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# 水体组分对聚苯乙烯纳米颗粒聚沉行为的影响

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**摘要:** 微/纳米塑料在环境水体中的团聚和沉降行为是影响其迁移和分布的重要因素。以聚苯乙烯纳米颗粒(PS-NPs)为对象, 研究了Na<sup>+</sup>和天然有机质(NOM)两种典型水体组分对其团聚粒径和沉降性能的影响规律, 分析了海水、湖水和生活污水等6种水体中团聚、沉降效果及潜在影响因子。结果表明,  $c(\text{Na}^+) < 80 \text{ mmol} \cdot \text{L}^{-1}$  时有利于PS-NPs沉降; 反之, 则促进其团聚和悬浮。NOM可借助Na<sup>+</sup>在颗粒表面形成多层吸附结构, 改变颗粒表面电势和相对密度, 进而影响PS-NPs团聚和沉降性能。 $\rho(\text{NOM}) > 10 \text{ mg} \cdot \text{L}^{-1}$  时可增强PS-NPs分散和悬浮性能, 可能归因于大量附着在颗粒表面的NOM降低了PS-NPs相对密度。环境水体较实验室合成水体更能促进颗粒团聚, 这可能与环境水体富含氨基酸和蛋白质等大分子有关。

**关键词:** 聚苯乙烯(PS); 纳米颗粒; 团聚; 沉降; 环境水体

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## Effect of Water Components on Aggregation and Sedimentation of Polystyrene Nano-plastics

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**Abstract:** The aggregation and sedimentation of micro/nano-plastics significantly affect their migration and distribution in the environment. This study investigated the effects of Na<sup>+</sup> and natural organic matter (NOM) on the aggregation and sedimentation of polystyrene nano-plastics (PS-NPs) in the aqueous phase. Six types of water, such as seawater, lake water, and domestic sewage, were used to evaluate the above effects and other potential influencing factors. The results indicated that Na<sup>+</sup> could facilitate the sedimentation of PS-NPs when it was less than  $80 \text{ mmol} \cdot \text{L}^{-1}$ , whereas it could promote the aggregation and suspension of PS-NPs when the concentration was greater than  $80 \text{ mmol} \cdot \text{L}^{-1}$ . NOM molecules affected the aggregation and sedimentation of PS-NPs by changing the  $\zeta$  potential and relative density of particles via forming a multilayer adsorption structure with Na<sup>+</sup> on the particle surface. It was observed that NOM greater than  $10 \text{ mg} \cdot \text{L}^{-1}$  enhanced the dispersion and suspension of PS-NPs, which might have been attributed to the decrease in relative density of the particles as a large amount of NOM was absorbed onto the surface. Compared with synthetic waters, environmental waters enhanced the aggregation of PS-NPs, which may have been related to the amino acid, protein, and other organic macro-molecules in the water.

**Key words:** polystyrene (PS); nano-plastics; aggregation; sedimentation; environmental waters

聚苯乙烯(polystyrene, PS)制品因透光性好、刚度大、易加工、抗腐蚀和绝缘等优点,被广泛用于日用装潢、产品包装和设备加工等领域<sup>[1]</sup>。由于回收率低,大量的PS塑料制品进入自然环境,受光照、生物和机械外力等作用而分解为微米或纳米级碎片(PS micro-nano plastics, PS-M/NPs)<sup>[2,3]</sup>。目前全球土壤、湖泊、河流和海洋中均检测到不同含量的PS-M/NPs<sup>[4~6]</sup>,如长江三峡库区<sup>[7]</sup>、黄河入海口<sup>[8,9]</sup>、环渤海区域<sup>[10]</sup>、曼谷湄南河<sup>[11]</sup>和西北太平洋<sup>[9]</sup>。有研究表明,PS-M/NPs能在生物体内富集且呈现多种毒性效应<sup>[12~14]</sup>,如抑制生物运动、诱导畸形发育、破坏免疫系统、DNA损伤和繁殖率降低等<sup>[13~18]</sup>。

微塑料在环境水体中的迁移和扩散性能是影响其生物可获得性及环境风险的关键因素,其中抗团聚和低沉降的颗粒的迁移和扩散性能更强<sup>[19,20]</sup>。PS-M/NPs密度在 $1.04 \sim 1.09 \text{ g} \cdot \text{cm}^{-3}$ 之间,与自然水体密

度较为接近;较传统工程纳米材料或高密度颗粒物,其团聚和沉降行为在受到各类环境水体组分的影响下更易于发生改变或对水环境条件更为敏感,如可能出现“聚而不沉”或者“沉而不聚”,进而影响其迁移、扩散性能以及水体界面的分布特征。如Borges-Ramírez等<sup>[21]</sup>调查发现,墨西哥湾底栖鱼类摄食的微塑料颗粒密度与浮游鱼类间存在较大差异,这与各类塑料颗粒本身密度属性及受水体组分作用分不开。当前关于水环境条件下PS-M/NPs团聚行为的研究报道较多,结果表明水体组分通过聚集或吸附在微塑料表面而改变其表面电化学属性,进而影响到

