锰化合物净水技术

2006

Beijing, China

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建设部科学技术司 组织编写

李圭白 杨艳玲 李 星 李 虹 著

中国建筑工业出版社

图书在版编目(CIP)数据

锰化合物净水技术/建设部科学技术司组织编写；李圭白等著. —北京：中国建筑工业出版社，2006
ISBN 7-112-08377-X

Ⅰ. 锰… Ⅱ. ①建…②李… Ⅲ. 锰化合物—净水—技术
Ⅳ. TU991.2

中国版本图书馆 CIP 数据核字(2006)第 051867 号

责任编辑：俞辉群
责任设计：崔兰萍
责任校对：王媛丽　王金珠

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建设部科学技术司　组织编写
李圭白　杨艳玲　李　星　李　虹　著
*
中国建筑工业出版社出版、发行(北京西郊百万庄)
新华书店经销
北京天成排版公司制版
北京云浩印刷有限责任公司印刷
*
开本：880×1230 毫米　1/16　印张：21¾　字数：690 千字
2006 年 8 月第一版　2006 年 8 月第一次印刷
印数：1—2500 册　定价：**60.00** 元
ISBN 7-112-08377-X
(15041)

本社网址：http：//www. cabp. com. cn
网上书店：http：//www. china-building. com. cn

内容提要

本书是一部应用科技类图书，书中主要介绍了近年来关于锰化合物净水技术，特别是高锰酸钾及其复合剂饮用水除污染技术的研究成果和生产应用情况。书中简要介绍了天然条件下和人工制造的锰化合物的形态及其物理化学性质。书中系统地阐述了高锰酸钾、高锰酸盐复合药剂及水合二氧化锰强化混凝除浊、除水中有机物及氯化消毒副产物前质、除水中微量有机污染物、除酚、除有机磷农药、除丙烯酰胺单体、除藻、除臭除味、强化氯和氯氨消毒、强化除砷以及天然锰砂接触氧化除铁除锰、二氧化锰除染料废水色度等技术的工艺原理、去除效果、影响因素、适用条件、工艺参数等。书中还介绍了该饮用水除污染技术在北京、大庆、哈尔滨、郑州、胜利油田、合肥、攀枝花、顺德、东莞等地的生产试验和应用实例。本书可供从事给排水工程、环境工程和水处理工程的工程技术人员，以及大专院校师生参考。

Summary

This is a book of applied science and technology. The new technique of water purification technique of manganese compound is mainly introduced in this book, especially research achievements and productive applications of the pollution removal technique of drinking water by potassium permanganate and potassium permanganate composite. The form and the physic and chemical properties of manganese compound under natural and artificial condition are briefly introduced. This book explains systematically technological principle, removal effects, influence factors, applicable conditions and technological parameters of potassium permanganate, potassium permanganate composite and hydrous manganese dioxide on enhanced coagulation for turbidity removal, organic matter removal, precursor removal of chlorination disinfection byproduct, microorganic pollutant removal, phenol removal, organic phosphorus pesticide removal, acrylamide removal, algae removal, odor and taste removal, enhancing disinfection of chlorination and chloramination, enhancing arsenic removal, iron and manganese removal with contact oxidation by natural manganese sand, and color removal of dye wastewater by manganese dioxide. Productive experiment and application examples of the pollution removal technique of drinking water in Beijing, Daqing, Harbin, Zhengzhou, Shengli oil field, Hefei, Panzhihua, Shunde and Dongguan are introduced. This book gives reference to engineering technical personnel, and teachers and students of colleges and universities who are engaged in water supply and sewerage engineering, environmental engineering and water treatment engineering.

序

水孕育了人类。

伴随着人类社会的进步和经济发展，“生命之水”面临日益巨大的危机和挑战，如今，在世界范围内出现的水危机对人类的发展构成了严重威胁。保障水安全，促进水资源可持续利用，实现人类与水环境和谐共存是世界各国十分关注的重大课题。近二三十年来，我国政府通过实施相关科技计划，水行业管理部门，科研开发、工程设计和水务运营等单位共同努力，在分析国际水领域技术发展趋势和典型案例的基础上，开展深入研究和技术攻关，取得了一批具有理论价值和应用价值的成果，拓宽了解决水问题的思路，发展了水处理技术，在保障城镇供水，改善水环境等方面取得了显著成效，形成了适合中国国情的技术体系和管理模式，培养了一支由国际知名专家为学科带头人的专业人才队伍，使我国水领域的技术和管理水平大幅度提高，为今后的发展奠定了很好的基础。

