

## Removal of Phenol from Olive Industry Liquid Waste Using Polyitaconic Acid

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This study focuses on a new approach for removal of phenol from an aqueous solution. In this approach cross-linked polyitaconic acid was used as phenol adsorbent. Cross-linked polyitaconic acid was prepared from itaconic acid and the cross-linking agent 1,4-butane diglycidyl ether using chain growth polymerization technique. The adsorption property of cross-linked polyitaconic acid was investigated in terms of adsorbent dosage, pH, temperature, contact time and contaminant concentration. The adsorption capacity of cross-linked polyitaconic acid was studied using Freundlich and Langmuir models at equilibrium to determine mechanism of adsorption process whether it is a chemical or physical process. It appears that analysis of the adsorption mechanism suggested that hydrogen bonding was the primary driving force for phenol adsorbed on the polymeric adsorbents in cyclohexane and multiple hydrogen bonding was involved for poly(*N*-methyl-*N*-*p*-vinylbenzylurea (PMVBU) with phenol. The results also showed that the adsorption properties of cross-linked polyitaconic acid model followed Langmuir model with B value of 0.031 which support our results in that the adsorption is favorable. The pseudo-second-order model was the best for describing the kinetic adsorption of phenol with correlation coefficient valued ( $R^2$ ) is being 0.9975 and,  $K_2$  and  $q_c$  of 0.0118, 11.933, respectively. This validated that the adsorption process was a chemical adsorption.

**Keywords:** Polyitaconic acid, Phenol, Adsorption, Wastewater, Isotherm, Olive waste.

### INTRODUCTION

The widespread wastewater that is contaminated by phenolic compounds and other organic compounds has become a major problem in recent years. As a result of that, the removal of pollutants from wastewater became the subject of many research studies in recent years<sup>1</sup>. One major source of phenolics contaminated waste water is the olive oil industry. The olive oil industry one of the most important industry in the Mediterranean region and has been strongly related to the culture, since ancient times. The worldwide olive oil production for the years 2002-2009 was reported to be about 2,775,800 MT<sup>2</sup>. Recent research revealed that there is a major contamination occurring through the olive oil production process. Olive mills wastewater (OMWW) (known in Palestine as Alzibar), was found to be the highest source of environmental pollution in the countries of Mediterranean region<sup>3</sup>.

In many countries such as Palestine, Spain, Syria and Tunisia the extraction of olive oil is performed by pressing or centrifuging processes. All the methods, currently used for

the extraction of olive oil, result in different wastes and pollutants. The olive industry liquid waste has produced a large amount of pollutants, especially, the phenolic compounds. Other sources of phenolic compounds in wastewater are gasoline, coal, petroleum, petrochemical and pharmaceuticals<sup>4</sup>.

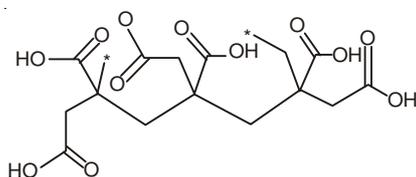
Disposing the olive industry waste on soil has a negative impact on soil and on ground water. Over the time it will reach the surface water and the ground there upon increasing water contents of poisoning organic matter<sup>5</sup>. All traditional methods used until now to remove these organic contaminants that are harmful to nature, human being and animals from olive mills wastewater were inefficient. For this reason several methods have been developed to deal with nature destructive issue<sup>6</sup>. The developed methods includes nano filtration using membrane, electrochemical methods and adsorption processes. The adsorption process is preferred since it can performed at low cost of processing without any need of large facilities<sup>7</sup>.

In general, water phenol has low toxicity, but may be converted to very toxic compounds *via* substitution with chlorine atoms and formation of organic radicals in a very short time,

which makes it dangerous on all living organism at low concentration and thus inhibit growth of organisms<sup>8</sup>.

Marvel and Shepherd<sup>9</sup> prepared polyitaconic acid by various methods in the presence of various initiators in water medium. The main purpose from synthesizing polyitaconic acid was to make an adsorbent with a large surface area for more sites of interaction with adsorbate, micro-porous properties, capacity of adsorption and easy to use<sup>10</sup>.

In this work a crosslinked polymer *i.e.*, cross-linked polyitaconic acid (x-PIA) with a high surface area and large number of adsorption sites was synthesized and used as an adsorbent for phenolic compounds from wastewater. To understand mechanism of adsorption of phenols by x-PIA, we studied the adsorption using the two models Langmuir and Freundlich. In addition the free energy of adsorption, thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ), kinetic and intra-particle diffusion parameters were evaluated **Scheme-I**.



**Scheme-I:** Chemical structure of polyitaconic acid

## EXPERIMENTAL

All chemicals used in this study were from Aldrich company (Germany) and used without any further purification unless otherwise stated. The chemicals used in this study were sodium hydroxide, hydrochloric acid, Itaconic acid, 1,4-butane diglycidyl ether, distilled, potassium persulfate.

**Equipment and devices:** IR analysis was performed using a Nicolet iS5 FT-IR Spectrometer by Thermo Scientific. UV spectroscopy was performed on UV-visible spectrophotometer Shimadzu-Model No. UV-1601, double beam spectrophotometer with a wave length range of 190-1100 nm, with an accuracy of  $\pm 0.004$ . SEM-EDS analysis was performed using Hitachi S-3400N variable pressure SEM system coupled with the oxford EDS system.