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颗粒团聚性能;其中 $\text{Na}^+$ 、 $\text{Mg}^{2+}$ 和 $\text{Ca}^{2+}$ 等无机离子通常增强塑料颗粒的团聚程度,而溶解有机质(DOM)则对塑料团聚行为呈抑制作用,但也因颗粒表面官能团而呈现差异<sup>[22-28]</sup>。然而,对于PS-M/NPs在环境水体中沉降行为的认识至今依然有限,尤其是各类水体组分对其团聚和沉降行为协同作用方面十分缺乏<sup>[29, 30]</sup>。

本研究以PS-NPs颗粒为对象,分析了典型环境水体组分对其团聚和沉降行为的影响规律,并测试了其在海水、湖水和生活污水等常见环境水体中的团聚、沉降性能及潜在影响因素,以期为深入理解PS-M/NPs的水环境行为及风险提供理论依据。

## 1 材料与方法

### 1.1 实验材料

PS-NPs分散液购自于苏州知益微球科技有限公司;NOM(2R101N)为天然水体有机质组分,其 $\omega(\text{TOC})$ (以C计)为 $469.6 \text{ mg} \cdot \text{g}^{-1}$ ,购自于国际腐殖酸协会(IHSS)<sup>[31, 32]</sup>。NaCl、HCl(36.0%~38.0%,质量分数)和KOH均为AR纯,购自于国药集团化学试剂有限公司。所有实验用水为超纯水,由Millipore integral 5系统提供,出水电阻率为 $>18.2 \text{ M}\Omega \cdot \text{cm}$ 。

### 1.2 实验方法

颗粒形貌与尺寸采用扫描电子显微镜(SEM, Hitachi Regulus8100)表征,工作电压为5.0 kV;颗粒表面主要官能团采用傅里叶变换红外光谱仪(FTIR, Nicolet iS5 Spectrometer)表征;颗粒 $\zeta$ (Zeta)电势和团聚粒径( $D_{\text{H}}$ )采用纳米粒度分析仪(Zetasizer Nano ZS90)测定;颗粒沉降率采用紫外分光光度计(Shimadzu UV-2600)进行测量。水体中的总有机碳(TOC)、无机离子分别采用TOC分析仪(Analytikjena multi N/C 2100)和离子色谱法(DIONEX ICS-2000)测定。水体荧光特征采用三维荧光光谱仪(HITACHI F-7000)表征。

相关实验在室温下开展,将一定量PS-NPs添加到NaCl溶液、NOM与NaCl混合溶液中,得到 $\rho(\text{PS-NPs})$ 为 $20 \text{ mg} \cdot \text{L}^{-1}$ 、 $c(\text{Na}^+)$ 为 $0 \sim 400 \text{ mmol} \cdot \text{L}^{-1}$ 和 $\rho(\text{NOM})$ 为 $0 \sim 200 \text{ mg} \cdot \text{L}^{-1}$ 的各类混合液。混合液pH采用 $1 \text{ mol} \cdot \text{L}^{-1}$ 的KOH和HCl测定。在 $\text{Na}^+$ 和NOM对PS-NPs $\zeta$ 电势、 $D_{\text{H}}$ 和沉降行为影响的实验中,调节溶液pH为 $6.5 \pm 0.2$ 并静置24 h,超声2 min后分别上机测定;其中沉降实验中,用 $\rho_0$ 和 $\rho_t$ 分别表示PS-NPs初始悬浮浓度和 $t$ 时刻对应悬浮浓度。吸附实验中,分别测定吸附前后溶液中NOM含量(以TOC计),溶液pH为 $6.5 \pm 0.2$ ,在加入PS-NPs摇匀静置24 h后高速离心30 min,并用 $0.22 \mu\text{m}$ 醋酸纤维素膜过滤去除颗

粒后上机测定。溶液相对密度采用玻璃比重计(精度为0.001)测量。为保证研究结果可靠,上述所有实验设置3个平行样。

### 1.3 水样采集与配制

海水(SW)、湖水(HdR)和生活污水(DS)分别采集于湛江市鹤地水库( $110^\circ 17' 52'' \text{E}$ ,  $21^\circ 44' 40'' \text{N}$ )、青岛市崂山区( $120^\circ 32' 46'' \text{E}$ ,  $36^\circ 06' 42'' \text{N}$ )和广州市大沙地污水处理厂( $113^\circ 28' 04'' \text{E}$ ,  $23^\circ 05' 35'' \text{N}$ );S1、S2和S3为实验室合成水体,为NaCl和NOM混合溶液,其中 $c(\text{Na}^+)$ 依次为20、20和 $100 \text{ mmol} \cdot \text{L}^{-1}$ , $\rho(\text{NOM})$ 依次为5、100和 $100 \text{ mg} \cdot \text{L}^{-1}$ 。天然水样经 $0.22 \mu\text{m}$ 醋酸纤维素膜过滤处理后与实验室合成水样一并保存在 $4^\circ \text{C}$ 环境中。

