

(HUANJING KEXUE)

ENVIRONMENTAL SCIENCE

第33卷 第12期

Vol.33 No.12

2012

中国科学院生态环境研究中心 主办



地 章 ENVIRONMENTAL SCIENCE (HUANJING KEXUE)

第33卷 第12期 2012年12月15日

次 目

特别策划:再生水灌溉利用生态风险研究专题 序 ——再生水灌溉利用的生态风险研究进展————————————————————————————————————	
序	陈卫平(4069)
再生水灌溉利用的生态风险研究进展	潘能,焦文涛(4070)
绿地再生水灌溉土壤微生物量碳及酶活性效应研究 潘能 侯振安 陈卫平 焦文流	年.彭驰.刘文(4081)
绿地再生水灌溉土壤盐度累积及风险分析	忠明.侯振安(4088)
再生水灌溉对土壤性质及重会属垂直分布的影响 数忠明 陈卫平 焦	文涛 王姜娥(4094)
超到模拟再生水灌溉对土壤水盐运动的影响	フ平 王美娥(4100)
横刑模拟十幢性质和植被轴光对重生水灌溉水卦运移的影响	エ → , 工 爻 巛 (4100) リ 平
医生长顶上板压负和低级作大利性工术压制小品色物的影响 ————————————————————————————————————	立 - , 工天
打工小准例从山上使用不6次次件快5次则几	入付, 上天
村士小催帆工场八上口风脚目示你保室快!N ————————————————————————————————————	上丁, 压入内(4121) 化工共
观印统化早叶丹生小催佩对地下小小贝影响研究	世玉分,
北京中井生水的公众认知度评估	卫平,焦义涛(4133)
研究报告 - 15-25-15-15-15-15-15-15-15-15-15-15-15-15-15	☆ 17
北京地区臭氧时空分布特征的飞机探测研究 ····································	局扬, 黄梦宇(4141)
世傳会期间上海市大气挥发性有机物排放强度及污染来源研究	
王红丽,陈长虹,黄海英,王倩,陈宜然,黄成,李莉,张钢锋,陈明华,楼,	晟荣,乔利平(4151)
贡嘎山本底站大气中 VOCs 的研究 张军科,王跃思,	吴方堃,孙杰(4159)
区域大气环境风险源识别与危险性评估 张晓春,陈卫平,马春,詹z	N芬, 焦文涛(4167)
稻草烟尘中正构烷烃和正构脂肪酸的碳同位素 刘刚,孙丽娜,3	李久海,徐慧(4173)
汽油轿车 NEDC 循环超细颗粒物排放特性 · · · · · · · · · · · · · · · · · · ·	丕强,楼狄明(4181)
城市道路绿化带不同植物叶片附尘对大气污染的磁学响应	孟颉,达良俊(4188)
一生红丽,陈长虹,黄海英,土情,陈宜然,黄成,季刹,张钢锋,陈明华,楼景 页嘎山本底站大气中 VOCs 的研究	清华,黄佳芳(4194)
模拟增温对冬小麦-大豆轮作农田土壤呼吸的影响 刘艳、陈书涛、胡正华、任士	景全, 沈小帅(4205)
广西大石围天坑中多环芳烃的大气传输与分异	孙骞, 黄保健(4212)
松花江流域冰封期水体中多环芳烃的污染特征研究 马万里,刘丽艳,齐虹,白杨,沈吉敏,陈	忠林 李一凡(4220)
温州城市河流中多环芳烃的污染特征及其来源	许世沅 潘琪(4226)
温州城市河流河岸带土壤中口及旧。的污染蜂行与来源	许世元,潘贯(1220)
温州城市河流河岸带土壤中 PAHs 的污染特征与来源 …	用
是内外部的内容,TATS 的力量的正众内壁中的	用 及 m ,同 由 (12 1 1)
本原面/ 医区切地上横可区区地上小助天门来付加切孔 甘于用作ル人加运池区地由夕环基场公司八五的八旦种柱尔	近近, 作工平(4231) 安县 比如田(4256)
某炼油厂退役场地土壤与浅层地下水酚类污染特征研究 某大型焦化企业污染场地中多环芳烃空间分布的分异性特征	及生, 平如田(4230) 主法 木仕匠(4262)
A.房中与作区有机或农约垂直万种村征及原辟机	月月, 学住尔(4203) 结片 共見切(4270)
工商印票明岛农田工集中多环方定分布和生态风险作价 ————————————————————————————————————	炭 成, 野京 超(42/0)
近50 年来深圳湾兰州外巡地 Hg、Cu 条积及其生态卮善评价	即国土, 货倍(42/6)
北运河源头区沙河水库沉积初里金属污染特征研究	张洪, 里保庆(4284)
太湖表层沉积物重金属赋存形态分析及污染特征 秦延又,张雷,	郑内辉,曹伟(4291)
典型李风型温冰川消融期融水化学日变化特征 朱国锋,蒲焘,何元庆,王培震,孔建龙,张	宁宁, 辛惠娟(4300)
螺-草水质净化系统氮素环境归趋的实验研究 周露洪,谷孝鸿,曾庆飞,毛志刚,高	华梅, 孙明波(4307)
固定化果胶酶抑制铜绿微囊藻生长研究	升燕,韩秀林(4316)
采用膜污染指数评估天然有机物在低压超滤膜中的污染行为 肖萍,肖峰,赵锦辉,秦潼,王东升,	冯金荣,许光(4322)
水体中甲基汞光化学降解特征研究 孙荣国,毛雯,马明,	张成,王定勇(4329)
土霉素在乙酸水溶液中的臭氧氧化降解研究 李时银,李小荣,朱怡苹,朱	江鹏,王国祥(4335)
酰胺咪嗪光降解效能与机制及其影响因素研究 陈超,赵倩,圭	対莉,张立秋(4340)
利用 FeS 去除水中硝基苯的试验研究 · · · · 王	夏琳,李睿华(4346)
利用 FeS 去除水甲硝基本的试验研究	晓磊,赵战坤(4352)
表面活性剂改性沸石对水中酚类化合物吸附性能研究 谢杰,王哲,吴	德意,李春杰(4361)
抗生素类制药废水厌氧消化产物急性毒性的检测 季军远,	邢雅娟,郑平(4367)
废砖块作为人工湿地填料的除磷能力研究 王振,刘超翔,李鹏宇,董健,	刘琳,朱葛夫(4373)
基干生物沸石复合滤料的间歇式脱氮水处理	陈冬,谢晶晶(4380)
硝酸盐对厌氧生物膜和颗粒污泥的同时产甲烷反硝化性能影响研究 钟晨字 叶杰旭 李若愚	陈胜 孙德智(4387)
水平电场作用下活性污泥的脱水研究 ————————————————————————————————————	干穀力 冯晶(4393)
多重环境因子对氟胺磺隆在土壤中降解的影响 宋宁 董 单正军 石利利 郭納 计	午静 孔德洋 (4400)
磁后外理对互花米草沼渣理化特性的影响研究	海芹 叶小梅(4406)
李确旁答言温悠结计程确的矿物相结构变化与环倍略前行为	皮泽壹
日本大学运动和建筑工程。 国家十年运动物排动标准体系研究	ハイラ,上供(サ12) 釉工需 任寿(1/17)
四次八、17不191H以191EP不明九	396. 14
小児至他門小児你他我化的你們你的 对"方妻重奏屋"实施了新首县於對此篇七子的利宝公坛	
刈 有母里並周 头爬 4 件尽里宜利益官刀入的利舌分析 ····································	(4428)
《	·············(4454)
硝酸盐对厌氧生物膜和颗粒污泥的同时产甲烷反硝化性能影响研究 —— 钟晨早,叶杰旭,季若愚,水平电场作用下活性污泥的脱水研究 —— 季雪元,多重环境因子对氟胺磺隆在土壤中降解的影响 —— 宋宁慧,单正军,石利利,郭敏,i碱后处理对互花米草沼渣理化特性的影响研究 —— 陈广银,郑正,常志州,王含砷废渣高温烧结过程砷的矿物相结构变化与环境释放行为 —— 王兴润,国家大气污染物排放标准体系研究 —— 工兴镇,和宝宁,张明慧,邹兰,环境基准向环境标准转化的机制探讨 —— 上,本,张国宁,张明慧,邹兰,环境基准向环境标准转化的机制探讨 —— 华岑岑,王对"有毒重金属"实施 2 种总量控制监管方式的利害分析 —— 《环境科学》第 33 卷(2012 年)总目录 —— 《环境科学》征订启事(4099) 《环境科学》征稿简则(4166) 信息(4180, 4219, 4225, 4275) 专	7 再 但 何 理 却 (41 / 2)

