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Liquid Chromatographic Determination of Aromatic Amines in Water Samples after Gold Nanoparticles Coated Membrane Microextraction

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A novel microextraction technique was developed for aromatic amines using gold nanoparticles coated membrane. The preparation of the extraction device involves with the synthesis of gold nanoparticles *via* the reduction of $AuCl_3$ by hydroxyethyl cellulose followed by coating to the polyethersulfone membrane. The simple extraction procedures involved placing the extraction device in a stirred aqueous sample solution, followed by desorption in an organic solvent using ultrasonication. The extract was analyzed by high performance liquid chromatography. Optimal extraction conditions include 50 min extraction time, 20 min desorption time, 30 mL sample volume, sample pH 10, 5 % NaCl content and 17 mg sorbent mass coupled with 100 µL desorption solvent. The performance of the extraction device in the absence and presence of gold nanoparticles was investigated. Enrichment factors ranged from 148 (for 3-nitroaniline) to 200 (for 3,4-dichloroaniline). The calibration results exhibited good linearity (r^2 = 0.9931-0.9988) within the range 0.5-20 µg/L. The limits of detection were 0.3-0.7 µg/L and RSDs (n = 6) 10-19%. Comparison was made with solid-phase extraction. The method was subsequently applied to municipal wastewater samples. The proposed microextraction method offers advantages such as easy operation, high recovery, faster extraction, minimal use of organic solvent and elimination of tedious solvent evaporation and reconstitution steps.

Keywords: Aromatic amines, Microextraction, Gold Nanoparticles, Membranes, Environmental applications.

INTRODUCTION

Aromatic amines are either decomposition product or synthesis intermediate species in azo dyes with wide applications in products including medicine, pharmaceuticals, pesticides, leather, textiles, plastics, food packaging and cosmetics [1-3]. They have also been reported as a major component in tobacco leaves and cigarette smoke [4,5]. These include 2-naphthylamine (2-ANP) and 4-aminobiphenyl (4-ABP), which are potential bladder cancer source. In addition, the International Agency for Research on Cancer (IARC) have also classified *o*-toluidine, 2-naphthylamine and 4-aminobiphenyl in the first group of human carcinogens, while *o*-anisidine and 2,6-dimethylaniline as possible human carcinogen and 1-naphthylamine as non-human carcinogen [5,6]. Incessant application of these compounds in industries will inevitably lead to their release into our environment and result to pollution problems [2]. Hence, adequate monitoring of their hazardous effects on the environment and ultimately, humans is highly significant.

Analytical methods which have been reported in literature for the determination of aromatic amines include high performance liquid chromatography (HPLC) [3,7,8], gas chromatography (GC) [9-11], capillary electrophoresis (CE) [12] and spectrophotometry [13]. Among them, HPLC and GC are the most effective for the determination of aromatic amines. Derivatization of aromatic amines is usually required prior in GC analysis [9,10]. Separation and detection of aromatic amines could be efficiently achieved using liquid chromatography such as HPLC due to their polarity [5,14].

Regardless of which analytical method is being used, appropriate sample pretreatment is essential prior to instrumental determination. Liquid-liquid extraction (LLE) and solid phase extraction (SPE) are established conventional pretreatment methods that have been employed for aromatic amines in aqueous samples [7,9]. Miniaturization has become the current trend in the development of new analytical methods. In recent years, microextraction techniques such as solid phase microextraction (SPME) [6-11] and liquid-liquid-liquid microextrac-

tion (LLLME) [3,8] have proven successful in the extraction of aromatic amines.

Solid-phase microextraction (SPME) has been known to be a viable pre-concentration step technique for diverse volatile and semi-volatile compounds from food, water, biological and environmental samples. It is usually combine with GC, GC-MS and HPLC analysis. Though, the HPLC application need suitable desorption optimize condition [15]. The advantages of microextraction methods over LLE and SPE are simple operation with fewer steps, less time-consuming, little or no solvent consumption and smaller sample volume requirement. LLE and SPE require drying the solvent and reconstitute the dry residue with a solvent suitable for HPLC, which can be tedious and prone to loss of analytes through adsorption and evaporation. Microextraction normally does not require solvent evaporation and hence avoids these problems [8,16].

This study aims to develop a novel microextraction technique for the extraction and preconcentration of four different aromatic amines. In recent years, there have been a growing interest in the use of gold nanoparticles in the development of new methods to detect and quantify nucleic acids [17-20] and proteins [21-25]. The feasibility of these methods is attributed to the high affinity of gold for the thiol and amine functional groups present in these biomolecules [21]. This property of gold shall become the working principle of the proposed extraction method named as gold nanoparticles coated polyethersulfone membrane (AuNPs-CPES). Polyethersulfone (PES) membrane was selected as the support material to bind the gold nanoparticles through the strong Au-S bonds. The performance of the gold nanoparticles coated membrane was investigated in the extraction of aromatic amines. Method optimization and its application to real wastewater samples was subsequently carried out.

