

An improved method for the purification of fullerene from fullerene soot with activated carbon, celite, and silica gel stationary phases

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Abstract

Extracting pure fullerene (C_{60}) from fullerene soot was accomplished in two steps. In the first step, extraction was carried out using a Soxhlet extractor. Different solvents, such as toluene, were used in this method. In this process, light and heavy fullerenes were separated from impurities such as soot and other compounds. The applied fullerene soot was produced using an electric arc method, and the obtained purity was close to 7%. In the next step, fullerene C_{60} can be separated from other fullerenes (particularly C_{70}) by column chromatography. The stationary phase in the chromatography column contained a mixture of activated carbon, silica gel, and celite, and in order to achieve a high efficiency for separation, the column was filled with a combination of these compounds. Organic solvents such as chlorobenzene and 1,2-dichlorobenzene were used as the mobile phase. Several experiments were designed and conducted to obtain optimal conditions, and consequently, the fullerene C_{60} was purified with proper efficiency. In this method, parameters including efficiency, low cost, and simplicity are of great importance in the aim of obtaining an optimized method. As a result, a suitable method with low cost and high efficiency was used in this research.

Keywords

Fullerene, Purification, Chromatography, Celite

Correspondence/Findings

Background

Fullerenes can be produced through several developing methods which have their own advantages and disadvantages. Fullerenes can be synthesized by ablating graphite with a laser [1], burning graphite in a furnace [2], and by producing an arc across two graphite electrodes in an inert atmosphere [3]. Other methods include using negative ion/desorption chemical ionization techniques [4-13], benzene flame [14,15], combustion method [16], and soot-free synthesis of C₆₀ [17]. At the present time, the most common method for synthesizing fullerenes is the Huffman-Kratschmer carbon arc technique [18]. In this method, pure carbon in the form of graphite was heated under plasma temperature by means of graphite electrodes in an inert atmosphere (usually helium). This method leads to the production of soot, in which the fullerenes have to be separated from. Until recently, only a few methods have been developed to separate fullerenes successfully. Most known separation methods employ a column chromatography technique [19]. Column chromatography uses a tube that is open at the top with a valve at the bottom to control the flow of liquid through the tube. The column is filled with a substance that has some affinity with the material that one is trying to separate (stationary phase). After the material to be separated is placed inside the top of the column, a solvent is passed through the column. The material to be separated has different interactions with the solvent and stationary phase; consequently, it moves through the tube slower than the solvent. The components will be carried along with the mobile phase to varying degrees, and a separation will be achieved. Most attempts to separate fullerenes involved using large amounts of stationary phase and solvent and an extended period of time for separation. The most common stationary phase for column chromatography is silica gel which is not able to separate the compounds effectively, and consequently, silica gel is used with alumina. Fullerenes have low solubility in common solvents, such as hexane. Their low solubility in inexpensive common solvents leads to ineffective separations with common stationary phases such as silica gel. An area of potential interest lies in the development of effective materials to separate the compounds properly for isolating gram quantities of 25 fullerenes. Recently, it was discovered that the use of an activated carbon (AC) and silica gel mixture can provide adequate and cost-effective separation of gram quantities of C₆₀ and C₇₀ [20,21].

One of the current interests in fullerenes is directed toward large-scale production and commercial applications. Although more than a decade has passed since fullerenes have been separated, an increasing number of researchers in both academic and industrial environment are still working on this subject [2]. Quite recently, industrial-scale fullerene extraction (a mixture of C₆₀, C₇₀, and C >70) began and lowered the price to less than one-fourth compared to the former prices [22]. With respect to the purification of fullerenes [19,23], chromatographic methods have been commonly employed [24-28]. Although these methods are quite useful for laboratory-scale purification, a few drawbacks were observed in the case of larger-scale production such as limited column loadings, duration of the process with constant attention, and the amounts of both required stationary and mobile phases. Non-chromatographic methods such as selective complexation [29-33] and fractional crystallization [34-37] are not always efficient especially for large-scale purification since they require a long stirring time, sometimes at elevated temperatures, and repeating the precipitation-filtration process a few times. Therefore, there is an increasing demand for a more efficient purification method that is applicable for the large-scale production of pure fullerenes. There are also several methods for the purification of fullerene derivatives [38]. In

