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Physico–chemical treatment techniques for wastewater laden with heavy metals

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Abstract

This article reviews the technical applicability of various physico–chemical treatments for the removal of heavy metals such as Cd(II), Cr(III), Cr(VI), Cu(II), Ni(II) and Zn(II) from contaminated wastewater. A particular focus is given to chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration. Their advantages and limitations in application are evaluated. Their operating conditions such as pH, dose required, initial metal concentration and treatment performance are presented. About 124 published studies (1980–2006) are reviewed. It is evident from the survey that ion exchange and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. Ion exchange has achieved a complete removal of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) with an initial concentration of 100 mg/L, respectively. The results are comparable to that of reverse osmosis (99% of Cd(II) rejection with an initial concentration of 200 mg/L). Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of higher than 1000 mg/L. It is important to note that the overall treatment cost of metal-contaminated water varies, depending on the process employed and the local conditions. In general, the technical applicability, plant simplicity and cost-effectiveness are the key factors in selecting the most suitable treatment for inorganic effluent.

Keywords: Electroplating industry; Heavy metal uptake; Inorganic effluent; Metal-contaminated water; Water pollution control

1. Introduction

Due to the discharge of large amount of metal-contaminated wastewater, electroplating industry is one of the most hazardous among the chemical-intensive industries [1]. Inorganic effluent from the industries contains toxic metals such as Cd, Cr, Cu, Ni and Zn [2], which tend to accumulate in the food chain.

Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. If the metals are ingested beyond the permitted concentration, they can cause serious health disorders (Table 1). Therefore, it is necessary to treat metal-contaminated wastewater prior to its discharge to the environment.

Different treatment techniques for wastewater laden with heavy metals have been developed in recent years both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Although various treatments such as chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration can be employed to remove heavy metals from contaminated wastewater, they have their inherent advantages and limitations in application.

Chemical precipitation is widely used for the treatment of electroplating wastewater in Thailand [7] and Turkey [8]. Coagulation–flocculation has also been employed for heavy metal removal from inorganic effluent in Thailand [7] and China [9]. Sorptive flotation has attracted interest in Greece [10] and the USA [11] for the removal of non-surface active metal ions from contaminated wastewater. In recent years, ion exchange

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Table 1
MCL of heavy metals in surface water and their toxicities

Heavy metal	Toxicities	Maximum effluent discharge standards (mg/L)		
		EPA[a] [3,4] (The USA)	EPD[b] [5] (Hong Kong SAR)	PCD[c] [6] (Thailand)
Cr(VI)	Headache, nausea, diarrhea, vomiting, carcinogenic to human	0.05	0.05–2.0	0.25
Cr(III)		0.10		0.75
Zn(II)	Depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst	1.00	0.60–5.0	5.00
Cu(II)	Liver damage, Wilson disease, insomnia	0.25	0.05–4.0	2.00
Cd(II)	Kidney damage, renal disorder, Itai-Itai, probable human carcinogen	0.01	0.001–0.2	0.03
Ni(II)	Dermatitis, nausea, chronic asthma, coughing, human carcinogen	0.20	0.10–4.0	1.00

[a] Environmental Protection Agency (EPA), The USA.
[b] Environmental Protection Department (EPD), Hong Kong SAR.
[c] Pollution Control Department (PCD), The Ministry of Natural Resources and Environment, Thailand.

has also received considerable interest in Italy [12] and Spain [13] as one of the most promising methods to treat wastewaters laden with heavy metals.

Due to its convenient operation, membrane separation has been increasingly used recently for the treatment of inorganic effluent. There are different types of membrane filtration such as ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). Membrane filtration has been used in Taiwan [14] and South Korea [15] to remove Cd(II), Ni(II), Zn(II) and Cr(III) ions from contaminated wastewater.

Electrotreatments such as electrodialysis [16], membrane electrolysis [17] and electrochemical precipitation [18] have also contributed to environmental protection. However, these techniques have been investigated less extensively due to the high operational cost caused by energy consumption. Although many techniques can be employed for the treatment of inorganic effluent, the ideal treatment should be not only suitable, appropriate and applicable to the local conditions, but also able to meet the maximum contaminant level (MCL) standards established (Table 1) [19].

This article presents an overview with critical analysis of the technical applicability of various physico–chemical treatments for wastewater laden with heavy metals. Their advantages and limitations in application are evaluated. To highlight their removal performance, the operating conditions such as pH, dose required, initial metal concentration and treatment efficiency are presented as well.

2. Physico–chemical treatment techniques for wastewater laden with heavy metals

2.1. Chemical precipitation

Chemical precipitation is widely used for heavy metal removal from inorganic effluent [20,21]. After pH adjustment to the basic conditions (pH 11), the dissolved metal ions are converted to the insoluble solid phase via a chemical reaction with a precipitant agent such as lime [22]. Typically, the metal precipitated from the solution is in the form of hydroxide [23]. The conceptual mechanism of heavy metal removal by chemical precipitation is presented in Eq. (1) [22]:

$$M^{2+} + 2(OH)^- \leftrightarrow M(OH)_2\downarrow \qquad (1)$$

where M^{2+} and OH^- represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

Lime precipitation was employed for the removal of heavy metals such as Zn(II), Cd(II) and Mn(II) cations with initial metal concentrations of 450, 150 and 1085 mg/L, respectively, in a batch continuous system [7]. In spite of their varying initial concentrations, an almost complete removal from synthetic wastewater was achieved for all the metals at pH 11, complying with the effluent limit of the Thai Pollution Control Department for Zn(II) and Mn(II) of less than 5 mg/L [6]. However, the treated effluent was unable to meet the stringent limit set by the

Table 2
Heavy metal removal using chemical precipitation

Species	Precipitant	Optimum dose of precipitant (g/L)	Initial metal concentration (mg/L)	Optimum pH	Contact time (h)	Removal efficiency (%)	References
Zn(II)	$Ca(OH)_2$	10	450	11.0	NA	99.77	[7]
Cd(II)	$Ca(OH)_2$	10	150	11.0	NA	99.67	
Mn(II)	$Ca(OH)_2$	10	1085	11.0	NA	99.30	
Cd(II)	$Fe(OH)_3$	NA	37	11.0	24	96	[8]
Cu(II)	$Mg(OH)_2$	NA	16	9.5	24	80	
Ni(II)	NA	NA	51.6	7.5	1	71	[25]
	NA	NA	51.6	10.5	1	85	

NA: not available.

US EPA of lower than 1 mg/L [3,4], thus suggesting that subsequent treatments using other physico–chemical methods were still required to comply with the US EPA discharge standard.

Some attractive findings were reported by Tünay and Kabdasli [8], who investigated the applicability of hydroxide precipitation in a closed system to treat synthetic wastewater containing Cd(II) and Cu(II) ions. Inorganic cations (Ca(II) and Na) were employed as ligand-sharing agents for EDTA (ethylenediaminetetraacetic acid) and NTA (nitrilotriacetic acid). They reported that Ca(II) was the only cation that effectively bound both ligands to form the hydroxide precipitations of the complexed metals. At pH 11, EDTA was also found to be the major component that determined Cd(II) solubility [24]. The removal performance of the precipitants is presented in Table 2.

