

## Adsorption of *P*-Aminodiphenylamine with Iodine Charge Transfer Complex on Surface Arundo Plant

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### Abstract

A charge transfer complex formed by interaction between the *p*-aminodiphenylamine (PADPA) as electron donor with iodine as electron acceptor in ethanol at 25<sup>0</sup>C as evidenced by color change and absorption. The spectrum obtained from complex PADPA – Iodine shows absorptions bands at 586 nm. All the variables which affected on the stability of complex were studied such as temperature, pH, time and concentration of acceptor. The linearity of the method was observed within a concentration rang (10–165) mg.L<sup>-1</sup> and with a correlation coefficient (0.9996), while the molar absorptivity and sandell sensitivity were (4643.32) L.mol<sup>-1</sup>.cm<sup>-1</sup> and (0.0943) µg.cm<sup>-2</sup>, respectively. The adsorption of complex PADPA–I<sub>2</sub> was studied using adsorbent surfaces arundo plant. The dynamics of isotherm were studied according to experimental conditions of contact time, adsorbent weight, pH and particle size. The results showed the adsorption isotherm according to the Gils classification indicated L<sub>1</sub>, when the temperature (10,25)<sup>0</sup>C of plant, but S<sub>2</sub> at (37.5,50)<sup>0</sup>C for plant. Analytical techniques including UV-Vis. & FTIR were applied to characterize arundo. The values of Gibbs free energy, enthalpy, entropy calculated from the thermodynamics of the process. [DOI: [10.22401/ANJS.22.4.01](https://doi.org/10.22401/ANJS.22.4.01)]

Keywords: charge transfer, *p*-aminodiphenylamine, iodine, UV-Vis, FT-IR, Arundo.

### Introduction

The charge transfer complex is a coordinate complex whose composition depends on the presence of a donor molecule and the acceptor of the electrons where the inhabitant electrostatic attraction causes the stability of the complex [1]. The notion of “molecular association” has long been celebrated as important in virtually all fields of chemistry. The notion is that of a comparatively electron-poor molecule, or acceptor (A), interacting in some way with an electron-rich molecule, or donor (D). The interaction is such that the binding between the components is weaker than a covalent bond. This definition is sufficiently spacious so as to take into consideration both weak and strong interactions between ionic and uncharged species. The literature also abounds with such expressions, as molecular complexes,  $\pi$  complexes, and charge-transfer complexes (CTCs), which all indicate to some sort of donor–acceptor interaction [2].

Considered as charge transfer complexes are of great importance because of their

physical and chemical properties. They can therefore be introduced into many applications such as the use of extraction processes through the design of new extraction systems that depend on the possibility of molecular charge on the molecular (donor-acceptor) [3], as well as used in optical materials, solar energy and surface chemistry [4,5] drug-receptor interaction mechanism [6], in addition to various biological applications [7], and play an important role in the science of materials[8], enzyme catalysis [9], DNA binding interactions [10] antibacterial agents[11], and probes for pharmaceuticals [12].

*p*-Aminodiphenylamine (PADPA) is a diaromatic amino compound that is chips of dark purple solid or soft dark purple, with chemical formula C<sub>12</sub>H<sub>12</sub>N<sub>2</sub> and molecular weight 184.242 g / mol and boiling point of 354<sup>0</sup>C; melting point of 69<sup>0</sup>C dissolved in water, Chloroform, ethanol, ethyl ether. The compound is an intermediate product in the preparation of alkyl derivatives that have been used as various polymers, stabilizers for monomers, antioxidants and antibiotics [13], It

can be used in dye technology because of its oxidizing ability [14].

Contaminating materials have become increasingly dangerous with increasing technological development and modern industries, prompted the organizations concerned with the preservation of the environment to develop limitation and laws for laboratories and about the treatment industrial waste before its emission into the environment so that toxic materials do not exceed the permissible limits [15]. Investigator have, thus, devoted efforts to find effective methods for the adsorption of contaminants from wastewaters, but, these processes are often economically expensive, like adsorption, flocculation, reverse osmosis, coagulation, photocatalytic degradation, membrane technology, and biological treatments. Adsorption technique is by far the most versatile and widely used furthermore, this process become economic if the adsorbent material used is available and cheap in cost [16,17]. adsorption methods have acquired a major attention due to simplicity, high sorption ability, eco-friendly, non-toxicity and efficiency for the removal a wide range of sorbents [18]. Many low-cost, effective natural materials used in adsorption have been discovered such as rice straw, vegetable peels, banana Peel, fruit and coffee grounds, cactus, wheat straw, and salvinia plant [19]. The plant arundo was also used to treat water from pollution, and the removal of odors unpleasant. and explained the studies on the impact of the plant on the purification of water from pollution as the roots of this plant contains substances that act as antibiotics antibiotic produced by the plant to protect itself from bacteria as well as to protect the environment in which the plant lives [20].

