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## Chapter

# Heavy Metals Removal from Water and Wastewater

*Lavinia Lupa and Laura Coheci*

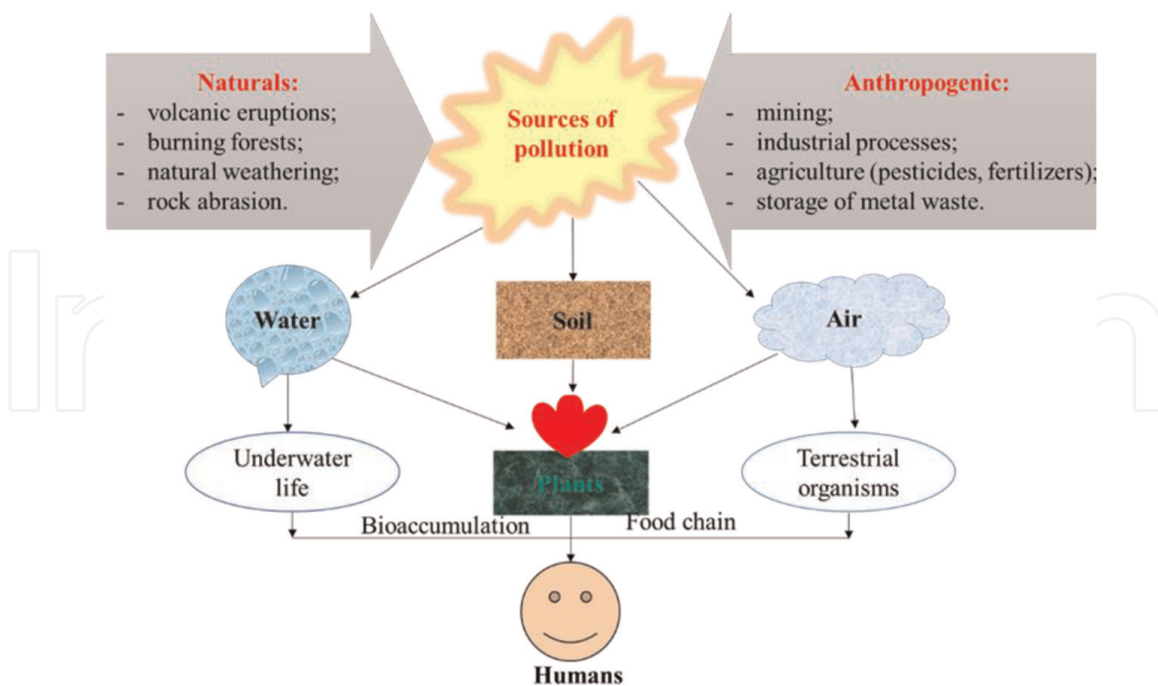
## Abstract

The chapter summarizes the main treatment processes used for the removal of heavy metals from water and wastewater. Heavy metals present a recalcitrant and persistent character, a bioaccumulating ability in the environment, therefore their removal from water and wastewater represents a worldwide concern. This chapter reviews the recent advances and technical applicability of the methods that have been used to treat heavy metal-containing water. The discussed technologies include chemical precipitation, coagulation-flocculation, flotation, ion exchange, adsorption, membrane filtration, and electrochemical methods. The main advantages/disadvantages and limits of each method are evaluated. It was observed that even if a lot of research on each mentioned method in practice is still necessary for intensive work for each case. In all methods, there are things that could be improved; therefore, future studies must be focused on the development of cost-effective materials and methods that involve low treatment costs, high efficiency, and minimal impact on the environment.

**Keywords:** heavy metals, water, wastewater, environmental issues, removal processes

## 1. Introduction

Metals present numerous benefits for everyday life. They have contributed to the development of civilization, to the modernization and development of industries. In some cases, they are essential for maintaining the metabolism of the human or animal body, or they are indispensable in the growth of plants as microelements [1, 2]. However, if metals exceed certain concentration levels (even trace amounts), they can contribute to environmental pollution and can lead to devastating effects on living organisms [3, 4]. **Figure 1** shows the main sources of metal pollution and their transport through an environment. Water is the most responsible environmental factor, with the help of which the heavy metals present at improper concentrations can reach living organisms. Furthermore, heavy metals have the property of bioaccumulation since they could not be biodegradable, leading to critical health issues [5–7]. Therefore, water pollution with heavy metals represents a global concern and the World Health Organization (WHO) established the maximum admitted level of heavy metal concentrations in drinking water [8].



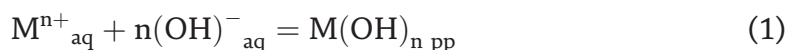
**Figure 1.**  
Sources and transport of heavy metals through an environment.

The removal of heavy metals from water sources or wastewater before discharge is an important problem that must be carried out to minimize pollution, reduce their interference with beneficial uses, and eliminate their negative effects on the environment. In some cases, in addition to eliminating the toxic effect of the metals present in waters upon the environment, these water treatment methods also have the purpose of recovering and revaluing the metals, especially if we are talking about rare and precious metals (such as gold, silver, platinum, palladium, rhodium, ruthenium, iridium, and osmium). The present chapter summarizes the treatment methods employed for heavy metals removal, describing new advanced developments, and highlighting the advantages and disadvantages of each in terms of efficiency, accuracy, feasibility, and kinetic.

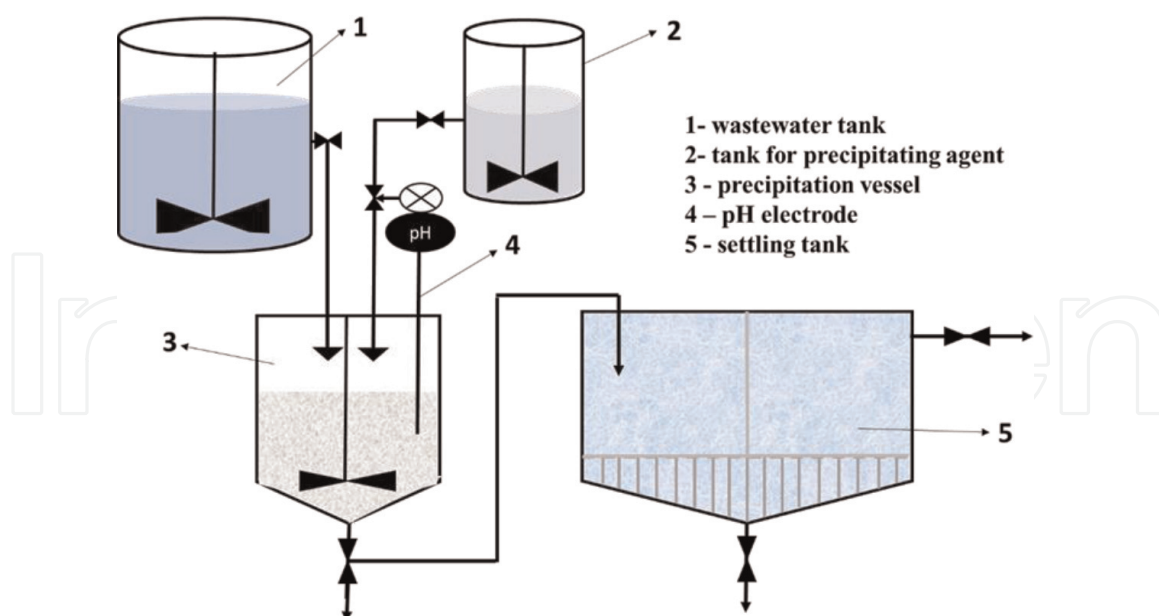
## 2. Chemical precipitation

Chemical precipitation (**Figure 2**) is the process of transforming soluble metal ions into insoluble metal compounds using various precipitating agents, such as hydroxides, carbonates, sulfides, sulfates, phosphates, chlorides, and sodium borohydride, usually followed by a separation step (sedimentation, filtration, settling, and centrifugation) [9–11].

