ARTICLE TYPE

Solid phase extraction and spectrofluorometric determination of leached bisphenol A from some polycarbonate products under simulated use conditions using surface molecularly imprinted magnetite nanospheres

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Abstract

This work reports on synthesis of a novel magnetic nanoadsorbent for solid phase extraction of leached bisphenol A (BPA) from some polycarbonate products. In order to improve the adsorbent selectivity 10 toward the analyte, the adsorbent was coated with a layer of BPA imprinted polymer. The prepared adsorbent has been fully characterized using Fourier transform infrared spectrometer, X-ray diffractometer and transmission electron microscope. The results showed that, after carful optimization of various affecting factors on the removal and desorption of BPA, the analyte can be determined in the concentration range of 5.0-1000.0 ng mL^{-1} with a detection limit as low as 1.5 ng mL^{-1} using the 15 spectrofluometric method. The results of the real samples analysis showed that the investigated samples release detectable and considerable amounts of BPA into the water under simulated use condition confirming the previous concerns about danger of polycarbonate products usage in daily human life.

Introduction

Bisphenol A (4,4'-(1-methylethylidene)bisphenol, BPA) is one of 20 the known endocrine disrupting chemicals, which is widely used in the production of polycarbonate plastics, epoxy resins used to line metal cans, and in many plastic consumer products including toys, water pipes, drinking containers, eyeglass lenses, sports safety equipment, dental monomers, medical equipment and 25 tubing, and consumer electronics.[1, 2] BPA has been shown to leach from food and beverage containers, and some dental sealants and composites under normal conditions of use. It has also been shown that BPA leached from lacquer coated cans and baby feeding-bottles [3]. BPA exposure has been associated with a 30 variety of health complications including obesity, type 2 diabetes, cardiovascular disease and reproductive disorders.[4] Specifically in men, the relationship between BPA levels and decreased semen quality, sperm DNA damage and changes in reproductive hormones have been reported.[5, 6]

35 The increasing global concern on BPA highlights the importance of developing selective and sensitive analytical methods to detect traces of this compound in environmental and food samples.[7-9] Certainly, many analytical methods involving high-performance liquid chromatography (HPLC), gas 40 chromatography coupled with mass spectroscopy (GC-MS), and capillary electrophoresis (CE) [10] have been developed for the determination of BPA in real samples and usually require a preliminary liquid–liquid or solid-phase extraction (SPE) step.[11] To achieve high selectivity and good recovery of pre-45 concentrating BPA by SPE, multifarious materials, such as C18,

surfactant-modified zeolite, microporous bamboo charcoal, and molecularly imprinted polymers (MIPs), have been adopted as sorbents.[12-15] The traditional sorbents are to some extent limited in their applications in SPE owing to their inefficient selectivity, 50 which can be improved by the use of MIPs.[16-19]

With the development of the molecularly imprinted adsorbents, some disadvantages of MIPs have emerged and greatly restricted its application. It was excited for scientists to find that giving MIP magnetism was an effective approach to 55 overcome the disadvantages of MIPs.[20, 21] MIP when used as a SPE sorbent, magnetic MIP bead can be dispersed into solution directly and separated via an external magnetic field, avoiding the operation of making packed columns as the traditional SPE adsorbents. Accordingly, an interest has been raised in 60 preparation and application of magnetic MIPs in recent years, and BPA was one of the selected targets.[22-25] These studies greatly extended the preparation method of magnetic MIPs and made them more efficient as SPE adsorbents. However, structure of the magnetic supporter (core), rather than a single Fe_3O_4 particle as 65 reported in the previous studies, should be better designed to improve the magnetic performance and enhance the stability of MIPs.

Herein, a highly selective magnetic molecularly imprinted polymers based on magnetite nanospheres (MNSs, as magnetic 70 core) were prepared using methacrylamide (MAA) as the functional monomer, ethylene glycol dimethacrylate (EGDMA) as the cross-linker, (2,2'-azoisobutyronitrile (AIBN) as the initiator and BPA as the template. The prepared BPA imprinted adsorbent (BPAMNSs) were characterized by Fourier transform

infrared spectrometer (FT-IR), X-ray diffractometer (XRD) and transmission electron microscope (TEM). The recognition and static adsorption of the BPAMNSs toward BPA were investigated in details. The results showed that the BPAMNSs exhibited good adsorption capacity towards BPA. Combined with spectrofluorometric (FL) studies, the BPAMNSs were successfully used for selective extraction and quantitative determination of leached BPA from some polycarbonate products under simulated use conditions.

Experimental

Chemicals

All the chemical reagents were at least of analytical grade. BPA, EGDMA, MAA, and AIBN were obtained from Sigma-Aldrich (St. Louis, MO, USA). The other chemical reagents were purchased from Merck Company (Darmstadt, Germany). The stock solutions of 100 mg L^{-1} of BPA were prepared in double distilled water (DDW) and maintained at 4°C and working standard solutions of different BPA concentrations were prepared daily by diluting the stock solution with DDW. Britton-Robinson universal buffer used for pH adjusting of working solutions.

