

SYNTHESIS AND APPLICATION OF MICROPOROUS CARBON SPHERES FOR
SOLID PHASE MEMBRANE TIP EXTRACTION OF NITROSAMINES FROM
WATER SAMPLES

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Specially dedicated to my beloved late parents, my wife and our children

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ABSTRACT

Microporous carbon spheres possess outstanding adsorptive properties and thus are advantageous in the development of solid phase microextraction sample preparation techniques. In this study, the feasibility of using microporous carbon spheres for the extraction of selected nitrosamines from water samples using solid phase membrane tip extraction (SPMTE) technique was investigated. Two types of adsorbents namely non-activated carbon spheres (NCS) and chemically activated microporous carbon spheres (MCS) were hydrothermally synthesized from sucrose. The prepared adsorbents were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption analysis, transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). Both adsorbents were spherical in shape as indicated by SEM. The FTIR spectra showed that the NCS and MCS have various surface functional groups such as OH, C=C and C-H which act as active sites. The surface areas of NCS and MCS are 7.88 and 308.10 m²/g, respectively as obtained from nitrogen adsorption analysis. The two prepared materials and a commercial activated carbon (granular activated carbon, GAC) were used in SPMTE to extract the selected nitrosamines namely N-nitrosodiethylamine (NDEA), N-nitrosodipropylamine (NDPA), N-nitrosopiperidine (NPIP) and N-nitrosodiphenylamine (NDPhA) from tap water and lake water matrices. Gas chromatography-mass spectrometry (GCMS) was used for quantitative analysis of the target analytes in the extracts. The optimized SPMTE conditions were conditioning solvent, extraction time, salt addition, pH, desorption solvent, desorption time and sample volume. Under the optimized conditions, the method showed good linearity in the range of 10 - 100 µg/L, good coefficients of determination ($r^2 = 0.9984 - 0.9994$), good precision (relative standard deviations, RSD < 9%, $n = 3$) and low limits of detection (LOD = 3.2 - 4.8 µg/L) for all the adsorbents. The extraction performance of each adsorbent was evaluated and compared in terms of percent recovery. The results showed that MCS gave better percent recovery in the range of 83.2 - 107.5% than both NCS (65.5 - 100.3%) and GAC (69.7 - 100.9%). This infers that MCS offered improved extraction efficiency and higher recovery of the tested nitrosamines compared to conventional activated carbon.

