学校编码：10384　　分类号_____　密级_____
学号：200434066　　UDC_____

厦门大学

硕　士　学　位　论　文

新型嵌入式被动采样膜的制备及其富集水体中溶解态 PAHs 的效能研究

Preparation of Cyclodextrin-Triolein Embedded Cellulose Acetate Membrane and Its Uptake Efficiency of Dissolved PAHs in Aqueous Solution

蔡宗群

指导教师姓名：张　勇　教授
专　业　名　称：环　境　科　学
论文提交日期：2007 年 10 月
论文答辩时间：2007 年 11 月
学位授予日期：2007 年　　月

答辩委员会主席：_____
评　　阅　　人：_____
_____

2007 年 11 月

厦门大学学位论文原创性声明

兹呈交的学位论文，是本人在导师指导下独立完成的研究成果。本人在论文写作中参考的其他个人或集体的研究成果，均在文中以明确方式标明。本人依法享有和承担由此论文产生的权利和责任。

声明人（签名）：

年　月　日

厦门大学学位论文著作权使用声明

本人完全了解厦门大学有关保留、使用学位论文的规定。厦门大学有权保留并向国家主管部门或其指定机构送交论文的纸质版和电子版，有权将学位论文用于非赢利目的的少量复制并允许论文进入学校图书馆被查阅，有权将学位论文的内容编入有关数据库进行检索，有权将学位论文的标题和摘要汇编出版。保密的学位论文在解密后适用本规定。

本学位论文属于

1、保密（　），在　　年解密后适用本授权书。

2、不保密（　）

（请在以上相应括号内打“√”）

作者签名：　　日期：　　年　　月　　日

导师签名：　　日期：　　年　　月　　日

目录

Contents

中文摘要

本论文共分为以下四个部分：

第一部分是绪论部分。首先介绍了多环芳烃(Polycyclic aromatic hydrocarbons , PAHs)的性质、来源、迁移以及对人类健康和生态环境的危害；详细综述了水体中 PAHs 生物有效性部分的研究进展，介绍了目前几种评价 PAHs 生物有效性的方法，其中着重论述了半透膜被动采样装置(Semi-permeable membrane device, SPMD)研究进展；介绍了 PAHs 几种常见的分析方法；随后介绍了环糊精(Cyclodextrins, CDs)的结构、性质及其在环境领域的应用；最后在上述讨论的基础上提出了本文的设想及研究内容。

第二部分是新型嵌入式被动采样膜的制备及表征。在嵌入式被动采样膜(Triolein embedded cellulose acetate membrane, TECAM)的基础上，采用具有疏水性空腔结构的 β-CD 作为致孔剂，制备了一种新型嵌入式被动采样膜(Cyclodextrin-Triolein embedded cellulose acetate membrane, C-TECAM)。采用沉浸凝胶相转化技术，以醋酸纤维素为膜材料，丙酮和二甲亚砜为混合溶剂，在制膜过程中将 β-CD 和三油酸甘油酯(Triolein)同时嵌入到高分子材料中。表征实验结果表明，C-TECAM 表观上是乳白色半透明的均匀膜，具备一定的厚度(115-122μm)；亲水性能良好，含水率介于 64.83%-65.77%之间，孔隙率介于 33.80%-35.65%之间；β-CD 和 Triolein 的加入能显著地提高膜的机械强度，拉伸强度平均较纯醋酸纤维素膜提高了 38.22%。C-TECAM 在典型的现实环境酸碱条件(pH=4.49-9.18)下基本性能保持稳定；在正己烷和环己烷中未发生溶胀、溶解或其他化学反应，但在二氯甲烷中则有部分溶解。纯净水可作为 C-TECAM 的保存液，己烷类溶剂可作为后续处理的透析溶剂。