Apparatus

Infrared spectra's of the polymeric adsorbent were collected using a FT-IR spectrometer (Perkin-Elmer model Spectrum GX) with the spectral range of 4000–400 cm^{-1}. A transmission electronic microscope (TEM, Philips-CMC) obtained the nanographs of the adsorbents with measurements operating at 300 KV. The crystal structure of the synthesized materials was determined by an X-ray diffractometer (XRD, 38066 Riva, d/G. Via M. Misone, 11/D (TN) Italy) at ambient temperature. A Metrohm model 713 pH-meter was used for pH adjustments. A 40 kHz universal ultrasonic cleaner water bath (RoHS, Korea) was used. A Perkin Elmer (LS50B) luminescence spectrometer was used for the determination of extracted BPA at λ_{em}= 307.5 nm (λ_{ex}= 248.0 nm).

Synthesis of the investigated nanospheres (Scheme 1)

Preparation of silica coated magnetite nanospheres (SCMNSs)

$FeCl_3 \cdot 6H_2O$ (1.35 g, 5 mmol) was dissolved in ethylene glycol (EG, 40 mL) to form a clear solution, followed by the addition of sodium acetate (NaAC, 3.60 g) and polyethylene glycol (PEG, 1.0 g). The mixture was stirred vigorously for 30 min and then sealed in a teflon lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to and maintained at 190 °C for 18 h, and then allowed to cool to room temperature. The black products (MNSs) were washed several times with ethanol and dried at 60°C for 6 h.[18]

MNSs were coated with a silica layer to prevent iron oxide cores from leaching into the mother system under any acidic circumstances. Briefly, 0.10 g of MNSs nanospheres were dispersed in the mixture of ethanol (50 mL), DDW water (10 mL) and concentrated ammonia aqueous solution (3 mL), followed by the addition of tetraethylorthosilicate (TEOS, 2.0 mL). After stirring at room temperature for 1.5 h, the silica coated MNSs nanospheres (SCMNSs) were separated and washed with ethanol and DDW water.[16]

Preparation of BPA-imprinted polymer coated SCMNSs (BPAMNSs) and non-imprinted polymer coated SCMNSs (NIPMNSs)

Typically 6 mmol of MAA (as the functional monomer), 20 mmol of EGDMA (as the cross-linker), and 0.40 g of SCMNSs agent were dispersed into a 45 mL acetonitrile solution of BPA (3 mmol, as the template). After sealing, shaking, and purging the mixture with nitrogen, a 5 mL acetonitrile solution with 0.05 g of AIBN (as the initiator) was added into the suspension with a sample injector. The resultant mixture was ultrasonicated at 60 ºC for 30 min under the nitrogen protection and then stirred overnight. The product was washed with methanol until no template molecule (BPA) was detected spectrofluorometrically in the washing solution. To ensure complete template removal, the product (BPAMNSs) was separated by a magnet and washed overnight with methanol in one batch. Then, the resulting nanospheres were dried under the vacuum for 12 h. As a reference, non-imprinted polymer coated SCMNPs (NIPMNSs), which did not contain the template, was also prepared in parallel with the BPAMNSs by using the same synthetic protocol in the absence of the template.[26]
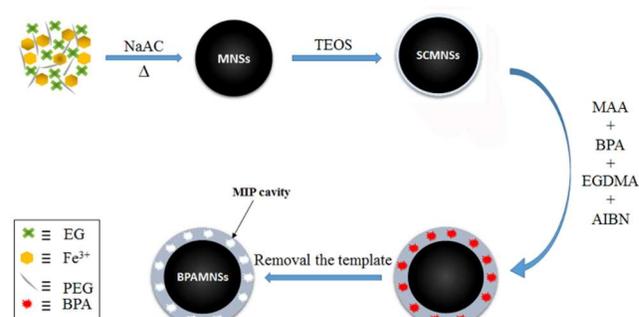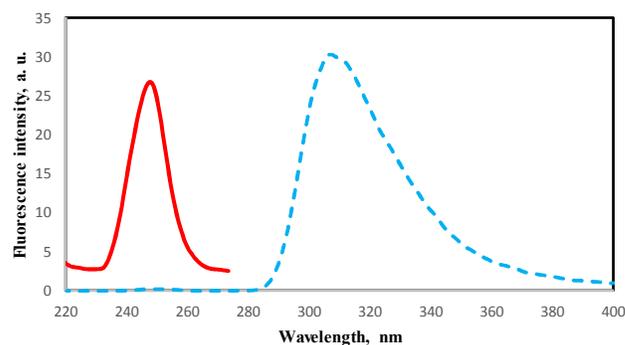

Scheme 1 Reaction involved in the synthesis of BPAMNSs

Fig. 1 Fluorescence excitation (——) at λ_{em}=307.5 nm and emission spectra (- - - -) at λ_{ex}=248.0 for BPA in water at pH=7.0 at room temperature.

