Synthesis of core/shell nanoparticles and their application in hydroxy-PAHs extraction

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Abstract. The study summarizes using a new synthesized core/shell type of nanoparticles to remove hydroxy-polycyclic aromatic hydrocarbons (PAHs). The Fe2O3 coated with several groups of compounds (Triethoxysilane, Trimethoxy (2-phenylethyl) silane, (3-aminopropyl) triethoxy silane ) and tested for removal of hydroxy PAHs from aqueous solution. The synthesized Core/shell nanoparticles characterized Using several techniques such as XRD analysis. The synthesized nanoparticles show the amorphous structure. However, utilizing the technique of room temperature fluorescence spectroscopy to determine the detection limit (LOD) and the quantitative limit (LOQ) of the hydroxyl PAHs, and it found (75%Triethoxysilane, 83%Trimethoxy (2-phenylethyl) silane, 90%(3-aminopropyl) triethoxy silane). An aqueous solution used to extract hydroxy PAHs to the synthesized nanoparticle, and the removal percentage was (91% 1-Hydroxy pyrene, 88% 9-Hydroxy fluorene, 86% 2-Naphthol). The results obtained showed the high value of the removal ratio that indicates the tremendous power of the synthesized nanoparticles on PAH removal.

Key words: Polymeric ocular prosthesis, Artificial eye, Polymethyl methacrylate, Enucleation, Evisceration, Orbital exenteration.

1. Introduction
Pollution is an increase in the number of certain materials in their gaseous, liquid, or solid forms affecting the environment, and this pollution is known as environmental pollution. This pollution includes all materials that harm the environment [1][2] or the organisms that live in it, dividing the main types of pollution into Water pollution, Air pollution soil pollution [3]. Where drinking water poses a severe threat from pollution problems, as a great emphasis on chemical pollution resulting from the use of renewable water for agricultural, industrial and domestic purposes that are human-made, and most of these activities lead to water pollution these pollutants are PAHs.

Polycyclic aromatic hydrocarbons) PAHs (are compounds consisting of aromatic fused rings and do not contain heteroatoms and no substitutes. [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]. The PAHs metabolizes in the human body via specific enzymes called CYP-450 [9]. The most abundant PAH metabolites in the human body are hydroxy PAHs. There are many hydroxy PAHs that consider being carcinogens and even more than the potent PAHs.

Modern techniques for extracting the concentration of hydroxylated PAHs from body fluids include several methods used, among which are liquid-solid extraction [10][11] and liquid-liquid extraction (LLE) [12]. In this research, we used the liquid extraction method (LLE) because it is an easy, environmentally friendly, safe, and fast method. To analyze and different materials from different samples, saving cost, cost, and very high selectivity [13]. The extraction of hydroxy PAHs from an aqueous solution is harrowing due to the complicated matrix; this requires a selective procedure. As a
novel signification technique, we consider synthesizing the modified nanoparticles (NPs) is a great consideration for removing hydroxy PAHs from an aqueous solution.

2. Materials and Methods
2.1. Materials
All the materials used were HPLC grade; the chemicals used were pure and needed no purification. Simultaneously (2-Naphtol, 1-HydroxyPyrene, 9-Hydroxy fluorene) were purchased from Sigma-Aldrich and all other chemicals from other commercial sources such as Merck.