the present paper, we report a novel method for purifying C_{60} with a Soxhlet extractor, column chromatography, and the characterization of purified fullerene by Fourier transmittance infrared (FT-IR), ultraviolet–visible (UV–vis) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, X-ray diffraction (XRD), and high-performance liquid chromatography (HPLC). As a result, these methods lead us to methods with low cost and high-efficiency purification.

Results and discussion

A process has been developed to separate the compounds effectively and recover pure amounts of C_{60} from the fullerene soot containing higher and lower molecular weight fullerenes. This process first extracts the fullerenes from carbon soot and then separates the C_{60} molecules sequentially with high-performance or low-adsorption chromatography packed column containing a silica gel, AC, or celite.

In this process, the first step of fullerene extraction is preferably accomplished by the Soxhlet method. Several solvents were examined on small scales using the Soxhlet method. The choice of solvent is important and is based on the solubility of C_{60} fullerene. Experimental solubilization of C_{60} has been carried out via different solvents. The used solvents are classified in the following groups: polars (*N*-methyl-2-pyrrolidone (NMP)), benzenes (toluene, chlorobenzene (CB), orthodichlorobenzene (ODCB), 1,2,4-trichlorobenzene (TCB)), naphthalenes (MN, dimethylnaphthalenes (DMN), 1-phenylnaphthalene (PN), 1-chloronaphthalene (CN)), and miscellaneous (carbon disulfide (CDS)). The measured solubilities confirm that C_{60} is poorly soluble in polar and H-bonding solvents and has low solubility in alkanes (the higher the number of carbons, the better the solubility), even though declining that solubilized C_{60} is more soluble in halogenated derivatives than in analog alkanes. In general, aromatics are proper solvents; increasing the number of rings increases solubility. As shown in Table 1, the most applicable solvent is CN (51 g/L, at room temperature) [39]. In addition to the high solubility, the solvent cost is also of great importance. As shown in Table 2, in the constant conditions of extraction, the highest efficiency is observed in run numbers of 4 to 9. The best solvent for extracting fullerenes from soot at a reasonable price that also showed high performance is ODCB. As illustrated in Figure 1, some of the solvents yield more than 100%, which means that the actual amount of fullerenes is 7% higher than the theoretical value. In the second step, fullerenes were extracted using ODCB solvent, and about 20 g of fullerenes were obtained by the Soxhlet extraction process. The solvent was then recovered using a rotary evaporator. The fullerenes were used for the purification in the second stage. Qualitative and quantitative tests were performed on fullerenes, such as IR, HPLC, and UV–vis spectroscopy. Analysis of the results showed that a mixture of fullerenes was extracted by the Soxhlet method.

Table 1 Solubility of C_{60} in various solvents

| Solvents | Solubility of C_{60} (mg/mL) |
|--------------------------------|--------------------------------|
| Toluene | 2.8 |
| <i>N</i> -methyl-2-pyrrolidone | 0.89 |
| Chlorobenzene | 7.0 |
| 1,2-Dichlorobenzene | 27 |
| 1,2,4-Trichlorobenzene | 8.5 |
| 1-Methylnaphthalene | 33 |
| Dimethylnaphthalenes | 36 |
| 1-Phenylnaphthalene | 50 |
| 1-Chloronaphthalene | 51 |
| Carbon disulfide | 7.9 |

