附件 3

重庆市高等学校巴渝学者青年学者候选人
推　荐　表

推 荐 学 校 : 长江师范学院

设岗名称：　化学工程

学科领域：工程技术领域

候选人姓名: 彭浩

侯选人国籍: 中国

现工作单位: 长江师范学院

填 表 日 期 : 2021 年 4 月 10 日

重庆市教育委员会制

2021 　　 3

填 表 说 明

一、填写本表前，请认真阅读《巴渝学者计划管理办法（试行 》。

二、本表第一至六项由候选人本人填写，内容必须全面、准确，实事求是，由学校负责审核。

三、设岗名称填写二级学科或学校自主设立的对接产业、交叉融合学科的岗位。

四、学科领域：选填自然科学、工程技术领域或人文社会科学领域。

五、本表内有关栏目不可更改格式，A4 纸双面打印。

一、候选人基本情况									
姓名	彭浩	性别	男	国籍	中国	民族	汉	出生年月	1990.03
最高学历	研究生	最高学位	博士	毕业院校	重庆大学				
现任职单位及职务	长江师范学院教师			现任专业技术职务	副教授				
从事专业	化学工程与技术			学科专业方向	化学工程				
手机号码	15123031643			电子邮箱	penghao@yznu.edu.cn				
主要学术及社会兼职	《当代化工研究》期刊编审，有色金属智库专家，Journal of Hazardous Materials, Hydrometallurgy 等 SCI 期刊审稿人。								

个人教育及工作经历

教育经历：

2012.09—2017.06　重庆大学 化学工程与技术 工学博士，导师：陶长元教授

2008.09—2012.06　重庆大学 化学工程与工艺 工学学士，导师：陶长元教授

工作经历

2021.1-至今，　长江师范学院化学化工学院，副教授

2017.06-2021.1　长江师范学院化学化工学院，讲师

二、教育教学情况

2.1 开设课程情况

序号	课程名称	学期数	总学时数	选学总人次	是否核心课程	是否市级及以上精品课程
1	计算机在化学化工中的应用	4	32	268	否	否
2	计算机在化学化工中的应用实验	4	24	268	否	否
3	化工基础	4	64	357	是	否
4	化工基础实验	4	24	357	否	否
5	化工实训	4	40	345	否	否

2.2 指导研究生情况

指导博士生	毕业人数：0	指导硕士生	毕业人数：0
	在读人数：0		在读人数：0

2.3 编写出版教材

序号	教材名称	出版社	出版年份	编著情况	排序

2.4 承担教学改革项目

序号	项目名称	年度	项目来源	排序

1	新工科背景下面向工程的教学模式改革-以化学工程与艺专业课程为例	2019-2021	长江师范学院	5
2	新工科视域下的化工专业人才能力矩阵解析与本科培养方案重构	2018-2019	长江师范学院	4

2.5 获得教学成果奖励

序号	奖励项目名称	奖励类型及等级	奖励年度	排序

三、候选人主要学术成就

3.1 近五年承担主要科研项目（5 项以内，请注明项目名称、项目来源、项目起讫时间以及项目完成人的顺序、解决问题）

序号	项目名称	项目性质及来源	项目经费	起止年度	排序	主要解决问题
1	电场强化转炉钒渣湿法浸出行为研究	重庆市基础研究与前沿探索专项项目，重庆市科学技术委员会	10 万	2018-2021	1	利用电催化氧化技术对转炉钒渣的湿法浸出过程进行强化，实现钒的高效湿法浸出，为转炉钒渣的资源化利用提供理论支撑和技术支撑。

2	电催化还原六价铬过程中的非线性行为及调控规律研究	重庆市教育委员会科学技术研究项目，重庆市教育委员会	4万	2019-2022	1	项目基于非线性非平衡态理论，研究电催化还原六价铬过程中电位振荡非线性动力学机制，建立电催化还原非线性物理模型，阐释电场对电催化还原过程中非线性行为的调控规律，建立电催化高效还原六价铬新模式。
3	废水中低价磷的转化与去除关键技术研究	涪陵区科技计划项目，涪陵区科技局	2.5万	2018-2020	1	系统研究废水环境中低价磷的采集和保存方法，建立水中低价磷酸盐分析与测试的方法
4	应用多组分悬浮造粒技术创制新型功能性控释肥料研究与示范	重庆市社会民生重点项目，重庆市科学技术委员会	50万	2017-2019	5	通过优化适应不同作物的肥料元素配比以促进大量元素与中微量元素配合，完成系列新型功能性控释肥料产品创制

3.2 近五年重要项目获奖情况（5 项以内，请注明获奖项目名称、获奖时间、奖励名称及级别、项目完成人的顺序）

序号	获奖项目名称	奖励名称	奖励等级	授奖单位及国别	奖励年度	排序

3.3 近五年代表性著作、论文（5 篇以内，请注明著作或论文名称、出版单位或发表的刊物名称、期号、出版或发表时间、所有著、作者姓名以及作者排序、创新点）

著作或论文名称	出版单位或发表刊物名称	期号、起止页码	所有著、作者姓名及排序	出版或发表年度	主要创新点
Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical	Environmental Chemistry Letters	18 (6): 2055-2068	**Hao Peng***, Jing Guo (1/2)	2020	本文对废水中六价铬的去除方法进行了概括综述，对六价铬的去除现状进行了总结和展望，为后续含铬废水的处理指明了方向。

reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review					
A Literature Review of Leaching and Recovery of Vanadium	Journal of Environmental Chemical Engineering	7（5）：103313	**Hao Peng*** (1/1)	2019	本文对钒的分离回收技术进行了概括综述，并对钒的提取现状进行了总结和展望，为转炉钒渣的高效湿法冶炼指明了方向。
Recovery of Vanadium with Urea in Acidic Medium	Environmental Chemistry Letters	17（4）：1867-1871	**Hao Peng***, Liu Yang, Lilian Wang, Jing Guo, Bing Li (1/5)	2019	利用尿素替代传统铵盐实现溶液中钒离子的高效回收。
High-efficient Recovery of Chromium (VI) with Lead Sulfate	Journal of the Taiwan Institute of Chemical Engineers	85: 149-154	**Hao Peng***, Jing Guo, Bing Li*, Zuohua Liu, Changyuan Tao (1/5)	2018	根据硫酸铅和铬酸铅的溶解度差异，以硫酸铅作为沉淀剂有效将废水中的铬离子除去且不产生二次污染。
Leaching kinetics of vanadium with electro-oxidation and H2O2 in alkaline medium	Energy & Fuels	30(9): 7802-7807	**Hao Peng***, Zuohua Liu, Changyuan Tao (1/3)	2016	以H2O2和电场为氧化手段对钒铬还原渣的碱性湿法浸出过程进行强化，实现钒和铬的高效湿法浸出。

3.4 近五年获得专利情况（5 项以内，请注明获得时间、国家、候选人作为专利所有人的顺序等）

序号	专利名称	专利授权国	专利号	授权公告日	排序

3.5 重要学术会议报告情况

序号	报告名称	会议名称	主办方	时间	报告类型
1	钒铬还原渣中钒铬的浸出工艺研究	第三届钒钛微合金化高强钢开发应用技术暨第四届钒产业先进技术交流会议	国家钒钛资源综合利用产业技术创新战略联盟、重庆大学、中国金属学会特钢分会微合金非调质钢学委会	2017 年 11 月	口头报告
2	转炉钒渣中锰的浸出行为研究	2016 年全国冶金物理化学学术会议	国家自然科学基金委员会工程与材料学部、中国有色金属学会冶金物理化学学术委员会、中国金属学会冶金物理化学分会	2016 年 8 月	口头报告

3.6 参与团队建设情况（参与平台、基地建设、创新团队、学术梯队情况等）
3.7 候选人获其他表彰奖励情况

四、候选人主要学术基础

　　候选人师从重庆大学陶长元教授，在教育部长江学者刘作华教授团队长期从事钒铬矿物的资源化利用方面的研究，并与相关高校和企业有着密切合作，在矿产资源高效利用、湿法冶金过程非线性动力学基础理论方面有较为丰富的研究经验。

　　近年来，采用电催化氧化技术、H_2O_2 氧化技术对低价钒铬矿物的湿法浸出过程进行强化，并利用三聚氰胺和硫酸铅对浸出液中钒铬离子进行回收，取得了一系列成果。目前主持重庆市基础研究与前沿探索项目 1 项，重庆市教委科学技术研究计划项目 1 项，涪陵区科技计划项目 1 项，入选长江师范学院青年科研人才成长计划，先后参与完成国家级、省部级和企业相关项目多项，**以第一作者或通讯作者身份在 Energy & Fuels、Journal of the Taiwan Institute of Chemical Engineers，Environmental Chemistry Letters 等期刊上发表 SCI/EI 检索论文 50 余篇，**相关研究成果在企业得到应用。

五、聘期工作设想

（主要填写对履行本学科专业青年学者岗位职责的工作思路、总体考虑，从事主要研究方向，学科专业建设、团队建设、成果转化、学术交流合作的预期目标等）

钒及其化合物作为重要的战略性资源，广泛应用于冶金、化工、航空航天、国防军事等核心领域，是国民经济发展和国家安全的重要保障基础。在自然界中，钒主要以低价态化合物赋存在钒钛磁铁矿、钒云母和钒铅矿中，此外还有大量的钒赋存于铝土矿和某些沉积物如含碳质的石油、页岩、沥青和石煤中。目前，生产五氧化二钒及其钒产品的主要原料为转炉钒渣和石煤。转炉钒渣是钒钛磁铁矿经高炉氧化吹炼得到的炉渣，其中富含大量的钒、铁、锰、硅和铝等元素，成分较为复杂。

研究表明，转炉钒渣主要的物相包括尖晶石相、硅酸盐相和夹杂相三种，其中钒主要以低价态的钒铁尖晶石结构存在。在提钒过程中，常常会采用高温氧化焙烧的方式将低价钒氧化成高价，旨在提高钒的浸出率。钠化焙烧-浸出（水浸、酸浸和碱浸）-沉淀-煅烧是最传统的提钒工艺之一，该工艺提钒效率较高，但存在严重的废气、废水和废渣污染问题。为减少"三废"问题，研究者采用钙盐替代钠盐开发了钙化焙烧工艺。在焙烧过程中，由于添加助剂的用量不同，低价钒的氧化产物形式多样。另外由于焙烧物料容易形成液相，引起物料聚集、包裹、粘结、烧结，炉料结圈、物料球团化等问题，使得含钒尖晶石相被硅酸盐相包裹，不易暴露出来，使得钒的转化率不高。为了提高浸出率，研究者开始关注转炉钒渣的湿法浸出过程（酸性浸出和碱性浸出）。在酸性浸出过程中，加入 MnO_2、$KClO_3$ 等氧化助浸剂可氧化低价钒提高钒的浸出率，另外改变反应体系压力也可强化钒的氧化浸出。但在浸出过程中转炉钒渣中的其他金属化合物也会溶出，其化学性质与钒相差无几，使得后续分离提纯困难较大。碱性浸出时，铁、锰等金属元素难以溶出而残留在滤渣中，实现了钒的选择性高效浸出。申请者发现在强碱条件下，反应体系中的水和氢氧根易被外加电场活化，形成具有强氧化性的羟基自由基和少量新鲜微纳尺度的氧气，可氧化反应体系中的低价化合物。申请者拟引入电场对转炉钒渣的碱性湿法浸出过程进行强化，活化反应体系中的氢氧根离子，实现低价钒向高价钒的氧化转化，提高转炉钒渣中钒的浸出率。

另外，候选人前期研究发现，低价钒在被电场氧化为高价钒的过程中存在着周期性的电流振荡

现象，这种非线性行为与钒的价态和体系环境有着密切的关系。另外，转炉钒渣的碱性湿法浸出过程具有体系开放性、状态非平衡性、机制非线性等特点，电场的引入使得钒价态呈现多样化，其价态变化过程蕴含丰富的非线性动力学机制。在钒价态变化过程中，中间价态的反应中间体，其在不同环节可分别扮演氧化剂、还原剂、催化剂等不同角色，为非线性机制的形成提供了必要的反馈机制，从而影响电场强化湿法浸出过程中钒的定向迁移转化和浸出效率。该项目基于非平衡态热力学和非线性动力学理论，深刻认识转炉钒渣碱性湿法浸出过程中钒价态变化时蕴含的非线性机制，并通过对这种非线性行为的调控，实现低价钒向高价钒的定向转化，可为转炉钒渣的高效冶炼和资源化利用提供创新性的理论基础和突破口。

综上所述，候选人拟引入电场对转炉钒渣碱性湿法浸出过程进行强化，研究钒的定向迁移转化与体系反应条件（电场强度，反应温度，反应时间等）之间的相互关系；提取转炉钒渣碱性湿法浸出过程中钒价态转化的非线性特征参数（混沌吸引子、分形维数、最大 Lyapunov 指数等），分析钒价态变化过程蕴含的非线性动力学机制，建立电化学振荡与钒元素价态转化之间的数理模型；调控电化学振荡规律，促进低价钒向高价钒的定向转化与迁移，实现转炉钒渣中钒的高效浸出，建立电场强化转炉钒渣高效湿法浸出新理论。本项目的研究成果将为转炉钒渣的高效冶炼和资源化利用提供理论基础与技术支撑。

通过项目的实施，拟建议一支由高校教师、钒产业技术人才组成的科研团队，瞄准钒产业技术和节能减排理论前沿，引入科学合理的激励竞争机制与团队协作机制，推动人才梯队建设，建设协作力、凝聚力强的高水平科研团队，形成一支始终围绕钒产业可持续发展与节能减排的协同创新团队，在钒资源高效利用的理论研究、工艺技术和装备研究、工程化应用方面取得突破，探索出面向钒产业节能减排的产学研合作新机制。

六、候选人承诺

　　承诺本表一至五项填写内容属实。若受聘上岗后，将完成规定时间或相应任务量工作，履行青年学者岗位职责。

<div align="center">候选人签名：</div>

<div align="right">年　　月　　日</div>

七、设岗学科专业领域的基本情况

（主要填写学校设岗理由和预期目标，包括设岗学科专业领域及具体研究方向、创新平台和重点科研基地建设情况，近五年取得重要科学成果、实验室及现有人员、设施等情况。）

八、学校拟为候选人提供的岗位支持条件（包括提供工作条件，配套科研经费、仪器设备，支持组建创新团队等）

九、学校推荐意见（对候选人立德树人成效、学术贡献、学风等总体评价，以及档案审核、廉洁自律、公示等情况）

负责人签名：

学校盖章：

年　月　日

十、专家评审委员会意见

专家评审委员会负责人签字：

年　月　日

十一、市教委审定意见

（盖章）

年　月　日

重庆市高等学校巴渝学者青年学者候选人

申报佐证材料

推荐学校：长江师范学院

设岗名称：　化学工程

学科领域：工程技术领域

候选人姓名：彭浩

候选人国籍：中国

现工作单位：长江师范学院

填表日期：2021 年 4 月 10 日

参考目录

立项编号： cstc2018jcyjAX0018

重庆市基础研究与前沿探索项目
（重庆市自然科学基金）任务书

项目名称	电场强化转炉钒渣湿法浸出行为研究
承担单位	长江师范学院（签章）
项目负责人	彭浩
通讯地址	重庆市涪陵区聚贤大道 16 号
联系电话	15123031643
起止年限	2018-08-01 至 2021-07-31

重庆市科学技术委员会

二〇一八年五月制

填 写 说 明

1、本任务书由重庆市科委、项目承担单位共同签订，甲方为重庆市科委，乙方为项目承担单位。

2、本任务书是项目经费拨付和结题的依据。任务书的内容根据《基础研究与前沿探索项目（重庆市自然科学基金)项目申报书》自动生成。

3、立项编号由项目管理系统统一分配。

填 写 说 明

一、考核指标

（一）考核指标概述

（1）研究电场强化转炉钒渣湿法浸出过程，分析电场强化过程中钒价态的转化规律，揭示钒化合物的转化机理；研究电场强化低价钒定向转化和钒选择性浸出的动力学行为，建立转炉钒渣钙化焙烧料电场强化湿法选择性浸出钒的非线性理论模型。

（2）项目研究将发表 SCI 收录学术论文 2 篇，参加高水平的国内、国际学术会议 2 人次。

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（2）项目研究将发表 SCI 收录学术论文 2 篇，参加高水平的国内、国际学术会议 2 人次。

（二）考核指标及验收依据

编号	考核指标	验收依据
1	项目研究将发表 SCI 收录学术论文 2 篇	SCI 论文 2 篇

二、项目组成员

姓　名	证件号码	性别	学历	职称	专业	工作单位	联系电话	项目中的分工	每年工作时间(月)	签　字
彭浩	421023199003290715	男	博士研究生	中级	化学工程与技术	长江师范学院	15123031643	主研	8	
郭静	500224199204127988	女	本科	初级	制药工程	长江师范学院	15823245513	实验数据分析	6	
林银河	51340119801030281x	男	博士研究生	副高	冶金工程	长江师范学院	18782300877	实验设计	6	

三、项目经费

甲方为乙方提供本项目研究经费＿＿5.0＿＿万，在签约后一次拨付；乙方自筹或匹配经费＿＿5.0＿＿万。

四、相关责任

1、甲方在项目执行过程中不得无故撤销或终止项目。

2、乙方及专项牵头单位在项目实施过程中应建立相应的规章制度，加强安全管理，确保人员及设备安全，对科研安全负全部责任。项目执行过程中应严格遵守重庆市科委科技计划项目管理的各项规定并承担相应权责，按约定保证项目实施所需的人力、物力、财力，督促项目负责人和本单位项目管理部门按重庆市科委的规定及时报送有关报表和材料并按期结题。

3、乙方及专项牵头单位要严格按照《重庆市科技计划项目资金管理办法（试行）（渝财教【2015】275号）》的要求，对项目资金单独设帐，严格按照预算专款专用，严禁挤占挪用项目经费、超预算范围开支的行为，严禁违反规定自行调整项目经费预算，严禁编制虚假预算套取项目经费，严禁项目结题后不及时进行财务结算、长期挂账报销费用，严禁提供虚假配套承诺或不及时足额提供配套资金。乙方及专项牵头单位在项目执行过程中，必须接受甲方对经费使用及项目进度的监督和检查，并按甲方要求及时提供年度计划执行情况报告，逾期不报，甲方有权暂停资助。

4、乙方在项目执行过程中，项目任务书中签订内容、人员和完成时间原则上不作变更；如因某种原因需对计划任务书内容作调整，应向市科委提交书面申请，并经市科委批准后签订修改（补充）任务书。专项牵头单位在项目执行过程中，依据签订的协议内容，对乙方实行监管，项目实施情况需及时向甲方报告。

5、乙方及专项牵头单位在项目执行过程中，如遇重大变化（如:与任务书研究内容有出入、技术措施或某些条件不落实等）致使计划无法执行，应主动及时要求中止任务或延长结题时间。对要求中止任务的，应视不同情况，部分或全部退还所拨经费；对要求延期结题的，延期结题时间不能超过一年，超出一年后结题的，视为总结结题，按照《重庆市科技计划项目管理办法》中规定，终止负责人三年项目申报资格。如乙方及专项牵头单位没有提出中止任务的要求，甲方根据调查情况有权提出终止任务的处理意见，有权延期或停止资助，甚至收回项目全部经费，并减少乙方申报数量；情节严重的，取消申报资格，直至追究法律责任。

6、乙方应在本计划任务书规定的完成时间前2个月向甲方提出结题申请，并根据甲方要求完成项目结题验收有关事宜。约束性指标未全部完成或选择性指标完成率未达85%的项目不能验收结题；结题验收未通过的，按《重庆市科技计划项目管理办法》中有关规定追究乙方及专项牵头单位责任。结题验收通过后，该项目才能作为

正式完成。

7、乙方及专项牵头单位应建立健全促进科研诚信、科技行为廉洁的规章制度，组织开展廉洁自律宣传教育，监督并认真查处本单位在科研过程中出现的违规违纪行为。乙方及专项牵头单位不得在有关人员职称、简历以及研究基础等方面提供虚假信息，不得在项目实施中抄袭、剽窃他人科研成果，不得捏造或篡改科研数据，不得在涉及人体的研究中违反知情同意、保护隐私等规定，不得违反实验动物保护规范等。

8、乙方及专项牵头单位不得向甲方工作人员行贿；不得报销应由甲方工作人员个人支付的任何费用；不得为甲方工作人员购置或提供通讯工具、交通工具、高档办公用品等贵重物品。乙方及专项牵头单位在项目立项和实施过程中贿赂甲方工作人员，或者为其报销应由个人支付的费用、购买贵重物品等，被纪检监察机关或司法机关查证属实的，甲方有权终止项目实施并追缴拨付的全部科研经费；若甲方工作人员主动向纪检监察机关上缴乙方及专项牵头单位提供的贿赂或者贵重物品，甲方同样有权终止项目实施并追缴拨付的全部科研经费。

9、乙方及专项牵头单位发现甲方工作人员在科技管理工作中有索贿、暗箱操作等违反廉政建设规定的行为，应及时向科技纪工委举报并积极协助查处工作。

其他约定：

责任约定签订的约定书、合同协议及签订的其他相关约定以附件形式上传

五、任务书签订各方

甲方：重庆市科委代表：　　科技人才与基础研究处　　处长　余国胜（签章）

项目管理人　熊新　（签章）

（单位签章）

二0　　年　　月　　日
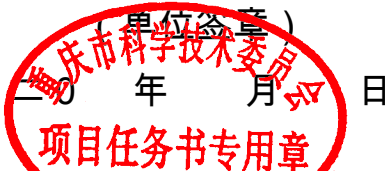
乙方：项目第一承担单位负责人　黄大勇　（签章）

项目负责人　彭浩　（签章）

帐 户 名：　长江师范学院

帐　　号：　31620101040009181

开户银行：　中国农业银行重庆涪陵城区支行

（单位签章）

二0　　年　　月　　日

重庆市教育委员会科学技术研究项目

合 同 书

项目下达方（甲方）：重庆市教委　　　合 同 编 号 ：KJQN201901403

项目承担方（乙方）：长江师范学院　　合同签订地点：重庆市教委

　　为保证重庆市教委科学技术研究项目的顺利实施和完成，依据《中华人民共和国合同法》，经甲乙双方协商，订立如下合同：

一、项目基本情况

　　项目负责人　　　：　彭浩

　　项目名称　　　　：　电催化还原六价铬过程中的非线性行为及调控规律研究

　　项目组成员　　　：　李兵　郭静

　　合作单位　　　　：　无

　　项目起止时间　　：　从 2019-10-30至 2022-10-30

二、项目主要研究内容

本项目应完成的主要研究内容如下：

项目基于非线性非平衡态理论，研究电催化还原六价铬过程中电位振荡非线性动力学机制，研究电位振荡与体系物质存在形态、浓度、pH、温度等的关系，建立电催化还原非线性物理模型，阐释电场对电催化还原过程中非线性行为的调控规律，建立电催化高效还原六价铬新模式。

（1）电催化还原过程中非线性行为的认识

六价铬还原过程中，体系中可能存在，体系中可能存在Cr^{3+}、CrO_2^-、$Cr_2O_7^{2-}$、CrO_4^{2-}物种，是一个非常复杂的体系。元素各价态之间的转化之间的转化及中间价态物种的存在将产生丰富的非平衡非线性现象。基于非平衡态热力学、非线性动力学理论及现代电化学分析方法，搭建能够实时在线监测的浸出-电化学测试一体化装置，监测还原过程中电位振荡的电化学信号，提取电位振荡的非线性特征参数（混沌吸引子、分形维数、最大Lyapunov指数等），分析振荡信号与体系反应条件，如温度、物质浓度、pH 值等之间的相互关系；运用现代仪器分析手段，分析还原体系中各价态存在的形态；分析电位振荡非线性特性参数变化与体系中物质存在形态变化之间的相互关系，建立电位振荡与物质存在形态之间相应的数理模型。

（2）电场对还原过程非线性行为的调控规律研究

废水中，物质存在形态、分布规律及转化途径与电位有着密切的联系。在前期研究建立的电位振荡与物质存在的形态相关模型的基础上，研究基于外加电场（直流或脉冲电场）强化调控下六价铬高效还原新模式。探索外加电场对电位振荡的影响；分析外场对体系中物质各价态迁移转化途径、方式及存在形态的影响规律，阐释电场对还原过程非线性行为的调控规律；建立六价铬高效还原与定向转化新模式。

三、考核指标：

论文、著作（篇/部）	SCI/EI/ISTP	核心期刊		其他论文		著作
	1	0		1		0
发明专利（项）	申请	0		授权		0
实用新型（项）	申请	0		授权		0
标准规范（项）	国家	行业		地方		企业
	0	0		0		0
新成果	新产品	新工艺	新装置	新材料		计算机软件
	0	0	0	0		0
获奖（项）	国家级	0	省部级	0	其他	0
人才培养（人）	博士后	0	博士	0	硕士	0
经济效益（万元）	0					
社会效益	无					

四、项目经费：

本项目经费总计 4 **万元**，大写：人民币肆万元整 ，其中：

1 甲方资助经费____万元，大写：人民币零元整
2 乙方自筹经费 4 万元，大写：人民币肆万元整
3 其他经费 0 万元，大写：人民币零元整

五、甲方的权利和义务：

1、甲方在本合同签字生效后及时按合同规定核拨经费。

2、甲方有权依据《重庆市教委科学技术研究项目管理办法》，在项目执行过程中检查监督研究进展和经费开支情况，要求乙方按甲方规定及时提供项目进展报告、结题总结报告和经费决算报告等全套资料。

3、甲方有权要求乙方及时转化本项目研究成果。

4、若乙方违反本合同规定，造成本项目不能正常实施和完成时，甲方根据调查情况有权提出终止合同的处理意见，有权延期或停止资助，甚至收回项目全部经费。情节严重的，甲方有权取消项目负责人申报资格，直至追究法律责任。

六、乙方的权利和义务：

1、乙方有权按照本合同的规定获得甲方项目拨款。经费拨付后，乙方要严格按照国家、教育部有关规定以及合同约定，组织科研人员合理使用项目经费，加强对科研经费的管理，完善经费支出、报销审核监督制度。

2、乙方须依据本合同规定和《重庆市教委科学技术研究计划项目管理办法》，提供配套研究经 费及相关条件，保证项目的顺利实施和按期完成。乙方应接受甲方的检查和监督，及时报送有关项目研究进展报告、结题总结报告和经费决算报告等全套资料。项目成果请标注"重庆市教委科学技术研究项目（KJ*******）资助"，英文"Supported by the Science and Technology Research Program of Chongqing Municipal Education Commission (Grant No. KJ*******)"。在项目完 成后，按甲方要求进行结题验收。

3、乙方应鼓励项目负责人使用本项目成果以技术转让、技术入股和联合生产等方式实施有偿转化，成果转化收益分配比例按照国家、重庆市有关政策执行。

4、方在项目执行过程中，本合同签订的内容、考核指标、人员和完成时间原则上不作变更，如需对合同书内容进行调整，应向甲方提交书面申请，并经甲方批准后签订修改（补充）任务书。

5、乙方在项目执行过程中，如遇重大变化致使项目无法继续实施，应主动及时要求终止任务或延长结题时间。对要求终止任务的，视情况，部分或全部退还所拨经费；对要求延期结题的，延期结题时间不能超过一年，超出一年的，暂停项目负责人三年本项目申报资格。

6、乙方应建立健全科研诚信体系、科研行为廉洁的规章制度，监督并认真查处本单位在科

研过 程中出现的违规违纪行为。

七、项目技术保密：

凡属技术保密的项目和内容，甲乙双方均有义务执行国家有关保密规定。在需要公开发表研究内容和用于国际合作、交流时，必须先送市技术保密管理部门审查批准。

八、 本合同自签字之日起生效。本合同由市教委科技处负责解释。

甲　方：市教委 单位公章（合同专用章签章）

年　　　月　　　日

乙　方：法人代表：＿＿＿＿＿＿＿＿＿＿（签章）

　　　　项目负责人：＿＿＿＿＿＿＿＿＿＿（签字）

　　　　账户名：＿＿＿＿＿＿＿＿＿＿

　　　　开户银行：＿＿＿＿＿＿＿＿＿＿

　　　　帐号：＿＿＿＿＿＿＿＿＿＿

单位(签章)