2006年9月，建设部与国际水协将在北京举办第五届世界水大会。大会将为中外学者和工程技术人员搭建一个传播国际先进理念、交流研究成果和实践经验，探讨技术和管理创新的平台。为增进国际水业界对中国的了解，展示我国水领域的学术水平和发展成就，促进国际交流与合作，建设部科学技术司组织国内水领域的部分院士和知名专家编写了这套书籍。它包括学术理论、水处理工艺和工程应用以及水业管理等方面的内容，是对几十年来我国水领域所取得的成果和经验的总结，对我国城镇供水、节水和污水处理及资源化工作的开展，对促进我国水领域的跨越式发展和机制创新会有很好的参考作用。

在此书即将出版，第五届世界水大会即将召开之际，我们借用先哲老子的名言“上善若水，水利万物而不争”来表达对我国水领域科技工作者和致力于水资源永续利用、创造美好人居环境的广大同仁的敬意，感谢他们做出的无私奉献。

谨以此书献给第五届世界水大会。

建设部科学技术司

2006年5月9日

前　言

目前世界范围内已出现较严重的水危机，我国的水危机尤甚。水危机以水资源短缺和水环境污染为标志。水环境污染使污染物随饮食、洗浴、水雾等方式进入人体，对人体健康构成危害，所以人类造成的水环境污染，受害者首先是人类本身。水环境污染对人体健康以及对生态环境的危害造成的经济损失不亚于洪涝灾害，所以被称为水质灾害。

人类社会带来的环境污染，只有通过人类自身的反思，和走可持续发展道路来逐步消除。我国的领导人倡导的科学发展观，人与自然和谐相处，建立节约型社会，开发绿色工艺，发展循环经济等理念，将引导我国走向社会可持续发展道路。

水处理是消除水环境污染的重要方法，研究和开发新的符合科学发展观理念的水处理技术，是水处理的主要发展方向。

锰化合物用于净水始于19世纪末和20世纪初。天然锰矿砂早期曾被用于地下水除铁除锰。高锰酸钾也曾用于地下水除铁除锰，饮用水除臭味等工艺。1963年美国有125个以上水厂使用高锰酸钾进行饮用水处理。1970年高达400个。到1999年美国在服务人口超过1万人的地面水源水厂中，有36.8%使用高锰酸钾，占人口的21%。

我国天然锰砂大规模用于地下水除铁始于20世纪60年代，那时笔者领导的课题组研发成功天然锰砂地下水曝气接触氧化除铁技术，并迅速推广，取代了原来的曝气法除铁。20世纪80年代初又研发成功天然锰砂地下水曝气接触氧化除锰技术，也得到大量推广。上述除铁除锰技术现已成为我国有代表性的地下水除铁除锰的主流工艺。

笔者领导的课题组于20世纪80年代开始将高锰酸钾用于饮用水除污染，研发成功一系列除污染技术：

- 高锰酸钾及其复合剂强化混凝除浊
- 高锰酸钾及其复合剂强化混凝去除水中有机物及氯化副产物前质
- 高锰酸钾及其复合剂强化混凝去除水中微量有机污染物
- 高锰酸钾及其复合剂强化混凝去除水中致突变物质
- 高锰酸钾及其复合剂强化混凝除藻除臭味
- 高锰酸钾及其复合剂去除地面水中高稳定性铁和锰
- 高锰酸钾及其复合剂强化预氯化和预氯氨化的杀菌和消毒效果
- 高锰酸钾及其复合剂强化对地下水中砷的去除
- 高锰酸钾及其复合剂对印染废水色度的去除

上述净水技术中使用的高锰酸盐复合剂(以PPC表示，以下同)是以高锰酸钾为主剂，多种化合物为辅剂复配而成。复合剂中的辅剂能增强高锰酸钾的净水效能，从而获得比单独使用高锰酸钾更好的除污染效果。

课题组还开发了多种与其他净水技术的组合工艺，例如：

- 高锰酸钾及其复合剂与粉末活性炭联用除有机污染物
- 高锰酸钾及其复合剂与颗粒活性炭联用除有机污染物
- 高锰酸钾及其复合剂与生物活性炭联用除有机污染物

- 高锰酸钾及其复合剂与臭氧联用除有机污染物
- 二氧化锰去除印染废水的色度

此外，国内还研发成功用锰化合物作催化剂臭氧催化氧化高稳定性有机物，用锰化合物去除水中重金属的技术等。

上述研究成功的锰化合物净水技术中，课题组与北京精密单因子水工程技术有限公司合作，使许多技术实现了向生产力转化。迄今，已开发出包括高锰酸盐复合剂制作、药液制备、投加、自动控制、参数在线检测等成套设备和系列产品，从而便于推广应用。

