ISSN No.: 2454- 2024 (online)

International Journal of Technical Research & Science

PREPARATION OF ACTIVATED CARBON FROM PEANUT HUSK AND REMOVAL OF POLYPHENOLS

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Abstract-Several activated carbon types were produced from peanut husk by using different activation methods and evaluated for removal of polyphenols. The best prepared activated carbon was utilized for removal of polyphenols from olive mills wastewater and the optimum conditions for adsorption process were determined. The adsorption data was correlated to Langmuir and Freundlich models. The results showed that activation of peanut husk using H_3PO_4 gives a highly porous activated carbon with a specific surface area 987 m^2/g thus enhancing adsorption. The peanut husk based activated carbon- olive mills wastewater system fits to Freundlich isotherm model and adsorption kinetics fits to pseudo second order rate model.

Keywords: activated carbon, adsorption, agricultural wastes, peanut husk, polyphenols.

1. INTRODUCTION

Agricultural waste represents sever environmental problem. In an agricultural country like Egypt, millions of tons of wastes are produced annually; most of these wastes are burned on field resulting in hazardous emissions. One of the methods to add values to these wastes is to convert it to activated carbon. The added value associated with transforming an agricultural cheap waste to a more valuable material can only compete with the necessity to abate the harmful environmental effects often associated with these wastes. Utilization of waste materials obtained from various sources in the preparation of highly porous activated carbon has been very common as it has high sustainability, economic viability besides being an ecofriendly approach. Among the various types of wastes which can be productively utilized for generating activated carbon, agricultural and food wastes are of prime significance as they are commonly available, have massive carbon content and their exclusion from the surroundings will help to keep the environment benign. Carbonaceous adsorbents, as they are also referred to, are particularly utilized owing to their large surface capacity, fast kinetics of adsorption and their recovery [1]. Tsaia et al [2] activated sugar cane bagasse using a solution of zinc chloride followed by firing the residue to 500^{o}C for 30 minutes. The produced material was used to adsorb Acid Orange 10 from wastewater solution. There was a steady increase in pore surface area with the time of impregnation of the waste in salt solution. Investigating the possibility of removing organic matter from the wastewater from a beverage industry was investigated by Amuda et al [3] who compared the efficacy of using activated carbon originating from coconut shells to that of a commercially available type (Calgon carbon F-300). Their results indicated that acid treatment of coconut waste resulted in an activated carbon that showed better adsorption efficiency than the commercial one.

Ash et al. [4] prepared activated carbon from coir pith. This latter is the residue left after extracting coir fibers from coconut shells. The chemical route was adopted by impregnation in either phosphoric acid or caustic soda solution with heating to temperatures in the range 823 to 873 K. It was concluded from raw data that this waste could be effectively used in removing dyes from textile industrial wastewater.

Lam et al [5] produced activated carbon by first charring sawdust waste in a fluidized bed furnace followed by heating the waste with steam. The authors concluded that maximum adsorption of MB dye could be obtained using a particle size of 500 µm, charring at 500^{o}C and steam activation at 800^{o}C.

On the other hand, Michailof et al [6] studied the adsorption of phenolic compounds from a synthetic solution prepared to simulate OMWW using activated carbon. The activation process was performed using potassium hydroxide solution as chemical activating agent at two different pyrolysis temperatures (800^{o}C and 900^{o}C) and a pyrolysis time reaching five hours. They concluded that three hours were sufficient to obtain an activated product of maximum surface area and highest adsorption capacity.

Using diverse agricultural wastes such as ferronia shell waste and jatropha seeds waste, Karthikeyan et al. [7] prepared activated carbon by heating the waste in different solutions including zinc chloride, calcium chloride, sulfuric acid, sodium carbonate or simply by calcining with calcium carbonate. The maximum firing temperature was kept every time at 800^{o}C. The authors compared phenol adsorption results obtained using different wastes and different chemical activation procedures.

Saeeda [8] studied the production of activated carbon from mung bean husk using a chemical activation method. This was subsequently used to remove cadmium ions from an aqueous solution. Foo and Lee [9] used Parkia speciosa pod also known as stink bean as a precursor for preparing activated carbon by means of phosphoric acid. The pore volume and porosity distribution was assessed as function of carbonization temperature and the mass ratio of acid to waste. The carbon yield obtained was comparable to that of commercial activated carbon.

Verla et al. [9] successfully prepared ten samples of activated carbon by carbonization and activation of fluted pumpkin seed shell. Physical activation followed the thermal route using temperatures ranging from 300°C to 700°C, while chemical activation was achieved by first impregnating the prepared raw material with diverse activating agents such as phosphoric acid and sulfuric acid, soda ash and sodium chloride. Carbonization followed at 500°C. The activated samples prepared were fully characterized and successfully used to remove phosphate ions from waste solutions.

Yusufu et al [10] investigated the effect of the mode of activation on the properties of activation carbon prepared from cattle bone, coconut-shell and wood carbon. Complete characterization of the prepared samples was performed and the authors concluded that the prepared activated material could be effectively used for adsorption purposes.

Kwaghger et al [11] activated mango nuts using a solution of zinc chloride followed by activation to temperatures reaching 500^{o}C. They used a statistical model to correlate the properties of the activation carbon obtained, namely, specific surface area, carbon content and ash content to experimental conditions of preparation. They concluded that the optimum conditions for preparing activated species were a carbonization temperature of 212^{o}C, hydrochloric acid concentration of 100%, a residence time of half an hour and 1ml/g mixture ratio. This resulted in an activated carbon with 5.92% ash content, 1142.3 m^2/g specific surface area and 63.2% carbon yield. These experimental values were in good agreement with the values predicted by the statistical model.

According to Alslaibi et al. [12] activated carbon with high specific surface area can be produced by chemical impregnation with microwave heating. The values of surface area obtained exceeded those obtained by traditional thermal means.

Rocha et al [13] studied the adsorption of phenol from synthetic solutions using chemically activated carbon based on corn cobs using phosphoric acid. The results indicated that phenol adsorption on corn cobs activated carbon was better described by the Freundlich model, indicating heterogeneous and multilayer adsorption.

The objective of this study was to transform peanut husk into activated carbon by different routes and identify the best route that produces the most affective activated carbon for removal of polyphenols from Olive Mills Wastewater (OMWW).

2. MATERIALS AND METHODS:

2.1 Materials

2.1.1 Olive Mills Wastewater

Industrial olive mill wastewater was obtained from Mina Factory for Oils and Grease located at 4th industrial area, El-Sadat city which is a medium sized three phase olive mill. The capacity of this facility is 30 tons olive oil/day; it works seasonally for 3-4 months/year producing about 3000 ton/year. The samples were filtered to remove suspended tissues and then were frozen at -18C till used.

2.1.2 Peanut Husk

Peanut husk was collected from local market, then was washed thoroughly with a lot of water until the removal of the brown coloration and then washed twice with distilled water. It was then dried using laboratory drying oven at 110 °C for 1 hour until constant weight. Peanut husk was ground in a laboratory hummer mill then sieved to 500 microns particle size. The clean, ground and sieved peanut husk was stored in glass jars until activation processes [14].