### Preparation and characterization of adsorbent

**Preparation of the polyitaconic acid adsorbent:** Polyitaconic acid, which was used as an adsorbent in this study, was prepared using the chain growth polymerization method. In this method itaconic acid was polymerized using a free radical initiator sodium persulfate in the presence of various amount of cross-linking agent as follows: Itaconic acid (50 g) was placed in a beaker (500 mL) and dissolved in 50 mL water. To the solution was added a crosslinking agent 1,4-butane diglycidyl ether (5.0 g, 10 % by weight of itaconic acid). In another reaction 1,4-butane diglycidyl ether (10 g, 20 % by weight of itaconic acid) was added. The polymerization was started by adding a solution of  $K_2S_2O_8$  (0.5 g in 10 mL water). The reaction was heated slowly, when the temperature reached 60 °C an exothermic reaction started. The reaction was kept at 60 °C for 2 h. Then cooled down slowly to room temperature in an oven at 80 °C. Then used as is with a further purification.

**Characterization of prepared polyitaconic acid adsorbent:** The study of the surface properties (surface area and SEM) of the adsorbent material is very important to confirm its ability to adsorption pores because the process of adsorption always occur on the surface of the adsorbent material<sup>11</sup>. The polyitaconic acid adsorption is influenced by two important factors. The surface area and porous structure. Therefore, it is important to explain the properties of this prepared polymer based on these two factors.

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

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

**Effect of pH:** The effect of pH on adsorption of phenol compound using polymer was studied with pH range of (3-13). The values of pH in the solution of phenol was changed by adding a few drops of sodium hydroxide and hydrochloric acid. Each sample of phenol solution (50 mL, 50 mg/L), contained 0.1 g of adsorbent. All samples were shaken for 1 h at 25 °C.

**Effect of temperature:** The influence of temperature on adsorption of phenol using the polymer was studied using solution [50 mL, 50 mg/L of (0.1 g) at pH of 13] using different ranges of temperatures (15-45 °C).

**Effect of contact time (kinetic study):** The effect of contact times on adsorption of phenol was studied at different times. Phenol solution (50 mL, 50 mg/L to each) with 0.1 g of the polymer at pH 13. All samples were shaken at 25 °C and then each sample was taken at different time until equilibrium adsorption reached after 130 min.

**Effect of phenol concentration:** In each glass bottle, different concentrations in the range of (10-50 mg/L, 50 mL), were added to 0.1 g of adsorbent, at initial pH of 13. Each glass bottle left to shake at 25 °C for 130 min.

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

$$\text{Percentage removal (\%)} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (1)$$

where PR is the percentage removal of phenol,  $C_o$  and  $C_e$  are initial and equilibrium concentration of phenol in a solution. The amount of phenol which adsorbed at equilibrium,  $q_e$  (mg/g), was measured using the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (2)$$

where  $C_o$  and  $C_e$  (mg/L) are the initial and equilibrium concentration of phenol, V is the volume of the solution (L) and W is the weight of adsorbent (g).

The whole data was fitted to the Langmuir and Freundlich eqns. 3 and 4, respectively, to describe the isotherm adsorption.

The Langmuir eqn. 3 is given as follows:

$$C_e/q_e = 1/bq_{\max} + C_e/q_{\max} \quad (3)$$

where  $q_e$  is the amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g) at equilibrium,  $q_{\max}$  is the maximum amount of phenol adsorbed per unit mass of polyitaconic acid polymer (mg/g),  $C_e$  is the equilibrium concentration of the adsorbate (mg/L) and  $b$  is the Langmuir constant (L/mg) (Langmuir, 1931).

The Freundlich eqn. 4 has form as this:

$$q_e = K C_e^{1/n} \quad (4)$$

where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L),  $q_e$  is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium,  $K_f$  and  $1/n$  are Freundlich constant,  $1/n$  is unit less and the unit of  $K$  is determined by the unit of  $q_e$  and  $C_e$ <sup>12</sup>.

**Thermal analysis:** About 0.346 g of both samples the one with phenol and the other with pure polymers were analyzed using DSC 250 manufactured by thermal analysis (USA) using nitrogen as purged gas. The heating was from 25 to 250 °C with 10 °C/min heating rate.

## RESULTS AND DISCUSSION

**Surface area of polyitaconic acid:** Surface area was measured using both the iodine number and BET method. The results show that the iodine number is 272.26 m<sup>2</sup>/g using equation. 3.1 and 355 m<sup>2</sup>/g using BET<sup>13</sup>.

**SEM analysis of the adsorbent:** The morphology of adsorbent was studied using SEM (scanning electron microscopy) technique to observe the surface physical morphology of the polyitaconic acid which used as adsorbent in this study. The SEM micrographs of polyitaconic acid show that the external surface of this polymer is rich with cavities and porous, as shown in Fig. 1a. After phenol adsorption occur the majority of these scattered cavities and pores on the surface had been filled and covered, indicating an adsorption process for phenol compounds (Fig. 1b).

**FTIR analysis of adsorbent materials:** In Fig. 2a FTIR analysis shows the functional groups which presented on the surface of adsorbent before the adsorption process occurs. The type of these functional groups help us to explain the mechanism of the adsorption process.