ABSTRAK

Sfera karbon berliang mikro mempunyai sifat penjerapan yang unggul, maka ia mempunyai kelebihan dalam pembangunan teknik penyediaan sampel pengekstrakan mikro fasa pepejal. Dalam kajian ini, kesesuaian penggunaan sfera karbon berliang mikro bagi pengekstrakan nitrosamina terpilih daripada sampel air menggunakan pengekstrakan muncung membran fasa pepejal (SPMTE) telah dikaji. Dua jenis penjerap iaitu sfera karbon tak teraktif (NCS) dan sfera karbon berliang mikro teraktif (MCS) telah disintesis secara hidroterma daripada sukrosa. Penjerap yang disediakan telah dicirikan menggunakan mikroskopi imbasan elektron (SEM), spektroskopi inframerah transformasi Fourier (FTIR), analisis penjerapan nitrogen, spektroskopi kehantaran elektron (TEM) dan analisis termogravimetri (TGA). Kedua-dua penjerap berbentuk sfera seperti yang ditunjukkan oleh SEM. Spektrogram FTIR menunjukkan bahawa NCS and MCS mempunyai pelbagai kumpulan berfungsi permukaan misalnya OH, C=C dan C-H yang bertindak sebagai tapak aktif. Luas permukaan NCS dan MCS masing-masing ialah 7.88 dan 308.10 m²/g, daripada analisis penjerapan nitrogen. Kedua-dua penjerap yang disediakan dan karbon teraktif komersial (karbon aktif butiran, GAC) telah digunakan sebagai penjerap dalam SPMTE bagi mengekstrak nitrosamina terpilih iaitu N-nitrosodietilamina (NDEA), N-nitrosodipropilamina (NDPA), N-nitrosopiperidina (NPIP) dan N-nitrosodifenilamina (NDPhA) daripada matriks air paip dan air tasik. Kromatografi gas-spektrometri jisim (GCMS) telah digunakan bagi analisis kuantitatif analit sasaran di dalam ekstrak. Keadaan optimum SPMTE ialah pelarut pengkondisi, masa pengekstrakan, penambahan garam, pH, pelarut penyaherapan, masa penyaherapan dan isipadu sampel. Di bawah keadaan optimum, kaedah ini menunjukkan kelinearan yang baik dalam julat 10 - 100 µg/L, pekali penentuan yang baik ($r^2 = 0.9984 - 0.9994$), kepresisan yang baik (sisihan piawai relatif, RSD < 9%, $n = 3$) dan had pengesanan yang rendah (LOD = 3.2 - 4.8 µg/L) bagi semua penjerap. Prestasi pengekstrakan setiap penjerap telah dinilai dan dibandingkan berdasarkan peratus perolehan kembali. Keputusan menunjukkan bahawa MCS memberikan peratus perolehan kembali yang lebih baik dalam julat 83.2 - 107.5% berbanding kedua-dua NCS (65.5 - 100.3%) dan GAC (69.7 - 100.9%). Ini menunjukkan bahawa MCS menawarkan kecekapan pengekstrakan yang lebih baik dan perolehan kembali lebih tinggi bagi nitrosamina yang diuji berbanding dengan karbon teraktif konvensional.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In recent times, non-polar hazardous compounds popularly known as persistent organic pollutants (POPs) and heavy metals are less relevant for the industrialized countries as a result of dramatic reduction in their emissions through adaption of appropriate measures and elimination of the dominant sources of pollution. However, the emergence of new unregulated contaminants so-called “new emerging pollutants” (NEPs) has become an environmental problem. Emerging pollutants are natural and synthetic chemical substances that are infrequently measured or controlled in the environment, but can lead to damaging effects on our surrounding environment as well as on human health. The term NEPs has recently been replaced by a new term called contaminants of emerging concern (CECs) by the US EPA in a published white paper document (Gerald *et al.*, 2008). This change of name from NEPs to CECs has also been narrated in a report published by water resources research center, the university of Arizona (Raghav *et al.*, 2013).

This group of pollutants includes the pharmaceuticals, steroids and hormones, personal care products, antiseptics, surfactants and surfactant metabolites, flame retardants, industrial additives and agents, gasoline additives and disinfection by-products. Major sources of emerging pollutants include untreated urban wastewaters and wastewater treatment plant (WWTP) effluents (Díaz-Cruz *et al.*, 2009). The emergence of these newly identified pollutants in our water resources is of great concern for the health and safety of consuming public since the existing

conventional water treatment plants were not designed to eliminate these endocrine disrupting chemicals (Bolong *et al.*, 2009).

Nitrosamines (NAs) constitute one class of the contaminants of emerging concern (Mhlongo *et al.*, 2009). NAs are compounds with chemical structure $R_2N-N=O$ formed from nitrites and amines. The history of environmental pollution by nitrosamines is quite lengthy and these compounds gained recognition when they were found to be extremely toxic and mostly carcinogenic in 1950s (Barnes and Magee, 1954). Environmental waters can be contaminated by nitrosamines through different means including primary effluents in wastewater treatment plants with concentrations in the range of 2-25 ng/L. Human urine has also been found to be a source of N-nitrosodimethylamine (NDMA) at 5 ng/L in raw wastewater and in higher concentrations by industrial waste (Cheng *et al.*, 2006). The enormous hydrophilic and less adsorbability nature of nitrosamines leads to a large risk of groundwater contamination. Nitrosamines are increasingly becoming known as a health risk with most serious threat from the formation of N-nitrosodimethylamine (NDMA) during final disinfection of drinking water with chloramines. However, the property of NDMA to strongly absorb radiation at 225-250 nm make the compound undergoes photolytic destruction in water (Nawrocki and Andrzejewski, 2011).