第三部分是水溶液和环己烷溶液中萘(Naphthalene, Na)、蒽(Anthracene, An)和苯并(a)芘(Benzo(a)pyrene, BaP)三组分 PAHs 同步荧光同时测定方法的建立。水溶液中，Na、An 和 BaP 线性范围分别为 0.5-20.0μg/L、0.5-20.0μg/L 和 0.5-5.0μg/L，Na 和 An 线性范围均在溶解度以内，而 BaP 在助溶剂无水乙醇的存在下则可扩展至溶解度以外；检测限分别为 0.37、0.021 和 0.048μg/L；三者相对标准偏差最高不超过 10%(n=5)；合成样品回收率介于 84.4%-123.9%之间。与标

准方法相比，本方法具有灵敏度高，无需复杂前处理的优点，能够为考察C-TECAM富集水体中PAHs的效能提供一种简便、灵敏、快速的研究手段，也为今后的在线研究奠定良好的方法基础。另一方面，为进一步从膜富集的角度研究C-TECAM富集水溶液中PAHs的效能，本文同时建立了环己烷溶液中Na、An和BaP三组分PAHs同步荧光同时测定方法。鉴于PAHs在环己烷中有较高的荧光量子产率，为使环己烷溶液中三种PAHs的分析灵敏度和水溶液中的灵敏度保持在一个相应的范围内，实验时对仪器参数作适当的调整。结果表明，分别在5.0-80.0μg/L、2.0-80.0μg/L和2.0-80.0μg/L范围内，环己烷溶液中Na、An和BaP的同步荧光光谱强度与其浓度有良好的线性关系；检测限分别为0.62、0.056和0.082μg/L；三者相对标准偏差不超过5%(n=5)；合成样品回收率则介于90.8%-103.8%之间。

第四部分是新型嵌入式被动采样膜的实验室模拟暴露实验研究。采用静水暴露实验系统，利用第三部分所建方法，初步考察了C-TECAM富集水体中Na、An和BaP的效能。在实验条件下，三种PAHs均可被C-TECAM快速富集，平衡富集量以及达到富集平衡所需的时间与PAHs的K_{ow}值呈正相关。Na($\log K_{ow}$=3.45)在2h左右就能基本达到平衡，但平衡富集量最小，An($\log K_{ow}$=4.54)达到富集平衡的时间约在6h，而BaP($\log K_{ow}$=6.35)至少需要暴露12 h以上才能接近富集平衡状态，但其平衡富集量在三种PAHs中最大。与“夹心式”SPMD相比，C-TECAM能够缩短富集达到平衡所需的时间。同时，与TECAM相比，β-CD的加入能够提高C-TECAM对Na、An和BaP的平衡富集量，但对Na和An的富集速率有所降低，而BaP在β-CD添加量为0.5%时富集速率有一定的提高。此外，三种PAHs在C-TECAM中的膜-水分配系数$\log K_m$与其辛醇-水系数$\log K_{ow}$以及生物富集系数$\log K_{BCF}$之间都有良好的线性关系，可作为研究PAHs生物有效性的评价手段。最后本文考察了C-TECAM的再生性能，达到富集平衡的膜经净化后可进行二次重复富集，是一种更为经济的富集技术。因此，C-TECAM有望提供一种更为高效、经济替代手段，用于PAHs的模拟生物富集研究，评估污染物的生物有效性。

关键词：环糊精；三油酸甘油酯；新型嵌入式被动采样膜；多环芳烃

Abstract

This dissertation is composed of four chapters.

Chapter one is the preface. First, the properties, sources, fate of polycyclic aromatic hydrocarbons (PAHs) and its effects on human and environment were present. The progress on bioavailability of PAHs and its estimated methods, especially the semi-permeable membrane device (SPMD) method, were introduced. The determination methods of PAHs were then discussed. Besides, the structure, properties of cyclodextrins (CDs) and their applications to environmental science were also introduced. Finally, the proposal of dissertation was illuminated.

