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Review

Studies on the occurrence and quantification of phenolic endocrine disruptors in water

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Global climate change has resulted in increasing advocacy for sustainable development. With continuing decline in freshwater resources, our generation is confronted with challenges in the wise use of this important natural resource. Population growth, urbanization, industrial development and associated changes in agricultural and other land use practices are inevitable activities for economic growth. Unfortunately, each of these either depletes (the quantity) or reduces the quality of freshwaters. An important class of pollutants in waters are endocrine disruptors which include phthalates, phenols and some metals. Phenols are particularly important because of their many exposure routes to man and the environment. The need to regularly assess these impacts and possibly, minimize them therefore, becomes imperative. This paper therefore reviews the different routes of phenols to man and the aquatic environment; their analysis as well as different abatement studies in water.

Key words: Abatement, endocrine disruptors, phenols, pollution, quantification.

INTRODUCTION

The human endocrine system, also known as the hormonal system, controls essential body functions ranging from gender differentiation during foetal development to the 'adrenalin rush' of extreme sports. The endocrine system is one of the major systems in the human body. It uses molecules called hormones to send signals to regulate sexual development, metabolism, puberty, a woman's menstrual cycle, bone growth and a host of other body functions (Vogel, 2004). Some chemicals while posing no direct threat to humans and wildlife, still pose an indirect threat by interacting with the endocrine system of the organism leading to unnatural, untimely and perhaps excessive release or suppression of hormones, a phenomenon known as endocrine disruption (Vogel, 2004).

Recently, there has been growing concern about the presence of this group of chemical compounds with endocrine activity in aquatic environments because of their adverse effects on humans and wildlife species (Kim et al., 2000;Segner, 2005; Sumpter, 2005; Mauricio et al., 2006; Game et al., 2006; Xue and Xu, 2006; Hecker and Giesy, 2008; Shin et al., 2007). An endocrine disruptor is an endogenous reproductive developmental toxicant that causes adverse health effects in an intact organism, or its progeny, secondary (consequent) to changes in endocrine activity (Vogel, 2004). On the other hand, a potential endocrine disruptor is a substance that possesses properties that might be expected to lead to endocrine disruption in an intact organism (Fenner-Crisp et al., 2000; Falconer et al., 2006; Gelbke et al., 2007).

Endocrine disrupting chemicals (EDCs) have also been described as a large and varied group of chemicals that are able to cause endocrine-mediated abnormalities in invertebrates, fish, avian, reptilian and mammalian species (Ferraz et al., 2007). Other deleterious health effects of these chemicals on wildlife and humans include dermal toxicity, immunotoxicity, carcinogenicity, neurobehavioural abnormalities, altered or reduced sexual behaviour, attention deficit/ hyperactivity disorder, altered thyroid and adrenal cortical function, pathological changes to the spleen, damaged digestive systems, amongst others (Vogel, 2004; Game et al., 2006; Xue and Xu, 2006; Dmitruk et al., 2008).

Endocrine disruption has been an overtly recognised issue since about 1992. Although, it has been known since the 1930's and even earlier that exogenous substances are capable of interfering with the endocrine sys-

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tem (Matthiesen, 2000). Researchers were first alerted to aquatic contamination by EDCs through obser-vation of a variety of reproductive changes in different species of fish and molluscs sampled immediately downstream of a sewage treatment plant outfall (Falconer et al., 2006).

The increasing concern about the possible impacts of exposure to these environmental chemicals has necessitated development of new guidelines for the screening and testing of potential EDCs in vertebrates (Hecker and Giesy, 2008). This becomes imperative because most EDCs are not readily degraded in the body, with high residence periods and so, may cause serious problems related to bioaccumulation in higher trophic level organisms (Kim et al., 2000; Dmitruk et al., 2008). Apart from known EDCs, numerous new chemicals are conti-nuously being synthesized and released into the environment with unforeseen consequences (Ferraz et al., 2007). Phenol and its derivatives however, have been identified as EDCs and are currently on EPA priority pollutants list. Therefore, this paper aims at reviewing in part, sources and effects of phenolic compounds on man and the environment; their quantification and abatement in waters.

