

百方知库
Eco-Environmental
Knowledge Web

环境科学

ENVIRONMENTAL SCIENCE

ISSN 0250-3301 CODEN HCKHDV
HUANJING KEXUE

■ 主办 中国科学院生态环境研究中心
■ 出版 科学出版社



2019

Vol.40 No.2
第40卷 第2期

目次

冬季山谷风和海陆风对京津冀地区大气污染分布的影响 李青春, 李炬, 郑祚芳, 王耀庭, 于淼 (513)

珠三角地区利用 PM_{2.5} 反演气溶胶数浓度谱方法 李菲, 谭浩波, 邓雪娇, 邹宇, 刘礼, 蔡明甫, 张芷言, 周声圳 (525)

广州冬季气溶胶中水溶性有机物和类腐殖质的吸光性和荧光光谱特性 范行军, 余旭芳, 操涛, 王艳, 肖新, 谢越, 李飞跃, 宋建中, 彭平安 (532)

扬州市 PM_{2.5} 中重金属来源及潜在健康风险评估 董世豪, 谢扬, 皇甫延琦, 史旭荣, 易睿, 史国良, 冯银厂 (540)

聊城市冬季 PM_{2.5} 中正构烷烃和糖类的污染特征及来源解析 刘晓迪, 孟静静, 侯战方, 衣雅男, 魏本杰, 伏梦璇 (548)

博斯腾湖流域大气多环芳烃污染特征、干沉降通量及来源 宋世杰, 黄韬, 赵留元, 毛潇萱, 穆熙, 高宏, 马建民 (558)

某集约化肉鸡饲养场 PM_{2.5} 中抗生素抗性基因的分布特征 刘菲, 许霞, 屠博文, 汪楚乔, 江晓栋, 王利平, 薛银刚 (567)

水汽源地和局地蒸发对大气降水氢氧稳定同位素组分的影响 胡勇博, 肖薇, 钱雨妃, 刘强, 谢成玉, 张秀芳, 张文庆, 温学发, 刘寿东, 李旭辉 (573)

滇池大气沉降氮磷形态特征及其入湖负荷贡献 任加国, 贾海斌, 焦立新, 王一茹, 杨苏文, 武倩倩, 高秋生, 崔志丹, 郝子峰 (582)

基于地统计学分析的太湖颗粒态和溶解态氮、磷营养盐时空分布特征及来源分析 吕伟伟, 姚昕, 张保华, 高光, 邵克强 (590)

湖泊蓝藻水华对连通河道水质的影响 余茂蕾, 洪国喜, 许海, 朱广伟, 朱梦圆, 权秋梅 (603)

异龙湖沉积物重金属人为污染与潜在生态风险 李小林, 刘恩峰, 于真真, 张恩楼, 林祺, 王荣, 沈吉 (614)

珠江河口悬浮物中重金属时空变化特征及其影响因素 杜佳, 王永红, 黄清辉, 戴琦, 杨远东 (625)

北运河粪源微生物分布特征及健康风险评估 陈磊, 李蕾芳, 郅晓沙, 张普, 戴莹, 肖月晨, 沈珍瑶 (633)

氧化还原循环过程中沉积物磷的形态及迁移转化规律 郝文超, 王从锋, 杨正健, 刘德富, 纪道斌, 赵萍, 丹勇, 胡子龙 (640)

磁性赭铁改性膨润土添加对河道底泥磷迁移与形态转化的影响 王艳, 林建伟, 詹艳慧, 张宏华, 张志斌, 何思琪, 赵钰颖, 吴小龙, 俞阳 (649)

钙预处理对磁性赭铁改性膨润土吸附水中磷酸盐的影响 赵钰颖, 林建伟, 张宏华, 张志斌, 詹艳慧, 姜博汇, 何思琪, 俞阳, 吴小龙, 王艳, 陈璐, 李十盛 (658)

NH₄⁺ 对镁改性生物炭除磷效果的影响 郭蒙蒙, 王鹏飞, 侯泽英, 曹晶, 储昭升, 杨永哲 (669)

3种吸附剂对污水磷污染去除性能与机制比较 吴露, 刘锋, 龙睿, 罗沛, 肖润林, 陈向, 吴金水 (677)

硝酸纤维素膜光降解水中对硝基苯酚的机制 代志峰, 赵同谦, 阴永光, 余加平, 武俐, 郅超, 孙静阳, 罗玉俊 (685)

ZnTiO₂-TiO₂ 复合光催化剂的制备及光催化降解有机污染物机制分析 张文海, 吉庆华, 兰华春, 李静 (693)

高指数晶面 TiO₂ 对铬的吸附及光催化去除 钟德健, 张健峰, 李尧, 谢晓丹 (701)

Fe⁰/海藻酸钙微球还原-Fenton 氧化协同降解酸性红 B 张环, 李爽爽, 魏俊富, 傅敏, 李雪曦, 丁琦, 白蓉 (708)

不同滤料滤池启动期内对铁锰离子的去除机制 蔡言安, 毕学军, 张嘉凝, 何睿, 董杨, 王海港 (717)

SGO 改性复合纳滤膜的制备及分盐性能 张彦君, 张少峰, 赵长伟, 王军 (724)

一体式铝盐絮体-超滤膜净水效能与机制 薛文清, 李文江, 刘娟, 马百文 (730)

臭氧-CNT 膜改性联用工艺通量及膜污染分析 王凯伦, 刘芳, 关羽琪, 祝学东, 董丹, 薛小雷, 马燕林, 栾桂荣, 郭瑾 (738)

多环芳烃及其衍生物在 SBR/MBBR 工艺中的分布与去除 刘淑惠, 田伟君, 周建仁, 赵婧, 王喆 (747)

微气泡曝气生物膜反应器处理低 C/N 比废水脱氮过程 刘春, 王聪聪, 陈晓轩, 张静, 张瑞娜, 张磊 (754)

从枝菌根强化型生态浮床处理煤化工模拟含盐废水 袁文清, 何皓, 宋文萍, 王曙光, 戴东伟 (761)

夏季高温下污水处理厂生物处理系统的硝化性能及强化方法 宋天伟, 盛晓琳, 王家德, 刘锐, 陈吕军 (768)

硝化包埋菌颗粒氨吸附性能及动力学特性 于德爽, 吕廷廷, 陈光辉, 王晓霞, 唐鹏, 黄硕, 刘诚诚, 杜世明 (774)

乙酸钠作为碳源不同污泥源短程反硝化过程亚硝酸盐积累特性 毕春雪, 于德爽, 杜世明, 王晓霞, 陈光辉, 王钧, 巩秀珍, 都叶奇 (783)

DPR-SNED 系统处理低 C/N 城市污水与硝酸盐废水的运行特性 杜世明, 于德爽, 毕春雪, 王晓霞, 陈光辉, 袁梦飞, 甄建园, 张帆, 吕廷廷 (791)

间歇曝气连续流反应器同步硝化反硝化除磷 赵智超, 黄剑明, 李健, 张为堂, 张力航, 吴雪晴, 陈永志 (799)

ABR-MBR 反硝化除磷工艺的启动及稳定运行 韦佳敏, 蒋志云, 程诚, 朱琳, 刘文如, 沈耀良 (808)

进水 C/N 对 SNEDPR 系统脱氮除磷的影响 都叶奇, 于德爽, 甄建园, 王晓霞, 陈光辉, 唐鹏, 王钧, 毕春雪, 巩秀珍, 黄硕, 刘诚诚 (816)

ABR 除碳-CANON 耦合工艺除碳脱氮特性 李田, 印雯, 王昕竹, 沈耀良, 吴鹏, 宋吟玲 (823)

