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生物体胃肠道中微塑料负载污染物的解吸行为和影响因素研究进展

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摘要：环境中大量分布的微塑料(microplastics, MPs)由于具有粒径小、比表面积大、且对生物体具有毒性危害等特点,因而近年来得到国内外越来越多的研究和关注。环境调查研究表明,环境 MPs 表面通常含有不同种类和含量的污染物(重金属和有机污染物),这些污染物通过摄食进入生物体胃肠道后在胃肠液作用下会发生解吸,并引起相应的生物毒性效应。本文系统综述了生物体胃肠道中 MPs 表面负载污染物的解吸行为、机制和潜在影响因素。生物胃肠道系统中 MPs 表面携带的重金属、有机物以及自身添加剂在胃肠液作用下能够大量解吸。解吸机制方面,胃肠中消化酶能够影响污染物与 MPs 之间界面结合力(范德华力、静电作用力和氢键等),结合力越小,解吸效率越高。此外,MPs 表面负载污染物在胃肠道中的解吸能力也受到塑料性质(结晶度、孔体积和疏水性)和胃肠液性质(消化酶种类、消化液组分和 pH)的共同影响,但具体机制当前仍不明确。笔者期望该综述能为进一步评估自然水体中生物体对 MPs 摄食所引起的生态风险提供科学依据。

关键词：微塑料;有机物污染物;重金属;胃肠道;水生生物;吸附解吸
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Desorption Behavior and Impacting Factors of Microplastic-loaded Pollutants in Biological Gastrointestinal Tract: A Review

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Abstract: Microplastic pollution in natural waters are of increasing concerns due to their widely distribution, specific physicochemical properties (i.e., small particle size, high specific surface area), and toxicity to aquatic organisms. During long-term retention in the water bodies, MPs are prone to absorb organic/inorganic environmental contaminants. When ingested by aquatic organisms, these harmful chemicals are readily to enter into biological gastrointestinal tracts and release under the impact of digestive enzyme, and pose adverse impacts on organisms. However, the desorption and factors controlling desorption efficiency in gastrointestinal tract remain unresolved. In this review, we aim to provide an overview over the desorption behavior and mechanism of MPs-loaded pollutants in the gastrointestinal tract. Many efforts have demonstrated the presence of MPs in biotic gastrointestinal tract, and

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distribution in various color, size and shape. During MPs retention in biotic gastrointestinal tract, many types of contaminants are prone to desorb from MP surface. The desorption efficiency of heavy metals in gastric phase is higher than that in intestinal phase, while the desorption efficiency of organic pollutants vary with pollutant types. The desorption of pollutants in the gastrointestinal tract partly depends on the intensity of the interaction between MPs and pollutants, which hinges on the physicochemical properties of MPs and pollutants. In addition, the gastrointestinal environment (pH, digestive enzymes, inorganic ions) is also available to influence the desorption behavior of pollutants from MP surface. The acidic condition of gastric phase facilitate the desorption of heavy metals. The digestive enzymes in the gastrointestinal tracts combine with MPs to form protein coronas, followed by the increase of MPs size and zeta potential, the change of residues and secondary structure of digestive enzymes. The interaction of MPs with digestive enzymes usually includes the synergistic effects of hydrogen bonding, van der Waals force, π-π interaction, electrostatic interaction and hydrophobic interaction. However, the interaction among MPs, pollutants, digestive enzymes and various ions involves complicated physicochemical changes, desorption and resorption coexist during the entire process. The mechanism and sites of the competitive adsorption among MPs, pollutants, digestive enzymes and various ions are still unknown. This review provides a new insight for understanding the desorption behavior and mechanism of pollutants from MPs in the gastrointestinal tracts, which was helpful to elucidate the additional ecological risk caused by MPs.

Keywords: microplastics; organic pollutants; heavy metals; gastrointestinal tract; aquatic organisms; sorption and desorption

塑料产品由于质量轻、价格低廉、耐用性强等优点被广泛应用于建材、包装、汽车装饰和电子产品等领域[1]。据统计,2018 年,全球 1 518 条河流每年向海洋环境中排放的塑料垃圾有 57 000 ~ 265 000 t[2]。在这些塑料垃圾中,粒径<5 mm 的微塑料(microplastics, MPs)在全球不同地区的河流[3]、湖泊[4]、海洋[5-7]、近岸海水[8-10]、沉积物[11-12]、高山雪域[13]甚至是极地地区[14]被大量检出,也因其环境持久性、生物富集性和毒性得到了广泛关注[15]。

由于 MPs 具有较小粒径和较大比表面积,其在水环境迁移过程中通常容易吸附重金属和有机污染物,如多环芳烃(polycyclic aromatic hydrocarbons, PAHs)[16-18]、多氯联苯(polychorinated biphenyls, PCBs)[19-21]、多溴联苯(polybrominated biphenyls, PBBs)[22-23],铝(Al)、铬(Cr)和铜(Cu)等[24-26]。MPs 与污染物发生相互作用的过程中分配作用和表面吸附是 2 种最主要的机制[27]。分配作用是 MPs 吸附亲脂性有机污染物的主要方式,该作用与表面吸附位点无关,与有机物的溶解度和 MPs 疏水性有关[27-28]。表面吸附是指固体表面吸附水中溶解污染物或胶体,主要通过亲电性原理,涉及双电层相互作用的污染物主要有离子态金属、有机碱和部分有机物。实际上,纳米颗粒物或天然矿物表面也同样具有这种特性。而且相对吸附位点要高出几个数量级。表面吸附通常分为化学吸附(生成化学键)和物理吸附(存在相互作用力)。化学吸附通常伴随着化学键的生成,具有不可逆性,除非发生共价键断裂,这使得化学物质从固相中解吸变得困难,含有羧基官能团(—COOH)、羰基(C ═ O)等含氧官能团的 MPs 易与污染物发生化学吸附,例如,老化后聚酰胺(polyamide, PA)羧基含量增加,并与 Pb(Ⅱ)发生表面络合[25];MPs 吸附 Cd(Ⅱ)后 C ═ O 比例的增加表明 Cd 离子吸附到 MPs 表面后形成更多的 C ═ O 键[29]。物理吸附通常涉及疏水作用、静电作用、π-π 相互作用和范德华力以及氢键等多种机制[30],例如聚苯乙烯(polystyrene, PS)吸附环丙沙星(ciprofloxacin, CIP)、甲氧苄啶(trimethoprim, TMP)和磺胺嘧啶(sulfanilamide, SDZ)的能力强于聚乙烯(polyethylene, PE),这是由于 PS 可以在芳香表面发生非特异性范德华相互作用和 π-π 相互作用,而 PE 只能发生范德华相互作用;而且在氢键的作用下 PA 对 3 种抗生素的吸附能力最强[31]。此外,MPs 对污染物的吸附机制受环境因素(pH、温度、离子强度和溶解性有机质)、污染物性质以及 MPs 自身性质(塑料类型、大小、结晶度、密度、极性、老化程度和生物膜)的影响[32-34]。

