Journal of Chromatography B, 1029–1030 (2016) 81–87

Contents lists available at ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

Hyperbranched polyglycerol/graphene oxide nanocomposite reinforced hollow fiber solid/liquid phase microextraction for measurement of ibuprofen and naproxen in hair and waste water samples

Zohreh Rezaeifar[a], Zarrin Es'haghi[b,*], Gholam Hossein Rounaghi[a], Mahmoud Chamsaz[a]

[a] Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran
[b] Department of Chemistry, Payame Noor University, 19395-4697, Tehran, Iran

ARTICLE INFO

Article history:
Received 16 April 2016
Received in revised form 4 July 2016
Accepted 6 July 2016
Available online 6 July 2016

Keywords:
Ibuprofen
Naproxen
Hyperbranched polyglycerol
Graphene oxid

ABSTRACT

A new design of hyperbranched polyglycerol/graphene oxide nanocomposite reinforced hollow fiber solid/liquid phase microextraction (HBP/GO –HF-SLPME) coupled with high performance liquid chromatography used for extraction and determination of ibuprofen and naproxen in hair and waste water samples. The graphene oxide first synthesized from graphite powders by using modified Hummers approach. The surface of graphene oxide was modified using hyperbranched polyglycerol, through direct polycondensation with thionyl chloride. The ready nanocomposite later wetted by a few microliter of an organic solvent (1-octanol), and then applied to extract the target analytes in direct immersion sampling mode.After the extraction process, the analytes were desorbed with methanol, and then detected via high performance liquid chromatography (HPLC). The experimental setup is very simple and highly affordable. The main factors influencing extraction such as; feed pH, extraction time, aqueous feed volume, agitation speed, the amount of functionalized graphene oxide and the desorption conditions have been examined in detail. Under the optimized experimental conditions, linearity was observed in the range of 5–30,000 ng mL^{-1} for ibuprofen and 2–10,000 ng mL^{-1} for naproxen with correlation coefficients of 0.9968 and 0.9925, respectively. The limits of detection were 2.95 ng mL^{-1} for ibuprofen and 1.51 ng mL^{-1} for naproxen. The relative standard deviations (RSDs) were found to be less than 5% (n = 5).

1. Introduction

Ibuprofen (IBU) and naproxen (NAP) are non-steroidal anti-inflammatory drugs (NSAIDs) that have been widely used treat pain and inflammation in rheumatic disease and other musculoskeletal disorders [1]. Because of their effectiveness in suppressing or preventing inflammation, NSAIDs are becoming the most commonly used medicines around the world [2]. Although NSAIDs are perceived as safe drugs within a short time usage, certainly long-term adverse effects can be associated such as gastrointestinal bleeding, acute kidney injury and cardiovascular risks [3]. Besides, NSAIDs serve as endocrine disruptors in environmental aqueous samples, leading to changes and damage of aquatic animals [4]. There is no doubt that the risks of NSAIDs can be serious, the degree of risk from NSAIDs varies greatly from one person to another. According to the report of American Gastroenterological Association (AGA), each year the side effects of NSAIDs endanger the lives of thousands of people and kill many of them in the USA [5]. Evenly, this goes the same for the other countries, including Iran [6]. Therefore, monitoring of NSAIDs in environmental and biological samples is of great importance to protect humans from the disturbance of NSAIDs. On the other hand, this class of compounds is of important due to their physicochemical properties: high water solubility, low pKa values, low adsorption coefficients [7].

Several methods for determination of concentrations of NSAID are described in the literature, such as high performance liquid chromatography [8,9] gas chromatography [10], capillary electrophoresis [11], spectrophotometry [12], and voltammetry [13]. Pharmaceutical residues are usually present in environmental and biological samples in trace levels; therefore, a preconcentration step is generally required for determination of them as the pollutants. A variety of extraction methods such as solid phase extraction (SPE) [14,15], solid phase microextraction (SPME) [16], stir bar sorptive extraction (SBSE) [17], single-drop microextraction

* Corresponding author.
E-mail address: eshaghi@pnu.ac.ir (Z. Es'haghi).

http://dx.doi.org/10.1016/j.jchromb.2016.07.010
1570-0232/

(SDME) [18], liquid–liquid–liquid microextraction (LLLME) [19], and hollow-fiber liquid-phase microextraction (HF-LPME) [20], have been applied to increase the concentration of NSAIDs existing at very low levels in environmental and biological samples. Among the various sample pre-treatment techniques, in-tube solid phase microextraction (in-tube SPME) has the advantages of low cost, simple operation, fast speed, high selectivity, low sample/reagent consumption as well as easy-to-automate and has been widely used for analysis of trace organic and inorganic analytes [21,22]. A large number of new SPME coatings have been increasingly developed, such as single-walled carbon nanotubes [23], chitosan [24], alumina [25] and silica modified coatings [21].

Recently, hollow fiber supported in-tube SPME (called in tube HF-SPME) developed due to its high porosity and superior stability [26]. Hollow fiber solid/liquid phase microextraction (HF-SLPME), which introduced for the first time by our research group, has been shown is one of the most effective methods for the removal of pollutants from contaminated water [27]. In this method, a conventional two phases hollow fiber liquid phase microextraction (HF-LPME) was developed, where the organic acceptor phase is reinforced with a nanocomposite. Therefore, we decided to promote the HF-LPME technique by inserting a dispersed mixture of *n*-octanol/functionalized graphene oxide into the pores of polypropylene hollow fibers.

