文章编号:1674-2869(2013)12-0027-08

吸油材料的研究进展

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摘　要:随着全球经济的快速发展,各国石油的需求量呈现出加剧的趋势.石油开采、油品运输等过程产生的泄露和油类废弃物对海洋和淡水生态环境造成了严重的破坏.因此,研究开发高效、清洁、循环使用的吸油材料实现油水分离成为近期研究热点.吸油材料可以分为无机吸油材料和有机吸油材料两大类.无机吸油材料因制备简单、成本低、吸油倍率高受到广泛关注;其中疏水亲油的海绵状石墨烯吸油材料因对各种油品适用性好、吸附速率快、吸油效率高、循环能力强得到较好的发展.有机类吸油材料在循环利用率、吸附速率方面明显高于无机吸油材料.有机吸油材料的研究旨在提高其吸油倍率、循环利用率和吸附速率等性能指标.针对两种吸油材料的特点,结合不同改性方法的制备工艺,开发新型、绿色、高吸油率的吸油材料是未来研究的重点.

关键词:吸附;溢油;吸油材料;研究进展
中图分类号:TQ6　　**文献标识码**:A　　**doi**:10.3969/j.issn.1674-2869.2013.12.006

0　引　言

随着石油及石油产品用量的增加,石油开采及石油产品的加工、提炼、储存、运输及使用过程中产生的泄露和各种油类废弃物对海洋生态环境和淡水生态环境造成了极大的破坏[1-3].水中的溢油、油渍不仅降低海洋和淡水环境的质量,影响食物链的循环,破坏生态平衡,还威胁着人类的健康[4].海上溢油造成的破坏具有危害程度大、波及范围广、清除困难等特点[5],要解决这些问题,迫切的需要开发出高效、耐用、清洁的吸油材料.吸油材料可归纳为无机吸油材料和有机吸油材料两种类型[6].

1　无机吸油材料

无机吸油材料又可以分为炭质吸油材料[7]、天然无机吸油材料[8]、人工合成无机吸油材料[9]和功能化改性无机吸油材料[10]4种类型.无机吸油材料来源广泛,吸油倍率高,制备方法简便、易操作,但是存在循环利用率低的问题.

1.1　炭质吸油材料

炭质吸油材料在无机吸油材料中占有很大的比例[11],它可以分为活性炭类吸油材料[12]、粉煤灰类吸油材料[13]和石墨类吸油材料等[14]几种类型.

1.1.1 *活性炭类吸油材料*　　活性炭可由木材、木屑、粉煤灰等制得,吸附油品后的活性炭可以用作固体燃料,处理较为容易,不会对环境造成破坏. Sun等[15]以商业的活性炭为基体,再用氢氧化钾和二甲基硅氧烷修饰,制得的活性炭具有很大的比表面积和孔隙率,具有很好的吸油效果,能够选择性的从水中去除多种有机物和油脂. Fan等[16]制备了一种大孔径的碳纳米管用来吸附溢油,与膨胀石墨吸附41 g/g相比,碳纳米管可以吸附69 g/g溢油,吸油倍率更高. Zhu[17]等和Gui等[18]制备的海绵状碳纳米管具有更好的吸油性能. Zhu等制备的碳纳米管吸油材料的吸油能力为92.30 g/g,传统吸附剂聚丙烯纤维织物和毛毡的吸油能力分别是7.45 g/g和6.74 g/g,新制备的吸油材料的吸附能力是传统吸油材料的15～16.5倍,吸油能力远大于两种传统的吸附剂. Gui等制备的吸油材料吸附柴油能力为56 g/g,在磁力和加热作用下可以循环1 000次,能重复使用. Kazuo[19]将粉末状的煤在400～500 ℃焦化、氧化、冷却,待加热到600～700 ℃时骤冷得到活性焦炭,再用含硅化合物进行憎水处理,得到的吸附剂具有憎水亲油性,可以很好的清除水中溢油.

