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Overview Scheme for Nickel Removal and Recovery from Wastes

Ahamed Ashiq, Viraj Gunarathne, and Meththika Vithanage

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14.1 Introduction

Trace metals can be described as the elements that have atomic weights from 63.5 to 200.6 amu and specific gravity higher than 5.0 (Srivastava and Majumder 2008). Release of trace metals into the natural environment through several industrial activities, including mining and metallurgical, electronic, electroplating, and metal finishing (Jadhav and Hocheng 2012), involved severe environmental pollution in the last few decades (Naaz and

Pandey 2010). Heavy metals are difficult to remove naturally by degradation and tend to accumulate in living organisms, generating highly toxic effects on them (Qin et al. 2012).

Most of the trace metals released into the environment through anthropogenic activities are in the form of aqueous solutions (Borbély and Nagy 2009). Therefore, the kind of wastewater generated from manufacturing processes in industries such as electronic and metal finishing typically contains higher concentrations of metals than acceptable levels established by law (Hunsoma et al. 2002). Other than wastewater, solid wastes including spent petroleum catalysts, fly ash, boiler ash, and waste electrical and electronic equipment (WEEE) contain considerable amounts of trace metals (Abdel-Aal and Rashad 2004; Akcil et al. 2015; Park and Fray 2009).

With increasing economic and environmental issues in mind, the removal or recovery of metals from wastes is an important concern (Kaminari et al. 2007; Qin et al. 2012).

14.1.1 Nickel as a Resource for Industry

Nickel has been recognized as an important strategic resource because of its optical, electrical, and catalytic performance; toughness; high corrosion resistance; thermal stability; chemical passivity; and ability to make super alloys (Farrell et al. 2010; Peng et al. 2014; Zahraei et al. 2015). It is a comparatively widespread element in nature (Förstner 1981), and raw materials including oxidic, silicate, sulfide, and laterite ore are the main production sources of nickel (Moskalyk and Alfantazi 2002; Panigrahi et al. 2009). However, after the 1960s, laterites became a major commercial source of nickel since sulfide ores declined with a drastic increase in world nickel consumption (Guo et al. 2009). Moreover, 70% of the world's nickel deposits are present in the form of laterites (Dalvi et al. 2004).

Nickel is extensively used in the stainless steel industry, accounting for two-thirds of the total nickel production. Also, the nickel consumption rate for this industry is increasing at a rate of 5%–6% annually (Anderson 1996; Anthony and Flett 1997).

Moreover, nickel is one of the most used element for coating of different industrial materials as it provides decorative appearances and improves resistance to corrosion (Schario 2007). Watts' baths containing chlorides and sulfates of nickel and boric acid are a widely used industrial method to improve surface finishing and appearance (Benvenuti et al. 2014).

Furthermore, nickel is used as a raw material for a wide variety of manufacturing processes such as mineral processing, paint formulation, phosphate fertilizers, electro chromic films, dye-sensitized solar cell, forging, battery manufacturing, magnets, semiconductors, gas sensors, non-ferrous metals, and special alloys (e.g., nickel steels, nickel cast irons, nickel brasses, and bronzes) as well as for minting of coins and tinting of glasses in green (Dizge et al. 2009; Mohammadijoo et al. 2014; Peng et al. 2014).

14.2 Sources of Nickel as Waste

Nickel-containing wastes have been released into the environment in two major forms: solid and aqueous. Regularly, nickel is discharged into water bodies through wastewater streams originating from various industries (Gupta et al. 2003). However, the rapidly growing production and consumption of nickel-based products (i.e., batteries, electronic equipment, etc.) are involved in the accumulation of nickel in the environment in the form of solid waste.

14.2.1 Nickel in Wastewaters and Solid Waste

Wastewater from industries such as nickel electroplating and textile or effluents comes from washing of nickel-contaminated soil that is used as a remediation technique, which often carries up to 1000 mg L^{-1} of nickel (Dermentzis 2010). However, according to industrial sources, nickel concentration varies from tens to thousands of milligrams per liter (Dermentzis 2010; Varma et al. 2013). Also, 60%–70% of all metals used in the plating process are not utilized effectively and removed with wastewater during rinsing of the plated article (Dermentzis 2010).

