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硕 士 学 位 论 文

植物法还原制备纳米铁颗粒及其去除水中
Cr(VI)和 As(V)的研究

Plant-mediated synthesis of iron nanoparticles and its
application in Cr(VI) and As(V) removal in aqueous medium

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肖正梨

指导教师姓名: 孙道华 副教授

梁榕源 高级工程师

专 业 名 称: 化 学 工 程

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摘要

水是人类赖以生存和发展不可或缺的基本资源，但随着社会发展和工业化进程的加快，大量工业废水的不合理排放对水环境造成了巨大的危害，其中重金属如铬和砷的广泛使用严重影响了周边动植物及人类的生命健康。近年来，纳米铁材料特别是零价纳米铁由于其较高的反应活性和可处理污染物的多样性在环境修复领域备受关注。但是，纳米铁在应用过程中存在易被氧化、稳定性差等问题，各种改性技术往往会带来合成成本的提高。本研究针对以上问题，利用植物法还原制备纳米铁颗粒，整个制备过程绿色简便、条件温和，不需要引入其他还原剂和改性剂，对所得纳米铁颗粒进行了一系列表征，并对其在水溶液中 Cr(VI)和 As(V) 的去除效果进行了研究。

采用福建省常见的 15 种植物树叶制备植物提取液，并将其与氯化铁反应用于纳米铁的合成。通过分析植物提取液中四种主要活性成分还原糖、多酚、黄酮、和蛋白质在还原制备纳米铁前后的含量变化，与提取液还原能力进行关联，以此确定植物法制备纳米铁过程中起关键作用的活性成分。结果表明多酚类物质是植物法制备纳米铁过程中起最关键作用的活性成分；并藉此结果，筛选出 15 种植物提取液中具有较好纳米铁合成效果的为蒲桃提取液 (*Syzygium jambos* (L.) Alston, SJA)。进一步，采用 UV-Vis、TEM、XRD、XPS 等技术对蒲桃提取液制得的纳米铁颗粒 (SJA-Fe NPs) 进行表征分析，发现 SJA-Fe NPs 为无定形、尺寸约为 15 nm 的近球形颗粒，主要以零价铁和二价铁氧化物的形式存在。通过模拟石英砂柱对 SJA-Fe NPs 迁移性能进行了考察，在两种尺寸石英砂填充、以纯水为流动相条件下，SJA-Fe NPs 在水平方向和垂直方向上通过率均为 50% 以上；流体中腐植酸和氯化钠的存在不会抑制 SJA-Fe NPs 的迁移性能。

将 SJA-Fe NPs 应用于水溶液中 Cr(VI) 的去除，考察了纳米铁投加量、Cr(VI) 初始浓度、温度以及 pH 等参数对 Cr(VI) 去除效果的影响，得到较适合的处理条件为：SJA Fe NPs 投加量为 0.5 mL，处理 20 mL 初始浓度为 50 mg/L 的 Cr(VI) 溶液，初始 pH 不加调整为 5.5，反应温度室温。在此条件下 SJA-Fe NPs 对 Cr(VI) 的去除能力为 983.2 mg Cr(VI)/g Fe。此外，还考察了溶液中共存物质对 Cr(VI)

的影响, 结果表明 SJA-Fe NPs 对 Cr(VI) 的去除过程受其它共存物质影响较小, 离子强度、腐植酸、阳离子等的存在不会影响 Cr(VI) 去除过程, 仅有个别的阴离子会抑制 Cr(VI) 的去除。对去除反应过程的动力学、反应机理进行了研究, 该过程符合准二级动力学模型; 结合 XPS 和反应过程不同价态 Fe、Cr 含量的分析, 推论 SJA-Fe NPs 对 Cr(VI) 去除的过程主要包括吸附、还原、共沉淀三个步骤。

