

## Preparing of Activated Carbon from Tyre Wastes and Using it in Adsorbing Spilled Oil on Water Bodies

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**Abstract:** The study involves on producing of activated carbon from tyre waste rubber by using chemical activation method with 50wt.% phosphoric acid followed with carbonization in  $N_2$  atmosphere at  $500^\circ C$ . The efficiency of the activated carbon was tested by the removal capacity of organic waste such as crude oil. The oil adsorption capacity of the prepared activated carbon was  $2.30 g_{oil}/g_{sorberent}$ . The Prepared activated carbon was characterized by using Fourier transform-infrared (FT-IR) spectroscopy, Nitrogen Adsorption/Desorption Isotherms and AFM images. The approached BET surface area has been reached  $41.27 m^2/g$  and pore volume  $0.0708 cm^3/g$  and mean pore radius  $0.002 nm$  for the prepared activated carbon. AFM images appeared that average of horizontal distance between nanosized particles of tyre rubber carbon was about  $90 nm$ .

**Key words:** Oil spill • Activated carbon • Adsorption • Phosphoric acid • Tyre waste rubber

### INTRODUCTION

Modern society continues to rely on the use of petroleum hydrocarbons for its energy needs. Despite recent technological advances, accidental spills of crude oil and its refined products occur on a frequent basis during routine operations of extraction, transportation, storage, refining and distribution. It is estimated that between 1.7 and 8.8 million metric tons of oil are released into the world's water every year, of which more than 90% is directly related to human activities including deliberate waste disposal. Contrary to popular perception, only one eighth of the oil released into the aquatic environment is from tanker accidents. It is also estimated that about 30% of the spilled oil enters freshwater systems [1].

It has been reported that 1 L of oil released into the environment can pollute 41.5 million L of fresh water, enough to supply 50 people for a whole year [2].

The crude oil (petroleum) predominantly hydrocarbons, comprising long chains of carbons and hydrogen is a widespread pollutant entering as waste from land or water and further, serious exposure is caused by the clean-up operations on shoreline: thus creating negative impact on the environment and seriously causing a variety of effects in marine life [3].

Figure 1 shows the major weathering and natural removal processes that can affect spilled oil on water, which include evaporation, photo-oxidation, spreading, dispersion, dissolution, emulsification, sedimentation and biodegradation [4].

Amongst the techniques that are extensively employed to remove pollution, the adsorption techniques are usually preferred because of their flexibility in operation and design. Adsorption techniques are known to be effective methods for removing toxic contaminants. Adsorbents such as carbon nanotubes and activated carbon have been largely explored by scientist for the removal of toxic contaminants in the environment [5-7].

Tire is one of the much used materials in modern life. The EU, the USA and Japan together were responsible for the disposal of a total of 5 million tons of scrap tires per year [8].

Used tyres are an alternative source of activated carbon due to the carbon content it has [5]. Rubber, the main ingredient of tyres, is an elastic hydrocarbon polymer. The most frequently employed rubbers in tyre manufacture are natural rubber (NR), polybutadiene rubber (PBR) and styrene butadiene rubber (SBR).

Fig. 2 illustrates a constructional cross-section of a modern passenger car tyre [9].