Phenols as endocrine disruptors

Phenols have been defined as hydroxyl derivatives of benzene and its condensed nuclei (Toniolo et al., 2007). Phenol and its derivatives are aromatic molecules containing hydroxyl, methyl, amide or sulphonic groups attached to the benzenoid ring structure (Huang et al., 2007). These compounds are produced *in situ* as chlorination by-products of municipal water and from degradation of other chemicals. They are toxic, persistent and very difficult to remove from the environment (Chaliha et al., 2008).

Phenols (and other EDCs) have been reported to exhibit disruption activities by either of three ways. First, as a consequence of their molecular structure, they may bind to hormone receptors thereby mimicking or antagonising the action of the natural ligand (Barcelo and Kettrup, 2004; Vogel, 2004). It is also possible for the chemicals to indirectly affect concentrations of hormones by altering their synthesis or metabolism. And lastly, by interfering with signals between different components of the hypothalamus-pituitary-endocrine gland axes (Dawson, 2000).The modes of action of these chemicals through the endocrine system typically lead to toxicity in specific endocrine target organs (Gelbke et al., 2007).

Occurrence of phenols in water

Phenols constitute an important class of contaminants which may occur in surface water or groundwater because of its solubility and volatility (Schmidt-Baumler et al., 1999; Amiri et al., 2004). Phenols may occur in domestic and industrial wastewaters, natural waters and potable water supplies (Toniolo et al., 2007). Some of these chemicals are used as pesticides, and remain as residues in fresh and processed food we eat. Other common sources of exposure that contribute to our total toxics load drinking water, lawn chemicals, consumer products, household insecticide use, plasticizers, etc. (Scippo et al., 2004; Vogel, 2004).

Phenols are widely present in our environment. They occur in nature as building blocks of plants and have several industrial applications (Baltussen et al., 1999). The presence of phenol and phenolic compounds in water has been of great public concern due to their widespread use, high toxicity and persistence (Gupta et al., 1998; Liao et al., 2006; Habibi-Yangjeh and Esmailian, 2008; Schmidt-Baumler et al., 1999; Kartal et al., 2001; Suliman et al., 2006). It is one of the most frequent contaminants in food, water and hazardous waste sites.

Phenols are used in large quantities in the production of plastics, plasticizers, drugs, dyestuffs, explosives, pesticides, detergents, stabilizers and antioxidants (Schmidt-Baumler et al., 1999; Gabriel et al., 2007). They are introduced into surface waters from industrial effluents such as those from coal tar, gasoline, plastic, rubber proofing, disinfectant, pharmaceutical, agricultural run-offs, chemical spills, steel industries, domestic waste-waters, wood preserving plants, brake and clutching industries, biocides application, etc. (Gupta et al., 1998; Chaliha et al., 2008; Sulisti et al., 1996; Amiri et al., 2004; Huang et al., 2007; Hartung et al., 2007). These com-pounds which are generally traceable to industrial effluents and landfills display a low taste threshold in potable waters and also may have a detrimental effect on human health at fairly high levels (Toniolo et al., 2007). Phenols can cause bad taste and odour in drinking water even at low concentration. Apart from anthropogenic emissions, phenolic residues can be formed naturally during decomposition of wood and leaves (Makoi and Ndakidemi, 2007; Schmidt-Baumler et al., 1999). Some phenolic compounds have been found to accelerate tumour formation (Gupta et al., 1998; Suliman et al., 2006).

The increasing quantities and types of industrial wastes generated require effective handling to minimise public health and environmental hazards. The problems which have resulted in the past from disposal of industrial affluents have related to their mismanagement (Sulisti et al., 1996).

Furthermore, associated adverse environ-mental and health effects of phenols have necessitated legislations in many jurisdictions worldwide on set limits for the maximum content of phenols in wastewaters (Toniolo et al., 2007; Hartung et al., 2007).

Analytical methods for quantification of phenols in water

Without appropriate tools, it will be impossible to investi-

gate the fate and behaviour of emerging pollutants at the wastewater treatment plants and receiving waters. In this sense, analysis of organic pollutants, including phenols, in wastewater is complex basically due to the variety of physicochemical and toxicological properties of compounds included in the same group, like pharmaceuticals (Barcelo and Petrovic, 2006). The necessity for the development of standard procedures for chemical analysis, risk assessment of compounds, which is more urgent for emerging contaminants, cannot be overemphasized. There is also the need for inter-comparison studies to validate the analytical protocols being used.