Table 2 Extraction of fullerenes from soot with the Soxhlet method

| Number of run | Solvent | Temperature (°C) | Fullerenes extracted (g) | Fullerenes extracted (%) | Efficiency (%) |
|---------------|------------------------|------------------|--------------------------|--------------------------|----------------|
| 1 | Carbon disulfide | 57 | 0.34 | 6.8 | 97.14 |
| 2 | NMP | 215 | 0.08 | 1.6 | 22.86 |
| 3 | Chlorobenzene | 142 | 0.352 | 7.04 | 100.0 |
| 4 | 1,2-Dichlorobenzene | 190 | 0.357 | 7.14 | 100.0 |
| 5 | 1,2,4-Trichlorobenzene | 225 | 0.357 | 7.14 | 102.0 |
| 6 | 1-Methylnaphthalene | 255 | 0.357 | 7.14 | 100.0 |
| 7 | Dimethylnaphthalenes | 280 | 0.357 | 7.14 | 100.0 |
| 8 | 1-Phenylnaphthalene | 335 | 0.357 | 7.14 | 100.0 |
| 9 | 1-Chloronaphthalene | 275 | 0.357 | 7.14 | 100.0 |
| 10 | Toluene | 120 | 0.16 | 3.2 | 45.71 |

Figure 1 Efficiency of fullerene extraction from soot by the Soxhlet method.

In the second step, C₆₀ was purified from the mixture of fullerenes by using column chromatography. As shown in Table 3, the purification efficiency can be optimized by changing parameters such as the combination of stationary phase and mobile phase. The various chromatographic methods used for fullerene separation have been investigated in several investigations, including stationary and mobile phases, conditions of detection, separation yields in some case, and a general discussion for each method. Stationary phases that have been reviewed include alumina [40], silica [41], molecular sieve, and AC [42-44]. In comparison with single materials, combinations of materials are more applicable and have been investigated more. In order to examine changes in the composition of the stationary phase material, 33 tests were designed. In addition to changing the mobile phase, four solvents were considered separately as a mobile phase. Large numbers of experiments have to be performed in order to evaluate all factors. The effects of all the parameters can be incorporated into designing the experiments. In runs 1 to 11, the effect of increasing AC and celite in the silica gel are shown. By adding these compounds to the silica gel, the purification efficiency increases significantly. Similarly, runs 12 to 22 show the effect of increasing the silica gel and celite on the AC. In runs 23 to 33, adding silica gel and AC to celite at first shows an increase in efficiency and purification, and then a reduction was observed. This trend of increase and decrease is shown in Figure 2. The increased efficiency in the first and second series of runs indicates that the exchange molecules of silica gel with celite and AC, and AC with celite and silica gel lead to increases in the separation process in columns. The reduced efficiency of separation in the third series of runs indicates that unlike previous series, the exchange of celite with silica gel and AC reduces the performance of the separation. The results in Table 3 and the slope of the curve in Figure 2 show that the purification efficiency of C₆₀ is increased by the addition of celite to the stationary phase. A comparison of efficiency in runs 1, 12, and 23 indicates that when celite is used individually, high separation performance will be observed.