锰化合物净水技术已用于我国各大水系的许多水厂中，不仅获得了成功，并且也积累了许多运行经验，使该技术在实践中又不断发展。

本书就是笔者领导的课题组与我的学生们50年来特别是近20年来在锰化合物净水技术方面的主要科研成果和生产应用经验。

全书共13章。第1章概论，主要介绍由于人类人口爆炸及社会发展造成水的不良社会循环及水危机对人类健康的危害；我国的水源水质标准、生活饮用水标准、污水排放标准等；锰化合物净水技术的发展。第2章主要阐述锰化合物及其物理化学性质；第3章至第12章主要阐述在除浊、除有机物、除氯化消毒副产物前质、除微量有机污染物、除致突变物质、除酚类化合物、除有机磷农药、除丙烯酰胺、除藻、除臭除味、强化氯化及氯胺化消毒、除铁除锰、除砷、染料废水除色等领域，锰化合物净水技术的基本原理、处理效果、影响因素、工艺条件、工艺流程、工艺参数等。第13章主要介绍若干锰化合物净水技术的生产应用实例，其中包括在松花江水系、海河水系、黄河水系、长江水系、珠江水系的应用。最后，参考文献中列出了笔者的课题组成员及学生们的博士学位论文、硕士学位论文、发表的学术论文，以及部分国内外有关科技文献的目录。

本书第1章、第4章、第5章、第6章、第12章由李圭白执笔；第3章、第10章、第11章、第13章中13—1、13—10、13—11、13—12等节由李星执笔；第2章、第7章、第8章、第9章由杨艳玲执笔；第13章中13—2、13—3、13—4、13—5、13—6、13—7、13—8、13—9等节由李虹执笔；全书由李圭白统稿。

本书可供从事给水排水工程、市政工程及环境工程技术人员、设计人员、技术管理人员、高校师生等参考。

对于多年来课题组成员和我的学生们在研发锰化合物净水技术的工作中做出的努力和贡献，以及水业同行们给予的支持和协助，表示衷心感谢。

由于作者水平有限，不足之处在所难免，望广大读者指正。

李圭白

2006年2月

Preface

Nowadays water crisis has already occurred in range of world, especially in China. The indications of water crisis are shortage of water resource and pollution of water environment. Pollution of water environment may cause pollutants to enter human body by food and drink, bathing, spray and so on to cause damage to health. The first victim is human itself from the pollution of water environment caused by human. Economic loss because of damage to human body health and ecological environment caused by pollution of water environment is not second to flood disaster. Therefore it is called water quality disaster.

The environment pollution produced by human society can be eliminated progressively only by introspection of human itself and sustained development. The government initiates idea of scientific development, getting on harmonious for human and nature, establishing economizing society, exploiting green technique and developing circulating economy, which can lead us to the way of sustained development.

Water treatment is an important method to eliminate the pollution of water environment. It is a major developing direction of water treatment to study and develop new water treatment techniques which are accorded with the idea of scientific development.

Manganese compound is applied to water purification from the end of 19th century and the beginning of 20th century. Natural manganese mineral sand was used for iron and manganese removal. Potassium permanganate was applied to iron and manganese removal, and taste and odor removal of drinking water too. Potassium permanganate was applied to drinking water treatment in more than 125 plants in USA in 1963, and up to 400 plants in 1970. Until 1999 up to 36.8% of plants had applications of potassium permanganate with surface water source which served over ten thousands people, which was about 21% of the population.

Natural manganese sand is applied to iron removal in groundwater in large-scale in China from the 1960s of 20th century. The research group lead by the author developed successfully the iron removal technique of aeration contact oxidation with natural manganese sand from groundwater. The technique was popularized rapidly to replace the former aeration method of iron removal. The manganese removal technique of aeration contact oxidation with natural manganese sand in groundwater was developed successfully in the 1980s of 20th century, and also popularized widely. The iron and manganese removal techniques above mentioned have been become the main techniques of iron and manganese removal in groundwater, typically representative in China.

