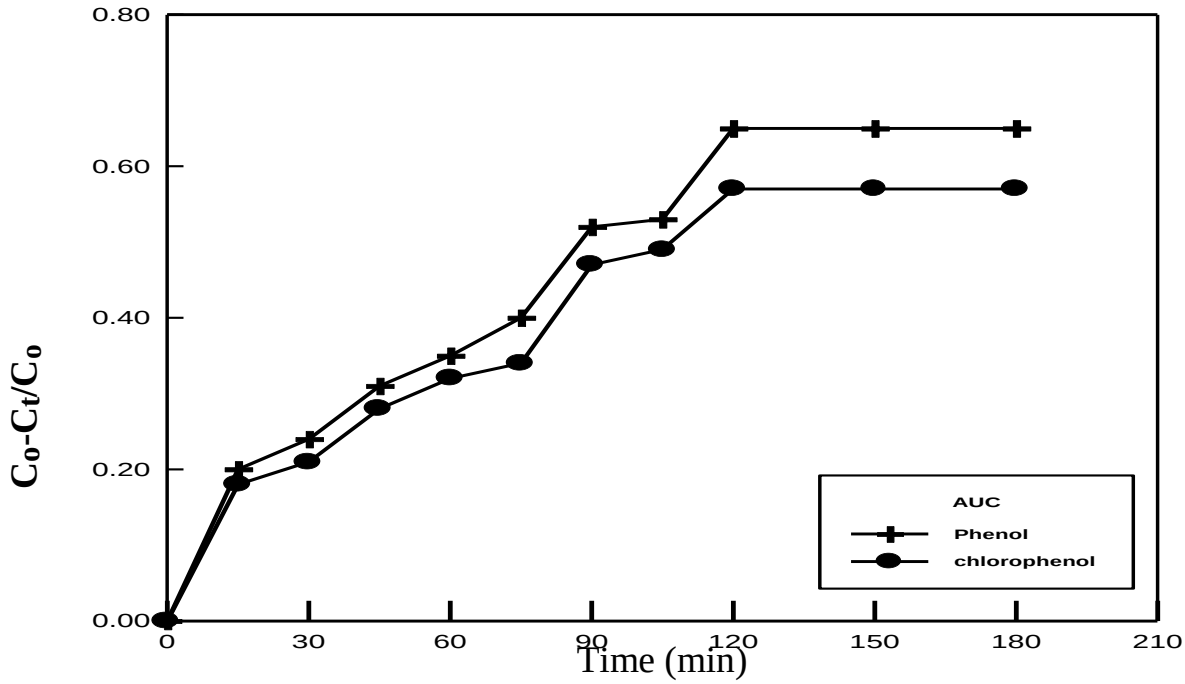


Figure 3.26. The uptake quantity of contact time of phenol and chlorophenol on the AUC surface at 298 K.

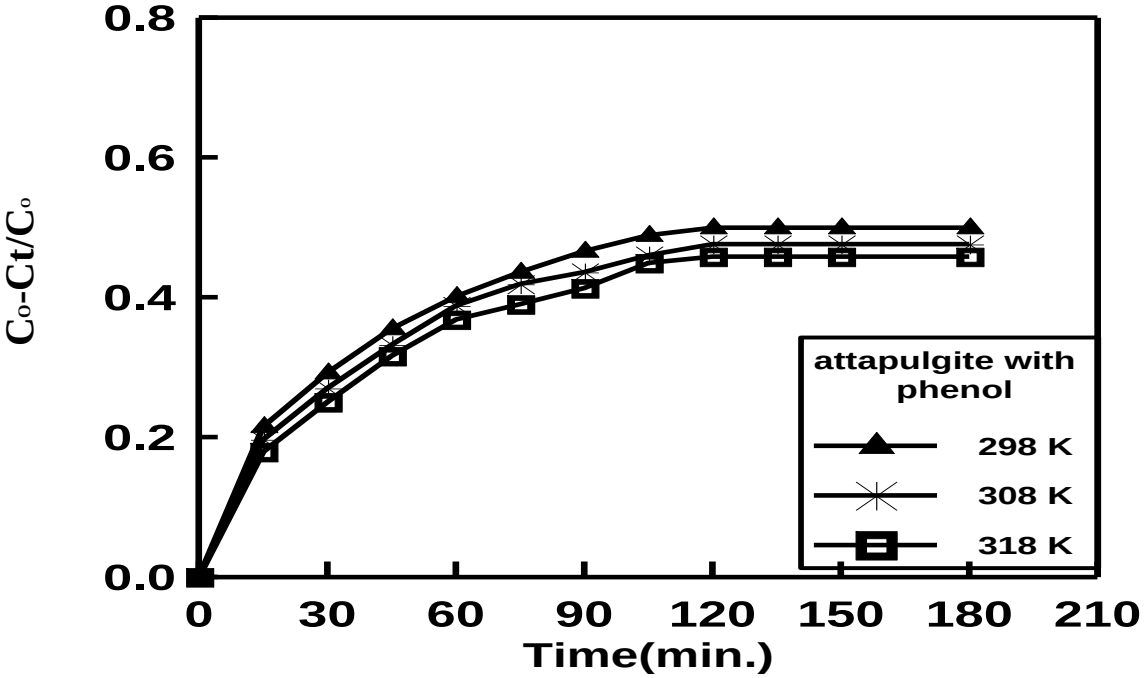


Figure 3.29. Temperature dependence of the contact time of adsorption of phenol on the attapulgite surface.

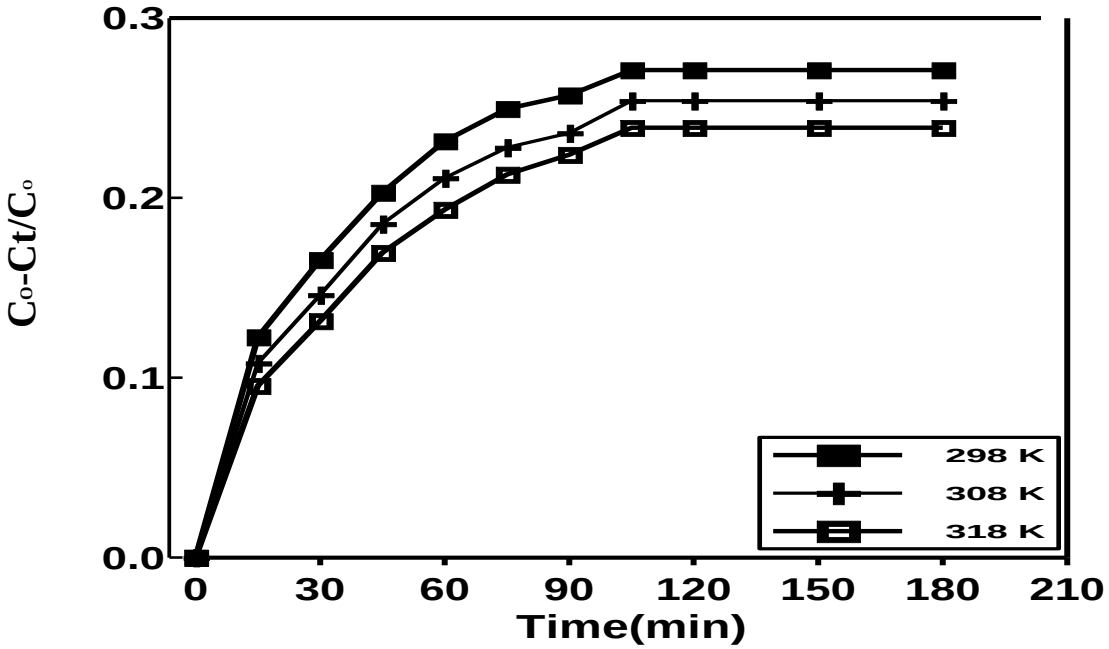


Figure 3.30. Temperature dependence of the contact time of adsorption of chlorophenol on the UFR surface.

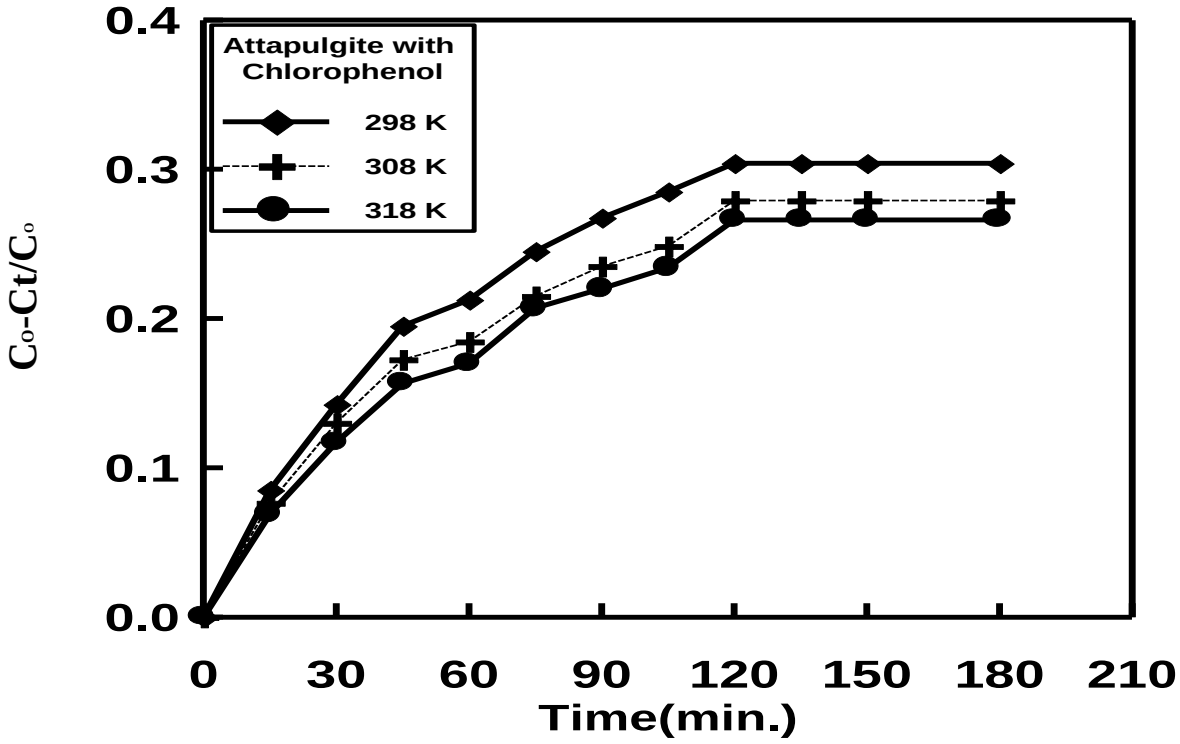


Figure 3.31. Temperature dependence of the contact time of adsorption of chlorophenol on the A surface.

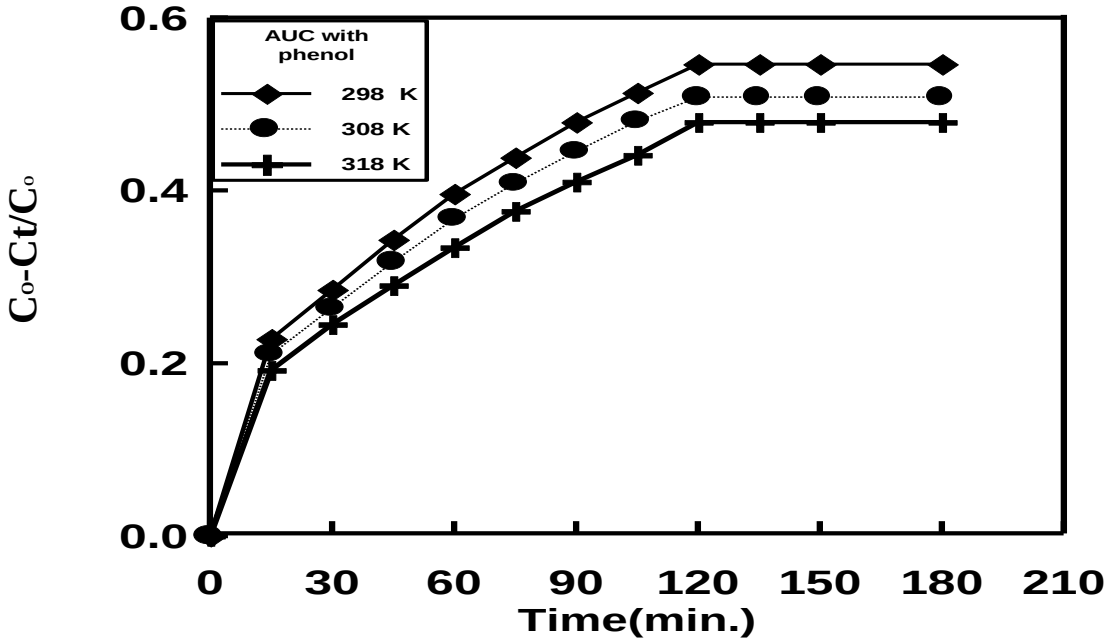


Figure 3.32. Temperature dependence of the contact time of adsorption of phenol on the AUC surface.

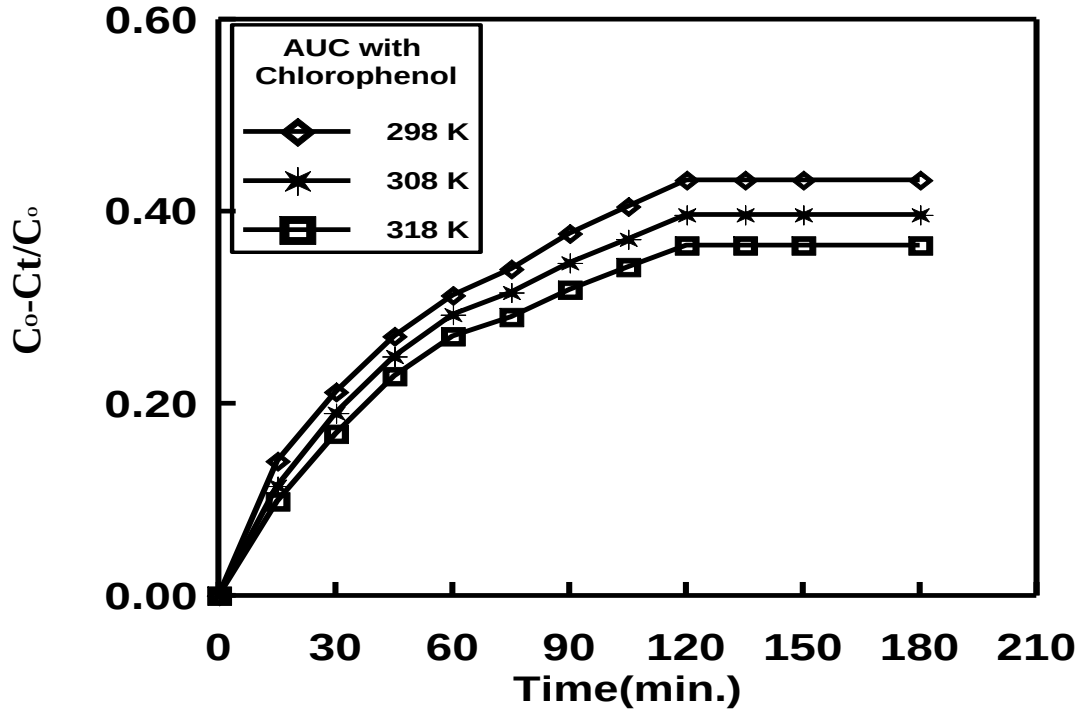


Figure 3.33. Temperature dependence of the contact time of adsorption of chlorophenol on the AUC surface.

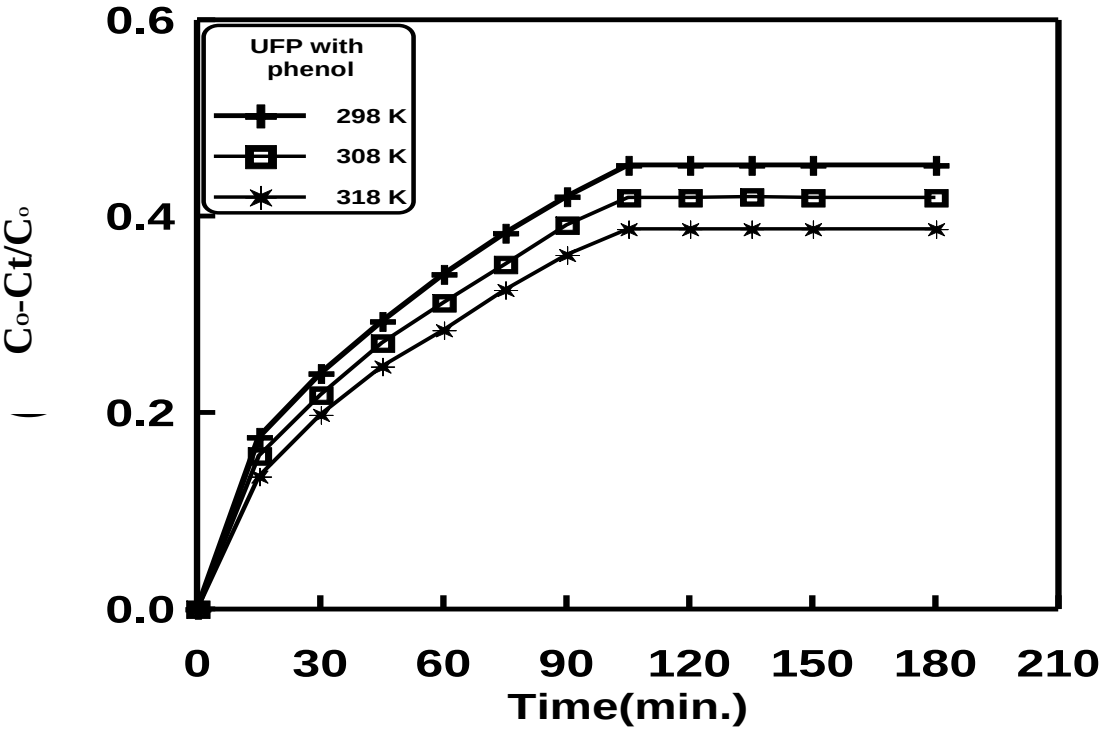


Figure 3.34. Temperature dependence of the contact time of adsorption of phenol on the UFR surface.

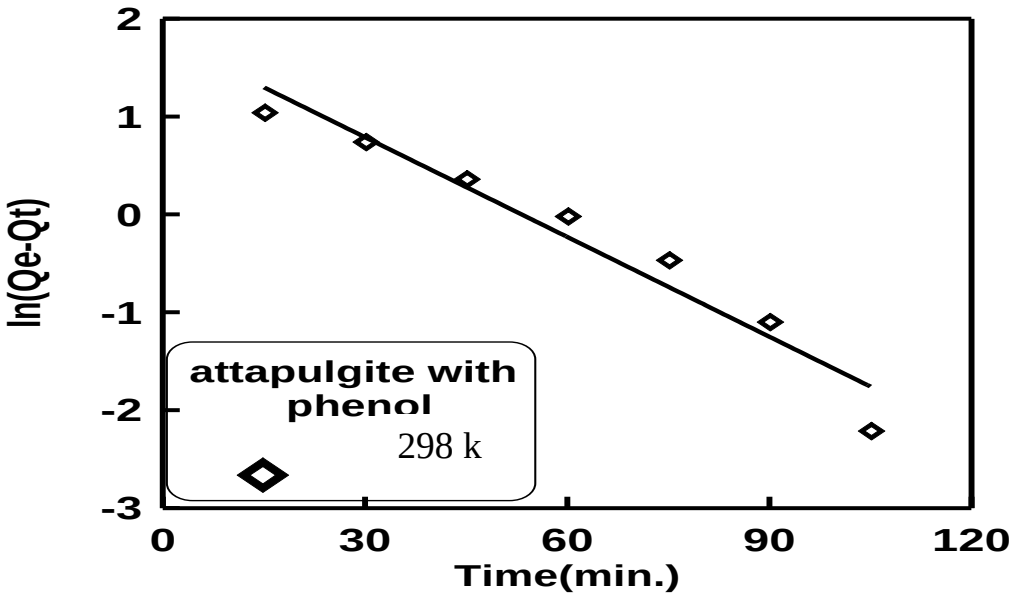


Figure.3.36. Kinetic adsorption of phenol on the attapulgite surface at 298 K.

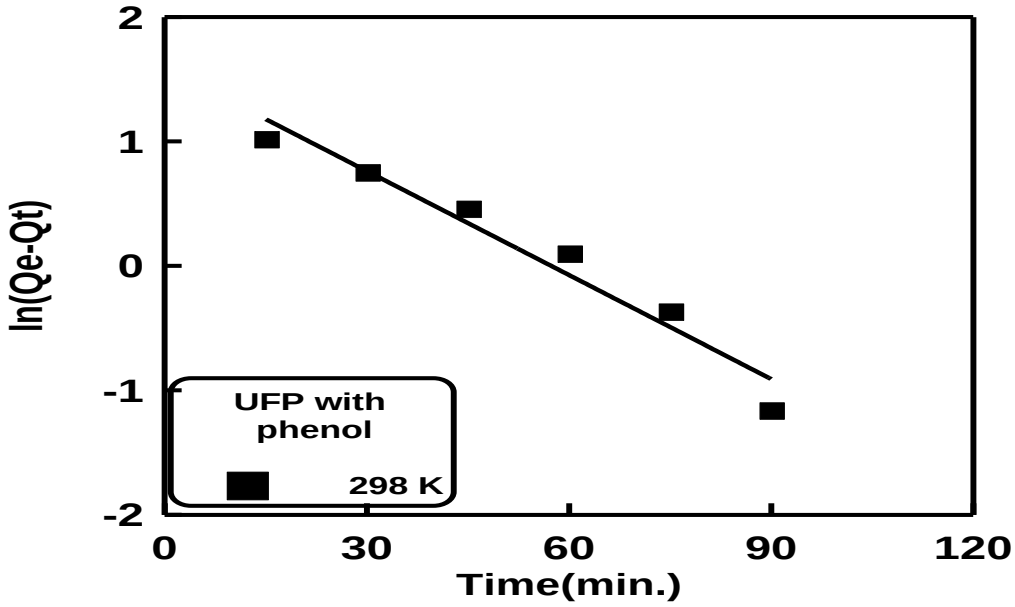


Figure.3.37. Kinetic adsorption of phenol on the UFR surface at 298 K.

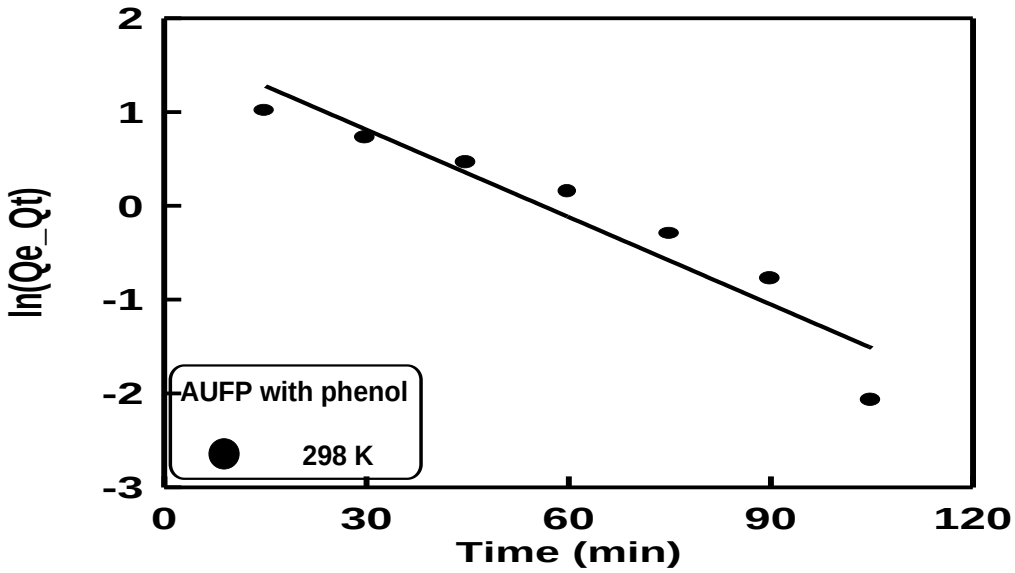


Figure.3.38. Kinetic adsorption of phenol on the AUFP surface at 298 K.

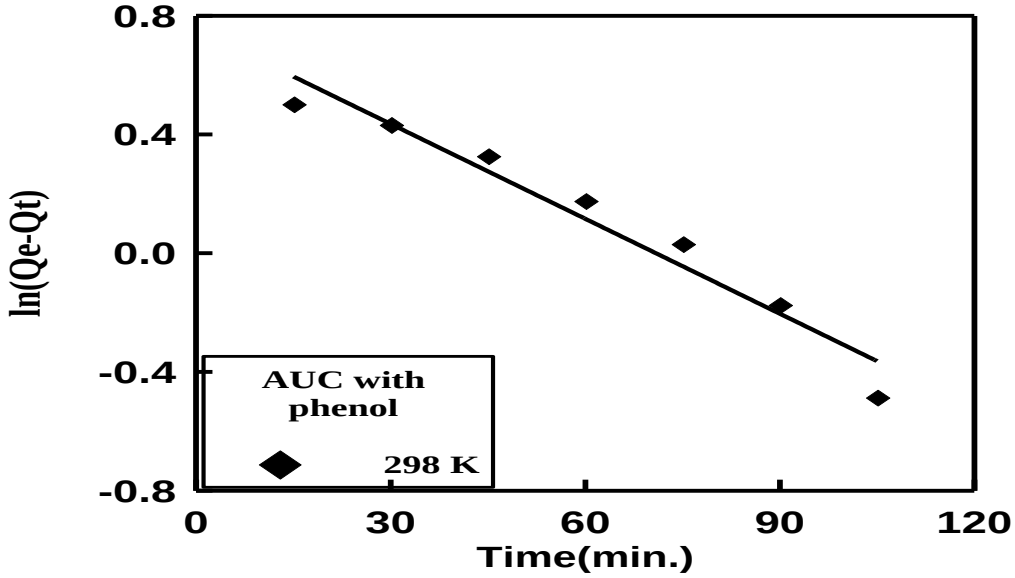


Figure.3.39. Kinetic adsorption of phenol on the AUC surface at 298 K.

