

磁性固相萃取在环境分析中的应用

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摘要: 样品前处理直接影响污染物分析的准确性并很大程度上决定了目标物质的检测限。磁性固相萃取作为一种新兴的样品前处理技术, 具有操作简单、消耗时间短、成本低等优点, 克服了传统柱式固相萃取的缺陷, 广泛应用于环境、化学、生物、药物分析等领域。文章介绍了磁性固相萃取技术及其流程, 概述了各种磁性材料在痕量污染物富集分离过程中的应用现状, 分析比较了不同表面修饰物质的磁性粒子的优缺点, 并展望了磁性固相萃取未来的研究方向。

关键词: 磁性; 固相萃取; 富集分离; 环境分析**中图分类号:** X832**文献标志码:** A

Application of Magnetic Solid Phase Extraction in Environmental Analysis

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Abstract: Sample pretreatment is an important process in environmental analysis, which directly influences the accuracy of analysis and strongly determines the detection limits of target pollutants. Magnetic solid phase extraction (MSPE) is a novel technology for sample pretreatment with the advantages of easy operation, short consumption time and low cost. MSPE overcomes the shortages of conventional column-type solid phase extraction (SPE) and thus has been widely applied in the fields of environmental, chemical, biological and pharmaceutical analysis. In this paper, the technology and process of MSPE are introduced and the current status of application of various magnetic materials in the process of enrichment and separation of trace pollutants is summarized. Moreover, the advantages and disadvantages of magnetic particles with different surface modification materials are compared and analyzed. Finally, orientation of MSPE study in the future is discussed.

Keywords: Magnetism; Solid Phase Extraction; Enrichment and Separation; Environmental Analysis**CLC number:** X832

环境水体中的微量污染物浓度低、成分复杂, 在分析检测过程中往往由于基体效应和杂质干扰而难以直接使用仪器分析^[1-2]。固相萃取 (Solid Phase Extraction, SPE) 是20世纪70年代中期发展起来一种样品预处理技术, 因其溶剂消耗少、固相萃取材料种类繁多、富集回收率高等特点^[3-4], 在环境、药物分析等众多领域得到了快速发展。然而这种富集分离技术仍然存在一定的缺陷^[5-6], 包括固相萃取柱价格昂贵、分析复杂环境样品时的柱堵塞现象、富集倍数低、大体积水

样处理时间长等。近年来, 磁性材料的出现为固相萃取的这些问题提供了解决途径。磁性材料出现之初, 铁氧化物 (如磁铁矿 (Fe_3O_4) 和磁赤铁矿 ($\gamma\text{-Fe}_2\text{O}_3$) 等)^[7-8] 是主要的研究对象, 并在信息储存、彩色成像、生物工艺和磁流体等领域发挥了重要作用。1996年, Tower et al^[9] 将负载二氧化锰的磁铁矿应用于海水中镉、铅和钋的萃取回收; 1999年 Šáfaríková et al^[5] 首次提出磁性固相萃取 (Magnetic Solid-Phase Extraction, MSPE) 的概念, 并使用磁木炭 (Magnetic Charcoal) 和负

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载铜酞菁染料的烷基化磁铁矿 (Blue Magnetite) 对水体中番茄红和结晶紫的萃取进行了研究。从此使用磁性吸附剂或可磁化吸附剂对大体积样品中目标物的预浓缩受到了人们的广泛关注。

1 磁性固相萃取

磁性固相萃取 (MSPE) 的核心是磁性萃取材料, 操作流程为: 将磁性萃取材料投加到含待测物质的溶液中, 目标物质被磁性材料吸附后, 在外加磁场作用下可轻易与溶液分离, 然后利用有机溶剂将目标物洗脱, 即可检测。与常规的固相萃取 (SPE) 柱相比, MSPE操作简单、省时快速、避免了柱堵塞^[10]。因此MSPE在环境检测、化学分析和生物分离等领域受到了广泛关注^[11-13]。

