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CHEN Y B, YE Q, QIAN G M, et al. Research progress on application of shells in industrial wastewater treatment process[J]. Water Purification Technology, 2025, 44(6): 17-25,46.

贝壳在工业废水处理工艺应用的研究进展

陈亚宝,叶 青*,钱功明,熊苓雅,马承启
(武汉科技大学资源与环境工程学院,湖北武汉 430080)

摘 要 **【目的】** 随着社会经济的蓬勃发展,冶炼、采矿、电镀、制革、印染等行业产生的工业废水成为环境治理的重要难题。贝壳是一种天然生物质碳酸钙,因其独特的有机-无机复合结构所表现出的理化性质,在工业废水处理处置领域受到广泛关注。**【方法】** 文章从工业废水中的重金属离子和有机污染物等污染源展开论述,阐述了吸附、光催化降解、化学沉淀、生物降解等方法的作用机理和主要影响因素,探讨了贝壳材料在不同处理处置方法中的应用。**【结果】** 探究了贝壳作为吸附材料对工业废水中重金属离子和有机污染物脱除的高效性;贝壳基载体在光催化降解有机污染过程中的适应性;贝壳基载体在化学沉淀法和生物降解法的稳定性。最后,系统阐述了物理改性和化学改性等手段对贝壳基材料性能调控方法,从反应动力学、吸附等温线、微观结构、热重等分析着手,概述了表面吸附、离子交换、催化降解等反应机制,对探索贝壳资源利用过程具有重要意义。**【结论】** 目前,贝壳去除水体污染物的研究仍处于探索阶段,尚未形成工业化应用技术体系。关于贝壳材料中重金属离子和有机污染物的二次溶出及循环利用的研究仍需要更多突破与发展。

关键词 贝壳 废水治理 重金属 有机污染物 吸附法 降解法
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Research Progress on Application of Shells in Industrial Wastewater Treatment Process

CHEN Yabao, YE Qing*, QIAN Gongming, XIONG Lingya, MA Chengqi
(*School of Resource and Environmental Engineering*, *Wuhan University of Science and Technology*, *Wuhan 430080*, *China*)

Abstract [**Objective**] With the vigorous development of the social economy, wastewater generated from industries such as smelting, mining, electroplating, leather making, printing, and dyeing is a serious challenge for environmental governance. Shell is a natural biomass of calcium carbonate, which has attracted widespread attention in the field of industrial wastewater treatment due to its unique organic-inorganic composite structure and physicochemical properties. [**Methods**] This paper reviews the pollution sources such as heavy metal ions and organic pollutant in industrial wastewater, elaborates on the mechanisms and main influencing factors of adsorption, photocatalytic degradation, chemical precipitation, and biodegradation process, and explores the application of shell materials in different treatment process. [**Results**] In addition, the high efficiency of shell as an adsorbent material for the removal of heavy metal ions and organic pollutant in industrial wastewater, the adaptability of shell-based carriers in photocatalytic degradation of organic pollutant, and the stability of shell-based carriers in chemical precipitation and biodegradation process is explored. Finally, the mechanism of physical and chemical modification to regulate the properties of shell-based materials is elaborated systematically. Combined with the analysis of reaction kinetics, adsorption isotherms, microstructure, and thermogravimetry, the reaction mechanisms of surface adsorption, ion exchange, and catalytic degradation are summarized, which is of great significance for exploring the process of shell resource utilization. [**Conclusion**] At present, the research on the removal of water pollutants by shells is still in the exploratory stage and has not yet formed an industrialized application technology system. The research on the secondary dissolution and

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[**作者简介**] 陈亚宝(1997—),女,硕士研究生,研究方向为改性贻贝壳去除废水中重金属离子的工艺及机理研究,E-mail: chenyabao2021@163.com。
[**通信作者**] 叶青(1992—),女,副教授,研究方向为固废资源利用及矿物功能材料,E-mail: yeqing@wust.edu.cn。

recycling of heavy metal ions and organic pollutants in shell materials still needs more breakthroughs and development.
Keywords　shell　wastewater treatment　heavy metal　organic contaminant　adsorption process　degradation process

随着我国工业的不断发展,废水污染也成为现阶段的主要环境问题之一。特别是电镀、冶金、制革等领域将含有大量重金属和有机污染物的废水排入到水体中,有毒有害组分的持续增加对人类的健康造成了严重威胁[1-3]。目前,工业废水的处理方法有多种,其中也包含利用天然矿物制备吸附材料治理工业废水的技术。由于该技术工艺流程简单、处理效果好,受到普遍关注[4-5]。

我国作为水产养殖大国,海水养殖面积总体上维持在 $2×10^6$ hm^2($1\ hm^2 = 10\ 000\ m^2$)左右,其中,贝类养殖面积可达 $1.20×10^6$ hm^2,约占总面积的60.0%[6-8]。贝类养殖业的快速发展产生了大量贝壳废弃物,其中仅有一小部分回收用作涂料和鱼粉的添加剂,60%以上的贝壳未得到有效的利用而作为固体废弃物被倾倒、堆积,不仅占用了土地资源还造成了严重的环境污染。因此,充分利用贝壳资源既能有效解决环境污染和土地占用等问题,还能实现可再生资源的高效利用。

贝壳主要成分为 $CaCO_3$(占总质量的 95%左右)、少量的有机质和微量元素。贝壳的结构十分丰富多样,最常见的微观结构有珍珠层、棱柱层以及交叉叠片。各片层间均通过有机质紧密相连,是一种天然的复合材料[9]。贝壳疏松多孔的结构使其具有良好的吸附性能,表面有机基团的存在也提供了进一步表面修饰改性的结合位点,有利于贝壳基功能性材料的开发和贝壳资源化利用工艺的探索。

1　工业废水的污染现状与危害

工业水体的污染主要包括重金属离子污染和有机物污染。其中,重金属污染最为严重,主要是指汞(Hg)、镉(Cd)、铜(Cu)、银(Ag)、铅(Pb)、铬(Cr)、锰(Mn)、铁(Fe)以及类金属砷(As)等生物毒性显著的金属元素,其含量一旦超过阈值,就会对生物产生毒害作用。此外,由于重金属离子本身结构稳定,能在环境中滞留几个月甚至几十年[10-11],给生态环境埋下重大隐患。有机污染物是指由天然有机质及某些其他可降解的人工合成有机物质组成的污染物,具体可划分为染料、卤化物、多环芳烃、表面活性剂、石油类污染物等。其中,染料的污染尤为严重。染料通常含有苯环、胺基和偶氮等有机基团,其化学结构稳定,难以被生物降解。有机污染物随水循环进入生物体内,造成生物积累,严重可导致重要器官中毒和损害[12-13],如表 1 所示。