2.2. Synthesis of Fe$_2$O$_3$ - SiO$_2$ – R Core / Shell Nanoparticles
We are utilizing the co-precipitation method under optimum conditions to prepare Fe$_2$O$_3$ NPs. On a side, using the stoichiometric equivalence relationship between ferric chloride hexahydrate FeCl$_3$.6H$_2$O with ammonia NH$_3$ were (5.4g) of FeCl$_3$.6H$_2$O. This mixture dissolves at a concentration of (0.2)M in (100) mL of water free of Nanomaterials and then add ammonium hydroxide with a concentration (12%) from ammonium hydroxide was added drop by drop to above solution under constant stirring (0.5) mL/min hydroxide every minute have formed a precipitate. The acidic function is equal (pH = 8). The precipitate is filtered and then washed with distilled water for four consecutive times to remove the base. The resulting residue from the addition of ammonium hydroxide measuring the acidic function after each wash then dried for 12 hours in (Korean Oven -LDO- 060S) and then Calcinated at (300 ° C) for four hours where we get the powder reddish- brown. The core of the Fe$_2$O$_3$-SiO$_2$ casing is prepared by adding (200) mL of nano pure water to (1) g of pre-prepared Fe$_2$O$_3$ NPs nanoparticle, and heat it by(Korean Hot- Plate with Magnetic Stirrer- LMS-1003)(80) ° C under nitrogen gas flow and then adding (40) mL of sodium silicate at a concentration of (1M) with continuous stirring and setting the acidic function pH to be (6) by adding hydrochloric acid at a concentration of (2M), and the reaction continues for three hours and the precipitate washed for three times with distilled water and then with ethanol and dry it at a temperature of (60) ° C in (Korean Furnace K-MF03).

1gm of the nanopowder (Fe$_2$O$_3$-SiO$_2$) and (0.5) mL Trimethoxy(2-phenylethyl) silane were dissolved in (60) mL toluene under nitrogen flow with stirring and continuous heating at (105 ° C -110) ° C 8 hours and then washed with methanol for four times and dried at 50 ° C for 12 hours or less to obtain (Fe$_2$O$_3$ - SiO$_2$ – R ) Core / Shell Nanoparticles.

2.3. Preparation of stock solution of PAHs
We prepare the Stock solutions of (9-Hydroxyfluorene, 2-Naphthol, and 1-Hydroxypyrene) by dissolving (3) mg of standards in (0.5) mL of methanol and compel the volume with distilled water to(10) mL. All the stock solutions keep in a dark place at (4) °C. However, it should be monitored via Room-temperature to fluorescence spectroscopy for possible photo-degradation of the PAHs. Moreover, All stock solutions use for a period of less than (6 months). Working solutions of PAHs were prepared daily by serial dilution of stock solutions.

2.4. Extraction Experiment
The extraction performed by preparing a standard solution for all hydroxy PAHs (9-Hydroxyfluorene, 2-Naphthol, 1-Hydroxypyrene) at a specific concentration, taking (0.01) g of nanoparticle and adding (3) mL from each solution in a separate way, then was placed in the shaker for (20) minutes followed by(Hettich, Germany centrifugation- EBA-20) for (30) minutes. To estimate extraction percentage (% E), using a fluorescent measuring device to measure the solution’s emission intensity before and after the extraction process.

3. Results & Discussion
3.1. Characterization of Fe$_2$O$_3$ - SiO$_2$ - R NPs:
The X-ray diffraction spectrum of the superposition (Fe$_2$O$_3$-SiO$_2$-R) shows the emergence of a broad peak in the range of 2θ = (19.84-23.21°) due to the amorphous nature of the silicon dioxide (SiO$_2$) nanoparticles. While sharp peaks at (2θ = 23.83°, 35.65°, 49.21°, 54.03°, 63.93°) are due to the presence of iron oxide (III). It noted the increased intensity of broad peak with an increase in the values of the full width of the mid-height of the peaks, a clear indication of the existence of a group of R, the value of the particle size ratio of the (Fe$_2$O$_3$-SiO$_2$-R) superposition calculated from the spark equation [14] up to (6.25nm). In contrast, the value of the distance between the crystal layers of the compound from the Prague equation [15]. It appears in the range of ((1.45-4.47 Ao)), and this evidence of the formation of a core/shell superposition.

![Figure 1. X-ray diffraction spectrum of a (Fe$_2$O$_3$-SiO$_2$-R) nanostructure.](image)

3.2. Fluorescence Spectroscopic Study

3.2.1. Excitation-Emission spectrum

Excitation and emission spectrum 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). Perform the wavelength scan at (5500 nm – min). Calculate the excitation and emission spectrum for multi-drug compounds (2-Naphthol, 1-HydroxyPyrene, 9- HydroxyFluorene). each of the three compounds dissolved in a certain amount of distilled water. Use the excitation spectrum to determine the excitation and emission wavelength. Measurements at room temperature, monitoring the performance of the device using standard materials, and choosing the radiation intensity at the highest spectrum, the results were as follows:

3.2.2. (2-Naphthol):

Where diluting a specific volume of the solution prepared with a concentration of (10 μg / L), then the Ex-Em spectrum of the compound 2-Naphthol was obtained, as shown in Figure (2).
3.2.3. (1-Hydroxy Pyrene):
A concentration (100 μg / L) prepared by diluting a specific volume of the solution stored with nanoparticles. Then an Ex-Em spectrum for 1-hydroxy pyrene was obtained, as shown in Figure (3).

