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微塑料对短流程膜工艺中膜污染的影响

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摘要: 微塑料作为新型污染物越来越受到关注. 随着微塑料在饮用水源地逐渐检出, 亟需了解当前水处理工艺对其去除效能与机制. 随着膜法饮用水处理技术的发展, 短流程膜工艺以其占地面积小、去污效能高成为重要研究方向. 因此, 考察了微塑料对短流程膜工艺尤其膜污染的影响. 结果表明, 微塑料混凝前后, 滤饼层始终是引起膜污染的关键诱因. 超滤膜由于孔径小 ($d < 0.1 \mu\text{m}$), 微塑料 ($d < 5 \text{ mm}$) 本身不会引起严重膜污染. 然而, 与铁盐混凝后, 由于絮体的存在使得滤饼层相对疏松, 但随着混凝剂投量增加, 小粒径微塑料容易进入絮体形成的网络空间, 形成致密滤饼层, 严重加剧膜污染. pH 7.0 时 $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 和 $0.9 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 水解絮体导致的膜比通量分别为 0.82 和 0.76. 然而, 0.1 g 小粒径微塑料 ($d < 0.5 \text{ mm}$) 分别与 $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 和 $0.9 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 混凝后导致的膜比通量分别降低至 0.76 和 0.62. 此外, 水环境中微塑料多呈负电. 与碱性环境相比, 氯化铁水解絮体在酸性环境中呈正电且粒径较小, 微塑料容易被絮体吸附、捕获, 进而形成相对致密滤饼层, 引起严重膜污染. pH 6.0 和 8.0 时, 0.1 g 小粒径微塑料 ($d < 0.5 \text{ mm}$) 与 $0.3 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 混凝后膜比通量分别为 0.55 和 0.79.

关键词: 微塑料; 铁盐; 超滤; 短流程膜工艺; 膜污染

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Effects of Microplastics on Membrane Fouling During a Shortened Ultrafiltration Membrane Process

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Abstract: Microplastics have garnered much attention worldwide as a new emerging pollutant. As they are gradually detected in freshwaters, understanding how microplastics will behave during current drinking water treatment processes is urgently needed. In recent years, the shortened process with an ultrafiltration (UF) membrane has shown excellent performance because of its low land use and high water purification efficiency. In this work, the membrane performance induced by microplastics was investigated with a shortened UF membrane process. The results showed that membrane fouling was always induced by the cake layer before and after coagulating with microplastics. Owing to the small UF membrane pore size ($d < 0.1 \mu\text{m}$), slight membrane fouling was caused by microplastics ($d < 5 \text{ mm}$) alone. However, although the loose cake layer was formed because of the existence of flocs, the cyberspace formed by flocs was easily entered by small microplastics with increasing coagulant dosage. As a result, server membrane fouling was induced because of the formation of a dense cake layer. It was shown that the specific membrane flux induced by flocs alone was 0.82 and 0.76 in the presence of $0.1 \text{ mmol} \cdot \text{L}^{-1}$ and $0.9 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. However, after coagulation the specific membrane fouling induced by the 0.1 g small microplastics ($d < 0.5 \text{ mm}$) was 0.76 and 0.62 with $0.1 \text{ mmol} \cdot \text{L}^{-1}$ and $0.9 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, respectively. In addition, microplastics were always negatively charged in water. In comparison with alkaline conditions, Fe-based flocs were positively charged under acidic conditions, which were also much smaller. Therefore, microplastics were more easily adsorbed by Fe-based flocs under acidic conditions, leading to severe membrane fouling because of the dense cake layer formed. After coagulating with $0.3 \text{ mmol} \cdot \text{L}^{-1}$ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, the specific membrane flux induced by 0.1 g small microplastics ($d < 0.5 \text{ mm}$) was 0.55 and 0.79 at pH 6.0 and 8.0, respectively.

Key words: microplastics; iron salt; ultrafiltration; shortened membrane process; membrane fouling

塑料及其制品在工业、农业以及日常生活中被广泛使用, 自 20 世纪 40 年代开始大规模生产以来, 塑料的产量迅速增加. 从 20 世纪 50 年代的 $1.5 \times 10^6 \text{ t} \cdot \text{a}^{-1}$ 大幅增加到 2011 年的 $2.8 \times 10^8 \text{ t}$, 估计目前全球每年产生的塑料产品超过 $3 \times 10^8 \text{ t}$, 进入海洋的塑料垃圾至少 $8 \times 10^6 \text{ t}^{[1-3]}$. 残存在环

境中的塑料具有化学性质稳定、密度低、粒径小等

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特点,但在长期的太阳辐射、风力、海浪等物理或化学作用下会分解成塑料碎片或者颗粒,当其粒径小于 5 mm 时被称为“微塑料”^[4~6].