年　　　月　　　日

合作单位：法人代表：＿＿＿＿＿＿＿＿＿＿（签章）

　　　　　负责人：＿＿＿＿＿＿＿＿＿＿（签字）

单位（签章）

年　　　月　　　日

项目编号：　FLKJ,2018BBA3074　　　　　　密级：＿＿＿＿＿

涪 陵 区 科 技 计 划 项 目
（指导性科研项目类）

任 　 务 　 书

项 目 名 称：　废水中低价磷的转化与去除关键技术研究及应用

项 目 类 别：　　　基础研究与前沿探索

承 担 单 位：　　　长江师范学院　　　　　　　（盖章）

项目负责人：　彭浩　　　　联系电话：15123031643

项目联系人：　彭浩　　　　联系电话：15123031643

起 止 年 限：　　2018 年 10 月 至 2020 年 10 月

重庆市涪陵区科学技术委员会

二 O 一八年版

填 写 说 明

1、本任务书系涪陵区科委为区级指导性科研项目而编制，任务书甲方为涪陵区科委，乙方为项目承担单位（或项目牵头单位）。

2、项目类别：基础研究与前沿探索、技术预见与制度创新、技术创新与应用示范项。

3、本任务书由涪陵区科委与项目承担单位签订，一式三份。其中：涪陵区科委二份，项目承担单位一份。提交项目任务书时，须提交项目任务书电子文档。

4、本任务书是项目指导、评估、总结、结题（验收）的依据。任务书的内容必须依据"科研项目征集申报表"所填报内容来填写。

5、本任务书要求文字及排版格式规范，需签字和填写部分要求字迹清晰，用 A4 纸双面打印填报。内容应简明扼要，主要技术和经济指标应量化。

6、项目编号在签订任务书后，由区科委统一编排。

7、项目密级由项目承担单位提出建议。

一、项目承担单位基本情况

<table>
<tr><td rowspan="3">项目承担单位
（第一承担单位）</td><td>名称</td><td colspan="4">长江师范学院</td></tr>
<tr><td>地址</td><td colspan="4">重庆市涪陵区聚贤大道 16 号</td></tr>
<tr><td>属地</td><td colspan="4">重庆市涪陵区聚贤大道 16 号</td></tr>
<tr><td colspan="2">单位性质</td><td>3</td><td colspan="3">1.企业 2.党政机关 3.事业单位 4.社会团体 5.其他</td></tr>
<tr><td colspan="2">工商登记
注册类型</td><td>1</td><td colspan="3">1.国有　　2.集体　　3.股份合作　　4.联营
5.有限责任公司　　6.股份有限公司　　7.私营
8.港、澳、台商投资 9.外商投资　　10.其他企业
11.无（行政、事业单位等没有工商注册的填此项）</td></tr>
<tr><td colspan="6" style="text-align:center">单位法人代表</td></tr>
<tr><td>姓名</td><td>黄大勇</td><td>职务</td><td>校长</td><td>联系电话</td><td>023-72790088</td></tr>
<tr><td colspan="6" style="text-align:center">项目负责人</td></tr>
<tr><td>姓名</td><td>彭浩</td><td>联系
电话</td><td>023-72792170</td><td>手机号码</td><td>15123031643</td></tr>
<tr><td colspan="2">项目主要
合作单位</td><td colspan="4">无</td></tr>
<tr><td colspan="2">项目所属
技术领域</td><td>10</td><td colspan="3">1.材料化工　　　　2.生物技术　　　3.装备制造
4.电子信息　　　　5.节能与新能源　6.现代农业
7.农产品加工与现代储运 8.现代服务业　9.医疗卫生
10.环境保护　　　　11.公共安全　　　12.教育体育
13.文化科技创新　　14.科学技术普及 15.其它</td></tr>
</table>

注：此简表的选择项均为单选项。

二、项目实施的必要性及可行性

1.国内外技术现状及发展趋势

1.1 低价磷的检测方法

磷元素是湖泊生态系统的生源要素之一，其在水生生物中的分布和含量直接影响着水体的初级生产力和蜉蝣生物的种类、数量和分布，是水体中富营养化的主要限制因子。亚磷酸盐等低价磷虽然已被证实在环境中存在但是却鲜有报道，亚磷酸盐作为磷循环的重要组成部分，越来越引起人们的关注。鉴于低价磷酸盐在环境中存在的浓度低以及环境介质本身的复杂性，环境中低价磷的检测是限制这一研究领域深入的瓶颈。

传统的磷划分理论是以常规的钼蓝比色-分光光度法测定磷为基础，但是该方法不能测定低价磷酸盐，故对水体中的低价磷酸盐的关注较少。对于天然水体中的检测鲜有报道，一方面时由于天然水体中的含量很少，另一方面是因为它们还原性很强，极不稳定，很容易被氧化成磷酸根。目前的测量方法主要分两类：一是纯粹的化学方法：如McCloskey法、Jenkin-Bruening法、Vogel法、Rao法等。化学测定法是基于：（1）在中性条件下，亚磷酸盐和碘能够完全反应，生成磷酸根，而次磷酸不会发生反应；（2）在强酸性介质中，次磷酸与碘会完全反应生成亚磷酸，而亚酸盐的反应非常慢。此类方法过程复杂、周期较长，检测限高，无法满足对天然水中痕量的低价磷酸盐的检测要求。二是利用先进的仪器分析手段如离子色谱、高效液相色谱、NMR、IC-ICP-ES等测定。Morten用钼蓝比色法和ICP-ES测定水样中溶解态磷时发现结果差异很大，经证实，差值为低价磷酸盐，并且在热黄磷厂、用铸铁输送的饮用水和含磷缓蚀剂的废水等环境中，测定出这些样品中含有次磷酸盐、亚磷酸盐、甲基磷酸和磷酸盐。同时用该技术证实了所研究的环境体系中存在低价磷酸盐。Ivey用IC-MS技术成功测定了模拟地热水中的次磷酸盐、亚磷酸盐和磷酸盐。

1.2 磷的去除工艺研究

（1）生物法除磷

生物除磷是目前比较经济的一种除磷方法。由一类统称为聚磷菌的微生物完成。聚磷菌能在厌氧状态下同化发酵产物，使得聚磷菌在生物除磷系统中具备了竞争的优势。在厌氧状态下（没有溶解氧和硝态氮存在），兼性菌（能在有氧和无氧的条件下适应生长和代谢的细菌）将溶解性有机物转化成挥发性脂肪酸；聚磷菌把细胞内聚磷水解为正酸盐，并从中获得能量，吸收污水中易降解的COD，同化成细

胞内碳能源存贮物聚β-羟基丁酸或β-羟基戊酸等。在好氧或缺氧条件下，聚磷菌以分子氧或化合态氧作为电子受体，氧化代谢内贮物质PHB或PHV等，并产生能量，过量地从污水中摄取磷酸盐。能量以高能物质ATP的形式存贮，其中一部分又转化为聚磷，作为能量贮于胞内，通过剩余污泥的排放实现高效生物除磷目的。
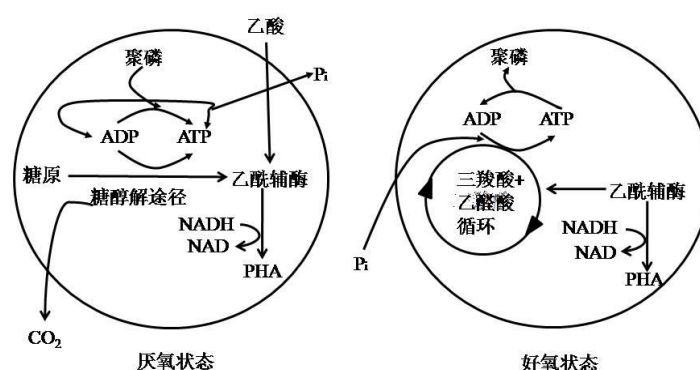
图1 除磷菌代谢模式示意图

但是这种方法有一定的局限性，如除磷效果不稳定、对高磷浓度的畜牧养殖废水及垃圾渗滤液处理效率有限，而且在除磷过程中会产生大量的剩余污泥，需进行妥善处理以防二次污染，很难达到当今工业生产中的需求。

（2）吸附法除磷

吸附法除磷具有容量大、耗能少、污染小、去除快和可循环等优势，其主要原理是利用一些物质自身多孔或者比表面积大的特性以及它们在溶液中对磷酸根离子的亲和力使磷在吸附剂表面实现离子交换、表面沉淀或物理吸附作用，将磷分离出来。

吸附法除磷自身也存在许多不足之处：吸附剂需保持定期更换，费用昂贵；共存离子对改性活性炭除磷影响显著；pH值的变化对金属氧化物吸附容量影响很大；几种特定的阴离子对硅基介孔分子筛影响较大；黏土矿物普遍存在吸附容量小的缺陷，在处理高磷浓度废水时很容易达到饱和，不适合处理高磷浓度的溶液。

（3）离子交换法除磷

离子交换法除磷主要是依靠多孔性的阴离子交换树脂来实现的。树脂具有容易中毒且难再生、选择性低、交换容量小以及只能去除某种单一离子等局限性，一次离子交换法在实际生产应用中很难得到推广，不适合高磷浓度的溶液处理。

（4）电化学法除磷

电化学法除磷是现今比较高效的一种除磷方法，具有操作简单，占地少等优点。

它有效地结合了电絮凝、气浮以及沉淀等多种作用，与生物法相比较而言，具有选择性强、去除率高、水力停留时间短等优势；而与一般的化学沉淀法相比而言，电场和气浮的作用在一定程度上强化了溶液中颗粒物的混凝效率，出水总溶解性的固体较少。利用电解法除磷工艺设备维护简单，污泥含水率低，而污泥又可以得到有效的利用。电絮凝技术用于污水中磷的去除在国内外已经有一定的研究，冯爽等研究了利用铁电极去除城市污水2级处理出水中的磷，结果表明，电絮凝除磷为零级反应，电解7 min后模拟污水中磷的去除率就可以达到70%左右。Rdemez等系统的研究了初始pH、电流密度、磷浓度等操作条件对铝电极或铁电极电絮凝去除污水中磷的影响，发现随着电流密度的增加，对于两种电极其相应的除磷效率和除磷速度都增加，但同时能耗也随之增加；对于铁电极电絮凝除磷工艺，较佳的pH值为7.0，除磷效率随着磷浓度的增加而下降；对于不同磷浓度的模拟污水，使用铝电极时，当电流密度为一定值时，几乎都可得到100%的磷去除率；根据研究结果，一般认为铝电极比铁电极能够更加有效得去除污水中的磷。Bektas等研究了在电流密度为2.5～10 mA·cm-2，水力停留时间为5～20 min的条件下，铝电极对磷质量浓度10～200 mg·L-1的模拟污水的净化效果，结果表明去除率几乎可以全部达到80%以上。

（5）电渗析法除磷

电渗析法除磷的本质就是一种膜分离的技术，它只是对溶液中的磷起到了一个浓缩的作用，无法从根本上除磷。它的工作原理是通过对电渗析室内的多对阴阳离子渗透膜之间施加直流电压，在直流电压的影响下，含磷及含氮的离子和其它的溶解离子中体积小的离子会通过渗透膜进入到另一侧的溶液中去，达到分离的目的。预处理及离子的选择性是利用电渗析法除磷是两个关键的因素，对浓度大的污染溶液必须进行预处理，而选择性高的渗透膜仍然在研究中。

（6）化学沉淀法除磷

化学沉淀法除磷是现今实际生产中运用最广的一种除磷方法，它具有操作简便、除磷效果好、简单易行等特点，适用于高浓度和超高浓度的含磷废水中除磷。近年来，化学沉淀法在湿法浸出液中的除磷工艺中有了很大的应用。取得了比较好的效果。陈红梅等在某湿法浸出液中利用可溶性的无机锆盐（硫酸锆、硝酸锆）进行深度除磷，除磷率达到99%以上。夏文堂等在高磷铁矿湿法除磷废水中利用氧化钙为除磷剂进行除磷实验，最终使废水中的磷的含量由原来3020 ug/mL降到了0.5 ug/mL，成功满足了废水排放的要求。

化学沉淀除磷是在含磷废水中加入铁、铝、钙等含有这些金属离子的化学试剂，

通过化学反应生成磷酸盐沉淀物，之后再利用固液分离的方法转移到污泥中，达到除磷的目的。

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2.项目立项的必要性

低价磷化合物的分析检测主要依赖于精密的仪器，且高价磷的去除工艺存在着成本较高等问题，本项目拟开展目标物质定向转化及工艺开发两方面的研究，建立低价磷快速分析的实验室检测方法，并结合刚柔组合搅拌桨对高价磷的去除过程进行强化，减少除磷剂的消耗，降低工艺成本，为政府在经济发展、环境保护方面实现可持续化发展提供共性关键技术。

3.申报单位现有工作基础或支撑条件

3.1 研究基础

申请人长期从事化工过程强化及节能减排方面的研究，在化工、冶金过程非线性科学领域开展了较为系统深入的研究，这为本申请项目的研究奠定了良好的基础。

（1）低价磷的检测分析

磷具有多种可变价态，在溶液中磷主要以各种形式的含氧酸盐形式存在。一般认为在水溶液中磷主要以正磷酸盐、次磷酸盐、焦磷酸盐以及聚合磷酸盐等高价态的形式存在。申请者在前期研究中发现，在水溶液磷还会以低价态的形式存在（表1和图3），且该形态的磷主要以络合物的形式存在，结构稳定，难以破坏且难以被除去，给生产生活带来较大不便。
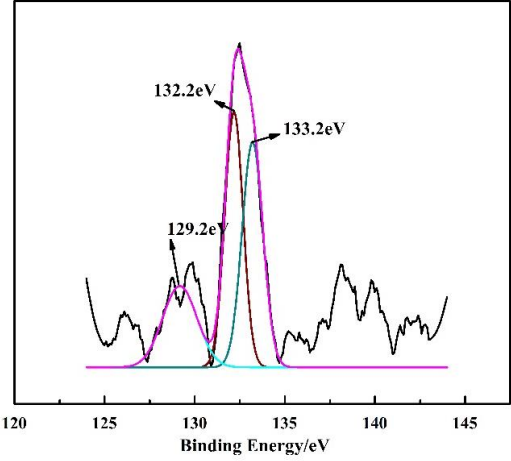
图 3 废水中磷的 XPS 谱图

表 1 废水中磷的价态与组成

	低价磷（%）	五价磷（%）
废水中磷含量	79.96	23.04

（2）磷的去除行为研究

申请者对转炉钒渣酸浸液中的磷酸盐的去除工艺进行了研究，重点研究了除磷剂种类、投加量以及反应pH条件对除磷效果的影响。

硅酸钙($CaSiO_3$)对转炉钒渣硫酸浸出液具有一定的除磷效果。当反应温度为20 ℃，加入的$m(CaSiO_3):m(P)=15:1$，反应时间为20 min，P的去除率可以达到78%，但是浸出液中剩余磷的浓度仍然很高，达140 mg/L。聚合硫酸铁对钙化转炉钒渣酸

性浸取液具有很好的除磷效果。当聚合硫酸铁的用量为n(Fe/P)到1.0，除磷率可以达到87.43%，溶液中磷的浓度从874 mg/L降低为76 mg/L。

采用聚合硫酸铁和硫酸铝复合除磷时，利用Al^{3+}促进酸性钒浸出液中钒磷杂多酸水解为PO_4^{3-}，再利用Al^{3+}、Fe^{3+}和OH^-、PO_4^{3-}之间的络合共沉淀以及含铁的羟基络合物的吸附作用，实现高效除磷。实验结果表明，在温度为50℃，反应时间为1 h，n (Fe:Al:P)=0.6:0.4:1时钒浸取液中的磷含量可从874 mg/L降低至79 mg/L，除磷率可达到91.09%。

由此可见，研究团队对本申请项目有关的研究已有相当的积累，已取得较显著工作成绩，本项目的有关准备工作是充分的，基础是扎实的。

3.2 工作条件

申请人所依托的长江师范学院拥有无机特种功能材料重点实验室、武陵山区特色资源开发与利用研究中心和三峡库区环境监测和灾害防治工程研究中心等，具有较好的研究条件，已经具备了本项目所需仪器设备。另外，申请人与之前重庆大学化工过程强化与反应国家地方共建工程实验室、洁净能源与特色资源高效利用化工过程重庆市重点实验室一直保持着合作关系，该实验室具有比较完备的测试条件，可以为本项目的完成提供支持。

3.3 经费支撑

申请人目前主持纵向项目项目2项，项目经费达30万，可以为本项目的实施提供财政支撑。

三、项目主要研究内容和目标

（要研究的内容，解决的主要技术难点和问题，项目的创新点等）

主要研究内容	1、系统研究废水环境中低价磷的采集和保存方法，建立废水中低价磷酸盐分析与测试的方法； 2、研究废水中低价磷酸盐的分布情况以及赋存状态，并探讨废水中其他因子对低价磷酸盐存在形态的影响； 3、采用化学沉淀法，结合电化学方法，实现磷酸盐的深度去除，并集合开发低价磷化合物转化与去除的关键科学技术。
解决的主要技术难点和问题	1、低价磷价态及赋存规律 建立废水中低价磷的检测分析方法，并弄清废水中多价态磷的存在形态，分析磷的赋存规律。 2、多重态元素价态演化过程中的非线性动力学机制。 元素变价过程中存在着丰富的非线性机制。分析低价磷的变价氧化过程，揭示多重态元素价态演化的非线性动力学机制。
创新点	1、建立低价磷化合物分析检测方法。 2、多重态元素价态演化过程中的非线性动力学机制。 3、刚柔组合搅拌桨强化除磷过程，降低除磷剂消耗。

四、项目考核内容与指标

1、主要技术指标（包括形成的专利、标准、新技术、新工艺、新产品、新装置、论文专著等成果、指标及其水平等。）：

> 1、建立测定废水中磷的价态及赋存形态的方法
>
> 2、开发出低价磷转化与去除的关键科学技术，
>
> 3、发表相关学术论文 1 篇，申请国家发明专利 1 项。

2、主要经济、社会、生态指标（包括项目实施中形成的示范基地、中试线、生产线及其规模，技术及产品应用所形成的市场规模、效益等。）：

> 1、针对废水中存在的低价磷化合物，开展低价磷化合物转化与去除关键技术研究。通过实验研究，建立一套分析测试磷化合物价态和赋存形态的方法，开发低价磷转化与高效去除的关键科学技术。
>
> 2、通过项目的实施，将研发出一套除磷关键技术，实现废水的无害化及资源化处理，将为政府在经济发展、环境保护方面实现可持续化发展提供共性关键技术。

五、项目实施的年度计划及目标

年度	实施计划及目标
2019年	文献调研拟定实验方案；分析废水样品组分，测试磷的价态和赋存形态。采用化学氧化法结合电化学处技术处理含磷废水，实现低价磷的氧化和解聚，认识元素从多重态定态到动态转化的非线性动力学机制。发表学术论文 1 篇。
2020年	开展高价磷化合物去除实验研究，实现磷的高效去除；结合刚柔组合搅拌桨强化除磷过程，降低除磷剂消耗；开发出低价磷转化与去除的关键科学技术；申请发明专利 1 项，项目结题。

六、项目承担单位、合作单位及主要研究人员

项目承担单位分工：

　　所有工作由项目承担单位负责完成。

主要合作单位分工：

主要研究人员：

序号	姓 名	年龄	职称/职务	从事专业	所在单位	任务分工
1	彭浩	28	讲师	资源化工	长师范学院	主持
2	郭静	26	实验员	化学工程	长师范学院	主研
3	李兵	43	正高级工程师	资源化工	长师范学院	主研

七、项目经费

项目经费由乙方（项目承担单位）负责落实。项目经费来源计划安排如下:

<div align="right">(单位：万元)</div>

经 费 来 源 计 划				
单位自筹	其他部门拨款	银行借款	其他资金	合计
2.5	0	0	0	2.5

八、其它

（指其它特殊约定，主要是指由 2 个以上单位承担项目时各自的任务等约定，没有填"无"）

无

九、廉洁责任

1、乙方应建立健全促进科研诚信、科技行为廉洁的规章制度，组织开展廉洁自律宣传教育，监督并认真查处本单位在科研过程中出现的违规违纪行为。

2、乙方不得向甲方工作人员行贿；不得报销应由甲方工作人员个人支付的任何费用；不得为甲方工作人员购置或提供通讯工具、交通工具、高档办公用品等贵重物品。

3、乙方发现甲方工作人员在科技管理工作中有索贿、暗箱操作等违反廉政建设规定的行为，应及时向纪检监察机关举报并积极协助查处工作。

4、乙方在项目立项和实施过程中贿赂甲方工作人员，或者为其报销应由个人支付的费用、购买贵重物品等，被纪检监察机关或司法机关查证属实的，甲方有权终止项目实施。

5、乙方要严格按照《重庆市涪陵区科研项目管理办法》的要求，制订和落实本单位项目管理和经费管理制度，对项目经费实行单独核算。

6、乙方要加强科研诚信建设，不得在有关人员职称、简历等方面提供虚假信息，不得在项目实施中抄袭、剽窃他人科研成果，不得捏造或篡改科研数据，不得在涉及人体的研究中违反知情同意、保护隐私等规定，不得违反实验动物保护规范等。

十、共同条款

1、乙方必须接受甲方对项目进度的监督和检查，并按甲方要求及时提供年度计划执行情况报告。

2、乙方因某种原因（如：与任务书研究内容有出入、技术措施或某些条件不落实等）致使计划无法执行，需向甲方书面说明情况。

3、项目执行过程中，所有经费由乙方自行解决。

4、如任务书没作约定，成果归乙方所有，但成果转让、产业化必须优先在涪陵区内进行。乙方因实施本项目而引起的各种知识产权纠纷由乙方负全部责任。

5、乙方在项目实施过程中应建立相应的规章制度，加强安全管理，确保人员及设备安全，并对科研安全负全部责任。

6、有两个及以上项目承担单位时，乙方需牵头做好项目分工与协作。

7、项目完成后，乙方应向甲方提出结题申请，并根据甲方要求进行项目结题（验收）。结题（验收）通过后，该项目才能作为正式完成。项目到期后必须及时结题（验收），延期结题（验收）时间不得超过半年。

8、项目完成后的三年内，乙方有义务每年向甲方报送一次项目应用及推广效果的资料。

十一、信用登记

下列情形之一的，区科委将对项目牵头单位和项目负责人实施科技信用记录。

1、项目任务变更未履行相关程序的；

2、经核实项目牵头单位或项目负责人发生重大变故，导致项目目标任务无法实现或项目无法继续实施的；

3、项目未通过验收的；

4、项目逾期未结题时间超过6个月的；

5、经核实在项目申报、项目实施过程中有违纪违规和弄虚作假行为的；

6、因知识产权不清晰，有严重知识产权纠纷或者侵权行为，经调解等方式无法解决问题，导致项目无法进行的。

十二、任务书签订各方

甲方：涪陵区科委（盖章）

　　　代　　　　　表（签字或盖章）：＿＿＿＿＿＿＿＿＿＿＿

　　　项目管理负责人（签字或盖章）：＿＿＿＿＿＿＿＿＿＿＿

乙方：项目承担单位（盖章）

　　　代　　　　　表（签字或盖章）：＿＿＿＿＿＿＿＿＿＿＿

　　　项 目 负 责 人（签字或盖章）：＿＿＿＿＿＿＿＿＿＿＿

　　　财 务 负 责 人（签字或盖章）：＿＿＿＿＿＿＿＿＿＿＿

　　　　　　　　　　　　　　　　20　　年　　月　　日

重庆市社会事业与民生保障科技创新专项
重点研发项目任务书

项目名称	应用多组分悬浮造粒技术创制新型功能性控释肥料研究与示范
承担单位	中化重庆涪陵化工有限公司（签章）
项目负责人	冯永刚
通讯地址	重庆市涪陵区龙桥街道南岸浦
联系电话	15826246222
起止年限	2017-10-23 至 2019-06-01

重庆市科学技术委员会

二〇一七年十月制

一、项目考核指标及验收依据

（一）根据项目目标任务要求明确的约束性指标（验收时对该类指标进行逐项考核，全部指标达成方可通过验收；研究成果表现形式仅为样品、样机、论文的，不得列入约束性指标）

编号	预期研究目标	考核指标	验收依据
1	开发一套肥料养分形态效应及协同调控技术	1.申请专利 20 件以上；2.培养新型功能性肥料研发及生产技术人才 20 名以上；	专利申请提供申请受理或授权文书
2	通过优化适应不同作物的肥料元素配比以及促进大量元素与中微量元素配合，完成系列新型功能性控释肥料产品创制	1.创制开发出含腐植酸、含脲甲醛、含低聚磷酸铵、含中微量元素、水溶性等功能型稳定性控释复合肥新产品 5 个以上；2.推广示范区域肥效试验磷元素利用率提高 5%以上、氮元素利用率提高 6%以上、农作物产量提高 10%以上；	1.产品开发提供农业主管部门登记认定依据；2.示范效果提供有资质的第三方机构检测报告；
3	长江流域肥料企业转型升级提供技术路径示范	形成 20 万吨/年产能，年创产值 5 亿元以上；	企业财务报表

（二）其他考核指标

二、项目研发团队

姓名	专业	工作单位	职称/职务	项目分工	每年工作时间（月）	签字
冯永刚	工商管理专业	中化重庆涪陵化工有限公司	中级	项目负责人	8	
冯永刚	工商管理专业	中化重庆涪陵化工有限公司	中级	项目负责人	8	
李兵	化学工程	长江师范学院	正高	项目技术负责人	6	
徐建华	物理化学	长江师范学院	正高	实验研究负责人	8	
韦莎	化学	中化重庆涪陵化工有限公司	中级	项目技术研发	8	
彭浩	化学工程与技术	长江师范学院	中级	项目实验技术开发	6	
郑义文	化工工艺	中化重庆涪陵化工有限公司	初级	项目管理	8	
马川	果树学	中化重庆涪陵化工有限公司	其他	项目实验肥料土肥实验	8	
李祥国	化学工程与工艺	中化重庆涪陵化工有限公司	中级	项目实验装置运行及管理	12	
张治平	化工工艺	中化重庆涪陵化工有限公司	初级	项目实验装置运行及管理	10	
姜贵华	机电一体化	中化重庆涪陵化工有限公司	初级	项目实验装置运行及管理	10	

江涛	化学工程与工艺	中化重庆涪陵化工有限公司	初级	项目知识产权管理	6
周小华	化工机械	中化重庆涪陵化工有限公司	中级	项目工程化设计及工程建设	6
郑开元	制药工程	中化重庆涪陵化工有限公司	初级	项目实验室开发	12
胡满川	工业分析	中化重庆涪陵化工有限公司	中级	项目样品及产品分析	4
冉东	环境科学	中化重庆涪陵化工有限公司	中级	项目工程化设计及工程建设	6
龚民	化工分析	中化重庆涪陵化工有限公司	中级	项目实验装置运行及管理	6

三、项目实施单位与任务、经费分配

项目承担单位 （盖章）	注册资金 （万元）	财政经费 （万元）	单位联 系人	联系电话	完成的研究任务
中化重庆涪陵化工有限公司	14800.00	37.50	江涛	15923710702	进行土壤分析、作物营养分析、肥料养分形态协同调控等基础研究，对原料及工艺路线筛选、工艺技术装备研究，示范装置改造及调试，新型肥料试生产及委托第三方单位进行性能肥效实验。
项目合作单位 （盖章）	注册资金 （万元）	财政经费 （万元）	单位联 系人	联系电话	完成的研究任务
长江师范学院	0.00	12.50	徐建华	13114028086	进行实验室研究及样品分析，重要实验仪器支持、专家咨询及技术支持。
财政科技经费合计	50				

备注：1、各单位的"注册资金"信息必须与该单位的统一社会信用代码证的注册资金（开办资金）一致。

2、任务及经费分配明确后，承担单位及合作单位需加盖单位公章。

四、主要实施内容(简要阐述技术路径、具体研究内容与应用方案，或技术集成思路与推广应用方案；1000字以内)