表 1　不同污染物的排放标准和健康危害

Tab. 1　Discharge Standards and Health Hazards of Different Pollutants

污染物		最高允许排放质量浓度/($mg·L^{-1}$)	典型的健康危害
重金属	Hg	0.05	神经系统损伤[14]
	Cd	0.1	肺部疾病、出生缺陷[15]
	Cr	1.5	皮肤溃疡、铬性鼻炎[15]
	As	0.5	皮肤病变、骨髓抑制[14]
	Pb	1.0	大脑、肾脏损伤[15]
	Cu	0.5	蛋白质变性、肝硬化、心脏疾病[14]
	Ag	0.5	皮肤产生蓝灰色色变、肝脏病变[16]
	Mn	2.0	永久性残疾、神经系统损伤[17]
	Zn	2.0	免疫功能下降、动脉硬化、诱发癌症[14]
	Ni	1.0	降低生育能力、致畸、系统紊乱[18]
	Fe	10	心力衰竭、骨质疏松[19]
有机物	亚甲基蓝	/	亨氏小体贫血、红细胞形态坏死、坏死性脓肿[20-21]
	罗丹明 B	/	皮肤和内脏红染、心肌纤维断裂[22]
	17-α-甲基睾酮激素	/	肝损伤、心血管疾病[23]
	双氯芬酸	/	多种慢性毒性症状,如神经毒性、心脏毒性[24]
	磺胺嘧啶	/	胃肠道的感染[25]

注:pH 值为 6~9,色度为 50 度,化学需氧量为 100 mg/L。

相关研究[26-30]表明,工业废水处理方法主要包括吸附法、化学沉淀法、降解法、生物处理法和膜分离法等。吸附法处理工业废水流程如图 1 所示,其中典型污染物所需吸附材料应具有比表面积较大、活性位点较多等特性。而在光催化降解有机污染物的工艺流程中,生物质材料作为良好的催化剂载体可有效增强催化剂的分散性,提高催化降解的效率。贝壳结构组织疏松多孔、孔隙分布均匀、比表面积较大,具有较强的吸附能力、离子交换能力,能够很好地吸附重金属离子。同时,贝壳可作为天然生物质载体,将催化剂负载在贝壳粉表面制备复合催化材料,增大催化剂与污染物的有效接触面积,提高降解效率。此外,贝壳中主要成分 $CaCO_3$ 也可作为复合盐通过化学沉淀处理废水中污染物。因此,将贝壳材料应用于工业废水的处理是实现贝壳高效资源化利用的重要途径。

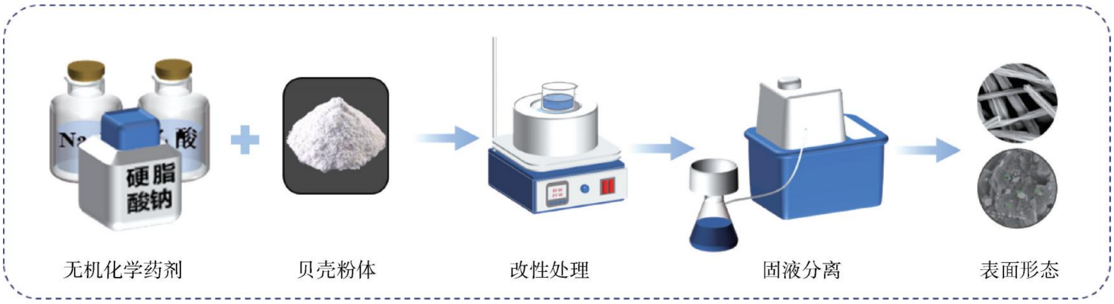

图 1 废水处理工艺流程

Fig. 1 Process Flow of Wastewater Treatment

2 贝壳材料处理工业废水的研究现状

由于贝壳具有实际密度较高、颗粒内孔体积较小等优点,通过改性处理、复合处理等手段,吸附废水中的重金属离子、光催化降解有机染料,可实现废弃贝壳的高值化利用,从而达到低成本、高效率治理废水的目的。

2.1 吸附法

2.1.1 重金属离子的吸附

贝壳由 3 层组成,即有机层、中间层、内层[30]。$CaCO_3$ 约占贝壳质量的 95%,有机物质仅占 5%左右。由于复杂的 3 层微观结构,贝壳具有坚固、稳定的特性。微观分析结果显示,贝壳的比表面积为 2.235 m^2/g,孔容和孔径分别为 0.005 6 cm^3/g 和 23.39 nm[31],即贝壳孔隙直径相对较大,具有较大的比表面积,能够有效去除重金属离子。吸附法具有操作简单、效率高、成本低、再生方便等优点,被学者大量地研究,贝壳去除重金属离子的部分应用总结如表 2 所示。

废水中重金属离子的吸附动力学研究[32]表明,初期贝壳表面附着许多吸附位点且浓度差较大,使得吸附传质动力学较大。因此,随着吸附时间的延长,贝壳吸附量迅速增大。随着吸附时间持续延长,贝壳表面活性位点减少,吸附传质动力学逐渐减小,吸附速率趋于稳定。进一步探究了 Cd^{2+} 吸附过程的吸附等温曲线,研究[33]结果表明,该过程为单分子层吸附,符合 Temkin 等温吸附模型。随着温度的升高,吸附质与吸附位点的接触率逐渐提高,贝壳的饱和吸附量增大,当温度从 10 ℃升至 40 ℃时,对 Cd^{2+} 的饱和吸附量由 149.39 mg/g 增加到 171.58 mg/g。此外,pH 的变化对 Cd^{2+} 的吸附量也产生影响[34]。pH 较低时,溶液中的 H^+ 与部分 CO_3^{2-} 反应,从而减少 Cd^{2+} 与吸附剂表面生成的碳酸盐沉淀;随着 pH 的增大,H^+ 浓度降低且 Cd^{2+} 可与羟基复合,促进 Cd 的吸附量增加。然而,贝壳粉饱和吸附容量较低、对金属离子选择性较差、极易团聚等问题导致吸附率不高,因此,可采用煅烧、化学改性、复合等方式对贝壳进行改性,以提高对重金属离子的吸附效果。