不同曝气密度对 CANON 工艺启动的影响 李冬, 高雪健, 张杰, 曹正美, 郭跃洲, 李帅 (829)

调控温度和沉降时间实现 ANAMMOX 颗粒快速启动及其稳定运行 李海玲, 李冬, 张杰, 刘博, 李帅 (837)

C/N 和污泥浓度对以 pH 值调控的亚硝化系统影响 张敏, 韦佳敏, 黄慧敏, 姜滢, 郭萌蕾, 陈重军, 沈耀良 (845)

基于活性微生物特征的供水管壁生物膜生长特性 王杨, 朱斌, 董俊, 白晓慧 (853)

黄山土壤细菌群落和酶活性海拔分布特征 姚兰, 胡立煌, 张焕朝, 方炎明, 王良梅 (859)

基于高通量测序分析的生物修复石油污染土壤菌群结构变化 祁燕云, 吴蔓莉, 祝长成, 叶茜琼, 徐会宁 (869)

硝化作用对盐碱湿地 N₂O 排放的影响及其环境因子分析 杨曲, 高伟峰, 刘凤琴, 王文锋, 马建华, 徐卓, 梁红, 高大文 (876)

长期定位施用牛粪对夏玉米-冬小麦体系农田 N₂O 和 NO 排放的影响 聂皇华, 张家升, 和周明, 安梅, 杨学云, 顾江新 (885)

地膜覆盖和施肥对菜地 N₂O 排放的影响 倪雪, 郝庆菊, 陈世杰, 李晓茜, 石孝均, 江长胜 (893)

双季稻品种根际特征与甲烷排放差异及其关系 肖志祥, 傅志强, 徐华勤, 苏姗, 郭昱, 张浪, 唐剑武 (904)

多年施用生物炭对河南烤烟种植区土壤呼吸的影响 李亚森, 丁松爽, 殷金玉, 李佳轶, 周迪, 刘国顺 (915)

桂林毛村不同土地利用方式下土壤呼吸空间变异特征 丁梦凯, 胡晓农, 曹建华, 吴夏, 黄芬, 王奇岗, 闵佳 (924)

工业发达城市土壤重金属时空变异与源解析 李锋, 刘思源, 李艳, 史舟 (934)

膨润土对不同类型农田土壤重金属形态及生物有效性的影响 林海, 靳晓娜, 董颖博, 罗明科, 赵一鸣 (945)

缙云山不同林分下土壤有机碳及矿化特征 陈仕奇, 吕盛, 高明, 黄容 (953)

复杂地形条件下根系对土壤有机碳的贡献 张彦军, 郭胜利 (961)

不同水平外源碳在稻田土壤转化与分配的微生物响应特征 王季斐, 童瑶瑶, 祝贞科, 陈珊, 邓悟悟, 葛东达, 吴金水 (970)

宝鸡市植被叶子重金属分布规律及生态风险评估 张俊辉, 林青, 姜珊, 刘滨, 李东兴, 王彦虎 (978)

生物炭对污泥堆肥及其利用过程重金属有效态的影响 周楫, 余亚伟, 蒋越, 杨雨滢, 张成 (987)

污泥停留时间对餐厨垃圾与剩余污泥中温厌氧混合发酵系统的影响 袁宏林, 马静, 邢保山, 温俊伟, 韩宇乐, 李倩, 王晓昌 (994)

热碱-分步酶水解-厌氧消化工艺处理秸秆畜粪混合物料及其甲烷高值化条件 卞爱琴, 远野, 张璐璐, 付强, 陈天明, 何磊, 丁成, 王爱杰 (1003)

《环境科学》征订启事(547) 《环境科学》征稿简则(828) 信息(581, 933, 952)

SGO 改性复合纳滤膜的制备及分盐性能

张彦君^{1,2}, 张少峰^{1*}, 赵长伟², 王军²

(1. 河北工业大学化工学院, 天津 300130; 2. 中国科学院生态环境研究中心环境水质学国家重点实验室, 北京 100085)

摘要: 近年来, 水资源短缺, 水源污染严重, 国家对水处理末端的资源化利用提出了更高的要求, 分盐过程也受到越来越多的关注. 纳滤膜表面通常带有电荷, 可以选择性地透过不同价态的离子. 基于纳滤膜表面电荷特性不同, 为很好地实现盐的分离, 将制备的带有磺酸基团的氧化石墨烯引入到纳滤膜材料中, 采用界面聚合法, 制备了 SGO 改性复合纳滤膜. Zeta 电位分析表明所制备的复合纳滤膜表面的电荷比不添加 SGO 的纳滤膜更负; 红外光谱分析中酯基基团特征峰的出现表明磺酸基团参与了聚合反应; SEM 结构表面, 膜表面出现了明显的图灵结构, 在 0.2 MPa 压力下, 纯水通量可达 $45.85 \text{ L} \cdot (\text{m}^2 \cdot \text{h})^{-1}$, 对 Na_2SO_4 截留率为 98.23%, 对 NaCl 截留率为 24.93%, 10 h 运行可以很好地实现对 SO_4^{2-} 、 Cl^- 的有效分离, 可实现盐的资源化回收.

关键词: 复合纳滤膜; 磺酸基; 氧化石墨烯; 电负性; 分盐

中图分类号: TU991.2 文献标识码: A 文章编号: 0250-3301(2019)02-0724-06 DOI: 10.13227/j.hj.kx.201807270

Preparation of Sulfonated Graphene Oxide Modified Composite Nanofiltration Membrane and Application in Salts Separation

ZHANG Yan-jun^{1,2}, ZHANG Shao-feng^{1*}, ZHAO Chang-wei², WANG Jun²

(1. School of Chemical Engineering, Hebei University of Technology, Tianjin 300130, China; 2. Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China)

Abstract: In recent years, water resources are in short supply and seriously polluted. Increasingly more attention has been paid to the process of salt separation. The surface of the nanofiltration (NF) membrane is usually charged and can selectively allow the permeation of different ions. Based on the different charges on the NF membrane surface, in order to achieve a good separation of salt, the prepared graphene oxide with the sulfonic acid group was introduced into NF membrane material. Additionally, the SGO modified composite NF membrane was prepared by interfacial polymerization. Zeta potential analysis showed that the charge on the surface of the prepared NF membrane was more negative than that of the NF membrane without SGO. The peak of the ester group in the FT-IR analysis indicated that the sulfonate group was involved in the polymerization reaction. A Turing structure present on the surface of the membrane was evident through SEM pictures of the membrane surface. At a pressure of 0.2 MPa, the pure water flux can reach $45.85 \text{ L} \cdot (\text{m}^2 \cdot \text{h})^{-1}$. The rejection of Na_2SO_4 was 98.23%, while that of NaCl was 24.93%. The 10 h operation can effectively separate SO_4^{2-} and Cl^- , which realized the salt recycling.

Key words: composite nanofiltration membrane; sulfonic group; graphene oxide; electronegativity; separation of salt

如何实现盐的有效分离是目前水处理技术中面临的难题和重点话题^[1,2]. 膜分离技术是一种新型的水处理技术, 与其他除盐技术如离子交换、电渗析、蒸馏等相比具有操作简单、维护方便、便于与其他技术耦合集成等优点, 在水中一价二价盐分离方面具有非常广阔的应用前景^[3,4].

纳滤(nanofiltration, NF)是膜分离技术中的一种, 是目前世界水处理领域研究的热点之一^[5]. 纳滤膜大多从反渗透膜衍化而来^[6,7], 纳滤膜的孔径介于反渗透膜和超滤膜之间^[8], 其范围在纳米级^[9], 纳滤膜表面通常具有荷电性^[8,10], 对不同电荷和不同价态的离子又具有不同的道南效应, 纳滤膜的孔径和表面特征决定了其独特的性能^[11]; 纳滤膜的分离机制主要由筛分和道南效应共同控制^[12,13], 不仅能有效去除相对分子质量在 200 ~ 1 000 的有机物, 通过调控电荷特性, 还可以实现不

同价态盐的分离^[14,15].