## 2 结果与讨论

### 2.1 材料表征

如图1(a)和1(b)所示,扫描电镜表征结果显示PS-NPs为均匀球形颗粒,对应统计学直径为 $(177.6 \pm 9.6) \text{ nm}$ ;本研究基于DLS测定,其 $D_{\text{H}}$ 约为 $160 \sim 200 \text{ nm}$ ,与扫描电镜表征结果较为一致。FTIR表征结果如图1(c)所示,PS-NPs有两处较强特征吸收峰,分别是 $696 \text{ cm}^{-1}$ 处的苯环CH弯曲振动峰, $1452 \text{ cm}^{-1}$ 和 $1493 \text{ cm}^{-1}$ 为芳香环C—H伸缩振动峰, $1601 \text{ cm}^{-1}$ 处为芳香环骨架振动吸收峰<sup>[33]</sup>。PS-NPs表面 $\zeta$ 电势变化如图1(d)所示,在pH 2.0~11.0范围内为负值,且随着pH增加而逐渐增强。Wu等<sup>[34]</sup>同时采用XPS和FTIR表征未经修饰的PS-NPs颗粒,表明颗粒表面带负电的主要原因是其表面分布着大量的C—O、C=O、O—C=O和OH等官能团。随着pH增加,溶液中越来越多的 $\text{OH}^-$ 离子因与 $\text{H}^+$ 结合,导致PS-NPs颗粒表面上述的官能团去质子化加剧,进而引起PS-NPs负电势不断增强<sup>[35]</sup>。

### 2.2 $\text{Na}^+$ 对PS-NPs聚沉行为的影响

#### 2.2.1 $\text{Na}^+$ 对PS-NPs团聚行为的影响

如图2(a)所示,当 $c(\text{Na}^+) < 80 \text{ mmol} \cdot \text{L}^{-1}$ 时,颗粒在各浓度梯度上的 $D_{\text{H}}$ 平均粒径维持在 $180 \text{ nm}$ 左右,即低浓度 $\text{Na}^+$ 对PS-NPs团聚行为的影响不明显;当 $c(\text{Na}^+) > 80 \text{ mmol} \cdot \text{L}^{-1}$ 时,颗粒 $D_{\text{H}}$ 随着离子浓度升高明显增加,在 $c(\text{Na}^+)$ 为 $400 \text{ mmol} \cdot \text{L}^{-1}$ 时达到 $310 \text{ nm}$ ,表明高浓度 $\text{Na}^+$ 会导致PS-NPs发生快速团聚。分析其原因,许多研究结果证实无机盐浓度增加会导致更多带相反电荷的离子通过静电、吸附等作用分布在颗粒表面区域,压缩颗粒表面双电层,且对颗粒的静电屏蔽作用增强,进而降低颗粒 $\zeta$ 电势而促使颗粒发生团聚<sup>[36, 37]</sup>。本研究中 $\text{Na}^+$ 浓度对颗粒表面 $\zeta$ 电势的影响如图2(b)所示,表明颗粒表面 $\zeta$ 电势随着 $\text{Na}^+$ 浓

