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磁颗粒在含油废水油水分离中的应用

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摘　要　含油废水因其环境危害大和难处理特征已成为全球性环境治理难题。磁颗粒处理含油废水展现出显著的技术优势，兼具分离效率高、环境友好和能够循环使用等优点，具有广阔的应用前景。本文基于含油废水的污染特征与处理难点，系统阐释磁颗粒应用于油水分离的原理与过程机制，全面评述其功能结构设计、分离效能评价及再生机制等研究进展，解析材料特性与作用条件对分离性能的影响规律，并对协同方法及装置设备的工作原理进行介绍，最后对该领域未来发展进行了前景展望。本文对于新型油水分离用磁颗粒的设计、制备及应用研究具有参考价值。

关键词　含油废水；磁颗粒；油水分离；净水装置；研究进展

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Application of magnetic particles in oil-water separation of oily wastewater

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ABSTRACT　Oily wastewater, a byproduct of various industrial processes such as petroleum refining, metal processing, and food production, poses significant threats to industrial production, economic development, and environmental sustainability. Its improper disposal can lead to equipment corrosion, pipeline blockages, and even fires, causing substantial economic losses. Moreover, the release of oily wastewater into the environment contaminates water bodies, harms aquatic ecosystems, and jeopardizes human health through the food chain. Therefore, developing efficient and environmentally friendly technologies for oily wastewater treatment is of paramount importance. Among various treatment methods, the use of magnetic particles has emerged as a promising approach due to its unique advantages. Magnetic particles exhibit excellent oil-water separation performance, enabling efficient removal of oil droplets from wastewater. Their simple preparation process, often involving co-precipitation or sol-gel methods, allows for cost-effective large-scale production. Furthermore,

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magnetic particles are environmentally friendly, as they can be easily recovered and reused through magnetic separation, minimizing secondary pollution. These advantages make magnetic particles highly attractive for practical applications in oily wastewater treatment. This paper provides a comprehensive review of the application of magnetic particles in oily wastewater treatment. It begins by discussing the sources and characteristics of oily wastewater, highlighting the complexity and challenges associated with its treatment. Subsequently, the principles and processes of oil-water separation using magnetic particles are introduced, emphasizing the role of surface properties, magnetic responsiveness, and particle size in determining separation efficiency. The paper then systematically summarizes the different structures of magnetic particles employed for oil-water separation, including core-shell structures, Janus particles, and magnetic composites. Each structure offers unique advantages in terms of oil adsorption capacity, selectivity, and recyclability. Practical applications of magnetic particles in various industries, such as oil spill cleanup, produced water treatment, and emulsion separation, are also discussed, demonstrating their versatility and effectiveness. Furthermore, the paper delves into the regeneration strategies for magnetic particles, which are crucial for their sustainable application. Thermal regeneration, solvent washing, and magnetic field-assisted regeneration are among the methods explored, with their advantages and limitations analyzed. The factors influencing the oil-water separation performance of magnetic particles, such as surface wettability, magnetic field strength, and operating conditions, are also thoroughly examined. To enhance the performance of magnetic particles, synergistic methods combining magnetic separation with other techniques, such as flocculation, filtration, and advanced oxidation, are reviewed. Additionally, the paper provides an overview of the equipment used for magnetic separation. Specifically, two prevalent operational principles are discussed: one involves fixing magnetic particles in place and allowing oily wastewater to flow through them, while the other entails adding magnetic particles to the wastewater, mixing them thoroughly to adsorb dispersed oil, and subsequently separating the magnetic particle-oil mixture from the water using magnetic selection. These two approaches are analyzed in terms of their efficiency, scalability, and suitability for different types of oily wastewater. Finally, the paper offers a forward-looking perspective on the future developments in this field. It identifies key research directions, such as the development of novel magnetic materials with enhanced performance, the integration of magnetic separation with other technologies for improved efficiency, and the exploration of new applications in emerging fields. This paper serves as a valuable reference for researchers and engineers involved in the design, synthesis, and application of magnetic particles for oil-water separation, contributing to the advancement of sustainable oily wastewater treatment technologies.

KEY WORDS Oily petrochemical wastewater; Magnetic particles; Oil-water separation; Water purification device; Research progress

含油废水因其来源广泛、组分复杂、排放量大及生态环境风险高等特征，已成为制约工业可持续发展的关键瓶颈[1]。同时，国内水体污染严重，水资源短缺的问题日益突出[2-4]，现行的物理法、化学法、生物法处理含油废水愈发难以满足处理需求。近年来，基于磁颗粒的油水处理技术因其磁响应性、可控表面功能化及循环稳定性等优势，展现出显著的工程应用潜力。本文从含油废水的特性出发，介绍了磁颗粒处理含油废水的原理、过程及应用案例，分析影响其油水分离性能的因素，并对基于磁颗粒的典型含油废水磁控处理装置进行介绍，并对磁颗粒应用于油水分离的未来前景进行展望，以期对含油废水绿色高效处理技术和装备研发提供理论与方法参考。

1 含油废水的来源、性质与危害

含油废水是工业生产过程中排放的含有油性物质的废水，是油和水在活性剂稳定或流体动力学扰动下形成的非均相分散体系[5]，尤其是石油石化工业（简易流程如图 1 所示），

从原油开采到油产品的加工都会产生大量的含油废水，如原油脱出污水、作业污水、钻井洗井污水、炼油污水等[6, 7]，约占全国工业废水排放总量的20%[8]。此外，食品行业、机械加工、纺织工业等其他工业及人类日常生活也会产生大量含油废水。