Table 3 Separation of C₆₀ (%) with different mobile phases and stationary phases

| Number of run | Combination of stationary phases (%) | | | Efficient separation of C ₆₀ (%) with different mobile phases | | | |
|---------------|--------------------------------------|-----|--------|--|-------|-------|---------|
| | Silica gel | AC | Celite | ODCB | CB | CDS | Toluene |
| 1 | 100 | 0 | 0 | 33.21 | 20.46 | 18.12 | 25.25 |
| 2 | 90 | 5 | 5 | 46.15 | 43.58 | 37.33 | 40.25 |
| 3 | 80 | 10 | 10 | 52.31 | 50.05 | 42.54 | 55.24 |
| 4 | 70 | 15 | 15 | 65.47 | 62.79 | 58.21 | 60.05 |
| 5 | 60 | 20 | 20 | 76.32 | 73.86 | 68.95 | 70.33 |
| 6 | 50 | 25 | 25 | 87.58 | 84.37 | 79.01 | 82.10 |
| 7 | 40 | 30 | 30 | 89.12 | 87.44 | 80.44 | 83.72 |
| 8 | 30 | 35 | 35 | 90.32 | 87.92 | 79.43 | 83.90 |
| 9 | 20 | 40 | 40 | 92.43 | 88.67 | 80.98 | 85.42 |
| 10 | 10 | 45 | 45 | 93.05 | 90.04 | 82.65 | 86.32 |
| 11 | 0 | 50 | 50 | 94.06 | 92.83 | 86.11 | 90.11 |
| 12 | 0 | 100 | 0 | 82.36 | 80.33 | 72.37 | 75.44 |
| 13 | 5 | 90 | 5 | 84.32 | 82.68 | 72.49 | 75.10 |
| 14 | 10 | 80 | 10 | 85.07 | 83.25 | 75.30 | 81.86 |
| 15 | 15 | 70 | 15 | 86.12 | 84.76 | 77.61 | 82.06 |
| 16 | 20 | 60 | 20 | 86.84 | 83.53 | 79.05 | 82.76 |
| 17 | 25 | 50 | 25 | 87.32 | 84.26 | 79.74 | 83.43 |
| 18 | 30 | 40 | 30 | 87.99 | 85.03 | 80.43 | 83.87 |
| 19 | 35 | 30 | 35 | 88.09 | 85.36 | 81.36 | 84.02 |
| 20 | 40 | 20 | 40 | 93.12 | 87.27 | 83.02 | 85.71 |
| 21 | 45 | 10 | 45 | 94.32 | 90.62 | 83.95 | 87.54 |
| 22 | 50 | 0 | 50 | 97.12 | 92.65 | 84.52 | 88.72 |
| 23 | 0 | 0 | 100 | 90.14 | 88.51 | 79.04 | 81.04 |
| 24 | 5 | 5 | 90 | 94.34 | 90.39 | 79.47 | 82.43 |
| 25 | 10 | 10 | 80 | 96.02 | 94.72 | 83.64 | 86.54 |
| 26 | 15 | 15 | 70 | 97.32 | 95.21 | 86.75 | 90.06 |
| 27 | 20 | 20 | 60 | 98.06 | 95.41 | 89.05 | 92.83 |
| 28 | 25 | 25 | 50 | 99.32 | 96.33 | 90.27 | 93.74 |
| 29 | 30 | 30 | 40 | 99.34 | 96.73 | 90.82 | 94.83 |
| 30 | 35 | 35 | 30 | 98.94 | 96.04 | 90.54 | 93.75 |
| 31 | 40 | 40 | 20 | 94.15 | 93.22 | 83.06 | 88.93 |
| 32 | 45 | 45 | 10 | 87.26 | 90.42 | 79.43 | 82.54 |
| 33 | 50 | 50 | 0 | 85.38 | 85.73 | 77.34 | 81.04 |

Figure 2 Efficiency of C₆₀ purification by column chromatography.

Comparing the results shown in Table 3, it can clearly be seen that celite is essential for the separation of fullerene C₆₀. For the stationary phase containing 100% of silica gel, AC, and celite, the efficiency of C₆₀ purification is 33.21, 82.36, and 90.14, respectively.

The maximum peak of four curves is related to run number 29 in which the mobile phase consisted of 30%, 30%, and 40% of silica gel, AC and celite, respectively. Four solvents, CB,

ODCB, CDS, and toluene, were used as the mobile phase in this method. As shown in Figure 2, the purification efficiency is as follows: ODCB > CB > toluene > CDS. The main impurity in fullerene C₆₀ is C₇₀. The highest obtained purity in these experiments was 99.34%. High purity can be confirmed by FT-IR, NMR, UV-vis spectroscopy, and XRD patterns.