FTIR spectra in the Fig. 2a interpreted each functional groups existence on the surface of adsorbent. The bands appeared at 3329.85 cm<sup>-1</sup> (O-H stretch an carboxylic acid) and 2941.66 cm<sup>-1</sup> (C-H stretch an alkanes). The bands around 2365.49 cm<sup>-1</sup> show the existence of (O-H stretch an carboxylic acid), the 1699.43 cm<sup>-1</sup> band, indicated the presence of (C=O of ester and carboxylic acid). The band observed at 1548.24 cm<sup>-1</sup> indicated the existence of (CH<sub>2</sub>-bend), the band at 1392.96 cm<sup>-1</sup> indicated the presence of (C-O stretch of an carboxylic acid), 1155.96 cm<sup>-1</sup> indicated the presence of [C-C-(O)-C stretch to all others].

Fig. 2b showed the FT-IR analysis for adsorbent prepared polyitaconic acid after adsorption occurs to phenol, from this

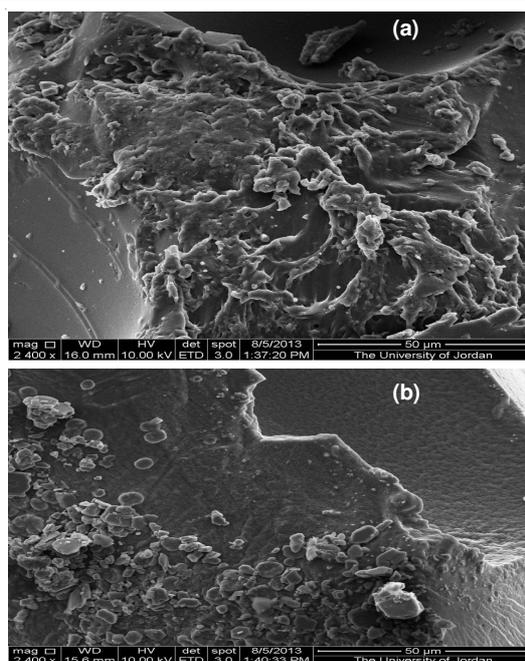


Fig. 1. SEM of polyitaconic acid before adsorption (a) and after the adsorption process to phenol (b)

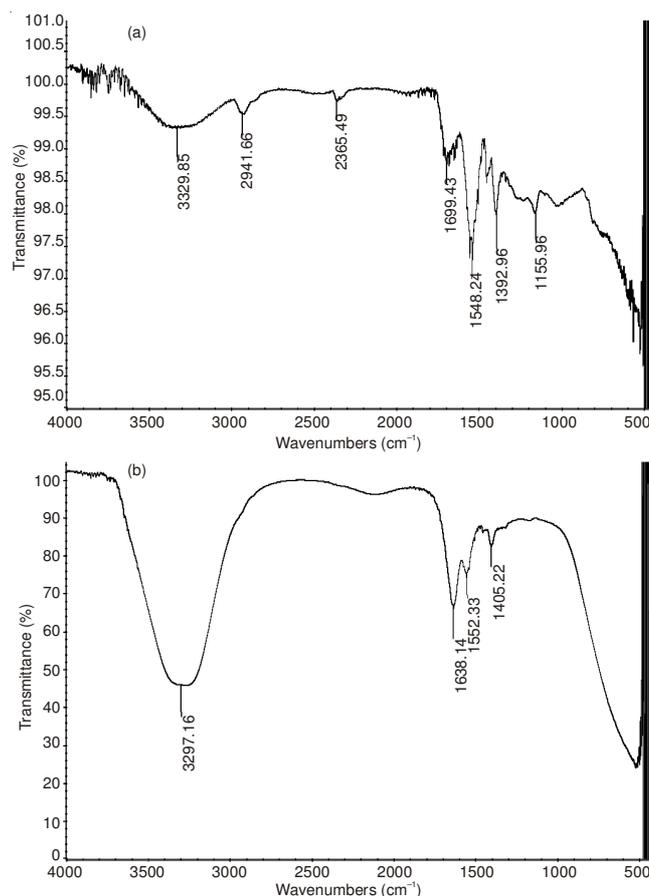


Fig. 2. FT- IR analysis for adsorbent prepared polyitaconic acid before (a) and after adsorption to phenol (b)

analysis it is noted that the appearance of broad band at 3297 cm<sup>-1</sup> and this indicated the presence of phenol molecules on polyitaconic acid surface. All the bands for functional groups are summarized in Table-1.

TABLE-1  
FUNCTIONAL GROUPS OF POLYITACONIC  
ACID USING FT-IR ANALYSIS

Functional group	Wave number (cm <sup>-1</sup> )
O-H stretch alcohol	3329.85
C-H stretch alkanes	2941.66
O-H stretch carboxylic acid	2365.49
C=O of ester and carboxylic acid	1699.43
CH <sub>2</sub> -bend	1548.24
C-O stretch of carboxylic acid	1392.96
C-C-(O)-C stretch to all others	1155.96

**DSC analysis of extracted cellulose:** The DSC analysis results of the prepared polymer show that it highly stable crystalline polymer. It shows only one endothermic peaks corresponding to melting at about 150 °C with an enthalpy of about 1447 J/g. The polymer showed no sign of degradation up to 300 °C. However, when the polymer is saturated with phenol, it went through glass transition temperature (softening) at about 80 °C. Another peak shows at about 170 °C which corresponding to phenol evaporation since phenol boiling point is about 182 °C. Again the polymer showed no sign of decomposition up to 200 °C.