2.1.3 Chemicals

Folin-Ciocaltu reagent, Potassium hydroxide, sodium sulphate and Sodium carbonate were provided from Acme Synthetic Chemicals, Mumbai. Hydrochloric acid, sodium hydroxide was provided from Sigma-Aldrich Corporation, ortho-phosphoric acid was supplied by Tiba chemicals.

2.2 Methods

2.2.1 Preparation of peanut husk based activated carbon

Various methods were used for the preparation of activated carbon from peanut husk using different activating agent as well physical activation.

2.2.2 Physical activation

In the physical activation process, no chemicals was used, the procedure adopted was as follows [15]:

10 grams of washed ground husk of 500 microns particle size was burned in muffle oven in absence of oxygen at 170 ^{0}C for one hour then the temperature risen to 450 ^{0}C for another hour. The pots were moved to a desiccator till the sample cooled to room temperature.

2.2.3 Chemical activation

Several chemicals of different natures (acids, alkaline, salts) were used. The adsorption efficiency for polyphenols from Olive Mill Waste Water (OMWW) was studied.

2.2.4 Activation Using Strong Alkaline Potassium Hydroxide (KOH)

In this activation process the method proposed by Sadiq et al [16] was followed. The procedure was as follows:

- A solution of 10 weight % KOH (10g in 100ml distilled water) was prepared.
- 6 grams of ground dry husk of 500 micron particle size was added to that solution.
- The sample was kept in an ultrasonic cleaner for 10 minutes at 30^{o} C, and then was shaken for 6 hours at 50 ^{o}C.
- The sample was filtered immediately and washed with plenty of doubled distilled water until the pH of the filtrate reached about 7. It was then placed in the muffle furnace for one hour at 170(±5^{o} C) and the temperature continuously was risen to 450(+/- 5^{0}C) for another hour and then lowered down to room temperature.
- The cooled sample was washed thoroughly with distilled water, dried at 110^{0}C for one hour and sieved to 100 m (0.147 mm).
- The sample was preserved in a desiccator for use.

2.2.5 Activation Using Different Salts Solutions

Three different salts (Na_2 CO_3, $CaCl_2$ and Na_2 SO_4) were used for the preparation of activated carbon. Preparation of activated carbon using different salt solutions followed the following procedure described by Skarthikeyan et al [17]:

- Salt solution with 10wt% concentration was prepared (10 gm/100ml) and 1 cm particle size dry husk was soaked in these solutions with a ratio of 1 gm / 5ml solution for 24 hours.
- After the samples were filtered, they left to dry for 12 hours in air at ambient temperature and humidity.
- The samples were then carbonized at 400 ^{o}C for 60 minutes then cooled down to room temperature and powdered to smaller particles.
- The samples were returned to the muffle furnace for another 60 minutes at 800 ^{o}C and then samples cool to room temperature.
- These carbon samples were washed with plenty of 4N HCl solution, filtered and washed with distilled water thoroughly till the pH of washing water reached 7, then dried at 110^{0}C for 1 hour.

2.2.6 Activation Using Phosphoric Acid

Activated carbon using phosphoric acid was prepared according to Al Othman et al [18] as follows:

- Clean sieved husk was soaked in phosphoric acid 33 vol. % solution for 24 hours in the ratio of 30% (30g husk/100ml. solution), after 24 hours the sample was filtered from excess acid.
- The sample was carbonized in a muffle furnace at 170 ^{o}C for one hour and then temperature was risen to 450 ^{o}C for another hour.
- After cooling the sample was washed thoroughly with distilled water till the pH of filtrate reached 7.
- The sample was washed again with boiled distilled water, then dried using oven drier at 110 ^{0}C for one hour and stored in a jar.

2.3 Batch Adsorption Process

2.3.1 Effect of pH

The effect of pH was studied by adjusting the initial pH of waste water solution between (2, 10) with diluted NaOH solution (1 M) and diluted HCl solution (1M). The optimum pH was determined using the following procedures:

- Six samples of filtered OMWW were prepared with different pH 2, 4, 6, 8, 10, and 12. The same amount of dried ground peanut husk with the same particle size (500 microns) was added to each sample.
- The samples were shaken at room temperature and 150 rpm for 24 hours.
- Samples were filtered and the total phenol content measured and the removal efficiency determined to obtain the optimum pH value which gives maximum removal efficiency.

2.3.2 Effect of Initial Concentration

The effect of initial concentration on the removal of phenols at constant optimum pH value was determined using the following procedure:

100 ml of different concentrations of OMWW were prepared by dilution using distilled water between 10-100 %.

The pH of these solutions was adjusted to optimum pH then the same amounts of peanut husk were added to diluted samples and shaken at room temperature and 150 rpm for 24 hours.

The samples were filtered and polyphenols concentrations were measured. The optimum initial concentration was determined according to the removal efficiency.

2.3.3 Effect of Adsorbent Dose (Adsorbent/ Adsorbate Ratio)

The effect of adsorbent dose using constant wastewater volume (100 ml) on removal efficiency was studied:
At optimum pH and optimum concentration, samples of OMWW with 100 ml volume were prepared. Different amounts of peanut husk (or peanut husk based activated carbon) with the same particle size (500microns) were added to the sample solutions these samples then shacked at 150 rpm for 24 hours.
Samples were then filtered and the removal efficiency for each dose calculated.
The optimum adsorbent dose was determined according to removal efficiency.

2.3.4 Effect of Contact Time

The increase in percent removal of total phenol content with respect to time helped in determining the equilibrium time.
The effect of contact time on the percentage removal of total phenol content at optimum conditions of the other factors was studied and the procedure was as follows:
Samples were prepared each containing 100 ml solution at optimum conditions for both of peanut husk and peanut husk based activated carbon separately.
Samples were taken at time intervals of 50 minutes for 8 hours. The changes in total phenol content with time were recorded.

2.3.5 Effect of Agitation

Agitation has a major influence in adsorption process and particularly in wastewater treatment where agitated tanks used in many treatment plants.
To study this effect, three different agitation speeds (100, 200 and 300 rpm) were used in the current search. The experimental procedure was as follows:
For both husk and peanut husk based activated carbon, three 100 ml. solutions prepared at optimum conditions, each solution agitated for 8 hours at different rpm. Samples were taken at different time intervals and analyzed.

