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新型吸附材料在处理含铀废水中的研究进展

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摘要: 如何处理核电、采矿过程中对水体环境产生的放射性铀污染是一个亟待解决的问题。吸附材料因其比表面积大、成本低、制备简单与吸附容量高等优点, 成为处理含铀废水的一种主要方式。首先梳理了现有处理含铀废水方法以及不同吸附材料的优缺点; 阐述了吸附现象、吸附机理等吸附材料理论基础; 重点分析了新型磁性纳米、偕胺肟、高分子纤维、新型金属有机骨架材料、生物炭、微生物等新型吸附材料的研究现状, 从材料特质、吸附性能、应用潜力等方面归纳了这些材料的吸附特性; 最后从贴近应用、避免二次污染、关注去污性能等角度展望了处理去铀废水的研究方向。简述了新型吸附材料对于含铀废水的去除, 并展望了未来吸附材料的发展方向。

关键词: 新型吸附材料; 含铀废水; 环境

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Research Progress of New Adsorption Materials in Treatment of Wastewater Containing Uranium

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Abstract: How to deal with radioactive uranium contamination in the water environment from nuclear power and mining processes is an urgent problem to be solved. Adsorption materials have become a major way to treat uranium-containing wastewater because of their large specific surface area, low cost, simple preparation and high adsorption capacity. This paper firstly compares the advantages and disadvantages of existing methods and different adsorption materials for the treatment of uranium-containing wastewater; secondly, the theoretical basis of adsorption materials such as adsorption phenomena and adsorption mechanisms are described; then the current research status of new adsorption materials such as new magnetic nano-, kaamine oxime, polymer fibers, new metal-organic skeletal materials, biochar, microorganisms, etc. is analyzed, and the adsorption properties of these materials are summarized

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in terms of material characteristics, adsorption performance and application potential; finally, the adsorption properties of these materials are summarized in terms of their specificity, adsorption performance and application potential. Finally, the research directions for the treatment of uranium-depleted wastewater are presented from the perspectives of application, avoiding secondary pollution, and focusing on decontamination performance. The new adsorbent materials for the removal of uranium-containing wastewater are briefly described, and the future directions of adsorbent materials are prospected.

Key words: new adsorbent materials; uranium-containing wastewater; environment

各类放射性废物中,铀元素是典型的 α 系元素,广泛存在于污染地区的地面、地表水与地下水中^[1]。污染源主要包括核废料丢弃与核泄漏、采矿选冶或磷肥使用等,其中核能产生的放射性废水包括含铀废水^[2];铀矿山开采过程和水冶过程同样排放含铀废水;农业中使用的磷肥也是常被忽略的铀污染源,以上原因导致周围生态环境受到含铀废水的污染^[3-7]。根据铀废水特有的放射性,美国国家标准规定铀废水中铀的最大排放浓度为 $30 \mu\text{g/L}$,世界卫生组织建议废水中铀的浓度要低于 $2 \mu\text{g/L}$,我国排放标准为 $50 \mu\text{g/L}$ ^[8],为世界卫生组织标准的 25 倍,我国的排放标准远高于美国与世界卫生组织标准。实际上,我国铀矿坑废水中铀浓度约为 5 mg/L ,磷肥的磷酸岩产生的放射性铀浓度通常可达 $2 \sim 200 \text{ mg/kg}$ ^[3],均远超国家标准。环境的轻微改变可导致铀在自然水体中溶解、迁移与沉淀,并最终危及食物链甚至整个生态系统的安全,对人类与动植物生命造成严重威胁。铀废水本身具有双重毒性特征,在一定时间范围内可以对人类健康和环境造成损害和危害^[9]。所以寻找有效的方法处理含铀

废水显得尤为重要。

目前,含铀废水的主要处理方法包括化学沉淀法^[9-11]、萃取法^[12-13]、离子交换法^[14-15]、膜处理法^[16]、植物修复法^[17-18]、吸附法^[19]等,其中化学沉淀法产生大量污泥,造成环境二次污染;萃取法处理废水成本较高,且需大量有机试剂,容易导致二次污染;离子交换法效率较低;膜处理法对操作要求过于精细;植物修复法容易受到外部条件干扰;吸附法具备材料来源广泛易得、制备较易、选择性优异、处理成本低及效果较好等优点,然而传统吸附剂存在二次污染、吸附容量低、选择性差等缺点,令吸附材料在实际工程上较难应用,制约其发展与应用前景等,不同方法优缺点总结如表 1 所示。

上述含铀废水处理方法大都存在成本高、环境不友好、局限性等缺点。相比之下,新型吸附材料具有成本低、环境友好、无二次污染、可多次重复利用、处理效果好、稳定性高等优势,为处理含铀废水开辟了新方式。根据新型含铀废水吸附材料相关国内外文献,梳理总结其优势与局限如表 2 所示,为研究吸附材料提供参考依据。