Graphene, are markable new member of carbon materials, has a great attention in the field of material science due to its strange electrical, thermal, mechanical, and structural properties [28–30]. It has been reported hat graphene possesses a high theoretical specific surface area (2630m2/g) [31], suggesting a high sorption capacity. In addition, due to its large delocalized π-electron system, graphene can form a strong π–π stacking interaction with the benzene ring [32]. Graphene oxide (GO), the oxidized derivative of graphene, is accessible through the oxidation of natural graphite powder [33]. GO contains a large number of oxygen atoms on its nano-sheet surface in the form of epoxy, hydroxyl, and carboxyl groups [34]. In this study, GO was modified by hyperbranched polymer in order to obtain a high adsorption capacity. Hyperbranched polymers have been broadly studied because of their capacity applications [35]. Their degree of branching, which explains the ratio of branches, terminals, and linear units in the polymer, is the most well-liked characteristic of them [36–38]. These unique polymers used in polymer electrolyte because of their lower degree of chain interactions that come with increased chain length, lower glass-transition temperature, and the greater number of cavities compared to linear polymers.

Hyperbranched polyglycerol (HBP) has been confirmed to be a type of extremely biocompatible polymer, which can be easily synthesized in a one-pot reaction in a high yield [39,40]. HBP macromolecule (Fig. 1a) includes of many hydroxyl groups and polyether parts, which equips a spherical structure and excellently branched structures. The embracing hydroxyl groups can create chemically bound with the various functional groups.

A functionalized polymer in the present context is a synthetic macromolecule to which a chemically functional group is bounded. In this work, graphene oxide has been functionalized with HBP (Fig. 1b) in the presence of thionyl chloride as a solvent.

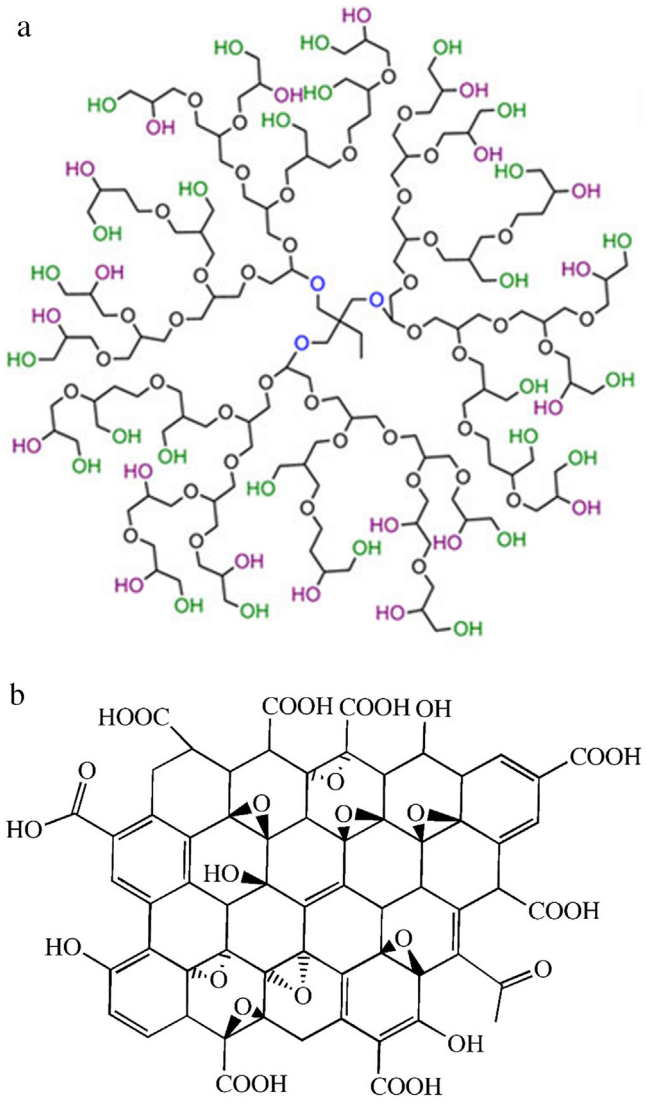

Fig. 1. a) Structure of Hyperbranched polyglycerol (HBP) [39], b) Structure of graphene oxide [34].

2. Experimental

2.1. Materials and methods

2.1.1. Standards and reagents

Ibuprofen and naproxen were purchased from the rouz darou Pharmaceutical Company (Tehran, Iran) and were of pharmaceutical quality. All of the solvents, were of HPLC grade and all chemical reagents were of analytical grade and they supplied by Merck chemical company (Darmstadt, Germany). Graphite powder (<150 μm, 99.99%) was purchased from Sigma-Aldrich. Q3/2 Accurel polypropylene microporous hollow-fiber membrane (200 μm wall thickness, 600 μm inner diameter, 0.2 μm pore size, 75% porosity) was obtained from Membrana (Wuppertal, Germany). Stock standard solutions of ibuprofen and naproxen (500 mg L^{-1}) were prepared by dissolving 5 mg of these analytes in 5 mL of methanol. Standard sample solutions were prepared daily at different concentrations by diluting the stock solutions with de-ionized water, which was purified in a Milli-Q filtering system (Millipore). The stock standard and sample solutions were stored at 4 °C. The pH of the solutions was adjusted by adding NaOH (1 M) and HCl (1 M).

