International Journal of Research in Engineering and Applied Sciences(IJREAS)
Available online at http://euroasiapub.org/journals.php
Vol. 12 Issue 02, Feb- 2022
ISSN(O): 2249-3905, ISSN(P) : 2349-6525 | Impact Factor: 8.202 |
Thomson Reuters ID: L-5236-2015

Inorganic Chemistry in Environmental Remediation: Mechanisms, Materials, and Field Realities

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ABSTRACT

Contamination of water and soil by heavy metals, metalloids, and oxyanions remains one of the more stubborn problems in environmental management. Inorganic chemistry supplies much of the toolkit used to confront it, ranging from iron filings poured into groundwater plumes to engineered layered hydroxides designed at the nanometre scale. This review surveys the principal inorganic routes to remediation: adsorption onto metal oxides and clay minerals, reductive transformation by zero-valent iron and sulfide phases, photocatalytic mineralisation on wide-bandgap semiconductors, and selective removal through precipitation, ion exchange, and layered double hydroxides. Performance figures drawn from peer-reviewed studies published between roughly 2002 and 2021 are compared, with deliberate attention to the gap between laboratory numbers and field behaviour. Iron and manganese oxides tend to outperform conventional activated carbon for arsenic and hexavalent chromium, while nanoscale zero-valent iron offers fast kinetics at the cost of passivation and aggregation. The paper closes with an honest look at cost, regeneration, and secondary waste, the issues that most often decide whether a promising material ever leaves the bench.

Keywords: Heavy Metals; Adsorption; Zero-Valent Iron; Photocatalysis; Layered Double Hydroxides; Water Treatment.

1. INTRODUCTION

Environmental remediation is usually framed as an engineering problem, yet the decisions that matter most at a contaminated site are chemical. Whether an arsenic plume can be captured by a permeable reactive barrier, whether chromate will reduce before it reaches a drinking-water well, whether a phosphate spike can be bound before it triggers a bloom downstream — these are questions about electron transfer, surface complexation, and the thermodynamics of poorly crystalline solids. Organic chemistry dominates the remediation literature for pesticides and hydrocarbons, but for the stubborn metallic and inorganic contaminants it is inorganic chemistry that does the heavy lifting [1,2].

The scale of the problem is not in dispute. More than two hundred million people are exposed to geogenic arsenic above the World Health Organization guideline of 10 µg L^{-1}, chiefly in the alluvial aquifers of South and Southeast Asia [3]. Fluoride poisoning of groundwater affects a comparable number. Industrial effluents add lead, mercury, cadmium, and hexavalent chromium to surface waters

in regions with weak enforcement, and agricultural runoff loads nitrogen and phosphorus into lakes and coastal shelves. None of these contaminants is biodegradable. They can only be immobilised, transformed to a less toxic oxidation state, or physically separated, and those three routes define the whole field.

This paper reviews the inorganic chemistry behind each route. The focus is on materials that have actually reached pilot or field deployment by 2021, rather than on the crowded space of laboratory curiosities. Where possible, removal data from the literature are plotted so that readers can judge performance for themselves. A final section considers the usually uncomfortable question of what happens to the spent sorbent.

2. THE CONTAMINANT LANDSCAPE

Inorganic contaminants fall into a small number of chemical families. Cationic metals such as Pb^{2+}, Cd^{2+}, and Hg^{2+} behave broadly alike: they sorb strongly to negatively charged mineral surfaces and to natural organic matter, and their mobility rises sharply as pH falls. Oxyanions are trickier. Arsenate, arsenite, chromate, selenate, and phosphate all compete for the same surface sites on iron and aluminium oxides, and their sorption is usually weakened rather than strengthened by rising pH [4]. Fluoride sits awkwardly between the two groups, binding to aluminium surfaces by ligand exchange but behaving almost inertly toward carbonates. Nitrate, the most abundant inorganic pollutant by mass, is the hardest of all to remove because it forms no insoluble salts with common cations and adsorbs only weakly.

