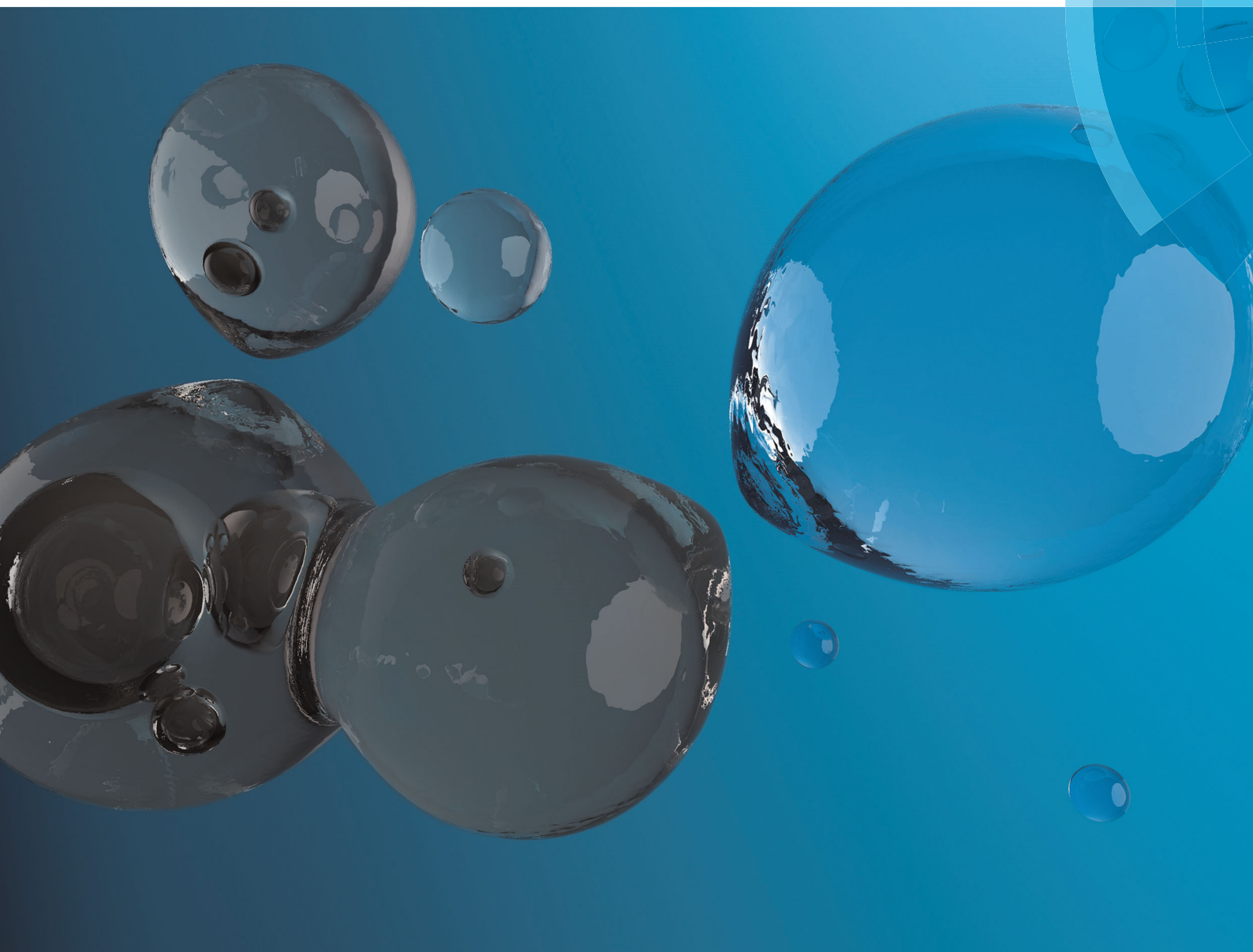


Chem Soc Rev

Chemical Society Reviews

rsc.li/chem-soc-rev



ISSN 0306-0012



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REVIEW ARTICLE

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Sustainable technologies for water purification from heavy
metals: review and analysis



Cite this: *Chem. Soc. Rev.*, 2019, 48, 463

Sustainable technologies for water purification from heavy metals: review and analysis

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Water pollution is a global problem threatening the entire biosphere and affecting the life of many millions of people around the world. Not only is water pollution one of the foremost global risk factors for illness, diseases and death, but it also contributes to the continuous reduction of the available drinkable water worldwide. Delivering valuable solutions, which are easy to implement and affordable, often remains a challenge. Here we review the current state-of-the-art of available technologies for water purification and discuss their field of application for heavy metal ion removal, as heavy metal ions are the most harmful and widespread contaminants. We consider each technology in the context of sustainability, a largely neglected key factor, which may actually play a pivotal role in the implementation of each technology in real applications, and we introduce a compact index, the Ranking Efficiency Product (REP), to evaluate the efficiency and ease of implementation of the various technologies in this broader perspective. Emerging technologies, for which a detailed quantitative analysis and assessment is not yet possible according to this methodology, either due to scarcity or inhomogeneity of data, are discussed in the final part of the manuscript.

Received 23rd August 2018

DOI: 10.1039/c8cs00493e

rsc.li/chem-soc-rev

1. Introduction

According to recent estimates, more than 1.2 billion people worldwide do not have access to the most vital component of life: clean drinking water.¹ Industrial development, energy plants, mining industries and environmental catastrophes have all contributed to an alarming increase of toxic pollutants in the environment, in various forms and concentrations, which is coupled with the simultaneous increase in the demand for

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accessible water caused by population growth.^{2,3} Everyday, approximately 2 million tons of industrial, sewage and agriculture waste are discharged into water worldwide,⁴ causing serious health problems and the death of approximately 14 000 people everyday. Water pollutants majorly consist of organic, inorganic, biological and macroscopic contaminants. Particularly, most heavy metal ions introduced into the environment by human activity biologically accumulate upon cumulative exposure, and cannot be easily decomposed, threatening human health *via* the entire food chain. Among naturally occurring contaminants, on the other hand, contamination of groundwater by arsenic is widespread worldwide. It is recognized that at least 140 million people in 50 countries regularly drink water containing arsenic at levels above the WHO guideline value of 10 $\mu\text{g L}^{-1}$. Fig. 1a summarizes the current global water scarcity resulting from inadequate natural water resources to supply local demand (physical water scarcity) and due to poor management of the available water resources (economic water scarcity). Superimposed on this chart is the distribution of the most dangerous sources of environmental toxins, consisting primarily of heavy metals (*e.g.* lead, mercury, chromium, *etc.*), obsolete pesticides and radionuclides.^{5,6} Fig. 1b details the composition of the major contaminants present at industrial and commercial sites in Europe^{7,8} whereas Fig. 1c describes the normalized volume of treated water by the field of use.

Consolidated and emerging water purification technologies are pressingly acclaimed to provide compelling solutions to the water pollution problem and indeed, an increasing number of available approaches for wastewater treatment and water purification have surfaced in recent years. Fig. 2a shows the current available technologies for global water purification in terms of their economic turnover contribution to the water purification market,¹⁰ while Fig. 2b presents some of the reported removal efficiencies for a selection of heavy

metals for four well-established technologies. A more comprehensive analysis of the efficiencies is provided later in Table 1 (*vide infra*).

Some technologies for water purification are claimed to have an efficiency of 99% or more, but this is true only under idealized conditions of pH, contaminant concentration and other operating parameters, and in reality, under industrially relevant conditions, their efficiency may decrease substantially, even down to $\approx 90\%$, or less, that is, 1 molecule of pollutant out of every 10 may still escape the purification process.²⁵ Furthermore, and perhaps more importantly, many of these techniques, such as ion exchange resins, are designed to target one contaminant at a time, which makes their use impractical for environmentally polluted waters, where several contaminants occur simultaneously nearly on a regular basis: in fact, it is well appreciated from the literature that simultaneous removal of heavy metal ions by exchange resins may decrease the efficiency of the process drastically, *e.g.* down to 80% or less.²⁶ Last but not least, most of the available technologies are unfeasibly expensive, and those, which are the most affordable, can often cause secondary pollution. Thus, purification of wastewater or polluted water bodies remains challenging, costly and highly inefficient, to such an extent that in several developing countries, this has led to irreversible environmental damage, with the availability of free drinkable water becoming a real challenge. What is certain is that the rapid development of technologies for water purification has not been able to cope, so far, with the even faster increase in demand for safe freshwater: in only two years, the number of people with no access to drinkable water has increased from 780 million in 2012 (WHO estimate) to 1200 million in 2014.¹ There is a general consensus among scientists that access to safe freshwater is the most urgent and serious problem humanity is asked to face over the next few decades.

A particular tricky problem in water purification is that associated with removal of heavy metal ions: on the one hand these contaminants are widely spread, from the naturally arsenic-contaminated groundwater bodies, to industrial wastewater, mining and energy sectors, increasing the pressure on the entire water supply chain, from environment, to agriculture, to drinking water (see Fig. 1); on the other hand, their ionic forms or ion specificity make often unsuitable or inefficient even the most established methods: a classical example is removal of arsenic(III) by nanofiltration or reverse osmosis:¹² since these technologies are highly inefficient with arsenic(III), an intermediate oxidation step to arsenic(V) is necessary before membrane removal. In this analysis, we focus therefore on heavy metal ions as a primary contaminant against which we review and benchmark the main technologies available, occasionally expanding the discussion to how the same technologies may also enable the purification of water from other pollutants. A particular perspective which is brought forward in this article is the aspect of sustainability of water treatment, which we view as a particularly stringent one, especially considering that the majority of geographical locations where water scarcity is most critical lack infrastructure, energy



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Raffaele Mezzenga finished his PhD at EPFL Lausanne (2001) and a postdoc at UCSB Santa Barbara, before joining in 2003 the Nestlé Research Center in Lausanne. In 2005 he was hired as Associate Professor of Physics at the University of Fribourg, and he then joined ETH Zurich in 2009 as Full Professor. His research focuses on the fundamental understanding of self-assembly processes in soft condensed matter. His work has

been internationally recognized by several prestigious distinctions such as the Biomacromolecules/Macromolecules Young Investigator Award (2013, American Chemical Society), the Dillon Medal (2011, American Physical Society), and the Young Scientist Research Award (2011, American Oil Chemist Society).

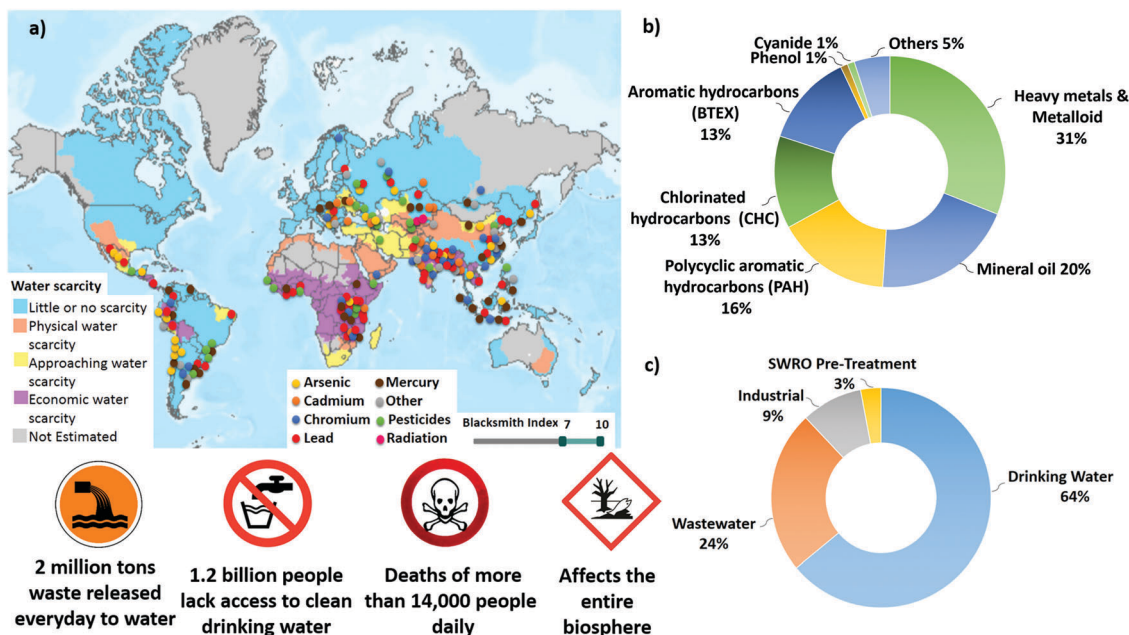


Fig. 1 Summary of worldwide global water pollution spread in numbers. (a) Superimposed geographical distribution of water scarcity and of pollution by the type of major pollutant, including heavy metals, pesticides and radionuclide.^{5,6} (b) Normalized composition of water pollutants in treated and recycled water streams.^{7,8} (c) Normalized volume of treated water by field of use.⁹