微塑料体积小、比表面积大和难降解,容易吸附环境中的重金属、持久性有机污染物,如农药、阻燃剂和多氯联苯等^[7~11]. 微塑料作为载体,可携带外来物种及潜在病原菌^[12,13],破坏生态环境,危害生物体健康. 还可以由地表径流在海洋中蔓延,改变海洋的生态环境,进入海洋生物食物链,对海洋生物造成危害,并且随着食物链的传递作用,微塑料最终进入人类的食物链,造成更严重的危害^[14~16].

前期的研究表明,微塑料普遍存在于表层海水、河口以及沉积物中,在极地冰川和河流湖泊沉积物中也有发现^[17~22]. 近年来,在淡水水源(河流、湖泊和水库等)也检测到了微塑料. 据报道,长江口微塑料平均丰度为 $(4.1 \times 10^3 \pm 2.5 \times 10^3)$ items·m⁻³^[23],三峡大坝附近地表水微塑料丰度为 $1.6 \times 10^3 \sim 1.23 \times 10^4$ items·m⁻³^[24]. 太湖的表层水体中也报道了微塑料的赋存,丰度甚至达到 $3.4 \times 10^6 \sim 25.8 \times 10^6$ items·m⁻³^[25]. 水体中已检测到的微塑料虽然种类繁多,如聚乙烯(PE)、聚丙烯(PP)、聚氯乙烯(PVC)和聚苯乙烯等,但 PE 的检出比例远高于其他种类^[26].

截至目前,混凝-膜滤工艺在饮用水处理工艺中已得到广泛应用^[27~29]. 短流程膜工艺以其除污效能高、占地面积小等优点成为近年来重要的研究方向. 随着微塑料在饮用水源地的逐渐检出,了解微塑料对短流程膜工艺的运行效能影响显得至关重要. 因此,本文以水环境中丰度较高的聚乙烯为目标污染物,考察了短流程膜工艺中,微塑料对超滤膜污染的影响机制.

1 材料与方法

1.1 实验材料

本实验所用试剂,如 FeCl₃·6H₂O、NaHCO₃、HCl 和 NaOH 均为分析纯,购自国药集团化学试剂有限公司(北京). 实验所用微塑料取自聚乙烯泡沫板,经砂纸细磨后,用分样筛将聚乙烯塑料分为不同粒径($2 < d_1 < 5$ mm、 $1 < d_2 < 2$ mm、 $0.5 < d_3 < 1$ mm 和 $d_4 < 0.5$ mm). 超滤杯(Amicon 8400)购自 Millipore 公司(美国). 平板超滤膜(100×10^3)购自安德膜科技有限公司(北京),材质为聚偏氟乙烯(PVDF).

1.2 实验装置与方法

本实验装置如图 1 所示. 向超滤杯内注入 300

mL 去离子水,随后加入一定量的 NaOH 或 HCl ($0.01 \text{ mol} \cdot \text{L}^{-1}$),为使体系中 pH 混凝后稳定在 6.0、7.0 和 8.0,加入 3 mL NaHCO₃ ($0.1 \text{ mol} \cdot \text{L}^{-1}$) 作为缓冲溶液. 之后,加入 0.1 g 微塑料. 快转 ($350 \text{ r} \cdot \text{min}^{-1}$) 1 min,慢转 ($100 \text{ r} \cdot \text{min}^{-1}$) 14 min,进行膜过滤. 采用 $10 \text{ mg} \cdot \text{L}^{-1}$ 氯化钠作为背景离子强度. 本实验过程中用膜比通量 J/J_0 代表膜污染状况,其中 J_0 为初始膜通量. 膜比通量越大,表示膜污染程度越轻. 所有实验至少两次平行.

