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# Removal of Benzene and Toluene from their Polluted Aqueous solutions by using Natural Adsorbent

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## Abstract:

Low cost activated carbon was produced from available consumed black tea with microwave technique and employed as an effective adsorbent for removal of benzene (Bz) and toluene (T) from water. The resulted activated carbon was characterized by utilizing dye (methylene blue (MB) and methyl violet (MV)) adsorption procedures and several techniques such as Fourier transform Infrared (FTIR), scanning electron microscopy (SEM), X-Rays diffraction (XRD). Commercial activated carbon and filter sand as individual and blend samples were also subjected to adsorption of MB, MV, Bz, and T. All obtained results were tabulated and discussed after qualitative and quantitative determinations by applying ultraviolet- visible spectroscopy (UV-VIS) for MB and MV dyes, and gas chromatography (GC) instrumentations for Bz and T.

**Keywords:** Activated carbon, consumed black tea, filters sand, methylene blue, methyl violet, benzene, toluene.

## Introduction:

Microwaves are considered as a form of electromagnetic energy within frequency range (300) MHz to (300) GHz located between Infrared and Radio regions [1]. There are many uses of microwaves through domestic or industrial ovens [2] in analytical chemistry, material science, waste treatment, food production processes, information-communication technologies …etc. [3].

Applicable microwaves methods provide several advantages compared with conventional heating methods such as energy source type, energy transfer mechanism, environmental –health consequences, method efficiency, engineering design, possibility of heat controlling, and uniform temperature distribution conjugated with rapid temperature rise [4]. The use of friendly environmental material with less cost for organic and inorganic pollutants removing prompted many researchers to investigate new methods including the activated carbon usage prepared from agricultural, food processes, and human consumption wastes [5].

Activated carbon is amorphous carbon with high qualities in porosity [6], surface area, penetration, adsorption capacity, and regenerations that enable it to be re-use in removing of inorganic (especially heavy and toxic elements) , organic (aromatic and polyaromatic hydrocarbons) [7-10] contaminants, paints, and pesticides.

Chemical, physical, and physico-chemical methods used in many absorbents such as activated carbon [11]. Chemical activation process determines the nature of treatment method that based on prior material and its accomplished possibility with unique step including thermal decomposition of the raw agricultural residues with acidic or basic reagents [12]. Table -1- shows carbon activation methods with the their applied activation reagents.

**Table (1) Carbon activation methods**

| Activation technique | Examples of materials | Ref. |
|---|---|---|
| Chemical | $H_2SO_4$, HCl, $H_3PO_4$, $Na_2CO_3$, $K_2CO_3$, KOH, NaOH, $ZnCl_2$ | 13-18 |
| Physical | Steam, $CO_2$, $CO_2$ and $N_2$ | 19-21 |
| Physico-chemical | KOH/$CO_2$ | 22-23 |

The aim of this study was directed to prepare activated carbon from largely consumed product in Iraq that is black tea after cooking and characterize it with available techniques, and remove benzene and toluene from aqueous solution.

## Experimental part:

**Chemicals (All chemicals were used without further purification):**

Sodium carbonate monohydrate (Riedel -DeHaen AG (Seelze -Hannover).Methylene blue (MB) (BDH). Methyl violet (MV) (Fluka). Commercial activated carbon (Fluka, Switzerland packed in metal container) according to the following specifications: Fe <0.3%, ash ~ 5%, mesh size 75% (<40 μ), loss on drying ~ 10%. Cooked black tea obtained from uncooked dried tea bought from Iraqi market. Benzene and toluene were purchased from BDH Company, UK.