Different results were obtained for the removal of Ni(II) uptake from a low-strength of real wastewater with a metal concentration of less than 100 mg/L [25]. At pH 7.5 and 10.5, the researchers found that about 71% and 85% of Ni(II) removal, respectively, with an initial metal concentration of 51.6 mg/L, could be attained. This could be attributed to the fact that a greater portion of the Ni(II) was precipitated and removed in the form of insoluble hydroxide compounds with the increasing pH.

Overall, pH adjustment to the basic conditions (pH 11) is the major parameter that significantly improves heavy metal removal by chemical precipitation (Table 2). Due to its availability in most countries, lime or calcium hydroxide is the most commonly employed precipitant agent. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations, making it a popular method for metal removal from contaminated wastewater.

In spite of its advantages, chemical precipitation requires a large amount of chemicals to reduce metals to an acceptable level for discharge [26]. Other drawbacks are its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal [27–29].

2.2. *Coagulation–flocculation*

Coagulation–flocculation can be employed to treat wastewater laden with heavy metals. Principally, the coagulation process destabilizes colloidal particles by adding a coagulant and results in sedimentation [30]. To increase the particle size, coagulation is followed by the flocculation of the unstable particles into bulky floccules [31]. The general approach for this technique includes pH adjustment and involves the addition of ferric/alum salts as the coagulant to overcome the repulsive forces between particles [32].

After lime precipitation, Charerntanyarak [7] employed subsequent coagulation process to remove Zn(II), Cd(II) and Mn(II) ions from synthetic wastewater. The optimum pH for coagulation process was found to be 11. At pH 11, the concentration of Zn(II) and Mn(II) in the treated effluent was reduced to less than 5 mg/L, the limit for the wastewater discharge set by the Thai Pollution Control Department [6].

To treat real electroplating wastewater containing copper, Li et al. [9] modified the conventional coagulation–flocculation process by using sodium diethyl-dithiocarbamate (DDTC) as a trapping agent and both poly-ferric sulphate and poly-acrylamide as the flocculants. DDTC is the most common chemical used as metal precipitant to form insoluble metal-dithio salts [33]. These insoluble dithio-metal salts are then coprecipitated, forming hydroxide-neutralized solids that precipitate prior to the discharge of the treated waste stream. When the mole ratio of DDTC to Cu was between 0.8 and 1.2, they found that an almost complete removal of Cu(II) could be achieved (Table 3).

In general, coagulation–flocculation can treat inorganic effluent with a metal concentration of less than 100 mg/L or higher than 1000 mg/L. Like chemical precipitation, pH ranging from 11.0 to 11.5 has been found to be effective to improve the heavy metal removal by the coagulation–flocculation process (Table 3). Improved sludge settling, dewatering characteristics, bacterial inactivation capability, sludge stability are reported to be the major advantages of lime-based coagulation [34,35].

In spite of its advantages, coagulation–flocculation has limitations such as high operational cost due to chemical consumption. The increased volume of sludge generated from coagulation–flocculation may hinder its adoption as a global strategy for wastewater treatment. This can be attributed to the fact that the toxic sludge must be converted into a stabilized product to prevent heavy metals from leaking into the environment [36].

To overcome such problems, electro-coagulation may be a better alternative than the conventional coagulation, as it can remove the smallest colloidal particles and produce just a small amount of sludge [37,38]. However, this technique also creates a floc of metallic hydroxides, which requires further purification [39], making the recovery of valuable heavy metals impossible.

Table 3
Removal of heavy metal using coagulation–flocculation

Species	Coagulant	Dose of coagulant (mg/L)	Initial metal concentration (mg/L)	Optimum pH	Removal efficiency (%)	References
Zn(II)	Na_2S	100	450	11.0	99.91	[7]
Cd(II)	Na_2S	100	150	11.0	99.73	
Mn(II)	Na_2S	100	1085	11.0	99.95	
Cu(II)	Poly-ferric sulfate	25	20	10–11.5	99.6	[9]
Cu(II)	Poly-acrylamide	5	20	10–11.5	95	

NA: not available.

2.3. Flotation

Flotation is employed to separate solids or dispersed liquids from a liquid phase using bubble attachment [40]. The attached particles are separated from the suspension of heavy metal by the bubble rise. Flotation can be classified as: (i) dispersed-air flotation, (ii) dissolved-air flotation (DAF), (iii) vacuum air flotation, (iv) electroflotation, and (v) biological flotation. Among the various types of flotation, DAF is the most commonly used for the treatment of metal-contaminated wastewater [41]. Adsorptive bubble separation employs foaming to separate the metal impurities. The target floated substances are separated from bulk water in a foaming phase.

Laboratory study was carried out by Rubio and Tessele [42] to investigate the flotation of Zn(II) and Ni(II) from synthetic wastewater using chabazite as the adsorptive particulate. They found that the removal performance was dependent on the interfacial chemistry and aggregation effectiveness. An almost complete removal (98.6%) of heavy metal ions with an initial concentration of 2 mg/L could be achieved by using 20 mg/L of $Fe(OH)_3$. The results are comparable to those of Blöcher et al. [43], who combined flotation and membrane separations to remove Ni(II) cations from synthetic plating solution by using CTABr (cetyl trimethyl-ammonium bromide) as the cationic collector (Table 4).

Other interesting results are reported by Zamboulis et al. [44], who studied the sorptive flotation for the removal of Zn(II) and Cu(II) ions from synthetic wastewater. SDS (sodium dodecyl sulfate) and HDTMA (hexadecyl-trimethyl-ammonium-bromide) were used as the cationic collectors. The addition of 2 g/L of zeolite was found to remove 99% of 50 mg/L of zinc(II), while 4 g/L of zeolite was required to remove 97% of 500 mg/L of the initial Cu(II) concentration (Table 4). The results confirmed that both the surface charge of the system and the solution pH significantly affected the metal removal by zeolite [10].

To explore their application as biosurfactants, Surfactin-105 and Lychenysin-A were applied to enhance the removal of Cr(VI) and Zn(II) ions from synthetic wastewater [45]. An almost complete removal of both metals with initial metal concentrations of 50 mg/L could be achieved at pH 4.0.

In the last decade, the trends of research had shifted from flotation alone to a combination of flotation and other physico–chemical treatment such as filtration or powder activated carbon [46,47]. Encouraging results were reported by Mavrov et al. [48], who examined a newly integrated process that combined adsorption, membrane separation and flotation for Cu(II) and Zn(II) removal from real wastewater with synthetic zeolite as the bonding agent. They found that about 97% of Cu(II) and Zn(II) removal were attained with an initial metal concentration of 60 mg/L. The binding capacities of Zn(II), Cu(II) and Ni(II) ions were found to be 270, 200 and 60 mg/g, respectively. The results were higher than those of Doyle and Liu [11], who employed triethylenetetraamine (Trien) as the collector for the flotation of Cu(II) ions from synthetic wastewater (Table 4).

