

# Preparation of Magnetite Nanoparticles Filters for the Removal of Benzene from Drinking Water

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**Abstract**— A simple method was described for the synthesis of magnetite nanoparticles by mixing and stirring two equivalents of iron(II) chloride tetrahydrate with three equivalent of iron(III) chloride hexahydrate in the presence of ammonium hydroxide. The precipitated magnetite nanoparticles were washed with 5% NH<sub>4</sub>OH. The nanoparticles formed were characterized by IR, SEM and X-ray diffraction and then applied for the removal of benzene from water samples..

**Index Terms**— Magnetite, benzene, metropolitan drinking water, ultraperformance liquid chromatography MS/MS.

## I. INTRODUCTION

Benzene is colourless liquid and is classified as carcinogenic hydrocarbon effect[1]. The sources of benzene include industrial usage, engine exhaust and tobacco smoke, it could also be formed from the reaction of benzoate and ascorbic acid under the influence of heat, uv light and metals ions as catalysts[2]. High levels of benzene can cause irritation vomiting, dizziness, sleepness, coma and may be death [3].

Many methods have been used for the removal of hydrocarbons from water, magnetic separation has been developed as a recovery and pollution control process for many environmental and industrial problems including waste water[4]and purification of drinking water[5]. The adsorption of contaminants in water was carried out using activated carbon/iron oxide magnetic composites[6]. Activated carbons offer an attractive and inexpensive option for the removal of contaminants from water[7]. Because of the high surface area and porous structure, it can efficiently adsorb compounds dissolved in liquids[8]. Magnetic filtration has been used for the removal of petrochemicals from water using activated carbon magnetic composites [9]. Luiz et.al[6] used the activated carbon/iron oxide magnetic composites for the adsorption of contaminants in water. The basics of heterogeneous photocatalysis was described for water purification and treatment using titanium dioxide. The method reported to be slow and poisonous[10]. Recent development in photocatalytic water treatment technology has been described using semiconductors[11]. The method was applied to the analysis of benzene in drinking water and other beverage samples.

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Danylchuk et.al[12] reported magnetic separation method for the purification of oil polluted water, they used a magnetic filtration for the purification of water from oil using a thin layer of magnetite.

Many gas chromatographic methods were applied for the determination a benzene. Ljungkiust and norlinder[13], described a method for the analysis of benzene in exhaled air by gas chromatography. Yamada et.al,[14] used activated charcoal to absorb benzene prior to analysis by G.C. Desorption of benzene was performed by solid-phase micro extraction before the analysis by G.C-MS[15]. Elke et.al[16] reported an improved analytical method for determination of benzene, toluene, ethyl benzene and xylene. The procedure consists of air sampling head-space SPME and GC. FID. Pekari et.al[17] determined benzene in blood using HS-GC equipped with a photoionization detector. Fiorentino and Coworkers[18] developed a method to evaluate low concentration of benzene in urine samples. Prado et.al[19] evaluated the effects of various factors to optimize urinary benzene determination using SPME and GC-MS.

Great attention has been made for the analysis of benzene in water samples.

Burnung and Grahl-Nielsen [20] applied purge and trap technique for the concentration of benzene from water samples. Benzene was purged from water by helium, using this method, benzene concentration of 0.1 µg/ dm<sup>3</sup> from 5 cm<sup>3</sup> water samples can be determined. Rosell et.al[21] optimized purge and trap G.C-MS for simultaneous determination of BTEX with other organics in ground water. Almieda and Boas[22] determined BTEX in water samples using SPME and GC-FID. The detection limit for benzene was 15 µg/cm<sup>3</sup>. Benzene in drinking water and beverages has also been determined using semiconductors [9]. A simple and rapid HS-GC procedure was developed for simultaneous determination of BTEX and alkyl ethers in water samples. The method was applied for the screening of contaminants in river water with the determination limit of benzene as 0.07 µg/ dm<sup>3</sup> [23].

## II. EXPERIMENTAL

### 2.1. Chemicals and Solutions

Iron(II) chloride tetrahydrate FeCl<sub>2</sub>.4H<sub>2</sub>O 99% BDH, iron(III) chloride hexahydrate FeCl<sub>3</sub>.6H<sub>2</sub>O 99% Lobacheie, ammonia NH<sub>3</sub> 35% Avoncheme all of analytical grade.

A Stock solution of benzene 1000 ppm was prepared by dissolving 1.14 ml in 40 ml ethanol and completing the volume to 1000 ml with deionized water, diluted solution are prepared as needed.

### 2.2 Apparatus :

Water acquity UPLC system equipped with quaternary pump (Milford MA, USA). The column used was an acquity BEH

C<sub>18</sub> column (50 × 2.1 mm) id 1.7-µm particle size) Waters, Milford, MA, USA). FT-IR spectra recorded by prestige-21 FT-IR spectrophotometer, Shimadzu. SEM spectra were recorded by JSM-6380 LA Scanning Electron Microscope. X-ray diffraction spectra were recorded by Jeol Altima 4 X-ray diffraction, Rigaco.