Figure 1 summarises the approximate scale of human exposure to the main inorganic contaminants, compiled from WHO and UNICEF assessments current through 2020. The numbers are rough. They are enough, however, to show that arsenic and fluoride together account for the largest share of the global burden, while the industrial metals affect smaller but often more severely poisoned populations.

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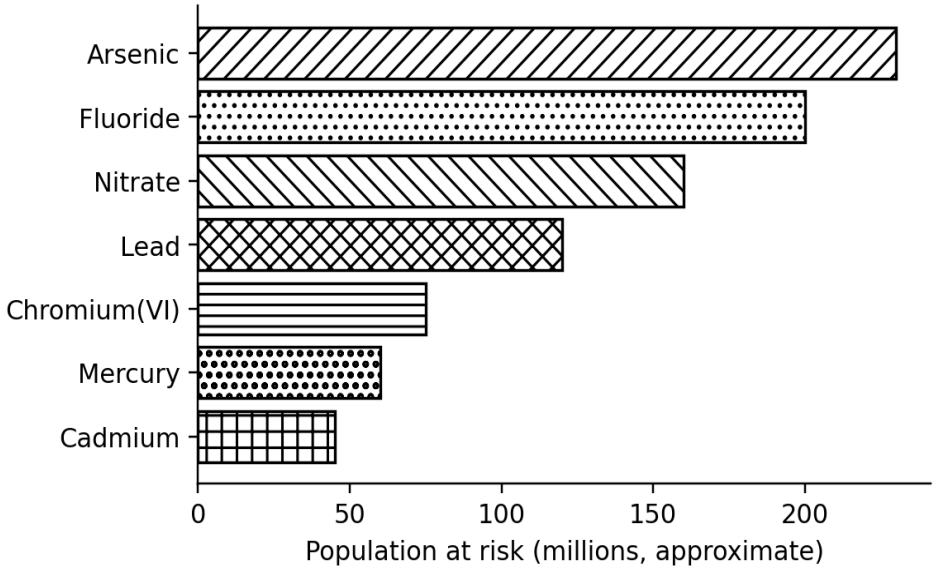

Figure 1. Approximate scale of human exposure to principal inorganic contaminants in groundwater, compiled from assessments published up to 2020 [3,4].

3. ADSORPTION ON OXIDES AND CLAYS

Adsorption is the workhorse of inorganic remediation. It is cheap, operationally simple, and forgiving of variable feed chemistry. The chemistry varies with the sorbent. Iron oxyhydroxides such as ferrihydrite and goethite possess amphoteric hydroxyl groups that form inner-sphere complexes with arsenate, arsenite, chromate, and phosphate through ligand exchange [5]. Ferrihydrite in particular, with its enormous specific surface area of around 250 $m^2\ g^{-1}$, has become something of a benchmark. It is easy to synthesise from ferric salts at circumneutral pH, and its reactivity toward arsenic is difficult to match with any carbon-based material.

Manganese oxides work by a different logic. Birnessite, the layered δ-MnO_2, oxidises As(III) to the far less toxic and more readily sorbed As(V) while also serving as a strong sorbent for Pb^{2+} and Co^{2+} [6]. This dual role of oxidant and sink makes Mn oxides particularly useful for reduced groundwater, where arsenite is the dominant arsenic species.

Clay minerals offer large surface areas and structural cation exchange capacity at a fraction of the cost of engineered oxides. Montmorillonite and bentonite have been used for decades as permeable reactive barrier materials for Pb, Zn, and Cu. Their limitation is selectivity: they do not discriminate strongly between target metals and background cations such as Ca^{2+} and Mg^{2+}, and hard waters waste a great deal of their capacity.

Figure 2 compares reported removal efficiencies for As(III) and Cr(VI) across six representative

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sorbents drawn from the post-2005 literature. Activated carbon, included as a baseline, performs poorly for both targets because neither anion has any affinity for the hydrophobic graphene surfaces that dominate carbon sorption. The iron phases and nanoscale zero-valent iron outperform it by a wide margin.