SPE procedure for BPA and its spectrofluorometric determination

The SPE procedure consisted of three steps. BPA was dissolved in DDW water at the concentration range of 5.0-1000.0 ng mL^{-1} with 100.0 mL total volume. The pH of the solution adjusted at 7.0 using 0.01-0.1 mol L^{-1} of HCl and/or NaOH. Then, 40 mg of BPAMNSs nanospheres was added into the BPA solution. The mixture was stirred at room temperature for 10 min. Then, the nanospheres were isolated rapidly from the solution

under an external magnetic field. Finally, the BPA was eluted from the BPAMNSs nanospheres with 2 mL of methanol.

The BPA concentration in the solution was determined spectrofluorometrically at λ_{em}= 307.5 nm (λ_{ex}= 248.0 nm) (Emission and excitation spectra of BPA are shown in Fig. 1). The adsorption percentage, i.e., the analyte removal efficiency (%Re), was determined using the following equation:

$$\%Re = \left[\frac{(C_0 - C_t)}{C_0}\right] \times 100 \qquad (1)$$

where C_o and C_t represent the initial and final (after adsorption) concentrations of BPA in mg L^{-1}, respectively.

Real samples treatment

In this study, three polycarbonate products (plastic cups, baby toy and baby milk bottle) have been investigated. The products have been provided from local stores. Three replicate experiments for each product were conducted to determine if BPA was released into the hot water stored in the products.

The effect of hot water on plastic cups was assessed by exposure of the cups with 100 mL of DDW water heated to 85°C for 2 h. Then the cups were separated and the solution was directly analyzed using the SPE procedure. In the case of the baby toy, the same procedure was conducted at 37°C for 24 h. The effect of hot water on baby milk bottle was assessed as described above except 100 ml of DDW water heated to 100°C was added to selected bottles. Filled bottles were shaken on an orbital shaker for 1 h at 100 °C. The bottles were shaken with the purpose of mimicking the motion of water during normal usage, and to ensure that the bottle's internal surface was in continuous

contact with the water sample.[27] Furthermore, in order to the method accuracy's evaluation, all of the polycarbonate products samples were spiked with BPA at ng mL^{-1} concentration levels.

Results and Discussion

Characterization of the synthesized adsorbents

The FTIR spectra for the products, in each step of the BPAMNSs synthesis, were recorded to verify the formation of the expected products. The related spectra are shown in Fig. 2. The characteristic absorption bands of Fe-O in Fe_3O_4 (around 435 and 592 cm^{-1}) are observed in Fig. 2a. A strong peak at about 1089 cm^{-1} in Fig. 2b is attributed to Si-O in SiO_2. The three new absorption peaks at 1732, 1320 and 1608 cm^{-1} in Fig. 2c are assigned to C=O, C-N and C=C bands in the polymer-coated final product (BPAMNSs), respectively. Moreover, new absorption peaks at 2957 and 2989 cm^{-1} are related to the stretching modes of the aliphatic C-H groups.[28] Based on the above results and by compare the product spectra with the initial materials (Fig. 2d), it can be concluded that the fabrication procedure has been successfully performed.

The XRD pattern of the BPAMNSs (Fig. 3) shows diffraction peaks that are indexed to (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), (4 4 0) and (5 5 3) reflection characteristics of the cubic spinel phase of magnetite (JCPDS powder diffraction data file no. 79-0418), revealing that the resultant nanoparticles are mostly Fe_3O_4. The average crystallite size of the BPAMNSs nanospheres was estimated to be 13 nm from the XRD data according to Scherer equation.[29]
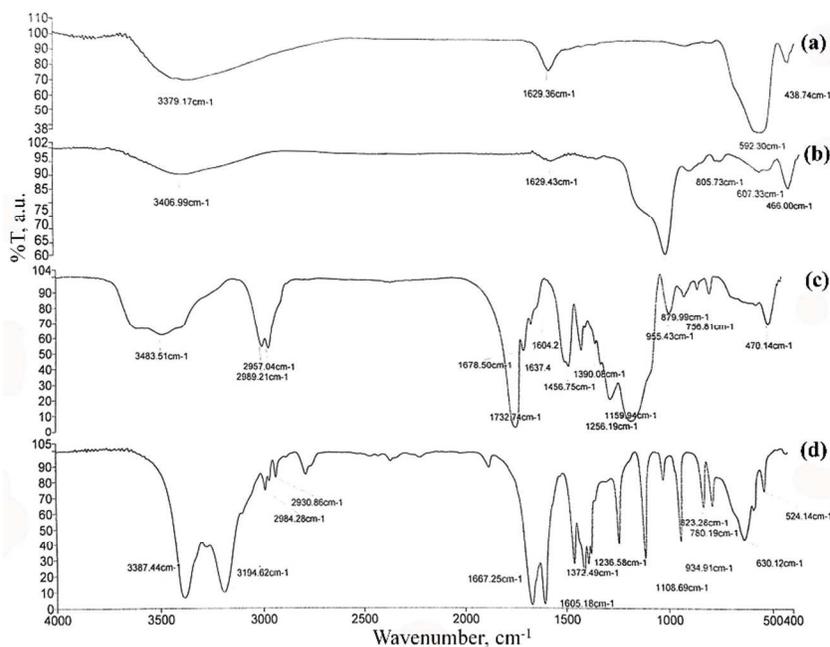