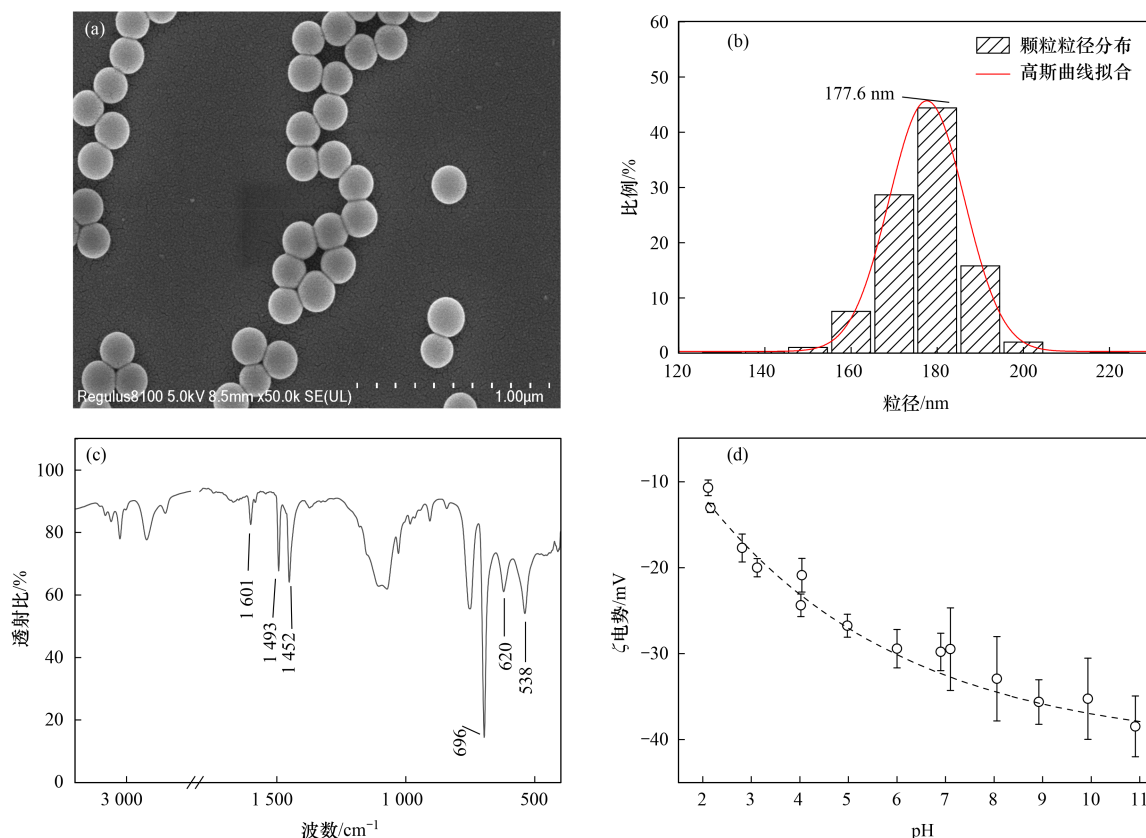


图1 PS-NPs形貌、粒径分布及表面官能团特征

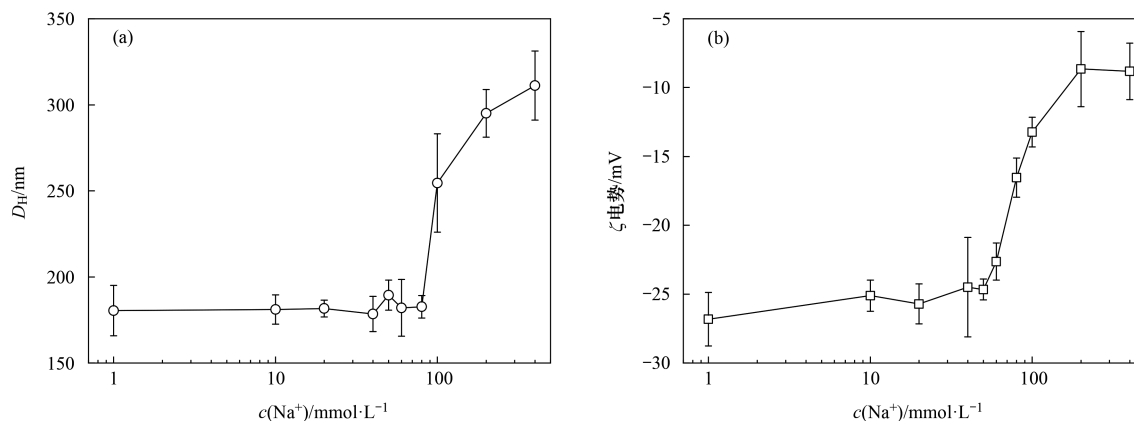
Fig. 1 Morphology, size distribution, and surface functional group of PS-NPs

度增加而逐渐降低;当 $c(\text{Na}^+) > 50 \text{ mmol} \cdot \text{L}^{-1}$ 时,颗粒表面 $\zeta$ 电势快速降低,直到 $\text{Na}^+$ 超过 $200 \text{ mmol} \cdot \text{L}^{-1}$ 时,颗粒表面 $\zeta$ 电势基本维持在 $-10 \sim -5 \text{ mV}$ 之间.因此,本研究中 $\text{Na}^+$ 导致PS-NPs表面 $\zeta$ 电势降低是促使PS-NPs团聚粒径增加的主要原因.此外,结合图2, $\text{Na}^+$ 诱导PS-NPs发生团聚的浓度阈值约为 $80 \text{ mmol} \cdot \text{L}^{-1}$ ,超过该浓度阈值的 $\text{Na}^+$ 将导致颗粒表面 $\zeta$ 电势 $< -15 \text{ mV}$ 且颗粒加速团聚,其粒径和表面 $\zeta$ 电势最终稳定在 $c(\text{Na}^+) 200 \sim 400 \text{ mmol} \cdot \text{L}^{-1}$ 之间.结合DLVO理论,当 $c(\text{Na}^+) > 80 \text{ mmol} \cdot \text{L}^{-1}$ 时,PS-NPs颗粒间的静电斥力将弱于范德华引力,进而引发颗粒快速团聚.Zhang

等<sup>[38]</sup>基于初始聚合速率常数(initial aggregation rate constant)拟合分析,得到 $\text{Na}^+$ 诱导尺寸为 $100 \text{ nm}$ 的PS-NPs发生团聚的初始浓度约为 $100 \text{ mmol} \cdot \text{L}^{-1}$ ,临界团聚浓度(CCC)为 $349.06 \text{ mmol} \cdot \text{L}^{-1}$ ,并认为范德华力主导了PS-NPs这一阶段的团聚行为,这一结果与本研究的基本一致.

## 2.2.2 $\text{Na}^+$ 对PS-NPs沉降行为的影响

本研究采用紫外分光光度法,于波长 $297 \text{ nm}$ 处测定PS-NPs不同添加量时的吸光度值,如图3(a)所示,拟合结果发现PS-NPs添加量与对应吸光度值有较高的线性相关性, $R^2$ 可达 $0.998$ ,表明采用紫外分

图2  $\text{Na}^+$ 对PS-NPs粒径及 $\zeta$ 电势影响Fig. 2 Effects of  $\text{Na}^+$  on  $D_H$  and  $\zeta$  potential of PS-NPs