Although it is only a kind of physical separation process, heavy metal removal by flotation has the potential for industrial application [49]. Low cost materials such as zeolite and chabazite have been found to be effective collectors with removal efficiency of higher than 95% for an initial metal concentration ranging from 60 to 500 mg/L (Table 4). Flotation can be employed to treat inorganic effluent with a metal concentration of less than 50 mg/L or higher than 150 mg/L. Other advantages such as a better removal of small particles, shorter hydraulic retention times and low cost make flotation one of the most promising alternatives for the treatment of metal-contaminated wastewater [50,51].

2.4. Membrane filtration

Membrane filtration has received considerable attention for the treatment of inorganic effluent, since it is capable of remov-

Table 4
Heavy metal removal using flotation

Species	Collector	Optimum dose of collector (g/L)	Precipitant	Optimum dose of precipitant (mg/L)	Initial metal concentration (mg/L)	Optimum pH	Removal efficiency (%)	References
Cu(II)	Chabazite	0.500	$Fe(OH)_3$	30.9	3.5	5.5	98.26	[42]
Ni(II)			$Fe(OH)_3$	20.0	2.0	5.5	98.6	
Zn(II)			$Fe(OH)_3$	20.0	2.0	5.5	98.6	
Cu(II)	Trien	0.015	SDS	NA	12.7	6.7	85	[11]
Ni(II)	Trien	0.015	SDS	NA	5.87	7.0	70	
Cr(VI)	Hydrotalcite		Magnafloc	3.0	58.8	NA	95	[10]
Cu(II)	CTABr	0.020	NA	NA	474.0	8–10	99.99	[43]
Ni(II)			NA	NA	3.3	8–10	98.50	
Zn(II)			NA	NA	167	8–10	99.97	
Cu(II)	Zeolite	0.8	NA	NA	60	8–10	97	[48]
Zn(II)	Zeolite	0.8	NA	NA	60	8–10	97	
Zn(II)	Zeolite	2	SDS	40.0	50	6.0	99	[44]
		2	HDTMA	20–40	50	9.0	96	
Cu(II)		4	SDS	50.0	500	5.0	97	
Cr(VI)	Surfactin-105	0.04	Ferric hydroxide	600	50	4.0	98	[45]
Zn(II)	Lycheny-sin-A	0.04	Ferric hydroxide	600	50	4.0	100	
Zn(II)	SDS	0.05	NA	20.0	50	7–9	100	[51]

NA: not available.

ing not only suspended solid and organic compounds, but also inorganic contaminants such as heavy metals. Depending on the size of the particle that can be retained, various types of membrane filtration such as ultrafiltration, nanofiltration and reverse osmosis can be employed for heavy metal removal and are presented as follows.

2.4.1. Ultrafiltration (UF)

UF utilizes permeable membrane to separate heavy metals, macromolecules and suspended solids from inorganic solution on the basis of the pore size (5–20 nm) and molecular weight of the separating compounds (1000–100,000 Da) [52]. These unique specialties enable UF to allow the passage of water and low-molecular weight solutes, while retaining the macromolecules, which have a size larger than the pore size of the membrane [53].

Some significant findings were reported by Juang and Shiau [14], who studied the removal of Cu(II) and Zn(II) ions from synthetic wastewater using chitosan-enhanced membrane filtration. The amicon-generated cellulose YM10 was used as the ultrafilter. About 100% and 95% rejection were achieved at pH ranging from 8.5 to 9.5 for Cu(II) and Zn(II) ions, respectively, with an initial Cu(II) concentration of 79 mg/L and Zn(II) concentration of 81 mg/L. The results indicated that chitosan significantly enhanced metals removal by 6–10 times compared to using membrane alone. This could be attributed to the major role of the amino groups of chitosan chain, which served as coordination sites for metal binding. In acidic conditions, the amino groups of chitosan are protonated after reacting with H^+ ions as follows:

$$RNH_2 + H^+ \leftrightarrow RNH_3{}^+, \quad \log K_p = 6.3 \qquad (2)$$

Having the unshared electron pair of the nitrogen atom as the sole electron donor, the non-protonated chitosan binds with the unsaturated transition metal cation through the formation of coordination bond [54]. For most of the chelating adsorbent, the functional groups with the donor atoms are normally attached to the metal ions, thus leading to a donor–acceptor interaction between chitosan and the metal ions [55], as indicated by the Eq. (3):

$$M^{2+} + nRNH_2 \leftrightarrow M\text{–}(RNH_2)_n{}^{2+} \qquad (3)$$

where M and RNH_2 represent metal and the amino group of chitosan, respectively, while n is the number of the unprotonated chitosan bound to the metal. Combination of Eqs. (2) and (3) gives the overall reaction as follows:

$$M^{2+} + nRNH_3{}^+ \leftrightarrow M\text{–}(RNH_2)_n{}^{2+} + nH^+ \qquad (4)$$

Eq. (4) suggests that an increase in pH would enhance the formation of metal–chitosan complexes.

To improve the rejection rates of metals by complexation–ultrafiltration, some modifications were conducted using polyethylene-imine (PEI), a water-soluble macroligand, to remove Cr(III) ions from a synthetic solution [56]. Technical parameters such as pH, ligand concentration, applied pressure and membrane pore size were found to significantly affect the rejection rate of metal ions. The researchers found that pH 6.0, pressure of 3 bar and 2 g/L of PEI were the optimum conditions to achieve the Cr rejection rate of 95% with an initial metal concentration of 20 mg/L (Table 5).

Another significant breakthrough in UF research was explored for the removal of Ni(II) ions from a synthetic solution using micellar-enhanced UF [57]. Both sodium dodecyl sulfate (SDS) and non-ionic mono-alkylphenol polyetoxilate were used to form micelles. An almost complete removal of Ni(II) could be achieved at 4 bar of pressure with 1 g/L of SDS concentration. This result was higher than that of Akita et al. [58], who studied the removal of Ni(II) ions from synthetic wastewater via micellar-enhanced UF. They found that only 60% of Ni(II)

Table 5
Uptake of heavy metals using UF, NF, or RO

Kind of process	Type of membrane	Species	Pressure (bar)	Initial metal concentration (mg/L)	Optimum pH	Rejection rates (%)	References
UF	YM1	Co(II)	NA	29.47	5–7	100	[58]
		Ni(II)	NA	29.35	5–7	60	
UF	YM10	Cu(II)	2	78.74	8.5–9.5	100	[14]
		Zn(II)	2	81.10	8.5–9.5	95	
UF	Carbosep M2	Cr(III)	3	20.00	6.0	95	[56]
UF	UPM-20	Ni(II)	4	10.00	NA	100	[57]
UF	HL	Ni(II)	2–5	25.00	NA	99.9	[59]
		Co(II)	2–5	25.00	NA	95.0	
UF	$ZnAl_2O_4$–TiO_2	Cd(II)	10	112.00	5.1	93	[60]
		Cr(III)	10	52	3.6	86	
NF	HL	Ni(II)	4	NA	4–8	96.49	[65]
NF	NTR-7250	Ni(II)	2.9	2000	3–7	94	[15]
RO	Polyamide	Cu(II)	7	200	4–11	98	[64]
		Cd(II)	7	200	4–11	99	
RO	Sulfonated polysulfone	Cu(II)	4.5	NA	3–5	98	[66]
		Zn(II)	4.5	NA	3–5	99	
RO	ULPROM	Cu(II)	5	50	7–9	100	[69]
		Ni(II)	5	50	7–9	100	
RO	CPA2	Ni(II)	15	21	7.0	97	[70]

with an initial metal concentration of 29 mg/L was removed at pH ranging from 5 to 7, confirming that the metal rejection rates were dependent on the degree of complexation between the cations and the extractant within the micelle [59].

