Preparation and use of maize tassels' activated carbon for the adsorption of phenolic compounds in environmental waste water samples

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Abstract The determination and remediation of three phenolic compounds bisphenol A (BPA), ortho-nitrophenol (o-NTP), parachlorophenol (PCP) in wastewater is reported. The analysis of these molecules in wastewater was done using gas chromatography (GC)×GC time-of-flight mass spectrometry while activated carbon derived from maize tassel was used as an adsorbent. During the experimental procedures, the effect of various parameters such as initial concentration, pH of sample solution, eluent volume, and sample volume on the removal efficiency with respect to the three phenolic compounds was studied. The results showed that maize tassel produced activated carbon (MTAC) cartridge packed solid-phase extraction (SPE) system was able to remove the phenolic compounds effectively (90.84–98.49 %, 80.75–97.11 %, and 78.27–97.08 % for BPA, o-NTP, and PCP, respectively) . The MTAC cartridge packed SPE sorbent performance was compared to commercially produced C18 SPE cartridges and found to be comparable. All the parameters investigated were found to have a notable influence on the adsorption efficiency of the phenolic compounds from wastewaters at different magnitudes.

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Introduction

The quality of water and wastewater streams in the urban settlements has been an issue of concern, thus calling for an increased attention in their monitoring, assessment, and purification. In the recent past, there has been an increase of release of organic compounds such as phenolic compounds mainly bisphenols A, 2, 2 bis (4-hdroxyphenyl) propane (BPA) (contained in polycarbonate plastic and epoxy resin), ortho-nitrophenol (o-NTP) (formed photochemically in the atmosphere from vehicle exhaust), and parachlorophenol (PCP) (generated from phenols in the chlorination of drinking water) into the hydrosphere (Rodríguez et al. 2000; Brossa et al. 2002; Zhao et al. 2010). These chemicals are often used as raw or synthesis intermediate materials in many manufacturing industries such as chemical plants, wood preservative plants, plastics, dye, epoxy, resins, pharmaceutical, oil refineries, textiles, leather industries, paper, and pulp (Jiang et al. 2007; Michailof et al. 2008; Gayatri and Ahmaruzzaman 2010; Mohamed et al. 2011). These compounds find their way into the aquatic environment through direct discharge of industrial wastewater or effluents (Mohamed et al. 2011).

The phenolic compounds that contaminate water systems have been identified to have organoleptic properties, carcinogenic and toxic to both aquatic and human life (Rodríguez et al. 2000; Gayatri and Ahmaruzzaman 2010). They are also known to produce unpleasant odor and taste in drinking water even when present at very low concentration (Rodríguez et al. 2000; Dabrowski et al. 2005). These compounds and their derivatives have been placed among the priority list of pollutant by both European Union and United State Environmental

Protection Agency (USEPA Report 1995; Yan et al. 2006; Uddin et al. 2007). The release of phenolic compounds into the environment has attracted great deal of attention, because of their potential estrogenic activity (Rodríguez et al. 2000; Dabrowski et al. 2005; Peng et al. 2006; Ahmaruzzaman 2008). Therefore, it is necessary to monitor and remove these chemicals from the environment by developing simple and cheap analytical methods.

Several analytical techniques are available for the determination of phenolic compounds which include high-performance liquid chromatography (HPLC) (Puig and Barcelo 1996, 1997; Rodríguez et al. 1996), gas chromatography (GC) (Rodríguez et al. 1996), using a variety of detectors, such as flame ionisation detection (FID) (Rodríguez et al. 1997, 2000; Puig and Barcelo 1996, 1997), and electron-capture detection (Puig and Barcelo 1996; Turves et al. 1996; Burke et al 2003), ion trap mass spectrometry/ mass spectrometry ion trap detection (Eskilssons and Bj rklund 2000; Żwir-Ferenc and Biziuk 2006), mass selective detection (Hengel and Shibamoto 2000), selected ion monitoring (Manirakiza et al 2000), gas chromatography electron capture negative chemical ionization mass spectrometry (Stout et al 1997), liquid chromatography/electrospray ionization mass spectrometry (LC/ESIMS) (Stout et al 1997), liquid chromatography/electrospray ionization tandem mass spectrometry (LC/ESIMS/MS) (Zhao et al 2010; Stout et al 1997), capillary electrophoresis in combination with ultraviolet detection (UV) (Khuhawar et al. 1993; Rodríguez et al. 1996; Turves et al. 1996; Patsias and Papadopoulou-Mourkidou 2000; Carabias-Martínez et al. 2004), fluorescence detection (Rodríguez et al. 1997; Khuhawar et al. 1993), electrochemical detection or mass spectroscopy (MS) (Thurman and Mills 1998; Turves et al. 1996), MS, or microwave-induced plasma atomic emission spectroscopy (Turves et al. 1996; Thurman and Mills 1998; Rodríguez et al. 1997; Turnes et al. 1997), electrothermal atomic absorption spectrometry (Tian et al 2011) . Nevertheless, a preconcentration step is necessary in the analytical scheme, for determination of phenolic compounds, as none of the above-mentioned combinations can achieve quantification limits required for the direct determination of phenolic compounds in drinking or wastewater stream (Rodríguez et al. 2000).

Furthermore, low concentrations of phenolic compounds in real water samples make direct determination difficult. Therefore, suitable sample pre-treatment methods are often employed. To have an ideal sample pre-treatment procedure, the following criteria are crucial for optimum selection (1) the set up should be simple, (2) able to extract the largest number of target compounds, (3) efficient, (4) inexpensive, and (5) compatible with various determination techniques; all these are the basis why these methods move toward simplification (Cai et al. 2003a, b; Zhao et al. 2007, 2010; Zhou et al. 2007a).