光光度法能准确测量溶液中悬浮颗粒浓度. 基于以上实验方法, 本研究分析了  $0 \sim 400 \text{ mmol} \cdot \text{L}^{-1}$  的  $\text{Na}^+$  对 PS-NPs 沉降行为的影响, 如图 3(b) 所示, 观察到随着  $\text{Na}^+$  浓度增加, PS-NPs 沉降率呈现先增加、再降低、后消失的趋势; 其中, 在  $c(\text{Na}^+)$  为  $20 \text{ mmol} \cdot \text{L}^{-1}$  时 PS-NPs 沉降性能达到最大值, 沉降率为  $24.2\%$ ; 当  $c(\text{Na}^+) > 80 \text{ mmol} \cdot \text{L}^{-1}$ , PS-NPs 沉降性能与对照组间未见明显差异. 结合图 2(a),  $c(\text{Na}^+) < 80 \text{ mmol} \cdot \text{L}^{-1}$  时 PS-NPs 未发生团聚, 其粒径均值维持在约  $180 \text{ nm}$ , 基于此可以推测导致 PS-NPs 沉降率增加的潜在原因为颗粒相对密度的改变. 由图 2(b) 可知,  $\text{Na}^+$  通过静电引力作用进入颗粒界面吸附层或吸附在带负电的官能团上, 进而降低颗粒表面  $\zeta$  电势. 因此, 随着溶液  $\text{Na}^+$  浓度增加, 更多的  $\text{Na}^+$  进入颗粒界面吸附层, 不仅削弱了颗粒  $\zeta$  电势, 也同时导致胶粒密度相对水溶液不断增加, 促进了 PS-NPs 沉降. 由于 PS-NPs 沉降率同时受胶体颗粒和水溶液相对密度的共同作用, 随

着  $\text{NaCl}$  不断加入, 水溶液密度逐渐增加而 PS-NPs 对  $\text{Na}^+$  吸附强度不断降低, 胶粒相对于水溶液的密度变小, 进而导致颗粒沉降率随之减弱. 本研究中, 当  $c(\text{Na}^+) > 20 \text{ mmol} \cdot \text{L}^{-1}$  时, 该促进作用因水体密度增强而不断被削弱, 最后消失于  $c(\text{Na}^+) > 80 \text{ mmol} \cdot \text{L}^{-1}$  时. 许多研究表明金属、金属氧化物等工程纳米颗粒的团聚、沉降效率会随着电解质浓度增加而不断增强, 这主要归因于金属、金属氧化物密度较大, 如  $\text{TiO}_2$ -NPs 为  $3.9 \text{ g} \cdot \text{cm}^{-3}$ 、 $\text{Fe}_2\text{O}_3$ -NPs 为  $5.24 \text{ g} \cdot \text{cm}^{-3}$ 、 $\text{ZnO}$ -NPs 为  $5.61 \text{ g} \cdot \text{cm}^{-3}$ 、 $\text{NiO}$ -NPs 为  $6.67 \text{ g} \cdot \text{cm}^{-3}$  和  $\text{SiO}_2$ -NPs 为  $2.6 \text{ g} \cdot \text{cm}^{-3}$ <sup>[39, 40]</sup>; 这导致其胶粒或团聚体的沉降行为受水体组分影响可以忽略, 即团聚和沉降行为近似同时发生<sup>[37, 41, 42]</sup>. 相比而言, 由于  $\rho(\text{PS-NPs})$  仅为  $1.05 \text{ g} \cdot \text{cm}^{-3}$ ,  $\text{Na}^+$  在其表面的吸附行为及其对水溶液密度的影响将明显干扰 PS-NPs 的沉降性能, 正如本研究发现的 PS-NPs 相继出现“沉而不聚”和“聚而不沉”两种行为.

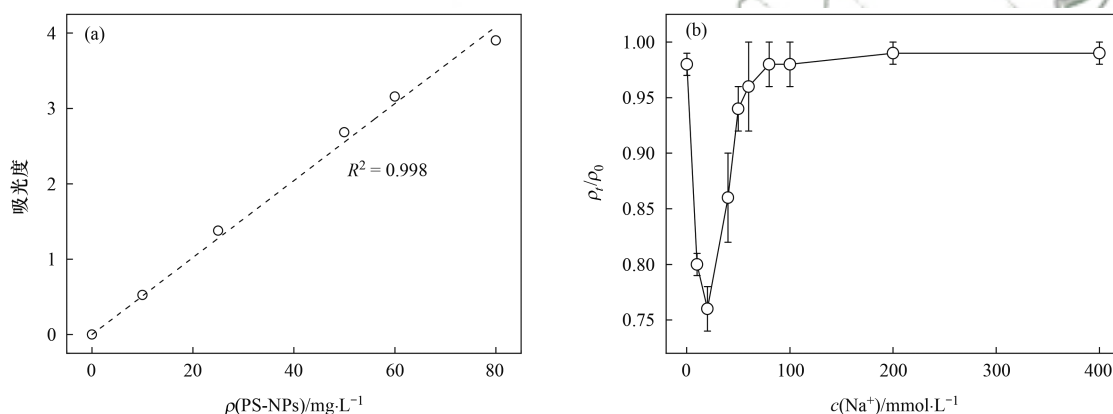


图3 PS-NPs添加量与吸光度相关性及  $\text{Na}^+$  影响下的沉降率

Fig. 3 Correlation between absorbance and dosage of PS-NPs and their sedimentation rates under the effect of  $\text{Na}^+$