2.4 Analytical Methods

2.4.1 Total Polyphenol Content Measurement

2.4.1.1 Standard (Calibration) Curve

In this study, a calibration (standard curve) was first prepared by using spectrophotometric analyzer for measuring total phenols in olive mill wastewater samples. The polyphenols (as gallic acid)-peanut husk based activated carbon system calibration curve is shown in figure (2.1)

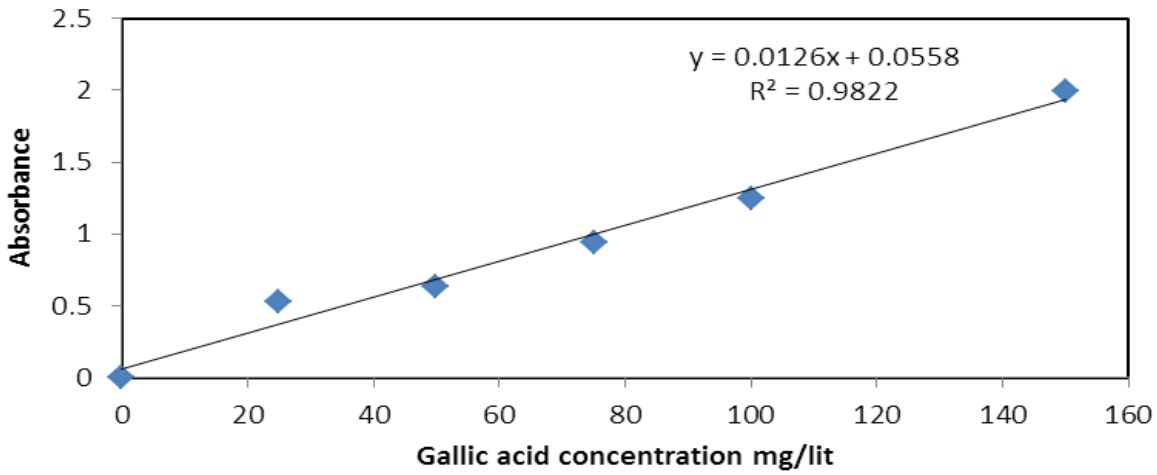

Fig. 2.1 The Polyphenols-Peanut Husk Based Activated Carbon System Calibration Curve

A standard curve from a specific polyphenolic compounds was determined to refer to the total phenols content of this compound. A High Performance Liquid Chromatography (HPLC, Agilent, 1200 series) was used for this purpose. The results from (HPLC) indicated that olive mill waste water (OMWW) contains Gallic acid as reference for measuring total phenols in waste water samples [19].
The procedure was as follows:

- Pure Gallic acid (0.05 gm) was dissolved in 100 ml. distilled water, so as to reach a concentration of 500 mg/lit.
- Different concentrations (10, 25, 50, 75, 100, 150) mg/lit. were prepared from this solution (According to equation $C_1V_1=C_2V_2$)
- 0.5 ml of each concentration was taken in a test tube by 1 ml. pipette.

- 2.5 ml of folded Folin Ciocalteu reagent (1:10) was added for each sample and shaken for 3 minutes.
- 2 ml of sodium carbonate solution (75 gm/lit) was added for each sample and left for 30 minutes standing in a test tube holder.
- The absorbance of samples was then measured using spectrophotometer at wave length 760 nm.

2.4.2 Measurement of Total Phenol Content in Waste Water Samples

Total phenols contents of waste water samples were determined as follow [19]:

- Waste water samples were centrifuged (or filtered) to produce clear solutions. 1 ml of the supernatant was diluted with distilled water to the ratio 1:20 if a high polyphenolic compounds concentration was expected or 1:10 if a lower concentration was expected or even without dilution if much lower concentration is reached.
- 0.5 ml of diluted solution was added to 2.5 ml of 1:10 diluent Folin-Ciocalteu reagent in a test tube, it was shaken and left for 3 minutes, after that 2 ml of sodium carbonate solution was added.
- Spectrophotometer was then used to read absorbance for each sample using a wave length of 760 nm.
- Samples were prepared in duplicates and the average readings were taken each time for more accuracy.

3. RESULTS AND DESCUSSION

3.1 Evaluation of Prepared Activated Carbon

Evaluating the activated carbon produced from different activation methods was according to two criteria, the first one is the yield of the produced carbon, and the yield was calculated according to the equation:

$$\%\text{Yield} = \frac{\text{W husk before activation} - \text{W of produced carbon}}{\text{W dry husk before activation}} * 100 \qquad 3.1$$

From fig. 3.1, the maximum yield for activated carbon production was obtained from activation using phosphoric acid (32%).

The second criterion for comparing the produced activated carbon was the adsorption efficiency for polyphenols from OMWW. For this comparison, three activated carbon were chosen, the one with the best yield (H_3PO_4), the second in yield with the lowest cost (physical activation) and the third was activation with KOH which despite its low yield had large specific volume (surface area).

Removal efficiency was calculated according to equation (3.2):

$$\%\ \text{Efficiency} = \frac{C_0 - C}{C_0} * 100 \qquad 3.2$$

Comparing the three chosen activated carbon, using phosphoric acid in chemical activation gave the highest yield (32%) and the highest percent removal of phenols (86%) under the preliminary adsorption experiment conditions (0.5 gm activated carbon at 100 ml volume of OMWW solution with 960 mg/lit initial concentration Fig. 3.2.