### Phenol adsorption experiments

**Effect of adsorbent dosage:** The result of adsorption of phenol compound using different amount of adsorbent is illustrated in Fig. 3.

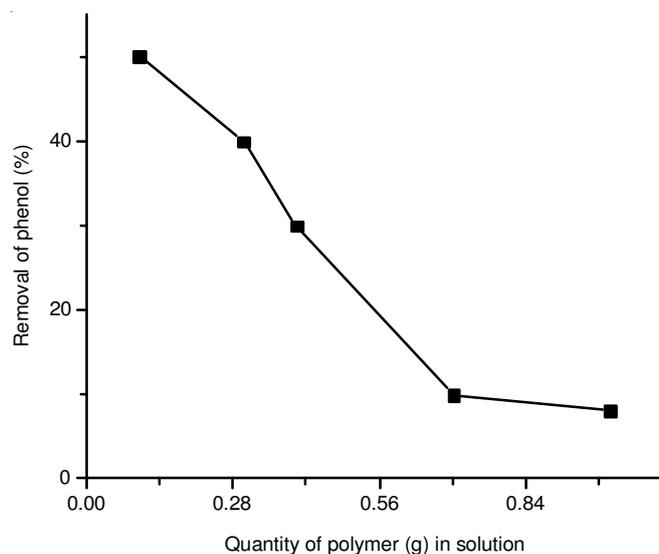


Fig. 3. Effect of adsorbent dosage on phenol removal by polyitaconic acid at (initial conc: 50 mg/L, initial pH: 13, temperature: 25 °C and contact time: 130 min)

The amount of phenol adsorbed decreased with increasing the amount of polymer polyitaconic acid, so the adsorption increased up to 50 % with adsorbent dosage of (0.1 g/50 mL). The occurrence of split in flux, concentration of phenol compound became as neutral between un adsorbed phenol in the solution and the adsorbed phenol on the surface of the adsorbent<sup>14</sup>.

**Effect of pH:** The impact of pH changes on the adsorption of phenol compounds was studied at adsorption time of 130 min to reach the equilibrium adsorption and at initial concentration

which was kept constant to all samples at 50 mg/L in 50 mL solution at 25 °C. Fig. 4 shows the effect of pH value on the adsorption of phenol compounds.

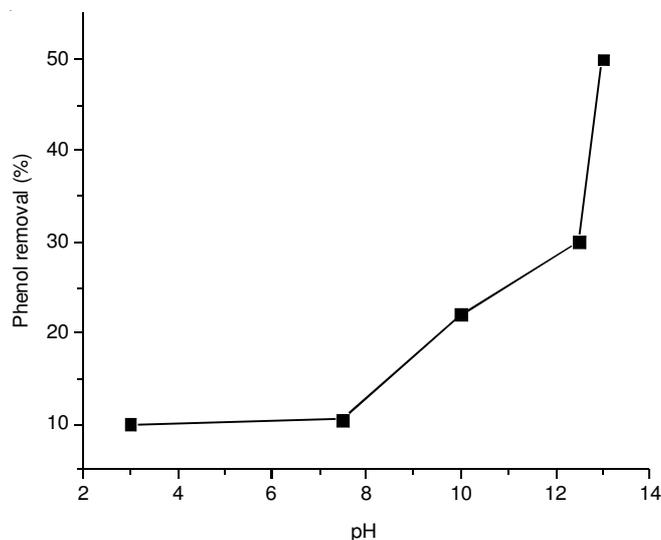


Fig. 4. Effect of pH on phenol removal by polyitaconic acid at (initial conc: 50 mg/L, temperature: 25 °C, contact time: 130 min)

Fig. 4 showed that the amount of phenol adsorbed increases with increasing the pH value. This behavior is due to the excess of hydroxide ions at higher pH value. This increase the amount of negatively charge on adsorbent surface. The polyitaconic acid is very rich with -COOH group on the surface as is clear to us from the figure, therefore increasing occurrence of H-bonding bonds between the phenol molecules and the OH groups which are attached on the surface of the adsorbent.

**Effect of temperature on adsorption:** The results showed in Fig. 5 indicate that the adsorption of phenol compound decreased as temperature increased. This can be explained as temperature increases the solubility and ionization of phenol in water is increasing, this lead to the probability of H-bonding between phenol and water molecules become stronger than

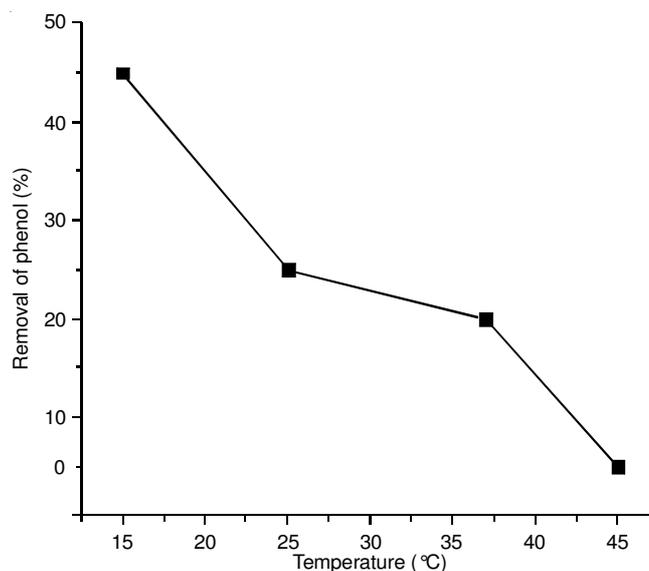


Fig. 5. Effect of temperature on phenol removal by polyitaconic acid at (initial conc: 50 mg/L, initial pH: 13, contact time: 130 min)