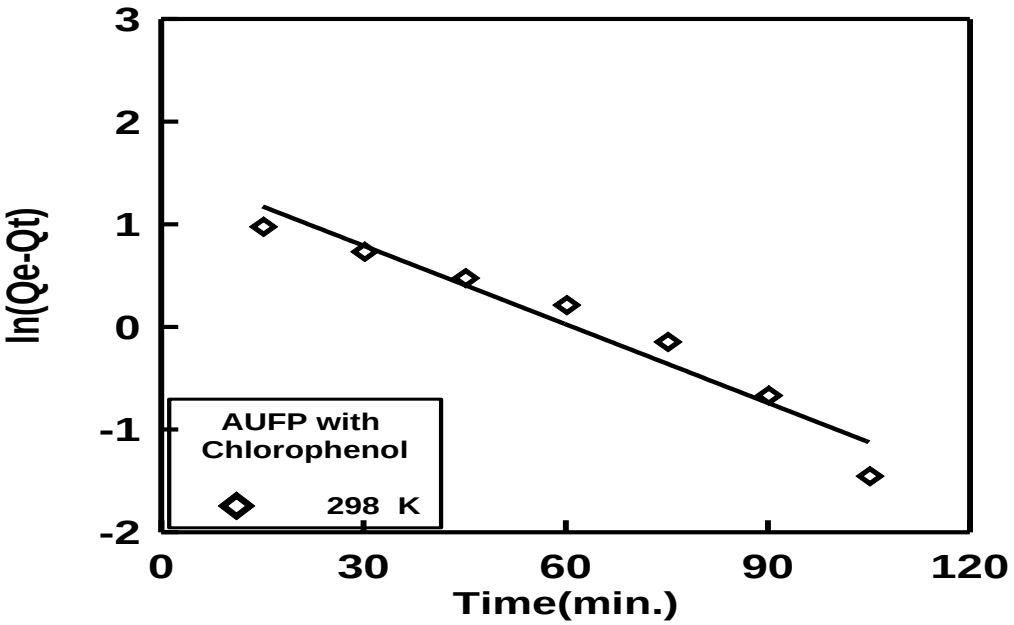


Figure.3.40. Kinetic adsorption of chlorophenol on the AUFP surface at 298 K.

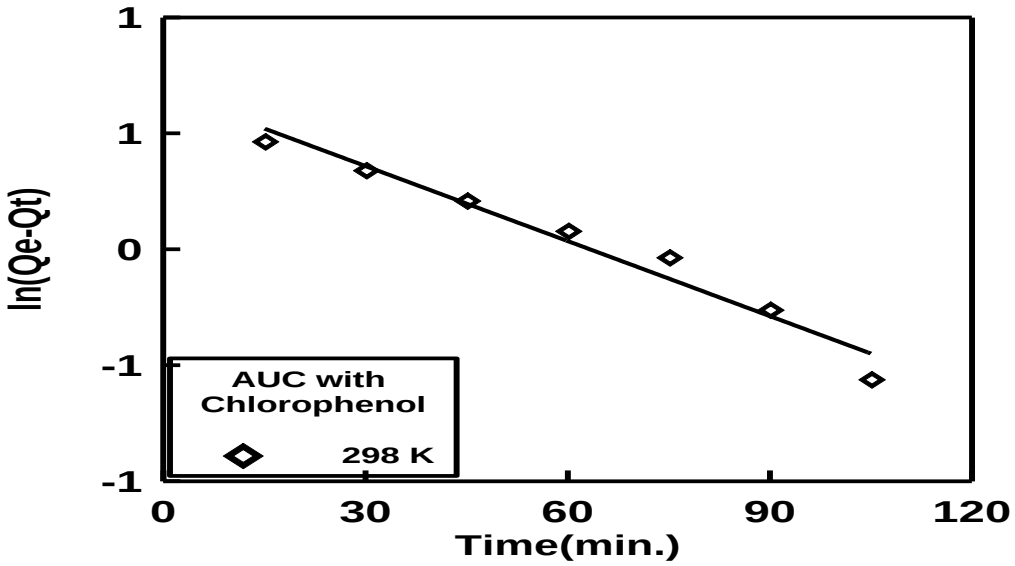


Figure.3.41. Kinetic adsorption of chlorophenol on the AUC surface at 298 K.

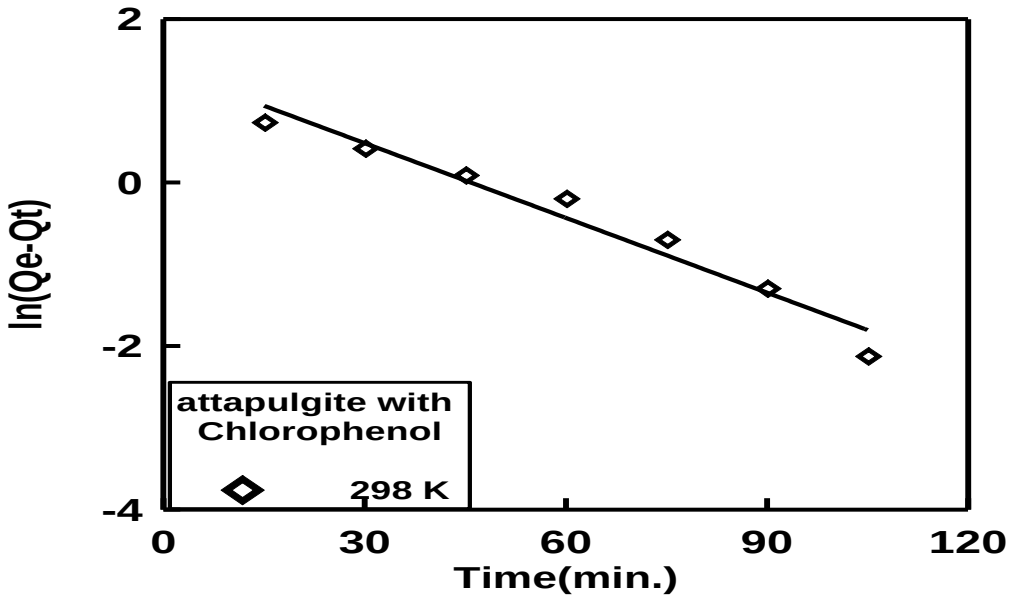


Figure.3.42. Kinetic adsorption of 2,3 dichlorophenol on the attapulgite surface at 298 K.

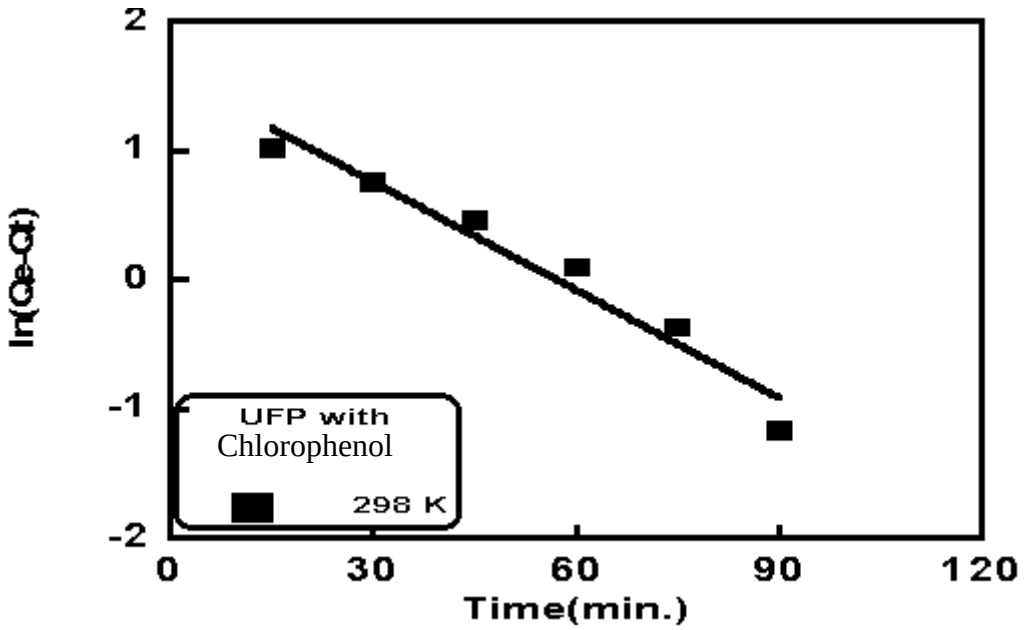


Figure.3.43. Kinetic adsorption of 2,3 dichlorophenol on the UFR surface at 298 K.

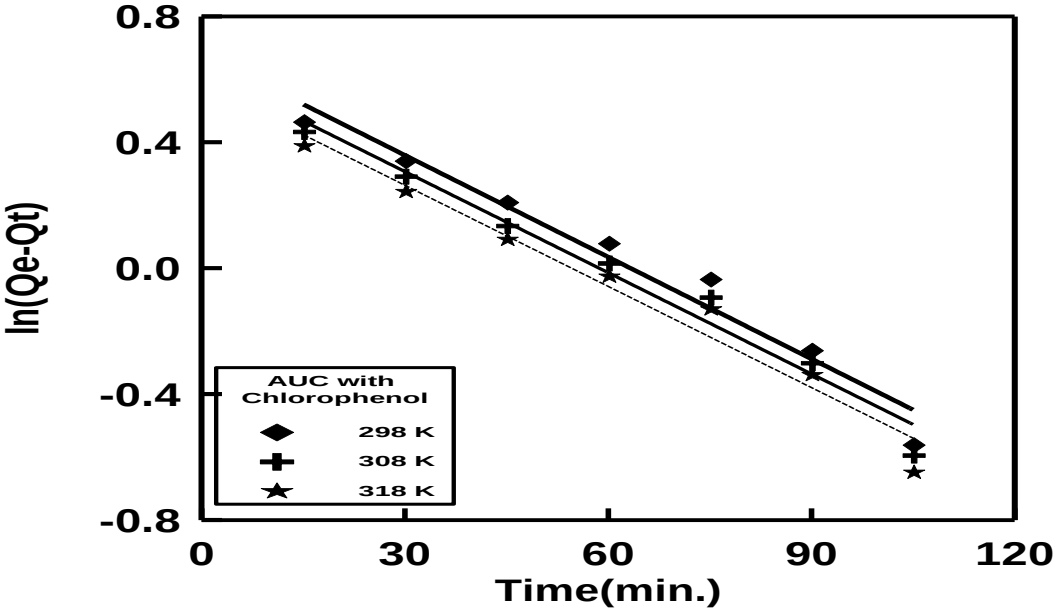


Figure. 3.44. Pseudo- first order adsorption kinetic of chlorophenol onto AUC at different temperature.

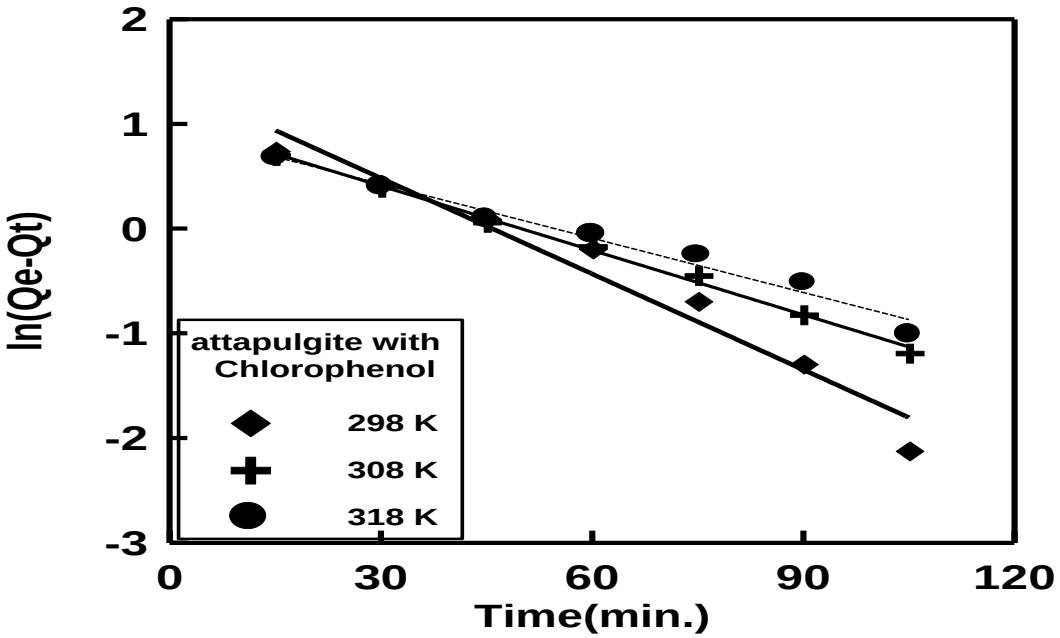


Figure. 3.45. Pseudo- first order adsorption kinetic of chlorophenol onto attapulgite at different

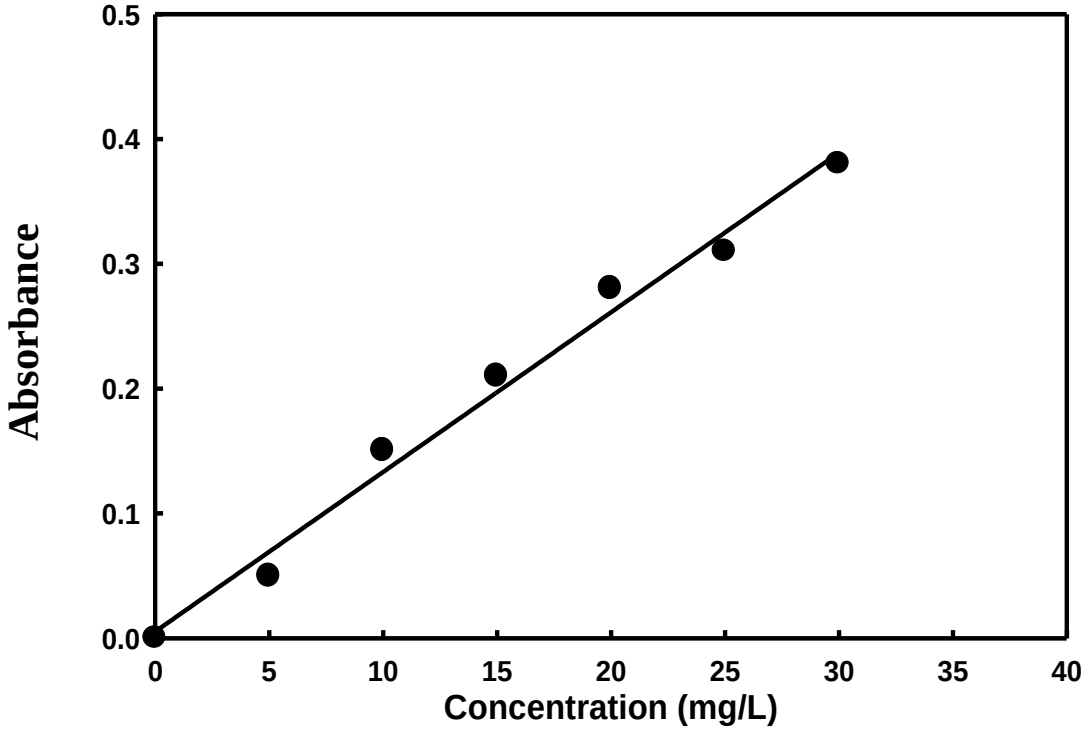


Figure 2.3. Calibration curve of phenol in aqueous solution.

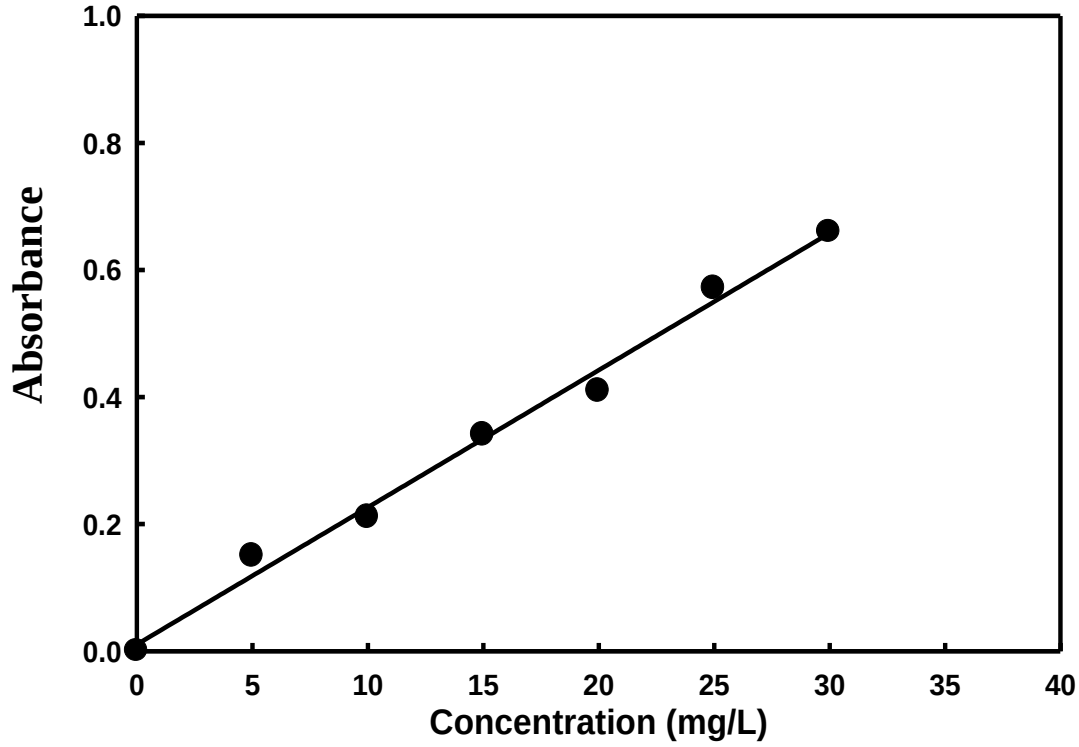


Figure 2.4. Calibration curve of chlorophenol in aqueous solution.

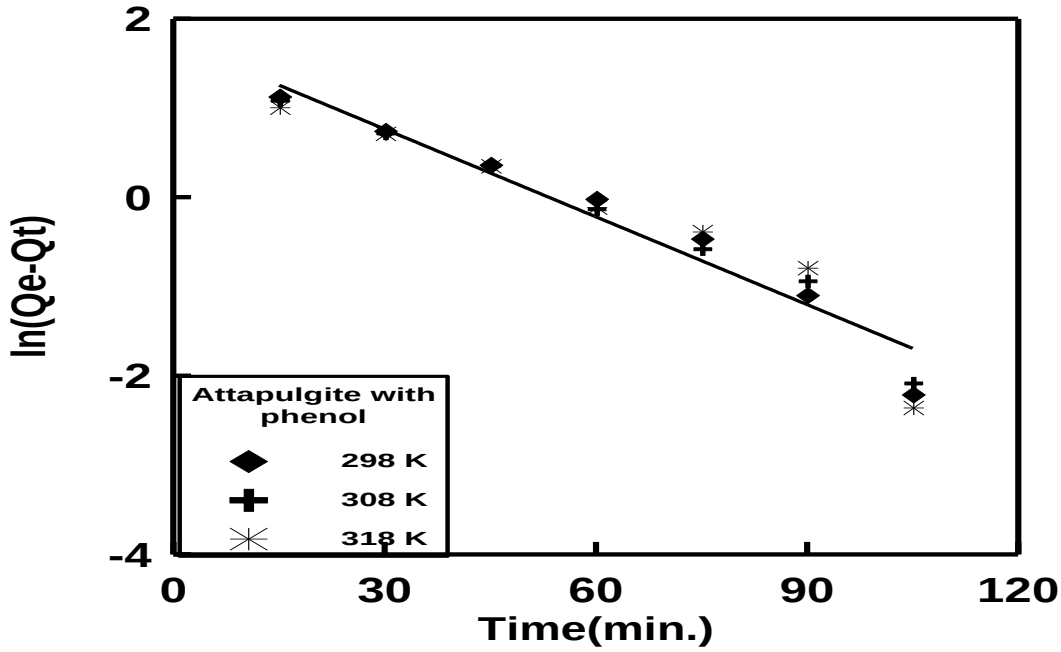


Figure. 3.48. Pseudo- first order adsorption kinetic of phenol onto A at different temperature.

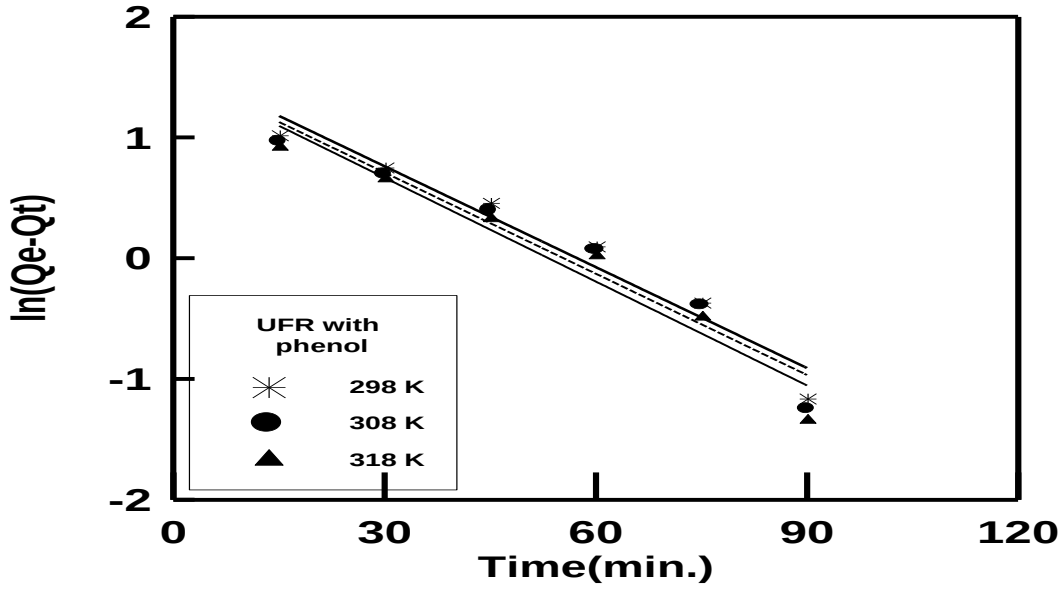


Figure. 3.49. Pseudo- first order adsorption kinetic of phenol onto UFR at different temperature.

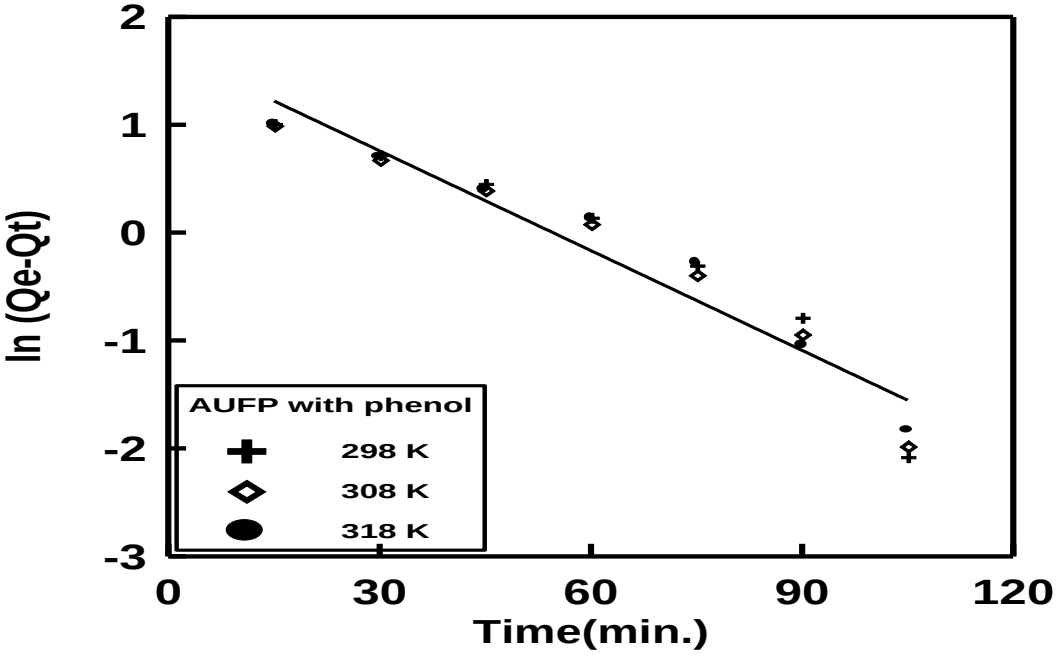


Figure. 3.50. Pseudo- first order adsorption kinetic of phenol onto AUFP at different temperature.