2 磁性固相萃取在环境分析中的应用

纯粹的纳米铁氧化物 (iron-oxide nanoparticles, NPs) 极易团聚, 致使磁性性能改变, 并且 NPs通常难以在复杂基质中使用。因此, 对 NPs进行修饰包裹是必要的。磁性粒子的表面修饰, 不仅能够改变其表面性质 (如亲疏水性、粘附性等), 还能够为目标物质的附着提供活性位点, 同时也能够防止磁性粒子的团聚和氧化^[14-15]。基于磁性粒子表面的修饰物质, 磁性固相萃取材料可以分为磁性硅基材料、磁性半胶束材料、磁性碳材料和磁性高分子聚合物材料等。

2.1 磁性硅基材料

硅基材料因其在水溶液中较稳定、易于表面改性和易于控制粒间相互作用等特点, 而在环境化学分析中得到广泛应用^[16]。近年来, 磁性硅基材料已应用于环境中多种污染物的富集分离,

表1 几种磁性硅基材料对不同污染物的富集分离

分析物	磁性材料	回收率/%	参考文献
铜、锌	2,6-二氨基吡啶修饰的磁性硅基颗粒	97~104	[17]
铅	邻 2-(2-羟基-5-磺基苯偶氮)亚苄基胍基苯甲酸修饰的磁性硅基颗粒	84~104	[18]
烟碱类农药	接枝石墨烯的磁性硅基颗粒	93.1~107.4	[19]
赭曲霉毒素 A	双 (巯基乙酸) 乙二醇修饰的磁性硅基颗粒	87~93	[20]
多环芳香烃	十八烷基硅烷修饰的磁粒子	35~93	[21]
雌激素	十八烷基三甲氧基甲硅烷修饰的磁粒子	23.0~91.6	[22]

介孔硅可以通过Fe-O-Si键与磁性Fe₃O₄纳米粒子结合形成核壳结构的磁性介孔硅材料, 通过调节介孔硅的用量和反应过程, 可以对磁性二氧化硅的包覆层厚度、孔体积和比表面积等进行调控。Tian等^[23]发现这种磁性介孔硅材料对水体中1,1-双 (对氯苯基) -2,2,2-三氯乙烷 (DDT) 具有快速、高效的去除性能。然而磁性介孔硅的萃取性能难以让人满意。磁性粒子表面的硅材料不但改变了磁性粒子的表面特性, 而且也提供了大量的硅烷醇基, 能够与众多的偶联剂反应以在磁性颗粒表面共价修饰特殊配体, 进而提高其吸附萃取性能^[24-25]。因此, 磁性硅材料表面修饰其他物质或基团的磁性复合萃取材料大量涌现。

Guan et al^[26]利用溶胶凝胶法制备表面负载羟基碳纳米管颗粒的二氧化硅磁性材料(Mag-

MWCNTs-OH), 并将其应用于水体中雌激素类物质的萃取分析。利用超声分散, Mag-MWCNTs-OH最短可在3 min内实现对水体中雌三醇、雌素酮和己烯雌酚的富集萃取, 其对三种雌激素物质的萃取回收率为52.4%~95.9%, 与非磁性MWCNTs-OH材料相比, 磁性材料对己烯雌酚的萃取性能明显提升。将该磁性固相萃取与胶束扫集电色谱法结合, 对3种雌激素的检测限为0.2 ng/mL。

十八烷基硅烷 (Octadecylsilane, ODS) 具有分离性能好、稳定性能高和使用寿命长等优点, 而被广泛应用在环境污染物的萃取浓缩领域^[27-28], 因此, 十八烷基硅烷包裹修饰的磁性材料也成为非常受欢迎的磁性固相萃取材料。Maddah et al^[29]将十八烷基三氯甲硅烷修饰在磁性Fe₃O₄粒子表面