将 SJA-Fe NPs 应用于水溶液中 As(V) 的去除, 考察了溶液 pH、温度、共存阴离子等对 As(V) 去除效果的影响。结果表明反应最适 pH 为 4; 低温有利于 As(V) 的去除; 被考察阴离子中仅有 HPO_4^{2-} 能够强烈抑制 SJA-Fe NPs 对 As(V) 的吸附。对吸附过程的动力学和等温线进行研究, 发现 SJA-Fe NPs 对 As(V) 的吸附过程符合准二级动力学模型; 吸附等温线更符合 Langmuir 模型, 由模型拟合得到的最大吸附量为 271.7 mg/g Fe。进一步, 对 SJA-Fe NPs 应用于 Cr(VI) 和 As(V) 共存溶液中两者的联合去除进行了考察, 初步结果显示 As(V) 浓度的升高抑制了 SJA-Fe NPs 对 Cr(VI) 的去除, 而适量 Cr(VI) 的存在则会极大地促进 SJA-Fe NPs 对 As(V) 的吸附。

关键词: 植物提取液; 生物还原; 纳米铁颗粒; 六价铬; 五价砷

Abstract

Water is essential to human survival and development, but with the development of society and the accelerated process of industrialization, the large-scale and unreasonable emission of industrial waste water causes enormous harm to the environment. The extensive use of heavy metals such as chromium and arsenic has serious impact on the surrounding flora and fauna as well as human life and health. In recent years, nano iron materials especially nanoscale zero-valent iron have received much attention in environmental remediation, due to its high reactivity and the diversity of pollutants it can handle. However, iron nanoparticles are usually unstable and can easily oxidize in the practical application. And the modification technologies would often increase the synthesis costs. In view of the above problems, this study employs plant-mediated method to prepare iron nanoparticles. The entire preparation process is simple and green, and no extra reagents and modifiers are needed. The obtained iron nanoparticles were characterized, and its performances on Cr(VI) and As(V) removal in aqueous solution were investigated.

15 common plant leaves in Fujian Province were selected to prepare plant extract, then reacted with ferric chloride for the synthesis of iron nanoparticles (Fe NPs). By analyzing content variation of the four main active ingredients (sugar, polyphenols, flavonoids, and protein) in plant extracts before and after the synthesis. And further be associated with the reducing ability of the extracts, hereby to determine which active ingredient plays the key role during the plant-mediated preparation of Fe NPs. The results indicated that polyphenols were the most critical active ingredient, and thereby screened out the *Syzygium jambos (L.) Alston* (SJA) as the good candidate for the green synthesis of Fe NPs among the 15 kinds of plant extracts. Characterizations such as UV-Vis, TEM, XRD, XPS and other techniques showed that the obtained Fe NPs by SJA (SJA-Fe NPs) were amorphous spherical particles with average size of about 15 nm. The migration performance of SJA-Fe NPs was investigated by quartz

sand column, with two sizes of quartz sand filled in and water as the mobile phase. The penetration rates of SJA-Fe NPs in horizontal and vertical directions were above 50%, and the presence of humic acid and sodium chloride would not inhibit migration performance of SJA-Fe NPs.

The SJA-Fe NPs were applied in the removal of Cr(VI) in aqueous solution and parameters such as the iron dosage, initial Cr(VI) concentration, temperature and pH for Cr(VI) removal were investigated. The obtained appropriate conditions were: 0.5 mL SJA-Fe NPs for the treatment of Cr(VI) solution with initial concentration of 50 mg/L, pH 5.5 without adjustment and room temperature. Under this condition, Cr(VI) removal capacity of SJA-Fe NPs is 983.2 mg Cr(VI)/g Fe. In addition, the influence of coexisting substances on Cr(VI) removal was studied. Cr(VI) removal by SJA-Fe NPs is less influenced by most coexisting substances, the presence of ionic strength, humic acid, and cations would not affect the Cr(VI) removal, only particular anions could suppress Cr(VI) removal. This process followed pseudo-second-order kinetic model, and based on the XPS analysis together with the content changes of Fe, Cr during the reaction, we concluded that the Cr(VI) removal by SJA-Fe NPs included three steps: adsorption, reduction and co-precipitation.