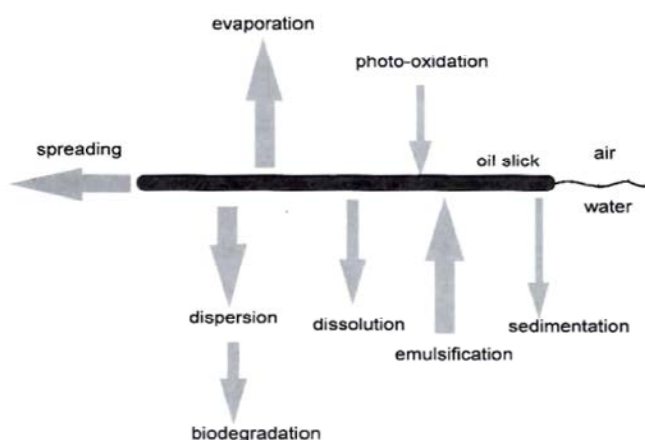


Fig. 1: Major weathering processes for oil slicks

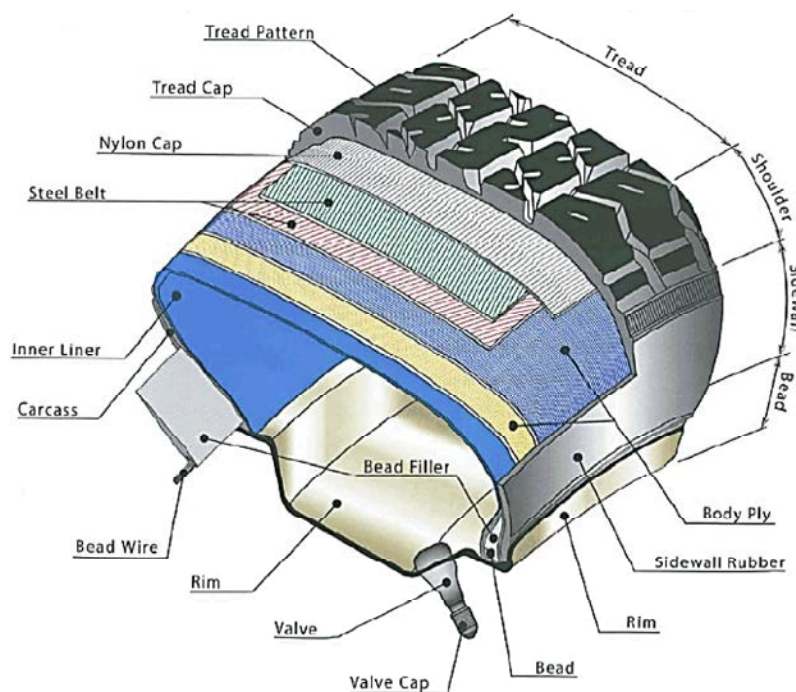


Fig. 2: Cross-section of a modern car passenger tyre

The preparation of activated carbons has been the subject of extensive research study for many years due to the diversity of their applications. Mainly though, activated carbons have been used as adsorbents and catalysts.

Although it is the porous structure of activated carbons that will determine their performance, the presence of surface groups containing heteroatoms will confer upon them different chemical properties that will contribute to determining their final application [10].

The methods used for activated carbon synthesis are physical activation and chemical activation. In physical activation, the precursor is first carbonized in an inert

atmosphere and then activated in a stream of carbon dioxide or steam; whereas for chemical activation, the precursor is impregnated with a dehydrating agent, usually zinc chloride or inorganic acids, prior to carbonization in an inert environment. In this study, chemical activation method is used due to the fact that the chemical activating agents play an important role in the carbonization process, in which they act as dehydration agents and minimize the formation of tar during carbonization. Furthermore, the temperature range used in chemical activation is lower in comparison to that used in physical activation. Phosphoric acid is selected as the activating agent instead of zinc chloride so as not to

aggravate environmental pollution by contamination with zinc compounds and also it is easier to recover the carbon product during processing stage i.e. only rinsing with water is required [11, 12].

### MATERIALS AND METHODS

#### Materials:

- Tires wastes rubber were collected from local resource (Aleppo-Syria).
- Iranian crude oil (medium density and viscosity type) was used as contaminant for water. The main physical properties of crude oil were summarized in Table 1.
- Phosphoric Acid with purity of 85%, Gas N<sub>2</sub> with purity of 99.995%, (Merk)

**Activated Carbon Preparation by Chemical Activating with Phosphoric Acid:** Tyre waste rubber was used for preparation of activated carbon which was obtained locally. The precursor was cut and sieved to desired mesh size (1-2 mm).

