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"Heavy Metals in Water: Presence, Removal and Safety"

Edited by Sanjay K. Sharma (Jaipur Engineering College and Research Centre (JECRC), India), Royal Society of Chemistry, Cambridge, UK, 2015, 357 pages, ISBN: 978-1-84973-885-9, £175.00, €218.75, US$290.00

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Introduction

"Heavy Metals in Water: Presence, Removal and Safety" is published by the Royal Society of Chemistry and consists of 16 independent chapters. The chapters can be broadly divided into two groups: those covering the techniques and processes used to deal with heavy metal pollution and those discussing a particular pollutant or pollution problem. The chapters are divided approximately equally between these two topics. The techniques presented include the use of modern approaches such as photocatalysis and nanotechnology (Chapters 2, 4 and 9) but by and large the volume emphasises the use of naturally occurring substances, waste products and bioremediation for removing heavy metals from water (Chapters 3, 10, 11, 14 and 15). This is understandable in light of the fact that most of the contributors come from developing countries where the emphasis for remediation is on low-cost readily accessible technologies. As a consequence the volume does not deal with heavy metal contamination resulting from high technology industries such as nuclear power, computer manufacturing and related electronics production where more technically advanced, but more expensive materials are employed in the industrially developed countries. The specific metal contamination problems presented are arsenic (Chapter 5), iron and manganese (Chapter 6), fluoride (Chapter 13) and chromium (Chapter 16), with the remaining chapters dealing with techniques and general surveys of heavy metal contamination. Chapters 7 and 8 stand out as chapters that deal with Chinese government policies on toxic metal contamination and should be very useful for foreign entrepreneurs wanting to establish new businesses in metals related industries.

The editor of this volume, Sanjay K. Sharma, is currently Professor and Head of the Department of Chemistry at JECRC University, India. He has edited many volumes closely related to this one and was recently appointed editor for the series 'Green Chemistry for Sustainability'.

Heavy Metals in Aquatic Media

It is beyond the scope of this review to give a detailed analysis of each chapter. A brief summary of each chapter will be provided with critical comments on the scientific contents, its relevance to the topic and where it complements or is redundant with the other chapters.

Chapter 1, 'Contamination of Heavy Metals in Aquatic Media: Transport, Toxicity and Technologies for Remediation' coauthored by the editor serves as a general introduction to the topic and deals with the

sources of heavy metal contamination, associated health risks and brief summaries of remediation methodologies, all of which are handled in more detail in later chapters. It concentrates on the removal of iron and manganese. This is strange as an entire chapter devoted to this subject is found later in the volume (Chapter 6). A useful summary of the health risks associated with heavy metals in water is provided in table form but several important contaminants are omitted. For example, uranium has become an important contaminant as a result of the development of nuclear energy and selenium remains a problem for the oil and coal industries. Both of these metals pose significant health risks. There are a few notable misstatements in the chapter. For example the authors define a heavy metal as having densities in the range of 3.5–7.9 g cm^{-3} while mercury has a density of 13.7 g cm^{-3} and many third row transition metals have densities of 19–22 g cm^{-3}. Cadmium is defined as the most toxic heavy metal although the allowable release level of mercury is lower than that of cadmium.

Photocatalysis and Nanotechnology

Chapter 2, 'Photocatalytic Processes for the Removal of Toxic Metal Ions' describes the photocatalytic reduction of metals using titanium dioxide (TiO_2) as the photocatalyst. The appeal of this method is that the electron holes created by the incident light can oxidise organic contaminants and the electrons released could be used to reduce metal ions in the same waste stream. In the absence of organic contaminants water needs to be oxidised. The authors do a good job of outlining the basic process and the relevant kinetic parameters, although one of the diagrams (taken from another source) is not adequately explained in the text. There is an appropriate discussion of the problems associated with scale-up of this technique followed by a case-by-case discussion of the reduction of specific metals on the bench scale. The tables in this chapter are basically redundant with those in Chapter 1 but it is interesting to note that the allowable release levels use the World Health Organization (WHO) values, which are different than those in Chapter 1.