The research group led by author applied potassium permanganate to pollution removal of drinking water in the 1980s of 20th century, and developed a series of pollution removal technique, including:

Enhanced coagulation for turbidity removal by potassium permanganate and potassium permanganate composite

Enhanced coagulation for organic matter and chlorination byproduct precursor removal by potassium permanganate and potassium permanganate composite

Enhanced coagulation for microorganic matter removal by potassium permanganate and potassium permanganate composite

Enhanced coagulation for mutagenic substance removal by potassium permanganate and potassium permanganate composite

Enhanced coagulation for algae and taste and odor removal by potassium permanganate and potassium permanganate composite

High stability iron and manganese removal by potassium permanganate and potassium permanganate composite

Sterilization and disinfection effect of pre-chlorination and pre-chloramination enhanced by potassium permanganate and potassium permanganate composite

Arsenic removal in groundwater enhanced by potassium permanganate and potassium permanganate composite

Color removal in dye wastewater by potassium permanganate and potassium permanganate composite

The potassium permanganate composite, applied in the water purification technique above mentioned, is made compositely by main agent of potassium permanganate, and subsidiary agents of various compounds. The subsidiary agents inside the composite can enhance the efficiency of water purification. Better pollution removal effects can be achieved compared with applied potassium permanganate individually.

Various combination processes with other water purification technique are developed by the research group, for example:

Removal of organic polluents by combined applications of potassium permanganate and potassium permanganate composite and powder active carbon

Removal of organic polluents by combined applications of potassium permanganate and potassium permanganate composite and granular active carbon

Removal of organic polluents by combined applications of potassium permanganate and potassium permanganate composite and biological active carbon

Removal of organic polluents by combined applications of potassium permanganate and potassium permanganate composite and ozone

Color removal in dye wastewater by manganese dioxide

In addition, the techniques to catalyze and oxidize high stability organic matters by ozone with manganese compound as catalyst, to remove heavy metal with manganese compound, and so on. are developed in China.

The research group cooperates with the Beijing High-Precision Uni-Tech. Water Engineering Ltd in the water purification technique of manganese compound and successfully transforms various techniques into production. Up to now, complete sets and series products convenient for application have been

developed , including equipments of manufacturing, solution preparation, dosing, automatic control and parameter online monitoring of potassium permanganate composite.

The water purification technique of manganese compound has been applied successfully to many water treatment plants in every major river system in China. Lots of operational experiences are accumulated to keep the technique developing in the practice.

This book is the major research achievements and productive application experiences of the research group of the author and the students in the aspect of water purification technique of manganese compound in fifty years, especially in recent twenty years.

The whole book adds up to thirteen chapters. Chapter one of introduction mainly introduces the harmfulness to human health of poor social circulation of water and water crisis caused by human population explosion and society development. Water quality standard of resource water in China, drinking water quality standard, wastewater discharge standard and so on, and development of the water purification technique of manganese compound are also introduced. Chapter two mainly explains the manganese compound and its physical and chemical properties. Chapter three to Chapter twelve mainly explain fundamental rules, treatment effects, influence factors, technical conditions, technological processes and technological parameters of the water purification technique of manganese compound, within the aspects of turbidity removal, organic matter removal, precursor removal of chlorination disinfection byproduct, microorganic pollutant removal, mutagenic substance removal, phenol compound removal, organic phosphorus pesticide removal, acrylamide removal, algae removal, odor and taste removal, enhancing disinfection of chlorination and chloramination, iron and manganese removal, arsenic removal and color removal in dye wastewater. Chapter thirteen gives some examples of productive applications of the water purification technique of manganese compound, including river systems of the Songhua River, the Haihe River, the Yellow River, the Yangtse River and the Zhujing River. Finally, the dissertation of doctor's degree and master's degree students and published academic papers of members of the research group, and parts catalogue of literature of science and technology related both at home and abroad are listed.

Chapter 1, Chapter 4, Chapter 5, Chapter 6 and Chapter 12 are written by Li Guibai. Chapter 3, Chapter 10, Chapter 11 and 13.1, 13.10, 13.11 and 13.12 of Chapter 13 are written by Li Xing. Chapter 2, Chapter 7, Chapter 8 and Chapter 9 are written by Yang Yanling. 13.2, 13.3, 13.4, 13.5, 13.6, 13.7 and 13.8 of Chapter 13 are written by Li Hong. The draft of whole book is united by Li Guibai

This book is for reference to technical personnel, design personnel, technical management, and teachers and students of colleges and universities who are engaged in water supply and sewerage engineering, municipal engineering and environmental engineering.

I express my heartfelt thanks to members of the research group and my students to make efforts and contribution during research and development of the water purification technique of manganese compound for many years, and thank to colleagues of water profession to give support and assistance.

The authors have made greatest effort to the book. Comments and opinions are welcome and very much appreciated.

Li Guibai
February 2006

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