XRD is another technique for the determination of fullerene purity. The XRD pattern of pure fullerene C₆₀ (shown in Figure 3) is clear and appears at $2\theta = 10.8, 17.6, \text{ and } 20.7$. Figure 3 shows the XRD patterns of a mixture of fullerenes extracted by the Soxhlet method. Solid C₆₀ forms a face-centered-cubic structure at room temperature [45,46]. The presence of impurities in the extracted product by the Soxhlet system is observable by broadening obtained peaks and observing other peaks that are related to C₆₀.

Figure 3 Comparison between XRD patterns of soot, mixture of fullerenes, and extracted fullerene (C₆₀).

The ¹³C NMR spectrum of purified C₆₀ shows one signal at 143.2. The amount of fullerene in the NMR samples is low, and the spin-lattice relaxation times are quite long (≥ 20 s for C₆₀) [47]. The FT-IR spectra of fullerene soot and purified C₆₀ are shown in Figure 4. Four absorption areas at 527, 576.5, 1,182.5, 1,429 cm⁻¹ are related to C-C bond stretching and bending frequencies [48].

Figure 4 FT-IR spectra of fullerene soot and purified C₆₀. (a) Fullerenes extracted by Soxhlet (toluene) and (b) fullerenes purified by column chromatography are related to samples no. 29.

The electronic absorption spectra (UV-vis) of C₆₀ and fullerene soot are characterized by stronger absorptions between 190 and 410 nm and the forbidden transitions in the visible region of the spectrum. For C₆₀, the number and the type of transitions were confirmed by means of theoretical calculation results. The assignment of the transitions has been carried out using the results of theoretical calculations [49,50]. The absorptions between 190 and 410 nm are related to the allowed ¹T_{1u} - ¹A_g transitions, while absorptions between 410 and 620 nm are related to orbitally forbidden singlet-singlet transitions. These absorptions that appeared in the visible part are responsible for the purple color of C₆₀ and the red color of C₇₀ [51].

Raw and pure samples of fullerene were also analyzed by HPLC (Figure 5). Chromatography was performed using Agilent 1200 HP HPLC (Agilent Technologies, Santa Clara, CA, USA) with Develosil ODS-5 column (Nomura Chemical Co., Ltd., Seto, Japan) at room temperature (*ca.* 15°C to 20°C) with mobile phase toluene/acetonitrile = 50/50, flow rate of 2 mL/min, and UV detector at 325 nm. Clearly, the peaks corresponding to fullerenes separated by means of an appropriate method of analysis.

Figure 5 HPLC chromatograms. (a) Fullerene soot, (b) fullerenes extracted by Soxhlet (toluene), and (c) fullerene purified by column chromatography are related to samples no. 2 (toluene); those in (d, f, g) are related to samples no. 29.

Methods

Materials and equipment

Fullerene soot was purchased from Sigma-Aldrich Chemise GmbH Company (purity 7%; Steinheim, Germany); celite R-630, silica gel 40, and powdered AC Norite A (particle size 1 to 150 μm) were purchased from the Merck company (Dramstadt, Germany). Toluene, ODCB, other chemical materials, and solvents were purchased from both Merck and Aldrich. These materials were used without further purification. IR spectra were recorded using a Shimadzu FT-IR 8400 (Kyoto, Japan); UV-vis spectrophotometers Scinco S-2100 (SCINCO, Twin Lakes, WI, USA), NMR Jeol 90 MHz (JEOL Ltd., Tokyo, Japan), HPLC Agilent 1200 HP, and rotary evaporator Heidolph Laborota 4000 (Schwabach, Germany) were used.

Soxhlet extraction procedure

Fullerene-containing carbon soot (5 g) was directly added to a cellulose extraction thimble. The extractions were performed using 50 mL of toluene for more than 1 h. Then, solids were separated from the solution by a rotary evaporator. The obtained solid was dried in an oven at 110°C (0.16 g). The extraction of fullerenes from soot was carried out by different solvents such as NMP, CB, ODCB, TCB, 1-ethylnaphthalene, DMN, PN, CN, or CDS. The fullerenes obtained were analyzed with FT-IR, NMR, UV-vis, XRD, and HPLC.