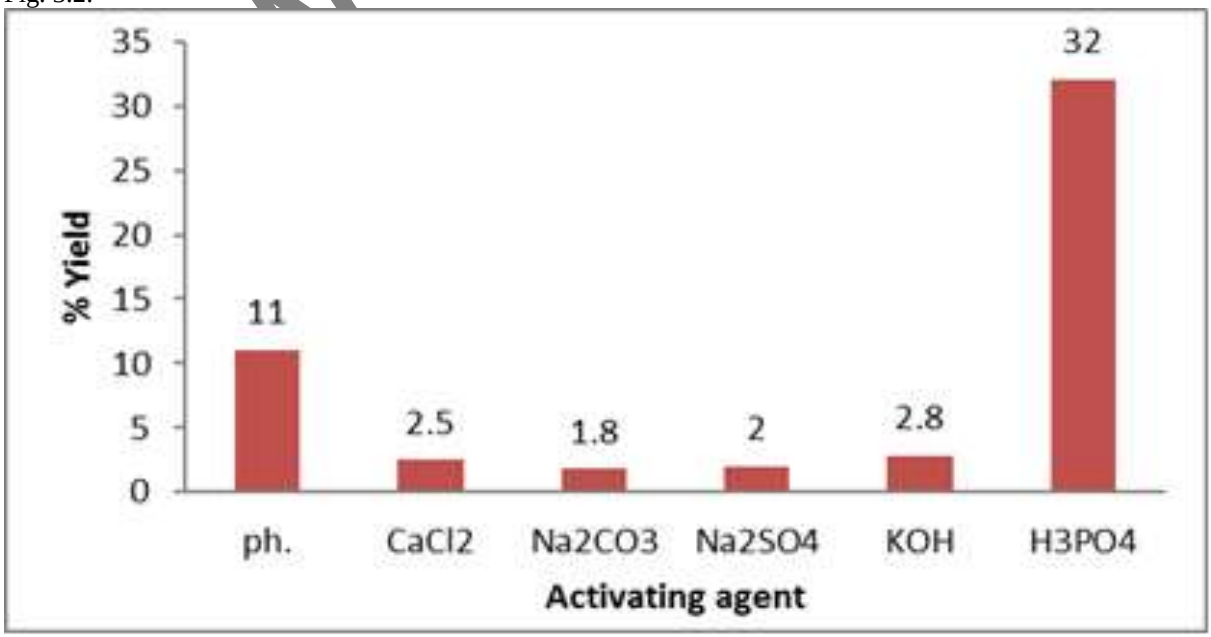

Fig. 3.1 The Yield for Different Activating Agent

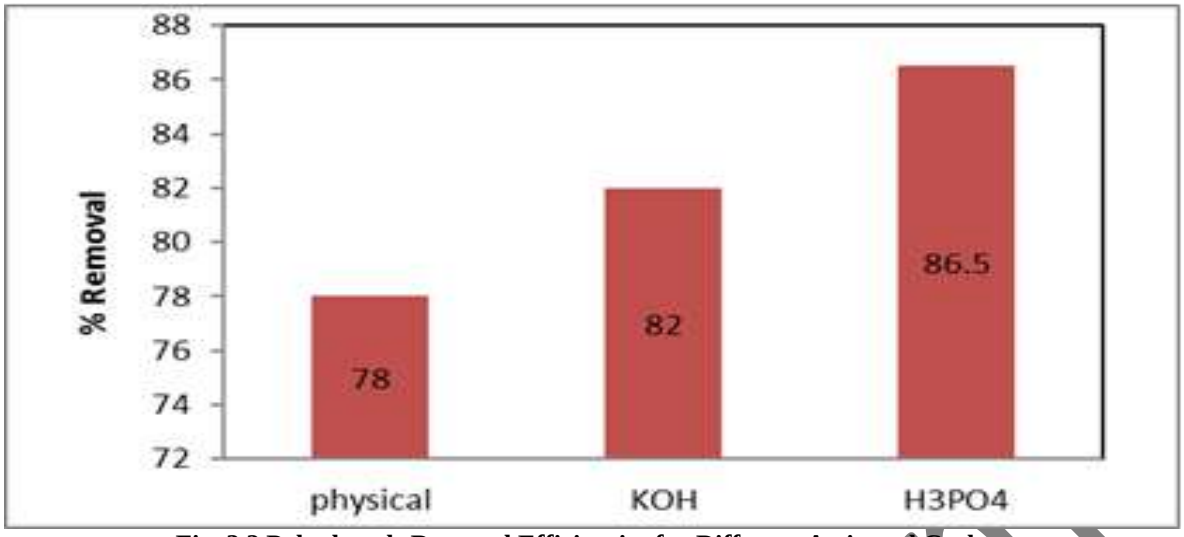

Fig. 3.2 Polyphenols Removal Efficiencies for Different Activated Carbon

3.2. Characterization of Phosphoric Acid Peanut Husk Based Activated Carbon

3.2.1 Bulk Density

The bulk density can be calculated from the equation (3.3):

$$\rho = \frac{m}{V_{bulk}} \quad 3.3$$

The density of activated carbon produced from activation by phosphoric acid was determined as 345 kg/m^3.

3.2.2 Solubility in OMWW

It represents the difference in weight of carbon before and after immersion in OMWW for 24 hours; this criterion estimates the decay or loss in the produced activated carbon during the adsorption process, it can be calculated as percentage ratio from equation (3.4):

$$\% \text{ Solubility} = \frac{m_o - m}{m_o} \times 100\% \quad 3.4$$

Where:
m_0 refers to the weight of carbon at time zero and m refers to the weight of carbon after 48 hours soaking in OMWW. The percent solubility for carbon was found to be 16%.

3.2.3 SEM Analysis

The Scanning Electron Micrographs (SEM) of the prepared carbon is shown in fig. 3.3. It is clear that the surface of carbon is rough and contains different porous sizes; this porous structure maximizes the inner surface area of carbon and provides cavities for internal diffusion.

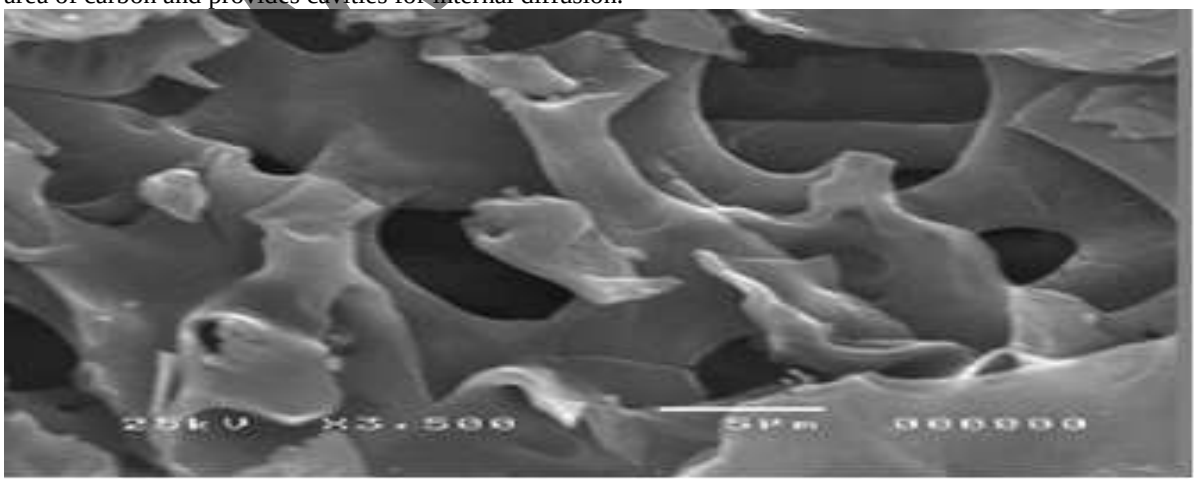

Fig. 3.3 The Scanning Electron Micrographs of Produced Activated Carbon

3.2.4 FTIR Analysis

The FTIR analysis for phosphoric acid Peanut Husk Based Carbon Activate (PHBAC) is shown in fig. 3.4.
The nearby located band at 1623 cm^{-1} after activation could be attributed to C – O vibrations [20]. This may be due to extraction of H elements and OH groups from the aromatic rings during impregnation and heat treatment stage as a result of the dehydration effect of phosphoric acid. The absorption peak around 1084 cm^{-1} indicated

the existence of C–O carboxylic bond or the P–O bond in phosphate esters. The absorption peak around 1084 cm^{-1} indicated the existence of C–O carboxylic bond or the P–O bond in phosphate esters [21].