表 1 现有处理含铀废水方法的优势与劣势

Table 1 Advantages and disadvantages of existing methods for treating uranium-containing wastewater

Removal method	Advantage	Disadvantage
Chemical precipitation	Simple, low cost, faster processing speed	The settled sludge is easy to cause secondary pollution of the environment
Extraction method	Low energy consumption	Prone to secondary pollution
Ion exchange method	Good removal effect	Higher price
Membrane treatment	High separation selectivity	High cost and complicated operation
Phytoremediation	Less secondary pollution	Susceptible to external influences
Adsorption method	Simple operation and low cost	Adsorption material selectivity needs to be improved

表 2 吸附材料种类与优缺点

Table 2 Types and advantages and disadvantages of adsorbent materials

Adsorbent type	Features	Defect	Ref.
Microbial adsorption material	Low cost and environmentally friendly	Easy to be disturbed by the surrounding environment	[20]
Nano adsorption material	Sufficient adsorption sites and larger comparative area	Currently limited to laboratories	[21]
Inorganic adsorbent material	Simple preparation, low cost, high specific surface area	Solid-liquid separation is difficult, and it is not easy to recycle and reuse	[22]
Polymer adsorbent material	Good stability, easy production, manual design	Expensive, expensive manpower and material resources	[23]

1 理论基础

1.1 吸附现象

吸附剂与吸附质之间的吸附现象普遍存在。当吸附剂与吸附质之间混合均匀且有效接触时,吸附质会在吸附剂中积累,这种富集现象即为吸附。根据吸附的作用力不同,吸附反应一般可分为三种不同类型:物理吸附、化学吸附和离子交换。

物理吸附指在吸附过程中分子间的吸附,受温度、浓度和吸附剂性质等不同因素的影响。化学吸附指当吸附剂与吸附质之间发生交换作用时,由于电子转移形成化学键的吸附作用。因为化学成键比较稳定,所以大部分吸附反应以化学吸附为主,目前吸附位点机理已经成为热点研究方向。离子交换指发生静电引力,并发生置换反应的吸附,在此类吸附中,吸附剂表面某些带相反电荷的离子将要与吸附质离子发生交换作用,因而被富集吸附。图1为吸附剂表面与内部原子的受力方式,由图1可以看出,吸附剂表面的原子没有被其他吸附剂原子完全包围,所以表面可以吸引吸附质。

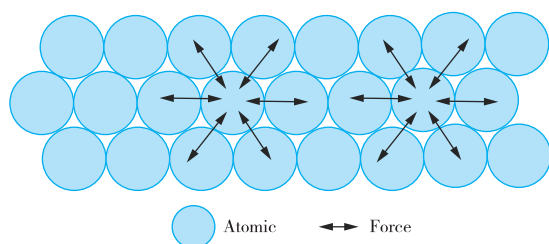


图1 吸附剂表面与内部原子受力方式^[24]

Fig. 1 The way of force on the surface and internal atoms of the adsorbent^[24]

1.2 吸附机理

广义吸附机理是由于吸附剂内部分子与吸附质分子间存在吸引力,吸附剂表面分子相对于外部作用力未能达到应有平衡,导致吸附剂表面分子受力不均存在表面能。根据化工原理热力学第二定律推断,吸附作用会引起表面能降低,原因为,吸附质到达吸附剂附近时,受到界面拉扯作用,吸附剂表面能降低,因此广义的吸附机理实质是一种传质过程^[25]。铈酰离子在吸附剂上一般会发发生氧化还原、离子交换、溶解沉降、配位解离、吸附解析与表面络合等过程。HUI等^[26]研究了 UO_2^{2+} 在 $\alpha\text{-SiO}_2(001)$ 的吸附机理, UO_2^{2+} 与吸附剂接触形成内球复合物而被去除。ZHANG等^[27]研究发现 UO_2^{2+} 在吸附剂表面会形成双齿配位作用,

并且发现O吸附位点占据主要作用,而羟基的作用大大减少,据此推断氢键的形成对于 UO_2^{2+} 的吸附起主要作用。OU等^[28]发现—OH基团的再分布和带负电荷表面区域的出现对 UO_2^{2+} 的吸附占据主要作用, UO_2^{2+} 主要与—OH基团发生配位作用。

2 研究现状

2.1 新型磁性纳米吸附材料

新型磁性纳米吸附材料自身具有易于回收利用、高吸附容量、超顺磁性等特点^[29],已成为科学家和学者研究热点之一,并在环境、磁共振成像、催化化学等领域得到广泛使用^[30]。