III. PREPARATION OF MAGNETITE :

Magnetite ferric oxide was prepared as follows: 122.52 g of FeCl<sub>2</sub>.4H<sub>2</sub>O and 250 g of FeCl<sub>3</sub>.6H<sub>2</sub>O were transferred into a 5 L measuring flask, followed by 250 ml of deionized water with stirring 200 ml of ammonia solution were added. The solution turned to black by the formation to magnetite. After filtration and washing with 5% ammonium hydroxide, the precipitate dried and grinded to give the nanoparticles(24).

IV. CHARACTERIZATION OF MAGNETITE

The nanoparticles of magnetite were characterized by IR, SEM and X-ray diffraction techniques to ensure the formation of magnetite ferric oxide and the size of the nanoparticles. The results obtained are shown in Figs. 1-3. The aim of this work is to remove benzene from drinking water by magnetite and apply UPLC-MS/MS for the determination of benzene in drinking water before and after treatment of water by the magnetite nanoparticles

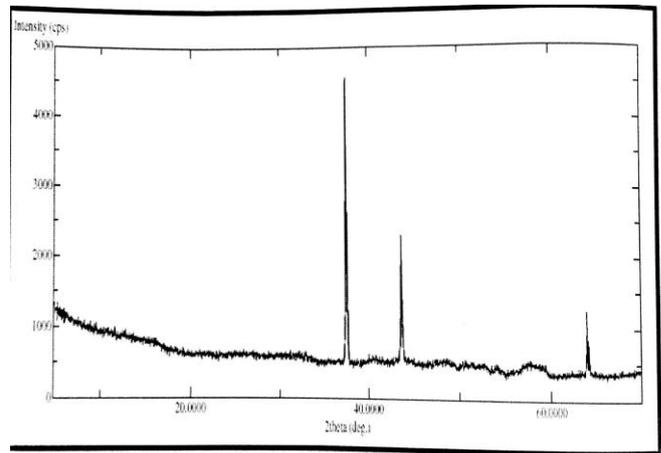


Fig. 3. X-ray diffraction of magnetite nanoparticles

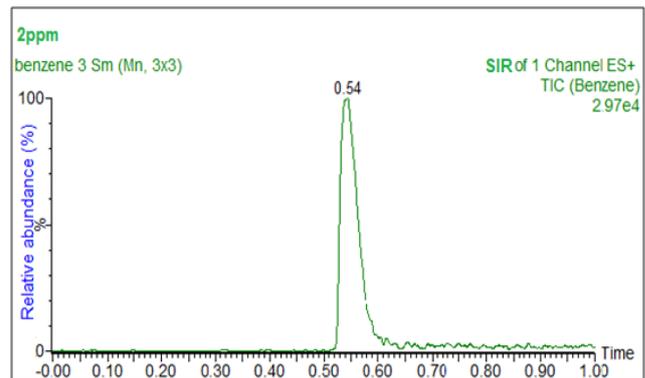


Fig. 4. The Chromatogram of 2 ppm benzene

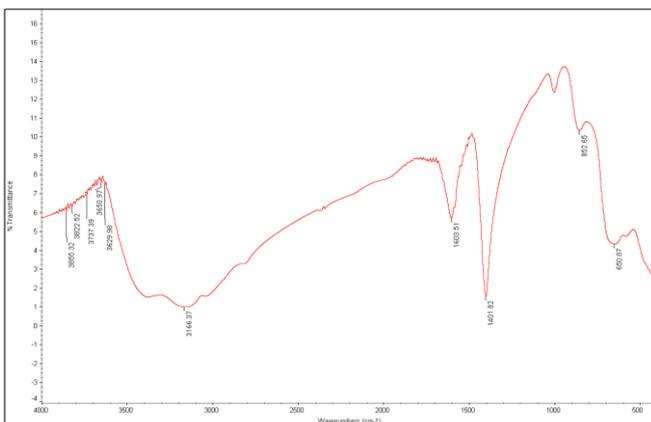


Fig1. IR spectrum of magnetite nanoparticles.