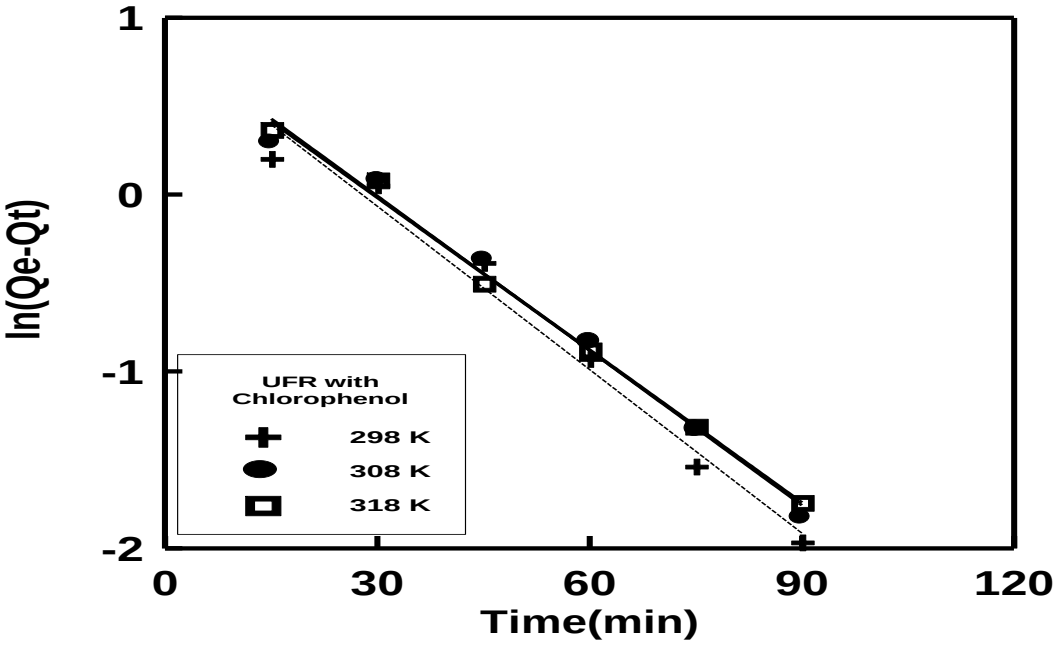


Figure. 3.51. Pseudo- first order adsorption kinetic of chlorophenol onto UFR at different temperature.

The Conclusions

1.The polymer AUFP was prepared by treating the clay with urea to form attapulgite-urea complex. The AUC the treated with formaldehyde to form the complex polymer AUFP, which has adsorption character properties.

2.the prepared adsorbents have been characterized by FTIR and UV/visible spectrometry.

3. The adsorption isotherms showed that the quantity of adsorption for phenol and chlorophenol by AUFP from their aqueous solutions increased on the four adsorbent surfaces by increased their concentration.

4. The adsorption of phenol and chlorophenol on the four adsorbent surfaces was of exothermic process.

5. The adsorptivity of phenol was better than that of chlorophenol on the four adsorbent surfaces (A, AUC, AUFP and UFR).

6. The adsorption capacity of phenol and chlorophenol on the AUFP and AUC were high when compared with UFR and attapulgite.

7. The adsorption kinetics of phenol and chlorophenol on the four adsorbent surfaces obeyed the pseudo-first order equation and showed that the adsorption was complex due to different factors that control the rate of reaction.

References

1. Maulood B.K.,Al-Saadi H.A.,and Al-Zubaidi F.S."**Ecology**" 1st edition, Mousel University Press, Mousel (1992).
2. World Health Organization, **International Agency on Cancer, Vol.71**, pp.762 (1999).
3. Ambient Water Quality Criteria Document **(4SEPA), phenol**, pp. III-346(1984).
4. State of Ohio Environmental Protection Agency (**Ohio EPA)**"**Pollution Prevention Opportunities for PBT Chemicals**" Report No.100 (2002).
5. Peyton, G.R and Gtaz, W.H.**Environ.Sci.Technology**, **22 (7)**, 76 (1988)
6. Kochany.J.R.,**Environ.Sci. Technol**., **26**,262 (1992)
7.Taube, W.C.,**J.Am.Chem.Soc., 62 (9)**,33579 (1980).
8.Chi.C.W.and Dranitt, S.S., **Chem.Eng.Proc.,52**,412(1979).
9. Kunin, R., **Chem.Eng.Pro.Vol.50**, 91(1977)
10.Shone, R.E and Mayer G.S., **J. Chem**., **54**,1164 (1982)
11.Adam, N.K.,"**Physical Chemistry** "3rd edition, Oxford University Press. (1962).
12.Weber, W.J.Asec, A.M. and Morris.J.C. **J.Saint Eng.Dir, Amer.Soc.Cir Enger.,89 (5A3)** 31 (1963).
13. Maron S.H. and Lando J.B., "**Fundamental of Physical Chemistry** ", Macmillan, Pulishing Co. London (1974).
14.Alfred M., **"Physical Pharmacy "**4th edition, Texas University press , Texas (1993).
15.Atkins, P.W.,**"Physical Chemistry "**,7thedition, Oxford University presses Oxford (2002).
16.Alexeyev V.N.,**"Quantitative Analysis"**2nd edition, Moscow University press. Moscow (1970).
17.Daniels F. and Alberty R.A., **"Physical Chemistry "**2ndedition, New York (1978).
18.Jalal K. and Abd A.A., **Scientific Conference, Scientific Research Council,** 4th , **Vol.1** part 1, (1980).

19.Jalal M.S., **"Surface Chemistry"** 1st Baghdad University press, Baghdad (1980).

20.Cal M. P.,Larson S. M. and Rood M. J.**,J.Chem.Eng.**, **Vol .13** ,No.1 pp:26-30 (1994).

21.Gilles, C.H., Smith, D.and Hurston, A., **J.Colloid Interface. Sci.**, **47**,755 (1974).

22. Gilles, C.H., Smith, Authony P.D.Silva and Jan A.Easton., **J.Colloid Interface. Sci., 74,**755 (1974).

23.Adamson, A.W.,**"Physical Chemistry of Surface "**Wiley, New York (2001).

24.Theng, B.K.G.,**"The Chemistry of Clay – Organic Reaction"**. Lower Hutt, New Zealand (1974).

25.Treybal R.E., **"Mass Transfer Operations** "Mc. Graw ,Hill ,New York pp:581 (1980).

26. Anliker,R.;Clarke ,E.A.;and Moser , P.,**J.Chemosphere** ,**Vol.10**, pp.263- 274.1981.

27.Puri B.N.,Bhardwaj S.S and Gupta U., **J.Indian Chem.Soci.,Vol 53**,pp 1095 -1098 ,1978.

28. Anaduria G.,Juang ,R.S.,and Lee,D.J., **J.Environ.Sci.Health** ,**A36** PP 715-725, (2001).

29.Albanis, T.A.,Danis,T.G.,and Kourgiu M.,**J.of Environ.Tech.**, **19,** PP: 25 –34 (1998).

30.Bekkouche S.,Bouhelassa M.,Sulah N.H.and Meghlaoni F.Z., **J. of Science chemistry Desalination 166** pp :355-362 (2004).

31.Adamson, A.W.,"**Physical Chemistry of Surface** "Wiley, New York (2001).

32.McGinity, J.W. and Hill J.A., **J.Pharm.Sci., 64(9)**, 1566(1979).

33. Grim, R.E. "**Clay Mineralogy"** 2nd edition, McGraw Hill , New York, (1968).

34. Farmer V.G., and .Genta V., **J.Soil Sci., 112,** PP: 62-68 (1971).

35.Peck G.and Leib F., "**Physical Chemistry** "3rd edition, (1979).

36.Minerals and Ores, **Sorptive Minerals Institute (SMI),** Washington (2004).

37. Ozin G. A. and Godber J., J. Phys. Chem., Vol.93 (1989).

38.Enviromental Science and Energy **"Attapulgite Clay and Its Applications to Water Treatment"** Summaries and Thesis (2003).

39.Jupp G.and Rau H., **J.Appl.Chem.,Vol 19**,pp 120-124,(1969).

40.Shmoyama A. and Johns W.P., **J.Nature Phys.Sci.**, **64,** pp237-243, (1972).

41. **Brief Introduction of The Attapulgite Clay,** Summaries and Theses " (2003).

42.Canant J.B.,and Blatt A.H.,"**The Chemistry of Organic Compounds"** 5th. edition.1952.

43.Adam G.A.and Gatta H.K.,"**Chemistry and Technology of Polymers** "1st edition. 1983.

44.Donald J.C. and Hammond G.S."**Organic Chemistry "** 2nd edition 1964.

45.Morrison, R.T.;and Boyd ,R.N.; "**Organic Chemistry** " 5th edition, New York press, New York University ,1987.

46. Nekrasov V.V.,"**Practical Organic Chemistry "**1st edition (1978).

47.Fred W.B.,**"Textbook of Polymer Science "**,2nd edition (1971).

48 . White, J.L. and Ledoux, R.L., **J.Colloid Interface Sci.**, **21,** 127(1966).

49.Ratanuman W.,David A.,White G.and Radu R.**,j.Chem.E.**,**Vol .77** , Part B, pp. 88-92 1999.

50.Al-Hayali W.E**., M.Sc.Thesis**, Collage of Education, Ibn-Alhaitham, University of Baghdad (2001).

51.Al-Timmimi, R.J. **M.Sc.Thesis**, College of Science, University of Baghdad (2002).

52. El-Bahrani, K.S and Martin, R.**J., Wat.Re.**, **17,**731 (1976).

53.Mattson, J.S., Mor K, H.B., Malbin, M.D., Webber, W.J and Crittenden, J.C**., J.Colloid Interface Sci., 31(1)**,116 (1969).

54.Brown, J.E., Feldkamp, J.R., White, J.L and Hem, S.L**., J. Pharm.Sci.**, **69(7)**, 816-823 (1980).

55.Mckay, G., Bino, M.J and Eltamemi, A.R**., Wat.Res.**,**19(14)**,491 (1985).

56.Statendra, K., Upadhyah, S.N.andUpadhaya.**J.Chem.Tech.Biotechnol.**, **37**,281(1987).

57.Al-Ameene A. **M.Sc.Thesis,** Ibn Al-Haitham, college of education , University of Baghdad (1996).

58. Albanis T.A., Hella D.G., Sakellaride T.M. and Danis T.g., **Int. J., Vol.2**, No.3, pp237-244, (2000).

59.Zawadzki, J., **J.of Chem.Phys.Carbon 21**, **Vol.147**, 1989.

60.Terzyk P., **J. of Colloid and Int. Sci.**, **Vol. 8**, PP 1-21 2004.

61.Rushed. I. and Maha F.T.,Ghazi A.W. and Salem M.M.,**J.of Colloid and Int. Sci., Vol.216**, PP.348_359,1999.

62.Reinik J., Viroja A. and Kallas J., Proc**. Estonian Acad.Sci.Chem.**,**50**,4 ,pp:205 –216 (2001).

63.Mattson,J.S., Mark. H.B.,Malbin M.D.,Webber W.J. and Crittenden,J.C ,**J.Colloid Int.Sci.**,**31(1)**,116(1969).

64.Nakamura T., Tamura T. and Tanada S., **J .of Health Sci**, **49 (46)** PP 520 –523 (2003).

70. Leasan H.M. and Bhandari A. "**Evaluation of Atrazine Binding to Surface Soils**", Proceeding of the 2000 conference on Hazardous Waste Research ,pp.76-89 . 2004.

71.Glasston S.Laider K.J.and Eyring H."**The Theory of Rate Processes** University of Utah Press,University of Utah (1941).

الخلاصة

تم في هذه الرسالة تحضير معقد داخلي لليوريا مع الاتابلكايت ومن ثم بلمرة جزيئات اليوريا الموجودة في قنوات الاتابلكايت وفجواته للحصول على بوليمر الاتابلكايت اليوريا فورمالديهايد. تم تشخيص الاتابلكايت - يوريا وكذلك معقد الاتابلكايت -بوليمر الأتابلكايت-يوريا-فورمالديهايد بواسطة تقنيتي حيود الإشعة السينية (XRD) ومطيافية الإشعة تحت الحمراء (FTIR) حيث أوضحت تلك القياسات بإن ارتباط جزيئات اليوريا مع الاتابلكايت كان عن طريق التآصر الهيدروجيني كما أن البوليمر كان قد تكون داخل قنوات الاتابلكايت.

درست عملية امتزاز وحركية الامتزاز وتأثير درجة الحرارة عليهما بالنسبة للفينول (ph) والكلوروفينول كمواد ممتزة على سطح معقد الاتابلكايت-بوليمريوريا-فورمالديهايد كمادة مازة بواسطة مطيافية الإشعة المرئية الفوق بنفسجية.

كما أن ايزوثرمات الامتزاز تأخذ الشكل (S) حسب تصنيف (Giles) ويكون الامتزاز باعث للحرارة لكل من هذه المركبات.

تم دراسة حركية امتزاز هذه المركبات على السطح المساز وفقاً لمعادلة Lagergreen حيث كانت حركية الامتزاز لهذه المركبات قريبة من حركية المرتبة الأولى وفقاً لهذة المعادلة بين الدقيقة (30) ولحين الوصول الى الإتزان ومنها تم استخراج ثابت معدل السرعة.

أوضحت دراسة تأثير درجة الحرارة على حركية الامتزاز أن التغيرات في قيمة ثابت معدل سرعة الامتزاز K_{ad} تكون طفيفة بتغير درجة الحرارة ومنها تم استخراج طاقة تنشيط (E_a) عملية الامتزاز حيث وجد إنها تتبع نفس ترتيب ثابت معدل سرعة الامتزاز بين المركبات الفينولية قيد الدراسة.

بينت قيم الانثالبي ΔH وطاقة التنشيط وK_{ad} على أن عملية الامتزاز يرافقها عملية تبادل ايوني لكل من الفينول والكلوروفينول على سطوح الاجسام المازة.

Table 3.1. The characteristic IR. absorption bands of A.

Group	**-OH**	**-OH**	**-OH**	**Si-O-Si(Al)**	**Si-O-Si(Al)**	**Si-O-Si(Al)**
νcm^{-1}	3720	3421	1645	1035	920	790

Table 3.2. The characteristic IR. absorption bands of AUC.

Group	**-NH_2 (asy)**	**-NH_2 (sym)**	**-OH**	**C=NH_2**	**N-C-N (asy)**	**Si-O-Si(Al)**	**Si-O-Si(Al)**
νcm^{-1}	3452	3348	2690	1627	1465	1039	785

Table 3.3. The characteristic IR. absorption bands of AUFP.

Group	**-OH**	**-NH_2 (sym)**	**-CH_2**	**C=O**	**N-C-N (asy)**	**C-H bending**	**Si-O-Si(Al)**
νcm^{-1}	3690	3354	2974	1645	1554.5	1384.8	1037.6

Table 3.4. The characteristic IR. absorption bands of UFR.

Group	-NH_2 (sym)	CH_2	C=O	C=NH_2	N-C-N	C-H bending	C-O
νcm^{-1}	3352	2968	1685	1639	1560	1384	1035

Table 3.5. The characteristic IR. absorption bands of Urea.

Group	-NH_2 (asy)	-NH_2 (sym)	-NH_2 H-bond	C=O	C=NH_2	N-C-N
νcm^{-1}	3450	3344	3259	1685	1606	1465

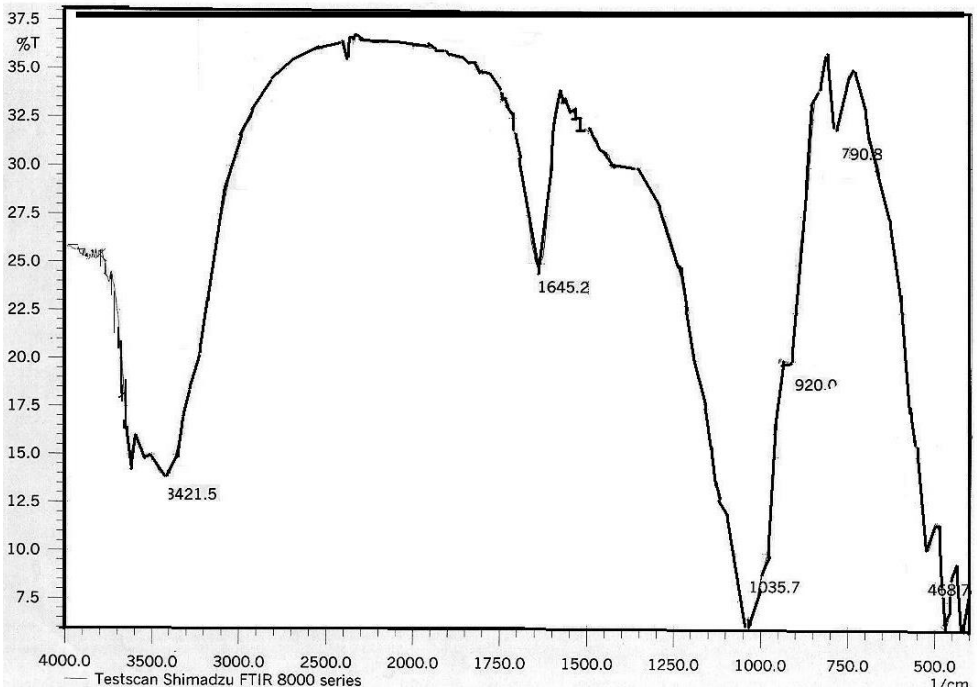


Figure 3.1. IR Spectrum of A.

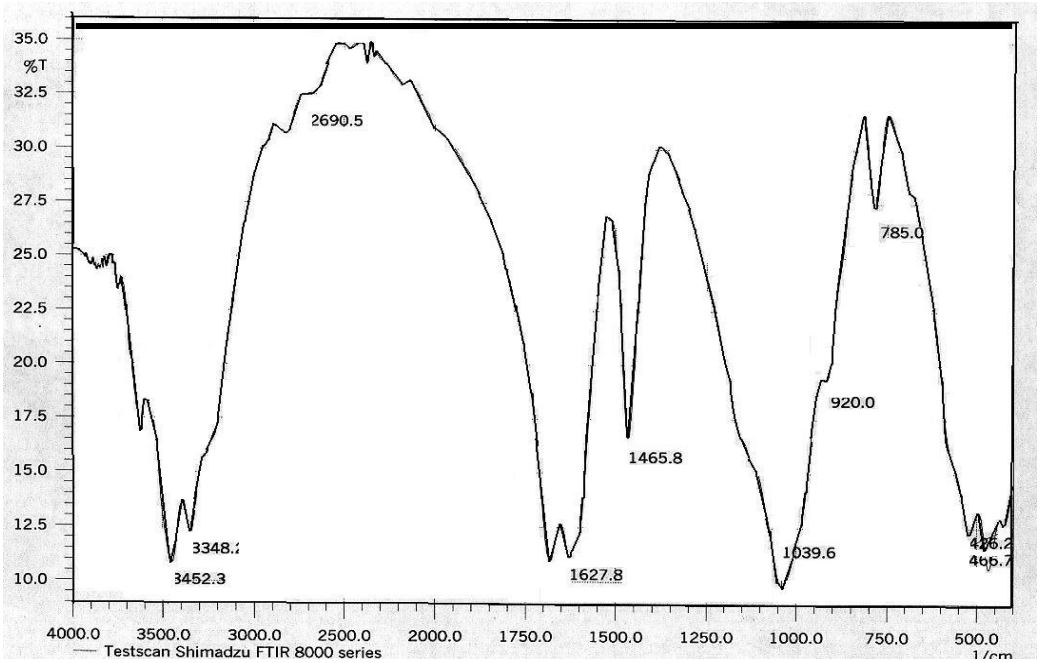


Figure 3.2. IR Spectrum of AUC.

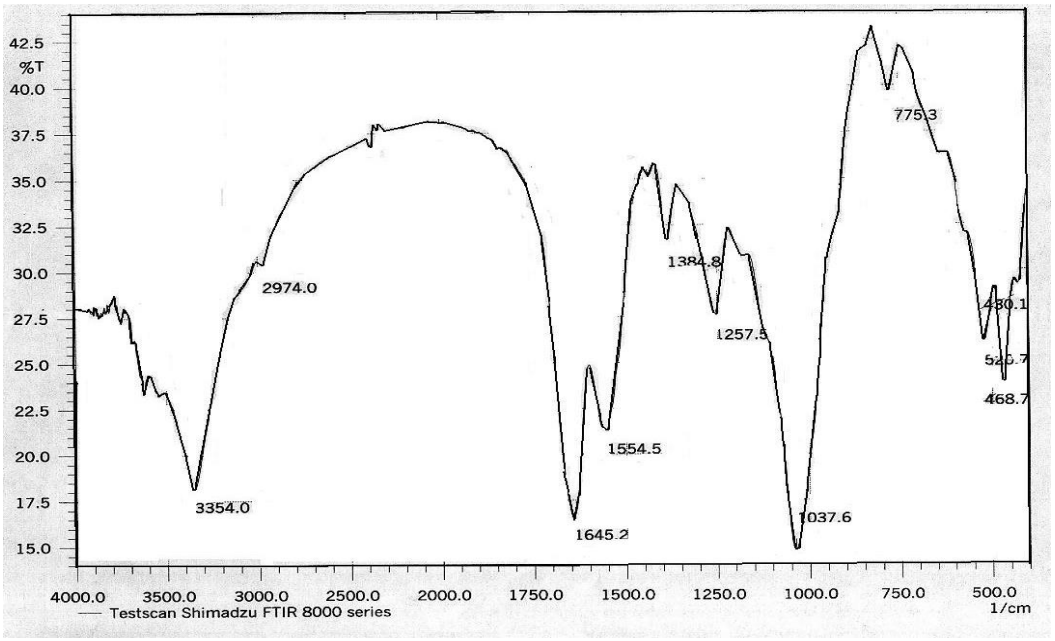


Figure 3.3. IR Spectrum of AUFP.

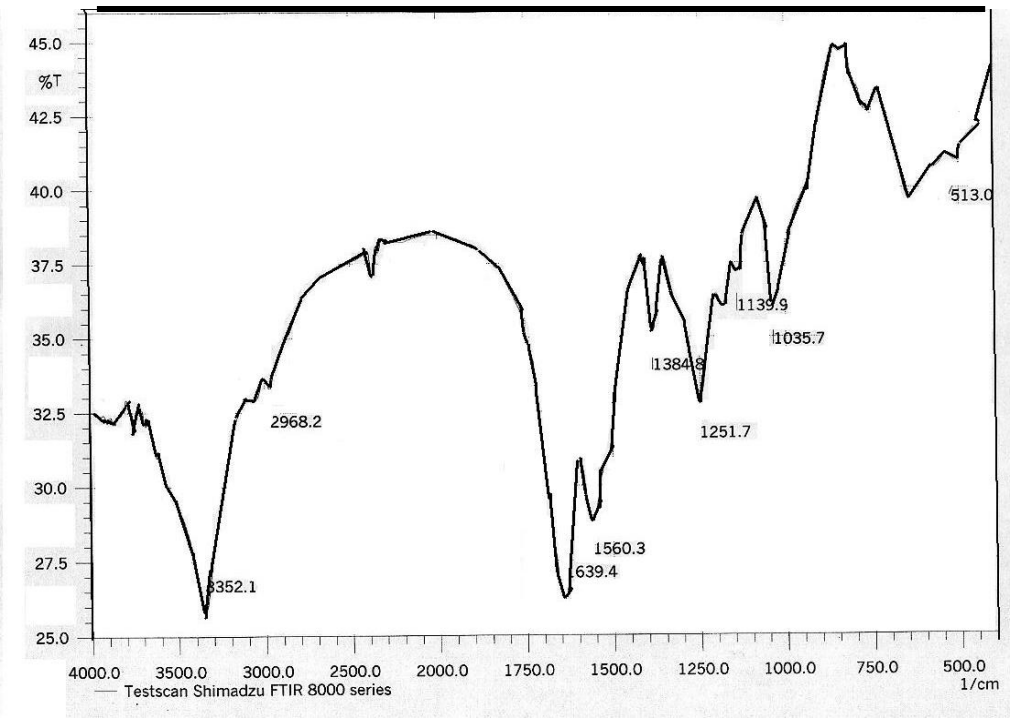


Figure 3.4. IR Spectrum of UFR.

Figure 3.1. IR Spectrum of UFR.