the occurring H-bonding between phenol and OH groups which is attached on adsorbent surface and water and known as an excellent solvent in the nature due to its polarity, high dielectric constant and small size and this character is suitable for polar and ionic compounds to dissolve in water<sup>15</sup>. Water ionizes and allow the proton to exchange in easy way between molecules; the highest amount of phenol are adsorbed at 15 °C which reach<sup>16</sup> to ~45 %.

**Effect of contact time:** The maximum amount of phenol removal was about 45 % after 130 min at pH 13 and 25 °C.

The adsorption of the phenol compound was increased with the increasing of contact time (Fig. 6). The equilibrium adsorption of phenol was reached at about 130 min.

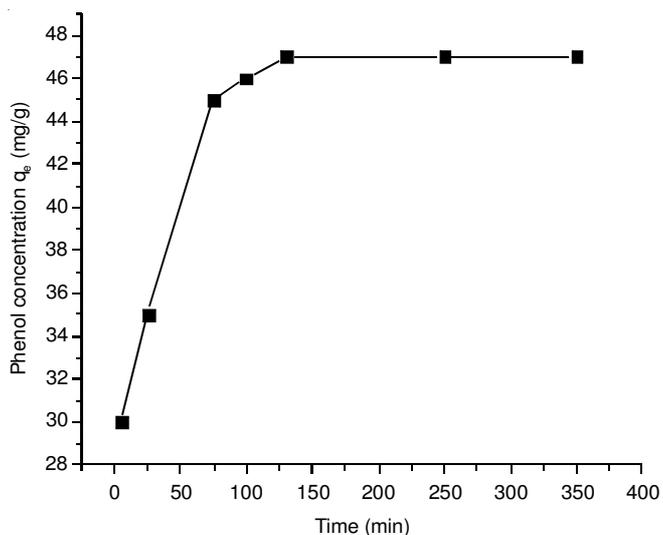


Fig. 6. Adsorption of phenol by polyitaconic acid (initial conc: 50 mg/L, initial pH:13, temperature: 25 °C)

At the beginning (10-30 min), the adsorption of phenol increased rapidly. The higher adsorption of phenol at the initial period of contact time is due to the higher availability of vacant sites on the external surface of adsorbent<sup>17</sup>.

**Effect of phenol concentration:** The effect of initial phenol concentration on percentage removal of phenol at equilibrium shows that the increase of concentration will increase the percentage of phenol removal (Fig. 7).

As phenol concentration increases from 10 to 50 mg/L, the percentage removal was increased from 24 to 56 %, because when the concentration of phenol increased this lead to increasing the mass of phenol molecules after that increase in driving force to these molecules and therefore acceleration the rate of mobility from solution to a surface of adsorbent<sup>18</sup>.

**Adsorption isotherms:** In this study, the adsorption isotherms equation was used to describe the relationship between the amount of phenol adsorbed by polyitaconic acid at equilibrium at 25 °C, pH 13, solid/liquid ratio 0.1 g/50 mL and the results are shown in Fig. 8a. The equilibrium adsorption isotherm has an important role to describe any adsorption system<sup>19</sup>.

The Langmuir, Freundlich and intra-particle diffusion are very important to determine the adsorption capacity of adsorbent in removal phenol compounds were used to describe the

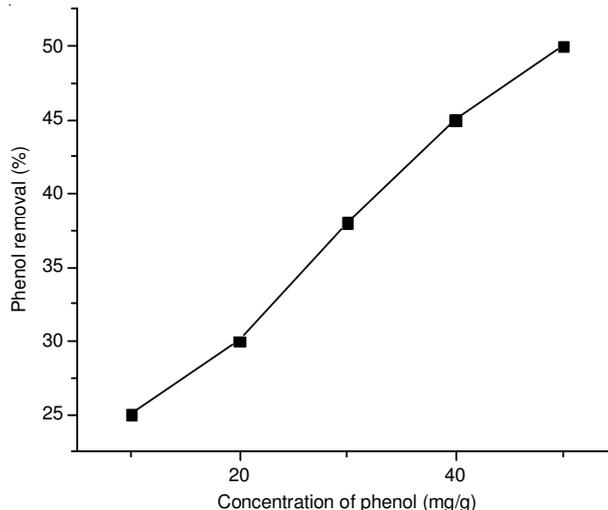


Fig. 7. Adsorption of phenol by polyitaconic acid at different initial concentrations (initial adsorbent dose: 0.1 g, initial pH:13, contact time: 130 min, temperature 25 °C)