To explore its potential to remove heavy metals, Saffaj et al. [60] employed low cost $ZnAl_2O_4$–TiO_2 UF membranes for the removal of Cd(II) and Cr(III) ions from synthetic solution. They reported that 93% Cd(II) rejection and 86% Cr(III) rejection were achieved (Table 5). Such high rejection rates might be attributed to the strong interactions between the divalent cations and the positive charge of the membranes. These results indicate that the charge capacity of the UF membrane, the charge valencies of the ions and the ion concentration in the effluent, played major roles in determining the ion rejection rates by the UF membranes [61].

Depending on the membrane characteristics, UF can achieve more than 90% of removal efficiency with a metal concentration ranging from 10 to 112 mg/L at pH ranging from 5 to 9.5 and at 2–5 bar of pressure (Table 5). UF presents some advantages such as lower driving force and a smaller space requirement due to its high packing density. However, the decrease in UF performance due to membrane fouling has hindered it from a wider application in wastewater treatment. Fouling has many adverse effects on the membrane system such as flux decline, an increase in transmembrane pressure (TMP) and the biodegradation of the membrane materials [62]. These effects result in high operational costs for the membrane system.

2.4.2. Nanofiltration (NF)

Nanofiltration has unique properties between UF and RO membranes. Its separation mechanism involves steric (sieving) and electrical (Donnan) effects. A Donnan potential is created between the charged anions in the NF membrane and the co-ions in the effluent to reject the latter [63]. The significance of this membrane lies in its small pore and membrane surface charge, which allows charged solutes smaller than the membrane pores to be rejected along with the bigger neutral solutes and salts.

To evaluate polyvinyl alcohol as the skin materials of the NF membrane, Ahn et al. [15] investigated the uptake of Ni(II) ions from real electroplating wastewater using NTR-7250 membranes. They found that the removal of Ni(II) was dependent on the applied pressure and the initial metal concentrations. It was observed that beyond 2.9 bar of pressure, the removal of Ni(II) did not improve with the increasing pressure, suggesting that 2.9 bar was the optimum pressure for NF application to remove Ni(II) ions from wastewater.

A comparative study of the removal of Cu(II) and Cd(II) ions from synthetic wastewater using nanofiltration (NF) and/or reverse osmosis (RO) was conducted [64]. At the same initial metal concentration of 200 mg/L, 98% of Cu(II) removal and 99% of Cd(II) removal could be attained by using RO, while NF was capable of removing more than 90% of Cu(II) and 97% of Cd(II). These results indicate that both types of the membrane filtration are effective for metal removal from contaminated wastewater. However, NF requires a lower pressure than RO, making NF more preferable due to its lower treatment costs [65].

In general, NF membrane can treat inorganic effluent with a metal concentration of 2000 mg/L. Depending on the membrane characteristics, NF can effectively remove metal at a wide pH range of 3–8 and at pressure of 3–4 bar (Table 5). However, NF is less intensively investigated than UF and RO for the removal of heavy metal.

2.4.3. Reverse osmosis (RO)

In reverse osmosis (RO), a pressure-driven membrane process, water can pass through the membrane, while the heavy metal is retained. This treatment has gained favor in Malaysia [66] and Spain [67]. Due to the increasingly stringent environmental legislation, RO has been developed with a membrane pore size down to 10^{-4} μm [68]. By applying a greater hydrostatic pressure than the osmotic pressure of the feeding solution, cationic compounds can be separated from water (solvent).

To examine the quality of polyamide as the skin material of the RO membrane, the removal performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) was investigated for the separation of Cu(II) and Ni(II) ions from both synthetic and real plating wastewater [69]. An almost complete rejection was attained for both Cu(II) and Ni(II) cations at 5 bar of pressure. It was pointed out that the higher the transmembrane pressure, the higher the flux and rejection rates. pH ranging from 7 to 9 was found to be optimum to achieve a maximum metal rejection.

Using polyamide as the same skin material for the membrane, Qin et al. [70] also employed RO for the treatment of Ni-contaminated wastewater directly discharged from a metal plating industry. They found that 97% of Ni(II) removal was achieved. The rejection rate of Ni(II) was enhanced at pH ranging from 3.5 to 7.0. Such a phenomenon might be due to the Donnan exclusion mechanism of the charged membranes, as the membrane acquired significantly more negative charge at pH 7.0 than at pH 3.5, thus inducing high rejection rates through electrostatics attraction.

In general, compared to UF and NF, RO is more effective for heavy metal removal from inorganic solution, as indicated by the rejection percentage of over 97% with a metal concentration ranging from 21 to 200 mg/L. Depending on the characteristics of the membrane such as the porosity, material, hydrophilicity, thickness, roughness and charge of the membrane [71], RO works effectively at a wide pH range of 3–11 and at 4.5–15 bar of pressure (Table 5). Unlike chemical precipitation, instead of pH, pressure is the major parameter that affects the extent of heavy metal removal by RO. The higher the pressure, the higher the metal removal efficiencies, and thus the higher the energy consumption. The other advantages of using RO include a high water flux rate, high salt rejection, resistance to biological attack, mechanical strength, chemical stability and the ability to withstand high temperatures [66]. The reuse of water from industrial process can be achieved and RO enables industrial users to comply with the effluent limit of the discharge standards imposed under environmental legislation.