The most frequently used method in industry is precipitation under hydroxide form. The method is based on the low solubility of metal hydroxides (reaction 1) at alkaline values of the mass reaction pH [1, 3].



The solubility of hydroxides is dependent on pH. For each metal, there are solubility diagrams that represent the graphical representation of the solubility function of



**Figure 2.**  
*Scheme of the precipitation system.*

pH, which present importance in the establishment of the pH value at which the desired metal ions present the lowest solubility [12]. Different metals have different values of the optimal precipitation pH, so maximizing the removal efficiency of a certain metal can lead to a significant decrease in the removal degree of another metal.

Sometimes for this reason it is necessary to use two stages of treatment to obtain a high removal degree of all the metals present in the wastewater. On the other hand, the fact that metals present in water precipitate at different pH values can lead to a selective separation of them. The main advantages of the method are: (1) easy of operation, could be applied without requiring a pretreatment; (2) could remove several parameters at once; (3) could be performed at ambient temperature; (4) could be automated; and (5) presents low costs if lime is used as a precipitating agent. At the same time, the method presents also some disadvantages, such as requires a high amount of precipitating agent, consequently generating a large amount of sludge (especially if lime is used as precipitating agent); the pH must be strictly controlled; does not remove complex metals; the efficiency of the separation step influence the treatment performance [13]. Among the metals that can be removed using this method, could be mentioned: iron, copper, zinc, cadmium, beryllium, cobalt, mercury, manganese, and aluminum. Chromium can only be removed if it is found in the trivalent form.

Besides pH, other parameters and factors must be considered (such as temperature, ionic strength, formation of complexes, formation of other solid phases, alkalinity, and formation of buffer solutions) because they affect the solubility of metal hydroxides and consequently the efficiency of metal ions removal through precipitation. The metal ions' solubility increases with the temperature increasing, with ionic strength increasing, or with the formation of complexes. Around the optimum pH value of metal ions precipitation under hydroxide form takes place in the formation of another solid phase, such as carbonates form. Certain anions present in wastewater from metal processing (chlorines, sulfates) can also precipitate the metals present. The carbonates and sulfates present in the water, as well as some organic anions can precipitate with the calcium ions added in the form of lime to adjust the pH. The metal

ions' solubility decreases as the formatted precipitate is subject to aging and is transformed into ideal crystals [12].

Instead of hydroxide precipitation or together with it is used precipitation under carbonates forms (reaction 2).



In contrast to metal hydroxides, metal carbonates are formed at lower values of the reaction mass pH, and present higher density, which leads to the improvement of the removal process performance. Lower metal solubilities can be obtained by increasing the carbonate dose at pH values lower than the optimal pH for the precipitation of hydroxides. The main disadvantages of this method are represented by its reduced kinetic and by the possible foaming of the reaction mass due to CO<sub>2</sub> release [14]. This method is frequently used for lead removal due to the high solubility of lead hydroxide [15, 16].

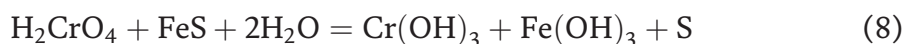
Metal sulfides are compounds that also present a much lower solubility than metal hydroxides. Thus, metal ions can be removed from aqueous solutions by precipitating them in the form of sulfides according to reactions 3–6 [1, 11, 17, 18].



For the precipitation of metals in the form of sulfides, soluble sulfides can be used, for example, sodium sulfide (Na<sub>2</sub>S), calcium polysulfide (CaS), or sodium hydrosulfide (NaHS), or insoluble sulfides, such as ferrous sulfide (FeS). The partially soluble ferrous sulfide is added as a suspension. Most metals have lower solubility than FeS, so heavy metals precipitate as sulfides, while FeS is solubilized (reaction 7). The reaction takes place around pH = 8, and Fe precipitates in the form of hydroxides [1, 11, 17].



Due to its reducing character, an important advantage of this method is the fact that FeS can be used directly in the removal process of Cr(VI) from water (reaction 8). The sulfur is oxidized to its basic state, and chromium precipitates in the form of hydroxide [19–21].



Another advantage of the precipitation under sulfide ions is the ability to direct the precipitation of complex metals. In this case, it does not require any pretreatment steps or multiple stages to remove different metals. Unfortunately, the sulfide precipitates are in the form of small particles that present poor sedimentation properties, sometimes requiring the use of coagulation agents. The main disadvantage of this method consists of the strict conditions for operation and handling of the resulting sludge due to the possibility of toxic hydrogen sulfide formation. The advantages and disadvantages of the main precipitation agents used for the removal of metal ions from water and wastewater are summarized in **Table 1**.

Precipitation agent	Advantages	Disadvantages
NaOH	<ul style="list-style-type: none"> <li>• Good kinetic</li> <li>• It is suitable for removing many parameters.</li> <li>• The process takes place under ambient conditions.</li> <li>• It could be automated.</li> </ul>	<ul style="list-style-type: none"> <li>• Expensive</li> <li>• Require high values of pH to obtain precipitates with lower solubility.</li> <li>• The pH must be strictly controlled.</li> <li>• Could not remove complex metals.</li> <li>• Treatment performance is determined by the separation stage.</li> </ul>
Ca(OH) <sub>2</sub>	<ul style="list-style-type: none"> <li>• Inexpensive</li> <li>• It is suitable for removing many parameters.</li> <li>• The process takes place under ambient conditions.</li> <li>• It could be automated.</li> </ul>	<ul style="list-style-type: none"> <li>• Require a higher amount of precipitation agent dose to achieve the optimum pH.</li> <li>• Formation of a higher quantity of sludge.</li> <li>• Could not remove complex metals.</li> <li>• Treatment performance is determined by the separation stage.</li> </ul>
Carbonates	<ul style="list-style-type: none"> <li>• Operation at lower pH values.</li> <li>• Easy sedimentation</li> </ul>	<ul style="list-style-type: none"> <li>• Slow kinetic</li> <li>• Foaming of the reaction mass.</li> <li>• Could not remove complex metals.</li> </ul>
Sulfides	<ul style="list-style-type: none"> <li>• Ability to directly eliminate Cr (VI) without other pretreatment steps.</li> <li>• Precipitates complex metals.</li> <li>• It does not require a final pH adjustment.</li> </ul>	<ul style="list-style-type: none"> <li>• Poor sedimentation characteristics.</li> <li>• It requires increased attention in the handling and storage stage of the sludge due to its hazardous nature.</li> <li>• Excess sulfides present in the effluent can lead to the development of H<sub>2</sub>S.</li> </ul>

**Table 1.**  
*The advantages and disadvantages of the main precipitation agents used for the removal of metal ions from water and wastewater.*