采用膜污染指数评估天然有机物在低压超滤膜中的污染行为

肖萍1,肖峰1,赵锦辉2,秦潼3,王东升1*,冯金荣2,许光4

(1. 中国科学院生态环境研究中心饮用水科学与工程中心,北京 100085; 2. 太平洋水处理工程有限公司,南通 226007; 3. 南通市自来水公司,南通 226007; 4. 北京市自来水集团门城污水处理有限公司,北京 102308)

摘要:针对超滤膜的过滤特性,采用膜污染指数(FI)来研究天然有机物(NOM)的膜污染行为.实验中,腐殖酸(HA)、牛血清蛋白(BSA)以及海藻酸钠(NaAlg)被用作模型有机物进行超滤膜污染研究.结果表明,NOM-膜滤先后经过快反应和慢反应污染阶段,其中快反应膜污染指数(TFI_F)远大于慢反应膜污染指数(TFI_S).说明短时间内 NOM 容易在低压膜上积累,造成通量迅速下降,引起较为严重的污染.因此,反应最初阶段,低压膜与有机物的作用决定了整个膜污染的趋势.经过水力清洗,通量有一定恢复,膜阻力降低,能够去除部分污染物,但仍有少量有机物附着在膜丝,从而造成不可逆污染.3种有机物造成的不可逆污染比例依次为 BSA > HA > NaAlg,而通过化学清洗后,其不可逆污染比例依次为:NaAlg > BSA > HA,腐殖酸和蛋白容易造成不可逆污染,但碱洗易于除去,多糖造成的不可逆污染相对较轻,但碱洗难以去除.污染物与膜之间的相互作用可能是造成污染的主要原因.总的说来,FI 计算方法简单,能够综合描述膜污染情况,具有一定的应用价值.

关键词:天然有机物(NOM); 低压超滤膜; 腐殖酸(HA); 牛血清蛋白(BSA); 海藻酸钠(NaAlg); 膜污染指数(FI)中图分类号: X703.1 文献标识码: A 文章编号: 0250-3301(2012)12-4322-07

A Novel Approach of Using Fouling Index to Evaluate NOM Fouling Behavior During Low Pressure Ultrafiltration Process

XIAO Ping¹, XIAO Feng¹, ZHAO Jing-hui², QIN Tong³, WANG Dong-sheng¹, FENG Jin-rong², XU Guang⁴ (1. Research Centre for Drinking Water, Research Centre for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China; 2. Pacific Water Treatment Engineering Co., Ltd., Nantong 226007, China; 3. Water Supply Plant of Nantong, Nantong 226007, China; 4. Mencheng Sewage Treatment Co., Ltd., Beijing Waterworks Group, Beijing 102308, China)

Abstract: In this study, fouling index (FI) was introduced as a novel approach to investigate NOM fouling behavior during low pressure membrane ultrafiltration process. Three kinds of typical NOMs, humic acid (HA), bovine serum albumin (BSA) and sodium alginate (NaAlg), were used in the experiments. The results indicated that the fouling caused by NOM can be considered as two steps with different FI values. One is the fast fouling phase, and the other is the slow phase. Apparently, the total fouling index of the fast phase (TFI_F) was much greater than that of the slow phase (TFI_S), which means the initial interaction between NOM and membrane would play a significant role in the whole fouling process. A higher TFI_F could lead to a faster fouling and the flux would decline more rapidly. After hydraulic washing, the flux was recovered and the resistance was reduced, indicating that physical cleaning could remove a part of foulants. Additionally, the results also represented that the sequences of NOM causing irreversible fouling and chemical clean irreversible fouling were BSA > HA > NaAlg and NaAlg > BSA > HA, respectively. Humic acid and protein tended to cause irreversible fouling and were easily removed by alkaline cleaning, while irreversible fouling caused by polysaccharide was difficult to remove by alkaline. The main cause of membrane fouling may be the interaction between foulants and membrane, which needs further research. Generally speaking, FI with a simple expression would play a significant role to describe the membrane fouling.