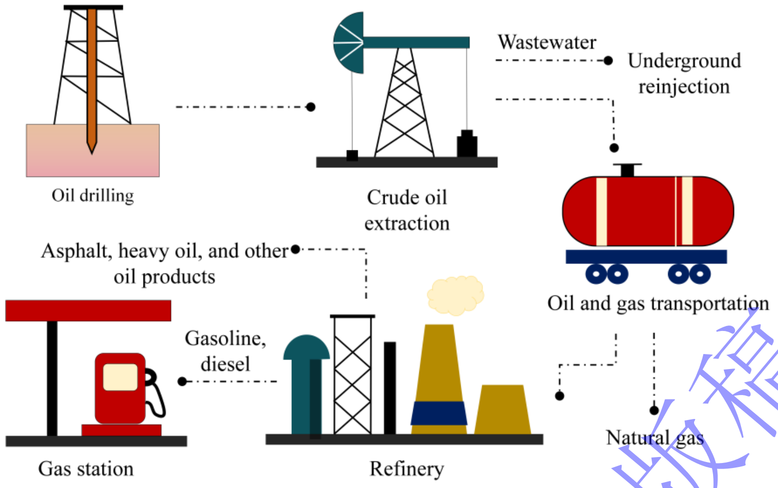

图 1　石油化工工艺简易流程

Fig.1　Simple Process of Petrochemical Technology

未经油水分离处理的含油废水会损害运输设备，导致管道的严重腐蚀和结垢，造成极大经济损失[9]。若直接排放进水体中，油类物质会在水体表面形成油膜隔绝空气，导致水生生物的死亡[10]。同时，经过不断渗透扩散，会危害地下水和饮用水源安全。此外，水中的油类污染物在光照条件下易分解，可能会威胁大气安全，并在风力作用下扩大污染范围；排放至土壤后也会对土壤形态和吸水能力产生危害，降低土壤吸湿性以及水力传导率，影响作物发芽和土壤微生物生长，这都给生态环境带来不可逆转的破坏[11]。对于城市管理而言，含油废水排入城市下水道还会对排水设施产生很大影响，甚至危害人体健康[12, 13]。因此，含油废水必须经过有效处理达标后方可排放。

根据油相分散度与界面稳定性的递变规律，含油废水中的油类物质可系统划分为三类。第一种是自由态油相，包括浮油和分散油，这类型的油类物质颗粒较大，通常较容易去除；第二种是亚稳态乳化油，粒径较小，呈乳化状态，同时在表面活性剂和固体颗粒的协同稳定作用下形成结构稳定的界面膜，使得油水分离较为困难；最后一种是分子态溶解油，只能通过高级氧化或生物代谢等才能将其转化去除，不过溶解油在水中的溶解度非常低[14, 15]。

2 磁颗粒处理含油废水的优势

目前含油废水处理技术主要包括生物方法、物理方法、化学方法。生物方法主要利用微生物或生物代谢产物进行净水[16-19]，过程可生物降解，绿色环保，但目前关于生物法处理油水分离问题的研究并不深入，处于探索阶段，在实际应用中对废水性质和处理条件要求苛刻。物理方法主要是根据油水两相的物理性质差异实现油水分离，如重力沉降[20]、离心破乳[21]、超声方法[22]、膜分离法[23]等，但通常物理方法设备较大，前期投资高，处理效果较为粗糙，难以凝聚含油废水中的超细分散油滴，处理效果有限。化学法主要通过投加化学药剂破坏油水界面膜，使两相失稳并最终实现油水分离[24-26]。因其分离迅速，流程简单，目前化学法的研究和应用最为深入，但残留的化学药剂容易造成污染，且药剂投加量大，导致油水分离成本较高。以上这些技术劣势都导致现有油水分离技术存在对化学品依赖性强、处理效果差、工艺繁琐等问题。

如果将不同性质的有机或无机材料复合成带有磁性的颗粒，这种颗粒保持高磁响应能力与亲油能力，依托外加磁场能快速实现油水分离[27]。同时这类型材料细胞毒性低，生物

相容性好，破乳性能优异，还可以利用外加磁场回收并循环使用，无二次污染产生。此外，循环再生能力在一定程度上能补偿其经济成本，这使得磁颗粒处理含油废水具有显著的性能和成本优势。

3 用于油水分离的磁性颗粒净水原理与过程

废水中的磁性颗粒在外加磁场中会受到磁场力（F_u）的作用[28]：

$$F_u = K_m V H \frac{dH}{dx}$$

其中，K_m 为颗粒磁化率，V 为颗粒体积（m^3），H 为磁场强度（A·m^{-1}），$\frac{dH}{dx}$ 为磁场梯度（T·m^{-1}）。当颗粒所受磁场力大于水流阻力时，磁颗粒即可被磁场吸引并从水相中分离。使用 Fe_3O_4 颗粒对含油废水进行油水分离时，利用分散油滴的磁化效应，油珠吸附在磁性颗粒上，以磁性颗粒为载体形成磁性絮体，在磁场作用下快速响应并实现两相分离。一些非磁性微粒（例如高岭土）虽也能吸附油，但不具备磁响应能力，只有通过混凝法才能去除且沉降效果并不理想。而 Fe_3O_4 不仅可以吸附在油水界面上，还能够在电性作用下破坏油水界面，使油滴聚并进而实现油水分离，其原理如图 2 所示[29, 30]。

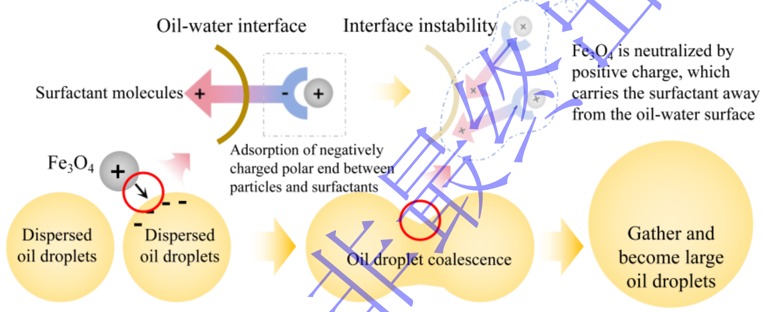

图 2 Fe_3O_4 颗粒破坏油水界面示意图

Fig.2 Schematic diagram of Fe_3O_4 particles damaging oil-water interface

纯 Fe_3O_4 颗粒比表面积大，表面能较高，易发生氧化和团聚[31]，严重制约其油水分离性能。若将其与目标分子或粒子复合，能够使其兼具磁响应能力和高油水分离性能。所制改性磁颗粒能够在油水界面发生吸附行为并形成多重排布结构来破坏油水界面从而实现分散油滴的聚结，此过程不可逆并最终在重力场或磁场中油水分离。在许多情况下，由于这些颗粒粒径细，表面活性很高，与油水界面上的活性物质发生竞争吸附后锚定在油水界面上，形成 Pickering 乳状液，这时的分散油滴具有磁响应能力，可在磁场辅助下快速富集聚并，如图 3 所示。