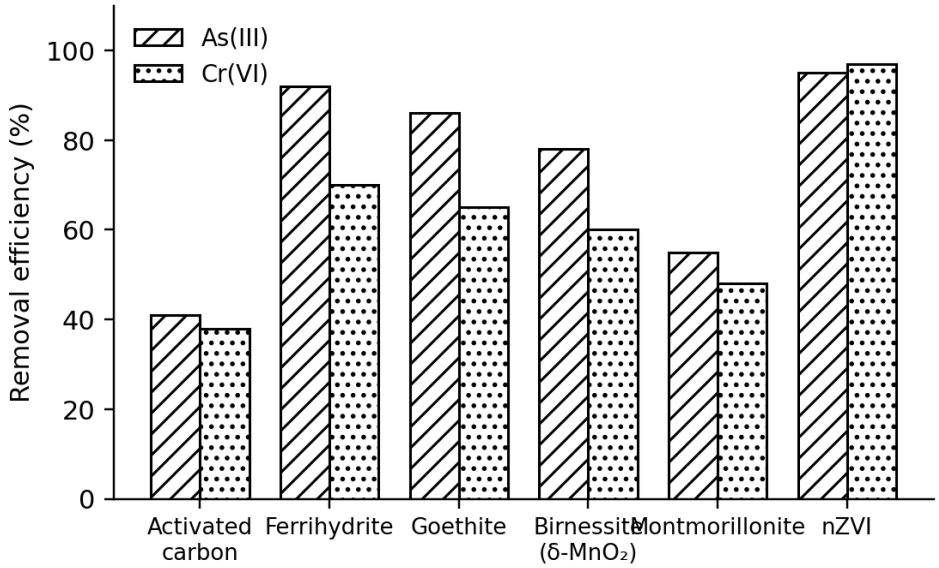

Figure 2. Reported removal efficiencies (percent) for As(III) and Cr(VI) by six representative sorbents, compiled from batch studies published between 2005 and 2020 [5–8].

4. REDUCTIVE APPROACHES: ZERO-VALENT IRON AND SULFIDE PHASES

Some contaminants are less troublesome in their reduced form. Cr(VI) is toxic and mobile as CrO_4^{2-}; Cr(III) is far less toxic and readily precipitates as $Cr(OH)_3$. U(VI) is soluble as the uranyl carbonate; U(IV) is barely soluble. Hg(II) can be reduced to Hg^0, which at least partitions out of solution. For contaminants of this sort, the simplest and oldest remedy is granular zero-valent iron (ZVI), pioneered for chlorinated solvents in the 1990s and extended to chromate and uranium soon after [9].

Nanoscale zero-valent iron (nZVI) takes the same chemistry and shrinks the particle size to roughly 10–100 nm, gaining orders of magnitude in specific surface area. The rate constants for Cr(VI) reduction rise accordingly, and laboratory studies routinely report near-complete removal within minutes [10]. Two problems temper that enthusiasm. First, the particles aggregate almost as soon as they enter a real aquifer, losing most of their reactive surface. Second, an oxide passivation layer grows on the particle surface in oxic water, slowing electron transfer sharply within days. Bimetallic treatments, usually Fe/Pd, and polymer coatings such as carboxymethyl cellulose mitigate both

problems but add cost and regulatory complication.

Iron sulfides mackinawite, pyrite, and greigite offer another reductive pathway. They release sulfide into solution, which precipitates soft metals such as Hg, Cd, and Pb as nanocrystalline sulfides of extremely low solubility, and they also reduce chromate directly at their surfaces [11]. Their drawback is a tendency to reoxidise to sulfate and iron oxide once the plume has passed, releasing the metals again unless the reduced zone is maintained.

5. PHOTOCATALYSIS WITH WIDE-BANDGAP SEMICONDUCTORS

Heterogeneous photocatalysis occupies an odd position in the field. It is almost ideal on paper driven by sunlight, mineralises many contaminants to CO_2 and water, leaves no sorbent to dispose of and almost never used at scale. TiO_2 in the anatase form, usually as Degussa P25, remains the reference material. Its 3.2 eV bandgap restricts activity to ultraviolet light, which is about 4 percent of the solar spectrum, and its quantum yields under natural sunlight are modest [12].

