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

S. Al-Tamrah, M. A. Abdalla and M. S. Mushab

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 equivalents of iron(III) chloride hexahydrate in the presence of ammonium hydroxide. The precipitated magnetite nanoparticles were washed with 5% NH₃·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 benzene, toluene, ethyl benzene and xylene. The procedure consists of air sampling head-space SPME and GC. FID. Pekari et.al[7] determined benzene in blood using HS-GC equipped with a photoionization detector. Fiorentino and Coworkers[8] developed a method to evaluate low concentration of benzene in urine samples. Prado et.al[9] 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/dm³ from 5 cm³ water samples can be determined. Rosell et.al[11] 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/cm³. 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/dm³ [23].

II. EXPERIMENTAL

2.1. Chemicals and Solutions

Iron(II) chloride tetrahydrate FeCl₂·4H₂O 99% BDH, iron(III) chloride hexahydrate FeCl₃·6H₂O 99% Lobache, ammonia NH₃ 35% Avonchemie 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...
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C₁₈ 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 FeCl₂.4H₂O and 250 g of FeCl₃.6H₂O 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.
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 µm), benzene in the filterate is determined by UPLC-MS/MS as mentioned before.

5.2 Filter Method:
The benzene polluted water sample is passed through a funnel (65 mm diameter) filled with magnetite for 10 min, thin filtered using 0.45 µm 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 obtain 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 removal benzene as shown in Figs. 8-10.

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 µm 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.
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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.

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:

<table>
<thead>
<tr>
<th>Station Riyadh Location</th>
<th>Water Source</th>
<th>Counc. of benzene before treatment ng/ml</th>
<th>Counc. Of benzene treatment in the station ng/ml</th>
<th>Counc of benzene after treatment by magnetite ng/ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malaz</td>
<td>Desalinated + Well water</td>
<td>344.8</td>
<td>280</td>
<td>Zero</td>
</tr>
<tr>
<td>Salbookh1</td>
<td>== ==</td>
<td>159.6</td>
<td>145.6</td>
<td>Zero</td>
</tr>
<tr>
<td>Salbookh2</td>
<td>====</td>
<td>201.3</td>
<td>157</td>
<td>Zero</td>
</tr>
<tr>
<td>Manfohah1</td>
<td>== ==</td>
<td>178.2</td>
<td>75.6</td>
<td>Zero</td>
</tr>
<tr>
<td>Manfohah2</td>
<td>== ==</td>
<td>127.3</td>
<td>100.2</td>
<td>Zero</td>
</tr>
<tr>
<td>Buaiib1</td>
<td>== ==</td>
<td>177.8</td>
<td>80.2</td>
<td>Zero</td>
</tr>
<tr>
<td>Buaiib2</td>
<td>== ==</td>
<td>216.3</td>
<td>121.4</td>
<td>Zero</td>
</tr>
</tbody>
</table>

Fig 16: Chromatogram of Buaiib2 sample
a) Before treatment by magnetite.
b) After treatment by magnetite

Fig. 17a) Chromatogram of Salbookh1 before treatment by magnetite treatment
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Fig. 18 a) chromatogram of salbookh2 before treatment by magnetite and b) after treatment.

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

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

Fig. 21. Chromatogram of salbookh2 a) before treatment by magnetite and b) after treatment.
Fig. 22. Chromatogram of Malaz sample a) before treatment by magnetite and b) after treatment

Fig. 23. Chromatogram of Manfoohah2 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, i.e. 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, Bowaih1 80 and Bowaih2 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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REFERENCES


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