Preparation Activated Carbon from Scrap Tires by Microwave Assisted KOH Activation for Removal Emulsified Oil

Najwa Saber Majeed, Huda Adil Sabbar and Nawar O. A. Al-Musawi*
Chemical Engineering Department-College of Engineering-University of Baghdad-Iraq
*Civil Engineering Department-College of Engineering-University of Baghdad-Iraq

Abstract

In this paper activated carbon adsorbents produced from waste tires by chemical activation methods and application of microwave assisted KOH activation. The influence of radiation time, radiation power, and impregnation ratio on the yield and oil removal which is one of the major environmental issues nowadays and considered persistent environmental contaminants and many of them are suspected of being carcinogenic. Based on Box-Wilson central composite design, polynomial models were developed to correlate the process variables to the two responses. From the analysis of variance the significant variables on each response were identified. Optimum conditions of 4 min radiation time, 700 W radiation power and 0.5 g/g impregnation ratio gave 205.8749 mg/g oil removal and 35.19618 % yield. The characteristics of the AC were examined by pore structure analysis, and scanning electron microscopy (SEM).The BET surface area and total pore volume were identified to be 374.594 m²/g and 0.2039 m³/g, respectively.

Key words: Waste tires, Activated Carbon, Activation, Microwave, Optimization, Adsorption.

Introduction

One of the major environmental issues nowadays is the vast and widespread occurrence of oil in industrial wastewater and ground water. Oils (Both mineral and synthetic) are considered persistent environmental contaminants and many of them are suspected of being carcinogenic [1], the removal of oily pollutants from wastewater poses a problem, particularly when they are present in low concentrations, such as in industrial water. Reliability and its inexpensiveness, the adsorption technology is extensively used in oil removal. Traditionally, activated carbon has been widely used as an adsorbent for removing [2]. Activated carbon is a material that is produced from carbonaceous source materials, such as coal, coconuts, nutshells, peat, wood, and lignite. It has highly developed internal surface area and porosity, its pore volume typically ranges from 0.20 to 0.60 cm^3/gm, and has been found to be as large as 1cm^3/gm. Its surface area ranges typically from 300 to 1500 m^2/gm [3]. A large capacity for adsorbing chemicals from gases and liquids.

Activated carbons are extremely versatile adsorbents of industrial significance and are used in a wide range of applications which are concerned principally with removal of undesired species by adsorption from liquids or gases, in order to effect purification or the recovery of chemical constituents [3], the forms and characteristics of Activated carbon are highly dependent on the precursors and activation methods adopted for its production [5] it is used in many fields both in industry and daily life of every person. The usage of carbon adsorbents depend on their surface area, pore size distribution and chemical surface characteristics. The quality (surface area, pore size distribution and hence adsorptive properties) of it are directly related to the nature of starting material, the type of the production method and the temperature of production [6]. Waste tires are good starting materials for activated carbon production because of it containing a high fixed carbon content and cheap and available In addition to maintaining the environment from the risks of throwing tires [7].

The preparation of AC involves of two stages, namely pyrolysis and activation [8]. Single step pyrolysis usually applied in the preparation of activated carbon using chemical activation method, which has low energy consumption, cheap shorter process duration and modest surface area and porosity. however, the conventional preparation of activated carbon using physical activation method was based on two step pyrolysis where carbonization and activation process takes place separately which has high energy consumption, expensive, longer process duration and high surface area and porosity. The product quality of two step pyrolysis is better compared

to the single step pyrolysis [9]. The thermal process may need several hours, even up to a week to make the desired level of activation another trouble related to the furnace is that the surface heating does not ensure a regular temperature for various shapes and sizes of samples [10]. Therefore, it is necessary to find a rapid and easy route for the preparation of AC. Although microwave heating is today a mature technique which finds wide applications in the area of material science, food processing and analytical chemistry [11], The major advantage of using microwave heating is: Heat emitted from microwave be fast and uniform, Direct using of big-sized feedstock, Treatment of non-homogeneous wastes, Minimize waste and material recovery, best production quality, Production of new materials and products .Total cost effectiveness, savings, and reduce dangers to humans and the environment [12]. In addition to use microwave heating in the production of char was found to produce desirable changes in its textural and chemical properties comparing to the char produced by conventional met hods. For instance, a cleaner porous structure has been reported by Miura et al., 2004 in the pyrolysis of wood, [13].

(RSM) approach. RSM has been found to be a useful tool to study the interaction of two or more factors [14]. A standard RSM design called Box-Wilson central composite design is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameter [15]. RSM has just recently been used for the optimization of activated carbon production from rattan sawdust [14].

The aim of this work is to optimize the preparation conditions of AC from

scrape tires by chemical activation for the removal of emulsified oil from waste water. The effects of radiation time, radiation power and impregnation ratio are also studied simultaneously to obtain a high oil removal using the Box-Wilson central composite design.

