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A review on water decontamination methods and future research trends

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Abstract. Pollution with heavy metals has become a dangerous threat due to global industrialization. The main sources that lead to the release of these pollutants in the environment are: agriculture, industrial wastewaters, mining and metallurgical processes. Moreover, armaments and ammunition industry also cause significant water pollution with heavy metals. In military sites, the highest degrees of heavy metals pollution were found in the proximity of shooting and test ranges. This study investigates a selection of modern methods for the decontamination of fresh water (or seawater), for a better comprehension of the mechanism of interaction between heavy metals and the environment and also for the investigation of the efficiency of the materials employed for decontamination. In addition, several proposals for improving the current water decontamination methods are presented herein together with some new methods that can become more effective in this field.

1. Introduction

Nowadays, even if the population has more and more access to drinking water, 1.8 billion people obtained access to basic services and the number of people collecting water directly from surface water sources reduced from 256 to 144 million according to World Health Organization and UNICEF reports, the potable water issue remains one of the greatest problems of humanity [1].

The process of water pollution is carried out through activities that introduce unwanted substances, intentionally or accidentally, into the water, subsequently changing the water quality and its composition and becoming toxic to humans and the environment [2]. Water plays a double role in urban development. The first is that aquatic systems are used as a sewerage system for the disposal of urban and industrial waste and the second is that water is used in various development activities such as agriculture, construction activities, industrial processes and nuclear power plants, to meet the needs of a growing population [3].

The main sources of water pollution are heavy metals, pesticides and radioactive materials [4]. Pesticides in the form of herbicides, fungicides, insecticides, rodenticides and fumigants are used in agriculture, being necessary to increase food production for a substantial growing demand [5]. The processes that use pesticides in agriculture are those to keep away weeds and unwanted pests [6]. The extensively use of pesticides in agriculture causes negative effects on the environment and organisms by contaminating them through runoff, leaching and spray drift [7]. Thus, in 2001 the Stockholm Convention established the elimination or minimization of the use of persistent organic pollutants (POPs) that have as negative characteristics in the environment the fact that they are toxic, persistent, bioaccumulative and have long-range environmental transport [8]. Although they can be found in the environment in low quantities, POPs are toxic and persistent substances that affect fauna and flora that are exposed to these substances. These compounds can be ingested or entered via the skin, thereby they are accumulated in the trophic chain. Because they can cause severe health problems for both animals and humans, POPs are a problem and their use must be regulated and minimized [9].

Another problem in water decontamination is radioactive pollution that occurs mainly from nuclear facilities, nuclear power plant waste or nuclear weapon testing. The most common radioisotopes that require removal from the environment because they have negative effects on human health are: Uranium (U), thorium (Th), radium (Ra), polonium (Po), strontium (Sr-90), cesium (Cs-137) or cobalt (Co-60) [10]. The half life of these radionuclides has a great significance in establishing the toxicity, therefore the most hazardous are long-lived isotopes like Cs-137 (half life of 30.17 years), Sr-90 (half life of 28 years) and Co-60 (half life of 5.27 years). Considering that they have a high transferability, high solubility and easy assimilation in living organisms these are considered the most harmful radionuclides. Although, naturally occurring uranium is not a problem for the environment it also been used as a nuclear fuel and can be found in radioactive liquid wastes. Radium-226 (Ra-226) is frequently found in the tailings and Thorium (Th) is used in medical applications or in U-233 production. Long-lived radionuclides are considered the most dangerous to human health due to their high transferability, high solubility, long half-lives and easy assimilation in living organisms among the fission by-products. Cs has a chemical similarity with potassium (K) and Sr with calcium (Ca), therefore Cs-137 and Sr-90 can transfer without difficulty and they have hazardous effects if they are in contact with the human body [11].

In the majority of situations, environmental pollution occurs due to heavy metals, that can contaminate water, soil and air. Environmental contamination caused by various metals such as: (Cd, Pb, Cr, Hg, Zn, Cu, Ni, Al, Fe, Mn, As, and Co) has been intensive studied, since it represents a serious threat to ecosystem and human health [12]. However, according to toxicological criteria, lead (Pb), mercury (Hg) and cadmium (Cd) possess the most dangerous impact on environment [10]. As a consequence of their high toxicity, prevalent existence and persistence in the environment of Pb, Hg, Cd, Cr and As should become a priority in water decontamination domain. Meanwhile, Ni (nickel) and V (vanadium) are extensively used and even though Cu and Zn are common metals and essential elements, they can also be toxic in high concentrations. Although they would not pose environmental threats, gold (Au), silver (Ag), palladium (Pd), and platinum (Pt) are noble or precious metals, thus being important to be recovered from diluted solutions [11]. Table 1 summarises the categories of compounds/elements which can constitute a water pollutant.