纳滤分离技术的核心是纳滤膜材料, 界面聚合是制备纳滤膜材料的最常用方法之一, 很多研究者致力于改性纳滤膜材料来提高膜的分离性能^[16]. 有研究发现, 主要的方法有调控纳滤膜材料表面的荷电性, 运用空间电荷模型, 对膜进行膜的结构参数、电荷密度、荷电膜内离子的场地情形等的分析讨论^[17,18]; 另外, 纳米粒子或者小分子有机物等的加入也可以有效改善膜的分离性能和通量^[19]. 氧化石墨烯(graphene oxide, GO)是石墨烯的一种衍生物, 自从 2010 年诺贝尔奖对“关于二维材料石墨烯进行开创性实验”引起关注后^[20], 它作为一种

收稿日期: 2018-07-31; 修订日期: 2018-08-23

基金项目: 国家自然科学基金项目(21476248)

作者简介: 张彦君(1994~), 女, 硕士研究生, 主要研究方向为纳滤膜的制备及应用, E-mail: 1441172447@qq.com

* 通信作者, E-mail: shfzhang@hebut.edu.cn

新的二维纳米材料, 由于其具有独特的物理特性和化学稳定性, 获得了更多的应用^[21,22]. Xie 等^[22] 采用浸入式沉淀法, 将 GO 与 SGO(sulfonated graphene oxide) 两种石墨烯纳米片融入 PES 基膜中, 制备了一种新型耐碱膜; Hu 等^[23] 将 GO 添加到水相溶液中, 再采用界面聚合法制备了复合纳滤膜, 通过调控膜表面的粗糙度和荷电性改善膜的分离性能和通量. 然而, 目前将 SGO 用于制备改性复合纳滤膜的研究报道很少.

本研究首先制备了 SGO, 采用界面聚合法, 将 SGO 用于调控纳滤膜表面的结构和荷电性, 制备了 SGO 改性复合纳滤膜 (PA-SGO), 一方面提高膜通量, 同时提高膜表面的电负性, 通过 FT-IR、EDS、SEM、Zeta 电位等手段表征复合纳滤膜的组成及形貌, 进一步用于一价、二价盐的分离.

1 材料与方法

1.1 实验材料和仪器

聚醚砜超滤底膜 (PES), 截留相对分子质量 30 000, 市购; 无水哌嗪 (PIP, 沪试, 分析纯, AR), 均苯三甲酰氯 (TMC, 阿拉丁, 98%), 三乙胺 (阿拉丁, AR, 99%), 正己烷 (分析纯 AR), 氧化石墨烯 (南京先丰纳米), 对氨基苯磺酸 (麦克林, AR, 99.5%), 浓盐酸 (分析纯, AR, 36% ~ 38%), 联胺标准溶液 (阿拉丁, 1 000 $\mu\text{g}\cdot\text{mL}^{-1}$), 硫酸钠 ($\geq 99\%$, 粉末), 硫酸镁 (分析纯, AR, $\geq 98\%$), 氯化镁 (99%, 粉末), 氯化钠 (优级纯, GR, $\geq 99.8\%$), 去离子水 (实验室自制) 等.

膜性能评测装置, 实验室自制; 场发射扫描电子显微镜 SEM (SU8020), 真空干燥箱 (DZF-6050),

鼓风干燥箱 (DGG-9140B), 纳米粒度及 Zeta 电位分析仪 (ZS90), 电导率测定仪 (S230), 傅里叶变换红外光谱仪 (Nicolet8700).

1.2 SGO 制备方法

1.2.1 对氨基苯磺酸重氮盐的配制

将对氨基苯磺酸、NaOH 加入到盛有 30 mL 去离子水的单口瓶中, 60°C 使其充分溶解后, 将单口瓶放入冰水中冷至 0 ~ 5°C, 并在磁力搅拌器的不断搅拌下, 加入 NaNO_2 并维持温度在 0 ~ 5°C 之间. 然后将盐酸缓慢滴加到上述混合溶液中, 并控制温度在 5°C 以下继续搅拌 30 min, 溶液颜色呈淡黄色 (重氮盐溶液即配即用)^[24].

1.2.2 制备 SGO

在不断搅拌的条件下, 将 GO 加入到配好的对氨基苯磺酸重氮盐溶液中, 保持温度在 0 ~ 5°C 搅拌反应 2 h, 然后在室温下搅拌反应 8 h. 反应完毕后, 将产物离心并清洗 10 次, 得到粗产物. 将粗产物与胍混合并加热到 100°C, 保温 2 h 用以去除部分氧化性基团 (羟基、羧基、环氧基). 经反应得到的产物即为 SGO 粉末^[25].

1.3 PA-SGO 膜的制备方法

将 30 mg SGO 加入到 1% 的哌嗪水溶液中, 形成水相溶液; 将 TMC 加入到正己烷有机溶剂中, 配成 0.2% 的有机相溶液. 首先, 将 PES 超滤底膜在去离子水中浸泡 48 h, 去除膜表面的杂质, 然后晾干, 将膜放入水相溶液中浸泡 3 min, 用橡胶辊去除表面多余的水分; 随后将膜放入有机相中, 浸泡 1 min, 用氮气吹干后放入 80°C 鼓风干燥箱中热处理 1 min, 然后放入超纯水中保存备用. 复合膜的制备过程如图 1 所示.

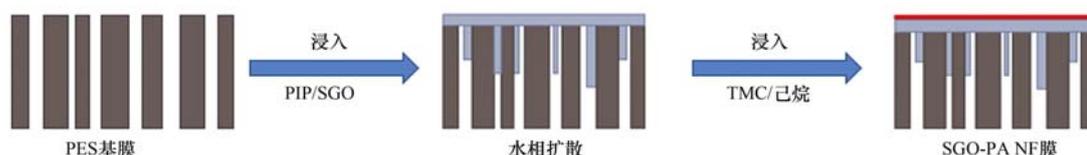


图 1 界面聚合示意

Fig. 1 Interface aggregation diagram

1.4 表征方法

磺酸基团在界面聚合中的反应情况采用傅里叶红外光谱仪进行表征; 膜表面中元素的存在情况用 EDS 能谱进行分析表征; 改性复合纳滤膜的表面和断面微观形态用 SU-8020 场发射扫描电子显微镜 (SEM) 进行观察; 膜表面的 Zeta 电位采用纳米粒度及 Zeta 电位分析仪进行测定分析, 每张膜选取 5 个不同位置进行测定, 取平均值.

1.5 分盐实验

本实验采用错流过滤, 先在 1.0 MPa 的压力下

进行预压以获得稳定的膜通量, 30 min 后, 在 0.2 MPa 压力下, 测定膜的纯水通量和截盐率. 纳滤平板膜性能测试实验装置如图 2 所示.

纯水通量 J 的计算公式为:

$$J = V / (At)$$

式中, V 为渗透过的液体体积, L; A 为膜的有效面积, m^2 (πr^2 , 其中 $r = 2.89$ cm); t 为时间, s. 溶质截留率 R 表示为:

$$R = \left(1 - \frac{c_p}{c_f}\right) \times 100\%$$

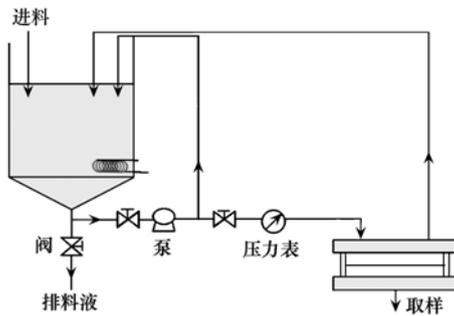


图2 平板膜性能测试装置

Fig. 2 Schematic diagram of flat membrane testing device

式中, c_p 为溶质在透过液的浓度; c_f 为溶质在原料液的浓度. 用电导率仪测定盐溶液的电导率, 根据标准曲线计算得到盐溶液的浓度.