这些改性磁颗粒的净水原理与 Fe_3O_4 类似，在酸性及中性条件下，静电相互作用能够促使油水分离，颗粒能有效絮凝油滴并促进磁选。碱性条件下，疏水相互作用是破坏油水界面的主要原因，颗粒可以克服静电斥力，通过疏水相互作用吸附到油滴表面，在磁场的作用下辅助两相分离[32-34]。

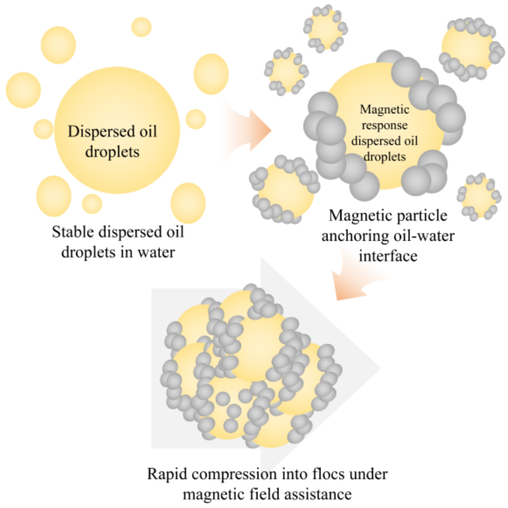

图 3　Fe_3O_4 颗粒锚定油水界面后磁场辅助油水分离过程

Fig.3　The process of magnetic field assisted oil-water separation after anchoring Fe_3O_4 particles at the oil-water interface

4 磁颗粒结构与油水分离实践

用于油水分离的磁性颗粒，以球形 Fe_3O_4 颗粒为结构基础，形成了不同尺寸、形貌的材料。结构上主要包括以下三种：核壳结构、镶嵌式结构复合材料与 Janus 结构[35]，如图 4 所示。

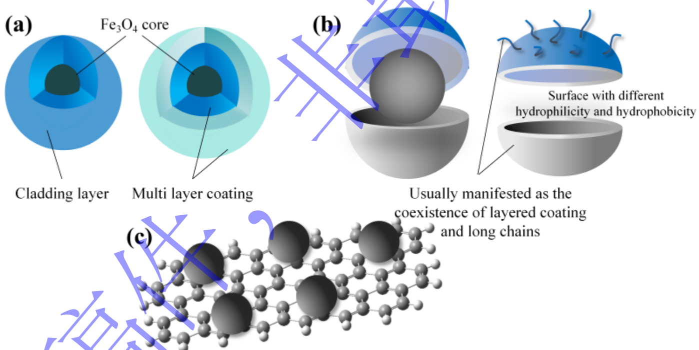

图 4　油水分离用磁颗粒的三种结构. (a)核壳结构; (b)Janus 结构; (c)镶嵌式结构复合材料

Fig.4　Three structures of magnetic particles for oil-water separation (a) Core-shell structure; (b) Uneven surface (Janus structure); (c) Embedded structural composite materials

4.1 核壳结构磁颗粒及其油水分离实践

核壳结构主要是使用改性材料包覆内核磁颗粒及包覆后继续接枝分子链的多层结构，主要形态呈现为球形，如图 4(a)所示。其复合类型主要包括 Fe_3O_4@化合物和 Fe_3O_4@SiO_2@化合物。

Fe_3O_4@化合物是在 Fe_3O_4 颗粒的表面直接包覆或接枝制备出的一系列用于油水分离的磁性材料。如将 OA 包覆在 Fe_3O_4 的表面制备的 Fe_3O_4@OA，具备捕捉油分的能力，在表面接触角为 90°时，颗粒表面活性最大油水分离效率能够达 98%[36, 37]。此外，包覆有机高分子材料也可以实现对表面亲疏水性的调控，如包覆聚乙烯亚胺（PEI）后就能够对废水中的油分进行有效捕收，且循环使用十次后油水分离性能都未见显著下降[38]。

Fe_3O_4@SiO_2@化合物的结构基础是 Fe_3O_4@SiO_2，研究表明 Fe_3O_4@SiO_2 能够捕收水中油分，循环 9 次后油水分离效率仍能保有 90%[39]。对 Fe_3O_4@SiO_2 可以进行硅烷化改性，

形成大量 $Fe_3O_4@SiO_2@$化合物材料。硅烷化试剂的烷氧基水解形成的硅醇与被改性颗粒表面羟基脱水缩合共价连接，结合强度也较为可观。硅烷偶联剂分子可以作为分子桥梁，连接两种性质截然不同的材料，而在材料表面先包覆 SiO_2 可以为硅烷偶联剂提供大量的作用位点。潘莲莲[40]利用硅烷化偶联剂 MPS 对 $Fe_3O_4@SiO_2$ 进行硅烷化修饰得到 $Fe_3O_4@SiO_2@MPS$，再与 NIPAAm 反应最终制得 M-PNIPAAm，结构改性示意图如图 5。图 5(b)为各阶段产物的接触角，可以看出，随着改性流程进行接触角的不断增加，愈发接近 90°，油水分离性能越来越好。将其用于处理模拟乳化含油废水和细粒乳化含油废水，两种废水处理后透光率分别提高到 90.2%和 78.7%，说明该材料能有效实现含油废水的油水分离。

核壳结构的磁颗粒制备工艺较为简单，成本较低，但其功能化程度也较为有限，有时很难达到处理需求。

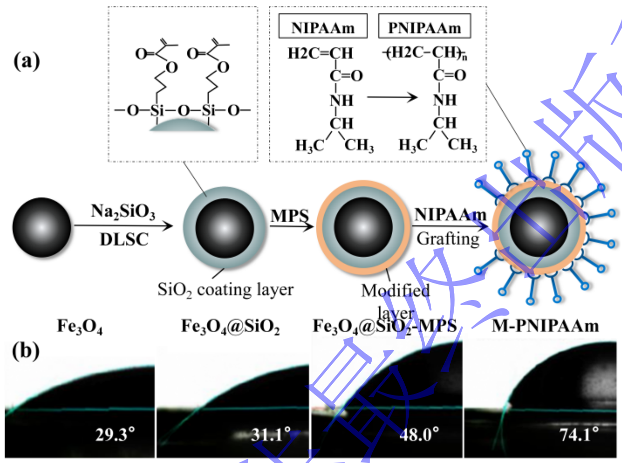

图 5 (a) M-PNIPAAm 制备过程及 (b) 阶段产物接触角[40]