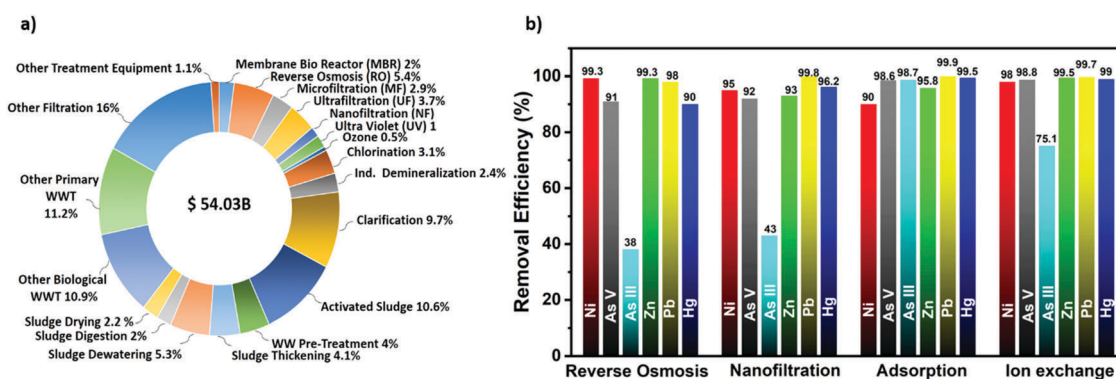


Fig. 2 Current technologies available for water purification: (a) in terms of global economic turnover by sector;¹⁰ (b) by efficiency (up to the first decimal) for a selected number of technologies and for a small representative selection of heavy metal ions.^{11–24}

and economic turn-over, severely restricting the implementation of many technologies. Current water treatment services need to deliver clean drinking water in a sustainable manner, that is *via* systems that are affordable, adaptable and resilient. Increasingly stringent drinking water quality and environmental discharge standards protect us from pollutants but require increasingly complex and energy-consuming treatments. Thus, sustainable water treatments also need to consider energy saving as one of the most stringent requirements; furthermore, it is necessary to find out today sustainable water treatments that have no adverse or minimal impact on the environment for the next generations to come. We therefore introduce in Section 3 of the article, a compact index, named the Ranking Efficiency Product (REP), by which the different techniques can be assessed by accounting for efficiency, operating flux, flexibility and ease of implementation,

but also capital and operating costs, energy consumption and other factors related to the sustainability aspect, which may play a pivotal role in field implementation for all resource-lacking countries. We conclude discussing those emerging technologies for which a quantitative assessment is not yet possible due to lack or inhomogeneity of data, but which show promise in alleviating this urgent global challenge.

2. Primary, secondary and tertiary water treatment processes

Water treatment is typically a multi-stage process, involving numerous steps and various technologies from the polluted water source to the final treated water. Generally, municipal and

Table 1 Summary of tertiary water treatment technologies and their performance in the removal of heavy metal ions

Technology/material	Heavy metal	Conditions	Ref.	Percentage and/or removal capacity (mg g ⁻¹)
Adsorption	Advantages/disadvantages: high removal efficiency, reversible nature allowing regeneration of adsorbents and flexibility in design and operation/disposal of both the spent media and the wastewater produced during regeneration; cleaning of the adsorption column, loss of adsorbent quality with cycles			
AC	Ni ²⁺ Cd ²⁺ Zn ²⁺ Pb ²⁺ Cr ³⁺	C ₀ = 30 ppm pH = 2	54	90.0% (27.0) 86.0% (25.8) 83.6% (25.1) 83.0% (24.9) 50.6% (15.2)
CNT	Pb ²⁺ Cu ²⁺ Cd ²⁺	C ₀ = 50 ppm C ₀ = 25 ppm C ₀ = 15 ppm pH = 5	67	80.4% (82.0) 59.2% (29.0) 31.5% (9.2)
CNT	Cu ²⁺ Pb ²⁺ Zn ²⁺ Co ²⁺ Mn ²⁺	C ₀ = 10 ppm pH = 9	17	99.8% (2.0) 96.3% (1.9) 95.8% (1.9) 93.4% (1.9) 72.6% (1.4)
Iminodiacetic acid-CNT	As ³⁺ Cd ²⁺ Co ²⁺ Cr ⁶⁺ V ⁵⁺ Pb ²⁺ Cu ²⁺	C ₀ = 3.6 ppm pH = 8	66	70.0% (6.27) 57.9% (5.21) 66.8% (6.01) 71.7% (6.45) 61.4% (5.53) 72.3% (6.51) 68.9% (6.20)
GO	Cu ²⁺	C ₀ = 1 ppm pH = 5	169	97.0% (9.7)
GO	Pb ²⁺	C ₀ = 25 ppm, pH = 7	170	76.3% (19.07)
GO	Zn ²⁺	C ₀ = 40 ppm, pH = 7	95	68.4% (196)
GO	Cd ²⁺ Co ²⁺	C ₀ = 20 ppm C ₀ = 30 ppm pH = 4	171	53.2% (106.3) 22.7% (68.2)
EDTA-magnetic GO	Pb ²⁺ Hg ²⁺ Cu ²⁺	C ₀ = 100 ppm pH = 4	98	96.6% (241.5) 96.1% (240.3) 94.3% (235.8)
Natural zeolite (clinoptilolite)	Pb ²⁺ Ni ²⁺ Cu ²⁺ Cd ²⁺	C ₀ = 20 ppm C ₀ = 20 ppm C ₀ = 20 ppm C ₀ = 2 ppm pH = 7.5	104	97.8% (7.8) 67.5% (5.4) 17.5% (1.4) 78.8% (0.6)
Natural zeolite (clinoptilolite)	Cu ²⁺ Cd ²⁺ Ni ²⁺ Cr ³⁺ Zn ²⁺	C ₀ = 100 ppm	108	90% (5.91) 90% (4.61) 90% (2.00) 90% (4.10) 90% (3.47)
Synthetic (NaP1) zeolite	Cu ²⁺ Cd ²⁺ Ni ²⁺ Cr ³⁺ Zn ²⁺	C ₀ = 100 ppm	108	(50.48) (50.80) (20.08) (43.58) (32.63)
Zeolite 4A	Co ²⁺ Cr ³⁺ Cu ²⁺ Ni ²⁺ Zn ²⁺	C ₀ = 50 ppm pH = 4	105	33.7% (16.8) 77.3% (38.7) 79.6% (39.8) 23.0% (11.5) 80.8% (40.4)

Table 1 (continued)

Technology/material	Heavy metal	Conditions	Ref.	Percentage and/or removal capacity (mg g ⁻¹)
Metal oxides				
Goethite (α -FeOOH)	Cu ²⁺	C ₀ = 500 ppm pH = 5.2	111	95.9% (151.9)
Hematite (α -Fe ₂ O ₃)	Cu ²⁺	C ₀ = 300 ppm pH = 5.2	111	92.0% (80.8)
Nano-alumina modified with 2,4-dinitrophenylhydrazine	Pb ²⁺ Cr ³⁺ Cd ²⁺ Co ²⁺ Ni ²⁺ Mn ²⁺	C ₀ = 50 ppm pH = 5	172	98.2% (35.1) 93.6% (33.4) 74.3% (26.5) 56.1% (20.1) 36.5% (13.0) 11.3% (4.0)
ZnO	Cu ²⁺	C ₀ = 2200 ppm pH = 4–6	118	36.1% (1580)
LDH based Fe–MoS ₄	Pb ²⁺ Ag ⁺ Hg ²⁺ Cu ²⁺ As ³⁺ Cr ⁶⁺	C ₀ = 20 ppm pH = (–)	173	≈ 100% (345) ≈ 100% (565) ≈ 100% (582) ≈ 100% (117) 76% (25.3) 82% (27.3)
βLG/AC hybrid membrane	Au ³⁺ Hg ²⁺ Pb ²⁺ Pd ²⁺ UO ₂ ²⁺ As ³⁺ As ⁵⁺	C ₀ = 71.3 ppm C ₀ = 120 ppm C ₀ = 252 ppm C ₀ = 25.2 ppm C ₀ = 1,980 ppm C ₀ = 258 ppb C ₀ = 239 ppb pH = (–) P = 1 bar PWF = (–)	16 and 24	≈ 100% (52.5) 99.5% (10.6) ≈ 100% (995.7) 99.8% (365.6) 99.4% 98.6% (1.1) 98.7% (0.3)
Activated carbon	Ni ²⁺	0.25 g adsorbent pH 2–5	15	≈ 100%
Membrane filtration		Advantages/disadvantages: high removal efficiency, no need of chemical additives or thermal inputs, no phase change involved, no secondary pollution, ease of fabrication, operation, scale up and control, and space-saving/selectivity and permeability trade-off, severe fouling and high energy consumption due to the pressure-driven inherent process; for drinking water treated by RO, mineral water composition needs readjustment <i>a posteriori</i>		
MEUF system comprising a cellulose UF membrane and SDS as a surfactant	Co ²⁺ Ni ²⁺ Mn ²⁺	C ₀ = 1 mM pH = 10 P = 40 psi PWF = 140–180 LMH	137	≈ 100% ≈ 100% ≈ 100%
MEUF system comprising a Membralox [®] Tl-70 ceramic UF membrane and SDS as a surfactant	Co ²⁺ Ni ²⁺ Zn ²⁺ Cr ³⁺	C ₀ = 10 ppm pH = (–) P = 2.8 bar PWF = 1200–1400 LMH	135	88% 87% 79% 80%
Poly(ionic liquid)/PSF NF	Co ²⁺ Ni ²⁺ Cu ²⁺	C ₀ = 5 mmol L ⁻¹ pH = 11 P = 6 bar PWF = 45.3 LMH	141	85.2% 84.9% 88.4%
Poly(ethyleneimine)/poly(dopamine)-MWCNTs/trimesoyl chloride NC NF	Zn ²⁺ Mg ²⁺ Cu ²⁺ Ca ²⁺	C ₀ = 1000 ppm pH = 6 P = 6 bar PWF = 91.92 LMH	174	93.0% 91.5% 90.5% 90.5%
Matrimid [®] /sulfonated pentablock copolymer NF	Pb ²⁺ Cd ²⁺ Zn ²⁺	C ₀ = 1000 ppm pH = 5.34 pH = 5.83	13	99.8% 98.2% 99.3%

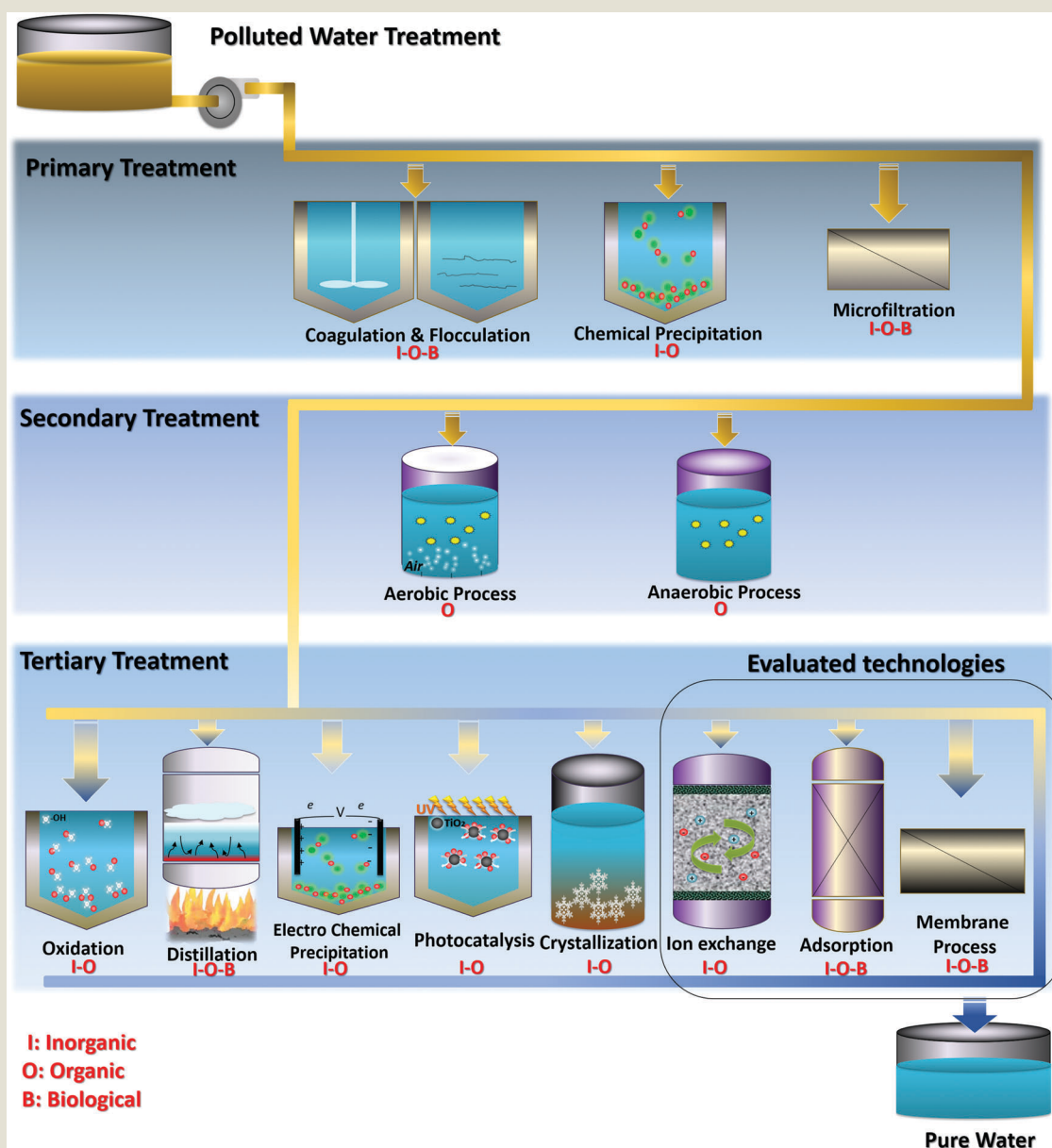
Table 1 (continued)