Materials and Method

Materials
Scrape tires were used as the precursor for the preparation of AC. waste tires were washed with water to get rid of impurities, then shredded using an electrical drill (BOSCH 305) adopted with crushing disk and sieved .Fraction with particle size of (1.18-2.36) mm was selected for the preparation. Potassium hydroxide (KOH), (purchased from Didactic company, Espuma) MW=56.10 of purity 99.9% was used as a chemical activator. Span 85 and Tween-80 materials that increases the emulsifying.
Cyclohexane (C_6H_{12}) which used as the extraction solvent, other chemical used such as hydrochloric acid were from analytical grades.
.
Preparation of Activated Carbon
A weighed amount (2g) of dried waste tires was mixed with 10 ml of KOH solution at various impregnation ratios (0.5 – 1.5 g/g) for 24 h at room temperature. The samples were next placed in an dryer (Model IH – 100, England) at 110 °C until completely dried then the dry samples were activated by using a quartz glass reactor in microwave at different radiation powers (400–700W) for different radiation times (4_12min), Samsung Mode (lMS23F301E), Malaisie, it can reach a maximum power of (800 watt) The upper surface of microwave had a removable cover connected to a stainless steel pipe of 5mm inside diameter from which pyrolysis gases were exit ,with quartz

glass reactor 2.5 cm diameter x 12.5 cm length as it is shown in Figure 1. After activation, the sample was withdrawn from the oven and allowed to cool. the sample was mixed with 0.1M HCl solution at 10 mg/l solid to liquid ratio. The mixture was left overnight at room temperature, and then filtered and subsequently the sample was repeatedly washed with distilled water to remove residual organic matters and alkalis, until the pH of filtrate reached (6.5 − 7). After that, the sample was dried at 110C° for 24 h. and subsequently was weighed. Finally the sample was stored in tightly closed bottles.
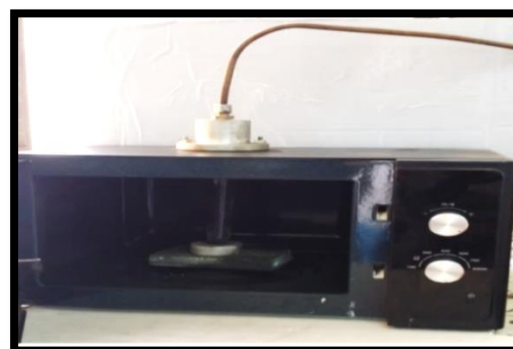

Fig. 1: photographic picture of microwave unit for preparation of Activated carbon

Process Performance
The performance of chemical activation process was determined by the product yield, along with its removal oil.

Yield
The yield is defined as the ratio of final weight of the obtained product after washing and drying to the weight of dried precursor initially used. The yield of AC was calculated based on the following equation:

$$\text{Yield (\%)} = \frac{W_f}{W_\circ} \times 100 \qquad \ldots(1)$$

Where Wf and Wo are the weight of final AC product (g) and the weight of scrape tires (g), respectively.

Removal of Oil

A solution of oily water prepared by mixing 0.225g of the motor oil and 0.025 of span$_{85}$ and tween$_{80}$ (which increase the stability of the emulsion) with 500 mL of water to prepared 500 ppm. The mixture was then stabilized in laboratory homogenizer Disperser at 10000 rpm speed for 30 second. The resultant solution was milky white, which exhibited the character of chemically stabilized solution Added 0.5gram of activated carbon to 200 ml of the resulting mixture(500 ppm) and then stirred with a magnetic stirrer (400 rpm) for 4 hour then the solution leaves a period of time and then be pulled 100 ml from the central region to avoid impurities. A sample of (100 ml) of solution was placed in conical flasks of (250 ml) and added drops of (1M)of HCL to neutralize the solution, and to extract the oil (10 ml) of cyclohexane, then it was shocked by hand for one minute and pulled a sample of the cyclohexane was added accumulated in the upper region for examination oil concentration by using TD500DTM Oil in Water Meter. The amount of adsorption at equilibrium, qe (mg/g), was found using Equation 2:

$$q_e = \frac{(C_\circ - C_e)V}{W} \qquad \ldots(2)$$

Where C0 and Ce (mg/L) are the liquid-phase concentrations of oil at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of activated carbon. Adsorption isotherms that were carried out in a set of 700 ml emulsion oil in water at 500ppm with different weights of activated carbon (0.35, 1.75, 3.5, 5.25, and 7) gram were placed in these beakers, at 400rpm and pH equal 7. Similarly the concentration of oil in water was calculated at different time (10 min, 30 min, 60 min, 90 min, 120 min, and 24 h) and by using Equation 2

the amount of adsorption at equilibrium, q$_e$ (mg/g).

Experimental Design

In order to organize the experiments of AC preparation from scrap tires, a standard RSM design, known as Box-Wilson central composite design was adopted. This design can reduce the number of experimental trails needed to evaluate multiple parameters and their interactions [16]. Box-Wilson design consists of 2n factorial points, 2n axial points, and one center point, where n is the numbers of variables. In order to design the experiments, the operating range of variables must be specified, thus: radiation power X1 (400-700 W), radiation and impregnation ratio X2 (0.5-1.5 g/g) radiation time X3 (4-12 min). The total number of experiments N is computed according to the following equation:

$$N = 2^n + 2n + 1 \qquad \ldots(3)$$

The relationship between the coded variable and the corresponding real variable is as follows:

$$X_{coded} = \frac{X_{actual} - X_{center}}{\frac{X_{center} - X_{MIN}}{n}} \qquad \ldots(4)$$

Characterization of Activated Carbon

1. Total surface area

Surface area is one of the key indicators attributed to the adsorptive properties of porous materials [17], it generally calculated by the BET method (Brunauer, Emmett and Teller 1). This method works at the low-pressure range of the adsorption isotherm of a molecule of known dimensions (commonly nitrogen). Nitrogen adsorption experiments were done to compute the specific surface area of the test samples using a Quantachrome Nova-1200 instrument

at 77k. The samples were out gassed overnight at 180 °C before the adsorption measurements. The BET model was used to be suitable for the nitrogen adsorption isotherms and estimate the specific surface area of the samples [18].