One of the most vital practices in any analytical procedure is sample preparation that often serves to isolate and concentrate the analytes of interest prior to final measurements. Most analyses are carried out in samples containing complex mixtures of very small amounts of chemicals or analytes that need to be identified. Many useful sample preparation methods have been developed over the years to address specific needs for analyzing waste water and drinking water, foods, medicinal, soil and air. Research on nitrosamines in waters requires the development of sensitive methods and analytical procedures. A previously developed method applied for the detection of nitrosamines involved enrichment of the compounds by solid phase extraction, analytes elution with methylene chloride, concentration of the eluate and chromatographic analysis (Cheng *et al.*, 2006).

In this work, microporous carbon spheres were prepared from a very cheap carbon precursor (sucrose) through hydrothermal reaction in an autoclave followed by pyrolytic KOH activation using the tube furnace. After various characterizations of the synthesized material, a simple microextraction technique incorporating the microporous carbon spheres was developed. The applicability of the developed method was examined by extracting selected nitrosamines from aqueous solution and the technique was compared with conventional SPE method.

1.2 Problem Statement

Trace analysis of environmental pollutants constitutes a difficult task due to complexity of the matrices and normally very low concentrations of the target analytes. Therefore, substantial analyte enrichment is necessary to isolate the target compounds from the matrix and to achieve the LODs required. A good analytical methodology for sample preparation is therefore imperative (Lopez de Alda *et al.*, 2003).

Conventional sample preparation methods used for nitrosamines analysis in water include liquid-liquid extraction and solid phase extraction (Rosenberg *et al.*, 1980). However, both extraction techniques turn out to deliver low nitrosamine recoveries since the nitrosamines have low partition coefficient in octanol/water system and are poorly adsorbed onto non polar activated carbon surfaces (Nawrocki and Andrzejewski, 2011). Therefore, development of new materials with suitable structures and better properties to act as adsorbents is very important. Carbon spheres among other carbon materials are attractive candidates due to their uniformity, high thermal stability and excellent conductivity as well as their numerous applications such as an adsorbent (Chen *et al.*, 2009).

In recent times, sensitive methods based on solid phase extraction using different carbonaceous adsorbents including coconut charcoal (Munch and Bassett, 2004) and Amborsorb 572 (Jurado-Sanchez *et al.*, 2007) have been developed for

the extraction of nitrosamines. In the present work, microporous carbon spheres were chosen and used as the SPMTE adsorbent because of its microporous nature and spherical shape as each of these factors enhances the adsorptive power of the carbon material (Munch and Bassett, 2004; Yang *et al.*, 2002).

Finally, an innovative solid phase extraction method called solid phase membrane tip extraction (SPMTE) incorporating the newly-synthesized microporous carbon spheres as adsorbent was developed in this work to overcome the shortcomings of conventional techniques in terms of extraction recoveries for nitrosamines from water samples.

1.3 Research Objectives

The objectives of this research are as follows:

- a. To synthesize and characterize microporous carbon spheres from sucrose.
- b. To develop SPMTE technique incorporating the synthesized microporous carbon spheres, non-activated carbon spheres and granular activated carbon for the extraction of nitrosamines from water samples.
- c. To apply the developed method to the analysis of nitrosamines in selected water samples and make comparisons with established SPE method.