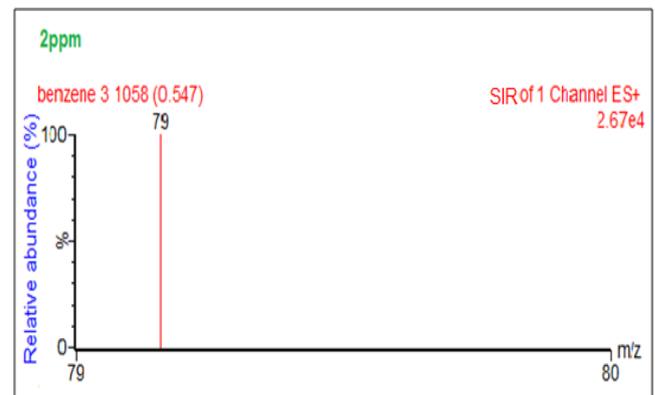


Fig. 5. Mass Spectrum of 2 ppm benzene

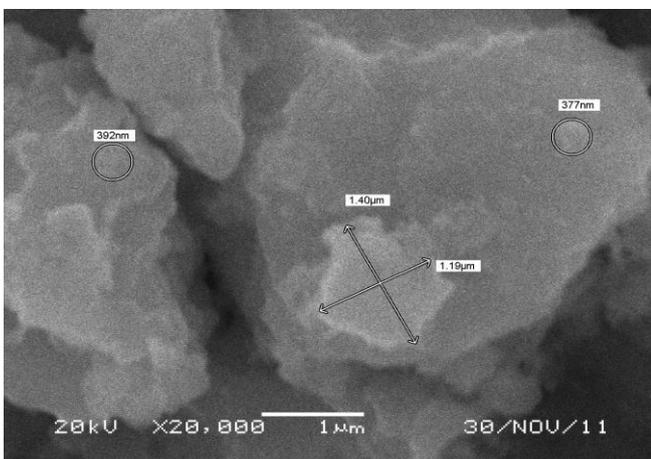


Fig. 2. SEM of Magnetite nanoparticles

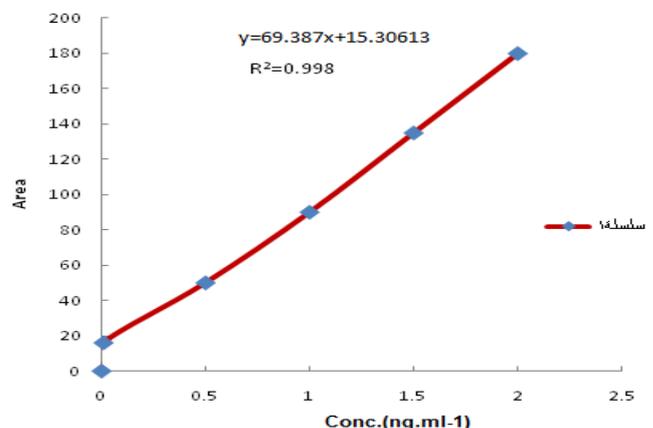


Fig.6 calibration graph for benzene

When benzene is injected to the UPLC-MS/MS system it gave a nice peak at 79 mass after 0.54 min. retention time Figs. 4-5. The area of this peak is related to the concentration of benzene as shown in Fig. 6.

V. THE METHODS USED:

5.1 Manual Method:

The benzene polluted water samples is transferred to a beaker followed by 1g of magnetite, the mixture is stirred for 10 minutes by the mechanical stirrer, filtered and refiltered by PVDF filter paper (0.45  $\mu$ m), benzene in the filtrate is determined by UPLC-MS/MS as mentioned before.

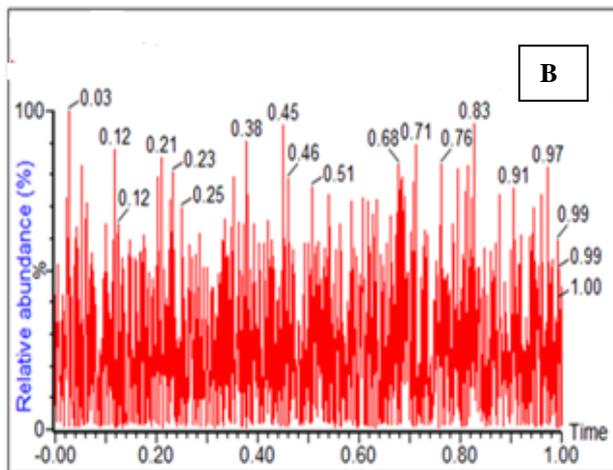
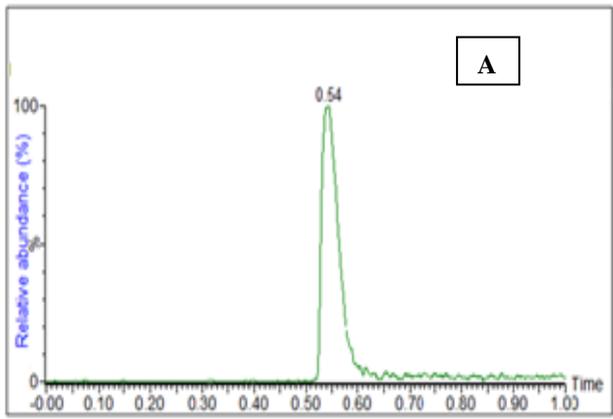


Fig. 7. Chromatogram of the water samples.

- a) before treatment by magnetite
- b) after treatment by 7g magnetite

5.2 Filter Method :

The benzene polluted water sample is passed through a funnel (65 mm diameter) filled with magnetite for 10 min, then filtered using 0.45  $\mu$ m PVDF filter paper before the UPLC-MS/MS measurement.

VI. REMOVAL OF BENZENE FROM WATER:

6.1. Manual Method :

When 7 g of magnetite is added to water sample containing 2 ppm of benzene, complete removal of benzene was obtained as shown in Fig. 7. The experiment was repeated by adding 5, 2 and 1g of magnetite to the same sample, complete removal

was also achieved indicating the high ability of magnetite to remove benzene as shown in Figs. 8-10.