制备得到磁性固相萃取材料,并将其应用于有机磷农药的萃取;萃取反应5 min即达到吸附平衡,其对噻磷和杀螟硫磷的萃取回收率为85%~92%;与高效液相色谱法联用,对两种有机磷农药的检测限为0.014~0.019 ng/mL。张小乐等^[30]将 Fe_3O_4 包裹在十八烷基三乙氧基硅烷功能化的介孔硅胶内,制备出磁性介孔硅胶颗粒。该材料比表面积大(273 m^2/g),饱和磁通量高(29 emu/g),可以对水样中痕量的酞酸酯类(PAEs)污染物进行有效的萃取,并对水体中的天然有机质有较强的抗干扰能力,回收率可达80%以上。

2.2 磁性半胶束材料

近年来,混合半胶束固相萃取引起了人们的关注。利用静电引力,将各种离子型表面活性剂(如十二烷基硫酸钠等)吸附于金属氧化物(如二氧化钛和氧化铝等)的表面形成混合半胶束,并以此为固相萃取材料,对环境样品进行富集浓缩预处理。混合半胶束材料具有萃取效率高、穿透体积大、易洗脱和可重复利用的特点^[31-32]。磁性固相萃取技术的出现也进一步拓展了半胶束材料的应用范围。Beiraghi et al^[33]通过化学沉淀法将表面活性剂(溴化十六烷基三甲铵)吸附在磁性 Fe_3O_4 纳米粒子表面,制得磁性半胶束材料,应用于自来水及地表水中异丁苯丙酸的萃取分析;该材料5~10 min即可达到吸附平衡,平均回收率为96%~99%,并表现出较好的抗天然有机质干扰性能;与高效液相色谱耦合,检测限为0.07 ng/mL。Li et al^[34]制备了以二氧化钛为磁性核心的磁性半胶束材料,并将其应用于水体中有机磷农药的萃取检测;其萃取富集倍数为1 000倍,对宽范围浓度(100~1000 ng/L)的多种有机磷农药有较高的萃取回收率88.5%~96.7%;与高效液相色谱检测联用,对有机磷农药的检测限为26~30 ng/L。

2.3 磁性碳材料

石墨化碳黑、多孔石墨碳和活性炭等碳材料对众多环境污染物具有极强的吸附性能,但是碳材料应用于固相萃取时,往往会与某些化合物

易于形成不可逆的吸附而难以脱附^[35-36]。近年来,有学者提出,将一层很薄的亲水性碳材料包覆在磁性纳米材料表面制备成磁性 $\text{Fe}_3\text{O}_4/\text{C}$ 纳米材料,就能够解决其难以脱附的问题。Bai et al^[37]利用水热反应制备了核壳结构的磁性 $\text{Fe}_3\text{O}_4/\text{C}$ 纳米材料;将该材料应用于环境水样中多环芳烃的萃取时,30 min达到吸附平衡,使用正己烷作脱附剂15 min完成脱附,富集倍数为35~133倍;与气相色谱-质谱仪联用,该技术对多环芳烃的检测限为0.015~0.335 ng/mL。张贵江等^[38]将磁性石墨烯作为磁性固相萃取的吸附剂,与气相色谱-质谱(GC-MS)相结合,对环境水样中7种三嗪类除草剂的残留进行了测定;该方法操作简单且富集倍数高,7种三嗪类除草剂的富集倍数在574~968之间。用该方法分析环境中的实际水样如湖水、井水等,萃取回收率为79.8%~118.3%,相对标准偏差为3.6%~10.5%。

2.4 磁性聚合物材料

多孔聚合物具有化学结构较稳定、孔道和比表面积易于调控、易于脱附等特点^[39]。将聚合物包覆在磁性粒子表面制备磁性聚合物萃取材料,不但保留了聚合物萃取剂的优点,而且具备了磁性性能。因此,聚合物固相萃取材料的应用愈来愈广泛。几种磁性聚合物材料在污染物萃取分离方面的应用见表2。