The activated carbon was prepared by impregnating the dried precursor with 50 wt.% H<sub>3</sub>PO<sub>4</sub> with ratio of 1:2.5 rubbers for 72hrs then filtrated and dried at 393K. Then the products were loaded in a stainless steel vertical tubular reactor placed in a tube furnace and carbonized at 500°C for 3hrs in absence of air and in flow of purified nitrogen (99.995 %) at 80ml/min. The Schematic diagram of the activated carbon preparation is shown in Fig. 3 [13-15].

Table 1: Characteristic of Crude Oil

| Properties                 | Crude Oil |
|----------------------------|-----------|
| Pouring Point, °C          | -16       |
| Density, g/cm <sup>3</sup> | 0.855     |
| Viscosity, CST             | 5.5       |
| Sulfur content, wt%        | 1.45      |
| Water content, ppm         | <0.05     |
| Salt content, ppm          | 50        |
| Sediment, ppm              | <0.1      |

The carbonized products were washed several times with hot water then cold bidistilled water until the pH value of the effluent reached 7, filtered and finally dried at 105°C. The dried activated carbon was crushed and sieved to desired mesh size (90µm).

The obtained activated carbon was designed as TC.

**Determination of Dynamic Oil Adsorption Capacity:** A 500mL sample of artificial sea water (3.5% NaCl) was placed in a 1L glass beaker 40g of oil was added to the beaker. The beaker containing crude oil and artificial sea water was mounted in a shaking apparatus; 4g of a sorbent material was added to the beaker, which was shaking for 15min at 150cycles/ min.

The oil content was weighed after a 30sec drain period. Oil content of the sorbent was analyzed according to ASTM F 726-99.

$$oil\ adsorbency\ (g_{oil}/g_{sorbent}) = \frac{S_S - S_0}{S_S} \quad (1)$$

S<sub>0</sub> = initial dry adsorbent weight.

S<sub>S</sub> = weight of adsorbent samples at end of oil test.

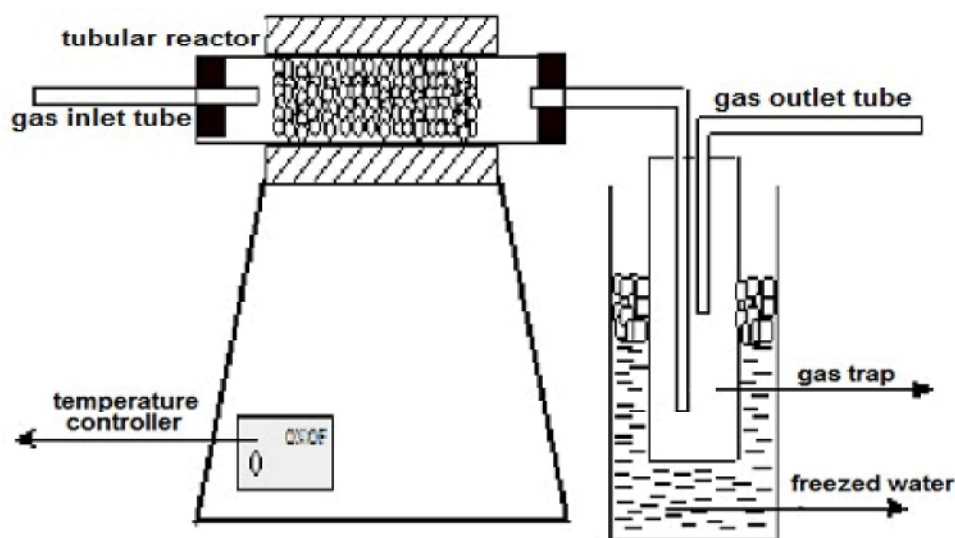


Fig. 3: Schematic diagram of the activated carbon preparation

This test was performed at  $23 \pm 4^\circ\text{C}$ . And all oil absorbency was measured three times and an average value was used [16, 17].