Spent rechargeable batteries (i.e., Ni-Cd, Ni-MH, and Li-ion batteries) are a major contributor to nickel-containing solid wastes. The cathode material of Ni-Cd batteries encompassed with nickel hydroxy-oxide in nickel form and anode consists of metallic cadmium embedded on a wire mesh of nickel (Sullivan and Gaines 2012). Generally, Ni-Cd batteries contain nearly 20% of nickel by weight (Gaines and Singh 1995; Rydh and Karlström 2002). However, cadmium is highly toxic in nature, and Ni-Cd batteries were eventually replaced by Ni-MH batteries. After commercializing them in 1990, Ni-MH batteries have been extensively used for a wide range of applications (Li et al. 2009). Electrodes and the active electrode material of Ni-MH batteries, which mainly consist of nickel, have a 30% total nickel content (Innocenzi and Vegliò 2012; Zhang et al. 1999). Also, in 2005, the total count of spent Ni-MH batteries reached up to 1 billion, containing 7500 tons of nickel, leading to severe environmental pollution from trace metals (Innocenzi and Vegliò 2012). At present, LiNiO_2 is also used as a cathode material for lithium-ion batteries (Chen et al. 2015; Nishi 2001), and their disposal may contribute to nickel release into the environment.

Also, different kinds of spent catalysts that are used in various industries may contain varied amounts of nickel, according to the nature of the industrial process and operating conditions. For instance, the number of spent catalysts from an ammonia plant that contain nickel at elevated quantities ranged from 12% to 30% (Singh 2009). Spent hydrodesulfurization catalysts from petroleum refining industries (Dufresne 2007; Szymczycha-Madeja 2011) and the Raney nickel catalyst (fine particles of Ni–Al alloy) used in the

pharmaceutical industry (Lee et al. 2010) contain high amounts of nickel. In addition, several other nickel-containing catalysts are extensively used in different manufacturing processes such as hydro cracking (NiS, WS₃/SiO₂Al₂O₃) and hydro refining (Ni, Mo/Al₂O₃) (Thomas 1970).

Moreover, most WEEE contain components that are made of nickel. As an example, metallic constituents of CRT monitors contain about 25%–45% nickel (Robotin et al. 2011). Manufacturing and consumption of WEEE have increased drastically during the last few decades and the waste stream of the products is rapidly growing (Guo et al. 2010). Thus, trace metals including nickel are accumulated in the environment at high concentrations.

14.2.2 Fractionation of Nickel in Soil

The types of nickel (both physical and chemical forms) that exist in wastes are strongly associated with their bioavailability for organisms (Schaumlöffel 2012). Speciation distribution of nickel in wastes is varied according to the type of waste, physicochemical properties, and waste management treatment. For example, nickel in WEEE is mostly associated with residual fraction and Fe-Mn oxide bound fraction than with organic matter fraction and carbonate bound fraction. However, the products resulting from incineration of WEEE contained significantly increased nickel contents in exchangeable and residual fractions (Long et al. 2013). The majority of nickel in fly ashes obtained from waste filter bags of steel plants existed in residual and acid-exchangeable fractions (Zhou et al. 2013).

14.2.3 Problems Associated with Nickel-Containing Wastes

Nickel occurs in sea water, petroleum, and coal at trace levels, and Ni²⁺ present in the environment can seep into plant and animal bodies. Minor quantities of Ni²⁺ serve as an activator of certain enzymes and have a beneficial effect on humans and other organisms (Peng et al. 2014). However, common compounds that contain elevated amounts of nickel have a toxic effect on humans and animals. Nickel ions can generate major genetic effects by binding with nucleic acids; a typically known local reaction to nickel is dermatitis (Gupta 1998). Also, exposure to Ni²⁺ at higher concentrations has wide-ranging effects, from minute symptoms such as dizziness, headache, extreme weakness, chest pain, rapid respiration, dry cough, gastrointestinal disorders, and cyanosis, to serious illnesses such as lung cancer and renal edema (Argun 2008; Pillai et al. 2009; Smith-Sivertsen et al. 1997), but acute toxicity is rarely observed (Borbély and Nagy 2009).