Fig.5 (a) Preparation process of M-PNIPAAm and (b) stage product contact angle[40]

4.2 镶嵌式结构复合材料及其油水分离实践

镶嵌式结构复合材料将磁性颗粒嵌入材料的外壁或内孔之间，如嫁接于碳纳米管与碳纤维、石墨烯的网状结构中，或使用磁性颗粒作为有机高分子材料合成的异相晶核等。但在有机高分子合成时，直接使用 Fe_3O_4 磁颗粒作为内核有时存在界面相容性差问题，其根源在于裸磁颗粒表面羟基密度不足且表面自由能过高，导致有机相难以均匀成核生长。采用 OA 预修饰策略，可以构建单分子层界面过渡带，使表面自由能下降，显著提升界面活性。预处理后再将有机高分子材料聚合在 $Fe_3O_4@OA$ 的表面，这种镶嵌式结构也可以看作是更复杂的包覆结构，如磺化聚苯乙烯@Fe_3O_4[41]、$Fe_3O_4@PS$[42]等。镶嵌结构的颗粒结构相较于核壳式更为复杂，尺寸也更大。

磁响应复合材料结构较为复杂，制备工艺更为繁琐，但其最大的优势是使磁性颗粒直接结合其他材料的优点，功能性更为强大，比如与天然矿物相复合时，原料易得且环境友好，循环使用性良好，发展潜力极大[43, 44]。近年来，碳材料也被应用于油水分离，如氧化石墨烯纳米片（GO）、碳纳米管（CNT）等，将其复合成磁响应复合材料后，磁颗粒可以镶嵌于材料的外壁或内孔，体现出较强油水分离性能的同时具备磁响应能力[45, 46]。图 6 为磁性碳纳米管（MCNTs）进一步制备三维材料 MCNTs/LDHs 的过程[47, 48]，更能体现磁响应复合材料功能性的强大，处理含油废水油水分离性能超 99%。尽管复合材料结构复杂，制备繁琐，但其往往都具有突出优势，功能性更强，油水分离效率也较好，应用潜力巨大。

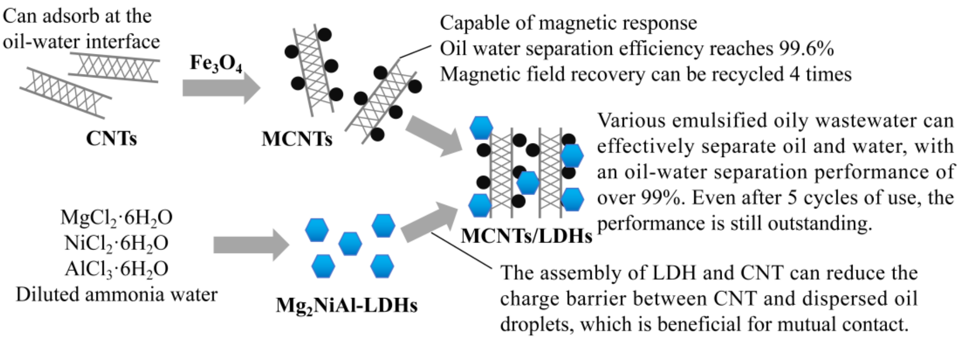

图 6 MCNTs/LDHs 制备流程[47]

Fig.6 Preparation process of MCNTs/LDHs[47]

4.3 Janus 结构磁颗粒及其油水分离实践

Janus 结构颗粒的表面性质不对称，同一颗粒表面的不同区域由于不同功能修饰使其具有两种不同形态、结构或性质的双功能结构，以球状居多，制备过程更为复杂，粒径介于包覆结构与镶嵌结构之间，体现为层状包覆及长链结构共存的表面形态。如表面不对称的 PGMA/PS/Fe_3O_4@OA 的复合颗粒，在三相之间的强不相容性驱动反应下制成，随着聚合物混合物的分离，Fe_3O_4 微粒能够嵌入到颗粒内部，最终形成具有表面不对称几何结构和相关化学组成的 MJPs 颗粒[49]。

Janus 颗粒具有表面不均匀的亲疏水性，使其在油水界面能够达到更优异的平衡状态，界面活性更高，锚定在油水界面处使得体系能量降到最低，能够在不破坏油滴稳定性的前提下利用磁场直接实现油水分离。He[50]在使用连续吸附羧甲基、乙基纤维素形成的 M-CMC-EC 基础上，对其部分区域再次吸附亲水的 CMC，最终在 Fe_3O_4 相反侧分别吸附了疏水的 EC 和亲水的 CMC，制备出 M-Janus，用于处理乳化含油废水油水分离效率达到 90%以上，且其适用于多种油水混合结构。同时，由于 Janus 颗粒可以占据油水界面，最大限度地降低体系的能量，所以这种磁颗粒也可以用来稳定油水混合体系，使其成为 Pickering 乳液[51]，由 Janus 颗粒稳定的 Pickering 乳液又容易对磁场响应从而被外部磁场分离，同时具备稳定和破坏油水体系的特征，能够同时解决石油开采中的乳化问题和含油废水油水分离的问题，还能够回收利用，这意味着具有不均匀表面结构的 Janus 颗粒在石油石化工业领域具有很大的开发潜力和应用前景。但这种颗粒由于需要精细控制表面，其制备过程往往更为复杂，对于制备的精细程度要求也较为严苛。

各种结构磁颗粒的油水分离效果与各类信息总结如表 1 所示，可以看出，尽管磁颗粒制备方法、结构以及复合类型大不相同，但各类磁颗粒普遍拥有较强的净水性能，能够实现高效油水分离。