水环境中 MPs 通常具有生物传递性,在长期停留过程中能够通过饮水、摄食和食物链传递等方式进入生物体内[35]。不同进食方式对生物体胃肠道中

MPs 赋存和分布特征有显著影响。例如,过滤和吸食性鱼类不会主动摄食 MPs 颗粒,误食后能通过自身口咽结构识别并吐出 MPs 颗粒,而吞食性鱼类则通过直接吞食食物方式进食,MPs 摄入的可能性较高。此外,纤维状 MPs 易在鱼呼吸过程中进入鱼嘴或鱼鳃中,当其含量在鱼嘴和鳃中积累超过耐受阈值,鱼可通过咳嗽行为排除一部分纤维[36]。然而,由于 MPs 尺寸微小难以被水生生物区分或识别,仍有大量的 MPs 在水生和底栖生物体胃肠道内被检出。生物胃肠道内 MPs 种类主要包括 PE、聚丙烯(polypropylene, PP)、PS、PA、聚氯乙烯(polyvinyl chloride PVC)、丙烯腈-丁二烯-苯乙烯共聚物(acrylonitrile butadiene styrene copolymers, ABS)、聚对苯二甲酸乙二酯(polyethylene terephthalate, PET)等[37],形状主要是纤维、碎片和薄膜[38],粒径以 1 mm 以下为主[39-40]。生物体胃肠道中 MPs 粒径的大小也与生物体摄食习性有关,鱼虾贝类中<1 mm MPs 居多[39, 41-44],但海洋食物链顶端的吞食性哺乳动物如海豚、白鲸胃肠道内存在大量 1 mm 以上的 MPs[45-49]。MPs 被生物摄入后,会在生物体胃肠道内停留过程中,释放添加剂和携带的外源污染物,加剧 MPs 毒性效应。然而,当前对于 MPs 负载表面污染物和添加剂在生物体胃肠道体系中的解吸、浸出行为的研究仍然较少。此外,进入生物体胃肠道中的 MPs 由于性质稳定难以被消化分解,因而会导致生物体消化道阻塞、营养不良和饥饿、游泳速度降低、易位到其他组织,从而导致存活率降低[50]。除此之外,MPs 也能通过食物链迁移在高营养级生物体内不断累积[51],并能进一步通过食物链迁移对人体健康造成威胁。

本研究系统综述了生物体胃肠道 MPs 污染现状,MPs 表面负载污染物的解吸行为、机制及潜在影响因素。笔者期望该综述可以为全面评价胃肠道体系中 MPs 及负载污染物的环境行为和毒性效应提供理论依据。

1 生物体胃肠道中 MPs 污染研究现状(Current status for MPs pollution in gastrointestinal tract of organisms)

为了考察当前生物体胃肠道中 MPs 污染的研究现状,笔者整理了近 10 年来国内外相关研究的论文发表数量和重点研究领域。截至 2021 年 12 月 21 日,在文献检索数据库 Web of Science 上以“microplastics”“gastrointestinal tract”为检索词共检索出 416 篇文章(2013—2021),其中包括综述论文 56 篇,研究性论文 360 篇。论文数量方面,2018—2021 年关于胃肠道中 MPs 污染研究论文总数量为 363 篇,占论文总数的 87.2%,且论文发表数量呈现逐年增加的趋势(2018:44 篇,2019:67 篇,2020:134 篇,2021:118 篇),说明生物体胃肠道中 MPs 污染近年来得到了广泛研究和关注。为了进一步考察生物体胃肠道中 MPs 污染重点研究领域,416 篇文章中选择核心合集文章 397 篇,通过 VOS viewer 1.6.16 软件对生物体胃肠道中 MPs 研究重点领域进行筛选。以论文关键词出现频率为排列方式统计出 1 558 个关键词,筛选出了出现频率 10 次及以上的关键词 83 个。图 1 的聚类分析结果表明,当前胃肠道中 MPs 污染研究领域主要关注摄食(ingestion)、累积(accumulation)和识别(identification),污染介质主要集中于海洋环境,而对于 MPs 及其携带污染物与胃肠道成分的相互作用方面研究较少。

2 胃肠道中 MPs 负载污染物的解吸行为(Desorption of pollutants form MPs surface in gastrointestinal tract)

2.1 MPs 负载的重金属在模拟胃肠液中的解吸

MPs 从水体进入生物体胃肠道后会在由胃、小肠和大肠区域组成的胃肠道(GIT)体系中停留[52],负载于 MPs 表面的污染物也会在胃肠液体系中发生一定程度的解吸,且胃肠道环境中污染物的解吸量高于自然水体[29, 53-55]。例如,Holmes 等[54]将英格兰西南部康沃尔的海滩获得的含 Fe、Mn、Co 和 Pb 的 PS MPs 颗粒置于模拟禽类胃液中,暴露 168 h 以探究重金属的解吸和生物可及性(bioaccessibility, 被生物利用的潜力,通常用释放量/负载总量表示),研究结果表明,Fe、Mn、Co 和 Pb 在模拟胃液中的最大解吸量分别为 38.9、0.81、0.014 和 0.10 $mg\cdot g^{-1}$,最大生物可及性分别为 60%、80%、50% 和 80%。Zhou 等[29]研究发现 5 种 MPs(PA、PVC、PS、ABS 和 PET)携带的 Cd 在模拟蚯蚓胃肠液中的解吸率高于 $CaCl_2$ 溶液。相应的,Liao 和 Yang[53]比较了模拟胃肠液和水体中 MPs 携带的 Cr(Ⅲ)和 Cr(Ⅵ)的解吸能力,发现相较于 $CaCl_2$ 背景溶液,模拟人体胃肠液对 Cr 解吸具有显著促进作用。总的来说,相比于非胃肠道环境,胃肠道环境能促进 MPs 表面重金属的解吸。此外,胃液和肠液中 MPs 表面重金属的解吸能力也存在差异。例如,Godoy 等[55]在连续解吸实验中发现 PE、PP 上的 Cr 和 Pb 释放量在胃阶段分别为