2. Pore size distribution

Pores in different sizes are important to the adsorbents overall capacity in adsorption processes. The presence of micro- and mesopores in activated carbons enhance the adsorption of large adsorbates [7].

3. Capacity

Capacity it is the amount which the adsorbent taken up from adsorbate by per adsorbent. It depends on the initial condition of the adsorbent, the fluid phase concentration and temperature. Adsorption capacity data are gathered at various adsorbate concentrations and a fixed temperature, and the data are plotted as an isotherm (loading versus concentration at constant temperature).

4. Bulk Density

Bulk density is defined as the ratio of the mass of the material to the total volume occupied by material. The total volume corresponds to the pore and inter-particle volume. Bulk density of the matter varies depending on it's composition.

Results and Discussion

Model Fitting and Statistical Analysis for Chemical Activation Sample

The response of experiments conducted according to Box – Wilson method, which represented by oil removal and activated carbon yield, is fitted to a second and third order polynomial mathematical model and the optimum response is calculated from this model, it determined the effect of each parameter. At first the predictions equation (Y=A+BX) used which represent first order equation for independent studied variables (Power:

X1, Ratio: X2, Time: X3, Responsible variables: Y and constant: A, so predictions equation become:

$$Y = const + B1*X1 + B2*X2 + B3*X \quad …(5)$$

Then second order polynomial mathematical model applied which give had form for three variable more accurate.

$$Y = B_o + B_1 X_1 + B_2 X_2 + B_3 X_3 + B_4 X_1 X_2 + B_5 X_1 X_3 + B_6 X_2 X_3 + B_7 X_1^2 + B_8 X_2^2 + B_9 X_3^2 \quad …(6)$$

$$\Sigma x_1 / n = \Sigma x_2 / n = \Sigma x_3 / n = \Sigma x_1 x_2 / n = \Sigma x_1 x_3 / n = \Sigma x_2 x_3 / n = 0, \text{ and:}$$

$$\Sigma x_1^2 / n = \Sigma x_2^2 / n = \Sigma x_3^2 / n = 0.933$$

The Equation 6 become:

$$Y = y + B1 X1 + B2 X2 + B3 X3 + B4 X1 X2 + B5 X1 X3 + B6 X2 X3 + B7 (X12 − 0.933) + B8 (X22 − 0.933) + B9 (X32 − 0.933) \quad …(7)$$

And third order

$$Y = const + B1*X1 + B2*X2 + B3*X3 + B4*X1*X2 + B5*X1*X3 + B6*X2*X3 + B7*(X1**2-0.933) + B8*(X2**2-0.933) + B9*(X3**2-0.933) + B10*(X1**3) + B11*(X2**3) + B12*(X3**3) + B13*X1*X2*X3 \quad …(8)$$

It used above equations which get to the correlation factor nearer to one. The final form becomes:

$$Yield(real) = -849.541 + 6.307 * X1 − 298.036 * X2 − 217.842 * X3 + 1.491 * X1 * X2 + 0.22811875 * X1 * X3 + 127.111 * X2 * X3 − 0.01489269396 * (X1\wedge 2 − 0.933) − 538.68 * (X2^2 − 0.933) + 11.349 * (X3\wedge 2 − 0.933) + 0.0000092 * (X1^3) + 163.368 * (X2^3) − 0.475 * (X3^3) − 0.22265 * X1 * X2 * X3 \quad …(9)$$

Oil removal (real) = 226.02924 − 0.027851 ∗ X1 − 68.3135 ∗ X2 + 2.246331 ∗ X3 + 0.03187 ∗ X1 ∗ X2 − 0.008071 ∗ X1 ∗ X3 + 5.4383 ∗ X2 ∗ X3 + 0.000059 ∗ (X1² − 0.933) + 2.250618(X2^2 − 0.933) − 0.176143 ∗ (X3^2 − 0.933)   …(10)

The Table 1 show values of the independent variables corresponding to the final form of the equation of yield and oil removal.

Table 1: Values of the Independent Variables Corresponding to the Final Form of the Equation of Yield and Oil Removal

Table 1a: Values of the Independent Variables Corresponding to the Final Form of the Equation of Yield and Oil Removal

no	Coded variables			Real variables			Yield (%)			Oil removal (mg∕g)		
								(coded variables)			(coded variables)	
	X1	X2	X3	X1	X2	X3	Y	y	Residuals	Y	y	Residuals
1	1	1	-1	463.4	0.71	5.7	88	86.11463788	1.885362	194.92	195.5772812	-0.65728
2	-1	-1	1	636.6	0.71	5.7	52	50.11463588	1.885364	198.2	198.2947812	-0.09478
3	1	-1	1	463.4	1.3	5.7	62	60.11463988	1.88536	185.2	185.2947812	-0.09478
4	-1	1	1	636.6	1.3	5.7	48.7	46.81463788	1.885362	190.48	191.1372812	-0.65728
5	1	1	1	463.4	0.71	10.3	54.2	52.31463788	1.885362	191.96	192.0547812	-0.09478
6	-1.732	0	0	636.6	0.71	10.3	74	72.11463588	1.885364	187.56	188.2172812	-0.65728
7	1.732	0	0	463.4	1.3	10.3	93.16	91.27463988	1.88536	195.8	196.4572812	-0.65728
8	0	-1.732	0	636.6	1.3	10.3	31	29.11463788	1.885362	195.9	195.9947812	-0.09478
9	0	1.732	0	400	1	8	65.9	68.41395525	-2.51396	194.52	194.0185477	0.501452
10	0	0	-1.732	700	1	8	68	70.51395432	-2.51395	195.52	195.0185472	0.501453
11	0	0	1.732	550	0.5	8	42.2	44.7139608	-2.51396	196	195.498549	0.501451
12	0	0	0	550	1.5	8	55	57.51396396	-2.51396	192.52	192.0185472	0.501453
13	1	1	-1	550	1	4	80	82.51395366	-2.51395	187.44	186.9385458	0.501454
14	-1	-1	1	550	1	12	39.8	42.31395515	-2.51396	194.28	193.7785493	0.501451
15	1	-1	1	550	1	8	63.6	63.59910988	0.00089	193.16	193.1601552	-0.00016
								R=.992415272			R=.99321325	