In spite of its benefits, RO has some limitations. Due to the suspended solids or oxidized compounds such as chlorine oxides, the small pores of the membrane make it more prone to

Table 6
Characteristics of some membranes and their treatment performance for inorganic effluent

Type of membrane	Type of application	Skin materials	Type of module	Pressure (bar)	Membrane area (cm^2)	Temperature (°C)	Manufacturer	Metal rejection rates (%)	References
YM1	UF	Cellulose acetate	NA	NA	28.7	25	Amicon (Japan)	100	[58]
YM10	UF	Cellulose acetate	NA	2	NA	25	Amicon (Taiwan)	100	[14]
Carbosep M2	UF	NA	Tubular	3	2.26×10^{-2}	NA	Tech-Sep	95	[56]
UPM-20	UF	Polyamide	NA	4	NA	NA	Vladipor (Rusia)	100	[57]
$ZnAl_2O_4$–TiO_2	UF	Silica and alumina	Tubular	10	8×10^4	25	–	93	[60]
NTR-7250	NF	Polyvinyl alcohol	Flat-sheet	2.9	60	NA	Nitto Denko (Japan)	94	[15]
NA	RO	Polyamide	Spiral-wounded	7.0	2.5×10^4	45	NA	98–99	[64]
Sulfonated polysulfone	RO	Sulfonated polysulfone	Spiral-wounded	4.5	NA	25	NWW-Acumem (Britain)	98–99	[66]
ULPROM	RO	Polyamide	Flat-sheet	5	60	25	Nitto Denko (Japan)	100	[69]
CPA2	RO	Polyamide	Flat-sheet	15	155	25	Hydranautics (Singapore)	97	[70]

NA: not available.

fouling [72]. Any cations such as Cd(II) and Cu(II) present in the contaminated wastewater promote membrane fouling, which might be irreversible. The membrane would then have to be replaced, thus increasing the operational costs. Membrane performance also decreases over time, resulting in the decreasing permeate flow rate [73]. Other major drawbacks are the high energy consumption, the scaling of $CaCO_3$ or $CaSO_4$ and the need for experienced personnel to run the process [74].

Table 6 summarizes the characteristics of some of the membranes and their treatment performance for wastewaters laden with heavy metals. It is observed that membranes with polyamide as their skin materials have a higher removal of heavy metals and can work at a wide range of temperature (5–45 °C). This may be attributed to the fact that polyamide membranes have a higher porosity and hydrophilicity than other materials such as cellulose acetate [71]. It is important to note that the selection of the appropriate membrane depends on a number of factors such as the characteristics of the wastewater, the nature and concentration of materials present in the wastewater, pH and temperature. In addition, the membranes should be compatible with the feeding solution and cleaning agents to minimize surface fouling [75].

2.5. *Ion exchange*

In addition to membrane filtration, ion exchange is also one of the most frequently applied treatments worldwide for wastewater laden with heavy metals. In ion exchange, a reversible interchange of ions between the solid and liquid phases occurs, where an insoluble substance (resin) removes ions from an electrolytic solution and releases other ions of like charge in a chemically equivalent amount without any structural change of the resin [52,76]. Ion exchange can also be used to recover valuable heavy metals from inorganic effluent [77]. After separating the loaded resin, the metal is recovered in a more concentrated form by elution with suitable reagents.

Since the acidic functional groups of resin consist of sulfonic acid, it is assumed that the physicochemical interactions that may occur during metal removal can be expressed as follows:

$$\underset{\text{(resin)}}{n\mathrm{RSO_3^-{-}H^+}} + \underset{\text{(solution)}}{\mathrm{M}^{n+}} \leftrightarrow \underset{\text{(resin)}}{n\mathrm{RSO_3^-{-}M^{n+}}} + \underset{\text{(solution)}}{n\mathrm{H}^+} \quad (5)$$

where ($–RSO_3^-$) and M represent the anionic group attached to the ion exchange resin and the metal cation, respectively, while *n* is the coefficient of the reaction component, depending on the oxidation state of metal ions [77].

The application of natural exchangers such as clinoptilolite and synthetic zeolite (NaPl) to purify synthetic wastewater was investigated [13]. It was found that synthetic zeolite demonstrated a sorption capacity about 10 times greater than that of clinoptilolite (Table 7a), despite having a comparable surface area (20–28 m^2/g). This could be attributed to the H^+ exchange capacity of zeolite and the strength of hydration shell cations that played major roles in the sorption capacities of both exchangers [25].

Other synthetic resins such as Amberlite IR-120 and Dowex 2-X4 were employed to investigate the total uptake of heavy metals from real plating wastewater containing Zn(II), Cr(III) and Cr(VI) ions [78]. The ion exchange system was found to completely remove all the heavy metals from the solution (Table 7b).

Similar results for Cr(III) uptake were also obtained by Rengaraj et al. [76], who investigated the removal performance of IRN77 and SKN1 resins in a synthetic solution. They reported that a complete removal of Cr(III) with a higher metal concentration of 100 mg/L could be achieved. Other resins such as 1200H, 1500H and IRN97H were also employed to study the kinetics of Cr uptake from real and synthetic wastewater [79].

Table 7a
Selective heavy metal uptake using ion exchange

Species	Ion-exchanger	Nature of ion exchanger	Dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Removal efficiency (%)	References
Cr(III)	Clinoptilolite	Weakly acidic ion exchanger	10	100	NA	4.10	90	[13]
	Synthetic (NaP1) zeolite	Weakly acidic ion exchanger	2.5	100	NA	43.58	100	
Ni(II)	Clinoptilolite	Weakly acidic ion exchanger	10	100	NA	2.00	90	
	Synthetic (NaP1) zeolite	Weakly acidic ion exchanger	2.5	100	NA	20.08	100	
Zn(II)	Clinoptilolite	Weakly acidic ion exchanger	10	100	NA	3.47	90	
	Synthetic (NaP1) zeolite	Weakly acidic ion exchanger	2.5	100	NA	32.63	100	
Cu(II)	Clinoptilolite	Weakly acidic ion exchanger	10	100	NA	5.91	90	
	Synthetic (NaP1) zeolite	Weakly acidic ion exchanger	2.5	100	NA	50.48	100	
Cd(II)	Clinoptilolite	Weakly acidic ion exchanger	10	100	NA	4.61	90	
	Synthetic (NaP1) zeolite	Weakly acidic ion exchanger	2.5	100	NA	50.80	100	
Ni(II)	Clinoptilolite	Weakly acidic ion exchanger	100	51.6	NA	8.89	75	[25]
Ni(II)	Zeolite tuffs	Weakly acidic ion exchanger	1.2	250	4.0–4.5	0.4	NA	[81]
Ni(II)	Zeolite	Weakly acidic ion exchanger	0.1	40	5.0	NA	60	[82]
Cu(II)			0.1	84	5.0	NA	64	

NA: not available.

Table 7b
Selective heavy metal uptake using synthetic ion exchange resin

Species	Ion-exchanger	Nature of resin	Dose (g/L)	Initial metal concentration (mg/L)	Optimum pH	Adsorption capacity (mg/g)	Removal efficiency (%)	References
Zn(II)	Amberlite IR-120	Strongly acidic resin with sulfonic acid functionality	NA	5.43	NA	NA	100	[78]
Cr(III)			NA	2.66	NA	NA	100	
Cr(VI)	Dowex 2-X4	Strongly basic resin with trimethylbenzyl-ammonium as the active group	NA	9.77	NA	NA	100	
Cr(III)	IRN77	Strong acidic resin with sulfonic acid functionality	3.0	100	3.5	35.38	100	[76]
	SKN1	Strongly acidic resin with sulfonic acid functionality	3.0	100	3.5	46.34	100	
Cr(III)	Amberjet 1200H	Strongly acidic resin with –SO$_3$$^-$ functionality	0.5	10	2–6	84.04	100	[79]
	Amberjet 1500H	Strongly acidic resin with sulphonates functionality	1.0	10	2–6	188.67	100	
	Amberlite IRN97H	Strongly acidic resin with –SO$_3$$^-$ functionality	1.5	10	2–6	58.14	100	
Ni(II)	Amberlite IR-120	Strongly acidic resin with sulphonates functionality	0.1	NA	NA	NA	NA	[80]
Cr(VI)	Ambersep 132	Strongly basic resin (H type)	0.4	750	NA	92.10	NA	[83]
			10.0	750	NA	100.00	NA	
Cr(III)	Lewatit TP 207	A strongly acidic resin with iminodiacetate functionality	0.4	3.12	4.5	17.73	NA	[86]
	Chelex-100	A strongly acidic resin with iminodiacetate functionality	0.8	3.12	4.5	14.98	NA	
Cr(VI)	Solvent impregnated resin (SIR) with aliquat 336	An acidic resin based on hydrophilic polymer	1.0	0.13	5.0	38.0	99.5	[85]

NA: not available.