## Instruments and equipment:

Domestic microwave oven type SHOWNIC China. FTIR spectra were recorded using infrared spectrophotometer ABB SPECTROLAB HORIZON MB$^{TM}$ (UK). Ultraviolet- Visible spectra were recorded using spectrophotometer UV- 1650, Shimadzu, Japan. X-Rays Diffraction also recorded using a Lab X (XRD-6000), Shimadzu, Japan and using the operational details of the following: Target: Cu Kα radiation, Wave: 1.54060 A, Voltage: 40.0 kV, Current: 30.0 mA, Speed: 5.0000 deg / min. Scanning Electron Microscope type VEGAS III Tescan Algiua origin. Gas Chromatography (GC-2014, Shimadzu, Japan), SPL1=200 $^{o}$C, Detector: FID, Det Temp., 200 $^{o}$C, Column oven= 100-200) $^{o}$C, flow rate= 50 mL/min., column: fused silica.

Preparation of activated carbon: (October 2013):[ 24]

Cooked or consumed black tea was dried in open air vessel to room temperature then in microwave oven (90% heating power) for 20 minutes and grinded in ceramic mortar. To the fine grinded tea, aqueous sodium carbonate solution added (2:1 wt: wt) then left for 24 hours. The filtrated tea washed several times with distilled water to reach pH 7.0, dried, and grinded with ceramic mortar.

## Measuring of adsorption capacity by using methylene blue (MB) or methyl violet (MV): [24]

At lab temperature, Accurate volume of (500) ppm of aqueous dye solution added to a certain weight of adsorbent, agitated with (140) rpm by using electrical shaker for (30) minutes then left to stand for (24) hours. To calculate the adsorption process efficiency (removal percentage (R%) and adsorption capacity (Q)), the absorbance of the filtrated solution was measured with UV-Vis spectrophotometer within range (500-700) nm.

### Benzene and Toluene removal from water

0.5 mL of pollutant (benzene, toluene, or their equal volume ratio) added to 250 mL deionized water then adsorption process was achieved with different types of adsorbent (activated carbon, filter sand, activated carbon: filter sand blends with different weight to weight ratios). The adsorbent and polluted water were shacked with electric device for 15 min. then filtrated. To the filtrate, 10 mL or 20 mL dichloromethane (DCM) were added and the pollutant were extracted then subjected to gas chromatography analysis to determine the pollutant residue after adsorption process and the removal efficiency (R%) of the applied material. After qualitative and quantitative determination of benzene and toluene by applying various pollutant volume in 10 mL of DCM, standardization curve were computed to determine the volume of Bz or T in each case.

## Results and Discussion:

It is well known that activated carbon as a porous material with surface area ranged (300-5000) $m^2$/gm used in adsorption processes, surface reactions, ion exchange, and mechanical filtration. Noncrystalline activated carbon classified to granular and powder where the first class used in gases adsorption while the second class for purification of liquids [25].

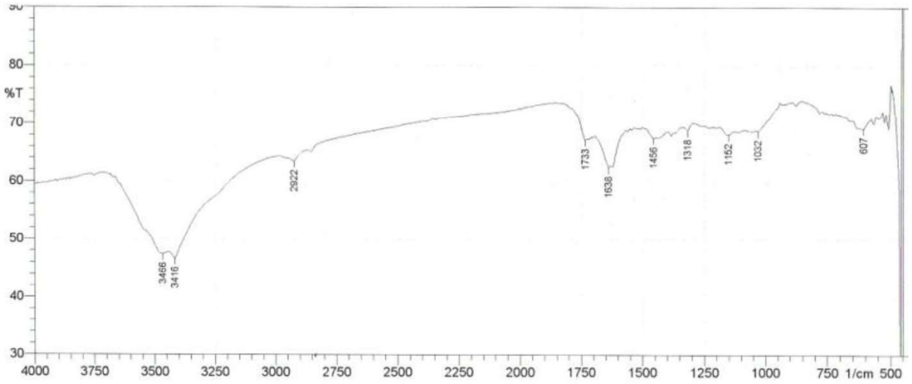
The inactivity of material surface in adsorption process is due to atoms saturation with electrons. Dispersion and van der Walls forces are resulted between adsorbent particles and surface with nonpolar properties for both of them. With polar property, dipolar interaction arises physical adsorption. The presence of electronically unsaturated atoms at surface configures chemical bonds with adsorbate atoms or molecules and arises chemical adsorptions [26].