Various techniques for sample enrichment for phenolic compounds have been reported and these include liquid–liquid extraction (LLE) which is still being used in the preconcentration step, for determining phenolic compounds in water and wastewater stream (Rodríguez et al. 2000; Zhao et al. 2010). Currently, solid-phase extraction (SPE) and solid-phase microextraction are being considered a better alternative to LLE (Rodríguez et al. 2000). This is due to the drawback presented by LLE which include foaming during the process, difficulties in the automation of LLE procedure, length of time of analysis, and consumption of large volume of organic solvents, making the technique uneconomical and environmentally unfriendly. SPE has been in operation in terms of development and usage for concentration of several pollutants for several decades (Cai et al. 2003a; Zhao et al. 2007; Zhou et al. 2007a; Zhou et al. 2007b). It is very effective as a sample handling technique, resulting in high pre-concentration factors: its simplicity, ease of automation and operation, having low usage of organic solvent, and being less time-consuming (Holadova and Hajšlová 1995; Zhao et al. 2000; Cai et al. 2003b; Zhou et al. 2007a; Zou et al. 2008; Zuo et al. 2009).

However, the choice of adsorbent is another crucial factor in order to obtain higher enrichment efficiency of analytes in SPE. Different types of solid-phase extraction sorbents such as C_{18}, or C_8 silica, (Pocurull et al. 1995; Fritz 1999; Simpson 2000), polystyrene-divinylbenzene polymer (Przyjazny 1985; Brouwer and Brinkman 1994; Pocurull et al. 1995; Rodríguez et al. 1996; Fritz 1999; Simpson 2000; Cai et al. 2003a), carbonaceous sorbents (Bacaloni et al. 1980; Rodríguez et al. 1997; Fritz 1999; Simpson 2000), and carbon nanotubes have been employed for the purpose of enrichment (Cai et al. 2003a). C_{18} has been the most widely used but shows low recovery for some polar analytes such as phenolic compounds (Pocurull et al. 1995; Fritz 1999; Simpson 2000; Cai et al. 2003a).

Activated carbon (AC) from lignocellulosic materials, especially that agricultural wastes residue-produced AC are renewable, abundant, readily available, and inexpesive, have attracted more attention in the recent time, due to their large surface area and pore diameter in environmental field application (Zuo et al. 2009; Zvinowanda et al. 2009; Demiral et al. 2011; Olorundare et al. 2012). This is due to their low cost and easy availability compared with other adsorbents. Annually, farming and agricultural processes generate millions of tonnes of these waste residues such as agro-based adsorbents (Srihari and Das 2008), almond shell (Marcilla et al 2000), banana peel (Achak et al 2009; Castro et al. 2011), carbonaceous adsorbent (Ioannou and Simitzis 2009), corn cob (Njoku and Hameed 2011; Ioannidou and Zabaniotou 2007; El-Hendawy et al. 2001; Tsai et al. 1998; Wu et al 2001), corn stover and oat hull (Fan et al 2004), corn hull (Zhang et al. 2004), cotton stalk (Putun et al 2005), date stone AC(Alhamed 2009), maize

tassel (Olorundare et al 2012), mungbean coat (Tian et al 2011), olive waste cake (Bacaoui et al. 2001), rattan saw dust AC(Hameed and Rahman 2008), rice husk (Nassar et al 2008; Yalcin and Sevinc 2000), vetiver root AC (Altenor et al 2009), etc., which have all been employed as precursor in AC production. The main advantage of these materials is their suitability for routine adsorption of pollutants due to their low consumption and cost.

From the above-mentioned facts, activated carbon from maize tassel maybe of great analytical potential as an effective SPE sorbent for extraction of some suitable compounds such as phenolic compounds. However, to the best of our knowledge, there have been no report on the usage of maize tassel produced activated (MTAC) carbon for phenolic compounds enrichment or preconcentration from aqueous solution. In this study, the applicability of MTAC as packing adsorbents for SPE was investigated using three phenolic compounds, BPA, o-NTP, and PCP as model compounds.

Experimental section

Experimental method

Chemical reagents and standards

All the phenolic compounds, BPA (>97 % purity), o-NTP (>98 % purity), and PCP (>99 % purity) were of analytical grade and obtained from Sigma-Aldrich (St Louis MO, USA). The standard stock solutions (100 mg/L) containing these compounds were prepared in methanol and stored at 4 °C. The working solutions were freshly prepared on daily basis by the appropriate dilution of the stock solution with deionized water. Acetic acid (96 % purity) and ammonia solution (25 %) were used to adjust pH values of the working solutions and were obtained from Associated Chemical Supplies Ltd, Fluka Analytical (Buchs, Switzerland) and Rochelle Chemicals Ltd (Johannesburg, South Africa). All the glassware were decontaminated overnight using 6 mol L^{-1} nitric acid and thoroughly washed with deionized water before use. Strata™ polypropylene C18-E SPE (EC) cartridges (0.5 g, 6 mL) were purchased from Phenomenex, Torrance, CA, USA.