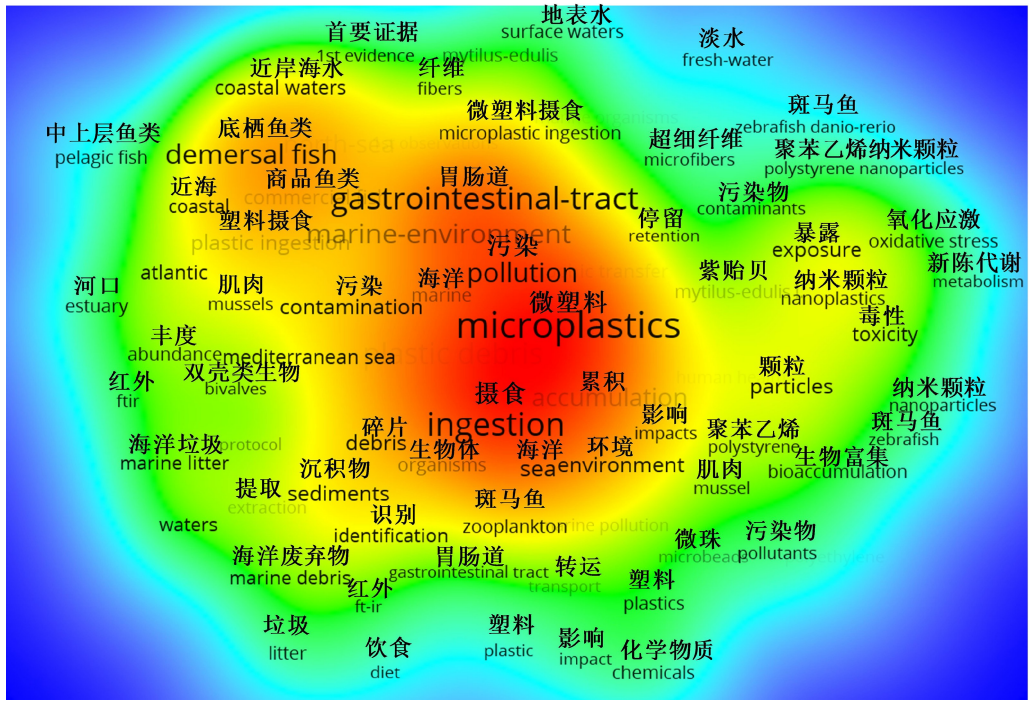

图 1　VOSviewer1.6.16 软件统计胃肠道中微塑料(MPs)研究重点领域密度视图

注:图中不同颜色区域表示关键词出现频率差异,出现频率从高到低依次为红色区域、黄色区域、绿色区域。

Fig. 1　Density view of the key areas of microplastics (MPs) research in the gastrointestinal tract by VOSviewer1.6.16

Note: Different color areas in the figure indicate the difference in the frequency of keywords, the order of higher frequency to lower frequency is red, yellow, green.

86.08% 和 32.41%。而在十二指肠阶段,Cr 和 Pb 的释放率分别为 29.58% 和 24.24%,小肠阶段 Cr 和 Pb 分别为 23.11% 和 23.17%,显著低于胃阶段。Liao 和 Yang[53]发现 PE、PP、PVC、PS 和聚乳酸(PLA)上的 Cr(Ⅵ)主要在胃消化阶段释放,推测主要的阴离子 Cr 物种(例如 CrO_4^{2-} 和 $HCrO_4^-$)与 MPs 的表面电负性位点相互作用可能会在酸性条件下丧失,导致 Cr 和 MPs 之间的亲和力降低,该结果也进一步验证了胃液更能促进重金属解吸。此外,不同种类重金属在胃肠液中解吸的能力和机制也会存在差异。例如,PE、PP 负载的 Cr(Ⅲ)在模拟胃液中的释放速率和释放量均高于 Pb(Ⅱ)[55]。Fe、Mn 和 Co 在模拟禽类胃液中的解吸量随时间逐渐增加而后达到平衡,而 Pb 在解吸初期释放迅速,但在之后的解吸过程中出现了次大值,推测 Pb 先快速脱落而后重新吸附到 MPs 上[54]。重金属价态同样影响胃肠道解吸过程,在胃液中,Cr(Ⅵ)的生物可及性显著高于 Cr(Ⅲ),两者在肠液接近于相似水平[53]。

2.2　MPs 负载的有机物污染物在模拟胃肠液中的解吸

除了重金属,胃肠道环境也能促进 MPs 表面负载有机物污染物的解吸行为。Bakir 等[56]发现 PE、PVC 负载的^{14}C-菲(phenanthrene, Phe)、^{14}C-全氟辛酸(perfluorooctanoic acid, PFOA)和^{14}C-邻苯二甲酸二乙基己酯(di-2-ethylhexyl phthalate, DEHP)在肠液中的解吸速率明显快于海水。与重金属不同,有机污染物在肠液中的解吸水平明显高于胃液。Liu 等[57]发现与聚氨酯(polyurethane, PU)、PET、PP 和 PE 结合的芘在肠道的生物可及性高于胃。相比之下,与 PU、PS、PVC 和 PE 结合的 4-壬基酚在肠道阶段表现出显著更高的生物可及性,这可能由于肠液高浓度的酶和胆汁盐提高了有机物的溶解度。

从塑料的组成上来说,水环境中大量赋存 MPs 的表面通常含有不同种类和含量的添加剂,包括阻燃剂、增塑剂、抗氧化剂、着色剂和润滑剂等[58−59],这些添加剂会在胃肠液体系中浸出。研究发现,在无脊椎动物和脊椎动物的模拟消化条件下(模拟脊椎动物:胃蛋白酶,pH=2.0,24 ℃;无脊椎动物模拟物:牛磺胆酸钠,pH=7,18 ℃),PS 表面添加剂 DEHP 在模拟消化液中的浸出效率比在海水中高(6.3±2.0)倍[60]。此外,Coffin 等[61]将含 12 种塑料添加剂的