## 2.3 NOM对PS-NPs聚沉行为的影响

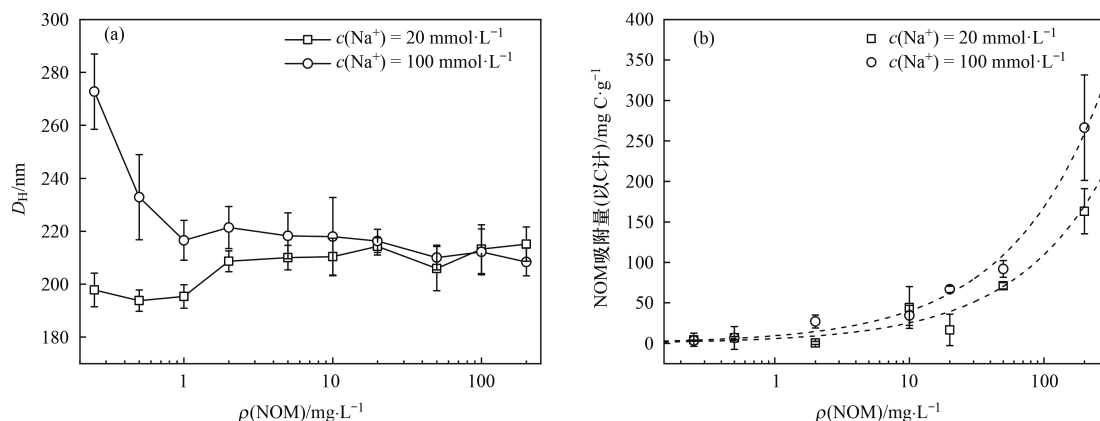
### 2.3.1 NOM对PS-NPs团聚行为的影响

考虑到  $\text{Na}^+$  对 PS-NPs 聚沉行为的影响, 本研究分别分析了  $c(\text{Na}^+)$  为  $20 \text{ mmol} \cdot \text{L}^{-1}$  和  $100 \text{ mmol} \cdot \text{L}^{-1}$  两种条件下 NOM 对 PS-NPs 的团聚和沉降行为的影响. 如图 4(a) 所示, 当  $c(\text{Na}^+)$  为  $20 \text{ mmol} \cdot \text{L}^{-1}$  时, NOM 浓度增加可促进 PS-NPs 的  $D_H$  略有增大, 可能归因于特定 NOM 大分子对部分颗粒的“桥连”作用<sup>[42]</sup>; 相比而言, 当  $c(\text{Na}^+)$  为  $100 \text{ mmol} \cdot \text{L}^{-1}$  时, NOM 导致 PS-NPs 的  $D_H$  减小至与前者相似粒径区域, 说明带负电的 NOM 在颗粒表面区域的吸附或聚集潜在增强了 PS-NPs 彼此间的电负性, 导致团聚体发生“解聚”现象. 上述两种条件下 PS-NPs 的  $D_H$  差异可能与 PS-NPs 对 NOM 分子和  $\text{Na}^+$  的吸附形态及对颗粒间作用力的影响有关. 依据图 4(b) 吸附实验结果, 两种条件下 PS-NPs 对 NOM 的吸附量均随着 NOM 添加量不断增加, 且较高的  $\text{Na}^+$

浓度能促进颗粒对 NOM 的吸附. 由于本研究未观察到吸附拐点, 说明 NOM 在颗粒表面可能均形成了多层吸附结构<sup>[43]</sup>; 结合图 2(b) 可知, 由于 PS-NPs 胶粒在两种条件下均呈现电负性, 说明带负电的 NOM 主要借助  $\text{Na}^+$  在颗粒表面形成多层吸附结构, 这一结构增强了水环境中 PS-NPs 的分散稳定性.

### 2.3.2 NOM对PS-NPs沉降行为的影响

NOM 对 PS-NPs 沉降行为的影响如图 5 所示, 当  $c(\text{Na}^+)$  为  $20 \text{ mmol} \cdot \text{L}^{-1}$  时, PS-NPs 沉降率随着 NOM 浓度增加呈现先上升后减弱现象, 在  $\rho(\text{NOM})$  为  $0.5 \text{ mg} \cdot \text{L}^{-1}$  时其沉降率达到最大值, 为  $42.4\%$ ; 随着 NOM 浓度持续增加, PS-NPs 沉降率逐渐减弱, 在  $\rho(\text{NOM})$  超过  $10 \text{ mg} \cdot \text{L}^{-1}$  时约等于空白组, 在  $\rho(\text{NOM})$  超过  $50 \text{ mg} \cdot \text{L}^{-1}$  时降至最低. 当  $c(\text{Na}^+)$  为  $100 \text{ mmol} \cdot \text{L}^{-1}$  时, PS-NPs 沉降率随着 NOM 投加而持续降低, 在  $\rho(\text{NOM})$  超过  $50 \text{ mg} \cdot \text{L}^{-1}$  时降至最低. 因此, PS-NPs 沉降率在上

图4 NOM对PS-NPs  $D_H$ 的影响和在颗粒表面的吸附特征Fig. 4 Influence of NOM on the  $D_H$  and their adsorption characteristics on PS-NPs

述两种条件下存在明显差异. 由于NOM借助 $\text{Na}^+$ 在颗粒表面形成多层吸附结构且增强颗粒分散稳定性,推断该吸附结构对PS-NPs沉降性能可能具有重要调节作用;且与 $\text{Na}^+$ 在颗粒表面富集能增强颗粒密度不同,NOM在颗粒表面的大量富集可能会降低PS-NPs相对密度而抑制颗粒沉降.