Adsorption process depends on the carbon porous structure and its chemical structure that may cause irregular microscopic crystalline structure with appearing of effective single electrons towards adsorption of polar and nonpolar materials. Hetero-atoms (S, N, O, H) presence in carbon composition contributes in chemical bond formation between organic parts in activated carbon [27].

Activated carbon can be prepared from raw materials with varying in quality and composition depending on chemical treatment methods based upon hydrogen removal linked to raw materials and carbonation reaction [27-35].

### - Analysis of Infrared spectroscopy (FTIR):

Infrared spectrum of tea residues after exposure to microwaves irradiation depicted in Figure -1- showed several absorption vibration bands such as hydroxyl group at 3478 $cm^{-1}$, carbonyl stretching at 1733 $cm^{-1}$ (for ketone, aldehyde, or acetyl derivatives) and 1638 cm-1, bending of (C-O) group at 1456 $cm^{-1}$, stretching of (N-O) group at 1375 $cm^{-1}$. While stretching vibration of (S=O and Si-O-Si) noticed at (1032 and 608) $cm^{-1}$ respectively. In this matter, asymmetrical and symmetrical vibrations of (C-H) appeared into (2920 and 2770) $cm^{-1}$ as identical characterization of methyl and alkyl methylene beside that the broad (OH) band indicated high degree of hydrogen bonding. FTIR spectrum of activated carbon after activation with sodium carbonate depicted in Figure -2- showed all previous mentioned bands beside (2360, 1618)cm$^{-1}$ that belong to stretching vibration of (C≡C) and (C-O) respectively.



**Fig(1) FTIR spectrum of tea residues after exposure to microwaves irradiation.**

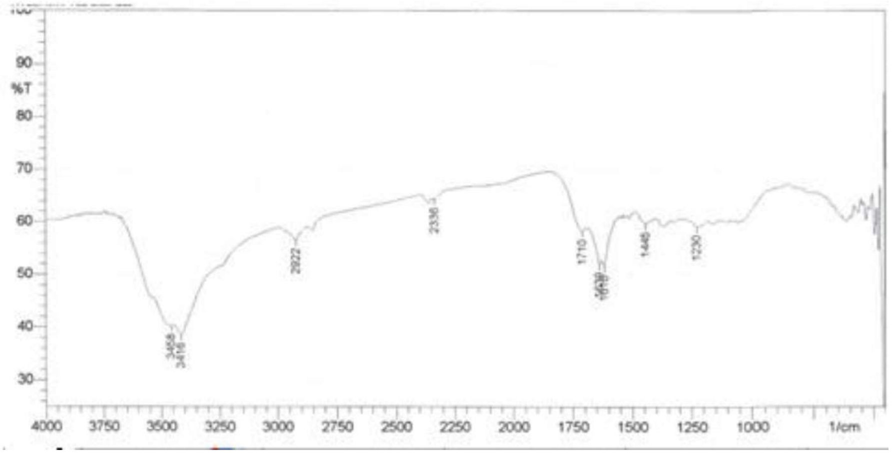


**Fig. (2) FTIR spectrum of activated carbon after activation with sodium carbonate.**

Both FTIR results can be compared with other published results of preparing activated carbon from residual tea with different activation methods [24,36, 37], such as using potassium carbonate, potassium acetate with tube furnace, or sodium hydroxide with microwave irradiation or heating with muffle oven. This comparison showed that presence of different hetero-atoms (N, S, O) as functional groups with demand oxygen in tea structure represented an important notice of effective centers in surface interactions and activated carbon behavior.