MPs 置于含胃蛋白酶的模拟海鸟和鱼消化液中 16 h,发现模拟海鸟消化道中双酚 A(bisphenol A, BPA)的浓度比率(204±129)% 和 DEHP 的浓度比率(175±97)% 明显高于淡水环境,模拟鱼类消化道条件下的邻苯二甲酸丁苄酯(benzyl butyl phthalate, BBP)(132±68)% 浓度显著高于海水,推测胃蛋白酶在促进 MPs 上添加剂的浸出方面发挥显著作用。Guo 等[62]发现在模拟鸟类胃肠道实验中,5 种尺寸的 ABS 上的溴化阻燃剂(brominated flame retardants, BFRs)在模拟胃液中的平衡浸出率为 0.15% ~36.7%,在模拟胃肠液中的总平衡浸出率能高达 80%,远高于在水中的比例。此外,模拟胃肠液中 MPs 表面添加剂的浸出受添加剂自身性质的影响。ABS 中阻燃剂(flame retardants, FRs)浸出到模拟禽类消化液的比例随着 FRs 的 $\log K_{ow}$ 升高而增加,说明亲脂性 FRs 更容易从 MPs 中释放到消化液[63]。

总的来说,MPs 表面负载的有机物、重金属以及 MPs 自身携带的添加剂在生物体胃肠液环境中会发生不同程度的解吸行为。解吸机制主要涉及 MPs、污染物和消化酶三者之间复杂的相互作用,且解吸与再吸附过程同时存在且同时发生。Mohamed Nor 和 Koelmans[64]分析肠道流体模拟系统,发现低密度 PE 和 PVC 上 14 种 PCBs 的化学转移是双向和可逆的,数小时内快速交换,然后是持续数周到数月的缓慢转移。在无污染物的肠道系统中,MPs 释放的 PCBs 在沙蚕和鳕鱼中的生物利用度分别为 14% ~42% 和 45% ~83%。然而,在被 PCBs 污染的肠道系统中,干净的 MPs 能够从肠道内的食物中快速提取 PCBs,这表明生物摄入 MPs 后化学污染和清洁过程很可能同时发生,且摄入的塑料是作为有机污染物的源还是汇,取决于生物体肠道与 MPs 之间的逸度梯度。然而当前对于 MPs 表面污染物解吸机制和影响因素的研究仍然较少,研究 MPs 表面污染物解吸机制对于评价 MPs、添加剂及负载的污染物对水生生物毒性和生态风险有重要意义。

3 胃肠液中 MPs 表面污染物解吸机制(Mechanism of pollutants desorption from MPs in gastrointestinal tract)

3.1 MPs 理化性质与污染物特性的影响

从解吸机制上来说,MPs 表面污染物从 MPs 表面解吸能力取决于污染物与 MPs 之间界面结合力的强弱。在胃肠道环境中,MPs 与污染物的界面结合力发生变化,导致污染物从 MPs 表面脱离,而界面结合力的强弱主要受到 MPs 理化性质(例如,官能团、比表面积、微孔体积和结晶度)和负载污染物自身性质的共同影响[29](图 2)。Liu 等[57]发现 MPs 结晶度、微孔体积、极性以及污染物的极性共同影响有机污染物的解吸,但影响解吸的最主要因素因有机污染物性质不同而存在差异。研究表明,MPs 结晶度和微孔体积是影响非极性有机污染物茫解吸的最重要因素,由于疏水性有机物优先占据聚合物的多孔区域,而且结晶性 MPs 更可能将茫截留在塑料中,故结晶性 MPs 的污染物解吸比非结晶性 MPs 更加滞后;对于极性有机污染物 4-壬基酚,MPs 的 O/C 是决定污染物在胃液中释放的最主要因素(贡献率 76%),由于高 O/C 的 MPs 具有更强的极性,与极性污染物的结合力更强,从而导致污染物解吸滞后,而 MPs 的微孔体积则是次要因素。Godoy 等[55]发现 PP 的比表面积(1.4 $m^2 \cdot g^{-1}$)、孔隙率(30×10^{-3} $cm^3 \cdot g^{-1}$)低于 PE,大原子 Pb 更易被截留在具有较低孔隙率的 PP 中从而导致解吸缓慢。MPs 结构是影响污染物胃肠道解吸的重要因素,胃肠液的高酸性条件、消化酶以及 MPs 的老化过程会导致 MPs 结构被破坏,从而促进污染物的释放。可降解聚乳酸(polylactic acid, PLA)在胃肠道溶液中降解加速,由于乳酸单体之间的酯键可以在酯酶和酸性条件下被催化水解,PLA 表面化学结构被破坏,Cr 与 PLA 的结合力减弱,从而导致 PLA 中 Cr 的释放速率增加[53]。研究发现,PE 在胃肠液中会发生表面降解,导致键断裂和裂缝的形成,促进重金属 Pb、Cr 的释放[55]。老化过程可导致 MPs 结构破坏,比表面积与微孔体积增加,疏水性与极性发生改变,从而改变 MPs 负载污染物在胃肠道内的解吸[65]。然而,由老化引起的 MPs 理化性质改变可能对污染物解吸产生多维度的影响。Liu 等[57]发现对于中等光老化程度的玻璃状 MPs,由于光老化后 MPs 含氧官能团增加,MPs 亲水性增强,极性污染物茫在胃液中的解吸高于原始塑料组,然而,对于高强度光老化处理后的 MPs,由于茫与 MPs 结合能力更强,茫在胃液中解吸明显低于原始塑料组,不过在肠道中 2 种老化程度的 MPs 相比于原始 MPs 茫的解吸率更大,这说明,MPs 上的污染物在胃肠道内的解吸受多种因素、多种相互作用共同调控,并且在胃肠道的不同阶段,解吸程度会因溶液环境变化发生动态改变。

3.2 胃肠道环境的影响

胃肠道消化系统成分复杂,环境条件特殊。胃

液 pH 在 0.9 ~ 1.5,主要含有盐酸、胃蛋白酶原、黏液和内因子;小肠液为弱碱性且成分更加复杂,主要含有胰酶和胆汁[66]。胃肠道的 pH、温度、无机离子和消化酶均影响污染物的释放(图 2)。低 pH 是胃液的最显著特征,高酸性环境可对部分污染物的解吸起促进作用。胃液的高酸性条件破坏阴离子 Cr(Ⅵ)物种(例如 CrO_4^{2-} 和 $HCrO_4^-$)与 MPs 的表面电负性位点相互作用,导致 Cr 和 MPs 之间的亲和力降低,从而促进 Cr(VI)解吸[53]。同时,胃液的酸性条件促进 PLA[53]和 PE[55]降解,导致重金属的释放速率增加。然而,Liu 等[57]在 5 种 MPs 上 4-壬基酚和芘的模拟胃肠液解吸实验中,发现胃液的酸性条件不是污染物在胃液和肠液解吸差异的原因,酸性环境对有机物的解吸基本无影响。胃肠道温度也影响 MPs 表面污染物的解吸。Liu 等[67]模拟了 18 ℃冷血和 37 ℃温血海洋生物的消化条件,发现与冷血条件相比,温血条件促进 MPs 携带的药物释放,生物可及性更高,这可能使温血生物面临更高的药物暴露风险。