技术路径:

```
┌─────────────────┐  ┌─────────────────┐  ┌─────────────────┐
│ 文献梳理、吸收创新  │  │ 市场调研、需求分析  │  │ 产品论证、产品设计  │
└─────────────────┘  └─────────────────┘  └─────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 土壤分析、作物营养分析、肥料              │
        │ 养分形态协同调控等基础研究                │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 原料及工艺路线筛选、工艺技术             │
        │ 装备研究                               │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 实验设计、实验实施、实验总结             │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 技术方案设计、示范装置改造及             │
        │ 调试，新型肥料试生产                    │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 新型肥料缓控释、螯合性、土壤             │
        │ 改良、增产增效性能肥效实验              │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 新产品示范推广                         │
        └──────────────────────────────────────┘
                              │
                              ▼
        ┌──────────────────────────────────────┐
        │ 项目总结、结题验收                      │
        └──────────────────────────────────────┘
```
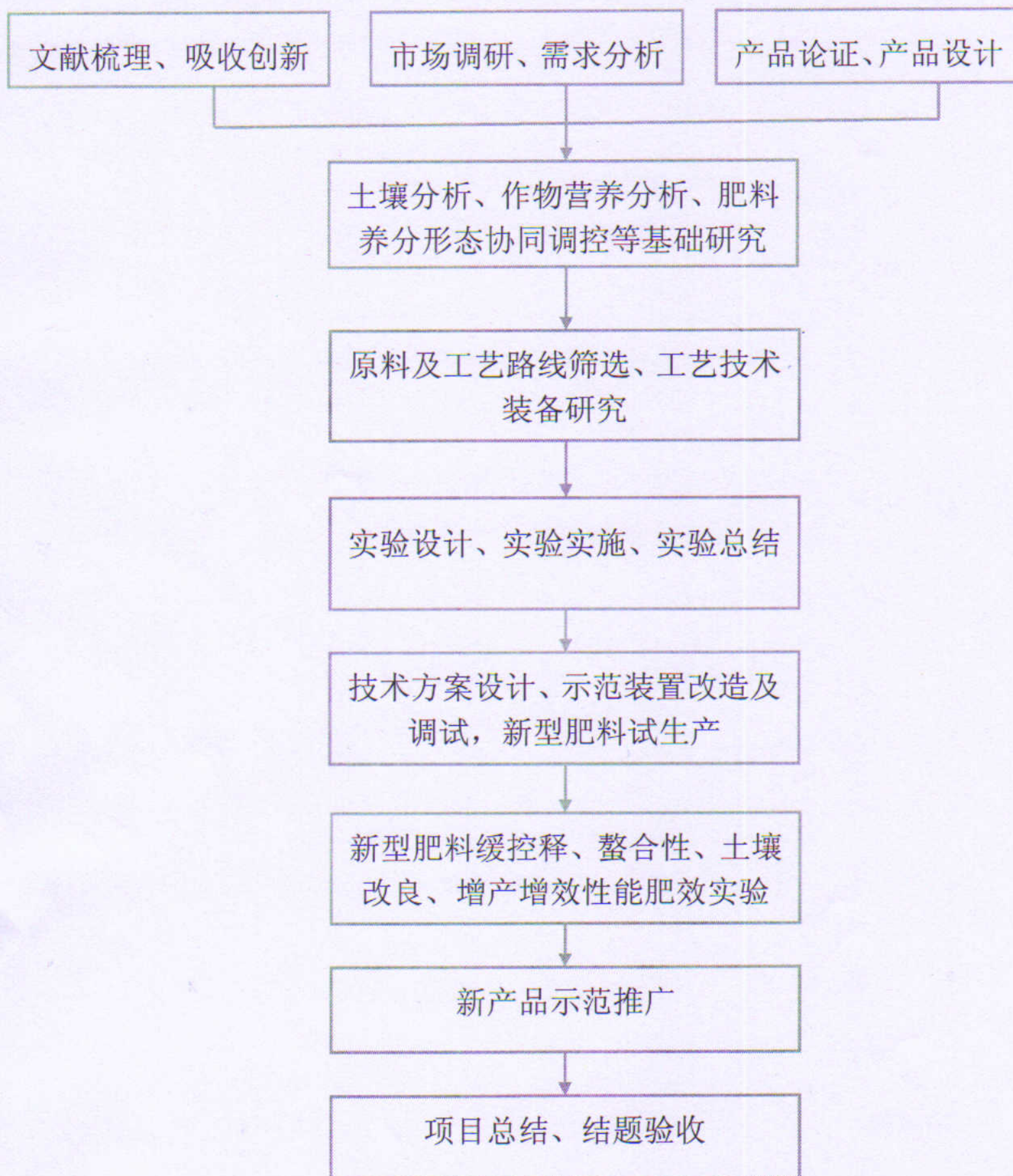
具体研究内容: 通过文献检索及对各种造粒生产工艺解析，结合行业实际情况进行原料、工艺路线筛选，进行多组分悬浮料浆造粒实验研究，优化工艺

指标,形成技术方案;在现有团粒法、喷浆法生产线基础上改造 20 万吨/年多组分悬浮料浆造粒复合肥工业性示范装置,开发合适的反应器及工艺流程,调试生产,优化完善工艺条件;在复合肥造粒工艺提升的基础上,开发出含腐殖酸的有机无机复合肥、含脲甲醛的缓释型复合肥、含低聚磷酸铵的复合肥、水溶性复合肥及复合功能的新型肥料;进行新产品实验,根据实验效果优化产品,进行新产品示范推广;总结研究内容,形成成套的技术方案。

应用方案:

（1）在剖析国外雅苒先进工艺产品基础上,研究不同料浆组分的性能,开展物热衡算,研究磷矿溶解与造粒技术的结合,开发不同的反应器及工艺流程;

（2）在多悬浮喷浆造粒技术研究基础上,研究腐植酸活化及融合利用技术,开发出含有活性腐植酸的复合肥产品,研究有机无机结合功能,研究螯合性能,进行肥效对比实验,研究土壤改良修复性能;

（3）在多悬浮喷浆造粒技术研究基础上,进行脲甲醛合成工艺研究,确定最优反应条件,设计建设脲甲醛合成装置,开发出含脲甲醛的复合肥产品,研究氮元素缓控释功能,进行肥效实验;

（4）在多悬浮喷浆造粒技术研究基础上,开发出含低聚磷酸铵复合肥,研究其螯合性能,并进行肥效实验,研究磷元素缓控释性能;

（5）进行作物营养研究,针对不同作物进行产品配方优化研究,进行营养元素形态研究,进行元素协同、防拮抗研究,进行作物套餐肥施用技术研究,进行肥料实验;

（6）进行技术耦合和功能集成,优选 5 种以上新产品,进行肥效实验,进行示范推广,形成一套从基肥到追肥、作物生长全周期都能配套使用的新型

稳定性缓释肥料生产使用技术，提高肥料利用率、减少化肥施用量、实现粮食增产提质。

稳定性缓释肥料生产使用技术，提高肥料利用率、减少化肥施用量、实现粮食增产提质。

五、经费概算(金额单位:万元)

经费来源概算		经费支出				
科目	概算数	序号	科目	概算数	其中市级财政资金拨款	
		一	直接费用:	335	49.5	
1 市级财政资金	50	1	设施设备费	69	0	
2 单位自筹资金	300	2	材料费	150	39	
		3	测试化验加工费	15	1.5	
		4	燃料动力费	50	0	
		5	差旅会议国际合作与交流费	8	2.0	
		6	出版/文献/信息传播/知识产权事务费	10	0.7	
		7	劳务费	25	4.3	
		8	专家咨询费	3	2.0	
		9	其他支出	5	0	
		二	间接费用:	15	0.5	
		1	管理费	11.5	0	
		2	绩效支出	3.5	0.5	
来源合计	350		支出合计	350	50	

备注: 1. "市级财政资金"必填。

2. "经费来源概算"和"经费支出"科目请参照《关于进一步完善我市财政科研项目资金管理等政策的实施意见》(渝委办发〔2017〕31号)相关规定进行编制。

六、相关责任

1、甲方在项目执行过程中不得无故撤销或终止项目。

2、乙方在项目实施过程中应按照《关于进一步完善我市财政科研项目资金管理等政策的实施意见》（渝委办发〔2017〕31号）的要求，制定和完善相应制度的操作实施细则，对项目资金单独设帐，严格按照预算专款专用。乙方在项目执行过程中，必须接受甲方对经费使用及项目进度的监督和检查，无故不接受监督和检查的，甲方有权暂停资助。

3、乙方在项目执行过程中，项目任务书中签订内容、人员和完成时间原则上不作变更；如因某种原因需对计划任务书内容作调整，应向市科委提交书面申请，并经市科委批准后签订修改（补充）任务书。

4、乙方在项目执行过程中，如遇重大变化（如：与任务书研究内容有出入、技术措施或某些条件不落实等）致使计划无法执行，应主动及时要求中止任务或延长结题时间。对要求中止任务的，按规定进行财务清算，不扣减乙方科研信用分值；对要求延期结题的，只能提出一次申请，且延期结题时间不能超过一年。如乙方没有提出中止任务的要求，甲方根据调查情况有权提出终止任务的处理意见，有权延期或停止资助，甚至收回项目全部经费，并减少乙方申报数量；情节严重的，取消申报资格，直至追究法律责任。

5、乙方应在本计划任务书规定的完成时间前向甲方提出结题申请，并根据甲方要求完成项目结题验收有关事宜。结题验收通过后，该项目才能作为正式完成。

6、乙方应按规定形成并按时提交科技报告。对未按规定形成并提交科技报告的，甲方根据调查情况有权提出终止任务的处理意见，有权停止资助，甚至收回项目全部经费，并扣减乙方科研信用分值。

7、乙方应建立健全促进科研诚信、科技行为廉洁的规章制度，组织开展廉洁自律宣传教育，监督并认真查处本单位在科研过程中出现的违规违纪行为。

8、乙方不得向甲方工作人员行贿；不得报销应由甲方工作人员个人支付的任何费用；不得为甲方工作人员购置或提供通讯工具、交通工具、高档办公用品等贵重物品。

9、乙方发现甲方工作人员在科技管理工作中有索贿、暗箱操作等违反廉政建设规定的行为，应及时向驻市科委纪检组举报并积极协助查处工作。

其他约定：

责任约定签订的约定书、合同协议及签订的其他相关约定以附件形式上传

七、任务书签订各方

甲方：重庆市科委代表： ___农村发展处 处处长___ ___卞雨昕___ （签章）

项目管理人 ___张振杰___ （签章）

（单位签章）

二〇 年 月 日

乙方：项目第一承担单位负责人 ___李仰景___ （签章）

项目负责人 ___冯永刚___ （签章）

帐 户 名： ___中化重庆涪陵化工有限公司___

帐 号： ___31-610101040003301___

开户银行： ___农行涪陵分行营业部___

（单位签章）

二〇 年 月 日

长江师范学院

教育教学改革研究项目

任 务 书

项 目 名 称 新工科背景下工程类课程面向工程的

教学模式改革——以化学工程与工艺专业

课程为例

项 目 类 别　　　　　一般项目

项 目 负 责 人　　　　　吕利平

联 系 电 话　　　　13896936313

起 止 时 间：　2019 年 3 月至 2021 年 3 月

所 属 单 位　　　化学化工学院　　（公章）

填表说明

一、《项目任务书》要逐项填写，不要减少栏目或改变栏目内容。填报内容应简明扼要。如因篇幅原因需对表格进行调整时，应当以"整页设计"为原则。

二、封面上的项目编号按学校立项文件公布的项目编号填写。

三、"成果形式"指教学改革方案、人才培养方案、教学大纲、教材、讲义、课件、软件、调研报告、论文、专著等。

四、此表要求一律用 A4 纸双面打印，于左侧装订成册。一式两份，教务处和项目负责人各一份。

一、项目组成员

	姓　名	出生年月	职称	本项目中的分工	签名
项目组主要成员	李兵	1976 年	高级工程师（博士）	教学模式构建，教学设计，简化工程案例	
	郭峰	1977 年	教授（博士）	教学模式改革，简化科研成果	
	杨甲	1985 年	讲师（博士）	主讲课程，教学设计	
	彭浩	1990 年	讲师（博士）	教学设计，构建理论评价体系，答疑，批改作业	
	贾乾发	1988 年	讲师（博士）	教学设计，构建实验评价体系，批改实验报告，答疑，简化科研成果	
	李航	1986 年	工程师（硕士）	简化科研成果，批改作业	

二、项目研究方案

（一）研究目标、研究内容和研究思路

1.1 研究目标

　　本项目以工程能力为导向，利用现代设计软件，结合简化的工程案例及科研成果，达到调动学生的学习积极性，提高学生的工程能力的目标，建立适应当前形势下工程类课程的教学模式，让工程教育回归工程。通过项目的建设，一方面提高学生的学习兴趣、学习目的性及学习自主性，强化学生的工程观念，让他们能够在有限的学习时间内掌握实用的工程技术，以期达到通过工程课程的学习具备解决实际工程问题的能力，加快学生向化工工程师的转变，实现工程教育与社会需求的"对接"；另一方面，通过这门课程的实践研究，促进教学质量及师资队伍的教学水平和教学研究水平的提高，同时，为本专业及其他工科专业工程类课程开展面向工程的教学模式提供可借鉴的路径和方法。

1.2 研究内容及研究思路

（1）通过本课题的研究，整合和优化相关课程内容，拓宽学生的视野；

（2）丰富课程教学资源，让学生在有限的学习时间内，能够学习到如何解决工程问题的能力；

（3）通过构建多元化的评价体系，激励学生长期保持学习的积极性和兴趣；

（4）通过本课题的研究提高相关教师的教学能力与教学效果，增强其教学科研能力。

（二）拟采取的研究方法与途径

2.1 以工程能力为导向，整合及优化课程内容

　　由于课程的课时有限，而涉及到两门课程的知识较多，如果完全按照课程本身的要求来进行讲解，势必会让学生感到知识点太多而抓不住重点。因此，根据本项目团队多年的教学经验，拟对课程的内容进行整合，而不是按照教材顺序进行讲解，这样会让学生更加明白前、后知识点的联系，使得学生更加容易掌握本课程的课程体系。初步的整合思路是根据化工专业毕业生需要具备的工程能力来进行整合，化工专业毕业生需要掌握阅读和绘制工艺物料流程图（PFD 图），带控制点的工艺流程图（PID 图），化工设备装配图，设备及车间布置图等。根据每种图样所需的工程制图的知识点进行匹配，将工程制图的知识分解到每种化工图样中，同时，根据化工专业的特点对该部分内容进行精简。初步构建的化工制图课程体系，如图 2-1 所示。

```
                      ┌────────────────┐
                      │  化工制图理论课  │
                      └────────────────┘
        ┌───────────┬───────────┬───────────┬───────────┐
   ┌─────────┐ ┌─────────┐ ┌─────────┐ ┌──────────────┐
   │制图基础知识│ │化工工艺流程图│ │ 投影基础 │ │设备及管道布置图│
   └─────────┘ └─────────┘ └─────────┘ └──────────────┘
                                  │
                            ┌─────────┐
                            │ 表达方案 │
                            └─────────┘
                                  │
                          ┌────────────┐
                          │化工设备装配图│
                          └────────────┘
   ┌─────────┐ ┌─────────┐ ┌──────────────┐ ┌──────────────┐
   │手工抄画图纸│ │PFD及PID图的│ │根据设备简图绘 │ │根据立体厂区图 │
   │         │ │  绘制    │ │制装配图     │ │绘制布置图    │
   └─────────┘ └─────────┘ └──────────────┘ └──────────────┘
                          ┌────────────┐
                          │化工制图实践课│
                          └────────────┘
```
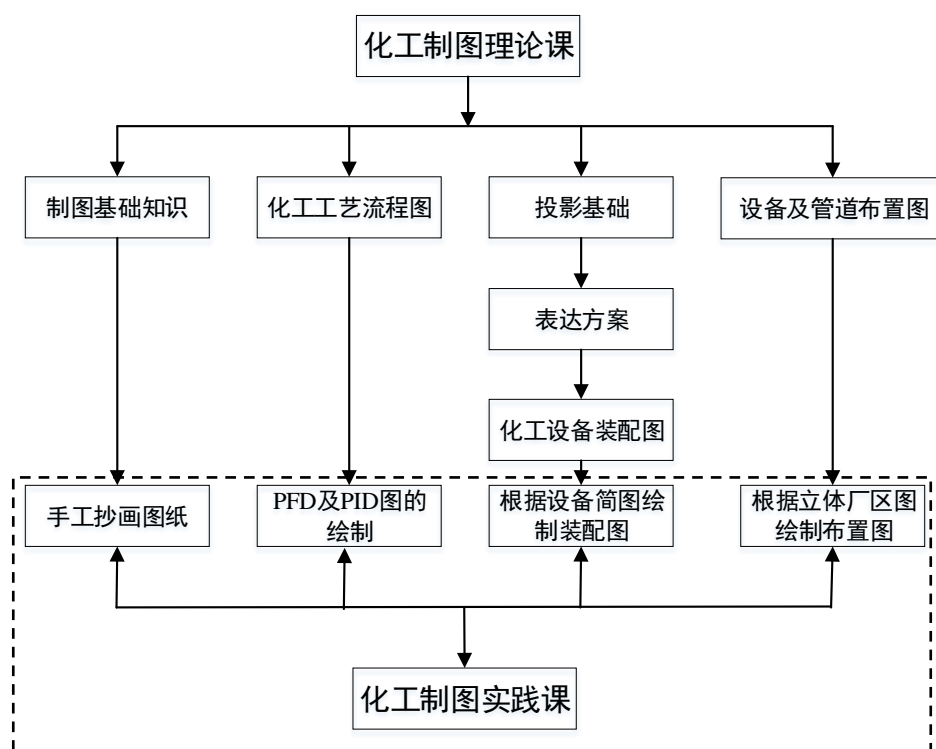
图 2-1 化工制图的课程体系

2.2 将工程案例及科研成果简化引入课堂，激发学生的学习兴趣

　　想要从根本上提高学生的学习积极性，培养学生的工程能力及创新意识，就应该从"为什么学，学什么，如何学及如何用"几个方面解决学生的兴趣驱动问题。美国教育专家兰本达说："学习是在学习者自身内部发生的过程，他越是卷入得深，就越是有动力，也就越能积极和这一过程合作"。因此，可以将工程案例或者较为前沿的科研成果进行简化后，对教学内容进行更新。同时，采用合适的教学方法，诱导和引发学生对当前学习内容的兴趣，以便调动学生参与的积极性。注意，在选用工程案例或者科研成果的时候，最好具有整体性及连续性，比如说：围绕某个产品的生产而绘制的 PFD 图，PID 图，关键设备的装配图，设备及管道布置图等。这样可以让学生能够更加明白，每种图在工程应用中表达特点及作用，能够结合工程需要绘制符合要求的图纸，从而增加学生获取绘图成果的成就感，并提高学生的工程分析能力，增强学生的设计及表达欲望，使学生能明显感到可以"学以致用"。

图 2-2 以绘制物料流程图（PFD 图）为例，说明如何将工程案例及简化的科研成果引入课堂，讲解"为什么学—>学什么—>如何学—>如何用"的问题。首先，给学生放映工厂全貌的 3D 视频，让他们对化工厂的设备有个初步的印象，再创设"建设化工厂的依据是什么？"的工程问题来激发学生的学习热情，而讲解的 PFD 图的内容及绘图标准与所看视频的 3D 厂区恰好匹配，学生就容易明白了 PFD 图纸的作用和意义；课后，再结合现代流程模拟软件 Aspen Plus 所模拟出的工艺流程及提供的方框图（简化的科研成果）绘制 PFD 图，这样就能很好的将所学的工程知识用于解决工程问题，达到兴趣驱动的目的。
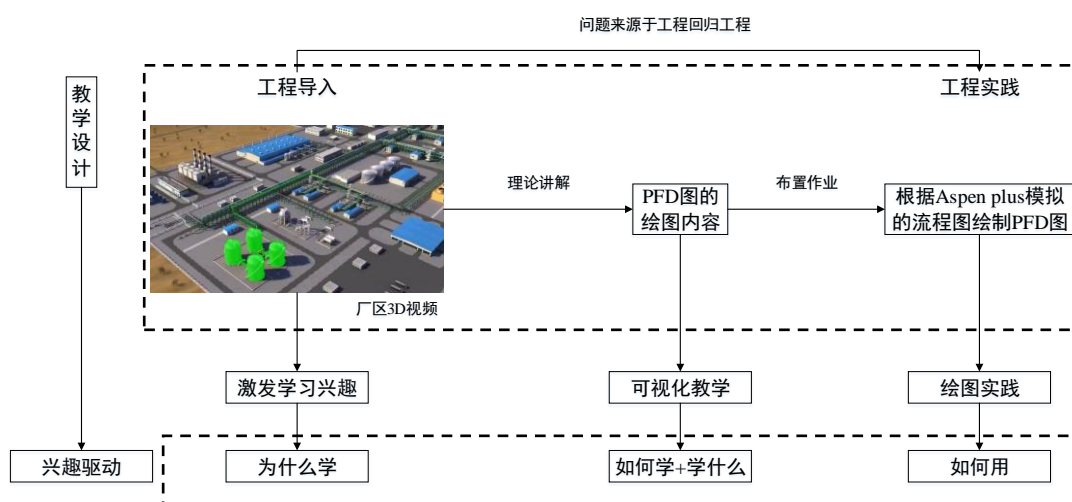
图 2-2 面向工程导向的教学设计（绘制 PFD 图）

2.3 利用多种设计软件及地方资源，解决理论和工程结合不紧密的问题

在整个教学过程中，不可能教授每个知识点，都领着学生去化工厂参观。那么，如何在常规的教学过程中，解决理论和实际结合不紧密的问题，一直是本项目团队所研究的难点。因此，本项目团队拟将简化的科研成果引入到实践课程中，并采用多种现代设计软件（Aspen Plus 流程模拟软件，Aspen Dynamics 动态控制软件，3D Max，Auto CAD 及 Visio 绘图软件），让学生能够利用所提供的资料，绘出比较满意的图纸，有效解决理论知识和工程实际结合不紧密的问题。拟采取的方案如图 2-3 所示。
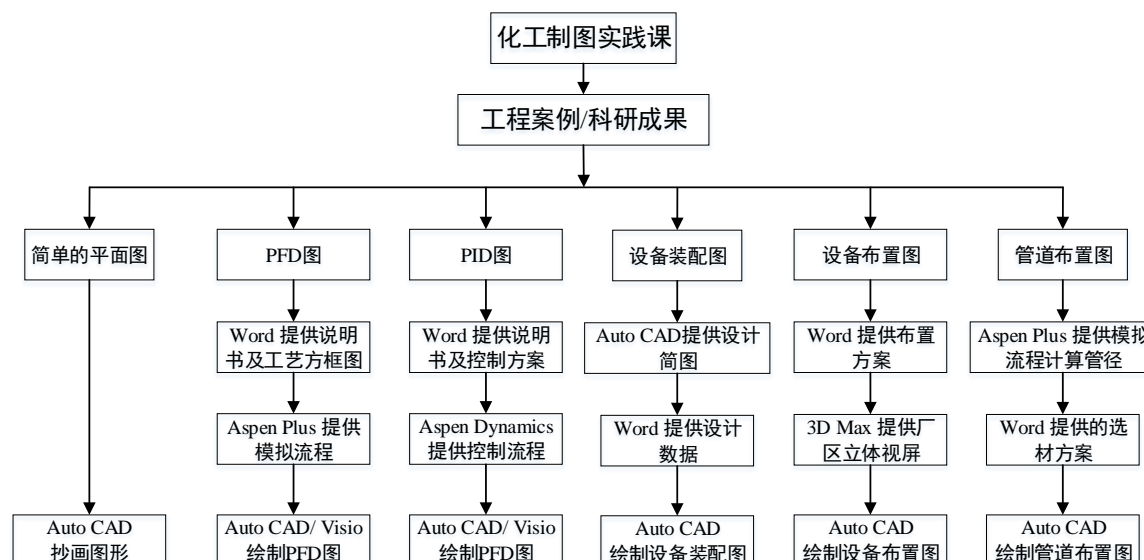
图 3 化工制图实践课程改革

另外，长江师范学院位于重庆市涪陵区，当地拥有非常多的化工园区，可以利用特殊的地方资源，加强校-企合作，更好的培养学生的工程应用能力，提高学生的工程素质。同时，该方式的实施也拓宽了教学资源，让课堂能够有机会从教室走向多种企业，避免了课程学习的封闭性。

2.4 基于 OBE 原则，构建多元化的评价体系

全面的评价体系不仅能够有效的反馈学生的学习效果，而且能够激励学生长期保持学习的积极性和兴趣。因此，本项目课题组拟在"学习过程"和"学习结果"两个维度上设置若干考核指标，在考查学生知识获得情况的同时，还对学生的创新意识、工程实践能力、分析与解决问题的能力、团队合作精神与协调能力等方面进行评价。

（三）项目实施计划与步骤

2019.05—2019.12　整合和优化教学内容，完成及细化教学大纲

主要通过与相关兄弟院校和相关的化工企业，工程公司，设计院等的交流，同时借鉴相关其他专业工程类课程改革的经验，相关文献的查阅，相关课本的参考。完成及细化化工专业工程类课程的模块设置，构建贴近专业和企业需求的工程模块应用体系，让课程的知识模块体系和企业能力需求更加契合。

2020.01—2020.06　收集整理简化的科研成果及工程案例

主要是针对每一种图样，寻找合适的案例，要求案例要比较适合教学。

2017.06—2017.12　构建多元化的课程评价体系

构建理论课程及实验课程的评价体系。

三、经费使用计划

分项写明经费使用计划

1．资料费/调查研究： 3000 元

2．论文发表等： 1000 元

3．项目结题及验收： 1000 元

　(1)整合和优化教学内容，完成及细化教学大纲，编写课程实践讲义一份;

　(2)收集整理并简化的科研成果及工程案例;

　(3)构建多元化的课程评价体系，提交详细的评价实施方案一份;

　(4)总结经验和成果，撰写并发表论文 2~4 篇;

　(5)实践总结报告。

四、预期研究成果

序号	完成时间	成 果 名 称	成果形式	完 成 人
1	2019.12	收集整理并简化的科研成果及工程案例;	作业/实验	李兵，郭峰
2	2020.12	整合和优化教学内容，完成及细化教学大纲，编写课程实践讲义一份	实验讲义	吕利平
3	2021.6	构建多元化的课程评价体系，提交详细的评价实施方案一份	课程体系评价实施方案	杨甲，彭浩
4	2021.12	总结经验和成果，撰写并发表论文 2~4 篇;实践总结报告。	论文及实践总结报告	贾乾发，李航

五、审核意见

项目负责人所在单位意见：

　　　　　　　　　　　　　　　　　　负责人：　　　　　　（公章）

　　　　　　　　　　　　　　　　　　　　　　年　　月　　日

学校意见：

　　　　　　　　　　　　　　　　　　（公章）

　　　　　　　　　　　　　　　　　　　　　　年　　月　　日

长江师范学院

教育教学改革研究项目

任 务 书

项 目 名 称　　新工科视域下的化工专业人才能力矩阵解析与

本科培养方案重构

项 目 类 别　　一般项目

项 目 负责人　　李兵

联 系 电 话　　13609470555

起 止 时 间：2018 年 4 月至 2019 年 6 月

所 属 单 位　　　　　　　　　　　　（公章）

填表说明

一、《项目任务书》要逐项填写，不要减少栏目或改变栏目内容。填报内容应简明扼要。如因篇幅原因需对表格进行调整时，应当以"整页设计"为原则。

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三、"成果形式"指教学改革方案、人才培养方案、教学大纲、教材、讲义、课件、软件、调研报告、论文、专著等。

四、此表要求一律用 A4 纸双面打印，于左侧装订成册。一式两份，教务处和项目负责人各一份。

1

一、项目组成员

项目组主要成员	姓 名	出生年月	职称	本项目中的分工	签名
	徐建华	1964.01	教授	方案推广	徐建华
	吕利平	1987.01	助教	需求调研	吕利平
	彭浩	1990.03	讲师	方案编制	彭浩

二、项目研究方案

（一）研究目标、研究内容和研究思路

研究目标：通过本课题的研究，目的在于全面认识新工科的真实内涵所在，从人才培养单位的供给侧和用人单位的需求侧两个角度，进一步调研感知新工科对人才培养，特别是工程类人才培养的能力矩阵内涵，并用人才培养方案的方式对这新的内涵进行逻辑分析，并一一对应，从而让新工科的能力素质要求真实体现下我们人才培养方案之中。基于此，提出对现有学院化工专业培养方案和课程体系进行修订，以适应新工科背景下的专业改造需要，并切实改变现有培养方案对人才实践能力培养力度不够的问题，为该专业的特色发展和建设以及化工类专业新工科改造提供建议。

研究内容：本课题主要研究内容是通过走访园区企业及政府人力资源管理部门，对新形势新产业背景下，重庆市支柱产业之一的化工医药产业的化工类人才能力需求进行实地调研，对调研结果进行分析归纳，建构出化工专业人才能力矩阵，并以此为要求，对我校现有化工专业本科培养方案进行修订，提出适应新工科的课程体系。

研究思路：一是通过广泛深入人才需求侧的工厂企业及工业园区进行化工人才需求调研，掌握需求侧对新工科背景下的化工专业能力具体要求。二是收集分析国内同类高校化工专业培养方案，比较研究同行对新工科的专业改造举措和培养方案改革实施情况，获取本课题研究可以借鉴的地方。

（二）拟采取的研究方法与途径

1、通过对国内特别是川渝地区化工本科院校人才培养方案进行调研，转换角度看问题，从人才需求侧进行调研，以新工科视域分析解构供需双向协同的化工专业人才能力需求矩阵。

克服现有培养方案重在从学校教学本位出发，更加倾向于落实教学任务，对新时代的新产业的新要求呼应不及时，甚至选择性反馈的弊病。真正转换角度，从实现供需两端有效对接的角度进行新工科视域下对化工专业人才能力需求的分析，构建能反应新工科内涵的能力矩阵。

2、将新发展理念和新时代新要求融入人才培养方案，构建更加适应"新工科"视域下的化工专业人才培养方案。

解构能力矩阵，然后根据能力矩阵要求，对照分析现有化工专业人才培养方案，并对专业课程方案进行重构，同时融入新时代绿色发展理念，研究应对新高考的全面实施，从教育端构建学生对化学化工专业的正确认识，以寻求一个更加适应"新工科"视域下的化工专业人才培养方案，并为化工专业适应新工科而进行专业改造提供建议。

3、积极探索以校企协同的人才培养双向对话模式，促进化工专业人才培养能力及培养方案的双向动态调整机制。

通过对现有人才培养方案，特别是承接培养方案的载体——化工专业课程体系进行修订，以重构适应新工科要求的课程设置方案。根据新的课程内容，重新设定教学计划等；并积极参与构建校企联合，建立工学结合、校企合作新模式，把课程搬到工厂，把工厂搬到学校，切实发挥企业和学校的资源优化组合，真正实现新工科视域下的化工人才协同培养。从而使得学校化工专业能够为新工科培养更多高素质人才。

（三）项目实施计划与步骤

第一阶段：2018/04—2018/09，制订调研方案，并选取国内有代表性的化工专业院校进行新工科培养方案情况调研；

第二阶段：2018/10—2018/12，进行研讨分析，解析需求侧对化工专业人才能力需要，并分析现存本科培养方案的响应情况，提出改进方案；

第三阶段：2019/01-2019/06，整理资料，形成研究成果，准备项目结题验收。

三、经费使用计划

分项写明经费使用计划

本项目申请经费 0.5 万元，具体开支如下：

1. 资料费：2000 元，购买资料、下载文献、打印与复印等。

2. 项目实施费：2000 元，购买试验耗材、化学试剂，与企业合作的接待、差旅等费用。

3. 会议费：500 元，项目组召开的实验教学研究会议费用。

4. 劳务费：500 元，开展实验研究的劳务费。

四、预期研究成果

序号	完成时间	成 果 名 称	成果形式	完 成 人
1	2019.6	化工专业人才培养方案修订版。	人才培养方案	李兵、徐建华、吕利平
2	2019.6	化工专业课程体系建议稿	人才培养方案	李兵、彭浩、吕利平
3	2019.6	课题研究总结报告	调研报告	李兵、彭浩、吕利平

五、审核意见

项目负责人所在单位意见：

同意实施

负责人： （公章）

年 月 日

学校意见：

同意实施

（公章）

年 月 日

4

A literature review on leaching and recovery of vanadium

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ABSTRACT

Vanadium as an important national strategy resource is widely used in many fields due to its excellent physicochemical properties. Much attention had been focused on recovering vanadium from vanadium titano-magnetite and stone coal as they were the main vanadium resources in China. Sodium roasting technology was the earliest technology applied in recovering vanadium, high recovery efficiency of vanadium was obtained along with serious environment problem like corrosive gases and hazardous wastewater. Calcium roasting technology avoided above problems, but high energy-cost and low recovery was remained. Non-salt roasting technology was suitable for limited vanadium resource. Vanadium was leached out after roasting and the leaching medium was divided into three parts according to the roasting technology. Recover process of vanadium depended on the vanadium species and pH in the leaching solution. Hydrolysis was the easily technology with most impurities. Ammonium precipitation was the common process for every technology. And high purity of V_2O_5 was obtained by calcining precipitation of recovery process. Overall, the industry of vanadium leaching was still under-developed, and much intensive research work was needed.