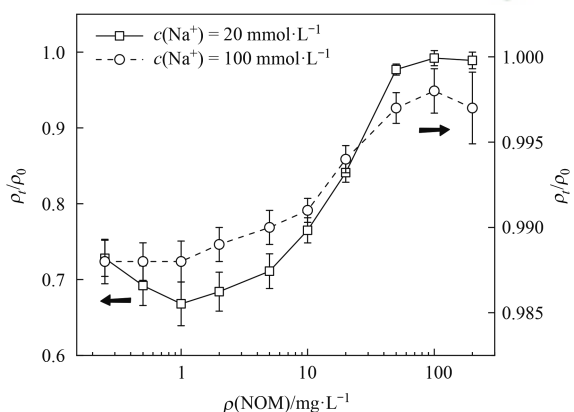


图5 NOM对PS-NPs的沉降行为的影响

Fig. 5 Effects of NOM on sedimentation rate of PS-NPs

为验证以上推测,本研究测定了NOM投加对水体密度的影响,结果发现在 $c(\text{Na}^+)$ 为 $20 \text{ mmol}\cdot\text{L}^{-1}$ 和 $100 \text{ mmol}\cdot\text{L}^{-1}$ 两种条件下,NOM浓度增加均能导致水体相对密度降低,且前者较后者更为明显(图6). 这一现象说明与 $\text{Na}^+$ 等无机盐会增强水体密度不同,NOM分子可降低水溶液相对密度. 当NOM分子大量吸附或富集在颗粒表面,亦可降低颗粒相对密度,进而抑制PS-NPs的沉降效率. 结合图5沉降实验结果,当 $c(\text{Na}^+)$ 为 $20 \text{ mmol}\cdot\text{L}^{-1}$ 时,少量的NOM加入会潜在促进大量 $\text{Na}^+$ 富集在胶粒吸附层,导致PS-NPs胶粒密度增大而加速沉降;当 $\rho(\text{NOM}) > 0.5 \text{ mg}\cdot\text{L}^{-1}$ 时,NOM在颗粒表面的大量吸附导致PS-NPs胶粒相对密度逐渐减小,最终在 $\rho(\text{NOM}) > 50 \text{ mg}\cdot\text{L}^{-1}$ 时基本消失.

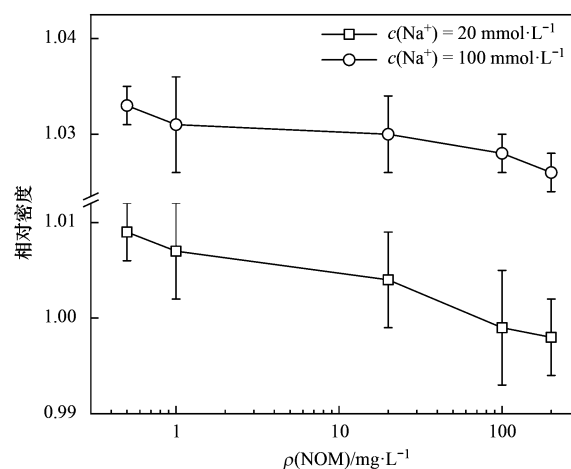


图6 NOM对水体密度的影响

Fig. 6 Effect of NOM on the relative density of water

## 2.4 环境水体中PS-NPs聚沉行为

6种水样中PS-NPs的 $D_H$ 和 $\zeta$ 电势变化趋势如图7(a)所示,除S1和S2两种水体,颗粒在其余4种水体中均发生不同程度的团聚, $D_H$ 由大到小依次为:SW > HdR > DS > S3;结合颗粒表面 $\zeta$ 电势变化,由于颗粒在SW、HdR和DS这3种环境水体中 $\zeta$ 电势均小于 $-15 \text{ mV}$ ,导致PS-NPs发生较大程度团聚,而颗粒在S3、S1和S2中的 $\zeta$ 电势不断增强且高于 $-15 \text{ mV}$ ,导致PS-NPs团聚程度较低或不发生,这一结果表明环境水体对PS-NPs团聚性能具有较实验室水体强的促进作用. PS-NPs在6种水体中沉降行为如图7(b)所示,15 min内颗粒沉降率表现为:S1 > DS > S2 > HdR > S3  $\approx$  SW,且未观察到这一结果与颗粒团聚程度相关. 结合表1中各水体组分含量,S1、S2和S3对应颗粒沉降率与3.2节和3.3节相应的结果较为一致,S1和S2表现为颗粒“沉而不聚”,S3表现为颗粒“聚而不沉”;相比实验室水体,环境水体组分的多样性导致PS-NPs聚沉行为更为复杂. SW较其他5种水体高的 $\text{Na}^+$ 、 $\text{Mg}^{2+}$ 、 $\text{Ca}^{2+}$ 和 $\text{Cl}^-$ 浓度是导致PS-NPs

颗粒 $D_H$ 不断增大的主要原因,而其较高的相对密度则造成PS-NPs团聚体“聚而不沉”. HdR 和 DS 两种水体离子强度较低,却促进了PS-NPs颗粒发生明显团聚,这可能归因于环境水体中氨基酸和蛋白质类大分子在颗粒表面的吸附作用促进了颗粒的自团聚<sup>[41, 44]</sup>. 本研究中SW、HdR 和 DS 较高的 IF 值表明

水体中氨基酸和蛋白质类分子浓度较高,印证了上述推测<sup>[45]</sup>. 同时,较高的 IF 意味着更多的氨基酸和蛋白质类大分子吸附在颗粒表面;较本研究使用的 NOM 标准品,前者可能有利于颗粒形成更为致密的团聚体,促进了DS中颗粒团聚体的沉降,相关机制有待深入研究.