Moreover, nickel has been considered as a nonbiodegradable toxic trace metal present in different kinds of waste materials (Peng et al. 2014). Therefore, removal of nickel from waste has been known as a difficult task and has been considered as a scientific challenge (Dermentzis et al. 2016).

14.3 Removal and Recovery Methods for Nickel from Wastes

Methods mentioned here are subcategorized either for removal or for recovery of the Ni^{2+} ions both from aqueous media and from solid wastes. Most of the extraction techniques revolve around the divalent nature of nickel either from wastewaters or solid wastes. Commercially used methods employed for nickel removal are leaching, ion exchange, ion flotation, adsorption, and membrane filtration (Figure 14.1). The most prominent commercial methods used to recover Ni^{2+} ions are electrochemical methods and a combination of electrochemical and ionization processes. A summary of the recovery and removal methods is provided in Table 14.1.

14.3.1 Leaching

Leaching is the extraction of a soluble component from a solid by means of a solvent. The process is utilized for the extraction of a very valuable solid material like nickel or for the removal of an insoluble solute from a contaminated solvent (Harker and Backhurst 2002).

To extract nickel from battery scraps, a systematic approach is used, such as leaching through mineral acids (e.g., sulfuric acid, hydrochloric acid, and nitric acid), followed by a filtration technique to remove the rest of the elements in the battery. Subsequently, precipitation is also carried out to concentrate nickel (Lee et al. 2010; Zhang et al. 1999); in the case of Ni-MH batteries, the electrode materials are treated with 2 M sulfuric acid and maintained at pH 0.4. Rare earths (other metal parts) are recovered at first from an external

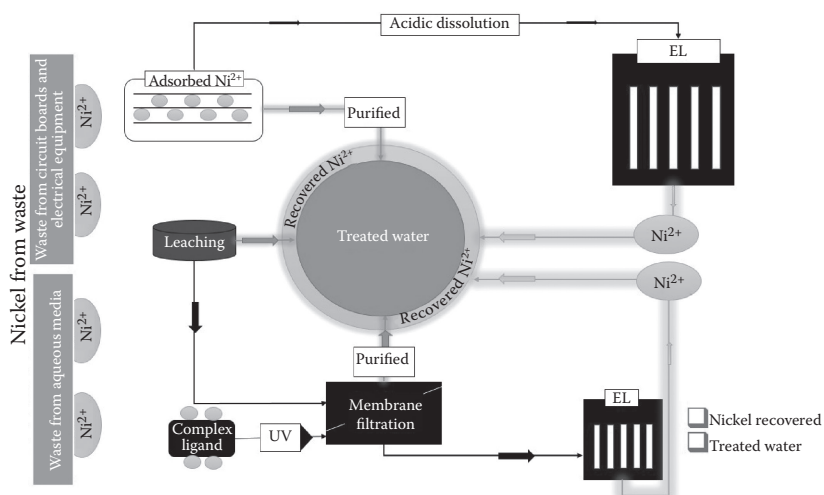


FIGURE 14.1

Nickel recovery from industrial wastewater. EL, electrochemical methods.

TABLE 14.1
Summary of Nickel Removal/Recovery Methods, Sources of Wastes, and Percentage Removal

Recovery Method	Ni ²⁺ Waste Source	Materials Used	Efficiency for Recovery (%)	Adsorption Capacity (mg/g)	Dosage (g/L)	References
Leaching	Ni ²⁺ from batteries	Bis (2,4,4-tri-methylpentyl) phosphinic acid Cyanex 272 and sulfuric acid	98	—	—	(Li et al. 2009)
		Sulfuric acid, citric acid and sodium hydroxide (precipitation)	99	—	—	(Innocenzi and Vegliò 2012)
		Tri-octyl/decyl amine (Alamine 336)	99	—	—	(Fernandes et al. 2013)
	Spent nickel metal	Sulfuric acid	98	—	—	(Siemens et al. 1986)
		Oxalic acid and hydrogen peroxide	65	—	—	(Mulak et al. 2006)
		Tartaric acid	83	—	—	(Marafi and Furimsky 2005)
		Citric acid	85	—	—	(Marafi and Furimsky 2005)
	Ni Mo / Al ₂ O ₃ hydro-treating catalyst	Sulfuric acid	98	—	—	(Valverde et al. 2008)
	Nickel molybdenum catalyst	Potassium bisulfate KHSO ₄	96–99	—	—	(Busnardo et al. 2007)
	Spent HDS catalyst	Nitric acid, sulfuric acid	90	—	—	(Lai et al. 2008)
	Ammonia leaching residue	Water leaching	91	—	—	(Chen et al. 2006)