Arundo Is a herb belonging to the Nephilian family, growing near the waterways and wetlands of its native habitat in southern Europe, North Africa, most temperate Asia, and in eastern Japan [21].

The aim of this work is to study the adsorption of PADPA-I<sub>2</sub> complex from water using arundo plant, which are considered environmentally safe and low-cost. The particle size, dose, solution pH, contact time, and temperature were investigated.

Thermodynamic parameters, kinetic equilibrium and adsorption isotherms were determined to analysis of the adsorption behavior.

## Experimental

### Materials

In this study, chemicals processed by international companies, characterized by their high purity, *p*-aminodiphenylamin (98), Iodine (99.5)%.

### Apparatus

UV / VIS double beam spectrophotometer, shimadzu 1800 (Japan) with 1 cm matched quartz cells was used for the absorbance measurements, thermostatic water bath shaker LabTech LSB-045S (Korea), electronic balance was used for weighing the samples, pH -meter with combined glass electrode i-Trans BP3001, Centrifuge 6000 rpm Hettich EBA20 (Germany), FTIR spectrophotometer Biotech FTIR-600 SIDCO (England).

### Preparation of standard stock solution (0.01M)

The stock solutions were prepared by dissolving an accurately weight 0.184 g of (PADPA) in 100 mL of ethanol absolute. and an accurately weight 0.254 g of iodine was dissolved in 100 ml of ethanol absolute. All the solutions were kept for later experiments.

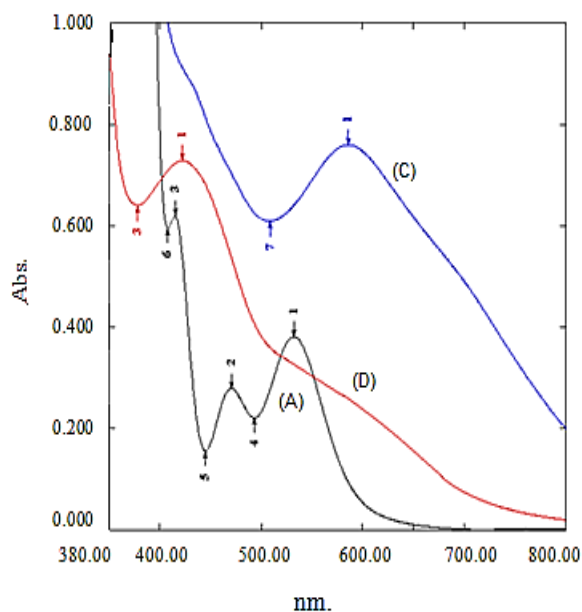
### Preparation of adsorbent

The plant was collected from the shores of the Tigris river from the area of Adhamiya on 15/11/2018 and was well cleaned, cut and then conducted a process of extraction using distilled water and several hours until a clear solution, then took the remainder of the first extraction and conducted it A second extraction process with absolute ethyl alcohol by using the soxhlet machine for several hours to remove all the existing plant, thus obtaining a wood surface composed of cellulose, hemicellulose and lignin, and then drying and grinding to obtain sizes of (75,150,250) μm and using sieves for this purpose.

## Results and Discussion Absorption

### Absorption spectra

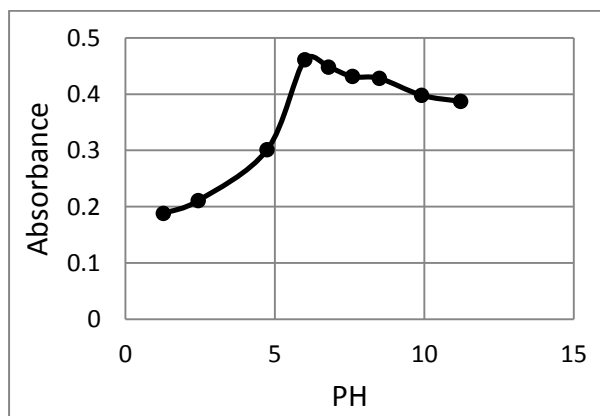
The complex for PADPA-I<sub>2</sub> giving maximum absorbance at  $\lambda_{\max} = 586\text{nm}$  as it is shown in Fig. (1).