Key words: natural organic matter (NOM); low pressure ultrafiltration membrane; humic acid (HA); bovine serum albumin (BSA); sodium alginate (NaAlg); membrane fouling index

低压膜分离技术(包含微滤和超滤)在过去的20年内飞速发展,获得众多行业的青睐.由于膜分离技术出水水质稳定、安全性高且易于操作,在饮用水行业成为水厂改造的首选.然而膜污染仍然是阻碍膜技术广泛应用的瓶颈.污染物在膜滤过程中,累积或吸附在膜表面以及膜孔内,导致膜有效过滤面积减少,引起通量下降.近年来,探讨膜污染的机制成为本领域的研究重点和热点.已有研究报

道^[1~6],某些特定的组分才可能导致膜污染,比如天然有机物(NOM)如腐殖酸、蛋白质和多糖类在很大程度上会造成可逆或者不可逆膜污染,这取决于膜材料与源水之间的相互作用.同时,膜污染并不

收稿日期: 2012-02-22; 修订日期: 2012-08-07

基金项目: 国家自然科学基金项目(50078051,51008293,51138008) 作者简介: 肖萍(1983~),女,博士研究生,主要研究方向为饮用水

膜处理技术, E-mail; suzy19831020@ yahoo. com. cn * 通讯联系人, E-mail; wgds@ reees. ac. cn

是由一种物质造成的,其组成成分复杂,许多物质共同作用,相互影响.正因为这样的特殊性,如何有效地评定或者预测膜污染成为一大难题.

许多学者利用 Heimia 公式或者其衍生公式,总 结出膜污染的几种典型机制[7],包括吸附污染、堵 塞污染、形成滤饼、形成沉淀以及形成凝胶层. Huang 等[8]通过数学推导,建立了针对膜污染特性 的标准膜污染指数(UMFI),能够在一定程度上描述 不同规模膜滤过程的污染趋势,并在低压膜处理废 水中得到验证. 同时得出 UMFI 与原水的浊度 (NTU)、总有机碳(TOC)没有直接的相关性,而膜 的特性如亲水性、膜孔大小则对其有一定的影响. 其它研究者[9,10]建立了恒通量低压膜的修正污染指 数模型,可逆和不可逆膜污染分别由滤饼和中间堵 塞造成. 不同类型的污染则根据相应的实验数据计 算其污染指数. 这些模型或者指数都能够描述膜污 染行为、预测膜污染趋势. 由于是在特定的污染机 制的基础上建立,存在着局限性. 膜污染并不是某 些特定污染物或者特定污染机制构成,而可能是多 种物质和多种污染机制同时发生,同时作用,最终导 致膜污染. 因此,建立一种普遍适用的膜污染模型, 用于描述污染具有重要的意义.

本研究以天然有机物(NOM)-低压膜滤过程为对象,以 Nguyen等[11]确定的膜污染指数(FI)为基础,评定3种典型有机物膜滤过程的污染行为.这种污染指数忽略了污染机制的类型,仅考察整体的污染行为和结果,能够应用于不同模式(恒通量或者恒压)的低压膜过滤过程,较好地描述膜污染的行为和趋势.并通过计算不同阶段(水力和化学清洗)的污染指数,确定膜的可逆和不可逆污染比例,全面了解 NOM 的膜污染过程.

1 污染指数评价指标的建立

通常可以用膜阻力来描述膜污染的情况,膜阻力 R 与膜通量 J、跨膜压差的关系可由公式(1)进行描述:

$$J = \frac{\Delta P}{\mu R} \tag{1}$$

式中, ΔP 为跨膜压差, μ 为水的黏度系数. 膜阻力 R 指液体过膜时可能产生的阻力的总和. 在任意一个过滤过程中,R 是膜自身阻力 R_m 和液体过膜产生的阻力 R, 的和,即:

$$R = R_{m} + R_{t} \tag{2}$$

根据产水量公式:

$$V = Qt/A \tag{3}$$

式中,V为单位面积上的产水量,Q为液体的流速,t为过滤时间,A为膜有效面积.

由于针对的是低压超滤膜,因此假定产水量与液体过膜产生的阻力 R_{ι} 呈线性关系^[11]. 即随着产水量的逐渐增大,液体过膜产生的阻力呈线性增加,因此:

$$R_{1} = kV \tag{4}$$

式中, k 是膜阻力随产水量增加的比例常数.

将公式(4)代入公式(2),可得:

$$R = R_{\scriptscriptstyle m} + R_{\scriptscriptstyle 1} = R_{\scriptscriptstyle m} + kV \tag{5}$$

结合公式(5)和公式(1)得到:

$$J = \frac{\Delta P}{\mu R} = \frac{\Delta P}{\mu (R_m + kV)} \tag{6}$$

对于新膜而言,产水量 V=0,因此有:

$$J_0 = \Delta P / \mu R_{\rm m} \tag{7}$$

产水量 V 不为 0, 而是等于 V'时,则有:

$$J' = \Delta P/\mu (R_{_m} + kV') \tag{8}$$

当跨膜压差 TMP 恒定,结合公式(7)和公式(8)可以推出:

$$\mu R_{\rm m} J_0 = \mu (R_{\rm m} + kV') J' \tag{9}$$

因此:

$$\frac{J_0}{J'} = 1 + \frac{k}{R_m} V \tag{10}$$

在公式(10)中,将 k/R_m 定义为膜污染指数 (fouling index, FI),即可得到:

$$J_0/J' = 1 + (FI)V$$
 (11)

由公式(11)可知,根据通量和产水量可以计算得出膜污染指数 FI 值(m²·L⁻¹). 其物理意义是:如果要获得一定的产水量,当通量恒定时,FI 的大小可以直接决定最终的压头损失;而当跨膜压差恒定时,FI 直接与最终产水量相关. 膜污染指数可以用于表征膜污染速率,即 FI 越小,污染越缓慢;反之,FI 越大,则污染越快. 根据公式(11),确定了污染指数 FI,根据产水量,则可以得知通量的变化. 在膜组件运行的各个阶段,通过对膜的表现以及清洗过程数据的监测,可以得到不同的污染指数. 根据不同的运行阶段,膜污染指数可以分别定义为总污染指数(TFI)、可逆污染指数(RFI),水力不可逆污染指数(HIFI)以及化学清洗不可逆污染指数(CIFI).

当膜过滤一个周期结束后,且并无任何物理或者化学清洗过程时,跨膜压差与产水量的关系可由公式(11)确定:

$$J_0/J' = 1 + (TFI)V$$
 (12)

其中 TFI 定义为一个运行周期内膜的总污染指数.公式(12)与已有研究^[9]有相同的数学意义,但是公式(12)不区分膜污染是由何种污染物造成或者污染的机制如何,而是将所有的污染物和污染机制均包含在内,用膜的总污染指数(TFI)描述污染情况,更加简明扼要.