2 结果与讨论

2.1 复合纳滤膜的分析表征

2.1.1 膜表面的红外光谱分析

为证明 SGO 成功引入聚酰胺膜中, 做了红外光谱分析, 结果如图 3 所示.

图 3 是 PA 膜与 PA-SGO 膜的 FT-IR 对照, 由于界面聚合会形成酰胺键, PA 和 PA-SGO 膜在 1600 cm^{-1} 均出现酰胺 ($-\text{CONH}-$) 的特征峰^[26]; 在 1715 cm^{-1} 处 PA-SGO 出现了酯基的特征峰^[27], 而 PA 膜在此处并没有酯基特征峰出现, 这可证明 SGO 存在于聚酰胺复合层中.

2.1.2 膜的表面和断面 SEM

图 4(a)~4(c) 分别是 PES 超滤底膜、PA 膜和 PA-SGO 膜的平面 SEM, 从中可以看出, PES 底膜膜表面平整; 通过界面聚合后, PA 膜表面形成致密的功能层, 膜表面有明显但不规则的凸起结构;

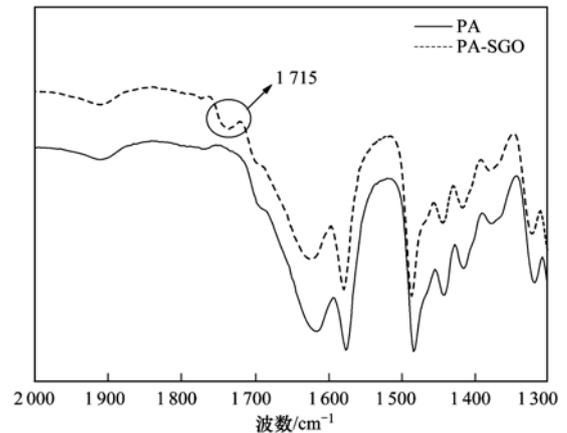


图3 膜表面的傅里叶红外光谱

Fig. 3 FT-IR spectrum of NF membrane surface

而 PA-SGO 表面则形成了交错的具有图灵结构的致密功能层, 这与文献[28]中膜的结构与性能的解释相吻合. 这使得膜的通量明显提高, 对 Na_2SO_4 的截留率仍可达到 98% 以上.

图 4(d)~4(f) 分别是 PES 超滤底膜、PA 膜和 PA-SGO 膜的断面 SEM. 从中可以看出, 界面聚合后, PES 底膜表层有明显的一层超薄致密层, 也就是聚酰胺功能层. 而且, 对比 PA 膜和 PA-SGO 膜的断面 SEM 图, SGO 的加入并没有破坏聚酰胺功能层的致密结构.

2.1.3 膜表面的 EDS 能谱分析

图 5(a) 和图 5(c) 分别为 PA 膜和 PA-SGO 膜表面的 EDS 能谱分析图, 与其对应的图 5(b) 和图 5(d) 分别是 PA 膜和 PA-SGO 膜的 EDS 图. EDS 数据表明, PA-SGO 膜中有明显的 S 元素的峰, 进一步说明了磺酸基团成功引入到了改性复合纳滤膜的功能层中.