**Determination of Textural Properties:** The pore structural characteristics of the as-prepared activated carbons were determined by nitrogen sorption/desorption measurements. Prior to the analysis, the sample was degassed for 3hrs under vacuum at 573K. The sample was transferred to the analysis system where it was cooled in liquid nitrogen. Analysis was carried out at 77K to obtain the nitrogen adsorption isotherm. The  $S_{\text{BET}}$  was calculated by the BET (Brunauer-Emmett-Teller) equation (2).

$$S_{\text{BET}} (\text{m}^2/\text{g}) = 4.37V_m \quad (2)$$

The total pore volume was estimated to be the volume of liquid  $\text{N}_2$  adsorbed at a relative pressure of 0.95. The mean pore radius ( $r_a$ ) was calculated from the equation (3) [18].

$$r_a (\text{nm}) = 2000 V_T / S_{\text{BET}} \quad (3)$$

## RESULTS AND DISCUSSION

**Brunauer-Emmett-Teller (BET) Equation:** Figure 4 shows the  $\text{N}_2$  adsorption-desorption isotherm of the prepared activated carbon. This adsorption isotherm gives information about the porous structure of the adsorbent. As can be seen, the adsorption isotherm is a type II in according to the IUPAC classification. No hysteresis loop was observed, i.e, the desorption branch was applied with

adsorption branch. The isotherm indicate that the prepared activated carbon has nonporous structure [18, 19].

The textural characteristics (surface area, total pore volume and mean pore radius) of the prepared activated carbon are summarized in Table 2. It has a low surface area and low pore size because it has non-porous structure and this is subsequently demonstrated by the application of the BET equation.

**IR Spectrums:** Infrared spectroscopy provides information on the chemical structure of the activated carbon. Fig. 5 shows the FTIR spectra of the synthetic carbon obtained by phosphoric acid activation from waste tyre rubber. Sample was prepared in the form of pellets using KBr as a matrix, in a ratio of 1mg of sample to 60mg of KBr. The pellet was dried at  $120^\circ\text{C}$  for 24h before analysis. The spectra were recorded from 4000 to  $400\text{cm}^{-1}$ .

In order to make a correct interpretation of the spectra it is important to bear in mind that each functional group gives rise to bands at different wavenumbers.

The wavenumbers associated to signals in the FTIR spectra from chemical functional groups of interest are listed in Table 3. The range between  $3136$  and  $2997\text{cm}^{-1}$  is associated to aromatic C-H stretching, whereas the range between  $2990$  and  $2770\text{cm}^{-1}$  is assigned to aliphatic C-H stretching. The  $1690$ - $1550\text{cm}^{-1}$  range corresponds to the C=O and C-C stretching modes. Taking into account that oxygen-containing groups are the most common groups on carbon surfaces, special attention was paid to the C-O bond.

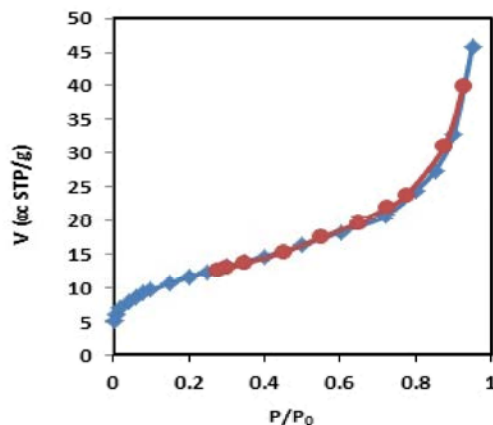


Fig. 4: Nitrogen adsorption isotherm of TC

Table 2: Porosity data of the activated carbon

| Sample | $S_{\text{BET}}$ surface area ( $\text{m}^2/\text{g}$ ) | $V_p$ Total pore volume ( $\text{cm}^3/\text{g}$ ) | $r_a$ (nm) | Adsorption Value ( $\text{g oil}/\text{g sorbent}$ ) |
|--------|---|--|------------|--|
| TC     | 41.27   | 0.0708   | 0.002      | 2.30   |