研究[35]采用硬脂酸钠对贝壳进行化学改性试验,进一步对微观结构分析可知,硬脂酸钠改善了贝壳粉的疏水性,团聚现象减弱,分散性得到明显提高。用 1% NaOH 溶液改性后的贝壳粉表面缺陷增多,对含 U 废液的处理过程中[36],随着初始浓度增加,吸附容量逐渐增大。另外,当溶液 pH 较低时,U 以 UO_2^{2+} 形式存在,与 H^+ 形成竞争关系;而当 pH 值>4 时,UO_2^{2+} 和负电性磷酸盐之间产生静电排斥,导致吸附容量降低[37]。采用水热法使用乙酸处理贝壳粉

体,可有效提高废水中 Cu^{2+} 的脱除。当 pH 较低时,溶液中的 H^+ 易与 Cu^{2+} 竞争吸附,导致吸附容量较低;随着 pH 的增大,Cu^{2+} 的去除率逐渐增大。结合吸附等温线及吸附动力学分析,表明该吸附过程为多层吸附,且吸附过程属于化学吸附反应。通过微观分析结果可知,微球具有更大的比表面积,表面分布较多均匀的孔隙。Cu^{2+} 可以通过多层吸附直接附着在微球表面,也可以通过孔吸附进入微球内部,如图 2 所示。同时,Cu^{2+} 与 Ca^{2+} 的离子半径相似,也存在离子交换过程,使得该材料的吸附能力进一步提高。

表 2　原始贝壳/改性贝壳去除重金属的应用效果

Tab. 2　Application Effect of Raw Shells or Modified Shells and for Heavy Metals Removal

吸附材料质量浓度/($g\cdot L^{-1}$)	目标重金属质量浓度/($mg\cdot L^{-1}$)	反应时间/h	pH 值	饱和去除容量/($mg\cdot g^{-1}$)
1($CaCO_3$)	50(Cd^{2+})	0.5	5.4	43.12[33]
50($CaCO_3$)	3.2(Pb^{2+})、225(Zn^{2+})	20	5.0	0.058、2.7
0.06(NaOH-$CaCO_3$)	10(U^{6+})	1	4.0	70[36]
0.1(NaOH-植酸-油酸-乙醇-$CaCO_3$)	200(UO_2^{2+})	0.5	4.0	2 140[37]
1(乙酸-$CaCO_3$)	60(Cu^{2+})	1	5.0	517[38]
2(聚乙烯醇-$CaCO_3$)	50(Cd^{2+})、50(Cu^{2+})	24	8.0	20、31[39]

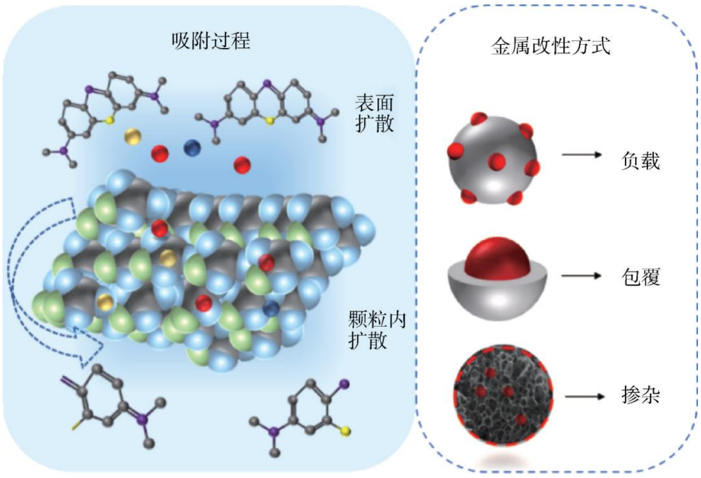

图 2　贝壳的吸附过程及金属改性方式

Fig. 2　Adsorption Process and Metal Modification Methods of Shells

高分子材料作为新型材料,具有良好的亲水性、稳定性以及耐高温等优点,使用高分子材料对贝壳进行改性,可以在一定程度上克服贝壳吸附容量低、可回收性差、选择性单一等问题。在贝壳粉上包覆聚乙烯醇(PVA),制备了一种分散性良好、选择性高的复合材料[39]。从微观结构可知,复合材料表面存在较小的缝隙,同时,聚合物中的—OH 与小分子间的相互作用,使体系中的游离水增多,孔隙结构得到改善。通过复合材料表面—OH、C═O 等官能团和金属阳离子的强配位作用,实现金属离子的高效脱除。该研究为复杂体系中污染物的去除奠定了基础,为改善粉体团聚、提高选择性提供了新思路。

2.1.2　有机污染物的吸附

物理吸附法是依靠比表面积大的多孔贝壳基材料与有机分子间的分子间作用力的吸附作用,因分子间作用力较弱,吸附和解吸速度也都较快。因此,被吸附的有机污染物容易解吸出来造成二次污染。化学吸附法是吸附质分子与固体表面分子发生电子的交换、转移、共有,形成吸附化学键。研究发现,为了提高对染料废水的处理能力,利用机械活化、煅烧、化学药剂改性等技术手段,可强化有机污染物的脱除效果,如表 3 所示。通过增大贝壳基表面缺陷、引入活性官能团、增大孔隙率及比表面积等方式,可

提高其吸附解吸性能，减少团聚现象，实现贝壳的高值化利用。

机械力可促进材料内部产生晶格畸变和局部破坏，增强反应活性。将贝壳研磨成超细粉末后，对 MB 的饱和吸附容量均得到明显提高[40]。研究[41]表明，贝壳材料的比表面积与球磨时间成正比关系。同时，由于球磨过程中会产生局部高温，可分解部分有机质形成微孔结构，进而增大贝壳粉体的比表面积。随着研磨时间的延长，颗粒中 CO_3^{2-} 的键合作用减弱，易与其他物质结合形成新基团，贝壳颗粒粒度减小；而当球磨时间过长，分子间的静电力促使颗粒团聚，反而导致粒径增大。