Fig. 2 FT-IR spectra of (a) MNSs, (b) SCMNPs, (c) BPAMNSs and (d) MAA

The TEM image of the BPAMNSs in Fig. 4 indicates that the MNSs nanospheres are enwrapped rather homogeneously in the SiO_2 shell, and further by the MIP layer. The average size of the synthesized nanospheres was estimated to be about 145 nm.

Point of zero charge (pH$_{PZC}$) of the BPAMNSs nanospheres

The pH$_{PZC}$ of the BPAMNSs was determined in degassed 0.01 mol L^{-1} NaNO$_3$ solution at room temperature. Aliquots of 20.0 mL 0.01 mol L^{-1} of NaNO$_3$ were mixed with 0.02 g of the nanoparticles in several beakers. The initial pH of the solutions was adjusted at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 using 0.01

mol L^{-1} of HCl and/or NaOH solutions as appropriate. The initial pHs of the solutions were recorded, and the beakers were covered with parafilm and shaken for 24 h. The final pH values were recorded and the differences between the initial and final pH (ΔpH) of the solutions were plotted against their initial pH values. The pH_{PZC} corresponds to the pH where ΔpH=0.[21] The pH_{PZC} for the BPAMNSs was determined using the above procedure and was obtained as 7.5. The results are shown at Fig. 5.
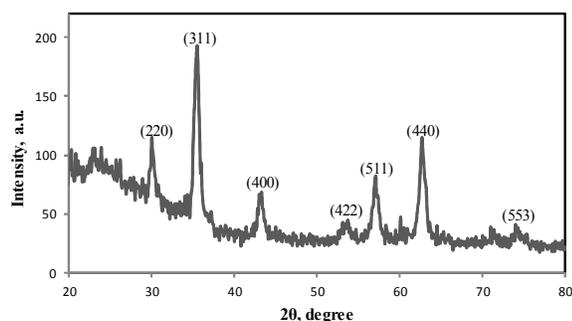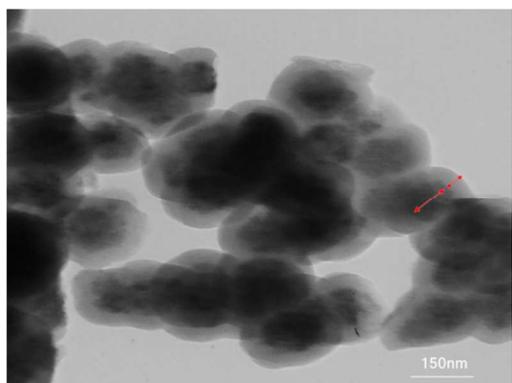

Fig. 3 XRD pattern for the BPAMNSs nanospheres

Fig. 4 TEM image of the BPAMNSs nanospheres
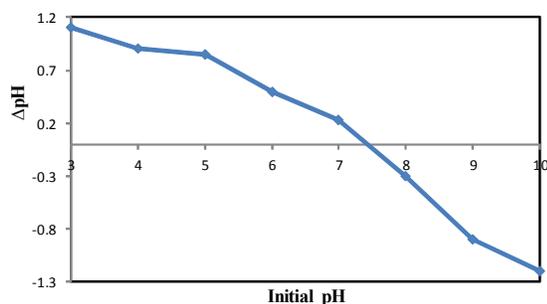

Fig. 5 Point of zero charge (pH_{pzc}) of the BPAMNSs nanospheres

Effect of various factors affecting the BPA removal efficiency

Various factors that can potentially affect the analyte removal efficiency (i.e. pH, contact time and nanospheres dosage) were optimized using "one-at-a-time" method. Here are the detailed results:

Effect of pH

The effect of pH on the BPA removal efficiency was investigated in the range 3.0–10.0 using an initial BPA concentration of 20.0 mg L^{-1} and a stirring time of 45 min, where the pH was adjusted with Britton-Robinson buffer. As elucidated in Fig. 6, the maximum value of BPA removal appeared in the range of pH 3.0 to 8.0. At pH>8.0 a significant decrease in BPA removal efficiency can be seen. Due to the pK_a value of BPA ranging from 9.6 to 10.2 [30], At pH>8.0, the predominant form of BPA is in its anionic form and electrostatic repulsion between negatively charged BPAMNSs (pH_{pzc}=7.5) and the BPA anion is responsible for the low removal efficiencies. At pH<7.5, the BPA has neutral form and the adsorbent is positively charged. So, electrostatic forces are not responsible for the high removal efficiencies. It can be suggested that hydrophobic interaction and hydrogen bonds between BPA and the MIP cavities (mainly the amine functional group of MAA) is responsible for the high observed removal efficiencies in pH range of 3.0-8.0. For further optimizations the pH=7 was chosen because of its more accommodation with biological pH.
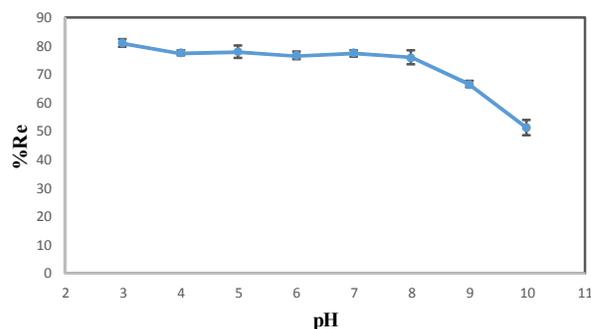

Fig. 6 Removal efficiency of BPA at different pHs (Conditions: 0.02 g of BPAMNSs, 20 mL of 20.0 mg L^{-1} of BPA, agitation time of 45 min, N=3)

Effect of nanoparticles dosage

The dependence of the adsorption of BPA on the amount of modified nanospheres was studied at room temperature and at pH 7.0 by varying the adsorbent amount from 0.01 to 0.05 g in contact with 20.0 mL solution of 2.0 mg L^{-1} of BPA with agitation time of 45 min. The results showed that the removal efficiency of BPA increased by increasing amount of the BPAMNSs due to the availability of higher adsorption sites. The adsorption reached a maximum with 0.04 g of adsorbent and maximum percentage removal was about 98%.

Effect of contact time

The effect of contact time on the adsorption of BPA was studied to determine the time needed to remove BPA by BPAMNSs from a 20.0 mg L^{-1} solution of the analyte at pH 7.0. A 0.04 g of the adsorbent was added into 20.0 mL of the BPA solution. Fluorescence intensity of BPA was monitored versus time to determine variation of the analyte concentration. It was observed that after a contact time of about 10.0 min, almost all the BPA was adsorbed (%Re>98) and this time was much enough to reach semi-equilibrium condition.

Effect of various factors on the BPA preconcentration efficiency

The aim of this step is providing the highest preconcentration factor and concentration of the adsorbed analyte into minimum possible volume of desorbing solvent. In this regard, various factors that can potentially affect the BPA desorbing efficiency

(i.e. type and volume of desorbing solvent, desorbing time and initial sample volume) have been optimized. The detailed results are given in bellow:

Desorbing solvent

For desorption studies, BPA loaded BPAMNSs were first washed by DDW to remove the unadsorbed BPA that loosely attached to the vial and adsorbent. In order to estimate the recovery of BPA from BPAMNSs, desorption experiments with different reagents (methanol, ethanol, acetonitrile, 0.01 mol L^{-1} NaOH, 0.05 mol L^{-1} NaOH and mixture of methanol: 0.05 mol L^{-1} NaOH (1:1 v/v)) were performed. After adsorption of BPA, the adsorbent was magnetically separated and washed with DDW. Then 2 mL of the eluent was added to the BPA loaded BPAMNSs. Samples were collected after 5, 10, 15, 20, 25, 30 and 45 min contact times to evaluate BPA recovery. The results (Fig. 7) showed that methanol is the most effective as a back-extracting solvent and can be used for the quantitative recovery of the analyte. Desorption rate was found to be rapid as almost 98% desorption completed at almost 15 min.
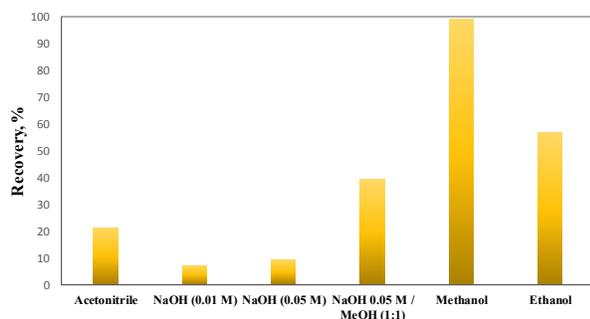