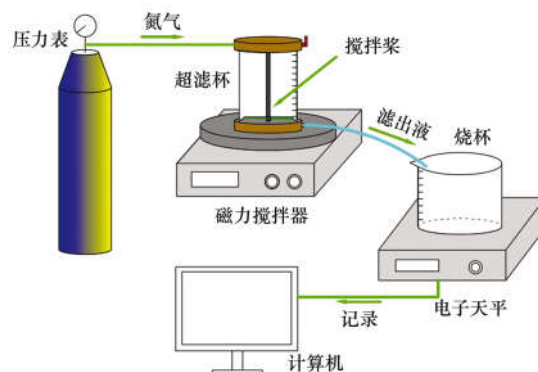


图 1 实验装置示意

Fig. 1 Schematic diagram of the experimental set up

1.3 分析方法

pH 通过 Orion pH Benchtop 测定;膜通量通过数字记录仪(HCB1002, Denver, USA)自动存储;膜表面形貌通过扫描电子显微镜(JEOL Ltd, Tokyo, Japan)和相机((Nikon, Coolpix P7100, Japan)测定,相机拍摄时,由于所用微塑料和超滤膜均为白色,拍摄前用亚甲基蓝将微塑料染色 2 h (除加 $0.9 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁时);絮体粒径通过 Mastersizer 2000 激光粒度仪测定(Malvern, UK);Zeta 电位通过 Delsa Nano C (Beckman Coulter, USA)测定.

2 结果与讨论

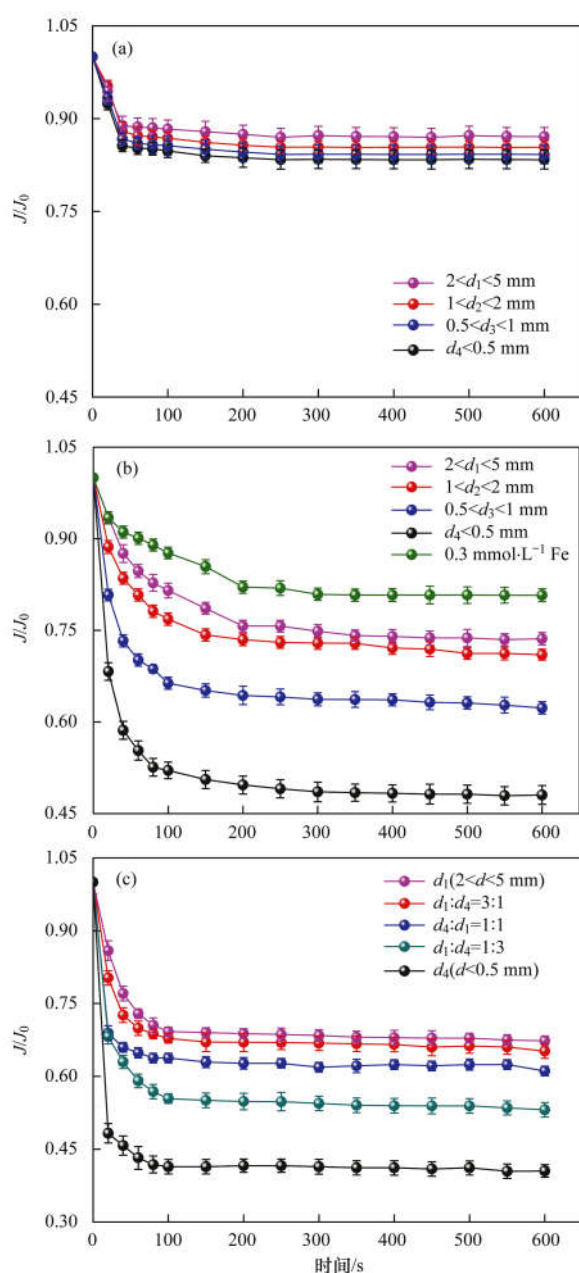
2.1 微塑料引起的膜污染

首先考察了 pH 7.0 时 0.1 g 不同粒径微塑料的膜污染行为. 由图 2(a)所示,微塑料粒径越小,膜比通量越低,膜污染程度越严重. 微塑料粒径分别为 $2 < d_1 < 5$ mm、 $1 < d_2 < 2$ mm、 $0.5 < d_3 < 1$ mm 和 $d_4 < 0.5$ mm 时,膜比通量依次降低为 0.87、0.85、0.84 和 0.83 (选取前 600 s 膜比通量变化,下同). 由于所用超滤膜的平均孔径为 (47.9 ± 6.4) nm,微塑料本身并不会吸附或者堵塞超滤膜孔,此时引起超滤膜污染的主要方式是微塑料形成的滤饼层. 微塑料粒径越小,在超滤膜表面形成的滤饼层相对致密,膜污染越严重,但膜污染加剧的趋势不

明显.