Fe_3O_4 具有易于固液分离、比表面积大等优点,成为研究最广泛的磁性纳米材料^[31-32]。早期的研究发现,单一的 Fe_3O_4 磁性纳米材料对 UO_2^{2+} 的吸附性能不佳,DAS等^[33]在2~50 mg/L含铈废水中进行吸附实验,发现,单一的 Fe_3O_4 对废水的吸附容量仅为5 mg/g,研究机理后发现,单一的 Fe_3O_4 容易在水中发生团聚现象,加之表面官能团较少,影响其对污染物的吸附能力^[34]。为此,后期开始把研究重点放在对 Fe_3O_4 进行改性上,ZHOU等^[35]将EPPTMS(3-丙基三甲氧基硅烷)与正硅酸乙酯作为材料的改性试剂, Fe_3O_4 作为基底材料,改性试剂与 Fe_3O_4 发生共聚反应,成功制备出新型磁性纳米材料EPPTMS-MN,材料制作过程如图2所示,在pH=6,温度为30℃,吸附反应时间为1 h条件下,对低浓度含铈废水的吸附效率达到98%,对浓度为20 mg/L含铈废水的吸附效率为97.6%。此外还发现,该材料以单层化学吸附为主要机理,同时伴随多层吸附与孔内扩散。DING等^[36]合成了Fungus- Fe_3O_4 复合磁性吸附材料,并将其用于含铈废水处理,该材料改善了 Fe_3O_4 的稳定性与分散性,并可以重复利用、多次吸附,相应机理如图3所示。YIN等^[37]成功制备出了核壳(Coll-shell Fe_3O_4 @TNS)与蛋黄壳磁性钛酸盐纳米片(Yolk-shell Fe_3O_4 @TNS)吸附材料,制备工艺图如图4所示,一系列试验结果表明,核壳 Fe_3O_4 @TNS在pH=5.0时,利用L吸附模型进行拟合,得到六价铈的最大吸附容量为68.59 mg/g,试验发现,蛋黄壳 Fe_3O_4 @TN的最大吸附容量大约是核壳材料的1.2倍,达到了82.85 mg/g,原因为后者具有较大的比表面积、较大的空隙空间、可交换的活性位点等优点。CHEN等^[38]通过试验发现,利用螯合反应将CFA与 Fe_3O_4 结合后,其对含铈酰离子废水的吸附容量高达

328 mg/g, 利用等温吸附方程对该吸附进行拟合, 拟合发现该吸附更符合 L 模型。因此, 吸附主要由化学吸附与单层吸附所控制, XPS 表征分析表明, Fe—OH、Fe(II)、Fe(III)、Fe—O 为该材料主要吸附的官能团, 相应吸附原理如图 5 所示。

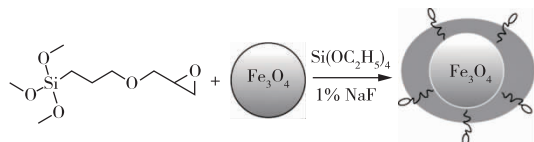


图 2 EPPTMS-MN 制备示意图^[35]

Fig. 2 Schematic diagram of preparation of EPPTMS-MN^[35]

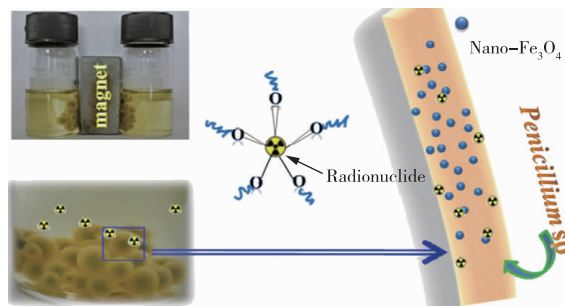


图 3 Fungus-Fe₃O₄ 对铀的吸附机理图^[36]

Fig. 3 Diagram of the adsorption mechanism of Fungus-Fe₃O₄ on uranium^[36]

