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Chapter 2

Resource recovery from industrial wastewater: what and how much is there?

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2.1 INTRODUCTION

Industrial production of goods and services is at the heart of our modern economy and society, and accounts for approximately 20% of global water consumption (FAO, 2020). This number increases significantly in developed and industrialized nations, as highlighted in Figure 2.1, with industry in Europe and Canada accounting for 54 and 80% of total water use, respectively (FAO, 2020; Statistics Canada, 2014). This water is key to the production of a variety of goods, such as processed food, clothing, chemicals, materials, and energy. Through its use in industry, a portion of this water will inevitably come into direct contact with a wide variety of raw resources, contaminants, or intermediate products, leading to its contamination. This contaminated water is defined as industrial wastewater, and it does not include contributions from agricultural and municipal wastewater discharge. Economic, environmental and safety regulations have driven industrial sectors to systematically manage and treat their wastewater, which can carry undesirable by-products, chemical residues, organics, pesticides, heavy metals, nutrients and minerals, to meet certain standards for process water, rendering it safe to be recycled and/or reused in processes, or returned to the environment. This treatment, which can take the form of mechanical, biological, physical, chemical, and thermal processes, often applied in series, represents a significant cost to industry. For example, in Canada, industrial wastewater treatment and discharge costs represent between 28% and 63% of total industrial water costs, averaging out at about 37% for all industries (Statistics Canada, 2014). Furthermore, in addition to continuous and ongoing growth in high-income countries, rapid industrialization and population growth in developing nations are expected to boost water demand by the manufacturing sector by 400% by 2050 (Marchal *et al.*, 2011). These treatment processes, which amount to annual costs of tens of billions of dollars at a global scale, can, however, present an alluring opportunity to recover resources, reducing the economic burden associated with industrial wastewater treatment.

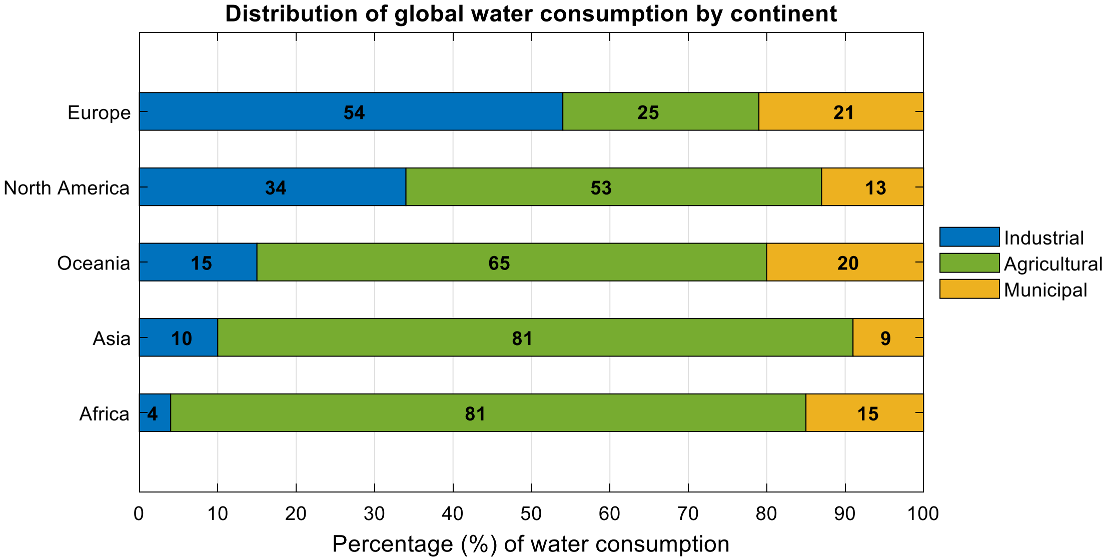

Figure 2.1 Distribution of global water consumption by continent (data from FAO, 2020). The industrial segment is generally made up of a variety of major sectors, each encompassing specific industries. Generally, regarding wastewater, we can consider major industrial sectors such as manufacturing, mining, and energy, each of which can then be further subdivided. For example, manufacturing encompasses industries such as textiles and leather, pulp and paper, chemicals, among many others.