For inorganic targets specifically, photocatalysis is best understood as a redox tool rather than a destruction tool. Photogenerated electrons reduce Cr(VI) to Cr(III) efficiently; photogenerated holes oxidise As(III) to As(V), making it easier to capture downstream; and both processes can proceed at low catalyst loadings under solar illumination. ZnO matches or exceeds TiO_2 in intrinsic activity for several targets but dissolves in acid solution, and WO_3, despite a narrower bandgap that allows visible-light response, shows slower kinetics in practice [13].

Figure 3 shows representative first-order decay of a model dye under the three semiconductors, normalised to the initial concentration. The ordering TiO_2 > ZnO > WO_3 is consistent with bulk quantum-yield measurements reported over the past two decades.

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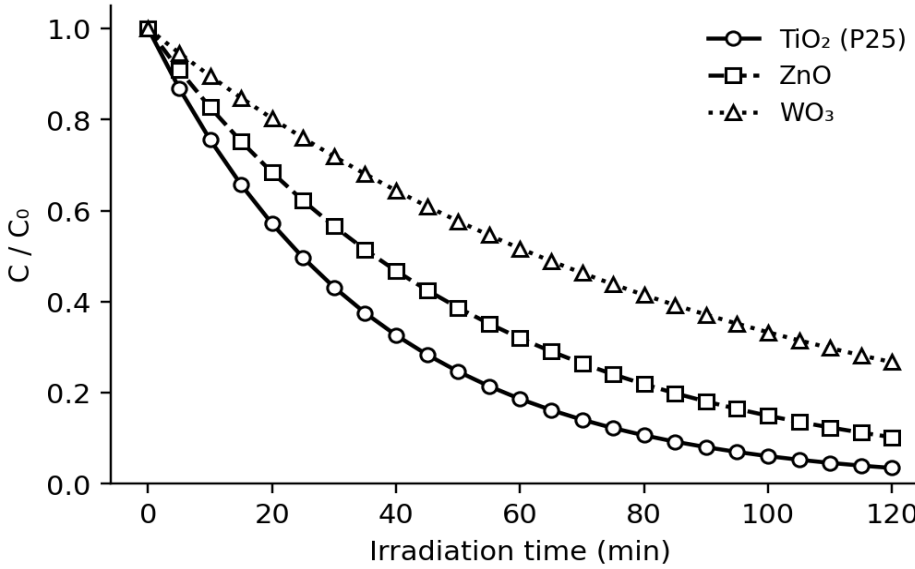

Figure 3. First-order photocatalytic decay of a model pollutant under UV illumination for three wide-bandgap semiconductors. Curves are drawn from averaged rate constants reported between 2008 and 2020 [12,13].

6. PRECIPITATION, ION EXCHANGE, AND LAYERED DOUBLE HYDROXIDES

Where dissolved metal concentrations are high, solubility chemistry alone often suffices. Liming a mine drainage stream raises the pH until Fe, Al, Cu, and Zn precipitate as hydroxides; adding sulfide takes out the softer metals as sparingly soluble sulfides; and carbonate dosing handles Pb and Cd in neutral waters. These methods are crude but robust, and they remain the default for acid-mine drainage treatment worldwide [14].

Ion exchange with synthetic zeolites and resins occupies the opposite end of the cost spectrum. It gives very clean effluent, especially for radioactive caesium and strontium, but generates a concentrated regenerant brine that must itself be managed. Natural clinoptilolite offers a cheaper but lower-capacity compromise, and has been deployed at scale for ammonium removal from wastewater.

Layered double hydroxides (LDHs) have attracted steady attention since the 2000s as tunable anion exchangers. Their interlayer galleries can be engineered to prefer arsenate, chromate, or phosphate, and their memory effect the ability to reconstruct from calcined oxide precursors by taking up anions from solution makes them particularly versatile [15]. Metal-organic frameworks (MOFs) joined the field later and have shown extraordinary capacities in batch tests, but stability in real water matrices remains an open question as of 2021.