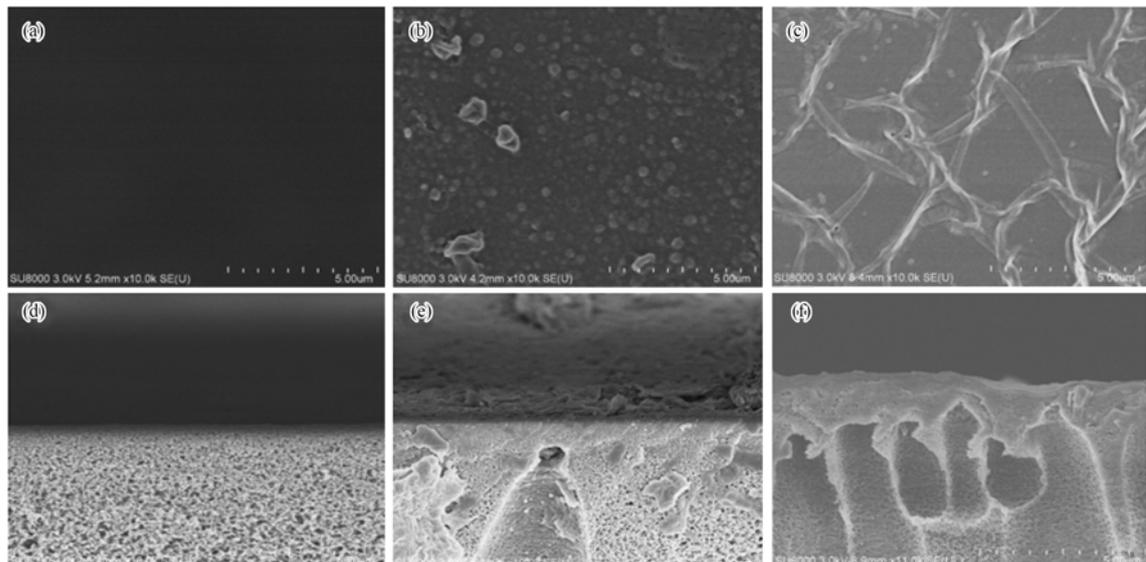


图4 膜的表面和断面形貌

Fig. 4 Surface and cross section images of the membranes

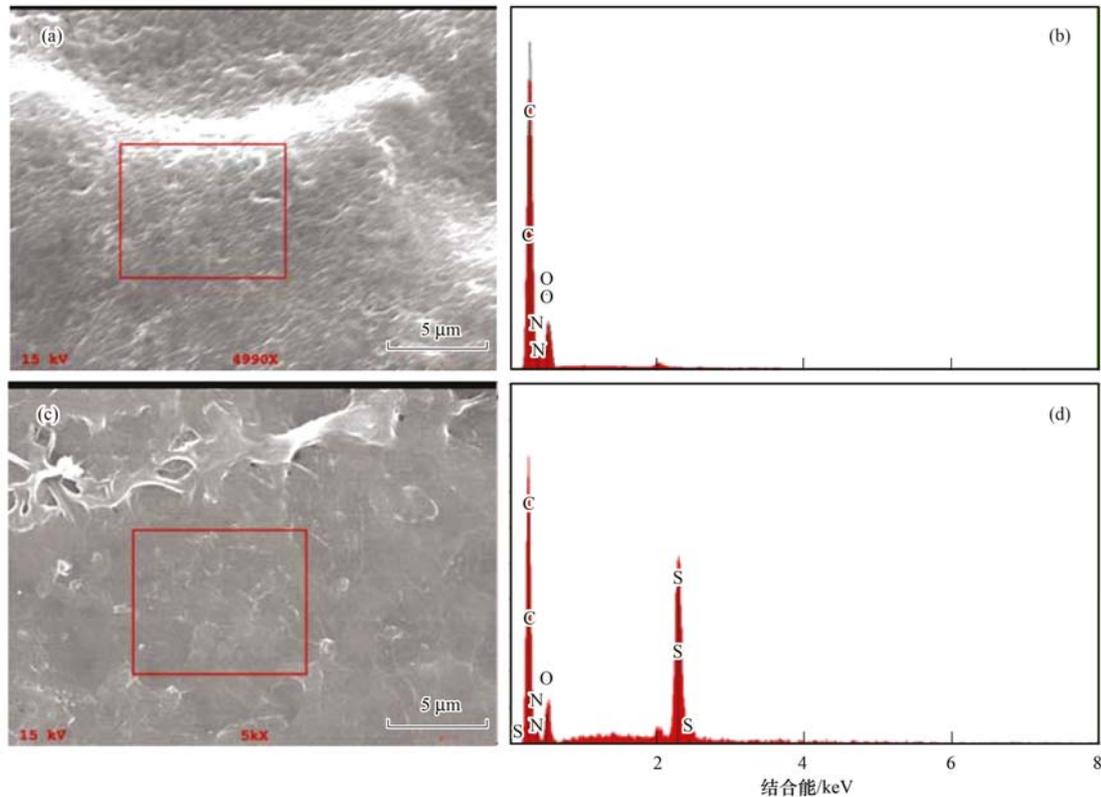


图 5 膜的能谱(EDS)分析图

Fig. 5 EDS patterns of the membranes

2.1.4 膜表面 Zeta 电位

为了对比 PA 膜和 PA-SGO 膜表面的电负性,做了膜表面 Zeta 电位的分析,如图 6 所示.

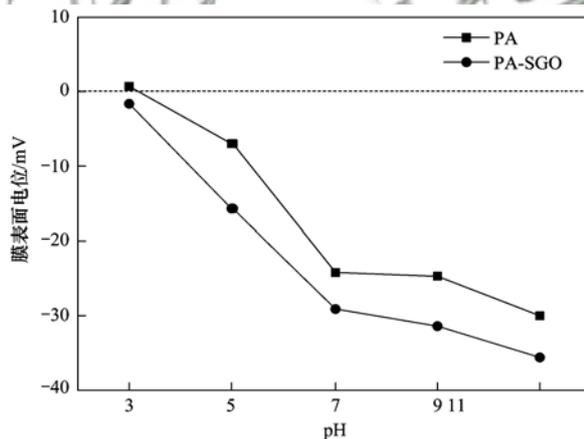


图 6 膜表面电位

Fig. 6 Zeta potential of the membranes

图 6 是复合膜表面的 Zeta 电位测试结果,从中可以看出,随着 pH 值的增大,Zeta 电位呈现逐渐减小的趋势,并且 PA-SGO 膜表面的电负性一直强于 PA 膜,当 pH=7 时,PA 膜表面的 Zeta 电位为 -24.2 mV,此 PA-SGO 膜表面的 Zeta 电位为 -29.1 mV,电负性的更负,结合纳滤道南效应分离机制,为一价盐和二价盐的有效分离提供了有力的证据.

2.2 复合纳滤膜的通量和截盐测试

图 7(a)和 7(b)分别展示了 SGO 含量对膜性能的影响和不同操作压力对纯水通量的影响.结果表明,随着 SGO 含量的增加,膜对 Na_2SO_4 的截留率基本保持不变,都在 98% 以上,对 NaCl 的截留率从 35.14% 降到 24.93%;这可能是由膜表面电位变的更负引起^[23].而纯水通量则从 26.2 增长到 $45.85 \text{ L} \cdot (\text{m}^2 \cdot \text{h})^{-1}$,SGO 含量为 0.03% 时,PA-SGO 膜的通量比 PA 膜增长了 75%,这与膜表面的图灵结构密切相关^[28].图 7(b)可以看出随着测试压力的增加,膜的纯水通量呈现逐渐增加的趋势,这与文献报道的规律相一致^[29].

由图 7(c)可知,PA 膜对盐的截留率为 Na_2SO_4 (98.81%) > MgSO_4 (94.96%) > MgCl_2 (39.5%) > NaCl (35.14%);当 SGO 含量为 0.03%,测试压力为 0.2 MPa 时,PA-SGO 膜对盐的截留率 Na_2SO_4 (98.23%) > MgSO_4 (92.45%) > MgCl_2 (33.57%) > NaCl (24.93%),PA-SGO 膜比 PA 膜更好地实现了一价盐和二价盐的分离.而从图 7 中可以看出,PA-SGO 膜的通量普遍比 PA 膜高.

2.3 膜的分盐性能

在操作压力 0.2 MPa,温度 25℃ 时,进一步研究了 PA-SGO 膜对 Na_2SO_4 和 NaCl 两种盐进行连续 10 h 的分离性能测试,结果如图 8 所示.

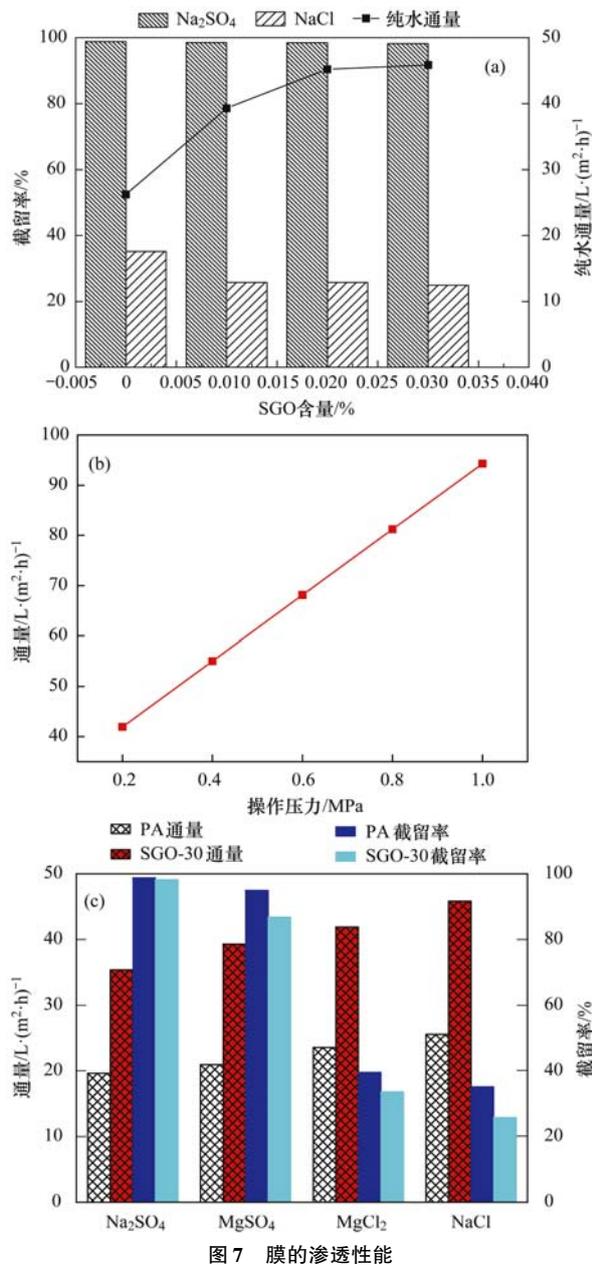


图7 膜的渗透性能

Fig. 7 Permeation performance of the membranes

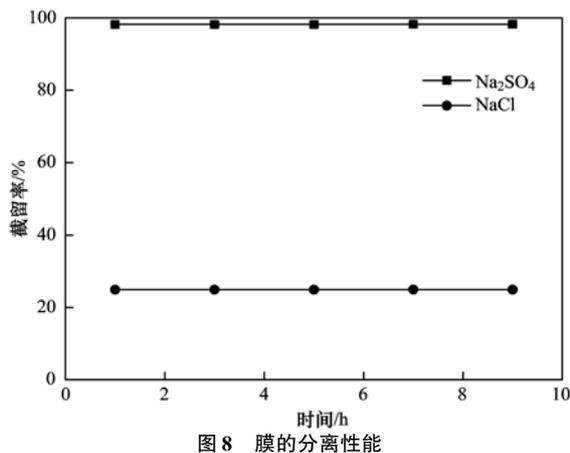


图8 膜的分离性能

Fig. 8 Separation properties of the membranes

随着测试时间的增加,膜对 SO_4^{2-} 和 Cl^- 的截留率基本保持不变.这主要是因为所制备的复合纳

滤膜稳定性良好,在分离运行过程中膜的耐压密性比较好,分离性能稳定.

