玉米秸秆油污吸附剂的制备及其在油水分离中的应用

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摘要 以玉米秸秆为原料, 粉碎后浸涂 ZnO 溶胶并经辛基三甲氧基硅烷(OTS)修饰后呈超疏水性和超亲油性, 水滴在其表面的接触角为 158.6° , 滚动角小于 5° , 而油滴在其表面则完全铺开. 利用玉米秸秆粉表面的超疏水性和超亲油性, 可将其用于水面油污的过滤、吸附、分离及循环利用, 其对油水混合物中油、水的分离效率分别为 98.0% 和 99.6%. 相关研究有望为玉米秸秆的加工、利用及油污吸附剂的制备提供新的思路.

关键词 玉米秸秆, ZnO 溶胶, 超疏水, 超亲油, 油水分离

海上原油泄漏、生活含油废水排放都易造成环境污染、危害人类健康. 发生油污泄漏, 常用物理、化学或生物方法处理. 化学法处理能耗高、易造成二次污染; 生物法处理, 耗时长、效率低. 近年来, 具有特殊润湿性的材料因其在自清洁^[1]、防腐^[2]、抗菌^[3]、防水^[4]、油水分离等领域^[5-7]有广泛应用前景而引起人们极度关注. 润湿性是指流体在固体表面的铺展能力, 通常用接触角衡量固体表面的润湿性, 将水滴/油滴在固体表面的接触角大于 150° 的表面称为超疏水/超疏油表面, 而将接触角小于 5° 的表面称为超亲水/超亲油表面^[8,9]. 荷叶表面^[10]、划蝽后翅翅面^[11]、水黾^[12]及黄斑大蚊腿部^[13]都存在超疏水现象. 材料表面的超疏水性源于其表面微纳米复合结构及低表面能化学组成的协同作用^[14]. 利用材料表面的超疏水-超亲油性、超疏油-超亲油性, 可将其用于油水混合物的有效分离, 如超疏水超亲油金属网^[15,16]、超疏油超亲水金属网^[17]、超疏水超亲油海绵^[18]、棉织物^[19]、颗粒^[20]及超亲水/水下超疏油材料等^[21].

上述油水分离材料虽然具有较好的分离效率, 但其制备过程繁冗复杂、成本高, 易形成二次污染.

植物秸秆是一种来源广泛、价格低廉的原料, 堆积闲置、腐烂易造成资源浪费, 焚烧处理又易引起污染环境. 相比于传统方法, 以植物秸秆为原料制备油污吸附材料, 具有原料广、成本低、质轻、吸油率高、漂浮性能好、易循环利用等优点. Wang 等人^[22,23]以玉米秸秆为原料, 浸涂 ZnO 溶胶、SiO₂ 溶胶并经十六烷基三甲氧基硅烷、含氟硅烷修饰后制得超疏水超亲油玉米秸秆粉, 可将其用于油水混合物的分离, 分离油污后的玉米秸秆粉经丙酮清洗后可循环利用. 本文以玉米秸秆为原料, 浸涂 ZnO 溶胶并经辛基三甲氧基硅烷修饰后制得超疏水超亲油玉米秸秆粉, 可将其用于水面油污的吸附、回收及循环利用. 相比于 Wang 等人^[22,23]的制备过程, 本方法成本低、无氟, 吸附油污后的玉米秸秆粉无需清洗, 经离心处理后即可循环使用. 相关研究有望为玉米秸秆的开发、利用及油污吸附剂的制备提供新的思路.

1 实验

(i) ZnO 溶胶的制备. ZnO 溶胶的制备参考 Spanhel 等人^[24]的方法并做了改进. 将 5.2 g Zn(CH₃COO)₂·

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2H₂O和250 mL乙醇置于圆底烧瓶中(配冷凝管),于80℃搅拌150 min后,70℃下旋转蒸发至溶液体积100 mL,然后加入0.35 g LiOH·H₂O,超声10 min.最后向上述溶液中逐滴加入2.0 mL蒸馏水,于60℃搅拌30 min,重复此操作过程2次即可制得白色乳状ZnO溶胶.