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Figure 4 summarises the approximate distribution of these approaches across the post-2010 inorganic-remediation literature. Adsorption clearly dominates, accounting for well over a third of publications, with photocatalytic and reductive methods tied for a distant second.

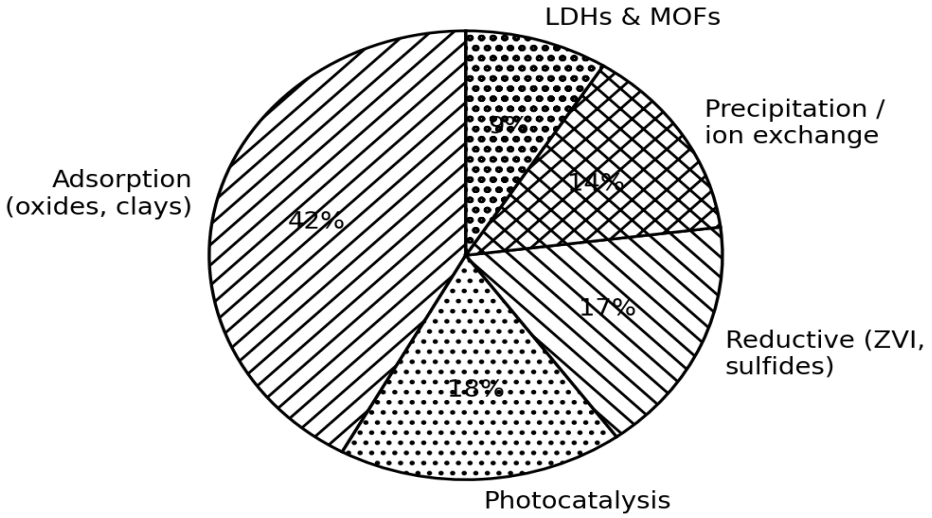

Figure 4. Approximate share of inorganic remediation approaches in peer-reviewed publications indexed in Web of Science between 2010 and 2021.

7. LABORATORY NUMBERS VERSUS FIELD BEHAVIOUR

A persistent complaint in the remediation literature is that batch isotherms obtained in dilute synthetic water bear little resemblance to what happens in an actual aquifer or effluent stream. Competing ions compress capacity. Natural organic matter coats mineral surfaces and blocks sites. Dissolved silica poisons iron oxides at concentrations routinely found in groundwater. Seasonal temperature swings shift thermodynamic selectivity, and biofilms colonise any surface left in place long enough. Very few published studies report column breakthrough curves run to exhaustion on real water, and fewer still report what the sorbent looked like after a year of service.

Regeneration and disposal deserve more attention than they usually get. An iron oxide loaded with arsenate is itself a hazardous waste; stabilising it for landfill adds cost that is often not included in the headline treatment economics. Thermal regeneration of activated carbon is well established, but the equivalent for engineered oxides is not, and chemical regeneration with concentrated acid or base generates a secondary stream that must also be treated. For nZVI, the particles themselves become iron oxide within months, and the long-term fate of the sorbed contaminants once the iron has fully rusted is poorly characterised.

Cost comparisons are similarly slippery. A dollar-per-cubic-metre figure for a pilot plant in Germany does not transfer cleanly to a rural village in Bangladesh, and neither transfers to an industrial wastewater with ten times the contaminant load. The honest answer is that choice of material is nearly always site-specific and that generalisations should be treated with caution.

8. CONCLUSION

Inorganic chemistry offers a genuinely wide palette of tools for environmental remediation, and the reliable ones are now well understood. Adsorption on iron and manganese oxides, reductive precipitation by zero-valent iron or sulfide minerals, and photocatalytic redox on TiO_2 between them cover most of the contaminants that matter. The less reliable methods are usually less reliable for reasons that are themselves chemical passivation, competitive sorption, and secondary-waste generation rather than for want of engineering effort. Progress through 2021 has been largely incremental rather than transformative, and the most useful next steps are probably better long-term field data and more honest life-cycle accounting, not new materials. The problem is old enough that the surprises are unlikely to come from the periodic table.