3 结论

(1)采用界面聚合的方法,成功制备了SGO改性复合纳滤膜.

(2)与PA膜相比,PA-SGO膜表面出现了明显的褶皱,增加了膜的比表面积,在0.2 MPa压力下,膜的纯水通量从 $26.2 L \cdot (m^2 \cdot h)^{-1}$ 增加到 $45.85 L \cdot (m^2 \cdot h)^{-1}$.

(3)SGO的加入使得膜表面电负性增强,对 SO_4^{2-} 的截留率仍维持在98%以上,对 Cl^- 截留率小于25%,实现了对一价盐和二价盐的有效分离.

参考文献:

- [1] 郭海燕,徐成燕,俞彬.石化行业高含盐废水的分盐零排放中试及应用[J].中国给水排水,2018,34(7):99-102.
- [2] 田晓媛.纳滤/反渗透膜技术处理高盐废水及高浓度重金属废水的研究[D].湘潭:湘潭大学,2014.
- [3] Eriksson P, Kyburz M, Pergande W. NF membrane characteristics and evaluation for sea water processing applications [J]. Desalination, 2005, 184(1-3): 281-294.
- [4] 方建慧,姜华,刘继全,等.纳滤膜在海水淡化中的应用研究[J].膜科学与技术,2006,26(1):50-54.
- [5] Fang J H, Jiang H, Liu J Q. *et al.* Study on desalination performance of seawater with nanofiltration membrane [J]. Membrane Science and Technology, 2006, 26(1): 50-54.
- [6] Luo J Q, Wan Y H. Effects of pH and salt on nanofiltration—a critical review [J]. Journal of Membrane Science, 2013, 438: 18-28.
- [7] 赵彦彦,袁其朋.有机相纳滤分离过程中浓度、电荷、溶剂对溶质截留行为的影响[J].膜科学与技术,2006,26(5):31-36.
- [8] Zhao Y Y, Yuan Q P. Effects of concentration, molecular charge and solvents on solute rejection with solvent-resistance nanofiltration membranes in non-aqueous system [J]. Membrane science and Technology, 2006, 26(5): 31-36.
- [9] Peng X S, Jin J, Nakamura Y, *et al.* Ultrafast permeation of water through protein-based membranes [J]. Nature Nanotechnology, 2009, 4(6): 353-357.
- [10] 魏源送,王健行,岳增刚,等.纳滤膜技术在废水深度处理中的膜污染及控制研究进展[J].环境科学学报,2017,37(1):1-10.
- [11] Wei Y S, Wang J X, Yue Z G, *et al.* Fouling and control of nanofiltration membrane in the advanced treatment of wastewater: an overview [J]. Acta Scientiae Circumstantiae, 2017, 37(1): 1-10.
- [12] 龙小庆,王占生.活性炭-纳滤膜工艺去除饮用水中总有机碳和Ames致突变物[J].环境科学,2001,22(1):75-77.
- [13] Long X Q, Wang Z S. Removal of TOC and Ames mutagens from drinking water using AC-NF process [J]. Environmental Science, 2001, 22(1): 75-77.
- [14] Nan Q, Li P, Cao B. Fabrication of positively charged nanofiltration membrane via the layer-by-layer assembly of graphene oxide and polyethylenimine for desalination [J]. Applied Surface Science, 2016, 387: 521-528.
- [15] Li Y F, Su Y L, Zhao X T, *et al.* Preparation of antifouling

- nanofiltration membrane via interfacial polymerization of fluorinated polyamine and trimesoyl chloride [J]. *Industrial & Engineering Chemistry Research*, 2015, **54** (33): 8302-8310.
- [12] 邱实, 吴礼光, 张林, 等. 纳滤分离机理[J]. *水处理技术*, 2009, **35**(1): 15-19.
Qiu S, Wu L G, Zhang L, *et al.* Separation mechanisms of nanofiltration [J]. *Technology of Water Treatment*, 2009, **35** (1): 15-19.
- [13] 黄裕, 张晗, 董秉直. 纳滤膜去除卡马西平的影响因素研究 [J]. *环境科学*, 2011, **32**(3): 705-710.
Huang Y, Zhang H, Dong B Z. Researches on factors affecting the removal of carbamazepine by nanofiltration membranes [J]. *Environmental Science*, 2011, **32**(3): 705-710.
- [14] 陈利, 沈江南, 林龙, 等. 纳滤分离机理及应用于高含盐溶液脱盐的进展[J]. *过滤与分离*, 2009, **19**(4): 9-12.
Chen L, Shen J N, Lin L, *et al.* Separation mechanism of nanofiltration and its application in desalination of high-salt concentration solution [J]. *Journal of Filtration & Separation*, 2009, **19**(4): 9-12.
- [15] 曹晓兵, 李涛, 周律, 等. 染整废水深度处理纳滤工艺膜污染成因分析[J]. *环境科学*, 2012, **33**(1): 117-123.
Cao X B, Li T, Zhou L, *et al.* Analysis of membrane fouling genesis in nanofiltration process for advanced treatment of dyeing and finishing wastewater [J]. *Environmental Science*, 2012, **33** (1): 117-123.
- [16] 文鹏. 氧化石墨烯改性聚酰胺复合纳滤膜的制备及其性能表征[D]. 天津: 天津工业大学, 2017.
- [17] Sasidhar V, Ruckenstein E. Anomalous effects during electrolyte osmosis across charged porous membranes [J]. *Journal of Colloid and Interface Science*, 1982, **85**(2): 332-362.
- [18] Smit J A M. Reverse osmosis in charged membranes: analytical predictions from the space-charge model [J]. *Journal of Colloid and Interface Science*, 1989, **132**(2): 413-424.
- [19] 王利颖, 石洁, 王凯伦, 等. 碳纳米管改性 PVDF 中空纤维超滤膜处理二级出水抗污染性能研究 [J]. *环境科学*, 2017, **38**(1): 220-228.
Wang L Y, Shi J, Wang K L, *et al.* Effect of PVDF hollow fiber ultrafiltration membranes modification with carbonnanotube on membrane fouling control during ultrafiltration of sewage effluent [J]. *Environmental Science*, 2017, **38**(1): 220-228.
- [20] Liu G P, Jin W Q. Graphene oxide membrane for molecular separation: challenges and opportunities [J]. *Science China Materials*, 2018, **61**(8): 1021-1026.
- [21] 王茜, 郭晓燕, 邵怀启, 等. 石墨烯及氧化石墨烯对分离膜改性的方法、效能和作用机理 [J]. *化学进展*, 2015, **27** (10): 1470-1480.
Wang X, Guo X Y, Shao H Q, *et al.* Methods, performances and mechanisms of separation membrane modified by graphene and graphene oxide [J]. *Progress in Chemistry*, 2015, **27**(10): 1470-1480.
- [22] Xie Q L, Zhang S S, Xiao Z Y, *et al.* Preparation and characterization of novel alkali-resistant nanofiltration membranes with enhanced permeation and antifouling properties; the effects of functionalized graphene nanosheets [J]. *RSC Advances*, 2017, **7**(30): 18755-18764.
- [23] Hu R R, He Y J, Zhang C M, *et al.* Graphene oxide-embedded polyamide nanofiltration membranes for selective ion separation [J]. *Journal of Materials Chemistry A*, 2017, **5**(48): 25632-25640.
- [24] 林菊香, 董菁, 陈丹青, 等. 基于对氨基苯磺酸重氮盐功能化制备亲水性磺化石墨烯的研究 [J]. *中国科学: 化学*, 2016, **46**(8): 791-799.
Lin J X, Dong J, Chen D Q, *et al.* Synthesis of hydrophilic sulfonated graphene based on diazonium salt of 4-aminobenzenesulfonic acid functionalized graphene [J]. *Scientia Sinica Chimica*, 2016, **46**(8): 791-799.
- [25] 郭长春. 氧化石墨烯(GO)与磺化氧化石墨烯(SGO)的制备及其修饰电极电化学研究[D]. 青岛: 青岛大学, 2012.
- [26] Bano S, Mahmood A, Kim S J, *et al.* Graphene oxide modified polyamide nanofiltration membrane with improved flux and antifouling properties [J]. *Journal of Materials Chemistry A*, 2015, **3**(5): 2065-2071.
- [27] Rolere S, Liengprayoon S, Vaysse L, *et al.* Investigating natural rubber composition with Fourier Transform Infrared (FT-IR) spectroscopy: a rapid and non-destructive method to determine both protein and lipid contents simultaneously [J]. *Polymer Testing*, 2015, **43**: 83-93.
- [28] Tan Z, Chen S F, Peng X S, *et al.* Polyamide membranes with nanoscale Turing structures for water purification [J]. *Science*, 2018, **360**(6388): 518-521.
- [29] 袁俊生, 焦亮, 刘杰. 利用纳滤膜软化浓海水研究 [J]. *水处理技术*, 2012, **38**(11): 81-83, 89.
Yuan J S, Jiao L, Liu J. Softening of concentrated seawater by nanofiltration membrane [J]. *Technology of Water Treatment*, 2012, **38**(11): 81-83, 89.