(ii) ZnO浸涂及表面修饰. 将张掖甘州区农场收割的玉米秸秆经剪碎后用研磨仪研碎(盛世致远仪器GY100型高速旋转粉碎机超离心研磨仪,转速6000 r/min),称取3.0 g研碎后的玉米秸秆粉加入50 mL上述ZnO溶胶中,24 h后弃去上层清液,将ZnO溶胶浸泡处理后的玉米秸秆粉于80℃烘干.烘干后的玉米秸秆粉置入50 mL体积分数为5%的辛基三甲氧基硅烷(octyltrimethoxy silane, OTS)溶液中(溶剂为

95%的乙醇),静置24 h后,弃去上层清液,将秸秆粉于120℃烘干即可得到超疏水超亲油玉米秸秆粉.

(iii) 测试与表征. 用扫描电子显微镜(SEM, Quanta 450 FEG)观察样品表面的微观形貌;用接触角测量仪(Kino SL200KS)测试水滴在样品表面的接触角,水滴体积为8 μL,选样品表面5个不同点测量(将秸秆粉末均匀铺于载玻片表面测量),结果取其平均值;用X射线光电能谱仪(XPS, PHI 5072)对秸秆粉表面元素及其元素化学价态进行分析.

2 结果与讨论

材料表面的润湿性由其表面微观结构及化学组成共同决定. 图1(a)和(b)是原始玉米秸秆经粉碎后的扫描电子显微镜图. 由图看出,粉碎后的玉米秸秆粉

图1 (网络版彩色)玉米秸秆粉表面的扫描电子显微镜图. (a), (b) 原始玉米秸秆粉; (c), (d) 浸涂ZnO溶胶后的玉米秸秆粉; (e), (f) 浸涂ZnO溶胶并经OTS修饰后的玉米秸秆粉; (f) 内嵌图为荷叶表面的扫描电子显微镜图

Figure 1 (Color online) SEM images of corn straw powder. (a), (b) Pristine corn straw; (c), (d) corn straw dip-coated by ZnO sol; (e), (f) corn straw treated by dip-coating ZnO sol and modifying with OTS. The inset in (f) is the SEM of lotus leaf

呈不规则几何状(片状、块状、褶皱状、卷曲状等), 粒径长约20~120 μm , 宽约25 μm . 原始玉米秸秆粉浸涂ZnO溶胶后, 玉米秸秆粉被ZnO溶胶覆盖, 生成一层ZnO的薄膜, 放大倍率观察发现, 薄膜由大量致密的团簇状的ZnO颗粒构成, 其表面呈乳突状, 粒径约100~200 nm, 见图1(c)和(d). 图1(e)是原始玉米秸秆粉浸涂ZnO溶胶并经OTS修饰后的表面形貌图, 其与硅烷偶联剂修饰前的秸秆粉表面形貌相比未见明显变化, 然而高倍率观察发现, 其表面乳突状的ZnO颗粒较修饰前更加明显, 团簇状颗粒由大量粒径为200~400 nm的ZnO颗粒堆积而成, 如图1(f)所示, 其表面与荷叶表面的微观形貌类似(图1(f)内嵌图)^[10]. 玉米秸秆粉、微米级团簇状颗粒及纳米级乳突微粒组成的复合阶层结构有利于其表面超疏水效应的形成^[14].

原始玉米秸秆粉、浸涂ZnO溶胶后的玉米秸秆粉表面均呈超亲水性, 水滴滴于其表面则完全铺开, 见图1(a)和(b). 玉米秸秆粉浸涂ZnO溶胶并经OTS修饰处理后, 其表面由超亲水性变为超疏水性, 水滴在其表面呈球状, 接触角为158.6°, 如图2(c)所示. 水滴在超疏水玉米秸秆粉表面极不稳定, 基底略微倾斜, 水滴便能轻易滚落, 滚动角约为4°, 如图2(d)所示.