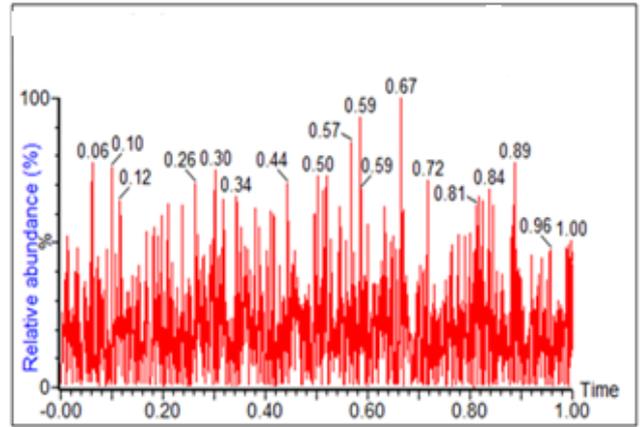


Fig. 8 Chromatogram of water samples after treatment by 5g of magnetite

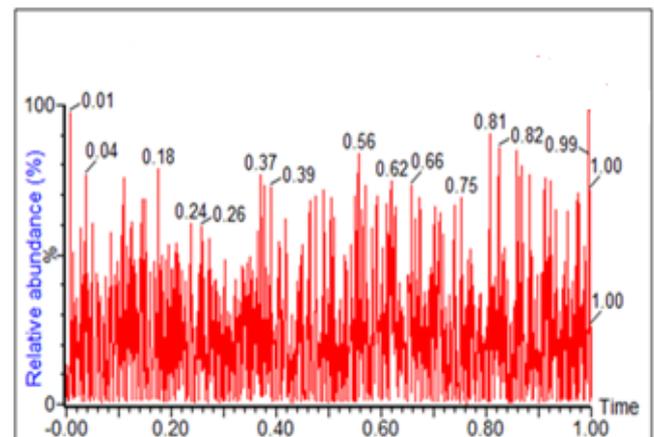


Fig. 9. Chromatogram of water sample after treatment by 2g of magnetite.

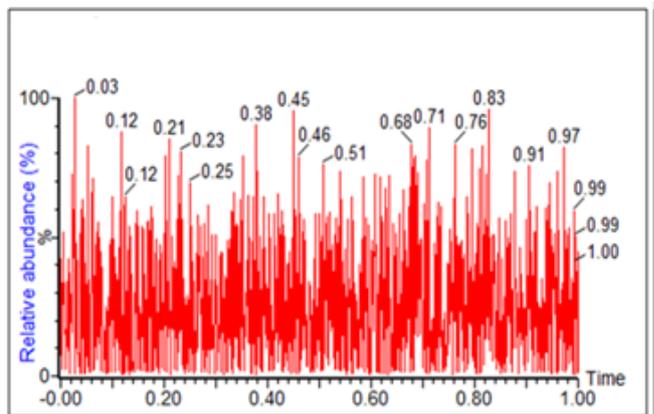


Fig. 10. Chromatogram of water sample after treatment by 1g magnetite

6.2 Filter Method:

In this method, 5 ml of the water sample containing 1 ppm of benzene were passed through the filter containing 1 g of magnetite, 30 minutes were found to be enough for the filtration. The sample was again filtered using 0.45  $\mu$ m PVDF filter paper prior to the injection to the UPLC-MS/MS system. Complete removal of benzene from water was obtained as shown in Figs. 11-12.

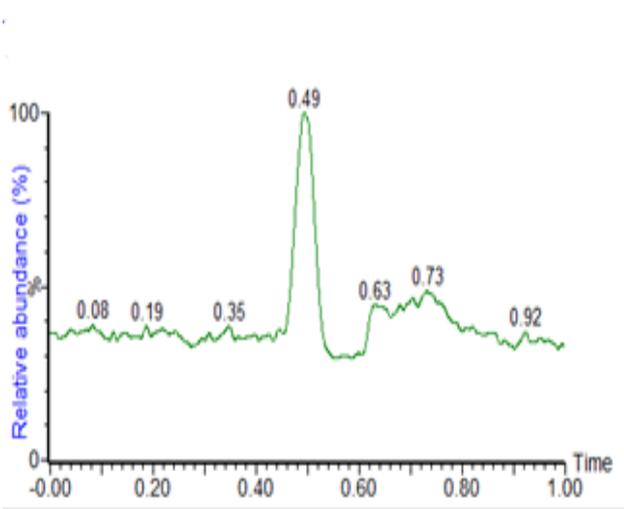


Fig. 11 Chromatogram of 5ml of sample containing 1ppm of benzene before filtration.

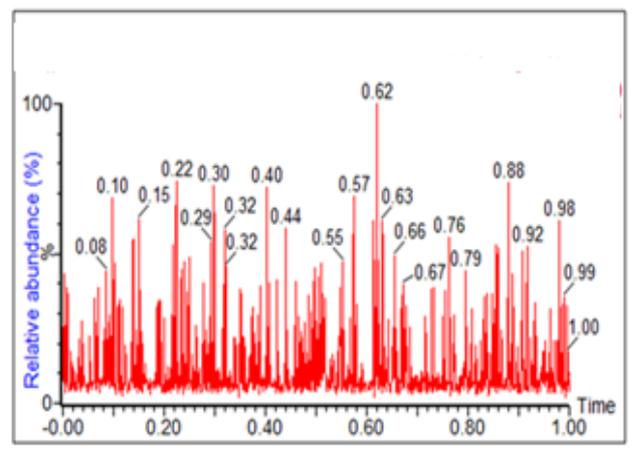


Fig. 14 Chromatogram of 40 ml of sample containing 1ppm of benzene after filtration.