1. Introduction

Vanadium is in the first transition series of the periodic table, specifically in the 5 group (group VB), which accounted Z = 23 in the periodic table, and being considered as a refractory metal due to its high melting point. It was discovered in 1831 by Andrés Manuel del Río, from a lead mineral from Zima pan, Mexico, and was named Vanadis, the Scandinavian Goddess of love, beauty and fertility, due to its multicolored compounds [1–3]. As it had an electronic configuration of $[Ar]3d^34s^2$, the vanadium valence could be V(II), V(III), V(IV) and V(V), and V(IV) and V(V) were the most common oxidation states [4]. The vanadium and its compounds as important national strategy resources were widely used in petrochemical industry, catalyst, iron steel, due to their excellent physicochemical properties and also being called "vitamins of modern industry" [5–10]. In China, the vanadium in low valence was deposited in vanadium titano-magnetite [11] and stone coal [12]. Usually the recovery of vanadium was in its high valence, and some pre-treatment was needed before leaching out vanadium, aiming at oxidizing the vanadium in low valence into high valence, which had high solubility and easy to be leached out [13,14].

2. Leaching out of vanadium

The converter vanadium slag was produced by the titan-magnetite smelting process [15], which amounts of lots of vanadium, iron, manganese, aluminum and silicon. The researchers found that the main phases in the converter vanadium slag were spinel phase, silicate phase and inclusion phase. The vanadium was commonly existed as spinel phase like Fe_2VO_4 [16–18] (showed in Fig. 1), which was hard to leach out with direct leaching. The principle of recovering vanadium was to oxidize V(III) to acid-soluble V(IV) compounds and/or water-soluble V(V) compounds, and then to dissolve it by acid leaching and/or water leaching. Often, some pre-treatment technologies like roasting [19–21], and intensified technologies were applied to enhance the recovery process of vanadium.

2.1. Roasting

2.1.1. Sodium roasting technology

The traditional roasting technology was sodium roasting technology which could be traced back to the first salt-roasting technology by Bleecker in 1912 [22]. The sodium salts (Na_2CO_3, Na_2SO_4 or NaCl) were mixed with vanadium slag and roasted in furnace at high temperature [23–25]. During the roasting process, V(III) in vanadium slag was oxidized by oxygen to maximal extent and transformed into sodium vanadates. The chemical reactions were as followed [26]:

$$4NaCl+O_2 \rightarrow 2Na_2O + 2Cl_2\uparrow \qquad (1)$$
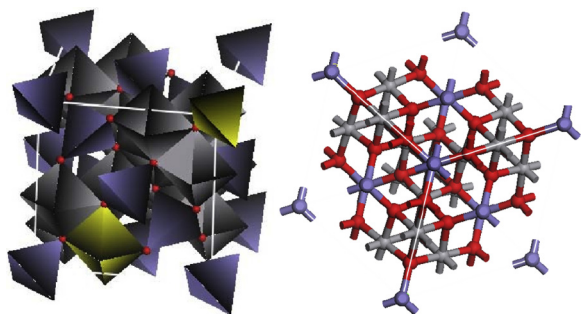
Fig. 1. The crystal structure of FeV_2O_4.

The formation of Cl_2 could catalyze the oxidation.

$$2V_2O_3 + O_2 \rightarrow 2V_2O_4 \tag{2}$$

$$3Cl_2 + 3V_2O_4 \rightarrow 2VOCl_3 + 2V_2O_5 \tag{3}$$

$$4VOCl_3 + 3O_2 \rightarrow 2V_2O_5 + 6Cl_2 \tag{4}$$

$$xNa_2O + yV_2O_5 \rightarrow xNa_2O \cdot yV_2O_5 \tag{5}$$

The ratio of x to y in Eq. (5) was closely related to the roasting conditions. And then the vanadium was leached out followed by water-leaching or acid leaching.

Jiang [27] investigated the leaching process of vanadium and chromium by sodium salt (Na_2CO_3) roasting-(NH_4)$_2SO_4$ leaching, the results showed that 94.6% vanadium and 96.5% chromium were leached out. Zhang [28] leached out vanadium from stone coal with 6 wt. % NaCl and 10 wt.% Na_2SO_4 as roasting additive. During the roasting process, the vanadium-bearing muscovite with quartz was converted to feldspar group minerals (albite, orthoclase and anorthite). The findings could produce some potential methods for recovery of vanadium from stone coal. Wang [19] roasted the red cake with 22.5 g NaOH/25 g red cake at 170 °C for 60 min, and then leached with water at 98 °C for 60 min with liquid-to-solid ratio of 3.3:1 mL/g, the leaching efficiency of vanadium was up to 97.0% and V_2O_5 with purity 99.3% was obtained after purified and roasting. Stepwise sodium roasting-water leaching technology [25] was applied to recover vanadium and chromium from high-chromium vanadium slag. About 87.9% of the vanadium could leach out at first step of Na_2CO_3-roasting-water-leaching at roasting temperature of 800 °C for 120 min. The V^{3+} was firstly activated by the oxidation of Fe^{3+} in the spinel lattice and then reacted with Na_2CO_3 and O_2 to generate high solubility vanadium oxides.

2.1.2. Calcium roasting technology

During the sodium roasting process, some corrosive gases like Cl_2, SO_2 and HCl emitted due to the addition of Na_2SO_4 or NaCl, and they were harmful to environment. Calcification roasting was a clean technology used as an alternative to sodium roasting.

In the calcium roasting technology, limestone, lime or other calcium compounds were mixed with vanadium slag and grounded to fine particles, and then roasted in vertical kiln [29–31]. During the roasting process, the vanadium reacted with calcium to form calcium vanadates and then leached out by acid leaching [29,32–34] and alkaline leaching with carbonate or bicarbonate solution [35,36]. The principle was investigated, and the roasting process were divided into four main parts ranged from the roasting temperature.

(1) FeO was oxidized at 300 °C.

$$2FeO + O_2 \rightarrow Fe_2O_3 \tag{6}$$

(2) The complex-compound decomposed at 400–500 °C.

$$Fe_2O_3 \cdot SiO_2 \rightarrow Fe_2O_3 + SiO_2 \tag{7}$$

(3) Spinel phase was oxidized as the temperature arose.

$$2Fe_2VO_4 + 2FeO + O_2 \rightarrow 2Fe_2O_3 \cdot V_2O_3 \tag{8}$$

$$2Fe_2O_3 \cdot V_2O_3 + O_2 \rightarrow 2Fe_2O_3 \cdot V_2O_4 \tag{9}$$

$$2Fe_2O_3 \cdot V_2O_4 + O_2 \rightarrow 2Fe_2O_3 \cdot V_2O_5 \tag{10}$$

$$Fe_2O_3 \cdot V_2O_5 \rightarrow Fe_2O_3 + V_2O_5$$
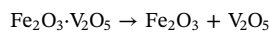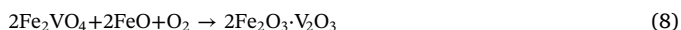
(4) The formation of calcium vanadates.

$$Fe_2O_3 + V_2O_5 \rightarrow 2FeVO_4 \tag{11}$$

$$2FeVO_4 + CaO \rightarrow CaV_2O_6 + Fe_2O_3 \tag{12}$$

$$VO_2 + CaO \rightarrow CaVO_3 \tag{13}$$

$$V_2O_5 + 3CaO \rightarrow Ca_3V_2O_8 \tag{14}$$

$$3VO_2 + CaO \rightarrow CaV_3O_7 \tag{15}$$

The calcined products were confirmed by the roasting temperature and also the addition ratio of Ca/V [37].

Calcification roasting-acid leaching of high-chromium vanadium slag was conducted to elucidate the roasting and leaching behaviors of vanadium and chromium [30]. The results showed that more of the CaO was likely to combine with vanadium and reacted to generate calcium vanadium which led to high leaching efficiency about 91.14% for vanadium, while chromium was remained in the leaching residue, only 8.48% was leached out. Xue [31] studied the isotherm and non-isotherm oxidation kinetics of converter vanadium slag with addition of calcium oxide. The results showed that the whole oxidation process could be divided into two parts, the first part followed the equation $[1–(1-x)^{2/3}] = kt$ with $Ea = 20.42$ kJ/mol at lower temperatures of 400–500 °C, and second part was followed $[(1- x)^{-1/3}-1]^2 = kt$ with $Ea = 227.66$ kJ/mol at temperature higher than 500 °C. Xue [21] investigated the roasting process of high-chromium vanadium slag with CaO and microwave heating. The roasting products of vanadium was changed with the dosage of CaO. At low $m(CaO)/m(V_2O_5)$, CaV_2O_6 was formed, and then converted into CaV_2O_7 and $CaVO_3$ as $m(CaO)/m(V_2O_5)$ increased. The microwave irradiation could decrease the particles size and shorten the roasting time and achieved leaching efficiency of 98.29% for vanadium under optimal conditions. Zhang [38] studied the roasting process of vanadium slag with lime. The heating rate had significant effect on the recovery of vanadium and lowering heating rate could achieve high recovery of vanadium. The formation of $Ca_2V_2O_7$ was more beneficial for vanadium leaching with sulfuric acid.

2.1.3. Non-salt roasting

Chromium spinel was commonly existed in the vanadium slag and could be oxidized to hexavalent chromium under alkaline roasting conditions. While the hexavalent chromium was a toxicity heavy metal contaminant and had being classified in Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (IARC). Du [15,35,39] introduced a new method for recovery of vanadium with non-salt roasting and ammonium leaching. This method had the following features. As there were no salts added during the roasting process, the chromium spinel existed in the vanadium slag could not converter to carcinogenic chromate salts, avoiding the cost and disposal of chromium waste. Also, the vanadium could be directly leached out as NH_4VO_3 and separated after cooling crystallization. The leaching efficiency of vanadium could up to 90% while the ammonium salt replaced with (NH_4)$_2C_2O_4$. Xue [40] compared the microwave blank roasting and conventional blank roasting on oxidation behavior, microstructure and surface morphology of high-chromium vanadium slag. They found that the normal spinel oxidized to inverse spinel at 400 °C and then decomposed at 600 °C. As roasting at high temperature, the minority of Cr^{3+} ions in the spinel phase were incorporated into VO_2 to form the $Cr_{0.07}V_{1.93}O_4$ or $CrVO_4$. Wang [41] found that the roasting technology was dependent on the occurrence state of vanadium in stone coal. If the vanadium existed in amorphous phase form, the non-salt-roasting technology was enough leaching out vanadium. While the vanadium was in vanadium-bearing crystalline phase, the additive agent was
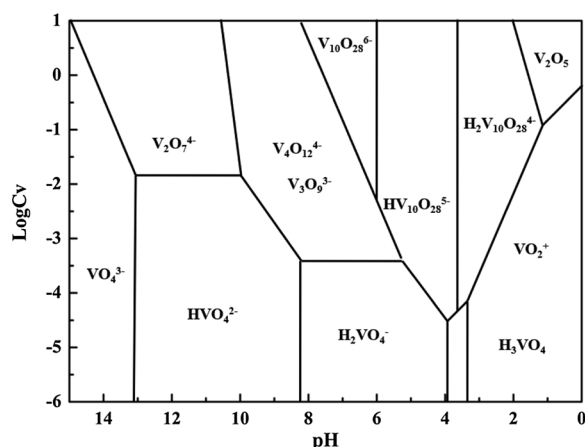
Fig. 2. Relationship between the status of vanadium in aqueous solution and the vanadium concentration and pH (25 °C).

needed in order to achieve high leaching efficiency of vanadium.

2.2. Leaching

The vanadium was leached out by water-leaching, acid-leaching or alkaline leaching after the vanadium slag/stone coal roasted.

2.2.1. Acid leaching

The calcium roasting technology was usually combined with acid leaching. The calcium vanadate was leached by H_2SO_4 and dissolved as VO_2^+, $V_{10}O_{28}^{6-}$ or other ions determined by the pH of the leaching solution and the vanadium concentration (showed in Fig. 2) [29,34,42].

$$Ca_3V_2O_8 + 4H_2SO_4 \rightarrow 3CaSO_4 + (VO_2)_2SO_4 + 4H_2O \quad (16)$$
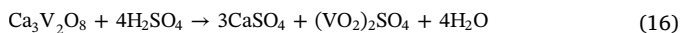
In order to enhance the leaching process and improve the leaching efficiency of vanadium, some technologies were applied. The addition of oxidant like NaClO, KClO$_3$ could improve the leaching efficiency [43]. Dai and Sun [44] found that the addition of oxidant could improve the leaching efficiency of vanadium from 14% to 73% during the direct acid leaching process. Tian [45] used an oxidant named SMTV01 to enhanced the acid leaching process of vanadium from stone coal and found that the leaching efficiency of vanadium was increased from 20% to 80% and also the dosage of H_2SO_4 was reduced 8%. Pressure leaching technology was also applied. Zhang [46] conducted the leaching process with microwave heating and electric heating under an oxygen pressure of 0.4 MPa, he found that the leaching efficiency of vanadium was up to 96% with microwave heating while only 46% with electric heating under the same conditions. Liu [47] introduced electro-oxidation technology to enhanced the leaching process of converter vanadium slag in acidic medium, a high vanadium leaching ratio (> 70%) was achieved under the optimal leaching condition. Li [48] found the leaching efficiency of vanadium was over 90% during the two-stage counter-current leaching procedure at partial oxygen pressure of 1.2 MPa and reaction temperature of 150 °C–180 °C. And the leaching kinetic was followed shrinking core model with a new variant, which the controlling step was both the interfacial transfer and diffusion. Otherwise, other technologies were also applied to leach out vanadium, like alkaline roasting-acid leaching [49], sulfuric acid baking and leaching [50], microwave-aided roasting [21,46,51,52].

2.2.2. Alkaline leaching

The metal elements like Fe, Al, and Mg in vanadium slag had high solubility in acidic medium, they could leach out along with vanadium during the leaching process and produced a large amount of impurities in the leaching solution, and they were hard to be separated. The alkaline leaching offered selective leaching of vanadium [53]. Vanadium

slag roasting with sodium salts or calcium salts could also being leach out in alkaline medium.

$$Ca_3V_2O_8 + 3Na_2CO_3 \rightarrow 3CaCO_3 + 2Na_3VO_4 \quad (17)$$

$$Na_2O \cdot V_2O_5 + 4NaOH \rightarrow 2Na_3VO_4 + 2H_2O \quad (18)$$
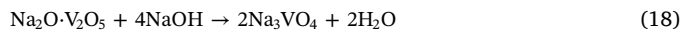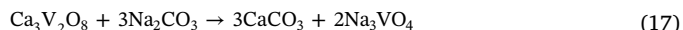
The sub-molten salt technology developed by the Institute of Process Engineering, Chinese Academy of Sciences had been successfully applied for treating amphoteric ores to extract valuable metals [54–60]. The core of this technology was continuous liquid phase oxide of vanadium slag in a sub-molten salt medium under atmospheric pressure which was associated with high alkaline concentration (usually above 50%), high boiling point, high ionic strength. The NaNO$_3$ was introduced to the decomposition process of vanadium slag in molten NaOH/KOH solution. The vanadium compounds were oxidized and formed Na$_3$VO$_4$ to leach out, as which had high solubility in alkaline medium. High pressure leaching technology was also applied. Wei [61] investigated the dissolution kinetic of pure vanadium trioxide in an alkaline-oxygen system. The vanadium dissolution rate was increased with the increasing of reaction temperature and oxygen partial pressure while the stirring speed and sodium hydroxide concentration had very little effect. Electro-oxidation technology and H_2O_2 were introduced to enhance the leaching process and improved the leaching efficiency of vanadium [53,62–65]. The OH^-/H_2O was activated by electricity and formed ·OH with high oxidation. The vanadium in low valence was reacted with ·OH and been oxidized to vanadium in high valence which had high solubility in alkaline medium. Li [25,36] used calcium-roasting technology combined ammonium carbonate to recover vanadium. She found that the ammonium carbonate could selectively leach out vanadium but maintain phosphorous and other impurities. Also, the ammonium could be recycled into the leaching process and made this technology environmental-friendly. While the leaching efficiency of vanadium could achieve 96.0% under optimal conditions.

3. Recovery of vanadium

3.1. Hydrolysis

In acidic medium, the vanadium was existed as polymer ions, like $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$, etc. It could hydrolyze and form precipitation (red cake) [66] at high temperature as followed:

$$6Na_4H_2V_{10}O_{28} + 7H_2SO_4 + (n+13)H_2O \rightarrow 5Na_2V_{12}O_{31}$$
$$\cdot nH_2O\downarrow + 7Na_2SO_4 + 13H_2O \quad (19)$$
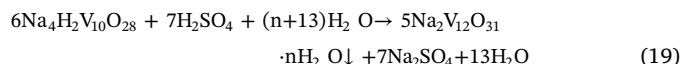
The red cake contained many impurities and the content of vanadium was only about 85% in common. In order to obtain high content vanadium oxides, the red cake needed further treatment.

3.2. Ammonium precipitation

Ammonium salts were widely used in precipitate vanadium in acidic/alkaline medium. In the acidic medium, the pH of vanadium solution was adjusted to 1.8–3.0, the vanadium was existed as polymer ions and precipitated as ammonium hexamethylate by adding ammonium salts like NH$_4$Cl, (NH$_4$)$_2$SO$_4$ and the reaction occurred as followed [67]:

$$3V_{10}O_{28}^{6-} + 10NH_4^+ + 8H^+ \rightarrow 5(NH_4)2V_6O_{16}\downarrow + 4H_2O \quad (20)$$
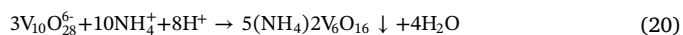
While in the alkaline medium, the vanadium was precipitated as ammonium metavanadate by adding NH$_4$Cl [68].

$$VO_3^- + NH_4^+ \rightarrow NH_4VO_3\downarrow \quad (21)$$

The final product, V_2O_5, was obtained by roasting the precipitation in kiln at 500 °C and the purity of V_2O_5 was more than 99%.

$$(NH_4)_2V_6O_{16} \rightarrow 3V_2O_5 + 2NH_3 + H_2O \tag{22}$$

$$2NH_4VO_3 \rightarrow V_2O_5 + NH_3 + H_2O \tag{23}$$
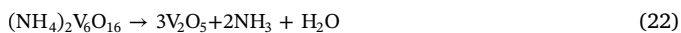
Zhang [68] investigate the ammonium salt precipitation process of vanadium in alkaline medium and ammonium salt precipitation of vanadium in acidic media from the stripping solution of N235-P507 synergistic extraction system. The precipitation in alkaline medium was easier while the purity of V_2O_5 was higher in acidic medium. The Na had little effect on the precipitation efficiency of vanadium and the purity of V_2O_5 while P had significant effect on the precipitation efficiency and the purity in acidic medium. Jiang [67] introduced a cleaner and novelty leaching medium, $(NH_4)_2SO_4$-H_2SO_4 synergistic system, to leach out vanadium after calcification roasting. About 99.75% of vanadium was precipitated as $(NH_4)_2V_6O_{16}$ as the system pH adjusted at 8.0 and the purity of 95.71% V_2O_5 was obtained after roasting. The whole recovery of vanadium from high-chromium vanadium slag was above 93%.

3.3. Adsorption

Adsorption technology played a vital role in wastewater treatment owing to high efficiency, simple operation and ease of regeneration [69–75]. Melamine possessing three free amino group and three aromatic nitrogen atoms in its molecule, was also used to absorb vanadium and showed great performance [42,76]. The results showed that the adsorption capacity was 1428.57 mg/g and the adsorption kinetics was followed pseudo-second-order kinetic model and the adsorption model was fitted well with Langmuir and Freundlich models. Xiao [77] investigated the adsorption performance of vanadium on natural kaolinite and montmorillonite. The results showed that the kinetics of V(V) adsorption on kaolinite and montmorillonite followed pseudo-second-order kinetic model. Also, the Langmuir model indicated that natural montmorillonite and kaolinite had low affinity for V(V) anions with maximum adsorption capacity of 0.98 mg/g and 0.78 mg/g, respectively.

3.4. Solvent extraction

Many researchers had focused on recovery of vanadium from solution with solvent extraction with various extractants [78–82]. A series of extractant had been used to leach out vanadium from aqueous solution, like di(2-ethylhexly) phosphoric acid (D2EHPA) [83–86], tributyl-phosphate (TBP) [87], 2-ethylexyl phosphoric acid mono 2-ethylexhyl ester (EHEHPA) [88], bis(2,4,4-trimethylpentyl) phosphoric acid (CYANEX 272) [79], trialkylamine (N235) [12,80,82] and tricapryl-methyl ammonium nitrate (A336) [81,89].

The vanadium (V) in the solution mainly existed as VO_2^+, $VO_2SO_4^-$, $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$ with the pH ranged from 0 to 4. The extractant N235 was able to leach out vanadium of anionic form through ion-exchange type extraction as followed [90]:

$$2[R_3N]_{org} + H_2SO_4 \rightarrow [R_3NH]_2^+(SO_4)^{2-}]org \tag{24}$$

$$[R_3NH]_2^+(SO_4)^{2-}]org + 2VO_2SO_4^- \rightarrow 2[R_3NH] + VO_2SO_4^-]org + 2SO_4^- \tag{25}$$

$$2[R_3NH]_2^+(SO_4)^{2-}]org + H_2V_{10}O_{28}^{4-} \rightarrow [R_3NH]_4^+H_2V_{10}O_{28}^{4-}]org + 2SO_4^- \tag{26}$$

$$5[R_3NH]2 + (SO_4)^{2-}]org + 2HV_{10}O_{28}5^- \rightarrow 2[R_3NH]5 + HV_{10}O_{28}^{5-}]org + 5SO_4^- \tag{27}$$
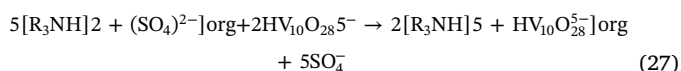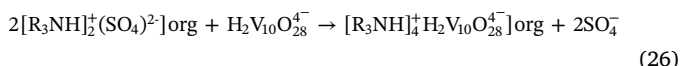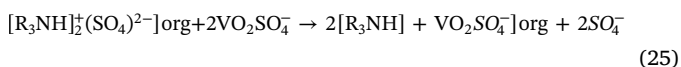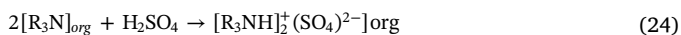
Then the organic phase was stripped in multi-stage count-current process by concentration NaOH solution, and then the vanadium was precipitated as ammonium metavanadate according to Eq. (21).

Zhang [91] investigated the selective extraction process of vanadium with N235 and P507. About 95% vanadium was leached out and

the impurity remained in the solution after one-stage extraction. Ning [92] investigated the vanadium species of vanadium in the extraction solution. They found that the extraction mechanism was similar to the CO_2 adsorption through amines, which was described as that the one N atom and two H atoms in $-NH_2$ group combined with one H atom (from V−OH group) and two O atoms (from V=O groups) in $H_xV_yO_z$ as (N−H) and (O−H) during the extraction process. Lee [93] used 5,8-diethyl-7-hydroxydodecane-6-oxime (LIX 63) and 2-ethylexyl hydrogen 2-ethylhexyl phosphonate (PC 88A) to leach out vanadium from sulfate solution under initial pH 1.2-6. The extraction of vanadium by PC88A was a cationic exchange process, while changed as the equilibrium pH increased by LIX 63. Hear-Kyung Park [94] investigated the extraction process of vanadium with mixture of 20% (v/v) Alamine-336 and 5% (v/v) tri-butyl phosphate (TBP). The extraction isotherm results showed that 99% vanadium was leached out through two-stage counter-current process and the purity of 98.4% V_2O_5 could be obtained after stripping, precipitated and roasting.

3.5. Ion exchange

In addition, there were also some reports about the recovery of vanadium with ion exchange or resin exchange in acidic medium [95–101]. The adsorption of vanadium by the resin was expressed as followed [102]:

$$R_3N + HCl \rightarrow (R_3NH)Cl \tag{28}$$

$$4(R_3NH)Cl + H_2V_{10}O_{28}^{4-} \rightarrow (R_3NH)_4 \cdot H_2V_{10}O_{28} + 4Cl^- \tag{29}$$

$$5(R_3NH)Cl + HV_{10}O_{28}5^- \rightarrow (R_3NH)_5 \cdot HV_{10}O_{28} + 5Cl^- \tag{30}$$

$$6(R_3NH)Cl + V_{10}O_{28}6^- \rightarrow (R_3NH)_6 \cdot V_{10}O_{28} + 6Cl^- \tag{31}$$
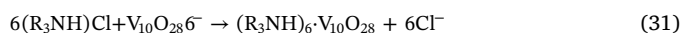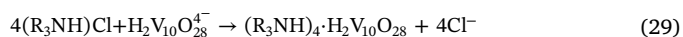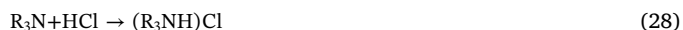
The adsorption process was stopped as the vanadium concentration decreased to an appropriate value. And then, the loaded resin was striped with concentration NaOH solution, and the reactions were described as followed:

$$(R_3NH)_4 \cdot H_2V_{10}O_{28} + 10NaOH \rightarrow 4R_3N + 10NaVO_3 + 8H_2O \tag{32}$$

$$(R_3NH)_5 \cdot HV_{10}O_{28} + 10NaOH \rightarrow 5R_3N + 10NaVO_3 + 8H_2O \tag{33}$$

$$(R_3NH)_6 \cdot V_{10}O_{28} + 10NaOH \rightarrow 6R_3N + 10NaVO_3 + 8H_2O \tag{34}$$
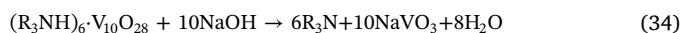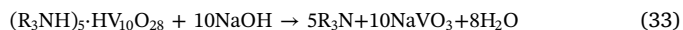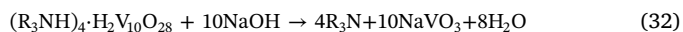
Last, the concentrated vanadium solution was used to produced V_2O_5 according to Eqs. (21) and (23). The recovery of vanadium by this method was generally above 99% [102].