玉米秸秆粉的主要成分为纤维素、半纤维素和木质素^[25], 其表面含有大量-OH, 呈亲水性, 水滴在其表面容易铺开. 玉米秸秆粉浸涂ZnO溶胶后, 表面形

成微纳米复合阶层结构, 含有大量-OH, 经水解后的OTS修饰处理后, 在ZnO表面形成长链烷基的自组装膜^[26], 表面能大大降低(-CH₃, -CH₂的表面能分别为36, 30 mN/m^[27]), 微纳米复合结构及低表面能化学组成的协同效应使其表面由超亲水性变为超疏水性, OTS的长链烷基在ZnO表面的自组装反应机理如图3(a)所示. 为验证硅烷长链烷基在其表面的自组装, 对原始玉米秸秆粉、浸涂ZnO溶胶并经硅烷偶联剂修饰后的玉米秸秆粉做XPS分析. 玉米秸秆主要成分为纤维素类物质, 由图3(b)的XPS谱图可以看出, 原始玉米秸秆粉表面主要含有C, O元素(图3(b)中b1曲线), 玉米秸秆粉浸涂ZnO溶胶并经OTS修饰后, 除了284.8, 532.5 eV处对应的C 1s, O 1s的特征峰外, 在88.9, 139.7, 1020.7, 1044.7 eV处出现Zn 3p, Zn 3s, Zn 2p_{3/2}, Zn 2p_{1/2}的特征峰, 在101.4, 153.0 eV处出现了Si 2p, Si 2s的特征峰, 如图3(b)中b2曲线所示. 原始玉米秸秆粉、浸涂ZnO溶胶并经硅烷偶联剂修饰后的玉米秸秆粉表面的XPS图谱的变化表明, 玉米秸秆粉浸涂ZnO溶胶并经OTS修饰后, 其表面形成了硅烷的长链烷基自组装膜.

根据Cassie理论^[28], 水滴滴于微纳米复合阶层结构的超疏水玉米秸秆粉表面时, 由于玉米秸秆粉表面的“乳突”及乳突间的“孔”、“洞”等微观结构的尺度远小于水滴, 致使水滴难浸入其下面的微纳米阶层结构, 水滴下的微观结构中有截留的空气, 表现上的水滴-玉米秸秆粉的接触实际上由水滴-空气-玉米秸秆粉组成的复合接触. 在复合阶层结构表面, 水滴犹如坐在“空气垫”上呈“球”状, 基底略微倾斜, 水滴便能从玉米秸秆粉表面轻易滚落, 表现出良好的超疏水性. 玉米秸秆粉表面的微纳米阶层结构及其低表面能化学组成使水滴在其表面的固-液-气三相接触线减小, 接触角高、滚动角低说明水滴在超疏水玉米秸秆粉表面具有较高的亚稳态能量和较低的能垒^[29].

玉米秸秆粉浸涂ZnO溶胶并经OTS修饰处理后, 其表面的微纳米复合阶层结构能有效阻止水滴的浸入, 水滴在其表面呈“球状”, 表现出良好的超疏水性, 而将十六烷、柴油滴于其表面时, 由于油滴的表面张力比水小(25 °C时, 水的表面张力约为72.8 mN/m, 十六烷、柴油的表面张力约为27.2, 26.8 mN/m), 油滴则能完全浸入其表面的微观结构, 表现为超亲油性. 利用玉米秸秆粉表面的超疏水性和超

图2 水滴在玉米秸秆粉表面的光学显微镜图. 水滴在原始玉米秸秆粉(a)、ZnO溶胶浸涂处理(b)、ZnO溶胶浸涂处理并经OTS修饰后(c)至(d)过程的玉米秸秆粉表面的光学显微镜图