EXPERIMENTAL

Aromatic amine compounds, which include 3-nitroaniline, 4-chloroaniline, 4-bromoaniline and 3,4-dichloroaniline were from Fluka (Neu-Ulm, Germany). Stock solutions (1000 mg/L of each aromatic amine) were prepared in methanol. HPLC grade organic solvents (acetonitrile and methanol) as well as ACS grade glacial acetic acid and sodium acetate were obtained from Merck (Darmstadt, Germany). Hyroxyethyl cellulose (HEC) with an average molecular weight of 250,000 and gold(III) chloride were procured from Sigma-Aldrich (Milwaukee, USA). The hydrophilic sulfonated polyethersulfone (PES) flat membrane used was from microPES (Membrana, Wuppertal, Germany). Ultrapure water was prepared in-house using Milli-Q (Millipore, Bedford, MA, USA) water purification system. The Oasis HLB 6cc SPE extraction cartridges were bought from Waters (Milford, MA, USA).

Sample collection: Real wastewater samples were collected from a municipal wastewater treatment plant in Saudi Arabia. The plant uses conventional activated sludge process for the treatment of wastewater. Both incoming wastewater and effluent leaving the secondary clarifiers were analyzed in this study. The samples were filtered through a 1.2 μm filter to remove suspended particles. They were then stored in amber glass bottles at 4 ºC and were analyzed within 3 days. The sample pH and sodium chloride concentration were adjusted. A portion of the effluent sample was spiked with 5 μg/L standards. All spiked and non-spiked samples were left to stand overnight prior to analysis.

Preparation of gold nanoparticles coated membrane: Gold nanoparticles were prepared by adding 303 mg of $AuCl_3$ to a 10 mL HEC solution, which was a mixture of 3 mL HEC of concentration 50 mg/L and 7 mL ultrapure water. The gold solution mixture was constantly stirred on a magnetic stirrer and maintained at 70 ºC for 2 h to allow the formation of gold nanoparticles. Pieces of polyether-sulfone (PES) membranes of dimensions 1.5 cm × 2.5 cm were added to the gold solution mixture for 1 h to allow coating to take place. The newly formed AuNPs-CPES membranes were then removed and air-dried.

Sample extraction and enrichment: The AuNPs-CPES membrane was soaked in ultrapure water followed by ultrasonication in acetonitrile for 20 min and stored in ultrapure water until use. During extraction, the membrane was hanged and immersed into the sample. This was to keep the membrane in suspension and to prevent the stirrer from breaking the membrane. The sample was stirred at 1000 rpm for 50 min. After extraction, the membrane was removed, rinsed in ultrapure water and dried with lint free tissue. It was inserted into a 250 μL microvial containing 100 μL of acetonitrile as the desorption solvent. The analytes were desorbed by ultrasonication for 20 min and the extract was later transferred to a clean 250 μL autosampler vial for HPLC analysis. The AuNPs-CPES membrane was cleaned by ultrasonication in acetonitrile for 10 min before reuse for the next extraction.

Solid phase extraction: A spiked solution (5 μg/L) was prepared with pH adjusted to 10. The Oasis HLB SPE cartridge (200 mg) was conditioned with 3 mL of methanol and 3 mL of ultrapure water. A 200 mL volume spiked solution was passed through the cartridge under gravity flow, followed by washing with 6 mL ultrapure water and drying. The amines on the cartridge were eluted with 2.5 mL of acetonitrile. The extract was concentrated under nitrogen gas to form a final volume of 0.5 mL.

HPLC system and conditions: HPLC was performed using a Shimadzu Prominence system (Shimadzu, Kyoto, Japan) consisting of a CBM-20A system controller, a LC-20AD pump, a SIL-20A autosampler, a CTO-20A column oven, a DGU-20A5 degasser and a SPD-20A UV-VIS detector. Separation was carried out using a 50 mm × 3.0 mm I.D. MetaSil 5u ODS column (Varian, Palo Alto, CA, USA) and a mobile phase of acetate buffer (pH 3.5)-acetonitrile (85:15, v/v). The flow rate was set at 0.3 mL/min and the detection wavelength was 254 nm. Fig. 1 shows the chromatogram obtained from an extract of a spiked ultrapure water sample at 7.5 μg/L concentration.