对于包含水洗而无化学清洗的运行周期,通过水洗后膜通量的恢复,确定通量与产水量的关系:

$$J_0/J_1 = 1 + (HIFI)V$$
 (13)

 J_1 为水力清洗后的纯水通量, HIFI 定义为水力不可逆污染指数,表示经过物理水洗后不能去除的污染.

而水力清洗后,再经过了化学清洗,通过清洗后的数据,则可以得到:

$$J_0/J_2 = 1 + (CIFI)V$$
 (14)

 J_2 为化学清洗后的纯水通量, CIFI 定义为化学清洗不可逆污染指数, 指经过化学清洗后不能去除的污染. 同时可以推出:

TFI = RFI + HIFI = RFI + CIFI + CRFI(15) RFI 为水力可逆污染指数,通常是指物理清洗(水力)可以去除的污染. CRFI 则是化学清洗可逆污染指数,为不可逆污染的一部分,可以由化学药剂去除但物理的水力清洗无法去除此部分污染.

同理,当通量J恒定时,由公式(7)和(8)可以推出:

$$\Delta P'/\Delta P = 1 + (FI)V \tag{16}$$

因此,如果要获得一定的产水量,当通量恒定的时候,膜污染指数的大小可以直接决定最终的压头损失.通过跨膜压差的变化同样可以得到膜污染指数 FI 值,且不同膜阶段的污染指数也可以通过相应的计算获得.而当跨膜压差恒定的时候,膜污染指数直接与最终的产水通量相关.

此外研究表明^[8],FI 与源水的 TOC、NTU 等水质特征并没有显著相关性,说明了膜污染指数 FI 能够较好地表征膜污染情况,并通过简单的计算即可得出,能够实时反映膜运行过程中的污染状况,适宜于饮用水低压膜滤过程.

2 材料与方法

2.1 源水水质与膜材料

实验采用腐殖酸(HA,Sigma-Aldrich,USA)、牛血清蛋白(BSA,Sigma,USA)和海藻酸钠(NaAlg,Sigma,USA)配水为原水.利用去离子水配制各有机物溶液,过0.45 μm 混合纤维滤膜,备用.分别测

定 HA、BSA 和 NaAlg 的总有机碳 TOC(TOC-V_{CPH}, Shimadzu, Japan) 为 10 ± 0.239 、 10 ± 0.27 、 10 ± 0.4 mg·L⁻¹, UV₂₅₄ (Spectrophotometer U-2910, Hitachi, Japan) 依次为 1.016 ± 0.001 、 0.025 ± 0.002 、 0.009 ± 0.0001 cm⁻¹, 计算得出其 SUVA 值 (specific ultraviolet adsorption) 分别为 10.16、0.25、0.09 L·(m·mg)⁻¹. 各溶液 pH 在 $6.8 \sim 7.3$ 之间, 保持中性酸度.

实验膜组件采用海南立升公司浸入式聚氯乙烯 (PVC)超滤膜. 组件由 10 根有效长度为 23 cm 的膜丝组成,膜孔外径 1.45 μ m,内径 0.85 μ m,膜有效面积为 0.01 m^2 ,截留相对分子质量为 5×10^4 .

2.2 实验装置和操作条件

使用浸入式 PVC 膜组件,进行过滤实验,操作 压力为恒压 30 kPa,利用天平(L-IC, Mettler Toledo, Switzerland) 进行通量 J 的记录(图 1). 首先测定新 膜纯水通量,记为 J_0 . 然后再进行有机物过滤实验, 考察膜通量J的变化情况,过滤时间为6h,得出通 量的比率 J/J_0 的变化趋势. 膜污染实验结束后,首 先使用去离子水进行曝气 5 min,强度为 1.8 L·min⁻¹,再将压力增加至80 kPa,水力清洗污染膜 30 min. 曝气水洗后,测定纯水通量 (J_1) ,考察通量 的恢复情况. 再使用 0.01 mol·L⁻¹ NaOH 浸泡膜 24 h,进行化学清洗. 用去离子水反复冲洗膜组件3 次,将残留在膜丝表面的化学清洗剂清洗干净后,再 次测定纯水通量 (J_2) ,考察化学清洗后膜通量的恢 复情况. 随后进行第2次过滤实验,如此循环,每种 有机物均进行3个周期的过滤实验. 每个实验重复 3次,所有数据均为实验平均值.

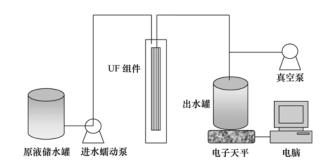


图 1 超滤膜系统装置示意

Fig. 1 Schematic diagram of the experimental ultrafiltration unit

3 结果与讨论

3.1 膜运行效能分析

由图 2 可知,随着过滤时间的增加,膜通量逐渐下降. 各有机物 3 个周期过滤实验膜通量的变化趋

势基本一致,在过滤结束时,通量下降比率大致相同. HA、BSA 和 NaAlg 通量平均下降至纯水通量的38.12%,25.38%和37.76%.值得注意的是,在过滤初始30 min 内,通量从最初的100%下降至40%~60%,下降率较快,而此后至过滤结束,通量的变化相对较为缓慢,仅下降10%~20%左右.因此,可将HA 膜滤过程分为2个阶段,分别称之为快反应和慢反应过程.出现这样的情况,可以认为是膜与污染物在不同阶段反应机制不同造成的.污染物首先进入膜孔,造成膜孔堵塞,与此同时附着或者沉淀在膜表面[12,13],这个过程发生时间短且污染迅速,认为其属于快反应过程.而随着过滤时间的增加,膜表面污染层逐渐增厚,分子不断的沉积,形成聚集体或者滤饼层.这种聚集体或滤饼层具有一定的缝

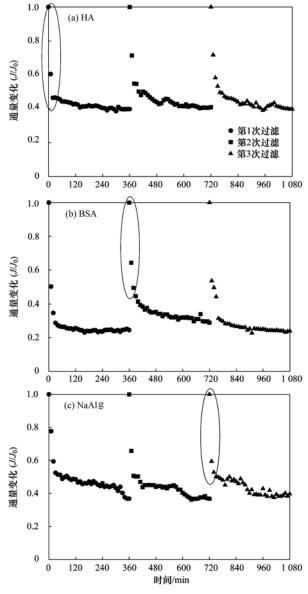


图 2 3 种有机物膜通量随时间的变化

Fig. 2 Variation of flux with time

隙,当分子之间相互作用达到平衡时,聚集体或滤饼层结构相对稳定,通量变化相对平稳^[14-16],进入慢反应过程.同时,对比3种有机物的膜滤过程,整个过程通量下降最多的是BSA,其次为HA,最后为NaAlg.3种有机物均在不同程度上使得通量下降,造成膜污染.