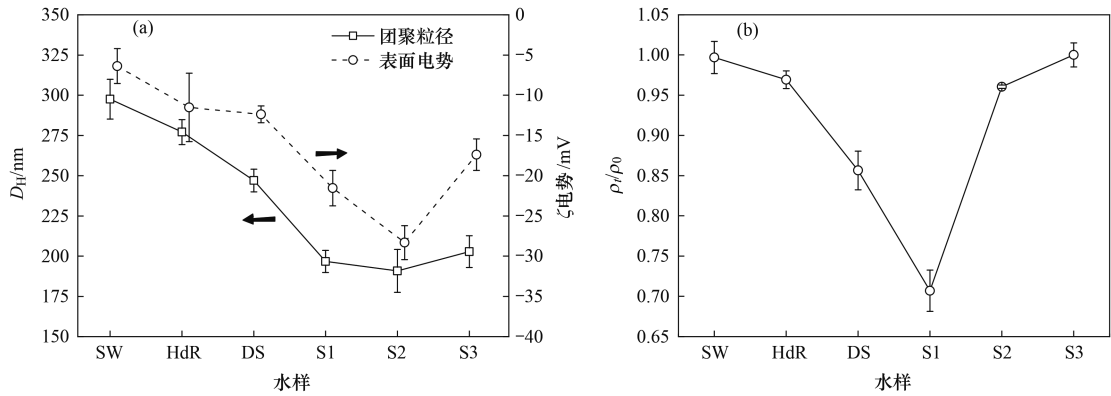


图7 各类水体中PS-NPs的 $D_H$ 、 $\zeta$ 电势及沉降率  
Fig. 7 Experimental  $D_H$ ,  $\zeta$  potential, and sedimentation rates of PS-NPs in water samples

表1 pH 6.5时各水体相关指标值<sup>1)</sup>  
Table 1 Parameters of waters at pH 6.5

| 水样  | 水体各组分浓度  |                 |                  |                  |                 | IF   | 相对密度  |
|-----|----------|-----------------|------------------|------------------|-----------------|------|-------|
|     | TOC      | Na <sup>+</sup> | Mg <sup>2+</sup> | Ca <sup>2+</sup> | Cl <sup>-</sup> |      |       |
| SW  | 11.5±0.0 | 244.7±1.7       | 28.1±0.4         | 5.6±0.1          | 288.9±1.9       | 1.92 | 1.100 |
| HdR | 12.1±0.3 | 0.2±0.0         | 0.1±0.0          | 0.2±0.0          | 0.2±1.8         | 1.81 | 0.992 |
| DS  | 44.9±2.2 | 2.9±0.0         | 0.5±0.0          | 1.0±0.1          | 2.4±2.1         | 2.11 | 1.003 |
| S1  | 3.2±0.1  | 20.5±0.1        | 0.0±0.0          | 0.1±0.3          | 21.2±1.6        | 1.38 | 1.011 |
| S2  | 44.7±0.7 | 20.9±0.2        | 0.0±0.0          | 0.1±0.0          | 21.4±1.4        | 1.36 | 1.009 |
| S3  | 46.0±0.7 | 88.3±0.7        | 0.0±0.0          | 0.1±0.1          | 89.9±1.4        | 1.36 | 1.017 |

1) TOC单位为 $\text{mg}\cdot\text{L}^{-1}$ ;  $\text{Na}^+$ 、 $\text{Mg}^{2+}$ 、 $\text{Ca}^{2+}$ 和 $\text{Cl}^-$ 单位为 $\text{mmol}\cdot\text{L}^{-1}$ ; IF为激发波长 $E_x$ 为370 nm时,发射波长 $E_m$ 为450 nm和500 nm对应的荧光强度比值

3 结论

(1)  $\text{Na}^+$ 导致PS-NPs的团聚、沉降行为发生在不同浓度区间. 当 $c(\text{Na}^+) < 80 \text{ mmol}\cdot\text{L}^{-1}$ 时, PS-NPs因其间较强的静电斥力作用而保持分散,但因 $\text{Na}^+$ 在其表面静电吸附作用而促进了颗粒沉降;当 $c(\text{Na}^+) > 80 \text{ mmol}\cdot\text{L}^{-1}$ 时, PS-NPs胶粒发生团聚,但因溶液较高的相对密度而呈现“聚而不沉”现象.

(2) NOM可增强PS-NPs分散稳定性,但对颗粒沉降行为的影响因 $\text{Na}^+$ 含量而存在较大差异. 当 $\text{Na}^+$ 浓度有利于颗粒沉降时(如 $20 \text{ mmol}\cdot\text{L}^{-1}$ ),低浓度的NOM可促进PS-NPs沉降;反之,则因NOM大量吸附在颗粒表面而抑制PS-NPs沉降行为.

(3) 海水、湖水和生活污水对PS-NPs团聚促进作用较实验室合成水体强,可能归因于前者富含氨基酸和蛋白质等组分对PS-NPs团聚行为的影响.

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