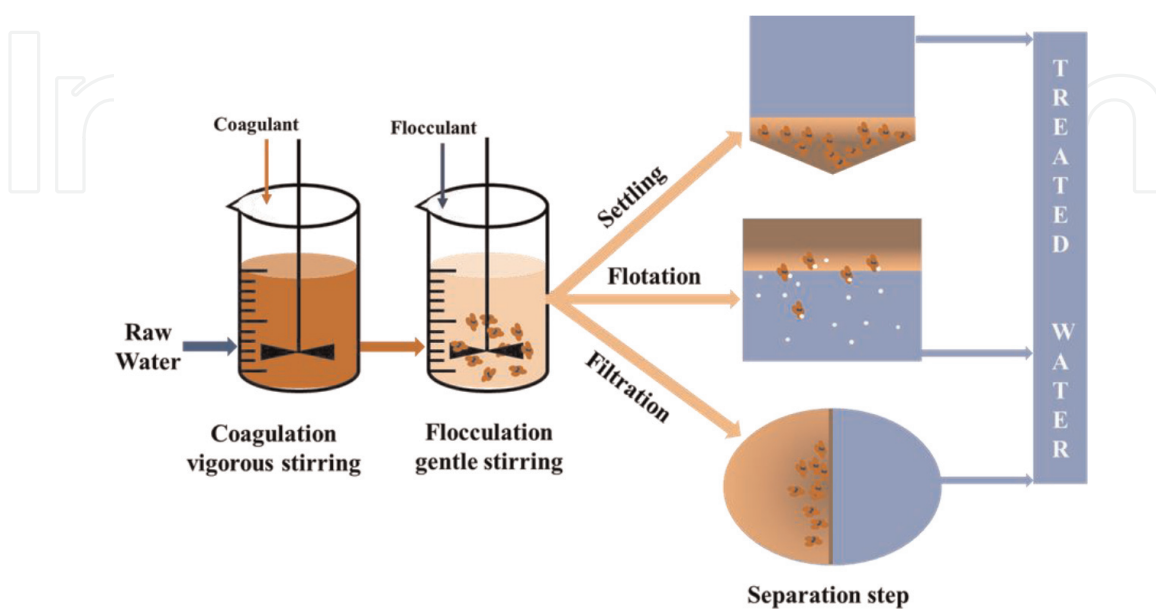
Precipitation in the form of sulfates is generally applied to remove barium from aqueous solutions [22–24]. Precipitation in the form of phosphates is generally applied for the elimination of trivalent metals (iron, aluminum, and chromium). The precipitation in the form of chlorides is particularly applied in combination with the oxidation of cyanides for the removal and recovery of silver [25]. Sodium borohydride is an effective reducing agent and is used to remove Pb, Hg, Ni, Cd, Co, Cu, and some precious metals [26, 27].

All these mentioned factors and variables that influence the precipitation raise difficulties in the evaluation of the treatment process. So that predicting the efficiency of the process requires the evaluation of a theoretical and experimental study for each individual case. For example, Serrano and his coworkers studied the removal of Fe (III), Cd(II), and Zn(II) using hydroxides precipitation combined with flotation. The precipitation efficiency was determined function of pH, metal ions initial concentration, treatment time, and dosage of the precipitating agent. The simultaneous removal of 99% for all three studied metal ions was obtained using a pH value of 10.3, an initial concentration of metal ions between 1 mol/L to 15 mol/L, and a treatment time of 15 minutes [9]. Zhang and Duan studied the removal of heavy metals by precipitation using magnesium hydroxy carbonate as a precipitating agent. They obtained a residual concentration under the maximum admitted value using a dosage of the precipitation agent of 0.3 g/50 mL of residual solution at a pH value of 7.1 [12]. Sadeghi et al. studied the removal of lead through precipitation using sodium sulfide and sodium carbonate as precipitation agents. In each case was obtained a removal efficiency

>95% at pH = 11 [15]. The lead ions removal was also studied by precipitation with sodium carbonate by Hu et al. In this case, the researchers used a ball milling process to increase the reaction between lead salts and the precipitation agent, achieving a removal degree of 99% [16]. Regarding precipitation in the form of sulfides, studies have been focused on minimizing the production of toxic hydrogen sulfide. In this regard, Phol studied the metal ions precipitation using other sulfur-containing precipitation agents, such as potassium/sodium thiocarbonate (STC), 2,4,6-trimercaptotiazine (TMT), sodium dimethyldithiocarbamate (SDTC), 1,3-benzenediamidoethanethiol (BDETH 2), 2,6-pyridinediamidoethanethiol (PyDET), or pyridine-based thiol ligand (DTPY) [17]. In this way, the metal ions are binding by the precipitation agent and form metal complexes and are avoided the H<sub>2</sub>S formation but to obtain an efficient removal of metal ions is necessary to use a higher dose of precipitation agents. Prokkola et al. studied the metal ions precipitation from acidic mine drainage (AMD) by using HS, resulting from sulfate reduction reaction. The resulted H<sub>2</sub>S gas and ionic HS<sup>-</sup> during anaerobic treatment were recycled in the precipitation process. The optimum pH value of the precipitation process was 5.5, when is achieved a residual concentration of metal ions <30 µg/L [18]. It is observed that regardless of the precipitation agent used, the degree of metal ions removal from aqueous solutions is influenced by the pH value, treatment time, precipitation agent dose, and initial concentration of metal ions in the solution. By adjusting these influencing factors, the removal capacity of metal ions from wastewater can be significantly improved, which provides the theoretical basis for the practical application of these technologies from the laboratory scale, updated to pilot scale, and further to the industrial level.

### 3. Coagulation – flocculation

Coagulation – flocculation is a physical-chemical process of metal ions removal from water and wastewater, which consist of three steps (**Figure 3**). In the first step, a coagulation agent is introduced under vigorous stirring having the role of colloidal



**Figure 3.**  
Scheme of the coagulation-flocculation system.

Coagulant/ flocculant agent	Water type	Methodology	Obtained results	Ref.
Alum	Landfill leachate	Coagulation/flocculation process combined with continuous adsorption using eggshell waste materials (CES). Optimum dose of alum is 3.0 g/L; CES adsorbent mass 25.5 g. Hydraulic loading rate HLR = 6.37 L/m <sup>2</sup> •min.	Removal efficiencies of Fe, Pb, Cu, Zn, Ni, and Cr of 92%, 93%, 87%, 76%, 65%, and 60%, respectively.	[28]
Ferric chloride: polymer	Industrial waste waters	Ferric chloride: polymer = 200 mg/L:20 mg/L	Removal efficiencies of Cr, Fe, and Zn of 97%, 92%, and 0%, respectively. Resulted volume sludge of 120 mL/L.	[29]
Ferric chloride	Industrial waste waters	Jar test, C <sub>1W</sub> = 321 ppm, Fe/W ratio = 4, or 8, pH = 4, 6, 8 and 10.	Tungsten removal efficiency of 99%, at pH < 6. Residual concentration of tungsten was <10 ppm.	[32]
Micro-alloyed aluminum composite (MAIC)	Wastewater containing Zn <sup>2+</sup> and Cu <sup>2+</sup>	Spontaneous reduction coagulation process in a laboratory semi-flow system varying several parameters (treatment time, pH, initial metal concentration, and flow rate).	Residual concentration of Zn and Cu ions under admissible level was obtained at 20 minutes of treatment, at neutral pH, and increased initial concentration of metal ions. The presence of copper favor zinc removal efficiency and copper removal is not affected by zinc presence.	[33]
Cationic polymers	Tannery wastewater	Jar test methodology using cationic polymers with different weights and charge densities.	A removal efficiency of Cr > 96% was obtained using cationic polymers with molecular weight between 4 and 6 and charge density between 40 and 55% and an optimum dose of 20%.	[34]
Cactus <i>Opuntia ficus indica</i> bioflocculant	River water with Pb <sup>2+</sup> , Zn <sup>2+</sup> , Cd <sup>2+</sup> , and Cu <sup>2+</sup> content.	The coagulation-flocculation process was optimized for pH, initial concentration of Pb(II) ions, particle size, dosage, ionic strength, contact time, and temperature.	Removal efficiency of Pb, Zn, Cd, and Cu of 100%, 85.74%, 84.16%, and 93.02%, respectively, were achieved at pH 5, natural ionic strength, dosage of 8 mg/L, corresponding to zero zeta potential, with particle size <75 µm, at 35°C for a floc settling time of 180 min.	[36]
Commercial tannin-based flocculant	Raw surface water with Cu <sup>2+</sup> , Zn <sup>2+</sup> and Ni <sup>2+</sup> content.	Jar-test procedure	Removal efficiency of Cu, Zn, and Ni of 90%, 85% and 70%, respectively, was achieved using pH value of 6, 7, and 8, respectively, and at a flocculant dose between 100 and 150 ppm.	[38]
Chitosan/montmorillonite	Synthetic water with Co <sup>2+</sup> , Ni <sup>2+</sup> , and Cu <sup>2+</sup> content	Synergic coagulation-flocculation process.	Chitosan: montmorillonite, weight ratio = 5% gave the highest cation removal yields at pH 6.8, and a concentration of 20–100 ppm of Co <sup>2+</sup> , Ni <sup>2+</sup> , and Cu <sup>2+</sup> .	[39]