2. Decontamination treatments

Heavy metals are toxic because they are not biodegradable and can accumulate in the living beings, therefore they require particular treatment in the process of water decontamination. Furthermore, the simultaneous removal of several types of heavy metals has a lower efficiency than the decontamination of a single type of metal [4]. Lead is amongst the metals that contaminates water, which creates bonds with the elements in the blood and can affect the kidneys, brain and nervous system of the living organisms [13]. However, another trace element that is harmful for humans and the environment is cadmium. Plants can accumulate Cd and this has a negative impact on soil organisms and soil ecology. The main toxic effect of Cd in human health targets the kidney or renal cortex, but other adverse health effects on pulmonary, cardiovascular, and musculoskeletal systems have also been reported, including Cd as a human carcinogen. Being introduced into the human diet, it can affect organs such as: kidney, lungs, heart, the muscular and skeletal system [14]. Even though people need Zn for a normal functioning of the body, in significant quantities it can cause health problems such as stomach cramps, vomiting, nausea, skin irritations and anemia, and at higher levels of Zn, it can even lead to arteriosclerosis and respiratory disorders [13]. Similar to Cd, Ni is carcinogenic and in addition, at high concentrations in the organism can cause kidney, gastro-intestinal, lungs and skin (dermatitis) problems [15]. Moreover, Hg poisoning can cause lung and kidney function failure, chest pain and dyspnea [16]. Pb can cause anemia, insomnia, headaches, dizziness, irritability, muscle weakness, hallucinations and kidney damage by affecting the liver, reproductive system and brain [17]. Cr is introduced into the body through diet because it bioaccumulates and in high quantities it can pose minimal health concerns such as skin irritation, but it can also lead to serious health problems as lung carcinoma [18].

Table 1. Types of water pollutants

Pesticides [19]	Radionuclides	Heavy metals [4]
Insecticides	*Nuclear power* [20]	Cu, Cu^{2+}
Organophosphates	*Activation Products*	Pb, Pb^{2+}
carbamates	Co-58, Co-60	Cr, Cr^{3+}, Cr^{6+}, $CrO4^{2-}$, $HCrO_4^-$
Organochlorines	*Fission Products*	Cd, Cd^{2+}
Pyrethrins pyrethroids	Sr-90	Co, Co^{2+}
Herbicides	Y-91	Ni, Ni^{2+}
Dipyridyl	Zr-95	Mn, Mn^{2+}
Chlorphenoxyacetate	Tc-99	Ag, Ag^{+}
Fungicides	Ru-106	Hg, Hg^{2+}
Chloroneb chlorothalonil	I-129, I-131	As, As^{3+}, As^{5+}, $HAsO_4^{2-}$
Thiocarbamates	Cs-134, Cs-137	Au, Au^{3+}
Organomercurials	Ce-144	Pd, Pd^{2+}
Rodenticides	*Neutron Capture Products*	Zn, Zn^{2+}
Aluminium phosphide	Pu-239, Pu-240, Pu-241	Ca, Ca^{2+}
Zinc phosphide	Am-241	
Warfarin and superwarfarin compounds	*Nuclear medicine* [21]	
Thallium-containing pesticides	Tc-99m (Technetium)	
Yellow phosphorus	Ga-67 (Gallium)	
	In-111 (Indium)	
	I-123 and I-131 (Iodine)	
	Tl-201 (Thallium)	
	F-18 (Fluorine)	
	N-13 (Nitrogen)	
	Rb-82 (Rubidium)	
	C-11 (Carbon)	
	Lu-177 (Lutetium)	
	P-32 (Phosphorus)	
	Re-186 (Rhenium)	
	Sm-153(Samarium)	
	Sr-89 (Strontium)	
	Y-90 (Yttrium)	

This study will focus only on the issues caused by heavy metals in the environment, because the decontamination of water of is a complex problem. Thus, heavy metal polluted waters treatment methods may vary, based on the type of metal that needs to be removed. In order to achieve this objective, a large number of methods for decontamination of toxic materials have been studied and developed. There are physical, chemical and biological approaches for heavy metal removal/recovery, as an instance: ion exchange, electrochemical methods, chemical precipitation, adsorption, coagulation, membrane filtration, flocculation, flotation, etc [22]. Then, polluted water treatment technologies can be divided into three classes, as indicated in Table 2.

The quality of the water used in households and in the aquatic environment is very important for a healthy life. There are no flawless methods for water decontamination, so this topic is intensively investigated. The methods of removing heavy metals are effective only under ideal operating conditions (a certain pH and a certain concentration of pollutants), but in industrial conditions it decreases from around 99% to 90%. In addition to this detrimental point, the simultaneous decontamination of several types of ions also decreases the efficiency of the method, which is reduced up to 80% or less [4].