Indeed, though often approached as waste streams, these industrial wastewaters can provide a rich source of water, nutrients, minerals, and compounds that can be recovered into valuable products. Besides the recovery of water as process water, there are two main fields of resource recovery, that is inorganic/organic compound recovery and energy recovery. In most industries, the largest driver is the water recovery, though recovery of high cost/value compounds in the wastewaters of certain processes, such as spent catalysts, can overtake this. The aim of this chapter is to outline these industrial wastewater resource recovery opportunities. The following sections will discuss major industries that contribute to the production of wastewater and their general characteristics, current practices in industrial wastewater treatment, and resources that can be recovered from industrial wastewater treatment processes.

2.2 LEARNING OBJECTIVES

At the completion of this chapter, you should be able to:

- Describe the sources and magnitudes of industrial wastewater generation and treatment, and understand its potential for resource recovery.
- Describe the key resources that can be recovered during the treatment of industrial wastewater.
- Identify recovery potential(s) in different types of industries.
- Understand that the added value from resource recovery processes can be evaluated not only by considering product value, but also through additional benefits for the overall treatment of the wastewater.

2.3 THE MAJOR INDUSTRIES THAT PRODUCE WASTEWATER AND THEIR CHARACTERISTICS

Industrial wastewaters stem from a variety of processes and industries, all being characterized by very different compositions, and physical and chemical characteristics. These waste flows are as unique as the processes that produce them and, therefore, require specific consideration when developing and implementing resource recovery processes. Examples of industries that produce large volumes of wastewater include: power generation, pulp and paper production, mining and refining processes, oil and gas production and refining, industrial food production and processing, chemical manufacturing, and textile production.

Indeed, as presented in Figure 2.2, the magnitude and share of industrial wastewater discharges from the major industrial sectors (each encompassing a variety of specific industries) vary greatly by region and depend on a variety of local factors. Though Figure 2.1 presents this distribution by continent and Figure 2.2 highlights how variable this can be between countries, the same kind of variability can be found between municipalities and regions within a country. This variability is a representation of local realities, reflecting the specific types of industries and sectors present in a region. For example, Figure 2.2 shows a stark contrast between the distribution of wastewater generation in Canada and the United States compared with the average across 20 countries (mostly based on countries in Europe), as well as with the three other example nations. However, these differences reflect and can be explained by national behavior. Indeed, on a per capita basis, we find that both Canada and the United States consume more than three times the amount of energy than the other countries in Figure 2.2; around 12 000–14 600 $\text{kWh}\cdot\text{person}^{-1}\cdot\text{year}^{-1}$ for the United States and Canada, compared to approximately 4000–4600 $\text{kWh}\cdot\text{person}^{-1}\text{year}^{-1}$ for Poland and China (EIA, 2019). Similarly, Figure 2.2 also reflects the central role mining plays in Poland's economy, being one of the world's main producers of coal, copper, silver, and rhenium (USGS, 2020). In contrast, China's dominance of global manufacturing, representing 28% of global output (World Bank, 2019), is mirrored in the distribution of the country's wastewater discharge.

Furthermore, all of the different industries contained within the industrial sectors presented in Figure 2.1 have unique characteristics based on the specific industrial processes and wastewater treatment scenarios applied. This can be seen in both Figures 2.3 and 2.4, where wastewater discharge characteristics for China and Europe are presented, respectively. In Figure 2.3, which presents the wastewater and chemical oxygen demand (COD) discharges from 22 industries in China, we can see just how variable these can be. This variability is observed both in the amount discharged, as well as the composition of the discharged wastewater, measured through COD. For example, based on Figure 2.3, the textile goods segment is responsible for the third largest quantity of wastewater discharged, while it represents the highest COD discharge in China, reflecting the high organic matter content of the textile industry's waste stream. Conversely, wastewater discharges from electricity and energy production (expressed as both 'Electricity, steam' and 'gas production') are large but contain a small COD load relative to the other segments.