Table 8
Exchange capacity of cations (meq/g) with different complex agents [80]

Species	Complex agent	Ion-exchanger	Dose of resin (g/L)	α[a]	Exchange capacity (meq/g)
Ni(II)	EDTA	Amberlite IR-120	1.0	0.5	0.30
	NTA				0.26
	Citrate				0.25
	EDTA	Amberlite IR-120	1.0	1.0	0.31
	NTA				0.27
	Citrate				0.25
Mn(II)	EDTA	Amberlite IR-120	1.0	0.5	0.34
	NTA				0.35
	Citrate				0.34
	EDTA	Amberlite IR-120	1.0	1.0	0.35
	NTA				0.36
	Citrate				0.34
Co(II)	EDTA	Amberlite IR-120	1.0	0.5	0.32
	NTA				0.28
	Citrate				0.32
	EDTA	Amberlite IR-120	1.0	1.0	0.34
	NTA				0.28
	Citrate				0.33

[a] α: the molar concentration ratio of complexing agent to the total metal.

Another investigation using Amberlite IR120 resin was performed on the uptake of multi-cations (Ni(II), Mn(II) and Co(II)) from complex synthetic solution containing EDTA, NTA and citrate [80]. Amberlite IR-120 is a strongly acidic resin with a sulfonic acid functionality. The researchers found that the equilibrium exchange of metal and resins was dependent on the pH and the complex agent used (Table 8), confirming the results of other studies [81,82].

Synthetic resin such as Ambersep 132 was also explored to recover chromic acid (H_2CrO_4) from synthetic plating solution [83]. Both batch and column tests were carried out to compare the performance of the recovery process. In the batch studies, the Langmuir isotherm (92.1 mg/g) was more representative than the Freundlich (24.56 mg/g) for the equilibrium sorption data of chromic acid. The metal exchange capacity in the column operation (100 mg/g) was higher than that of the batch studies (92.1 mg/g) at the same concentration of 750 mg/L. This could be attributed to the fact that in the batch studies, the concentration gradient decreased with an increasing contact time; while in the column operation, the resin had continuous physico–chemical contact with fresh feeding solution at the interface of the adsorption zone, when the adsorbate solution passed through the column. Consequently, more cations were exchanged in the column operation than in the batch studies [84–87].

In general, ion exchange is effective to treat inorganic effluent with a metal concentration of less than 10 mg/L, or in the range of 10–100 mg/L, or even higher than 100 mg/L (Tables 7a and 7b). Depending on the characteristics of the ion exchanger, heavy metal removal by ion exchange works effectively in acidic conditions with pH ranging from 2 to 6. Among the ion-exchangers, low-cost material such as clinoptilolite can give a comparable metal removal (90%) to commercial resins such as IRN77 and SKN1 (100%) for the same Cr(III) concentration of 100 mg/L (Tables 7a and 7b). Unlike chemical precipitation, ion exchange does not present any sludge disposal problems [88], thus lowering the operational costs for the disposal of the residual metal sludge. Other advantages of ion exchange include its convenience for fieldwork since the required equipment is portable, the speciation results are reliable and the experiments can be done quickly. Resins also have certain ligands that can selectively bond with certain metal cations, making ion exchange easy to use and less time-consuming [89].

Despite these advantages, ion exchange also has some limitations in treating wastewater laden with heavy metals. Prior to ion exchange, appropriate pretreatment systems for secondary effluent such as the removal of suspended solids from wastewater are required. In addition, suitable ion exchanger resins are not available for all heavy metals, the capital and operational cost is high [90].

2.6. *Electrochemical treatment techniques*

2.6.1. *Electrodialysis (ED)*

Electrodialysis is a membrane separation in which ionized species in the solution are passed through an ion exchange membrane by applying an electric potential [91]. The membranes are thin sheets of plastic materials with either anionic or cationic characteristics. When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion-exchange and cation-exchange membranes [92,93].

Some interesting results were reported by Tzanetakis et al. [94], who evaluated the performance of the ion exchange membranes for the electrodialysis of Ni(II) and Co(II) ions from a synthetic solution. Two cation exchange membranes, perfluorosulfonic Nafion 117 and sulfonated polyvinyldifluoride membrane (SPVDF), were compared under similar operating conditions. By using perfluorosulfonic Nafion 117, the removal efficiency of Co(II) and Ni(II) were 90% and 69%, with initial metal concentrations of 0.84 and 11.72 mg/L, respectively.

Different results were reported from a laboratory scale study of Cd(II) treatment from synthetic plating wastewater using ED [95]. Two commercial cationic and anionic exchange membranes, Nafion 450 and Selemion, were employed. About 13% of Cd(II) with an initial metal concentration of 2 g/L was removed within 120 min.

The literature review above indicates that ED cannot effectively treat inorganic effluent with a metal concentration higher than 1000 mg/L, thus suggesting that ED is more suitable for a metal concentration of less than 20 mg/L (Table 9). In spite of its limitation, ED offers advantages for the treatment of wastewater laden with heavy metals such as the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water. Moreover, valuable metals such as Cr and Cu can be recovered. Since ED is a membrane process,

Table 9
Electrochemical treatment technologies for removal of heavy metals

Species	Anode	Cathode	Electrical current (A/m^2)	Power consumption ($kW\,h/m^3$)	Initial metal concentration (mg/L)	Optimum pH	Removal/ recovery efficiency (%)	Cost of treatment ($US\$/m^3$)	References
Ni(II)	Platinum oxide-based coated Ti	Stainless steel	400.0	NA	11.72	NA	69	NA	[94]
Co(II)			25.0	NA	0.84	NA	90	NA	
Cd(II)	Nafion 450	Selemion	150.0	NA	2000	NA	13	NA	[95]
Ni(II)	Activated Ti	Metal granule	325.0	4.2×10^3	2000	5.5	90	NA	[99]
Cr(VI)	Carbon aerogel	Carbon aerogel	0.8	NA	8	2.0	98.5	NA	[97]
	Iron rotary	Iron rotary	113.0	7.9×10^3	130	8.5	99.6	NA	[98]
	Fe_2O_3	NA	1.7	12	NA	10–11	77–100	5.54	[18]
	Fe_2O_3	NA	6.7	20	2100	10–11	85.1	5.54	[100]
Ni(II)	Ti(II)	Stainless sheet	600.0	3.43×10^3	40000	NA	80–85	NA	[101]

NA: not available.

it requires clean feed, careful operation, periodic maintenance to prevent any damages to the stack.