(Continued)

TABLE 14.1 (CONTINUED)
 Summary of Nickel Removal/Recovery Methods, Sources of Wastes, and Percentage Removal

Recovery Method	Ni ²⁺ Waste Source	Materials Used	Efficiency for Recovery (%)	Adsorption Capacity (mg/g)	Dosage (g/L)	References
Ion exchange	From wastewaters	Chelex-100	99	—	—	(Leinonen et al. 1994)
		Sodium titanate	99.9	—	—	(Lehto et al. 1996; Leinonen et al. 1994)
Ion flotation		Dowex HCR S/S	98	—	—	(Alyüz and Veli 2009)
		Dodecyl-diethylenetriamine (Ddien)	93	—	—	(Liu and Doyle 2009)
		Ethylhexadecyldimethylammonium bromide (EHDABr)	88	—	—	(Hoseinian et al. 2015)
Adsorption		Citrus limettioides seed carbon (CLSC)		1.5	35.54	(Sudha et al. 2015)
		<i>Parthenium hysterophorus</i> L.		17.24	20	(Lata et al. 2008)
		Carbon aerogel		2.80	12	(Goel et al. 2005)
		Walnut shell carbon		15.34	30	(Wang et al. 2010)
		Bentonite clay		112.69	0.5	(Yang et al. 2009)
		Thermally treated attapulgite		2	10	(Ren et al. 2014)
		Turkish zeolite		119.7	8	(Kocaoba et al. 2007)
Natural zeolitic tuff		16.64	10	(Rajic et al. 2010)		
ZrO-montmorillonite		(40%)				
TBA-montmorillonite				0.05		(Gupta and Bhattacharyya 2006)

solvent extraction by adding bis(2-ethylhexyl)phosphoric acid (D2EHPA) followed by precipitation with oxalic acid. The nickel in the raffinates are then extracted through bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) followed by precipitation with oxalic acid, recovering about 99.8% of the nickel (Zhang et al. 1999). Other recovery techniques employed after leaching are electrolysis and electrowinning, which will be described later.

The other solvent that is commonly used for the extraction of Ni²⁺ ions from the batteries that showed promising results is D2EHPA with 6 M nitric acid. Nickel is then made to precipitate easily from the latter using oxalic acid, leaving behind the rest of the elements (the rare metals in the case of Ni-MH batteries) (Lyman and Palmer 1993a,b).

Nickel-based catalysts have been extensively used in oil and gas processes and are disposed as solid waste either in their pure form or as composites (Idris et al. 2010; Yang et al. 2011). Nickel found in these sources employs the leaching procedure as explained above through the use of other mineral acids, hydrogen peroxide, and potassium bisulfite (Akcil et al. 2015; Lai et al. 2008; Mulak et al. 2006).

The most common practice to recover nickel from used storage batteries (i.e., Ni-Cd batteries or Ni-MH batteries) and spent catalysts is through leaching, and it is becoming more popular because it is easy and can be carried out on a larger scale as the consumption and wastage of these batteries are exponentially increasing (Table 14.2). Majority of the hydrometallurgical processes in the literature proposed the combination of leaching and selective precipitations of the liquid–liquid phase (Innocenzi and Vegliò 2012).