**- Analysis of X-rays diffraction (XRD):**

One of the most effective technologies that used to identify the nature of crystalline materials is X-Rays Diffraction. The obtained results of prepared activated carbon figure (3) illustrated that spaces between interlayers with weak crystalline character as non-graphitized carbonaceous structure are larger than graphite. XRD pattern figure (3) shows different Bragg angle (2θ, deg.) with maximum intensity in all measured samples (21-22) degrees and around (44) degrees corresponding to (002) and (100) diffraction of the disordered stacking of the microstructures. Also, the obtained results of prepared activated carbon samples figure (3) illustrated that spaces between interlayers with weak crystalline character as non-graphitized carbonaceous structure are larger than graphite as calculated by Scherrer equation [38]:

$d=k\lambda/\beta.\ \text{Cos}\theta$

Where: d= average crystallite size (or mean size of the ordered crystalline) in (nm).

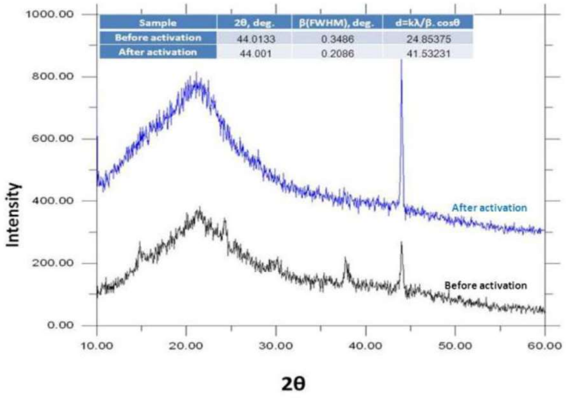
λ= X-ray wavelength in (nm)

β= the peak width of the diffraction peak profile (or the line broadening) at half maximum (FWHM) in (radius); [β (radian) =2π β (deg.)/ 360].

K= shape factor (or constant related to crystalline shape= 0.91).

θ= Bragg angle in (radius); θ (radian) =2π θ (deg.)/ 360].

These results coincide with many published documents of preparation and characterization of activated carbon from plants or non-vegetarian sources [4, 30-34].



| Sample | 2θ, deg. | β(FWHM), deg. | d=kλ/β. cosθ |
|---|---|---|---|
| Before activation | 44.0133 | 0.3486 | 24.85375 |
| After activation | 44.001 | 0.2086 | 41.53231 |

**Fig.(3) XRD analysis of both prepared activated carbon before and after activation with sodium carbonate**

### - Analysis of Scanning Electron Microscopy (SEM):

Analysis of Scanning Electron Microscopy (SEM) of carbon sample before activation process (after microwave irradiation) and activated carbon sample (after treatment with sodium carbonate depicted in figures (4&5) respectively had been done. The obtained results clarify that first sample (before activation process) have partial porous structures outputted from microwaves heating effects on residual tea. While the second sample (after activation) has gaps, channels, or slits of porous structure as Microscopic porous character. This character of the second sample conjugated with irregularity in shape and size with dispersed distribution making this material with high surface area and adsorption capacity. These pores configuration linked with carbon monoxide and carbon dioxide formation during preparation within activation effect of sodium carbonate according to the following equations:

$$Na_2CO_3 + 2C \longrightarrow 2Na + 3CO$$

$$Na_2CO_3 \longrightarrow Na_2O + CO_2$$

$$Na_2O + C \longrightarrow 2Na + CO$$

Also, it can be noticed presence of a particle on some pore surface of carbon after thermal treatment and before activation process that help in reducing of surface area. These particles disappeared after treatment with sodium carbonate with presence of micropores within prepared activated carbon structure. Previous mentioned notices of our prepared activated carbon were similar in characteristic properties with others that prepared from tea or vegetarian sources [38, 39].