Chapter 4, 'Functionalized Magnetic Nanoparticles for Heavy Metals Removal from Aqueous Solutions' addresses the timely and interesting topic of magnetic nanoparticles as adsorption media for heavy metals. The chapter begins with a repetition of the same topics summarised in Chapters 1–3, sources and health effects of heavy metals, but does include selenium in the list. The chapter then goes on to discuss the synthesis of magnetic nanoparticles, focusing heavily on iron, and then goes on to explain the different materials and methods for coating the iron nanoparticles. This is a useful summary of the currently available technologies. The kinetic and isotherm models for the nanoparticles as applied to adsorption of heavy metals are also discussed. This is fairly standard for all adsorptive materials and the authors would have been better off giving more details on the synthesis of the iron-glutamic acid nanocages and on regeneration of magnetic nanoparticles in general. A minor point is that one of the equations given is not correct, it should read Fe_2O_3, not Fe_2O_4. The correct equation (Equation (i)) is given below.

$$Fe_3O_4 + 2H^+ \rightarrow \gamma\text{-}Fe_2O_3 + Fe^{2+} + H_2O \quad \text{(i)}$$

Chapter 9, 'Use of Nanotechnology against Heavy Metals Present in Water', provides a brief overview of nano-adsorbents. This is a developing area of research that has not seen much use in the remediation industry. The author does a good job of putting this field in perspective including a discussion of the environmental dangers of nanomaterials, a topic that is often sidestepped by other workers in this area.

Removing Heavy Metals From Water

Chapter 3, 'Removal of Dissolved Metals by Bioremediation', is perhaps the least useful and most superficial chapter in the book. The usual list of metals is followed by a cursory summary of the same remediation techniques outlined in Chapters 1 and 2. The actual subject of the chapter is bioremediation, which is summarised in three or four pages and consists of a laundry list of bacterial strains that absorb heavy metals with no conceptual or mechanistic insights.

Chapter 10, 'Modified and New Adsorbents for Removal of Heavy Metals from Wastewater' presents a survey of industrial waste byproducts and modified agricultural and biomaterials for heavy metal adsorption. Like the other chapters in this volume, the author starts out with the usual list of toxic metals,

their sources, health risks and methods of removal. The use of industrial and agricultural wastes is a good addition to this volume as is the discussion of modified biopolymers. A very interesting magnetic core-shell particle modified with a bio-hydrogel is reported but this figure is barely readable and should have been corrected prior to publication. An otherwise useful chapter is compromised by the statement that batch equilibrium studies can be used for designing industrial processes. This is a significant misstatement as this type of study is only the beginning of the process, followed up by kinetic studies, adsorbent regeneration studies and evaluation of usable lifetime.

Chapter 11, 'Natural Clays/Clay Minerals and Modified Forms for Heavy Metals Removal' presents a thorough and comprehensive survey of the use of clays and modified clay. The first few pages are devoted to allowable limits and then methods of treatment for activation of the clays. A comprehensive list of the applications of the various mineral clays to specific heavy metals is provided. The complex structures and structural modifications of the wide range of clay minerals available has prompted workers in the field to develop new isotherm mathematical models for evaluating adsorption parameters. The chapter presents a list of the more recently developed isotherm models in addition to the more common Langmuir and Freundlich models and the clays to which they have been applied. Unfortunately, the chapter is already quite long and there was no critical evaluation of these models.

Chapter 14, 'Use of Industrial and Agricultural Waste in Removal of Heavy Metals Present in Water' describes a wide range of materials for this application (everything from banana peel to walnut dust), along with the methods used to modify them and their capacities for divalent metals and chromium. The authors discuss the methods in detail and some interesting images are included that describe the surface changes resulting from modification of the surface of the waste product.

Chapter 15, 'Biosorption of Metals – From the Basics to High Value Catalysts Production' targets biosorption by living organisms. The first six pages of the chapter, devoted to the sources and toxic effects of the metals arsenic, cadmium, chromium, copper, nickel, lead and zinc, are probably not necessary in light of the other chapters. The chapter goes on to briefly describe the mechanisms of biosorption and the parameters affecting efficiency. The chapter would have benefitted from more details on these topics rather than devoting half the chapter to information already covered elsewhere in the book.