Instrument

The chromatographic separations were performed using a LECO Pegasus® 4D GC×GC time-of-flight mass spectrometry (TOFMS) instrument (LECO Corporation, 3000 Michigan, USA). A Restek GC column (Rxi®-5 ms (crossbond is 5 % diphenyl/95 % dimethyl polysiloxane) 30 m, 0.25 mm ID, 0.25 μm df with max temperature, 340 °C min bleed at 320 °C, and second dimension column
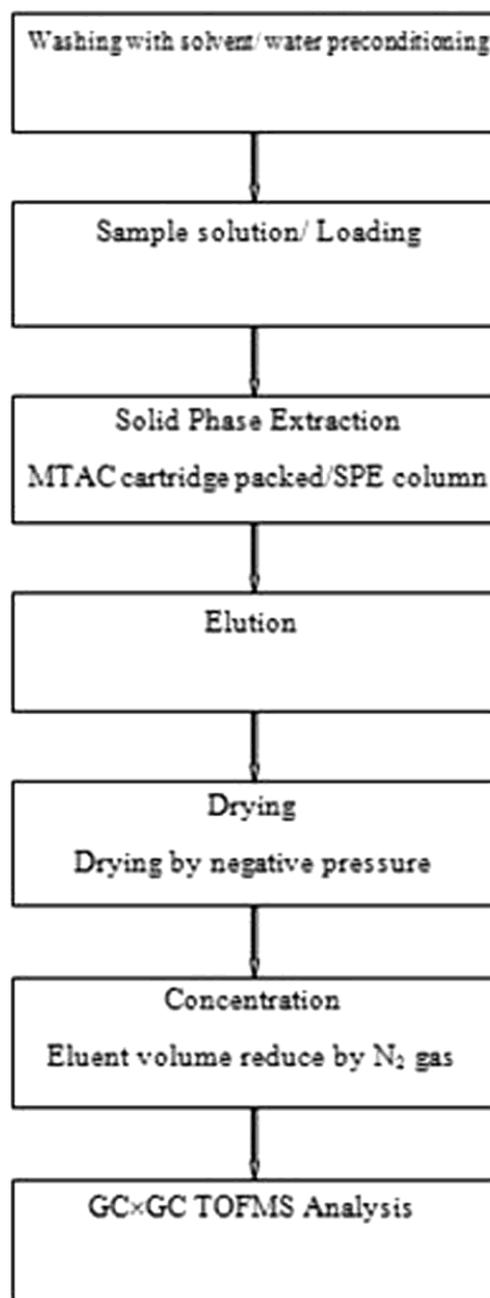

Fig. 1 Sample flow analysis during SPE extraction process

(Rtx®200 2m, 0.18 mm ID, 0.18 μm df with maximum programme temperature 350 °C min, bleed at 330 °C) were used for all separations.

Sample preparation

In this experiment, the sorbent used for cartridge packing MTAC was produced by chemical method according to Olorundare et al. (2012). An aliquot of 20 g of the milled maize tassel powder was added to 20 mL of phosphoric acid solution (85 % by weight) and manually stirred for

Fig. 2 SEM image of MTAC powder
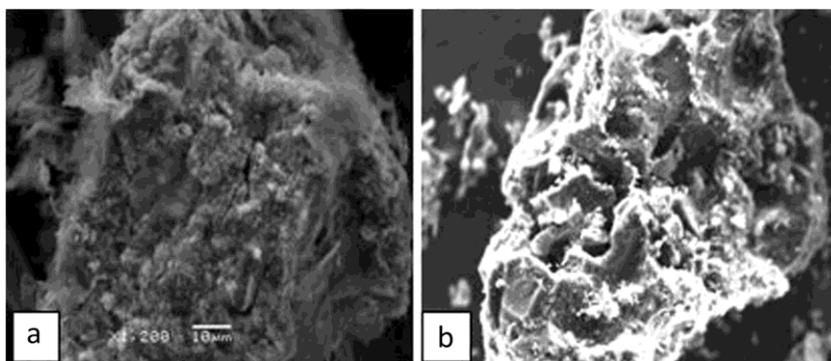
few minutes and left to stand for 1 h. The impregnated materials were dried at 110 °C for 24 h and then activated at 500 °C under an inert atmosphere, i.e., nitrogen flow at 200 $cm^3 \cdot min^{-1}$. The produced activated carbons were coded as MTAC. The residual phosphoric acid was eliminated from the activated carbon by washing with hot deionized water until the pH of the leachate was between pH 5 and pH 6, after which the powder was dried at 110 °C for 3 h; the final material was then ground and stored for further analysis. The MTAC used was the one with highest BET surface area.

The MTAC prepared was characterized by using nitrogen adsorption/desorption isotherm measured at 77 K using ASAP 2020 Micrometrics instrument for the BET surface area at relative pressure range ($P/P_o = 0.05-0.3$) and total pore volume at relative pressure of 0.995. The surface morphology of the sorbent MTAC was determined using scanning electron microscope (SEM) (Nano 2000 High resolution SEM (HRSEM), Jeol, Japan) which gives rough ideas about the porosity of the material. Two water samples were selected

from local dam situated in Johannesburg city. Before application, all the environmental water samples were filtered through 0.45 µm micropore membranes filter and stored under low temperature.

Solid-phase extraction cartridge

The SPE commercial cartridge was replaced with an MTAC packed cartridge which was prepared by modifying a Strata™ C18-E SPE C_{18} (EC) (0.5g, 6 mL) cartridge. The C_{18} packing of the cartridge was evacuated, and then 0.5g of MTAC was packed into the cartridge. The 20 µm polypropylene lower and upper frits remained at each end of the cartridge to serve as support holder for MTAC packing. The outlet tip of the cartridge was connected to a vacuum pump (Shimadzu, Japan), and the inlet end of the cartridge was connected to PTFE suction tube whose other end was inserted into sample solution. The entire solid-phase extraction setup assembly was carefully washed with