TABLE 14.2

Spent Catalyst and Their Leaching Methods

Spent Catalyst	Leaching Agent Used	Nickel Recovered (%)	References
Spent nickel metal	Sulfuric acid	98	(Siemens et al. 1986)
	Oxalic acid and hydrogen peroxide	65	(Mulak et al. 2006)
	Tartaric acid	83	(Marafi and Furimsky 2005)
	Citric acid	85	(Marafi and Furimsky 2005)
Ni Mo/Al ₂ O ₃ hydro-treating catalyst	Sulfuric acid	98	(Valverde et al. 2008)
Nickel molybdenum catalyst	Potassium bisulfate KHSO ₄	96–99	(Busnardo et al. 2007)
Spent HDS catalyst	Nitric acid, sulfuric acid	90	(Lai et al. 2008)
Ammonia leaching residue	Water leaching	91	(Chen et al. 2006)

14.3.2 Ion Exchangers

Ion exchange is a highly selective method and clearly depends on the solution type and the desired contaminant or valuable metal to be extracted. Ion exchangers consist of solid materials that could carry cations or anions interchangeably. The ions are exchanged at a fixed stoichiometric rate with the particles in the solution. The materials with exchangeable cations are called cation exchangers and the materials that could carry anion are called anion exchangers (Helfferich 1962). Ion exchangers are specific to definite metals that have affinity toward that material. Mostly, the ions are exchanged or replaced with the desirable ion or displaced by the undesirable ion from the solution, say, Ni^{2+} from waters. The most commonly utilized exchanger types nowadays are mostly resin based with defined lattices (Barakat 2011; DaBrowski et al. 2004). Some other exchangers are coupled with electric current as in electrolysis for the recovered Ni^{2+} ions from the surfaces of the resins onto a concentrated solution, the details of which can be found in later sections.

For recovery, the important factor to take into consideration is the selectivity of ion and its medium for binding and unbinding, which is closely bound to the surface area of the exchangers used (Chitpong and Husson 2017). The ion exchangers are highly dependent on the functional group attached to the surface; carboxylate, sulfonate, amino, thiol, and amide groups as well as specialty ligands are commonly used to extract Ni^{2+} and to form a complex that can be recovered at a later stage through acidification (Chitpong and Husson 2017; Ma et al. 2013). Traditionally, zeolites were commonly used in ion exchangers and have now been replaced with synthetic resins that have been proven effective and inexpensive. The advantages were faster exchange rates, longer life cycles, higher capacity to withhold the nickel, and the ability to adsorb other metals as well (Alyüz and Veli 2009; Clifford 1999). Macro porous carboxylic cation exchangers showed positive results for the removal of nickel ions (Halle et al. 1982). Sulfonic-based cation exchangers with Styrene matrix were also suggested for commercial application for the removal of nickel from wastewaters (Alyüz and Veli 2009). Some of the commercially utilized resins specific to nickel ions are listed in Table 14.3.

TABLE 14.3

Commercially Used Ion Exchange Resins

Commercially Used Resin	Removal Efficiency for Ni^{2+}	References
Wofatit CA-20	Carboxylic acid	(Halle et al. 1982)
Chelex-100	99%	(Leinonen et al. 1994)
Sodium titanate	99.9%	(Lehto et al. 1996; Leinonen et al. 1994)
Dowex HCR S/S	98%	(Alyüz and Veli 2009)

Source: Lewinsky, A. A. 2007. *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*, Nova Publishers.

The commercial application of resins utilizes the divalent ion removal resin for the removal of nickel. There are certain criteria in which the selection of a resin is looked upon (Alyüz and Veli 2009):

- i. Higher charge on the ion than the resin preferred.
- ii. Less hydrated ions.
- iii. Ions with a strong affinity toward a particular functional group that contains the resins are to be considered.

Ion exchangers have shown promising results when it comes to nickel recovery mainly due to its low cost and high efficiency. The major attributes notable in the literatures are high recovery, less sludge, and being able to meet the requirements of the specifications (Rengaraj et al. 2001). Among the materials used in ion exchange processes, synthetic resins are commonly preferred because they are effective and inexpensive and can be modified to certain functional groups to have higher affinity toward Ni^{2+} (Clifford 1999). Cation exchange resins generally contain sulfonic acid groups. These groups can also be carboxylic, phosphonic, or phosphinic (Alyüz and Veli 2009). The drawbacks of ion exchange include the fouling of the surfaces of the resin matrices as it cannot handle high concentrations of the solutions with organics and solid wastes and it is quite dependent on the pH of the solution (Barakat 2011).