CONTENTS

Influence of Mountain Valley Breeze and Sea Land Breeze in Winter on Distribution of Air Pollutants in Beijing-Tianjin-Hebei Region	LI Qing-chun, LI Ju, ZHENG Zuo-fang, <i>et al.</i>	(513)
A Method of Aerosol Particle Number Size Distribution Inversed by PM _{2.5} Mass Concentration in PRD	LI Fei, TAN Hao-bo, DENG Xue-jiao, <i>et al.</i>	(525)
Light Absorption and Fluorescence Characteristics of Atmospheric Water-soluble Organic Compounds and Humic-like Substances During the Winter Season in Guangzhou	FAN Xing-jun, YU Xu-fang, CAO Tao, <i>et al.</i>	(532)
Source Apportionment and Health Risk Quantification of Heavy Metals in PM _{2.5} in Yangzhou, China	DONG Shi-hao, XIE Yang, HUANGFU Yan-qi, <i>et al.</i>	(540)
Pollution Characteristics and Source Analysis of <i>n</i> -alkanes and Saccharides in PM _{2.5} During the Winter in Liaocheng City	LIU Xiao-di, MENG Jing-jing, HOU Zhan-fang, <i>et al.</i>	(548)
Pollution Characteristics, Dry Deposition Fluxes, and Sources for Atmospheric Polycyclic Aromatic Hydrocarbons in the Bosten Lake Watershed	SONG Shi-jie, HUANG Tao, ZHAO Liu-yuan, <i>et al.</i>	(558)
Distribution Characteristics of Antibiotic Resistance Genes in PM _{2.5} of a Concentrated Broiler Feeding Operation	LIU Fei, XU Xia, TU Bo-wen, <i>et al.</i>	(567)
Effects of Water Vapor Source and Local Evaporation on the Stable Hydrogen and Oxygen Isotopic Compositions of Precipitation	HU Yong-bo, XIAO Wei, QIAN Yu-fei, <i>et al.</i>	(573)
Characteristics of Nitrogen and Phosphorus Formation in Atmospheric Deposition in Dianchi Lake and Their Contributions to Lake Loading	REN Jia-guo, JIA Hai-bin, JIAO Li-xin, <i>et al.</i>	(582)
Temporal-spatial Distribution of Nitrogen and Phosphorus Nutrients in Lake Taihu Based on Geostatistical Analysis	LÜ Wei-wei, YAO Xin, ZHANG Bao-hua, <i>et al.</i>	(590)
Effects of Cyanobacterial Blooms in Eutrophic Lakes on Water Quality of Connected Rivers	YU Mao-lei, HONG Guo-xi, XU Hai, <i>et al.</i>	(603)
Contamination and Potential Ecological Risk Assessment of Heavy Metals in the Sediments of Yilong Lake, Southwest China	LI Xiao-lin, LIU En-feng, YU Zhen-zhen, <i>et al.</i>	(614)
Temporal and Spatial Characteristics of Heavy Metals in Suspended Particulate Matter in Pearl River Estuary and Its Influencing Factors	DU Jia, WANG Yong-hong, HUANG Qing-hui, <i>et al.</i>	(625)
Pollution Characteristics and Health Risk Assessment of Microorganism Pollutions in the Beiyun River	CHEN Lei, LI Lei-fang, ZHI Xiao-sha, <i>et al.</i>	(633)
Speciation and Transformation of Phosphorus in Sediments During the Redox Cycle	HAO Wen-chao, WANG Cong-feng, YANG Zheng-jian, <i>et al.</i>	(640)
Effect of Magnetic Zirconium/Iron-Modified Bentonite Addition on Phosphorus Mobilization and Species Transformation in River Sediments	WANG Yan, LIN Jian-wei, ZHAN Yan-hui, <i>et al.</i>	(649)
Influence of Calcium Ion Pre-treatment on Phosphate Adsorption onto Magnetic Zirconium/Iron-modified Bentonite	ZHAO Yu-ying, LIN Jian-wei, ZHANG Hong-hua, <i>et al.</i>	(658)
Effect of Nitrogen on Magnesium Modified Biochar Adsorption to Phosphorus	ZHI Meng-meng, WANG Peng-fei, HOU Ze-ying, <i>et al.</i>	(669)
Removal Performance and Mechanism for Treating Phosphorus in Agricultural Wastewater by Three Adsorbents	WU Lu, LIU Feng, LONG Rui, <i>et al.</i>	(677)
Photolysis Mechanism of <i>p</i> -Nitrophenol by Nitrocellulose Membrane in Aqueous Solution	DAI Zhi-feng, ZHAO Tong-qian, YIN Yong-guang, <i>et al.</i>	(685)
Preparation of ZnTiO ₃ /TiO ₂ Photocatalyst and Its Mechanism on Photocatalytic Degradation of Organic Pollutants	ZHANG Wen-hai, JI Qing-hua, LAN Hua-chun, <i>et al.</i>	(693)
Adsorption and Photocatalytic Removal of Chromium on High-index TiO ₂ Facet	ZHONG De-jian, ZHANG Jian-feng, LI Yao, <i>et al.</i>	(701)
Reduction Cooperated Fenton Oxidation of Zero-valent Iron (ZVI) Immobilized in Alginate Microsphere for Degradation of Acid Red B	ZHANG Huan, LI Shuang-shuang, WEI Jun-fu, <i>et al.</i>	(708)
Mechanism of Removing Iron and Manganese from Drinking Water Using Manganese Ore Sand and Quartz Sand as Filtering Material	CAI Yan-an, BI Xue-jun, ZHANG Jia-ning, <i>et al.</i>	(717)
Preparation of Sulfonated Graphene Oxide Modified Composite Nanofiltration Membrane and Application in Salts Separation	ZHANG Yan-jun, ZHANG Shao-feng, ZHAO Chang-wei, <i>et al.</i>	(724)
Purification Efficiency and Mechanism of Integrated Al Salt Flocculation-ultrafiltration Membrane Process	XUE Wen-jing, LI Wen-jiang, LIU Jian, <i>et al.</i>	(730)
Threshold Flux and Membrane Fouling Analysis of the Hybrid Pre-ozonation and CNTs Membrane Modification Process	WANG Kai-lun, LIU Fang, GUAN Yu-qi, <i>et al.</i>	(738)
Distribution and Removal of Polycyclic Aromatic Hydrocarbons and Their Derivatives in SBR/MBBR Process	LIU Shu-hui, TIAN Wei-jun, ZHOU Jian-ren, <i>et al.</i>	(747)
Biological Nitrogen Removal Process in a Microbubble-aerated Biofilm Reactor Treating Low C/N Wastewater	LIU Chun, WANG Cong-cong, CHEN Xiao-xuan, <i>et al.</i>	(754)