Zhang [103] compared the ion exchange technology and solvent extraction technology for recovery of vanadium from sulfuric acid leach solutions. The results indicated that vanadium (V) was more favorable being leached out by ion exchange technology and vanadium (IV) was easily being leached out by solvent extraction technology. During the ion exchange experiments, five kinds of resins were tested and the results showed that the vanadium (V) was significantly adsorbed by ZGA414 resin, the adsorption efficiency was about 99.9% at pH 2.5 and the process would be affected by concentration Fe (III). About 99% of the vanadium (IV) could be leached out by five-stage counter-current extraction process during the solvent extraction experiments. Li [104] used resin 201, D314 and 717 recovered more than 99% vanadium from hydrochloric acid leaching solution. And these three resins had their own merits, resin D201 was suitable for adsorption in strong acidic medium and had maximum loading of vanadium, resin 717 had fastest adsorption rate in weak acidic medium.

4. Discussion

In summary, the measurement and technology for recovery of vanadium could be described in Fig. 3. Although some techniques for vanadium recovery had been proposed and developed, it was also needed to further development. For the purpose of meeting the world's
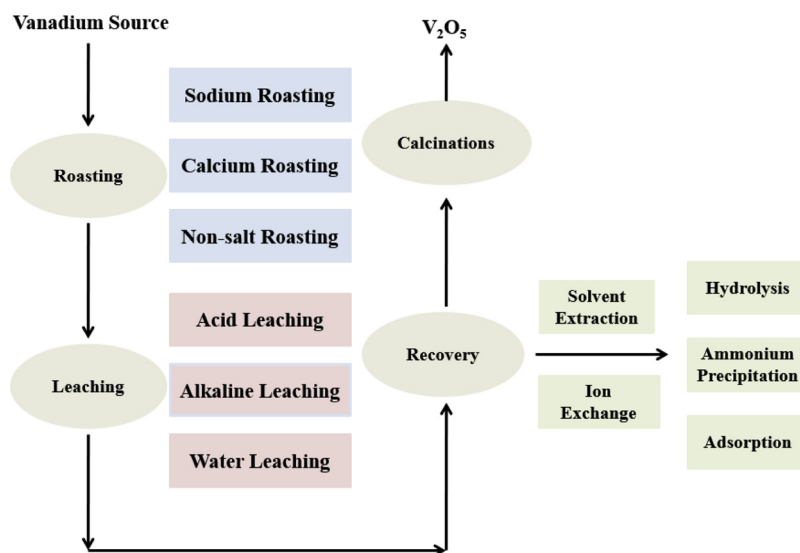
Fig. 3. Flowsheet of recovery of vanadium from vanadium source to V_2O_5.

increasing demand for vanadium, these following aspects which should be strengthened and paid more attention to are listed below.

1 The vanadium valence and species existed in vanadium-bearing resources. Although some researches had been done, the effect of existing form and valence of vanadium on the leaching efficiency of vanadium from vanadium-bearing resources had not been completely understood until now. The development of innovative technology and the improvement in the leaching process depended on breakthroughs of studies on their existing forms.
2 Recovery of vanadium from all vanadium-bearing resources. Vanadium and its compounds were widely used in many fields, it could be recycled and reused. The technology for recovery of vanadium from all vanadium-bearing resources should be developed.
3 Reaction mechanism during every step of recovery of vanadium. Dialyzing the reaction mechanism was beneficial to choose the right technology for vanadium treatment.
4 The development of specialized equipment for leaching out vanadium. The suitable equipment for vanadium extraction would enlarge production scale and reduce specific energy consumption and costs, also realize auto control in vanadium leaching process and relieve environmental stress.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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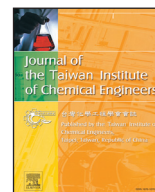
High-efficient recovery of chromium (VI) with lead sulfate

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ABSTRACT

Lead sulfate was chose to precipitate chromium (VI) based on the difference of the solubility between lead sulfate and lead chromate. The effects of parameters on the precipitation efficiency of chromium including reaction temperature, reaction time, and initial pH of solution and dosage of lead sulfate were investigated. Results showed that the initial pH of solution and dosage of lead sulfate had big influence while reaction time and reaction temperature had little. The concentration of chromium (VI) could reduce from 0.2 mol/L to 0.0015 mmol/L (0.08 mg/L) at pH value of 13.90 and the dosage of lead sulfate as n $(PbSO_4)/n$ $(K_2CrO_4) = 4$. The XRD result of precipitation was consistent with the result predicted by Visual MINTEQ software and the precipitation was composed of $PbCrO_4$, $PbSO_4$ and other oxides containing lead. Otherwise, XRF and ICP were used to analyze the residual lead (II) in the filtrate and results indicated that the concentration of Pb (II) in the filtrate was acceptable.

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1. Introduction

Chromium is an important metal used for metal plating, leather tanning, metal corrosion inhibition, and pigment productions [1–3]. Chromium (VI) discharged from industrial activities including electroplating, petroleum refining, alloy manufacturing and battery production [4–9]. It is known that chromium (VI) species such as dichromate $(Cr_2O_7^{2-})$ and chromate $(HCrO_4^-, CrO_4^{2-})$ could cause a series of problems for humans and animals because they could form non-biodegradable compounds that affect aquatic life and cause serious health issues such as digestive tract cancer, anemia, neurological damage, circulatory shut down and death [10–12]. In China, it has become one of the most commonly detected contaminants in groundwater due to improper storage and disposal practices. Chromium (VI) has been considered as a hazardous contaminant and there is increasing interest in developing effective measures to remove chromium from chromium-contaminated wastewater.

Many treatment technologies for removal of heavy metals from wastewater have been conducted [13]. Adsorption methods based on the high porosity, specific surface and high surface activity of adsorbents are used to remove chromium (VI) species from wastewater [14–16], while it is only applicable for treatment of low concentration wastewater. Membrane filtration methods seriously suffer from lack of resistance of the membranes to the harsh conditions typically found in industry wastewaters [17]. Ambient chromium mainly exists in the oxidative states of chromium (VI) and chromium (III). The chromium (III) species are relatively stable and have low solubility and mobility in environmental conditions. In contrast, the chromium (VI) species are highly soluble and mobile and also more poisonous than chromium (III). Mostly, chromium (VI) species are reduced to chromium (III) species and then treated with other technologies, like adsorption or precipitation [18–21], but occupied with high dosage of reducing agent and acid or alkaline, also large amount of chromium-containing sludge.

In this paper, chemical precipitation was chosen to recover chromium from the solution. Lead sulfate was selected as precipitation agent to precipitate chromium (VI) based on the difference of the solubility constant between lead sulfate and lead chromate, for which was 1.6×10^{-8} and 2.8×10^{-13}, respectively. The effects of parameters on the precipitation efficiency of chromium including initial pH of solution, reaction temperature, reaction time and dosage of lead sulfate were studied.

2. Experimental

2.1. Materials

All the reagents were analytical grade, including sulfuric acid, potassium dichromate, sodium hydroxide, lead sulfate used for precipitation reaction and phosphoric acid and ammonium ferrous sulfate, hexamethylenetetramine, potassium permanganate, and *N*-phenylanthranilic used in the chemical analysis.

(a) c(K$_2$CrO$_4$)=0.2 mol/L, n(PbSO$_4$)/n(K$_2$CrO$_4$)=1

(b) c(K$_2$CrO$_4$)=0.2 mol/L, n(PbSO$_4$)/n(K$_2$CrO$_4$)=2

(c) c(K$_2$CrO$_4$)=0.2 mol/L, n(PbSO$_4$)/n(K$_2$CrO$_4$)=3

(d) c(K$_2$CrO$_4$)=0.2 mol/L, n(PbSO$_4$)/n(K$_2$CrO$_4$)=4
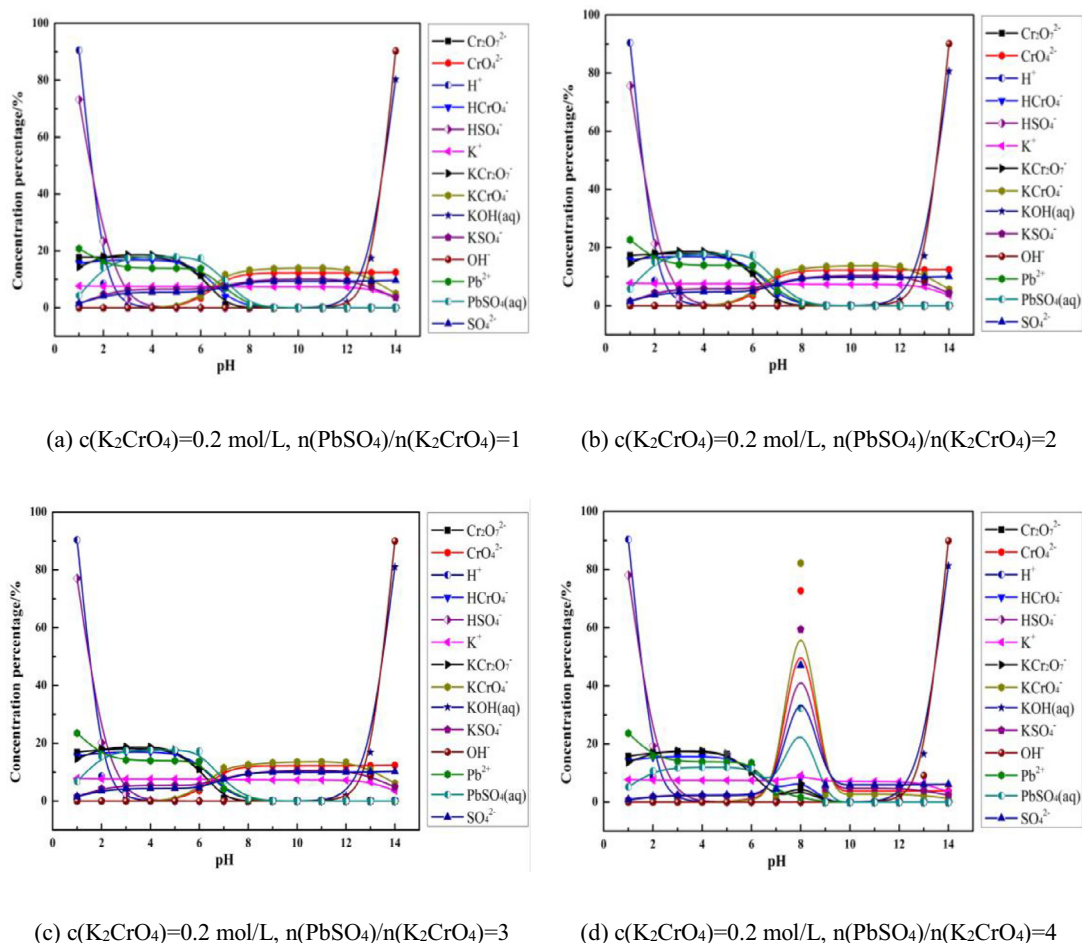
Fig. 1. Effect of pH value on species of the solution of K^+–CrO_4^{2-}–Pb^{2+}–SO_4^{2-}.

The chromium solution for the experiment was prepared by dissolving potassium dichromate in deionized water. The deionized water used in the experiments was produced by a water purification system (HMC-WS10).

2.2. Apparatus and procedures

All experiments were performed in a glass beaker with a thermostatic mixing water bath pot.

A predetermined amount of potassium dichromate and deionized water was added to the beaker to produce a homogeneous solution under constant stirring. Subsequently, the pH value of the solution was adjusted with sulfuric acid and sodium hydroxide. The solution was heated to a predetermined temperature. Next, the lead sulfate was added to the beaker. After the required reaction time had lapsed, the filtrate was separated from the precipitation through vacuum filtration.

Titration with ammonium ferrous sulfate is used to determine the concentration of chromium in the filtrate [22]. Precipitation efficiency of chromium is calculated using the following formula:

$$\eta = \frac{(C_1 \times V_1 - C_2 \times V_2)}{C_1 \times V_1} \times 100\% \tag{1}$$

where η is the chromium precipitation efficiency, %; C_1 is the total chromium concentration in the chromium aqueous, g/L; V_1 is the volume of chromium aqueous, mL; C_2 is the total chromium concentration in the filtrate after the reaction, g/L; and V_2 is the volume of filtrate after the reaction, mL.

3. Results and discussion

3.1. Technology principle

3.1.1. The composition in the solution of K^+–CrO_4^{2-}–Pb^{2+}–SO_4^{2-}

The composition in the K$_2$CrO$_4$ solution was calculated by Visual MINTEQ software, including the presence form, the dissolution and equilibrium and the saturated state of the solid. The calculating conditions were set with concentration of K$_2$CrO$_4$ solution at 0.2 mol/L, the dosage of lead sulfate was set as molar ratio at n (PbSO$_4$)/n (K$_2$CrO$_4$) = 1, n (PbSO$_4$) /n (K$_2$CrO$_4$) = 2, n (PbSO$_4$)/n (K$_2$CrO$_4$) = 3, n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4, reaction temperature of 25 °C, pH varied from 1 to 14. The activity coefficient of the charged materials was calculated with Davies equation [23]. The results were shown in Fig. 1.

The results shown in Fig. 1 indicated that the main species in the solution were $Cr_2O_7^{2-}$, CrO_4^{2-}, H^+, $HCrO_4^-$, HSO_4^-, K^+, $KCr_2O_7^-$, $KCrO_4^-$, SO_4^{2-}, KSO_4^-, OH^-, and Pb^{2+}. The chromium (VI) was mainly existed in form of $Cr_2O_7^{2-}$, $HCrO_4^-$ and $KCr_2O_7^-$ at pH < 7, and then converted to $KCrO_4^-$ and CrO_4^{2-} as pH value increased. When the pH value of solution was below 7, the lead in the solution existed in Pb^{2+} and PbSO$_4$ (aq) which was poisonous and harmful to the environment. When the pH value increased above 8, the concentration of Pb^{2+} and PbSO$_4$ (aq) was nearly 0. Therefore, the precipitating process of chromium with lead should be reacted at high pH value in order to avoid the environment pollution caused by lead. Otherwise, the results showed that the dosage of lead sulfate had little influence on the species of the solution according to the results shown in Fig. 1.

(a) c(K_2CrO_4)=0.2 mol/L, n(PbSO_4)/n(K_2CrO_4)=1

(b) c(K_2CrO_4)=0.2 mol/L, n(PbSO_4)/n(K_2CrO_4)=2

(c) c(K_2CrO_4)=0.2 mol/L, n (PbSO_4)/n(K_2CrO_4)=3

(d) c(K_2CrO_4)=0.2 mol/L, n (PbSO_4)/n(K_2CrO_4)=4
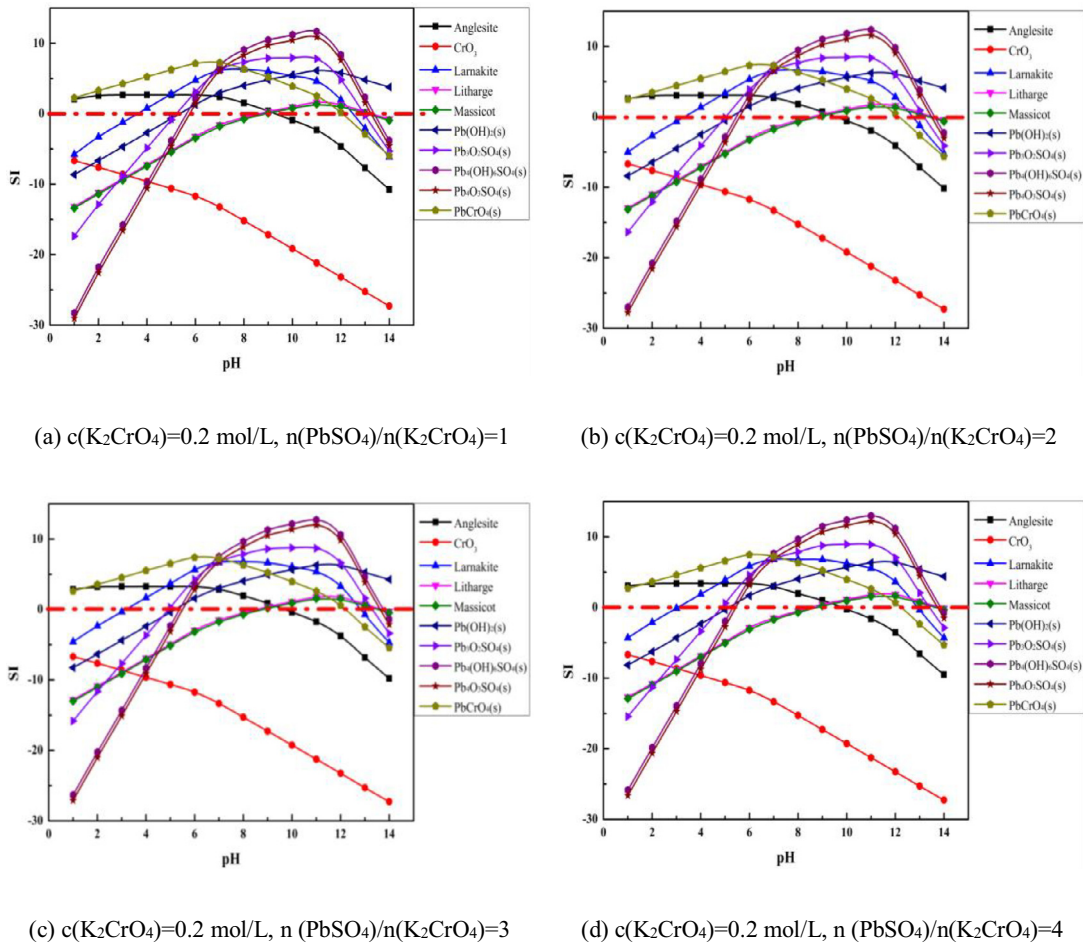
Fig. 2. Effect of pH value on SI of predicted precipitation.

3.1.2. The composition of precipitation

Saturation index (SI) was used to predict the trend of precipitated and dissolved species, and was calculated based on Eq. (2). If SI > 0, the content was in oversaturation and might precipitate; SI = 0, the content was in equilibrium state; SI < 0, the content existed in form of ions in the solution:

$$SI = \log IAP - \log Ks \tag{2}$$

where IAP is the selected ion activity in Visual MINTEQ software, and Ks is the solubility product constant.

The content of reaction products were predicted by Visual MINTEQ software, the results were shown in Fig. 2. The main products of the reaction were anglesite (PbSO_4), CrO_3, larnakite (Pb_2OSO_4), litharge (PbO), massicot (PbO), Pb(OH)_2, Pb_3O_2SO_4, Pb_4(OH)_6SO_4, Pb_4O_3SO_4, PbCrO_4. While the SI of CrO_3 was below 0, it might not exist in the precipitate. SI of the main products increased first with the increasing of pH value and then decreased, different solid components occurred in different reaction pH value. As pH below 4, the precipitation was composed of anglesite and PbCrO_4 and not affected by dosage of lead sulfate. As pH > 6, anglesite, larnakite, Pb(OH)_2, Pb_3O_2SO_4, Pb_4(OH)_6SO_4, Pb_4O_3SO_4 and PbCrO_4 all occurred in the precipitation. Especially among pH at 10–13, the precipitation was most complicated almost contained all contents in which Fig. 2 showed except CrO_3.

During the precipitation process, some new oxides containing lead would form, which was competed with chromium (VI) and would consumed much more Pb^{2+}, which was not beneficial for chromium (VI) precipitation. In order to achieve effective precipitation performance of chromium (VI), excessive dosage of lead sulfate was required.

3.2. Effect of initial pH value of solution

The results in Fig. 1 showed that the pH value of the solution affected the species in the solution and also the precipitation process should be conducted at high pH value. The experiments about the effect of the initial pH value of the solution on the precipitation efficiency of chromium was preferentially investigated under the following conditions: reaction temperature of 30 °C, concentration of chromium (VI) of 0.2 mol/L, reaction time of 60 min, and dosage of lead sulfate set as molar ratio at n (PbSO_4)/n (K_2CrO_4) = 1.

The results shown in Fig. 3 indicated that the precipitation efficiency increased with the increasing of the initial pH value of the solution. First, the precipitation efficiency was about 18.9% at pH value of 6.92 and increased smoothly at pH < 12. It increased sharply to 51.90% at pH value of 13.90, while the concentration of chromium (VI) was much high. During the precipitation process, some new content containing lead might form which competed with chromium (VI) and would decreased the precipitation efficiency of chromium (VI). Therefore, it should increase the dosage of lead sulfate to achieve high precipitation efficiency of chromium (VI). Other way, the pH value of the filtrate was between 6.7 and 9.0 according to the results showed in Fig. 3, which was easy to treat.
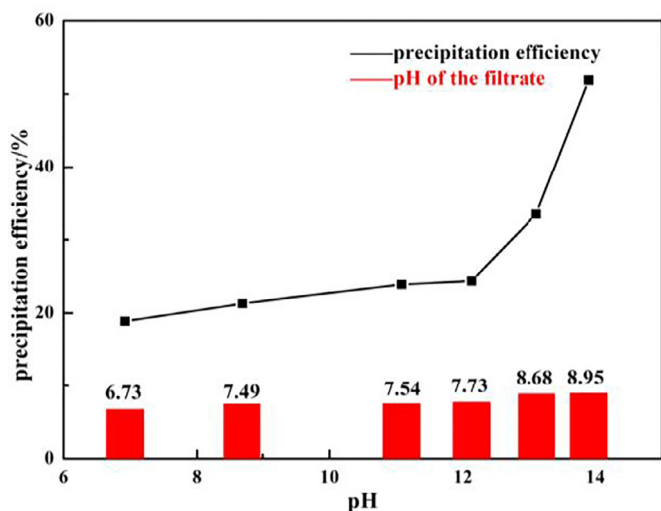
Fig. 3. Effect of pH on the precipitation efficiency of chromium.
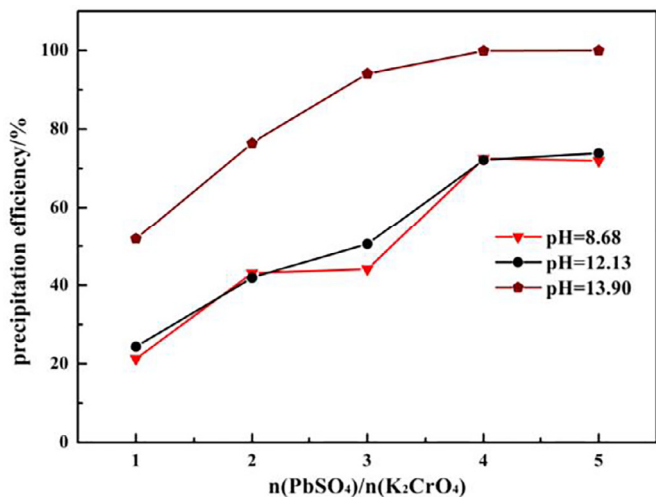
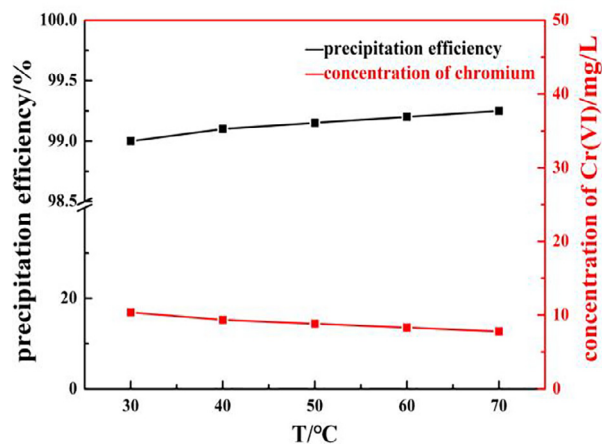Fig. 4. Effect of dosage of lead sulfate on the precipitation efficiency of chromium.

Fig. 5. Effect of reaction temperature on the precipitation efficiency of chromium.
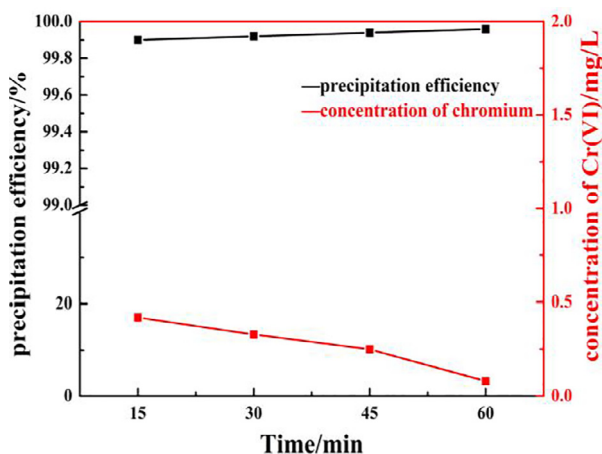
Fig. 6. Effect of reaction time on the precipitation efficiency of chromium.

3.3. Effect of dosage of lead sulfate

During the precipitation process, the dosage of precipitation agent had big influence on the precipitation efficiency of chromium (VI). The effect of dosage of lead sulfate was studied under the following conditions: reaction temperature of 30 °C, concentration of chromium (VI) of 0.2 mol/L, and reaction time of 60 min. The results were shown in Fig. 4.

The precipitation efficiency increased sharply with the increasing of dosage of lead sulfate, especially at pH value of 13.90. The precipitation efficiency was about 99.9% and the concentration of chromium (VI) reduced to 0.15 mmol/L at n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4 and pH of 13.90. And continue increasing the dosage of lead sulfate, the concentration of chromium (VI) would be reducing more. In order to reduce the mass of precipitation and also achieve high precipitation efficiency, the dosage of lead sulfate was chosen as molar ratio at n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4 for further experiments.

3.4. Effect of reaction temperature

During the process, the reaction velocity is followed the diffusion laws and reaction temperature is an important parameter affected the reaction during the diffusion process. High temperature will decrease the diffusion resistance while accelerate the sol-

ubility of the precipitation. The effect of reaction time of lead sulfate was studied under the following conditions: concentration of chromium (VI) of 0.2 mol/L, initial pH value of 13.90, reaction time of 60 min, and the dosage of lead sulfate set as molar ration at n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4.

The results in Fig. 5 showed that the reaction temperature had little influence on the precipitation efficiency of chromium (VI) at high dosage of lead sulfate of n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4. The concentration of chromium (VI) reduced from 0.2 mol/L to 0.15 mmol/L.

3.5. Effect of reaction time

Reaction time also plays an important role during the precipitation process. It is eager for producing as many products as possible at the shortest time and earned more economic benefits in the industry. The effect of reaction time was studied under the following conditions: reaction temperature of 30 °C, the dosage of lead sulfate of n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4, initial pH value of 13.90 and concentration of chromium (VI) of 0.2 mol/L. The results were shown in Fig. 6.

From Fig. 6, it was concluded that lead sulfate played a fast precipitate rate. The precipitation efficiency could up to 99.9% at only 15 min. The concentration of residual Cr (VI) in the filtrate could reduce to 0.08 mg/L as the reaction time increased to 60 min. In summary, the initial pH value of solution and dosage of lead sulfate had big influence on the precipitation efficiency of chromium

(a) pH =13.90, n (PbSO₄)/n(K₂CrO₄)=1   (b) pH =13.90, n (PbSO₄)/n(K₂CrO₄)=4
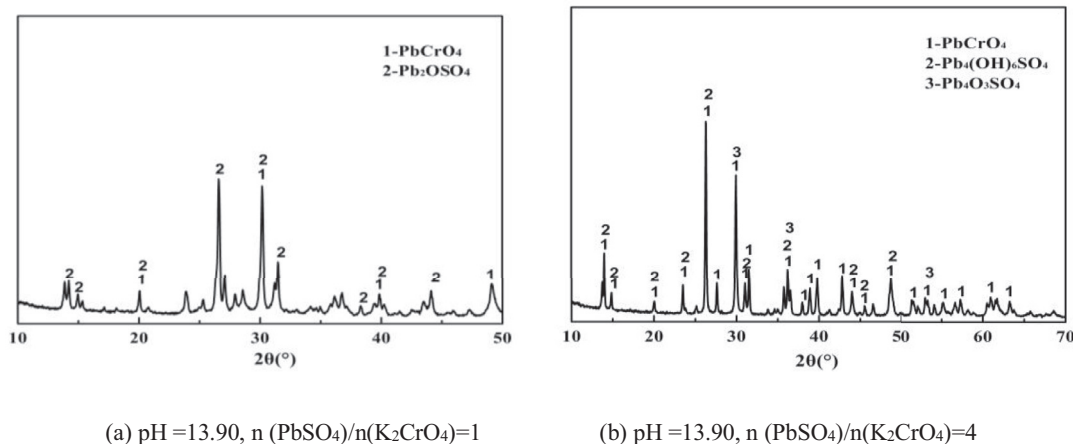
Fig. 7. XRD pattern of the precipitation.