Preparing the column

The following steps were performed to prepare the column. In this step, a clean column (1.5 \times 50 cm) with a glass wool at the bottom was used. It is notable that the applied glass container and column have to be washed with soapy water, rinsed with distilled water and a small amount of acetone, and ultimately dried in an oven. A small amount (0.5 cm) of dry sand was added to the column on top of the glass wool. The column was filled with the stationary phase including different percentages of silica gel, AC, and celite. Hexan was added to the beaker containing stationary phase as a solvent. The contents of the beaker were stirred to remove air bubbles, and solid particles were allowed to get wet. A funnel was placed on top of the column, and the stationary phase was poured quickly into the column. If necessary, the columns' stopcock will be opened, and some of the hexane was drained away to the stationary phase. This process was repeated until most of the stationary phase transferred to the column. The column was then gently tapped in order to remove the bubbles and compress the stationary phase; 1 cm of sand was smoothly added to the top of the stationary phase. The stopcock was opened, and the excess hexane was drained until its level reaches above the sand level.

Running the column

The extracted fullerene (50 mg) was poured into an Erlenmeyer flask, and then 20 mL of the solvent was added to the flask for purification purpose. The mixture was stirred properly and transferred to the top of the sand layer in the column. The opened stopcock in the column allows the fullerene to pass through the sand and the stationary phase. Subsequent to this step, 5 mL of the solvent was added to the solution. The components were collected as the solvent drips from the bottom of the column, and a rotary was used to evaporate the solvent

and isolate the fullerenes. The obtained solid fullerenes were analyzed. This process was repeated for different stationary phases, and the efficiency of each test was also evaluated.

Conclusions

Celite is a naturally occurring, soft, chalk-like sedimentary rock that is easily crumbled into a fine white to off-white powder. This powder has an abrasive characteristic, similar to pumice powder, and is very light due to its high porosity. The typical chemical composition of diatomaceous earth is 86% silica, 5% sodium, 3% magnesium, and 2% iron. It is used as a filtration aid, mild abrasive, mechanical insecticide, absorbent for liquids, cat litter, activator in blood clotting studies, and heterogeneous catalyst [52-55].

Celite is a cheap material, which together with activated carbon and silica gel increases the efficiency of purification. This material with good pores traps the heavier fullerenes of C_{60} and allows fullerene C_{60} to pass through the column. The use of this material with silica gel and activated carbon can increase the efficiency significantly. Here are a series of chemical and physical interactions of fullerene with celite and also celite with AC and silica gel. This method is a simple and yet efficient method to use. In addition to the laboratory base, this method can be used in the bench base. The applied solvents are easily recyclable by rotary evaporators for use in the next stages. The mobile phase can be recovered using a suitable solvent. In this method, parameters including efficiency, low cost, and simplicity are of great importance in the aim of obtaining an optimized method. As a result, a suitable method with low cost and high efficiency was used in this research.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

MN participated in the experimental section. MN and AR participated in the design of the study and performed the statistical analysis. HK, as the supervisor, participated in this work. HK, MN, and AR carried out the manuscript preparation. All authors read and approved the final manuscript.