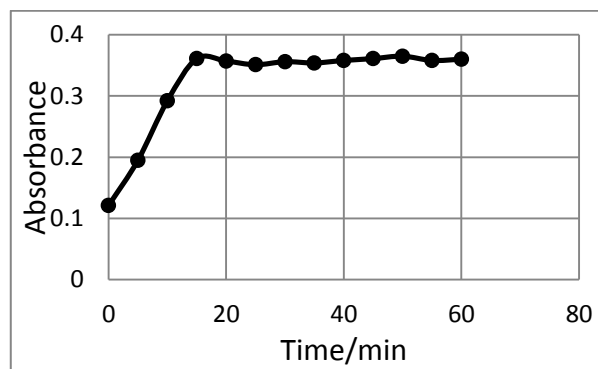
**Fig.(1):** Electronic absorption spectrum of (A) iodine, (D) PADPA, and (C) PADPA-I<sub>2</sub> complex reaction in ethanol, ( $10^{-4}\text{M}$ ).

### Univariate method

The effect of the pH, and reaction time on the formation of PADPA-I<sub>2</sub> complex were studied. The results show that the best acidic function and reaction time for the complex formation was when pH = 6 at 20 minutes as shown in Fig.(2,3).

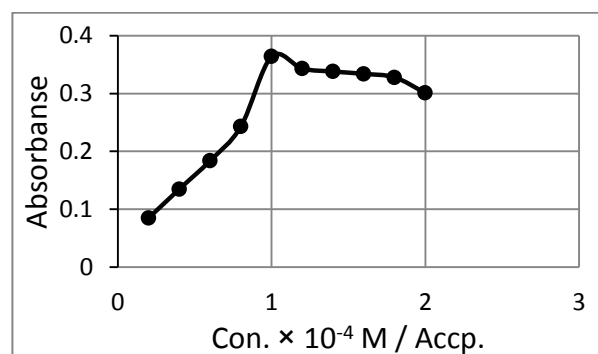


**Fig.(2):** Effect of pH on the complex formation.

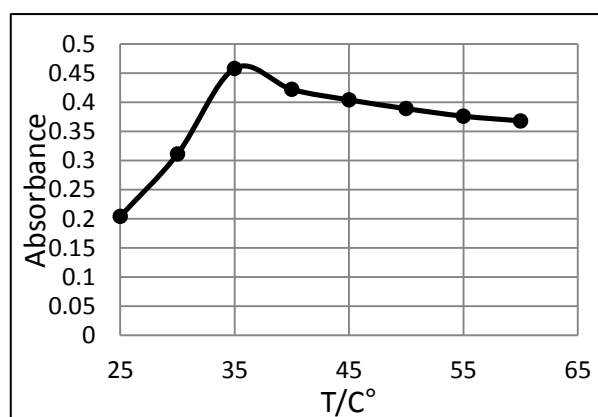


**Fig.(3):** Effect of time on the complex formation.

In addition, the effect of the acceptor concentration and temperature of the complex was studied. The results show that the best concentration is  $1 \times 10^{-4}\text{M}$  at  $35^\circ\text{C}$  as shown in Fig. (4,5).



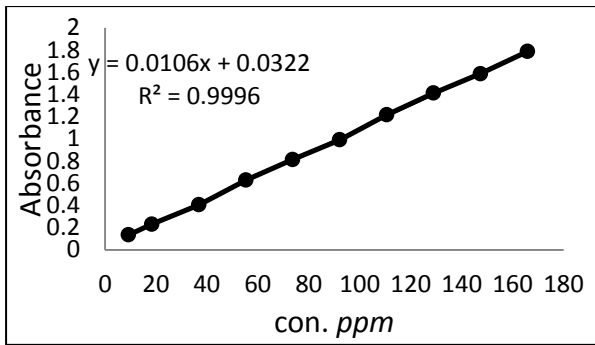
**Fig.(4) :** Effect of the acceptor concentration on the stability of complex.



**Fig.(5):** Effect of temperature on the complex formation.

### Calibration Curve

Absorbance values of the solutions of concentrations range (10-165) mg/L are measured at a selected wavelength ( $\lambda_{\max} = 586\text{ nm}$ ) and plotted against the concentration of the complex, Fig.(6) shows the calibration curve of complex.