(VI), while the effect of reaction temperature and reaction time could be ignored.

3.6. XRD of the precipitation

XRD (X-ray diffraction) analysis of the precipitation was conducted. Fig. 7 showed the XRD pattern of the precipitation (a) pH = 13.90, n (PbSO$_4$)/n (K$_2$CrO$_4$) = 1, (b) pH = 13.90, n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4. The results showed that the contents in the precipitation were PbCrO$_4$ and other lead oxides. Upon an increase in the dosage of lead sulfate, the species in the precipitation became more complicated. The results were consistent with the results calculated in Visual MINTEQ software.

XRF and ICP [24–28] were used to analyze the residual lead (II) in the filtrate and results indicated that the concentration of Pb (II) in the filtrate was acceptable. In other words, it would not make secondary pollution used lead sulfate as precipitation agent [25,27].

4. Conclusions

Lead sulfate was used as a precipitation agent to precipitate chromium (VI) from the solution according the difference of solubility compared with lead chromate. The concentration of chromium (VI) could reduce from 0.2 mol/L to 0.0015 mmol/L (0.08 mg/L) at pH value of 13.90 and the dosage of lead sulfate as n (PbSO$_4$)/n (K$_2$CrO$_4$) = 4. The initial pH value of solution and dosage of lead sulfate had big influence on the precipitation efficiency of chromium (VI), while the effect of reaction temperature and reaction time could be ignored. Analysis results indicated that lead sulfate was all gone into the precipitation not dissolved in the filtrate and would not cause secondary pollution during the precipitation process.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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Leaching Kinetics of Vanadium with Electro-oxidation and H_2O_2 in Alkaline Medium

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ABSTRACT: A residue containing vanadium and chromium was precipitated from a wastewater mill. Electro-oxidation technology and H_2O_2 acting as reinforcement methods were introduced for vanadium leaching from the residue. During the leaching process, sodium hydroxide could provide an appropriate reaction medium and promote the reaction rate of the acidic oxides. Electro-oxidation technology and H_2O_2 could produce some fresh and nano-/micrometer-size oxygen bubbles, which could oxidize vanadium in low valence to high valence. The kinetics investigation indicated that the leaching process was followed by a surface chemical reaction model, and the leaching efficiency increased along the increase of the temperature and reaction time. The apparent activation energy decreased with the intensification of electro-oxidation technology and H_2O_2. Electro-oxidation technology coupled with H_2O_2 exhibited the lowest apparent activation energy as 6.48 kJ mol^{-1}.

1. INTRODUCTION

Vanadium is an important metal used for manufacturing iron and steel non-ferrous metals and petrochemicals because of its excellent physicochemical properties.[1−4] It becomes necessary and urgent to exploit and use the secondary resources as the increasing market demand for vanadium compounds, including fly ashes[5] and spent catalysts.[6] The main vanadium resources in China were titanomagnetite[7] and stone coal (carbonaceous shale).[8,9]

Some traditional hydrometallurgy technologies were conducted to leach out vanadium from vanadium resources. Sodium salt roasting was the commonly used technology,[10,11] but some toxic gases, such as HCl and SO_2, would emit during the process and were harmful for the environment. Acid leaching was also an efficient way to extract out vanadium.[6,9,12−14] However, it would lead to high acid consumption and a high concentration of impurities. An environmentally friendly technology called electro-oxidation was applied in leaching out vanadium from the residue.[15−17] Vanadium in low valence could be oxidized to high valence and formed a soluble phase during the leaching process. Some other oxidants, such as MnO_2 and $KClO_3$, were also added to enhance the leaching process.[18]

Because the residue used in the study consisted of vanadium in low valence, the electro-oxidation technology and H_2O_2 were applied in leaching out vanadium from the residue. The effects of the temperature and reaction time on the leaching efficiency of vanadium were systematically investigated, and apparent activation energy was calculated.

2. MATERIALS AND METHODS

2.1. Materials. The wastewater containing chromium(VI) and vanadium(V) was reduced and precipitated from a mill. The residue was the precipitation containing vanadium and chromium in low valence. Before the experiment, the residue was first dried in an oven overnight and then sieved for further treatment. The X-ray fluorescence (XRF) analysis of the residue was shown in Table 1.

Vanadium in the residue existed as $VOSO_4$ and $Na_2(Cr,V)Si_2O_9$, shown in Figure 1.

Table 1. XRF Analysis Results of the Residue

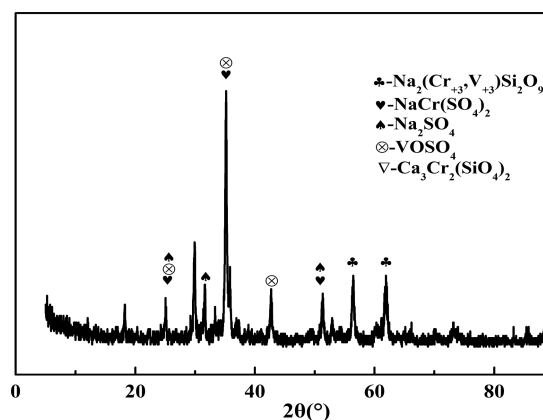| component	O	Cr	Si	Na	S	V
amount (wt %)	41.09	14.36	12.02	9.76	12.02	1.63
component	Ca	Cl	Fe	K	Mg	
amount (wt %)	1.42	4.09	0.33	0.29	0.20	

Figure 1. XRD pattern of the original residue.

2.2. Apparatus and Procedure. The leaching reaction was conducted in a 250 mL beaker placed in the water bath pot equipment. The temperature was controlled by the bath pot, with a precision of ±0.1 K. Sodium hydroxide (NaOH) and deionized water were added to the beaker to make a homogeneous solution. Then, the residue was added after the temperature of the solution stabilized. After the

leaching process, the solution was separated by vacuum filtration. The experiments conducted with electro-oxidation and H_2O_2 were also carried out in the batch reactor.

The concentration of vanadium in the filtrate was determined by the titration with ammonium ferrous sulfate. The leaching efficiency (X) of vanadium for each experiment was calculated in eq 1

$$X = \frac{VC}{MW_x} \tag{1}$$

where V is the volume of leaching solution (mL), C is the concentration of vanadium in the leaching solution (g/mL), M is the initial mass of the residue added into the reactor (g), and W_x is the mass percentage of vanadium in the residue (wt %).

3. RESULTS AND DISCUSSION

3.1. Alkaline Leaching (LP1). The leaching experiments were conducted under the following conditions: liquid/solid
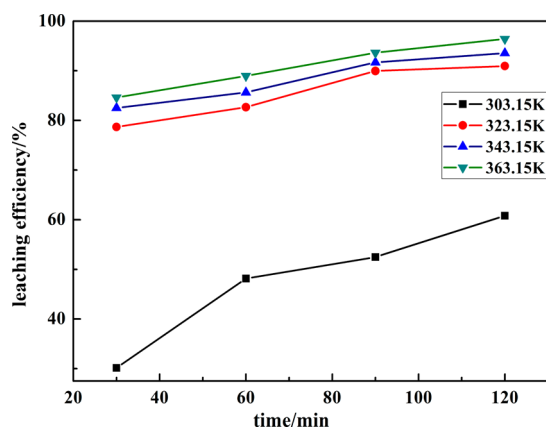
Figure 2. Effect of the time on leaching efficiency of vanadium at various temperatures in LP1 (alkaline leaching).
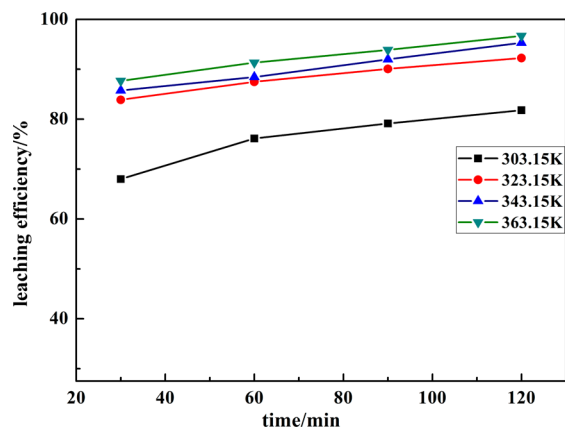
Figure 3. Effect of the time on leaching efficiency of vanadium at various temperatures in LP2 (electro-oxidation leaching).

ratio of 4 (mL/g) and NaOH/residue mass ratio of 1.0:1.0 (g/g). The results were shown in Figure 2.

As shown in Figure 2, the increase of the temperature could accelerate the reaction of vanadium with NaOH in the medium. The leaching efficiency was about 60% at 303.15 K after 120 min, while at 323.15 K, it was nearly 91%. A high temperature would increase the leaching efficiency. This was because the viscosity of the medium decreased with the increase of the temperature, and the diffusion efficiency was also affected by
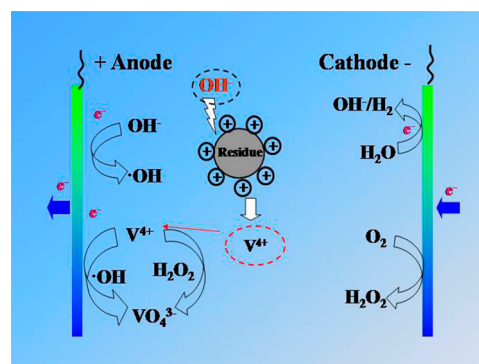
Figure 4. Oxidation model for the electric field in alkaline medium.
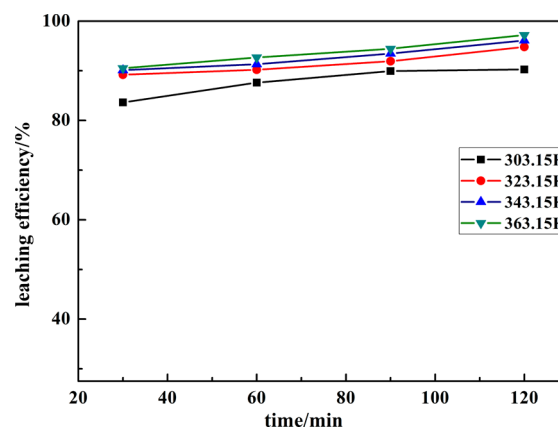
Figure 5. Effect of the time on leaching efficiency of vanadium at various temperatures in LP3 (oxidation leaching with H_2O_2).
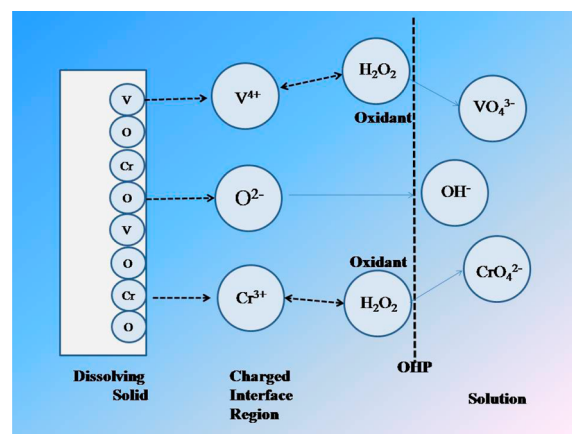
Figure 6. Oxidation model for H_2O_2 in alkaline medium.

the increase of the temperature[16,19,20] and facilitated the transportation of reactants as a sequence.

3.2. Electro-oxidation Leaching (LP2). Electro-oxidation as an environmentally friendly technology[16,17] was introduced to leach out vanadium from the residue. The experiments carried out were intensified with the current intensity of 1000 A/m^2, liquid/solid ratio of 4 (mL/g), and NaOH/residue mass ratio of 1.0:1.0 (g/g). The results were presented in Figure 3.

In comparison to the results showed in Figure 2, the leaching performance was intensified within the presence of the electric field. The mechanism had been discussed in early experiments,[16] and the reaction model was expressed in Figure 4. A new oxidant, •OH, would be formed under the electric field
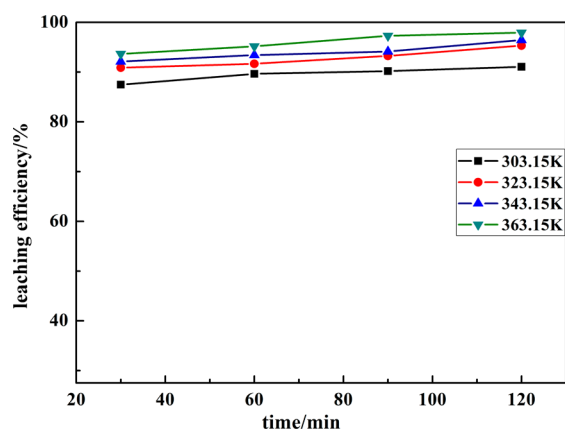
Figure 7. Effect of the time on leaching efficiency of vanadium at various temperatures in LP4 (oxidation leaching coupled electro-oxidation and H_2O_2).
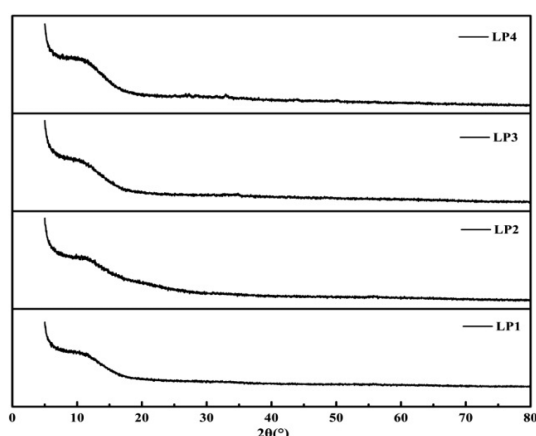

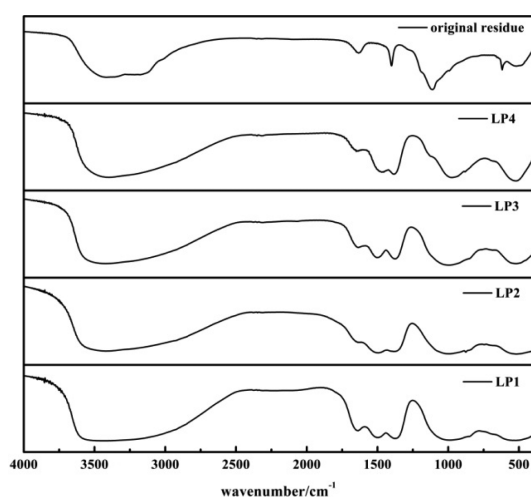Figure 8. XRD pattern of the leaching residue.

Figure 9. FTIR spectrum of the residue before and after leaching.

during the leaching process. Also, the anodic oxidation of hydroxyl ions might produce some fresh and nano-/micro-meter-size oxygen bubbles.[15,21] These two oxidants might oxidize vanadium in low valence to vanadium in high valence, which made a contribution to improving the leaching efficiency.

3.3. Oxidation Leaching with H_2O_2 (LP3). H_2O_2 was added to enhance the leaching performance of vanadium from

Table 2. Wavenumber and Peaks in FTIR Spectra

peak	original residue	NaOH (LP1)	NaOH + eletro-oxidation (LP2)	NaOH + H_2O_2 (LP3)	NaOH + eletro-oxidation + H_2O_2 (LP4)
1	516	511	514	518	520
2	619				
3	1111	983	995	999	975
4	1400	1373	1377	1375	1384
		1496	1490	1498	1435
5	1633	1635	1629	1635	1645
6	3415	3419	3415	3419	3415

Table 3. Kinetic Models and Equations

controlling step	equation[a]
liquid boundary layer diffusion	$K_1 t = X$ (4)
surface chemical reaction	$K_2 t = 1 - (1 - X)^{1/3}$ (5)
diffusion through a product layer	$K_3 t = 1 - 2/3 X - (1 - X)^{2/3}$ (6)

[a]X is the leaching efficiency of vanadium; K_1, K_2, and K_3 were the apparent rate constants for each kinetic model (min^{-1}); and t is the reaction time (min).

Table 4. Apparent Rate Constants K_1, K_2, and K_3 and Correlation Coefficients

parameter	liquid boundary layer diffusion, X		diffusion through the product layer, $1-2/3X-(1-X)^{2/3}$		surface chemical reaction, $1 - (1 - X)^{1/3}$	
	K_1 (min^{-1})	R^2	K_2 (min^{-1})	R^2	K_3 (min^{-1})	R^2
NaOH (LP1)						
303.15 K	0.0032	0.9223	0.0005	0.9503	0.0010	0.9703
323.15 K	0.0015	0.9344	0.0009	0.9156	0.0012	0.9356
343.15 K	0.0019	0.9534	0.0009	0.9663	0.0023	0.9463
363.15 K	0.0024	0.9694	0.0011	0.9761	0.0027	0.9961
NaOH + electro-oxidation (LP2)						
303.15 K	0.0015	0.9187	0.0006	0.9317	0.0011	0.9528
323.15 K	0.0009	0.9262	0.0008	0.9621	0.0013	0.9977
343.15 K	0.0011	0.9167	0.0009	0.9763	0.0015	0.9813
363.15 K	0.0010	0.9439	0.0009	0.9627	0.0019	0.9948
NaOH + H_2O_2 (LP3)						
303.15 K	0.0007	0.8803	0.0003	0.9034	0.0009	0.8997
323.15 K	0.0006	0.9515	0.0005	0.9136	0.0011	0.9252
343.15 K	0.0008	0.9347	0.0007	0.9413	0.0014	0.9501
363.15 K	0.0010	0.9219	0.0008	0.9291	0.0016	0.9687
NaOH + electro-oxidation + H_2O_2 (LP4)						
303.15 K	0.0004	0.9130	0.0003	0.9282	0.0012	0.9395
323.15 K	0.0005	0.9326	0.0005	0.9433	0.0013	0.9416
343.15 K	0.0007	0.9204	0.0005	0.9244	0.0016	0.9561
363.15 K	0.0009	0.9147	0.0006	0.9729	0.0018	0.9829

the residue.[18] The experiments were conducted under the following conditions: liquid/solid ratio of 4.0 (mL/g), mass ratio of NaOH/residue of 1.0 (g/g), and volume ratio of H_2O_2/residue of 1.6 (mL/g), respectively. The results are shown in Figure 5.

Figure 5 showed that the presence of H_2O_2 made a great contribution to leach out vanadium from the residue. In the residue particle, vanadium primarily existed in the central area as $VOSO_4$ and $Na_2(Cr,V)Si_2O_9$ and could be oxidized to produce water-soluble vanadate in the presence of H_2O_2. The reaction was described as below.
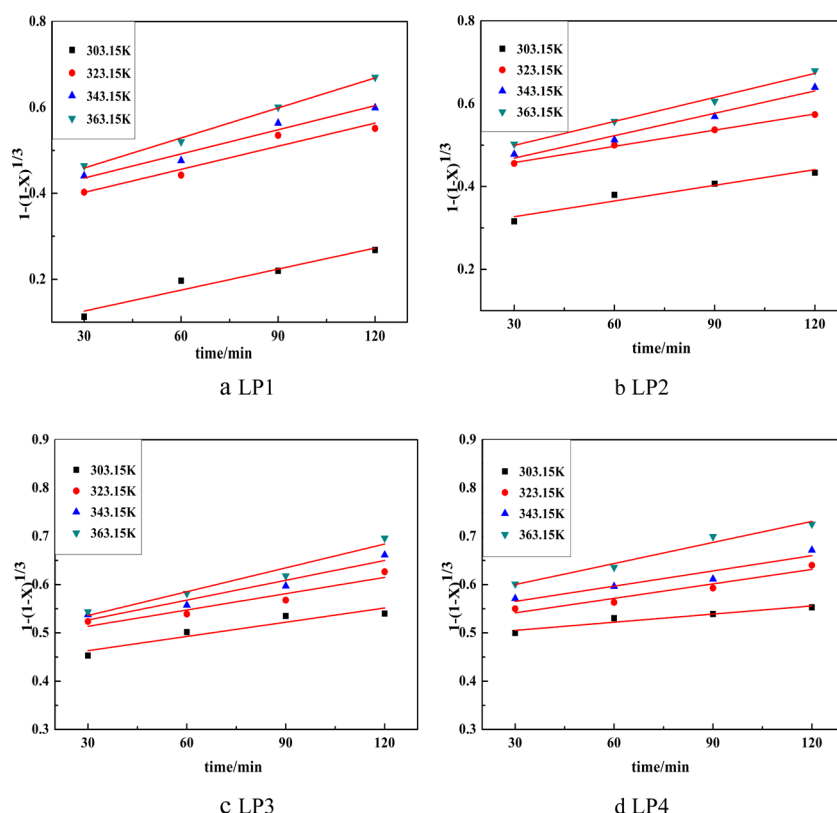
Figure 10. Plot of leaching kinetics of vanadium at various reaction temperatures in different leaching processes (LP1, leached with NaOH; LP2, leached with NaOH + eletro-oxidation; LP3, leached with NaOH + H$_2$O$_2$; and LP4, leached with NaOH + electro-oxidation + H$_2$O$_2$).
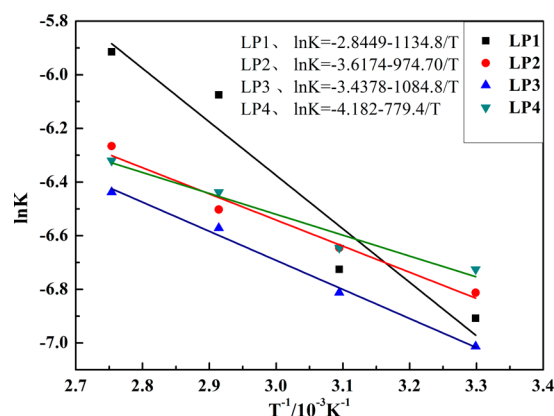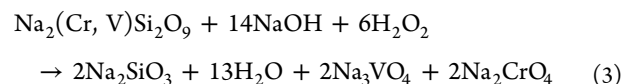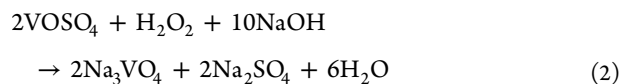

Figure 11. Natural logarithm of the reaction rate constant versus reciprocal temperature in different leaching processes (LP1, leached with NaOH; LP2, leached with NaOH + eletro-oxidation; LP3, leached with NaOH + H$_2$O$_2$; and LP4, leached with NaOH + electro-oxidation + H$_2$O$_2$).

$$2VOSO_4 + H_2O_2 + 10NaOH$$
$$\rightarrow 2Na_3VO_4 + 2Na_2SO_4 + 6H_2O \qquad (2)$$

$$Na_2(Cr, V)Si_2O_9 + 14NaOH + 6H_2O_2$$
$$\rightarrow 2Na_2SiO_3 + 13H_2O + 2Na_3VO_4 + 2Na_2CrO_4 \qquad (3)$$

During the leaching process, vanadium and chromium in the residue broke their bonds Cr−O−V (Figure 6), formed ions, V^{4+} and Cr^{3+}, and then moved into the solution.[22] The ions in low valence would be oxidized by H$_2$O$_2$ and formed ions in high valence. The reaction model was expressed in Figure 6.[23]

3.4. Oxidation Leaching Coupled Electro-oxidation and H$_2$O$_2$ (LP4). Electro-oxidation technology and H$_2$O$_2$ were coupled to enhance the leaching performance under the optimal conditions: liquid/solid ratio of 4.0 (mL/g), mass ratio of NaOH/residue of 1.0 (g/g), current density of 1000 A/m^2, and volume ratio of H$_2$O$_2$/residue of 1.6 (mL/g), respectively. The results were summarized in Figure 7.

From Figures 2 to 7, we could see that the leaching efficiency of vanadium increased sharply at low temperatures and slowly at high temperatures. Partially because the oxidation intermediates O$_2$, generated by anodic oxidation of hydroxyl ions and decomposition of H$_2$O$_2$, had low solubility at high temperatures, the oxidizing of vanadium was blocked, which led to a slow increase of leaching efficiency. In addition, the

Table 5. Apparent Activation Energy with Different Leaching Processes

	NaOH (LP1)	NaOH + eletro-oxidation (LP2)	NaOH + H$_2$O$_2$ (LP3)	NaOH + electro-oxidation + H$_2$O$_2$ (LP4)
Arrhenius equation	ln K = −2.8449 − 1134.8/T	ln K = −3.6174 − 974.70/T	ln K = −3.4378 − 1084.8/T	ln K = −4.182 − 779.4/T
apparent activation energy (kJ mol^{-1})	16.58	8.10	9.02	6.48

increase of leaching efficiency was obvious in the presence of electro-oxidation coupled with H_2O_2.

3.5. Residue Morphology. The change of the residue before and after leaching was analyzed by X-ray diffraction (XRD). Figure 8 showed the XRD pattern of the leaching residue of LP1, LP2, LP3, and LP4. The main characteristic peaks of main content phases disappeared and left the leaching residue composed with an amorphous structure.

Figure 9 showed the Fourier transform infrared (FTIR) spectra of the residue before and after leaching. The peaks and corresponding wavenumber were displayed in Table 2. The original residue had six peaks at 516, 619, 1111, 1400, 1633, and 3145 cm^{-1}. After leaching, peak 1 at 516 cm^{-1} assigned to the symmetric stretching vibration of the Si−O band and peak 5 at 1633 cm^{-1} and peak 6 at 3145 cm^{-1} assigned to the antisymmetric stretching vibration of the −OH band in H_2O were left, while peak 2 at 1111 cm^{-1} with respect to the antisymmetric stretching vibration of the Si−O−Si band had a little blue shift. Peak 4 disappeared, and two new peaks occurred at around 1375 and 1496 cm^{-1}, which represented the compounds of Fe_2O_3.

After all, after leaching, the main components left in the residue were SiO_2 and Fe_2O_3 with an amorphous structure according to Figures 8 and 9.

3.6. Kinetics Analysis. The shrink core model was often used to described the kinetics of the liquid solid-phase reaction,[6,16,24−26] and there were three equations that described the kinetic models,[27−29] as shown in Table 3.

The experimental data were fit into equations shown in Table 3 to determine the kinetic parameters and rate-controlling step. The results reported in Table 4 showed that both eqs 5 and 6 fit the experimental data perfectly. Therefore, it was clear that both the diffusion of the product layer and the surface chemical reaction were the controlling steps. From Figures 2, 3, 5, and 7, the leaching efficiency increased steadily, affected by the temperature, and the leaching reaction occurred between the residue and the concentrated NaOH solution. Therefore, it was reasonable to describe the leaching reaction of vanadium as mainly being controlled by the surface chemical reaction. Therefore, eq 5 was used to express the shrinking core model.

The reaction rates and apparent rate constant were calculated, and the results were expressed in Figure 10. The apparent activation energy was calculated on the basis of the Arrhenius equations, and the results were shown in Figure 11

$$\ln K = \ln A - E_a/(RT) \qquad (7)$$

where E_a is the apparent activation energy, A is the pre-exponential factor, and R is the molar gas constant.

The apparent activation energy of each leaching process (LP1, leached with NaOH; LP2, leached with NaOH + eletro-oxidation; LP3, leached with NaOH + H_2O_2; and LP4, leached with NaOH + electro-oxidation + H_2O_2) was calculated and expressed in Table 5.

Results in Table 5 showed that the apparent activation energy was decreased in the presence of reinforcement methods. The apparent activation energy was decreased from 16.58 to 8.10 kJ mol^{-1}, intensified with an electric field in comparison of LP1 to LP2. Oxidized by H_2O_2 made the leaching of vanadium more easy; the apparent activation energy was decreased 7.56 kJ mol^{-1} from LP1 to LP3. In LP4, the electric field and H_2O_2 were coupled to enhance the leaching process; it exhibited the lowest apparent activation energy, 6.48

kJ mol^{-1}. In other words, the presence of electro-oxidation and H_2O_2 during the leaching process could reduce the apparent activation energy and enhance the leaching performance of vanadium from the residue.