**Table 2.**  
 The efficiency of various coagulation/flocculation processes applied to different wastewater treatment.



substance destabilization. Vigorous stirring facilitates the contact between the metal ions and the coagulant. In the second step, under gentle stirring, a flocculant is introduced, which has the role of inducing the union of destabilized particles with the aim of forming large flocs, easily separable. The collision between particles and the growth of flocs is facilitated by the gentle stirring of the reaction mass. In the third stage, the resulting sludge and clarified effluents are separated. Separation can be done by settling, flotation, or filtration [2, 3].

The first and most intensive coagulants used in water treatment are those based on  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , such as ferric sulfate— $\text{Fe}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ; ferrous sulfate— $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ; ferric chloride— $\text{FeCl}_3$ ; aluminum sulfate— $(\text{Al}_2\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$ ; aluminum chloride— $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ; poly aluminum chloride— $(\text{Al}(\text{OH})_{1.5}(\text{SO}_4)_{0.125}\text{Cl}_{1.25})_n$ ; and sodium aluminate— $\text{NaAlO}_2$  [28–33]. Among the two trivalent metal ions, coagulants based on  $\text{Al}^{3+}$  are preferred because red coloring is avoided, as can happen when using coagulants based on  $\text{Fe}^{3+}$ . In both cases, a subsequent pH adjustment is needed, and a great dose of coagulant is required for efficient flocculation. The main disadvantage of using inorganic coagulants is a large amount of resulted sludge and its toxic nature, which leads to serious health problems. For this reason, researchers have turned their attention to the use of organic coagulants, especially polymers [34–37]. Even if the polymers are user-friendly, they do not require pH adjustment, and the obtained flocs are large and easily separated, their high price minimizes their use on a large scale. Thus, an alternative to the drawbacks of synthetic polymers is the use of natural polymers, which are found in abundance and are environmental-friendly, due to their biodegradable property [38–40]. But this characteristic, biodegradability, limits their applications, because the formed flocs present instability and loss of strength in time, the natural polymers presenting a shorter lifetime of the active compound. Coagulation–flocculation cannot achieve a 100% heavy metals removal efficiency; therefore, these techniques must be followed, or combined with other treatment processes. **Table 2** summarizes the methodology and the results of various studies of single or combined coagulation/flocculation processes applied on different waste waters with their metal ions removal efficiencies.

Coagulation/flocculation processes could be applied as primary or tertiary treatment of different types of water. The operating parameters (such as coagulant/flocculant dosage, pH, stirring speed, stirring time, settling time, and temperature) present a significant influence on the metal ions removal efficiency. In order to improve the obtained performance, in some cases the coagulation/flocculation process is combined with different treatment methods.

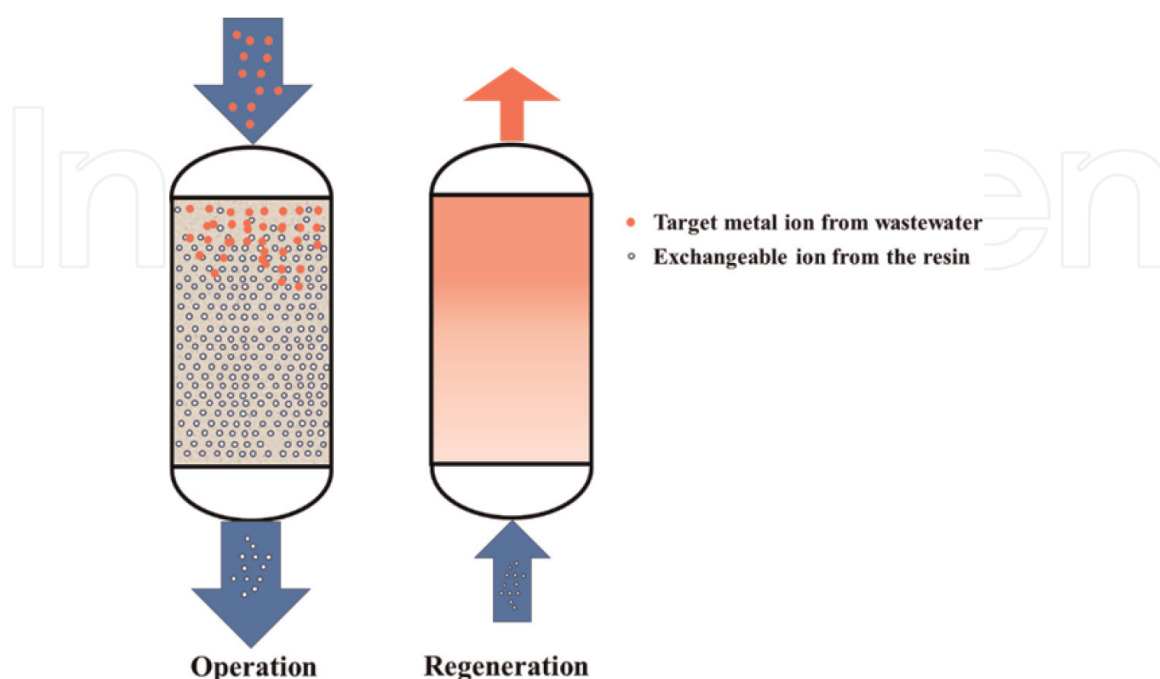
#### 4. Ion-flotation

The process which uses different surfactants for the destabilization of the metal ions present in the wastewaters, and their transformation into hydrophobic compounds, followed by removal through flotation using air bubbles is called ion-flotation [41, 42]. The principle of the ionic flotation process consists on the one hand of attaching the metal ion to the polar end of the surfactant and on the other hand of the interaction between the nonpolar end of the surfactant and the air bubbles, which leads to the concentration and separation of the metal ions on the surface of the residual water by froth forming. In addition to surfactants, foaming agents/frothers (such as ethanol, polypropylene glycol, and methyl isobutyl carbinol), can also be used, which have the role of obtaining air bubbles of the smallest possible size to increase the surface of

interaction between them and the target metal ions [42]. Ionic flotation can be used both for the treatment of wastewater and for the recovery of precious or rare metal ions. As surfactants/collectors were studied sodium dodecyl sulfate [42], polyethylenimine [43], hexadecyltrimethyl ammonium bromide [44], 4-thiazolidinone derivatives [45], etc. This treatment method does not require high energy consumption and sophisticated and large equipment, it is easy to operate, and can be used for selective separations presenting high efficiency and obtaining low amounts of sludge. Ion-flotation could be conducted at different work conditions (pH, flow rate, treatment time, and molar ratio of surfactant/metal ions), function of the metal ions which need to be removed, and function of the used surfactant/collector. The results presented in the specialty literature describe this treatment method as a simple, rapid, and economic one, but also underline the necessity of developing new low-cost collectors, with greater selectivity, environmentally friendly, and present a higher efficiency using a lower dosage, all these leading to a decreasing of the treatment costs.