Technology/material	Heavy metal	Conditions	Ref.	Percentage and/or removal capacity (mg g ⁻¹)
	Ni ²⁺ HAsO ₄ ²⁻ HCrO ₄ ⁻	pH = 5.88 pH = 6.58 pH = 8.55 pH = 4.81 P = 10 bar PWF = 24.0 LMH		99.8% 99.9% 92.3%
Aromatic polyamide skin layer on a polysulfone substrate AFC 80-NF	Pb ²⁺	5 ppm, 50 bar	175	≥ 99.5%
Polydopamine functionalized halloysite nanotube-polyetherimide MMM	Pb ²⁺ Cd ²⁺	C ₀ = 1000 ppm pH = 6 P = 10 bar PWF = 225.0 LMH	150	78.5% 75.6%
Desal AG4021FF RO	Ni ²⁺ Zn ²⁺	C ₀ = 170 ppm pH = 6 P = 11 bar PWF = (—)	11	99.3% 98.9%
Polyamide RO TFC	Ni ²⁺ Cu ²⁺	C ₀ = 1000 ppm pH = (—) P = 3 bar PWF = (—)	176	98.1% 98.6%
Polyamide TFM-100 RO	As ³⁺ As ⁵⁺	C ₀ < 500 ppb pH = 6.2 pH = 9.0 P = 6 bar PWF = (—)	12	55.0% 99.0%
Polyamide (ES 20) ULP-RO	Cr Cu Ni	pH 7, 500 kPa pH 7, 500 kPa pH 7, 500 kPa	177	≈ 100% 99.7% 99.2%
ED cation exchange membrane by 2-acrylamido-2-methylpropane sulfonic acid	Pb ²⁺ Ni ²⁺	C ₀ = 50 ppm P = (—); <i>i.e.</i> vacuum PWF(—)	153	≈ 100% 97.0%
Polyimide TFC FO	Pb ²⁺ Cd ²⁺ Cu ²⁺ Hg ²⁺ HAsO ₄ ²⁻ HCrO ₄	C ₀ = 2000 ppm pH = (—) P = 5 bar PWF = 11 LMH	178	99.4% 99.9% 99.8% 99.8% 99.7% 99.9%
Ion exchange resins	Advantages/disadvantages: high efficiency, selective removal, no sludge generation/not universal, high cost			
DOWEX™ HCR S/S resins	Ni ²⁺ Zn ²⁺	pH = 4, 100 mg L ⁻¹	168	98% 98%
Duolite C-467	Zn ²⁺	153 mg L ⁻¹ ; pH ≥ 4	179	99.5%
Zirconium sulfate	As(III) As(V)	5 mg L ⁻¹ ; pH 10 5 mg L ⁻¹ ; pH 7.5	19	75.1% 98.8%
Sodium titanate Hexacyanoferrate FIBAN AK-22 Duolite C467	Ni ²⁺ ¹³⁷ Cs CrO ₄ ²⁻ Zn ²⁺	2.7 meq g ⁻¹ , pH = 5 182 m ³ , pH = 11.5 5 ppm cr, pH 5–8 153 ppm, pH ≥ 4	18	≈ 100% ≈ 100% 99.6% 99.5%

Notes: (1) PWF: pure water flux; LMH: L m⁻² h⁻¹.

industrial water treatment units combine primary, secondary and tertiary treatment processes, so that water is treated with high efficiency against all types of pollutants, *i.e.* inorganic, organic

and biological pollutants. The main primary, secondary and tertiary water and heavy metal-contaminated water treatment processes are summarized in Box 1.



Box 1: The typical water purification flowchart: combined primary, secondary and tertiary treatments against organic, inorganic and biological pollutants, with major technologies highlighted along with their application to different classes of pollutants. Re-designed with an original layout starting from ref. 27. Technologies for tertiary treatment which are evaluated quantitatively in the present work are highlighted in the box.

Water bodies, streams and industrial wastewater contaminated by heavy metals, with substantial levels of contamination, with or without the presence of suspended solids, oxidized metals, and scaling minerals, need to be pre-treated before entering into the high quality tertiary treatment process. This is necessary to prevent membrane fouling and saturation of the adsorbent or to avoid that resins can cause higher operational cost and drop of the efficiency. The most common pre-treatment for heavy metal removal is the chemical precipitation process; especially lime precipitation is considered as an effective conventional treatment for extreme heavy metal concentrations, *e.g.* several orders of

ppm. This work focuses on reviewing, analysing and assessing the technologies for tertiary water treatment for heavy metal ion removal. Before tackling this part, however, and for the sake of completeness, the discussion below briefly reviews the common primary treatment technologies for water pre-treatment and secondary water treatments, mostly classified into aerobic and anaerobic biological processes.

2.1. Technologies for primary water treatment

Primary treatment is the preliminary water purification process before further refined treatments are applied. It can be of

physical and/or chemical nature and includes screening and microfiltration, centrifugation, sedimentation, chemical precipitation, coagulation, gravity and flocculation methods. In the case of high concentration heavy metal polluted water, microfiltration, chemical filtration, coagulation and flocculation are the most important primary technologies. Although the efficiencies are generally much lower compared to tertiary treatment processes, massive quantities of pollutants can be removed by these cost-effective simple processes.

2.1.1. Microfiltration. Microfiltration has the largest pore size range (100–1000 nm) among the wide variety of membrane filtration technologies and may be based on both ceramic and polymer membranes. Media and microfiltration not only remove heavy metal ions but also efficiently filter TDS, bacteria, algae, microorganisms larger than viruses and micropollutants.²⁸ Water pre-treated by the microfiltration process can then be used directly in the tertiary heavy metal purification processes such as adsorption, ion exchange and membrane filtration.

2.1.2. Chemical precipitation. Chemical precipitation is effective and by far the most widely used process in industry for heavy metal primary purification because it is relatively simple and inexpensive to operate.²⁹ In this process, pH adjustment (basic pH) of heavy metals and reaction with chemical reagents (for example, lime, hydroxides and sulfides) result in the formation of insoluble particles, which are then removed by simple sedimentation. The major advantage of this process it is inexpensive and is of simple operational nature. The major drawback, however, is that the heavy metal concentration does not reach ranges acceptable for discharge, mandating additional post-treatments. Large sludge generation, disposal of sludge and possible secondary pollution are additional major disadvantages of this process.

2.1.3. Coagulation and flocculation. Coagulation is one of the most important methods for wastewater treatment; this method majorly destabilizes the particles suspended in the polluted streams by the addition of coagulants or flocculants, resulting in the sedimentation of particles. Ferric and aluminium salts are commonly used as coagulant and flocculating agents.³⁰ Improved sludge settling and biological pollutant removal are the advantages of this technique, while the major chemical consumption costs and sludge disposal are their drawbacks.

2.2. Technologies for secondary water treatment

Secondary water treatments rely on naturally occurring microorganisms capable of converting pollutants into simpler and safer substances. This type of treatment is divided into two broad categories: anaerobic and aerobic treatments.

In the aerobic treatment, microorganisms convert pollutants into carbon dioxide and new biomass in the presence of oxygen. Aerobic microorganisms require oxygen, so air must be continuously circulated through the tanks. Forced air from an air blower or compressor is mixed with the wastewater, where the aerobic bacteria feed on the waste present in the water source.

Anaerobic treatment is an energy-efficient process in which microorganisms transform pollutants in the wastewater into biogas in the absence of oxygen. Methane-rich biogas is also

produced through the anaerobic process, which can be treated and used as a renewable energy source.

Secondary treatments are most commonly used in removing organic pollutants. Microorganisms, as heavy metal bio-adsorbents, offer a new alternative for the removal or detoxification of toxic or valuable metals in industrial wastewater. Recent research studies show that microbes may also be efficient in removing the heavy metals.³¹ For example, bacterial biofilms may be genetically programmed to aid in the sequestration of mercury.³² Aerobic upflow systems show efficient removal of zinc (Zn), copper (Cu), manganese (Mn), and iron (Fe) with immobilized yeast *Issatchenkia orientalis* (*Io*) and *Candida tropicalis* (*Ct*) on zeolites.³³ Copper and iron removal by the acidogenic biomass immobilized on clinoptilolite in an anaerobic packed bed reactor was also studied.³⁴ A removal efficiency beyond 90% was achieved by this anaerobic process. Nonetheless, cost effective and highly efficient industrial scale water treatment by the microbes from heavy metal ions is not yet widespread in the market and is expected to expand in near future.

2.3. Technologies for tertiary water treatment

We divide the sections related to tertiary treatment of water from heavy metal ions into two main parts. First, in Section 2.3, we briefly introduce chemical oxidation, electrochemical precipitation, crystallization, distillation, and photocatalysis, for which the data availability is still somehow scattered and not comprehensive or consistent enough to allow a full evaluative assessment against the main discriminants of interest in this review (*e.g.* sustainability, cost, energy, *etc.*). We then proceed with a more detailed discussion on those technologies for which such a detailed metrical assessment becomes possible, and in Section 2.4 we review adsorption, membrane technologies (including reverse osmosis), and ion exchange technologies, for which we then present a detailed sustainability assessment in Section 3.

2.3.1. Chemical oxidation. This is a well-established, reliable technology requiring minimal equipment. Chemical oxidation involves the introduction of an oxidizing agent into the wastewater, causing electrons to move from the oxidant to the pollutants, which undergo structural modification. Oxidation can be employed to remove organic and some inorganic compounds such as iron and manganese from water. Oxidants commonly used in water treatment applications include chlorine, chlorine dioxide, permanganate, oxygen, and ozone. Advanced oxidation technologies, through processes such as steam stripping or activated carbon adsorption, can help in removing the toxic by-products of chemical oxidation. The outstanding advantage of this method compared to other typical technologies is its destructive nature without causing secondary pollution.^{35,36}

2.3.2. Electrochemical precipitation. Electrochemical methods involve the plating-out of metal ions on a cathode surface and can recover metals in the elemental metal state.³⁷ The electrochemical process, which is simple and environmentally friendly, requires less labour, and can save significant energy over other processes.

This method can also remove the chemical oxygen demand (COD); however, the removal efficiency of heavy metal ions is not high compared to the tertiary heavy metal water treatment technologies discussed below.

2.3.3. Crystallization and distillation. Most typical methods for tertiary water treatment are based on thermal and crystallization technologies. In thermal technologies, such as distillation and evaporation, sufficient energy is provided to bring the polluted water to its boiling temperature and then to vaporize, transforming a portion of the water into steam. The final step is to condense the process steam as pure water.³⁸ In the crystallization process, the pollutant concentration is increased until crystallization occurs. Struvite crystallization is a particularly efficient technique to remove ammonia, nitrogen and phosphorus from wastewater.