RESULTS AND DISCUSSION

In present work, the effects of various factors that would influence extraction efficiency were investigated. These factors include extraction time, desorption time, sample volume, pH, ionic strength and sorbent mass. Optimization studies were

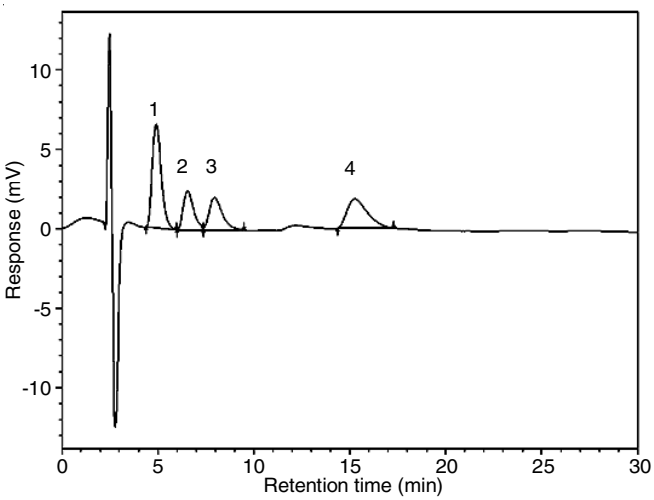

Fig. 1. HPLC chromatogram obtained from the extract of a 7.5 µg/L spiked solution after AuNPs-CPES membrane microextraction. Peak: (1) 3-nitroaniline, (2) 4-chloroaniline, (3) 4-bromoaniline and (4) 3,4-dichloroaniline

conducted by performing analysis of triplicate ultrapure water samples spiked with 5 µg/L of each aromatic amine analyte. Desorption of the analytes were carried out using ultrasonication in 150 µL of acetonitrile. The extraction performance of the proposed method was compared with that of SPE. Optimal conditions obtained from the results were subsequently applied in the quantitative evaluation studies as well as wastewater analysis.

Extraction time: Extraction was carried out at different durations ranging from 20 min to 60 min to determine their effect on extraction performance. The results are shown in Fig. 2. Since adsorption of analytes to the sorbent is a time dependent process [26], peak area is expected to increase with longer extraction time till it reaches a maximum. Highest extraction was observed at 50 min and beyond that there was no considerable improvement in the peak area. Hence, 50 min was selected as the optimum extraction time.

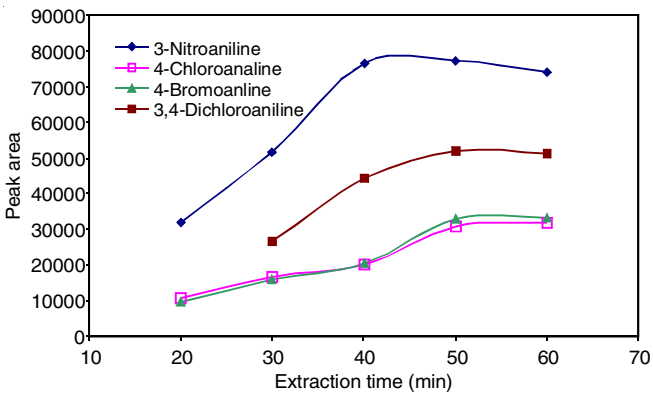

Fig. 2. Effect of extraction time on extraction performance

Desorption time: The extent of desorption of the analyte compounds in acetonitrile was investigated. After extraction, the AuNPs-CPES membrane sorbent was ultrasonicated at various time periods ranging from 10 to 30 min. As shown in Fig. 3, complete desorption of 3-nitroaniline occurred at 10 min

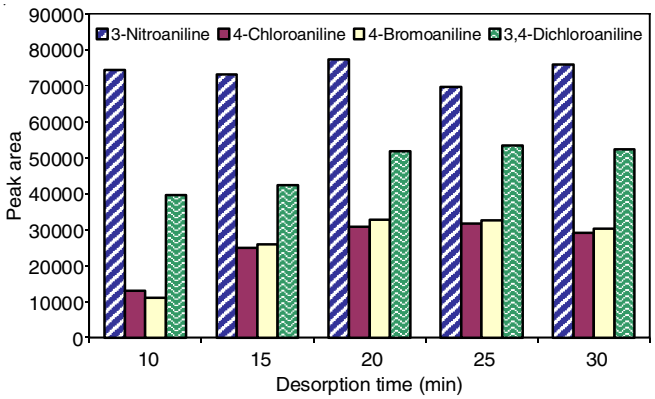

Fig. 3. Effect of desorption time on peak area

with no observable improvement in peak area at longer desorption times. The remaining three aromatic amines required at least 20 min for complete desorption. Therefore, the optimum desorption time was set at 20 min. After the first desorption, the AuNPs-CPES membrane sorbent after clean-up was further desorbed to examine any carryover effect. The analytes were not detected in the second desorption.

Sample volume: The effect of different sample volumes from 15 to 40 mL on extraction performance was investigated. All samples contained 5 µg/L of analytes. As shown in Fig. 4, smaller sample volumes contributed to lower analyte enrichment. This was due to the smaller amount of analytes present in the samples. Maximum analyte enrichment was observed when 30 mL of sample was used. No significant improvement to the peak area was observed when sample volume was greater than 30 mL. The AuNPs-CPES membrane sorbent could be already saturated or longer extraction time would be needed to reach equilibrium at higher sample volumes. Therefore, the optimum sample volume was 30 mL in this study.