## 5. Ion exchange

Chemical precipitation and coagulation-flocculation are used to treat water with a high content of metal ions. Their efficiency decreases if the metal ions are found in trace concentrations. In this situation, it is necessary to use advanced water treatment methods. Ion exchange is one such method that can be successfully used to remove metal ions found in low concentrations from water. Ion exchange treatment of waters with metal ions content requires the use of ion exchangers (IX), a water-insoluble compound, that release in water some harmless ions, such as  $H^+$ ,  $Na^+$ , or  $OH^-$ , retaining in return the target metal ions, which present a higher affinity for the used IX, according to reaction (9). This process is reversible and takes place until the exhaustion of IX. Usually, the treatment is carried out with two columns filled with IX (Figure 4), one is used for operation, while the other is regenerated. After



**Figure 4.**  
Scheme of the ion exchange process.

Ion exchanger	Water type	Methodology	Obtained results	Ref.
Dowex M4195, and Lewatit® MonoPlus TP 220	Acidic streams with Cu <sup>2+</sup> content	Batch tests	The highest removal capacity of Cu (86.44 mg/g) was obtained using Lewatit® MonoPlus TP 220 in chloride form, at pH around 2, resin dose of 10 g/L, and treatment time of 60 min.	[48]
C107E, MTS9301 and TP214 resins	Synthetic acetic acid leachate containing Cu <sup>2+</sup> , Fe <sup>2+</sup> , Pb <sup>2+</sup> and Zn <sup>2+</sup>	Batch tests	C107E developed the highest sorption capacity for the studied metal ions (q <sub>mCu</sub> = 5 mmol/g; q <sub>mFe</sub> = 2.1 mmol/g; q <sub>mPb</sub> = 9 mmol/g; q <sub>mZn</sub> = 20 mmol/g)	[50]
Clinoptilolite	Synthetic waters containing Pb(II), Cd(II), and Cr(VI)	Batch experiments and fixed-bed reactors	Pb and Cd were efficiently removed (>95%) from the single and binary system but were significantly affected by the presence of Cr ions or organic contaminants.	[52]
Clinoptilolite	Synthetic waters containing Cu <sup>2+</sup> , Fe <sup>3+</sup> , and Cr <sup>3+</sup>	Batch tests, C <sub>i</sub> = 0.01 N, T = 25°C, treatment time = 4 days, pH = 2–2.5.	The presence of SO <sub>4</sub> <sup>2-</sup> and HPO <sub>4</sub> <sup>2-</sup> anions affect the ion exchange of Cu <sup>2+</sup> and in a lower measure of Fe <sup>3+</sup> and Cr <sup>3+</sup> .	[53]
Thomsonite	Synthetic waters containing Pb <sup>2+</sup> , Fe <sup>3+</sup> , and Ni <sup>2+</sup>	Batch tests, C <sub>iMe</sub> = 100 ppm	Extraction efficiency of ~100%, 99.9%, and 98.6%, for Pb <sup>2+</sup> , Fe <sup>3+</sup> , and Ni <sup>2+</sup> , respectively.	[54]
Zeolite	Synthetic waters containing Cu <sup>2+</sup> , Cd <sup>2+</sup> , Cr <sup>3+</sup> , Ni <sup>2+</sup> , and Pb <sup>2+</sup>	Batch tests S:L ratio = 5 g: 45 mL C <sub>iMe</sub> = 5, 10, 30 mg/L, T = 23°C, treatment time = 5–60 min.	Removal efficiency 99%.	[56]
Strong base anion exchange resin	Synthetic water containing heavy metal (Cu <sup>2+</sup> , Cd <sup>2+</sup> , Zn <sup>2+</sup> ) and cyanide ions.	Semi-fluidized and fluidized beds using a transparent acrylic resin tube, d = 20 mm h = 600 mm, m <sub>resin</sub> = 20 g	The ion exchange efficiency of the studied heavy metal cyanide systems decreases as the concentration ratio of cyanide and heavy metal increases.	[58]
Dowex HCR-S synthetic resin	Synthetic water containing Cd <sup>2+</sup> , Ni <sup>2+</sup> , and Zn <sup>2+</sup>	Batch experiments at different initial solution pH, stirring speeds, temperatures, initial concentrations, and resin dosages	The exchange level of 99.76%, 93.66%, and 83.1% for Cd <sup>2+</sup> , Ni <sup>2+</sup> and Zn <sup>2+</sup> , respectively, at T = 293 K, C <sub>i</sub> = 250 mg/L, t = 60 min, pH = 2, resin dose = 2 g.	[60]
Amberlite IRC-50/IRC-86 and Amberlite IRA-67	Synthetic water containing Pb <sup>2+</sup> , Cu <sup>2+</sup> and Cd <sup>2+</sup>	Column experiments, d = 17.2 mm h = 490 mm.	The most efficient resin was IRC-86. The order of adsorption capacity for the metal ions tested was Pb <sup>2+</sup> > Cd <sup>2+</sup> > Cu <sup>2+</sup> . A 99% desorption of the studied metal ions was achieved using CO <sub>2</sub> .	[61]

**Table 3.**  
Efficiency of various ion exchangers applied on different wastewater treatment.

regeneration, smaller volumes of solutions containing the target metal ions in much higher concentrations are obtained so that they can be recovered, capitalized, or further processed using other methods [46–49].



where:

R: ion exchanger matrix.

A: the mobile ion of the ion exchanger.

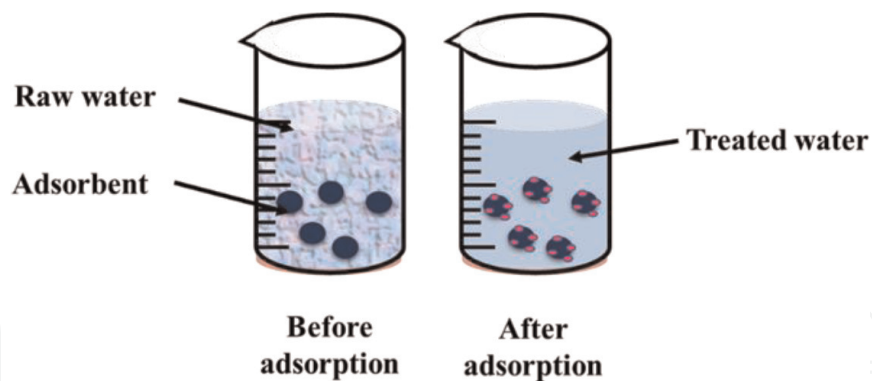
Me: the target metal ion from the residual water of the same sign as A.

Depending on their nature, IX can be: (i) inorganic-natural (zeolites, clinoptilolite) or synthetic (layered double hydroxides) [50–56]; (ii) organic-natural (cellulose, alginic acid, chitin), or synthetic (polycondensation ion exchangers; polymerization ion exchangers) [48, 57–63]. Depending on the type of mobile ion they can exchange, IX are classified as cationic, anionic, or amphoteric. The most important property of IX is the exchange capacity. The exchange capacity represents the number of ions exchanged during the process, equal to the number of functional groups capable of exchange. It is expressed in equivalents per dry product unit or wet product volume unit. In practice, two notions are used: total capacity and useful exchange capacity. The exchange capacity is influenced by constructive factors (the ratio between the column height and diameter), functional factors (percolation speed, specific load, and regeneration level), and chemical factors (the chemical composition of the water to be treated). The disadvantage of ion exchange treatment consists in the fact that the method is sensitive to the pH variations of the influent, and a pre-treatment must be carried out both to remove the particles in suspension and to avoid the precipitation of metal ions on the used resin to avoid the clogging of the exchange column. **Table 3** summarize the experimental conditions and the results of various ion exchanger applied on different wastewater treatments and the obtained metal ions removal efficiencies.

Not all ion exchangers could be used for the removal of metal ions, therefore further studies must be carried on regarding the stability and reusability of various ion exchangers [64, 65]. The challenge in the heavy metals removal from aqueous solution is the development of nontoxic, easily available, and low-cost ion exchangers. For a good design and modeling of the ion exchange process is necessary for each case to study the effect of the main parameters, such as pH, time, flow rate, dosage, initial concentration, bed height, and types of resin.