This variability in industrial wastewater characteristics continues when looking at more specific compounds/pollutants, such as chlorinated organic compounds, heavy metals, and other organic and inorganic pollutants, such as COD, hydrocarbons, and phenols (organic), and chlorides, cyanides, fluorides, and nutrients (inorganic), as shown in Figure 2.4. As mentioned, these flows are extremely variable based on sectors, processes, and treatment scenarios, with a deeper dive into these sectors being provided throughout the following section. Generally, we can note that chlorinated organics mainly stem from the pulp and paper and chemical industries, while heavy metals are present across all industries, being particularly present in general manufacturing and metal and mining related industries. Other organic compounds are prevalent in most sectors (with the exception of metal and mining related industries), while inorganic compounds are the main pollutants discharged from the chemical industry.

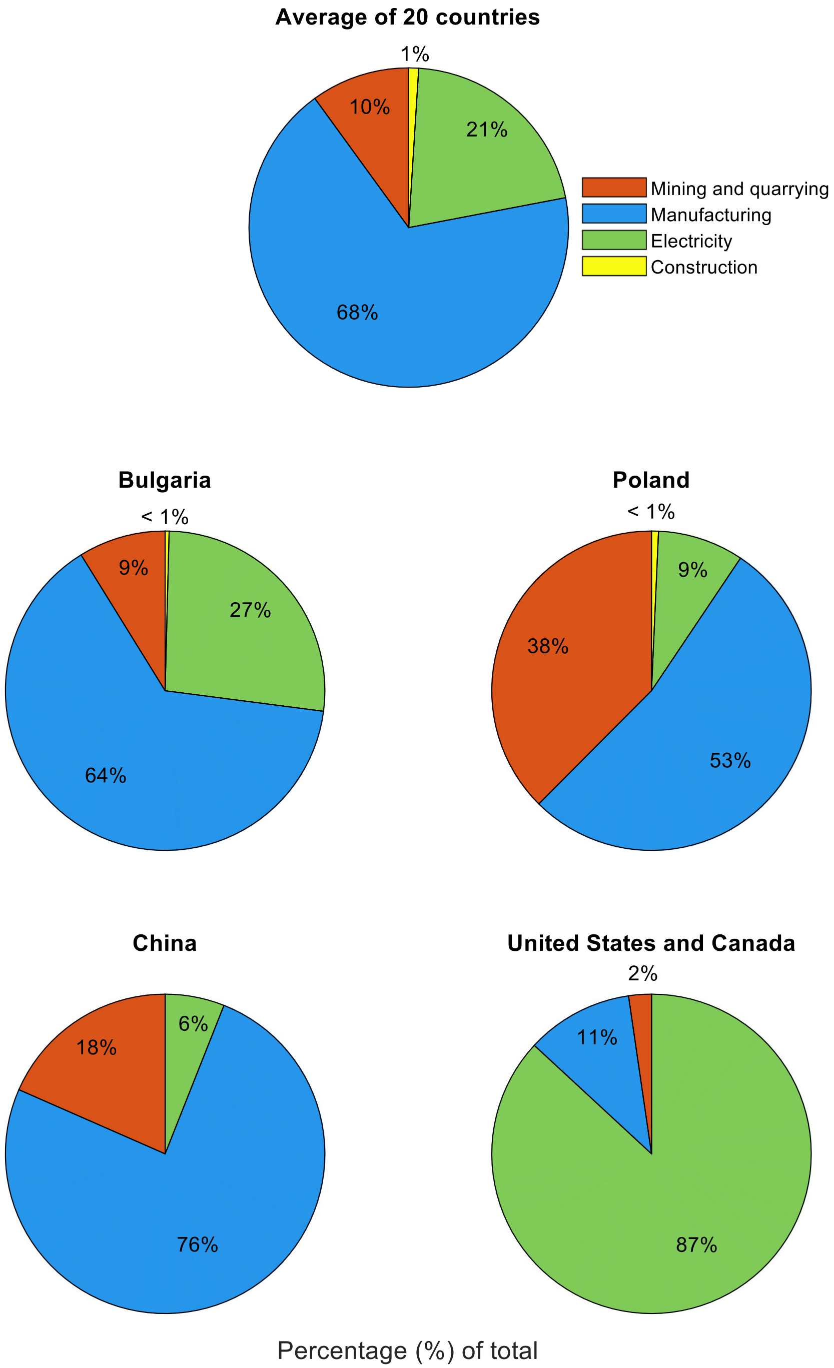

Figure 2.2 Breakdown of wastewater generation by major industrial sectors for various countries. Note that no data was available for the contribution of construction to the totals given by Canada, China, and the United States. Based on data and estimates from the United Nations World Water Assessment Program (WWAP) (2017), Dieter *et al.* (2018), Statistics Canada (2014), and Guo *et al.* (2018).