2.3.4. Photocatalysis. In this technology, photons from a light source are absorbed by a catalyst surface, which generates free radicals (e.g. hydroxyl radicals: $\bullet\text{OH}$) able to undergo secondary reactions, such as water electrolysis.³⁵ Photocatalytic reduction and photocatalytic oxidation are reactions induced by photons or UV light and sensitized by photocatalysts such as TiO_2 . A representative example of the photocatalysis process by TiO_2 particles for the removal of arsenite was reported by Zhang *et al.*³⁹ In the presence of TiO_2 under UV-light irradiation, arsenite was initially oxidized to arsenate and then was removed by a second step adsorption mechanism. Indeed, TiO_2 has a semiconductor structure, in that an electron filled valence band and an empty conduction band are present, separated by an energy bandgap. When TiO_2 is irradiated by light, one electron in the valence band can be transferred into the conduction band generating a hole, which is actually a positive radical. When the hole comes into contact with water and the TiO_2 photocatalyst surface, $\bullet\text{OH}$ radicals are formed. The $\bullet\text{OH}$ radicals can act as strong oxidizing agents, which can then be used for removing pollutants through photodegradation,⁴⁰ as well as Pb(II) from the solution through a photooxidation mechanism.⁴¹ Furthermore, the electrons can be used for reducing targeted metal ions, including Hg(II) ⁴² and Cr(VI) ,⁴³ or, as in the case of Ag, even recovering them in the elemental form from the wastewater treatment process. Solution pH, initial concentration of the metal ions, photocatalyst mass and light intensity have a strong effect on the photocatalytic metal reduction. Metal-organic frameworks are another example of photocatalysts for organic pollutant degradation.^{44–47} In particular, iron based metal-organic frameworks can serve as stable and efficient photocatalysts for Cr(VI) treatment under visible-light irradiation.^{48,49}

2.4. Technologies for tertiary water treatment evaluated in this review

In this section, we review the state-of-the-art of the remaining technologies (and the corresponding materials) for tertiary water treatment from heavy metal ions from groundwater, surface water and wastewater, for which a more extensive dataset is available. This allows a quantitative assessment of their performance against several critical discriminants, as well as the evaluation of their sustainability fingerprint.

These technologies encompass adsorption, membrane technologies (including reverse osmosis) and ion exchange resins.

2.4.1. Adsorption. Adsorption is the increase in substance concentration at a surface owing to a mass transfer process.⁵⁰ The application concept of this approach in wastewater treatment is based on removing pollutants by promoting their adsorption on the adsorbent surface.⁵¹ Adsorption has become a well-known, effective and economical method to remove heavy metals²⁶ due to the high removal efficiency, the possibility of regenerating adsorbents and the flexibility in design and operation. Because the specific area is a primary factor in adsorption, nanoparticles with a high surface/volume ratio are ideal candidates for this process and technologies producing new types of adsorbents with high chemical activity and specific surface area are rapidly expanding.⁵² Adsorbents primarily used in wastewater treatment are categorized as carbon-, metal- and zeolite-based nanosorbents.

2.4.1.1. Carbon-based nanosorbents. Carbon-based nanosorbents have been widely used for heavy metal wastewater remediation. Although activated carbon (AC) is the most common carbon-based commercial adsorbent for wastewater treatment applications,⁵⁰ in recent times other carbon-based materials such as carbon nanotubes (CNTs) and graphene have also emerged as efficient nanosorbents.

Due to its large surface area, which can reach $3000 \text{ m}^2 \text{ g}^{-1}$, a highly porous structure and high surface reaction affinity, AC is recognized as an efficient and common adsorbent for the removal of organic and inorganic pollutants in the aqueous environment.^{53,54} However, research on AC in the last decade has been slowed down by the rise of other carbon adsorbents such as CNTs,⁵⁵ and has focused on its chemical functionalization or its coupling with other adsorbents,^{56–59} or on the development of cheaper AC precursors.^{60–63}

Compared to AC, CNTs have more accessible adsorption sites per unit mass and shorter intraparticle diffusion distance, which are at the basis of their higher heavy metal removal performance.⁶⁴

CNTs, available in their two main allotropes of single walled (SWCNTs) and multi-walled (MWCNTs) carbon nanotubes, have been successfully employed in the removal of heavy metals such as arsenic,^{65,66} cadmium,^{17,66–71} chromium,^{66,68,72} cobalt,^{17,66,68,69,73} copper,^{17,66,67,69,70} europium,⁷⁴ lead,^{17,66–71,75,76} manganese,^{17,68} mercury,⁷³ nickel,^{69,71,77–79} strontium,⁷⁹ thorium,⁸⁰ uranium,^{81–83} vanadium⁶⁶ and zinc.^{17,69,70} The heavy metal adsorption mechanisms onto CNTs are complex and are attributed to the combination of chemical interaction, electrostatic attraction (when these are chemically modified) and sorption precipitation.⁶⁴ The adsorption properties of CNTs depend on several factors. The fraction of opened and unblocked nanotubes and the contribution of individual adsorption sites are important morphological factors.⁸⁴ The number of active sites in opened CNT bundles is larger than that in capped CNTs.⁸⁵ There are four types of adsorption sites in CNTs including internal sites, interstitial channels, outer surfaces and grooves.⁸⁶ Because the outer surfaces and grooves are directly exposed to the

adsorbing material, adsorption reaches equilibrium much faster on them than on the internal sites, *i.e.* inside the tube and the interstitial channels.⁸⁴ The purity of CNTs is also an important factor. Impurities such as soot, catalyst particles and other carbon-based contaminants can coat the surfaces of CNT bundles and consequently reduce the number of CNT active adsorption sites.⁸⁷

Previous studies showed that CNTs modified by oxygen exhibit greatly improved adsorption capacity. Some oxygen functional groups, such as $-OH$, $-CO$, and $-COOH$, can be attached to the CNT surface during the synthesis procedure or by oxidation, using various acids, ozone and plasma treatments.⁸⁶ In addition to improving dispersibility in aqueous solution, oxidation induces negative charges on the surface of CNTs, consequently increasing their cation exchange capacity.⁸⁸ For instance, SWCNTs with functional acidic sites on their surface and negative zeta potential have improved adsorption performance for Ni^{2+} and Zn^{2+} .⁶⁴ Promising heavy metal removal results were also reported by modification of CNTs by metal oxides, such as iron oxide,⁷⁹ manganese dioxide⁸⁹ and aluminum oxide.^{90,91} Although the mechanisms for enhanced adsorption capacity of these composites are not yet fully understood, it has been suggested that this could arise from the synergistic effect between CNTs and metal oxides.⁷⁹

Graphene, as the latest member of the carbon allotrope family, has also been used in combination with metal oxides to fabricate new adsorbents for heavy metal ion removal.^{92,93} For example, Gollavelli *et al.* successfully synthesized smart magnetic graphene *via* microwave irradiation of graphene oxide (GO) and ferrocene precursors. The adsorbent had high demonstrated removal efficiencies ($\sim 99\%$) down to the ppb level, for Cr^{6+} , As^{5+} and Pb^{2+} . Additionally, it also exhibited effective antibacterial activity (at $40 \mu g L^{-1}$) towards *E. coli* and low toxicity (at $0.1 ng nL^{-1}$) towards zebrafish. The good adsorption properties, effective disinfection control and cost-effective nature make it a potential adsorbent for safe drinking water in future decentralized water systems.⁹⁴

GO in the different forms of powder,⁹⁵ aerogel⁹⁶ and foam⁹⁷ has also been widely used for heavy metal removal. The GO aerogel for Cu^{2+} removal has a faster adsorption rate (15 min to reach equilibrium) compared to oxidized CNT sheets (24 h) and AC (40 min).⁹⁶ To achieve further heavy metal adsorption capacity, effective surface functionalization of GO with other compounds such as ethylene diamine tetra acetic acid (EDTA),⁹⁸ poly(amidoamine),⁹⁹ polydopamine,¹⁰⁰ poly-3-aminopropyltriethoxysilane,¹⁰¹ cyclodextrin and chitosan¹⁰² was successfully performed. For instance, EDTA was shown to improve the performance of GO for heavy metal ion adsorption, by forming stable chelates with metal ions.¹⁰³

2.4.1.2. Zeolite based nanosorbents. Zeolites and related inorganic crystalline materials have also been systematically employed for heavy metal ion removal.^{104–106} Zeolites are crystalline hydrated aluminosilicate materials with uniform-sized pores widely used in numerous industrial applications, due to their unique adsorption, catalytic and ion-exchange properties.¹⁰⁷

Although zeolite particle sizes typically range between 1 and $10 \mu m$, due to their pore sizes, between 0.4 and 1 nm, they are considered nanomaterials.⁵⁰ For heavy metal treatment, the natural zeolite clinoptilolite has been mostly used; however, some results with synthetic zeolites such as zeolite 4A¹⁰⁵ and zeolite X¹⁰⁶ have also been reported.

Sprynskyy *et al.* investigated the ability of natural zeolites to remove Ni^{2+} , Cu^{2+} , Pb^{2+} , and Cd^{2+} .¹⁰⁴ They concluded that the sorption has an ion-exchange nature, and it occurs over three distinct stages of fast adsorption on the clinoptilolite microcrystal surface, inversion stage and diffusion flow from the zeolite microcrystal's interior. In addition, the same authors found that pH plays a major role in the ion-exchange adsorption. At lower pH, due to hydrogen ion competition, adsorption decreases rapidly.¹⁰⁴ The removal efficiency of the heavy metal ions by zeolite exchangers was tested by comparing the natural zeolite clinoptilolite and the synthetic zeolites (NaPl).^{108,109} The synthetic zeolites have greatly improved exchange capacity compared to the natural ones. Hui *et al.* synthesized zeolite 4A and applied it for the removal of Co^{2+} , Cr^{3+} , Cu^{2+} , Zn^{2+} and Ni^{2+} .¹⁰⁵ Zeolite 4A showed good performance for heavy metal ion removal, with adsorption capacity ranking as $Cu^{2+} > Cr^{3+} > Zn^{2+} > Co^{2+} > Ni^{2+}$. The difference in adsorption performance is related to hydration free energy, metal ions' hydrated radii and the zeolite 4A crystal structure.¹⁰⁵ Luo *et al.* proposed a sustainable and green approach to synthesize needle-like nanocrystalline zeolites from metakaolin (MK) as a precursor clay mineral. The hydrothermally synthesized zeolite showed higher porosity and specific surface area, due to a particular needle-like morphology compared to raw MK with a layered structure. Accordingly, Cu^{2+} and Pb^{2+} adsorption capacities of zeolites were $431.0 mg g^{-1}$ and $337.8 mg g^{-1}$, respectively, which showed a 20-fold increment compared to raw MK. The main adsorption mechanism of MK-based zeolites relies on ionic exchange reactions between the sodium ion of zeolites and heavy metal ions.¹¹⁰

2.4.1.3. Metal-based nanosorbents. Nano metal oxides, such as ferric oxides including goethite ($\alpha-FeOOH$) and hematite ($\alpha-Fe_2O_3$),¹¹¹ hydrous ferric oxide,¹¹² maghemite ($\gamma-Fe_2O_3$)¹¹³ and magnetite (Fe_3O_4),¹¹⁴ manganese oxides including hydrous manganese oxide¹¹⁵ and mixed-valence manganese oxides,¹¹⁶ titanium oxides, aluminum oxides, magnesium oxides,¹¹⁷ zinc oxides¹¹⁸ and cerium oxides,¹¹⁹ are effective and low-cost materials for heavy metal ion wastewater treatment. Essentially, the common separation mechanism relies on the complexation of the oxygen in the metal oxides with the heavy metal ions in the aqueous environment.¹²⁰ Recently, hierarchically structured metal oxides have gained considerable interest due to their high reactivity with heavy metal ions, excellent surface to volume ratio, desirable mechanical stability and ease of regeneration.^{121,122}

Granular ferric hydroxide is one of the most widely used metal-based materials, and has already been commercialized for arsenic removal from drinking water. Basically, it consists of akaganéite ($\beta-FeOOH$) with a ferrihydrite ($Fe(OH)_3$) component.

This material has high adsorption capacity for use in fixed bed adsorbers. The porosity and specific area of granules are 75% and $330 \text{ m}^2 \text{ g}^{-1}$ and they present high arsenic adsorption capacity.^{123–125}

Besides the main classes of adsorbents discussed above, several readily available low-cost bioadsorbents have been collected from agricultural waste, seafood waste, food waste, industrial by-products and cellulose waste materials, which are economically attractive for alternative heavy metal ion treatments.^{126,127} The literature shows evidence on how these low cost adsorbents can perform with moderate to high efficiency in removing metal ions from aqueous solutions or wastewater.¹²⁸

2.4.2. Membrane processing. Membrane separation processing includes several advanced and diverse technologies showing great potential for removing various types of pollutants with high efficiency. When used for heavy metal removal, membrane processing can provide a reliable solution, which generally does not require chemical additives or thermal inputs, does not involve phase changes, is environmentally friendly, and relatively simple in fabrication, operation, scale-up and control.^{129–131} The separation mechanisms for these membranes consist of size sieving, solution-diffusion and Donnan exclusion.^{132,133} Notwithstanding the aforementioned advantages, membrane technologies suffer from selectivity and permeability trade-off, severe fouling and high energy consumption due to the pressure-driven inherent process.⁵⁵ Membrane based technologies for water purification can further be classified into ultrafiltration, nanofiltration, reverse osmosis, nano-hybrid membranes and electrodialysis.