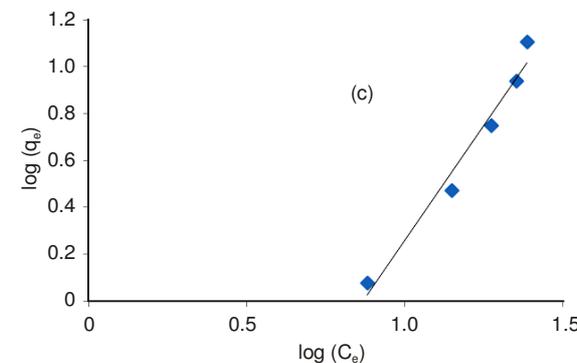
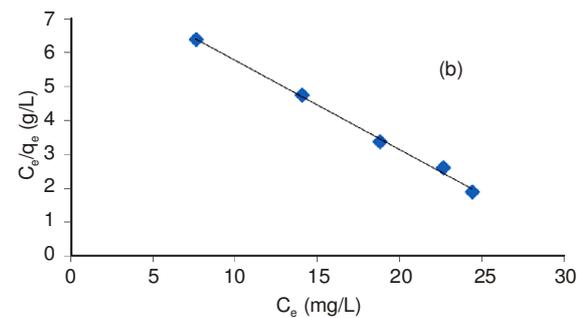
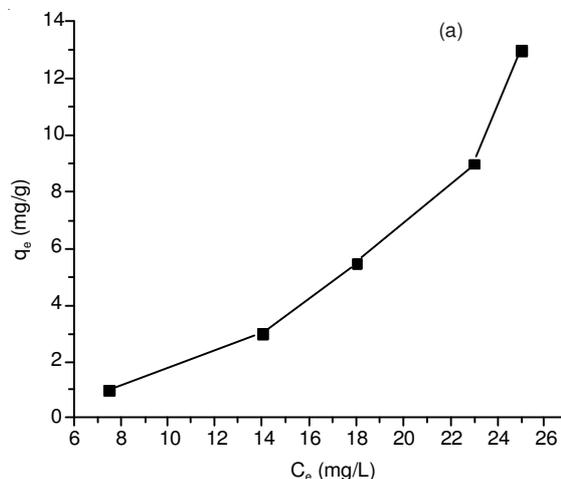


Fig. 8. Equilibrium adsorption isotherm (a) Langmuir isotherm (b) Freundlich isotherm plot for phenol adsorption on polyitaconic acid (temperature; 25 °C, initial pH:13 and solid/liquid ratio 0.1 g/50 mL)

equilibrium phenomenon between adsorbed phenol on the surface of adsorbent and unadsorbed phenol in solution<sup>20</sup>. The value of Langmuir and Freundlich constants are obtained by plotting  $C_e/q_e$  versus  $C_e$  (Fig. 8b) and  $\log q_e$  versus  $\log C_e$  (Fig. 8c).

The adsorption isotherm data are calculated from the slope and intercept of the linear plots used the Langmuir eqn. 3 and Freundlich eqn. 4, together with  $R^2$  value to both equations are given in Table-2.

Langmuir Isotherm			Freundlich Isotherm		
$R^2$	B (L/mg)	$Q_{(MAX)}$ (mg/g)	$R^2$	$K_F$ ((mg/g) (L/mg) <sup>1/n</sup> )	N
0.9965	0.031	3.796	0.9708	49.52	0.511

It is clear that  $R^2$  value for Langmuir is closer to 1; while the value for Freundlich isotherm is 0.97 which means that Langmuir isotherm model describe data better than Freundlich. The Langmuir isotherm model shows that the adsorption increases with increases in phenol concentration until it reaches the saturation point.

This describes the adsorption process which occurs by formation monolayer to phenol molecules on the surface of the adsorbent and after that no further adsorption will occur<sup>21</sup>. All sites on the surface of the adsorbent are occupied by phenol molecules so any further increase in concentration of phenol compound in the solution will not increase the amount of adsorbed phenol.

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

A favorable adsorption does not tend to have Freundlich. The n constant is not between 1 and 10. Smaller value of n (larger value of 1/n), indicates that it does not cause strong interaction between the phenol molecules and adsorbent. From the n value we are sure that the assumption of monolayer chemical adsorption between adsorbate and adsorbent which was used in this research was achieved completely, on the contrary the multilayer physical adsorption was not achieved<sup>22</sup>.

**Kinetics of phenol adsorption:** The mechanism of adsorption have been studied using the following models: pseudo-first-order, pseudo-second-order and the intra particle diffusion model were all used to test the experimental data.

Taking the pseudo-first order as follows:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303)t \quad (5)$$

where  $q_e$  is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at equilibrium,  $q_t$  is the amount of phenol adsorbed per unit mass of adsorbent (mg/g) at time t (min),  $K_1$  ( $\text{min}^{-1}$ ) is the pseudo-first order rate constant<sup>23</sup>.

The pseudo second order models type of equation was used to describe the adsorption process that occur to the ions and compound which containing of polar functional groups such as ketones, aldehydes, carboxylic acids and phenolic compounds. The relationship is used to describe this equation as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

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

The results of all these kinetic models are shown in Fig. 9 and Table-3. From Table-3 the correlation coefficient values ( $R^2$ ) of the pseudo-second-order model for adsorbent are greater than those obtained for the pseudo-first-order model. The values of the equilibrium of adsorption  $q_e$  that have been calculated to the pseudo-second-order model, are very close to the  $q_e$  of experimental value.