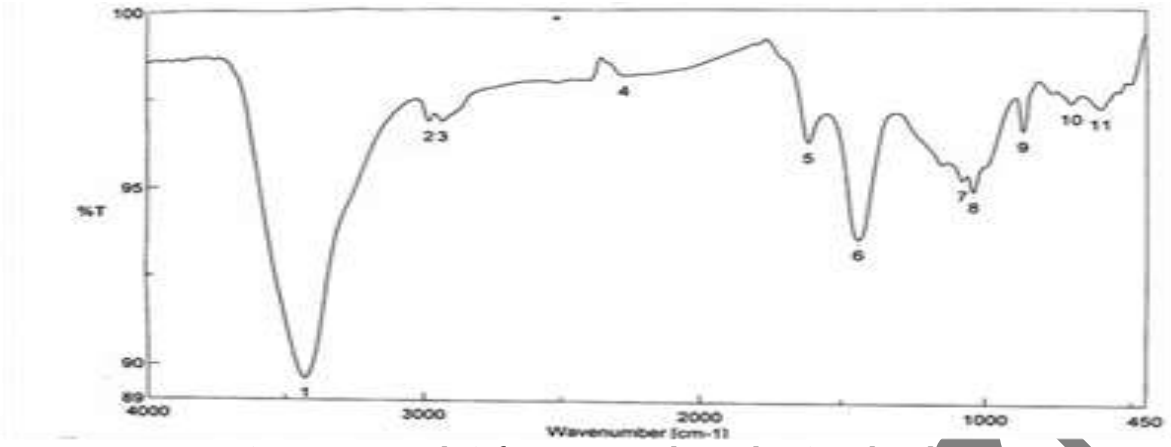

Fig. 3.4 FTIR Analysis for Peanut Husk Based Activated Carbon

3.2.5 BET Surface Area Analysis

The BET analysis for chemically activated peanut husk shows great enhancement in surface characterization than peanut husk, the sample used was 0.5 in mm particle size. The adsorption isotherm for N_2 on activated carbon surface is shown in fig. 3.5. The adsorption isotherm simulate type 1 of adsorption isotherm according to IUPAC classification which indicates that adsorption inside micro-pores takes place in monolayers behavior associated with narrow silt like pores of adsorbents [22]. The BET surface area calculated by BET equation is 987 m^2/ g which is an acceptable value. Total pore volume equal 0.6163 cc/g.

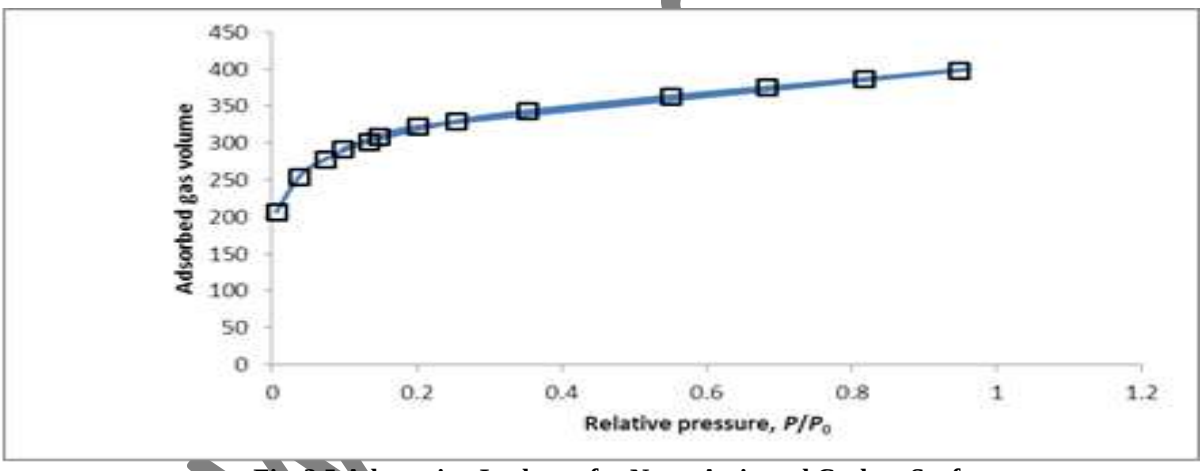

Fig. 3.5 Adsorption Isotherm for N_2 on Activated Carbon Surface

3.3 Effect of pH Value of OMWW

The natural *pH* value for OMWW effluent is 5.2 for the sample taken from the case study factory; this pH value was modified during batch and continuous treatment experiments to the optimum pH value for each adsorbent. Generally, phenolic compounds are weak acids, slightly soluble in water with *pKa* = 9.89. Zero point charge (PZC) for peanut shell activated carbon as reported by Zhong et al [23] is 3.9. Above PZC the surface of adsorbent is negatively charged which increases the electrostatic repulsion between phenolic anions and the surface of the activated carbon. These results are shown in fig. 3.6.

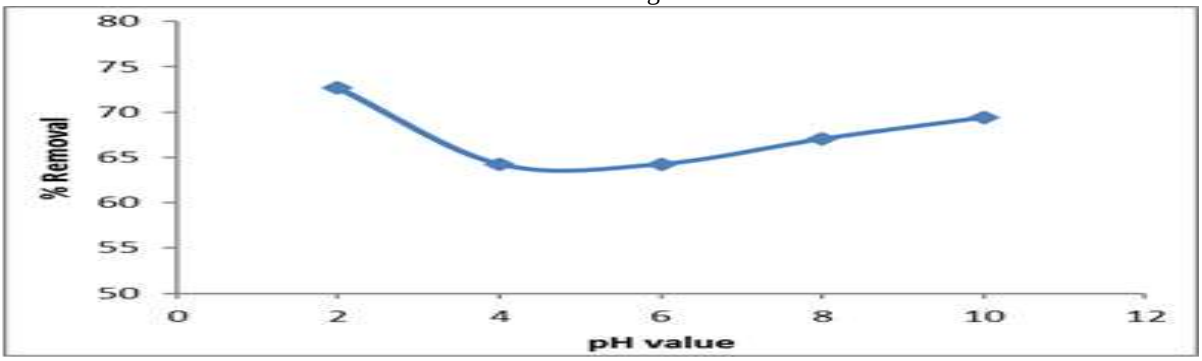

Fig. 3.6 Effect of pH Value on Percent Removal of Polyphenol from OMWW by PHBAC

3.4 Effect of Initial Concentration

A certain amount of activated carbon (4 g) was added to 100 ml of OMWW solutions with different initial polyphenols concentrations (480, 960, 1440, 1920, 2880 and 3800 mg/lit equivalent to 10, 20, 30, 40, 60, 80 and 90% dilution) of effluent concentration and were shaken for 24 hours at room temperature.
The results indicates that increasing initial concentration of polyphenols is associated by a decrease in removal efficiency due to saturation of active sites and pores existing on the adsorbent surface by adsorbates molecules as shown in Fig. 3.7. Thus the concentration used in further experiment was taken as 480 mg/lit (10% dilution).