## 6. Adsorption

Another advanced water treatment that is efficient use in the removal of trace amounts of metal ions from water and wastewater is adsorption. Adsorption is a separation process consisting of the adhesion of metal ions dissolved in aqueous solutions to the surface of a solid, called adsorbent (**Figure 5**). Separation mechanisms of metal ions from water through adsorption are influenced both by their characteristics and by the characteristics of the adsorbent, being determined by the interactions between these two. These interactions can be of a physical nature, exerted by forces with low energies (e.g., van der Waals-type forces). In this case, the metal ions are adsorbed in the pores of the adsorbent without the involvement of electron transfer. In this case, the process is reversible, the metal ion molecules retained on the



**Figure 5.**  
*Scheme of the adsorption process.*

adsorbent surface can be removed by desorption, regenerating the adsorbent. If the interaction between metal ions and adsorbents involves the transfer of electrons and the formation of chemical bonds, then the process is called chemical adsorption, or chemisorption. In this case, the metal ions are not attracted to the entire surface of the adsorbent materials, but only to the active zones, which contain functional groups that react with the metal, involving higher energies than those of physical adsorption, a fact that explains the greater selectivity of the chemical adsorption [11, 66, 67].

In adsorption processes, the used adsorbent material represents the essential element for obtaining effective separations. Thus, a multitude of adsorbent materials was studied. The most frequently used is activated carbon both in its powder form and in its granular form, due to its high specific surface area [68–71]. The powder-activated carbon (PAC) could be used together with other treatment processes, for example, in the coagulation-flocculation processes, for obtaining a better separation of the heavy metals. This presents an advantage that it is not necessarily an alternative equipment, those the separation costs are reduced. Unfortunately, in this case, it is not possible to recover the activated carbon from the resulted sludge. Another disadvantage is represented by the fact that is required a great amount of PAC for a specific volume of water to be treated. The use of granular activated carbon (GAC) requires a smaller amount for the treatment of a specific volume with heavy metals content, but in this case, it is necessary to use separate devices for water treatment and for the regeneration of the exhausted GAC. Sometimes the adsorbed metal ions could be instantaneously removed from the surface of GAC appearing in the effluent at higher concentrations than they were initially in the influent [11, 68–71]. With the recent development of nanotechnologies, researchers have turned their attention to the uses of carbon nanotubes as adsorbent materials [72, 73]. Numerous studies have been carried out regarding the use of activated carbon obtained from vegetable waste as an adsorbent material, or various natural adsorbent materials [74–82], or on different wastes [83, 84]. They have the advantage of low costs, but also the disadvantage of developing low adsorption capacities and low selectivity. To obtain high selectivity and increased efficiency for certain specific adsorption processes, various materials were synthesized and studied such as ferrites or oxides [85–87]. Adsorbent materials with magnetic properties have also been developed to improve the separation stage [88–92]. Since the structure of the adsorbent greatly influences the adsorption process, compounds with well-ordered structures, such as layered double hydroxides and metal-organic frameworks, have also been intensively studied [93–97]. To obtain materials with high selectivity and improved adsorbent properties, functionalized

materials have been developed by impregnating numerous solid supports with compounds containing various functional groups [51, 98–105]. **Table 4** summarizes the experimental conditions and the efficiency of various adsorbent materials used for the removal of various metal ions from different wastewater.

Adsorbent materials	Water type	Methodology	Obtained results	Ref.
Microporous (CS-1501) mesoporous activated carbon cloths	Synthetic wastewater containing $\text{Cu}^{2+}$ and $\text{Pb}^{2+}$	Batch mode adsorption studies using mono or bicomponent systems ( $V = 250$ ml, $m = 500$ mg, $C_i = 0.1$ – $1.4$ mmol/L, $t = 12$ h, $\text{pH} = 3.5/5$ ).	The adsorption capacities of the studied metal ions are between 0.080 and 0.175 mmol/g. In binary system, a decrease of adsorption capacities is observed.	[68]
Activated carbon produced from the biomass recovered from the medicinal plant residue	Synthetic wastewater containing $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ , and $\text{Pb}^{2+}$ and leachate waters.	Batch adsorption studies $C_i = 0.1$ – $50$ mg/L; $\text{pH} = 4$ , $T = 25^\circ\text{C}$ , $t = 15$ min– $5$ h.	Optimum condition in synthetic waters for adsorption of $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$ , and $\text{Cd}^{2+}$ were $\text{pH} = 5$ , $T = 25^\circ\text{C}$ , adsorbent dose = $5$ g/L, $t = 1.5$ h. The rate of heavy metal adsorption from landfill leachate was lower than that from artificial wastewater.	[69]
Carbon nanosheet (CNS) functionalized with amine derivatives	Seawater containing $\text{Zn}^{2+}$ , $\text{Cd}^{2+}$ , and $\text{Hg}^{2+}$	Quantum mechanics studies.	The studied adsorbent present a negative adsorption energy (range: $-75$ to $-93$ kJ/mol). The metal ions adsorption was confirmed by the natural bond orbital and quantum theory of atoms in molecules.	[72]
Multi-walled carbon nanotubes (MWCNTs)	Synthetic waters containing $\text{Cu}^{2+}$ , $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , and $\text{Zn}^{2+}$	Kinetic experiments, $C_i = 0.5$ mg/L, $\text{pH} = 7$ , $T = 278$ – $333$ K, adsorbent dose = $125$ mg/100 mL.	At 298 K, the binding of the metal ions by MWCNTs follows the order: $\text{Cu(II)} > \text{Pb(II)} > \text{Zn(II)} > \text{Cd(II)}$ .	[73]
Activated carbon obtained from seeds of <i>Albizia lebbek</i> and <i>Melia azedarach</i> trees	Synthetic waters containing $\text{Pb}^{2+}$ and $\text{Cd}^{2+}$	Batch adsorption studies $C_i = 10$ – $50$ mg/L, adsorbent dose = $0.1$ – $0.5$ g/50 ml, $\text{pH} = 2$ – $7$ , $T = 20$ – $70^\circ\text{C}$	Removal efficiency of 62% form Pb and 66% for Cd using $t = 120$ min, $\text{pH} = 5$ , $T = 20^\circ\text{C}$ adsorbent dose = $0.2$ g/100 mL, $C_{i\text{Me}} = 40$ mg/L.	[74]
Keratin biomasses (human hair—HH and sheep fur—SF)	Waste waters containing $\text{Cu}^{2+}$ , $\text{Cr}^{6+}$ , $\text{Cd}^{2+}$ , and $\text{Pb}^{2+}$	Batch adsorption varying the operation parameters ( $\text{pH}$ , contact time, and temperature)	Adsorption kinetic rates between 0.054 and 0.261 g/mmol·min have been obtained.	[75]
Treated ajwa date pits (TADP) Produced ajwa date pits (ADP)	Synthetic waters containing $\text{Cu}^{2+}$	Batch mode varying the operation parameters	$q_{\text{mTADP}} = 1428.57$ mg Cu/g $q_{\text{mADP}} = 1111.1$ mg Cu/g at $\text{pH} = 6.5$ , $T = 328$ K	[77]