高温热解也是贝壳改性的常用方法，微观形貌分析表明，贝壳粉经 700 ℃下热解 2~5 h 后，颗粒尺寸减小且颗粒表面呈不规则层状结构，可有效提高染料废水中 17-α-甲基睾酮激素等难处理有机污染物的脱除率[42]。进一步通过吸附动力学研究[43]表明，热处理后的贝壳粉与激素的吸附过程是一个分步反应，即第一阶段为激素在热解贝壳外层的扩散，第二阶段为颗粒内扩散，第三阶段为孔内扩散。热处理过程中贝壳有机质充分分解形成发达的孔隙，可明显改善吸附性能。

利用乙酸处理的贝壳材料对结晶紫染料及原油表现出良好的吸附效果，并且在甲醇中可实现解吸，解吸率可达 82%[44]。通过循环试验可知，循环 10 次后，贝壳材料在解吸过程中表现出较好的回收性。采用 HCl、Na_2CO_3 等试剂处理贝壳材料，具有更大的比表面积、更高的介孔率和更多的活性位点数[45]。研究[46]表明，随着 pH 的增大，吸附剂表面的羟基负离子增多，从而增加了催化剂和染料分子间的静电相互作用。

吸附法具有吸附效率高、吸附材料制备简单、吸附能力强等优点，是目前应用最广泛的废水处理技术，但该技术仍存在二次污染。因此，仍需进一步研究来完善该工艺。

2.2 化学沉淀

贝壳的主要成分为 $CaCO_3$[47]，通过与盐溶液络合沉淀废液的重金属离子，使其以氢氧化物或碳酸盐的形式沉降去除。重金属的形态受到 pH 和共存阴离子的显著影响，当溶液中的 OH^- 增多，可与重金属离子反应生成沉淀，将部分重金属离子去除[48-49]。试验结果表明，贝壳粉能提高酸性废水的 pH，达到降低溶液的重金属浓度的目的。然而 $CaCO_3$ 中和沉淀工业废水时，会产生大量含重金属离子的污泥，需占用大量面积去存放处理，且金属离子易重新溶解和迁移，造成二次污染。而光催化技术作为一种绿色环保的工艺手段，能够将有机染料降解为无害的无机物，为处理工业废水，提供了崭新的技术手段，具有良好的应用前景。

2.3 光催化降解

在废水治理工艺流程中，光催化技术常用于降解染料及其他有机物。其原理是光催化剂在光照条件下，将有机污染物降解成 H_2O 和 CO_2，如图 3 所示。贝壳的主要成分为 $CaCO_3$ 和少量氨基酸，在光催化降解工艺中，贝壳作为一种良好的光催化载体，可减少颗粒团聚现象，改善光催化性能。

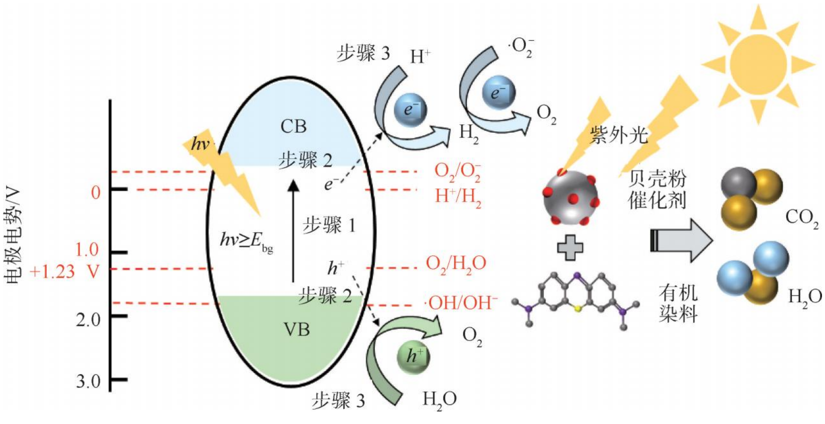

图 3 贝壳粉光催化降解机理

Fig. 3 Photocatalytic Degradation Mechanism of Shell Powder

通过热活化处理贝壳，可去除材料中的结合水和部分有机质。随着温度的升高，贝壳晶体结构、孔

结构及比表面积均产生一定程度的变化,从而改善贝壳的性能,提高贝壳对废水中有机物的去除能力[50]。研究[51]表明,当温度为400~500 ℃时,有机物部分被分解成水分并蒸发,霰石向方解石转换;当温度升高至600~700 ℃时,贝壳材料质量变化明显下降,该过程中方解石转化为CaO和CO_2并形成空腔,表面由层状结构转变为多孔结构。在富氧条件下,热活化后的贝壳材料对有机物的降解率明显提高,这是由于溶解氧作为氧化剂,生成了部分促进降解反应的自由基,如OH^-、HO_2^-等。但由于煅烧过程并不能产生新的活性基团,对于难以去除的污染物如激素等,脱除效果仍未明显改善。因此,考虑采用化学改性的方式,有效提升废水中污染物的去除效果。

采用NaOH浸泡去除贝壳表面脂质,再经过HCl处理的贝壳材料表面裂缝和凹陷交错,形成排列不均的中孔,比表面积增加了57.5倍[52]。光催化降解试验研究表明,经光照300 min后,改性贝壳材料对刚果红/亚甲基蓝(MB)和罗丹明B的吸附量分别为72 mg/g和38.4 mg/g,并达到吸附平衡。经4次连续循环试验,改性贝壳材料对MB和罗丹明B的去除率仍可达到86.103%、75.844%,表明该材料具有较好的可回收性及较高的稳定性。进一步研究染料的降解机制表面发现,光照过程中产生的OH^-、O^{2-} 2种基团破坏N-脱乙基和共轭结构,再通过脱甲基和脱氨基反应催化降解是实现有机污染物高效降解的主要原因[53]。

事实上,由于金属纳米粒子具有较丰富的电子性质,表现出优异的催化活性,制备金属与贝壳基的复合材料已成为光催化降解领域的热点[54]。金属或金属氧化物利用掺杂、包覆、负载等手段对贝壳改性,如图2所示。改性后的贝壳能够有效促进材料相变、抑制晶粒生长、增大比表面积,同时,对加速电荷的转移、表面氧的生成、去除能力的提高和反应位点的增加均产生正向影响。通过铁浸渍法,制备了一种具有棒状结构的贝壳基复合材料[55]。微观分析表明,复合材料的结晶度增加、热稳定性提高,而棒状结构归因于α-Fe_2O_3相的形成,该相可促进有机污染物的催化降解。对响应面模型分析表明,少量的催化剂产生的活性氧能够促进双氯芬酸(DFC)与催化剂相互作用,致使其失活。