2.4.2.1. Ultrafiltration. Ultrafiltration (UF) membranes have pore sizes ranging from 10 to 100 nm and typically are used to remove viruses, bacteria, color pigments, and some natural organic colloids.¹³⁴ UF has the further advantage to be an energy-saver technology compared to reverse osmosis (RO), where the considerable higher transmembrane pressure requires substantially larger energy consumption. However, since UF membranes' pore size is larger than metal ions' hydrated radius, metal ions generally pass through the membranes and the heavy metal ion rejection is not satisfactory. To obtain high metal separation efficiency, the addition of surfactants to wastewater becomes essential, realizing the so called "micellar-enhanced ultrafiltration (MEUF)", which may allow reaching heavy metal rejection of 99% and beyond.¹³⁵ MEUF has several operating stages, including addition of surfactants with concentrations higher than their critical micelle concentration (CMC) to wastewater, micelle formation by surfactant monomer aggregation, binding of metal ions and micelles *via* electrostatic interactions and eventually their separation by a typical UF technique.¹³⁶ Lin *et al.*, for example, applied the MEUF system comprising cellulose UF membranes and sodium dodecyl sulfate (SDS) as a surfactant to achieve rejections above 90% for Cu^{2+} , Co^{2+} and Ni^{2+} .¹³⁷

2.4.2.2. Nanofiltration. Nanofiltration (NF) membranes are designed to remove pollutants smaller than 10 nm and are best

suited for water softening applications and removal of most heavy metals. The NF separation mechanism relies on a combination of steric and Donnan exclusion.¹³⁸ According to Donnan exclusion theory, membranes with a positive surface charge have higher flux and rejection for cations such as heavy metals, however, due to fabrication materials and procedures, typical NF membranes have either neutral or negatively charged surfaces. Thus, the development of positively charged NF membranes for effective heavy metal removal has recently garnered renewed interest.¹³⁹ A novel positively charged polyamide NF membrane with a dendrimer-decorated surface was prepared by Li *et al.*¹⁴⁰ Grafting the poly(amidoamine) dendrimer onto the surface of the polyamide causes high density of free protonated amino groups, thus resulting in excellent metal ion rejections (above 90%), in the order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Pb}^{2+}$, following ions' hydrated radii.¹⁴⁰ Tang *et al.* reported a novel technique to prepare positively charged NF membranes on a microporous polysulfone (PSf) support, by rapid hydrophilic–hydrophobic transformation of poly(ionic liquid) (PIL) in aqueous solutions.¹⁴¹ The synthesized PIL/PSf NF membrane showed a good retention performance (above 90%) for Cu^{2+} , Ni^{2+} and Co^{2+} .¹⁴¹ A positively charged Matrimid[®] 5218 NF membrane with a sulfonated pentablock copolymer rejection layer was synthesized successfully by Thong *et al.*¹³ The resulting membrane shows an excellent rejection rate exceeding 98% for cations such as Pb^{2+} , Cd^{2+} , Zn^{2+} , and Ni^{2+} but performs well also in the case of anions, such as HAsO_4^{2-} (99.9%) and HCrO_4^- (92.3%).¹³

2.4.2.3. Reverse osmosis. Reverse osmosis (RO) is the most common worldwide used desalination technology, and in such an application field, it is referred more specifically as seawater reverse osmosis (SWRO). In the case of heavy metal removal, RO is mostly used to treat large volumes of brackish groundwater. Apart from the notable exception of As(III),¹² RO is very efficient in removing most ions, and it is widely used in aerospace, food, oil and gas, galvanic, dairy, pulp and paper industries and power plants. In RO, ions are separated from water through a semipermeable membrane by applying a hydrostatic pressure against the osmotic pressure. Hence the threshold of hydrostatic pressure is settled by the osmotic pressure, although the hydrophilic nature of RO membranes definitely facilitates water transport through the membrane.¹⁴² However, high losses of processed water, high-energy consumption and large initial investments are the major drawbacks of RO. Furthermore, precisely because RO leads to a manifold concentration of the pollutant solution, efficient disposal of residual water volumes is also an important issue. Finally, specifically to drinking water, since RO removes ions in a non-selective way, the mineral composition of water oligo-elements always needs post treatment and readjustment. Over the past few decades remarkable advances have been made to improve RO, such as fabrication of new material precursors, minimizing fouling, concentration polarization (*i.e.* the phenomenon of depletion of permeable component concentration in the adjacent layer of the membrane surface which decreases

the mass transfer driving force), enhancement of water flux and reduction of energy consumption, which has decreased from the average 12 kW h m^{-3} in the 1970s to less than 2 kW h m^{-3} in the early 2000s. However, 87% of the total RO cost arises from electricity (energy), labor and chemicals, so that this improvement is still not satisfactory when sustainability aspects are considered. Thin film composite (TFC) polyamide membranes are typical RO membranes which consist of a polyester structural support, a micro-porous interlayer and an upper ultra-thin barrier layer.¹⁴³ In one of the new applications of RO, Khedr *et al.* showed that RO could remove efficiently (above 99%) radionuclides including radium, $^{226}\text{Ra}^{2+}$ and $^{228}\text{Ra}^{2+}$, uranium, as uranyl cation, UO_2^{2+} , carbonate complexes, such as $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$, and radon, ^{222}Rn .¹⁴⁴

2.4.2.4. Nanohybrid membranes. Nanohybrid membranes are a new generation of membranes, which are made by the incorporation of inorganic particles with the aim of improving the properties of the polymeric membrane precursors.¹⁴⁵ There are two types of nanohybrid membranes: mixed matrix membranes (MMMs) and nanocomposite membranes (NCMs).¹³⁰ MMMs are formed by the incorporation of high separation performance porous inorganic molecular sieves, such as zeolites,¹⁴⁶ and carbon-based molecular sieves,^{147,148} in polymer matrixes to combine the advantages of polymeric membranes with the superior separation performances of inorganic molecular sieves.^{107,149} In addition to changing the surface properties of the membranes, these molecular sieves form selective and preferential pathways for the water molecules within the polymeric matrices, enhancing water permeability and ion rejection.¹³⁰ For example, Hebbar *et al.* synthesized poly-dopamine functionalized halloysite nanotube-polyetherimide MMMs for heavy metal ion removal in an aqueous environment.¹⁵⁰ Their results showed improvement in Pb^{2+} and Cd^{2+} separation performance and antifouling properties compared to untreated polymeric membranes.¹⁵⁰ The other type of nanohybrid membrane, NCMs, is made by incorporation of nanoparticles such as silver oxides¹⁵¹ within the thin layer of the polymer to improve the surface properties of the membranes, such as hydrophilicity and antibacterial and photocatalytic properties.¹⁵²

2.4.2.5. Electrodialysis. Electrodialysis (ED) is an electrically driven membrane technique, which can be used for heavy metal removal. This process can be scaled-up and combined with other processes.¹⁵³ Due to the inherent high water recovery and low use of chemicals, ED is widely used in industrial heavy metal water treatment.¹⁵⁴ The heart of ED systems is ion exchange membranes (IEMs), both cation- and anion-exchange membranes, with fixed ionic groups on their backbones. Nowadays the research focus on ED is towards fabricating new types of IEMs with lower electrical resistance, improved permeability and higher selectivity for specific ions, and these, together with higher chemical, mechanical and thermal stabilities, are coupled to lower costs. Efficiency may

reach high values: by the preparation of new ED cation exchange membranes by using 2-acrylamido-2-methylpropane sulfonic acid, Nemati *et al.* successfully removed K^+ (99.9%), Pb^{2+} (99.9%) and Ni^{2+} (96.9%).¹⁵³

Lienhard *et al.* tried to reduce the cost of ED by considering the entropy generation rate arising from ion passage, aiming at achieving a more uniform spatial distribution of ions across the membrane.¹⁵⁵ To this end, they studied two ED configurations, *i.e.* operation in a counterflow and in two electric stages at different voltages. Their results showed that by using these configurations a significant reduction in a system's energy consumption could be obtained, especially for systems with large membrane areas.¹⁵⁶ Researchers in the Winter group developed the first robust model for the prediction of ED full energy consumption and the desalination rate without any experimental parameter estimation or system characterization requirements. In fact, in this model both electrochemical and hydraulic contributions in total ED power consumption were taken into account. Based on this powerful tool, ED operating behavior can be significantly modelled and predicted, before an actual ED system is built.^{157,158}

2.4.3. Ion exchange resins. Ion exchange is a well-established method commonly applied to drinking water treatment for hardness removal, but it is also increasingly being studied for the removal of heavy metal ions.^{159,160} In this water purification technology, porous ion exchange microbeads trap the specific ions by releasing the pre-saturated non-toxic ions.¹⁶¹ Because the technology relies on exchange surfaces, as in adsorption, an important requirement is to have nanoporous resins with accessible high specific surface area. Anion and cation resins are most common exchangers which have the capacity to exchange negatively charged (arsenate, selenate, chromate, uranium, *etc.*) and positively charged ions (barium, strontium, radium, calcium, magnesium, *etc.*), respectively.¹⁶² These resins are categorised depending on their available functional groups as either strong or weak exchangers and may be acidic or basic in nature. Most common ion exchange resins available in the market are sodium silicates, zeolites, polystyrene sulfonic acid, and acrylic and methacrylic resins. In order to achieve the high purity required in conventional water treatment applications, the mixed bed approach is typically used to remove both the cations and anions. Ion exchange resins' performance is highly sensitive to process parameters such as pH, temperature, initial concentration of the adsorbent and sorbate, anions and contact time.^{163,164}

A distinct advantage of ion exchange resins is the reversibility of the reactions, which allows regeneration once the resin is saturated. Ion exchange resins can also be used to recover valuable heavy metals present in the wastewater effluents, by elution with suitable reagents.¹⁶¹

The synthetic ion exchange resins Amberlite IR-120 and Dowex 2-X4 almost completely exchange Zn(II) , Cr(III) and Cr(VI) ions from the electroplating wastewater.¹⁶⁵ Ambersep 132 (strong basic resin) and cation exchange resin called IRN-77 both have high capacity to remove the Cr(VI) and Cr(III) heavy metal ions, respectively.^{166,167} Commercially available

ion exchangers removing Pb(II), Hg(II), Cd(II), Ni(II), V(IV,V), Cr(III,VI), Cu(II) and Zn(II) from water and industrial wastewaters are discussed in detail elsewhere.¹⁶¹ Dowex HCRS/S resins, considered as economically beneficial exchange resins due to their high regeneration properties, have a removal efficiency of 98% for Ni and Zn at pH 4.¹⁶⁸ The recovery of chromic acid from the ion exchange resin Ambersep 132 was studied by Lin *et al.*¹⁶⁶

Ion exchange resins are typically installed in fluidized, packed bed configurations, and are easy to use. They can operate with minimal energy demand, quickly and without producing sludge or secondary pollution. Despite these advantages, they also have some important limitations: for example, pre-treatment is compulsory, operational costs are relatively high and their performance is highly specific and dependent on the ions, which make them unsuitable for simultaneous ion removal from polluted water streams.

2.5. Summary of tertiary water treatment technologies

The removal efficiency and capacity of various heavy metal pollutants by diverse adsorbents, membranes and ion exchange resins along with the experimental conditions (initial pollutant concentration, pH, water flux, and pressure) are summarized in Table 1. The advantages and disadvantages of different heavy metal removal technologies are mentioned in each case. Efficiencies in the table are given in percentages up to the first decimal; efficiencies above 99.9% are approximated to 100%. As observed in the table, LDH based Fe-MoS₄, amyloid fibril adsorbents, polyimide TFC forward osmosis membranes and sodium titanate hexacyanoferrate ion exchange resins have the highest efficiencies among the materials considered.

