Modified nano particles method for fluorescent dye removal from aqueous samples

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Abstract:

This work reports the synthesis of iron oxide (Fe₃O₄) nanocomposites (NCs) such as, Fe₃O₄/GO using CO-sedimentation method. The synthesized NCs were characterized by X-ray diffraction (XRD). Through experiments and measurements, it was found that the compound (Fe₃O₄-GO) achieved the highest extraction rates of cyclic hydrocarbons from aqueous solutions, with a percentage of pyrene extracting 96% and fluorine 94%. Then the detection limit (LOD) and The quantitative limit (LOQ) of The hydroxy PAHs were determined using room temperature fluorescence spectroscopy technique and it was found (95% Graphene oxide, 58% Tannic acid, 53% Hummic acid). Then The synthesized nanoparticle was used to extract cyclic PAHs from an aqueous solution and The removal percentage were (96% pyrene, 94% fluorene). The results obtained showed the high value of the removal ratio that indicates of the tremendous power of the synthesized nanoparticles on removal of PAH.

1. Introduction:

Aromatic hydrocarbons can be defined as chemical compounds consisting of a huge number of rings in which more than one normal compound is mixed. Usually, these compounds are white, colorless, or pale green and tend to yellow, and are generally used in many industries, including the pharmaceutical industry and the manufacture of dyes.¹

These compounds may be a major cause of polluting the environment when they enter the atmospheric air components and may lead to forest fires or cause volcanoes. Often we notice these compounds do not dissolve in the water but are attached to the solid particles in the water.² These may enter The compounds in the components of the soil are tightly attached to the compounds present in it and cause pollution of the groundwater and through the studies that have been conducted it has been shown that these compounds may be a major cause of cancer and it has been observed that some people who have touched or inhaled aromatic hydrocarbons for a long period have cancer, for example when inhaling them through the air Cause lung cancer or through food cause stomach cancer, or using it as a skin cream causes skin cancer.³ Polycyclic aromatic hydrocarbons (PAHs) have been the subject of
interdisciplinary research in the fields of chemistry, physics, materials science, and biology. Notably, PAHs have drawn increasing attention since the discovery of graphene, which has been regarded as the “wonder” material in the 21st century. Different from semi metallic graphene, nanoscale graphenes, such as graphene nanoribbons and graphene quantum dots, exhibit finite band gaps owing to the quantum confinement, making them attractive semiconductors for next-generation electronic application(4). Many of these compounds are known to be carcinogenic. (5) It results from incomplete combustion of carbon-containing fuels such as wood, coal, diesel, grease, (6)(7)(8).

Nanomaterials can be defined as chemicals that are produced from a class of advanced materials ranging in size (1 nanometer) to (100) nanometers and due to its small size, it has characteristics that differ from the characteristics of larger materials, and among these materials is the fluorine compound, which is a nanoparticle consisting of 60 carbon atoms, and the shape of this compound is spherical, similar to a football.(9) Other materials may be added to the nanocomposites during manufacture to improve the properties and use this material in many areas.(10)

2. Chemicals

All the materials used were HPLC grade, the chemicals used were, pure and needing no purification, while (pyrene, fluoren) were purchased from Sigma- Aldrich as well as all other chemicals from other commercial sources such as Merck.

3. Methods

3.1 -Synthesis of Fe₃O₄-GO-R Core/Shell Nanoparticles

GO was prepared according to modified Hummers method. Graphite 1g was added 1g NaNO3 and 46 ml H2SO4 (98%), the rate of addition was controlled carefully. Avoiding a sudden increase of temperature reaction was performed on ice bath. The stirring was continued for 2 h at temperatures below 20 C°. Then 6 g KMnO4 was slowly added to the reaction, with stirring for 2 h. The ice bath was removed and then the reaction was covered by aluminum foil, stirring for 30 min the form a brown paste. After that, the reaction mixture was diluted with 200 ml of deionized water and temperature was kept below 100 C°. the mixture was stirred for 1 h, After that 5 ml of 30% H2O2 was added which changed its color. The resultant was filtered and washed several times with 5% HCl aqueous solution and deionized water. Finally the resultant solid was dried at 60°C for 24 h. GO was analyzed using XRD instrument.(11)

3.2 Preparation of GO-Fe₃O₄ NPs

In a typical process, 0.2 g of Fe₃O₄ GO was dispersed in 50 ml deionized water by ultrasonic treatment for 15 min, and then 25ml (0.25 g) Fe₃O₄ mixed water solutions were slowly added to the GO solution. And stirred and heated up to 60°C. After cooling to room temperature, the product (GO-Fe₃O₄) was washed with deionized water three times and dried in oven at 80°C.(12)
3.3- Preparation of Standard Solution for PAHs