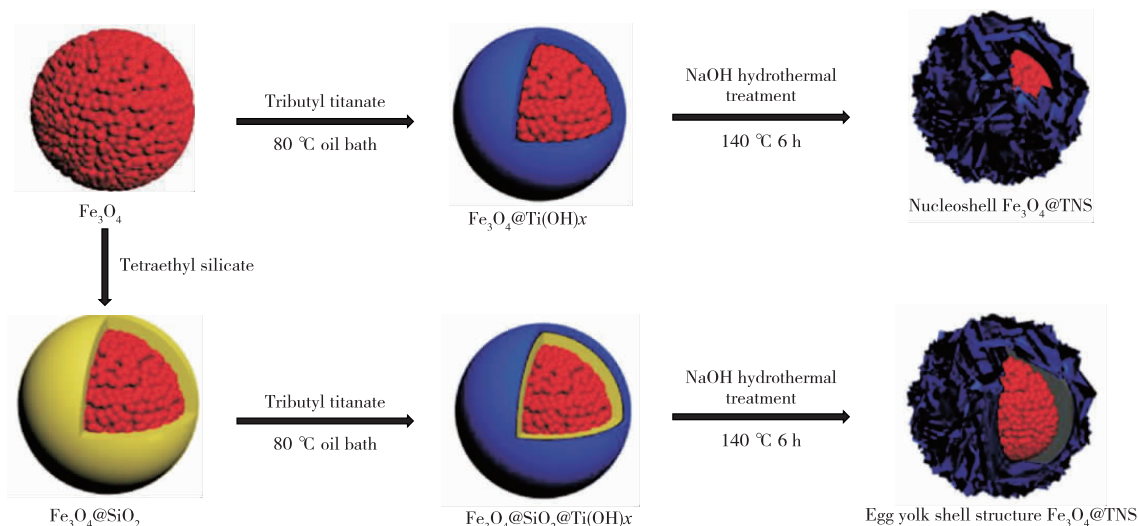


图 4 核壳及蛋黄壳磁性纳米粒子的合成工艺图^[37]

Fig. 4 Synthesis process diagram of core-shell and egg-yolk-shell magnetic nanoparticles^[37]

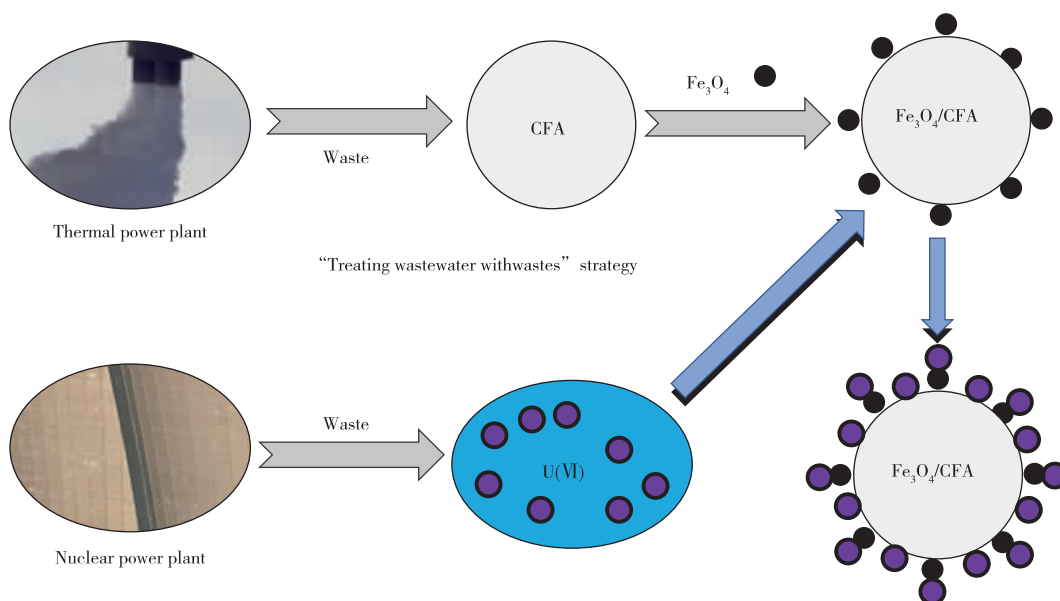


图 5 Fe₃O₄/CFA 对铀的吸附原理图^[38]

Fig. 5 Schematic diagram of the adsorption of uranium on Fe₃O₄/CFA^[38]

相比传统的吸附剂,新型磁性纳米材料具有磁响应性、分散性、表面效应、尺寸小、比表面积大、易于高效回收等优点,因此,磁性纳米材料是一种具有较大应用潜力的吸附材料^[31]。

2.2 偕胺肟吸附材料

偕胺肟吸附材料存在形式主要包括树脂型、纤维型以及新型无机固体载体型等,偕胺肟配体体 $[-C(NO_2)NH_2](AO)$ 可与铈酰离子形成有效配位,偕胺肟具有酸、碱两性官能团,具有较好的金属离子捕获性能,引起许多学者对其开展了详尽的应用研究。