Few analytical methods for environmental monitoring that are fast, low-cost and continuous are currently available. The monitoring of water contamination can be classified into two main categories. These are first, screening or diagnostic techniques in which only yes-or-no (qualitative) answer is required and secondly, semi-quantitative or quantitative techniques in which the detection of unwanted chemicals and the testing of the residues of the contaminants to determine if they are within required permissible levels. It is possible for both methods to generate false positive or negative results if the sensitivities are insufficient for detection of threshold levels (Sadik et al., 2000).

Phenols are currently determined using chromatogramphic techniques. Gas chromatography (GC) is often adopted because its advantage of high resolution, rapid separation, low cost and easy linkage with sensitive and selective detectors (Zhao et al., 2008). Many workers have utilized this analytical tool to measure levels of phenols in different water samples (Larreta et al., 2007; Ribeiro et al., 2002; Bagheri et al., 2004; Zhao et al., 2008).

A method of simultaneous determination of phenolic and steroid EDCs in aqueous and solid samples was developed by Arditsoglou and Voutsa (2008). Levels of alkyl phenols (nonylphenol, octylphenol) and their ethoxylate oligomers (mono- and di-ethoxylate of nonyl-phenol and octylphenol), bisphenol A and steroids (estriol, estrone, 17β-estradiol, 17α-estradiol, mestranol and 17α-ethynylestradiol) in aqueous and solid samples were determined. The analytical protocol for water samples was based on a Solid-phase extraction (SPE)-gas chromatography-mass spectrometry (GC-MS) method. The recoveries of target compounds were assessed using Oasis HLB extraction cartridges and different elution solvents. A derivatization step was carried out to enhance selectivity and sensitivity of the analysis. The concentration of phenols reported ranged between 11.2 - 113 ngL^{-1}, 13.4 - 277 ngL^{-1} and 19.5 - 43,860 ngL^{-1} in seawater, river water and runoff/wastewater samples respectively. The instrument detection and method detection limits for the phenols ranged between 0.011 - 0.056 and 1.5- 14.1 ngL^{-1} respectively.

Levels of nonylphenol and octylphenol were assessed in water samples by Mauricio et al. (2006) using SPE followed by high-performance liquid chromatography (HPLC)-MS. Measurement of these chemicals were made in samples from a wastewater treatment plant using a commercial enzyme-linked immunosorbent assay kits and also, HPLC-MS/MS. The results revealed that the wastewater treatment plant process is efficient on the removal of target EDCs. However, environmentally significant concentrations are still present in the treated effluent. The enzyme-linked immunosorbent assay kit was also shown to be suitable for routine analysis of the selected compounds.

The composition, distribution and characterization of 31 suspected EDCs in surface water, pure water and sediments from a reservoir have been studied (Xue and Xu, 2006). SPE and capillary gas chromatography with electron capture detection was used. It was shown that water pollution with the chemicals was moderate in the study area and the reservoir's tributaries while residues in a few sites were considerably high with respect to endocrine disrupting effects and chronic health effects. Observed variations in concentration of chemicals were adduced to factors such as agricultural runoffs from fields, chemical diffusion through pores in the sediments and increases in agricultural production.

Heberer and Stan (1997) derivatized more than 50 substituted phenols with *N*-(*t*-butyldimethylsilyl)-*N*-methyl trifluoroacetamide (MTBSTFA) by forming their *t*-butyldimethyl silyl derivatives. The determination and detection of the derivatives were performed by capillary GC-MS. Two capillary columns of different polarities were used for the gas chromatographic separation of all phenol derivatives. Application of solid phase extraction (SPE) with polymetric adsorbents enabled phenols detection at ngL^{-1} level, even in environmental samples with high matrix contents. The derivatization procedure was applied to trace-level determination of various phenols with detection limits of 5 - 10 pgL^{-1} applying GC with electron ionization (EI)-MS detection in the SIM mode.