**Fig.(6): the calibration curve of complex Factors Affecting Adsorption Process.**

**Contact Time**

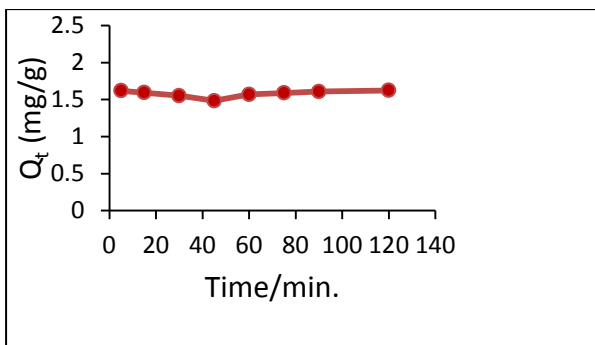
Fig.(7) is showing the relation between contact time and adsorption of the complex on arundo plant at different time ranges (15-120min) in 25 ° C and constant concentration of the complex (110.544 mg / L), and particle size (75µm). Results showed that the amount of adsorbent material increases quickly during the first few minutes of the process and then at 45 minutes we reach a roughly stable value for the amount of adsorbent material.

Quantity of complex adsorbed at equilibrium time (Q<sub>e</sub>) is calculated by using Eq.1

$$Q_e = \frac{x}{m} = \frac{V(C_0 - C_e)}{m} \dots\dots\dots(1)$$

Where: X the quantity adsorbed (mg), m weight of adsorbent (g).

C<sub>0</sub> and C<sub>e</sub> (mg/L) are the concentrations of adsorbent material at initially and at equilibrium, respectively and V is the volume of solution (L).



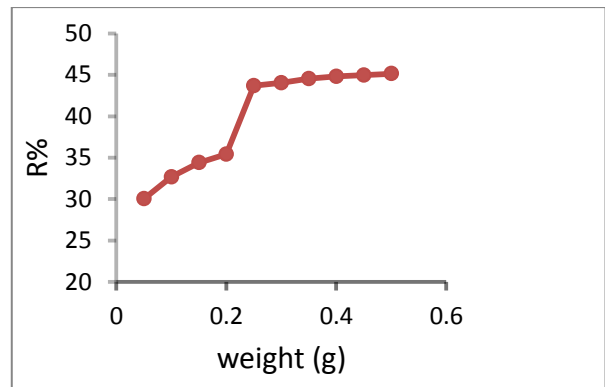
**Fig.(7): Effect of Contact Time on the Adsorption of complex.**

**Adsorbent Weight**

The effect of the weight of the adsorbent on the adsorption process was studied using a

fixed concentration of the complex solution and different weights of the adsorbent material (plant) at (25°C) and the size of the adsorbent (75 µm). The results are shown on Fig.(8). it will be there a jump between (0.2-0.3) g and after weight (0.3) g, the amount of adsorbent material is proven which means that the best amount of adsorption in this study is 0.25 (g). Percentage of complex removal (R%) is calculated by using Eq.(2) [22].

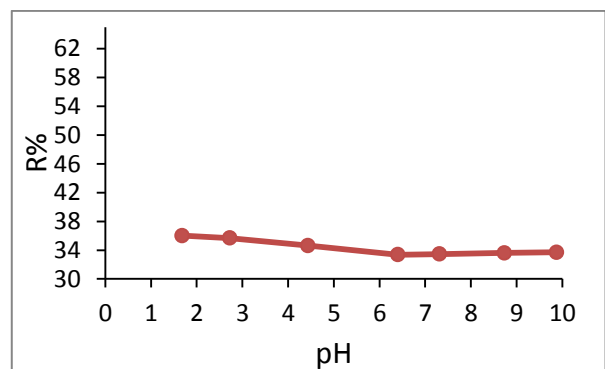
$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots(2)$$



**Fig.(8): Effect of Adsorbent Weight on adsorption of complex by the adsorbent.**

**Effect of pH**

Fig.(9) is showing the relation between R% and pH of the complex on arundo plant at different pH in 25°C and particle size (75) µm. The study showed a decrease of R% with increasing pH in the range of (2.0-6.5) and then a slight increase is similar to stability at pH=10.



**Fig.(9): Effect of pH on adsorption of complex on plant surface.**

**Effect of Particle Size**

To study the effect of the particle size on the adsorption process using a fixed

concentration of the complex solution and the weight of the plant adsorbent material (0.25) g with different size of the adsorbent (75, 150, and 250)  $\mu\text{m}$ . Note that the relationship between the amount of adsorption and the adsorbent material particle size is an reverse relationship, which increases the adsorption by increasing the granular size due to the availability of more adsorption sites for the plant, as shown in Fig.(10).