20 世纪 80 年代,WITTE 等^[39]通过 X 射线表征研究,首次解释了铈酰偕胺肟配合物的配位机理,即偕胺肟上的 O_2 通过 0.25 的配位比在赤道平面上与铈结合。随后该学者发现胺和肟也可以双齿方式结合铈酰^[40]。UKOVIC 等^[41]利用 DFT 与晶体学研究配位机理,研究结论为过 η^2 配位方式最为稳定。我国学者研究发现,当铈酰离子与偕胺肟配位比为 1:2 时最稳定,偕胺肟可由中性与负离子状态与铈酰离子配位^[42]。WANG 等^[43]制备出了亲水性好、螯合位点多的聚酰亚胺二肟纳米纤维(PIDO-NFs)吸附材料,并对模拟含铈废水进行吸附,吸附容量高达 951 mg/g。MA 等^[44]研究出了一种基于偕胺肟(PAO)水凝胶的简便快速方法,对水中铈的吸附容量可达 $(1\,279 \pm 14.5)$ mg/g。王宁等利用吹吹旋法制备出了蒙脱石复合聚丙烯的多孔偕胺肟基纳米纤维吸附剂(SMON-PAO),该材料对海水中

铈的吸附容量达到 $(1\,089.36 \pm 64.31)$ mg/g^[45]。WONGSAWAENG 等^[46]通过辐射的方法制备出了低成本的聚丙烯腈(PAN),用于吸附海水中的铈,试验发现最大吸附容量可达 32.28 mg/g。YUAN 等^[47]用自由基聚合方法制备了偕胺肟化磁性纳米材料 $Fe_3O_4/P(GMA-AA-MMA)$,在最适宜条件下该材料对铈的最大吸附容量为 200.5 mg/g,并具有较高的稳定性与铈酰离子选择性,可至少重复利用 5 次。近期,对含铈废水吸附材料偕胺肟化改性的科学研究受到国内外学者越来越多的重视,比如引入含氰基、羟基、巯基与氨基等官能团对吸附材料进行改性^[48-52],从而制备出了不同的偕胺肟吸附材料。

对偕胺肟吸附材料的合成及吸附性能研究结果表明,其对低浓度含铈废水具有选择性高等特点,可以有效用于重金属离子分离与富集,非常适合处理含铈废水。另一方面,研究力学强度高、吸附容量大、选择性多、循环利用性强的新型偕胺肟吸附材料,将会具有更高的实际应用价值。

2.3 高分子纤维吸附材料

高分子纤维对金属离子具有较好的吸附与分离特性。传统的纤维吸附材料由棉花、麻和纤维素等天然纤维材料合成与制备。随着人类科学的不断进步、化工技术的突飞猛进,纤维吸附材料逐渐采用化学纤维代替天然纤维,纤维材料目前已进入快速发展阶段,当前已经开发出了聚乙烯醇纤维、聚丙烯腈纤维等新型化工合成纤维材料,不同高分子纤维吸附材料之间的对比如表 3 所示。

表 3 几种高分子纤维的优势与劣势比较

Table 3 Compares of the advantages and disadvantages of several high-scoring fibers

Polymer fiber substrate	Advantage	Disadvantage
Polyolefin fiber	Good mechanical properties,acid and alkali resistance	Poor water solubility
Polyacrylonitrile fiber	Good adaptation to climate	Higher requirements for pH
Polyolefin fiber	Good chemical stability and strength	Poor temperature adaptation,poor thermal conductivity
Polyvinyl Alcohol Fiber	Good mechanical properties,acid and alkali resistance	Smaller requirements for temperature
Other new fibers	Has a special function	Complex synthesis and expensive

YAN 等^[53]利用以聚丙烯腈纤维为基础材料,通过交联反应使聚丙烯腈与叠氮腈环发生化学加成反应,成功制备出了新型纤维材料聚四唑纤维(PVT),PVT 对 $Cu(II)$ 、 $Cd(II)$ 、 $Ni(II)$ 、 $Zn(II)$ 的吸附容量分别为 323、278、200、175 mg/g,通过降低溶液的 pH 值,可以解析吸附剂上的重金属离子。HUANG 等^[54]利用自组装技术在聚丙烯腈纤

维(PANF)表面生成氧化锌(ZnO)纳米棒,成功制备出了 $ZnO/PANF$ 复合纤维材料,对铈酰离子的最大吸附容量可达 248.14 mg/g。CHI 等^[55]采用乙烯基膦酸制备了新型 PVA 纤维,并对模拟废水中的 $U(VI)$ 进行了吸附试验,试验结果表明,在室温与 $pH=4.5$ 情况下,对铈酰(VI)的最大吸附容量可达 32.1 mg/g。RAO 等利用聚乙烯醇纤维与