Adsorbent materials	Water type	Methodology	Obtained results	Ref.
Surface-modified sawdust-based cellulose nanocrystals	Aqueous solutions containing $\text{Cu}^{2+}$ , $\text{Fe}^{2+}$ , and $\text{Pb}^{2+}$	Combination of adsorption and coagulation techniques	$q_m = 111.1 \text{ mg Cu/g}$ $q_m = 2.82 \text{ mg Pb/g}$ $q_m = 81.96 \text{ mg Fe/g}$	[84]
Cobalt ferrite nanoparticles	Aqueous solutions containing $\text{Pb}^{2+}$ , $\text{Zn}^{2+}$ , and dyes.	Fixed bed column adsorption	$q_m = 275 \text{ mg Pb/g}$ $q_m = 390 \text{ mg Zn/g}$	[85]
Nickel ferrite nanoparticles (NFN's)	Aqueous solutions containing $\text{Cr}^{6+}$ , $\text{Pb}^{2+}$ , and $\text{Cd}^{2+}$	Batch mode varying the operation parameters (pH 3–7, dose: 10, 20, 30, 40, and 50 mg and contact time: 30, 60, 90, and 120 min)	Removal efficiencies of Cr(VI), Pb(II), and Cd (II) were obtained at 89%, 79%, and 87%, respectively, under optimal conditions.	[86]
Sol-gel derived nano metal ferrites, $\text{MFe}_2\text{O}_4$ (M = Ni, Zn, Cu)	Aqueous solutions containing $\text{Cr}^{6+}$	Batch mode adsorption varying the operation parameters.	$q_{\text{mZnFe}_2\text{O}_4} = 1.46 \text{ mg Cr/g}$ $q_{\text{mNiFe}_2\text{O}_4} = 1.34 \text{ mg Cr/g}$ $q_{\text{mCuFe}_2\text{O}_4} = 1.14 \text{ mg Cr/g}$ The efficiency is kept for three adsorption-desorption cycles.	[87]
Ultrafine mesoporous magnetite ( $\text{Fe}_3\text{O}_4$ ) nanoparticles	River water containing $\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$	Batch mode adsorption varying the operation parameters	$\text{Pb}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Cu}^{2+}$ , and $\text{Ni}^{2+}$ have been successfully removed simultaneously from river water, obtaining a removal efficiency >50% for Ni and > 80% for the other metals.	[88]
Sultone-modified magnetic activated carbon	Aqueous solutions containing $\text{Pb}^{2+}$ , $\text{As}^{3+}$ , and $\text{Cd}^{2+}$	Batch mode adsorption varying the operation parameters	$q_m = 147.05 \text{ mg Pb/g}$ $q_m = 151.51 \text{ mg As/g}$ $q_m = 119.04 \text{ mg Cd/g}$	[92]
Ni-based phosphonate metal-organic frameworks using various phosphonic acid (phosphonoacetic (CP), vinyl phosphonic acid (VP) and N,N-bis(phosphonomethyl) glycine (Gly))	Aqueous solutions containing $\text{Cr}^{6+}$	Batch mode adsorption varying the operation parameters: pH (range: 1–7), contact times (15–180 min), $\text{Cr}^{6+}$ initial concentration (range: 2.5–250 mg/L)	$q_{\text{mNi-CP}} = 45.9 \text{ mg Cr/g}$ $q_{\text{mNi-Gly}} = 76.9 \text{ mg Cr/g}$ $q_{\text{mNi-Ni-VP}} = 77.0 \text{ mg Cr/g}$	[93]
MgFe layered double hydroxide from iron-containing acidic residual solution.	Aqueous solutions containing $\text{Mo}^{6+}$	Batch mode adsorption varying the operation parameters	$q_{\text{mMg}_4\text{Fe}} = 42.1 \text{ mg Mo/g}$ $q_{\text{mMg}_4\text{Fe-450}} = 55.2 \text{ mg Mo/g}$	[94]
Cu- and Co-based metal organic frameworks.	Aqueous solutions containing $\text{Cs}^+$ and $\text{Tl}^+$	Batch mode adsorption varying the operation parameters	$q_{\text{mCo-SP}} = 4.25 \text{ mg Cs/g}$ $q_{\text{mCo-CP}} = 3.71 \text{ mg Cs/g}$ $q_{\text{mCu-CP}} = 3.64 \text{ mg Cs/g}$ $q_{\text{mCo-SP}} = 3.27 \text{ mg Tl/g}$ $q_{\text{mCo-CP}} = 2.96 \text{ mg Tl/g}$ $q_{\text{mCu-CP}} = 2.76 \text{ mg Tl/g}$	[95]

Adsorbent materials	Water type	Methodology	Obtained results	Ref.
Ionic liquid functionalized Zn-Al layered double hydroxides (Zn <sub>3</sub> Al-IL)	Aqueous solutions containing Pd ions	Batch mode adsorption varying the operation parameters	q <sub>mZn3Al-IL</sub> = 100 mg Pd/g	[97]
Cross-linked polyethylene-graft-polystyrene sulfonic acid (PE-g-PSSA)	Aqueous solutions containing Co <sup>2+</sup> , Cu <sup>2+</sup> , Ni <sup>2+</sup> , and Ag <sup>+</sup>	Batch mode adsorption varies the operation parameters (contact time, initial metal ion concentration, pH, and temperature)	q <sub>m</sub> = 73 mg Ni/g q <sub>m</sub> = 59 mg Co/g q <sub>m</sub> = 67 mg Cu/g q <sub>m</sub> = 61 mg Pb/g q <sub>m</sub> = 53 mg Ag/g	[99]
Ionic liquid impregnated Florisil	Aqueous solutions containing Tl <sup>+</sup>	Batch mode adsorption varying the operation parameters.	The phosphonium-based ionic liquid impregnated with Florisil developed a higher efficiency in the removal process of thallium ions from an aqueous solution than the materials obtained through impregnation of Florisil with imidazolium-based ionic liquids.	[102]
Polyethyleneimine-functionalized alumina nanopowder	Aqueous solutions containing Pd ions.	Batch mode adsorption varying the operation parameters.	q <sub>m</sub> = 97.7 mg Pd/g	[104]
Mg <sub>3</sub> Al-LDH functionalized with ionic liquid (IL)	Aqueous solutions containing Pd ions	Batch mode adsorption varying the operation parameters.	q <sub>m</sub> = 277.8 mg Pd/g	[105]

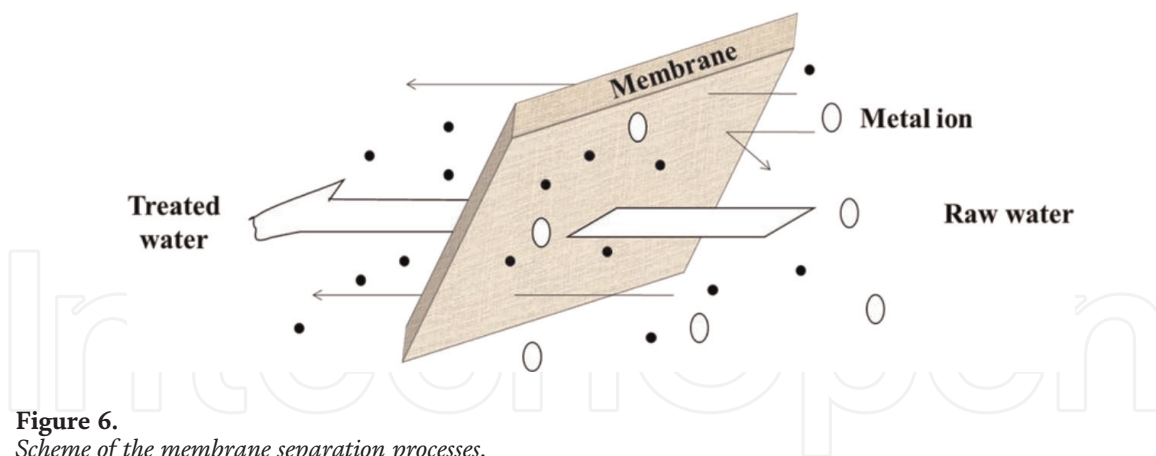
**Table 4.** Research results of various adsorbent materials used for the removal of various metal ions from different wastewater.