Y: observed value   y: calculated value

Table 1b: Values of the Independent Variables Corresponding to the Final Form of the Equation of Yield and Oil Removal

no	Coded variables			Real variables			Yield (%) (Real variables)		Oil removal (mg∕g) (real variables)	
	X1	X2	X3	X1	X2	X3	y	Residuals	y	Residuals
1	1	1	-1	463.4	0.71	5.7	87.0284781	0.971521903	195.05277	0.1327663
2	-1	-1	1	636.6	0.71	5.7	52.44198703	-0.441987025	197.45902	-0.7409794
3	1	-1	1	463.4	1.3	5.7	60.86207183	1.13792817	184.41962	-0.7803832
4	-1	1	1	636.6	1.3	5.7	49.04515041	-0.345150407	190.08274	-0.3972646
5	1	1	1	463.4	0.71	10.3	53.5071943	0.692805702	192.97879	1.0187855
6	-1.732	0	0	636.6	0.71	10.3	74.81534444	-0.815344435	188.95471	1.3947126
7	1.732	0	0	463.4	1.3	10.3	92.39491428	0.76508572	197.10518	1.3051821
8	0	-1.732	0	636.6	1.3	10.3	31.71814296	-0.718142957	196.33797	0.4379737
9	0	1.732	0	400	1	8	69.08168428	-3.181684283	193.75079	-0.7692064
10	0	0	-1.732	700	1	8	73.81767748	-5.817677483	195.12248	-0.3975164
11	0	0	1.732	550	0.5	8	46.42729498	-4.227294983	195.05562	-0.9443824
12	0	0	0	550	1.5	8	59.25529498	-4.255294983	192.27897	-0.2410314
13	1	1	-1	550	1	4	83.92604498	-3.926044983	188.57718	1.1371786
14	-1	-1	1	550	1	12	44.41254498	-4.612544983	191.99552	-2.2844774
15	1	-1	1	550	1	8	64.98529498	-1.385294983	193.10464	-0.0553614
							R=0.99204284		R=0.99321325	

Y: observed value   y: calculated value

Process Optimization

At optimum conditions, the prepared AC should have a high yield and high removal oil. However, it is difficult to optimize both these responses under the same condition because the interest region of variables is different, when oil removal increases, carbon yield

decrease and vice versa. Therefore, the optimum conditions have been determined depending on achieving high removal oil. The optimum operating conditions has been determined by studying each independent variable alone [19]. Thus, the optimum conditions corresponding to a maximum removal oil are 4 min radiation time, 700 W radiation power, and 0.5 g/g impregnation ratio which determined by study every parameter with changing two other parameter as show in Table 2. At these conditions, 205.8749 mg/g oil removal with 35.19618 % yield were reported experimentally.

Effect of Process Variables

Effect of Radiation Time
The effect of radiation time on yield and oil removal of prepared activated carbon at different radiation powers and different impregnation ratio is shown in Figure 2. Shows that the yield of AC decreases with increasing of radiation time at impregnation ratio (0.5, 0.75, 1, 1.25, and 1.5) g/g.

At 400 w radiation power, the radiation time increasing from 4 to 12 min leads to decreases in yield from 88 to 70 % when impregnation ratio equal 0.5 g/g. this is probably due to rapid evolution of volatile materials to form stable compounds, and this situation corresponds to the explanation by Foo and Hameed [20]. They showed that a steep decrease in yield occurs for production of AC from coconut husk by microwave KOH activation [3].
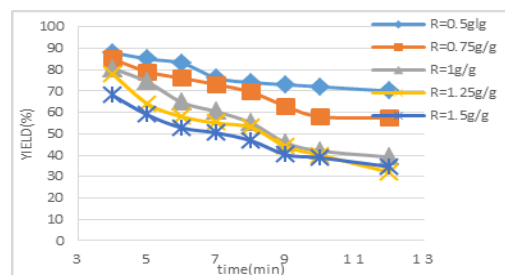

Fig. 2: Effect of radiation time on yield at different impregnation ratio (radiation power=400 w)