消化酶是胃肠道系统的重要组成部分,胃蛋白酶、胰酶(蛋白酶、淀粉酶和脂肪酶)是最主要的消化酶类。已有研究表明生物体胃肠液中的消化酶对碳基材料表面污染物的解吸行为有重要影响。Wang 等[68]研究了碳纳米管上的菲在模拟胃肠液中的生物可及性,发现生物分子(如胃蛋白酶和胆汁酸盐)可促进碳纳米管中残留的疏水有机化合物在消化液中的释放,从而增加菲的生物可及性。Liu 等[57]发现肠液中高浓度的酶和胆汁盐能明显提高芘和 4-壬基酚的溶解度,促进 MPs 上芘和 4-壬基酚在肠道阶段的释放。Liu 等[67]推测 PS 上抗高血脂药物阿托伐他汀(antihyperlipidemia atorvastatin, ATV)、抗高血压药物氨氯地平(antihypertensive amlodipine, AML)在肠道中的高解吸量主要依赖于肠道成分(即牛血清白蛋白和胆汁盐)的溶解作用和胆汁盐的竞争性吸附。MPs 在胃肠道内会与消化酶发生相互作用,形成蛋白冠,随之塑料颗粒的尺寸增加,ξ 电位增加[69],MPs 会改变消化酶的残基和二级结构,导致酶活性降低[70−73]。Wang 等[69]发现 PS-NPs 诱导胃蛋白酶、α-淀粉酶和胰蛋白酶上酪氨酸(tyrpsine, Tyr)和色氨酸(tryptophan, Trp)残基荧光猝灭,并改变其二级结构,并且热力学参数表明(ΔH<0,ΔS<0),络合过程可以由氢键或范德华力驱动,静电相互作用不是两者之间相互作用的唯一驱动力。Tan 等[70]发现与 PS 相互作用 2 h 后,脂肪酶的 α-螺旋比例降低(从 11.6% 到 7.3%),β-折叠比例增加(从 35.5% 到 38.9%)。这说明 α-螺旋序列上氢键网络被破坏,脂肪酶失去一部分 α-螺旋结构并在较小直径的基团上获得 β-折叠结构[73];并且二者发生相互作用后,荧光光谱显示 Trp 残基发生红移和荧光猝灭,这分

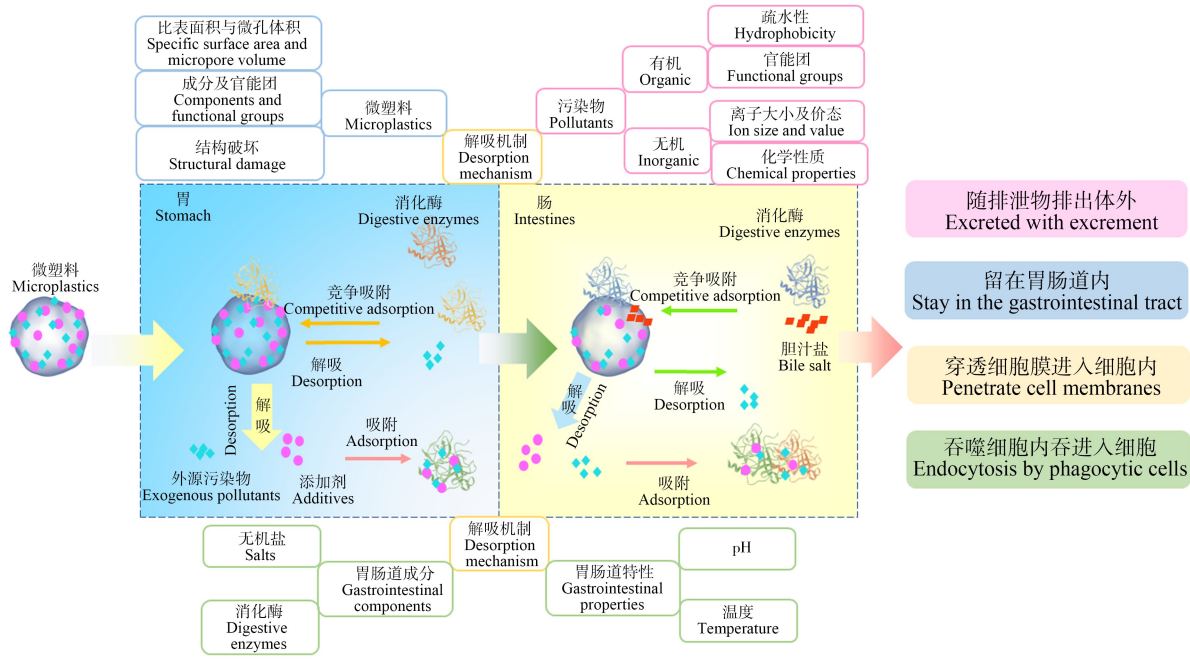

图 2　胃肠道中 MPs 表面污染物的解吸行为、解吸机制和 MPs 在生物体内的归趋

Fig. 2　Desorption behavior and mechanism of MPs loaded pollutants in the gastrointestinal tract, and fates of MPs in organisms

别说明暴露于水溶液中的 Trp 残基数量增加、PS 和脂肪酶之间存在非共价相互作用(例如,π-π 和疏水相互作用)。以上结果说明,进入到胃肠道中的塑料会与消化酶发生一种或多种相互作用,如氢键、范德华力、π-π、静电以及疏水相互作用,一定程度上可能促进 MPs 表面污染物的解吸,但目前有关胃肠道解吸的研究匮乏,消化酶促进污染物解吸的机制尚不明确,消化酶是否会通过竞争吸附到 MPs 上而促进污染物的解吸尚未可知。此外胃肠道内成分复杂,多种酶系之间相互作用对于 MPs 表面污染物解吸行为和解吸机制的研究仍然较少,且胃肠道内食物的存在加剧 MPs 表面污染物解吸机制的复杂程度。