2.1.2. Apparatus

The HPLC system was a Knauer Smart Line (Berlin, Germany) with a Knauer (S-2500) UV detector. The column was a Perfectsil Target RP-18 column (4.6 mm diameter, 250 mm length, ODS3, 5 μm) from Knauer. An RP-18 guard column (4 × 4 mm i.d., 5 μm) which was fitted upstream in the analytical column. The mobile phase consisted of 0.1% (v/v) o-phosphoric acid:acetonitrile (45:55)

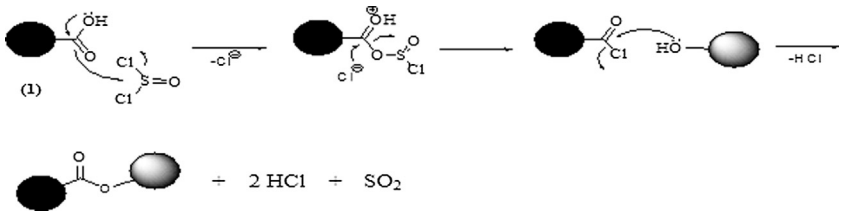

Fig. 2. Proposed mechanism of graphene oxide functionalization.

and was run in isocratic mode at a flow rate of 1.0 mL min^{-1}.The mobile phase was filtered by a Milli-Q filtering system before use and delivered by a Knauer (S-1000) HPLC pump. The signals were monitored at 232 nm. An Ultrasonic Processor, model UP 400S, made in Germany was used for functionalizing the surface of graphene oxide with HBP. The FT-IR spectra were recorded using Buck ScientificM-500 Fast-Scan IR Spectrometer (East Norwalk, CT, USA). A UV–vis Spectrophotometer, model T80 (PG Instruments,UK), was used for recording the absorbance spectra. A Metrohm 780 pH-meter equipped with a combined glass electrode was used for determination of the pH values during the experiment (Herisau, Switzerland). Transmission electron microscopic (TEM) images were obtained by a HITACHIS-600 (Japan) transmission electron microscope operating at 200 kV.

2.2. Synthesis and functionalization of nano-graphene oxide with HBP

GO was prepared from graphite powders using a modified Hummer's method [41]. Although sometimes the pure graphene oxide can be used in extraction and removal of organic and inorganic pollutants without the need for further functionalization, but it is needed to modify the surface of graphene oxide by attaching some functional groups in order to obtain a specific surface in separation purposes. HBP synthesized by Masoodi et al. in Payame Noor University of Mashhad (2nd International Symposium Frontiers in Polymer Science 29–31 May ***2011***, ***Lyon, France***, *The synthesis of Azo (PAMAM –DIPA Core(G1))2 Dendrimer*). For functionalizing the surface of graphene oxide, 1.0 gr HBP, 1.0 gr graphene oxide and 5 mL thionyl chloride were added in a round-bottom flask. The solution was stirred at reflux condition for 8.0 h. After completion the reaction, 50.0 mL of ethanol was added to the solution and it was allowed to cool at room temperature. The precipitated products were separated by filtration and washed with ethanol. The proposed mechanism for the reaction is shown in Fig. 2.

2.3. Hair samples treatment

The treatment o the hair samples, differs from the other materials used for toxicological analysis because of its distinctive ability to work as a long-term storage of external substances with respect to the temporal appearance in blood. In the field of drug analysis, great interest has been taken in hair analysis due its substantially longer detection window (months to years) [42]. A bulk sample of the hair, necessary to develop the method and validate it, was obtained from a person in a barber shop in Mashhad, Iran, who didn't use any of these drugs for the past one year. The hair sample with potential drug content was collected from volunteer's patient who had treated with these drugs. Both blank and sample hairs were cut with a round-point scissor about 5 mm in diameter from the vertex posterior region of the scalp. Some samples of 2–4 cm long were selected for analysis. The hair samples were washed with 20 mL dichloromethane, 15 mL acetone, and twice with methanol (15.0 and 10.0 mL), respectively to remove the hair surface contaminations. After drying at room temperature,the hair samples were cut into approximately 1.0 mm pieces and digested by the following steps: 2.0 mL methanol as an extracting solvent was added to the hair sample, in a 10.0 mL screw-cap tube. The samples were incubated at 50 °C for 5 h . The extracts were filtered and diluted with appropriate de-ionized water [43].

2.4. Extraction procedure

20 mg of functionalized GO was dispersed in 1 mL 1-octanol. The extraction procedure for target analytes was as follows: first, the hollow fiber was cut into segments with a length of 2 Cm. The fiber segment cleaned with acetone to remove impurities and directly dried in air. Then, the fiber submerged in the 1-octanol for a few seconds to fill the membrane pores of the hollow fiber wall. This solvent is compatible with polypropylene and easily occupies the pores. Then, 2.0 μL of the acceptor solution (functionalized GO in 1-octanol) injected into the lumen of the hollow fiber with a micro syringe. After that, the end of the hollow fiber sealed with heated tweezers and then washed with water to remove the excessive organic solvent. This fiber placed into the sample solution present in a proper vial (25 mL volume). The vial covered and stirred at 400 rpm for 20 min. In the time, the analytes from the sample solution diffuses through the porous polypropylene membrane into the acceptor solution. After the extraction process, the hollow fiber was removed and plunged into 1 mL of methanol in a closed vial, and the analyte desorbed from the fiber with sonication. The extracted samples were measured by HPLC. The volume of methanol as the extractor solvent for HPLC analysis was 40 μ L (the HPLC loop volume was 20 μL).