The solution was prepared by dissolving (0.01) g of each of the flourene and pyrene each in 0.5mL of methanol and completing the volume with pure empty water to the specified mark using a 10 mL volumetric flask and then the mother solution was kept in a dark place at 4 °C. ° C Before each measurement the mother solution is monitored using fluorescence spectroscopy for the photolysis potential of these compounds. All mother solutions have been used for a period of less than 6 months

3.4- Extraction experiment

We take a certain weight from the nanocomposite (Fe3o4.GO), this weight is 0.01, and add (3 ml) of the pyrene solution once and the fluorine solution again, and put the prepared solution in the engine for a period of (20) minutes, and then we separate with the magnet and take the solution The intensity of absorption and emission is measured by the fluorescent device, and the intensity is measured before extraction and after extraction.

4. Results and Discussion

4.1- Characterization of Fe3O4 GO NPs :

Xrd patterns of Fe3O4-GO nanocomposites are shown in Fig -1.Its shows a wide range of peaks but shows three strong peaks for 2Θ values of 35.31 °, 62.21°, 57.20°. The peaks at 35.31° might refer to the characteristic peak of GO , That there are interaction between Fe3O4 and GO NPs. The average crystallite size was determined from the full-width half maximum (FWHM) of the strongest reflection of the (1.05) peak using the scherrer formula(13).

![Figure (1): X-ray diffraction spectrum of a (Fe3O4-GO)NPs nanostructure](image)

4.2- Fluorescence Spectroscopic Study

4.2.1- Excitation-Emission spectrum

Excitation and emission spectrum are obtained using the commercial spectrometer (Shimadzu RF-5301pc).The excitation source is a( 150-watt xenon lamp),( 220 – 900) nm.
The precision reached a uniform color (± 1.5 nm). The wavelength scan was performed at (5500 nm – min). The excitation and emission spectrum was calculated for multi-drug compounds (Pyrene, Fluorene). Each of the two compounds is dissolved in a certain amount of distilled water. The excitation spectrum was used to determine the excitation and emission wavelength. Measurements at room temperature, monitoring the performance of the device using standard materials and determining the radiation intensity at the highest spectrum, the results were as follows:

4.2.1.1 (Pyrene):

Where the concentration is (20ug / L) was prepared by diluting a specific volume of that solution. Then the absorption and emission spectrum of the compound is measured as in the following figure. Then the Ex-Em spectrum of the compound pyrene was obtained as shown in Figure (2).

![Figure 2 Ex-Em spectrum of Pyrene](image)

4.2.1.2 (Fluorine):

We notice in the following figure when the concentration is (80) as it was prepared by diluting a certain volume of fluorine with the nanocomposite as shown in Figure (3).
4.2.2- Calibration curve

Several concentrations of fluorine and pyrene were prepared in distilled water using the serial dilution method and the following calibration curves were obtained for the behavior of ((Graphene oxide, ) non-polar absorbent material to extract the compounds (2- pyrene, fluorene) from the aqueous solution as is Shown in Figure (4,5).
4.2.3- LOD and LOQ of Fluorescence Spectroscopy

The detection limit (LOD) and the quantity limit (LOQ) were measured for the detection of (fluorene and Pyrene) in an aqueous solution and the values were in the following table:

| Names of compound | LOD µg/L | LOQ µg/L | R²  
|------------------|----------|----------|------
| Pyrene           | 9.071514674 | 27.48943841 | 0.9974 |
| Fluorene         | 21.21412493  | 64.28522707  | 0.9901 |

Table (1) Determination and Quantification Limit Values for (Pyrene, Fluorene) using Fluorescence Spectrometry for PAHs in aqueous solution.

4.3-Using of Fe₃O₄- GO-R Core/Shell NPs for extraction of PAHs

The Fe₃O₄-GO-R core/shell was used to study the interference with Pyrene and fluorine PAHs and obtain the extraction process. as shown in Figure (6,7). Extraction ratios of 96% Pyrene, 94% Fluorene)
5. Conclusion:

In this research, an advanced method was used to extract cyclic hydrocarbons (PAHs) from aqueous solutions, as well as the results showing that the use of graphene oxide with magnetic ferric oxide had an important role in obtaining high extraction rates that reached 96%. In addition, it is possible to reuse the nanomaterials. For more than once, by using a suitable solvent, the PAHs are separated from the nanocomposite. The solvent may be propanol, methanol, ethanol and its other solvents.

6. References

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