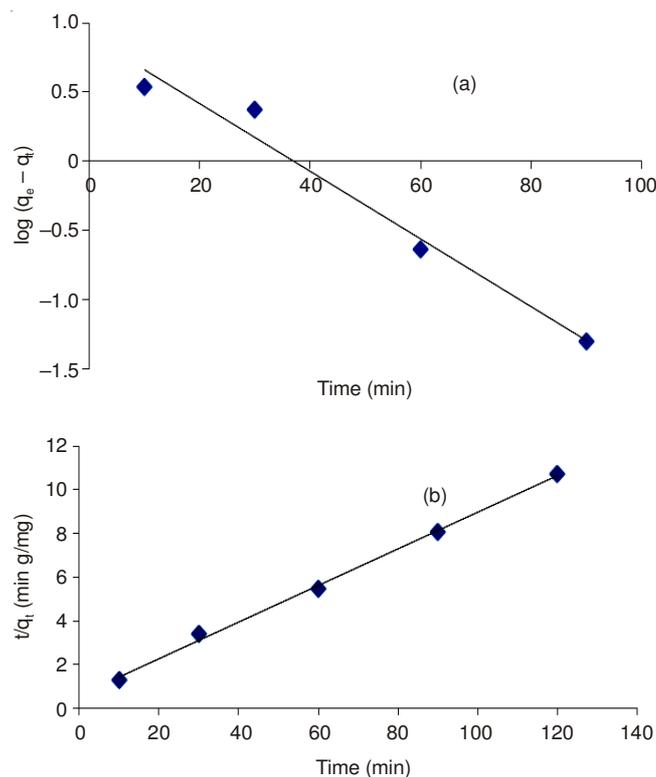


Fig. 9. Pseudo-first order (a) and pseudo-second order kinetics model of phenol adsorption on polyitaconic acid (b)

Pseudo-First Order		
$k_1$ ( $\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$
0.0564	8.105	0.9726
Pseudo-Second Order		
$k_2$ (mg/(g min))	$q_e$ (mg/g)	$R^2$
0.0118	11.933	0.9975

As a result, it can be concluded that the higher correlation coefficient of pseudo-second-order model and the close value of  $q_{e(\text{calc.})}$  values to  $q_e$  of the experimental value, the adsorption follows the pseudo-second-order kinetic model. The chemisorption processes between the adsorbent surface of polyitaconic acid and phenol adsorbate can explain the adsorption

process for phenol<sup>24</sup>. Weber and Morris discovered the theory to explain the mechanism or system of adsorption material from the media center by using a solid material as adsorbent. The relationship was shown by eqn. 7:

$$q_t = K_{bt}^{0.5} + A \quad (7)$$

where  $q_t$  is the amount of adsorbate (mg/g) at time  $t$  (min),  $k_b$  (mg/g min<sup>1/2</sup>) is the rate constant of intra-particle diffusion and ( $A$ ) expresses about of the thickness to the surface of adsorption.

The value of  $k_b$  and  $A$  were calculated<sup>25</sup> from the slope and intercept of plotting  $q_t$  vs.  $t^{0.5}$ .

Through the study, which used the intra-particle diffusion model, the values obtained as the correlation coefficient  $R^2$  and  $K_b$  constant are 0.992 and 0.487 (mg/g min<sup>-0.5</sup>) for  $K_b$  and 6.2 for  $A$ . From the data it implies that the rate of phenol adsorption into polyitaconic acid is not limited by mass transfer across the boundary layer on adsorbent.

**Adsorption thermodynamics:** In order to describe the thermodynamic adsorption of phenol molecules under the influence of thermal effect by changing temperature, the Gibbs free energy ( $\Delta G^\circ$ ), the entropy ( $\Delta S^\circ$ ) and the enthalpy ( $\Delta H^\circ$ ) were calculated so the spontaneity of adsorption process can be interpreted by thermodynamic parameters such as enthalpy change ( $\Delta S^\circ$ )<sup>26</sup>.

The thermodynamic values are calculated using the following equations:

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (8)$$

where,  $R$  is the universal gas constant (8.314 J/mol K),  $T$  is the temperature in Kelvin and  $K_d$  is the distribution coefficient which can be calculated from eqn. 9:

$$K_d = C_{Ac}/C_c \quad (9)$$

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

Gibbs free energy ( $\Delta G^\circ$ ) can be calculated by eqn. 10:

$$\Delta G^\circ = -RT \ln K_d \quad (10)$$

The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  are calculated from the slope and intercept of the linear equation which results from the plotting of  $\ln K_d$  versus  $1/T$  as shown in Fig. 10. The thermodynamics parameters are summarized in Table-4.

TABLE-4  
THERMODYNAMICS PARAMETERS FOR PHENOL  
ADSORPTION BY POLYITACONIC ACID AT  
DIFFERENT TEMPERATURES WITH INITIAL  
CONCENTRATION OF 50 mg/L

T (K)	$K_d$	$\Delta H^\circ$ (Kj/mol)	$\Delta G^\circ$ (Kj/mol)	$\Delta S^\circ$ (j/mol k)
288	0.383		2.29	
298	0.197	-51	4.02	-184.5
308	0.151		4.84	
318	0.043		8.31	

The positive value of Gibbs free energy ( $\Delta G^\circ$ ) at various temperatures indicates that the adsorption process which occurred to phenol by this adsorbent polyitaconic acid is feasible but not spontaneous<sup>27</sup>. The increases in the value of  $\Delta G^\circ$  with increases in temperature shows that the adsorption is more favorable at lower temperature.