3. Sustainability of the different technologies

Although efficiency in the removal of heavy metal ions is the first discriminant when implementing any water treatment technology, the limiting factors are most often of different nature and involve primarily costs, power consumption and ease of implementation. This becomes a particularly stringent criterion when sustainability aspects are considered.¹⁸⁰ For example reverse osmosis is a reliable, widespread technology, with high rejection efficiencies, but it can be extremely energy-intensive, requires substantial investments and has very low portability, in short, it cannot be applied in most rural or remote areas where water scarcity is critical; ultrafiltration, nanofiltration, and core-shell nanofibers may be equally efficient, but generally require high processing pressures which may not always be easily available; similarly some advanced materials, such as latest generation adsorbents, ion exchange resins or heterogeneous photocatalysts, may not be compatible with largely accessible drinking water needs for cost aspects, at least in many disfavoured environments.

The literature over the last ten years has come to acknowledge that the sustainability cannot be judged by a technology

or technology qualities alone, and that it is the technology plus the business model or implementation model together that determines sustainability in the broadest sense.^{181,182}

Nonetheless, a sustainable technology for water purification should have the following key and universal characteristics: (i) maintain the cost of processed water as low as possible, (ii) require little to no investment; (iii) be operative at low energy and processing pressures; (iv) allow recovering most of the treated water and (v) keep a low environmental fingerprint, that is, ideally rely on renewable, recyclable and environmentally friendly materials.

Fig. 3 reviews some of these critical characteristics for the five main classes of technologies considered: reverse osmosis, nanofiltration, adsorption, ion exchange and electrodialysis. Fig. 3a gives the total cost per million liters of processed water. Although there is significant spread in the data, it appears evident that technologies such as adsorption and ion exchange tend to provide the most affordable solutions for water purification in terms of costs. To understand why, it is important to distinguish between capital investment and operative running costs, discussed in detail in Fig. 3b and c, respectively. These figures illustrate that both technologies require the lowest initial capital investment among the five analysed, with adsorption offering also the lowest operating costs. These conclusions are further supported by an analysis of the average energy consumption to operate the five technologies considered, which is summarized in Fig. 3d: there, it is apparent how adsorption is best performing also in terms of energy requirements, with only minimal energy demand. These considerations, together with the high portability of the technology, make it an ideal candidate for water purification in rural and remote areas or underdeveloped countries, where often no energy is available to process water, other than natural resources (*e.g.* gravity). Is this enough to conclude that adsorption is a more sustainable technology compared to reverse osmosis? Certainly not, if one also considers that reverse osmosis can process up to one order of magnitude larger volumes of water compared to adsorption (although at a lower efficiency in recovering processed water). This is another critical and central aspect to be considered and will remain so as long as more than one billion people worldwide remain without access to safe drinking water. This illustrates well the difficulties in evaluating each individual technique, especially without a careful and comprehensive assessment, which accounts for all possible critical factors. To this end, in the following section we propose a simple, compact, yet powerful and comprehensive tool to evaluate individual technologies in the broadest possible perspective, including technical aspects, efficiency performance and sustainability aspects.

3.1. General assessment of individual technologies parameterized by a single compact index, the ranking efficiency product (REP)

From the discussion above, it appears evident that evaluating a single technology to draw conclusions on its advantages

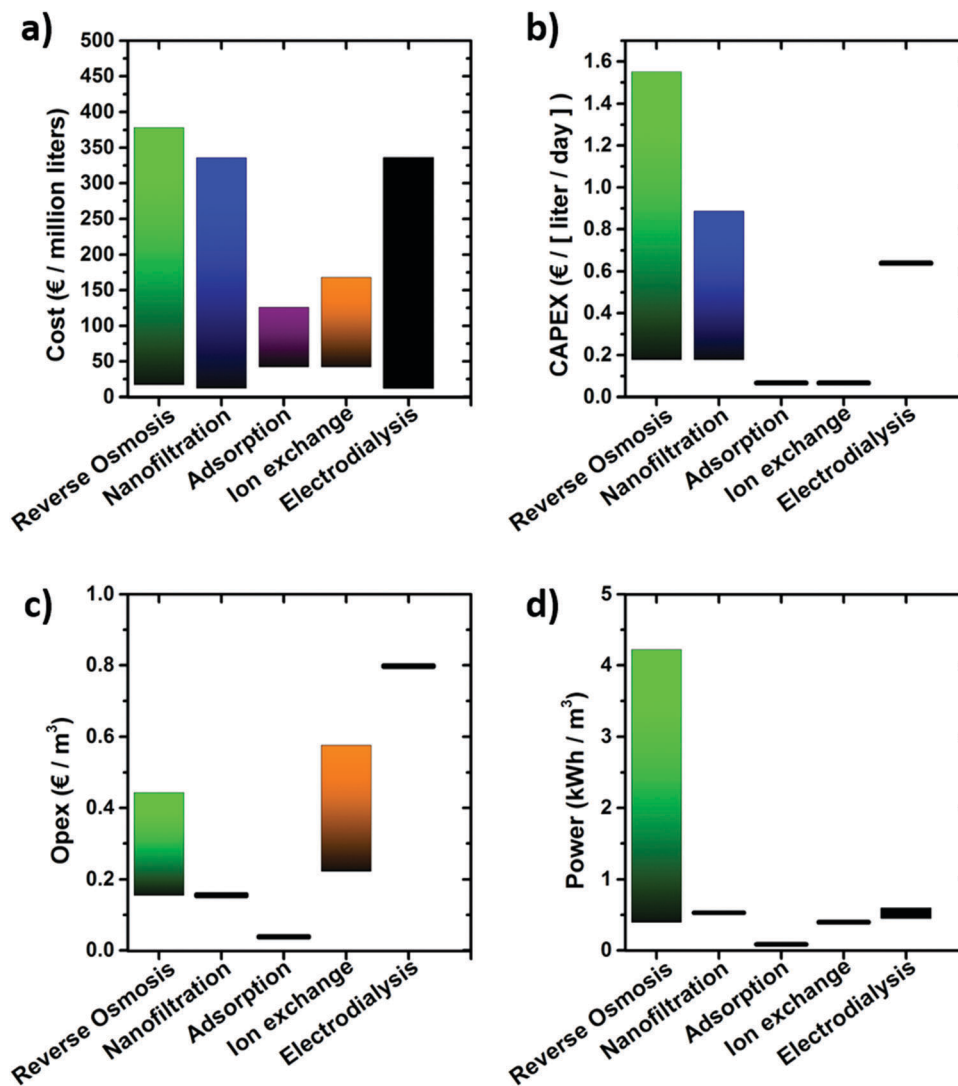


Fig. 3 Cost (upper and lower limits) of technologies in wastewater and drinking water treatment: (a) total cost per volume of treated water;²⁷ (b) installation costs;^{183–187} (c) running costs;^{183,184,188,189} and (d) energy consumption.^{183,185,188,190–192}

and disadvantages remains a challenging task, which needs to account for several factors simultaneously. Furthermore, under real conditions there is most likely not a single gold technology capable of delivering solutions to all the multiple issues, contexts and problems related to water purification and solutions remain specific to individual problems, which all differ from each other. We nonetheless introduce a compact index, named the Ranking Efficiency Product (REP), by which the different techniques can be assessed against the main criteria discussed in this article, in particular with respect to their performance and sustainability aspects, which can serve as a basis to evaluate the trade-off between the advantages and disadvantages of each individual technology.

The approach is stochastic in nature and based on rank product statistics. According to this simple approach a technology j can be evaluated by ranking each i of the n independent characteristics between a minimum r_{i-MIN} and a maximum

rank, r_{i-MAX} . We then define the overall ranking efficiency product of a technology j as

$$REP_j = \left[\prod_{i=1}^n (r_i/r_{i-MAX})_j \right]^{1/n} \quad (1)$$

where r_i is the individual ranking score for the characteristic i of the technology j . REP as defined above varies between (r_{i-MIN}/r_{i-MAX}) and 1 for worst and best performing technologies, respectively. Graphically, the REP can be assimilated to the fractional area covered by an n -fold web with corners placed at r_i distance from the centre over that of the homologue n -fold web with all corners placed at r_{i-MAX} distance from the centre. Fig. 4a–e give the evaluation of reverse osmosis, nanofiltration, adsorption, ion exchange and electrodialysis, respectively, evaluated on a 5-rank basis according to 8-fold characteristics from those detailed in Table 2. Fig. 4f summarizes the REP index evaluated by both 8-fold and 7-fold characteristics

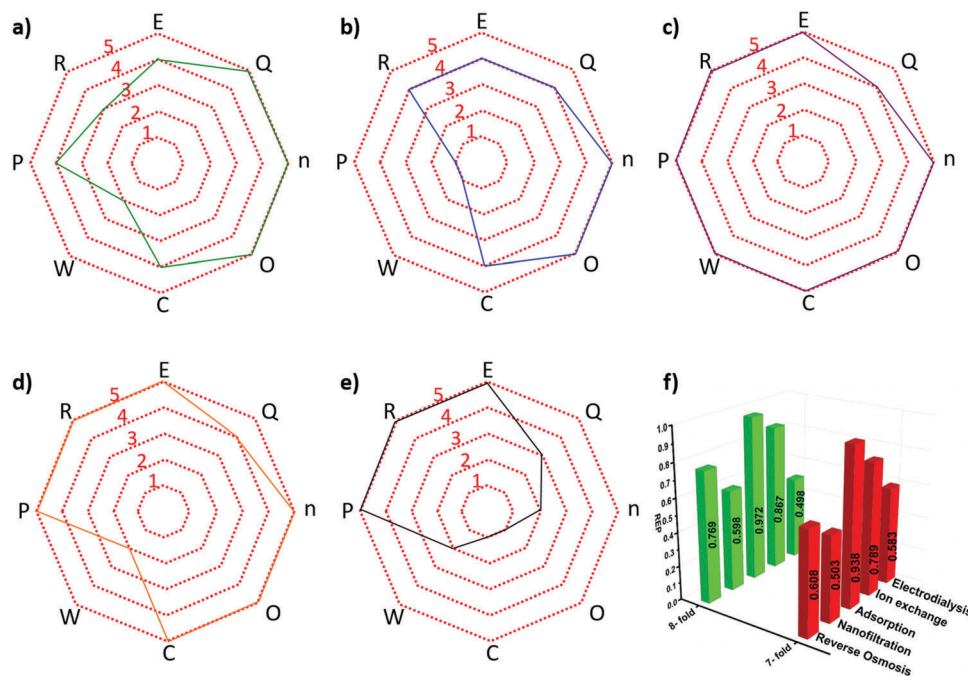


Fig. 4 General assessment of individual water purification technologies according to the rank product statistics. (a) Reverse osmosis, (b) nanofiltration, (c) adsorption, (d) ion exchange, and (e) electrodialysis sorted following an 8-fold, 5-ranked assessment. The characteristics considered are efficiency (E), operating flux (Q), number of fields of application (n), operating costs (O), capital costs (C), consumed power (W), operating pressure (P) and water recovery efficiency (R). Panel (f) gives the REP index evaluated by both these 8-fold characteristics and an alternative 7-fold where only the total cost (T) is considered.

among the 9 given in Table 2. The characteristics considered are efficiency (E), operating flux (Q), number of fields of application (n), total cost (T), operating costs or OPEX (O), capital cost or CAPEX (C), consumed power (W), operating pressure (P) and water recovery efficiency (R). The 8- and 7-fold differs only in the way the cost is accounted: in the first case, individual OPEX and CAPEX costs are both considered in the REP. This approach is robust because it considers individually the two main cost components, but since the CAPEX is not inclusive of the lifetime of the technology, a 7-fold evaluation is also provided using total cost T as a single characteristic. Independent of the way cost components are evaluated, the picture emerging from the rank product statistics remains substantially the same, pointing at adsorption as the most sustainable technology, followed by ion exchange and reverse osmosis.

The method is general, robust and simple enough to be generalized to additional, fewer or different characteristics; thus technologies can be sorted out differently, shall one or more characteristics lose weight in the evaluation. For example, if water purification needs to be performed in an environment where energy can be provided at low or no cost by recycling energy produced from large plants (nuclear, hydroelectric, *etc.*), a different evaluation can immediately be implemented by simply dropping the power consumption characteristic, which becomes then of minor importance in such a context. Details on the way individual ranks are sorted are given in the method section.