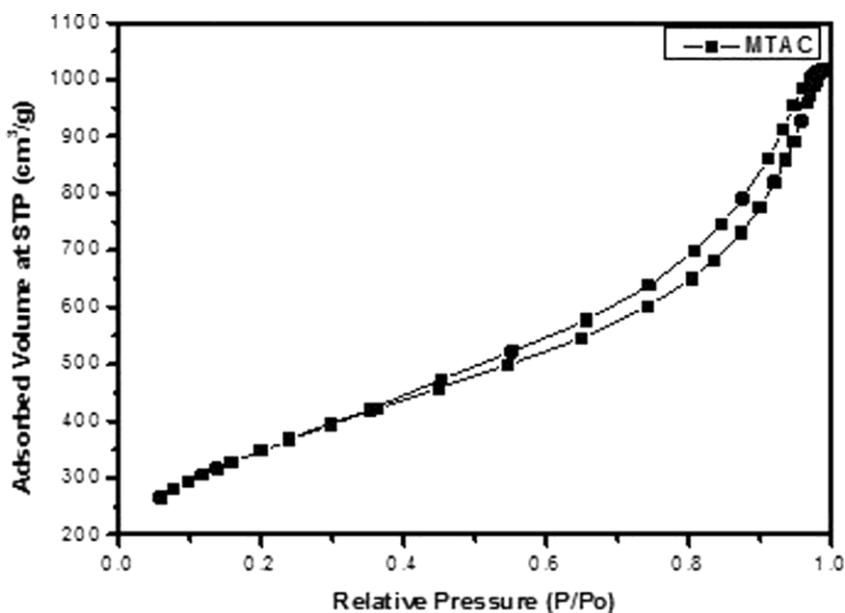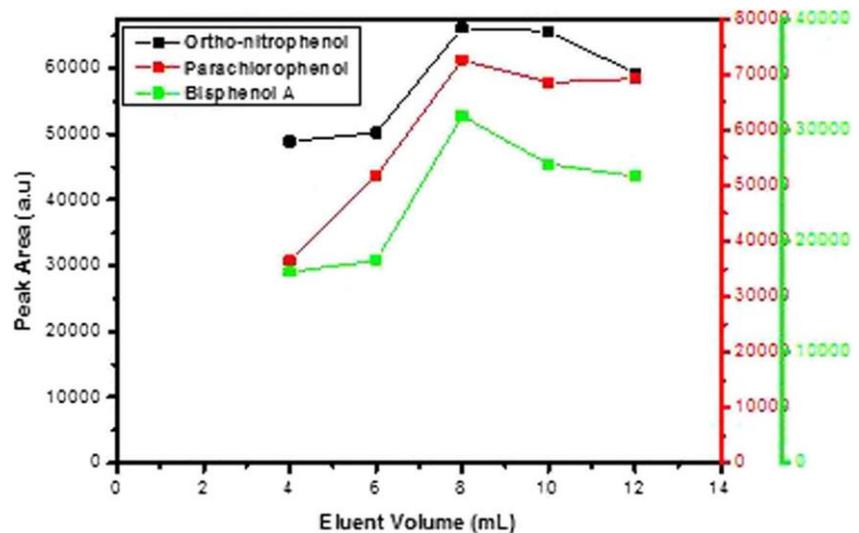Fig 3 Adsorption/desorption isotherm of N2 at 77 K on MTAC

methanol before use in order to reduce the interferences of the organic and inorganic contaminants.

Procedure for SPE extraction

Before the preconcentration enrichment step (Fig. 1), the MTAC packed cartridge was firstly preconditioned by washing with 6 mL of methanol, and then 10 mL of purified water was added before a new SPE preconcentration procedure started. The pH of samples was adjusted accordingly with 1 mL of acetic acid or ammonia solution. Then a known volume of spiked water samples was aspirated through the modified SPE C18 column at controlled flow rate, and the eluate obtained was discarded. However, when the whole sample had passed through the SPE column, 10 mL of purified water was used to clean the impurity or the co-adsorbed matrix materials from the cartridge. The SPE column was then

dried by negative pressure for 10 min, and the targeted analytes were eluted with optimum volume of methanol. The resulting eluate was later air-dried with gentle flow of nitrogen gas to 1 mL before subsequent determination by injecting 2 μL of the final eluate into GC×GC TOFMS.