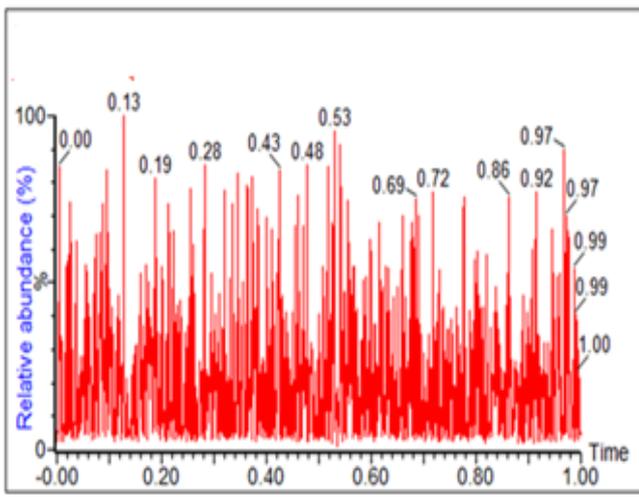


Fig. 12 Chromatogram of 5ml of sample containing 1ppm of benzene after filtration

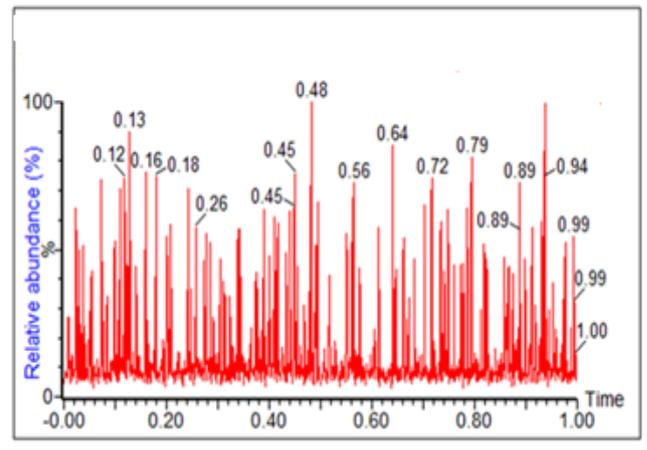


Fig. 15 Chromatogram of 70ml of sample containing 1ppm of benzene after filtration..

The experiment was repeated by taking 20, 40 and 70 ml of the sample also 100% removal of benzene was achieved as shown in Figs. 13-15.

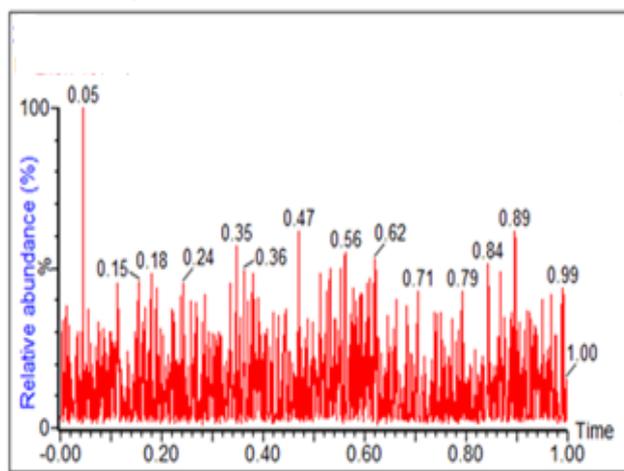


Fig. 13 Chromatogram of 20 ml of sample containing 1ppm of benzene after filtration.

#### VII. APPLICATION OF THE METHOD FOR METROPOLITAN STATIONS:

The results obtained from the various authentic benzene polluted water samples showed a high activity of magnetite in removing benzene using both methods, the manual and filters., this encouraged the application of these methods for the removal and analysis of water samples containing benzene.

Samples are collected from Bowaib1, Bowaib2, Manfohah1, Manfohah2, Salbokh1, Salbookh2 and Malaz stations in Riyadh area.

##### 7.1. Manual Method

Four samples were analysed by this method Manfohah1, Salbookh1, Salbookh2 and Bowaib2. 20-30 ml of the samples are transferred to a beaker containing 1g of magnetite following the procedure of the manual method mention before.

Results obtained showed complete removal of benzene from all water samples as shown in Figs. 16-19.