对过硫酸盐体系中Fe^{3+}难以被还原导致催化性能下降的问题,相关研究[56]采用双金属体系,以贝壳粉为载体,制备了Fe-Co/贝壳粉催化剂。试验结果表明,催化剂的添加量为0.3 g/L、光照时间为20 min时,对20 mg/L的MB的降解率为93.5%。随着双金属体系中铁原子与钴原子摩尔比(n_{Fe}:n_{Co})的增大,MB的降解率呈先增大后减小的趋势。事实上,由于少量的Co起到还原Fe^{3+}的作用,而当体系中Co含量过高时,在催化剂表面形成$CoFe_2O_4$,从而影响对染料的催化性能。

表3　原始贝壳/改性贝壳去除有机污染物的应用效果

Tab. 3　Application Effect of Raw Shell or Modified Shells in Organic Contaminants Removal

吸附材料质量浓度/($g\cdot L^{-1}$)	目标有机物质量浓度/($mg\cdot L^{-1}$)	反应时间/h	饱和去除容量/($mg\cdot g^{-1}$)
10(球磨$CaCO_3$)	100(MB)	2	16.5/8.32[40]
10(700 ℃热解$CaCO_3$)	5(17-α-甲基睾酮激素)	2	0.778[42]
5(乙酸-$CaCO_3$)	5(结晶紫)	48	0.4[44]
25(乙酸-$CaCO_3$)	40(原油)	0.16	15.52[44]
1(HCl-Na_2CO_3-$CaCO_3$)	20(中性红)	2.3	14.2[45]
2.5(Fe_3O_4@SiO_2/HAP)	550(甲基橙)	2	196[46]
2.5(900 ℃煅烧$CaCO_3$)	5(MB)	24(光照)	1.894[51]
0.5(NaOH-HCl-$CaCO_3$)	60(MB)、24(罗丹明B)	5(光照)	72、38.4[52]
0.015 2(Fe@MSBC)	60(DFC)	0.5(光照)	58.974[55]
0.3(Fe-Co/$CaCO_3$)	20(MB)	0.33(光照)	18.7[56]
0.1(Ag_2O/Ag_2CO_3)	10(磺胺嘧啶)	1.5(光照)	10[57]
0.5(柠檬酸-$CaCO_3$-石油烃降解菌)	1 000(原油)	168	810.3[58]

以贝壳粉为前驱体制备了 Ag_2O/Ag_2CO_3 新型光催化剂,由于复合材料在异质结构表面形成丰富的氧空位,扩大了光响应区域[57-59]。此外,贻贝壳中微量金属元素的部分掺杂,形成了更多的光催化反应活性位点。选用贝壳粉作为载体,可以较好地解决金属氧化物等其他催化剂的粒子团聚问题,促进电子与空穴复合、提高界面电荷传输效率,为制备高效贝壳基复合光催化剂、改善光催化剂效率提供理论基础和科学依据。

3 结论与展望

贝壳具有发达的孔隙结构和生物活性,可广泛应用于工业废水中污染物处理。本文综述了贝壳材料的制备与改性方法,通过优化设计贝壳材料的微观结构,如增大比表面积、增大孔隙率、增多反应活性位点等,提高对重金属离子、有机污染物的处理能力。进一步阐述了贝壳材料对污染物处理过程的反应机制,主要包括表面吸附、化学沉淀、离子交换等作用。此外,改性贝壳材料可作为载体与纳米粒子结合制备复合材料,通过调控材料相变与晶粒生长,实现对污染物的高效降解。目前,贝壳去除水体污染物的研究仍处于探索阶段,尚未形成工业化应用技术体系。关于贝壳材料中重金属离子和有机污染物的二次溶出及循环利用的研究仍需要更多突破与发展。

参考文献

[1] BERHE R N, KASSAHUN S K, KANG J W, et al. Performance evaluation of Fe_3O_4 @ ACF-supported bio-electro Fenton system for simultaneous sewage treatment and methyl orange degradation [J]. Materials Today Communications, 2023, 35: 106331. DOI: 10.1016/j.mtcomm.2023.106331.

[2] YIN Q Q, LIU M T, REN H P. Biochar produced from the co-pyrolysis of sewage sludge and walnut shell for ammonium and phosphate adsorption from water[J]. Journal of Environmental Management, 2019, 249: 109410. DOI: 10.1016/j.jenvman.2019.109410.

[3] ALJOHANI M M, AL-QAHTANI S D, ALSHAREEF M, et al. Highly efficient adsorption and removal bio-staining dye from industrial wastewater onto mesoporous Ag-MOFs[J]. Process Safety and Environmental Protection, 2023, 172: 395-407. DOI: 10.1016/j.psep.2023.02.036.

[4] FEI Y H, HU Y H. Recent progress in removal of heavy metals from wastewater: A comprehensive review[J]. Chemosphere, 2023, 335: 139077. DOI:/10.1016/j.chemosphere.2023.139077.

[5] LAN D, ZHU H, ZHANG J, et al. Adsorptive removal of organic dyes via porous materials for wastewater treatment in recent decades: A review on species, mechanisms and perspectives[J]. Chemosphere, 2022, 293: 133464. DOI: 10.1016/j.chemosphere.2021.133464.

[6] LIN C Y, DAI G L, LIU Y, et al. Ecological value of mariculture shellfish resources in China: Assessment and management[J]. Marine Policy, 2023, 148: 105406. DOI: 10.1016/j.marpol.2022.105406.

[7] MAHARI W A W, WAIHO K, AZWAR E, et al. A state-of-the-art review on producing engineered biochar from shellfish waste and its application in aquaculture wastewater treatment[J]. Chemosphere, 2022, 288: 132559. DOI: 10.1016/j.chemosphere.2021.132559.