In another study (Schimidt-Baumler et al., 1999), the presence of 22 substituted phenols was investigated in surface water samples. SPE with styrene divinylbenzene adsorbent was used for extraction followed by derivatization with MTBSTFA. The samples were analyzed by capillary gas chromatography- mass spectrometry (GC-MS). Phenol concentrations ranged between 0.02 - 7.80 μgL^{-1}. The distribution of the residues of water samples showed that phenols with the exception of pentachlorophenol and 2-ethylphenoldid not originate from municipal sewage treatment plant discharges. Rather, some of the phenols were formed naturally or occur as ubiquitous anthropogenic contaminants in the aquatic system.

Bagheri et al. (2004) developed an immersed single-drop microextraction (SDME) method for the trace enrichment of phenols from aqueous samples. A micro-drop of butyl acetate was suspended from the tip of a micro-syringe needle, immersed in an aqueous spiked solution for a preset time. The micro-drop was then re-

tracted into the micro-syringe and injected directly into a GC-MS injection port. Effects of parameters such as solvent type, extraction time, stirring rate and temperature were investigated and optimized. Detection limits obtained was in the range of 5 - 22 ngL^{-1}. The method was applied to the extraction and determination of some environ-mentally important phenols in water samples. The method is reported to be rapid, simple, linear and reproducible while small volumes of sample and micro scale size of organic extracting solvent are required.

Various sensors were developed for the detection of EDCs (pesticides, organochlorines, PCBs, alkyl phenols) using electro optical detection. Low detection limits were realized for cyanazines, PCBs and alkyl phenols with values as low as 0.30 - 3.3 $ngmL^{-1}$, 0.1 - 0.25 $ngmL^{-1}$, 0.39 - 3.3 $ngmL^{-1}$ and 0.5 - 0.8 mM for cyanazines, aromatic phenols, PCBs and alkyl phenols respectively (Sadik et al., 2000).

The occurrence and distribution of some EDCs including chlorophenols have been investigated in a river (River Pistula) bin Poland. Solvent extraction of chlorophenols was carried out prior to esterification with anhydrous acetic acid. Levels of chemicals were measured with GC equipped with an electron capture detector (ECD). Chlorophenols and PAHs occurred similarly along the river course but were highest further downstream. The study indicated pollution of the river by the studied chemicals (Dmitruk et al., 2008).

An automated method of analysis of organic micro-pollutants in water samples was evaluated for the determination of phenols. The phenols were derivatized off-line with acetic anhydride which was added directly to the water sample. The GC apparatus was connected to a mass spectrometer detector operated in the SIM mode. Detection limits for the method were in the 1 - 5 ngL^{-1} range (Baltussen et al., 1999).

Leachates from different landfills were analyzed for phenols using solid phase microextraction (SPME)–GC with flame ionization detection (FID). In order to prevent thermal destruction prior to chromatographic analysis, the fibre was preconditioned in the GC injector for 1 h at 250°C. Phenols identified and quantified include 2,4-dichlorophenol, 2,6-dichlorophenol, 2,3,4-trichlorophenol, 2,3,4,5-tetrachlorophenol and 2,3,4,6-tetrachlorophenol at concentration ranges of 15 - 130, 18 - 65, 8 - 40, 5 - 20 and 10 - 25 μL^{-1} respectively (Ozkaya, 2005).

Ribeiro et al. (2002) reported the evaluation of SPME/GC-MS for the analysis of 13 chlorophenols and phenol in landfill leachate. The overall analysis was performed in 90 min and detection limits ranged between 0.005 μgL^{-1} (pentachlorophenol) and 2.5 μgL^{-1} (phenol). Percentage recovery was evaluated at 86. Optimized extraction conditions were obtained with an 85 µm PA coated fibre, immersion sampling at 40°C for 30 min and stirring at 750 rpm with saturated salt conditions; sample pH <2 and desorption for 3 min at 280°C.