表 1 磁颗粒制备方法、结构及其处理含油废水的油水分离性能

Table 1 Preparation method, structure and oil-water separation performance of magnetic particles in the treatment of oily wastewater

Magnetic particle name	Composite type	Preparation method	Structure	Oil-water separation efficiency	Recycle cycles	Refer ences
Fe_3O_4@OA	Fe_3O_4@compound	Co-precipitation	Core-shell structure	98%	6	[36]
Fe_3O_4@SiO_2	Fe_3O_4@compound	Sol-gel	Core-shell structure	90%	9	[39]
Fe_3O_4@PEI	Fe_3O_4@compound	Hydrothermal	Core-shell structure	>90%	10	[38]
Fe_3O_4@PVP	Fe_3O_4@compound	Hydrothermal	Core-shell	>99%	5	[52]

			structure			
M-5010	Fe_3O_4@SiO_2@compound	Two-step coating	Core-shell structure	97.3%	5	[53]
MP@PDMAEMAx	Fe_3O_4@SiO_2@compound	SI-ATRP	Core-shell structure	Approaching complete	6	[54]
Fe_3O_4@SiO_2@NH_2	Fe_3O_4@SiO_2@compound	Hydrolytic synthesis	Core-shell structure	97%	-	[55]
M-PNIPAAm	Fe_3O_4@SiO_2@compound	Two-step coating	Core-shell structure	The transmittance increased to 90.2%	7	[40]
M@NH_2	Fe_3O_4@compound	APTES coating	Core-shell structure	99.7%	6	[56]
MMZ-CDs	Magnetic-responsive composite	Co-precipitation	Embedded composite structure	99%	5	[43]
SP@Fe_3O_4/APTES-CD	Magnetic-responsive composite	Hydrothermal synthesis and dehydration condensation	Embedded composite structure	99.8%	10	[44]
M-GO	Magnetic-responsive composite	Silanization modification	Embedded composite structure	99.98%	6	[45]
CNTs/Fe_3O_4	Magnetic-responsive composite	Hydrothermal	Embedded composite structure	99.6%	4	[48]
Fe_3O_4@OA/GO	Magnetic-responsive composite	Solution self-assembly	Embedded composite structure	99.99%	6	[57]
MCNTs/LDHs	Magnetic-responsive composite	Solution self-assembly	Embedded composite structure	>99%	5	[47]
Fe_3O_4@SiO_2@OxdC-DDSA	Fe_3O_4@SiO_2@compound	Silanization modification	Embedded composite structure	98%	3	[58]
MPB	Magnetic responsive composite	Co-precipitation	Embedded composite structure	83.9%	5	[59]
EP@APTES-Fe_3O_4	Magnetic amphiphilic particle	Silanization modification	Embedded composite structure	Significant	4	[60]
M-Janus	Magnetic amphiphilic particle	Pickering emulsion method	Uneven surface (janus)	>90%	5	[50]
Fe_3O_4@P(MMA-AA-DVB)	Magnetic amphiphilic particle	Soap-free emulsion polymerization	Uneven surface (janus)	95%	5	[61]

4.4 油水分离用磁颗粒在循环中的脱油

由表 1 可以看出，将磁颗粒用于含油废水处理，实现高效油水分离的同时，还能够在磁场的作用下得以回收并循环使用，循环过程简图如图 7 所示[60]。其循环使用性一方面大幅度降低了处理成本，另一方面不产生副产物和二次污染，对环境比较友好，实现经济和环境的双收益。

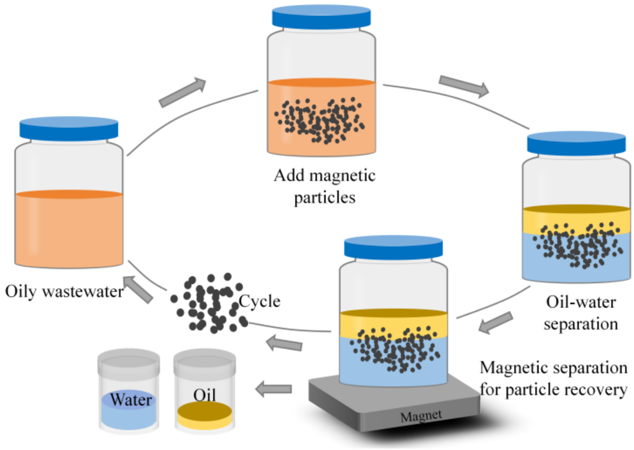

图 7 油水分离与颗粒循环示意图[60]

Fig.7 Schematic diagram of oil-water separation and particle circulation[60]

磁颗粒经过磁场回收后，在再次投加至废水之前还需进行脱油，从磁颗粒-油絮体中分离出来才能进行循环使用。目前使用较多的方法是溶剂洗脱，通过有机溶剂溶解并去除颗粒上的油分，洗脱后的颗粒经干燥后再次循环使用，常见的洗脱剂有氯仿[36]、正己烷[38]、石油醚[53]、甲苯[45]、甲醇[55]、乙醇[56]等。除使用有机溶剂回收黏附油分外，还可以使用化学洗脱法[54, 62]，使用化学试剂（如酸、碱等）对磁性颗粒表面进行清洗，破坏油污与颗粒表面的结合力去除吸附的油污和其他有机物，恢复磁颗粒的吸附能力。

此外，还有使用物理方法进行磁颗粒脱油回用的研究。热处理方法通过温度调节对油分进行去除，如在 60 ℃下对所回收的材料进行热磁洗，能够对颗粒和油分进行有效分离，达到循环使用的目的[40]；超声波能够剥离并清除磁颗粒表面所黏附的物质，德国 Universität Stuttgart 的污水处理试验站即采用超声波进行磁颗粒的再生[63]。

虽通过磁分离并脱出油分后颗粒能够循环使用，但由于在循环过程中可能会发生磁性颗粒的磨损、团聚、形状变化及磁性损失，或洗脱过程不充分、废水水质发生变化等，磁性颗粒的油水分离性能可能会略有下降。经过多次循环使用后，颗粒的再生效率会逐渐降低，需要定期更换或补充新的颗粒。尽管如此，使用可再生循环的磁颗粒处理含油废水带来的环境和经济效益仍然显著。在实际应用中，可以通过优化再生工艺和控制循环次数来提升颗粒的循环性能，如优化溶剂选择、洗脱时间、处理温度等再生工艺参数，能够提高再生效率，延长磁性颗粒的使用寿命；根据磁性颗粒的再生效率和成本效益设定合理的循环次数，当颗粒的再生效率下降到一定程度时，可以选择更换或混合新颗粒使用。