Figure 2 Optical micrographs of water droplet on the surface of corn straw powder. Correspond to the optical micrographs of water droplet on pristine corn straw (a), corn straw (b) dip-coated by ZnO sol and corn straw treated (c), (d) by dip-coating and modifying with OTS, respectively

图3 (网络版彩色)反应机理及组成分析. (a) 辛基三甲氧基硅烷在ZnO表面的自组装膜形成机理图; (b) 原始玉米秸秆粉及玉米秸秆粉浸涂ZnO溶胶并经OTS修饰后的XPS图

Figure 3 (Color online) Reaction mechanism and analysis of chemical composition. (a) Schematic of octyltrimethoxy silane self-assembled on ZnO; (b) XPS spectra of pristine corn straw and corn straw treated by dipping ZnO sol and modifying with OTS

亲油性, 可将其用于油水混合物的有效分离.

3 油污吸附及分离

将0.50 g超疏水超亲油玉米秸秆粉置于漏斗中(漏斗底部垫60目铜网), 将50.0 mL的油水混合物(柴油、蒸馏水分别用油溶红、亚甲基蓝染成红色和蓝色, 体积均为25.0 mL)倾倒在玉米秸秆粉表面时, 油能透过超亲油玉米秸秆粉流入漏斗下方的量筒被收集, 而水难透过超疏水玉米秸秆粉, 滞留在漏斗内, 可对油水混合物进行“一进二出”的有效分离. 初次分离后收集到的柴油、水分别为22.0, 24.8 mL, 其对油和水的分离效率分别为88%和99.2%. 初次分离后, 玉米秸秆粉对油的吸附达到饱和, 后续分离时, 收集到的柴油、水的体积分别约为24.5, 24.9 mL, 对应油、水的分离效率分别为98.0%和99.6%, 超疏水超亲油玉米秸秆粉对油水混合物的分离过程如图4(a)~(c)所示.

用上述过滤的方法分离时, 流速慢、耗时长, 且难以做到完全、高效的分离, 收集后的水面依然有少量油污漂浮. 为进一步高效、快速去除、回收水面的油污, 可将玉米秸秆粉撒向泄露油污的水面, 其能选择性的吸附水面的油污, 进而实现油污的吸附、回收及循环利用.

图5为玉米秸秆粉用于水面油污的吸附、去除及

分离过程. 将油溶红染色的1.00 mL的十六烷滴于水面, 将超疏水玉米秸秆粉、原始玉米秸秆粉分别撒向水面油污, 超疏水玉米秸秆粉能稳定漂浮在水面, 快速吸附水面油污于其表面, 原始的玉米秸秆粉有些漂浮在水面吸附油污, 有些则沉入水底, 如图5(a)和(b)所示. 用铜网捞出水面的玉米秸秆粉, 用超疏水玉米秸秆粉处理后的水面, 已观察不到明显的油污, 而用原始玉米秸秆粉处理的水面依然有少量油污漂浮, 如图5(c)所示. 将吸附油污的玉米秸秆粉捞出后置于双层套管的内管(内管下端有微孔), 高速离心, 可实现玉米秸秆粉和油污的有效分离. 实验结果表明, 吸附1.00 mL的十六烷, 需要超疏水玉米秸秆粉、原始玉米秸秆粉各0.24和0.74 g. 超疏水玉米秸秆粉能选择性吸附水面的十六烷, 离心分离后回收的十六烷约0.85 mL, 回收率约为85%. 而原始玉米秸秆粉既能吸附水面油污, 又能吸水, 玉米秸秆粉经离心分离后, 收集到的水、十六烷共计约1.5 mL(其中十六烷约0.62 mL, 回收率约为62%, 水约0.88 mL), 如图5(d)所示. 吸附油污后的玉米秸秆粉经离心回收、120℃烘2 h后, 水滴在其表面依然呈“球状”(图5(d)内嵌图), 其表面依然具有很好的超疏水性. 回收后的超疏水玉米秸秆粉可继续用于油水混合物的有效分离, 其对十六烷的回收率均保持在70%以上. 连续分离