Results and discussion

Physical characterization of MTAC

Scanning electron microscopy (SEM) studies

In order to study the morphology and porosity development of MTAC prepared, SEM was employed. The SEM results reveal that MTAC is characterized with distinct cells and
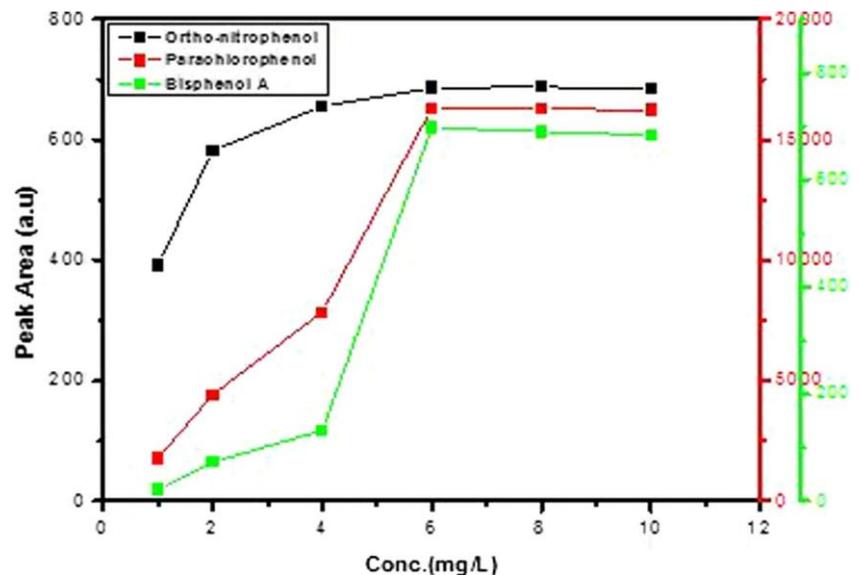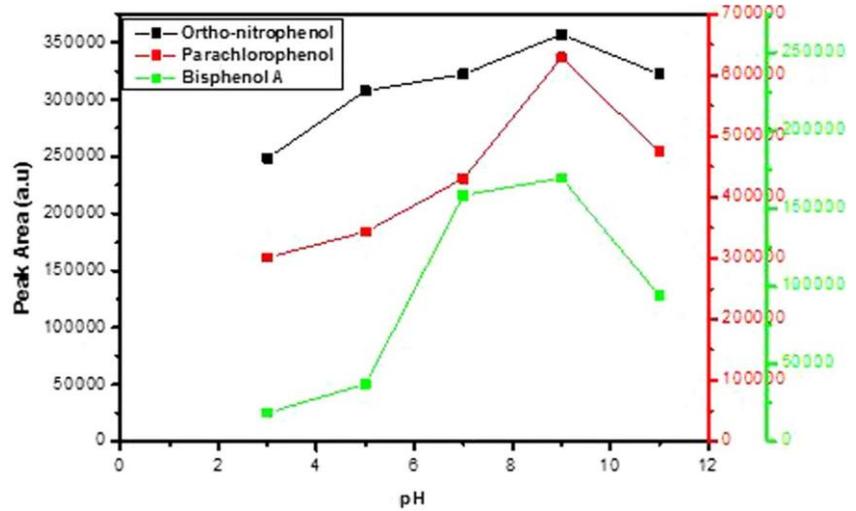
Fig. 6 Effect of sample pH on the adsorption of phenols by MTAC. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scale

specific surface structure. The SEM images of the MTAC at high magnification are shown in Fig. 2a, b, and from the micrograph presented, wide pores can be observed with characteristic spongy surfaces. The micrograph shows the changes in the microstructure of maize tassel after being impregnated with phosphoric acid and subsequent isothermal holding at 500 °C. It was observed that there was pore enlargement on the surface of AC produced (Fig. 2b), while its original cell structure is completely preserved (Fig. 2a). It could also be seen that a closer look on AC surface (Fig. 2b) revealed that the large pores on the surface are connected with smaller pores, thus forming a whole network in the interior of the carbon material.

BET N$_2$ adsorption

However, identifying the pore structure of an adsorbent is a crucial factor in adsorption process, and inert gas adsorption is a good method using adsorption instrument for this function

(Ruthven 1984; Geundi 1997). Figure 3 shows the isotherms of N$_2$ adsorption/desorption at 77 K on the MTAC. The isotherm for the MTAC overlap completely at low relative pressure, but the hysteresis exists at high relative pressure (P/P$_o$>5), irrespective of the precursor source. The factor such as the presence of the 'inkbottle types of pores' and slit-shaped pores are major influences on the types of hysteresis produced (Ruthven 1984; Geundi 1997). Furthermore, a common feature to hysteresis loops is that the steeps region of desorption branch leads to the lower closer point at a relative pressure for a given adsorption, which also depends mainly on the nature of the adsorption rather than the nature of pores adsorbent (Sing et al 1985; Wu and Tseng 2005). Thus, this explains the reason for large pores and high BET surface area of about 1,263 m^{2}g^{-1} and total pore volume of 1.54 cm^{3}g^{-1} on MTAC. The pore diameter also play crucial role in phenolic compounds adsorption, because the smaller the pore diameter, the larger the available surface area for adsorption. This factor came into play, for example, when substance such as humic

Fig. 7 Effect of sample volume. The graphing was on the first and secondary y axis in order to accommodate the value differences, which needed different scale
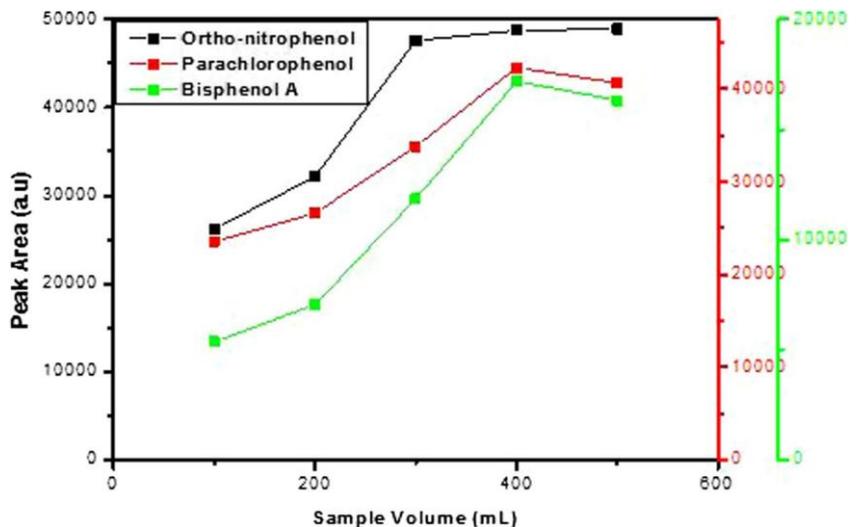
Table 1 Analytical performance of the proposed enrichment/extraction procedure

Analytes	Calibration equations	Linear correlation coefficients (r^2)	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)
o-Nitrophenol (ONPT)	$Y = 4.1e^{+05x} - 2.93e + 05$	0.993	0.0593	0.1779	1.648
p-Chlorophenol (PCP)	$Y = 3.01e^{+07x} - 3.01e + 07$	0.997	0.0559	0.1577	1.561
Bisphenol A (BSP A)	$Y = 2.01e^{+06x} - 1.01e + 06$	0.984	0.0622	0.1866	1.709

acid, which may interfere with phenolic compounds adsorption in later analytical process, will be prevented from entering the pore matrix (Rodríguez et al 2000).