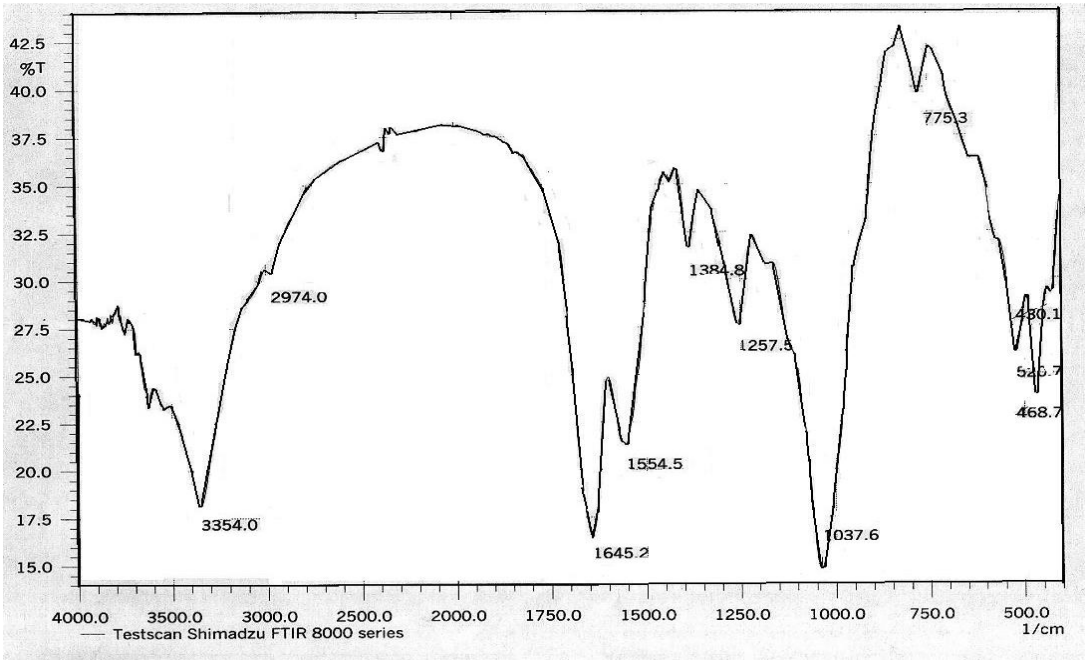
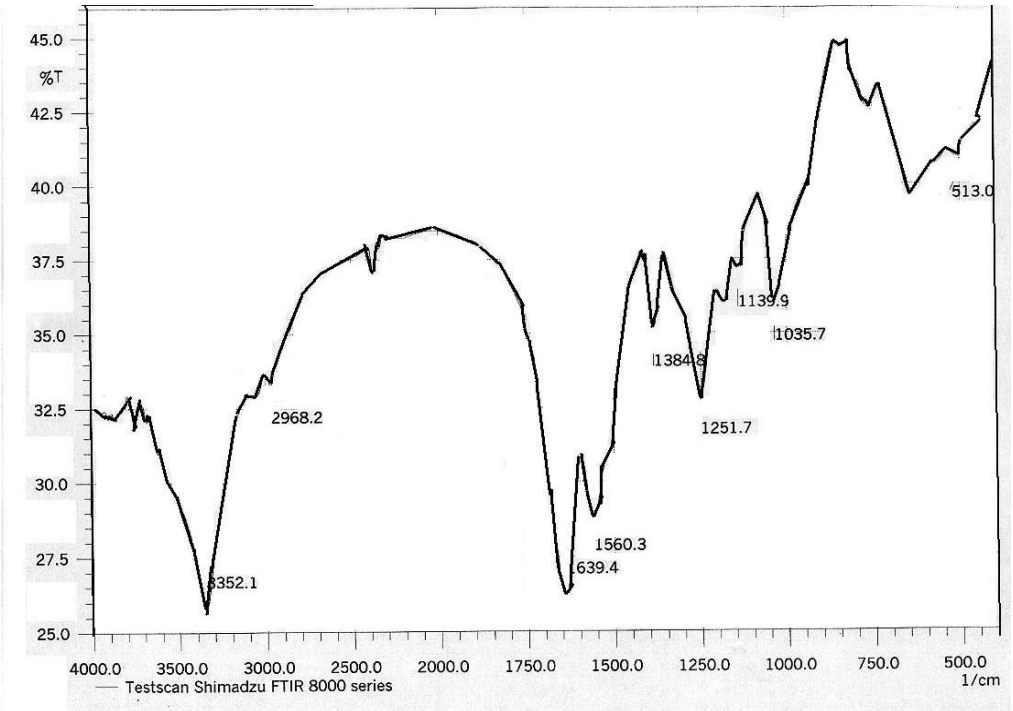


Figure 3.3. IR Spectrum of AUFP.



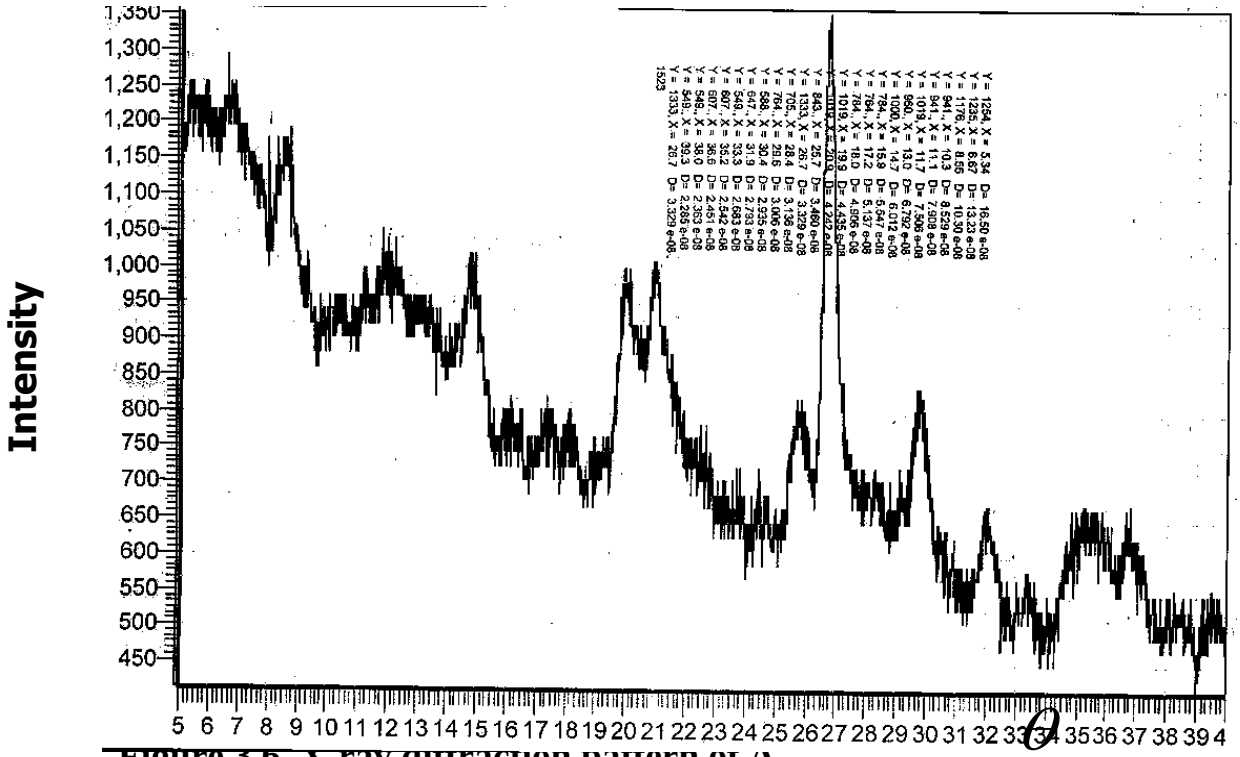


Figure 3.6. X-ray diffraction pattern of A.

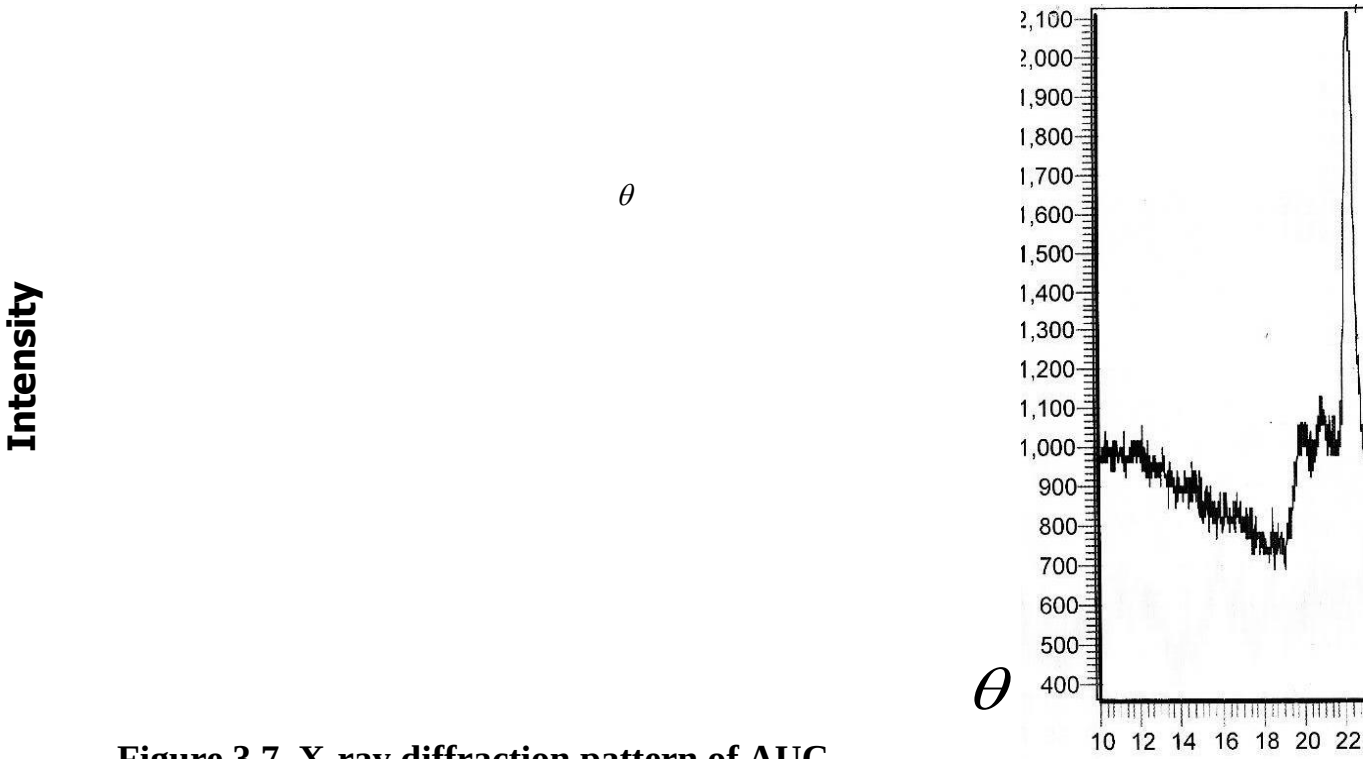


Figure 3.7. X-ray diffraction pattern of AUC.

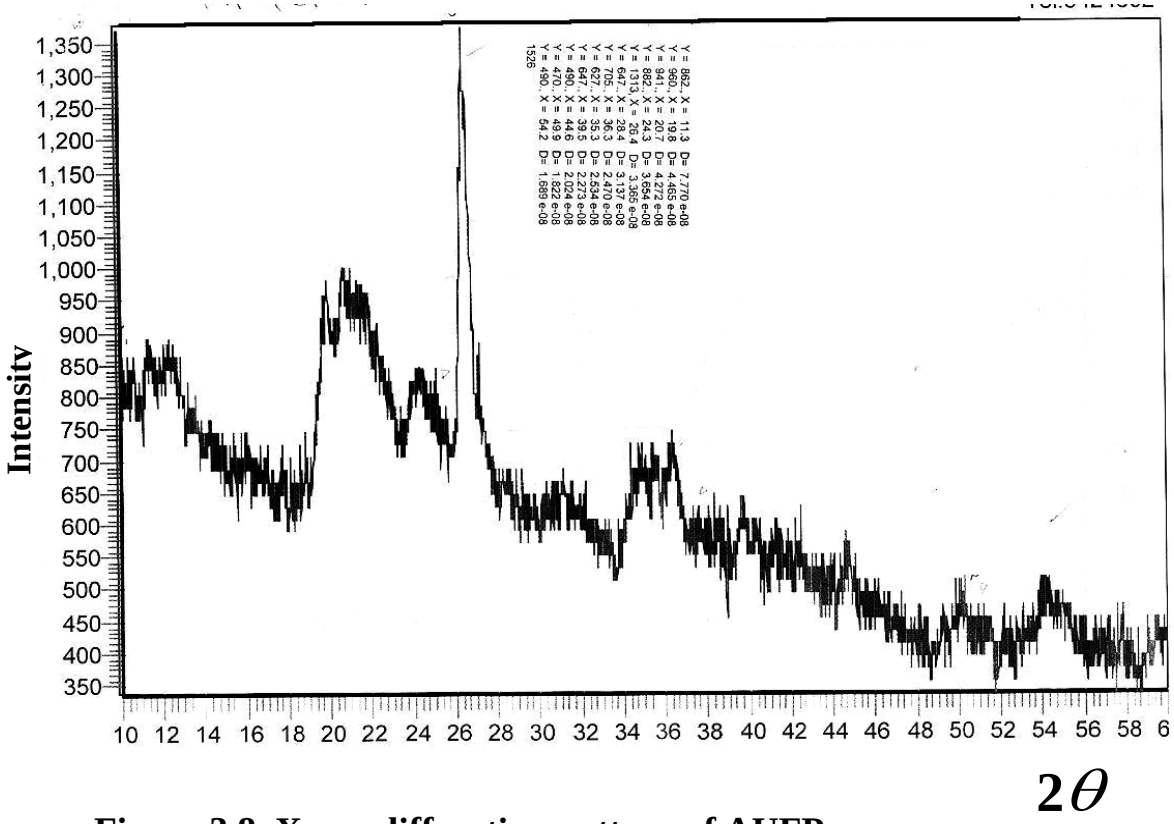


Figure 3.8. X-ray diffraction pattern of AUFP.

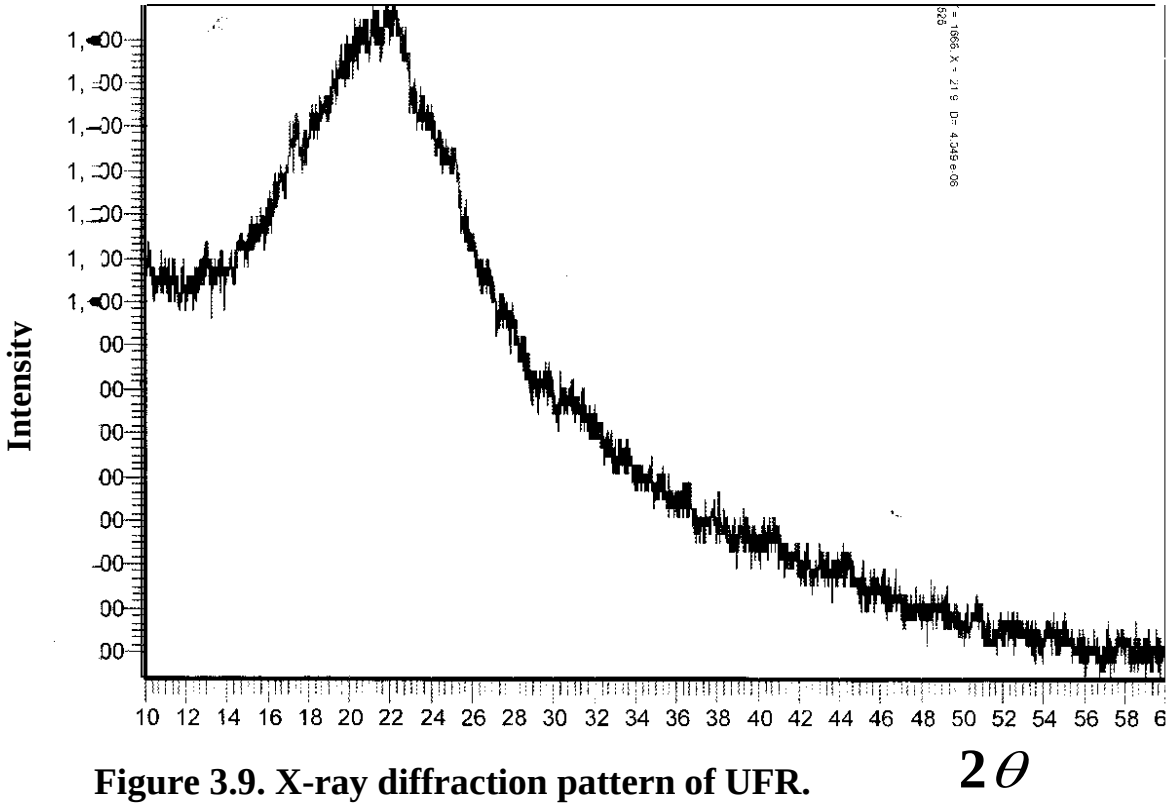


Figure 3.9. X-ray diffraction pattern of UFR.

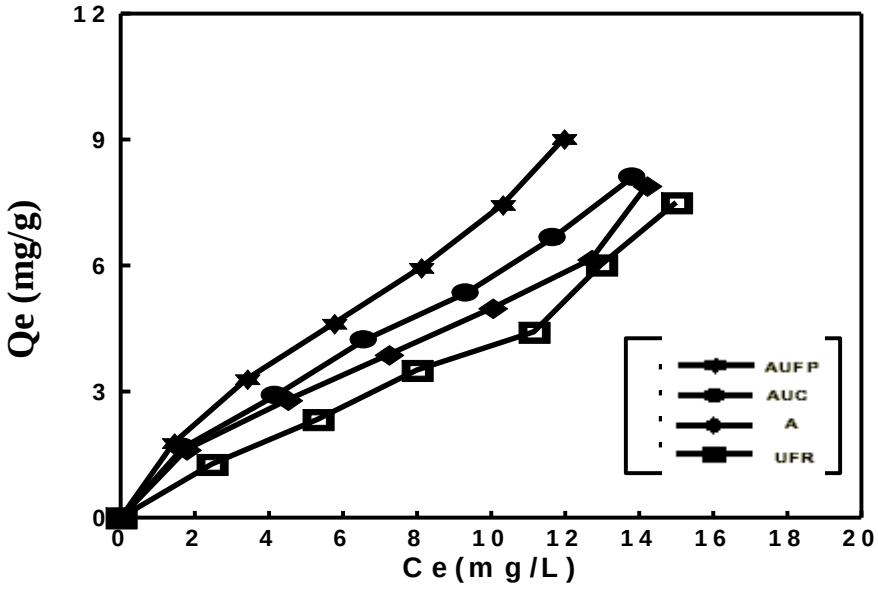


Figure 3.10. Adsorption isotherm of phenol on A, AUC, AUFP and UFR at 25 ^{0}C.

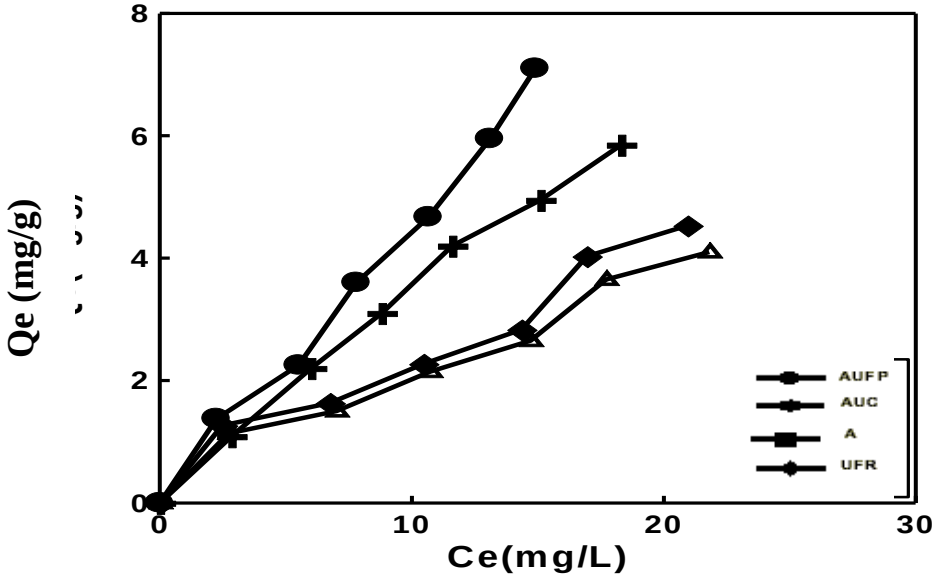


Figure 3.11. Adsorption isotherm of 2,3 dichlorophenol on A, AUC, AUFP and UFR at 25 ^{0}C.

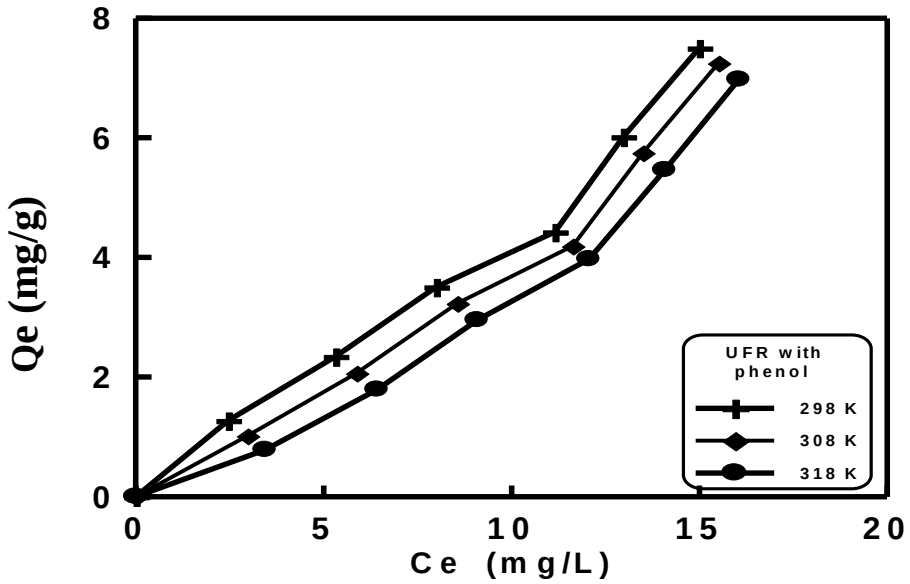


Figure 3.14. Temperature dependence of the adsorption of phenol on the UFR surface.

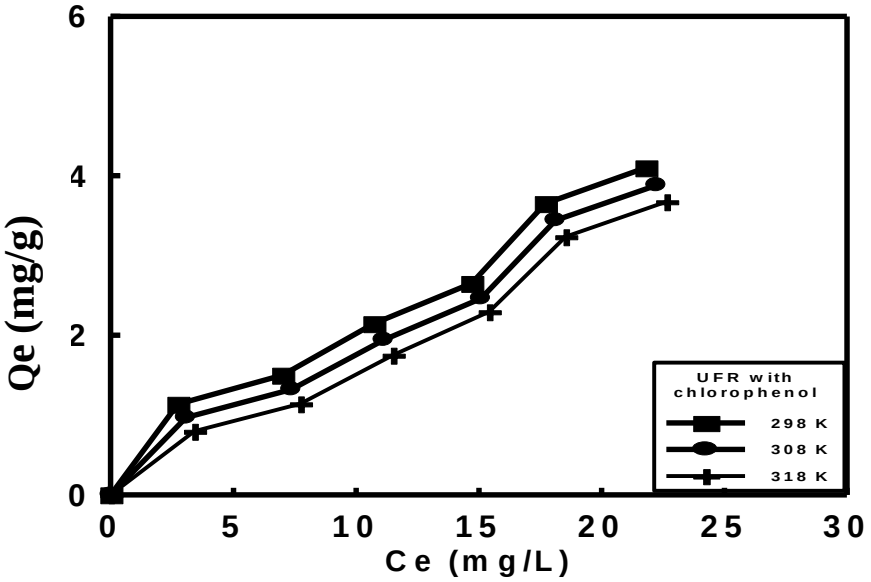


Figure 3.15. Temperature dependence of the adsorption of 2,3 dichlorophenol on the UFR surface.

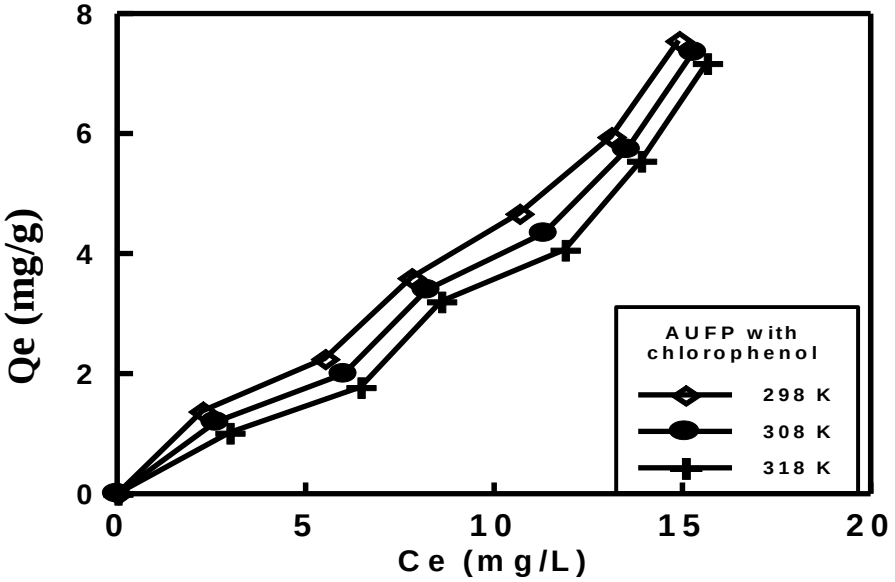


Figure 3.16. Temperature dependence of the adsorption of 2, 3 dichlorophenol on the AUFP surface.