14.3.3 Ion Flotation

The flotation method is a gravity separation method. This method follows the usage of a surfactant that is foamed with an inert gas. The foam is then made to accumulate the trace metal values using the metal-ion complex that is formed. This is usually viable when there is an appropriate surfactant utilized to separate the required cation and the foaming conditions are taken into account as well (Sebba 1962). This technique utilizes two properties of the material: surface charge and surface energy. These properties need to be controlled by precisely choosing the right surfactants, followed by flotation (Sancio et al. 1992). After the selective attachment of the cation with the froth or foam, the solids are concentrated and transferred from the body of water to the surface. Thus, unlike settling by gravity only, it is a solid-liquid separation technique that has been utilized only after the density of the particles is made lower than that of the liquids (Deliyanni et al. 2017). This makes the recovery of Ni^{2+} plausible using separation and by further employing acid treatment and electrolysis.

Most of the metals in the periodic table are recovered by this method, especially at low concentrations, and in comparison with the other methods, flotation promises higher recovery of Ni^{2+} (Jafari et al. 2017). Table 14.4 shows a few notable surfactants available commercially and their removal percentile.

TABLE 14.4

Notable Surfactant and Their Efficiency

Surfactant Used	Ni ²⁺ (Recovered)	References
Dodecyl-diethylenetriamine (Ddien)	93%	(Liu and Doyle 2009)
Ethylhexadecyldimethylammonium Bromide (EHDABr)	88%	(Hoseinian et al. 2015)

Source: Carolin, C. F., Kumar, P. S., Saravanan, A., Joshiba, G. J. & Naushad, M. 2017. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *Journal of Environmental Chemical Engineering*, 5, 2782–2799.

The probability for the flotation separation to occur is highly dependent on the bubble and the particle collision. Its behavior tremendously varies at different nickel particle sizes (Dai et al. 2000). Recent studies have shown the different behaviors when the bubble–particle collision is enhanced by decreasing the bubble size or by increasing the particle size (Miettinen et al. 2010). From a nickel recovery perspective, the following are the major advantages of using this method: much lower energy requirements, lesser sludge with nickel concentrates, higher recovery, and continuous operation. This method is used for other trace metals as well (Rubio et al. 2002; Salmani et al. 2013).

14.3.4 Adsorption

This method is especially used for the removal of trace metals in aqueous media. Most of the Ni²⁺ ions are in parts-per-million levels and have several advantages over other processes. Adsorption is the most simplified and the oldest method for nickel recovery. In adsorption, nickel ions are diffused from the bulk solution onto the surface of the solid adsorbent, thereby forming a layer of adsorbed phase. The major drawback of this recovery is that the adsorbate does not hold at a certain level and thus several criteria are made to select the right adsorbents for nickel recovery (Harker and Backhurst 2002). Adsorbents that have a large surface area and that are chemically stable with the adsorbate are the basic criteria. Some of the adsorbents are modified through chemical treatments to have an enhanced surface area (Ren et al. 2015). Activated carbon (AC), clays, and zeolites are the commonly used adsorbents and have shown promising results for nickel removal from aqueous solutions (Raval et al. 2016).

14.3.4.1 Activated Carbon

ACs are commonly used commercial adsorbents for trace metal removals because of their large surface area and can withstand huge amounts of particles. It was found that a typical surface area for AC is 10⁶ m²/kg with a pore diameter of 2 nm (Harker and Backhurst 2002). Table 14.5 summarizes the best AC and sources of AC used for nickel recovery.

TABLE 14.5

Summary of the Major Activated Carbon Used with Their Dosages Used in Ni Recovery

Source of AC	Adsorption Capacity (mg/g)	Dosage (g/L)	References
Citrus limettioides seed carbon (CLSC)	1.5	35.54	(Sudha et al. 2015)
<i>Parthenium hysterophorus</i> L.	17.24	20	(Lata et al. 2008)
Carbon aerogel	2.80	12	(Goel et al. 2005)
Walnut shell carbon	15.34	30	(Wang et al. 2010)

Source: Raval, N. P., Shah, P. U. & Shah, N. K. 2016. Adsorptive removal of nickel (II) ions from aqueous environment: A review. *Journal of Environmental Management*, 179, 1–20.