Evaluation of MTAC as solid-phase extraction adsorbent

To determine the analytical potential of MTAC as sorbent in SPE, BPA, o-NTP, and PCP were adopted as a model samples. In this experiment, there are few parameters that may influence the enrichment efficiency, including initial concentration, pH of the sample solution, sample volume, the eluent, and its volume. All these parameters were critically investigated, because they play important role in the concentration of the target analytes. And also, they have impact on the optimization of the adsorption efficiency.

Influence of eluent types and volume on the MTAC adsorption capacity

In achieving the above goal, four types of eluates including acetone, acetonitrile, dichloromethane, and methanol were experimentally tested. The results showed that BPA was the least eluted one among the analytes. It was difficult to elute BPA with dichloromethane. The difficulty in elution has to do with different the behavior of phenolic compounds in terms of acidity and polarity (Rodríguez et al 2000). This could also be due to

difference in pKa and octanol-water partition coefficient log K_{ow} between the three analytes which influences the mobile phase for all the three analytes differs (Rodríguez et al 2000). However, methanol was found to elute all the three analytes effectively. This is because methanol is a water-miscible solvent which can enhance the hydrophobic surface of the sorbent and also helps in the partitioning process, which involves the differences in solubility of the analytes between the aqueous and the solid polar phase (Rodríguez et al 2000; Zhao et al 2010). Therefore, methanol was used in this study as eluent. The volume of methanol used was also investigated, and the results show that optimal recoveries were achieved when the volume of methanol was 8 mL (Fig. 4), after varying the volume between 4 and 12 mL. Thus, 8 mL of methanol was then used throughout this experiment. Methanol has the optimum elution at 8 mL because there is high mass transfer between water and the sorbent at this methanol volume. Methanol has more than 90 % recovery for all of the analytes at this volume. However, from Fig. 4, it was observed that increase in volume of methanol increased the recovery of the analytes from 4 to 8 mL. When the volume of methanol is greater than 8 mL, there was a slightly reduction on the recovery of all the three analytes; this might me due to reduction in mass transfer efficiency at volume greater than 8 mL (Rodríguez et al 2000).

Table 2 Analytical results of phenolic compounds in river and tap water samples using MTAC packed cartridge

Analytes	Tap water			River 1			River 2		
	Real (ng/mL)	Added (ng/mL)	R^b (%)	Real (ng/mL)	Added (ng/mL)	R^b (%)	Real (ng/mL)	Added (ng/mL)	R^b (%)
(O NTP)	BDL[a]	10	97.55	0.2895	10	97.11	0.1056	10	89.44
	BDL[a]	100	95.67	0.4740	100	95.26	0.1925	100	80.75
(PCP)	BDL[a]	10	97.84	0.2916	10	97.08	0.1966	10	80.34
	BDL[a]	100	94.99	0.5674	100	94.33	0.2173	100	78.27
(BSP A)	BDL[a]	10	98.83	0.0191	10	98.08	0.0813	10	91.87
	BDL[a]	100	98.43	0.0505	100	98.49	0.0916	100	90.84

[a] Below detection limit
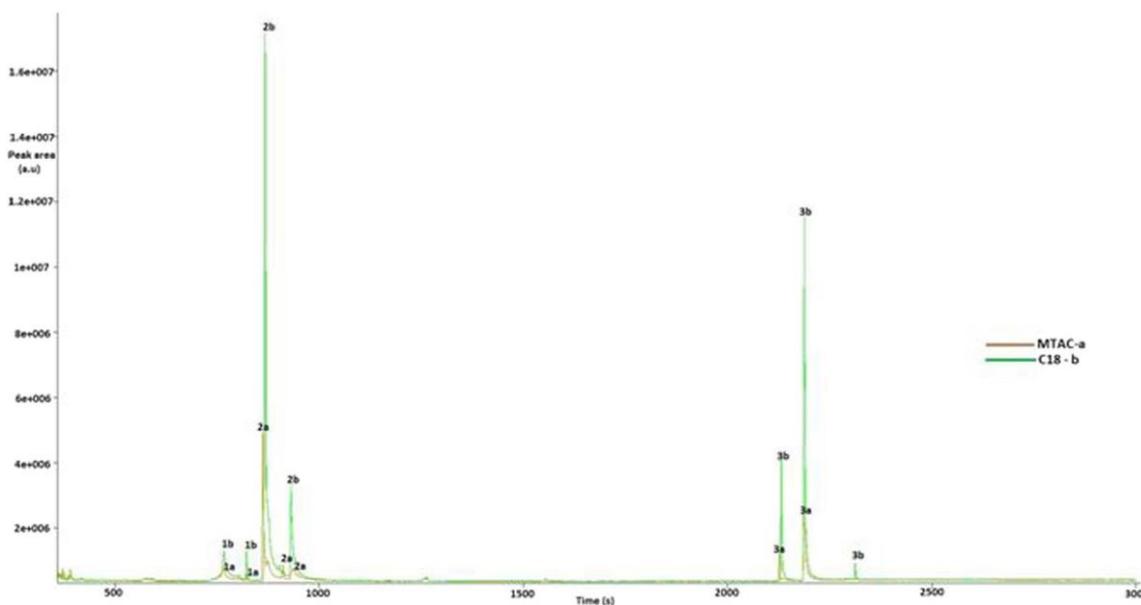
[b] Recovery percentage