Fig.7 Effect of various eluents on BPA recovery

Initial sample volume

The effect of initial sample volume on the analyte adsorption was studied in the range 20.0–200.0 mL; 0.5 mL samples containing 100.0 mg L^{-1} of BPA were diluted to 20.0, 50.0, 75.0, 100.0, 125.0, 150.0 and 200.0 mL with DDW. Then adsorption and desorption processes were performed under the optimum conditions (pH 7.0; contact time, 10.0 min; BPAMNSs dosage, 0.04 g) as described in the experimental section. The results showed that the analyte content in the volumes up to 100.0 mL was completely and quantitatively adsorbed by the nanoparticles, but there was a decrease in the amount adsorbed at higher volumes. Therefore, for the determination of trace quantities of the analyte, a sample volume of 100.0 mL was selected in order to having highest preconcentration factor.

Adsorption isotherms

The capacity of the adsorbent is an important factor that determines how much sorbent is required to quantitatively remove a specific amount of the analyte from solution. For measuring the adsorption capacity of BPAMNSs and NIPMNSs, the absorbents were added into BPA solutions at various concentrations (under optimum condition), and the suspensions were stirred at room temperature, followed by magnetic removal of the absorbent. An adsorption isotherm describes the fraction of the sorbate molecules that are partitioned between the liquid and the solid phase at equilibrium. Adsorption of the BPA by BPAMNSs and NIPMNSs adsorbents were modelled using Freundlich [31] and Langmuir [32] adsorption isotherm models. The remained analyte in the supernatants was measured spectrofluorometrically, and the results were used to plot the isothermal adsorption curves as shown in Fig. 8. The equilibrium adsorption data were fitted to Langmuir and Freundlich isotherm models by linear regression. The resulting parameters are summarized in Table 1.
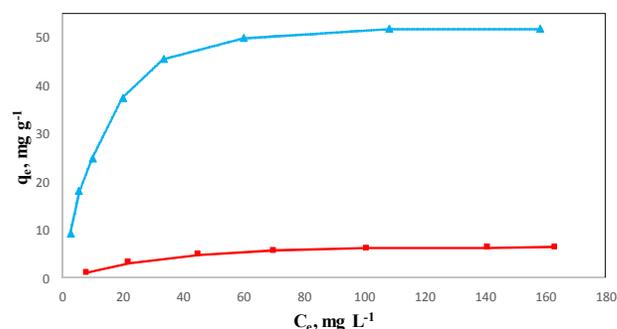

Fig. 8 Isothermal adsorption curves of BPA on (▲) BPAMNSs and (■) NIPMNSs adsorbents

The higher correlation coefficient obtained for the Langmuir model (> 0.99) indicates that the experimental data are better fitted into this model, and adsorption of BPA onto BPAMNSs adsorbents is more compatible with Langmuir assumptions, i.e., adsorption takes place at specific homogeneous sites within the adsorbent. The Langmuir model is based on the physical hypothesis that the maximum adsorption capacity consists of a monolayer adsorption, that there are no interactions between adsorbed molecules, and that the adsorption energy is distributed homogeneously over the entire coverage surface. This sorption model serves to estimate the maximum uptake values where they cannot be reached in the experiments.

Table 1 Adsorption isotherm parameters of Langmuir and Freundlich models for the adsorption of the analyte onto BPAMNSs and NIPMNSs adsorbents

Isotherm models	Langmuir			Freundlich		
	K_L (L mg^{-1})	q_{max} (mg g^{-1})	R^2	K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n (g L^{-1})	R^2
BPAMNSs	4.76	58.76	0.997	0.77	2.44	0.872
NIPMNSs	0.20	8.33	0.983	0.20	1.78	0.893

According to the results (Table 1), the maximum amount of BPA that can be adsorbed by BPAMNSs and NIPMNSs was found to be 58.76 and 8.33 mg g^{-1} at pH 7.0, respectively. The relatively

high adsorption capacity of BPAMNSs in comparison with NIPMNSs, shows that the adsorption of BPA molecules takes place at a large number of specific homogeneous sites within the

adsorbent (specific cavities of the MIP layer), besides non-specific interactions which are approximately identical for both BPAMNSs and NIPMNSs adsorbents.