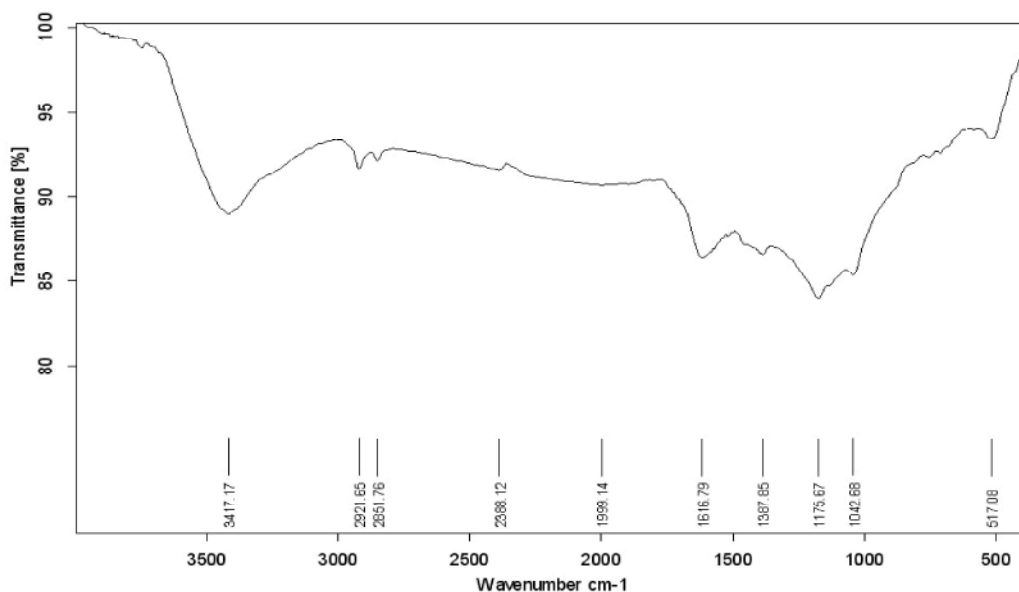


Fig. 5: IR spectrum of TC

Table 3: Band assignments for the FTIR spectra.

| Wavenumber (cm <sup>-1</sup> ) | Assignment  |
|--------------------------------|---|
| 3400                           | -OH and -NH stretching  |
| 2920                           | Aromatic compounds C-H stretching   |
| 2850                           | Aliphatic compounds C-H stretching  |
| 2390                           | C=C vibration in alkyne group   |
| 1615                           | C-C aromatic compounds - ring stretching  |
| 1400                           | Bending vibrations of C-H bonds in -CH <sub>2</sub> - and -CH <sub>3</sub> groups |
| 1387                           | -CH <sub>3</sub> symmetric bend   |

The sample contained a variety of aromatic compounds, aliphatic compounds and oxygenated functional groups, such as hydroxyl, carboxyl or carbonyl groups.

The band at 2388cm<sup>-1</sup> correspond to  $\nu(\text{C}\equiv\text{C})$  vibration in alkyne group.

Curve-fitting of the peak in the 1500-1800 cm<sup>-1</sup> region provided integrated areas of the oxygenated and aromatic carbon groups. The FTIR spectra of activated carbon indicates the presence of surface groups such as lactones, reflected in the bands in the ranges of 1160-1370cm<sup>-1</sup> and 1675-1790cm<sup>-1</sup>; quinones reflected in the C-O band between 1550 and 198 cm<sup>-1</sup> and carboxylic acids with bands in the ranges of 1120-1200, 1665-1760 and 2500-3300cm<sup>-1</sup> [10, 14, 19, 20].

**AFM Images:** The morphology of the synthesized tyre rubber carbon nanomaterial has been studied by AFM images which were obtained by 2×2μm area of the sample surface (x-y accessible area) at 0.5Hz scan rate.