3. Results and discussion

3.1. Characterization of HBP/GO nanocomposite

FT-IR analysis was used to characterize the HBP functionalized with graphene oxide (HBP-GO) (Fig. 3a–c). As shown in the Figures, the FT-IR spectrum of the functionalized product (Fig. 3a) is clearly different from the spectrum of graphene oxide (Fig. 3b) and HBP (Fig. 3c). In the spectrum of GO, the strong absorption bands at 1722, 1045 and 3426 cm^{-1} correspond to the stretching vibration of C=O, C—O (epoxy) and O—H, respectively. The peaks at 1619 and 1223 cm^{-1} correspond to the vibration of the carboxyl groups (Fig. 3b). The spectrum of HBP, shows strong absorption bands at 1000–1300 cm^{-1} and a broad absorption band at 3413 cm^{-1} relating to the stretching vibration of C—O and O—H, respectively, and the peaks at 2876, 2917 cm^{-1} are assigned to symmetric and asymmetric stretching vibration of CH_2 group (Fig. 3c). The IR spectrum of HBP-GO (Fig. 3a) also shows peaks at 2855, 1713, 1573, 1067 and 3321 cm^{-1} that can be attributed to the presence of GO and HBP in HBP-GO nanocomposite.

Also, Fig. 4 shows XRD spectra for graphene oxide functionalized with HBP. Usually, GO shows a broad band over low diffraction angles ($2\theta = 11.2^{\circ}$), suggesting some degree of re-aggregation of the exfoliated GO sheets (Fig. 4a). Upon functionalization with HBP, the XRD band of GO downshifted to $2\theta = 10^{\circ}$, indicating that the cova-

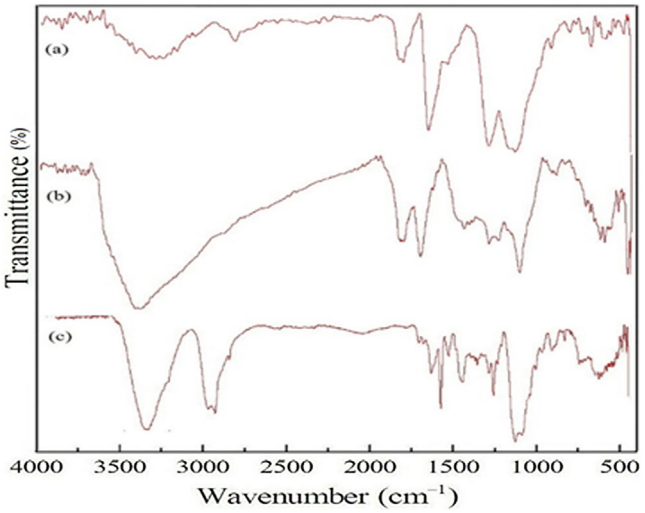

Fig. 3. FT-IR spectrum of; a)HBP-GO, b) GO, and c) HBP.

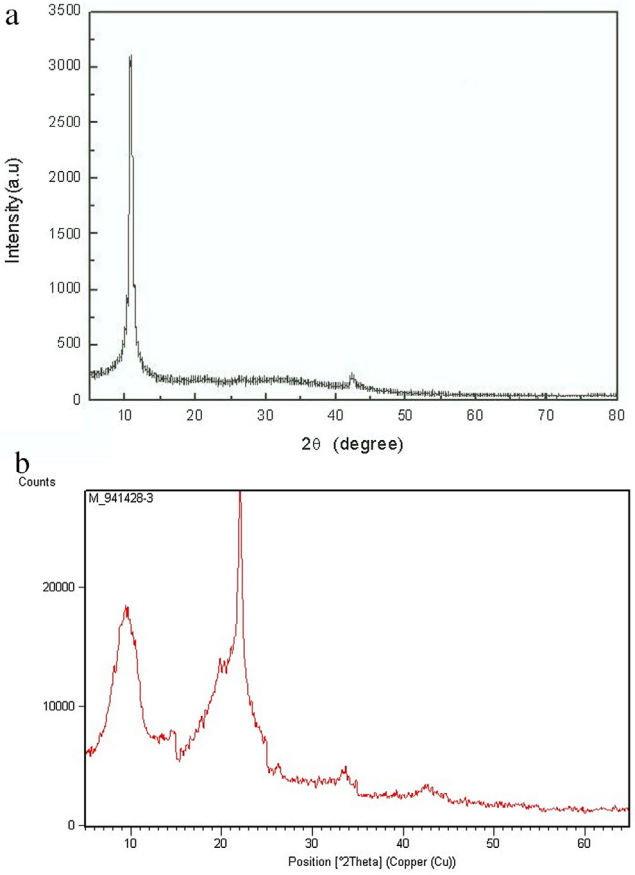

Fig. 4. XRD spectra for graphene oxide and GO functionalized with HBP.

lently bonded HBP moieties increased the interlayer space between graphene sheets in the HBP-graphene hybrid. The newly appearing broad amorphous bands over $2\theta = 15 - 25^{\circ}$ in the XRD profile of the HBP-graphene indicate, most probably, that the intercalated HBP moieties, show a largely disordered structure with a low crystallinity (Fig. 4b).

The nanosheets morphology of HBP-GO were investigated by TEM imaging as displayed in Fig. 5a and b.The Figures show that GO nanosheets are very thin and have some folds and wrinkles, and some black regions on the surface of HBP-GO can be observed.