2.6.2. *Membrane electrolysis (ME)*

Membrane electrolysis, a chemical process driven by an electrolytic potential, can also be applied to remove metallic impurities from metal finishing wastewater. There are two types of cathodes used: a conventional metal cathode (electrowinning) and a high surface area cathode [17]. When the applied electrical potential across an ion exchange membrane, reduction–oxidation reaction takes place in electrodes [96]. In the anode, oxidation reactions occur as follows:

$$M_1(\text{insoluble}) \leftrightarrow {M_1}^{n+}(\text{soluble}) + ne^- \qquad (6)$$

$$4OH^- \leftrightarrow 2H_2O + O_2 + 4e^- \qquad (7)$$

$$2Cl^- \leftrightarrow Cl_2 + 2e^- \qquad (8)$$

In the cathode, the following reduction reactions take place:

$${M_2}^{n+}(\text{soluble}) + ne^- \leftrightarrow M_2(\text{insoluble}) \qquad (9)$$

$$2H^+ + 2e^- \leftrightarrow H_2(g) \qquad (10)$$

M and *n* represent the metal and the coefficient of the reaction component, respectively. The *n* coefficient depends on the state oxidation of the metal ions.

The feasibility of electrochemical Cr(VI) removal from synthetic wastewater using carbon electrodes was investigated [97]. More than 98% of Cr removal with an initial metal concentration of 8 mg/L could be achieved at pH 2.0. This result is slightly lower than that of Martínez et al. [98], who studied Cr(VI) removal from synthetic plating wastewater. An almost complete Cr removal could be achieved with an initial metal concentration of 130 mg/L, consuming 7.9 kW h/m^3 of energy. Martínez et al. [98] reported that the higher the current density, the shorter the treatment time required and the lower the energy spent for agitation.

Ni(II) recovery from synthetic rinse water of plating baths using ME was studied [99]. About 90% of Ni(II) was recovered from an initial metal concentration of 2 g/L. However, this process required 4.2×10^3 kW h/m^3 of energy consumption, significantly higher than that of Kongsricharoern and Polprasert [18,100], which consumed 12–20 kW h/m^3 using electrochemical precipitation (Table 9).

Unlike ED, ME can be employed to treat plating wastewater with a metal concentration of higher than 2000 mg/L or less than 10 mg/L (Table 9). The major drawback of ME is its high energy consumption.

2.6.3. *Electrochemical precipitation (EP)*

To maximize the removal of heavy metal from contaminated wastewater, electrical potential has been utilized to modify the conventional chemical precipitation. Some work using electrochemical precipitation (ECP) was carried out for the removal of Cr(VI) from real electroplating wastewater [18]. Over 80% of Cr removal could be attained and the treated Cr effluent was less than 0.5 mg/L, the effluent limit allowed in Thailand. The result is comparable to that of Kongsricharoern and Polprasert [100], which also employed bipolar ECP for Cr(VI) removal using the same type of wastewater. Bipolar ECP was also technically applicable for 85% of Cr removal with an initial Cr concentration of 2100 mg/L.

In general, electrochemical precipitation processes can treat inorganic effluent with a metal concentration higher than 2000 mg/L (Table 9). Depending on the characteristics of the electrodes, the electrochemical process can work at either acidic or in basic conditions [101]. Grebenyuk et al. [102,103] reported that heavy metal removal can be carried out through electrochemical oxidation/reduction processes in an electrochemical cell without a continuous feeding of redox chemicals, thus avoiding a costly space, time and energy consumption.

2.7. *Adsorption*

Recently, adsorption has become one of the alternative treatment techniques for wastewater laden with heavy metals [104]. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and becomes bound by physical and/or chemical interactions [105]. Due to its large surface area, high adsorp-

Table 10
Summary of the highest reported adsorption capacities of low-cost adsorbents and activated carbon

Source of adsorbent	Type of adsorbent	Adsorption capacity (mg/g)					References
		Cd(II)	Cr(VI)	Cu(II)	Ni(II)	Zn(II)	
Agricultural waste	Hazelnut shell		170				[112]
	Orange peel				158		[113]
	Citric acid-modified soybean hull			154.9			[114]
Industrial by-products	Red mud				160		[115]
	Blast-furnace slag			133.35		103.33	[116]
Natural materials	HCl-treated clay			83.3	80.9	63.2	[117]
Activated carbon	GAC type Filtrasorb 400		145				[118]
	HNO_3^- treated ACF	146					[119]

tion capacity and surface reactivity, adsorption using activated carbon can remove metals such as Ni(II) [106], Cr(VI) [107], Cd(II) [108], Cu(II) [109] and Zn(II) [110] from inorganic effluent.

Kurniawan et al. [111] reviewed over 100 papers (1984–2005) on the application of various low-cost adsorbents derived from agricultural waste, industrial by-product or natural material for the removal of heavy metals (Cd(II), Cr(III), Cr(VI), Cu(II), Ni(II) and Zn(II)) from metal-contaminated wastewater. Table 10 presents the highest reported metal adsorption capacities of low-cost adsorbents from various sources and activated carbon. The table indicates that low cost adsorbents from agricultural waste can be viable alternatives to costly activated carbon for the treatment of metals-contaminated wastewater. In general, technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat inorganic effluent.

3. Evaluation of heavy metal removal by different physico–chemical treatments

To evaluate the performances of all the treatments described above, a comparative study is presented in terms of pH, dose required (g/L), initial metal concentration (mg/L), and metal removal efficiency. Although it has a relative meaning due to the different testing conditions (pH, temperature and strength of wastewater), this comparison is useful to evaluate the overall removal performance of each treatment in the decision-making process.

Table 11 summarizes the most outstanding metal removal performance among the various physico–chemical treatments presented in this study. Depending on the initial metal concentration of the contaminated wastewater, it is evident from the table that ion exchange has achieved a complete removal of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) with an initial concentration

Table 11
Comparison of the outstanding removal performance among treatment technologies for metal uptake

Type of treatment	Metal species	Type of precipitant/ coagulant/ ion exchanger/ membrane/ collector/ electrode	Optimum dose (g/L)	Initial metal concentration (mg/L)	Pressure (bar)	Optimum pH	Power consumption (kW h/m^3)	Removal efficiency/metal rejection rate (%)	References
Chemical precipitation	Mn(II)	$Ca(OH)_2$	10	1085	–	11.0	–	99.30	[7]
Coagulation	Cu(II)	Poly-ferric sulfate	25	20	–	10.0–11.5	–	99	[9]
Flotation	Zn(II)	Surfactin-105	0.04	50	–	6.0	–	100	[45]
	Zn(II)	SDS	0.05	50	–	7–9	–	100	[51]
Ion exchange	Cr(III)	Synthetic (NAP1) zeolite	2.5	100	–	NA	–	100	[13]
	Ni(II)		2.5	100	–	NA	–	100	
	Zn(II)		2.5	100	–	NA	–	100	
	Cu(II)		2.5	100	–	NA	–	100	
	Cd(II)		2.5	100	–	NA	–	100	
	Cr(III)	IRN77	3.0	100	–	3–5	–	100	[76]
		SKN1	3.0	100	–	3–5	–	100	
Ultrafiltration	Cu(II)	YM1	–	79	2	8.5–9.5	–	100	[14]
Nanofiltration	Cd(II)	Polyamide	–	200	7	4–11	–	99	[64]
Reverse osmosis	Cu(II)	ES20	–	50	5	7–9	–	100	[69]
	Ni(II)	ES20	–	50	5	7–9	–	100	
Membrane electrolysis	Cr(VI)	Iron rotary	–	130	–	8.5	7.9×10^3	99.60	[98]