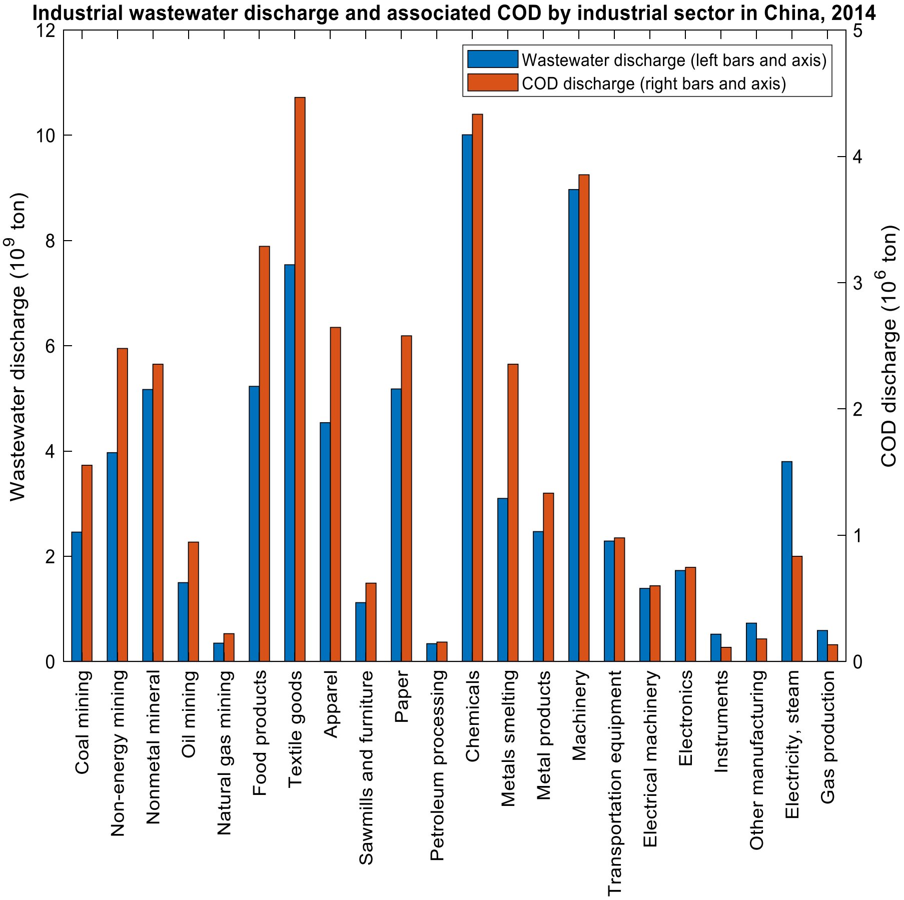

Figure 2.3 Industrial discharge by sector in China for the year 2014. Based on the estimates of Guo *et al.* (2018).

The figures presented thus far have provided a good picture of the different industrial segments that generate wastewater and some of the main pollutants in those wastewater streams. However, resource recovery processes are often aimed at specific compounds, and not general pollutant classes. Table 2.1 presents a list of the major types of contaminants found in industrial wastewater and the industries with which they are generally associated. These include substances with significant impacts to public and/or environmental health, such as heavy metals, synthetic organic substances, inorganic substances, nutrients (such as N, P, K), organic matter and emerging contaminants. Some of the contaminants in Table 2.1 can be recovered, recycled and/or reused, as described in Section 2.5 and later chapters of this book. Other contaminants in Table 2.1 are not recovered but may still impact the selection of treatment technologies and the value of recovered resources.