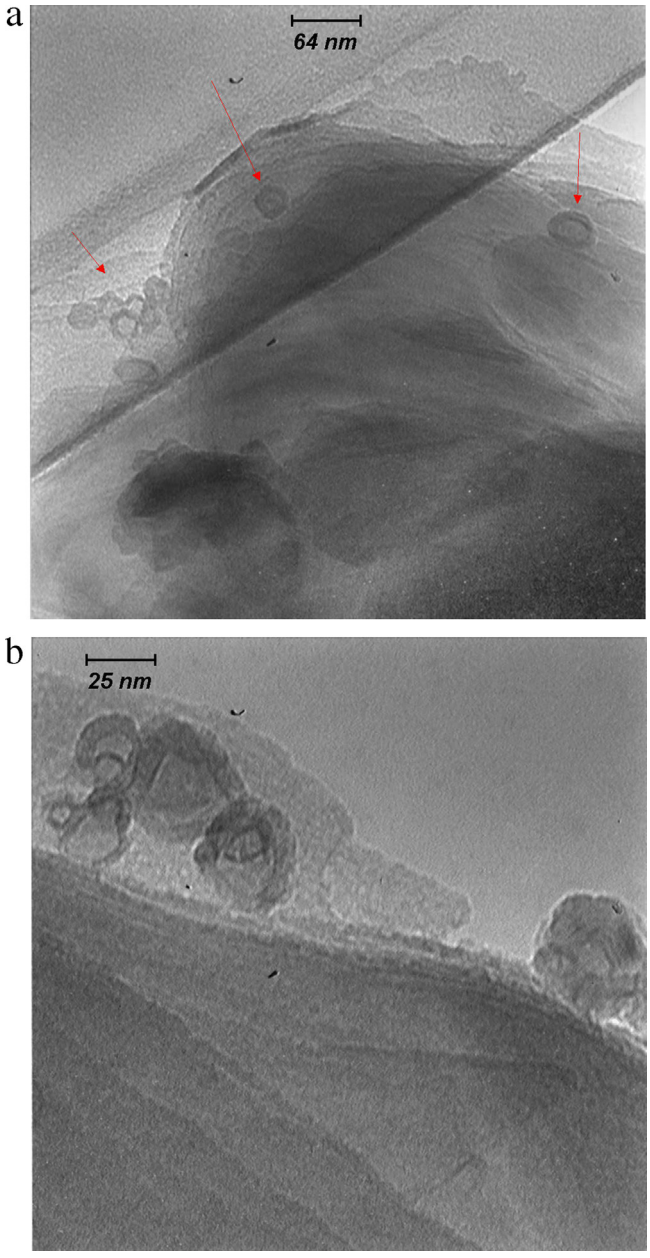

Fig. 5. TEM images of HBP-GO with different scales.

The black spots of HBP-GO can be attributed to the hyperbranched polyglycerol layer attached onto the GO surface from both sides.

3.2. Optimization procedure

In order to obtain the optimum extraction conditions for extraction of the analytes, the main parameters expect pH of the aqueous samples were investigated only for ibuprofen. The parameters such as effect of the amount of GO, pH of the aqueous sample solutions, extraction time, volume of the aqueous sample, agitation speed and also the desorption conditions, were optimized. The concentration of the analytes in the optimization steps was 5 $\mu g\,mL^{-1}$.

3.2.1. Effect of the amount of GO in extraction process

For investigation the effect of the amount of GO, upon extraction process, 5–20 mg of functionalized GO,was dissolved in 1 mL of 1-octanol. The results are shown in Fig. 6.As is shown in this Figure, the extraction efficiency increases up to 20 mg of Go. Since at

Table 1
Analytical performance of HF-SLPME method for extraction of ibuprofen and naproxen.

Analyte	Pre-concentration factor	LDR(ng ml^{-1})	R^2	LOD(ng ml^{-1})	LOQ(ng ml^{-1})	RSD%
Ibuprofen	1156	5–30000	0.9968	2.95	5.83	3.95
Naproxen	1212	2–10000	0.9925	1.51	2.04	3.66

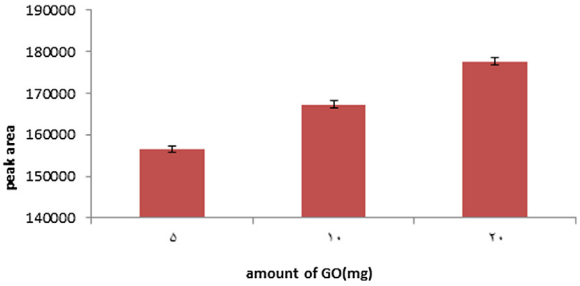

Fig. 6. Effect of amount of GO on the extraction efficiency.

higher amounts of GO,the injection of sample in to the hollow fiber, becomes difficult, therefore, we selected 20 mg of Go per 1 mL of 1-octanol solution.

3.2.2. Effect of pH

A suitable pH value of a sample aqueous solution, can improve the extraction efficiency and reduce the matrix interferences [44]. Changes in pH of the solution, may results in the ionization form of the basic and acidic analytes and, thereby, it will affect their water-solubility and extractability. Since ibuprofen and naproxen are acidic compounds with pKa of 5.2 and 4.15, respectively, the sample solution should be acidized to convert the analytes to their molecular form. We studied the effect of pH between 2 and 7, and according to the results the selected optimum pH value was 5.0 for the feed solution.