进一步考察了铁盐与不同粒径微塑料混凝后导致的膜污染. 由图 2(b) 可知, 单独铁盐 ($0.3 \text{ mmol} \cdot \text{L}^{-1}$) 时, 松散的水解絮体引起的膜污染程度较轻, 膜比通量为 0.81. 而铁盐与微塑料混凝后, 滤饼层厚度增加, 膜污染加剧, 尤其小粒径微塑料. 此时膜比通量分别为 $0.74(d_1)$ 、 $0.71(d_2)$ 、 $0.62(d_3)$ 和 $0.48(d_4)$, 膜污染加剧程度远高于无混凝剂时[图 2(a)].

为进一步验证小粒径微塑料能严重加剧膜污



(a) 单独微塑料; (b) 微塑料混凝后;

(c) 不同粒径比例微塑料混合物混凝后

图 2 pH 7.0 时不同粒径微塑料混凝前后引起的膜污染

Fig. 2 Membrane fouling caused by microplastics with different particle sizes before and after coagulating at pH 7.0

染, 考察了不同粒径微塑料 ($2 < d_1 < 5 \text{ mm}$ 、 $d_4 < 0.5 \text{ mm}$) 以不同比例混合后膜污染程度. 如图 2(c) 所示, 粒径 $2 \sim 5 \text{ mm}$ 的微塑料与氯化铁絮体混凝后导致的膜比通量为 0.68. 然而, 在保持投加总量一致的情况下, 随着小粒径微塑料比例的增大, 膜污染程度严重加剧, 此时膜比通量逐渐降低为 0.65 ($d_1:d_4 = 3:1$)、0.61 ($d_1:d_4 = 1:1$)、0.53 ($d_1:d_4 = 1:3$) 和 0.43 ($d_4 < 0.5 \text{ mm}$).

2.2 铁盐浓度的影响

一方面, 膜污染随微塑料粒径减小而加剧. 另一方面, 混凝剂投量随水质不同而改变^[30~32]. 进一步研究了小粒径微塑料 ($d_4 < 0.5 \text{ mm}$) 与不同浓度铁盐混凝后导致的膜污染. 首先考察了混凝剂本身对膜污染的影响. 结果表明, 膜比通量随铁盐投量的增加而逐渐降低. 当混凝剂浓度分别为 0.1 、 0.3 、 0.6 和 $0.9 \text{ mmol} \cdot \text{L}^{-1}$ 时, 膜比通量为 0.82、0.81、0.77 和 0.76[图 3(a)]. 仅 $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 铁盐时, 膜污染程度最轻[图 4(a)], 尽管膜污染程度随混凝剂投量增加而加剧, 但混凝剂水解絮体松散, 膜污染加剧程度也不明显, 运行结束后膜比通量仅变化 0.06.

而与小粒径微塑料 ($d_4 < 0.5 \text{ mm}$) 混凝后, 膜污染程度明显加剧, 此时, 膜比通量分别降低为 0.76、0.74、0.70 和 0.62[图 3(b)]. 从图 4 中可以看出, 混凝后絮体与微塑料相对均匀地分布在超