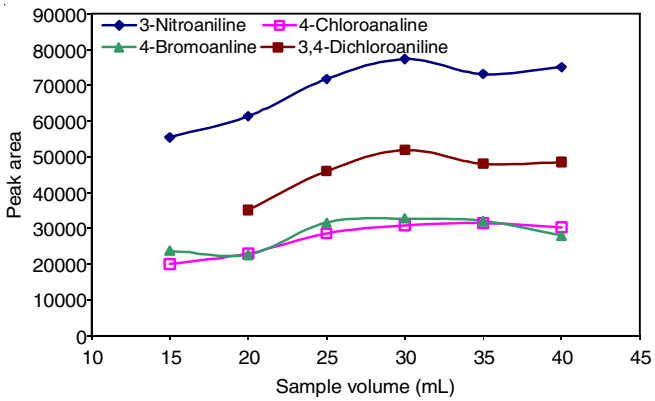

Fig. 4. Effect of sample volume on extraction performance

Sample pH: Extraction runs were carried out to determine the effect of sample pH on the method's performance. Sample pH was adjusted in the range from 2 to 12 with the addition of aqueous NaOH or aqueous HCl. A trend in Fig. 5 showed that extraction was poorer at low pH values. At pH 2, only 3-nitroaniline was detected. The extraction improved significantly as sample pH increased from 2 to 10 and decreased slightly at pH 12 for some aromatic amines. This was because of the incre-

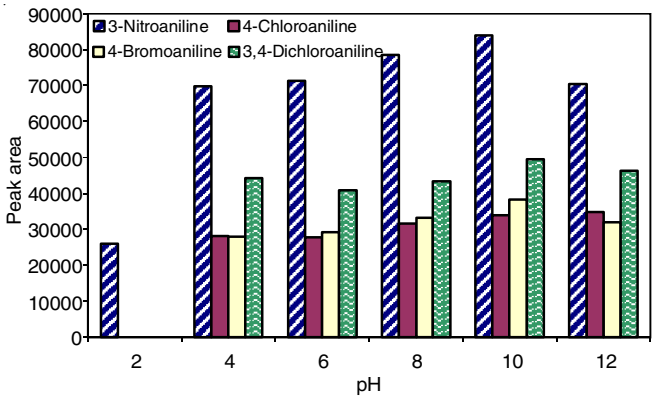

Fig. 5. Effect of sample pH on extraction performance

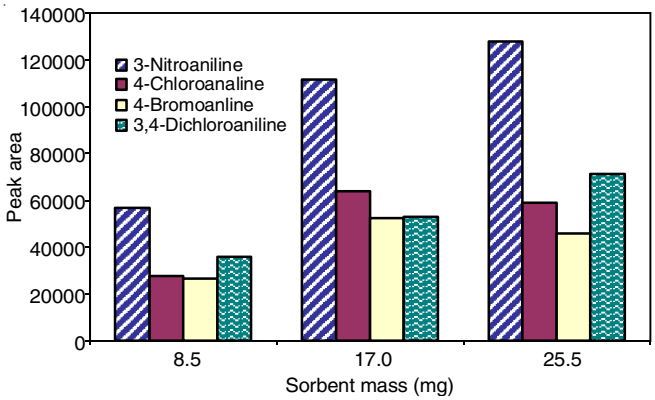

Fig. 7. Effect of sorbent mass on extraction performance

asing dominance of the protonated species over the neutral species as pH decreased. The acid dissociation constants (pK_a) of the individual aromatic amines are presented in Table-1. Due to their positive charge, the protonated amines have relatively higher aqueous solubility than their neutral counterparts, which make extraction less favorable. The optimum sample pH was set at 10.

Ionic strength: The role of the sample′s ionic strength in affecting extraction performance was examined. Experiments were conducted with the addition of anhydrous sodium chloride to form 5 to 20% concentrations. The presence of salt reduces the analytes' solubility in aqueous samples, hence helping the sorbent to extract the analytes better. Comparing the results without salt addition (Fig. 6), better extractions were achieved for 4-chloroaniline and 4-bromoaniline at salt concentrations 5% or greater. Extraction of 3-nitroaniline was most favorable at 20% salt concentration. On the other hand, 5 to 20% salt concentrations had no positive effect on the extraction of 3,4-dichloroaniline. Thus, 5% was chosen as the optimum salt content.