14.3.4.2 Clay Adsorbents and Zeolites

Both these adsorbents are known for their crystalline lattice that facilitates the adsorption of trace metals. Because of this, the positively charged trace metals are easily adsorbed and exchanged in their closely knit frameworks (Kim and Keane 2002; Qiu and Zheng 2009). These tetrahedral structures possess large channels containing negatively charged sites that could take advantage of adsorbing a cation, say, Ni²⁺ (Bailey et al. 1999).

Zeolites are aluminosilicates that have SiO₄ and Al₂O₃ linked to each other with a shared oxygen atom in a three-dimensional crystal lattice (Deer et al. 1992). They have the capability of counterbalancing with a cation because of their negatively charged sites (Malamis and Katsou 2013).

Clays are naturally occurring minerals and are hydrated aluminosilicates as well. They too possess crystal structures as in zeolites but exist in both tetrahedral and octahedral crystal lattices, which allow more affinity for adsorption of trace metals (Uddin 2017).

However, these minerals are almost completely modified to increase the cation uptake onto the adsorbents either chemically or thermally. Table 14.6 summarizes some notable and the highest adsorbent capacities with the least dosage of these materials.

14.3.5 Membrane Filtration

This method is completely driven by pressure and very selective toward the kind of membrane to be used for nickel recovery and its isolation from the aqueous solution (Carolin et al. 2017). Membrane filtration can be varied in types depending on the sizes of the particles; in nickel, the most prominent techniques used are ultrafiltration, nanofiltration, and reverse osmosis (Barakat 2011; DaBrowski et al. 2004).

Particles in the range of 10–100 nm are separated by ultrafiltration. To enhance the separation process, polymeric agents are used to clog the ions, say, Ni (II) ions. Macromolecules are formed when these polymeric agents

TABLE 14.6

Brief of Clays and Zeolites Used with Adsorption Capacity for Nickel Removal

Adsorbents	Adsorption Capacity (mg/g)	Dosage (g/L)	References
Bentonite clay	112.69	0.5	(Yang et al. 2009)
Thermally treated attapulgite	2	10	(Ren et al. 2014)
Turkish zeolite	119.7	8	(Kocaoba et al. 2007)
Natural zeolitic tuff	16.64	10	(Rajic et al. 2010)
ZrO-montmorillonite TBA-montmorillonite	(40%)	0.05	(Gupta and Bhattacharyya 2006)
Gibbsite	9×10^{-5} (mol/m ²)	5	(Rajapaksha et al. 2012)
Goethite	2×10^{-5} (mol/m ²)	-do-	(Rajapaksha et al. 2012)
Laterite	4×10^{-5} (mol/m ²)	-do-	(Rajapaksha et al. 2012)
Natural red earth	6×10^{-6} (mol/m ²)	-do-	(Rajapaksha et al. 2012)

Source: Raval, N. P., Shah, P. U. & Shah, N. K. 2016. Adsorptive removal of nickel (II) ions from aqueous environment: A review. *Journal of Environmental Management*, 179, 1–20.

TABLE 14.7

Membrane and Polymer Combinations for Complexion–Ultrafiltration for Nickel Recovery

Polymer	Membrane	References
Polyethyleneimine (PEI)	Poly(ether sulfone) (PES)	(Molinari et al. 2008)
Polyethyleneimine (PEI)	Carbon-zirconia composite	(Cañizares et al. 2002)
Polyallylamine (PAA)	Poly(ether sulfone) (PES)	(Moreno-Villoslada and Rivas 2003)
Chitosan	Ceramic	(Taha et al. 1996)

combine with the metal ions and are conglomerated, thereby making the separation easier (Crini et al. 2017; Rivas et al. 2011). These macromolecules congregate containing the metal ions and are thus recovered. Table 14.7 shows the use of the membrane and the polymer for the removal of nickel.