脒胺反应进行改性,并对水溶液中 Cu 离子进行了吸附试验,发现该材料具有吸附容量大、合成简单、亲水性较好等特点,吸附机理研究发现螯合作用是该材料的吸附机制^[55]。LEI 等^[56]研究了 PEI/PVC 交联纤维(PEI/PVCCF)对铂(IV)的吸附能力,热力学分析发现,该材料对于铂(IV)的吸附是自发进行的,并且具有较好的吸附效果。ZHOU 等^[57]利用聚丙烯纤维,通过接枝技术制备出 PP-g-AA 和 PP-g-AA-DETA 两类不同的纤维材料,并利用模拟含铅溶液进行了吸附试验,试验结果表明,PP-g-AA 和 PP-g-AA-DETA 对铅最大吸附容量分别为 12.2 和 25.7 mg/g。

为应对不断加深的环境污染,科学家已开发出如超细纤维、中空纤维、皮芯复合纤维等新型纤维^[58-60]。超细纤维与中空纤维扩大了传统纤维的比表面积。利用超细纤维与中空纤维作为基地材料,可增加材料的吸附位点,改善材料的流体性能,受水的阻力较小。采用两种及以上聚合物通过纤维的纵向可以制备出皮芯复合纤维。该种纤维更容易与功能基团嫁接,继而制备出新型功能化纤维吸附材料,增强该材料的发展潜力。

2.4 MOFs 新型吸附材料

新型金属有机骨架材料(metal organic frameworks)简称 MOFs,利用金属族与金属有机桥连配体作用形成杂化晶体新型材料,是近期研发的一类新型多孔吸附材料,如图 6 所示^[61]。该类材料具有易于改性、尺寸可设计、比表面积大等特点,在生物、催化、分类等领域表现出了优异的效果。

ZHANG 等^[62]通过接枝技术,将羟甲基香豆素与 Zn-MOF-74 中锌的不饱和位点发生化学反应,试验发现,该材料在 pH 为 4 时对模拟含铈废水中六价铈离子的吸附容量为 360 mg/g。WU 等^[63]利用溶剂热法成功制备出了含氧官能团的 MOFs 材料 MOF-5,试验发现当 pH 为 5 时,该材料对铈酰离子吸附容量为 237 mg/g,并在 300 s 达到吸附平衡。YANG 等^[64]通过 MOF-76 处理含铈废水,pH 为 3 时 MOF-76 对六价铈的吸附容量高达 314.5 mg/g。CARBONI 等^[65]通过有机桥连法,利用 2,5-二溴苯胺和 4-(甲氧羰基)苯基硼酸合成了 H_2L_1 和 H_2L_2 , $Zr(Cl_4)$ 分别与上述两种物质发生化学反应,制备出了多孔 MOFs 材料,并命名为

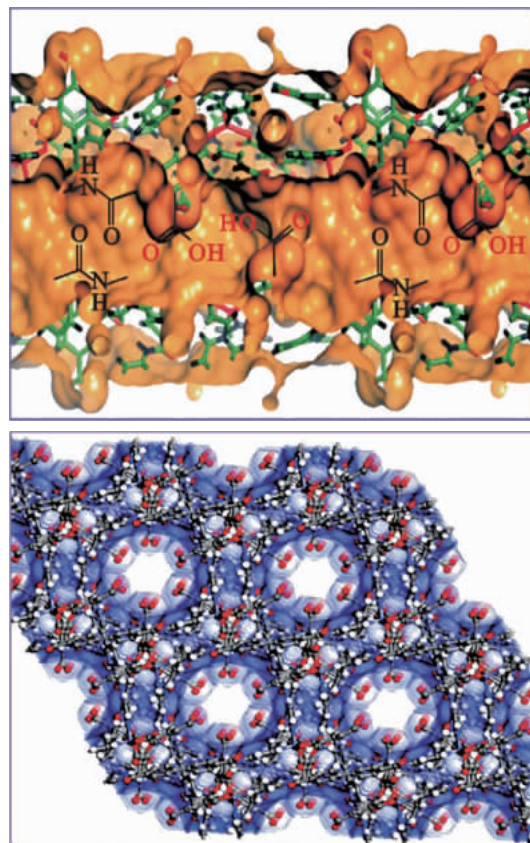


图 6 MOFs 的模拟 3D 结构图^[61]

Fig. 6 Simulated 3D structure diagram of MOFs^[61]

MOF1 和 MOF2,利用 Me_3SiBr 与 MOF2 反应成功制备出 MOF3,在水溶液 pH = 2.5 时,MOF2 和 MOF3 对水体中 UO^{2+} 最大吸附容量分别为 217.4 与 208.9 mg/g。

从以上研究可以看出,MOFs 材料在种类、结构、功能等方面不断丰富,且凭借纯度高、结晶度高、结构可控等优点,表明 MOFs 对含铈废水处理具有巨大优势,同时展现出了在该领域巨大的应用潜能。但与此同时,进一步改善材料的结构,加强稳定性仍然是未来的发展方向。