活性炭除了自身改性制成吸油材料还可以与其它材料复合增加吸附能力. Klymenko N A等[20]将活性炭与生物膜结合起来制备了一种新型

收稿日期:2013-09-29
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吸附材料，并将其应用于被油品污染的自来水的处理，取得了很好的效果，经过处理的水质可以达到饮用标准. Chun 等[21]用聚苯乙烯微球和硝酸铁为基体制备了一种三维大孔 Fe/C 的纳米复合材料，具有很高的疏水性，对油品和有机溶剂有很好的吸附效果，而且有很好的循环性. Chen 等[22]用三氧化二铁、镍、钴与碳结合制备了一种超轻的疏水亲油性材料，在 400 ℃时将金属与碳接枝到聚氨酯上，发现它们会形成一种中空的管状结构，管状结构的大小可以通过丙烯酸或金属阳离子的含量来调节，制备的材料吸油倍率可达到 100 g/g. Bi 等[23]将碳纤维和未加工的棉花制备成气凝胶作为吸油材料，通过实验发现它对菜籽油、橄榄油、泵油等油品和甲苯、氯仿等有机物有很好的吸附效果，其中对泵油吸附效果为自身重量的 192 倍，对氯仿的吸附效果为 115 g/g，而且能多次循环利用.

活性炭具有良好的吸附特性和稳定的化学性质，既能耐强酸、强碱，又能经受水浸、高温、高压作用. Muhammad 等[24]将石墨烯用硫酸、盐酸等酸化得到一种新的吸油材料，并且测定了容积密度、空隙体积和碳氧比、原油粘度对其吸附量的影响，测定得到吸油材料的吸附量为 131 g/g. 徐静莉等[25]利用活性炭的大的比表面积来吸附含油废水中的 *COD*，发现粉炭对 *COD* 的去除效果最好，当吸附时间为 50 min，pH 值为 7，活性炭用量为 6 g的条件下，*COD* 去除率大于 65%.

1.1.2 *粉煤灰类吸油材料* 粉煤灰不仅可以用来制成活性炭作为吸油材料，其本身经过改性也具有很好的吸油性能[26]，粉煤灰改性后制得的吸油材料对油品的清除有较好效果. 姚乐[27]用聚二甲基二烯丙基氯化铵对粉煤灰进行改性，并将改性后的粉煤灰在含油废水中进行吸附测试，结果表明吸附时间为 90 min，废水 pH 值为 10，改性粉煤灰用量为 100 g/L 时改性粉煤灰除油效果最佳，去除率为 96%. Shashwat 等[28]将粉煤灰用阳离子表面活性剂十六烷基三甲基溴化铵进行改性，发现它能有效的吸附风化的原油. Tamilselvan 等[29]将粉煤灰通过化学改性改变了其亲水性，先通过碱处理，再在其表面增加疏水性官能团改变亲水性，制备成一种疏水亲油的吸油材料，吸油能力是未改性材料的 5 倍. Karakasi 等[30]将工业副产品高钙粉煤灰制备了吸油材料，用吸油材料对燃油、轻循环油和伊朗轻质原油进行吸附测试，同时测试了时间、温度、吸附剂与油品的质量比和溶液浓度等与吸附量的关系，发现了吸油材料的吸附特性.

除了直接将粉煤灰改性制得吸油效果较好的材料外，也可以将粉煤灰和其它材料复合以增加其吸附能力. Kolemen 等[31]用粉煤灰、膨润土和糖蜜在 30 MPa 的压力下造粒制备吸附剂，发现 10 g 粉煤灰和 0.25 mL 糖蜜与膨润土反应 2.5 h 制备的吸附剂吸附效果最好，对含油废水的去除率为 90%. 郝志涛等[32]的研究结果表明在搅拌时间为 15 min，转速为 300 r/min，pH 值为 7.2～7.8，灰水比为 1∶50 时，粉煤灰对采油废水中的石油类和 COD 去除效果最佳，去除率分别为 70%～80% 和 20%左右. Liu 等[33]以三元乙丙橡胶为基质，粉煤灰为填料，过氧化二异丙苯为催化剂，制备了一种吸油材料，结果表明过氧化二异丙苯为 2%(质量分数)，粉煤灰含量为 25%(质量分数)时，制备的吸油材料的吸附性能最好.

1.1.3 *石墨类吸油材料* 石墨类吸油材料通常包括两种，一种是石墨烯类吸油材料，另一种是膨胀石墨类吸油材料.