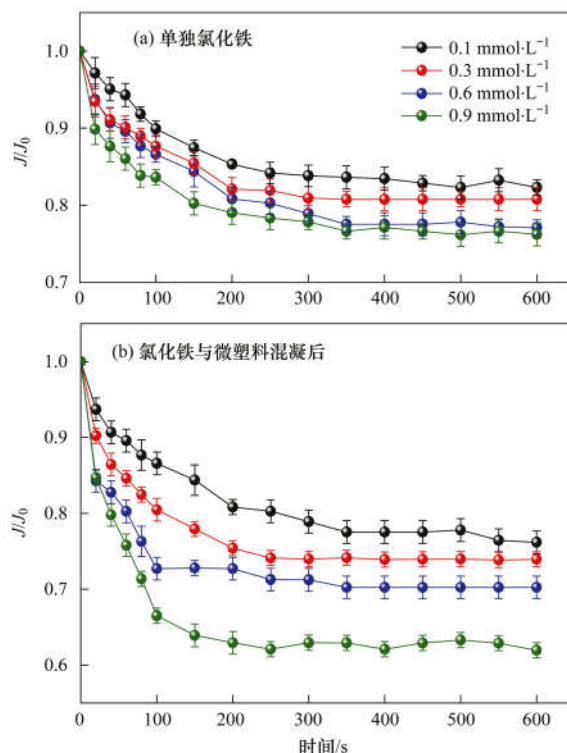
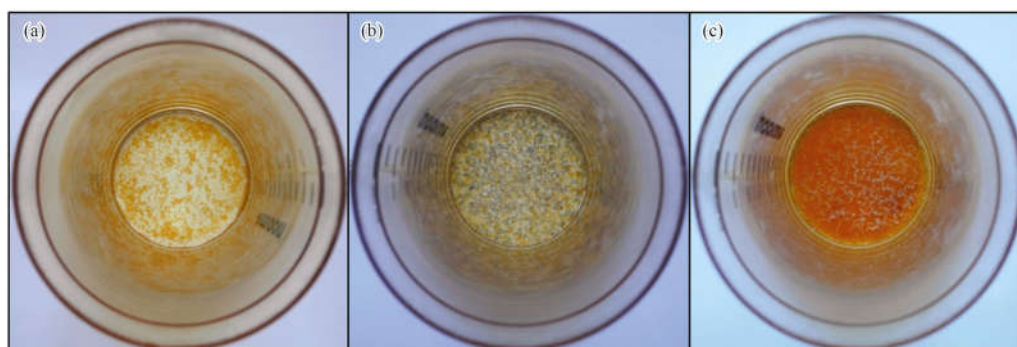


图 3 pH 7.0 时微塑料混凝前后膜比通量

Fig. 3 Membrane specific flux caused by microplastics before and after coagulation at pH 7.0

滤膜表面[图 4(b)和 4(c)], 滤饼层更致密, 因而膜污染程度更严重. 随着铁盐浓度的增加, 滤饼层

厚且致密, 膜污染程度进一步加剧, 运行结束后膜比通量变化 0.14.



(a) $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁; (b) $0.1 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁与 0.1 g 微塑料($d_4 < 0.5 \text{ mm}$) 混凝;
(c) $0.9 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁与 0.1 g 微塑料($d_4 < 0.5 \text{ mm}$) 混凝

图 4 pH 7.0 时微塑料混凝前后超滤膜表面形貌

Fig. 4 Surface morphology of membrane caused by microplastics before and after coagulation at pH 7.0

2.3 pH 的影响

絮体的性质受 pH 影响较大^[33], 进一步研究了不同 pH 条件下微塑料对膜污染程度的影响. 从图 5 可以看出, 膜污染程度随 pH 升高而降低. pH 为 6.0、7.0 和 8.0 时, 单独 $0.3 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁水解絮体造成的膜比通量分别为 0.70、0.76 和 0.81. 与小粒径微塑料($d_4 < 0.5 \text{ mm}$) 混凝后, 膜污染程度加剧, 尤其酸性条件下, 相应膜比通量分别为 0.55、0.69 和 0.79.

进一步研究表明, 膜污染程度随 pH 降低而加剧归因于以下原因: ① pH 6.0、7.0 和 8.0 时, $0.3 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁水解絮体的表面电荷大部分呈正电, 分别为 (10.16 ± 2.81) 、 (3.96 ± 0.84) 和 $(-23.68 \pm 0.69) \text{ mV}$, 而此时微塑料的表面电位呈负电, 分别为 (-6.98 ± 1.11) 、 (-13.32 ± 6.89) 和 $(-15.05 \pm 4.66) \text{ mV}$ [图 6(a)], 低 pH 时微塑料更易被絮体吸附; ② 氯化铁水解絮体平均粒径(d_{50})随 pH 增加而增大[图 6(b)], pH 6.0、7.0 和 8.0 的平均粒径分别为 $413 \text{ } \mu\text{m}$ 、 $622 \text{ } \mu\text{m}$ 和 $694 \text{ } \mu\text{m}$. 低 pH 时絮体粒径小, 在超滤膜表面形成的滤饼层更致密[图 6(c)和 6(d)], 加剧膜污染.