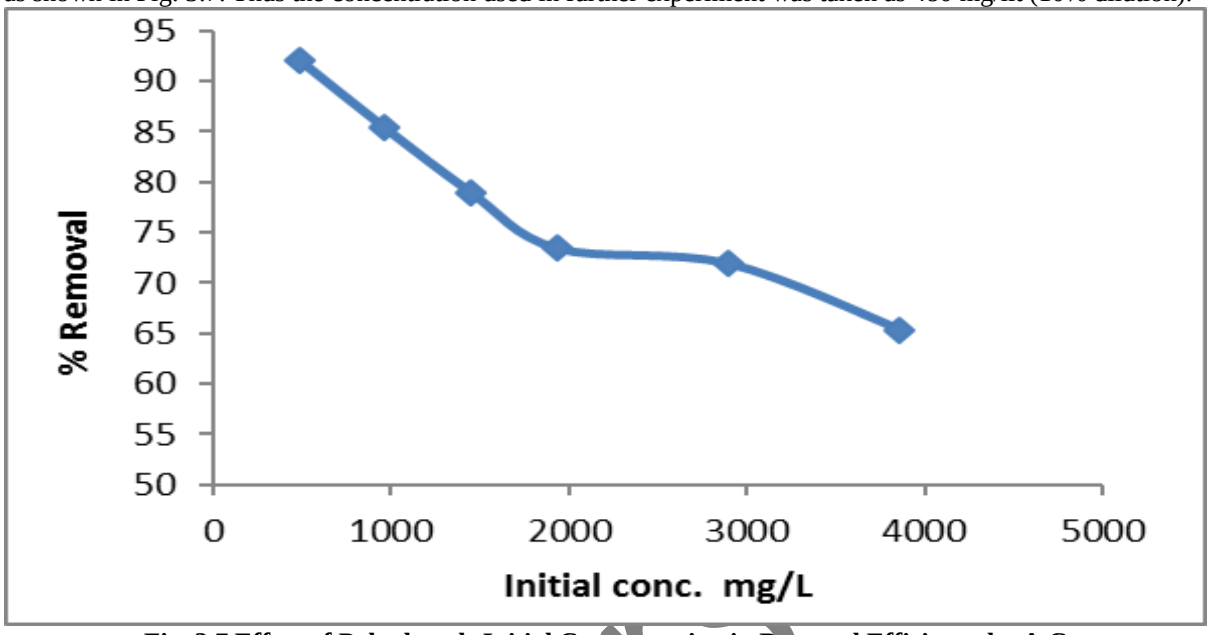

Fig. 3.7 Effect of Polyphenols Initial Concentration in Removal Efficiency by A.C

3.5 Effect of Adsorbent Dose

Fig. 3.8 shows the relation between adsorbent dose and percent removal of polyphenols. The results indicate that increasing adsorbent dose from 0.4g/100 ml to 2.4 g/100 ml had a significant effect on the percent removal as it increases from 65% to 91%. Upon further increase of the adsorbent dose beyond 2.4 g/100 ml and up to 6 gm/100 ml, the percent removal of polyphenols only slightly increased from 91% to 94.675%.
This result can be explained by the fact that adsorption process occurs on the adsorbent surface and by increasing the dose, the surface area increases and more active sites are available for adsorption. However, as available sites get saturated less removal takes place as evidenced by the plateau shown in fig (4.34) when the dose exceeds 2.4 g/100 ml.

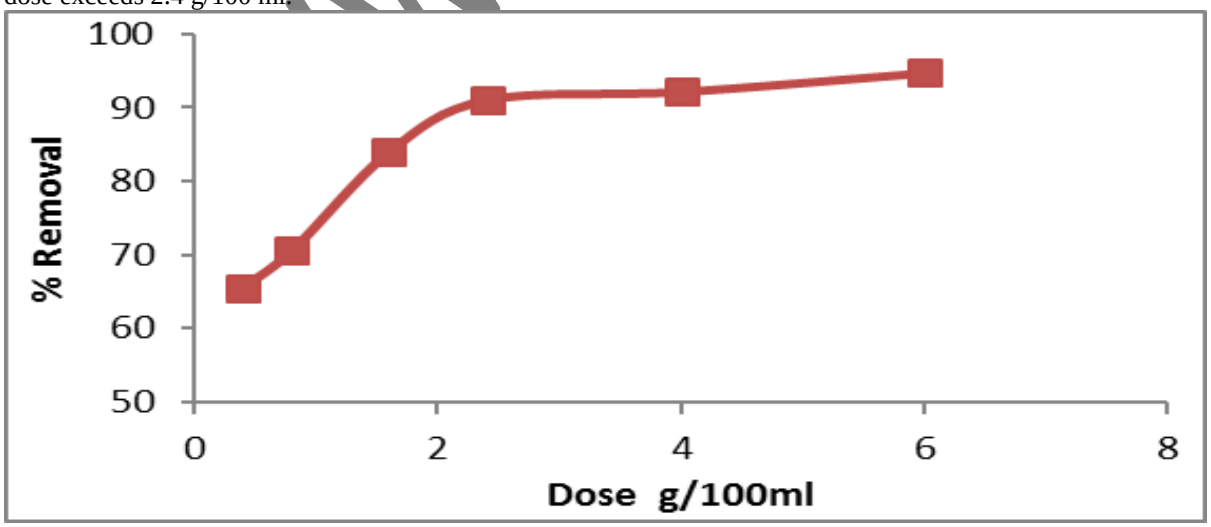

Fig. 3.8 Effect of Adsorbent Dose on Removal Efficiency

3.6 Effect of Agitation Speed

Three different agitation speeds were used to follow the effect of agitation speed on polyphenols removal efficiency. The results are illustrated in Fig. 3.9, the figure shows that when using an agitation speed of 100 rpm, removal was enhanced to 93% after 400 minutes and the maximum removal was reached at 300 rpm agitation speed (99% after 400 minutes).

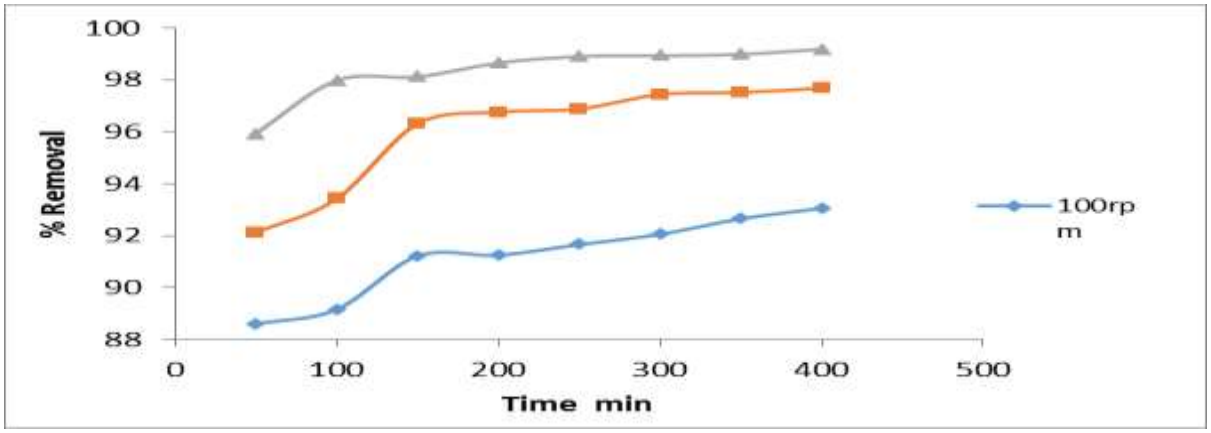

Fig. 3.9 Effect of Agitation Speed on Percent Removal of Polyphenols

3.7 Effect of Contact Time

The effect of contact time (50 – 480 min.) on the removal of polyphenols from olive mill waste water using activated carbon is shown in fig. 3.10. Most of the adsorption process is accomplished within the first 50 minutes where 70% of polyphenols content of OMWW adsorbed; after that, adsorption proceeds at a slower rate till reaching 85 % removal after 480 minutes (The adsorption equilibrium removal after 24 hours is 91%). This is due to that initially, a large amount of active sites is available for the adsorption process and the driving force which is the difference between bulk concentration of polyphenols in solution and that in adsorbent surface is large. Polyphenols accumulating on active sites result in repulsive forces forming between phenolic compounds in bulk and thus on the surface and molecules of phenolic compounds need to penetrate deeper into pores developing more resistance.