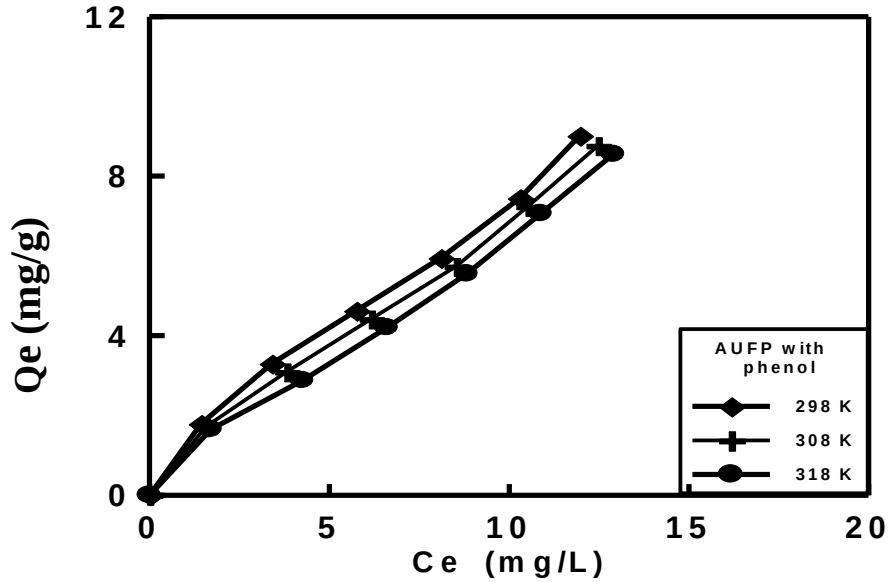


Figure 3.17. Temperature dependence of the adsorption of Phenol on the AUFP surface.

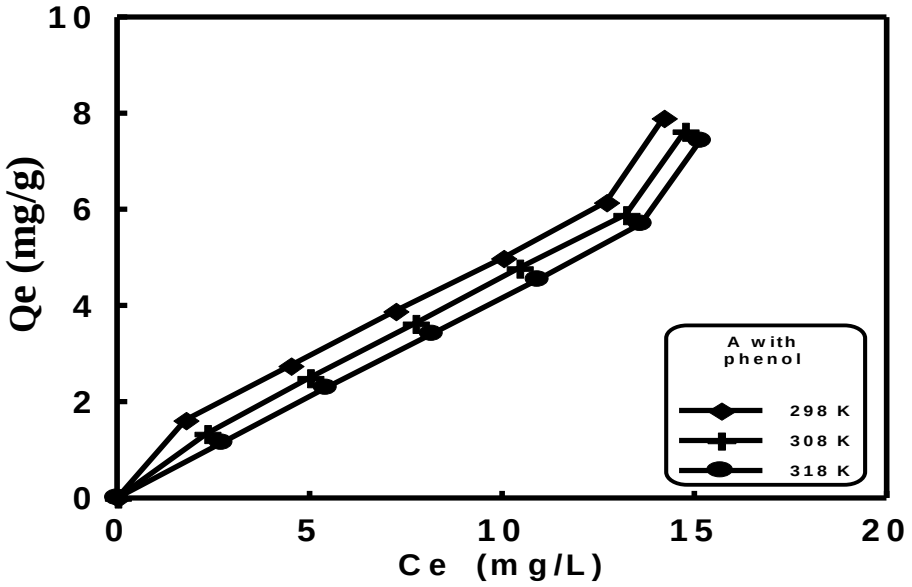


Figure 3.18. Temperature dependence of the adsorption of phenol on the A surface.

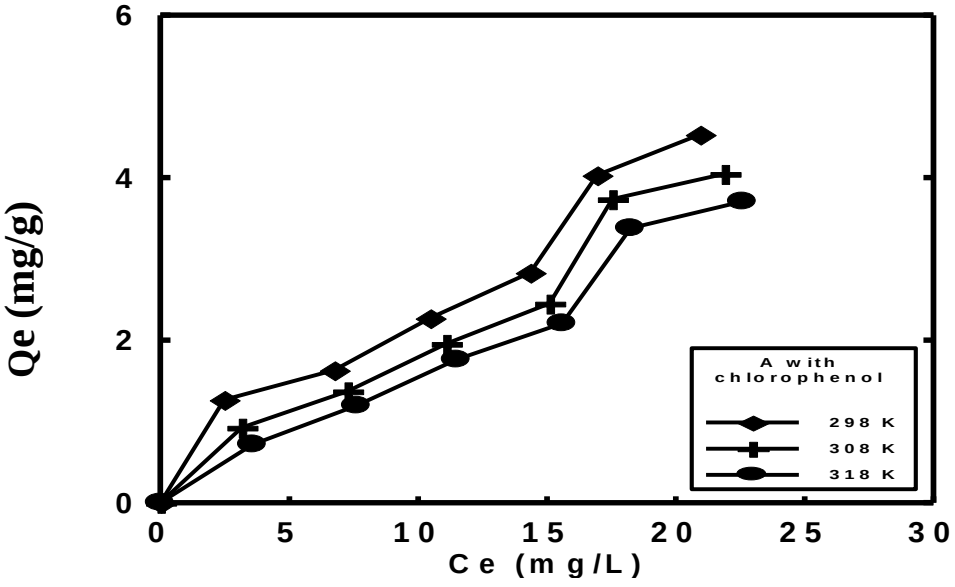


Figure 3.19. Temperature dependence of the adsorption of chlorophenol on the A surface.

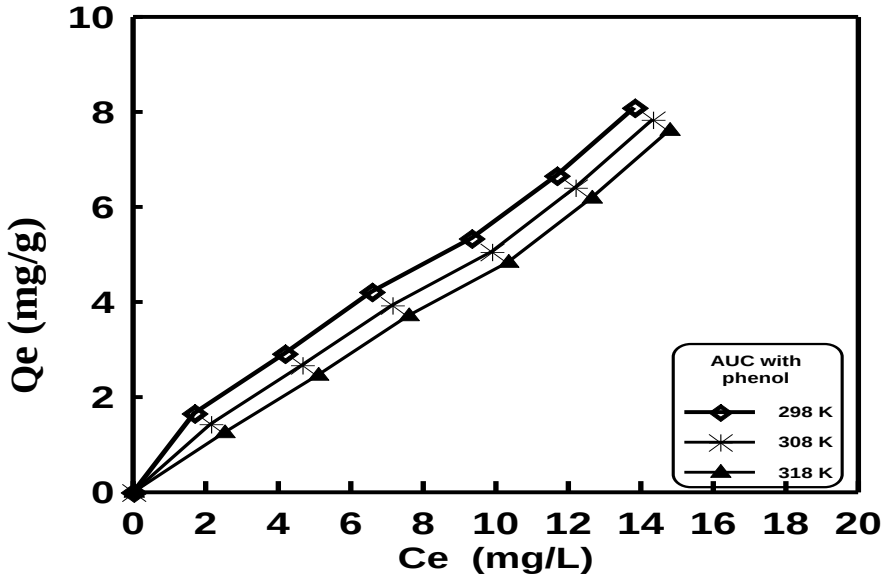


Figure 3.20. Temperature dependence of the adsorption of phenol on the AUC surface.

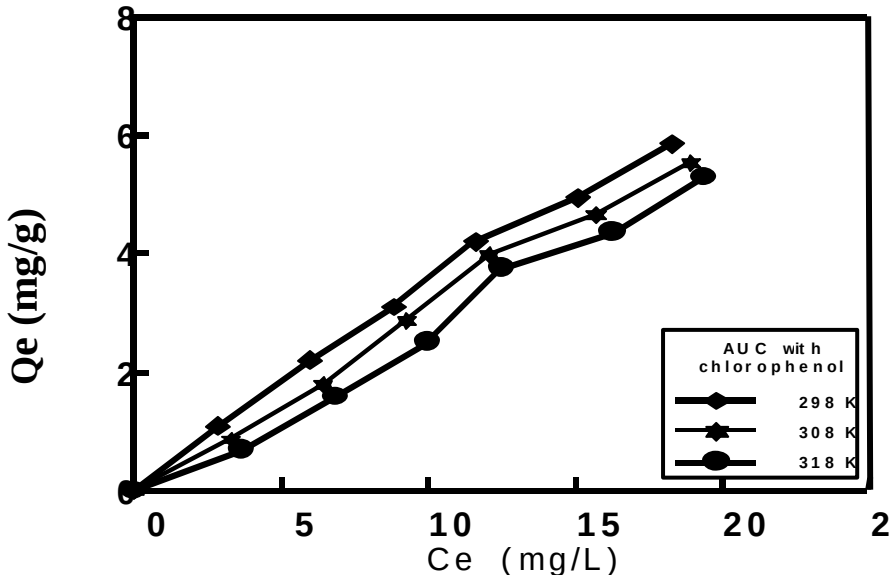


Figure 3.21. Temperature dependence of the adsorption of 2,3 dichlorophenol on the AUC surface.

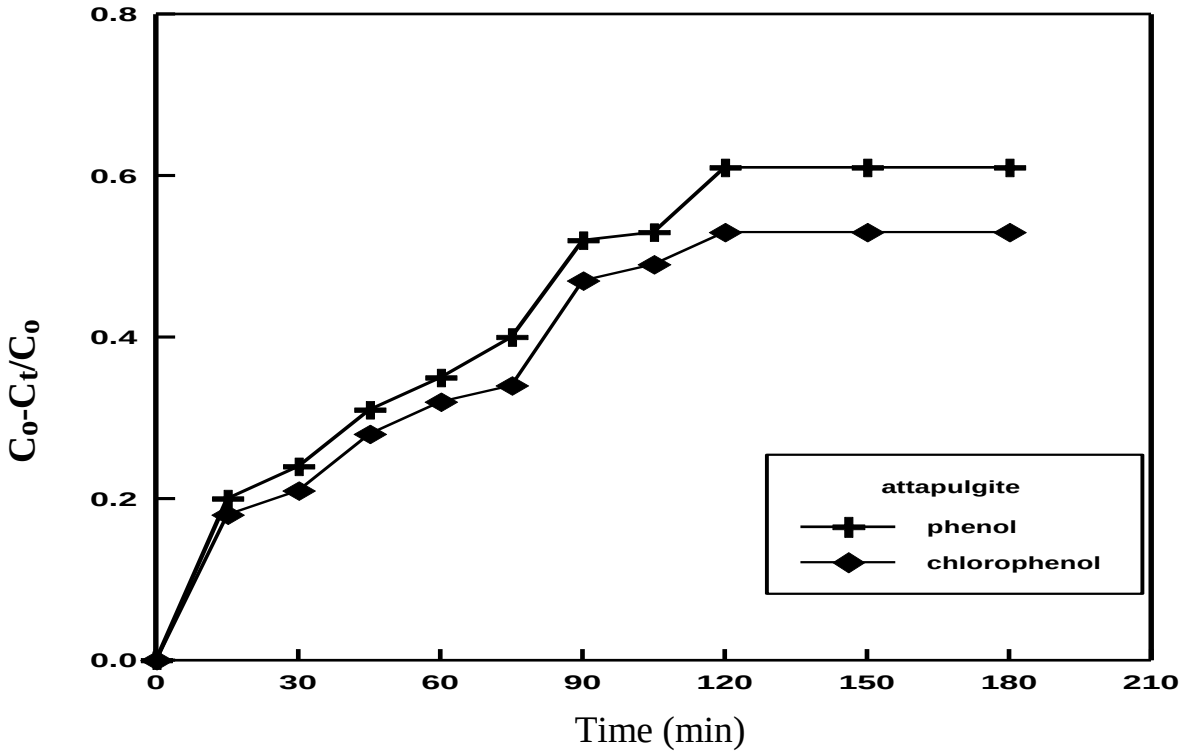


Figure 3.25. The uptake quantity of contact time of phenol and chlorophenol on the attapulgite surface at 298 K.

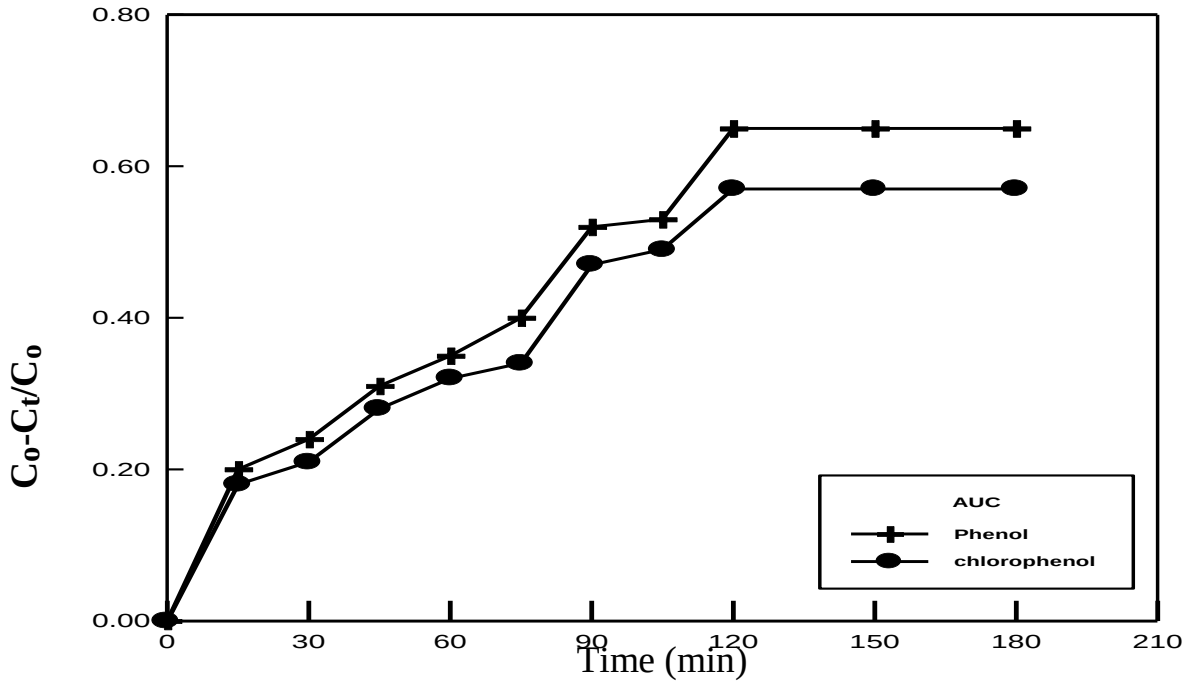


Figure 3.26. The uptake quantity of contact time of phenol and chlorophenol on the AUC surface at 298 K.

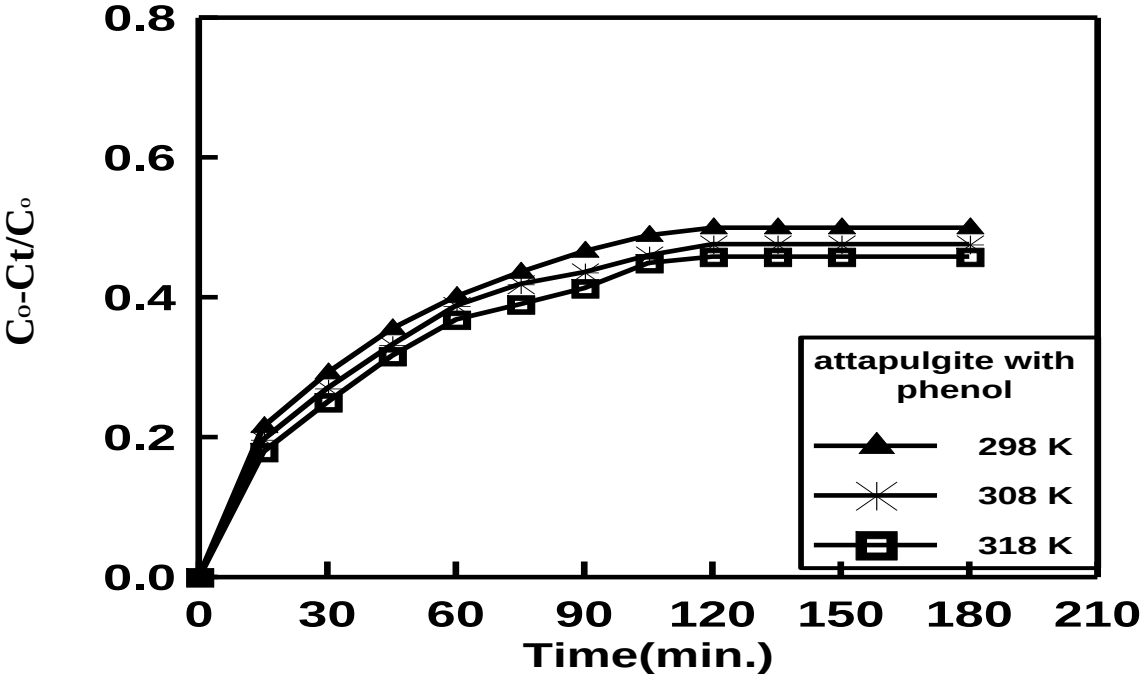


Figure 3.29. Temperature dependence of the contact time of adsorption of phenol on the attapulgite surface.

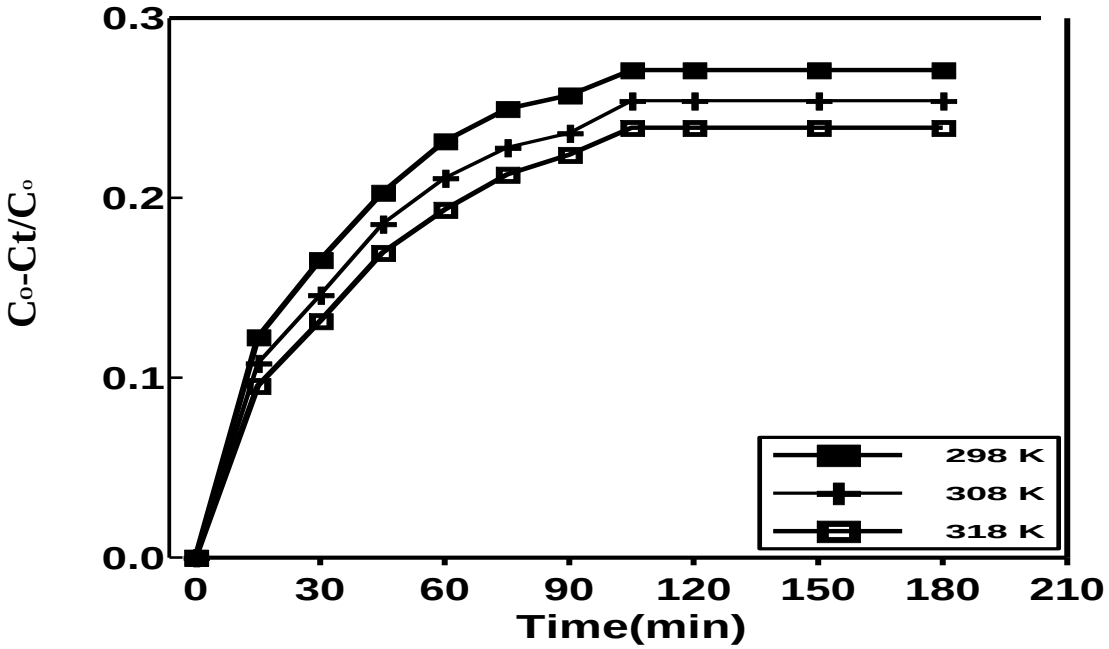


Figure 3.30. Temperature dependence of the contact time of adsorption of chlorophenol on the UFR surface.

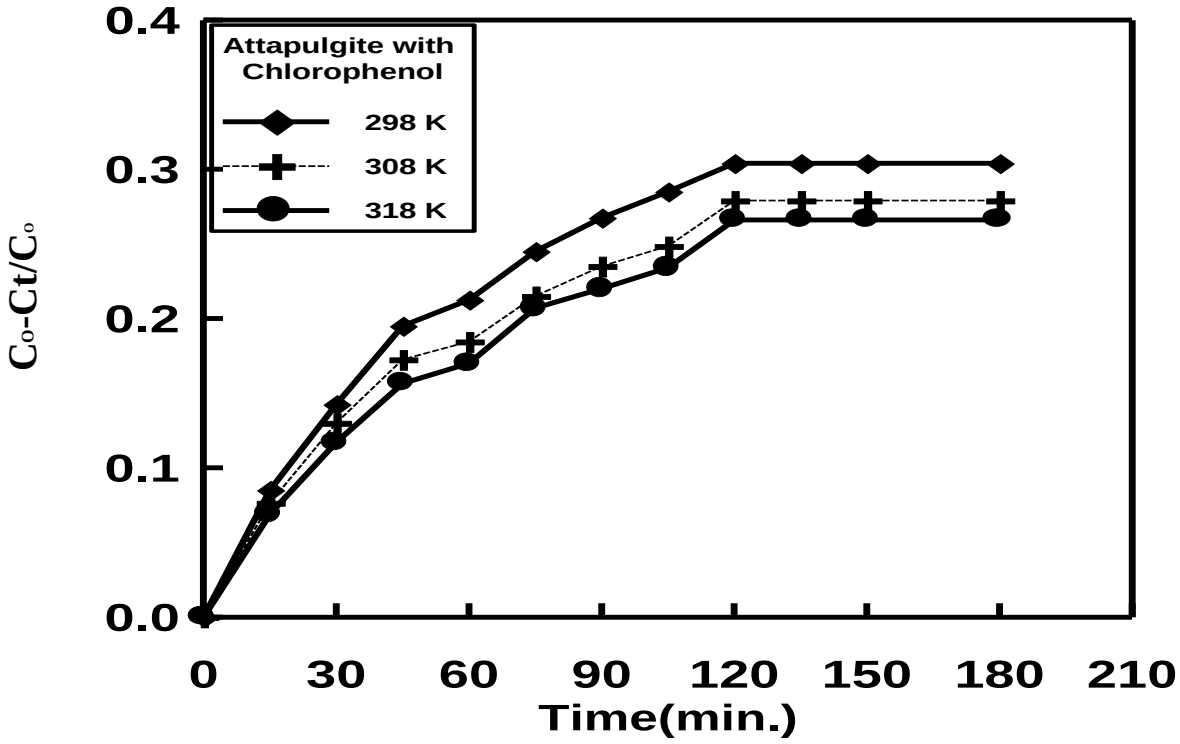


Figure 3.31. Temperature dependence of the contact time of adsorption of chlorophenol on the A surface.

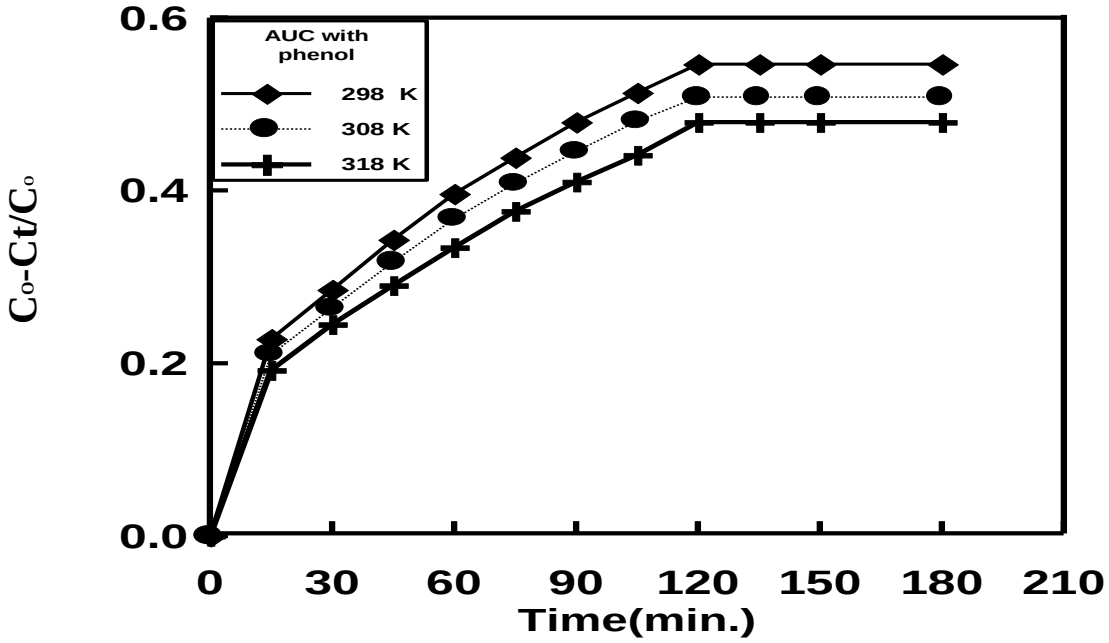


Figure 3.32. Temperature dependence of the contact time of adsorption of phenol on the AUC surface.