3.2.3. Volume of the feed solution

The extraction efficiency can be improved by increasing the volume ratio of donor to acceptor phase, but a larger sample volume can be disadvantageous due to poorer mass transfer kinetics which results in a poor extraction efficiency [44]. In the present work, the phase ratio of donor and acceptor solutions was optimized by changing the volume of the donor phase between 1 and 7 mL while the volume of acceptor phase was kept constant at 2.0 μL. The results showed that optimum donor phase volume is 5 mL.

3.2.4. Effect of extraction time

Extraction time is an important factor for improving the extraction efficiency, because it influences the partition of the analytes between the donor phase and the sorbent in the lumen of the fiber. SPME is not an exhaustive extraction technique. The maximum amount of analyte that can be extracted by the sorbent is achieved at equilibrium. Thus, the extraction time was examined to give the highest microextraction efficiency. The partition of the analyte,was controlled by the physicochemical properties of the analyte, the sample matrix, the acceptor phase, thickness and porosity of the sorbent.For a thicker sorbent, the time needed for the analyte diffusion into the sorbent was longer than for the thinner materials. However, a thicker sorbent,provides a better sensitivity because the kinetics of the microextraction is dependent on diffusion of the analyte in the bulk solution and the sorbent. The effect of different extraction time(10–40 min) was studied at room temperature. The extraction efficiency was increased up to 20 min and then decreased. Therefore, 20 min was chosen as an optimum extraction time.

Table 2
RSD% and relative recovery% (RR%) of ibuprofen and naproxen in clinical waste water.

Analyte	RSD%	RR%
Ibuprofen	3.55	102
Naproxen	2.42	94

3.2.5. The influence of stirring rate

A high stirring rate can increase the extraction rate by increasing the mass-transfer rate of the analyte to the membrane and reducing the thickness of the boundary layer at the outer membrane surface [27]. The effect of different stirring rate (200–500 rpm), was tested on the extraction efficiency. The experimental results show that the extraction efficiency increases by increasing the stirring speed up to 400 rpm, and then decreases at higher stirring rate, which may be due to the formation of air bubbles on the fiber surface, which results in a decrease the amount of analytes extracted into the sorbent. Therefore, 400 rpm was selected as an optimum stirring speed throughout the experiments.

3.2.6. Desorption condition

As in the case of SPME, the analytes were desorbed by an organic solvent from the surface of the GO,after extraction.Both the polypropylene membrane and GO are insoluble in most common organic solvents such as acetone, methanol, dichloromethane and hexane. Since, acetonitrile and methanol as widely-used mobile phases do not show strong and clear interferential peaks,therefore, extraction efficiencies of the two desorption solvents were investigated. The results showed the extraction efficiency is higher in methanol than acetonitrile. Therefore, methanol was selected as a desorption solvent in these experiments.The analytes extracted by the membrane were desorbed ultrasonically for the appropriate amount of time and then analyzed by HPLC. The effect of different desorption times (5–15 min)was studied at room temperature. The obtained results, indicate that the highest extraction efficiency is obtained at 10 min of desorption time. But at longer desorption time, the extraction efficiency decreases, because the desorbed analytes are absorbed by GO and diffuse to the pores of the lumen of hollow fiber due to the concentration difference and ultrasonication process.

3.3. Validity of the method

The linear dynamic range(LDR), limit of detection (LOD),limit of qualification (LOQ) and the relative standard deviation(RSD)for the extraction of ibuprofen and naproxen drugs from aqueous samples were determined under optimized experimental conditions. The results are summarized in Table 1.

3.4. Analysis of real samples

In order to test the reliability of the proposed method, it was applied for determination of ibuprofen and naproxen drugs in clinical waste water (See Table 2). A reversed-phase high performance liquid chromatography method was validated for the determination of analytes in real samples.

To investigate the matrix effects and applicability of the method to a biological sample, final experiments were carried out on a