3.2 不同阶段膜污染指数的变化

通过公式(12)分段计算快、慢反应过程的膜污 染指数,见图 3. 快反应膜污染指数 TFI。远大于慢 反应膜污染指数 TFIs. 3 种污染物慢反应指数在 0.2~1.2之间, 快反应污染指数为5~20. 在过滤0 ~30 min 内,有机物迅速地附着在膜表面或者进入 膜内部堵塞膜孔,导致通量大幅度下降,污染严重. 在这个快反应过程中,通量迅速下降,污染也较为快 速. 随后的慢反应过程,通量变化缓慢而稳定,膜污 染指数 TFI。相对较小,说明污染较轻. 膜污染指数 可以用来表征膜污染的情况,污染指数越大,说明污 染速率越快,反之则污染速率越慢, 在有机物膜滤 过程中,快反应相对于慢反应而言,更为重要,决定 了污染过程的整体趋势. 总体而言,污染速度最快 的为 BSA (均值 TFI = 3.55), 其次为 NaAlg (均值 TFI = 1.76),最后为 HA(均值 TFI = 0.96),但快慢 反应的 FI 比值则有不同的变化趋势.

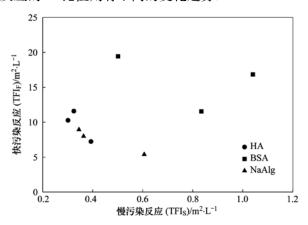


图 3 快反应和慢反应膜污染指数

Fig. 3 Membrane fouling index of fast and slow phases

过滤结束后,先进行曝气水洗,然后再用化学药剂清洗污染膜丝,并测定相应的通量,考察清洗后通量的恢复情况(图4).3种有机物在3个过滤周期内,污染造成的膜通量平均下降率分别为: HA 38.12%,BSA 25.38%,NaAlg 37.76%,而经过物理的曝气水洗后,通量有一定的恢复,分别恢复至73.82%、28.78%和74.36%,增加了35.7、3.41和36.6个百分点.不同有机物水力清洗和化学清洗效

果不同. 水力清洗对 BSA 通量恢复作用相对较小, 通量恢复率较低(斜率 a = 0.034),增加率仅为 3.41%. 化学清洗后,急剧增加(a=0.514),通量恢 复至80.19%.物理清洗对BSA污染膜丝几乎无作 用. 这可能是由于蛋白类与有机聚合膜之间存在强 烈的吸附作用,能造成膜不可逆污染,水力清洗无法 去除. 曝气水洗能够有效地去除 HA 和 NaAlg 在膜 丝表面形成的滤饼,使得通量有一定的恢复(35.7 个百分点和36.6个百分点). 使用化学药剂则进一 步恢复膜通量,HA 污染后的膜丝经过 NaOH 浸泡 后,通量平均恢复率增加至99%以上. 经过化学药 剂浸泡后的膜,表面接触角和形态均发生一定的变 化,同时由于使用 NaOH,清洗剂中的—OH可能附 着在膜丝表面,从而提高膜表面的亲水性,使得膜丝 通量上升,可能恢复至初始纯水通量[17]. 而在化学 清洗后, NaAlg 污染膜丝通量则恢复至83.52%,相 比之下,增长速率低于物理清洗.

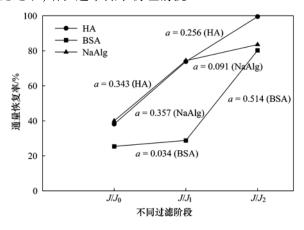


图 4 不同阶段通量比率的变化

Fig. 4 Variation of flux during different phases

物理和化学清洗后,通过计算得出水力可逆污染指数(RFI)、化学清洗不可逆污染指数(CRFI)的相对比值(图 5).可逆污染造成的通量下降,可以通过水力冲洗恢复,而不可逆污染只有依靠化学清洗,才能使通量有一定恢复^[18,19],但不能完全恢复,即部分污染物是连化学清洗都无法去除的.从水力不可逆污染指数与总膜污染指数的比值得出(图 5),3 种有机物,BSA 造成的不可逆污染比例最大,但是这种污染,经过碱液浸泡后,较大部分能够被去除,造成化学清洗不可逆污染的比例仅占 10%左右. 3 种有机物的不可逆污染比例依次为 BSA > HA > NaAlg,而化学不可逆污染比例从大到小依次为 NaAlg > BSA > HA. 腐殖酸和蛋白更容易造

成 PVC 超滤膜的不可逆污染,但是通过碱洗能够有效去除蛋白质和腐殖酸的不可逆污染. 这部分污染为化学可逆污染. NaAlg 是 3 种有机物中污染速度处于中间状态的物质,其通量下降率和不可逆污染比例最低,但是其造成的不可逆污染相对而言确是最难以被碱洗去除,即化学不可逆污染比例较大. 从不同有机物各阶段污染指数可知,NOM 能够在短时间膜滤过程中迅速造成膜的不可逆污染,且其中 1%~10% 左右的污染是化学清洗都无法去除的.

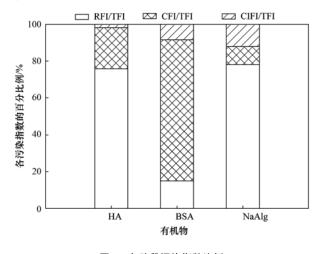


图 5 各阶段污染指数比例

Fig. 5 Proportion of membrane fouling index in different phases

膜表面的粗糙度、溶液和膜的 Zeta 电位、分子 大小和结构、亲疏水性以及污染物与膜之间的相互 作用都可能影响膜污染. pH 为 6.8~7.3 时, HA 呈 现伸展的线性结构, BSA 则为球状, NaAlg 也为线 状[20~23]. 相比线性结构,球形结构更容易造成膜的 堵塞,从实验结果看 BSA 造成的不可逆污染最高, HA 和 NaAlg 相对较低. 同时,利用体积排阻色谱法 (HPSEC),对3种有机物进行相对分子质量的测 定. 由结果可知(图 6),有机物相对分子质量均分 为2段,一是小分子段,集中在650~700;另外一个 则是高分子量段. HA 在4000, BSA 位于18000~ 25 000, NaAlg 最高为40 000. 分子质量大小依次为: HA < BSA < NaAlg, 与各有机物造成的化学不可逆 污染顺序相同. 但水力不可逆污染则呈现不同的变 化规律. 蛋白质造成的不可逆污染最高,可能是由 于蛋白质与膜存在强烈的吸附作用[24,25],这种吸附 无法利用水力清洗去除,只能依靠化学药剂. 而海 藻酸钠造成的化学不可逆污染最高,其原因还有待 进一步研究. 分子量的大小与膜污染似乎并无直接 的联系.