2.5 生物炭吸附材料

通过缺氧或无氧条件下将果皮、秸秆等原生生物质,历经热裂解热化学反应后制备成多孔含碳物质固体称为生物炭^[66]。生物炭除了拥有较大的孔隙度和比表面积之外,还存在稳定的芳香环片层结构,以上特点使生物炭拥有优异的吸附效果。该材料表面电荷密度较大,并且电荷呈现负电形式,有利于带正电的金属阳离子的吸附^[67]。生物炭对重金属的吸附机理如表 4 所示。

表 4 生物炭对重金属的吸附机理

Table 4 Biochar's adsorption mechanism for heavy metals

Adsorption mechanism	Mechanism explanation	Ref.
Cation- π	Conjugated aromatics on the surface of biochar. The more structure, the stronger its effect	[71]
Coordination	Biochar contains functional groups such as uranium -OH and -COOH, which can coordinate with metals	[72]
Ion exchange	There are certain ions in the synthesis of biochar, which can exchange with heavy metal ions	[73]
Electrostatic adsorption	Since biochar itself has a negative charge, it is easy to adsorb positively charged metal ions	[74]

YAKKALA 等^[68]根据温度的不同合成了水牛杂草生物炭,试验发现,700 ℃条件下生物炭会产生更大的比表面积,对铬和铅具有较好的去除效果。TAN 等^[69]通过硫代乙酰胺改性甘草渣生物炭。当 pH 为 2~6 时,对模拟含铀 1 mg/L 的废水去除率为 98.2%,最大吸附容量为 340 mg/g。AMERKHANOVA^[70]等利用松树废料混合冶金渣成功制备了生物炭,采用 H₃PO₄ 进行改性处理,改性后的生物炭产生了更多的孔隙,对 I 的去除率为 90.13%,对二价铁、二价钴、二价镍等金属离子均具有一定的去除效果。SHENG 等^[71]成功制备出了二乙烯三胺五乙酸功能化的磁性壳聚糖纳米粒子(DTPA-MCS),该吸附材料 N/O 基团的密度较大,对铀酰离子的最大吸附容量高达 178.20 mg/g。ZHOU 等^[72]通过印记分子技术制备了离子印迹磁性壳聚糖微球(IMCR),IMCR 对水体中六价铀的最高吸附容量为 187.26 mg/g,高于无印记技术 IMCR 的 26.49 mg/g。

目前,生物炭因多孔结构与表面的大量官能团,在环境治理领域发挥着越来越大的作用,可广泛应用于废水与土壤中的污染物治理。生物炭在治理环境污染的同时,又能改善土壤和节能减排,显示出广阔的应用前景。

2.6 微生物吸附材料

微生物一般包含人们所熟知的细菌、真菌、藻类等。微生物吸附重金属一般会发生生物沉淀、生物积累与生物吸附等。微生物表面含铀大量的挂能团(羧基、氨基、磷酸基、羧基),可对水中的重金属离子进行吸附^[75-77]。微生物去除水体中重金属的机理一般包括表面络合作用、离子交换作用、物理吸附、

氧化还原、无机微沉淀等。基于上述机理,微生物吸附材料可以用于重金属离子的吸附。

CHEN 等^[78]采用饱和硼酸-海藻酸钙交联固定酿酒酵母制备了吸附剂微球(PVA-SA-GO Yeast gel beads),当 pH = 5,铀的模拟废水浓度为 1~127 mg/L,固液比为 4.60 g/L,吸附时间为 120 h 时,对铀的吸附容量为 30.62 mg/L。JIANG 等^[79]采用冷冻干燥诱导自组装技术,通过壳聚糖为基底,负载小球藻,制备了壳聚糖复合气凝胶(CP/CTS),在一定温度下对模拟含铀废水吸附 7 h 后,试验测得吸附容量为 571 mg/g,分析机理发现材料中的羧基、羟基、氨基是该材料吸附的主要官能团。马佳林等^[80]采用真菌(酵母菌)、细菌(枯草芽孢杆菌)、小球藻吸附模拟废水中的铀,发现枯草芽孢杆菌吸附容量最大达到 512.50 mg/g,酵母菌吸附容量最小为 341.20 mg/g。

微生物通过自身丰富的官能团,可以对含铀废水进行高效净化处理,但是,微生物的培育较慢并且复杂,这限制了微生物材料的发展,因此,今后对于微生物吸附材料还需进一步探索与应用。

