



Review

Metal–organic frameworks for heavy metal removal from water

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ABSTRACT

The pollution of surface and groundwater with heavy metals is a serious global concern, both environmentally, as well as with respect to human health. Overabundance of these elements poses severe health risks for humans, and also for other life forms through bioaccumulation along food chains. Therefore, steps should be taken to reduce the amount of such elements in water to acceptable levels. This review looks at metal–organic frameworks (MOFs) which have been recently developed and studied for potential applications in heavy metal removal from water. We provide an overview of the current capabilities and important properties of MOFs used for this purpose.

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1. Introduction

1.1. Sources of heavy metals in water

Geological sources: Heavy metals (that is metals with density over 5 g cm^{−3} such as arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc) [1] polluting our water is a rapidly growing global concern. These elements can be found within the

environment – be it in water reservoirs, the atmosphere or soil – in excess, due to various anthropogenic actions. It is also important to note the natural sources of heavy metal pollution. These include all types of rocks (igneous, sedimentary and metamorphic), which, through their interactions with the surrounding environment (i.e., weathering, erosion, soil formation and the rock cycle in general), transport and redistribute heavy metals [2]. Heavy metals most commonly found in rock-forming minerals include those which most easily leach due to mineral weathering such as nickel, cobalt, manganese, zinc, copper, and vanadium, in addition to metals that have intermediate stability such as scandium, yttrium and other

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Table 1

Anthropogenic sources for common heavy metal pollutants [3] along with their provisional guideline limits according to WHO [9] and their toxicity [7].

Heavy metal	Anthropogenic sources	Provisional maximum tolerable daily intake (PMTDI) (g L ⁻¹)	Toxicity
As	Animal feed additive, algacides, herbicides, insecticides, fungicides, pesticides, rodenticides, sheep dip, tanning and textile, pigments, veterinary medicine, ceramics, special glasses, metallurgy, electronic components, non-ferrous smelters, electrical generation (coal and geothermal), light filters, fireworks	0.01	Phytotoxic (toxic to plants), arsenicosis (i.e., blackfoot disease), keratosis, possible vascular complications, carcinogenic
Cd	Neutron absorbers (within nuclear reactors), nickel–cadmium batteries, anti-corrosive metal coatings, alloys, plastic stabilizers, coal combustion, pigments	0.003	Phytotoxic, bio-accumulative, <i>itai-itai</i> disease, carcinogenic
Cr	Data storage, plating, ferro-alloys manufacturing, textiles and leather tanning, wood treatment, passivation of corrosion of cooling circuits, pigments	0.05	Cr ³⁺ not detrimental to mammals, Cr ⁶⁺ very toxic, carcinogenic
Cu	Water pipes, chemicals and pharmaceutical equipment, kitchenware, roofing, alloys, pigments	2	Relatively not detrimental, narrow tolerance for plants
Pb	Alloys, ceramics, plastics, glassware, lead-acid batteries, cable sheathings, sheets, solder, pipes and tubing, sheets, ordinance, antiknock agents, tetramethyllead, pigments	0.01	Pb poisoning (a world-wide issue) through gasoline, plumbing and paints
Hg	Amalgamation (the process of metal extraction), electrical and measuring apparatus, catalysts, dental fillings, Hg vapor lamps, solders, X-ray tubes, pharmaceuticals, fungicides, scientific instruments, electrodes, rectifiers, oscillators, chloralkali cell's mobile cathode.	0.006	Biomagnification in aquatic environments, Minamata disease
Ni	An alloy in the steel industry, computer components, catalysts, ceramic and glass molds, electroplating, nickel–cadmium batteries, dental and surgical prostheses, arc-welding, rods, pigments	0.07	Contact dermatitis, asthma, chronic respiratory infections carcinogenic
Zn	Zn alloys, PVC stabilizers, gold precipitation from cyanide solution, in chemicals and medicines, anti-corrosion coating, cans, barriers, rubber industry, welding and soldering fluxes, paints	0.3–1.0 mg kg ⁻¹ of body weight per day	Relatively not detrimental to mammals (may affect cholesterol metabolism in humans)

rare earth elements, all the way to uranium or hafnium, which can be found in zircon and are resistant to weathering. These elements are then concentrated when hot hydrothermal fluids permeate the rocks, inducing chemical reactions that cause precipitation of minerals and creation of ores [3]. Such deposits are often found within sedimentary rocks, which, due to their porous structure and high permeability, are well suited for storage of solids.

Soils are another medium responsible for heavy metal storage. Heavy metals in soil are found in relocated rock debris, insoluble minerals and organic matter (i.e., the solid phases), as well as in the water and air trapped within the soil (i.e., the fluid phases). These solid and fluid phases interact with each other and various ions passing through the system [4]. The concentration and identity of heavy metals in soil is directly related to the type of rock that the soil originated from. Most heavy metals can be found within the third layer – or horizon – of soil called the B-horizon. This layer contains elements which were once dissolved within the upper layer (the A-horizon) and then underwent eluviation (movement of the dissolved material downwards or sideways) into the lower layer, where they were deposited [5]. The B-horizon attracts heavy metals because it has a high concentration of iron oxyhydroxides and clay which are able to absorb the cationic elements [3].

Surface waters (from springs and streams to lakes and rivers) can carry heavy metals over a large distance and their chemical composition varies depending on the geological features over/around which they flow. Other factors contributing to the identity and concentration of heavy metals in surface water include biological, chemical and physical influences such as living organisms, adsorption from sediments or organic and inorganic matter, dilution and evaporation, redox potential, pH and finally temperature [3]. For instance, increasing acidity (as the water flows over pyrite, which causes minerals to oxidize) influences the solubility of heavy metals and so increases their mobility within the water

[6]. Heavy metals carried by water can be adsorbed by oxyhydroxides or onto aquatic vegetation such as algae, introducing them into the food web. This leads to bioaccumulation of heavy metals within living organisms, causing toxicity and damage [2]. It is important to note that even though many heavy metals are essential to biological systems (e.g., copper, zinc), their intake over the provisional maximum tolerable daily intake can cause toxicity (see Table 1).

Anthropogenic sources: Groundwater reservoirs which are the main source of drinking water and of great importance to humankind, are contaminated mainly by organic and inorganic pollutants of anthropogenic origin. This pollution may lead to the poisoning of both aquatic and land animals, and ultimately poses a risk to human health. Monitoring and controlling potential sources of pollution is therefore vital. This includes sources such as runoff from agricultural and industrial sites, urban areas, mining and hazardous disposal sites, landfills, dredged sediments, sewage systems, railways and motorways [3]. Groundwater contamination can also result in redistribution of heavy metals throughout the environment, be it *via* uptake by plants or sorption/complexation (to particulate organic matter). A general overview showing the transportation of heavy metals within groundwater systems is illustrated in Fig. 1. Many human activities that contribute to heavy metal pollution can be tied, in broad terms, to the processes of production, consumption and disposal of products, across areas ranging from industry to agriculture and transportation. A summary of selected heavy metals and some of their anthropogenic sources are summarized in Table 1. The elements released by such activities can come both from diffuse, as well as point sources and are introduced into the environment as either gasses or particulates in aqueous or solid forms. Agricultural sources of pollution include substances used for crop management such as fertilizers. Phosphatic fertilizers for example contain cadmium and zinc in proportions dependent upon the type of rock they are derived

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