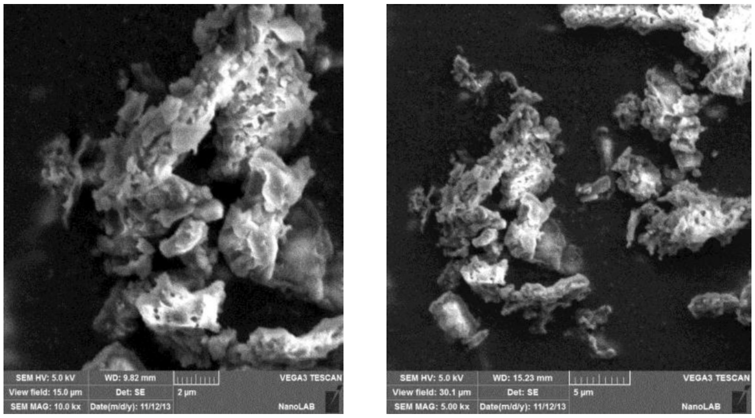


**Fig.(4) SEM images of residual tea before activation**

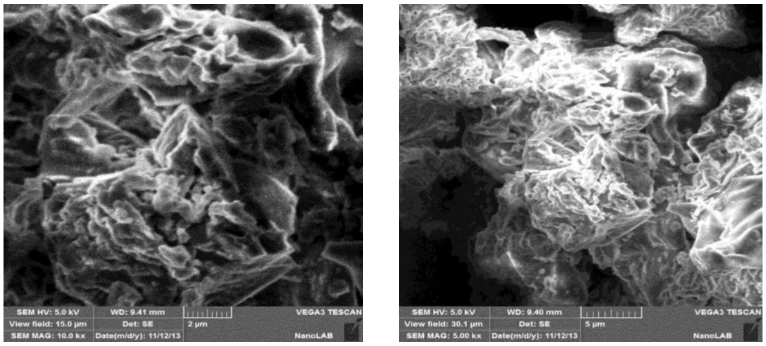


**Fig.(5) SEM images of activated carbon after activation**

- **Determination of prepared activated carbon, commercial adsorbents, and/ or their blends adsorption efficiencies and capacities to methylene blue (MB) or methyl violet (MV) and comparison it with:**

Methylene blue (MB) considers as most likely used dyes in scientific researches especially in adsorption (kinetic studies) or characterization of prepared adsorbent efficiency due to its cationic dyeing property in dyes industries for cotton, wool, or silk [40] besides its effects on many living species even within very low concentration (less than 1 ppm).

UV-Vis spectra (Figure -6-)were done for standard solutions of methylene Blue (MB). After MB was subjected to adsorption process, its UV–Vis. Spectrum was used to determine the percentage removal (R%) and adsorption capacity (Q) through the application of the following equations (1 and 2):

**Removal % = $[(C_o - C_t) / Co] \times 100$ ………… (1)**

Where

$C_o$ : initial concentration (ppm).

$C_t$: concentration after adsorption (after a specific time) (ppm).

**Adsorption capacity (Q) = $[(C_o - C_t) / m] \times v$ ……… (2)**

Where

$C_o$ : initial concentration (ppm) of adsorbate.

$C_t$: concentration of adsorbate after adsorption (after a specific time) (ppm or mg/L); m: weight of adsorbent (g); v: volume of solution (L)

Q: Adsorption capacity of adsorbent after a specific time (mg/g).

The obtained results of standard MB solutions showed good correlation coefficient ($R^2$) at characteristic λmax value (Figure -7-).

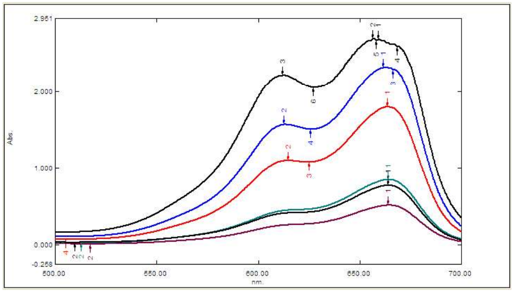


Fig.(6) UV-Vis. Spectra of Standard MB solutions

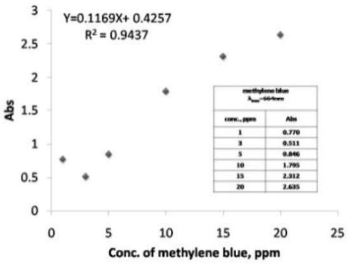


Fig.(7) Standard MB curve at (1-20) ppm range

MB adsorption can be affected by surface functional groups and micropore presence. The applied materials adsorbed 500 ppm MB with excellent efficiency (both R% and Q values) where commercial activated carbon was more influence in MB adsorption than our prepared material as shown in table(2). Adsorption capacity Q or MB number (in mg/g) of our prepared material from waste tea was in same range of other activated carbon prepared from tea sources table (3).