在金属冶炼、加工、开采、以及后续使用过程中经常会产生重金属的污染,会导致地表水、土壤甚至地下水受到重金属元素污染^[81-89]。铀元素具有化学毒性,还兼具放射性,一旦含铀废水流出便会对周围生态系统产生巨大影响,金属资源目前日益短缺,并且是不可再生资源,因此,对于受污染水体中某些有用金属离子的回收、提取与吸附,在环境保护与可持续发展中具有重要的现实意义。表 5 总结了不同新型吸附材料对铀吸附试验的试验结果。

表 5 不同吸附材料对铀的吸附性能

Table 5 Adsorption performance of different adsorbent materials for uranium

Adsorption material	Adsorbent	Test conditions	Adsorption capacity	Ref
New type of magnetic nano	EPPTMS-MN	pH=6, T=30℃, t=1 h	Adsorption efficiency: low concentration 98%, concentration 20 mg/L is 97.6%	[35]
	Fe ₃ O ₄ @TNS	pH=5.0	82.85 mg/g	[37]
	Combination of CFA and Fe ₃ O ₄	pH=6.0-10.0	328 mg/g	[38]
Amidoxime	PIDO-NFs	In the sea	951 mg/g	[43]
	PAO hydrogel	In the sea	1 279±14.5 mg/g	[44]
	SMON-PAO	In the sea	1 089.36±64.31 mg/g	[45]
	PAN	In the sea	32.28 mg/g	[46]
	Fe ₃ O ₄ /P(GMA-AA-MMA)	pH=4.5	200.5 mg/g	[47]
High score fiber	PVT	—	Cu(Ⅱ): 323 mg/g, Cd(Ⅱ): 278 mg/g, Ni(Ⅱ): 200 mg/g, Zn(Ⅱ): 175 mg/g	[53]
	ZnO/PANF	T=298.15 K, pH=6	248.14 mg/g	[54]
	PVA	pH=4.5, Room temperature	32.1 mg/g	[55]
	PP-g-AA/PP-g-AA-DETA	—	12.2 mg/g/25.7 mg/g	[80]
MOFs	Hydroxymethylcoumarin and Zn-MOF-74	pH=4	360 mg/g	[62]
	MOF-5	pH=5	237 mg/g	[63]
	MOF-76	pH=3	314.5 mg/g	[64]
	MOF2/MOF3	pH=2.5	217.4 mg/g/208.9 mg/g	[65]
Bio-charcoal	Modified licorice residue biochar	pH=2-6	Removal rate: 98.2%, 340 mg/g	[69]
	Pine waste mixed with metallurgical slag	—	Removal rate: 90.13%	[70]
	DTPA-MCS	T=298 K, pH=5	178.20 mg/g	[71]
	IMCR	pH=5, T=298 K, t=3 h	187.26 mg/g	[72]
Microbe	PVA-SA-GO Yeast gel beads	pH=5, concentration 1-127 mg/L, Solid-liquid ratio 4.60 g/L, t=120 h	30.62 mg/L	[77]
	CP/CTS	T=313 K, t=7 h	571 mg/g	[78]
	Yeast/Bacillus subtilis	—	341.20 mg/g/512.50 mg/g	[79]

3 结论与展望

未来吸附材料的发展应该朝着更清洁、更高效、更廉价以及能够实际应用的方向发展,具体来说,新型吸附材料处理含铀废水可以考虑从以下几个方面开展进一步研究。

1)当前大多数材料的研发工作还是以实验室为主,离实际应用还存在着不小的距离。为此,应重点研发与实验室材料相对应的工业应用工艺,探索研究工业水平吸附材料,为含铀废水处理实际应用提供技术基础。

2)处理含铀废水的吸附材料在吸附铀的同时,一般会产生金属离子或新的有毒有害物质,继而造成新的污染。为此,在新型材料研发过程中应考虑如何避免有毒有害物质的使用,确保吸附材料清洁高效。

3)实验中对铀的吸附容量表示吸附材料对铀核素的吸附能力,实际用于指示吸附剂上的活性位点

的数量,其受铀浓度、吸附剂用量、溶液 pH 值、反应温度等因素的影响。但是对于处理含铀废水而言,吸附材料的去污性能是最关键的,并用铀的去除率指标表征。为此,今后应将实验评价重点转移到考核吸附材料的去铀能力。

4)天然水体复杂多变,需要进一步探究铀酰离子与多种离子共存条件下,吸附剂对铀酰离子的选择能力。

5)未来的吸附材料对水体 pH 值与温度变化要有较强的适应能力,并且要有较高的重复利用能力,延长吸附材料的使用时长。

6)某些吸附材料在选择性、成本、制备时间、合成方法需要做进一步改进,需研发出价格低廉、制备简单,选择性好、无二次污染的新型吸附材料。

7)含铀废水吸附材料的机理研究报道较少,应增强机理研究,为新型吸附材料的研发打下必要的基础。

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