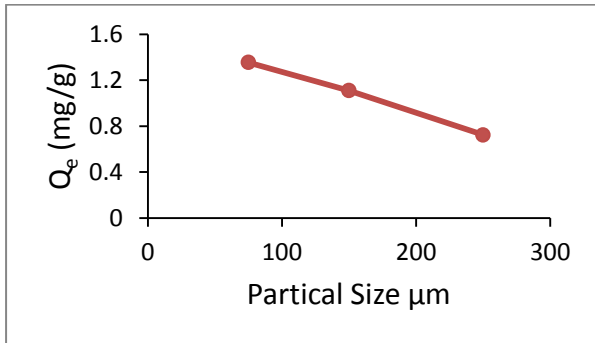


Fig.(10): Effect of Adsorbent Particle Size on the Adsorption.

**Adsorption Isotherms**

Adsorption of complex from aqueous solution on arundo plant is studied at four temperatures (10.0, 25.0, 37.5 and 50.0) $^{\circ}\text{C}$  keeping the other parameters of adsorption unchanged. The weight of the adsorbent material ( $Q_e$ ) corresponding to each value of equilibrium concentrations  $C_e$  was calculated as shown in Fig. (11).

The results show an increase in adsorptive capacities of arundo plant as the concentration of the complex increases until reaching a limited value. The general shape of the adsorption isotherm of complex on arundo plant consistent with ( $L_1$ -type) on the Giles classification at (10,25) $^{\circ}\text{C}$  the adsorption to more than one layer, a second adsorption site appears at (37.5,50) $^{\circ}\text{C}$  and the adsorption pattern becomes ( $S_2$ - type).

The experimental adsorption data are applied to the empirical Langmuir isotherm (eq.3) and Freundlich isotherm (eq.4)[23].

$$\frac{c_e}{Q_e} = \frac{1}{a \cdot b} + \left(\frac{1}{a}\right) \cdot C_e \dots\dots\dots (3)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots\dots\dots (4)$$

The adsorption isotherm at the studied temperatures shows good compatibility of the

Langmuir adsorption model With high values of  $R^2$  and slope, and positive cross for all isotherm which means that it gives realistic estimates of the constant adsorption of  $K_L$  and the value of  $Q_{\text{max}}$ .as shown in Fig. (12).

According to Isotherm Frondlich for adsorption as shown in Fig. (13), we find that most of the isotherm seem to be an excellent conformant to Isotherm frindlish.

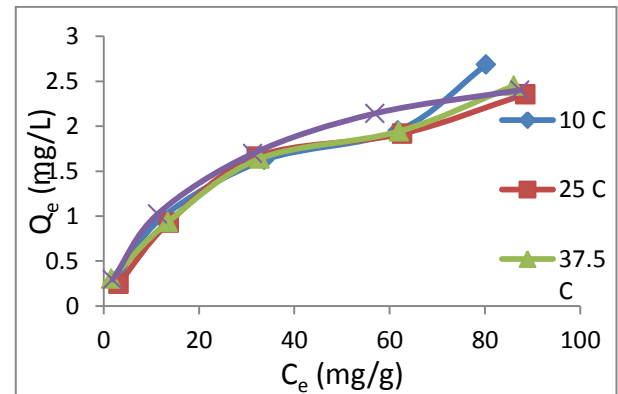


Fig.(11): Adsorption Isotherm of complex on Plant at Different Temperatures.

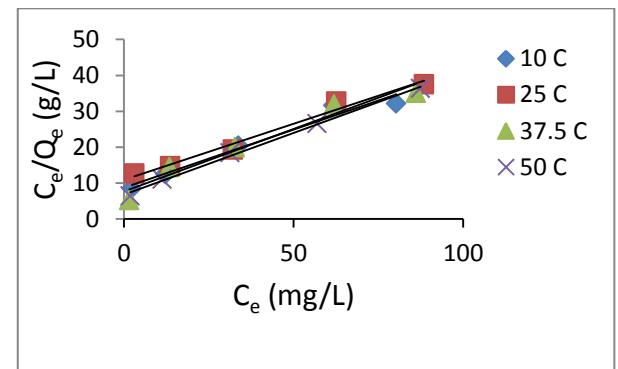


Fig.(12): Langmuir Isotherm of complex on Plant at Different Temperatures.