A methodology based on the cloud point extraction (CPE) using non-ionic surfactant (oligoethylene glycol monoakyl ether-Genapol X-080) as extractant has been used for the extraction and preconcentration of phenolic compounds in water (Santana et al., 2002; Liu et al., 2004; Lopez-Darias et al., 2008; Wang et al., 2006). The HPLC system was equipped with a diode array detector (DAD). Optimum conditions for the extraction and concentration of phenolic derivatives were established and detection limits lower than 10 μgL^{-1} were obtained for all studied compounds. The method was applied for phenolic determination in sea water and depurated wastewater.

A headspace single-drop microextraction (HSDME) based on ionic liquid (IL) was developed for the gas chromatographic determination of phenols in water and wastewater. The volume of IL used was 1 µL. Optimized conditions for analysis were 25 min for extraction at 50°C in solutions (pH 3) containing 0.36.gmL^{-1} sodium chloride. The limit of detections (LODs), relative standard deviations (RSDs) and the average enrichment factors of phenols were 0.1 - 0.4 $ngmL^{-1}$, 3.6 - 9.5% (n = 5) and 35 - 794 respectively. The spiked recoveries were in the range of 81-111% at a spiked level of 0.4 μgmL^{-1}. The IL-HSDME-GC does not suffer from solvent loss during headspace extraction, no interference of big solvent peak, has sufficient sensitivity and highly reproducible (Zhao et al., 2008).

A branched chain, fluorocarbonaceous, silane-bonded silica gel material was prepared by silation and used as packing material for HPLC columns. The columns were use for the separation of phenol and its halogenated derivatives. The HPLC system used was equipped with a variable-wavelength UV detector. Results showed that the column packing have a high selectivity for the geometrical isomers of substituted phenols. Polyphenols such as flavonoids were separated with a sharp peak shape and excellent durability under extreme eluting conditions in contrast to ordinary hydrocarbon-bonded silica gel columns (Monde et al., 1996).

Amiri et al. (2004) used HPLC to study the influence of pH on the sorption of 3 different phenols (2-methyl-4,6-dinitrophenol, 2,4,6-trichlorophenol and pentachlorophenol) on a natural sandy aquifer material in flow through column experiments. 25 mL samples were enriched on a solid phase polymer. The polymer phase was preconditioned with methanol and pure water; dried in N_2 gas after which the cartridge was flushed with acetonitrile-methanol (50/50) solution. The extract was concentrated to 1 mL under N_2 gas and made up to 2 mL with 1% acetic acid solution. The final solution was then analyzed with a HPLC-diode array detection (DAD) using a C18 column. The experiments were performed at pH values in the range of 4.4 - 6.9. Sorption was reported to increase with decreasing pH indicating stronger sorption of the neutral species in comparison to that of anions formed by dissociation. The anions of 2-methyl-4,6-di

nitrophenol and 2,4,6-tichlorophenol did not show significant sorption. On the contrary, pentachlorophenol showed sorption not only to neutral form but also in ionic form significantly.

The applicability of liquefied dimethyl ether DME was evaluated as an extractant for phenol from water. Phenol concentration was analyzed with a HPLC equipped with a silica-ODS column and UV detector using methanol as solvent. Extraction ratio of phenol was defined as the percentage of phenol extracted from the water phase to that from liquefied gas phase based on the charged phenol. Phenol extraction ratio was 79 and 67% using 5.45 and 0.11 wt% phenol solutions respectively with a liquefied DME/water volume ratio of 1.5:1. Phenol isolation from DME phase by extraction with a water phase containing an initial phenol concentration of 1.09 wt% or more was achieved (Sato and Matsumura, 2003).

The use of coumarin-6-sulphonyl chloride (C6SCl) as a fluorescence-labelling reagent for the analysis of some environmentally important phenols was investigated by Suliman et al. (2006) using a simple, sensitive and rapid reversed-phase (RP) HPLC method. The compound (C6SCl) reacts with phenols within 20 min under mild conditions (ambient temperature, pH 9.0) to give sulphonates that could be separated by RP-HPLC employing fluorescence detection. The optimum conditions for fluorescence, derivatization and chromatographic separation were established and detection limits in the range of 0.1 - 0.9 μgL^{-1}were obtained for the studied compounds. The practical applicability of the method to environmental samples was demonstrated by analyzing drinking and industrial water samples spiked with phenolic compounds.