图4 (网络版彩色)超疏水超亲油玉米秸秆粉用于油水混合物的分离。(a) 分离前的油水混合物;(b) 油水分离装置;(c) 分离后收集的油和水;油和水分别用油溶红、亚甲基蓝染色

Figure 4 (Color online) Separation of oil-water mixtures by employing superhydrophobic and superoleophilic corn straw powder. (a) Oil-water mixtures before separation; (b) device and process of separating oil-water mixtures; (c) recovered oil and water after oil-water separation. Water and oil were dyed with methylene blue and oil red, respectively

图5 (网络版彩色)原始玉米秸秆粉及超疏水超亲油玉米秸秆粉对水面油污的吸附及分离。(a) 水面的十六烷;(b) 秸秆粉吸附油污后的水面;(c) 去除吸附油污后的玉米秸秆粉表面的水面;(d) 秸秆粉经离心后回收的十六烷。内嵌图为水滴在回收后的超疏水玉米秸秆粉表面的相机图,十六烷用油溶红染成红色

Figure 5 (Color online) Images of adsorption and separation of oil stain on water surface by employing pristine corn straw powder and superhydrophobic-superoleophilic corn straw powder. (a) Dodecane floating on water surface; (b) water surface after being treated by corn straw powder; (c) water surface after the adsorbed oil being removed by corn straw powder; (d) recovered hexadecane after the corn straw adsorbed oil being treated by centrifugal separation. The inset in (d) is the image of water droplet on the recovered corn straw powder with superhydrophobicity, hexadecane was dyed with oil red dye

1~10次后,水滴在其表面的滚动角约为 8° ,接触角约为 $156^\circ \pm 1^\circ$,吸附油污后的超疏水玉米秸秆粉经离心分离后其表面的接触角与分离次数的关系如图6(a)

所示。依据标准ASTMF726-2006^[30]测试原始玉米秸秆粉、超疏水玉米秸秆粉对十六烷的吸附能力,发现其吸附容量分别为2.1和3.8 g/g。

图6 (网络版彩色)玉米秸秆粉循环利用及油污吸附、分离和回收机理。(a) 油水分离次数与超疏水玉米秸秆粉表面的接触角关系图; (b) 超疏水玉米秸秆粉的制备及其油污吸附、回收及油水分离应用机理图

Figure 6 (Color online) Recycling and mechanism of corn straw powder in oil adsorption, recovery and oil-water separation. (a) Correlation diagram of water contact angles varying with times of oil-water separation; (b) schematic diagram of preparation of superhydrophobic corn straw powder and its application in oil adsorption, recovery and oil-water separation

以玉米秸秆为原料制备油污吸附剂, 原料丰富、成本低, 能在水面稳定漂浮, 质轻、油污吸附性能好、能循环利用。超亲油玉米秸秆粉的制备及其在油水分离、油污吸附、去除及回收方面的应用机理如图6(b)所示。

4 结论

以玉米秸秆为原料, 粉碎后浸涂ZnO溶胶, 表面形成微纳米复合阶层结构, 经OTS修饰后, 表面形成

长链烷基的自组装膜, 表面能降低。微纳米复合阶层结构及低表面能物质的协同作用使其表面变为超疏水性, 水滴在其表面的接触角约为 158.6° , 基底略微倾斜, 水滴便能滚落, 滚动角约为 4° 。油滴在其表面则能完全铺开, 表现为超亲油性。利用玉米秸秆粉表面的超疏水性和超亲油性, 可将其用于油水混合物的有效分离及水面油污的吸附、回收及循环利用, 相关研究有望为玉米秸秆的加工、利用及油污吸附剂的制备提供有益的借鉴。

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Summary for “玉米秸秆油污吸附剂的制备及其在油水分离中的应用”

Preparation of oil sorbents of corn straw and its application in oil-water separation