Table 2. Heavy metal polluted water treatments [11]

Chemical reaction for metal removal	Chemical precipitation Chemical reduction Electrolysis
Sorption/enrichment/ separation processes for metal removal without alteration of metal state	Active carbon Adsorption Extraction Ion exchange Reverse osmosis Electro dialysis Evaporation
Biological process with adsorption	Biosorption Bioflocculation Constructed wetlands

In order to convert polluted water into clean water, this must go through several stages that involve numerous types of processes and in which different technologies are involved. These can be divided into 3 categories: primary, secondary and tertiary treatments. These methods aim to decontaminate the water from inorganic, organic and biological pollutants. Since secondary biological treatments use aerobic and anaerobic degradation treatments and target the removal of organic pollutants, they will not be mentioned here [4]. Figure 1 shows a flow chart summarizing the most popular methods of decontamination of heavy metals from wastewater, that will be detailed below.

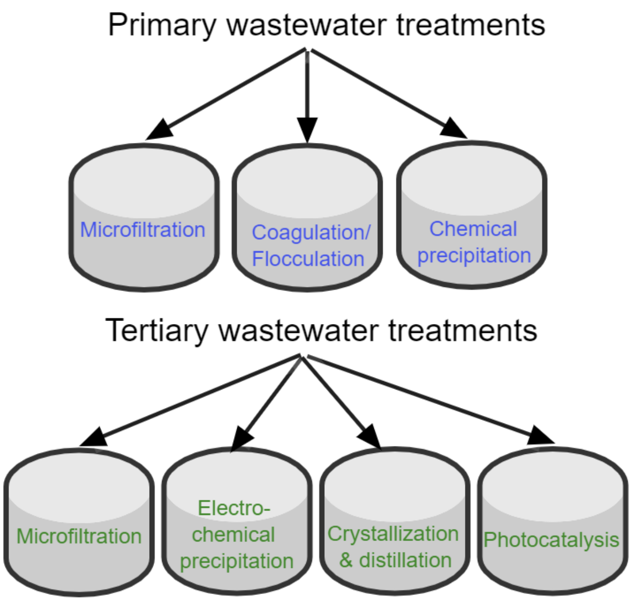

Figure 1. Heavy metals removal methods

3. Primary wastewater treatments

Primary treatments consist in simple and inexpensive technologies. Even if they have lower yields than tertiary treatment methods, they can significantly reduce the amount of heavy metals, having the advantage that they are less expensive.

3.1. *Microfiltration*

The first step in microfiltration is the rapid binding of metals to selective binding agents (chelates) to form precipitating or floating compounds. Then, the contaminated water is filtered through different membranes (polymeric membranes, polymer-ceramic membranes, electrospinning nanofiber membranes, and nano-enhanced membranes) that retain metal complexes [23].

3.2. *Coagulation and Flocculation*

Due to the fact that is an inexpensive method, it is used to treat wastewater resulting from textile industry, but its efficiency depends on the amount of flocculent added and the pH of the solution. Metal polluted waste water can be treated through coagulation flocculation methods that can eliminate colloidal particles, soluble compounds and solid suspension [24]. Initially, positively charged coagulation agents are added to wastewater (aluminum sulfate, aluminum salts, ferric chlorides, polyferric sulfate) which stabilize the colloidal particles (with sizes between 0.001 and 1 micron) that are negatively charged and exhibit Brownian motion.

3.3. *Chemical precipitation*

Considering it involves low costs and good results, chemical precipitation is widely used in decontamination of heavy metals from wastewater. Through this process water-soluble metals are removed. By adjusting the pH of the wastewater, heavy metals reach the lowest point of solubility, which decreases with increasing pH. Thus, alkaline agents (lime or caustic soda) are added so that the metal ions precipitate out of the solution in the form of hydroxides. The problem with these methods is that they form a residue that requires further expensive treatments [25].

4. Tertiary wastewater treatments

Even if the effectiveness of the primary treatment for heavy metals decontamination from wastewater is reasonable in the first phase, however, in order to be able to discharge water into rivers or oceans, to reuse it for recreational purposes or as potable water, it must undergo supplementary processes. Through tertiary treatment, the amount of heavy metals can be further reduced, reaching acceptable levels of contamination, situated below the levels regulated by law [26].

4.1. *Chemical oxidation*

The purpose of chemical oxidation is represented by the structural transformation of certain pollutants (usually organic, but also iron and magnesium) so that they are less harmful or harmless. The degradation of these compounds is performed by introducing oxidizing agents such as ozone, hydrogen peroxides, permanganates, persulfates, etc. into the wastewater, which cause electrons to move from oxidant to pollutant and convert it to inorganic salts [27]. Because it is a reliable and cheap technology, it is widely used, but it also has the disadvantage of producing secondary pollution [4].