表2 几种磁性聚合物材料对不同污染物的富集分离

分析物	磁性材料	回收率/%	参考文献
多环芳烃	聚多巴胺包裹磁粒	76.4~107	[40]
邻苯二甲酸酯	磁性聚吡咯微球	91.1~113.4	[41]
双酚 A	磁性分子印迹聚合物	89~106	[42]
喹诺酮类抗生素	磁性分子印迹聚合物	94~124.4	[43]
阿特拉津	磁性分子印迹聚合物	71.6~126.7	[44]
苏丹红	磁性分子印迹聚合物	78~103	[45]

Tahmasebi et al^[46]在噻吩聚合过程中加入 Fe_3O_4 粒子,成功制备了聚噻吩磁性纳米颗粒($\text{Fe}_3\text{O}_4@\text{PThNPs}$),应用于水样中几种典型塑化剂化合物(邻苯二甲酸二丁酯、聚己二酸二辛酯等)的萃取和预富集;与气相色谱联用,该法检测限为0.2~0.4 $\mu\text{g/L}$,相对标准偏差为4.0%~

12.3%；将该方法应用于河水、瓶装矿泉水等水样的分析，萃取回收率可达85%~99%。本实验室Zhangetal^[47]利用膜乳化法，通过聚合、后交联反应制备了磁性超高交联微球，该微球比表面积为1 303.59 m²/g，并具有超顺磁性。将该磁性微球应用于水样中西玛津、阿特拉津、卡巴咪嗪等8种微污染有机物的检测分析，仅需要少量吸附剂(50 mg/L)即能在30 min内完成大体积水样(5 L)中多种微污染有机物的萃取；在优化条件下，8种微污染有机物的萃取回收率为91.7%~99.4%，与HPLC联用的检测限为1.76~27.56 ng/L，该检测限达到甚至低于SPE-HPLC-MS的水平，这表明磁性固相萃取对大体积样品中微污染有机物的快速富集萃取极大地降低了水质安全评价过程中对检测仪器的要求。

分子印迹聚合物具有极强的选择性，因而在固相萃取中得到广泛应用^[48-49]。大量交联剂与分子模板混合聚合后，将分子模板洗脱或解离出来而在聚合物中留下大量的与模板分子大小和形状相匹配、官能团互补的立体孔穴，这便赋予该聚合物特异的“记忆”功能，即类似生物自然的识别系统，这样的空穴将对模板分子及其类似物具有选择识别特性。Lin et al^[50]制备了以17 β -雌二醇分子为模板的磁性分子印迹材料，并将其应用于环境水体中多种雌激素类物质的同步萃取分析；该材料对雌二醇、雌三醇、17 β -雌二醇及双酚A等内分泌干扰物质均有较高的萃取效率；在对自来水、饮用水、地表河流等水样的萃取分析中，该材料对多种雌激素类物质的萃取回收率为72%~102%。Zhang et al^[51]合成的以Pb²⁺为模板的磁性分子印迹材料，在Cu²⁺、Zn²⁺、Cd²⁺、Hg²⁺等离子存在下表现出对Pb²⁺的高选择性(相对选择性系数>3.75)；其对环境水体中Pb²⁺的萃取回收率为98%~104%。Guo et al^[52]利用高岭石/Fe₃O₄制备的磁性分子印迹复合物用于水样中双酚A的富集分离，解吸效率高达95.75%。

3 结语与展望

磁性固相萃取技术是目前环境样品预处理

领域的研究热点，越来越多的磁性固相萃取材料被研究出来，但迄今为止仍未有商业化的磁性固相萃取材料，这是因为现有的磁性固相萃取材料往往只是针对某一类物质，其广泛适用性较弱，难以实现大范围的推广应用。因此，面向社会应用需求，开发研究稳定性高、制备简便、使用寿命长、吸附容量大、萃取效率高、重现性好、具有广泛适用性的新型磁性固相萃取材料，并将其在环境样品预处理中推广应用，将是今后磁性固相萃取技术研究的重要方向。

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