[8] SONG C, XIONG Y L, JIN P, et al. Mariculture structure adjustment to achieve China's carbon neutrality and mitigate climate change[J]. Science of the Total Environment, 2023, 895: 164986. DOI: 10.1016/j.scitotenv.2023.164986.

[9] OSA J L, MONDRAGON G, ORTEGA N, et al. On the friability of mussel shells as abrasive[J]. Journal of Cleaner Production, 2022, 375: 134020. DOI: 10.1016/j.jclepro.2022.134020.

[10] KHAN B N, ULLAH H, ASHFAQ Y, et al. Elucidating the effects of heavy metals contamination on vital organ of fish and migratory birds found at fresh water ecosystem[J]. Heliyon, 2023, 9(11): e20968.

[11] MENG Y M, ZHI H H, XIANG Q X, et al. Simultaneous immobilization of multiple heavy metals in polluted soils amended with mechanical activation waste slag[J]. Science of the Total Environment, 2023, 894: 164730. DOI: 10.1016/j.scitotenv.2023.164730.

[12] MUTALIB A A A, JAAFAR N F. ZnO photocatalysts applications in abating the organic pollutant contamination: A mini review[J]. Total Environment Research Themes, 2022, 3/4: 100013. DOI: 10.1016/j.totert.2022.100013.

[13] 中华人民共和国生态环境部. 污水综合排放标准: GB 8978—1996[S]. 北京: 中国环境科学出版社, 1996.
Ministry of Ecology and Environment of the People's Republic of China. Comprehensive sewage discharge standard: GB 8978—1996[S]. Beijing: China Environmental Science Press, 1996.

[14] TRAVEN L, PUPAVAC S M, ŽURGA P, et al. Arsenic (As), copper (Cu), zinc (Zn) and selenium (Se) in northwest Croatian seafood: A health risks assessment[J]. Toxicology Reports, 2023, 11: 413-419. DOI: 10.1016/j.toxrep.2023.10.012.

[15] YU X N, JIANG N J, YANG Y, et al. Heavy metals remediation through bio-solidification: Potential application in environmental geotechnics[J]. Ecotoxicology and Environmental Safety, 2023,

263：115305. DOI：10.1016/j.ecoenv.2023.115305.

[16] MA L J, WANG Q, ISLAM S M, et al. Highly selective and efficient removal of heavy metals by layered double hydroxide intercalated with the MoS_4^{2-} ion[J]. Journal of the American Chemical Society, 2016, 138(8): 2858-2866.

[17] FUCHIDA S, TAJIMA S, NISHIMURA T, et al. Kinetic modeling and mechanisms of manganese removal from alkaline mine water using a pilot scale column reactor[J]. Minerals, 2022, 12(1): 99.

[18] SUNDERMAN F W, DINGLE B, HOPFER S M, et al. Acute nickel toxicity in electroplating workers who accidently ingested a solution of nickel sulfate and nickel chloride[J]. American Journal of Industrial Medicine, 1988, 14(3): 257-266.

[19] MIA B, AMC D, HA E, et al. Appraisal of heavy metals exposure risks via water pathway by using a combination pollution indices approaches, and the associated potential health hazards on population, Red Sea State, Sudan[J]. Physics and Chemistry of the Earth, 2022, 127: 103153. DOI: 10.1016/j.pce.2022.103153.

[20] GILLMAN P K. CNS toxicity involving methylene blue: The exemplar for understanding and predicting drug interactions that precipitate serotonin toxicity[J]. Journal of Psychopharmacology, 2011, 25(3): 429-436.

[21] CHEN A, WONG A. The role of angiotensin Ⅱ in poisoning-induced shock-A review[J]. Journal of Medical Toxicology, 2022, 18(2): 145-154.

[22] LUO Y D, HAN Y, XUE M S, et al. Ball-milled bismuth oxybromide/biochar composites with enhanced removal of reactive red owing to the synergy between adsorption and photodegradation[J]. Journal of Environmental Management, 2022, 308: 114652. DOI: 10.1016/j.jenvman.2022.114652.

[23] CAO P, LUAN S Q, WANG W X, et al. Metabolites identification of 17α-methyltestosterone mediated by *Aspergillus niger* RG13B1 and their cytotoxicity on cancer cells[J]. Phytochemistry Letters, 2023, 54: 153-157. DOI: 10.1016/j.phytol.2023.02.011.

[24] SATHISHKUMAR P, MOHAN K, MEENA R A A, et al. Hazardous impact of diclofenac on mammalian system: Mitigation strategy through green remediation approach[J]. Journal of Hazardous Materials, 2021, 419: 126135. DOI: 10.1016/j.jhazmat.2021.126135.

[25] DUAN Y, DENG L, SHI Z, LIU X, et al. Efficient sulfadiazine degradation via in-situ epitaxial grow of graphitic carbon nitride ($g\text{-}C_3N_4$) on carbon dots heterostructures under visible light irradiation: Synthesis, mechanisms and toxicity evaluation[J]. Journal of Colloid and Interface Science, 2020, 561: 696-707. DOI:10.1016/j.jcis.2019.11.046.

[26] BISWAL B K, BALASUBRAMANIAN R. Use of biochar as a low-cost adsorbent for removal of heavy metals from water and wastewater: A review[J]. Journal of Environmental Chemical Engineering, 2023, 11(5): 110986.

[27] MAQBOOL A, SHAHID A, JAHAN Z, et al. Development of ZnO-GO-NiO membrane for removal of lead and cadmium heavy metal ions from wastewater[J]. Chemosphere, 2023, 338: 139622. DOI: 10.1016/j.chemosphere.2023.139622.

[28] HE S, SUN J, JIN X, et al. Adsorption enhancement of Congo red dye from wastewater based on edamame shell originated activated carbon by the cations: Experimental and theoretical studies[J]. Diamond and Related Materials, 2023, 136: 109930. DOI: 10.1016/j.diamond.2023.109930.

[29] TANG M Q, SNOUSSI Y, BHAKTA A K. Unusual, hierarchically structured composite of sugarcane pulp bagasse biochar loaded with Cu/Ni bimetallic nanoparticles for dye removal[J]. Environmental Research, 2023, 232: 116232. DOI: 10.1016/j.envres.2023.116232.

[30] SVETLANA D, PETER K, YULIYA K, et al. Mineral-free biomaterials from mussel (*Mytilus edulis L.*) shells: Their isolation and physicochemical properties[J]. Food Bioscience, 2023, 56: 103188. DOI: 10.1016/j.fbio.2023.103188.