2.4 微塑料混凝前后膜污染机制及环境意义

综上所述, 微塑料单独存在时, 由于其粒径远大于膜孔, 膜污染程度较轻. 在短流程膜工艺中, 微塑料与铁盐混凝后直接进入膜池, 且相对均匀地分散在膜表面. 随着铁盐投量增加, 滤饼层厚度相应增加, 此时小粒径微塑料可能进入絮体内部网络空间, 滤饼层更致密, 进一步加剧膜污染. 与碱性环境相比, 酸性环境时, 铁盐絮体表面带正电荷且粒径较小, 更容易吸附/捕获水环境中呈负电性的微塑料, 在膜表面形成的滤饼层也更致密, 膜污染程度严重.

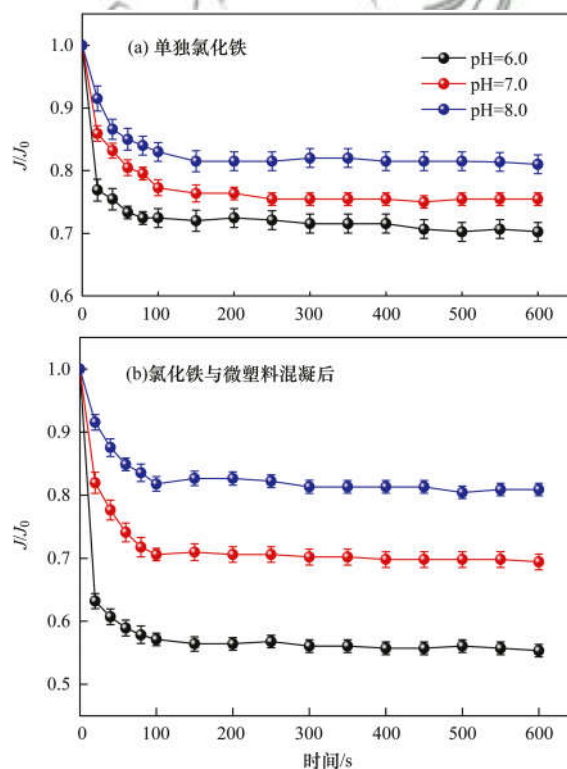
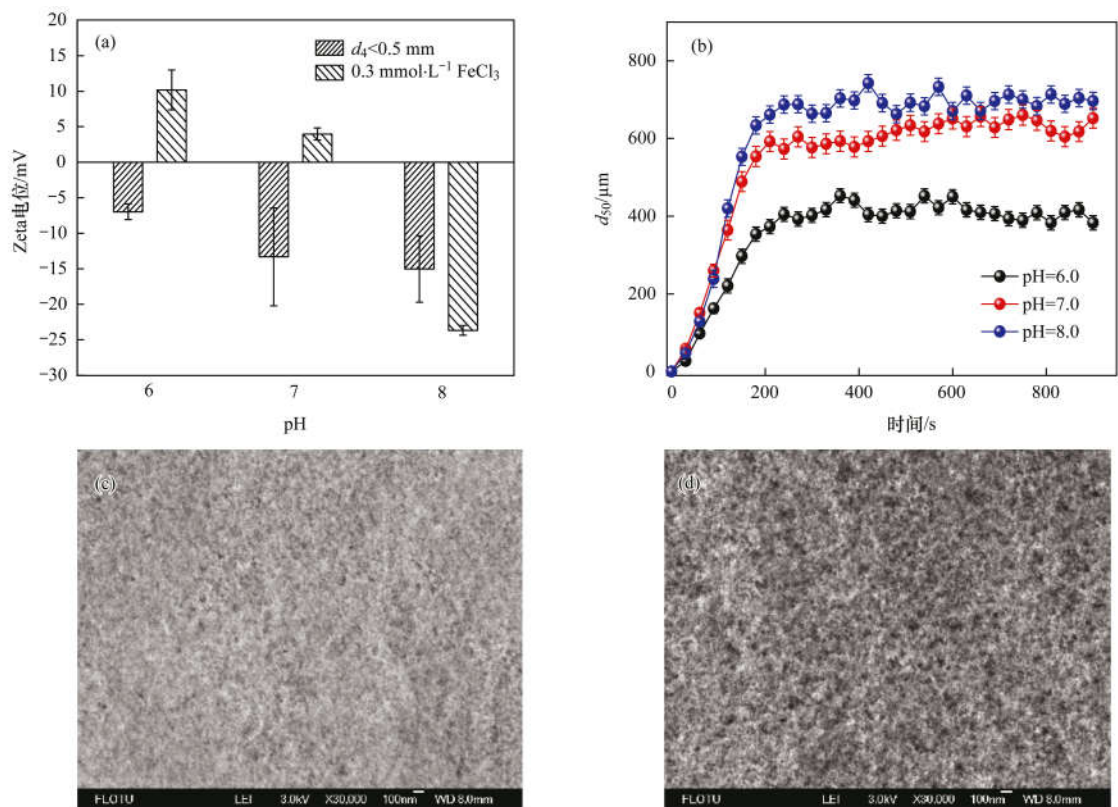