The SJA-Fe NPs then were applied in As(V) removal in aqueous solution, and the effect of pH, temperature, coexisting anions on As(V) removal were investigated. The pH of 4 and low temperature is favorable for As(V) removal. Moreover, HPO_4^{2-} could strongly inhibit the adsorption of As(V) on SJA-Fe NPs among the anions investigated. As(V) adsorption by SJA-Fe NPs followed the pseudo-second-order kinetic model, and the adsorption isotherm is more fitted with Langmuir model with the maximum adsorption of 271.7 mg/g Fe. Next, the SJA-Fe NPs in the removal of co-existed Cr(VI) and As(V) were investigated. The preliminary results showed that Cr(VI) removal was restrained with the increase of As(V) concentration, while the presence of Cr(VI) would greatly promote the As(V) adsorption by SJA-Fe NPs.

Keywords: Plant extract, Bioreduction, Iron nanoparticles, Hexavalent chromium, Arsenate

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厦门大学博硕士论文摘要库

第一章 绪论

1.1 水资源及其污染

1.1.1 水污染现状

水是地球上所有生物体赖以生存、不可或缺的基本条件，是组成生物体和生态环境的基本要素。随着全球人口的快速增长和人类活动的迅猛发展，人类对水的需求量日渐增多（每十五年用量翻倍）^[1]，水资源危机已成为世界各国面临的全球性问题。

我国水资源总量丰富，大小河川总长 42 万公里，湖泊 7.56 万平方公里，占国土总面积的 0.8%，淡水资源总量为 28000 亿立方米，占全球淡水资源的 6%，居世界第 4 位，但人均不到 2200 立方米，只占世界人均拥有量的 1/4，居 121 位，为 13 个贫水国之一^[2]。目前中国 640 个城市有 300 多个缺水，2.32 亿人年均用水量严重不足。随着现代工业的发展，污染问题日益严重，2008 年中国环境质量公报公布的数据显示，大水系的水质总体为中度污染，浙闽区河流的水质为轻度污染，湖泊(水库)富营养化问题突出。海河、辽河、淮河、巢湖、滇池、太湖污染严重，七大水系中，不适宜作饮用水源的河段已接近 40%，其中淮河流域和滇池最为严重。工业较发达城镇河段的污染更突出，78%的城市河段不适宜作饮用水源，受到污染的城市地下水达 50%。水污染加剧了我国水资源短缺的矛盾，对工农业生产和人民生活带来了巨大影响^[3]，国内水污染事件频繁发生（图 1-1），对水资源的保护显得迫在眉睫。其中，随着城市化进程的加快和工农业的迅猛发展，重金属排放造成的水环境污染问题不断凸显。据统计，自 2009 年以来，我国已连续发生 30 多起重特大重金属污染事件^[4]。而重金属污染物在环境中毒性大而且不易代谢，因此对重金属污染的防治与治理显得尤为重要，表 1-1^[5]列出了美国环境保护署（US EPA）和世界卫生组织（WHO）规定的饮用水中重金属最高允许浓度。在国内，2011 年国务院将《重金属污染综合防治“十二五”规划》作为我国第一个“十二五”专项规划，并提出将对 Pb、Hg、Cr、As、Cd 等重金属污染物进行重点防控^[6]。



图 1-1 近年来我国发生的水污染事件

Figure 1-1 Water contamination accident occurred in China in recent years

表 1-1 美国环境保护署和世界卫生组织规定的饮用水中重金属最高允许浓度^[5]

Table 1-1 WHO and US EPA limitations of selected heavy metal in drinking water

污染物	US EPA		WHO 指导浓度值 (mg/L)
	最高允许浓度 (mg/L)	最高允许浓度控制目 标 (mg/L)	
铅	0.015	0	0.01
铬	0.1	0.1	0.05
镉	0.005	0.005	0.003
砷	0.010	0	0.01
汞	0.002	0.002	0.006
铜	1.3	1.3	2
锌	5	-	3
镍	-	-	0.07

1.1.2 铬简介及其污染

铬 (Cr) 为 VI 族元素, 单质铬为钢灰色、质脆而硬金属, 化学性质比较活泼, 广泛存在于土壤、大气、水和动植物体内, 天然水体中的铬主要存在两种价态: Cr(VI)和 Cr(III), 前者的毒性为后者的数百倍。Cr(III)较稳定, 在水体中 Cr(III)

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