Table (2): Adsorption results * of methylene blue (MB).

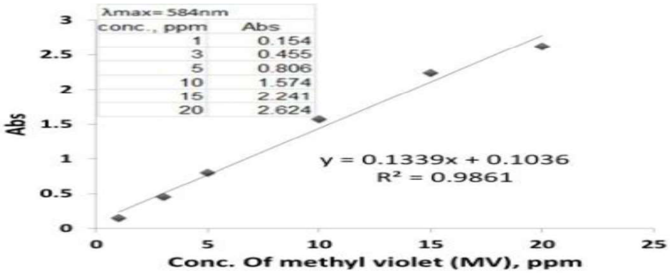
| Adsorbent | Volume of added MB dye, L | Percentage removal (R %) | Adsorption capacity (Q), mg/g |
|---|---|---|---|
| Commercial AC | 0.05 | 98.43062 | 24.60766 |
| Prepared AC | 0.025 | 96.0391 | 24.00977 |
| Filter sand | 0.05 | 95.8797 | 23.96993 |
| 1:3 AC : Sand | 0.05 | 101.0462 | 25.26155 |
| 2:2 AC : Sand | 0.05 | 101.05 | 25.2625 |
| 3::1` AC : Sand | 0.05 | 101.048148 | 25.26204 |

* Dye initial concentration = 500 ppm.

**Table (3): Published methylene blue results for activated carbon prepared from different tea sources.**

| Tea source | MB number, mg/g | Ref. |
|---|---|---|
| tea industry waste carbon (only carbonized material)<br>tea industry waste activated carbon (produced with ½:1activating agent/precursor) | 27.8<br>31.9 | 24 |
| Tea-industry waste | 39.1 | 41 |
| Spent tea waste<br>thermally activated carbon from spent waste tea | 39.30<br>43.0 | 42 |

Also, methyl violet (MV) applied as adsorption dye qualifications with the same MB experimental conditions and showed good correlation coefficient ($R^2$) at characteristic $\lambda_{max}$ value (Figure -8-).The obtained results of MV adsorption can compared with methylene blue (MB) adsorption as shown in Table (4).



**Fig(8) Standard MV curve at (1-20) ppm range**

**Table (4): Adsorption results * of methyl violet (MV)**

| Adsorbent | Percentage removal (R%) | Adsorption capacity (Q), mg/g |
|---|---|---|
| Commercial AC | 100 | 25 |
| Prepared AC | 96.0391 | 24.0098 |
| Filter sand | 95.9940 | 23.9985 |
| 1:3AC:sand | 100.1624 | 25.0406 |
| 2:2AC:sand | 100.1669 | 25.0417 |
| 3::1`AC:sand | 100.1624 | 25.0406 |

* Dye initial concentration = 500 ppm, Volume of added MV dye = 0.05 L

Our prepared activated carbon from tea residues showed excellent results MV adsorption in both R% and Q values but less than commercial activated carbon. Also, MV adsorptions were more effective than MB with commercial, prepared activated carbon and filter sand samples. But these conclusions cannot be considered finally for both activated carbon samples because of using different sample weight and with this note MB adsorption precedes MV adsorption.

It can be observed that filter sand gave good R% and Q values less than both applied activated carbon materials. With implementation of commercial activated carbon – filter sand blends with different ratio, several points can be concluded from R% and Q values such as all applied blends were more effective in MB adsorption than MV with same (R% and Q) values in the same dye.