The effects of radiation time on oil removal are demonstrated in Figure 3 that show oil removal increase with increasing radiation time at higher impregnation ratio and it decrease with increase radiation time at low impregnation ratio. At radiation power 400 w, at impregnation ratio equal 1.5 g/g, oil removal is demonstrably increase from 170.28 to 205.144 mg/g while at impregnation ratio equal 0.5 g/g oil removal decrease from 199.5987 to 190.94 mg/g with increase radiation time 4-12 min .At higher impregnation ratio, prolonging radiation time promotes an acceleration of temperature or energy, which in turn increase the reaction rates , de volatilization and led to opening of micropores and mesopores which resulted in expansion of the average diameter thus developed the porosity and rudimentary of the pore structure. But in low impregnation ratios, oil removal decreased with increasing radiation time, probably due to turn mesopores to macropores and sintering effect, which hugely crashed the pore walls between relative pores (Foo and Hameed, 2012) [20].
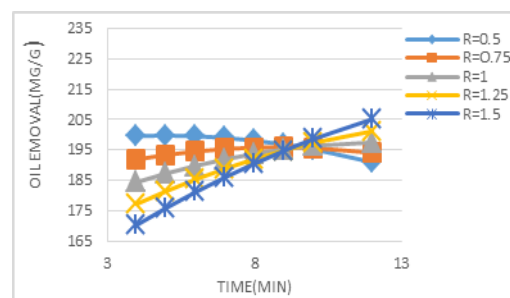

Fig. 3: Effect of radiation time on oil removal at variable impregnation ratio (radiation power=400 w)

Effect of Radiation Power
The effect of radiation power on yield and oil removal of prepared activated carbon at different radiation time is shown in Figures 4 and 5. Figure 4 shows that the yield of AC decreases with increasing of radiation power at radiation time 4-12 min.

At impregnation ratio 0.5 g/g when radiation power change from 400 to 700 w, yield decrease from 86 to 55% at radiation time equal to 4 min, it illustrated that loss of the volatile materials with increasing power. Then the lower rate of yield decrease was noticed where a stable structure is formed. However, at a high radiation power over-gasification might occur causing destruction of pore structures, thus the removal oil and carbon yield decreased gradually. The weight loss of carbon increased proportionally to the microwave power, mainly attributable to the robust reaction at higher thermal radiation which massive devolatilization, dehydration and putridity [20].
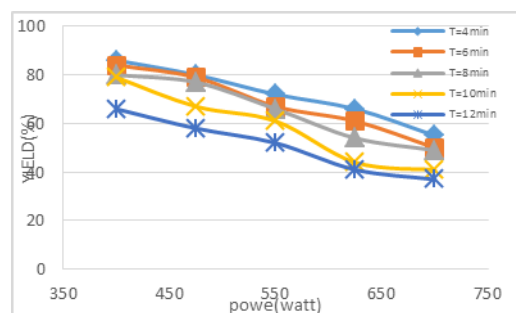
Fig. 4: Effect of radiation power on yield at variable radiation time (impregnation ratio =0.5)

The effects of radiation power on oil removal are demonstrated in Figure 5 that show oil removal increase with increasing radiation power at low radiation time. But in high radiation time, oil removal decrease with increasing radiation power.

At impregnation ratio equal 0.5 g/g, oil removal increased from 199.5987 to 205.87 mg/g at 4 min radiation time while oil removal decrease from 190.949 to 177.8548 mg/g at 12 min radiation time with increases the radiation power from (400-700), at low radiation time, increasing the microwave power was to induced higher internal and volumetric heating leading to the development of new

pores thereby enhancing the adsorption capacity and possibly ascribed to the joint effect of internal and volumetric heating responsible for the expansion of the carbon structure creation of raise porosity and a bigger surface area [20]. But in high radiation time increase in power might be due to the sintering effect at high power, followed by shrinkage of the char, and realignment of the carbon structure which resulted in reduced pore areas as well as volume this situation corresponds to the explanation by Deng et al. [21] who reported for MB uptake on AC prepared from cotton stalk by microwave assisted KOH activation.
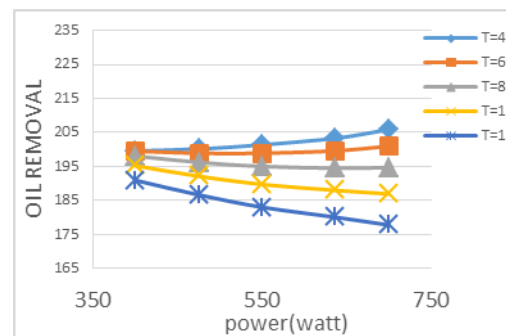

Fig. 5: Effect of radiation power on oil removal at different radiation time (impregnation ratio =0.5)

Effect of Impregnation Ratio

The effect of impregnation ratio on yield and oil removal of prepared activated carbon at different radiation time and different radiation power is shown in Figures 6 and 7.

Figure 6 shows that the yield of AC decreases with increasing of radiation ratio at radiation time 4 and 6 min at radiation power (400, 475, 550,636.6, and 700) watt.