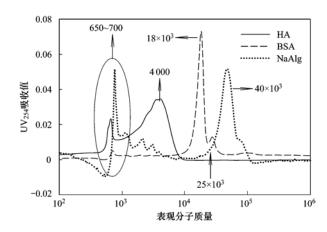


图 6 有机物相对分子质量分布

Fig. 6 Distribution of apparent molecular weight

4 结论

- (1)NOM 膜滤过程可以分为快反应和慢反应, 快反应膜污染指数 TFI_F 较大,污染速率较快,而慢 反应膜污染指数 TFI_S 较小,污染速率缓慢. 在短期 过滤周期中,快反应相对更为重要,决定了整个过程 的膜污染趋势.
- (2) NOM 能在短时间内即造成膜不可逆污染, 且化学清洗无法全部去除. 经过水力清洗,通量有 一定恢复. 物理和化学清洗能够去除部分污染物, 但仍有少量有机物附着在膜丝,造成化学不可逆污染. HA 和蛋白更容易造成 PVC 超滤膜的不可逆污染,但碱洗能够有效去除. NaAlg 造成的不可逆污染 比重最低,但是化学不可逆污染的比例最高,难以被碱洗去除. 有机物相对分子质量的大小与膜污染似乎并无直接的联系.
- (3)膜污染指数(FI)不区分污染机制,计算方法简明扼要,能够较好地描述膜污染状况,表征污染速率和污染程度.通过计算不同阶段的污染指数(总污染指数、水力不可逆污染指数和化学清洗不可逆污染指数),得到各污染相对比例,确定各阶段的污染情况.

参考文献:

- [1] Howe K J, Clark M M. Fouling of microfiltration and ultrafiltration membranes by natural waters [J]. Environmental Science & Technology, 2002, 36(16): 3571-3576.
- [2] Howe K J, Marwah A, Chiu K P, et al. Effect of coagulation on the size of MF and UF membrane foulants [J]. Environmental Science & Technology, 2006, 40 (24): 7908-7913.
- [3] Fan L H, Harris J L, Roddick F A, et al. Influence of the characteristics of natural organic matter on the fouling of microfiltration membranes[J]. Water Research, 2001, 35(18): 4455-4463.

- [4] Yamamura H, Kimura K, Watanabe Y. Mechanism involved in the evolution of physically irreversible fouling in microfiltration and ultrafiltration membranes used for drinking water treatment [J]. Environmental Science & Technology, 2007, 41 (19): 6789-6794.
- [5] Peter-Varbanet V, Margot J, Traber J, et al. Mechanism of membrane fouling during ultra-low pressure ultrafiltration [J]. Journal of Membrane Science, 2011, 377 (1-2): 42-53.
- [6] Huang H, Lee N, Young T, et al. Natural organic matter fouling of low-pressure, hollow-fiber membranes: effects of NOM source and hydrodynamic conditions [J]. Water Research, 2007, 41 (17): 3823-3832.
- [7] 许振良. 膜法水处理技术[M]. 北京: 化学工业出版社, 2001: 148-149.
- [8] Huang H O, Thayer Y T, Jacangelo J G. Novel approach for the analysis of bench-scale, low pressure membrane fouling in water treatment[J]. Journal of Membrane Science, 2009, 334(1-2): 1-8.
- [9] Huang H O, Thayer Y T, Jacangelo J G. Unified membrane fouling index for low pressure membrane filtration of natural waters: principles and methodology [J]. Environmental Science & Technology, 2008, 42(3): 714-720.
- [10] Huang H, Spinett R, O'Melia C R. Direct-flow microfiltration of aquasols I. Impacts of particle stabilities and size[J]. Journal of Membrane Science, 2008, 314(1-2): 90-100.
- [11] Nguyen A H, Tobiason J E, Howe K J. Fouling indices for low pressure hollow fiber membrane performance assessment [J]. Water Research, 2011, 45(8): 2627-2637.
- [12] Yuan W, Zydney A L. Humic acid fouling during ultrafiltration
 [J]. Environmental Science & Technology, 2000, 34 (23):
 5043-5050.
- [13] Costa A P, Pinho M N. Effect of membrane pore size and solution chemistry on the ultrafiltration of humic substances solutions[J]. Journal of Membrane Science, 2005, 225 (1-2): 49-56.
- [14] Bolton G, LaCasse D, Kuriyel R. Combined models of membrane fouling: development and application to microfiltration and ultrafiltration of biological fluids [J]. Journal of Membrane Science, 2006, 277(1-2): 75-84.
- [15] Mitnik D M, Shaw J A, Pindzola M S, et al. Treating different types of raw water with micro-and ultrafiltration for further desalination using reverse osmosis[J]. Desalination, 1998, 117 (1-3): 40-60.
- [16] Lahoussine-Turcaud V, Wiesner M R, Bottero J Y, et al. Fouling in tangential-flow ultrafiltration: the effect of colloid size and coagulation pretreatment[J]. Journal of Membrane Science, 1999, 52(2): 173-190.
- [17] Li Q L, Elimelech M. Organic fouling and chemical cleaning of nanofiltration membranes: measurements and mechanisms [J]. Environmental Science & Technology, 2004, 38 (17): 4683-4693.
- [18] Noble R D, Stern S A. Membrane separation technology:

- principles and applications[M]. Elsevier: Amsterdam, 1999.
- [19] Hilal N, Ogunbiyi O O, Miles N J, et al. Methods employed for control of fouling in MF and UF membranes: a comprehensive review[J]. Separation Science and Technology, 2005, 40(10): 1957-2005.
- [20] Huisman I H, Pradanos P, Hernandez A. The effect of proteinprotein and protein-membrane interactions on membrane fouling in ultrafiltration [J]. Journal of Membrane Science, 2000, 179 (1-2): 79-90.
- [21] Ghosh K, Schnitzer M. Macromolecular structures of humic substances[J]. Soil Science, 1980, 129(5): 266-276.
- [22] Tipping E, Cooke D. The effects of adsorbed humic substances

- on the surface-charge of goethite (Alpha-Feooh) in fresh-waters [J]. Geochimica et Cosmochimica Acta, 1982, **46**(1): 75-80.
- [23] 张振海, 吕慧侠, 周建平, 等. 应用1 H NMR 法比较7 种海藻酸钠序列结构[J]. 分析测试学报, 2009, **28**(4): 497-500.
- [24] Tu K L, Chivas A R, Nghiem L D. Effects of membrane fouling and scaling on boron rejection by nanofiltration and reverse osmosis membranes [J]. Desalination, 2011, 297 (1-3): 269-277
- [25] Hashinoa M, Hiramia K, Ishigamia T, et al. Effect of kinds of membrane materials on membrane fouling with BSA[J]. Journal of Membrane Science, 2011, 384(1-2): 157-165.