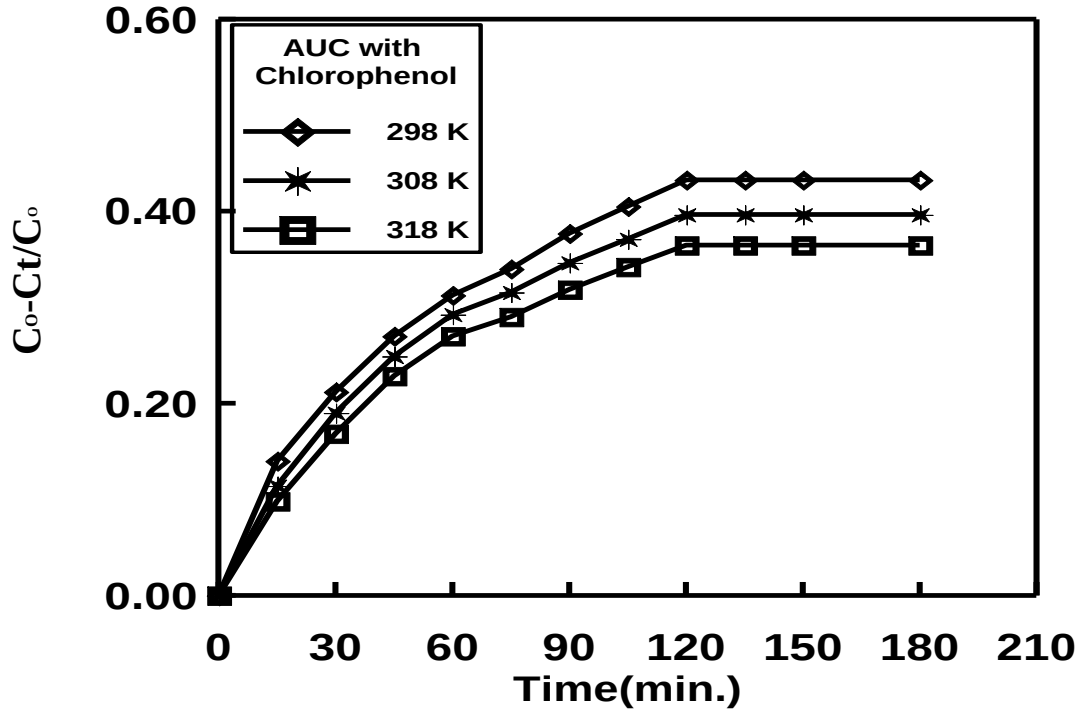


Figure 3.33. Temperature dependence of the contact time of adsorption of chlorophenol on the AUC surface.

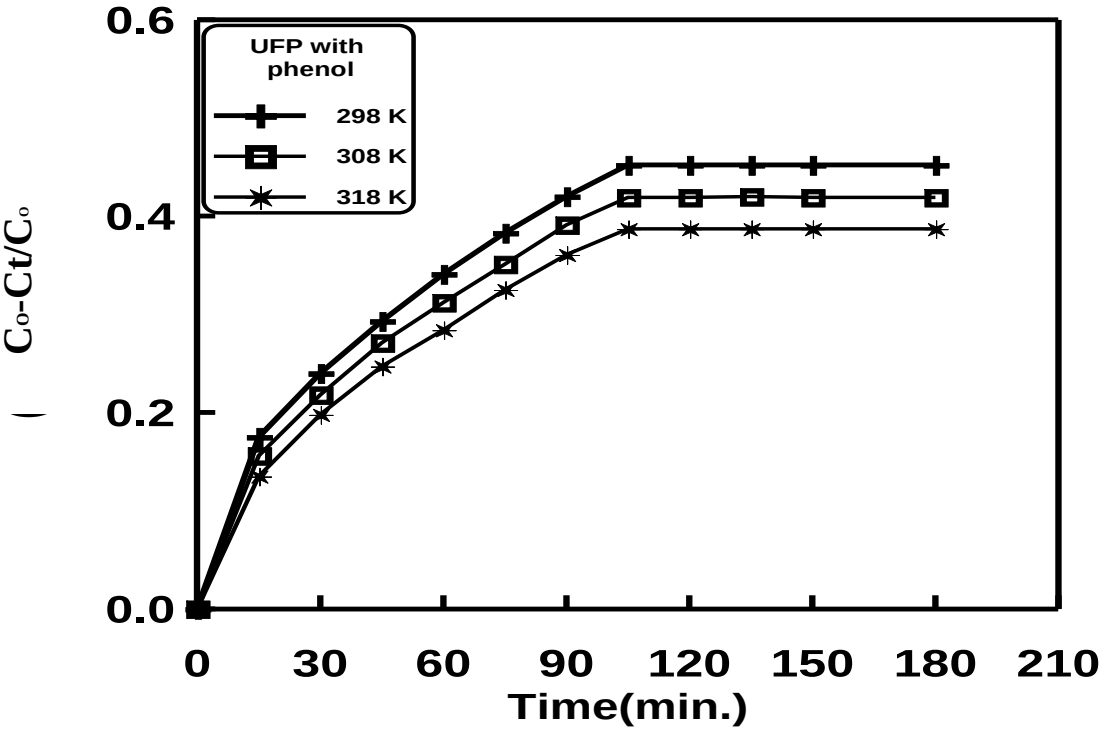


Figure 3.34. Temperature dependence of the contact time of adsorption of phenol on the UFR surface.

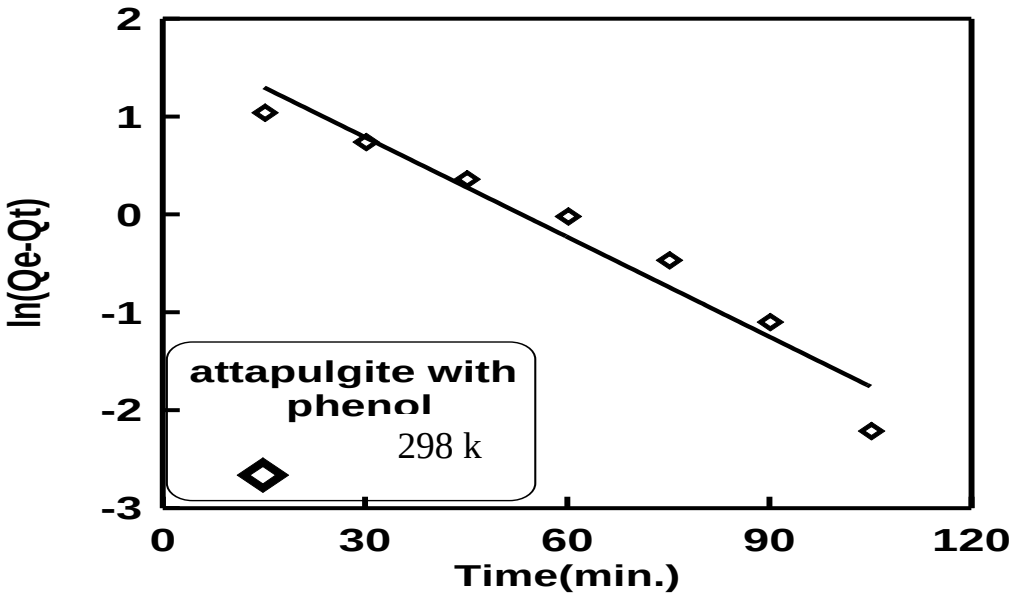


Figure.3.36. Kinetic adsorption of phenol on the attapulgite surface at 298 K.

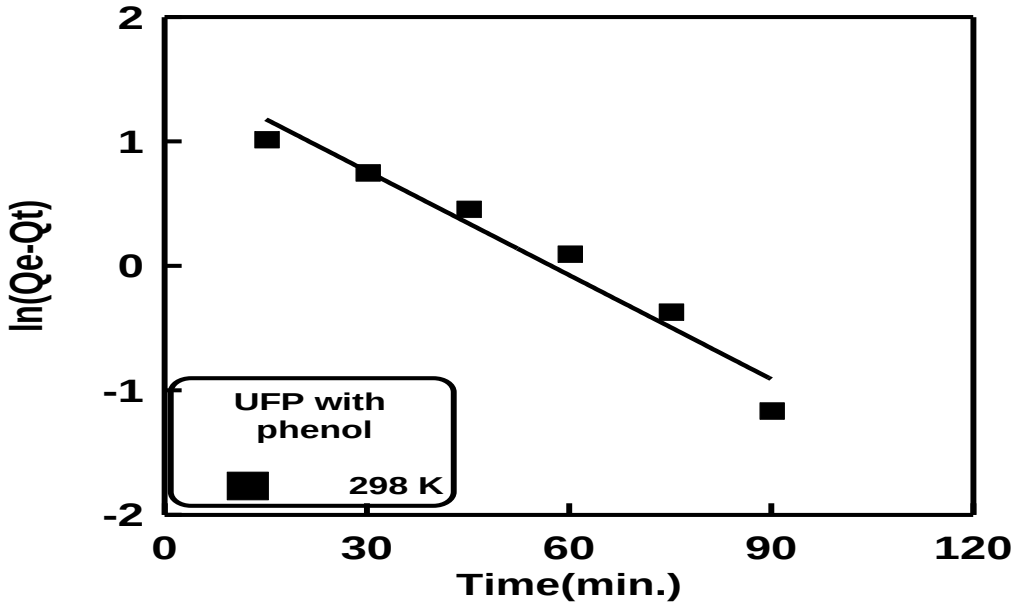


Figure.3.37. Kinetic adsorption of phenol on the UFR surface at 298 K.

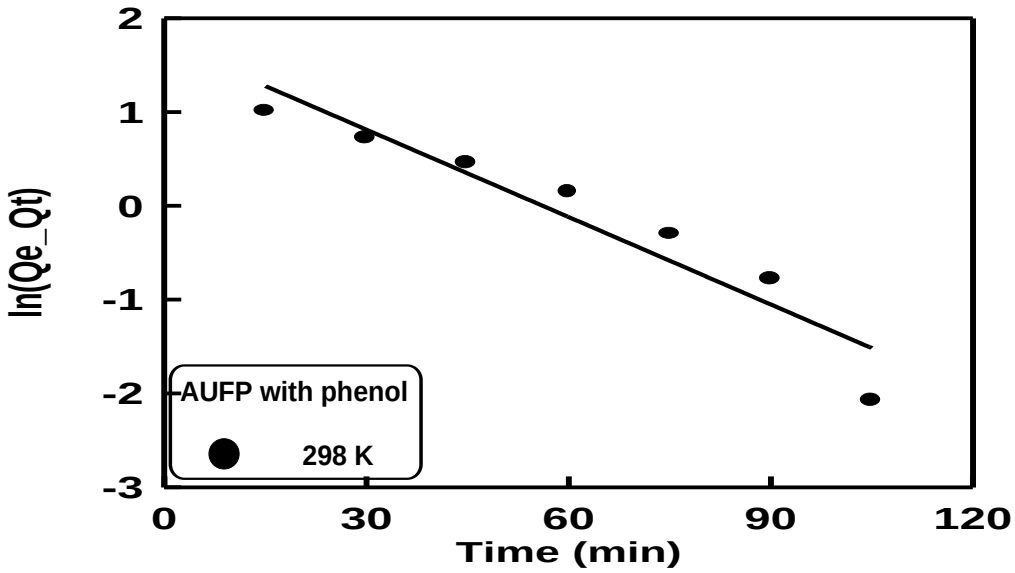


Figure.3.38. Kinetic adsorption of phenol on the AUFP surface at 298 K.

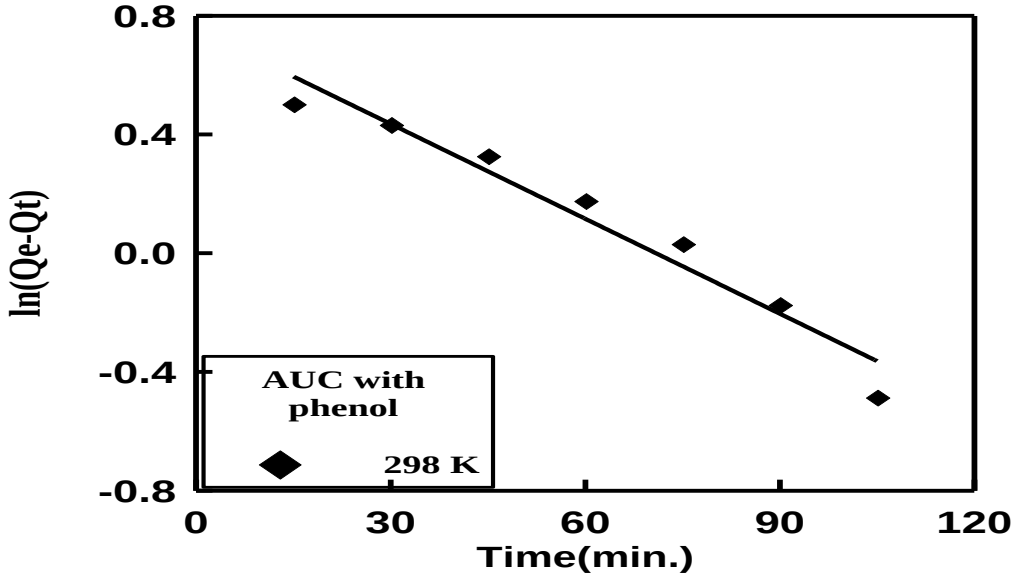


Figure.3.39. Kinetic adsorption of phenol on the AUC surface at 298 K.

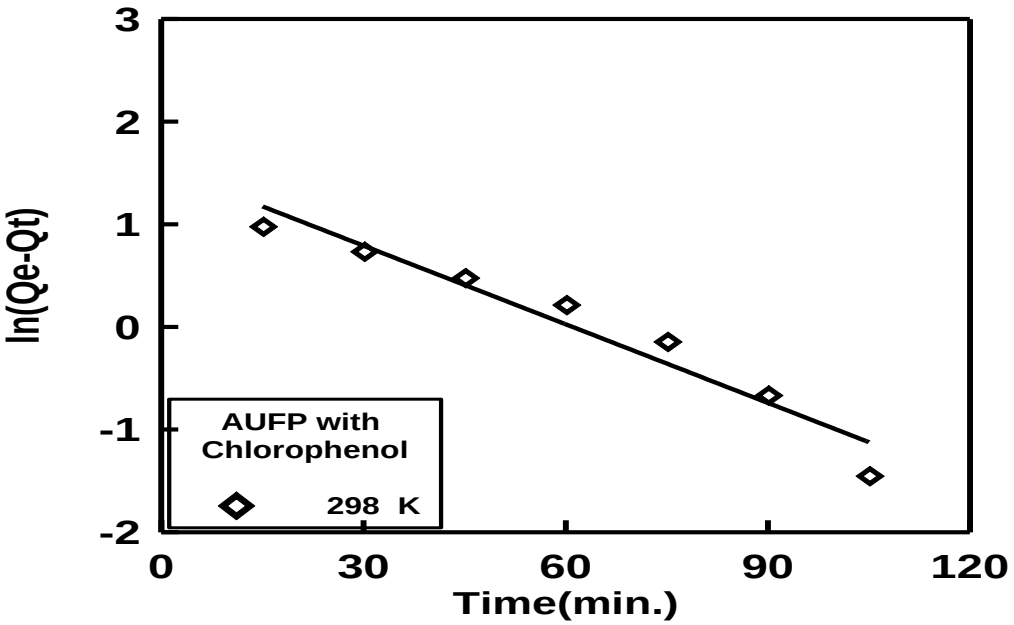


Figure.3.40. Kinetic adsorption of chlorophenol on the AUFP surface at 298 K.

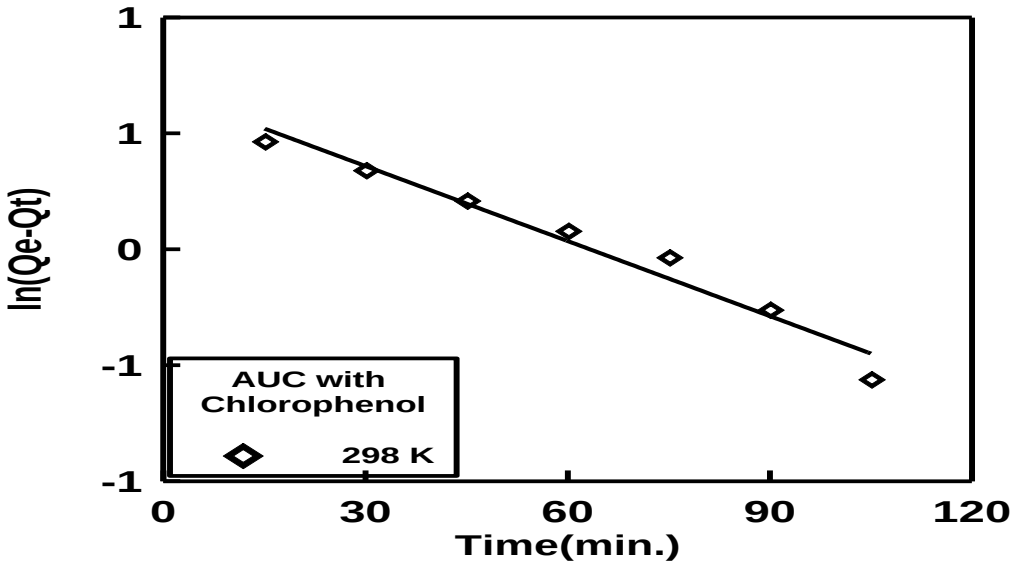


Figure.3.41. Kinetic adsorption of chlorophenol on the AUC surface at 298 K.

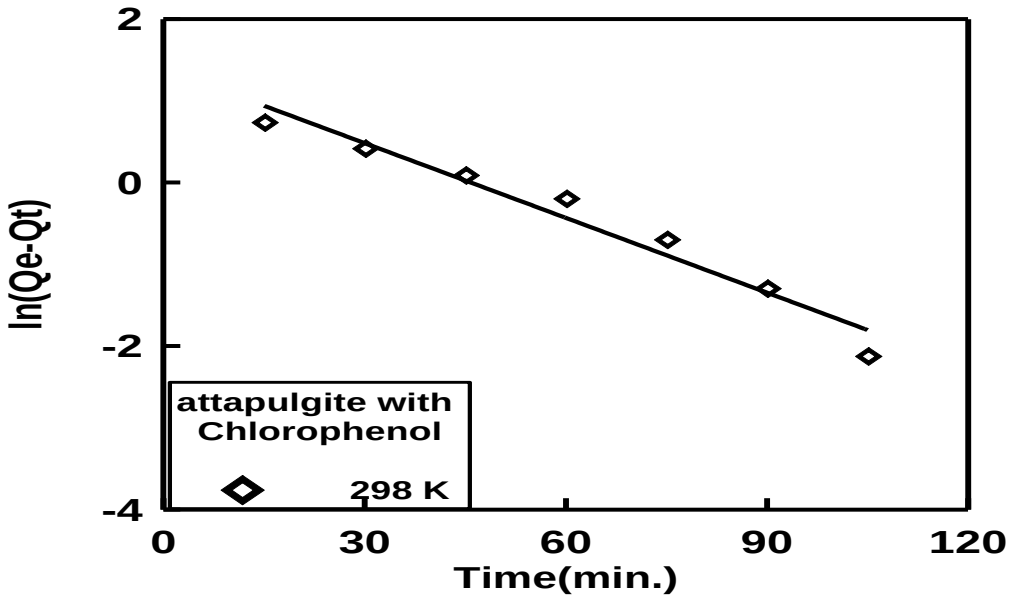


Figure.3.42. Kinetic adsorption of 2,3 dichlorophenol on the attapulgite surface at 298 K.

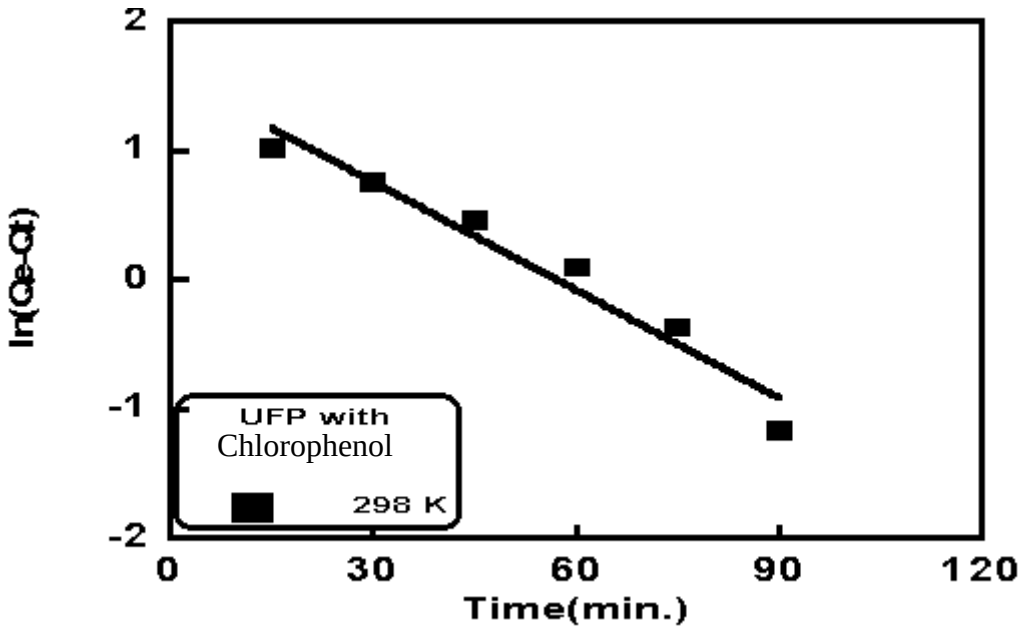


Figure.3.43. Kinetic adsorption of 2,3 dichlorophenol on the UFR surface at 298 K.

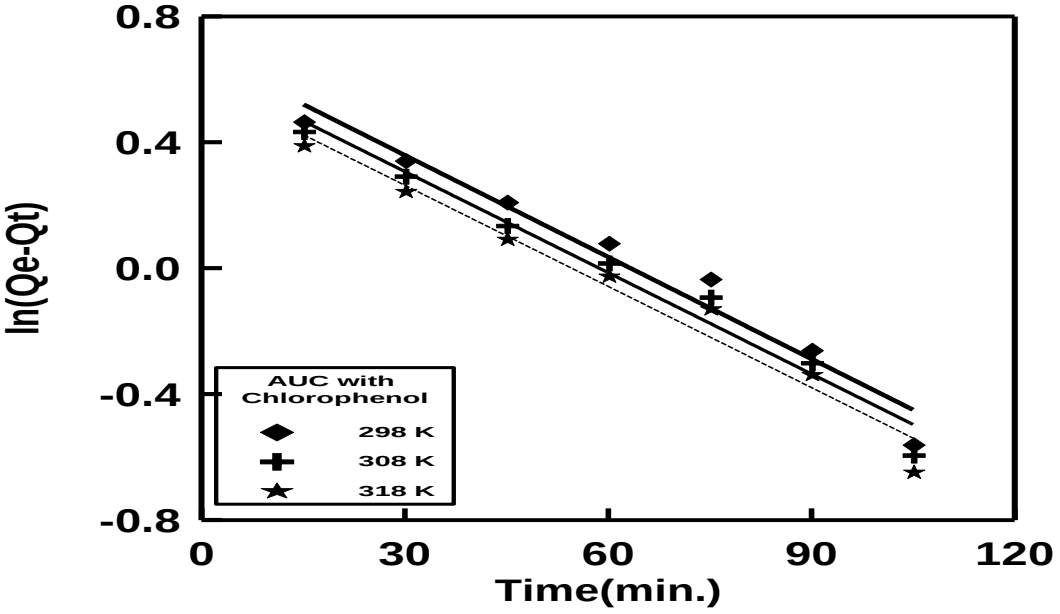


Figure. 3.44. Pseudo- first order adsorption kinetic of chlorophenol onto AUC at different temperature.