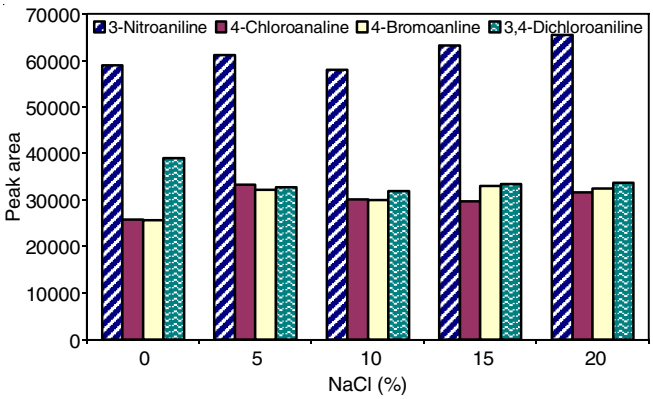

Fig. 6. Effect of salt concentration on extraction performance

Sorbent mass: Experiments were repeated with various AuNPs-CPES membrane sorbent masses as shown in Fig. 7. A larger sorbent offers more sites for the sorption of analytes and hence higher extraction efficiency is expected. This was reflected in the results when peak areas doubled as sorbent mass increased from 8.5 mg to 17 mg. However, similar trend was not observed in the results for 25.5 mg sorbent. Comparing the results of 17 mg and 25.5 mg sorbent, the latter showed a smaller magnitude of increase in the peak areas for 3-nitroaniline and 3,4-dichloroaniline while the peak areas for the other two aromatic amines were reduced slightly. This could be due to the difficulty encountered for the 25.5 mg sorbent to maintain full contact with the desorption solvent during desorption. In view of that, the optimum sorbent mass selected would be around 17 mg and desorption solvent volume was reduced from 150 µL to 100 µL for subsequent experiments to achieve higher enrichment.

Effect of gold nanoparticles: The proposed method was performed on 5 µg/L spiked solutions using a plain PES membrane without gold nanoparticles. The PES membrane by itself was found to extract the aromatic amines. From the molecular structures of the aromatic amines (Fig. 8a) and PES (Fig. 8b), the binding of the aromatic amines to the PES membrane could be due to non-covalent interactions such as π-π stacking, hydrogen

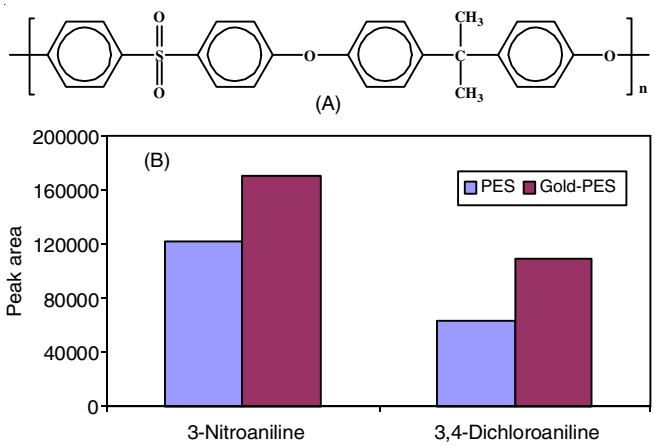

Fig. 8. (a) Molecular structure of PES, (b) Peak areas of aromatic amines (5 µg/L) after extraction with PES and AuNPs-CPES membranes

TABLE-1
pKa VALUES FOR THE AROMATIC AMINES [Ref. 27]

Analyte	3-Nitroaniline	4-Chloroaniline	4-Bromoaniline	3,4-Dichloroaniline
pKa	2.47	4.15	3.86	3.00

bonding and hydrophobic interactions between the compounds and PES.

In comparison with the data obtained from AuNPs-CPES membrane (Fig. 8b), gold nanoparticles enhanced the extraction efficiency by 28% and 43% for 3-nitroaniline and 3,4-dichloroaniline, respectively. PES membrane alone gave very poor peak resolutions for 4-chloroaniline and 4-bromoaniline. Therefore, their peak areas cannot be determined accurately. AuNPs-CPES membrane on the other hand, produced better peak resolution for the two aromatic amines.

Quantitative evaluation: Performance parameters such as repeatability, linearity, limit of detection (LOD), limit of quantification (LOQ) and recovery were investigated by testing spiked solutions of aromatic amines in ultrapure water. The experiments were carried out in triplicates (n = 3). External calibration curves were created for the four aromatic compounds by plotting peak areas against the respective spiked solution concentrations (Figs. 9-12). Good linearity is observed for all the compounds as shown by the high correlation coefficients (r^2) 0.9931- 0.9988 in the range of 0.5-20 µg/L.