Fig. 8 GCTOFMS chromatogram of environmental samples containing the phenolic compounds with both MTAC-a and CI8-b SPE result. Peaks: A MTAC; 1a o-NTP, 2a PCP, and 3a BPA while Peaks: B C18 SPE; 1b o-NTP, 2b PCP, and 3b BPA

Influence of initial concentration

The influences of initial concentration play a significant role in the adsorption of phenolic compounds onto MTAC sorbent. Figure 5 shows the amount of analytes adsorbed for all the three phenolic compounds. The results show that, among all the analytes, PCP has the highest extraction shown by the peak area, while the least extractive analyte was BPA. It was observed that an increase in initial concentration of the solute results in increasing uptake of all the solutes. This is more pronounced in PCP than others due to the fact that increasing the initial concentration generally increases the overall mass transfer driving force between the solid and liquid phase of the adsorbate (Banat et al 2000; Mohamed et al 2011), thus leading to an increase in the interaction between the adsorbent and the adsorbate, which consequently enhances the adsorption process (Banat et al 2000; Dabrowski et al 2005; Michailof et al 2008). Furthermore, the bonding between adsorbent and water must be broken first before adsorption can take place, and also, greater solubility provides stronger bonding between the adsorbate and adsorbent (Weber 1985) which explains why BPA is the least adsorbed among all the analytes.

Influence of sample solution pH

The sample solution pH also plays important role in SPE procedure, because the pH values of the solution reveal the analyte's state and also the target analyte's extraction efficiency.

In this study, sample pH range of 3 to 11 was investigated. The difference in the extracted amounts by means of peak area versus sample pH was shown in Fig. 6. The maximum enrichment efficiency was achieved with a sample solution pH of 9. pH above or below this value resulted in decrease in extraction efficiency; this might be due to the pKa value of the three compounds which also may decompose in either acidic or alkaline condition (Weber 1985; Rodríguez et al. 2000; Dabrowski et al. 2005). The adsorption capacity for all the three analytes increases with pH values. The pH values of water constitute a major influence on the adsorption capacity of compounds that can be ionized (Myers and Zolandz 1981). The increase in the pH value is because of the alkali species of the solution produce changes on the carbon surface by reacting with the surface functional groups (Cai et al. 2003a; Zhao et al. 2010).

By considering the pKa values of the solutes and taking it into account, it is expected that electrostatic interaction between adsorbent and adsorbate was not dominant in adsorption process. But, in this case, the adsorption of o-NTP is controlled by the dispersive interaction between the π electron of the aromatic ring of the analytes and those of the graphene layers of the carbon surface of AC (Rodríguez et al 2000; Alvarez et al 2005). This is because the presence of electron-donating groups on the ring of the hydroxyl group of phenolic compounds would lead to higher adsorption of energy while the electron-withdrawing groups would lead to lower analyte affinity for AC. Thus, the order of affinity for adsorption capacity is PCP>o-NTP>BPA. A similar result was reported by Alvarez et al. (2005). This result confirms an earlier observation.

Table 3 Comparison of analytical performance and represented methods with other methods for the determination of phenolic compounds

Sorbents	Volume (mL)	Method	Analytes	Recoveries (%)	LOD (ng/mL)	LOQ (ng/mL)	RSD (%)	Technique	References
βCD-BIMOT-TDI	15	SPI	2CP, 2NP, DCP, 4CP, 4CMP, TCP	87–116	0.23–0.35	0.79–1.18	0.1–1.7	GC-FID	Raoov et al. 2014
C18, C18, membrane extraction disk, PS-DVD	250	SPE	Ph, 2CP, 2,4,6 TCP, 2,4DMP, 4C-3MP, 2,4DCP, PCP	C18(35–86) C18D(58–83) PS-DVB(70–1080)	0.03–0.12 0.01–0.05 0.01–0.1	–	C18(3–13) C18D(4–13) PS-DVB(5–12)	LC-ED	Galceran and Jauregui 1995
Empore disk, bond elute certify	15	SPE	Bisphenol A BSP A	Water (83.8 - 98.2) Serum (79.0 - 87.3)	0.01 0.02	0.01 0.05	3.4–6.1 5.1–13.5	HPLC-ED	Inoue et al. 2000
Chemically modified polymeric resin with o-caboxyl moiety	100	SPE	Ph, 4NP, 2,4DNP, 2CP	41–85	0.3–0.6	–	3–6	HPLC	Masque et al. 1998
Chemically modified polymeric resin with an acetyl group (PS-DVB)	100	SPE	Ph, 4NP, 2,4NDP, 2CP, 2NP, 2,4DMP, 2M-4,6-DNP, 4C-3-MP, 2,4-DCP, 2,4,6TCP, PCP	56–99	0.2–0.6	–	3–5	LC-UV LCFLD	Masque et al. 1997
			Res, catec, orcinol, Ph, 4NP, guaiacol,2,4dnp	4–86	0.2–0.6	–	8–18	LC-UV LC-FLD	Masque et al. 1997
Polypyrrole (PPy) polymer	25	SPE	Ph, 2CP,4CP, 2,4DCP, 2,4,6TCP	84–96	0.16–0.15	–	2.8–6.9	RPLC-UV	Bagheri et al. 2004
MWCNT-CN	200	SPE	4CP, 1Naphthol, 2Naphtol,2,4DCP	83.43–103.13 80.28–91.46	0.08–3.00	0.27–10.00	1.47–5.69 2.50–9.62	HPLC-UV	Gao et al. 2012
BAC	100	SE	BSP A, TBB A	80.5 - 119.8	0.01–0.01	–	6.2–8.3	LC-ESI	Zhao et al. 2010
BAC	200	SPE	BSP A, N-Ph, OC-Ph	79.5 - 104.3	0.17–0.37	–	3.0–5.5	MS/MS HPLC-UV	Zhao et al. 2009
MWNT	500	SPE	BSPA 4n-N-Ph, 4tert-OC-Ph	89.8–104.2	0.018–0.083	–	5–8	HPLC-FLD	Cai et al. 2003a, b
MWNT	200	SPE	4CP, 3CP, DCP, TCP, PCP	88–109	0.08–0.8	–	5–8	HPLC	Cai et al. 2005
MTAC	100	SPE	Bisphenol A, parachlorophenol, ortho-nitro phenol	94.33 - 98.49	0.055–0.062	0.17–0.19	1.56–1.71	GC×GC TOFMS	This study