5 磁颗粒处理含油废水性能影响因素

磁性油水分离体系的性能调控受控于材料本征属性与环境参数的协同作用[64]。有的磁颗粒可以对废水环境中的多种条件进行响应，如与聚(2-二甲氨基)甲基丙烯酸乙酯复合成聚甲基丙烯酸甲酯（PDMNC）复合材料[65]，其具备对磁场和 pH 的双重响应，pH 会直接影响其油水分离性能，在实践中能够通过 pH、磁场强度等多维度进行油水分离过程的调控。

表 2 总结了较常见的因素在净水时所产生的影响，实际进行油水分离时，需要根据废水性质、现场条件、场地限制、颗粒本身等进行调试，找寻最适宜的操作参数，以达到最佳净水效果。

表 2　磁颗粒处理含油废水性能影响因素

Table 2　Factors affecting the performance of magnetic particle treatment of oily wastewater

Influenceing factor	The impact of low parameter setting	The impact of high parameter setting
Temperature	At lower temperatures, the viscosity of oil-containing wastewater increases, complicating the oil-water separation process.	Increasing the temperature reduces viscosity but raises energy consumption. Further temperature increases may lead to oxidation, decomposition, and gas bubble formation, reducing oil removal efficiency. Additionally, there is a risk of particle performance degradation.
Stirring intensity	Insufficient stirring intensity results in inadequate interaction between particles and oil droplets, leading to lower reaction efficiency.	Higher stirring intensity enhances particle-oil droplet interaction and increases reaction efficiency, but it also increases energy consumption. Excessively high stirring intensity may induce shear forces that stabilize the oil-water emulsion, reducing separation efficiency.
Magnetic particle dosage	Insufficient dosage fails to achieve the necessary concentration for effective interaction with dispersed oil, resulting in low oil-water separation efficiency.	Excessive dosage strengthens inter-particle interactions, leading to agglomeration, which negatively affects dispersibility and the efficiency of magnetic separation.
Reaction time	Short reaction times may prevent particles from reaching the oil-water interface, resulting in inadequate reactions.	Prolonged reaction times may lead to side reactions that reduce oil removal efficiency, such as oxidation of Fe^{2+} in magnetic particles to Fe^{3+}, weakening their adsorption capacity.
Initial oil content	Low initial concentration results in insufficient interaction between particles and oil droplets, impairing oil-water separation efficiency.	High initial oil content may cause the active sites on magnetic particles to become saturated too quickly, requiring increased particle dosage or optimization of processing time.
Magnetic induction strength	Weak magnetic fields may fail to generate sufficient force for particle-oil floc separation, hindering oil-water separation.	Once magnetic particles are saturated with adsorbed oil, further increases in magnetic field strength provide minimal improvement in oil removal efficiency and may cause particles to deposit in the separator, hindering regeneration and recycling.
Interaction time	Short interaction times may result in insufficient contact between particles and oil droplets, leading to poor oil-water separation.	Excessive interaction time may cause particle aggregation or re-dispersion of oil droplets, thus reducing separation efficiency.
Fluid dynamics conditions	Similar to stirring intensity, low flow rates result in insufficient contact between particles and oil droplets, reducing adsorption efficiency.	High flow rates may cause excessive kinetic energy in oil droplets, preventing their capture by the magnetic particles. Additionally, high flow rates may cause particle loss due to the movement of the particles with the water flow.

6 磁颗粒协同处理含油废水

除直接投加磁性颗粒并在外加磁场辅助下进行油水分离之外，还有一些研究利用其他手段来协同磁性颗粒处理含油废水，如接枝生物制剂[66]、协同絮凝[67]、微波辅助[68]等，表 3 列举了几种常见的协同方法。

表 3 协同方法简介

Table 3 Introduction to collaborative methods

Collaborative methods	Brief introduction	Advantages	Performance	references
Biological method	Magnetic particles are grafted onto microorganisms with oil-water separation capabilities, such as the strain alcaligenes sp. S-xj-1.	Improves oil-water separation efficiency, accelerates the separation process, and is environmentally friendly.	Oil-water separation efficiency: 80%	[66]
Magnetic flocculation	Magnetic particles are coupled with flocculants, which can flocculate dispersed oil while also providing magnetic response.	Accelerates flocculant-water separation, significantly reducing separation time from 180-240 minutes to under 15 minutes.	Chemical oxygen demand removal rate: 81%, turbidity reduction: 89%	[67]
Microwave-assisted	Microwave assistance is added during the separation of oil-water phases with magnetic particles.	Reduces the amount of magnetic particles used and improves oil-water separation performance.	Oil-water separation efficiency: 93%	[68]
Photocatalysis	Photocatalysis is added during the separation of oil-water phases with magnetic particles; magnetite and adsorbed hydroxyl groups generate hydroxyl radicals that further degrade the oil-water interface film through oxidation.	Shows a positive photocatalytic effect at low Fe_3O_4 loadings.	Photocatalysis improves by more than 10 percentage points	[69]
Redox reaction	Materials grafted on the surface of magnetic particles (e.g., ferrocene nitrogen fc+a) can change hydrophilicity/oleophilicity upon the addition of oxidizers/reducers, providing multi-response capabilities.	Enables cycle control of oil-water phase stability and separation by adding oxidizers/reducers.	Organic matter extraction efficiency: 97.5%, oil-water stability/separation can cycle at least 3 times	[70]
Air flotation synergy	Pre-treatment of water with air flotation to remove oil, followed by mixing with reagents, then magnetic particle separation, and recycling of the magnetic particles after further processing.	Fast oil-water separation, can quickly meet oilfield reinjection standards, low treatment cost, long equipment life.	Both oil and suspended solids concentrations are below 5 mg/l	[71]
Chemical method	The demulsifier dmea used in oilfields reacts with triacetate iron to form a magnetic demulsifier m-dmea.	Demulsifier can be recovered and recycled using electrical current or permanent magnets.	Oil-water separation efficiency: 96%	[72]
Aerogel adsorption	A new graphene aerogel-Fe_3O_4 polystyrene mesh composite material, which combines the strong adsorption capabilities of porous materials to adsorb oil in wastewater.	Can be recycled after magnetic recovery and oil removal.	Oil absorption capacity: 40 times its own volume	[73]