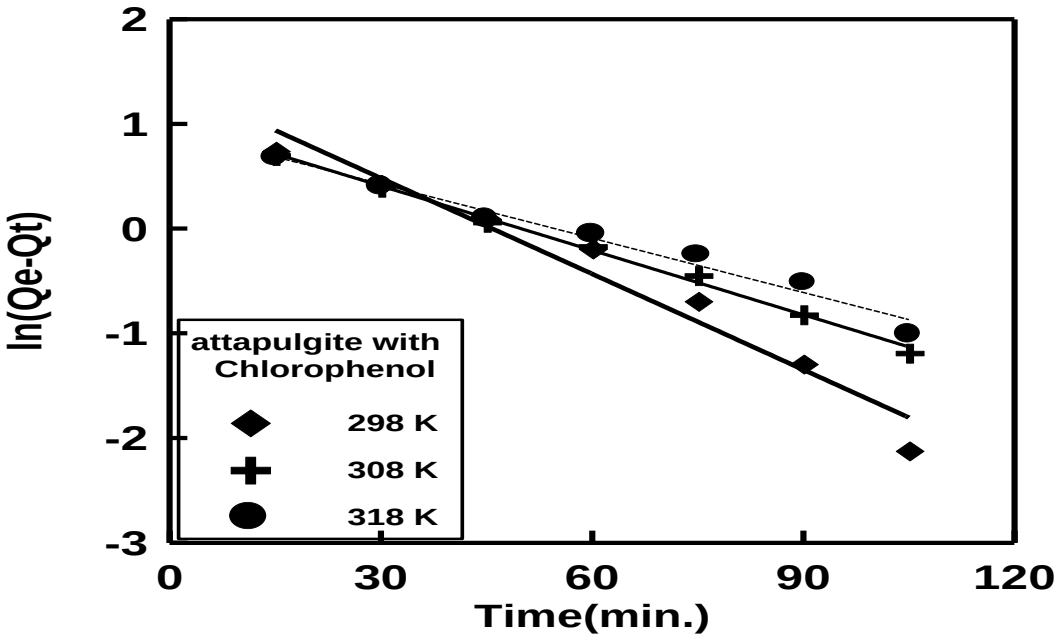


Figure. 3.45. Pseudo- first order adsorption kinetic of chlorophenol onto attapulgite at different

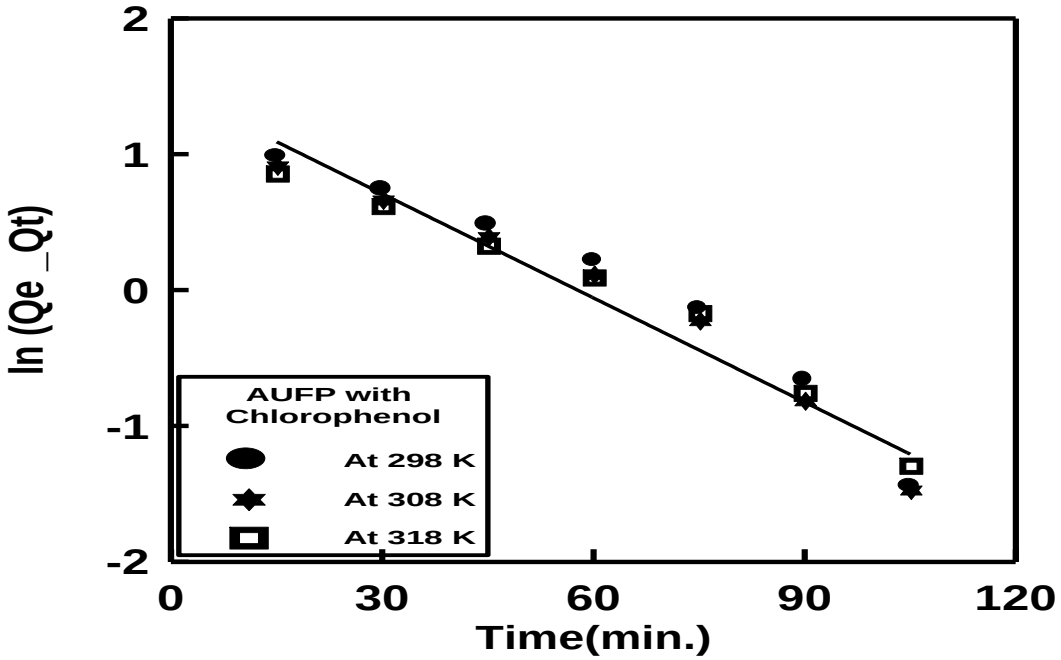


Figure. 3.46. Pseudo- first order adsorption kinetic of chlorophenol onto AUFP at different temperature.

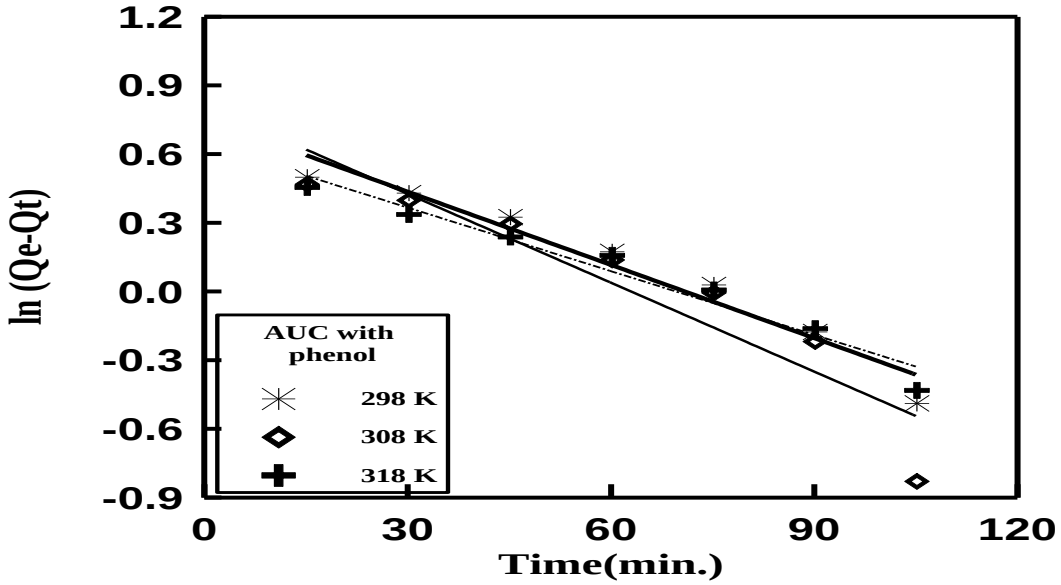


Figure. 3.47. Pseudo- first order adsorption kinetic of phenol onto AUC at different temperature.

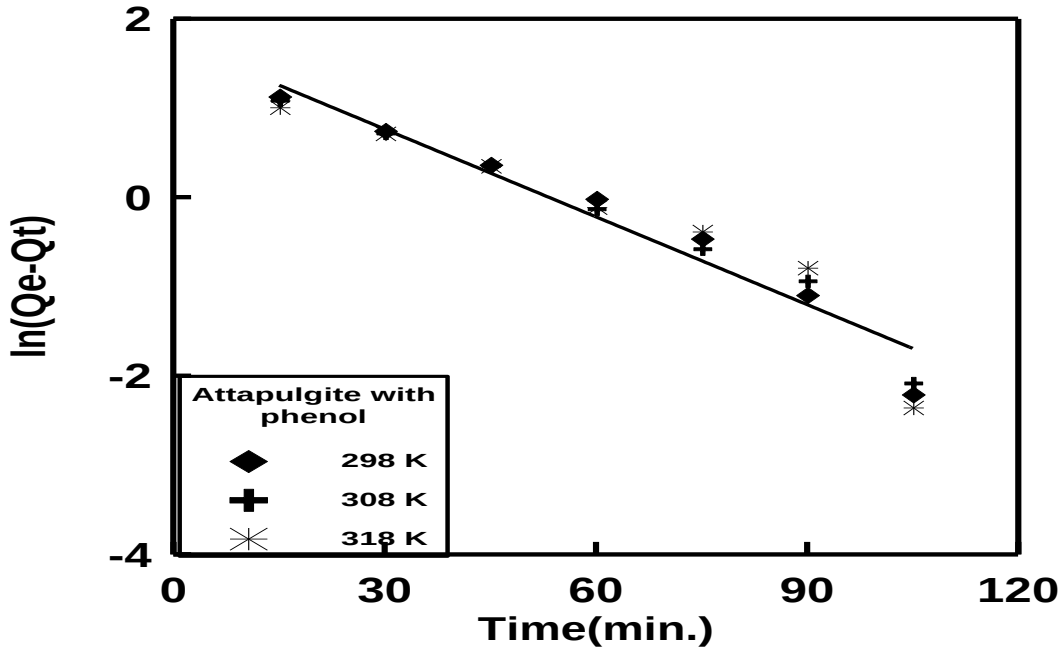


Figure. 3.48. Pseudo- first order adsorption kinetic of phenol onto A at different temperature.

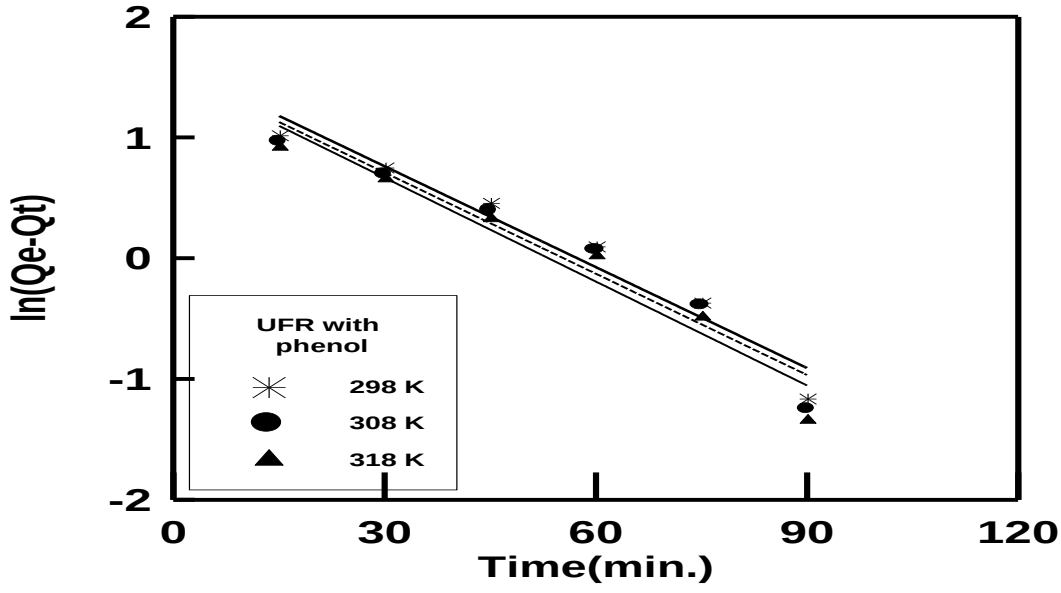


Figure. 3.49. Pseudo- first order adsorption kinetic of phenol onto UFR at different temperature.

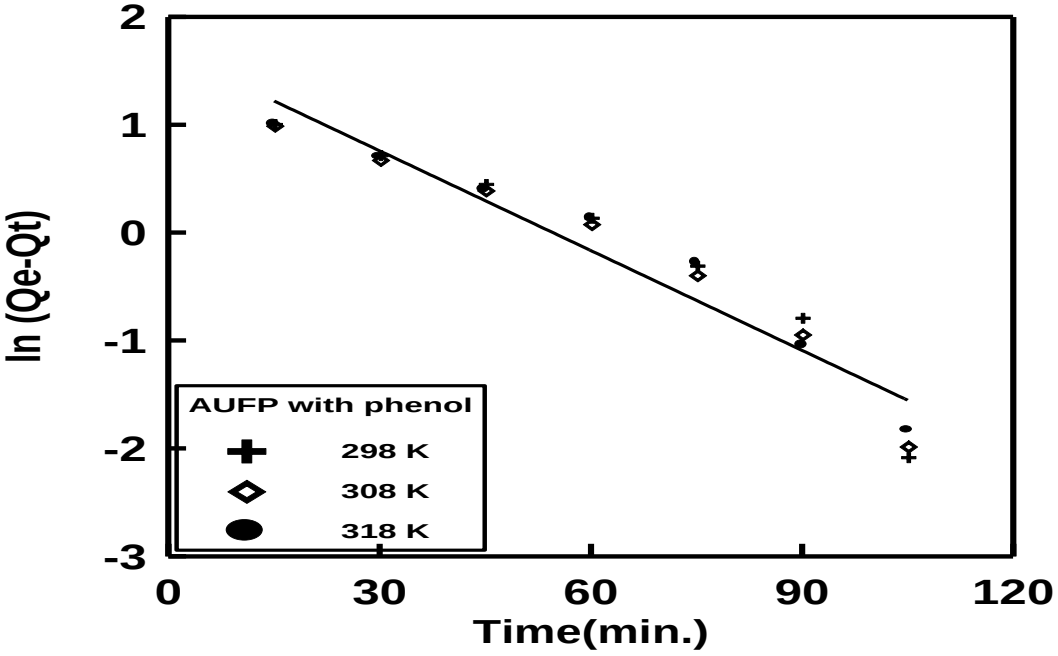


Figure. 3.50. Pseudo- first order adsorption kinetic of phenol onto AUFP at different temperature.

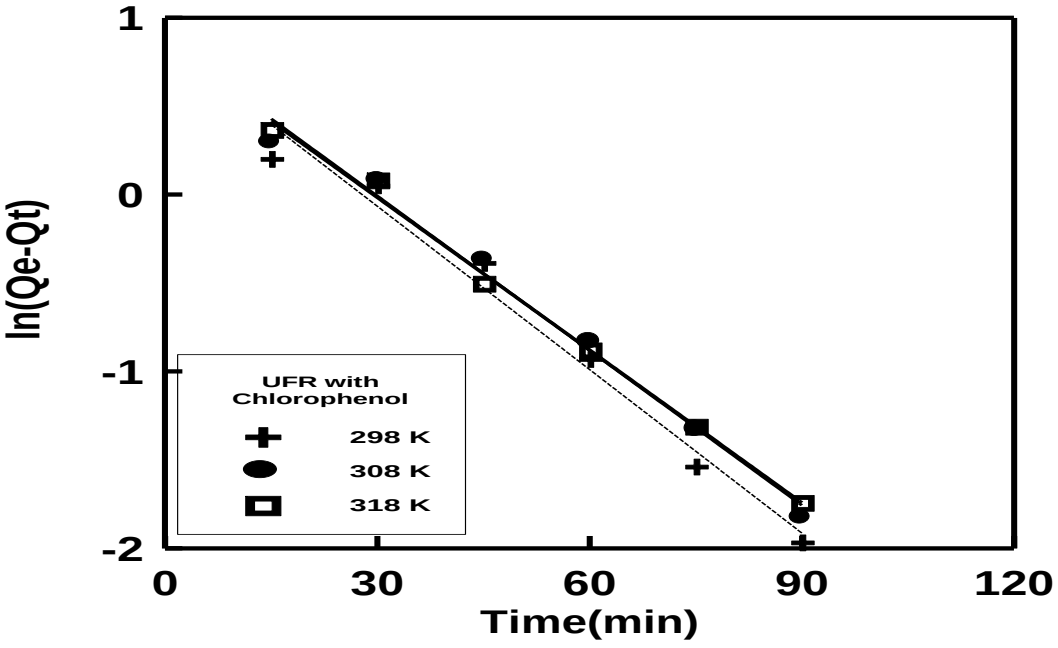


Figure. 3.51. Pseudo- first order adsorption kinetic of chlorophenol onto UFR at different temperature.

The Conclusions

1.The polymer AUFP was prepared by treating the clay with urea to form attapulgite-urea complex. The AUC the treated with formaldehyde to form the complex polymer AUFP, which has adsorption character properties.

2.the prepared adsorbents have been characterized by FTIR and UV/visible spectrometry.

3. The adsorption isotherms showed that the quantity of adsorption for phenol and chlorophenol by AUFP from their aqueous solutions increased on the four adsorbent surfaces by increased their concentration.

4. The adsorption of phenol and chlorophenol on the four adsorbent surfaces was of exothermic process.

5. The adsorptivity of phenol was better than that of chlorophenol on the four adsorbent surfaces (A, AUC, AUFP and UFR).

6. The adsorption capacity of phenol and chlorophenol on the AUFP and AUC were high when compared with UFR and attapulgite.

7. The adsorption kinetics of phenol and chlorophenol on the four adsorbent surfaces obeyed the pseudo-first order equation and showed that the adsorption was complex due to different factors that control the rate of reaction.

Chapter One

Introduction

1.1 Water Pollution

Water quality can be affected by different form of pollution, chemical, biological and physical [1]. These polluting factors can influence natural and human environment directly by creating conditions that limit water utilization for specific purpose. Where possible, states identify the pollutants that degrade water quality and indicators that document impacts of water quality degradation.

Indicators of water quality degradation include physical, chemical and biological parameters. Examples of biological parameters include species diversity and abundance. Examples of physical and chemical parameters include pH, turbidity and temperature.

1.2 The Main Types of Pollution

1.2.1 Chemical Pollution

Chemical pollutants can be divided into non-persistent pollution, degradable and persistent, degrade slowly. Persistent pollution is the most rapidly growing type of pollution and includes substances that degrades very slowly or cannot be broken down at all; they may remain in the aquatic environment for years or longer periods of time. Which include some pesticides (e.g. DDT deil drain), some leachate components from landfill sites, petroleum and ploy aromatic hydrocarbons. The damage they cause is either irreversible or reversible only over decades or centuries. Non persistent pollutants include domestic sewage, fertilizers, and some industrial wastes. These compounds can be broken down by chemical reactions or by natural bacteria into sample [2].

1.2.2 Physical Pollution

Physical pollution includes warm water from cooling towers (thermal pollution), floating debris, garbage and foam. In power plants that generate electricity is certainly the most important type of physical pollution. Power plants need cool water to start with and they generally release warmer water back to the environment. The temperature of the released water can affect downstream habitats. Temperature also can be affect on the ability of organisms to resist certain pollutants.

1.3 Advanced Methods of Water Treatment

The main aim from this treatment is to improve water. There are many methods for this aim such as using oxidation chemicals for water pollution treatment by using strong oxidizing agent as the ozone [6], molecular oxygen [7], and hydrogen peroxide [8]. Ditto the industrial resins can be used as an ion exchanger [9], or used the natural substances for the same purpose such as (zoelite)[10]. But when it found high concentration from the pollutants in water can use (chemical extraction method)[11] . Adsorption method on the surface of activated carbon, silica gel and porous clay can be used when the concentration of the polluted substances become very low, and can not be removed by methods used previously. [12.13].

1.5 Adsorption

Adsorption process can be defined as the attachment of particles to a surface [14, 15], or is the collection of a substance on to the surface of adsorbent solids [16]. It occur on the surface of the solid and results from valence forces or molecules in the outer – most layer of the solid which are not so fully utilized as in the interior of the solid. The extent of adsorption depends also on the

concentration or pressure and on the temperature [17]. There are two types of adsorption:

1.5.1 physical adsorption (physisorption)

There is a Van der Waals interaction, for example, a dispersion or dipolar interaction between the adsorbate and the substrate. Van der Waals interactions have a long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation. The enthalpy of physisorption can be measured by the monitoring the rise in temperature of sample of known heat capacity, and typical value is in the region of (20 kJ/mole). This small change is insufficient to lead to bond breaking [18]. So a physisorbed molecule retains its identity, although it might be distorted by the presence of the surface.

1.5.2 Chemical adsorption (Chemisorption)

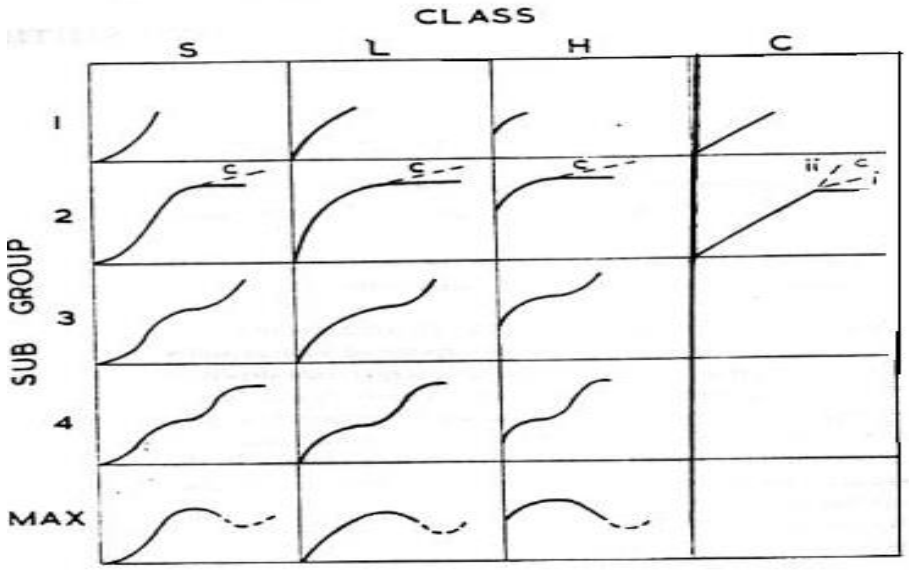
In chemisorption the molecules or atoms stick to the surface by forming a chemical "usually covalent " bond, and tend to find sites that maximized their coordination number with substrate, the enthalpy of chemisorption very much greater than for physisorption; and typical values are in the region of (200kJ/mole). The distance between the surface and the closest adsorbate atom is also typically shorter for chemisorption than for physisorption [15] The theoretical treatment of adsorption from solution, however is generally more complicated than that of gas adsorption, since adsorption from solution always involves competition between solute and solvent or, between the component of a liquid mixture for the adsorption site. Adsorption from solution behavior can often be predicted qualitatively in terms of the polar /non-polar, nature of their solid of the solution component. In solution, physical adsorption is far more common than chemisorption [19].

1.6 Adsorption Isotherm

The variation of amount of solute adsorbed by a given amount of adsorbent (Q_e) with pressure or concentration at chosen temperature is called the adsorption isotherm [15]. It is standard method for characterizing the adsorption capacity of adsorbents and is constructed for equilibrium adsorption of individual components over arranges of concentration [20]. Graphic representation of the adsorption isotherm obtained by plotting Q_e against the equilibrium concentration of solute in the liquid phase after it attains equilibrium.

Classification of isotherm is a stated necessary to their theoretical treatment and interpretation. A classification system of solid solute adsorption (SSA) isotherms has been described by Gilles and co-workers [21] as represented in Figure 1.1. They divided them all by their initial slope into four main classes, termed for convenience, the S-curve, slope at first increases with concentration because in cooperative adsorption, sites capable of retaining a solute molecule increase, i.e., The S-curve formation by competition of an adsorbed impurity and refers to highly polar adsorption. S-curve is usually taken to mean an end – on orientation provided the possibility of the competitive effects[22] . L, Langmuir, L-curve, there are relatively strong attractive forces between solute molecules and substrate but very week forces between solute molecules themselves, H (high affinity), H -curve can be happen if the cooperating molecules move as a large unit from solvent to substrate and C (constant Partition) classes in all other C -curve systems so far discovered, there is good reason to believe that the solute initiates the adsorption by penetrating into the structure of the substrate, and farther into several sub groups (1, 2, 3, etc) or max by subsequent variation as shown in Figure 1.1. Curves in subgroup 1 represent systems in which the adsorbate monolayer has not been completed. In subgroup 2 and higher we confidently the plateau.

Equilibrium Concentration of Solute in Substrate.



Equilibrium Concentration of Solute in Bath.

Figure 1.1. Gilles classification of adsorption isotherm.

1.6.1 Langmuir Equation:

The adsorption process can be written as:

N_2 (solute in solution) + N_1^S (adsorbed solvent) = N_2^S (adsorbed solute) +

N_1 (solvent in solution) (1.1)

The equilibrium constant K for this process is

$$K=(N_2^S a_1 / N_1^S a_2) \quad (1.2)$$

Where a_1 and a_2 are the solvent and solute activities in solution, the activities in the adsorbed layer are given by the respective mole fractions N_2^S and N_1^S.

Since the treatment is restricted to dilute solutions, a_1 is constant, and we can write $b=K/a_1$; also $N_1^S + N_2^S = 1$, so that equation 1.2 becomes

$$N_2^s = \frac{n_2^s}{n^s} = \theta = \frac{ba_2}{1+ba_2} \quad (1.3)$$

Where θ is the fraction of surface occupied by solute and $n_2^S = n^S N_2^S$, where n^S is the number of moles of adsorption sites per gram. In sufficiently dilute solutions, the activity coefficient, a_2 can be replaced by C_2.

$$N_2^s = \frac{n_2^s}{n^s} = \theta = \frac{bC_2}{1+bC_2} \quad (1.4)$$

At sufficiently high concentrations, n_2^S approaches the limiting value n^S. Thus n^S is a measure of the capacity of the adsorbent and b of the intensity of the adsorption .the two constant n^S and b are conveniently evaluated by putting equation 1.4 in the form

$$\frac{C_2}{n_2^s} = \frac{1}{bn^s} + \frac{C_2}{n^s} \quad (1.5)$$

that is, a plot of C_2 / n_2^S versus C_2 should give straight line of slope $(1/n^s)$ and intercept $(1/bn_s)$ [23]. Equation 1.5 represents the Langmuir equation for adsorption in solution. Also, we can write the linear form of this equation as:

$C_e /x/m = 1/kv_m + C_e /v_m$ (1.6)

Where C_e is the equilibrium concentration; x is the amount adsorbed per a unit weight m of clay; k and v_m are constants, the latter being identifiable with the monolayer capacity of the adsorbent. Conformity of data to equation 1.5 is indicated by the straight line observed when (C_e/x/m) is plotted against C_e. Plotting, C_e/x/m (C_e /Q_e) viruses C_e gives straight line of slope $1/v_m$ and intercept $1/kv_m$ as shown in figure 1.2 However, this in itself does not provide information on the mechanisms of adsorption [24].

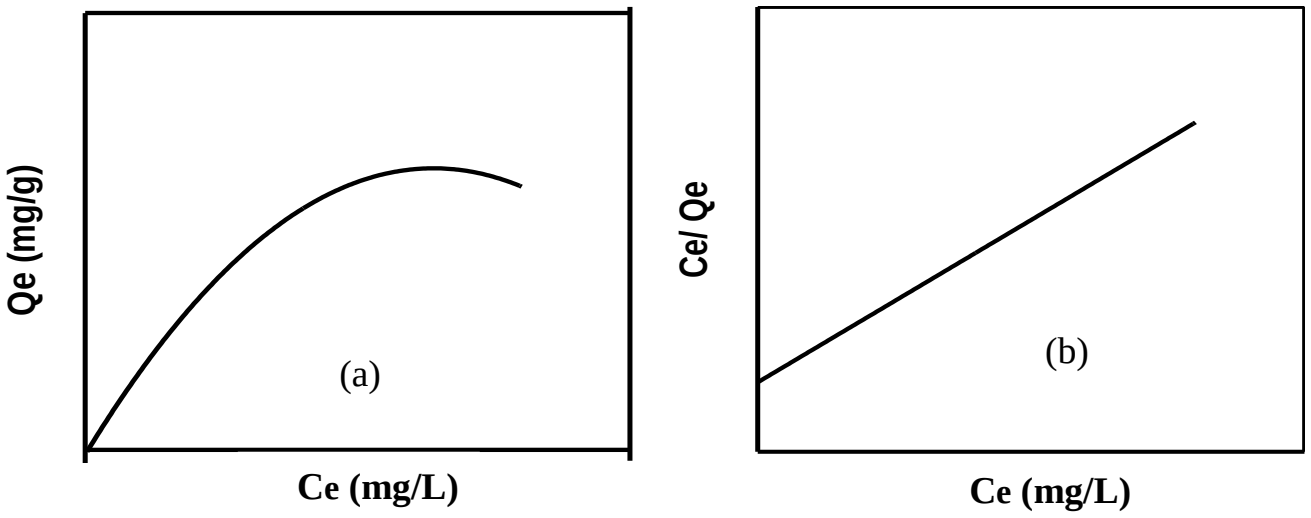


Figure 1.2 (a) Langmiur isotherm, (b) The linear form of Langmuir isotherm.