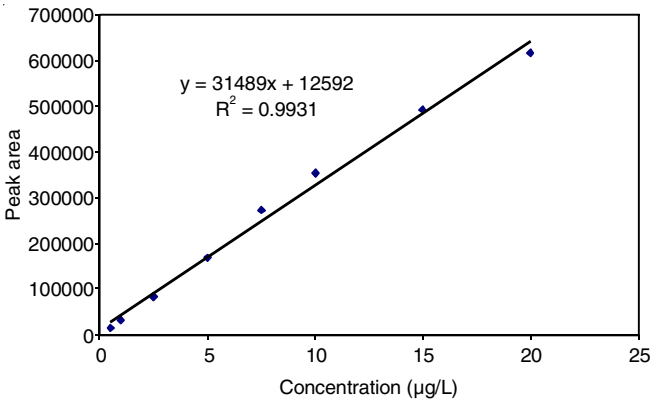

Fig. 9. Calibration curve for 3-nitroaniline in spiked solutions

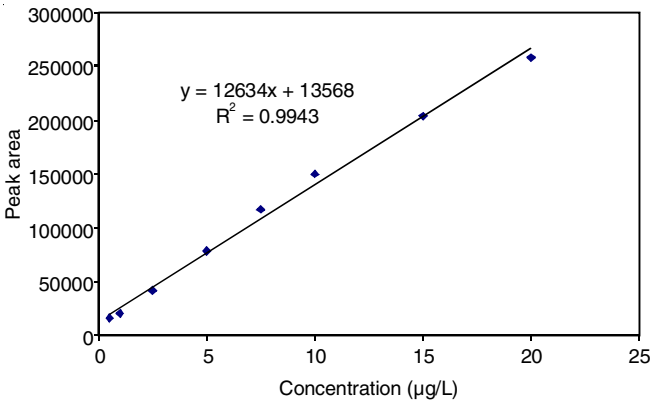

Fig. 10. Calibration curve for 4-chloroaniline in spiked solutions

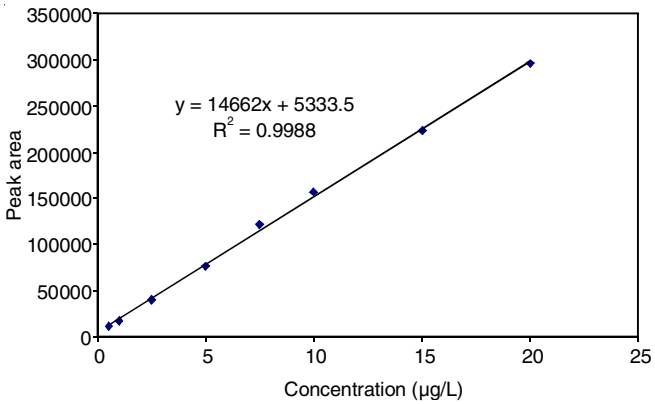

Fig. 11. Calibration curve for 4-bromoaniline in spiked solutions

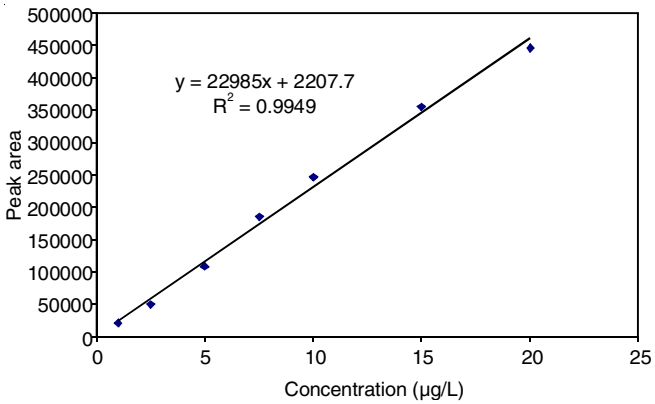

Fig. 12. Calibration curve for 3,4-dichloroaniline in spiked solutions

The performance data of the remaining parameters are shown in Table-2. LODs and LOQs were derived based on the signal to noise ratios of 3 and 10, respectively. Due to time constraints and the tight schedule for the study, only intra-day precision was determined for the spiked solutions at 1 µg/L (n = 6). The RSDs obtained were satisfactory, within 20% for all the compounds. Enrichment factors for the AuNPs-CPES microextraction were 148-200 and recoveries 49-67%.

Comparison with SPE: SPE was selected to compare with the AuNPs-CPES microextraction. Both methods were applied to spiked ultrapure water solutions (5 µg/L). The recovery and RSD data are tabulated in Table-3. With the exception of 3-nitroaniline where SPE gave a higher recovery than AuNPs-CPES microextraction, the recoveries of the remaining three aromatic amines were similar in the two extraction methods. Increasing the sample volume could further enhance the sample enrichment of SPE. However, AuNPs-CPES microextraction was much faster than SPE. The longer extraction time for SPE was due to the greater number of steps involved and the larger sample volumes applied to the cartridge.