CP chlorophenol, NP nitrophenol, DCP dicholopenol, TCP trichlorophenol, CMP choromethylphenol, Ph phenol, DMP dimethylphenol, MP methylphenol, DNP dinitrophenol, C-MP chloromethylphenol, PCP pentacholophenol, NP nitrophenol, M-DNP methyl-dinitrophenol, PC para-cresol, TMP trimethylphenol, MWCNT-CN cyano-functionalized carbon nanotube, MWNT multiwalled nanotube, MTAC maize tassel activated carbon, BAC bamboo activated charcoal, PS-DVB polystyrene–divinylbenzene polymer, BPA bisphenol A, TBBA tetrabromobisphenol A, βCD BIMOT-TDI beta cyclodextrin ionic liquid polymer, Res resorcinol, Catec catechol, N-Ph nonyl phenol, OC-Ph octylphenol

Influence of analyte nature

Generally, AC is majorly hydrophobic and displays strong affinity for organic molecules with a partial solubility in water. Thus, compounds which are hydrophilic are less adsorbed than those that are hydrophobic, because hydrophobic compounds will tend to be pushed to the adsorbent surface. This explains why PCP and o-NTP, which are hydrophobic compounds, tend to adsorb better than BPA which is hydrophilic (EPA Report 1995; Moreno-Castilla et al. 1995; Rouquerol et al. 1999; Bansal 2005).

Influence of sample volume

The sample volume is another important parameter that influences the sensitivity of the SPE method. To investigate its influence, a sample volume in the range of 100–500 mL spiked with purified water was investigated and optimized. Figure 7 shows the result of sample volume. It was found that the increasing sample volume has obvious influence from 100 to 400 mL, after which there was no significant increase on the recovery of the analytes. Sample volume for 400 mL was adopted as the sample volume to reduce extraction time based on the excellent adsorption properties of MTAC; the results were shown in Fig. 7. The extraction of PCP and o-NTP was similar to that of BPA, but smaller in terms of the peak area when compared with the other two analytes.

However, during the enrichment process, it was observed that the analytes were well retained by the sorbent (MTAC) and not eluted by water. The removal of interferences was done by proper washing before the elution stage, and this enhanced the sensitivity of the analytes without much background noise. There is non-polar interaction between the MTAC sorbent and the analytes. This is because the analytes have non-polar structure that can be adsorbed onto the non-polar MTAC sorbent via Van-der-Waal forces. This potential interaction enables the analytes to be retained and subsequently eluted (Gao et al. 2012; Zhao et al 2009, 2010; Rodríguez et al. 2000). The retention of organic analytes through adsorption is essentially an exchange process; hence, molecules are retained not only because they are attracted by the sorbent but also by the solution rejection (Moreno-Castilla et al. 1995; Rodríguez et al 2000; Alvarez et al 2005).

Application

Analytical performance and real sample analyses

The optimum conditions revealed the limit of detection (LOD), limit of quantification (LOQ), and repeatability (relative standard deviation (RSD)) for the extraction/enrichment procedure as shown in Table 1. The linearity was observed over the range of 10–100 ng/mL for all the analytes. The linear correlation coefficient (r^2) ranged from 0.984 to 0.997. The limit of detection was based on signal-to-noise ratio of 3, and this ranged from 0.056 to 0.062 as shown in Table 1.

In order to validate the feasibility of this method used in this study to analyze these three compounds BPA, o-NTP, and PCP, the performance of the method was evaluated with two environmental water samples from a local dam with more than one river serving as its feeders. Tap water was also employed for validation purposes under optimum conditions as shown in Table 1. It was discovered that there were no peaks at the related location for tap water sample solution, while the two river waters showed some peaks in the sample solution. In order to show the merit of this method, the environmental water sample was spiked with the three compounds, at 10 and 100 ng/mL, even though the MTAC was reused more than 20 times; a good spiked recovery (78.27 to 98.49 %) was achieved for the entire river water samples as shown in Table 2.

Comparison of the enrichment performance

The enrichment performance comparison between MTAC and C18 was performed using two environmental river water samples. The optimal conditions for the recoveries of the spiked water samples were obtained at the highest peak area for all the compounds. The results are shown in Fig. 8. It was observed that good recoveries were obtained for all the analytes employed on packed MTAC cartridge. Figure 8 reveals that MTAC was as effective as C18 cartridge for all of the analytes used. The comparison with other reported studies (Table 3) show that MTAC cartridge packed recoveries from the environmental water samples are satisfactory. This result also shows that packed MTAC cartridge has great advantage as SPE adsorbent on extraction of BPA, o-NTP, and PCP.

Conclusion

This study describes a cheap and simple method of analysis of BPA, o-NTP, and PCP in an environmental sample. The method was based on SPE and GC×GC TOFMS. MTAC, activated carbon produced from agricultural waste residue, is a cheap and an excellent material that can be employed in SPE column for enrichment of BPA, o-NTP, and PCP. This method allows concurrent determination of multiples phenolic compounds without complicated protocols. MTAC packed cartridge can be reused as many times as possible.

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