4 结论与展望(Conclusion and recommendation for further research)

环境中 MPs 具有较小的粒径和较大的比表面积,能够作为污染物的载体,并容易被水生生物摄食从而进入到生物体胃肠道中,MPs 携带的污染物在生物体胃肠道内能发生一定程度的解吸,从而增加了对水生生物的毒性风险。MPs 负载的污染物在胃肠道的释放能力一部分取决于 MPs 与污染物相互作用的强度,这与 MPs 的特性(结晶度、孔隙率、比表面积和表面官能团、结构破坏程度)和污染物特性(有机/无机、官能团等)密切相关。此外,胃肠环境(pH、消化酶和无机离子)对污染物的释放也有重要影响。胃的酸性条件显著促进重金属的释放。胃肠道消化酶与 MPs 结合形成蛋白冠,MPs 大小和 zeta 电位增加,消化酶残基和二级结构发生变化,MPs 与消化酶的相互作用通常包括氢键、范德华力、π-π 相互作用、静电相互作用和疏水相互作用的协同作用。然而,MPs、污染物和消化酶之间的相互作用仍不清楚。

当前国内外关于生物胃肠道内 MPs 表面负载污染物的解吸行为研究仍然较少,在解吸机制和潜在影响因素方面仍需继续探索,未来研究应聚焦以下几个方面。

(1)在 MPs 表面污染物解吸机制方面,原始和老化的 MPs 上的添加剂、污染物在胃肠道内的释放机制不明确,需要进一步完善人体胃肠道中 MPs 及其污染物行为的研究。

(2)当前生物体胃肠液中 MPs 表面污染物解吸研究主要基于模拟胃肠液体系,且实验中的 MPs 浓度和污染物浓度普遍较高,未来应开展更贴近实际环境浓度解吸实验。而且模拟胃肠液体系存在一定的局限性,无法模拟胃肠道蠕动,无法真实还原胃肠道消化过程,未来还应探索胃肠道模型,进一步评估 MPs 负载污染物的暴露风险。

(3)当前涉及 MPs 胃肠道解吸的研究大多聚焦于 MPs 吸附的污染物,对 MPs 本身携带的添加剂关注较少。塑料添加剂普遍存在于塑料制品中,在塑料使用、回收和自然老化过程缓慢释放到环境中,并在生物体内迁移,对生态环境和人体健康造成极大威胁,因此未来深入探究胃肠道塑料添加剂的释放行为及机制将更具有环境意义。

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参考文献(References):

[1] Plastic Europe. Plastics—The Facts of 2019: An analysis of European latest plastics production, demand and waste data [R]. Brussels: Plastic Europe, 2019: 1-64

[2] Mai L, Sun X F, Xia L L, et al. Global riverine plastic outflows [J]. Environmental Science & Technology, 2020, 54(16): 10049-10056

[3] Tsering T, Sillanpää M, Sillanpää M, et al. Microplastics pollution in the Brahmaputra River and the Indus River of the Indian Himalaya [J]. Science of the Total Environment, 2021, 789: 147968

[4] Li L, Geng S X, Wu C X, et al. Microplastics contamination in different trophic state lakes along the middle and lower reaches of Yangtze River Basin [J]. Environmental Pollution, 2019, 254: 112951

[5] Desforges J P W, Galbraith M, Dangerfield N, et al. Widespread distribution of microplastics in subsurface seawater in the NE Pacific Ocean [J]. Marine Pollution Bulletin, 2014, 79(1-2): 94-99

[6] Eriksen M, Lebreton L C M, Carson H S, et al. Plastic pollution in the world's oceans: More than 5 trillion plastic pieces weighing over 250, 000 tons afloat at sea [J]. PLoS One, 2014, 9(12): e111913

[7] Auta H S, Emenike C U, Fauziah S H. Distribution and importance of microplastics in the marine environment: A review of the sources, fate, effects, and potential solutions [J]. Environment International, 2017, 102: 165-176

[8] Gündoğdu S, Çevik C. Micro- and mesoplastics in Northeast Levantine coast of Turkey: The preliminary results from surface samples [J]. Marine Pollution Bulletin, 2017, 118(1-2): 341-347

[9] Antunes J, Frias J, Sobral P. Microplastics on the Portuguese coast [J]. Marine Pollution Bulletin, 2018, 131(Pt

A): 294-302

[10] Zhang K, Xiong X, Hu H J, et al. Occurrence and characteristics of microplastic pollution in Xiangxi Bay of Three Gorges reservoir, China [J]. Environmental Science & Technology, 2017, 51(7): 3794-3801

[11] Cunningham E M, Ehlers S M, Dick J T A, et al. High abundances of microplastic pollution in deep-sea sediments: Evidence from Antarctica and the southern ocean [J]. Environmental Science & Technology, 2020, 54(21): 13661-13671

[12] Wang J D, Peng J P, Tan Z, et al. Microplastics in the surface sediments from the Beijiang River littoral zone: Composition, abundance, surface textures and interaction with heavy metals [J]. Chemosphere, 2017, 171: 248-258

[13] Materic D, Kasper-Giebl A, Kau D, et al. Micro- and nanoplastics in alpine snow: A new method for chemical identification and (semi) quantification in the nanogram range [J]. Environmental Science & Technology, 2020, 54(4): 2353-2359

[14] Mishra A K, Singh J, Mishra P P. Microplastics in polar regions: An early warning to the world's pristine ecosystem [J]. Science of the Total Environment, 2021, 784: 147149

[15] Worm B, Lotze H K, Jubinville I, et al. Plastic as a persistent marine pollutant [J]. Annual Review of Environment and Resources, 2017, 42: 1-26

[16] Liu X M, Shi H H, Xie B, et al. Microplastics as both a sink and a source of bisphenol A in the marine environment [J]. Environmental Science & Technology, 2019, 53(17): 10188-10196

[17] Ma Y N, Huang A N, Cao S Q, et al. Effects of nanoplastics and microplastics on toxicity, bioaccumulation, and environmental fate of phenanthrene in fresh water [J]. Environmental Pollution, 2016, 219: 166-173