Nguyen 等[34]制备了一种超疏水亲油的海绵状石墨烯，它能高效的吸收油类和有机溶剂，其吸油能力最高为 165 g/g，且有很好的循环能力. Bi 等[35]制备的海绵状石墨烯具有很高的比表面积，形状可塑性高，除了能高效的吸收石油产品和脂肪类物质，对有毒溶剂甲苯、氯仿等也有较好的吸附能力，它对氯仿的吸收能力为 80 g/g，循环 10 次后仍然有很好的吸附效果. He 等[36]人用单项冻结干燥、无方向冷冻干燥和空气冷冻干燥技术制备具有疏水性的氧化石墨烯泡沫，它对汽油、柴油、泵油和润滑油等的吸附能力均高于 100 g/g，对于橄榄油的吸附能力高达 122 g/g. Dong 等[37]在镍的催化下用两步化学气相沉积法合成了三维的石墨烯混合泡沫，通过测试证明它对机油等多种油品和甲苯等有机溶剂都有较好的吸附效果.

王淑钊等[38]选用氧化插层法制备了膨胀石墨，测定了膨胀体积对柴油饱和吸附量的影响，研究表明膨胀石墨的膨胀体积越大，对柴油的饱和吸附量越大，最高可达 54 g/g. 庞秀言等[39]研究了膨胀石墨对不同黏度油类的吸附量大小和膨胀容积对吸附量的影响，发现吸附量随吸附质的黏度增大而增加，吸附量与膨胀石墨的膨胀容积呈正相关性. Wang 等[40]用柠檬酸溶胶凝胶法制备了一种磁性膨胀石墨，研究发现有磁性的膨胀石墨比普通的膨胀石墨来说孔隙结构更加明显，磁性膨胀石墨对机油和原油的吸附率为 48.93 g/g 和 42.75 g/g，相较于普通膨胀石墨的 41.46 g/g 和

40.46 g/g，吸油率提高了 18.01%和 5.65%.

1.2　天然无机吸附材料

现在研究的天然无机吸油材料大多数是将矿物粘土如沸石、膨润土、蛭石等经过改性或者将其与其他物质复合得到[41]. Tina 等[42]选用一种疏水亲脂的矿物粉末碳酸钙作为吸附剂从油水混合物中吸附溢油，发现吸附效果较好. Shavandi 等[43]采用天然沸石从棕榈油厂废水中吸附剩余的残渣油，并且对 pH、吸附剂的剂量、搅拌速率、接触时间等影响因素进行了探讨.

Flávia 等[44]用化学气相沉积法将碳纳米管和碳纳米纤维沉积到膨胀蛭石表面，制备了一种高疏水性低密度的吸油材料，这种材料具有“海绵结构”，可以吸附自身 6 倍重量的油品. Miguel 等[45]将甘油在膨胀蛭石表面进行处理制备了一种新型的吸油材料，对柴油等油品具有很好的吸附效果. Zhao 等[46]用插层法将石墨插入蛭石内制备一种新的吸油材料，制备的材料具有多孔的结构，未改性前蛭石对柴油的吸油能力为 26.7 g/g，改性后吸油效果为 70.6 g/g，且具有良好的循环性.

Dikla 等[47]通过研究发现滑石对食用油的吸附能力强于海泡石，海泡石强于蒙脱石，但是海泡石对油品的吸附速度更快，清除相同量的溢油，海泡石清除完时滑石清除了 60%左右，而蒙脱石清除了 45%，并且发现通过热处理，海泡石的吸油率会提高.

1.3　功能化改性无机吸附材料

以一种天然无机材料为基质，对其表面进行功能化制得的吸油材料称为功能化改性无机吸附材料[48]. 马希璐等[49]介绍了以无机材料硅胶为基质，对其表面进行有机功能化，制备出针对某种组分具有选择性吸附性能的吸附材料. Barbey[50]将具有菱面体晶体结构和含水量质量分数 0.1%～1.6%的碳酸钙用微波加热至 100～145 ℃，加热 60～90 min制得吸油效果良好的吸油材料.