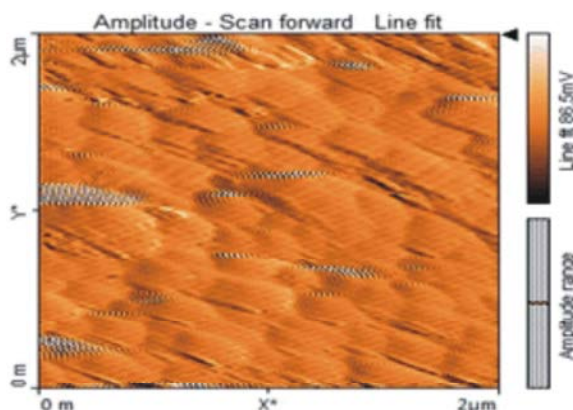


Fig. 6: Topographical AFM images of TC (2D)

Measurements were based on true contact mode with a silicon cantilever consisting of a < 10 nm tip radius and 42N/m force constant [21].

Fig. 6 depicts topographical AFM image of TC (2D). Whereas the existence of nanosized particles in the TC is more clearly reflected in three dimensional (3D) AFM image (Fig. 7). This image shown wave type projection in the Z direction from the fine surface and smaller size of TC was clearly noticed. These corresponding cross-sectional views indicates that the average thickness of TC is about 54nm and we note that the carbon surface is heterogeneous and it can be explained that there are residues of rubber additives such as metal oxides. Fig. 8 shows Cross sections of height trace (top) and amplitude

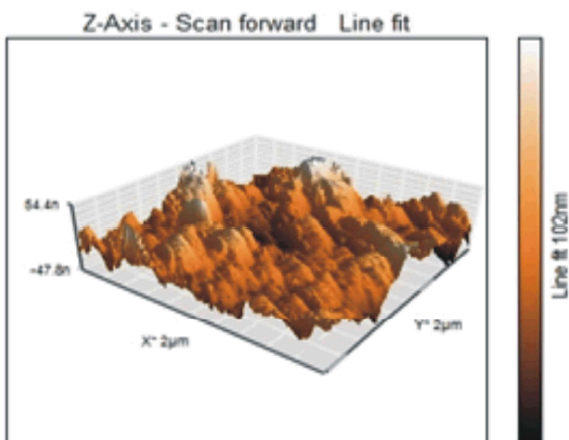


Fig. 7: Three-dimensional AFM images of TC (3D)

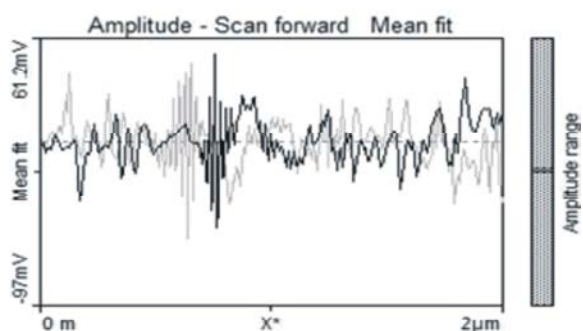


Fig. 8: Cross sections of height trace (top) and amplitude trace (bottom) images of an 2 $\mu$ m scan of AFM images of TC

trace (bottom) images of an 2 $\mu$ m scan of TC. The average of horizontal distance between nanosized particles of tyre rubber carbon about 90nm [22, 23].

### CONCLUSIONS

In summary, this research is described as practical research in the interests of the environment and society and aims to get rid of oil pollution, The adsorption mechanism is summarized by placing oil particles on the surface of the activated carbon pores. As a result, we successfully prepared a well-developed porous texture of activated carbon by using tyre waste rubber. It was found that this synthetic waste can serve as potential source for manufacturing activated carbon, which can operate as a capable adsorbent for water treatment. The BET surface area of prepared activated carbon was 41.27m<sup>2</sup>/g and its oil adsorption capacity was 2.30g<sub>oil</sub>/g<sub>sorbent</sub>. This activated carbon can be reused by extracting oil from them in a variety of ways (solvent extraction or squeezing).

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