NA: not available.

of 100 mg/L, respectively. The results are comparable to that of reverse osmosis (99% of Cd(II) rejection with an initial concentration of 200 mg/L). Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration of higher than 1000 mg/L. It is interesting to note that flotation also offers comparable metal removal (100%) to RO, an advanced treatment technique, at the same metal concentration of 50 mg/L, but with a lower cost.

In general, physico–chemical treatments offer various advantages such as their rapid process, ease of operation and control, flexibility to change of temperature. Unlike biological system, physico–chemical treatment can accommodate variable input loads and flow such as seasonal flows and complex discharge. Whenever it is required, chemical plants can be modified. In addition, the treatment system requires a lower space and installation cost. Their benefits, however, are outweighed by a number of drawbacks such as their high operational costs due to the chemicals used, high energy consumption and handling costs for sludge disposal. However, with reduced chemical costs and a feasible sludge disposal, physico–chemical treatments have been found as one of the most suitable treatments for inorganic effluent.

4. Cost comparison of treatment technologies for electroplating wastewater

To estimate a reliable treatment cost for metal-contaminated wastewater is difficult due to the many cost components such as pumping equipment and treatment facility involved. In addition, changes in the quality and quantity of the plating wastewater due to the fluctuating market demand also contribute to the variations of its treatment cost. Therefore, information on the treatment cost of plating wastewater is rarely reported (Tables 2–10).

Basically, the treatment cost of contaminated wastewater varies, depending on its strength and quantity, the process employed, the amount and composition of impurities, as well as the extent of purification [120,121]. The overall treatment cost includes the construction costs as well as the operational and maintenance costs (O&M). The construction costs normally depend on the effluent quality required and the capacity of the installation, while the O&M costs cover manpower, energy, chemicals and maintenance. The manpower cost varies from one country to another. To obtain an accurate assessment of the operational cost for the treatment of electroplating wastewater, a pilot-scale study needs to be carried out [122].

Although this article has featured some pilot studies [98,123], most of the data presented above are derived from research conducted on a laboratory scale. Consequently, further experiments on a pilot scale are needed to quantify the overall treatment cost associated with the proposed treatment. A direct comparison of the overall treatment cost of each technique presented above may be difficult due to their different operating conditions.

In addition, the overall treatment cost for electroplating wastewater varies depending on the process employed and the local conditions. This may be attributed to the fact that most of the electroplating industries (especially in the Southeast Asia) are located either in the commercial area of a town or in industrial estates, where wastewater is discharged into sewers after neutralization with acids/alkalis [124]. Wastewater treatment plants of other engineering industries that have electroplating sections are designed to handle the entire wastewater, including those from the electroplating process. As a result, the cost of installation and operation of such plants do not represent the actual cost of an independent plating industry. Wide variations in the flow and the characteristics of the effluent wastewater also present difficulties in estimating the treatment cost accurately. Such inconsistency in data presentation makes a cost comparison among the available treatment technologies for wastewater laden with heavy metals difficult to materialize.

5. Concluding remarks

Over the past two decades, environmental regulations have become more stringent, requiring an improved quality of treated

Table 12
Summary of the treatability of physico–chemical treatments for inorganic effluent

Number	Type of treatment	Target of removal	Advantages	Disadvantages	References
1	Chemical precipitation	Heavy metals, divalent metals	Low capital cost, simple operation	Sludge generation, extra operational cost for sludge disposal	[22,28,29]
2	Coagulation–flocculation	Heavy metals and suspended solids	Shorter time to settle out suspended solids, improved sludge settling	Sludge production, extra operational cost for sludge disposal	[30,103]
3	Dissolved air flotation	Heavy metals and suspended solids	Low cost, shorter hydraulic retention time	Subsequent treatments are required to improve the removal efficiency of heavy metal	[10,40]
4	Ion exchange	Dissolved compounds, cations/anions	No sludge generation, less time consuming	Not all ion exchange resin is suitable for metal removal, high capital cost	[52,76]
5	Ultrafiltration	High molecular weight compounds (1000–10000 Da)	Smaller space requirement	High operational cost, prone to membrane fouling	[52,56]
6	Nanofiltration	Sulphate salts and hardness ions such as Ca(II) and Mg(II)	Lower pressure than RO (7–30 bar)	Costly, prone to membrane fouling	[15]
7	Reverse osmosis	Organic and inorganic compounds	High rejection rate, able to withstand high temperature	High energy consumption due to high pressure required (20–100 bar), susceptible to membrane fouling	[52,68]

effluent. In recent years, a wide range of treatment technologies such as chemical precipitation, coagulation–flocculation, flotation, ion exchange and membrane filtration, have been developed for heavy metal removal from contaminated wastewater. It is evident from the literature survey of 124 articles (1980–2006) that ion exchange and membrane filtration are the most frequently studied and widely applied for the treatment of metal-contaminated wastewater. Ion exchange has achieved a complete removal of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) with an initial concentration of 100 mg/L, respectively. The results are comparable to that of reverse osmosis (99% of Cd(II) rejection with an initial concentration of 200 mg/L). Lime precipitation has been found as one of the most effective means to treat inorganic effluent with a metal concentration higher than 1000 mg/L.

Table 12 summarizes the treatability of various physico–chemical techniques for electroplating wastewater. Among the treatments presented in the table, some of them have been tested successfully in laboratory or even on a pilot scale. Some may even be ready for commercialization. However, no individual treatment has been found to be universally effective and applicable for heavy metal removal. As future regulations focus upon the ability of industrial users to comply with the legal requirements of the residual metal concentration in discharge, it would be very beneficial to investigate various treatments, which can assist industrial users to comply with the environmental law.

Although many techniques can be employed for the treatment of wastewater laden with heavy metals, it is important to note that the selection of the most suitable treatment for metal-contaminated wastewater depends on the initial metal concentration, the overall treatment performance compared to other technologies, plant flexibility and reliability, environmental impact as well as economics parameter such as the capital investment and operational costs (energy consumption and maintenance). Finally, technical applicability, plant simplicity and cost-effectiveness are the key factors that play major roles in the selection of the most suitable treatment system for inorganic effluent. All the factors mentioned above should be taken into consideration in selecting the most effective and inexpensive treatment in order to protect the environment.

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