[18] Frias J P G L, Sobral P, Ferreira A M. Organic pollutants in microplastics from two beaches of the Portuguese coast [J]. Marine Pollution Bulletin, 2010, 60(11): 1988-1992

[19] Velzeboer I, Kwadijk C J A F, Koelmans A A. Strong sorption of PCBs to nanoplastics, microplastics, carbon nanotubes, and fullerenes [J]. Environmental Science & Technology, 2014, 48(9): 4869-4876

[20] Lo H S, Wong C Y, Tam N F Y, et al. Spatial distribution and source identification of hydrophobic organic compounds (HOCs) on sedimentary microplastic in Hong Kong [J]. Chemosphere, 2019, 219: 418-426

[21] Yeo B G, Takada H, Yamashita R, et al. PCBs and PBDEs in microplastic particles and zooplankton in open water in the Pacific Ocean and around the coast of Japan [J]. Marine Pollution Bulletin, 2020, 151: 110806

[22] Jeong C B, Kang H M, Lee Y H, et al. Nanoplastic ingestion enhances toxicity of persistent organic pollutants (POPs) in the monogonont rotifer *Brachionus* koreanus via multixenobiotic resistance (MXR) disruption [J]. Environmental Science & Technology, 2018, 52(19): 11411-11418

[23] Wardrop P, Shimeta J, Nugegoda D, et al. Chemical pollutants sorbed to ingested microbeads from personal care products accumulate in fish [J]. Environmental Science & Technology, 2016, 50(7): 4037-4044

[24] Besson M, Jacob H, Oberhaensli F, et al. Preferential adsorption of Cd, Cs and Zn onto virgin polyethylene microplastic versus sediment particles [J]. Marine Pollution Bulletin, 2020, 156: 111223

[25] Tang S, Lin L J, Wang X S, et al. Pb(Ⅱ) uptake onto nylon microplastics: Interaction mechanism and adsorption performance [J]. Journal of Hazardous Materials, 2020, 386: 121960

[26] Vedolin M C, Teophilo C Y S, Turra A, et al. Spatial variability in the concentrations of metals in beached microplastics [J]. Marine Pollution Bulletin, 2018, 129(2): 487-493

[27] Tourinho P S, Kocí V, Loureiro S, et al. Partitioning of chemical contaminants to microplastics: Sorption mechanisms, environmental distribution and effects on toxicity and bioaccumulation [J]. Environmental Pollution, 2019, 252(Pt B): 1246-1256

[28] Wang F, Zhang M, Sha W, et al. Sorption behavior and mechanisms of organic contaminants to nano and microplastics [J]. Molecules (Basel, Switzerland), 2020, 25(8): 1827

[29] Zhou Y F, Yang Y Y, Liu G H, et al. Adsorption mechanism of cadmium on microplastics and their desorption behavior in sediment and gut environments: The roles of water pH, lead ions, natural organic matter and phenanthrene [J]. Water Research, 2020, 184: 116209

[30] Fred-Ahmadu O H, Bhagwat G, Oluyoye I, et al. Interaction of chemical contaminants with microplastics: Principles and perspectives [J]. Science of the Total Environment, 2020, 706: 135978

[31] Li J, Zhang K N, Zhang H. Adsorption of antibiotics on microplastics [J]. Environmental Pollution, 2018, 237: 460-467

[32] Torres F G, Dioses-Salinas D C, Pizarro-Ortega C I, et al. Sorption of chemical contaminants on degradable and non-degradable microplastics: Recent progress and research trends [J]. Science of the Total Environment, 2021,

757: 143875

[33] Rochman C M, Hentschel B T, Teh S J. Long-term sorption of metals is similar among plastic types: Implications for plastic debris in aquatic environments [J]. PLoS One, 2014, 9(1): e85433

[34] Liu X M, Xu J, Zhao Y P, et al. Hydrophobic sorption behaviors of 17β-estradiol on environmental microplastics [J]. Chemosphere, 2019, 226: 726-735

[35] Markic A, Gaertner J C, Gaertner-Mazouni N, et al. Plastic ingestion by marine fish in the wild [J]. Critical Reviews in Environmental Science and Technology, 2020, 50 (7): 657-697

[36] Li B W, Liang W, Liu Q X, et al. Fish ingest microplastics unintentionally [J]. Environmental Science & Technology, 2021, 55(15): 10471-10479

[37] Sequeira I F, Prata J C, da Costa J P, et al. Worldwide contamination of fish with microplastics: A brief global overview [J]. Marine Pollution Bulletin, 2020, 160: 111681

[38] Li J N, Qu X Y, Su L, et al. Microplastics in mussels along the coastal waters of China [J]. Environmental Pollution, 2016, 214: 177-184

[39] Zhang C N, Wang S D, Pan Z K, et al. Occurrence and distribution of microplastics in commercial fishes from estuarine areas of Guangdong, South China [J]. Chemosphere, 2020, 260: 127656

[40] Jaafar N, Azfaralariff A, Musa S M, et al. Occurrence, distribution and characteristics of microplastics in gastrointestinal tract and gills of commercial marine fish from Malaysia [J]. Science of the Total Environment, 2021, 799: 149457

[41] Ferreira M, Thompson J, Paris A, et al. Presence of microplastics in water, sediments and fish species in an urban coastal environment of Fiji, a Pacific small island developing state [J]. Marine Pollution Bulletin, 2020, 153: 110991

[42] Nan B X, Su L, Kellar C, et al. Identification of microplastics in surface water and Australian freshwater shrimp *Paratya* australiensis in *Victoria*, Australia [J]. Environmental Pollution, 2020, 259: 113865

[43] Ghosh G C, Akter S M, Islam R M, et al. Microplastics contamination in commercial marine fish from the Bay of Bengal [J]. Regional Studies in Marine Science, 2021, 44: 101728

[44] Lin F, Zhang Q Z, Xie J, et al. Microplastics in biota and surface seawater from tropical aquaculture area in Hainan, China [J]. Gondwana Research, 2021, 25: 1

[45] Battaglia F M, Beckingham B A, McFee W E. First report from North America of microplastics in the gastrointestinal tract of stranded bottlenose dolphins (*Tursiops truncatus*) [J]. Marine Pollution Bulletin, 2020, 160: 111677

[46] Moore R C, Loseto L, Noel M, et al. Microplastics in beluga whales (*Delphinapterus leucas*) from the eastern Beaufort Sea [J]. Marine Pollution Bulletin, 2020, 150: 110723