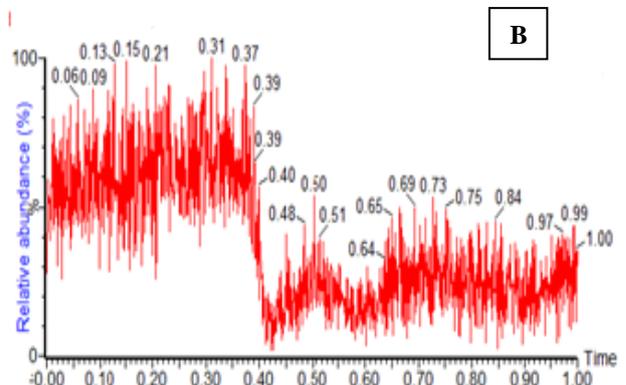
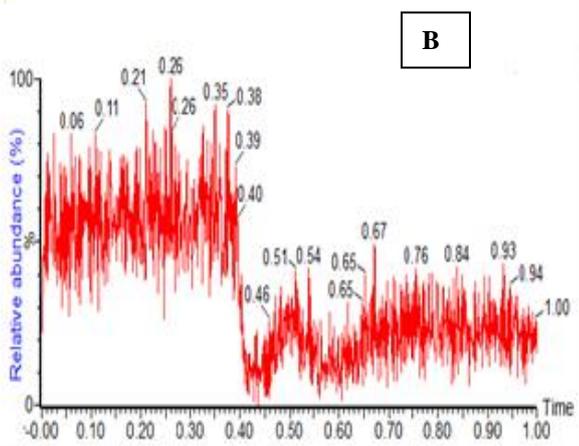
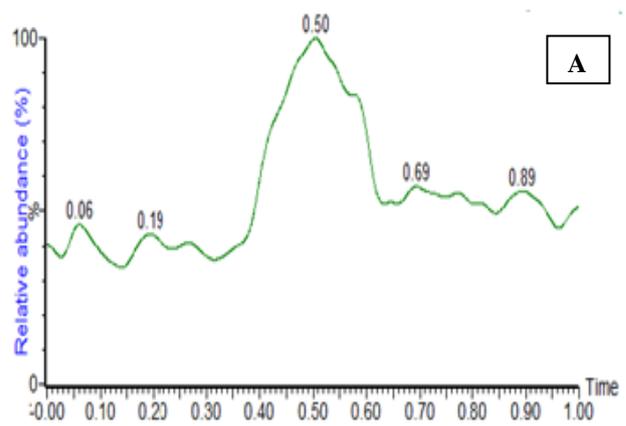
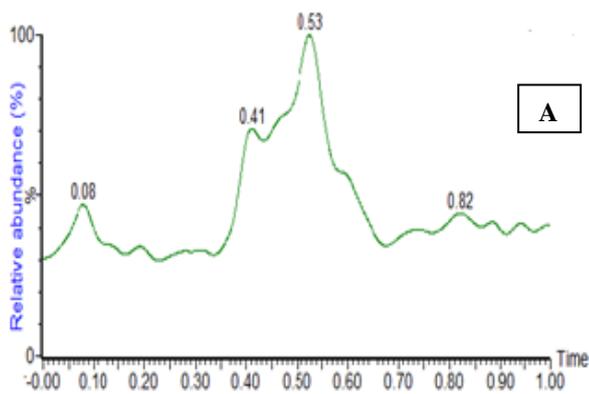
##### 7.2 Filter method:

In this method, filter was used for the removal of benzene. Four samples were chosen, Bowaib1, Salbookh2, Malaz and Manfohah2. 5 ml of each samples were passed through the

filter using 1g of magnetite. Results obtained are shown in Figs. 20-23. The results obtained are summarized in Table 1 below:

**Table 1 Analysis of benzene in water metropolitan stations Riyadh Area:**

Station Riyadh Location	Water Source	Counc. of benzene before treatment ng/ml	Counc. Of benzene treatment in the station ng/ml	Counc of benzene after treatment by magnetite ng/ml
Malaz	Desalinated + Well water	344.8	280	Zero
Salbookh1	===	159.6	145.6	Zero
Salbookh2	=====	201.3	157	Zero
Manfohah1	===	178.2	75.6	Zero
Manfohah2	===	127.3	100.2	Zero
Buaib1	===	177.8	80.2	Zero
Buaib2	===	216.3	121.4	Zero