4. CONCLUSION

In this paper, the leaching kinetics of vanadium from the residue with electro-oxidation and H_2O_2 in alkaline medium was investigated. The results showed the following: (1) The leaching kinetics of vanadium followed the shrinking core model, and the controlling step was the surface chemical reaction. (2) Electro-oxidation technology was an efficient way to enhance the leaching performance of vanadium. (3) H_2O_2 was used to intensify the leaching process. It could oxidize vanadium in low valence, reduce the apparent activation energy of the leaching reaction, and then make the reaction easier. (4) The apparent activation energy was calculated as 16.58, 8.10, 9.02, and 6.48 kJ mol^{-1} for LP1 (leached with NaOH), LP2 (leached with NaOH + eletro-oxidation), LP3 (leached with NaOH + H_2O_2), and LP4 (leached with NaOH + electro-oxidation + H_2O_2), respectively.

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The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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Recovery of vanadium with urea in acidic medium

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Abstract

Classical hydrometallurgy methods such as chemical precipitation, ion exchange, solvent extraction and adsorption have been used to recover vanadium from aqueous solutions, but the last step of these methods involves precipitation with ammonium salts, which are harmful to the environment at high concentration. Therefore, here we tested urea as a new precipitant to replace ammonium salts. We studied the effect of various parameters on the precipitation efficiency of vanadium. Results showed that urea is hydrolyzed to form NH_4^+ in acidic medium at 90 °C. Then, NH_4^+ reacts with $V_6O_{16}^{2-}$ and precipitates as $(NH_4)_2V_6O_{16}$. Nearly 95% of the vanadium was precipitated within 120 min in the system containing 2.8 g/L vanadium and $n(CON_2H_4)/n(V)$ of 0.6. The Avrami model was used to describe crystallization kinetics and analysis of the dimensions of crystal growth. Model results show that the crystalline growth was one-dimensional and that the crystals were shaped in columns. Overall, this study introduced a new way for urea utilization as a new precipitant to recover vanadium.

Introduction

Vanadium is an important national strategic resource and widely used in petrochemical industry, catalyst and iron steel, due to their excellent physicochemical properties (Anjass et al. 2017; Efremenko et al. 2013; Lübke et al. 2016; Smirnov et al. 2014; Wei et al. 2014; Zadorozhnyy et al. 2014). The main resource for vanadium recovery is titanium magnetite and stone coal in China (El Hage et al. 2019; Xiang et al. 2018; Zhang et al. 2019a, b). Many methods had been applied to recover vanadium from leaching solution, like chemical precipitation (Kang et al. 2019), ion exchange (Bashir et al. 2019; Bao et al. 2018; Zhu et al. 2018), solvent extraction (Yang et al. 2016; Ye et al. 2018) and adsorption (Peng et al. 2017a, b; Prathap and Namasivayam 2009). What these technologies had in common was that the vanadium was precipitated with ammonium salts and then roasted to produce V_2O_5 at the last step. The key point was to find a new precipitant to replace ammonium

salts during the precipitation process as excessive ammonium was harmful to the environment (Shu et al. 2019).

Urea $[CO(NH_2)_2]$ was widely used in agriculture as a conventional fertilizer (Hermida and Agustian 2019). It was absorbed in the form of ammonium (NH_4^+) by the plant, which was produced by hydrolysis process of urea. In this paper, urea used as a new precipitant was applied to recover vanadium from solution. The effect of experimental parameters including dosage of urea, reaction temperature and reaction time was investigated. Also, the possible reaction mechanism was proposed.

Experimental section

Materials

All the chemicals were of analytical grade, including sodium vanadate (Na_3VO_4) and urea (CON_2H_4), and all solutions were prepared with deionized water with a resistivity greater than 18 MΩ/cm (HMC-WS10).

Procedures

The vanadium solution for the precipitation tests was prepared by dissolving a certain amount of sodium vanadate in

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distilled water. Batch precipitation experiments were conducted by adding urea and sodium vanadate solution into a 250-mL beaker with a thermostatic mixing water bath pot at an agitation speed of 500 rpm. Various operating parameters on vanadium precipitation, such as dosage of urea, dosage of H_2SO_4, reaction time and reaction temperature, were investigated. The solution was rapidly separated from the precipitation by vacuum filtration after the reaction. And the precipitation efficiency of vanadium (η) was calculated using Eq. (1):

$$\eta = \frac{C_1 V_1 - C_2 V_1}{C_1 V_1} \times 100, \tag{1}$$

where C_1 is the initial concentration of vanadium, g/L; C_2 is the concentration of vanadium in the filtrate, g/L; and V_1 and V_2 are the volume of the vanadium solution before and after the precipitation experiments, L.

Characterization

The concentration of vanadium in the solution was measured by inductively coupled plasma optical emission spectrometry. The crystalline phases of the precipitation were measured by X-ray diffraction meter (SHIMADZU-6000, Japan) with a Cu Kα radiation source under the conditions of $\lambda = 0.15418$ nm, 40 kV and 40 mA at 10° to 90°, and the surface morphology was recorded by metallographic microscope.

Results and discussion

Precipitation experiments

The effect of dosage of urea on the precipitation efficiency of vanadium is shown in Fig. 1. The precipitation efficiency was increased with the increase in molar ratio of $n(CON_2H_4)/n(V)$. The precipitation was about 63.03% without the addition of urea, as vanadium was easy to hydrolyze and formed V_2O_5 in acidic medium at high reaction temperature. The addition of urea could favor the reaction and improve the precipitation efficiency of vanadium. Nearly 95% of the vanadium was precipitated within 120 min in the system containing 2.8 g/L vanadium and $n(CON_2H_4)/n(V)$ of 0.6. And the residual vanadium concentration in the filtrate was decreased to 0.14 g/L.

Also, the effect of reaction temperature was also examined, and the results are shown in Fig. 2. The vanadium was still existed as ions and did not precipitate at low reaction temperature. The precipitation efficiency increased from 4.17 to 95.06% as the reaction temperature increased from 60 to 90 °C. In other words, high reaction temperature was beneficial for vanadium precipitation. The results shown in Fig. 3 expressed that the precipitation efficiency of vanadium was increased along the reaction time. Further reaction time could improve the precipitation efficiency of vanadium.

Fig. 1 Molar ratio of $n(CON_2H_4)/n(V)$ had significant effect on the precipitation efficiency of vanadium and residual vanadium concentration. When the molar ratio was $n(CON_2H_4)/n(V) = 0.6$, the precipitation efficiency of vanadium was about 95.06% and the residual vanadium concentration in the filtrate was decreased to 0.14 g/L
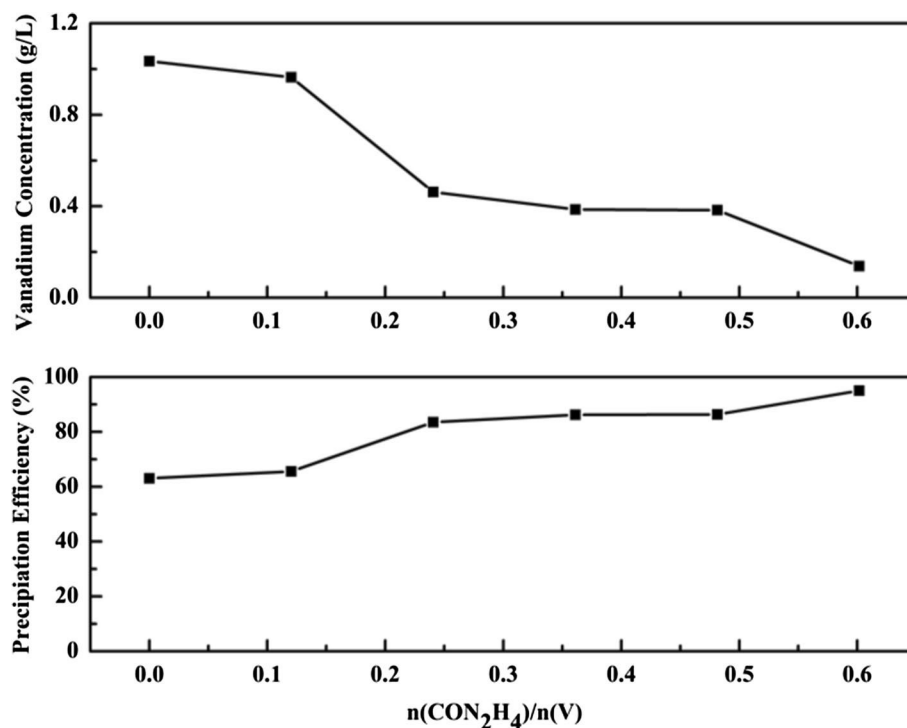
Fig. 2 Precipitation efficiency increased with the increase in reaction temperature. High temperature could favor the precipitation process and achieve high precipitation efficiency and low residual vanadium concentration
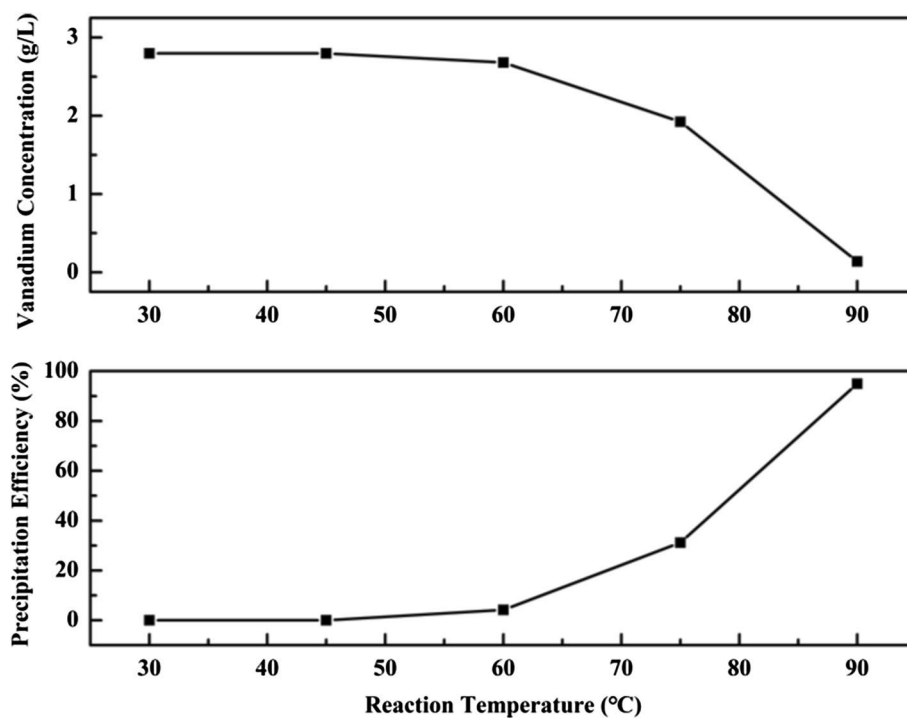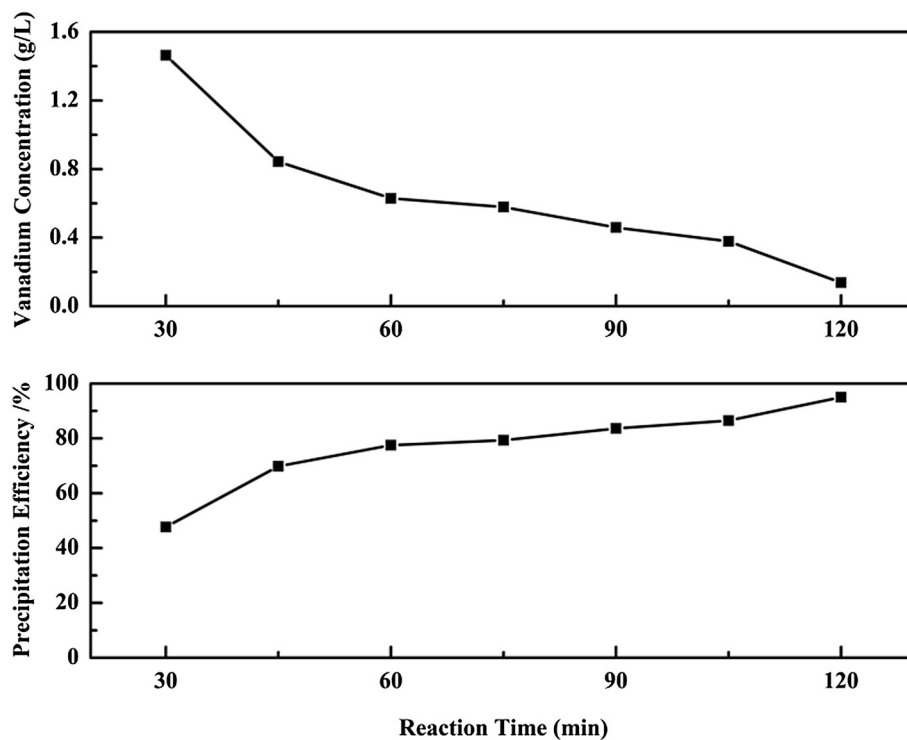

Fig. 3 Vanadium was precipitated along the reaction time. The more the reaction time, the higher the precipitation efficiency and the lower the residual vanadium concentration


Characteristics of precipitation

The X-ray diffraction pattern of crystalline phases of the precipitation is shown in Fig. 4a; the peaks were fitted perfectly with the crystalline phases of $(NH_4)_2V_6O_{16}$, which indicated that the precipitation was just as $(NH_4)_2V_6O_{16}$. The surface morphology recorded by metallographic microscope (Fig. 4b) showed that the precipitation was one-dimensional and seemed like a stick.
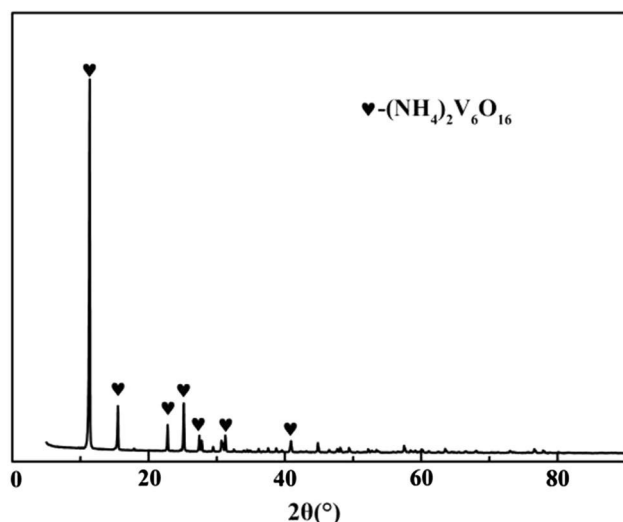
(a) X-ray diffraction pattern
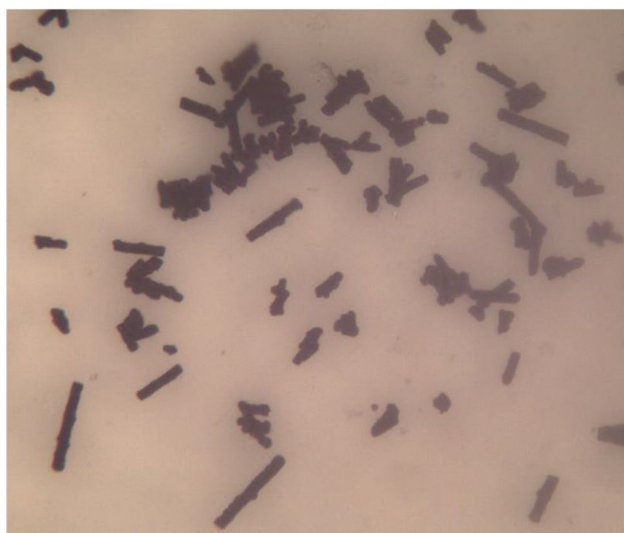
(b) metallographic microscope image

Fig. 4 X-ray diffraction pattern indicated that the precipitation was $(NH_4)_2V_6O_{16}$, and metallographic microscope image for precipitation showed that the precipitation shape of crystals was in column

Kinetic analysis

The Avrami model is widely used for the description of crystallization kinetics and analysis of the dimensions of crystal growth (Avrami 1939, 1940; Hubbes et al. 2018). The equation is as follows:

$$\varphi = \varphi_\infty[1 - \exp(-kt^n)], \tag{2}$$

where φ is the absolute amount of crystalline at time t; φ_∞ is the maximum amount of crystalline; k is the reaction constant, represented both the nucleation and growth rates; and n is the Avrami exponent, represented the dimension of crystal growth.

Setting x as the relative amount of crystallization at time t, Eq. (2) could be changed to Eq. (3):

$$1 - x = \exp(-kt^n). \tag{3}$$

And then by taking the logarithm of Eq. (3), Eqs. (4) and (5) are obtained.

$$Ln(1 - x) = -kt^n \tag{4}$$

$$Ln(-Ln(1 - x)) = Ln\,k + n\,Ln\,t. \tag{5}$$

The obtained experimental data are fitted as Eq. (5) at reaction temperature of 90 °C, and the fitted result is shown in Eq. (6) as follows:

$$Ln(-Ln(1 - x)) = 0.93 Ln(t) - 3.51. \tag{6}$$

The results shown in Eq. (6) indicated that the reaction constant was calculated as 0.0299 min^n, and the Avrami exponent was calculated as 0.93, which was nearly to 1, and the crystalline growth model was one-dimensional growth and the crystalline was in column (Celik and Kazanc 2013; Celik et al. 2011; Hu et al. 1994). The results were consistent with the results shown in Fig. 4b.

Proposal mechanism

Based on the experimental results, we proposed a reaction mechanism for the precipitation of vanadium. The vanadium was existed as single ion like VO_2^+ or polymer ions like $V_6O_{16}^{2-}$ in acidic medium, and it was hydrolyzed to form V_2O_5 which had low solubility in acidic medium following Eq. (7). Nearly 63% of vanadium could precipitate at this stage. The addition of urea could improve the precipitation efficiency of vanadium belonged to the reaction occurred according to Eqs. (8) and (9). The urea was hydrolyzed to form NH_4^+ in acidic medium at reaction temperature of 90 °C. And then NH_4^+ was reacted with $V_6O_{16}^{2-}$ and precipitated as $(NH_4)_2V_6O_{16}$ (Wen et al. 2018, 2019).

$$VO_2^+/V_6O_{16}^{2-} + H^+ \rightarrow V_2O_5 \downarrow + H_2O \tag{7}$$

$$CON_2H_4 + H_2O + 2H^+ \rightarrow 2NH_4^+ + CO_2 \tag{8}$$

$$2NH_4^+ + V_6O_{16}^{2-} \rightarrow (NH_4)_2V_6O_{16} \downarrow. \tag{9}$$
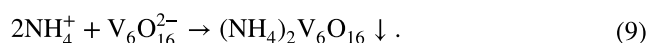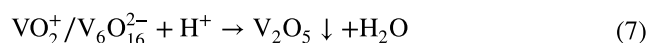
Conclusions

In this paper, urea used as a new precipitant was applied to recover vanadium from solution. The effect of experimental parameters on the precipitation efficiency of vanadium was investigated, and the reaction mechanism about urea hydrolyzed in acidic medium was proposed. The Avrami model was also used to describe the crystallization kinetics and analysis of the dimensions of crystal growth. This work introduced a new method for vanadium recovery.

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REVIEW

Removal of chromium from wastewater by membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology: a review

Hao Peng[1] · Jing Guo[1]

Abstract

Chromium is a potentially toxic and carcinogenic metal originating from natural processes and anthropogenic activities such as the iron steel, electroplating and leather industries. Therefore, chromium should be removed from wastewater to avoid environmental pollution and to recycle chromium in the context of the future circular economy. Here we briefly review aqueous Cr species, their toxicity and methods to remove Cr such as membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology.

Keywords Chromium · Treatment · Wastewater · Removal · Physicochemical technology · Electrocoagulation · Electrochemical reduction · Electrodialysis · Photocatalysis · Nanotechnology

Introduction

Wastewater containing heavy metal ions is a serious environmental problem in the world (Kyzas and Matis 2015; Nogueira et al. 2015; Song et al. 2011). The heavy metal present on the surface of microorganisms and inside the cell can cause significant alterations to the biochemical cycles of living things (Liu et al. 2019; Shakoor et al. 2020). The Comprehensive Environmental Response Compensation and Liability Act is categorized heavy metals in order of their toxicity: Pb (2) > Hg (3) > Cd (7) > Cr (17) > Co (52) > Ni (57) > Zn (75) > U (97) > Cur (125) > Mn (140) and the maximum contaminant level values as per Environmental Protection Agency (EPA) is defined: Pb (0.015 mg/L), Hg (0.002 mg/L), Cd (0.005 mg/L), Cr (0.1 mg/L), Zn (5 mg/L), Cu (1.3 mg/L), Mn (0.05 mg/L) (Anfar et al. 2019a). Among them, Cr is a toxicity heavy metal ion and qualifying for inclusion in Group 1 (carcinogenic to humans) by the International Agency for Research on Cancer (Peng et al. 2019a,

b). It is also one of the top 20 toxic substances in super fund controlled contaminated sites in the USA. Furthermore, Cr(VI) has several negative environmental impacts, including reducing germination and growth of some plants, increasing mortality and reproduction rates in earthworms, organ damage in crayfish, detrimental effects on survivability, growth and post-exposure reproduction of marine fish larvae and copepods, toxic effects on gill, kidney and liver cells of freshwater fish, and possible diatom demise. Therefore, it is important in order to develop proper treatment technologies for Cr(VI) removal (Adhoum et al. 2004a; Hunsom et al. 2005) (Gallios and Vaclavikova 2008; He et al. 2020; Liu et al. 2011).

In the past decades, many researchers have done their best to promote efficient treatment technologies for chromium removal. These technologies are mainly classified into three kinds: physicochemical technology, electrochemical technology and advanced oxidation technology. Physicochemical technologies included membrane filtration, chemical precipitation, ion exchange, and adsorption (Azimi et al. 2017). Electrocoagulation, electrochemical reduction, electrodialysis and electrodeionization have belonged to electrochemical technology (Zhao 2018). Photocatalysis and nanotechnology are advanced oxidation technology which is a practical

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approach in treating wastewaters (Zhao et al. 2019). All the mentioned technologies in this paper are shown in Table 1.

Chromium species

Cr(VI) species in the Cr–H_2O system are in the form of H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$ and CrO_4^{2-}. The reaction relationships of the species could be expressed as Eqs. (1) to (3), and the thermodynamic studies Cr-H_2O system were conducted to determine the chemical state of ions in the wastewater; the calculated results are shown in Table 2.

$$[HCrO_4^-][H^+] = 10^{0.75}[H_2CrO_4] \tag{1}$$

$$[CrO_4^{2-}][H^+] = 10^{6.45}[HCrO_4^-] \tag{2}$$

$$[HCrO_4^-]^2 = 10^{2.2}[Cr_2O_7^{2-}][H_2O] \tag{3}$$

To investigate the reaction mechanisms of chromium removal technologies, the species of chromium in the Cr(III)–H_2O system and Cr(VI)–H_2O system was simulated with Visual MINTEQ software (Kocaoba and Akcin 2002). The results shown in Fig. 1a indicated that the main species in the Cr(III)–H_2O system were $Cr(OH)^{2+}$, $Cr(OH)_3(aq)$, $Cr(OH)_4^-$, Cr^{3+}, $Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$ and $CrOH^{2+}$. The Cr(III) mainly existed in the form of Cr^{3+} at pH < 4. With the increase in pH value, Cr^{3+} was transformed to $CrOH^{2+}$, while $Cr_2(OH)_2^{4+}$ was appeared at its highest mole fraction of 12.3% at pH = 3 and then decreased to nearly zero along with the increase in pH. The form of $CrOH^{2+}$ reached its maximum mole fraction at pH = 4 (93.6%) and then transformed to $Cr(OH)_2^+$ and $Cr(OH)_3$ (aq). At pH = 4–7, Cr(III) was mainly existed as $CrOH^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3$ (aq), while the form of $Cr_3(OH)_4^{5+}$ only appeared at pH = 6–8 and its maximum mole fraction appeared at pH = 7 (22.1%). The form of $Cr(OH)_3$ (aq) existed at pH = 5–14 and reached its maximum at pH = 9 (99.4%) and transformed to $Cr(OH)_4^-$. The form of $Cr(OH)_4^-$ appeared with the increase in medium alkalinity and became the only form of Cr(III) in the solution at pH > 14.

While the species in the Cr(VI)–H_2O system was quite simple than Cr(III), only four species appeared: $Cr_2O_7^{2-}$, CrO_4^{2-}, H_2CrO_4 and $HCr_2O_7^-$ according to the results shown in Fig. 1b. Among these four species, H_2CrO_4 only

Table 1 Treatment technologies for chromium removal

No.		Methods	Advantages	Disadvantages
1	Physicochemical processes	Chemical precipitation	Simple, effective	Secondary pollution
2		Membrane	Higher removal efficiency, no pollution loads and sometimes lower energy consumption	Highly depend on materials, membrane pore size and composition
3		Ion exchange	HIGH efficiency, low cost, less sludge volume and high selectivity	Highly depend on resin structure and solution environment
4		Adsorption	High efficiency, simple operation and ease of regeneration	Highly depend on the solution environment
5	Electrochemical Technologies	Electrocoagulation	Simple, productive, ease of operation	Poor systematic reactor design and sacrifice of electrodes
6		Electrochemical Reduction	No further reagent	Dependent on the electrode materials and electrochemical surface area of the electrode
7		Electrodialysis	Low energy consumption	Highly cost of electrodes
8	Advanced Technologies	Photocatalysis	Simple design, low-cost operation, high stability and high removal efficiency	Producing unwanted byproducts
9		Nanotechnology	Higher removal efficiency, low waste generation and specific uptake	Increase the risk of nano-pollutants in the environment

Table 2 Equilibrium and corresponding constants of Cr-H_2O system at 298 K

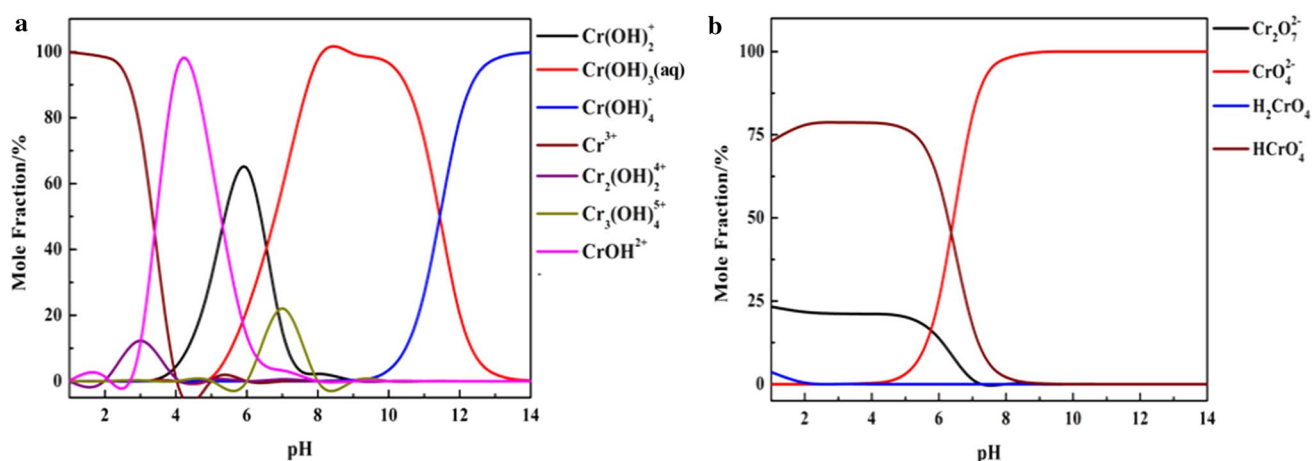| No.	Equilibrium reactions	Equilibrium constants (log K)	References
1	$H_2CrO_4 = HCrO_4^- + H^+$	0.75	Cotton and Wilkinson (1980)
2	$HCrO_4^- = CrO_4^{2-} + H^+$	6.45	Cotton and Wilkinson (1980)
3	$2HCrO_4^- = Cr_2O_7^{2-} + H_2O$	2.2	Cotton and Wilkinson (1980)

Fig. 1 Species of chromium in the Cr(III)-H$_2$O system and Cr(VI)-H$_2$O system were simulated with Visual MINTEQ software (Kocaoba and Akcin 2002). The results shown in **a** indicate that the main species in the Cr(III)-H$_2$O system are Cr(OH)$^{2+}$, Cr(OH)$_3$(aq), Cr(OH)$_4^-$, Cr^{3+}, Cr$_2$(OH)$_2^{4+}$, Cr$_3$(OH)$_4^{5+}$ and CrOH^{2+}; the results shown in **b** indicate that only four species appear: Cr$_2$O$_7^{2-}$, CrO$_4^{2-}$, H$_2$CrO$_4$ and HCr$_2$O$_7^-$

existed at low pH and accounted for little fraction. Thus, it could be ignored. At pH < 8, the Cr(VI) had existed both in the form of Cr$_2$O$_7^{2-}$ and HCr$_2$O$_7^-$, and HCr$_2$O$_7^-$ was nearly three times to Cr$_2$O$_7^{2-}$. As pH increased, Cr$_2$O$_7^{2-}$ and HCr$_2$O$_7^-$ were transformed to CrO$_4^{2-}$, which was the one that existed in the alkaline medium.