图 5 不同 pH 条件下 $0.3 \text{ mmol} \cdot \text{L}^{-1}$ 氯化铁与微塑料混凝后引起的膜污染

Fig. 5 Membrane fouling caused by microplastics after coagulating with $0.3 \text{ mmol} \cdot \text{L}^{-1} \text{ FeCl}_3 \cdot 6\text{H}_2\text{O}$ under different pH conditions

微塑料混凝前后引起膜污染的机制示意图见图 7.

以上研究表明, 小粒径微塑料能急剧加剧膜污染. 理论上讲, 低压滤膜(微滤和超滤)由于孔径小, 可将混凝前后微塑料全部截留, 所形成的滤饼层相对松散, 且绝大部分为可逆污染. 然而, 受机械、光解和微生物等作用, 微塑料会进一步分解成纳米尺度塑料. 随着微纳塑料在环境中的检出, 其对水质尤其膜污染的影响更严重. 在实际水环境



(a)氯化铁水解絮体和微塑料 Zeta 电位; (b)氯化铁水解絮体粒径变化; (c)和(d) pH 6.0 和 pH 8.0 絮体在超滤膜表面形貌

图 6 不同 pH 时絮体性质及膜表面形貌

Fig. 6 Properties of flocs and surface morphology of membranes at different pH value

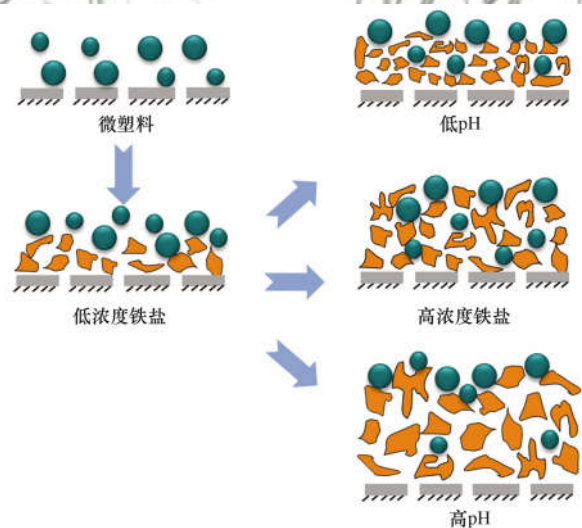


图 7 微塑料混凝前后超滤膜污染机制示意

Fig. 7 Schematic diagram of UF membrane fouling mechanisms induced by microplastics before and after coagulation

中,微纳塑料本身是污染物,更重要的是,微纳塑料可作为优良载体,不仅能有效吸附重金属、持久性有机污染物等有毒物质,也容易滋养、携带病原菌等微生物,成为严重的污染源。微纳塑料作为一种新型污染物,当前的研究多以检测方法、吸附效能和毒理学效应等为主,后续应多关注微纳塑料作为载体滋养微生物对膜污染的影响,尤其纳塑料。

3 结论

(1)微塑料对超滤膜污染程度影响较低,但小粒径微塑料,尤其混凝后形成致密的滤饼层能显著加剧膜污染。

(2)超滤膜污染程度随混凝剂投量增大而加剧。混凝过程中,大粒径微塑料往往被拦截于絮体表面,而小粒径微塑料容易进入絮体形成的内部网络,形成致密滤饼层,加剧膜污染。

(3)水体中微塑料多呈负电,酸性条件下氯化铁水解絮体粒径较小且带正电荷,易吸附微塑料形成致密滤饼层,引起严重的膜污染。

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