1.6.2 The Freundlich Equation

The Freundlich equation is an empirical expression used to describe adsorption isotherms. The equilibrium adsorption data could be described satisfactorily by the Freundlich isotherm:

$X/m = k. C^{(1/n)}$ (1.7)

Where X is the amount adsorbed per a unit of adsorbent (m); C is the equilibrium concentration of the adsorbate in the liquid phase [25]. The constant K and n in

equation (1.8) are determined by measuring (X/m) as a function of C. as shown in figure (1.3a), and when plotting log (C) on the abscissa and log (x /m) on the ordinate, and finding the slope (equal to 1/n) and ordinate intercept equal to log (K) of the best fit line through the experimental point as shown in equation below:

$$\log (Q_e) = \log K + 1/n \log C_e \qquad (1.8)$$

The constant K, partition coefficient in equilibrium is positively related to the extent or degree of adsorption or adsorbent capacity. While the constant (n) provides a rough estimation of the intensity of adsorption [26] .The Freundlich equation is especially useful, where the actual identity of the adsorbate is not known .The disadvantage of using the Freundlich plot is that, it is only useful for limited adsorbate concentration ranges and it has limited predictive ability with regard to adsorption isotherms for similar adsorbate.[20]

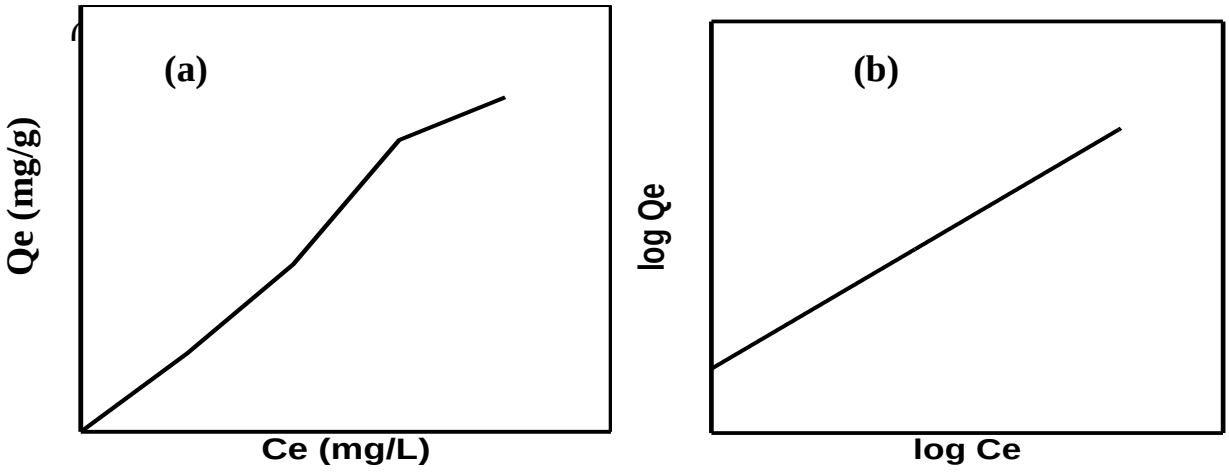


Figure 1.3. (a) The Freundlich isotherm,(b) The Freundlich linear isotherm.

1.7 Factor Influencing Adsorption Process

1.7.1 Concentration of Adsorbate

In general when the concentration of adsorbed increases the capacity of adsorption increases [27], but in some cases, adsorption may be confined to only one layer of adsorbed molecules. Further increase of concentration of adsorbate can produce no further adsorption because the surface of the crystal lattice of adsorbent is covered.

1.7.2 Surface Area of Adsorbent

The dominate factor of adsorption for substance is the specific surface area and pore volume [28], therefore when the surface area increases it refers to high active sites that cause increase in the capacity of adsorption [29].

1.7.3 Temperature

The important factor of adsorption is the temperature, when increases, the effective layers thickness for adsorption decreases. That means The adsorption process in general (exothermic) [15].

1.7.4 Effect of pH

pH plays a major role in the phenomena of adsorption, the ability of adsorption may increase, decrease, or remain unchanged as a result of changing pH.Many variables can take part in this process, such as, the nature or chemical state of the adsorbent, adsorbate and solute .The adsorption of the adsorbent presents an optimum for a pH understood the capacity of adsorption change with the pH [30].

1.7.5 Ionic Strength

The solubility of ionic salts is effected in adsorption process, because when the ionic salts having solubility are better than the adsorbent substances caused increased in adsorption [31], or decrease because the ionic salts caused interference

on the surface adsorption [32].

1.7.6 Effect of Agitation Velocity

The increase of the agitation velocity acts favorably on the adsorption. It is obvious that the effect of agitation speed cannot be indefinite and quantities adsorbed at equilibrium (Q_e) seem tender toward the values constant for greater speed. Indeed, after certain speed limits, the effect must become constant when the phenomena of mass transfer is not limited by diffusion [30].

1.8 The Clay

Clays are composed mainly of silica, alumina, and water; frequently with appreciable quantities of iron, alkalis, and alkali earth [33] .Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of closely packed oxygen or hydroxyls in which alumina, iron or magnesium atoms are embedded in one octahedral combination, so that they are equidistant from six oxygen's or hydroxyls. The second unit is built of silica tetrahedrons. Which are arranged to form a hexagonal network that is repeated indefinitely to form a sheet of composition $SiO_6(OH)_4$ [33]. The surface oxygen in layer silicates, however, is a weak electron donor. The (Si - O) bond, of prime important, is marked by a considerable degree of polarity [34]. Every silicon atoms is a tetrahedral arrangement, the second valence of the oxygen atoms, as a rule, links them either to another atom of silicon or to on atom of a metal such as aluminum. In the latter case the oxygen atoms become monovalent negative ions. In more complex cases the silicate groups are linked up forming planner networks or three–dimensional structures that comprise the framework of the crystal [35].

1.9 Classification of Clay Mineral

The most common clay minerals can be classified into five groups:

A –Sepolite (sepolite, and palygorskite "attapulgite").

B – Illite (illite, and glauconite).

C-Smectite (montmorillonite, beidellite, and nontronite).

D – Kaolinite (kaolinite, halloysite, and others).

E – Chlorite (chlorite and others). [36].

1.9.1 Attapulgite Clay

Attapulgite structure is commonly called a chain layer. It is unique mineral structure that manifests ribbons of alumino–silicate layers to be joined at their edges. Attapulgite crystals are needles shaped (circular) rather than flat or flake – like [37], which have high surface area [38]. Attapulgite is superior kaolinite, because it is an open structure enclosing channels into which organic compound [39,40]. It is composed of arimorphic layer arranged in chain (bands) which are joined through oxygen. It has smaller trimorphic unit, intermediate between di – and trioctahedral in character. These minerals have been considered to belong to the category of (chain –lattice silicates). However; since they bear a closer relationship to the phyllosilicates than to the chain silicates [24].

Phyllosilicates are essentially made up of layers formed by condensation of sheets of linked $Si(O,OH)_4$ tetrahedral with those of linked $M_2(OH)_6$ octahedral, where M is divalent cation [24]. The attapulgite is a kind of crystalloid hydrous magnesium aluminum silicate mineral having a special laminated chain structure in which there [41], the chemical structure of one layer of attapulgite can be written in the form

$2[(OH_2)_4(Mg,Al,Fe)_5(OH)_2Si_8O_{20}]4H_2O$ see Figures 1.4 and 1.5, Table 1.1 lists

the main oxides content in the attapulgite clay .

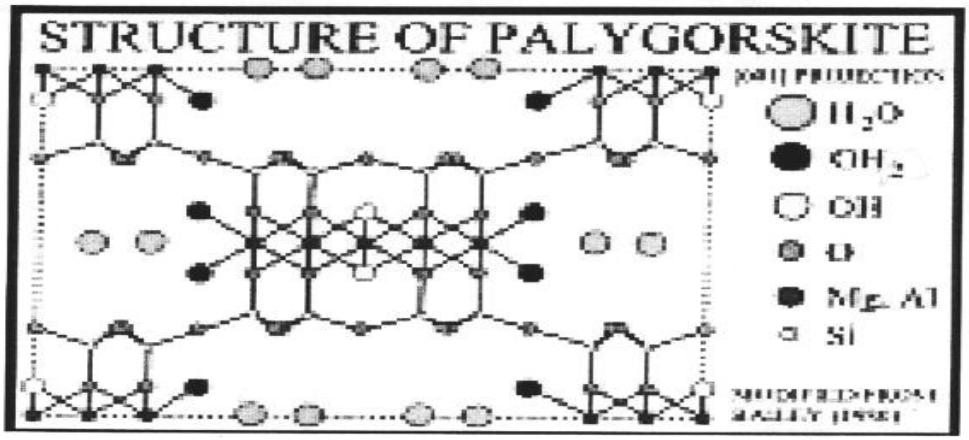


Figure (1.4): Stereo structure of attapulgite clay

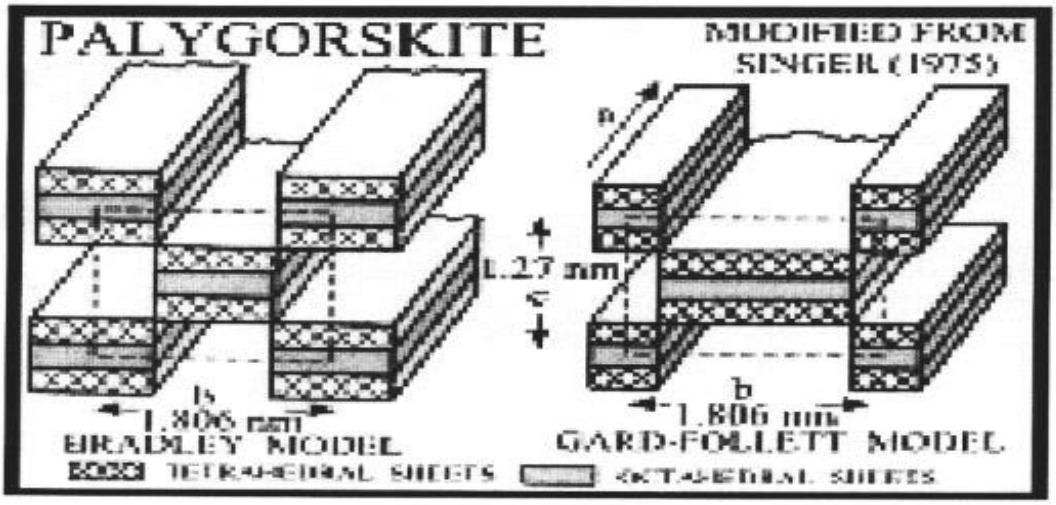


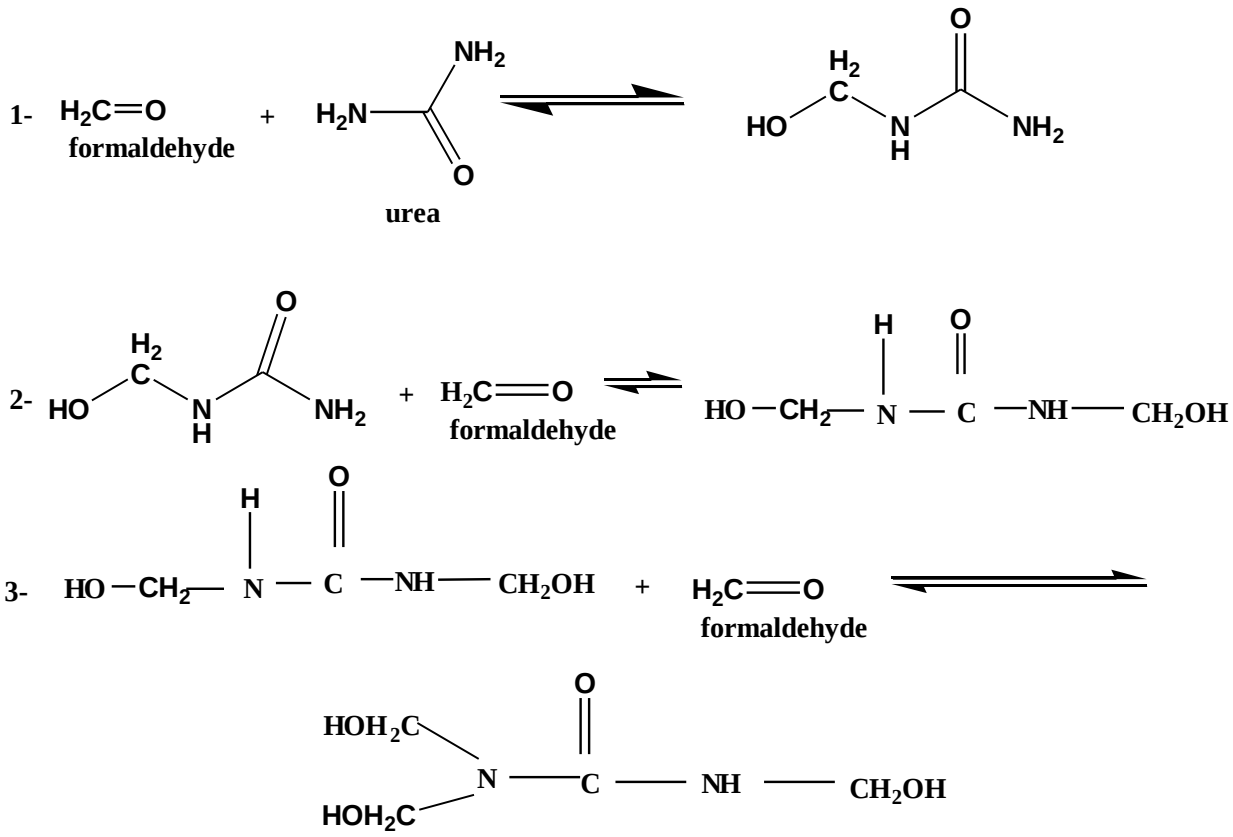
Figure 1.5: Pore Volume of Attapulgite Clay.

Table (1.1) the main oxides content in the attapulgite clay [42].

Oxides	%
SiO_2	55.6-60.5
Al_2O_3	9-10.1
Fe_2O_3	5.7-6.7
Na_2O	0.03- 0.11
K_2O	0.28-1.3
CaO	0.22-1.95
MgO	10.7-11.35
MnO	0.61
TiO_2	0.32- 0.63
L.of I.	10.53-11.8

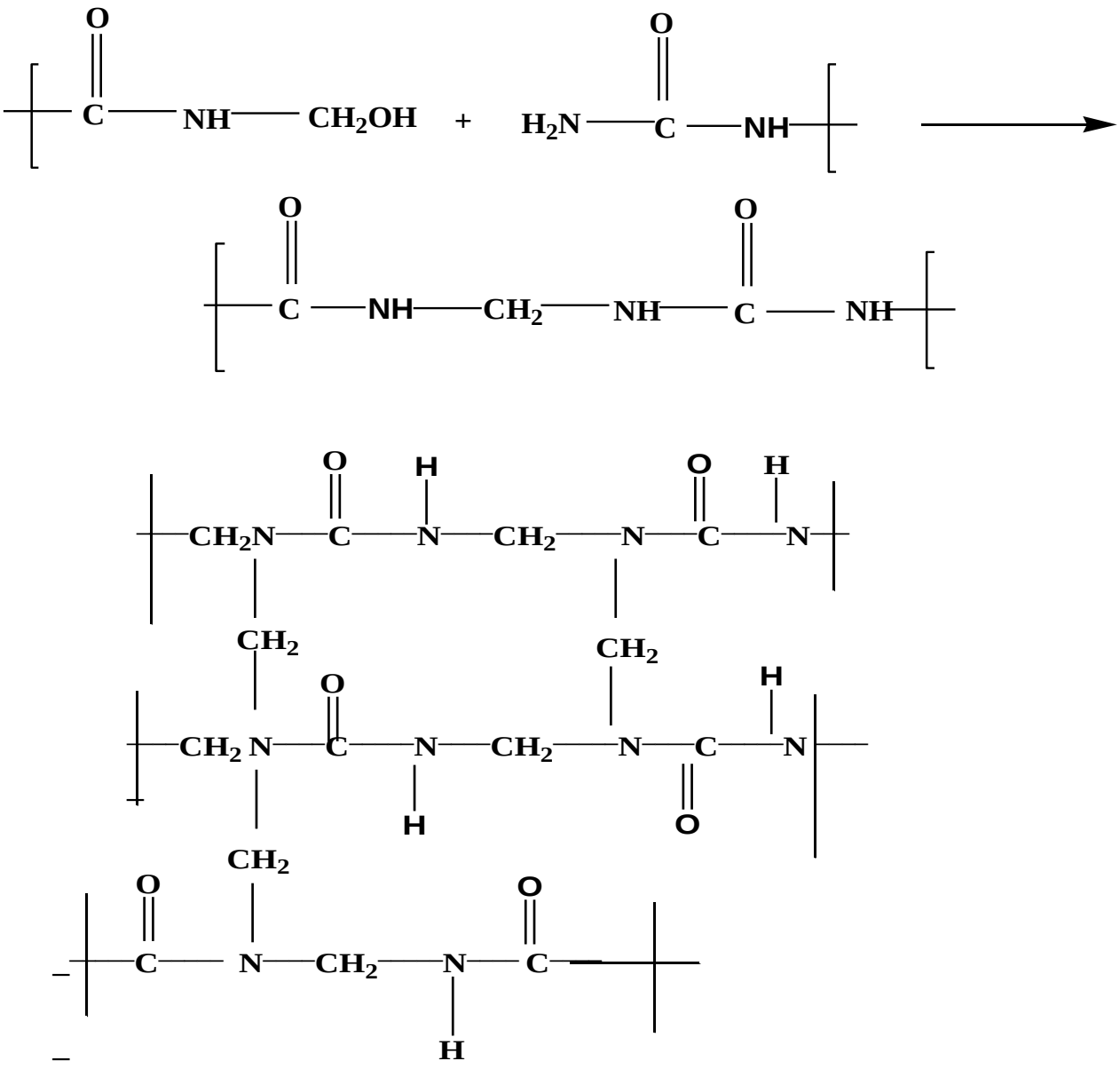
1.10 Condensation of Urea with Formaldehyde

Urea and poly functional amides condense with formaldehyde to form important class resins that are thermosetting materials [43]. The reactants condense to form linear polymer, which form infinite networks on heating. Plastics are called thermosetting, since the fluid material is heated in a mold to form an infusible product. [44]. The obtained product does not contain hydroxyl groups,but has very large macromolecules, and is insoluble in water [45]**.** The character and rate of the reaction between urea and formaldehyde in an aqueous solution depend on the reaction conditions. The preparation of polymer urea-formaldehyde is depens on the main step [42] described in scheme 1.1



Scheme 1.1

The reaction (1) happens by using alkaline agent or acidic agent. It becomes reversible reaction when using acidic agent, and the reaction (1) capable to formation condensation reaction therefore is very fast. In the formaldehyde –urea resins the long chains are tied together with many methylene cross-links as indicated in scheme 1.2



Scheme 1.2

1.11 X-ray Diffraction Analysis

The x-ray diffraction method is a powerful tool for investigating orderly arrangements of atoms or molecules through the interaction of electromagnetic radiation to give interference effects with structures comparable in size to the wavelength of the radiation. If the structures are arranged in an orderly array or

lattice. The interference is sharpened so that the radiation is scattered or diffracted only under specific experimental conditions. Knowledge of these conditions gives information regarding the geometry of the scattering structure. The wavelengths of X-rays are comparable to inter atomic distances in crystals; the information obtained from scattering at wide angles describes the spatial arrangements of the atom [46, 47].

1.12 Literature survey

There are many studies of adsorption in different fields such as, pollution, medicine, and chromatography. The adsorption of phenol and chlorophenol on different adsorbents has been studied extensively.

White, and Ledox [48] are studied the (IR) and hydrogenic bond between the kaolin surface and formaldehyde and hydrazine, they found the interaction of hydrazine with kaolin increase the stretching in-group (NH_2) from 2738$cm^{-1}$to 2765 cm^{-1} in complex.

Ratanuman et.al,[49] are studied the adsorption of phenolic compounds from water by surfactant modified pillared clays and they found that the presence of the Hexa Decayl Tri Methyl Ammonium (HDTMA) enhanced the adsorption ability of the clays towards phenolic compounds from aqueous systems. And they proved the adsorption affinity decreasing in following sequence: 3,4 dichlorophenol > 3-monochlorophenol > phenol.

Al –Hayali [50] studied the adsorption from solution of two widely used antibiotic drugs, the adsorption of the drugs on kaolin and bentonite surfaces was found to be an endothermic reactions while the adsorption process on attapulgite surface was exothermic.

Al-Timmimi [51] investigates the activity of kaolin, bentonite, and attapulgite as antidotes in treatment of poisoning, and was found that the bentonite surface

possesses the highest activity for adsorption of these drugs.

El-bahrani and Martin [52] studied some types of phenols on carbon by using (GLC) technique. They found the adsorption is obeyed to langmuire and freundlich equations and they found the group which are capable to formation hydrogenic bond such as (OH, NH_2) caused decrease in adsorption process.

Mattson et. al., [53] studied adsorption of phenol and paranitro phenol on activated carbon. They found the adsorption process was found to depend on the charge transfer between of these compounds and the surface of carbon.

Brown et. al.,[54] studied the ability of attapulgite, bentonite, and kaolin to adsorption of tetracycline and found the adsorption process is depending on the ion exchange between the surface and the drug.

Mckay et. al.,[55] studied the adsorption of phenol and para chlorophenol from aqueous solution by activated carbon have been studied by system were found obeyed to Langmuire and Freundlich equation.

Statendra et. al.,[56] studied the adsorption of phenol, cresol and the mixture of these compounds on fly ash. They found that the adsorption obeyed to Freundlich equation.

Al-Ameene [57] studied the adsorption of some phenol compounds from aqueous solution by carbon and asphalt surface .He found that the adsorption process on carbon surface obeyed the Freundlich equation and also found the substituted group on the ortho and para position, the adsorption when the substitution groups has been electron withdrawing groups.

Albanis et. al.,[58] used the flash ash and soil for the removal of dyes from aqueous solutions. They found that the logarithmic form of Freundlich equation gave high linearity and the constant (K) are increasing with increase of fly ash content in adsorbent mixture and the affinity between the adsorbent surface and

adsorbent solute.

Zawadzki [59] using FTIR technique to study the adsorption of phenol on clay, showed exactly the opposite effect, concluded that phenol creates hydrogen bond with surface oxides, and the adsorption of water on active site can be neglected. Thus it can be seem that the process of hydrogen bonding and the competition between the solute and solvent are important and can not be neglected.

Terzyk [60] studied the adsorption of biological active compounds from aqueous solutions on two unmodified activated carbons. He found that the rate of adsorption for unmodified carbon increased with temperature.

Jordanian zeolitic tuffs and their admixtures with urea and thiourea studied by Rushed et. al., [61], the chemical and structure properties from point of with urea and thiourea and they used as potential scavengers for phenolics in aqueous medium. They found that the time and temperature dependence adsorption experiments both indicated that (zeolitic-urea). Which displayed the largest surface area and they also found that showed the greatest ability to remove phenolic compounds from water.

Reinik et. al.,[62] studied the adsorption of (2,4-xylidien) on granulated activated carbon (GAC), they found that the adsorption isotherm by using Freundlich equation on (GAC) better than the Langmuir isotherm.

The effects of temperature on the adsorption have been studied by Mattson et. al.,[63] they found that the temperature dependence of adsorption is mainly due to decrease in the number of electrostatically interacting molecules with surface groups.

Nakamura et. al.,[64] studied the decolorization of acidic dye by charcoal from coffee grounds and they found also that the dominate factor of adsorption for organic pollutants is the specific surface area and pore volume.

The adsorption of phenol on titanium oxides (TiO_2) has been investigated by the Bekkouche et. al.,[30]. They found that the equilibrium of adsorption was reached after 1h, and they found also the kinetics of adsorption were slow and obeyed the Lagergreen model.

1-13 Aim of The Study

The project includes synthesis of the complex AUC and AUFP by the treatment of the clay attapulgite with urea then by the polymerization of the complex AUC with formaldehyde to obtained attapulgite urea formaldehyde polymer by the interaction the polymer urea – formaldehyde with holes of the clay. Then it studies the ability of clay A, AUC, AUFP and UFR as the adsorbent surfaces of phenol and chlorophenol from its aqueous solution and studies the effect of temperature on adsorption of all adsorbent surfaces.