A summary of the analysis of phenols in waters by some workers is presented in Table 1.

Abatement of phenols in water

Current technologies for treatment of organic pollutants include many physical, chemical and biological methods (Hao et al., 2003).Other methods that have been proposed for the removal of phenols from industrial effluents include ozonolysis and activated carbon adsorption (Kartal et al., 2001; Huang et al., 2007; Ugurlu et al., 2008).

Recently, a popular means for the removal and recovery of organic water pollutants is by adsorption. Indeed, there has been an increasing large amount of literature devoted to the study of adsorption for the removal of aqueous organic species such as phenols and substituted phenols (Tatsumi et al., 1996; Gupta et al., 1998; Rege et al., 1998; Amiri et al., 2004; Bassi et al., 2004; Liao et al., 2006; Huang et al., 2007).

Photocatalytic oxidation of phenol in an aqueous suspension of illuminated Titanium dioxide at a typical concentration value for a petroleum effluent was investigated by Kartal et al. (2001). Effects of pH, TiO_2 loading, O_2 flow rate ad temperature of destruction were studied. Samples were analyzed using GC-FID for residual phenol content. Maximum phenol removal was achieved at pH 6.6 while degradation rate of phenol increased with increasing TiO_2 loading up to 2 gL^{-1}. Flow rate of O_2 had no considerable effect on photocatalytic oxidation of phenol over a range of 2.0 - 3.5 $Lmin^{-1}$.

A catalytic dehydrohalogenation method was used to break down chlorinated phenols in wastewater (using palladium on charcoal as catalyst and sodium formate as reducing agent) was studied by Hartung et al. (2007). A GC-MS splitless system was used for separation and detection. The method competed well with 11 other methods that were compared with it. The method did not require organic solvent nor complicated apparatus. Reaction conditions were mild: room temperature and appropriate use of a non-toxic and cheap reagent (sodium formate). The catalyst can be recycled.

In another work, Trillas et al. (1996) studied photocatalysis of phenol, 2,4-dichlorophenol, phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid using Titanium dioxide as photocatalyst. Concentration of the phenols was determined by HPLC equipped with a Vis-UV detector. The stationary phase was a Hypersil ODS column (10 cm x 4.5 mm i.d; 5 µm particle size). Rate of photodegradation was reported to be dependent on the pH of the solution, the point of zero charge of TiO_2 and the pK_a of the chemicals used. Long-term irradiations using phenol as a model compound showed high degrees of photodegradation; only a periodic evacuation of the effluent out of the reactor is needed to sustain high percentages of photodegradation.

Chaliha et al. (2008) attempted catalytic destruction (wet oxidation) of 4-chlorophenol in water. MCM-41 (mesoporous material) based catalysts impregnated with Fe(III), Co (II) and Ni (II) were used. Catalyst characterization was achived using X-ray diffraction, scanning electron microscopy, FTIR, CEC and atomic absorption spectrophotometric measurements. Optimized parameters for the catalysts include reaction time, pH, mole ratio of reactants and oxidant, catalyst load, feed concentration and temperature. A GC-MS apparatus was used for 4-chlorophenol analysis using 0.6 µL sample volume.

Gabriel et al. (2007) demonstrated the ability of *Sphingobium xenophagum* Bayram to metabolize phenols. The metabolites were characterised unambiguously by HPLC-UV, HPLC-MS and HPLC-MS/MS. Formation of metabolites were adduced to ipso-substitution and ipso-hydroxylation mechanisms. It was established that ipso-substitution is a versatile degradative principle utilized by diverse organisms to degrade α-quaternary 4-nonylphenols, 4-alkoxyphenols and Bisphenol A.

Genetic engineering techniques have also been employed for the oxidation of 4-bromophenol in water using re-suspended immobilised enzyme in cellulosic matrix. The immobilised enzyme was packed into a

Table 1. Some extraction/analytical techniques being used for phenols quantification.