Of course, any attempt to sketch down to a simple number a technology related to a problem as complex as water

purification is, by definition, simplistic at least. In this context, the REP method cannot escape this rule of thumb. For example, as presented above, the REP index does not account for relative weights of the different characteristics, which are all considered equally important; this, however, can be readily implemented in eqn (1) by introducing a multiplicative factor b_i , with $0 < b_i < 1$, for each i of the n independent characteristics, shall the importance of each of them be considered or perceived different: this adds for flexibility on the REP ranking, but also introduces somewhat arbitrariness to the analysis. Additionally, the REP metric does not accommodate or account for the large uncertainties in the qualities used as inputs. Some of the inputs, such as cost, have significant uncertainty ranges (see Table 2), while the REP as presented above is based for this specific characteristic only on the average value (see the Sorting method section). All other characteristics are processed by considering only maxima (for favorable characteristics) or minima (for unfavorable characteristics), without implementing the variance or spread of their available range (see the Sorting method section). Once again, however, the modular form of the REP analysis easily allows for the implementation of such a range of each characteristic in the final metric: it would be sufficient to add for each i of the n independent characteristics a multiplicative term v_i , varying between a minimum value and 1 to rank the range width as an unfavourable characteristic (see the Sorting method section), and averaging the REP to a $1/2n$ power, instead of $1/n$, to account for the doubling of the sorting characteristic entries. In the spirit of a simple and accessible, yet robust and compact number, these unnecessary complications are avoided in the

Table 2 Technical specifications used for sorting the ranking and ranking efficiency product for the various technologies considered

	Reverse osmosis	Nanofiltration	Adsorption	Ion exchange	Electrodialysis
<i>E</i> : efficiency	Brackish water: 0.91–0.9991 ^{127,132–134,177} Note: As(III): 0.2–0.55 ^{11,12,176,193,194} Desalination: 0.99	0.47–0.999 ^{195–197}	0.3–0.9998 ^{24,54,67,105,198}	0.5–0.9999 ^{18,161,199–201} Note: efficiency depends strongly on metal	0.69–0.9999 ^{199,202,203}
<i>Q</i> : operating flux	From 1900 m ³ day ⁻¹ up to 55 000 m ³ day ⁻¹ ²⁰⁴	Up to 3700 m ³ day ⁻¹ ²⁰⁵	1300–4800 m ³ day ⁻¹ average flux ^{183,206}	1300–4800 m ³ day ⁻¹ (average flux assumed as in adsorption)	1270 m ³ day ⁻¹ (average flux) ^{184,189}
<i>n</i> : number of fields/domain of application	1 Municipal 2 Industrial 3 Household	1 Municipal 2 Industrial 3 Household	1 Municipal 2 Industrial 3 Household	1 Municipal 2 Industrial 3 Household	1 Industrial
<i>T</i> : total cost (€ per one million liters of treated water)	197.4 ± 180.6 ²⁷	174 ± 162 ²⁷	84 ± 42 ²⁷	105 ± 63 ²⁷	174 ± 162 ²⁷
<i>O</i> : OPEX, operating cost per volume of treated water (€ per m ³)	0.155 (brackish) 0.443 (desalination) ¹⁸⁴	0.155 ¹⁸⁴	Down to 0.039 at a water flux of 1300 m ³ day ⁻¹ ¹⁸³	0.421–0.576 (at 1200 m ³ day ⁻¹) 0.222–0.377 (at 4796 m ³ day ⁻¹) ¹⁸⁸	0.798 ¹⁸⁹
<i>C</i> : CAPEX, capital investment normalized by operating flux [€ per (day ⁻¹)]	0.177–0.887 (brackish) ¹⁸⁴ 0.665 to 2.551 (desalination) ^{184,186}	0.177–0.887 ¹⁸⁵	0.066 at a water flux of 1300 m ³ day ⁻¹ ¹⁸³	0.066 (assuming identical cost as adsorption)	0.638 (at a current of 88 A m ⁻²) ¹⁸⁷
<i>W</i> : power required per volume (kW h m ⁻³)	0.396 to 0.792 ^{185,190} (brackish) 2.902–4.221 (desalination) ¹⁹⁰	0.528 ¹⁹¹	0.084 ¹⁸³	0.396 ¹⁸⁸	0.449–0.596 ¹⁹²
<i>P</i> : operating pressure	2–17 bar (brackish) 30–70 bar (desalination) ²⁰⁷	4.5–7.5 bar ²⁰⁵	0.5–2 bar It works with gravity, vacuum and pressure ²⁰⁸	0.5–2 bar It works with gravity, vacuum and pressure	1–3.4 bar ²⁰⁹
<i>R</i> : water recovery efficiency	50–60% (brackish) 30–60% (desalination) ¹⁹⁰	60–70% ^{186,190,210}	100% ¹⁸⁴	98% ¹⁸⁴	80–90% ¹⁸⁴

analysis presented in Fig. 4, but can be easily implemented should the analysis be pushed further into specific aspects of interest.

4. Emerging technologies

In this last section, we briefly discuss emerging technologies which are still in their infancy or the incubation stage but which show high promise in mitigating the global water purification issue. For the technologies discussed below, current availability of data does not allow a comparative analysis as the one based on the REP sorting method, and only a partial, non-comprehensive assessment is possible. Furthermore, cutting-edge nanomaterials, hybrid adsorbents and newest generation of membranes are also discussed in what follows. Some of these emerging technologies and materials are summarized and depicted in Fig. 5.

4.1. Graphene oxide microbots

GO-Based tubular micromotors, dubbed microbots, propelled by a catalytic reaction are among the rapidly emerging materials for heavy metal removal.²¹¹ These microbots consist of four layers: an outer GO layer, an inner Pt layer and two Ni/Pt and Ni

intermediate layers. Heavy metals are adsorbed on the surface of the GO outer layer, the Pt inner layer acts as the engine decomposing hydrogen peroxide fuel for self-propulsion and intermediate layers control microbots' motion by an externally applied magnetic field. Vilela *et al.* showed that the GO-microbots are active self-propelled systems for lead capture, transfer, removal and subsequent recovery.²¹¹ Due to strong complexation of Pb²⁺ with the surface oxygen moieties of GO, high adsorption of Pb²⁺ on the surface of microbots can be obtained. Microbots' propulsion force is then obtained by ejection of water and oxygen microbubbles, produced by the decomposition of hydrogen peroxide in the platinum layer. Eventually, owing to their magnetic properties, microbots can easily be collected and removed from water using a magnet. Microbots can be reused after Pb²⁺ recovery by pH adjustment. By applying mobile GO-microbots, lead removal efficiency one order of magnitude above that of nonmotile GO-microbots was obtained, from the initial 1000 ppb down to 50 ppb in just two hours.²¹¹

4.2. Layered double hydroxides

Jawad *et al.* introduced layered double hydroxide (LDH)-based Fe–MoS₄ as a powerful adsorbent for the selective

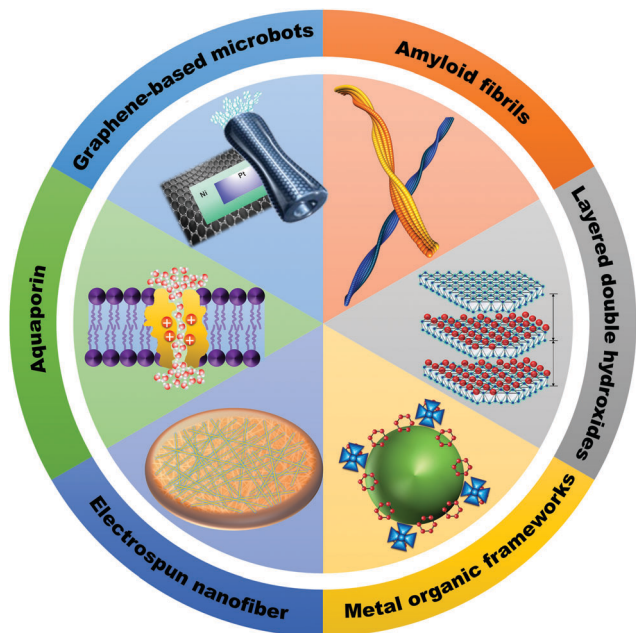


Fig. 5 Summary of some emerging technologies and materials for water purification.

removal of heavy metals.¹⁷³ Mineral sulfides such as MoS_4^{2-} anions have an inherent ability to coordinate strongly with heavy metals through the M–S linkage, however, their ability is typically limited by their non-porous structure, solubility in water and sensitivity to atmospheric oxygen. Protective shields for intercalated MoS_4^{2-} anions could be provided by chemical binding of thiol ($-\text{S}-$)²⁻ groups in protective lamellar LDH structures. Heavy metal adsorption approached 100% removal efficiency for Ag^{2+} , Hg^{2+} , Pb^{2+} and Cu^{2+} and 76% and 82% removal efficiency for As^{3+} and Cr^{6+} , respectively. Furthermore, due to the fact that Fe– MoS_4 is principally based on the soft acid–base Lewis concept, removal of harmful radioactive soft metals such as Sr, Cs, and U in nuclear waste could also be performed by this novel adsorbent.¹⁷³

4.3. Metal–organic frameworks

Metal–organic frameworks (MOFs), also known as porous coordination polymers (PCPs), are multifunctional materials emerging as promising candidates in a multitude of different applications.²¹² MOFs consist of metal nodes and organic linkers and owing to self-assembly *via* strong bonds between the metal-containing moieties and the organic linkers, these synthetic crystalline materials have high porosity, large area-to-mass ratios and ideal flexibility in tuning both their pore size and shape from the microporous to the mesoporous scale.^{213–215} For example, a MOF reported by Farha *et al.* in 2012 with a BET area of $7000 \text{ m}^2 \text{ g}^{-1}$ and a computer simulated surface area of $14\,600 \text{ m}^2 \text{ g}^{-1}$ has the largest surface area of any porous material reported to date.^{216,217}

For considering MOFs as an adsorbent in an aqueous environment, their behavior in the presence of water might be taken into account because they may undergo hydrolysis.^{213,215,218}

The metal–ligand coordination bonds make MOFs more susceptible to hydrolysis than other covalent materials such as activated carbon and zeolites. However, this issue has been addressed in recent literature and to date a growing number of highly stable MOF structures have been reported.^{219–221} In addition to their excellent stability under harsh conditions, MOFs can be synthesized on a large scale through affordable and simple techniques, which make them an emerging class of adsorbents to tackle environmental pollution, with outstanding efficiencies in the removal of heavy metals.²²² MOFs have mainly been used for the removal of As, Cd, Cr, Pb and Hg from wastewater.^{217,223}

There are five different modification strategies for improving the heavy metal adsorption performance of MOFs. These approaches consist of (i) using large organic linkers to improve porosity, (ii) introducing defects in the structure in order to increase their pore size and produce additional adsorption sites, (iii) and (iv) functionalization of metal nodes and organic linkers to produce additional adsorption sites and improve selectivity compared to the pristine MOFs, and (v) hybridization of MOFs with other functional materials, such as magnetic materials, to benefit from their properties and synergistic effects.²²²

In one pioneering work, Sun *et al.* synthesized a water-stable MOF/polymer composite with environmentally and biologically friendly materials. This composite consists of 1,3,5-benzenetricarboxylate (Fe-BTC), alternatively known as MIL-100, as a MOF and polydopamine (PDA) as a polymer phase. Fe-BTC/PDA composites showed superior heavy metal adsorption efficiencies, as high as 99.8% with adsorption capacities of 1634 mg of mercury and 394 mg of lead per gram of composite. Besides high separation performance in short time, these novel composites are regenerable and present high stability in water and against fouling.²²⁴

In addition to high adsorption capacity, another important feature of MOFs is that their pore window can range from 0.3 nm to over 10 nm, depending on composition. This makes it possible to fabricate nanofiltration membranes based on MOFs as separating agents.^{225,226} For instance, an amino functionalized MOF/GO composite was used to decorate a PDA-coated substrate surface to produce NF hybrid membranes with a Cu^{2+} rejection of 90% and a flux of $31 \text{ L m}^{-2} \text{ h}^{-1}$ at a pressure of 7 bar.²²⁷ The excellent adsorption efficiency, the high capacity and the possibility of tuning their pore size down over more than an order of magnitude make MOFs emerging water treatment materials with a broad range of applications.