HUANJING KEXUE

Environmental Science (monthly)

Vol. 33 No. 12 Dec. 15, 2012

CONTENTS

Preface	
Ecological Risks of Reclaimed Water Irrigation: A Review	CHEN Wei-ping, ZHANG Wei-ling, PAN Neng, et al. (4070)
Study on Soil Enzyme Activities and Microbial Biomass Carbon in Greenland Irrigated with Reclaimed Water	
Soil Salinity in Greenland Irrigated with Reclaimed Water and Risk Assessment	
Effect of Reclaimed Water Irrigation on Soil Properties and Vertical Distribution of Heavy Metal	··· ZHAO Zhong-ming, CHEN Wei-ping, JIAO Wen-tao, et al. (4094)
Simulation of Effect of Irrigation with Reclaimed Water on Soil Water-Salt Movement by ENVIRO-GRO Model	LÜ Si-dan, CHEN Wei-ping, WANG Mei-e (4100)
Simulation of Effects of Soil Properties and Plants on Soil Water-salt Movement with Reclaimed Water Irrigation by ENVIRO-GR	RO Model ······ LÜ Si-dan, CHEN Wei-ping, WANG Mei-e (4108)
Modeling the Cd Accumulation in Agricultural Soil Irrigated with Reclaimed Water	···· ZHAO Zhong-ming, CHEN Wei-ping, JIAO Wen-tao, et al. (4115)
Model Simulation of the Transportation, Transformation and Accumulation of Synthetic Musks in Soils Input Through Recycle W	ater Irrigation
Impacts of Reclaimed Water Irrigation of Urban Lawn on Groundwater Quality	
Public Awareness Assessment of Water Reuse in Beijing	
Temporal and Spatial Distribution of Ozone Concentration by Aircraft Sounding over Beijing	
Emission Strength and Source Apportionment of Volatile Organic Compounds in Shanghai During 2010 EXPO	
Study on Atmospheric VOCs in Gongga Mountain Base Station	
Regional Atmospheric Environment Risk Source Identification and Assessment	
Carbon Isotopic Compositions of n-Alkanes and n-Alkanoic Acids in the Smoke from Combustion of Rice Straw	
Research on NEDC Ultrafine Particle Emission Characters of a Port Fuel Injection Gasoline Car	
Magnetic Response of Street Tree Leaves to Particulate Pollution in Shanghai	
Diurnal Variations of Greenhouse Gas Fluxes at the Water-Air Interface of Aquaculture Ponds in the Min River Estuary	
Effects of Simulated Warming on Soil Respiration in a Cropland Under Winter Wheat-Soybean Rotation	
Transport and Differentiation of Polycyclic Aromatic Hydrocarbons in Air from Dashiwei Karst Sinkholes in Guangxi, China	
Pollution Characteristics of Polycyclic Aromatic Hydrocarbons in Water of Songhua River Basin During the Icebound Season · · ·	
Pollution Characteristics and Sources of Polycyclic Aromatic Hydrocarbons in Urban Rivers of Wenzhou City	
Pollution Characteristics and Sources of Polycyclic Aromatic Hydrocarbons in Riparian Soils Along Urban Rivers of Wenzhou Cit	
Spatial Distribution and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Partial Surface Sediments of Liaohe River $$	
Phenols Pollutants in Soil and Shallow Groundwater of a Retired Refinery Site	
Heterogeneous Characteristic of PAHs' Spatial Distribution in a Large Coking Site of China · · · · · · · · · · · · · · · · · · ·	
Vertical Distribution and Source Analysis of Organochlorine Pesticides in Sewage Irrigation Area, Taiyuan City	
Distribution and Ecological Risk Assessment of Polycyclic Aromatic Hydrocarbons in Agricultural Soil of the Chongming Island i	n Shanghai
Mercury and Copper Accumulation During Last Fifty Years and Their Potential Ecological Risk Assessment in Sediment of Mang	grove Wetland of Shenzhen, China
Characteristics of Heavy Metal Pollution in the Sediments from Shahe Reservoir, the Upper Reach of the North Canal River	
Speciation and Pollution Characteristics of Heavy Metals in the Sediment of Taihu Lake	
Chemical Composition and Daily Variation of Melt Water During Ablation Season in Monsoonal Temperate Glacier Region: A Ca	ase Study of Baishui Glacier No. 1
Experimental Study on the Environmental Fate of Nitrogen in Snail-Macrophyte Ecosystem for Water Purification	
Growth Inhibition Effect of Immobilized Pectinase on Microcystis aeruginosa	
A Novel Approach of Using Fouling Index to Evaluate NOM Fouling Behavior During Low Pressure Ultrafiltration Process	
	NY D 1510 W 151 151 1 (1990)
Characteristics of Monomethylmercury Photodegradation in Water Body	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent	LI Shi-yin, LI Xiao-rong, ZHU Yi-ping, et al. (4335)
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors	LI Shi-yin, LI Xiao-rong, ZHU Yi-ping, et al. (4335) CHEN Chao, ZHAO Qian, FENG Li, et al. (4340)
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS)	LI Shi-yin, LI Xiao-rong, ZHU Yi-ping, et al. (4335) CHEN Chao, ZHAO Qian, FENG Li, et al. (4340) WANG Xia-lin, LI Rui-hua (4346)
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field Effects of Multiple Environmental Factors on Triflulsulfuron-methyl Degradation in Soils	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field Effects of Multiple Environmental Factors on Triflulsulfuron-methyl Degradation in Soils Effect of Alkaline Post-Treatment on Physicochemical Property of Digested Spartina alterniflora	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field Effects of Multiple Environmental Factors on Triflulsulfuron-methyl Degradation in Soils Effect of Alkaline Post-Treatment on Physicochemical Property of Digested Spartina alterniflora Structural Changes in Mineral Phases and Environmental Release Behavior of Arsenic During Sintering of Arsenic-containing Wa	LI Shi-yin, LI Xiao-rong, ZHU Yi-ping, et al. (4335) CHEN Chao, ZHAO Qian, FENG Li, et al. (4340) WANG Xia-lin, LI Rui-hua (4346) GUO Lei, JIA Yong-gang, FU Teng-fei, et al. (4352) XIE Jie, WANG Zhe, WU De-yi, et al. (4361) JI Jun-yuan, XING Ya-juan, ZHENG Ping (4367) WANG Zhen, LIU Chao-xiang, LI Peng-yu, et al. (4373) QING Cheng-song, BAO Tao, CHEN Tian-hu, et al. (4380) ZHONG Chen-yu, YE Jie-xu, LI Ruo-yu, et al. (4387) JI Xue-yuan, WANG Yi-li, FENG Jing (4393) SONG Ning-hui, SHAN Zheng-jun, SHI Li-li, et al. (4400) CHEN Guang-yin, ZHENG Zheng, CHANG Zhi-zhou, et al. (4406) uste WANG Xing-run, NONG Ze-xi, WANG Qi (4412)
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field Effects of Multiple Environmental Factors on Triflulsulfuron-methyl Degradation in Soils Effect of Alkaline Post-Treatment on Physicochemical Property of Digested Spartina alterniflora Structural Changes in Mineral Phases and Environmental Release Behavior of Arsenic During Sintering of Arsenic-containing Wa Study on Emission Standard System of Air Pollutants	
Degradation of Oxytetracycline with Ozonation in Acetic Acid Solvent Photodegradation Performance and Mechanisms of Carbamazepine and Its Impact Factors Investigation of Nitrobenzene Removal by Iron Sulfide (FeS) Experimental Research on In-Situ Auto-Monitoring for Underground Sewage Pipeline Leakage Adsorption of Phenol Chemicals by Surfactant-Modified Zeolites Acute Toxicity of Antibiotics and Anaerobic Digestion Intermediates in Pharmaceutical Wastewaters Study on Phosphorus Removal Capability of Constructed Wetlands Filled with Broken Bricks Denitrification Water Treatment with Zeolite Composite Filter by Intermittent Operation Influence of Nitrate on the Simultaneous Methanogenesis and Denitrification Reaction of Anaerobic Biofilm and Granular Sludge Study on Dewatering of Activated Sludge Under Applied Electric Field Effects of Multiple Environmental Factors on Triflulsulfuron-methyl Degradation in Soils Effect of Alkaline Post-Treatment on Physicochemical Property of Digested Spartina alterniflora Structural Changes in Mineral Phases and Environmental Release Behavior of Arsenic During Sintering of Arsenic-containing Wa	LI Shi-yin, LI Xiao-rong, ZHU Yi-ping, et al. (4335) CHEN Chao, ZHAO Qian, FENG Li, et al. (4340) WANG Xia-lin, LI Rui-hua (4346) CHEN Chao, ZHAO Qian, FENG Li, et al. (4346) WANG Xia-lin, LI Rui-hua (4346) XIE Jie, WANG Zhe, WU De-yi, et al. (4352) WANG Zhen, LIU Chao-xiang, LI Peng-yu, et al. (4361) WANG Zhen, LIU Chao-xiang, LI Peng-yu, et al. (4373) WANG Zhen, LIU Chao-xiang, LI Ruo-yu, et al. (4387) ZHONG Cheng-song, BAO Tao, CHEN Tian-hu, et al. (4387) ZHONG Chen-yu, YE Jie-xu, LI Ruo-yu, et al. (4387) JI Xue-yuan, WANG Yi-li, FENG Jing (4393) SONG Ning-hui, SHAN Zheng-jun, SHI Li-li, et al. (4400) CHEN Guang-yin, ZHENG Zheng, CHANG Zhi-zhou, et al. (4406) uste WANG Xing-run, NONG Ze-xi, WANG Qi (4412) JIANG Mei, ZHANG Guo-ning, ZHANG Ming-hui, et al. (4417)