We do think that the increasing in (R% and Q) with MB is attributed to dye size optimized with surface functional group presence and micropore size. Also, blends effectively adsorbed both dyes more than individually activated carbon or filter sand besides commercial activated carbon was more effective than filter sand. With these notes, it can deduce that blend qualification attributed to activated carbon more than filter sand.

### - Benzene and Toluene removal from water

Benzene and toluene are toxic volatile monoaromatic compounds with high vapor pressure and low molecular weight. They contaminate water as results of different petroleum industries and their solubility in water (18 and 25) ppm respectively [43]. Monoaromatic compounds removal methods were physical, chemical, and biological techniques [44-47] that allowed both compounds to be less than maximum allowed levels (0.005 and 1) ppm for benzene and toluene respectively [48].

In this work, benzene and toluene in water underwent to adsorption with different activated carbon: filter sand ratio after qualitative and quantitative determination for both pollutants with gas chromatography (GC) instrumentation (Tables -5- and -6-) to estimate standard curve equations and their correlation coefficients ($R^2$) followed by calculation of removal percentage (R%) in each case.

From Table -6-, it can be noticed that presence of activated carbon (AC) strongly affected the removal of benzene or toluene. Also, comparing removal (R% ) of [1:3 and 3:1] AC: filter sand ratios for both pollutants showed that AC plays an effective role in adsorption process and this may be related to differences in surface functional group presence and micropore size.

**Table (5) Adsorption of benzene or toluene with different activated carbon: filter sand blends**

| Pollutant | Equation, $R^2$ | Condition | Adsorbent Ac: Sand (wt : wt) | Area | Removal (R%) |
|---|---|---|---|---|---|
| Benzene | y= 7E+06x + 49321<br>$R^2 = 0.876$ | 0.5 mL benzene in 20 mL DCM | **AC Only** | 151424 | 97.08277 |
| | | | **1 : 3** | 523558 | 86.45037 |
| | | | **2 : 2** | 332502 | 91.90911 |
| | | | **3 : 1** | 293139 | 93.03377 |
| Toluene | y= 8E+06x + 43128<br>$R^2 = 0.961$ | 0.5 mL toluene in 20 mL DCM | **AC Only** | 390260 | 91.3217 |
| | | | **1 : 3** | 210270 | 95.82145 |
| | | | **2 : 2** | 229707 | 95.33553 |

Table -6- summarizes the influence of mixing both pollutants under study on adsorption with AC, filter sand, and their various ratio blends and clarifies the effects of adsorbent type, pollutant physical properties, mixing ratio as shown in the following points:

1. Using individually filter sand was more effective in adsorption process than AC.
2. Applying AC: filter sand blends gave clear images on molecular pollutant size effect on R% values.
3. Comparing 1:3 and 3:1 (AC: Sand) ratios showed the demonist role of AC on adsorption process.

**Table (6) Adsorption of benzene and toluene with different activated carbon: filter sand blends**

| Adsorbent | Condition | Pollutant | Area | Removal (R%) |
|---|---|---|---|---|
| 5 gm AC | 0.5 mL benzene<br>0.5 mL toluene<br>10 mL DCM | Benzene | **713009** | 81.03749 |
| | | Toluene | **515889** | 88.18098 |
| 5 gm Sand | 0.5 mL benzene<br>0.5 mL toluene<br>10 mL DCM | Benzene | **458231** | 88.31686 |
| | | Toluene | **258523** | 94.61513 |
| 1:3 AC:Sand | 0.5 mL benzene<br>0.5 mL toluene<br>10 mL DCM | Benzene | **781914** | 79.06877 |
| | | Toluene | **1748176** | 57.3738 |
| 2:2 AC:Sand | 0.5 mL benzene<br>0.5 mL toluene<br>10 mL DCM | Benzene | **142432** | 97.33969 |
| | | Toluene | **284289** | 93.97098 |
| 3:1 AC:Sand | 0.5 mL benzene<br>0.5 mL toluene<br>10 mL DCM | Benzene | **352795** | 91.32931 |
| | | Toluene | **434401** | 90.21818 |

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