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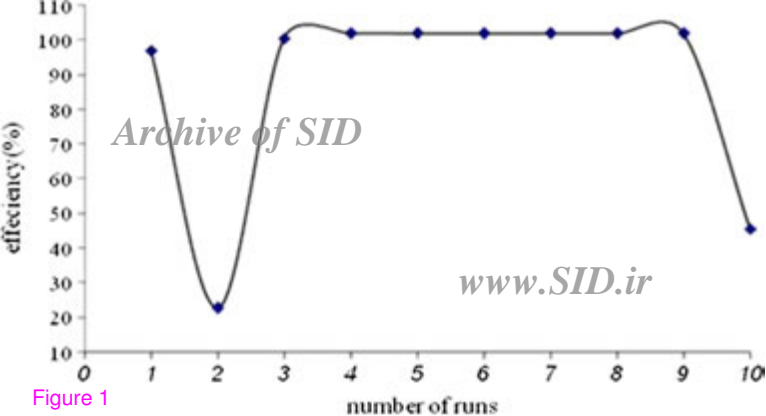
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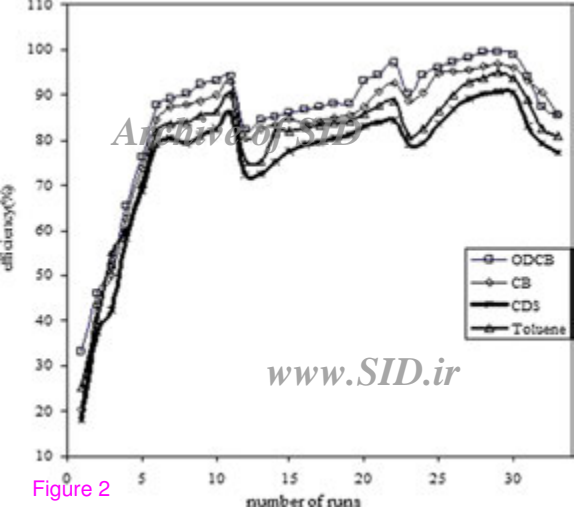