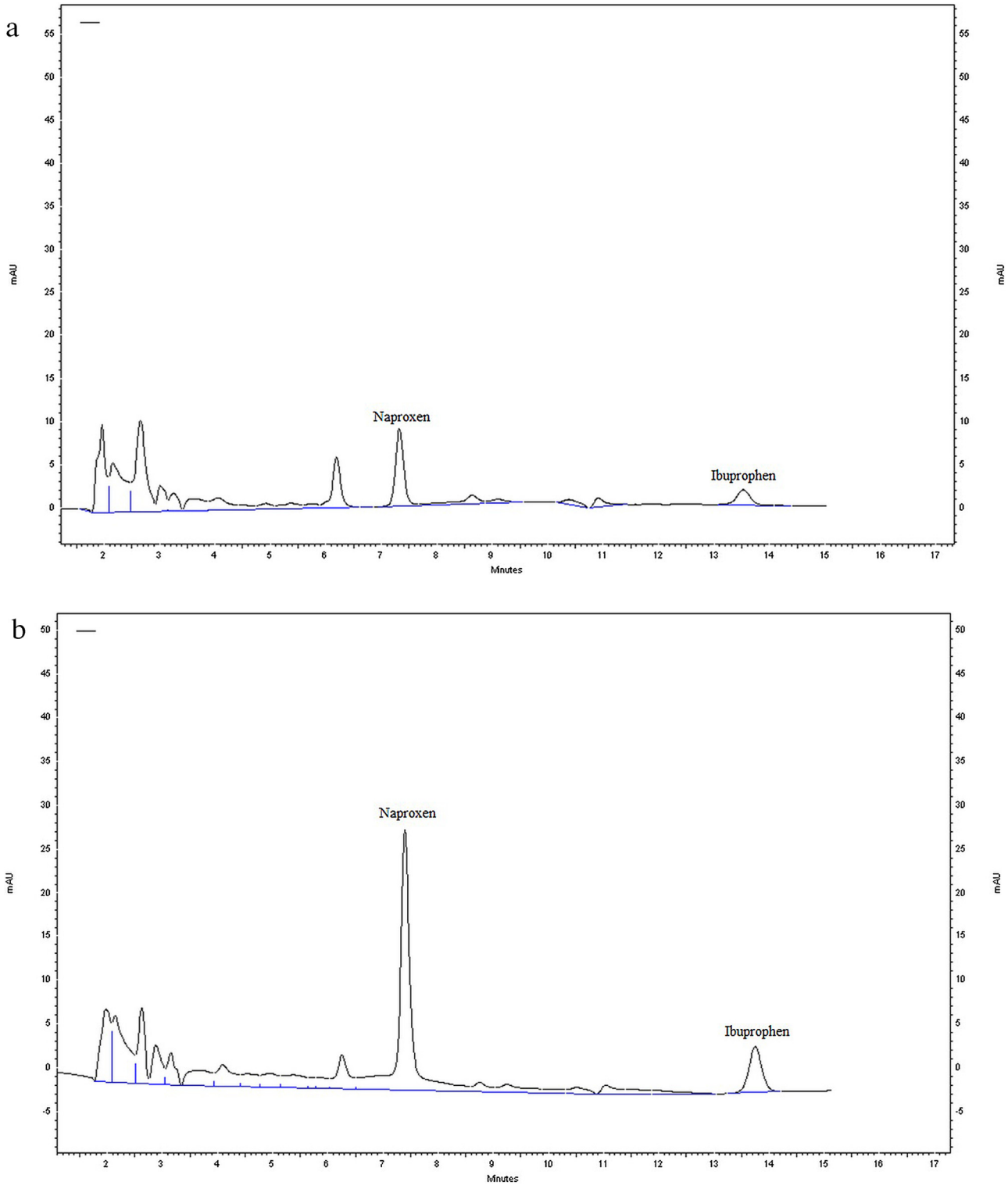

Fig. 7. The chromatograms of the hair samplea) before and b) after spike (1 μg mL^{-1} of naproxen and 5 μg mL^{-1} ibuprofen).

hair sample that was taken from a patient who was being treated with these two drugs. The results are summarized in Table 3.The hair samples were prepared as mentioned in Section 2.3. The chromatograms of the hair sample before and after spike,containing 1 μg mL^{-1} of naproxen and 5 μg mL^{-1} ibuprofen, are shown in Fig. 7a and b respectively.

Table 3
Founded concentrations (μg/mg) and relative percent recoveries of NSAIDs in the hair sample.

Analyte	Founded amounts (μg mg^{-1})	Spiked amount(μg mg^{-1})	RR%
Ibuprofen	10.87	1	82
Naproxen	1.23	0.2	94

4. Conclusions

A novel producer based on hyperbranched polyglycerol/graphene oxide (HBP/GO) nanocomposite reinforced hollow fiber solid/liquid microextraction has been developed to determine trace amounts of ibuprofen and naproxen in hair and waste water samples.GO reacted with HBP via its functional groups using thionyl chloride. The HBP/GO was supported by a macro-porous polypropylene membrane wall that protected the composite network structure. Functionalized GO is also compatible with the polypropylene fiber structure.The proposed method is fast, simple, sensitive and it needs low solvent consumption.The disposable nature of the hollow fiber, totally eliminates the possibility of sample carry over and ensures a high reproducibility.In addition, the small pore size of the hollow fiber, prevents from large molecules in the matrix and also unsolved particles in the donor solution from entering the acceptor phase, thus yielding a very clean extract.Also, the present technique shows a good linear range, low detection limit and acceptable precision to measurement of these two drugs,and it can be used for determination some organic compounds such as targeted drugs in aqueous and biological samples.

Acknowledgments

The present work was supported by theFerdowsi University of Mashhad, Iran and Payame Noor University, Mashhad, Iran (Grant No.32138)