1.4　人工合成无机吸附材料

人工合成无机吸附剂主要是指由铝、铁等金属的化合物制备的吸附剂及一些磁性物质[51].

Chi 等人[52]证明了氟的金属有机框架(FMOFs)是高度疏水性的多孔材料，在疏水性和毛细管作用下能够很好的与碳氢化合物结合，具有高吸油倍率，特别是对 C6～C8 的油品有很好的吸附效果，在清除溢油方面起到很好的作用. Hu 等[53]利用等离子体诱导嫁接技术将 β-环糊精接枝到多壁碳纳米管铁氧化合物上得到磁性碳纳米管复合材料，并将复合材料用于清除水中无机和有机污染物. 研究结果表明制备的复合材料对 1-酚萘的吸附量达到 57.47 mg/g. Fernando 等[54]利用聚合物醇酸树脂和磁赤铁矿制备了一种磁性纳米复合材料，这种材料被用于清除水中溢油，可以清除 8 g/g.

2　有机吸油材料

一般来讲，有机吸油材料可以分为天然或天然改性的有机吸油材料[55]和人工合成的有机吸油材料两类[56]. 有机吸油材料相较于无机吸油材料来说吸油速率快，循环利用率好，但是合成较为复杂，还不能普遍单独的用于溢油的清理，一般将其与其他方法或者无机吸油材料一起处理溢油事故.

2.1　天然或天然改性的有机吸油材料

天然有机改性吸油材料已经在水上溢油回收和含油废水处理等方面得到了应用[57]，一般是采用将农产品的废弃物改性制备吸油材料. 天然有机物高分子往往含有亲水基，目前很多研究多集中在提高它们的疏水性上.

Hussein M 等[58]将甘蔗渣在 300 ℃下进行碳化 2 h 处理，发现处理后的蔗渣对重油、低粘度油水、高粘度油都有很好的吸附能力，处理后的蔗渣对汽油和柴油的最高吸油倍率分别为 23 g/g 和 25 g/g，并能循环使用，也可自然降解. Bayat 等[59]以稻壳和蔗渣为原料制备出疏水的吸油材料，并将制备的材料与商业用聚丙烯相比较，得到的结果发现稻壳和蔗渣的吸油率较商业用吸附剂更高，且稻壳和蔗渣作为农作物废弃物，来源广泛，能够自然降解. Teik 等[60]用木棉制备吸油材料，并将用木棉制备的吸油材料与商业用吸油材料聚丙烯比较，发现用木棉制备的新材料对柴油、液压用油和机油的吸油倍率分别为 36、43 g/g 和 45 g/g. 同时，用木棉制备的吸油材料还有很好的疏水性和保油性，能够循环利用. Suni 等[61]研究了羊胡子草纤维、羊胡子草毡片对几种油品的吸收倍率和吸收速率，并把它们同商业吸油材料作比较，发现羊胡子草制备的吸油材料吸收石油量大约是商业吸油材料的 2～3 倍，速度也是它的2～3 倍，在测试中羊胡子草纤维几乎不吸水，去除水面柴油时效率超过了 99%，吸附剂吸附量为自身重量的 20 倍，而且具有生物降解性，是一种很好的吸油材料. Kathiresan 等[62]以香蕉树干的纤维为原料经过油酸、硬脂酸、蓖麻油和棕榈油改性后用于溢油回收，发现在硫酸催化作用下，经过油酸改性后的橡胶树干纤维的吸油效果最好，对机油的吸

收倍率最高,并且具有很好的保油性,能够多次循环使用.

Sun 等[63]通过油酸酰氯和羧甲基壳聚糖反应制备了一种改性壳聚糖作为水面溢油吸油材料,用于处理采油过程中产生的废水和回收水面上的浮油,制备的吸油材料吸油速率明显增加且能多次循环使用. Juuso 等[64]用真空冷冻干燥技术出一种高孔隙率的纳米纤维素气凝胶,在二氧化钛作用下纤维素水凝胶具有疏水亲油性,可以有选择的吸附油品,吸附油品后的材料通过清洗或者灼烧表面可以清除表面的油品,能够多次循环利用.

2.2 人工合成的有机吸油材料

合成有机吸油材料是 20 世纪 60 年代后期诞生的一种新型吸油材料[65],主要是指高吸油树脂[66].