Adsorption kinetics

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. The adsorption capacities of adsorbents were calculated from the difference between the initial and the final concentration at any intermediate time. The sorption dynamics of the adsorption by BPAMNSs were tested with the pseudo-first order and the pseudo-second order kinetic models. [29, 33]

To study the adsorption kinetics of BPA on BPAMNSs, 20.0 mg L-1 initial concentration of corresponding BPA solutions which were stirred in the presence of 0.04 g adsorbents at pH 7 and for different times, ranging 0–30 min, were used at room temperature. The solution was separated with magnetic decantation to remove adsorbent and analysed spectrofluorometerically. The removal of BPA by adsorption on BPAMNSs was found to be rapid at the initial period (in the first 5 min) and then became slow and stagnate with the increase in the contact time (≈5th to ≈15th min), and nearly reached a plateau after approximately 20 min. Different kinetic parameters of BPA adsorption onto BPAMNSs are shown in Table 2. All the experimental data showed better compliance with pseudo-second order kinetic model in terms of higher correlation coefficient value ($R2 > 0.99$) and lower RMS value. Moreover, the q values (qe, cal) calculated from pseudo second order model were more consistent with the experimental q values (qe, exp) than with those calculated from the pseudo-first-order model. Hence, it could be found that pseudo-second order kinetic model was more valid to describe the adsorption behaviour of BPA onto BPAMNSs

Reusability and stability of the adsorbent

The reusability and stability of BPAMNSs for the extraction of BPA was assessed by performing twenty consecutive separations/desorption cycles under the optimized conditions (Conditions: 0.04 g of BPAMNSs, 100.0 mL of 0.02 mg L-1 of BPA , agitation time of 10 min). Desorption of BPA from the adsorbent was performed with methanol as described above. There was no significant change in the performance of the adsorbent during these twenty cycles, indicating that the fabricated BPAMNSs is a reusable and stable solid phase sorbent for the extraction of BPA.

Interference studies

The influences of some coexisting substances on the determination of BPA were investigated and the results are shown in Table 3. Possible interference was investigated by addition of various ions and biological compounds to Britton-Robinson buffer (pH 7.0) in the presence of 500 ng mL-1 BPA.

The common cations such as Na^+, K^+, Ca^{2+} and anions such as Cl^- and NO_3^- did not show significant interference manner (signal change < %5) with BPA determination. But some structurally similar organic compounds, such as 2, 2-dihydroxybiphenyl, have serious interference manner. The main Interferents of this compounds are in the removal step and, because of the selective detection method (spectrofluorometric determination), it can be resolved with using higher amount of the adsorbent.

Analytical applications

Calibration graph was constructed from spectrofluorometric measurements of the desorbed BPA after performing its adsorption/separation under the optimum conditions as described above. The calibration graph was linear in the range 5.0 - 1000.0 ng mL-1 for a sample volume of 100 mL. The calibration equation is $I_F = 0.989C + 3.11$ with a determination coefficient of 0.9997 (n = 9), where I_F is the fluorescence intensity of the eluate at $\lambda_{em} = 307.5$ nm ($\lambda_{ex} = 248.0$ nm) and C is the concentration of the analyte in ng mL-1. The limit of detection, defined as $LOD = 3S_b/m$, where LOD, S_b and m are the limit of detection, standard deviation of the blank and the slope of the calibration graph, respectively, was found to be 1.5 ng mL-1 of BPA . As the analyte in 100 mL of the sample solution was concentrated into 2 mL, a maximum preconcentration factor of 50 was achieved in this method. The enrichment factor (the ratio of the slope of the calibration graphs with and without preconcentration in the desorbing solvent) was 50.5 and shows good match with its corresponding experimental value (i.e. the preconcentration factor).The relative standard deviations (RSD) for 500.0 and 10.0 ng mL-1 of the analyte were 1.56% and 2.69% (n = 5), respectively.

The analytical applicability of the proposed method was evaluated by determining the leached BPA from some polycarbonate products. The results are given in Table 4 and show that all of the investigated samples released detectable amounts of BPA into the water under simulated use conditions. The results of the spiked samples show good recoveries of the proposed method and suggest that the method is a good candidate for BPA determination in the investigated samples.

Table 5 shows a comparison between the results obtained by the present method with those of obtained by some other methods reported for the determination of BPA. This comparison shows that the proposed method analytical performance is comparable with some sensitive instrumental method, such as HPLC, and in some cases, the method is not superior on the analytical figure of merit bases. However, other advantages of the proposed method are simplicity, less expensive, low LOD, wide linear range, easy adsorbent separation and high removal capacity of the adsorbent.

Table 2 The values of parameters obtained by different kinetic models.

Kinetics models	Pseudo-second order				Pseudo-first order				
Parameters	$q_{e, cal}$ (mg g-1)	k_2 (g mg-1h-1)	R^2	RMS	$q_{e, cal}$ (mg g-1)	k_1 (h-1)	R^2	RMS	$q_{e,exp}$ (mg g-1)
	10.57	0.084	0.991	0.51	8.63	0.140	0.924	1.87	9.84

Table 3 Interference of some coexisting substances for 500 ng mL^{-1} of BPA

Interferents	Tolerance level (mg L^{-1})
Na$^+$, K$^+$, NO$_3^-$, Cl$^-$, Zn^{2+}, Al^{3+}, Ca^{2+}, Cr^{2+}, Ba^{2+}, Pb^{2+}, Mn^{2+}	500
3,4-dihydroxybenzaldehyde	40
Phenol, 4-nitro phenol, 4-amino phenol	20
p-hydroquinone	10
2,2-dihydroxybiphenyl	5