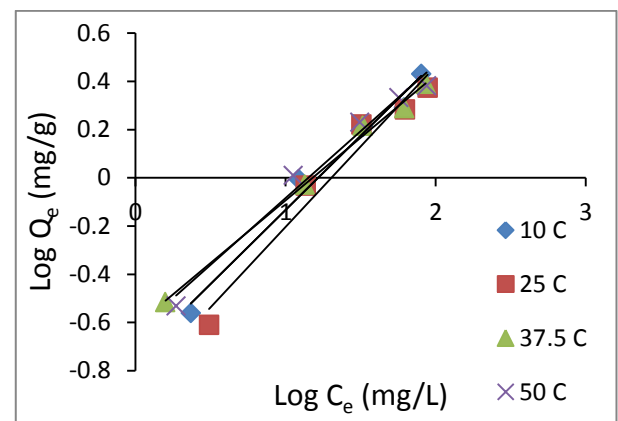


Fig.(13): Freundlich Isotherm of complex on Plant at Different Temperatures.

### Thermodynamics of Adsorption Process

The thermodynamic parameters are linked to the adsorption of complex, such as, Gibbs free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ).

Thermodynamic parameter values can be found from the following equations.

$$\Delta G = -RT \ln K_{ads} \dots\dots\dots (5)$$

$$\ln K_{ads} = (-\Delta H / RT) + \text{constant} \dots\dots\dots (6)$$

$$\Delta G = \Delta H - T \Delta S \dots\dots\dots (7)$$

Where

$K_{ads}$  :is adsorption equilibrium constant which is calculated at each temperature

R :is the gas constant (8.314 J/mol.deg)

$K_{ads}$  which is calculated from the following equation.

$$K_{ads} = \frac{Q_{e\max} \times 800}{C_{e\max}} \dots\dots\dots (8)$$

The values of  $\Delta H$  is determined from the slope and intercept of the linear plot of ( $\ln K_{ads}$ ) vs. ( $1/T$ ), Fig.(14).  $\Delta G$ ,  $\Delta S$  and  $\Delta H$  values are listed on Table (1).

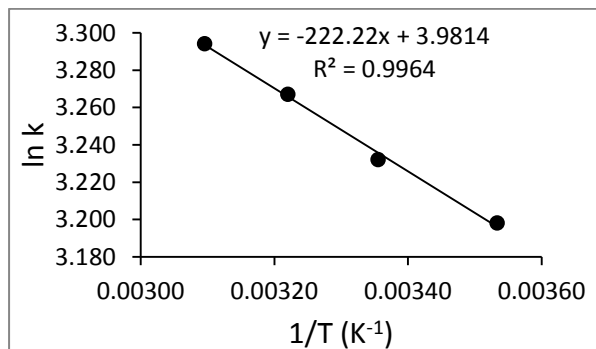


Fig.(14): The linear plot of ( $\ln K_{ads}$ ) vs. ( $1/T$ ) for Adsorption of complex on plant.

Table (1)

Values of Thermodynamic Functions for the Adsorption of complex on the plant at Different Temperatures.

$\Delta G$ (kJ.mol <sup>-1</sup> )	$\Delta H$ (kJ.mol <sup>-1</sup> )	$\Delta S$ (J.mol <sup>-1</sup> .K <sup>-1</sup> )
-7524.453	+1847.565	33.117
-8007.513		33.071
-8433.751		33.112
-8845.780		33.106

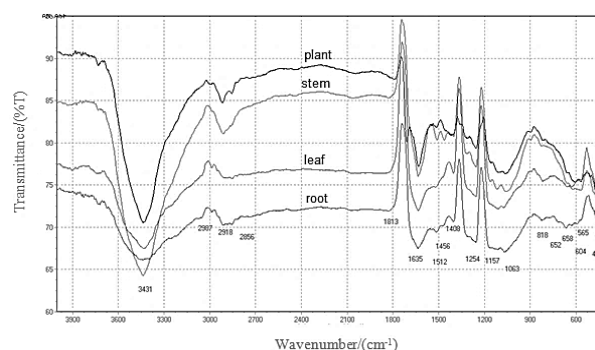


Fig.(15): FTIR Spectra of plant, root, leaf and stem.

### Conclusion

In this research, the adsorption of PADPA-I<sub>2</sub> was investigated under different conditions including contact time, adsorbent dosage weight, pH and particle size. The adsorption isotherms were found to fit well to Langmuir and Freundlich models. Results of thermodynamic studies indicate that the adsorption of the PADPA-I<sub>2</sub> is spontaneous. According to results, arundo can be used as a highly affective adsorbent for the removal of contaminants.

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