[47] Stockin K A, Pantos O, Betty E L, et al. Fourier transform infrared (FTIR) analysis identifies microplastics in stranded common dolphins (*Delphinus delphis*) from New Zealand waters [J]. Marine Pollution Bulletin, 2021, 173: 113084

[48] Zhang X Y, Luo D Y, Yu R Q, et al. Microplastics in the endangered Indo-Pacific humpback dolphins (*Sousa chinensis*) from the Pearl River Estuary, China [J]. Environmental Pollution, 2021, 270: 116057

[49] Moore R C, Noel M, Etemadifar A, et al. Microplastics in beluga whale (*Delphinapterus leucas*) prey: An exploratory assessment of trophic transfer in the Beaufort Sea [J]. Science of the Total Environment, 2022, 806: 150201

[50] Wang W F, Ge J, Yu X Y. Bioavailability and toxicity of microplastics to fish species: A review [J]. Ecotoxicology and Environmental Safety, 2020, 189: 109913

[51] Huang W, Song B, Liang J, et al. Microplastics and associated contaminants in the aquatic environment: A review on their ecotoxicological effects, trophic transfer, and potential impacts to human health [J]. Journal of Hazardous Materials, 2021, 405: 124187

[52] Jeong C B, Won E J, Kang H M, et al. Microplastic size-dependent toxicity, oxidative stress induction, and p-JNK and p-p38 activation in the monogonont rotifer (*Brachionus* koreanus) [J]. Environmental Science & Technology, 2016, 50(16): 8849-8857

[53] Liao Y L, Yang J Y. Microplastic serves as a potential vector for Cr in an *in-vitro* human digestive model [J]. The Science of the Total Environment, 2020, 703: 134805

[54] Holmes L A, Thompson R C, Turner A. *In vitro* avian bioaccessibility of metals adsorbed to microplastic pellets [J]. Environmental Pollution (Barking, Essex: 1987), 2020, 261: 114107

[55] Godoy V, Martínez-Férez A, Martín-Lara M Á, et al. Microplastics as vectors of chromium and lead during dynamic simulation of the human gastrointestinal tract [J]. Sustainability, 2020, 12(11): 4792

[56] Bakir A, Rowland S J, Thompson R C. Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions [J]. Environmental Pollution (Barking, Essex: 1987), 2014, 185: 16-23

[57] Liu X L, Gharasoo M, Shi Y, et al. Key physicochemical

properties dictating gastrointestinal bioaccessibility of microplastics-associated organic xenobiotics: Insights from a deep learning approach [J]. Environmental Science & Technology, 2020, 54(19): 12051-12062

[58] Campanale C, Massarelli C, Savino I, et al. A detailed review study on potential effects of microplastics and additives of concern on human health [J]. International Journal of Environmental Research and Public Health, 2020, 17 (4): 1212

[59] Bridson J H, Gaugler E C, Smith D A, et al. Leaching and extraction of additives from plastic pollution to inform environmental risk: A multidisciplinary review of analytical approaches [J]. Journal of Hazardous Materials, 2021, 414: 125571

[60] Coffin S, Lee I, Gan J, et al. Simulated digestion of polystyrene foam enhances desorption of diethylhexyl phthalate (DEHP) and *in vitro* estrogenic activity in a size-dependent manner [J]. Environmental Pollution, 2019, 246: 452-462

[61] Coffin S, Huang G Y, Lee I, et al. Fish and seabird gut conditions enhance desorption of estrogenic chemicals from commonly-ingested plastic items [J]. Environmental Science & Technology, 2019, 53(8): 4588-4599

[62] Guo H Y, Zheng X B, Luo X J, et al. Leaching of brominated flame retardants (BFRs) from BFRs-incorporated plastics in digestive fluids and the influence of bird diets [J]. Journal of Hazardous Materials, 2020, 393: 122397

[63] Guo H Y, Zheng X B, Ru S L, et al. The leaching of additive-derived flame retardants (FRs) from plastics in avian digestive fluids: The significant risk of highly lipophilic FRs [J]. Journal of Environmental Sciences, 2019, 85: 200-207

[64] Mohamed Nor N H, Koelmans A A. Transfer of PCBs from microplastics under simulated gut fluid conditions is biphasic and reversible [J]. Environmental Science & Technology, 2019, 53(4): 1874-1883

[65] Sun Y R, Yuan J H, Zhou T, et al. Laboratory simulation of microplastics weathering and its adsorption behaviors in an aqueous environment: A systematic review [J]. Environmental Pollution, 2020, 265: 114864

[66] Chu S S, He F L, Yu H M, et al. Evaluation of the binding of UFCB and Pb-UFCB to pepsin: Spectroscopic analysis and enzyme activity assay [J]. Journal of Molecular Liquids, 2021, 328: 115511

[67] Liu P, Wu X W, Liu H Y, et al. Desorption of pharmaceuticals from pristine and aged polystyrene microplastics under simulated gastrointestinal conditions [J]. Journal of Hazardous Materials, 2020, 392: 122346

[68] Wang Z Y, Zhao J, Song L, et al. Adsorption and desorption of phenanthrene on carbon nanotubes in simulated gastrointestinal fluids [J]. Environmental Science & Technology, 2011, 45(14): 6018-6024

[69] Wang Y H, Li M, Xu X F, et al. Formation of protein *Corona* on nanoparticles with digestive enzymes in simulated gastrointestinal fluids [J]. Journal of Agricultural and Food Chemistry, 2019, 67(8): 2296-2306

[70] Tan H W, Yue T T, Xu Y, et al. Microplastics reduce lipid digestion in simulated human gastrointestinal system [J]. Environmental Science & Technology, 2020, 54 (19): 12285-12294

[71] Trestrail C, Walpitagama M, Miranda A, et al. Microplastics alter digestive enzyme activities in the marine bivalve, *Mytilus galloprovincialis* [J]. Science of the Total Environment, 2021, 779: 146418

[72] Zhao X C, Hao F, Lu D W, et al. Influence of the surface functional group density on the carbon-nanotube-induced α-chymotrypsin structure and activity alterations [J]. ACS Applied Materials & Interfaces, 2015, 7(33): 18880-18890

[73] Zhao X C, Lu D W, Hao F, et al. Exploring the diameter and surface dependent conformational changes in carbon nanotube-protein *Corona* and the related cytotoxicity [J]. Journal of Hazardous Materials, 2015, 292: 98-107 ◆