3.2.4. (9-Hydroxy Fluorene):
A concentration of (15 μg / L) prepared by diluting a specific stock solution volume with nanoparticles. Then an Ex-Em spectrum for 9-Hydroxy Fluorine was obtained as shown in Figure (4).
3.3. Calibration curve

Specific concentrations of each compound were prepared in distilled water using the serial dilution method. Then the titration curves were obtained for the behavior of (3-aminopropyl) triethoxy silane non-polar absorbent material to extract the compounds (9-Hydroxyfluorene, 2-Naphthol, 1-Hydroxypyrene) from the aqueous solution as is Shown in Figure (5,6,7).

**Figure 4.** Ex-Em spectrum of (9-Hydroxy Fluorene).

**Figure 5.** Calibration curve of 2-Naphthol.

**Figure 6.** Calibration curve of 1-Hydroxy Pyrene.
3.4. LOD and LOQ of Fluorescence Spectroscopy
The detection limit (LOD) and the quantity limit (LOQ) measured for the detection of (9-Hydroxyfluorene, 2-Naphthol, and 1-HydroxyPyrene) in an aqueous solution, and the values were in the following table:

| Names of compound        | LOD  | LOQ   | R²  |
|--------------------------|------|-------|-----|
| 2-Naphtol                | 0.035414 | 0.118047 | 0.9806 |
| 1-HydroxyPyrene          | 0.239598 | 0.798659 | 0.9908 |
| 9-HydroxyFluorene        | 0.07474 | 0.249133 | 0.9917 |

3.4.1. Using of $\text{Fe}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{R}$ Core/Shell NPs for extraction of PAHs
The $\text{Fe}_2\text{O}_3\text{-SiO}_2\text{-R}$ core/shell used to study the interference with hydroxy PAHs and obtain the extraction process, as shown in Figure (8). Extraction ratios of (91% 1-Hydroxy Pyrene, 88% 9-Hydroxy Fluorene, 86% 2-Naphthol)

![Figure 7. Calibration curve of 9-Hydroxy Fluorene.](image7)

![Figure 8. Emission spectra of 1-HydroxyPyrene before and after extraction.](image8)
Figure 9. Emission spectra of 9-HydroxyFlourene before and after extraction.

Figure 10. Emission spectra of 2-Naphthol before and after extraction.

4. Conclusion
In this research, an advanced method for synthesis and using core/shell nanoparticles to remove hydroxy PAHs from the aqueous solution demonstrates the advantage of using ((3-aminopropyl) triethoxy silane) as a shell of nanoparticles. The extraction ratios were around 90%, which indicates the benefit for the extraction of hydroxy PAHs. The table shows the removal ratios.

Table 2. Showing removal ratio ratios for the PAHs and composite nanoparticles.

| Names of the PAHs       | Removal ratio of the PAHs | Names of composite nanoparticles | Removal rate for composite nanoparticles |
|-------------------------|--------------------------|----------------------------------|------------------------------------------|
| 1-Hydroxy Pyrene        | 91%                      | (3-aminopropyl) triethoxy silane | 90%                                      |
| 9-Hydroxy Fluorene      | 88%                      | Trimethoxy (2-phenylethyl) silane | 83%                                      |
| 2-Naphthol              | 86%                      | Triethoxysilane                  | 75%                                      |
The prepared nanoparticles used to extract PAHs from aqueous solution, the results obtained showed the high value of the removal ratio, which indicates the tremendous strength of the nanoparticles installed on the removal of PAHs, ((3-aminopropyl) triethoxy silane) the best nanoparticle has the highest removal rate of (1-Hydroxy Pyrene).

5. References

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