Treatment of Simulated Saline Wastewater from the Coal Chemical Industry Using Ecological Floating Beds Enhanced with Arbuscular Mycorrhiza	DOU Wen-qing, HE Hao, SONG Wen-ping, <i>et al.</i>	(761)
Nitrification and Bioaugmentation of Biological Treatment System of Sewage Treatment Plant at High Temperature in Summer	SONG Tian-wei, SHENG Xiao-lin, WANG Jia-de, <i>et al.</i>	(768)
Characteristics of Ammonia Adsorption and Kinetics by Nitrifying Sludge Immobilized Pellets	YU De-shuang, LÜ Ting-ting, CHEN Guang-hui, <i>et al.</i>	(774)
Nitrite Accumulation Characteristics of Partial Denitrification in Different Sludge Sources Using Sodium Acetate as Carbon Source	BI Chun-xue, YU De-shuang, DU Shi-ming, <i>et al.</i>	(783)
Operating Characteristics of a DPR-SNED System Treating Low C/N Municipal Wastewater and Nitrate-containing Sewage	DU Shi-ming, YU De-shuang, BI Chun-xue, <i>et al.</i>	(791)
Simultaneous Nitrification and Denitrifying Phosphorus Removal in Continuous Flow Reactor with Intermittent Aeration	ZHAO Zhi-chao, HUANG Jian-ming, LI Jian, <i>et al.</i>	(799)
Start-up and Stable Operation of ABR-MBR Denitrifying Phosphorus Removal Process	WEI Jia-min, JIANG Zhi-yun, CHENG Cheng, <i>et al.</i>	(808)
Effect of Influent C/N Ratio on the Nutrient Removal Characteristics of SNEDPR Systems	DU Ye-qi, YU De-shuang, ZHEN Jian-yuan, <i>et al.</i>	(816)
Carbon and Nitrogen Removal Characteristics of ABR Decarbonization-CANON Coupling Process	LI Tian, YIN Wen, WANG Xin-zhu, <i>et al.</i>	(823)
Effect of Aeration Density on Start-up of CANON Process	LI Dong, GAO Xue-jian, ZHANG Jie, <i>et al.</i>	(829)
Adjusting Temperature and Settling Time to Achieve ANAMMOX Particles Rapid Start-up and Stable Operation	LI Hai-ling, LI Dong, ZHANG Jie, <i>et al.</i>	(837)
Effect of C/N and Sludge Concentration on the pH-Regulated Nitrosation System	ZHANG Min, WEI Jia-min, HUANG Hui-min, <i>et al.</i>	(845)
Growth Features of Water Supply Pipeline Biofilms Based on Active Microorganisms	WANG Yang, ZHU Bin, TONG Jun, <i>et al.</i>	(853)
Elevational Distribution Characteristics of Soil Bacterial Community and Enzyme Activities in Mount Huangshan	YAO Lan, HU Li-huang, ZHANG Huan-chao, <i>et al.</i>	(859)
Microbial Community Structure Shift during Bioremediation of Petroleum Contaminated Soil Using High Throughput Sequencing	QI Yan-yun, WU Man-li, ZHU Chang-cheng, <i>et al.</i>	(869)
Effect of Nitrification on N ₂ O Emissions and Their Environmental Factors in Saline-alkali Wetlands	YANG Qu, GAO Wei-feng, LIU Feng-qin, <i>et al.</i>	(876)
Effect of Long-term Dairy Manure Amendment on N ₂ O and NO Emissions from Summer Maize-Winter Wheat Cropping Systems	NIE Huang-hua, ZHANG Jia-sheng, HE Zhou-ming, <i>et al.</i>	(885)
Effects of Plastic Film Mulching and Nitrogen Fertilizer Application on N ₂ O Emissions from a Vegetable Field	NI Xue, HAO Qing-ju, CHEN Shi-jie, <i>et al.</i>	(893)
Differences and Relationship Between Rhizosphere Characteristics and Methane Emissions of Double-cropping Rice Variety	XIAO Zhi-xiang, FU Zhi-qiang, XU Hua-qin, <i>et al.</i>	(904)
Effect of Long-Term Biochar Application on Soil Respiration in Flue-Cured Tobacco Planting Fields in Henan Province	LI Ya-sen, DING Song-shuang, YIN Quan-yu, <i>et al.</i>	(915)
Spatial Variability in Soil Respiration Under Different Land Use Patterns in Maocun Village, Guilin	DING Meng-kai, HU Xiao-nong, CAO Jian-hua, <i>et al.</i>	(924)
Spatiotemporal Variability and Source Apportionment of Soil Heavy Metals in a Industrially Developed City	LI Feng, LIU Si-yuan, LI Yan, <i>et al.</i>	(934)
Effects of Bentonite on Chemical Forms and Bioavailability of Heavy Metals in Different Types of Farmland Soils	LIN Hai, JIN Xiao-na, DONG Ying-bo, <i>et al.</i>	(945)
Characteristics of Soil Organic Carbon and Mineralization with Different Stands in Jinyun Mountain	CHEN Shi-qi, LÜ Sheng, GAO Ming, <i>et al.</i>	(953)
Contribution of Root Biomass to Soil Organic Carbon Under Complex Landforms Conditions	ZHANG Yan-jun, GUO Sheng-li, <i>et al.</i>	(961)
Transformation and Distribution of Soil Organic Carbon and the Microbial Characteristics in Response to Different Exogenous Carbon Input Levels in Paddy Soil	WANG Ji-fei, TONG Yao-yao, ZHU Zhen-ke, <i>et al.</i>	(970)
Analysis of Heavy Metal Pollution and Ecological Risk Assessment on Vegetation Leaves in Baoji City	ZHANG Jun-hui, LIN Qing, JIANG Shan, <i>et al.</i>	(978)
Effect of Biochar on Available Heavy Metals During Sewage Sludge Composting and Land Application of Compost	ZHOU Ji, YU Ya-wei, JIANG Yue, <i>et al.</i>	(987)
Influence of Sludge Retention Time on the Performance and Stability of Mesophilic Anaerobic Co-digestion of Food Waste with Waste Activated Sludge	YUAN Hong-lin, MA Jing, XING Bao-shan, <i>et al.</i>	(994)
Performance of Treating Straw and Animal Manure Mixture by an Integrated Process of Thermo-alkali-bi-enzyme Hydrolysis-anaerobic Digestion and Conditions of High Methane Yield	BIAN Ai-qin, YUAN Ye, ZHANG Lu-lu, <i>et al.</i>	(1003)