References

[1] C.K.S. Ong, P. Lirk, C.H. Tan, R.A. Seymour, Clin. Med. Res. 5 (2007) 19–34.
[2] I. Pountos, T. Georgouli, H. Bird, P.V. Giannoudis, Int. J. Infereron Cytokine Mediator Res. 3 (2011) 19–27.
[3] C.A. Misurac, J.D. Knoderer, C. Leiser, A.C. Wilson, S.P. Andreoli, J. Pediatr. 162 (2013) 1153–1159.
[4] A. Gentili, Anal. Bioanal. Chem. 387 (2007) 1185–1202.
[5] K.D. Rainsford, Am. J. Med. 107 (1999) 27–35.
[6] M. Saberi-Firoozi, F. Khademolhosseini, M. Yousefi, D. Mehrabani, N. Zare, S.T. Heydari, World J. Gastroenter. 13 (2007) 5486–5491.
[7] G.G. Noche, M.E. Laespada, J.L. Pavon, B.M. Cordero, S.M. Lorenzo, J. Chromatogr. A 1218 (2011) 6240–6247.
[8] M.R. Payan, M.A.B. Lopez, R.F. Torres, M.V. Navarro, M.C. Mochon, Talanta 85 (2011) 394–399.
[9] M.D. Gil Garcia, F.C. Canada, M.J. Culzoni, L. Vera-Candioti, G.G. Siano, H.C. Goicoechea, M. MartínezGalera, J. Chromatogr. A 1216 (2009) 5489–5496.
[10] E.A. Suchara, D. Budziak, E. Martendal, L.L.F. Costa, E. Carasek, Anal. Chim. Acta 613 (2008) 169–176.
[11] A. Macia, F. Borrull, M. Calull, C. Aguilar, TrAC Trends Anal. Chem. 26 (2007) 133–153.
[12] C. Sajeev, P.R. Jadhav, D.R. Shankar, R.N. Saha, J. Anal. Chim. Acta 463 (2002) 207–217.
[13] M. Starek, J. Krzek, Talanta 77 (2009) 925–942.
[14] N.H. Hashim, S.J. Khan, J. Chromatogr. A 1218 (2011) 4746–4754.
[15] C. Wu, A.L. Spongberg, J.D. Witter, Int. J. Environ. Anal. Chem. 88 (2008) 1033–1048.
[16] M.D.G. García, F.C. Cañada, M.J. Culzoni, L. Vera-Candioti, G.G. Siano, H.C. Goicoechea, M.M. Galera, J. Chromatogr. A 1216 (2009) 5489–5496.
[17] C.-X. Yang, Y.-J. Chen, H.-F. Wang, X.-P. Yan, Chem. Eur. J. 17 (2011) 11734–11737.
[18] A. Sarafraz-yazdi, H. Assadi, Z. Es'haghi, N.M. Danesh, J. Sep. Sci. 35 (2012) 2476–2483.
[19] X. Wen, C. Tu, H.K. Lee, Anal. Chem. 76 (2004) 228–232.
[20] N. Larsson, E. Petersson, M. Rylander, J.A. Jönsson, Anal. Methods U.K. 1 (2009) 59.
[21] F. Zheng, B. Hu, Talanta 73 (2007) 372–379.
[22] Y. Fan, Y.Q. Feng, S.L. Da, Z.G. Shi, Anal. Chim. Acta 523 (2004) 251–258.
[23] L.M. Yuan, C.X. Ren, L. Li, P. Ai, Z.H. Yan, M. Zi, Z.Y. Li, Anal. Chem. 78 (2006) 6384–6390.
[24] X.J. Huang, Q.Q. Wang, B.L. Huang, Talanta 69 (2006) 463–468.
[25] W.L. Hu, B. Hu, Z.C. Jiang, Anal. Chim. Acta 572 (2006) 55–62.
[26] B.B. Chen, B. Hu, M. He, X.J. Mao, W.Q. Zu, J. Chromatogr. A 1227 (2012) 19–28.
[27] Z. Es'haghi, M. Ahmadi-Golsefidi, A. Saify, A.A. Tanha, Z. Rezaeifar, Z. Alian-Nezhadi, J. Chromatogr. A 1217 (2010) 2768–2775.
[28] A.A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, C.N. Lau, Nano Lett. 8 (2008) 902–907.
[29] C. Lee, X. Wei, J.W. Kysar, J. Hone, Science 321 (2008) 385–388.
[30] J.C. Meyer, A.K. Geim, M.I. Katsnelson, K.S. Novoselov, T.J. Booth, S. Roth, Nature 446 (2007) 60–63.
[31] M.D. Stoller, S.J. Park, Y.W. Zhu, J.H. An, R.S. Ruoff, Nano Lett. 8 (2008) 3498–3502.
[32] Y. Cai, G. Jiang, J. Liu, Q. Zhou, Anal. Chem. 75 (2003) 2517–2521.
[33] Y. Zhu, S. Murali, W. Cai, X. Li, J.W. Suk, J.R. Potts, R.S. Ruoff, Adv. Mater. 22 (2010) 3906–3924.
[34] H. He, J. Klinowski, M. Forster, A. Lerf, Chem. Phys. Lett. 287 (1998) 53–56.
[35] Y.H. Kim, J. Polym. Sci. A: Polym. Chem. 36 (1998) 1685–1698.
[36] V. Brigitte, J. Polym. Sci. A: Polym. Chem. 38 (2000) 2505–2525.
[37] J.M.J. Fre'che, M. Henmi, I. Gitsov, S. Aoshima, M.R. Leduc, B. Rrubbs, Science 269 (1995) 1080–1086.
[38] C.J. Hawker, F. Chu, P.J. Pomery, D.J.T. Hill, Macromolecules 29 (1996) 3831–3838.
[39] R.K. Kainthan, J. Janzen, E. Levin, D.V. Devine, D.E. Brooks, Biomacromolecules 7 (2006) 703–709.
[40] R.K. Kainthan, S.R. Hester, E. Levin, D.V. Devine, D.E. Brooks, Biomaterials 28 (2007) 4581–4590.
[41] D.C. Marcano, D.V. Kosynkin, J.M. Berlin, A. Sinitskii, Z. Sun, A. Slesarev, L. Alemany, B. Lu, W. Tour, J. M, ACS Nano 4 (2010) 4806–4814.
[42] F. Pragst, M.A. Balikova, J. Clin. Chim. Acta 370 (2006) 17–49.
[43] M. Ebrahimi, Z. Es'haghi, F. Samadi, F.F. Bamoharram, M.S. Hosseini, J. Chromatogr. A 1225 (2012) 37–44.
[44] E. Psillakis, N. Kalogerakis, J. Chromatogr. A 938 (2001) 113.