John 等[67]用 $(CH_3O)_4Si$ 和 $CF_3(CH_2)_2Si(OCH_3)_3$ 在甲醇中用氨催化再进行超临界萃取制得一种疏水气凝胶,经过测试得到其吸附的油品质量可以达到自身的 237 倍,但是制备比较昂贵. Deniz 等[68]将丁基橡胶用一氯化硫硫化,得到一种多孔性的聚合物,经过测试发现它对原油和石油产品以及多环芳烃具有很好的吸附效果,制备的吸油材料可以吸附 15～23 g/g 的油品. Chitsan 等[69]利用 PP 短纤废料及废旧轮胎的粉末制备一种吸油材料,它既能像 PP 短纤一样具有吸油性,又具有轮胎的弹性可以多次循环利用. 可以用作油品紧急泄露应急处理时浮油回收的材料. Zhu 等[70]在金属铜的催化作用下,用聚氨酯制备了一种海绵状的疏水性材料,这种材料能够很好的吸附溢油,吸附倍率可以达到 13 g/g,而且通过简单的机械挤压可以使吸附的油品脱离出来,能够循环使用多次,有很好的稳定性. Zhou 等[71]也用普通的商业聚氨酯制备了一种海绵状的疏水性材料,使吸油倍率得到了提高,对油品的吸附多于 20 g/g,也可以通过反复的挤压后循环使用. Li 等[72]首次研究了超疏水共轭微孔聚合物对油水分离的作用,共轭微孔聚合物的空隙为开孔结构,表面具有较强的疏水性,便于油分子进入聚合物空间网格中,故而制备的吸油树脂吸油速率非常快,方便油水分离后的回收处理. 周爱军等[73]将丁苯橡胶和自制的高吸油树脂为原料,以炭黑为补强剂、石油树脂为软化剂,用物理共混的方法制备了一种遇油膨胀橡胶,并对其吸油性能等进行了研究,结果表明高吸油树脂和炭黑用量的增加对制备的吸油橡胶的吸油性能有较大影响. Swarnalatha 等[74]将吸油性较差的天然橡胶与磁铁矿纳米粒子制备了一种复合材料,在环氧化作用下天然橡胶保留弹性的同时提高了吸油性,制备的材料选择性吸附溢油而且吸附的油品可以完全解吸,可以循环多次使用. Yuan 等[75]提出了一个全新的方案,用正辛烯、苯乙烯和二乙烯基苯单元交联制备一种聚烯烃三元共聚物,制备的共聚物具有很好的疏水亲油性,能够吸附本身 45 倍重量的油品.

3 结 语

吸油材料作为清除溢油的一种方法,已经越来越多的被用作溢油突发事故以及石油泄露等的清除. 吸油材料不仅在清除水上溢油方面取得了一些进展,同时在清除水中的多环芳烃、金属离子等方面也取得了一些成就. 尽管吸油材料还存在一些不足,但是可以预料经济高效的吸油材料的研究仍能得到大力发展.

致 谢

感谢武汉工程大学研究生处对本项目的支持!

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Development in oil-absorption materials

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Abstract:Oil demand presents the intensified trend with the rapid development of the world's economy. Spill and waste oil have caused damaging impacts on the marine and freshwater environment during crude production and oil shipment processing. Therefore,recent research was carried out to provide efficient,clean,reusable materials to clean up oil spill. Oil-sorbent materials can be grouped into two major classes,namely organic oil-sorbent material and inorganic oil- sorbent material. Inorganic oil- sorbent material has received extensive attention for its property advantages of simple preparation,low cost, high oil absorption. Superhydrophobic and superoleophilic graphene-based sponges are demonstrated as efficient absorbents for their high selectivity,fast adsorption rate,excellent absorption capacities and good recyclability. Recyclability and adsorption rate of organic oil-sorbent material are much better than those of inorganic oil-sorbent material. The study of organic oil-sorbent material focuses on improving adsorption rate,absorption capacities and recyclability. The study of new green oil-sorbent material with high sorption capacities should be paid attention in the future.

Key words:adsorption; oil spill; oil-spill material; research prospect

本文编辑:张 瑞