A combination of processes (ultrafiltration and electrolysis techniques) is thus employed for the recovery of Ni²⁺ ions from industrial wastes (Chaufer and Deratani 1988). First, the ions are mixed with certain ligands to form a complex as mentioned above. A concentrated solution of nickel is obtained through ultrafiltration of the complex. Then, the Ni²⁺ ions are desorbed or decomplexed from the complex aggregate through acidification, allowing the recycle of the complex ions. Finally, through electrolysis, we can recover the Ni²⁺ ions using appropriate solutions. Mostly, the complexes used are polycarboxylate and polyethylenimine based. The decomplexation or extraction of Ni²⁺ from the complex formed is achieved by using suitable acids (Baticle et al. 2000; Chaufer and Deratani 1988).

Around 99% of nickel can be recovered by this complexation process using sodium polyacrylate (PAAS) and polyethylenimine (PEI) (Shao et al. 2013). This membrane process is based on the principle that if the polymers used have a larger molecular weight than the membrane used, then they can bind the trace metals to form the macromolecular complex, which is retained in the membrane. Further electrolysis and acid treatment are performed to recover the entire Ni^{2+} ions (Baticle et al. 2000; Shao et al. 2013).

Nanofiltration membranes are mostly made of polymers that are either positively or negatively charged depending on the ion to be isolated. There is a close relation with the electrostatic forces of the ions and the membrane and thus lesser energy or pressure is utilized unlike the other membrane techniques (Carolin et al. 2017).

The notable advantages of nanofiltration are lesser energy utilization and much lower pressure required than the other methods and operations. However, it is highly dependent on pH, pressure, temperature, configuration, and the incoming feed concentrations (Fu and Wang 2011; Tao et al. 2016). These filters are made up of synthetic polymers that have a certain positive or negative charge that enhances the trace metal removal (Mohammad et al. 2015).

Reverse osmosis is based on the particle size and the charges on the particle. It uses a semipermeable membrane for the removal of the solid present in the aqueous medium (Bilal et al. 2013). The pore sizes for the membrane range from 0.1 to 1.0 nm and are increasingly familiarized in the removal of trace metals as well. Reverse osmosis requires high energy for its operation compared to other membrane techniques (Carolin et al. 2017).

14.3.6 Electrodialysis and Ion Exchange

These recovery processes are primarily driven by electric current in the aqueous media. Electrodialysis is a membrane process that is based on the selective migration of Ni^{2+} ions through a suitable membrane using an electric current source. It is most prominent method used to recover the cations from rinse water in electroplating (Njau et al. 2000; Shao et al. 2013; Tzanetakos et al. 2003). Low concentrations of trace metals are usually removed by this method, and the effluent water is mostly recycled for use (Benvenuti et al. 2014). Electrodeionization is a combination of techniques for Ni^{2+} recovery. It includes electrolysis, electrodialysis, and ion exchange where the system to be purified is stacked with ion exchange resins, most of which are explained as above, and an external power source is applied as in electrodialysis (Alvarado and Chen 2014). Basically, a series of steps were followed to ultimately recover the Ni^{2+} and obtain 100% purity in water. Electrolysis–electrodialysis and ionization combination processes recover both high and low concentrated solutions. Around 94% purity/recovered nickel can be obtained with this method (Peng et al. 2014).

14.4 Future Outlook

In recent years, a wide range of studies have been made and have been extended for removal and recovery of trace metals before disposing them to the environment, whether they are in solid form or aqueous media; the recovery of nickel has been of primary importance due to its threat to humans and to the environment as well as its high economic value to the industry.

From the different methods of nickel extraction from wastes, membrane separation and adsorption remain the most conventionally employed method to obtain reusable water. To date, there has been not much focus on the recovery of nickel. The electricity-driven methods seem to be more promising for recovery of nickel, but the plausibility of having it in a large-scale facility to treat nickel-containing sludge is challenging, keeping in mind the energy consumed for the recovery.

Another major drawback is the clogging of the membranes at the downstream processes for filtration of the trace metals. Ongoing studies have proven that adsorption and ion exchange would be effective for the treatment of nickel from wastewaters or for any trace metal for that matter (Carolin et al. 2017; Dermentzis et al. 2016; Raval et al. 2016). Further investigation is needed to optimize the adsorption process because it gives a promising outcome and is currently plausible only at low concentrations. Improvement and modifications are needed in order to enhance the surface area of these adsorbents through the right kind of modification for the right trace metal removal, say, Ni²⁺ ion extraction.

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