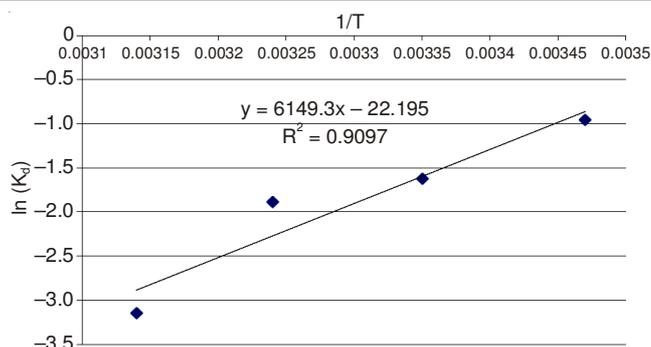


Fig. 10. Thermodynamics adsorption of phenol on polyitaconic acid

The negative value of the enthalpy ( $\Delta H^\circ$ ) indicates that the adsorption is an exothermic process and this indicates the affinity of adsorbent material for phenol.

**Theoretical analyses of phenol/polyitaconic acid complexation:** This observed trend may be due to the formation of ions. Phenoxide ions have more resonance energy than phenol itself due to no charge separation in the canonical structures as well as having negative charge on the more electronegative element, oxygen. Thus the ion is more stable in water<sup>28</sup>. Therefore, it is expected that the adsorbed phenol should be eluted more easily with sodium hydroxide than with simple water. Hydrochloric acid can protonate the oxygen of phenol but the ion formed is less stable due to charge separation in the canonical structures and positive charge on the more electronegative element (oxygen) (Fig. 11).

So the present study indicates that the adsorption of phenol from concentrated aqueous solutions corresponds to a process of micropore filling and that it is not limited to the coating of the micropore walls, as observed for dilute solutions. This means that, in case of phenol, depending on its concentration, two distinct mechanisms have to be considered for its selective adsorption by active carbons<sup>29</sup>.

Recently, it was confirmed the hypothesis proposed above by working on similar polymeric adsorbents (PMVBU = poly(*N*-methyl-*N*-*p*-vinylbenzylurea)). It appears that analysis of the adsorption mechanism suggested that hydrogen bonding was the primary driving force for phenol adsorbed on the polymeric adsorbents in cyclohexane and multiple hydrogen bonding was involved for PMVBU with phenol<sup>30</sup>.

## Conclusion

The polyitaconic acid polymer in basic medium was effective for phenol adsorption from olive mills wastewater more than in neutral medium which lead to a higher percent of phenol removal about 50 % occurs when the amount of dosage is 0.1 g with phenol concentration of 50 mg/L. other observation is phenol adsorption decreases when temperature increases as a result of phenol dissolving in water which leads to lowering an adsorption of phenol from water. Other conclusion is the pseudo-second-order model is more suitable to describe the kinetics adsorption more than pseudo-first-order model. The last thing we observed that it appears that analysis of the adsorption mechanism suggested that hydrogen bonding was the primary driving force for phenol adsorbed on the polymeric adsorbents in cyclohexane and multiple hydrogen bonding was involved for PMVBU with phenol.

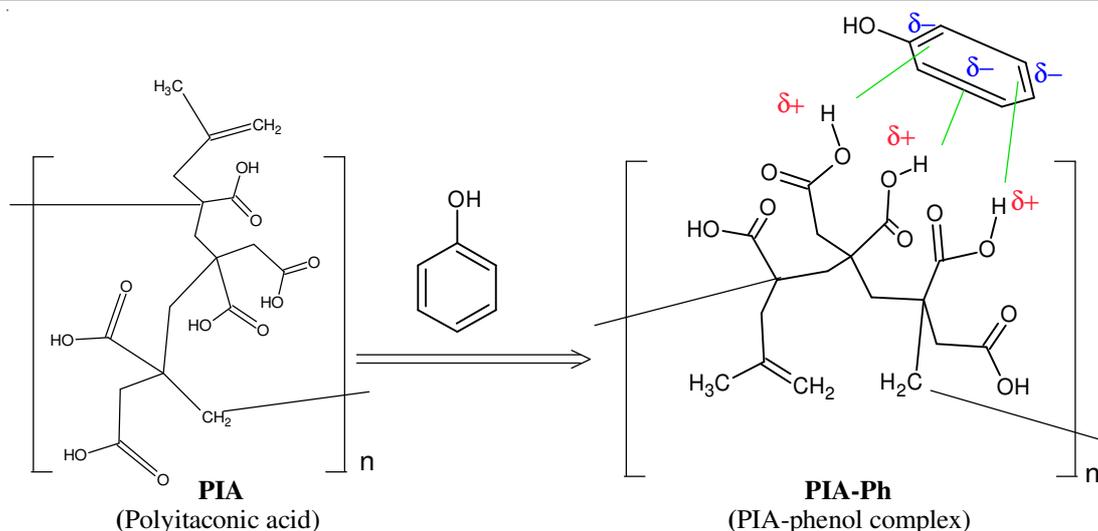


Fig. 11. Proposed mechanism of phenol/polyitaconic acid complexation

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