At 4 min radiation time yield decrease from 91.3 to 61.6% when impregnation ratio increase from 0.5 to 1.5 g/g at 400 watt power radiation This decrease is due to the continuous removal of tar material from the pores.. This behavior agrees with results obtained by Sudaryanto [22] for AC production

from cassava peel by chemical activation with potassium hydroxide. This is the same in the case at radiation time 6 min with decrease in yield with increase radiation time.
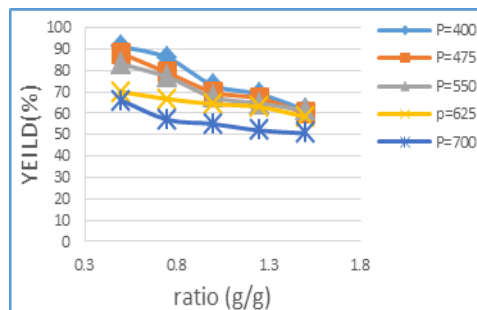

Fig. 6: Effect impregnation ratio on yield at different radiation power (radiation time =4min)

The effects of impregnation ratio on oil removal are demonstrated in Figure 7 that show oil removal increase with increase impregnation ratio at height radiation time, but at low radiation time it decrease with increase impregnation ratio. Figure 8, at 12 min radiation time and 400 w radiation power, removal oil increase from 190.95 to 205.149 mg/g while oil removal decrease from 199.59 to 170.2881 mg/g at 4 min radiation time. At height radiation time, the potassium compound created during the activation step would spread into the internal structure of tires matrix and expansion existing pores. Therefore, by rising the ratio of KOH to tires, the activation process would play a key role in pore modelling. The pore width was successively broadened and new micropores - mesopores were formed in the off-center pore walls, giving a self-sustaining increase in BET surface area and pore volume. Correspondingly, but in low radiation time, the oil removal was extra enhanced., increase KOH and metallic potassium did not take enough time to gas left in the carbon surface caused blockage of the pores leading to carbon burn of and mutation of micropores-

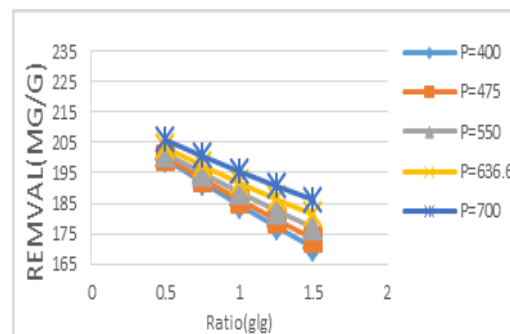mesopores into macropores lessening the oil removal [20].

Fig. 7: Effect impregnation ratio on oil removal at variable radiation power (radiation time =4min)
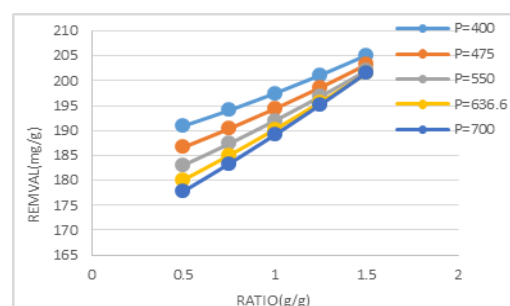

Fig. 8: Effect impregnation ratio on oil removal at variable radiation power (radiation time =12min)

Table 2: studying best variable that achieve maximums oil removal

constant variable	Best variables in constant certain variable		Maxim oil removal(mg/g)
Effect of Radiation Time			
Radiation power (watt)	impregnation ratio(g/g)	Radiation time (min)	Maxim oil removal (mg/g)
400	1.5	12	205.144
475	1.5	12	203.26
550	1.5	12	202.04
625	0.5	4	203.068
700	0.5	4	205.87
Effect of Radiation power			
impregnation ratio(g/g)	impregnation time(min)	radiation power (watt)	Maxim oil removal (mg/g)
0.5	4	700	205.87
0.75	4	700	200
1	12	400	197
1.25	12	400	201
1.5	12	400	205.14
Effect of impregnation ratio			
impregnation time(min)	radiation power (watt)	impregnation ratio(g/g)	Maxim oil removal (mg/g)
4	700	0.5	205.87
6	700	0.5	200.98
8	400	0.5	198.09
10	700	1.5	199.854
12	400	1.5	205.144

Adsorption Isotherms of Emulsified Oil on Activated Carbon Prepared at Optimum Condition

The adsorption isotherm is the most extensively employed method for representing the equilibrium states of an adsorption system. The adsorption isotherm gives useful information regarding the adsorbate, the adsorbent, and the adsorption process**,** the results of this fitting, as summarized in Table 3 show that Sips isotherm has the highest R^2 value as compared to that of both Langmuir and Freundlich isotherms. The Sips model correlates the equilibrium data with R^2 values.
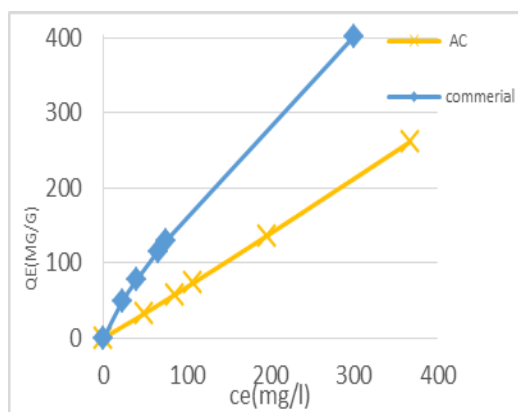
Fig. 9: sips adsorption isotherm of oil on activated carbon at 25 ℃

Table 3: Isotherm parameters for oil Adsorption onto activated carbon with the Correlation Coefficient