4.4. Emerging membrane technologies

Electrospun nanofiber membranes are a new generation of membranes, which can efficiently be applied to heavy metal removal. Owing to their high surface-to-volume ratio, high porosity, and small pore sizes once processed into membranes, nanofibers with diameters of less than 100 nm can be efficiently used to provide filtration and adsorption together. Among the various methods for producing high performance nanofiber membranes, such as melt fibrillation, gas jet techniques and electrospinning, the last method could be used to produce membranes with higher porosity compared to

conventional membrane systems, such as RO and NF.²²⁸ Chitpong and Husson synthesized ion-exchange cellulose acetate nanofiber membranes by grafting poly(acrylic acid) (PAA). The separation results showed a superior Cd²⁺ adsorption capacity of up to 160 mg g⁻¹, well above that of traditional ion-exchange media.²²⁹

Forward osmosis (FO) is another emerging membrane technology for water reuse and desalination, which has drawn increasing attention in recent years. The driving force is the osmotic pressure difference between the draw solution (DS) and feed solution (FS), so that water transports naturally through the semi-permeable membrane. Compared to RO, FO does not need high pressures, and the membrane is less prone to fouling.⁵³ Cui *et al.* synthesized novel TFC FO membranes by interfacial polymerization on a polyimide support. In order to minimize reverse solute flux, bulky hydroacid complex Na₄ [Co(C₆H₄O₇)₂].2H₂O (Na-Co-CA) was used as a DS.¹⁷⁸ Eventually, the proposed FO system showed a high water flux of up to 16.5 L m⁻² h⁻¹ and superior rejections, up and beyond 99.7%, for six heavy metals *i.e.* Cd²⁺, Pb²⁺, Cu²⁺, Hg²⁺, As³⁺ and Cr⁶⁺.¹⁷⁸

Size-exclusion based last generation membranes represent a very fast-evolving sector of water purification technologies, including from heavy metals, due to the emergence of new classes of functional materials, such as the highly selective membrane protein aquaporin,²³⁰ or graphene nanosheets designed to perform tunable sieving of specific ions.²³¹ A recent review discusses in detail the evolution in materials science behind last-generation membranes and the reader is addressed to that review for a comprehensive discussion on the topic.²³²

Recent developments in supramolecular chemistry and engineering as well as related analytical techniques have allowed mimicking natural biological structures for water purification. These inspired biological membranes benefit from either biological elements or bio-related concepts and could present similar efficient water purification mechanisms to those evolved by nature over billions of years.²³³ Since Agre *et al.*'s discovery of aquaporin, who were awarded Nobel prize in 1993, this membrane protein has become the most known biomolecule allowing exclusively water gating through biological membranes.¹³⁰ Aquaporin-based membranes were therefore made by incorporation of this membrane protein into the matrixes of amphiphilic molecules, such as lipids or polymers deposited on the surface of polymeric membrane substrates, thus mimicking the natural cellular membrane, where aquaporin naturally occurs.²³⁴ The separation mechanism in aquaporin membranes is based on the combination of size exclusion *via* channels of 0.28 nm, electrostatic repulsion by positively charged arginine residues, which repel positively charged ions from the surface of membranes, and water dipole reorientation, which facilitates individual water molecules' transport.²³³ Nowadays, aquaporin membranes are commercially produced by a Danish company, Aquaporin A/S, and are mainly used in RO and FO processes.^{235–238} In one of the related works, Xia *et al.* achieved water fluxes

of 8.8 L m⁻² h⁻¹ with low reverse salt fluxes of 4.0 g m⁻² h⁻¹, by use of the aquaporin membrane in a model FO process.²³⁵

Among the new families of adsorbers recently proposed in both the literature and market, protein-based amyloid nanofibrils have been shown to play a potential leading role in heavy metal removal, offering a solution, which is simple, efficient, low cost and sustainable.²⁴ Amyloid nanofibrils exploit the ultra-high surface-to-volume ratio, combined with the multitude of available essential amino acids offering simultaneously twenty distinct metal-ligand binding constants to heavy metals.^{16,24} The distinct advantages of this new technology are the possibility of removing non-specifically a high number of metal ions simultaneously, with demonstrated efficiencies as high as 99.98% for gold, 99.5% for mercury, 99.97% for lead, 99.84% for palladium, 99.35% for radioactive uranium²⁴ and more than 98.6% for both arsenate and arsenite,¹⁶ the last being particularly difficult to remove by size exclusion technologies such as RO and NF.¹² Possibly, however, the most appealing aspect of this new class of adsorbers is their extremely low cost: when produced from whey protein, which is a by-product waste from the cheese-making industry, amyloid fibrils stand as unchallenged adsorbers from a sustainability and environmental fingerprint perspective.²⁴ Furthermore, the scale up process of amyloid-carbon hybrid membranes is possible on an industrial scale due to their inexpensive nature. These hybrid membranes can provide cost effective and highly efficient solution for removing various pollutants (heavy metal ions and biological pollutants) from both industrial and drinking water. Additionally, recovery of precious and rare earth metals, such as those found in mining and electroplating wastewater, is at easy reach using these hybrid membranes by chemical or thermal reduction of metal ions to elemental metals.²⁴

Recently, there has been a significant increase of interest in fabricating new classes of membranes by molecular design of selective layers. Lyotropic liquid crystal (LLC) membranes based on amphiphilic lipids with controlled pore size are considered as a new generation of polymeric membranes.^{239–244} The molecular precursors used to generate LLC by self-assembly are amphiphilic molecules with hydrophilic head groups and hydrophobic organic tails. These molecules in the presence of an immiscible liquid, typically water, can self-organize into ordered structures with continuous aqueous domains and uniform feature sizes of 1–10 nm. LLC phases are categorized on the basis of packing symmetry of the ordered domains and water content. On the basis of the first criterion, the most common phases are bicontinuous cubic (Q), lamellar (L) and hexagonal (H); on the basis of the second criterion they are water-excessive (type I) or water-deficient (type II).²³⁹

L. Gin *et al.* have pioneered the use of LLC membranes for water purification and showed that a type I and Q phase (with either the *Ia3d* or *Pn3m* symmetry) is the best LLC phase for fabricating membranes for water desalination applications.²⁴⁵ This QI-LLC membrane has a pore size of 7.50 Å which is around the metal ions' hydrated diameters but larger than water molecules of size 2.75 Å. This feature enables this

membrane to separate metal ions from water molecules very efficiently. The QI-LLC membrane rejection for Na^+ ions was 95% and for Ca^{2+} and Mg^{2+} ions was higher than 99%. The thickness-normalized water permeability of QI-LLC membranes was $5.9 \times 10^{-2} \text{ L m}^{-2} \text{ h}^{-1}$ at 400 psi, which is comparable to the reported fluxes for typical RO membranes at this pressure.²⁴⁰

4.5. Electrocoagulation

Another emerging technology for heavy metal removal is electrocoagulation (EC), which is a combination of coagulation, flotation and electrochemistry. As for coagulation/flocculation, EC benefits from destabilizing the system by neutralizing the repulsive forces between particles, resulting in the aggregation of particles and subsequently formation of larger particles, which are then easily separated from water. The major advantage of EC compared to chemical coagulation is that there is no need to add external chemical coagulants such as metal salts or polyelectrolytes and coagulants are generated *in situ* by the electrolytic oxidation of a sacrificial anode electrode by applying electric current through the electrodes.^{246,247} Conversely, in some chemical coagulation processes there is a need to add up to three chemicals and pH adjustment for achieving the best performances, which makes chemical coagulation expensive and labor-intensive.²⁴⁸ Typically, EC electrodes are made of aluminium and iron due to their availability, low price, high valence and non-toxicity;^{247,249,250} however, in a recent study by Gilhotra *et al.*, arsenic was removed from water successfully by the EC process using stainless steel electrodes.²⁵¹

Chen *et al.* removed zinc ions from wastewater by EC using aluminium electrodes. Their findings showed that current density is the key parameter in zinc removal efficiency and EC energy consumption, by affecting the production of Al^{3+} and speed of coagulant formation. They performed the experiments with a wide range of initial zinc concentrations, from 50 to 2000 ppm. Higher removal efficiencies were obtained at lower concentrations, which shows that it is more favourable to use EC as a final treatment step after given pre-treatments. In this process, besides the precipitation by aluminium hydroxide, electrochemical reactions by reduction of Zn^{2+} at the cathode also play an important role.²⁵² Furthermore, effective separation of iron from wastewater following a similar EC process was demonstrated in another work by Doggaz *et al.*²⁵³

4.6. Capacitive deionization

Capacitive deionization (CDI) can separate and recover heavy metal ions and salt ions from wastewater using electrodes and an electric field. This technology could separate and remove Pb^{2+} and Na^+ with efficiencies as high as 99.9% and 98.7%, respectively, at an operating voltage of 1.4 V. Selective electrodes and addition of selective ion exchange resins on the surface of electrodes are some of the emerging approaches for the removal of target heavy metal ions.²⁵⁴

5. Concluding remarks

In this work, we have reviewed and evaluated the most established technologies in water treatment from heavy metal ions,

by considering technical characteristics, efficiency performance and sustainability aspects. The picture emerging is that a single technology, which can offer alone a universal solution to the multiple facets of water pollution from heavy metals in the broadest possible context, is still to be found, and possible combination of different technologies may significantly expand the portfolio of solutions to the existing water problems. Furthermore, it is important to note that there is not a single technique that can perform at a nominal, perfect 100% efficiency under real conditions. In the case of adsorption and ion exchange, this limit is thermodynamically forbidden by the equilibrium nature of the process between bound and unbound ions on a physical adsorption/exchange surface; in the case of size exclusion technologies, the nominal 100% efficiency is impeded by defects present on real membranes, which lead to small, yet not negligible leakage. Nonetheless, technology is progressing at such a speed that today the theoretical 100% efficiency limit is asymptotically, yet rapidly being approached through the design of new generations of high performance membranes or adsorbents and resins with unprecedented strong binding constants. Thus, efficiency is no longer the main discriminant for implementing a specific technology in water purification, at least among the considered technologies, which are all available at efficiencies exceeding 99.9% among the literature we have reviewed.

While improvements have been extremely rapid on the technical side, the cost, affordability and sustainability aspects of each technology have progressed at a much slower pace. The reasons behind this are multiple and diverse. For example, while application of nanomaterials in water and wastewater treatment is steadily increasing, there are also growing concerns about their potential toxicity to the environment and human health. In fact, gold standards for assessing the toxicity of nanomaterials are still relatively scarce at present times. Hence, comprehensive evaluation of the potential toxicity of nanomaterials is an urgent need to enable and secure the full use of nanomaterials in real water treatment applications. Established and widely accepted technologies, such as reverse osmosis, nanofiltration and electrodialysis, are still characterized by high capital and operating costs, and improvements along these lines are still highly sought for these technologies. Adsorption and ion exchange have significantly lower costs while maintaining high efficiencies, although ion exchange remains highly ion-specific.

In order to provide a compact assessment of the various technologies we have sorted out a rank for each individual characteristic of interest and a compact ranking efficiency product has been proposed as a simple tool to evaluate individual technologies against specific criteria. In the present analysis, nine different intrinsic characteristics have been considered and evaluated so as to maintain an equilibrium between performance and sustainability, but the method proposed is simple and general enough to be easily adaptable to varying scenarios describing any potential case of water purification. Despite all these efforts, it must be highlighted that water purification remains a very diverse, complex problem

with many case-specific discriminants, and any attempt at ranking a process over another, despite its comprehensiveness, can only be taken as a guidance, each water treatment problem remaining highly specific to the context in which it has to be performed.

Sorting method

In order to sort the ranking of each characteristic i for the five technologies j considered, the various values a_{ij} in Table 2 have been processed as follows. First, when a range is available for a_{ij} , the best value of the range is systematically used ($\max a_{ij}$ for E, Q, n, R ; $\min a_{ij}$ for O, C, W, P) in order to evaluate each technology according to the best performing conditions. For the total cost T , average values have been considered. For the efficiency (E measured in decimal), because additional digits after zero are particularly important to target higher orders of magnitude in contamination of polluted water, entries were reprocessed by taking $-\log_{10}(1 - a_{ij})$, that is, $-\log_{10}(1 - E)$. Similarly, the operating flux, which presented the highest differences among the various technologies considered, was reprocessed by taking $\log_{10}(W)$. Proceeding as above, a single value A_{ij} for each characteristic i among each technology j is generated. Then, to order each A_{ij} value according to ranks between 1 and 5 (5 best, 1 lowest performing) for any given characteristic (fixed i), the maximum value per characteristic is first taken as the reference value $(A_{ij})_{\text{MAX}}$ and the incremental step of a characteristic i is then generated by taking this reference value divided by 5 ($(A_{ij})_{\text{MAX}}/5$). For favorable characteristics (E, Q, n, R), the final ranks r_{ij} are obtained by dividing each value by the corresponding incremental step $[(A_{ij}/(A_{ij})_{\text{MAX}}/5)]$ of the characteristic and approximating to the closest integer between 1 and 5, i.e. $r_{ij} = \text{integer} \lfloor 5A_{ij}/(A_{ij})_{\text{MAX}} \rfloor_1^5$. For unfavorable characteristics (O, C, T, W, P), the final rank is obtained as $r_{ij} = 6 - \text{integer} \lfloor 5A_{ij}/(A_{ij})_{\text{MAX}} \rfloor_1^5$, that is, the complementary integer to reach 6 (e.g. an intermediate rank 1 becomes 5; an intermediate rank 2 becomes 4).

Author contributions

S. B. and M. P. performed the literature search. R. M. performed the sorting and ranking analysis. All authors wrote the manuscript.

Conflicts of interest

The authors declare no competing financial interests.

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