TABLE-2
PERFORMANCE DATA OF INDIVIDUAL AROMATIC AMINES: LODs, LOQs, RSDs AND RECOVERIES

Analyte	LOD (µg/L)	LOQ (µg/L)	RSD[a] (%, n = 6)	Enrichment factor[b]	Recovery[b] (%)
3-Nitroaniline	0.3	0.9	16	148	49
4-Chloroaniline	0.5	1.8	10	195	65
4-Bromoaniline	0.7	2.4	19	193	64
3,4-Dichloroaniline	0.6	2.0	17	200	67

[a]RSDs determined from results of spiked solution of 1 µg/L.
[b]Mean enrichment factors and recovery values determined from results for the spiked solutions 0.5 to 20 µg/L.

TABLE-3
RECOVERIES OF THE AROMATIC AMINES IN SPIKED SOLUTIONS OF 5 µg/L AFTER SPE AND AuNPs-CPES MICROEXTRACTION FOLLOWED BY HPLC ANALYSIS (n =3)

Analyte	SPE		AuNPs-CPES microextraction	
	Recovery (%)	RSD (%, n = 3)	Recovery (%)	RSD (%, n = 3)
3-Nitroaniline	81	6	50	15
4-Chloroaniline	58	17	58	9
4-Bromoaniline	61	15	59	5
3,4-Dichloroaniline	65	12	64	10

Wastewater sample analysis: The developed AuNPs-CPES was applied on two grab wastewater samples under the derived optimal conditions. Triplicate samples were tested (n = 3). Results are tabulated in Table-4. With the exception of 3,4-dichloroaniline, other aromatic amines were detected in the raw wastewater prior to treatment and the concentration of 4-bromoaniline was highest at 2.64 µg/L. On the other hand, none of the compounds was detected in the secondary effluent. This may be due the fact that the wastewater has already undergone biological treatment with denitrification and nitrification processes carried out for nitrogen removal.

TABLE-4
AROMATIC AMINES DETERMINED IN WASTEWATER SAMPLES (n = 3)

Analyte	Raw wastewater	Secondary effluent
3-Nitroaniline (µg/L)	< 0.9	ND
4-Chloroaniline (µg/L)	< 1.8	ND
4-Bromoaniline (µg/L)	2.64	ND
3,4-Dichloroaniline (µg/L)	ND	ND

The HPLC chromatogram of the extract obtained from the raw wastewater is shown in Fig. 13. There was a high intensity interfering peak beside the peak of 4-bromoaniline but its retention time did not coincide with the amine compounds. Humic acids and other organic compounds are inherently present in wastewaters. Tong *et al*. [7] reported that presence of humic acids in surface waters can disturb the HPLC analysis of aromatic amines. This problem was not severe in the present study as shown by the relatively clean baseline. The method in general has demonstrated good selectivity, despite the high complexity of the wastewater matrix.

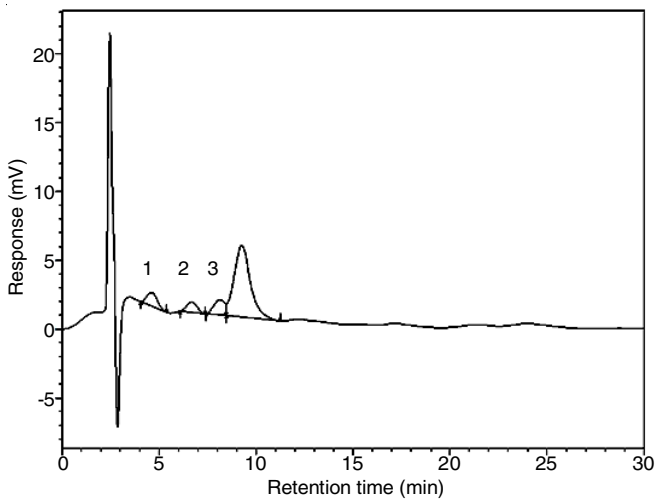

Fig. 13. HPLC chromatogram obtained from the extract of the raw wastewater sample after AuNPs-CPES membrane microextraction. Peaks: (1) 3-nitroaniline, (2) 4-chloroaniline and (3) 4-bromoaniline

Spiking was carried out at a concentration of 5 µg/L in the secondary effluent sample and the relative recovery data are shown in Table-5. Recoveries are acceptable within the 70 to 130% guideline.

Comparison of figures of merits of this work with some previous ones: The efficiency of this method for effective determination and quantification of the tested aromatic amines was compared with some previous findings (Table-6). The figures of merit results suggested that the method is efficient for the selected analytes. The LODs of present work method are comparable with the other methods. It has a well refined repeatability and the RSDs are also comparable to the considered previous reports. In addition, the EFs of the spiked secondary effluents are far higher than those methods as it can be seen in Table-5.