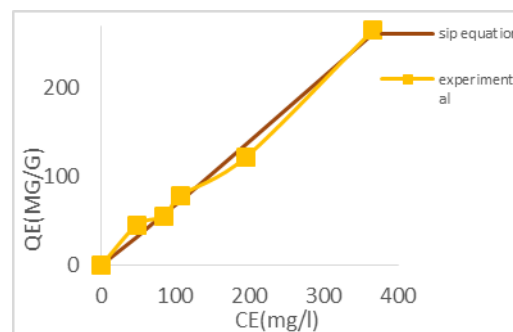| Model	Parameters	Values
Langmuir $q_{e} = \frac{q_m\,k_L\,c_e}{1+k_L\,c_e}$	K_L(l/mg)	0.003054
	$q_{,max}$(mg/g)	230.5
	R^2	0.993
	R_L	0.395
Freundlich $q_e = k_f c_e^{1/n}$	K_f	0.571428
	N	0.9639
	R^2	0.99
Sips $q_e = \frac{q_m k_s C_e^{1/m}}{1 + k_s C_e^{1/n}}$	q_m(mg/g)	265
	K_s((l/mg)$^{1/m}$)	0.002155
	n	0.96445
	R^2	0.997

Fig. 10: adsorption isotherm for oil by activated carbon ($C_\circ$=500mg/l, temp=25 and dp= 1.18-2.36mm)

Characterization of Activated Carbon

BET Surface Area and Pore Volume

The BET surface area, total pore volume of AC prepared at optimum conditions are found to be 374.594 m²/g, 0.2039 m³/g These values higher than that reported by Skodras et al [22] who show the BET surface area of activated carbon from tires by KOH activation were 358.5 m^2/g AC. Table 4 shows the Comparison on the application of microwave heating to the production of activated carbon from different material.

Table 4: summary of previous works on preparation of activated carbons produced by waste tires [5]

| References	Activating Agent	Activation conditions	BET surface Area ($m2$ / g)
This study	KOH	Power=625w, Time=6min and Ratio=0.75 g/g	374.59
Skodras *et al.*, (2007)	Steam	Temp=900 ,Time= 2	358.5
Helleur *et al.*, (2001)	Steam CO2	Temp=900 ,Time=3 Temp=875 ,Time= 7	272 270
Sainz-Diaz and Griffiths, (2000)	CO2	Temp=1000 ,Time=5 Temp=1000 ,Time=7	431 284
Cunliffe and Williams, (1999)	Steam	Temp=935 Time= -	640
Streat *et al.*, (1995) -	Steam	Temp=800 ,Time= 24 Temp=900 ,Time= 18	346 155
Belgacem et al., 2013	phosphoric acid	Temp=650 Time= 2hand 30min	400

Surface Morphology

Figures 11a and b show SEM images of scrap tires and AC production by two ways: physical and chemical activation methods. It can be found that the surface of tires is free of any pores, constricted and blocked by deposited tray substance. However, the microwave irradiation sample demonstrated a well-developed and uniform surface, forming an orderly pore structure. The development of porosity is associated with gasification according to the following reduction reactions [23]:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$$

K_2CO_3 was reduced by carbons to form K, K_2O, CO and CO_2 so that more pores were formed as follows:

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$
$$K_2CO_3 \rightarrow K_2O + CO_2$$
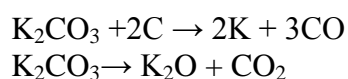
It was assumed that metallic potassium K formed during the gasification process would diffuse into the internal structure of carbon matrix widening the existing pores and created new porosities. Figure 11b also shows that the surface of prepared carbon contains some cavities which are resulted from the evaporation of impregnated KOH derived compounds, leaving the space previously occupied by the reagent. Theses cavities provide channels for the adsorbate molecules to access the micropores and mesopores inside a carbon particle.
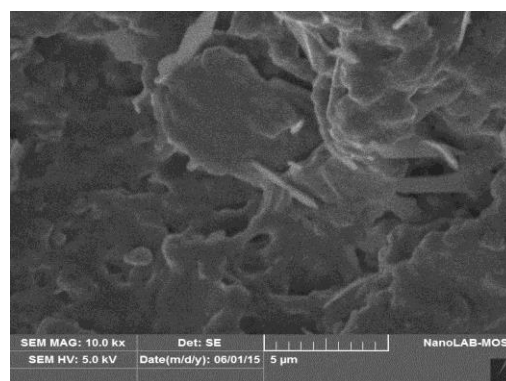
(a)
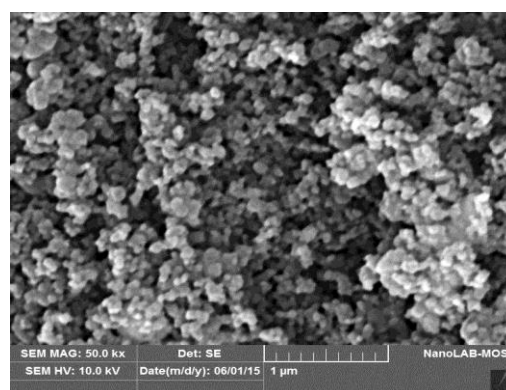
(b)
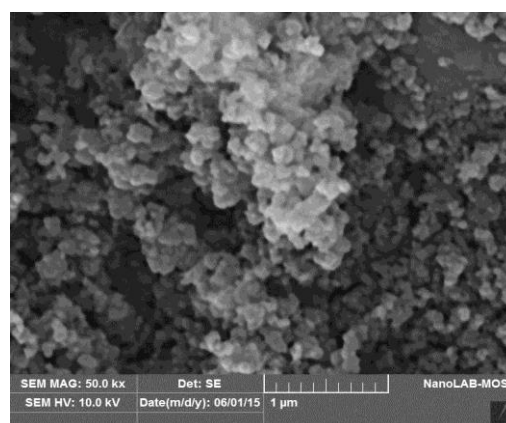
(c)

Fig. 11: SEM micrographs (10 kx) of srape tires (A) and (50kx) AC by physcal method (B) AC method (C) by chemicl

Conclusion

Activated carbons were prepared from scrape tires by microwave assisted KOH activation. 205.8749 mg/g removal oil with corresponding yield of 35.1961 % were obtained at optimum conditions of 4 min radiation time, 700 W radiation power, and 0.5 g/g impregnation ratio. Also, the

surface area, pore volume of AC were 374.59 m²/g, 0.2039 m³/g .Box-Wilson central composite design was adopted for arrangement of preparation experiment. Two second order polynomial models were successfully used to correlate the process variables to the two responses.