Contamination Problems

Overall Chapter 5, 'Arsenic Contamination: An Overview' is an excellent chapter that summarises all aspects of the most pervasive water contaminant worldwide. The natural and anthropogenic sources of arsenic contamination are nicely described and the health risks and the different methods of arsenic removal are explained. In the conclusions section the reader is left with the impression that none of the currently available removal techniques are in widespread use. Although all the current methods have their disadvantages, processes using iron(III) chloride ($FeCl_3$) precipitation, adsorption onto Fe particles (the ferrihydrite process) and composite materials are commercially available and are being used effectively. The most recent advances using ion exchange technologies are not covered at all and this is a glaring omission in an otherwise excellent review. The properties of elemental arsenic are listed, however, this has nothing to do with the topic of this chapter and should have been deleted.

Chapter 6, 'Removal of Iron and Manganese from Water – Chemistry and Engineering Considerations' deals with removal of these metals from ground and surface waters. The chapter begins with an excellent description of the aqueous redox chemistry of iron and manganese. These metals rank low on the toxicity index and are mainly a problem for the construction industry. Indeed, this chapter is a contribution from a civil engineering firm. The chapter goes on to describe the effective oxidation-filtration systems used to remove these metals in the construction industry. There are many other commercially available adsorbents for removal of these metals but none of these are discussed in this chapter and so it is a narrowly conceived contribution to the volume.

Chapter 13, 'Fluorides in Different Types of Aquatic Systems and their Correlation with Metals and Metalloids' deals with fluoride contamination arising primarily from the use of fluorine containing industrial chemicals. Sulfur tetrafluoride (SF_4) used for termite extermination in the USA is missing from the otherwise

fairly complete list. The chapter was hard to follow. The salt contents of an apparently random list of water sources are given in a table but are not discussed in the text. The authors attempt to correlate the presence of fluoride with various cations and estimates of Al/F speciation as a function of pH are discussed in detail. The authors go on to explain the correlation between the presence of fluoride with arsenic in ground waters but the discussion and the data presented are confusing and unconvincing. A useful but, perhaps over interpreted chapter overall.

Chapter 12, 'Heavy Metals in Tannery Wastewater and Sludge: Environmental Concerns and Future Challenges' and Chapter 16, 'Chromium in Tannery Wastewater' both deal with the problem of chromium in the wastewater and sludge associated with tanning leather. The chapters are complementary rather than redundant. Chapter 12 focuses more on the distribution of tanning sites worldwide and the demographics of risk from the toxic effects of Cr(VI). The legal discharge limits for Cr in various countries are included with some countries providing only Cr(III) limits, and estimates of the most at-risk populations are given. Chapter 16 contains much more detail on the chemistry of the tanning process and methods of treatment (**Figure 1**) including recovery and reuse of the chromium salts. Taken together the two chapters provide an excellent overview of the challenges facing the tanning industry today.

Chinese Economy

Chapter 7, 'Heavy Metal Pollution in Water Resources in China – Occurrences and Public Health Implications' and Chapter 8, 'Heavy Metals Distribution in Surface Water Samples of Taihu Lake, China' are unique in this volume in that they both deal with the distribution of heavy metals in the environment. Chapter 7 deals with the sources of heavy metals across the Chinese economy while Chapter 8 focuses on the details of metal pollutants in one of China's largest lakes (**Figure 2**). Both chapters contain an enormous amount of information that will be useful for planning future environmental clean-up in China and for foreign investors in the Chinese economy looking to get involved in balancing Chinese economic growth with sustainability.

Summary

The volume covers the field of heavy metals in water very well for the most part. In general the chapters