可以看出，磁性颗粒与其他方法协同油水分离，或可以提高分离效率或速率，或降低处理成本、减少过程污染，但能够综合其他方法，对磁颗粒处理含油废水的油水分离过程起到积极作用。目前，协同处理的研究并不丰富，需要进一步探索，构建一种有磁性颗粒参与的低成本、高效率、无污染的综合处理方法。

7 典型含油废水磁控处理装备

用于油水分离的磁颗粒的结构及其在实际应用中的表现已在上文进行了详细讨论。虽然这些磁颗粒在油水分离过程中表现出优异的性能，但为了充分发挥其效果，合适的处理装备和装置同样必不可少。这些装备和装置不仅能够优化磁颗粒的使用效率，还可以提高整体分离过程的稳定性和可靠性。表 4 为使用高梯度磁分离器（HGMS）和重力法处理炼油厂的含油废水出水水质对比。可以看出，HGMS 的分离效果相较于重力设备在各项指标上都要更好，油水分离性能优势显著，出水含油量仅为重力设备的 10%左右。实践证明，通过磁颗粒处理含油废水能够将含油废水处理过程中所需药剂量缩减一半[74]。

将磁分离技术装备化，能够为实现高效、经济和环保的含油废水处理提供更高效的解决方案。利用磁颗粒进行含油废水油水分离处理的装备主要有磁颗粒滤料过滤和磁分离（磁选）两类。

表 4 装备处理含油废水性能对比

Table 4 Comparison of performance in treating oily wastewater

Device	Outflow oil content（$mg \cdot l^{-1}$）	Outflow SS content（$mg \cdot l^{-1}$）	Outflow phenol content（$mg \cdot l^{-1}$）
Gravity device	190 ~ 240	142 ~ 204	1500 ~ 4100
High gradient magnetic separator (Magnetic particles)	19 ~ 23	3 ~ 5	1663
High gradient magnetic separator (Magnetic particles+coagulant)	5 ~ 20	1 ~ 18	260

7.1 磁颗粒滤料过滤装置

磁颗粒滤料过滤装置与纤维聚结滤油原理类似，主要以含油废水为流动相，使废水流经磁颗粒作为滤料的油水分离区域，水中分散油滴会不断沉积在磁颗粒滤料的表面上，在滤料内腔流经一段厚度后即可完成油水分离。

图 8 为较典型的磁颗粒过滤含油废水装置[75]，设置了两段并联的过滤段 A、B，两过滤段相通并平行放置，管内使用磁颗粒充填作为过滤含油废水的滤料，两管外围缠绕电磁线圈，通电时提供外加磁场，将滤料固定在管内，同时管末端通常增添针对磁颗粒的过滤器，以防止磁颗粒在装置运行时被水流冲走。装置运行时，含油废水从进水口进入装置，此时 B 段的阀门关闭，废水进入 A 段过滤。由于磁颗粒对油分较为亲和，在废水通过 A 段时，分散油分会被磁颗粒吸附并沉积在磁颗粒滤料的表面，在流经一段滤料后，废水即可实现油水分离。

完成油水分离后的废水经由 A_2 口达标排放，A_2 口装配有光电检测来检测出水口的含油量，含油量达标后才能够排放。而如若光电检测结果显示处理不达标，表明磁颗粒表面沉积的油分已超负荷，不再具备油水分离能力。此时，装置关闭 A 管道的进水阀和电磁线圈，打开 B_1 进水阀及 B 的电磁线圈，使得含油废水进入 B 管道进行油水分离。同时，在 A 管中更换磁颗粒，失活的颗粒洗涤循环备用。在 B_2 光电检测到含油废水未达标后，再使用 A 管处理，B 管颗粒回收，以此二管交替循环。

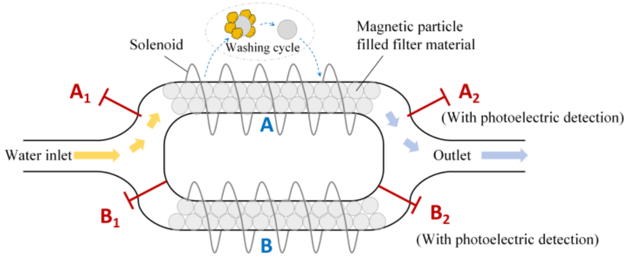

图 8 磁颗粒过滤装置净化含油废水示意图

Fig.8　Schematic diagram of purifying oily wastewater with magnetic particle filtration device

7.2 磁分离（磁选）装置类

磁分离（磁选）类装置工作时一般为“磁颗粒混合-磁分离”工艺。处理含油废水时，会首先将磁颗粒与含油废水进行混匀，在混匀后泵入或流入磁选设备，磁颗粒和油分的絮体会被磁场选别出，与水相进行分离，简易工艺流程如图 9 所示。

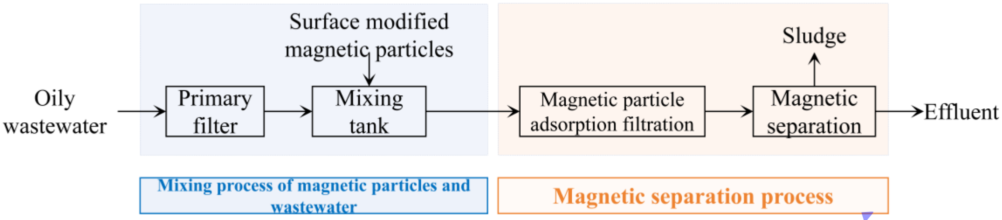

图 9　“磁颗粒混合-磁分离”工艺简图[76, 77]

Fig.9　Process diagram of "magnetic particle mixing magnetic separation"[76, 77]