《环境科学》第6届编辑委员会

主 编:欧阳自远

副主编:赵景柱 郝吉明 田 刚

编 委: (按姓氏笔画排序)

万国江 王华聪 王凯军 王绪绪 田 刚 田 静 史培军

朱永官 刘志培 汤鸿霄 陈吉宁 孟 伟 周宗灿 林金明

欧阳自远 赵景柱 姜 林 郝郑平 郝吉明 聂永丰 黄 霞

黄耀 鲍强潘纲潘涛魏复盛

环维种草

(HUANJING KEXUE)

(月刊 1976年8月创刊)

2012年12月15日 33卷 第12期

ENVIRONMENTAL SCIENCE

(Monthly Started in 1976)

Vol. 33 No. 12 Dec. 15, 2012

主	管	中国科学院	Superintended	by	Chinese Academy of Sciences
主	办	中国科学院生态环境研究中心	Sponsored	by	Research Center for Eco-Environmental Sciences, Chinese
协	办	(以参加先后为序)			Academy of Sciences
		北京市环境保护科学研究院	Co-Sponsored	by	Beijing Municipal Research Institute of Environmental
		清华大学环境学院			Protection
主	编	欧阳自远			School of Environment, Tsinghua University
编	辑	《环境科学》编辑委员会	Editor-in -Chief		OUYANG Zi-yuan
7 11 1	14	北京市 2871 信箱(海淀区双清路	Edited	by	The Editorial Board of Environmental Science (HUANJING
		18 号,邮政编码:100085)			KEXUE)
		电话:010-62941102,010-62849343			P. O. Box 2871, Beijing 100085, China
		传真:010-62849343			Tel:010-62941102,010-62849343; Fax:010-62849343
		E-mail; hjkx@ rees. ac. cn			E-mail; hjkx@ rcees. ac. cn
		http://www.hjkx.ac.cn			http://www. hjkx. ac. cn
出	版	4 望 出 版 社	Published	by	Science Press
щ	///	北京东黄城根北街 16 号			16 Donghuangchenggen North Street,
		邮政编码:100717			Beijing 100717, China
印刷装	订	北京北林印刷厂	Printed	by	Beijing Bei Lin Printing House
发	行	斜学出版社	Distributed	by	Science Press
		电话:010-64017032			Tel:010-64017032
		E-mail:journal@mail.sciencep.com			E-mail:journal@mail.sciencep.com
订 购	处	全国各地邮电局	Domestic		All Local Post Offices in China
国外总发	行	中国国际图书贸易总公司	Foreign		China International Book Trading Corporation (Guoji
		(北京 399 信箱)			Shudian), P. O. Box 399, Beijing 100044, China

中国标准刊号: ISSN 0250-3301 CN 11-1895/X

国内邮发代号: 2-821

国内定价:70.00元

国外发行代号: M 205

国内外公开发行