References

1. Harvey, R. G. (1991). Polycyclic aromatic hydrocarbons: chemistry and carcinogenicity. Cambridge University Press,Cambridge, England.
2. Simonović, B. R., Aranđelović, D., Jovanović, M., Kovačević, B., Pezo, L., & Jovanović, A. (2009). Removal of mineral oil and wastewater pollutants using hard coal. Chemical Industry and Chemical Engineering Quarterly, 15(2), 57-62.
3. Kareem R.A. (2014)" Sustainable Production of Local Adsorbent Material from Waste Tires for Removal of Lead from Aqueous Solution". University of Baghdad. College of Engineering. M.Sc. Thesis.
4. Manocha S. M. (2003). Porous carbons. Sadhana, 28(1-2), 335-348.
5. Abbas A.F. 2014," Preparation of activated carbon from date stones by K_2CO_3 activation for methylene blue dye adsorption", M.Sc. Thesis ,College of engineering, Baghdad University.
6. Yagsi N. U. (2004). Production and characterization of activated carbon from apricot stones (doctoral dissertation, Middle East technical university).
7. Mui, E. L., Ko, D. C., & McKay, G. (2004). Production of active carbons from waste tyres—a review. Carbon
8. T.H. Liou, (2010), Development of mesoporous structure and high adsorption capacity of biomass based activated carbon by phosphoric acid and zinc chloride activation, Chem. Eng. J. 158(2), 129-142.
9. Hameed, B. H., Tan, I. A.W. and Ahmed, A. L.(2009) "Preparation of oil palm empty fruit bunch. Based activated carbon for removal of 2, 4, 6-trichlorophenol:Optimization using response surface.
10. Chaied M. A.(2015)" Microwave Assisted Preparation of Activated Carbon from Phragmites (Reed) for Antibiotics Adsorption" ,M.Sc. Thesis ,College of engineering, Baghdad University.
11. M. Komorowska, G.D. Stefanidies, T. Van Gerven, A. L. Stankiewicz, (2009), Influence of microwave irradiation on a polyesterification reaction, Chem. Eng. J. 15 (3), 859-866.
12. Fernández, Y., Arenillas, A., & Menéndez, J. Á. (2011). Microwave Heating Applied to Pyrolysis, Advances in Induction and Microwave Heating of Mineral and Organic Materials, Stanisław Grundas (Ed.), ISBN: 978-953-307-522-8, InTech.
13. Miura, M., Kaga, H., Sakurai, A., Kakuchi, T. I. & Takahashi, K. I. 2004. Rapid pyrolysis of wood block by microwave heating. Journal of Analytical and Applied Pyrolysis ,71, 187-199.
14. A. A. Ahmad, B. H. Hameed, A. L. Ahmed, (2009), Removal of disperses dye from aqueous solution using waste derived activated carbon: optimization study, J. Hazard. Mater.170, 612-619.

15. A. M. M. Varagas , C. A. Garcia , E. M. Reis , E. Lenzi , W.F. Costa , V. C. Almeida , (2010), NaOH-activated carbon from flamboyant (Delonixregia) pods ; Optimization of preparation condition using central composit rotatable design , Chem. Eng. J. 162,43-50.

16. Tan I. A. W., Ahmed A. L., Hameed B. H., (2008) , Preparation of activated carbon from coconut husk: Optimization study on removal of 2, 4, 6-trichlorophenol using response surface methodology, J. Hazard. Mater, 153, 709-717.

17. Mui, E. L., Ko, D. C., & McKay, G. (2004). Production of active carbons from waste tyres—a review. Carbon.

18. Cleiton A. Nunes; Mário C. Guerreiro 2011"Estimation of surface area and pore volume of activated carbons by methylene blue and iodine numbers", Quím. Nova vol.34 no.3 São Paulo.

19. Edger T. F., Himmelblau D. M, (2001), Optimization of chemical process, 2nd Ed, McGraw-Hill Chemical Engineering series.

20. Foo. K. Y. & Hameed B. H. (2012). Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid reside: influence of operational parameters. Bioresource technology, 103 (1), 398-404.

21. Deng, H., Li, G., Yang, H. and Tang, J. 2010a, "Preparation of activated carbon from Cotton stalk by microwave assisted KOH and K_2CO_3 activation", Chem. Eng. J., 163, 373-381.

22. Sudarynto, Y., Hartono, S. B., Irawaty, W. and Ismadji, S. 2006, "High surface area activated carbon prepared from cassava peel by chemical activation", Bioresour. Technol., 97, 734-739.

23. D.W. McKee, (1983), Mechanisms of the alkali metal catalyzed gasification of carbon, Fuel, 62, 170-175.