如图 9 所示，通过搅拌作用加强磁颗粒与废水中油滴的吸附结合，然后由高位水箱将混合了磁颗粒的废水接入磁颗粒过滤器，磁性颗粒吸附过滤对乳化态油和细微杂质具有较好的处理能力。在磁场作用下，磁颗粒的磁性速度（V_m）[63]为：

$$Vm = \frac{V \cdot M \cdot gradB}{3\pi \cdot \eta \cdot d}$$

其中，V 为颗粒的体积（m^3），M 为单位体积颗粒之磁化强度（$A{\cdot}m^{-3}$），B 为磁感应强度（T），η为含油废水的粘滞度（Pa·S），d 为颗粒的直径（m）。施加磁场后，V_m 应足够大以克服过滤时的流体动力，此时磁性絮体被捕集在磁性颗粒上，水经过磁颗粒的缝隙排出，从而实现废水净化[76, 77]。而回收磁颗粒时，断开磁场，V_m=0，反冲洗颗粒或剥落颗粒也较为容易[63]。

图 10 为一种桶罐式强磁磁选分离装置[78]，可以分为上下两个区域，下部区域为净水（油水分离）区域，上半部分则为磁颗粒回收区域。工作时，磁颗粒先与含油废水混合后由进水口进入油水分离区域，磁棒经由伸缩活动杆的推动进入净水区域，将油滴-磁颗粒的絮体磁吸附在表面，实现水相与絮体的分离，并从出水口排出。在完成净水后，磁棒又通过伸缩活动杆缩回颗粒回收区域，通过推料盘将其表面吸附的油滴-磁颗粒絮体剥落至接料盘中，完成一次净水流程。在此分离装置中，颗粒的回收过程为间歇式的，在工作过程中需要间歇地将磁棒提出。

此外，还有连续式工作的磁回收装置，图 11 为连续式磁盘分离机，能够做到对磁颗粒的连续回收。装置中设有能够缓慢旋转的磁力盘，永久磁铁按一定方式排列在磁力盘上形成磁回路，当含油废水与磁颗粒在混合后由进水口进入装置中，通过磁圆盘时，磁颗粒与分散油分形成的絮体会被吸附至永磁体上，并随着磁盘的缓慢旋转带出水面，含油废水实现油水分离后从出水口排除，完成净水。而磁颗粒形成的絮体被带离水面后继续旋转，开始沥水，再次转至水面时被刮板刮下，实现颗粒的回收，分离絮体后的洁净永磁铁则又进入水中进行再次进行吸附。这种设计使废水流向与磁盘旋转方向相反，不断通过永磁铁，流动过程中逐级变清，同时净水时无须暂停，实现油水分离与颗粒回收的连续运行[74]。

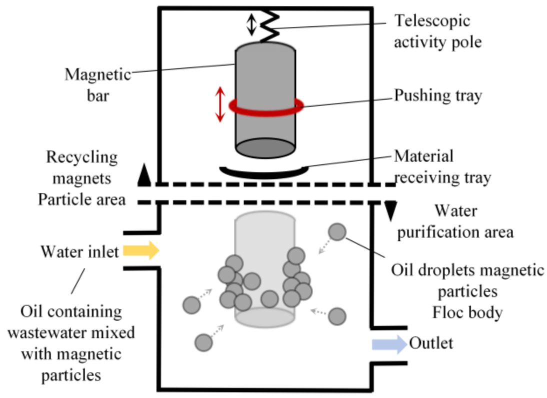

图 10 一种桶罐式强磁磁选分离装置[78]

Fig.10 A bucket type strong magnetic separation device

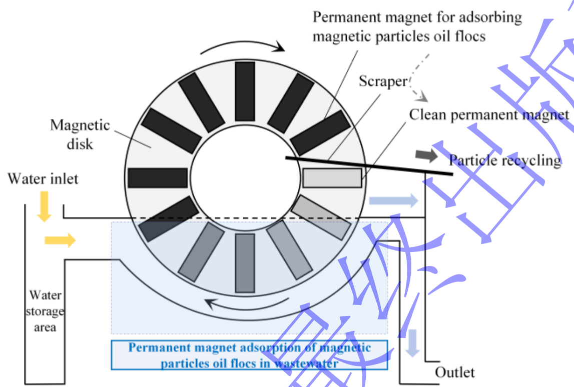

图 11 连续式磁盘分离机回收磁颗粒

Fig.11 Continuous disk separator for recycling magnetic particles

8 总结与展望

磁颗粒处理含油废水绿色经济，具有优良油水分离性能的同时能够在磁场辅助下循环使用，具备极大的应用潜力和研究价值。本文简要介绍了含油废水的性质与危害，系统总结了磁颗粒处理含油废水的油水分离过程与原理、各种结构磁颗粒的油水分离实践，介绍了颗粒循环再生中主要的脱油方法，并分析了影响磁颗粒油水分离性能的因素，最后对协同处理方法和典型含油废水磁控处理装置进行了介绍。基于此，对该领域未来一段时间的研究进行展望：

（1）优化颗粒制备，增强再生研究。目前关于磁颗粒的制备仍有待提升，制备过程应更为绿色经济；同时提升制备过程精细化，增强颗粒形貌和粒径的可控制程度；对材料使用后颗粒与油的分离进行进一步研究，提升材料再生性，增加循环使用次数，延长颗粒服役时间。

（2）加强多学科交叉，促进油水分离。物理法简易经济，化学法快速高效，生物法环保清洁，磁颗粒净水技术应与物理、化学、生物法相结合，兼容并蓄，博采众长，作为技术耦合的核心载体，建立多机制联动的油水分离体系。此外，在材料研发层面，应突破单一场响应的局限，设计具有多物理场耦合响应的功能颗粒。如对油水分离过程进行流场调控，建立多流态调控-磁场协同聚结的高效油水分离技术。这种融合多机制协同作用的技术路线能够应对复杂多变的工业工况，实现油水分离过程的多维度精细调节。

（3）加快规模化和智能化装备开发，推进工业化应用，[79]。磁性颗粒油水分离研究大部分仍停留在实验室阶段，需要推进工业化应用研究[80]；同时需要加快磁颗粒净水设备

的规模化和智能化水平，使之简单易用，经济高效，进一步推动该技术和装备的工业化推广应用。

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