**Fig 16: Chromatogram of Buwaib2 sample**  
a) Before treatment by magnetite.  
b) After treatment by magnetite

**Fig. 17a) Chromatogram of Salbookh1 before treatment by magnetite treatment**

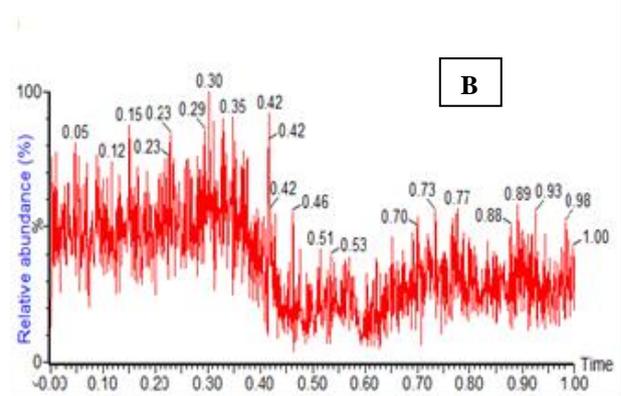
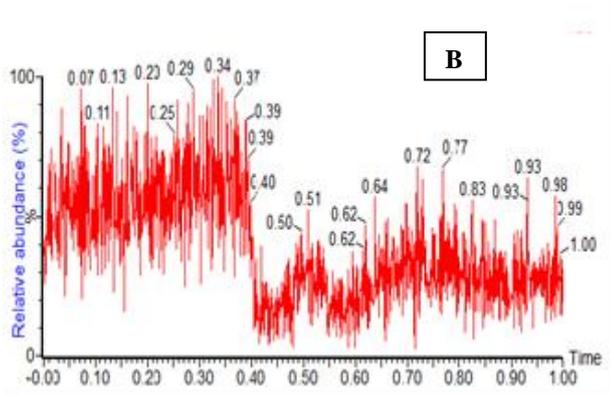
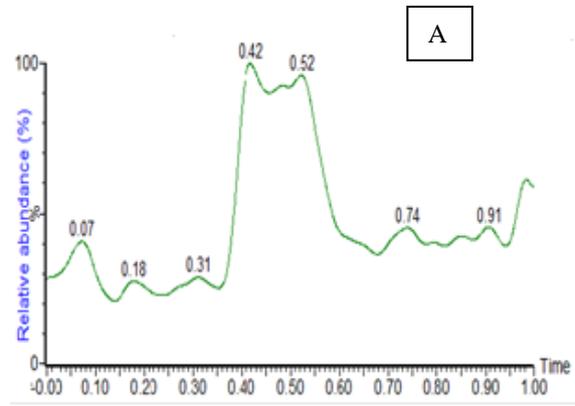
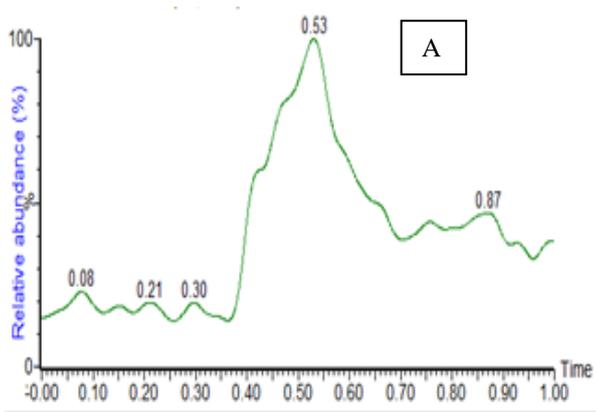


Fig. 18 a) chromatogram of salbookh2 before treatment by magnetite and b) after treatment.

Fig. 20 chromatogram of Buwaib1 sample a) before treatment by magnetite and b) after treatment

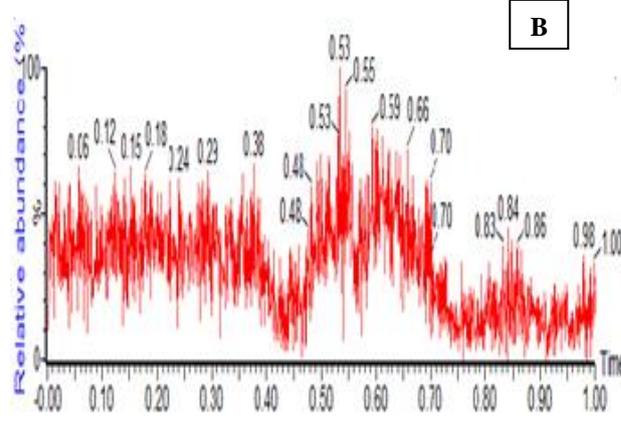
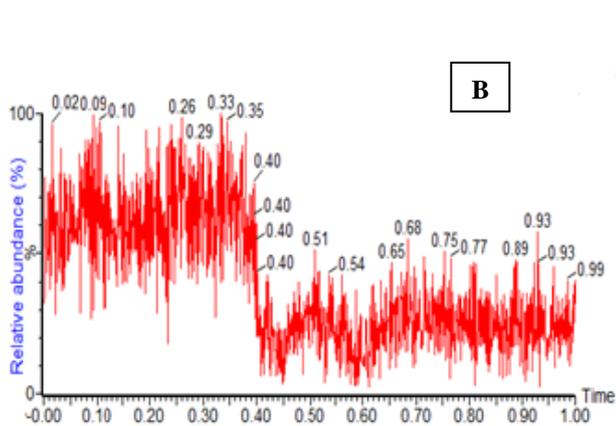
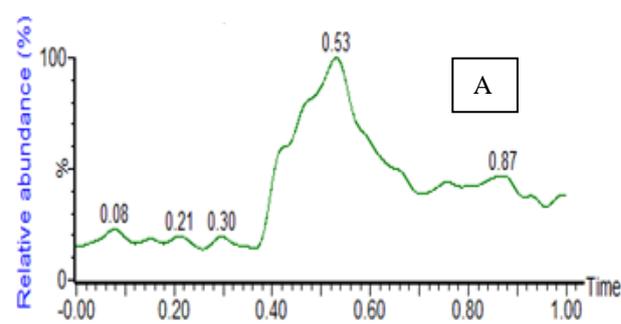
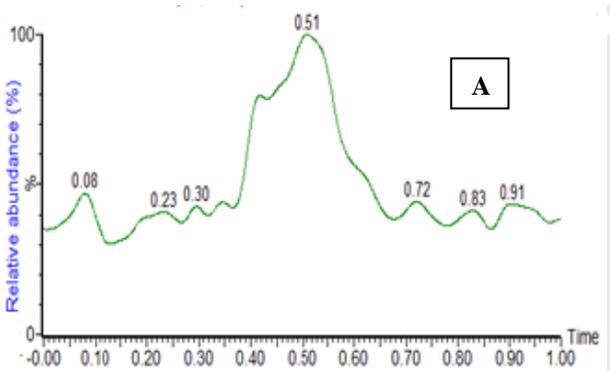