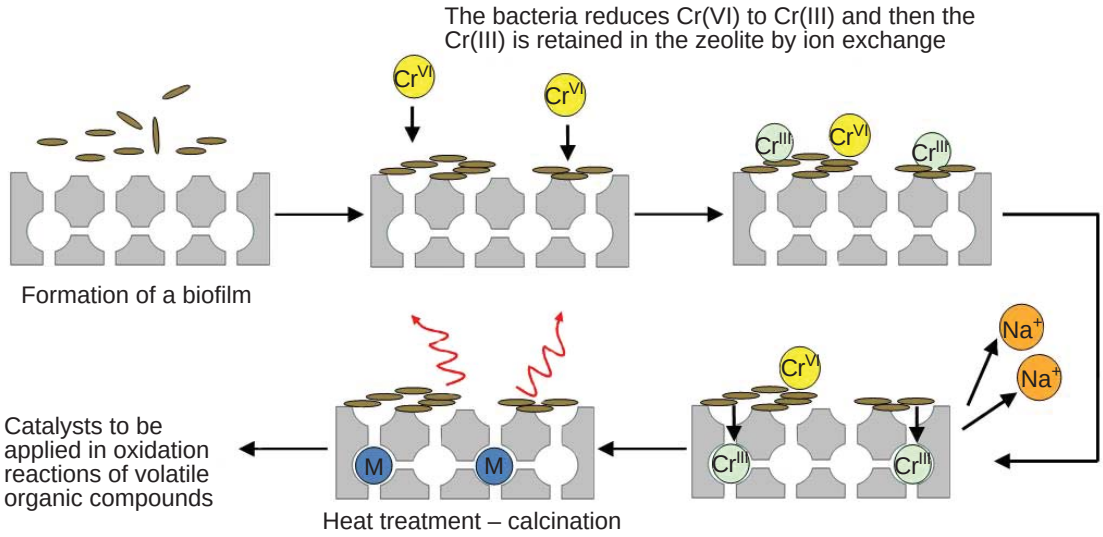


Fig. 1. New method of chromium removal from wastewater and catalytic reutilisation in volatile organic compounds oxidation (Reproduced by permission of Royal Society of Chemistry)

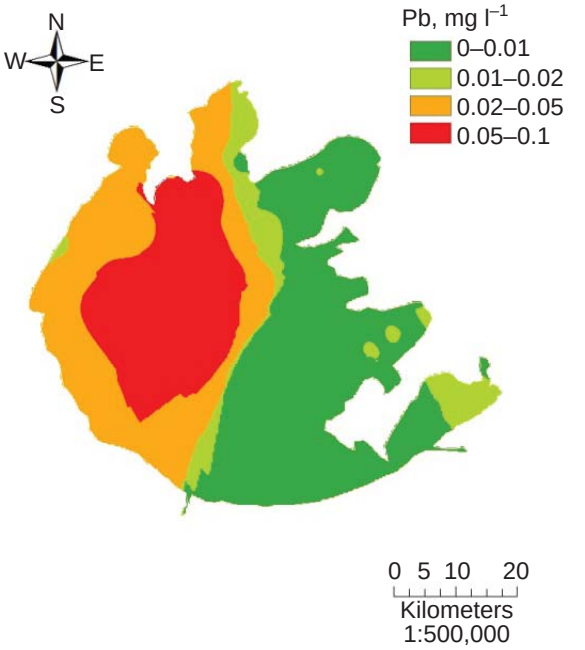
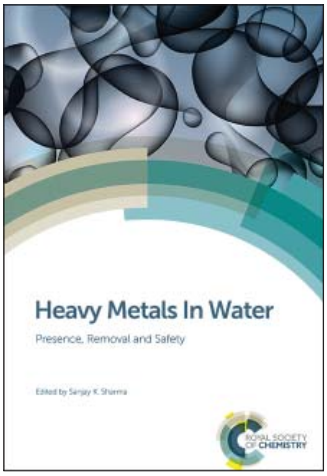


Fig. 2. Lead concentration distribution in Taihu Lake, China (Reproduced by permission of Royal Society of Chemistry)

are well written and organised for facile retrieval of data. The references are recent and cite the most important journals in the field. The one glaring omission is the cursory treatment of ion exchange. In the USA the use of ion exchange materials constitutes a US$5 billion dollar a year market and represents the go-to technology for heavy metal removal from water. The volume would also have benefitted from more careful editing. As mentioned several times in this review there is too much repetition of the sources, health effects and allowable release levels of the various heavy metal pollutants. This could have been covered in one introductory chapter (as it is) and omitted from the subsequent chapters. Overall however, this volume is a useful addition to the area of heavy metal pollution and remediation.



"Heavy Metals in Water: Presence, Removal and Safety"

The Reviewer

Edward Rosenberg received his doctorate at Cornell University, USA, and held post-doctoral fellowships at the University of London, UK, and the California Institute of Technology, USA. He is the author of 180 peer-reviewed publications, five book chapters, eight patents and one book in the areas of environmental and organometallic chemistry. He has received awards for his research and student mentoring from the University of Montana and has had visiting faculty fellowships in Italy, Israel and South Africa.