Table 4 Assay of leached BPA from some polycarbonate products under simulated use condition

Sample	Spiked value (μg g^{-1})	Found (μg g^{-1})	Recovery percent
Plastic cups			
	-	2.47±0.06[*]	-
	5.10	7.30±0.20	96.5
	25.60	29.00±0.99	103.6
Baby toy			
	-	2.10±0.06	-
	1.70	3.8±0.15	99.2
	8.70	10.50±0.25	96.7
Baby milk bottle			
	-	0.05±0.01	-
	0.63	0.68±0.02	99.5
	3.15	3.19±0.12	99.8

[*]N=3

Table 5 Comparison of the proposed method with some previously reported methods for BPA determination

Method	LOD (ng mL^{-1})	Linear range (ng mL^{-1})	Sample	Ref.
SPE–MS [a]	0.7	5-200	Milk	34
HPLC	3.6×10^{-4}	2-70	Surface water	35
LLME [b]	0.07	0.5-100	Water samples	36
SPE-GC-MS [c]	0.1	-	Baby milk bottle	37
LLME-GC-MS [d]	0.4×10^{-3}	10-250	Water samples	38
MIP/SPE/FL	1.5	5-1000	Plastic cups, toy and baby milk bottle	This work

[a] Solid phase extraction followed by mass spectrometry
[b] Liquid-liquid microextraction
[c] Solid phase extraction followed by gas chromatography- mass spectrometry
[d] Micro liquid-liquid extraction followed by gas chromatography- mass spectrometry

Conclusion

The novel molecularly imprinted nanoadsorbent, used for recognizing of BPA, was prepared using MNSs as the magnetic core, MAA as the functional monomer, EGDMA as the cross-linker, AIBN as the initiator and BPA as the template. The recognition properties and applications based on the SPE of BPAMNSs were evaluated. The resulting BPAMNSs showed a relatively large adsorption capacity and fast binding kinetics for recognizing BPA, and the BPAMNSs-SPE-FL method showed high recovery, good selectivity and repeatability in determining the leached BPA from some polycarbonate products under simulated use condition. These excellent properties make the BPAMNSs one of the most promising candidates in various applications, especially in the analysis of environmental water samples based on SPE.

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Notes

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Acknowledgements

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Table of Contents (TOC)
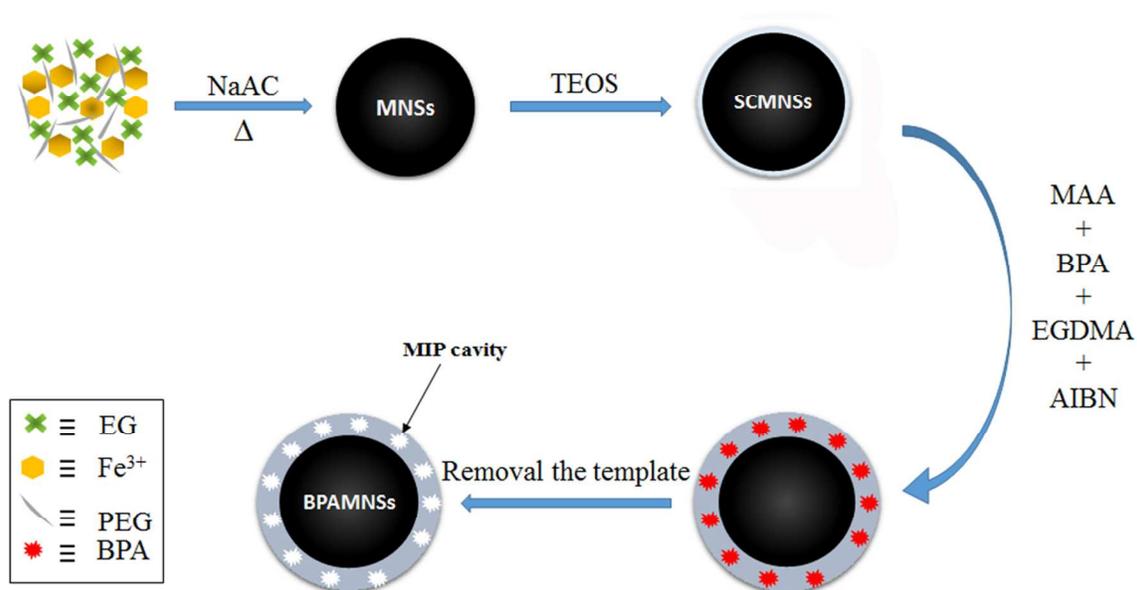
Solid phase extraction of leached bisphenol A from some polycarbonate products using surface molecularly imprinted nanospheres