[31] CHAKRABORTY A, PARVEEN S, CHANDA D K, et al. An insight into the structure, composition and hardness of a biological material: The shell of freshwater mussels[J]. RSC Advances, 2020: 10. DOI: 10.1039/D0RA04271D.

[32] ZHAO G L, WANG X F, CHEN Q F, et al. Efficacy of phosphorus loaded oyster shell in heavy metal removal: A combined study on adsorption behavior, structure characterization and comparative mechanism[J]. Environmental Technology & Innovation, 2024, 33: 103484. DOI: 10.1016/j.eti.2023.103484.

[33] 罗文文. 含钙生物吸附剂及其改性材料对 Cd(Ⅱ)吸附效应及机理研究[D]. 北京：中国农业科学院，2023.
LUO W W. The adsorption properties and mechanism of Cd(Ⅱ) removal onto calcium-containing biosorbents and its modifided materials[D]. Beijing: Chinese Academy of Agricultural Sciences, 2023.

[34] ALI A, LI M, SU J, et al. Brevundimonas diminuta isolated from mines polluted soil immobilized cadmium (Cd^{2+}) and zinc (Zn^{2+}) through calcium carbonate precipitation: Microscopic and spectroscopic investigations[J]. Science of the Total Environment, 2022, 813: 152668. DOI:10.1016/j.scitotenv.2021.152668.

[35] 纪登杰，许依能，杨威，等. 改性扇贝壳粉与壳聚糖复合膜的制备及性质研究[J]. 食品工业科技，2022，43(14)：268-275.
JI D J, XU Y N, YANG W, et al. Preparation and properties of modified scallop shell powder and chitosan composite film[J]. Science and Technology of Food Industry, 2022, 43(14): 268-275.

[36] 陈拓,彭捍,肖海鹏,等. 贝壳基吸附材料的制备及其铀吸附性能研究[J]. 应用化工, 2022, 51(12): 3481-3485, 3491.
CHEN T, PENG H, XIAO H P, et al. Preparation of shell based adsorbent materials and its adsorption properties of uranium [J]. Applied Chemical Industry, 2022, 51(12): 3481-3485, 3491.

[37] LIU Y X, XU Z Y, XIA C J, et al. Extremely effective removal of U(Ⅵ) from aqueous solution by 3D flower-like calcium phosphate synthesized using mussel shells and rice bran[J]. Separation and Purification Technology, 2023, 310: 123235. DOI: 10.1016/j.seppur.2023.123235.

[38] WANG H B, YAN K Q, XING H R, et al. Effective removal of Cu^{2+} from aqueous solution by synthetic abalone shell hydroxyapatite microspheres adsorbent [J]. Environmental Technology & Innovation, 2021, 23: 101663. DOI: 10.1016/j.eti.2021.101663.

[39] ZHOU Z F, WANG Y N, SUN S, et al. Preparation of PVA/waste oyster shell powder composite as an efficient adsorbent of heavy metals from wastewater[J]. Heliyon, 2022, 8(12): e11938.

[40] SU H X, GUO X, ZHANG X P, et al. Ultrafine biosorbent from waste oyster shell: A comparative study of congo red and methylene blue adsorption[J]. Bioresource Technology Reports, 2022, 19: 101124. DOI: 10.1016/j.biteb.2022.101124.

[41] 王亚会,高文元,唐玲,等. 高能球磨时间对牡蛎贝壳粉体性能与结构的影响[J]. 大连工业大学学报, 2017, 36(4): 295-299.
WANG Y H, GAO W Y, TANG L, et al. The effect of high energy ball milling time on the structure and properties of oyster shell powder[J]. Journal of Dalian Polytechnic University, 2017, 36(4): 295-299.

[42] HENRIQUE D C, QUITELA D U, IDE A H, et al. Mollusk shells as adsorbent for removal of endocrine disruptor in different water matrix [J]. Journal of Environmental Chemical Engineering, 2021, 9(4): 105704.

[43] CHAUAHARI R R, BHONGALE C J. Simultaneous TG-FTIR analyses on molluscan shells: Characterization and thermal stability of organic-inorganic components[J]. Chemical Geology, 2022, 611: 121132. DOI: 10.1016/j.chemgeo.2022.121132.

[44] MURPHY J N, SCHNEIDER C L M, HAWBOLDT K, et al. Hard to soft: Biogenic absorbent sponge-like material from waste mussel shells[J]. Matter, 2020, 3(6): 2029-2041.

[45] THAKUR S, SINGH S, PAL B. Superior adsorption removal of dye and high catalytic activity for transesterification reaction displayed by crystalline CaO nanocubes extracted from mollusc shells[J]. Fuel Processing Technology, 2021, 213: 106707. DOI: 10.1016/j.fuproc.2020.106707.

[46] CHENG M Q, HU L, PAN P P, et al. Abalone shell-based magnetic macroporous hydroxyapatite microspheres with good reusability for efficient dye adsorption[J]. Colloids and Surfaces B: Biointerfaces, 2023, 231: 113561. DOI: 10.1016/j.colsurfb.2023.113561.

[47] JO Y H, JEONG W G, PARK J, et al. Partially calcined $CaCO_3$ for remediating multi-heavy metals-contaminated groundwater [J]. Chemical Engineering Journal, 2023, 471: 144652. DOI: 10.1016/j.cej.2023.144652.

[48] HO H J, TAKAHASHI M, IIZUKA A. Simultaneous removal of fluoride and phosphate from semiconductor wastewater via chemical precipitation of calcium fluoride and hydroxyapatite using byproduct of recycled aggregate[J]. Chemosphere, 2023, 340: 139875. DOI: 10.1016/j.chemosphere.2023.139875.

[49] 张琢,王梅,任杰,等. 贝壳粉对污染土壤中Pb、Zn、Cd的稳定化作用[J]. 环境污染与防治, 2016, 38(1): 14-18.
ZHANG Z, WANG M, REN J, et al. Effects of sea shell powder on the stabilization of Pb, Zn and Cd in contaminated soil[J]. Environmental pollution and prevention, 2016, 38(1): 14-18.