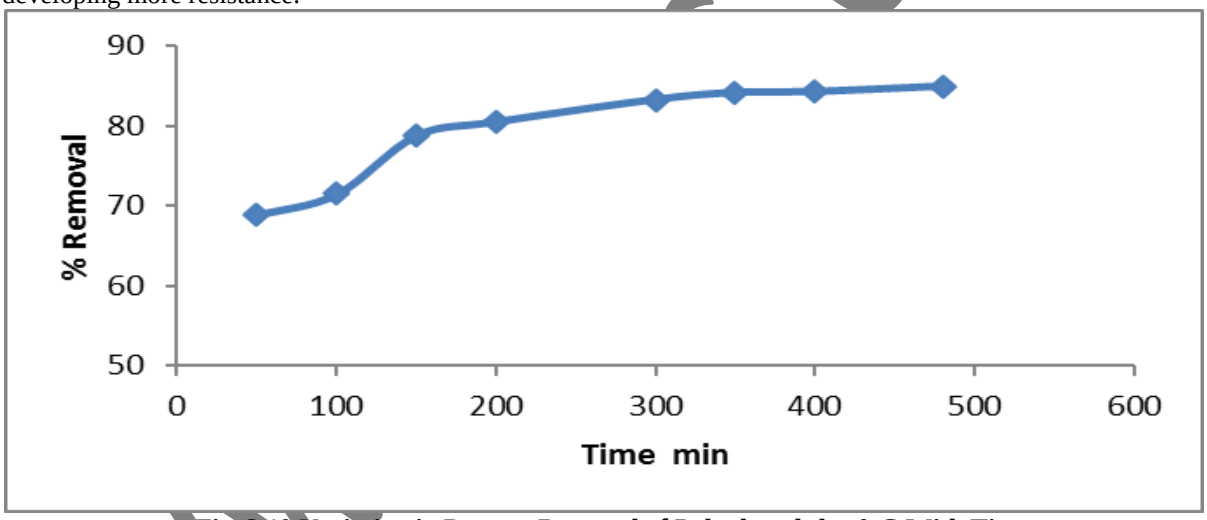

Fig. 3.10 Variation in Percent Removal of Polyphenols by A.C With Time

3.8 Adsorption Isotherm Modeling

3.8.1 Langmuir model:

Fig. 3.11 represents the fitting results of total phenols adsorption onto activated peanut shell to Langmuir isotherm model at optimum conditions.

Langmuir isotherm model is a theoretically derived isotherm that was first proposed to describe adsorption in gas-solid systems; later it was proved that it is also valid for some liquid-solid systems. Langmuir assumed that the surface of adsorbent is homogeneous and smooth and consists of finite number of identical sites with homogeneous adsorption energy and also that adsorbate molecules accumulate in the surface of adsorbent in monolayer behavior and interaction between solute molecules on the adsorbent surface was neglected.

The equation for Langmuir model in linear form is:

$$\frac{Ce}{qe} = \frac{1}{Q_m} C_e + \frac{1}{Q_m\, KL} \qquad 3.5$$

Where:

q_e refers to the equilibrium adsorption capacity (mg/g), Q_m is the maximum adsorption capacity (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), and K_l refers to Langmuir constant (L/mg) related to the energy of adsorption. As can be seen from this figure, the Langmuir plot displayed poor fitting of experimental data, suggesting that this model does not apply to the present case.

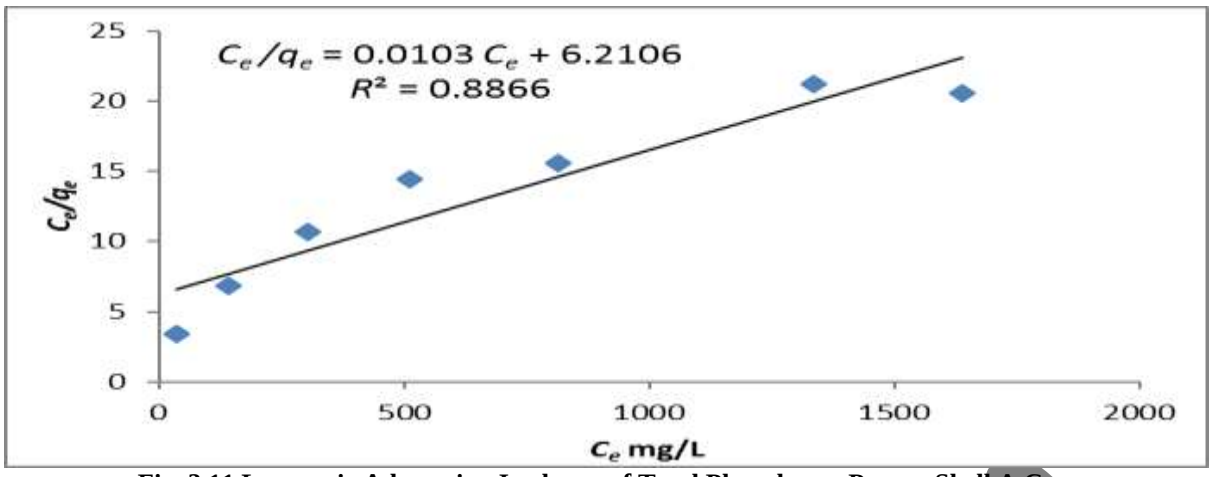

Fig. 3.11 Langmuir Adsorption Isotherm of Total Phenol onto Peanut Shell A.C

3.9 Fraundlich Isotherm

Fig (3.12) shows the fitting of experimental results obtained to Fraundlich isotherm model. Freundlich assumed that adsorption occurs on heterogeneous surfaces of different adsorption affinities. He assumed that the most active sites are first occupied and that the binding strength decreases with the increasing degree of site occupation [24]. He then obtained the following semi – empirical equation:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad 3.6$$

The elevated value of the determination coefficient R^2 seems to favor this model. The Freundlich constants K_f and n were calculated from fig. 3.12 as follows:

Log K_f = 0.2158 Hence: K_f = 1.64

1/n = 0.5103 Hence: n =1.96

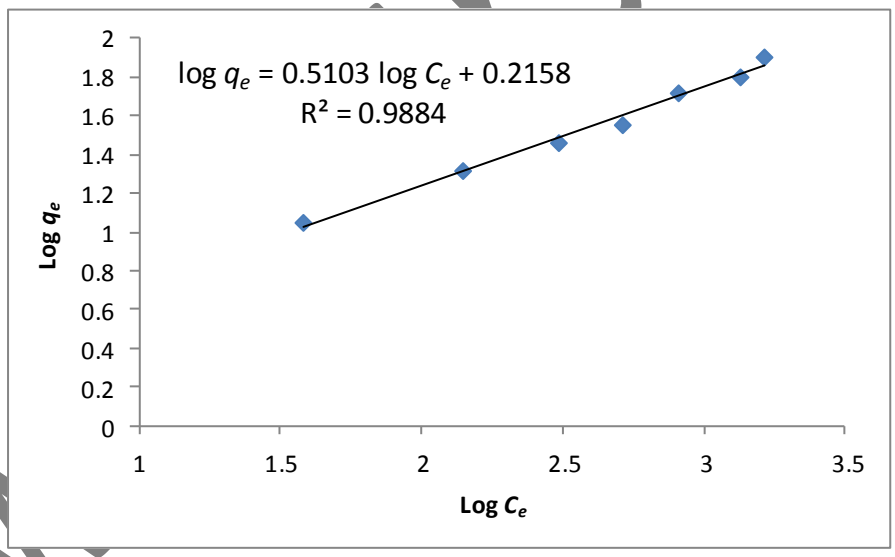

Fig. 3.12 Fraundlich Adsorption Isotherm of Total Phenol onto Peanut Shell A.C

3.9.1 Adsorption Kinetics of Polyphenols onto Peanut Husk Based A.C

Removal of total polyphenols by peanut shell activated carbon as a function in time is represented in fig (3.10). These results were fitted to different kinetic models of either diffusion models or reaction type. The results show that best model describes the mechanism of adsorption process for OMWW and Peanut Husk Based Activated Carbon is pseudo second order model as shown in figure (3.13) with determination coefficient (R^2) exceeds 0.9996. pseudo-second order rate equation as follows:

$$\frac{1}{q_t} = \frac{1}{V_0} + \frac{1}{q_e} t \qquad 3.7$$

Where:

V_0 (mg/g.min) is the initial adsorption rate, and the constants V_0 and q_e can be determined experimentally by plotting of 1/q_t against t.

$$V_0 = K q_e^2 \qquad 3.8$$

Table (3.1) shows the parameters obtained for different reaction models as reaction models was found to fit the results better than diffusional models.

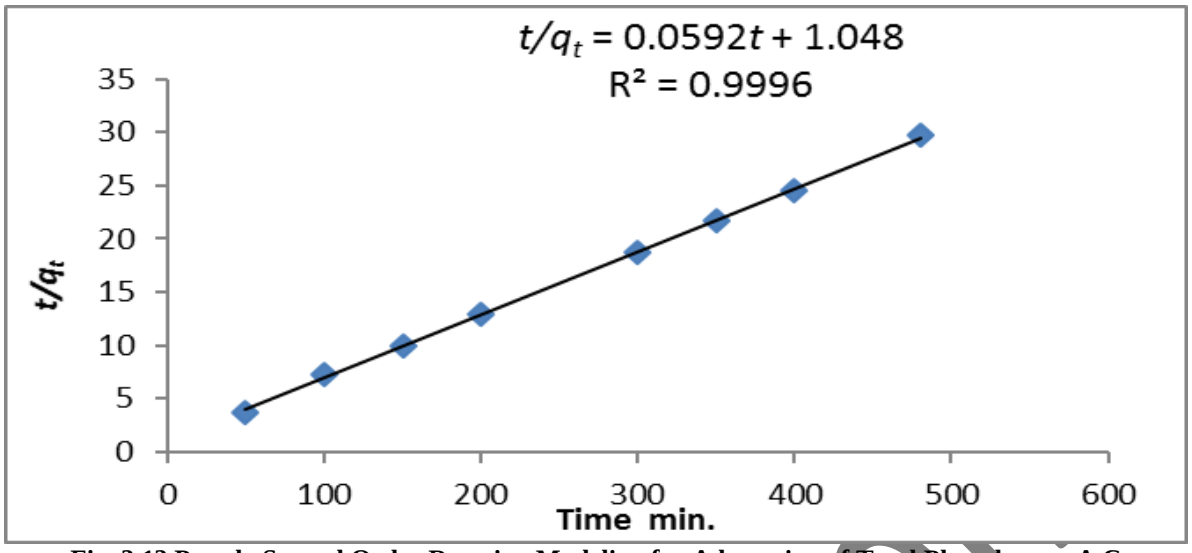

Fig. 3.13 Pseudo Second Order Reaction Modeling for Adsorption of Total Phenols onto A.C

Table-3.1 Parameters obtained for different reaction models

Pseudo first order model			**Pseudo second order model**			**Second order model**		
K	q_e	R^2	$33V_0$	q_e	R^2	K_l	C_0	R^2
0.003	4.3	0.885	0.9542	16.892	0.9996	$2*10^{-5}$	151.5	0.8914

In The following table (Table 3.2), the different adsorption kinetics models for which the results were applied and the determination coefficient for each are explained:

Table-3.2. Comparison for the Determination Coefficient for Different Kinetics Models Fitted to Obtained Results for OMWW- PHBAC System

Model	**Describing equation**	**Determination coefficient**
Liquid film diffusion model	$\ln(1-\frac{q_t}{q_e}) = -Kt$	0.8845
Dumwald-Wagner intra particle diffusion modeling	$\ln[1-\left(\frac{q_t}{q_e}\right)^2] = K\,t$	0.7923
Pseudo first order reaction modeling	$\ln(q_e - q_t) = \ln q_e - K\,t$	0.8845
Pseudo second order reaction modeling	$\frac{1}{q_t} = \frac{1}{V_0} + \frac{1}{q_e}t$	0.9996
second order reaction modeling	$\frac{1}{C_t} = K\,t + \frac{1}{C_0}$	0.8914

CONCLUSION

- Different activation methods were used and activation by H_3PO_4 was chosen as it yielded highly porous activated carbon with BET surface area = 988 m^2/g.
- The peanut husk activated carbon was used in batch process to optimize and study adsorption process. The optimum removal conditions were at pH value equal 2, initial polyphenols concentration 480 mg/lit, adsorbent adsorbate ratio equal 2.4g/100ml, 500 micron particles size and 300 rpm agitation speed. Under these conditions adsorption capacity (q_{max}) reached 240 mg/g.

Here also the Freundlich isotherm model accounted for experimental data and adsorption kinetic data fitted to a -second order rate model.

- This may conclude that transforming peanut husk into activated carbon numerously increase polyphenols adsorption efficiency and hence enhanced treatment process.

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