Figure 2

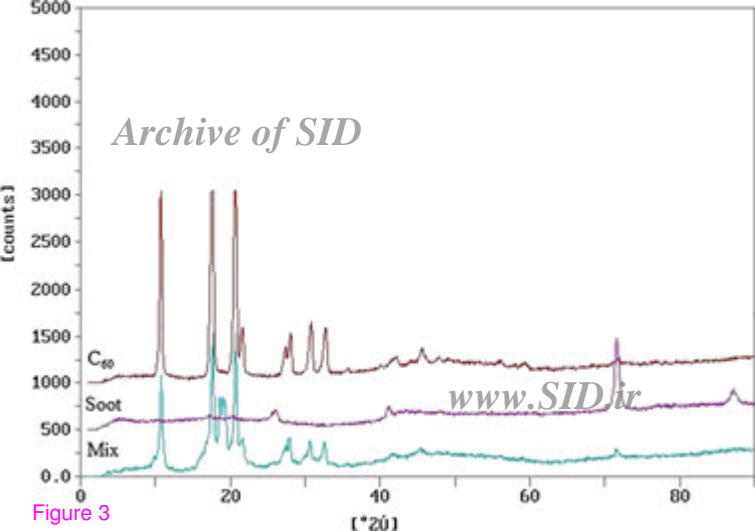


Figure 3

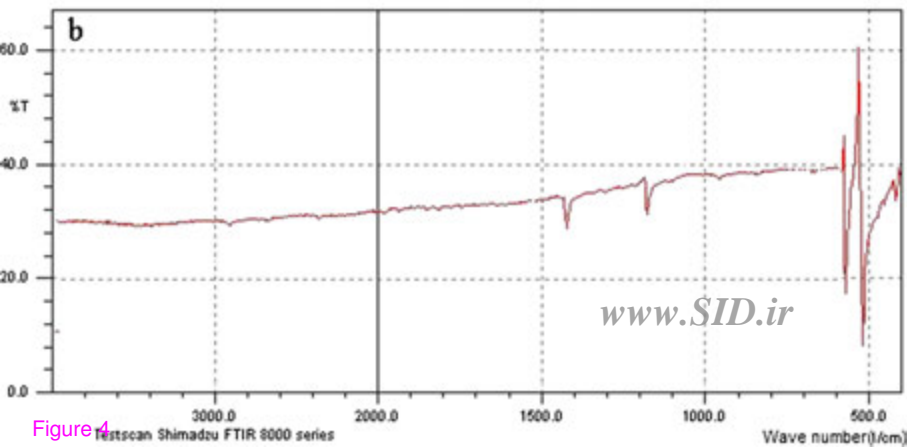
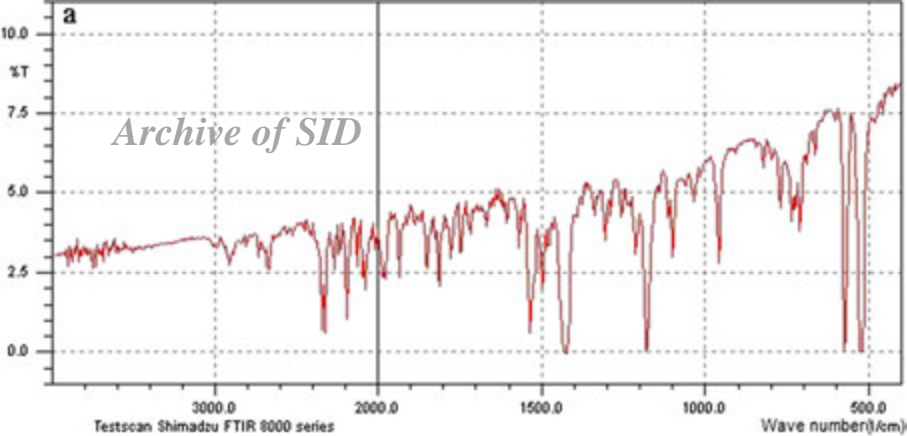


Figure 4

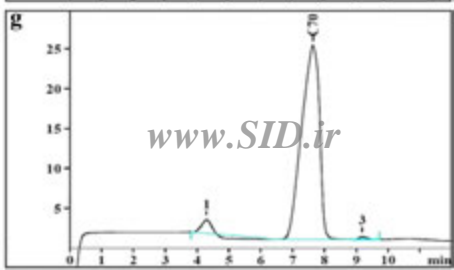
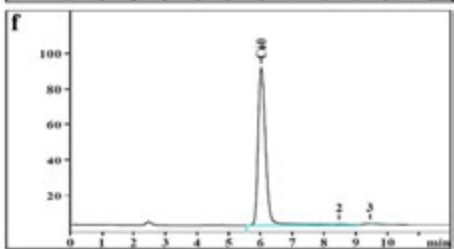
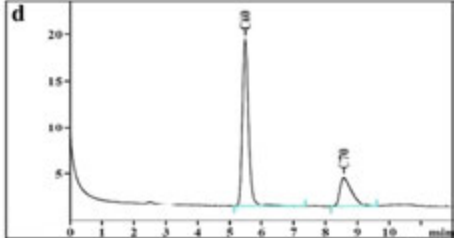
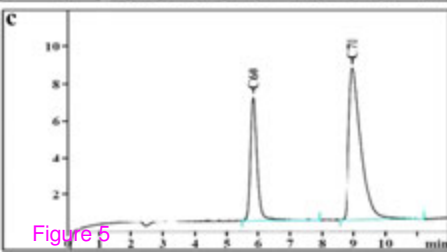
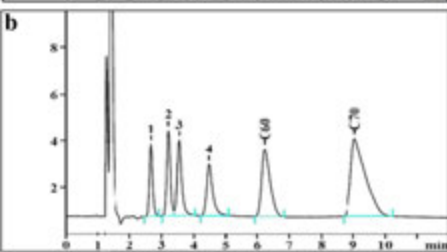
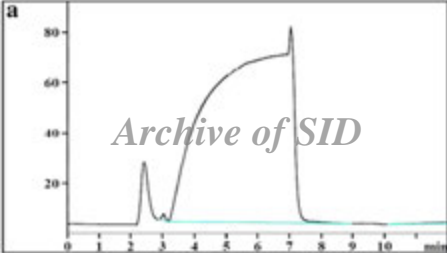


Figure 5