[50] LIU G, ZHANG R X, GU Z L, et al. Evaluation of calcined coal slime in binary and ternary ordinary portland cement composites: The role of calcination temperature [J]. Construction and Building Materials, 2023, 403: 133091. DOI: 10.1016/j.conbuildmat.2023.133091.

[51] SHARIFFUDDIN J H, YEAN W C, GHAZALI S S. Investigating the catalytic properties of calcium compounds derived from marine based shell waste for wastewater treatment [J]. Materials Today: Proceedings, 2018, 5(10): 21718-21727.

[52] WANG Z, XIA L P, CHEN J L, et al. Fine Characterization of natural SiO_2-doped catalyst derived from mussel shell with potential photocatalytic performance for organic dyes [J]. Catalysts, 2020, 10(10): 1130.

[53] WANG W, LIN F, YAN B, et al. The role of seashell wastes in TiO_2/seashell composites: Photocatalytic degradation of methylene blue dye under sunlight[J]. Environmental Research, 2020, 188: 109831. DOI: 10.1016/j.envres.2020.109831.

[54] YANG Y, ZHANG C, HUANG D, et al. Boron nitride quantum dots decorated ultrathin porous g-C_3N_4: Intensified exciton dissociation and charge transfer for promoting visible-light-driven molecular oxygen activation [J]. Applied Catalysis B: Environmental, 2019, 245: 87-99. DOI: 10.1016/j.apcatb.2018.12.049.

[55] EHAL J C C, MARCHADESCH A N R, ORO R A G, et al. Fenton-like degradation of diclofenac in water using iron-impregnated mussel shell biochar (Fe@MSBC)[J]. Materials Today: Proceedings, 2023. DOI: 10.1016/j.matpr.2023.04.158.

[56] 薛瑶佳,黄文豪,白书立,等. 染料废水的贝壳粉负载铁-钴双金属催化降解[J]. 印染, 2021, 47(7): 63-66, 71.

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LIU J M, XU B, ZHU W Q, et al. Analysis of trace I-DBPs in drinking water by SPME-GC/MS [J]. Water & Wastewater Engineering, 2015, 41(8): 9-15.

[32] 王存进, 代文彬, 钟志雄. 离子色谱测定饮用水中一碘乙酸和二碘乙酸[J]. 化学分析计量, 2020, 29(4): 62-66.
WANG C J, DAI W B, ZHONG Z X. Simultaneous determination of monoiodoacetic acid and diiodoacetic acid in drinking water by ion chromatography [J]. Chemical Analysis and Meterage, 2020, 29(4): 62-66.

[33] ZHAO X D, SALHI E, LIU H L, et al. Kinetic and mechanistic aspects of the reactions of iodide and hypoiodous acid with permanganate: Oxidation and disproportionations [J]. Environmental Science & Technology, 2016, 50(8): 4358-4365.

[34] JONES D B, SAGLAM A, TRIGER A, et al. I-THM Formation and speciation: Preformed monochloramine versus prechlorination followed by ammonia addition [J]. Environmental Science & Technology, 2011, 45: 10429-10437. DOI: 10.1021/es202745t.

[35] HUA G H, RECKHOW D A, KIM J. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination [J]. Environmental Science & Technology, 2006, 40(9): 3050-3056.

[36] HUA G, RECKHOW D A. Characterization of disinfection byproduct precursors based on hydrophobicit and molecular size [J]. Environmental Science & Technology, 2007, 41(9): 3309-3315.

[37] 李明阳. 不同消毒方式和工艺条件对碘代三卤甲烷生成的影响[J]. 净水技术, 2018, 37(2): 42-52.
LI M Y. Effect of different disinfection methods and process conditions on formation of I-THMs [J]. Water Purification Technologys, 2018, 37(2): 45-52.

[38] BICHSEL Y, GUNTEN U V. Oxidation of iodide and hypoiodous acid in the disinfection of natural waters [J]. Environmental Science & Technology, 1999, 33: 4040-4045. DOI: 10.1021/es990336c.

[39] GILCA A F, TEODOSIU C, FIORE S, et al. Emerging disinfection byproducts: A review on their occurrence and control in drinking water treatment processes [J]. Chemosphere, 2020, 259: 127476. DOI: 10.1016/j.chemosphere.2020.127476.

[40] ALLARD S, NOTTLE C E, CHAN A, et al. Ozonation of iodide-containing waters: Selective oxidation of iodide to iodate with simultaneous minimization of bromate and I-THMss [J]. Water Research, 2013, 47(6): 1953-1960.

[41] KORMOS J L, SCHULZ M, TERNES T A. Occurrence of iodinated X-ray contrast media and their biotransformation products in the urban water cycle [J]. Environmental Science & Technology, 2011, 45(20): 8723-8732.

[42] LIU W, ZHANG Z L, YANG X, et al. Effects of UV irradiation and UV/chlorine co-exposure on natural organic matter in water [J]. Science of the Total Environment, 2012, 414: 576-584. DOI: 10.1016/j.scitotenv.2011.11.031.

(上接第 25 页)

XUE Y J, HUANG W H, BAI S L, et al. Degradation of dye wastewater by Fe-Co bimetal oxide supported activated shell powder [J]. China Dyeing & Finishing, 2021, 47(7): 63-66, 71.

[57] CAO J Z, JU P, CHEN Z Y, et al. Trash to treasure: Green synthesis of novel Ag_2O/Ag_2CO_3 Z-scheme heterojunctions with highly efficient photocatalytic activities derived from waste mussel shells [J]. Chemical Engineering Journal, 2023, 454: 140259. DOI: 10.1016/j.cej.2022.140259.

[58] 陈钰, 刘梅, 郭靖, 等. 改性贻贝壳固定化微生物降解海洋溢油研究[J]. 浙江海洋大学学报(自然科学版), 2022, 41(6): 529-535.
CHEN Y, LIU M, GUO J, et al. Study on marine spilled oil degradation by modified mussel shell immobilized microorganisms [J]. Journal of Zhejiang Ocean University (Natural Science), 2022, 41(6): 529-535.

[59] LU X Y, ZHANG M L, REN Y X, et al. Design of Co-MOF nanosheets for efficient adsorption and photocatalytic degradation of organic dyes [J]. Journal of Molecular Structure, 2023, 1288: 135796. DOI: 10.1016/j.molstruc.2023.135796.