Adsorption is a low-cost and easy-to-operate method for the treatment of water with metal ion content. It presents economic feasibility to be scaled up to the industrial application. The existence of various adsorbent materials and low-cost adsorbent materials increases the versatility of this treatment method. Unfortunately, this method is not suitable for automation. Due to the multitude of adsorbent materials with different adsorptive properties (see **Table 4**), intensive studies are continuously carried out, and the selection of one must be based on a preliminary study performed for the specific effluent that is to be treated.

## 7. Membrane separation processes

Membrane separation processes are also an advanced water treatment that could be used for the removal of trace concentrations of metal ions from water and wastewater. Membrane separation processes (**Figure 6**) consist of passing the water flow through semipermeable membranes with certain properties (pore size or electrical





**Figure 6.**  
*Scheme of the membrane separation processes.*

charge) that allow the passage of water molecules but retain the dissolved metal ions [11, 106–109].

Depending on the forces-actions used for separation and the size of the separated particles, the membranes can be classified into.

- Membranes that work under pressure (MF—microfiltration, UF—ultrafiltration, NF—nanofiltration, RO—reverse osmosis).
- Membranes actuated by electrical voltage (ED—electrodialysis, RED—reverse electrodialysis).

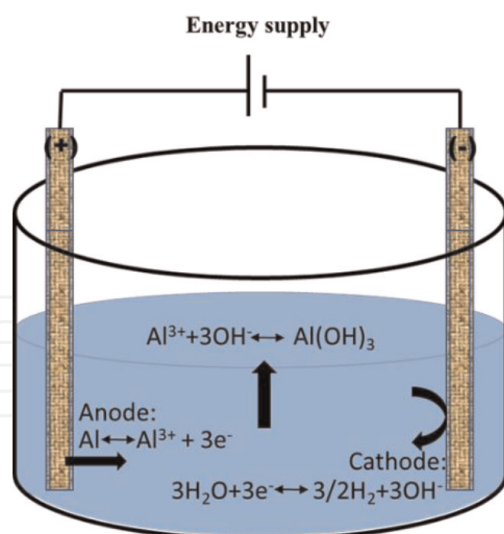
Since membrane treatment technologies require operation at high pressures, the membranes must present compressive strength. The properties that characterize membranes are permeability, porosity, hydrophilicity, surface charge, and thermal/mechanical stability.

Most of the studied membranes are composite materials based on polymer supports [110–112]. The use of these processes presents the following advantages: they constantly ensure good water quality, no chemical reagents are used, they lend themselves to automation, and they are compact. At the same time raise technical issues: insufficient selectivity, relatively weak transmembrane fluxes, exploitation problems, possibility of membrane fouling, requiring pretreatment step and periodic membrane cleaning, and also economic problems: many and different manufacturers with different technologies and prices.

## 8. Electrochemical separation processes

Electrochemical treatment processes were first used for ores electrorefining in the mineralogical industry. Researchers were reluctant to use them due to the need for energy consumption and initial investment in special equipment, which leads to increased processing costs. After studies that demonstrated their efficiency and the need for low maintenance of the equipment, the use of these methods in the water treatment processes with metal ions content became more and more promising. Electrochemical processes for treating water with metal ions content can be divided into electrocoagulation, electro flocculation, and electrodeposition.

The electrocoagulation process takes place in a simple electrolysis cell, which contains sacrificial electrodes, which could be from the same or different materials (**Figure 7**). In most of cases, the electrodes are formed from  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$ . The

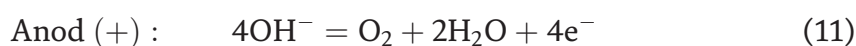
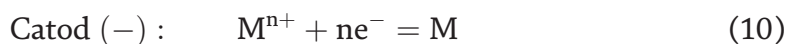


**Figure 7.**  
 Scheme of electrocoagulation processes.

electrocoagulation process consists of the dissolution of the anode,  $H_2$  and  $HO^-$  generation at the cathode, coagulant ( $Al(OH)_3$ ) formation, destabilization and neutralization of metal ions by introducing electric current, aggregation of the destabilized metal ions and flocks/sludge formation [113–118]. The main advantage of this process consists in the fact that no additional reagents are required, and the coagulant is formed *in situ* due to the electrical dissolution of the sacrificial electrodes. The obtained flock/sludge is stable and easy to be removed. The hydrogen formation contributes to the removal of tiny particles. The main disadvantages are represented by the possibility of cathode passivation and the need of the periodical replacement of the sacrificial anode.

In the case of electroflotation, the destabilized heavy metals adhere to the oxygen and hydrogen molecules released by the reactions from the electrodes and float to the surface of the liquid from where they are removed. The formed sludge presents better stability in this case and the process requires a shorter time. Most of the time, a combination of electrocoagulation and electroflotation is used [119–121].

Electrodeposition is an effective method of selective recovery of dissolved metals in order to recycle/reuse them. It is advantageous because it does not require additional reagents and no sludge is formed. Dissolved metals from wastewater are deposited at the cathode according to the reaction (10). In this case, it is preferable for the anode to be insoluble in order not to contaminate the recovered metals. At the anode, the reaction takes place according to the reaction (11). Side reactions such as the formation of hydrogen gas may occur during the process, reaction (12). This method is selective but is sensitive to the composition of water to be treated, and the efficiency is negatively influenced by the side reaction of hydrogen formation [11, 123].



## 9. Conclusions, remarks, and future perspectives

It can be seen from the literature study that each method of removing metal ions from water has both advantages and disadvantages. The choice of one or another is

made following several conditions, such as knowledge in the field, experience in a certain method, the composition of the influent, the desired removal efficiency to be achieved, and the operating conditions. Sometimes two or more methods are combined and used to obtain the desired results. Chemical precipitation is frequently used in the treatment of waters with a high content of heavy metals. It presents low capital costs, simple operation condition, and a high treatment efficiency, it can be easily automated, but in some cases, even if high removal degree is obtained, residual concentrations below the maximum allowed concentrations are still not reached, so it is necessary to be followed by an advanced treatment method. The main disadvantages of chemical precipitation are underlined by the need for chemical reagents addition for pH adjustment and by the fact that great quantities of sludge are obtained, which need further treatment or special disposal. The same disadvantages are encountered in the case of using coagulation-flocculation processes. The efficiency of chemical precipitation or coagulation-flocculation processes also depends on the efficiency of the method used to remove the resulting sludge. Ion exchange processes and adsorption processes are used to treat large volumes of wastewater with a low content of metal ions. In the case of ion exchange processes, the initial investment in ion exchange columns is necessary, the problems raised in this case are given by the costs of ion exchange resins and their selectivity, stability, and reusability. Adsorption processes are the most promising treatment process of heavy metals removal from aqueous solutions due to low costs, easy operation, and the multitude of existing adsorbent materials, especially low-cost adsorbent. Also, in this case, the problem of regeneration and reuse of adsorbent materials arises. Membrane separation processes develop very high removal degrees of metal ions, but in this case, the costs of the technology and the possibility of membrane fouling limit their use at a large scale. Electrochemical processes have the advantage of selective removal of metal ions and the possibility of their recovery and reuse without the need for additional consumption of chemical reagents. At the same time, it presents the disadvantage of high energy consumption. Accordingly, for each case, studies must be carried out starting from the laboratory scale and then updated to the pilot scale to determine the optimal treatment method. Most of the studies were carried out on synthetic water. To clearly specify the efficiency of a certain treatment process or another, for different situations encountered in practice, it is necessary to carry out studies on real waters. Besides the metal of interest, the sample matrix also presents a major influence on the performance of the process treatment. Future studies must be focused on the development of cost-effective materials and methods that involve low treatment costs, high efficiency, and minimal impact on the environment.

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