Physicochemical processes

Chemical precipitation

Chromium occurs primarily in Cr(III) and Cr(VI) oxidation states in aqueous solution. In the chromium removal process, the Cr(VI) was often reduced to Cr(III), which remained relatively stable and less poisonous and then followed with chemical precipitation technologies (Azimi et al. 2017; Fenglian and Hong 2014). In chemical precipitation processes, chemical precipitant agents reacted with heavy metal ions and changed them into insoluble solid particles (Fig. 2) (Fu and Wang 2011). Then, the precipitation could be separated from the solution by sedimentation or filtration (Zamboulis et al. 2004).

Hydroxide precipitation

In this process, some chemical precipitant agents like iron salt and aluminum salt might enhance the precipitation process and accelerate the filtration process. Heavy metal ions had low solubility in alkaline medium; thus, the precipitation process was often conducted in alkaline medium and the chemical reaction was described as follows:

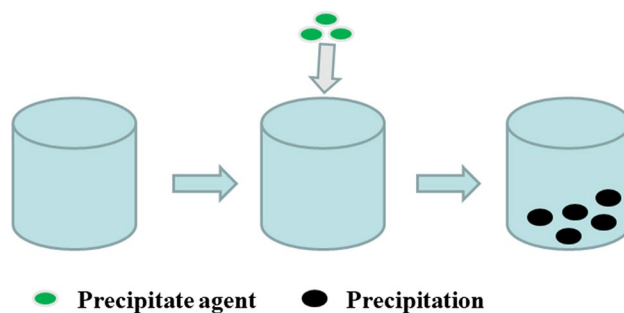● **Precipitate agent**   ● **Precipitation**

Fig. 2 Chemical precipitation model. The chemical precipitant agents were added into the solution containing Cr(VI) or Cr(III) and then generated precipitation after stirring

$$M^{n+} + nOH^- \rightarrow M(OH)_n \downarrow \tag{4}$$

in which M^{n+} was the soluble metal ions.

For chromium removal process, the Cr(VI) was first reduced to Cr(III) and then some alkaline like NaOH or NH$_3$·H$_2$O was added; thus, Cr(III) was precipitated as Cr(OH)$_3$.

Direct precipitation

A direct precipitated Cr(VI) technology was conducted with lead sulfate (Peng et al. 2018). The Cr(VI) was removed in the form of PbCrO$_4$ based on the large difference of solubility constant of PbSO$_4$ and PbCrO$_4$.

$$2PbSO_4 + CrO_4^{2-} + 2OH^- \rightarrow PbCrO_4 \downarrow + 2SO_4^{2-} + Pb(OH)_2 \tag{5}$$
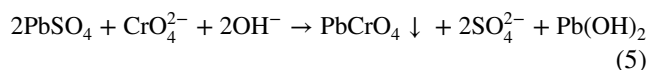
The concentration of Cr(VI) was reduced from 0.2 mol/L to 0.0015 mmol/L at pH = 13.90 and n (lead sulfate)/n(Cr(VI)) = 4. Though the residual Pb concentration in the solution was acceptable, the technology could be implemented in a large scale as Pb was a poisonous metal and showed harmful to the environment. In other way, the large amount of precipitation was another limitation for the industrial application.

Membrane filtration

Membrane filtration processes were developed and used due to their higher removal efficiency, no pollution loads and sometimes lower energy consumption than conventional methods (Choudhury et al. 2018; Kumar et al. 2019). Membrane processes are employed in treating water and wastewater because of the simple separation method (Anarakdim et al. 2020; Semghouni et al. 2020; Zhao et al. 2019). This simple procedure is divided between different membrane processes with minor differences. In general, three kinds of membranes are used in separation processes called liquid, pressure-driven and hybrid membranes. There are many parameters that can affect the membrane process, like materials in use, membrane pore size and composition, which lead to highly efficient and economic separation (Duan et al. 2018; Ibrahim Turgut et al. 2019). Membrane processes are often coupled with other technologies and are divided into five kinds: reverse osmosis (Kurniawan et al. 2006), ultrafiltration (Sandoval-Olvera et al. 2019), microfiltration (Azimi et al. 2017), nanofiltration (Giagnorio et al. 2018) and electrodialysis (Chen et al. 2017). Giagnorio et al. used NF270 and NF90 achieved 98.8% and 76.5% chromium removal and also overcame the drawbacks like fouling and system operational performance (Giagnorio et al. 2018). A magnetite membrane produced by oxidation of 316L stainless steel was achieved 100% chromium removal at pH = 4, and it also showed excellent stability and strength for industrial applications (Shi et al. 2015; Yao et al. 2018). Membrane technique was also coupled with other technologies, like ion exchange, adsorption, electrochemical technology, etc.

Ion exchange

Historically, ion exchange was an ancient technique documented more than 100 years ago. Since then, this technique has been used for softening water to an incomparable wider scale of applications and has become an integral part of new technical and industrial processes (Alyuz and Veli 2009; Kurniawan et al. 2006; Lin and Kiang 2003; Mazurek 2013; McGuire et al. 2007; Xiaobo et al. 2017; Xuewen et al. 2011). Ion exchange is a reversible stoichiometric chemical reaction wherein an ion from solution or electrolyte or molten salt is exchanged for a similarly charged ion attached

to an immobile and insoluble solid material, maintaining the overall electroneutrality (Dabrowski et al. 2004; Dharnaik and Ghosh 2014; Elwakeel 2010; Li et al. 2014a; Rengaraj et al. 2001b). In this process, an insoluble resin was used to Cr(III) from the wastewater and release other ions of similar charge without any structural change of the resin itself (Bao et al. 2018; Fengliang et al. 2013)(Anirudhan and Radhakrishnan 2011). The Cr(III) was recovered in a more concentrated form by elution with suitable reagents, after separation of the loaded resin. Resin with acidic functional groups contained sulfonic acid in its structure; hence, it could be supposed that during Cr(III) capturing, the physicochemical interactions might take place:

$$3RO_3^- - H^+ + Cr^{3+} \rightleftharpoons (RO_3^-)_3 - Cr^{3+} + 3H^+ \tag{6}$$
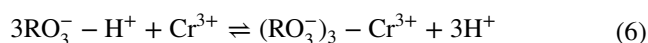
The processes demanded ion-exchange materials with high thermal stability, good resistance toward ionizing radiation and efficient sorption capacity. Organic resins and inorganic ion exchanges were both attracted much more attention, such as zeolites, sodium titanites, titan silicates, metal sulfides, layered double hydroxides, metal phosphates, metal tungstate and hexacyanoferrates (Bashir et al. 2018). Among all the available kinds, synthetic polymer resins were preferred, such as styrene–divinylbenzene (Banno and Yabuki 2020), gel-like resins (Ju et al. 2020), macropore resins (Xiao et al. 2020). 5-Methyl-2-thiophene carboxaldehyde possessed high surface area (623 m^2/g) and showed high removal efficiency of Cr(III) at pH = 6.5 with 6 h (Parambadath et al. 2015). Tenorio found that the concentration of Cr(III) in the wastewater could be reduced to below 0.3 mg/L with ion exchange. Two commercial ion-exchange resins named Diaion CR11 and Amberlite IRC 86 both showed effective performance in the removal of Cr(III) from wastewater (Cavaco et al. 2007). Gode et al. observed that the new ion-exchange resin named Lewatit S 100 showed great removal efficiency of Cr(III) at pH = 3.5 and the adsorb kinetics followed first-order reversible kinetics model (Gode and Pehlivan 2006). Cation-exchange resins called IRN77 and SKNI were applied to remove chromium from water and wastewater; the results showed that nearly 95% chromium was removed under optimal reaction conditions (Rengaraj et al. 2001a).

Adsorption

Adsorption technology was widely used in wastewater treatment due to its high efficiency, simple operation and ease of regeneration (Anfar et al. 2019a, b, c, d, 2020; El Haouti et al. 2019; Li et al. 2009; Liu et al. 2006, 2010; Meirong et al. 2012; Ouasfi et al. 2019; Shu et al. 2018a, b, 2019; Zbair et al. 2019). Melamine possessing three free amino groups and three aromatic nitrogen atoms in its molecule

was also used to absorb vanadium and showed great performance (Peng et al. 2017a; b). Our recent studies showed that melamine achieved high adsorption capacity (2843 mg/g) at removal efficiency of chromium (III) (98.63%) within 60 min at n (melamine)/n (Cr) = 1.5 and reaction temperature at 90 °C (Peng et al. 2020). The adsorptive isotherm and kinetic indicated that the main adsorption mechanisms for the adsorption of chromium (III) were confirmed as electrostatic attraction and stacking interaction and the adsorption process was a spontaneous, endothermic and physisorption process.

Adsorption by activated carbon is one of the most studied phenomena (Anfar et al. 2019a). Many researchers have established the efficiency of activated carbon and activated carbon composites as adsorbents to remove many types of pollutants including heavy metals and dyes (Elwakeel et al. 2015; Shakoor et al. 2020; Yavuz et al. 2006). The adsorption processes are often well described with pseudo-second-order model, and the adsorption mechanism studied by intraparticle model suggested that the adsorption processes include four steps (Fig. 3): (1) bulk transport (the heavy metal ions transport in the solution phase); (2) film transport (the heavy metal ions are transported from the bulk liquid phase to the adsorbent's external surface through a hydrodynamic boundary layer or film); (3) intraparticle (diffusion of the heavy metal ions from the exterior of the adsorbent into the pores of the adsorbent); and (4) adsorption (Anfar et al. 2019a).

In recent years, biosorption as an eco-friendly technique for toxic metals removal had attracted much more attention (Escudero et al. 2006; Fiol et al. 2003). In this process, the ligands and functional groups of biomaterials were reacted with heavy metal ions and formed complex compounds. The major advantages of biosorption over conventional methods were low cost, high adsorption capacity and good selectivity (Aditya et al. 2011; Avila et al. 2014; Kanagaraj et al. 2014; Mishra et al. 2020). The most common biomaterials for Cr(VI) removal were chitosan (Ngah and Liang 1999), sludge biomass (Colla et al. 2015), nanofibers (Avila et al. 2014; de Oliveira et al. 2014; Feng et al. 2020; Mohamed et al. 2017) and others (Arshid Bashir et al. 2019; Blázquez et al. 2009; Mangwandi et al. 2020; Niu and Volesky 2006). During the biosorption process, adsorption of Cr(VI) was affected significantly by the pH value of the reaction medium. At low pH, the active sites of the biosorbents were protonated and the anionic species could be bound on the sorbent by electrostatic forces. Maximum uptake values of Cr(VI) were observed at pH 2.0 for tea waste (Malkoc and Nuhoglu 2007), hazelnut shells (Bayrak et al. 2006), osage orange (Pehlivan and Kahraman 2011) and rice straw (Chang et al. 2012). In other studies, pH 3.0 and 1.5 were found to be optimal for the hexavalent chromium sorption onto cork and grape stalks (Machado et al. 2002).

Fig. 3 Adsorption mechanism studied by intraparticle model suggests that the adsorption processes includes four steps: (1) bulk transport (the heavy metal ions transport in the solution phase); (2) film transport (the heavy metal ions are transported from the bulk liquid phase to the adsorbent's external surface through a hydrodynamic boundary layer or film); (3) intraparticle (diffusion of the heavy metal ions from the exterior of the adsorbent into the pores of the adsorbent); and (4) adsorption
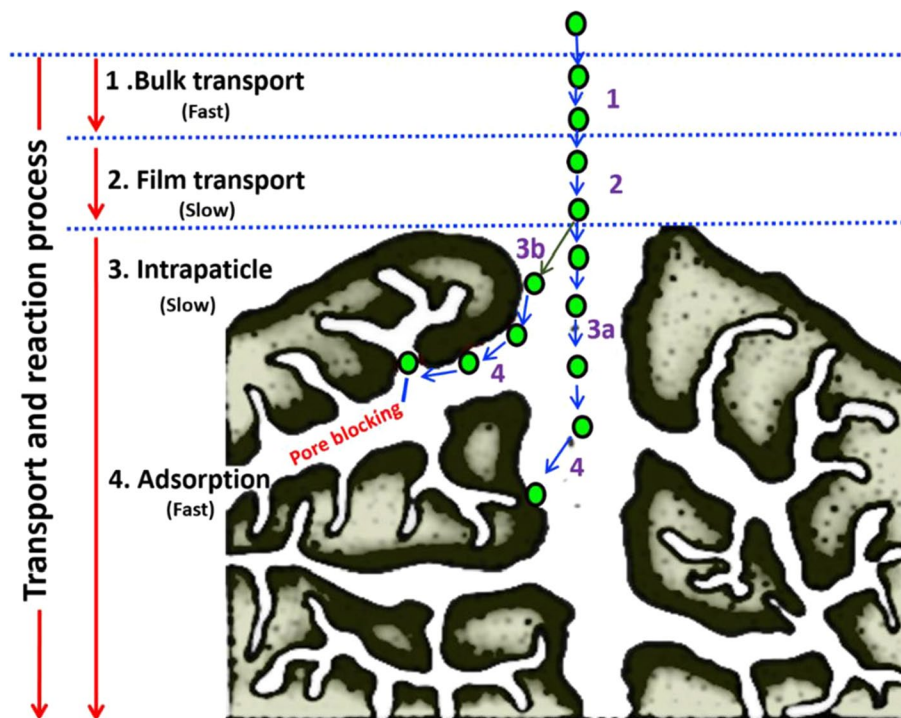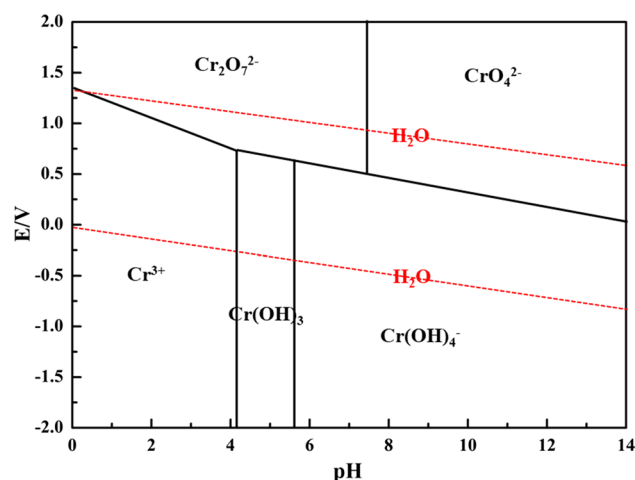
Fig. 4 Eh-pH diagram of conversion of Cr(VI) and Cr(III). Chromium occurs mainly as Cr(III) and Cr(VI) in the aqueous solution, and Cr(VI) is easily reduced to Cr(III) with electrochemical technology
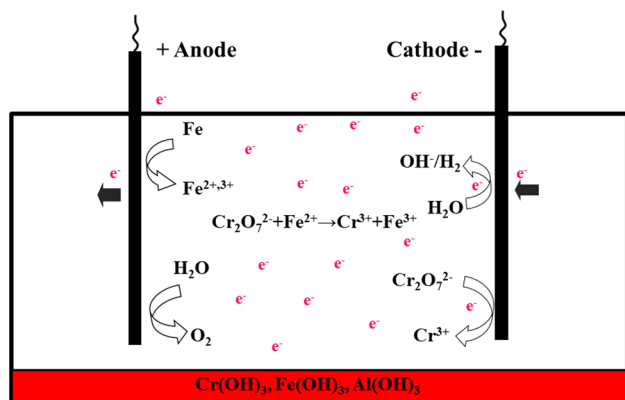

Fig. 5 Electrochemical technology model. The electrochemical process for chromium removal often involves three steps: (1) The first step is the formation of electrogenerated Fe(II) species; (2) the second step is the reduction of Cr(VI) to Cr(III); and (3) the third step is the precipitation of Cr(III)

Electrochemical technology

The electrochemical technology had shown great potential for Cr(VI) removal and attracted much more attention in recent years. The main advantage was the clean reagent (electron) used in the process, which was environmental-friendly, facilitating its potential application due to the stringent pollution regulation (Duarte et al. 1998) (Figs. 4 and 5). Besides, it also contained some other advantages like operation versatility, amenability of automation, production safety in mild reaction conditions (Breslin et al. 2019; Dhal et al. 2013; Rajkumar and Palanivelu 2004; Zongo et al. 2009). Golder compared the Cr(VI) removal

performance using electrocoagulation and chemical coagulation and identified that electrocoagulation efficiency was nearly 3 times higher than chemical coagulation using Al or aluminum sulfate (Akbal and Camcı 2010). It was clear that electrochemical techniques could offer enormous prospects for the development of clean, efficient and cost-effective Cr(VI), meeting the increasingly stringent environmental regulation.
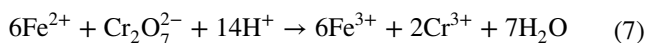
Electrocoagulation

Among the electrochemical technologies, the most effective one was electrocoagulation, which was the electrochemical production of destabilization agents from sacrificial anodes (such as Al, Fe) for removing pollutant and pathogens (Adhoum et al. 2004; Ait Ouaissa et al. 2013; Aoudj et al. 2015; Can and Bayramoglu 2010; Cheballah et al. 2015; Fajardo et al. 2014; Heidmann and Calmano 2008; Li et al. 2019; Moersidik et al. 2020; Xu et al. 2019). In the chromium process, the use of Al and Fe electrodes was suggested because the elimination of chromium species (Cr^{3+}, CrO_4^{2-} and $Cr_2O_7^{2-}$) was around 80% depending on the experimental conditions. The selective of electrode materials had a significant effect on the removal efficiency of heavy metals or organic pollutants during the electrocoagulation process (Fajardo et al. 2014; Graça et al. 2019; Kabdasli et al. 2009; Kim et al. 2020; Olmez-Hanci et al. 2012; Sharma et al. 2019; Zongo et al. 2009). Aluminum, iron and stainless steel were the most common electrode materials. The electrocoagulation process of chromium (VI) (Al-Shannag et al. 2015; Ali Maitlo et al. 2019; Garcia-Seguraa et al. 2017; Lu et al. 2016; Sahu et al. 2014; Zaroual et al. 2009; Zewail and Yousef 2014) involved the following three steps:
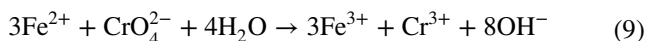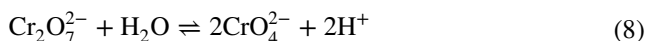
The first step was the formation of electrogenerated Fe(II) species:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + +2H_2 + O_2 + 2e^- \tag{6}$$
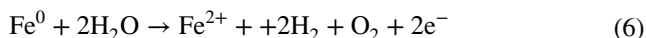
The second step was the reduction of Cr(VI) to Cr(III). The reactions were described as follows: $0.5 < pH < 6.5$:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \tag{7}$$

$6.5 < pH < 7.5$:

$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+ \tag{8}$$

$$3Fe^{2+} + CrO_4^{2-} + 4H_2O \rightarrow 3Fe^{3+} + Cr^{3+} + 8OH^- \tag{9}$$

$pH > 7.5$:

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \tag{10}$$

$$3Fe(OH)_2 + CrO_4^{2-} + 4H_2O \rightarrow 3Fe(OH)_3 + Cr(OH)_3 + 2OH^- \tag{11}$$
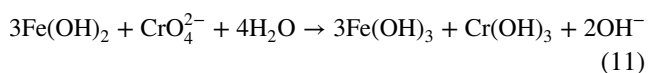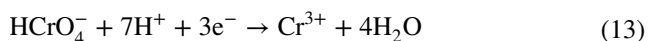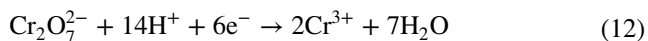
For aluminum electrode electrocoagulation process, Cr(VI) was reduced to Cr(III) in contact with cathodes (Heidmann and Calmano 2008; Zongo et al. 2009):

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \tag{12}$$

$$HCrO_4^- + 7H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O \tag{13}$$

$$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^- \tag{14}$$

The third step was the precipitation of Cr(III):

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \tag{15}$$

T. M. Zewail et al. investigated the removal behavior of Cr(III) and Cr(VI) from synthetic wastewater with vertical expanded Fe anode (Zewail and Yousef 2014). The results showed that the Cr(III) removal efficiency was slightly increased with the increase in current density and then achieved its maximum at pH = 8. In contrast, Cr(VI) removal efficiency was slightly decreased with the current density and reached its maximum at pH = 4.5. The presence of NaCl could promote the removal efficiency of both Cr(III) and Cr(VI). Feryal Akbal et al. applied the electrocoagulation process to remove copper, chromium and nickel from metal plating wastewater with Fe and Al electrodes (Akbal and Camcı 2011). The results showed that the Cr(VI) removal efficiency was reached up to 100% at a reaction time of 20 min, current density of 10 mA/cm^2 and pH = 3. Tugba Olmez used response surface methodology to investigate the effect of operating conditions on the removal of Cr(VI) (Olmez 2009). The results showed that after reaction 70 min under 7.4 A current in 33.6 mM NaCl solution, the removal efficiency of Cr(VI) could achieve 100%.

Electrochemical reduction

Another popular technique was the electrochemical reduction, which could take place through direct reduction and indirect reduction pathways (Frenzel et al. 2006; Jin et al. 2012; Scialdone 2009). The Cr(VI) remediation in this technology was largely dependent on the electrode materials and electrochemical surface area of the electrode. The most common electrodes were made of PbO$_2$ coatings or dimensionally stable anodes coatings on Ti (Almaguer-Busso et al. 2009; Peng et al. 2019b; Rodriguez-Valadez et al. 2005). In order to improve the removal efficiency of Cr(VI), some new cathode materials were developed. Carbon-based electrodes, mercury-based electrodes, bismuth film electrodes, gold electrodes,

conducting polymers and fuel cell system had attracted much more attention.

Roberts used porous carbon felt electrodes to remove Cr(VI), and the Cr(VI) was reduced from 50 mg/L to less than 5 mg/L within a reaction time of 230 min at pH = 3.5 (Roberts and Yu 2002). Wang (Wang and Na 2014) used carbon nanotube arrays to remove Cr(VI), and he found that the carbon nanotube arrays could increase electrode surface area up to 13 times to stainless steel mesh and the increase in electrode surface area directly benefitted Cr(VI) reduction without compromising the electrode's ability to adsorb Cr(III). Some results showed that the gold electrode exhibited a good reduction performance of Cr(VI) in aqueous solution (Duarte et al. 1998; Jin and Yan 2015). Jin used gold nanoparticle-decorated TiO$_2$ nanotubes arrays for the electrochemical removal of trace Cr(VI). The new electrode achieved 23 times activity improvements than usual gold electrode due to its highly ordered with metal–semiconductor heterojunction infrastructures and high surface areas. The Cr(VI) was reduced and adsorbed at pH = 2.0 and then precipitated as Cr(OH)$_3$ at pH = 11.0, which was easily separated (Jin et al. 2014).

Other electrochemical technologies

Some other electrochemical technologies also had attracted much more attention in removing Cr(VI) and Cr(III) from wastewater, like electrodialysis, electro-electrodialysis and electrodeionization. Electrodialysis was a membrane separation process based upon the selective transport of aqueous ions through ion-exchange membranes under the electrical driving forces (Dharnaik and Ghosh 2014; Hosseini et al. 2019; Sadyrbaeva 2016; Strathmann 2010; Wang et al. 2013). The recent research (Sadyrbaeva 2016) investigated the removal performance of Cr(VI) with galvanostatic electrodialysis, the results showed that the chromium(VI) transport rate increased with the increase in current density and initial Cr(VI) concentration, and nearly 99.5% Cr(VI) could be removed from the feed solution. Electro-electrodialysis (EED) was a method that integrated features of electrolysis and electrodialysis (Chen et al. 2017; Duan et al. 2018; Tanaka et al. 2019). The issues of this technology applied in Cr(VI) removal were usually linked to the poor stability of the anion-exchange membrane, the increase in the membrane resistance (Xu and Huang 2008) and concentration polarization (Zhang et al. 2014). Thus, the development of stable, highly conductive and selective membranes was needed to improve the removal efficiency of Cr(VI) from wastewater.

Advanced technologies

Photocatalysis

Photocatalysis picked up its thought because of the capacity to debase a wide extent of substance contaminants (Wang et al. 2004). Photocatalysis oxidizes or lessens different poisonous metal particles including Hg(II), Cd (II), Cu (II), Cr(VI), etc. During the photocatalysis process, the heavy metals were reduced by receptive oxygen species which were produced on acquaintance photocatalyst with UV or visible radiation. The advantage of this technology was the low generation of secondary pollution, harmless products, less time and reaction requirement, while the interfacial charge transfer and bandgap dependency would limit the removal efficiency of Cr(VI). TiO_2 was the main material for the photocatalytic decrease of Cr(VI) (Feng et al. 2017; Han et al. 2017; Sane et al. 2018). The experiment results indicated that 79% Cr(VI) was reduced at optimal reaction conditions and the photocatalysis process was favored in acidic medium. Zheng et al. (Zheng et al. 2019) synthesized a carbon-coated Mg–Al layered double oxide nanosheets to remove Cr(VI) from aqueous solution. The result showed that the sorption capacity of Mg–Al layered double oxide nanosheets increased and then decreased with the increasing Mg/Al molar ratio, of which Mg_5Al_1 layered double oxide nanosheets exhibited the best sorption capacity. The adsorption behavior of Mg–Al layered double oxide nanosheets was fitted well with the Langmuir isotherm model, and the adsorption kinetics of chromium (VI) was described by the pseudo-second-order model.

Nanotechnology

Nanoscale objects were great adsorbents and widely used in treating wastewaters due to their large surface area (Al-Rashdi et al. 2013; Liu et al. 2014; Nogueira et al. 2015; Qu et al. 2013; Serrano et al. 2009; Tang et al. 2014). There were three kinds of nanoparticles for wastewater treatment: adsorptive, reactive and hybrid magnetic. Nanomagnetic oxides were widely used in wastewater treatment systems due to their high surface area, stability and mesoporous structure, and the removal efficiency of Cr(VI) was depended on the reaction condition and adsorbent (Hua et al. 2012). Nano-zero-valent iron was another useful nanoparticle used for Cr(VI) removal from wastewater (Chen et al. 2019; Fan et al. 2020; Fenglian and Hong 2014; Fengliang et al. 2013; Fu et al. 2017; Rongbing et al. 2017; Vilardi et al. 2019). During the reaction process, the addition of nano zero-valent iron decreased the pH and redox potential of the solution; chromium (VI) was easily reduced to Cr(III), which was harmless for the environment (Fengliang et al. 2013; Yoshino and Kawase 2013). Another nanoparticle was hybrid magnetic nanoparticles, which were widely used due to their convenient magnetic properties, low toxicity, low price and high surface-to-volume ratio (Giraldo et al. 2013; Hao et al. 2010; Yu et al. 2013). Hu et al. (Hu et al. 2007) prepared various types of nanoparticles for Cr(VI) removal; the results showed that the adsorption capacities for Cr(VI) followed the order: $MnFe_2O_4 > MgFe_2O_4 > ZnFe_2O_4 > CuFe_2O_4 > NiFe_2O_4 > CoFe_2O_4$.

Some other removal technologies not mentioned in this paper were also attracted much more attention, like solvent extraction (Balogh et al. 2000; Kalidhasan and Rajesh 2009; Pourmohammad et al. 2019; Semghouni et al. 2020; Zhang et al. 2007), ultrafiltration (Huang et al. 2019; Li et al. 2014b; Sandoval-Olvera et al. 2019), foam separation (Ghosh et al. 2019; Lee et al. 2017; Stergioudi et al. 2015).

Conclusion

Rapid industrialization has resulted in increased utilization of Cr ions in the last few decades to make a serious worldwide environmental issue. Due to its hazardous and bioaccumulate nature, there have been numerous attempts to find a suitable remedial action. Various conventional methods such as membrane filtration, chemical precipitation, ion exchange, adsorption electrocoagulation, electrochemical reduction, electrodialysis, electrodeionization, photocatalysis and nanotechnology have been developed and used for water and wastewater treatment to decrease Cr concentrations. Each method has its own removal efficiency and the specific parameters that affect the removal process. The results are different for each method and their experimental conditions. We conclude that in order to remove the Cr completely and efficiently, many technologies discussed above should be used together and also some new technologies needed to be developed.

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2019年9月1日