1.4 Scope of the Study

This study was carried out in three major parts. In the first part, carbon spheres were hydrothermally synthesized from a very cheap and readily available carbon precursor (sucrose) through hydrothermal reaction in an autoclave followed

by pyrolytic KOH activation under nitrogen environment in a tube furnace. Besides its availability and low price, sucrose was chosen as carbon precursor in this work because it requires lower carbonization temperature than other complex carbon precursor molecules like cellulose or starch (Mi *et al.*, 2008). It was also found that direct mixing of carbonaceous material with metal hydroxides (KOH or NaOH) and heat treatment of up to 760°C is a good way to obtain activated carbons with large surface areas and micropore volumes (Lillo-Rodenas *et al.*, (2003). In this work, KOH was selected as the activating agent over NaOH because it produces higher yield of activated carbons and reactions between carbon/KOH begins at lower temperature (400°C) as compared to carbon/NaOH which begins at around 570°C (Lillo-Rodenas *et al.*, (2003). It has also been reported that the differences noticed in the efficiency between KOH and NaOH during activation of multiwalled nanotubes of various crystallinity were mainly due to the fact that K metal has better intercalating ability than Na metal (Raymundo-Piñero *et al.*, 2005).

The synthesized materials were characterized in the second part of the study using different techniques including scanning electron microscopy (SEM), transmission electron microscopy, thermogravimetric analysis (TGA), Fourier transform infra-red spectroscopy (FTIR) and Brunauer, Emmett and Teller surface area analysis.

In the third part of the study, SPMTE technique was developed using the synthesized carbon spheres as adsorbent and the method was applied to the determination of selected nitrosamines in aqueous samples. In this part, several important extraction parameters such as types of organic conditioning solvent, total extraction time, extracts desorption time, pH value, effect of salt and sample volume were optimized. Both qualitative and quantitative analyses of the tested nitrosamines were carried out using GCMS with a HP-Wax column. Results from established method and the present method were compared.

1.5 Significance of the Study

Conventional LLE and SPE methods for extraction of nitrosamines in water are based on the use of organic solvents or activated carbon adsorbents. LLE in particular is less environmentally friendly and both methods are not cost effective apart from their low recovery turn out (Nawrocki and Andrzejewski, 2011). The use of SPMTE technique incorporating microporous carbon spheres for the extraction of nitrosamines from water has not been reported. This study therefore exposes a marvellous alternative method for extraction of nitrosamines from aqueous matrices. It has been shown that the current method has advantages over the conventional methods in terms such as low costs, eco-friendly, use of minute amounts of adsorbent, use of simple apparatus and good analyte recoveries.

1.6 Organization of Study

Chapter 1 compiles the introduction to the background theories of the study. It outlined the problem statements as well as the research objectives followed by the scope and significance of the study.

Chapter 2 provides a survey of relevant literatures covering contaminants of emerging concern (CEC) formally known as new emerging pollutants (NEPs) in general with nitrosamines (NAs) as key members, carbon spheres (CSs) and various conventional analytical methods for the extraction of nitrosamines from aqueous samples. It also describes the general sample preparation techniques for chemical analysis.

Chapter 3 explains the general methodology used in the study. It includes procedures of hydrothermal synthesis of carbon spheres, KOH activation of the synthesized carbon spheres and various steps taken during characterization of the material. The chapter also demonstrates SPMTE procedure used in the extraction of nitrosamines from aqueous samples.

Chapter 4 discusses the study carried out for the synthesis, activation and characterization of microporous carbon spheres. The chapter deliberates on the effects of some synthetic parameters (i.e. precursor and KOH concentrations) towards the size and morphology of the material. Furthermore, the foreseen paths leading to pore formation in the carbon spheres during activation and the anticipated causes for structural destruction of the sphere shape at certain KOH concentrations are also been explained.

Chapter 5 discusses the results obtained from solid phase membrane tip extraction using the synthesized material and a commercial activated carbon as adsorbents. Optimizations of several important extraction parameters such as types of organic conditioning solvent, total extraction time, extracts desorption time, pH value, effect of salt and sample volume are fully discussed. The chapter also discusses comparisons between the developed method and an established method in terms of efficiency.

Finally, chapter 6 provides the general conclusions and future directions for subsequent studies. This chapter summarizes the overall results obtained in chapters 4 and 5. Future directions are presented and discussed for further improvement of the study.

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