Fig. 19 chromatogram of manfoohah1 a) before treatment by magnetite and b) after treatment

Fig 21. Chromatogram of salbookh2 a) before treatment by magnetite and b) after treatment.

VIII. CONCLUSION :

From the results obtained we observed that the treatment of water samples by reverse osmoses is not enough to remove benzene from water, ie. only about 40% of benzene can be removed as shown in table (1), which showed high concentration of benzene remains in the samples which is very dangerous on the human health, Malaz 280, Salbookh1 146, Salbookh2 157, manfohah1 75, Manfohah2 100, Bowaib1 80 and Bowaib2 121 ng/ml, these concentration are very high. The concentration of benzene should not exceed 5 ng/ml(25). However, the treatment of water polluted samples by magnetite gave very good results with 100% removal of benzene because of the high ability of magnetite, magnetite has also the advantage of being cheap, available and easy to be prepared.

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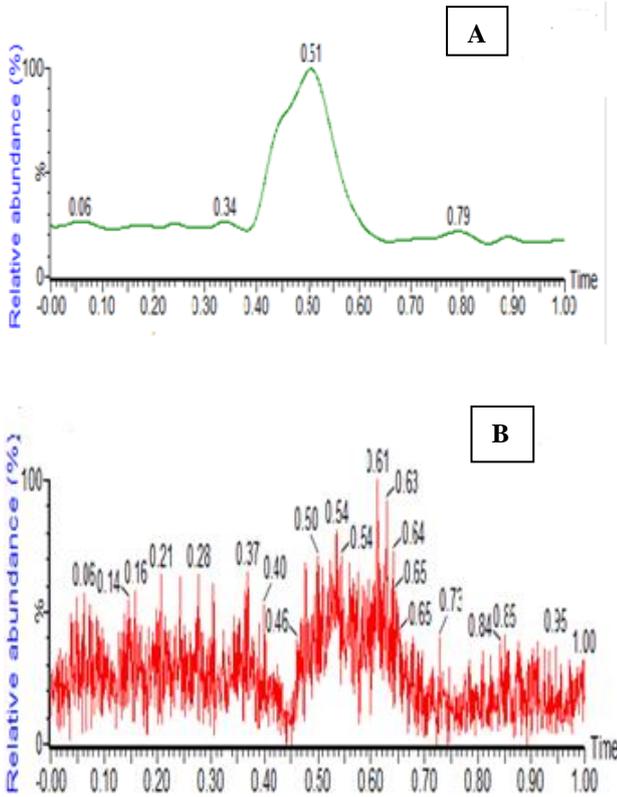


Fig. 22. Chromatogram of Malaz sample a) before treatment by magnetite and b) after treatment

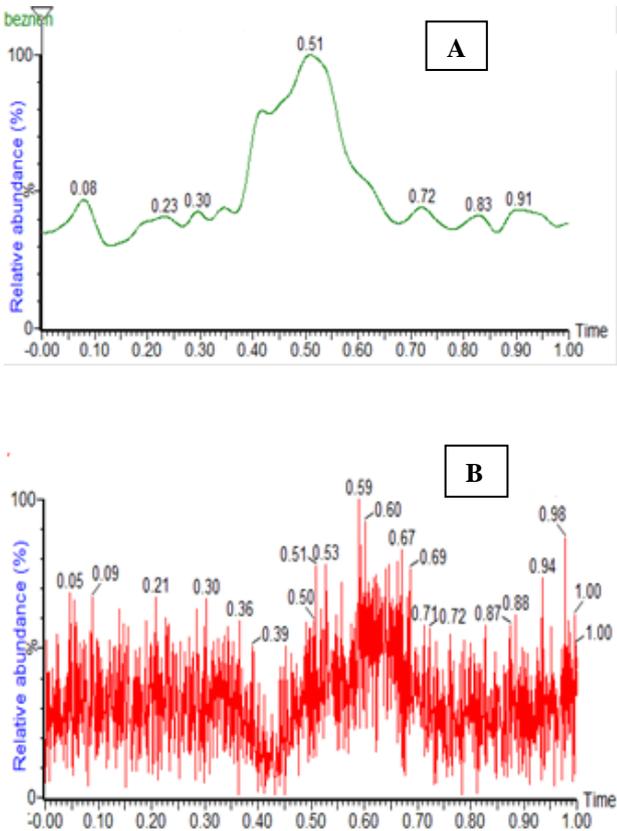


Fig. 23. Chromatogram of Manfohah2 a) before treatment by magnetite and b) after treatment

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