Conclusion

The present study has successfully shown the feasibility of using gold nanoparticles coated membrane for the extraction of aromatic amines followed by HPLC analysis. The optimal conditions for the extraction process were determined. This method has the potential of becoming a better alternative over conventional extraction methods with the advantages of easy operation, elimination of sample preparation step, high recovery, faster extraction, minimal use of organic solvent and elimination of tedious solvent evaporation and reconstitution steps.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-5
RELATIVE RECOVERIES OF AROMATIC AMINES IN SPIKED SECONDARY EFFLUENT SAMPLES AT 5 µg/L

Analyte	3-Nitroaniline	4-Chloroaniline	4-Bromoaniline	3,4-Dichloroaniline
Relative recovery (%)	117	109	86	73

TABLE-6
COMPARISON OF THIS WORK TO OTHER METHODS THAT HAVE BEEN USED IN THE AROMATIC AMINES PRECONCENTRATION AND DETERMINATION

Analyte	Sample	Method	[a]LOD (μg L^{-1})	[b]LR (μg L^{-1})	[c]ER (%)	[d]EF	[e]RSD (%)	Ref.
Aniline	Wastewater	[f]DLLME-GC-MS	0.08	0.25-70	69	449	10.6	[28]
p-Chloroaniline			0.04	0.25-70	77	645	8.1	
p-Toluidine	Water	[g]DLLME-HPLC-VWD	1.8	5-5000	–	41.3	4.1	[29]
p-Chloroaniline			1.3	5-5000	–	56.5	4.8	
Anilne	Water and wastewater	[h]AALLME-SFO-DES-GC-MS	0.003	0.011-2000	89	890	4.2	[30]
p-Toluidine			0.006	0.023-2000	94	940	3.9	
p-Chloroaniline			0.0018	0.006-2000	92	920	3.3	
p-Anisidine			0.0024	0.009-2000	86	960	4.0	
4-*tert*-Butyl aniline			0.0053	0.018-2000	79	790	2.6	
Anilne	Water and food	[i]HS-SPME-GC-MS	0.025	0.080-100	–	–	5.2	[31]
p-Toluidine			0.080	0.5-100	–	–	5.6	
p-Chloroaniline			0.060	0.4-100	–	–	6.1	
p-Anisidine			0.070	0.1-100	–	–	4.1	
[j] 4-CA, [k] 3,4-DCA	Tap, rain and mineral water	[n]I*P*-LPME-HPLC-DAD	0.2-0.6	0.6-200	–	–	6.9	[32]
3,4-DCA	River water	[o]HF-LPME-GC-FID	2.2	6.6-1000	–	–	8.2	[33]
[l] 3-NA, 4-CA, [m] 4-BA	Well and river water	[p]SPE-MLC-HPLC-UV	1.0-4.5	3.1-125	–	–	5.1	[34]
4-CA	Wastewater	[q]CE-SPE-LC-MS	2.4	8.0-60	–	–	13.4	[35]
3-NA	Tap, river and ground water	[r]DSD-LLLME-HPLC-UV	1.0	5.0-1500	–	–	4.9	[36]
4-CA, 3,4-DCA	Sewage sludge, soil and sediment	[s]MASE-CSPE-GC-MS	0.1-0.3	0.4-150	–	–	5.8	[37]
3-NA, 4-CA, 4-BA, 3,4-DCA	Hookah and river water	[t]D-μ-SPE-HPLC-DAD	0.1-0.25	0.25-500	–	–	5.6	[38]
3-NA	Wastewater	[u]AuNPs-CPES-HPLC-UV-vis	0.3	–	49	148	16	This work
4-CA			0.5	–	65	195	10	
4-BA			0.7	–	64	193	19	
3,4-DCA			0.6	–	67	200	17	

[a]Limit of detection (S/N ¼ 3); [b]Linear range; [c]Extraction recovery; [d]Enrichment factor; [e]Relative standard deviation; [f]Dispersive liquid-liquid microextraction-gas chromatography-mass spectrometry; [g]Dispersive liquid-liquid microextraction-high performance liquid chromatography-variable wavelength detector; [h]Air-assisted liquid-liquid microextraction based on solidification of deep eutectic solvent-gas chromatography-mass spectrometry; [i]Headspace-solid phase microextraction-gas chromatography-mass spectrometry; [j]4-Chloroaniline; [k]3,4-Dichloroaniline; [l]3-Nitro-aniline; [m]4-Bromoaniline; [n]Ion-pair based surfactant assisted microextraction-high performance liquid chromatography-diode array detector; [o]Hollow fiber liquid phase microextraction-gas chromatography-flame ionization detection; [p]Solid phase extraction-micellar liquid chromato-graphy-high performance liquid chromatography-UV; [q]Cation exchange-solid phase extraction-liquid chromatograph-mass spectrometer; [r]Directly suspended droplet liquid-liquid–liquid microextraction-high performance liquid chromatography-UV; [s]Microwave-assisted extraction combined with continuous solid-phase extraction-gas chromatography-mass spectrometry; [t]Dispersive micro-solid phase extraction- high performance liquid chromatography-diode array detector; [u]Gold nanoparticles coated Polyethersulfone membrane-high performance liquid chromatography-UV-Vis.

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