4.2. *Electrochemical precipitation*

Through the electrolysis of effluents, heavy metals can be removed by electro-plating process, by collecting them on a cathode and then extracting them in the metal form, without forming by-products. Electrochemical precipitation is a clean and low-cost treatment. It has a low efficiency compared to other tertiary processes, therefore it is a less used method [28].

4.3. *Crystallization and distillation*

In this process wastewater is brought to a boiling point, then the vapours are condensed and separated from the residue, which is concentrated and crystallised becoming salts [4].

4.4. *Photocatalysis*

Photocatalysis is one of the advanced oxidation processes used for the removal and recovery of heavy metals that. This process can ensure both oxidation and reduction of metal ions. It is based on the absorption of light from a UV source by the surface of the photocatalyst which as a result generates free radicals. Factors that may influence the efficiency of decontamination by photocatalytic treatment are: pH of the solution, initial concentration of metal ions, light intensity and mass of the photocatalyst.

5. Evolving and future trends in heavy metals decontamination

The provenience of the wastewater and the contaminants contained, impose the selection of a certain technology to be adopted for decontamination. Besides the classical decontamination methods listed above, three new decontamination technologies, membrane separation methods, microalgal adsorption method and microbial fuel cells, are detailed below. These relatively new, promising technologies, have already been successfully used for heavy metals decontamination, proving their efficacy.

5.1. Membrane separation methods

This method of decontamination is used for the separation of the heavy metals from the waste waters through a filtration technique which implies the use of a performant especially designed membrane. Membranes usually consist of a thin sheet barrier employed for the separation of particles with a well-known dimension, but they can also possess chemical functional groups or microorganisms, that can enhance the decontamination efficacy through a better interaction with the contaminant. Membranes are sometimes used as a standalone system in secondary treatment of wastewater. The permeation of a membrane and the selective rejection depend on the size of the pores inside the membrane and also on its chemical structure. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) or forward osmosis (FO) are the main membrane technologies used for the purification of the wastewaters. Both MF and UF sometimes serve as pre-treatment for NF and RO procedures, in order to reduce the fouling of membrane. A particular example of membranes highly efficient for heavy metals removal are ion exchange membranes (IEM): anion exchange membrane or cation exchange membranes. Depending on the type of effluent, membranes can be employed for heavy metals removal through: electrodialysis (ED), reverse electrodialysis (RED), diffusion dialysis (DD) and the Donnan membrane process (DMP). All these processes involve the exchange of ions between solutions across the employed membrane [29].

5.2. Microalgal adsorption methods

Some algal consortia demonstrated efficient heavy metals removal from the wastewater. Specific microalgal strain / microalgae consortium can be selected to treat a given wastewater source. Besides the remarkable capacity of microalgae to isolate organic contaminants, microalgae also remove heavy metals from waste waters, thus preventing secondary pollution. Even if this method has proved its efficiency, there are also some drawbacks to be mentioned: many of the highly efficient microalgae cannot be easily filtered and need to be separated through centrifugation, which is a more expensive operation; algae can be harvested by sedimentation, but this is a slow process and requires considerable time and space resources; metal salts could be used as flocculants to facilitate sedimentation, but this results in subsequent water contamination [29].

5.3. Microbial fuel cells

An microbial fuel cell (MFC) is a device that converts matter to electricity, using microorganisms as biocatalyst. Many recent studies have demonstrated that several biological processes can be used to produce bioenergy or bio-chemicals at the same time as treating industrial wastewater. For this purpose, microbial fuel cells (MFCs) are used to simultaneously treat wastewater and produce bioenergy in the form of bioelectricity, by converting the organic and chemical energy contained in wastewater to electrical energy. The advantages of MFCs in wastewater treatment include: sustainability, use of renewable sources, degradation of organic and inorganic waste, bio-hydrogen production and an efficient removal of contaminants. The successful removal and recovery of heavy metals through biocatalytic and electrochemical reduction in the cathodic chamber of MFCs had also been reported in literature [29].

6. Conclusions

Even though there is a wide range of methods for removing heavy metals from wastewater, the most efficient method remains the chemical precipitation in which lime is used as a pH changer. However, in recent years the regulations on the quantities of heavy metals are becoming more rigorous, so new innovative methods of decontamination of polluted water are needed. They must take into account that the treatments must be inexpensive, simple and cost effective. Photocatalysts-based treatments have a promising future in the field, but they require to accomplish some parameters in order to be effective, such as: pH, initial metal concentration, treatment performance compared to other technologies, environmental impact and economic impact [30].

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