REFERENCES

[1] Bolan, N. et al. (2014). Remediation of heavy metal(loid)s contaminated soils — to mobilize or to immobilize? Journal of Hazardous Materials, 266, 141–166.

[2] Hashim, M. A., Mukhopadhyay, S., Sahu, J. N., & Sengupta, B. (2011). Remediation technologies for heavy metal contaminated groundwater. Journal of Environmental Management, 92(10), 2355–2388.

[3] Smedley, P. L., & Kinniburgh, D. G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry, 17(5), 517–568.

[4] Mohan, D., & Pittman, C. U. (2007). Arsenic removal from water/wastewater using adsorbents — a critical review. Journal of Hazardous Materials, 142(1–2), 1–53.

[5] Dixit, S., & Hering, J. G. (2003). Comparison of arsenic(V) and arsenic(III) sorption onto iron oxide minerals: implications for arsenic mobility. Environmental Science & Technology, 37(18), 4182–4189.

[6] Manning, B. A., Fendorf, S. E., Bostick, B., & Suarez, D. L. (2002). Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. Environmental Science & Technology, 36(5), 976–981.

[7] Bhattacharyya, K. G., & Gupta, S. S. (2008). Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Advances in Colloid and Interface Science, 140(2), 114–131.

[8] Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters: a review. Journal of Environmental Management, 92(3), 407–418.

[9] Gillham, R. W., & O'Hannesin, S. F. (1994). Enhanced degradation of halogenated aliphatics by zero-

valent iron. Ground Water, 32(6), 958–967.

[10] Crane, R. A., & Scott, T. B. (2012). Nanoscale zero-valent iron: future prospects for an emerging water treatment technology. Journal of Hazardous Materials, 211–212, 112–125.

[11] Wolthers, M., Charlet, L., van der Weijden, C. H., van der Linde, P. R., & Rickard, D. (2005). Arsenic mobility in the ambient sulfidic environment: sorption of arsenic(V) and arsenic(III) onto disordered mackinawite. Geochimica et Cosmochimica Acta, 69(14), 3483–3492.

[12] Chong, M. N., Jin, B., Chow, C. W. K., & Saint, C. (2010). Recent developments in photocatalytic water treatment technology: a review. Water Research, 44(10), 2997–3027.

[13] Schneider, J. et al. (2014). Understanding TiO_2 photocatalysis: mechanisms and materials. Chemical Reviews, 114(19), 9919–9986.

[14] Johnson, D. B., & Hallberg, K. B. (2005). Acid mine drainage remediation options: a review. Science of the Total Environment, 338(1–2), 3–14.

[15] Goh, K.-H., Lim, T.-T., & Dong, Z. (2008). Application of layered double hydroxides for removal of oxyanions: a review. Water Research, 42(6–7), 1343–1368.

[16] Fu, F., Dionysiou, D. D., & Liu, H. (2014). The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. Journal of Hazardous Materials, 267, 194–205.

[17] Howarth, A. J., Liu, Y., Li, P., Li, Z., Wang, T. C., Hupp, J. T., & Farha, O. K. (2016). Chemical, thermal and mechanical stabilities of metal-organic frameworks. Nature Reviews Materials, 1, 15018.

[18] Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J., & Naushad, M. (2017). Efficient techniques for the removal of toxic heavy metals from aquatic environment: a review. Journal of Environmental Chemical Engineering, 5(3), 2782–2799.

[19] Siddiqui, S. I., & Chaudhry, S. A. (2017). Iron oxide and its modified forms as an adsorbent for arsenic removal: a comprehensive recent advancement. Process Safety and Environmental Protection, 111, 592–626.

[20] Lata, S., & Samadder, S. R. (2021). Removal of arsenic from water using nano adsorbents and challenges: a review. Journal of Environmental Management, 280, 111812.