Extraction method	Analytical technique	Detection limit	Reference
Sequential pre-concentration	-	0.2 µM at 80°C	Toniolo et al. 2007
Single drop micro-extraction	GC-FID	0.4 ng/mL	Zhao et al., 2008
Headspace solid-phase microextraction	GC-MS	0.02 µg/L	Larreta et al., 2007
Solid-phase microextraction	GC-MS	0.005 µg/L	Riberio et al., 2002
Signal drop microextraction	GC-MS	5 ng/L	Bagheri et al., 2004
Solvent extraction	HPLC-UV	-	Sato and Matsumura, 2003
Automated sorptive extraction thermal desorption	GC-MS	-	Baltussen et al., 1999
Thermal desorption	HPLC-DAD	0.1 µg/L	Suliman et al., 2006
Solid phase extraction	GC-MS	1.0 ng/L	Heberer and Stan, 1997
Solid phase extraction	GC-MS	0.02 µg/L	Schimidt-Baumler et al., 1999
Solid-phase microextraction	GC-FID	2.00 µg/L	Ozkaya, 2005
Solid-phase extraction	GC-MS	12.30 ng/L	Arditsoglou and Voutsa, 2008
Solid-phase extraction	LC-MS/MS	0.15 µg/L	Mauricio et al., 2006
Cloud point extraction	HPLC-DAD	2.00 µg/L	Santana et al., 2002
Automated sorptive extraction/thermal desorption	GC-MS	0.2 pg/mL	Kawaguchi et al., 2005

Key: GC-MS = Gas chromatography- mass spectrometry, HPLC-DAD = High performance liquid chromatography- diode array detection, GC-FID = Gas chromatography- flame ionization detection, LC-MS/MS = Liquid chromatography- mass spectrometry/mass spectrometry = Not stated by authors.

Table 2. Phenol removal from wastewaters using different materials.

Compound	Material used	Reference
Phenol and p-Nitrophenol	Baggase fly ash	Gupta et al., 1998
Chlorophenol	Cavitational-induced pyrolysis	Hao et al., 2003
Chlorinated phenols	Pd and charcoal/sodium formate	Hartung et al., 2007
Phenol and reactive dye	Activated carbon	Nakagawa et al., 2004
Phenol	Colliery waste	Stafford and Callely, 1973
Chlorophenols	Immobilized enzyme on magnetite	Tatsumi et al., 1996
Lignin and phenol	Fe and Al electrocoagulation	Ugurlu et al., 2008

column connected to a HPLC equipped with a DAD. The quaternary pump of the HPLC system was employed to separately pump bromophenol, hydrogen peroxide and potassium phosphate buffer (pH 6.0) into the column. Immobilised substrate exhibited enhanced stability to H_20_2 thereby enhancing oxidation. Inclusion of gelatine, which suppresses product dependent inactivation, further increased the amount of bromophenol oxidation. However, the resistance to degradation (that is, ring deactivation) and toxicity of halogen substituted phenols is dependent on both the degree of substitution and the position of the substituent in the aromatic ring. The application of this finding is limited by factors such as susceptibility to H_2O_2, product dependent inactivation and the need for the continuous supply of fresh enzyme (Levy et al., 2003).

The immobilization of horseradish peroxidase on magnetic particles and its use for the removal of chlorophephenols in an aqueous solution was investigated by Tatsumi and co-workers (1996). Phenols removal was monitored by HPLC equipped with a UV detector. The immobilized enzyme was able to remove almost 100% of each of the phenol species contained in simulated wastewater. A summary of some attempts to remove phenols from wastewaters is presented in Table 2.

Since many studies have established the presence of phenols in water from different sources in diverse places, it is almost obvious that the trend will be similar in a developing economy like South Africa. It will therefore be necessary to assess the levels of these economically and environmentally important contaminants in water, their potential health risks to aquatic life and to suggest an efficient cost-effective method of abatement from sources.

Conclusion

This review highlighted the importance on phenols to man, its sources into the environment, different methods that has been used for quantification. Some abatement studies that has been carried out on this group of che-

micals were also reviewed. The used of cellulosic materials were however minimal in the literature. This may be a potential area for exploration in developing economies like Africa where technology is scarce and expensive. Some agricultural materials that have been effectively used to remove inorganic pollutants from waters may also be applicable to this group of chemicals. It is therefore recommended that research be focussed in this area using locally available agricultural waste biomass to solve environmental problems.

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