Chapter two is the preparation and characterization of a novel passive sampling membrane, cyclodextrin-triolein embedded cellulose acetate membrane (C-TECAM). On the basis of the triolein embedded cellulose acetate membrane (TECAM), β-CD was introduced to C-TECAM as a novel pore-forming material. C-TECAM was prepared by wet phase inversion technique in which triolein and β-CD were embedded. C-TECAM was ivory-white apparently and 115-122μm in thickness. C-TECAM was hydrophilic with water content between 64.83%-65.77% and porosity between 33.80%-35.65%. The mechanical strength of C-TECAM was improved 38.22% averagely compared to cellulose acetate membrane. C-TECAM was stable in typical acidic and basic conditions (pH=4.49-9.18) and in organic solvents such as hexane and cyclohexane, except dichloromethane.

Chapter three is the establishment of simultaneous determination of Naphthalene (Na), Anthracene (An) and Benzo(a)pyrene (BaP) by synchronous fluorimetry. With the new method, Na, An and BaP can be simultaneously determined in a mixture aqueous solution and in a mixture cyclohexane solution respectively. The linear ranges for the determination of Na, An and BaP in aqueous solution were 0.5-20.0μg/L, 0.5-20.0μg/L and 0.5-5.0μg/L with the limits of detection 0.37、0.021 and 0.048μg/L, respectively and the relative standard deviations were less than 10% (n=5). Satisfactory recovery experimental results were between 84.4%-123.9% in

spiked water samples. The advantage of the established method was sensitive and did not necessitate a complex pretreatment. It could be a simple, sensitive and rapid method to investigate the accumulation efficiency of C-TECAM to PAHs in aquatic environment and be a useful method for further on-line study. On the other hand, simultaneous determination of Na, An and BaP by synchronous fluorimetry in cyclohexane solution was also established to study the accumulation efficiency of C-TECAM from the membrane phase. As the fluorescence quantum yield of PAHs was higher in cyclohexane solution, apparatus parameters were changed to get a corresponding sensitivity in cyclohexane solution as well as that in aqueous solution. The linear ranges for the determination of Na, An and BaP in cyclohexane were 5.0-80.0μg/L、2.0-80.0μg/L and 2.0-80.0μg/L with the limits of detection 0.62、0.056 and 0.082μg/L, respectively and the relative standard deviations were less than 5% (n=5). Satisfactory recovery experimental results were between 90.8%-103.8% in spiked cyclohexane samples.

Chapter four is the laboratory simulated exposure experiment of C-TECAM to Na, An and BaP. The exposure of C-TECAM to three PAHs in aquatic environment was studied in static exposure system by synchronous fluorimetry. Na, An and BaP could be accumulated rapidly by C-TECAM, concentrations of three PAHs increased in C-TECAM while those decreased in aqueous solution till uptake equilibrium. Equilibrium time was directly proportional to octane-water partition coefficient ($\log K_{ow}$). Na, with $\log K_{ow}$ 3.45, could reach equilibrium in about 2 hours, while An and BaP, with $\log K_{ow}$ 4.54 and 6.35, needed 6 and 12 hours to equilibrium, respectively. C-TECAM was proved to be a more rapid accumulation method which could shorten equilibrium time compared to “sandwich” SPMD. The equilibrium concentrations of Na, An and BaP were increased with the introduction of β-CD to C-TECAM. Meanwhile, the uptake rates of Na and An were decreased and the uptake rate of BaP were improved with the addition of 0.5% β-CD.The membrane-water partition coefficient ($\log K_m$) of three PAHs in C-TECAM was linear correlated to their $\log K_{ow}$ as well as bioconcentration factors ($\log K_{BCF}$). Besides, C-TECAM could be regeneration for another accumulation of three PAHs. The results indicated that

C-TECAM could be a more efficient and economic method for the estimation of the bioavailable concentrations of PAHs.

Key words: β-cyclodextrin, Triolein, Cyclodextrin-triolein embedded cellulose acetate membrane, Polycyclic aromatic hydrocarbons