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The leakage of crude oil at sea and the discharge of domestic oily wastewater are likely to cause environmental pollution and threaten human health. Therefore, the development of techniques for the collection and recovery of the large amount of oil from water is attracting worldwide attention. To deal with the polluted water by spilled oil, materials with special wettability have been designed and developed over the past decades. Currently, metal meshes, sponges and cotton fabrics as well as particles with superhydrophobicity/superoleophilicity or superhydrophilicity/superoleophobicity have often been employed to separate oil and water mixtures. However, how to remove the spilled oil from water *via* techniques of low operation cost, high separation selectivity and efficiency as well as good recoverability for reuse without causing secondary contamination to environment is still a big challenge. Consequently, it is highly desirable to develop a new and advanced oil-water mixtures separation material that can selectively absorb oil while completely repelling water. Cellulose is the most abundant organic polymer, which is mainly used as a raw material to produce paper and cotton fabrics. Plant-derived cellulose is an important structural component of the primary cell wall of green plants, and usually found in a mixture with hemicellulose, lignin, pectin and other substances. Corn is a very common crop and widely planted in the Zhangye district of Gansu Province in China, and the corn straw are very abundant after harvest in autumn. However, the unused and accumulated corn straw can be easily rotted and hence cause the waste of resources, and the traditional treatment of burning can also induce serious environment pollution. With the consideration of the wide source, low cost, light weight, high oil adsorption capacity, good floatability in water as well as easy recycling, the corn straw is an ideal raw material which can be employed to prepare oil sorbent.

In this research, corn straw was employed to fabricate oil sorbent. Corn straw was first crushed and then immersed into ZnO sol for 24 h, subsequently, corn straw powders were taken out and dried in air at 80°C. Finally, the dip-coated corn straw powders were immersed in octyltrimethoxy silane (OTS) solution for 24 h, taken out and dried at 120°C, and then, the corn straw powders began to exhibit superhydrophobicity and superoleophilicity. Water contact angle on the superhydrophobic corn straw powders is 158.6° and the sliding angle of water droplet is about 4°, but the oil droplets can spread out completely on the corn straw powders due to the superoleophilicity. Synergy effects between surface morphology and surface chemical composition are known as the crucial factors to realize the opposite wettability to oil and water. The surface morphology and surface chemical composition of the obtained corn straw powders with superhydrophobicity and superoleophilicity were characterized by scanning electron microscopy (SEM) and X-ray photoelectron spectrum (XPS), respectively, and the wettability were measured with an optical contact angle meter at ambient temperature. The research indicates that both the dip-coating ZnO sol and surface modification with OTS play an important role for the performance of superhydrophobicity and superoleophilicity of corn straw powders. Because water and many oils are intrinsically immiscible, and the corn straw powders with extremely different affinities towards oils and water can be employed to separate oil-water mixtures by ways of filtration, and the separation efficiency towards water and oil is up to 99.6% and 98.0%. In addition, the spilled oil on water can also be removed by adsorption. Compared with the adsorption capacity of the pristine corn straw powder to spilled oil, the adsorption capacity of superhydrophobic corn straw powder is much high, and the corresponding adsorption capacity is 2.1 and 3.8 g/g, respectively. Moreover, the corn straw and spilled oil adsorbed by superhydrophobic corn straw can be reused and recovered by treatment of high speed centrifugation. When the adsorption time increased from 1 to 10, the water contact angle on the recovered corn straw powders is still about 156°±1°, and the corresponding sliding angle of water is about 8°, and the average percentage of recovery of superhydrophobic corn straw to hexadecane is above 70%. The design and fabrication of oil sorbent of superhydrophobic-superoleophilic corn straw made by dip-coating ZnO sol and modifying with OTS are expected to provide a new idea for the processing and utilization of corn straw as well as preparation of oil sorbents.

corn straw, ZnO sol, superhydrophobic, superoleophilic, oil-water separation

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