Currently, on-site industrial wastewater treatment often focuses on managing organics (COD) or toxic compounds (e.g., heavy metals and chlorinated organics), while other inorganic substances (including nitrogen and phosphorus) are important discharges from industrial wastewater treatment. Indeed, in 2011, the European Environment Agency reported that inorganic substances made up more than 98% in mass of the directly released (i.e., from the industrial plant directly into waterbodies)

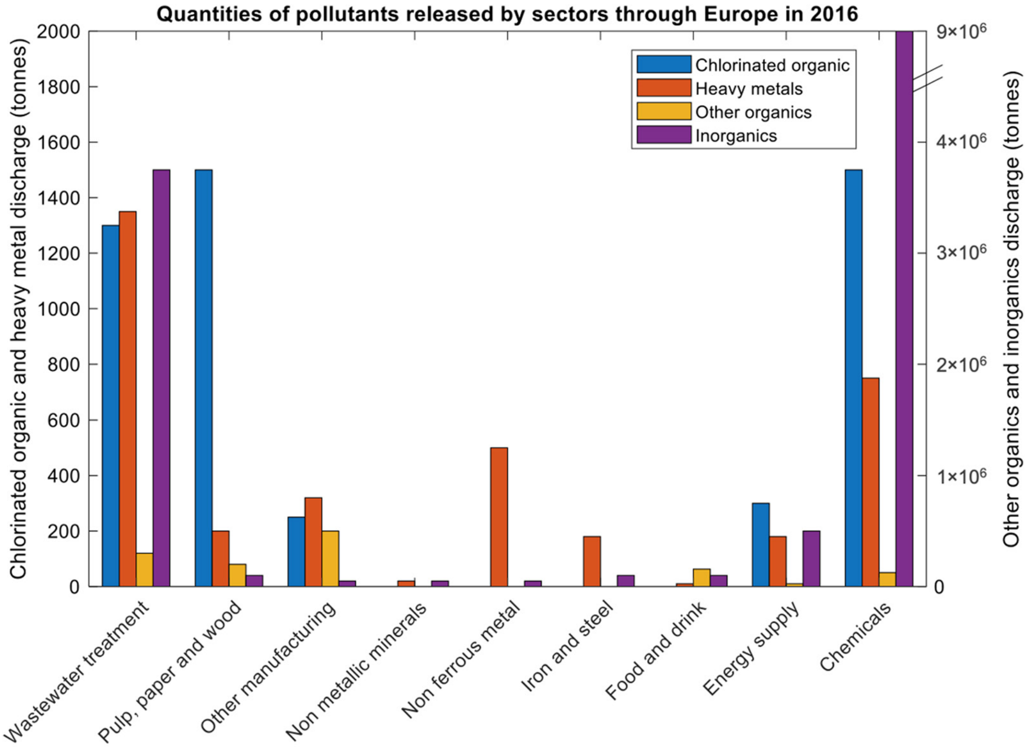

Figure 2.4 Pollutant discharge by sector throughout Europe in 2016, adapted from EEA (2019).

substances (EEA, 2019), while Canada's 2009 inventory showed the importance of nutrients, with nitrogen representing 90.4% of industrial discharge (47.1% nitrate and 43.3% total ammonia), followed by phosphorus at 5.1% (Statistics Canada, 2011). Organic substances account for 2% of total release, with all other contaminants making up the remainder. Indeed, despite higher discharge limits for COD than most other contaminants, the massive amount of inorganics used, produced, and released during industrial processes generally outweighs the mass of discharged organics. This is highlighted in Figure 2.4, where the release of inorganic substances through Europe is in the order of 10^7 tons·year^{-1}, compared to about 10^6 tons·year^{-1} of organic compounds, mostly stemming from the chemical manufacturing industry. Furthermore, chemical manufacturing is one of the primary industrial sectors in many countries (e.g., China; see Figure 2.3) and is thus an important source of industrial wastewater discharge. Another factor leading to the prominence of inorganics release is that regulations on the nutrient loads of discharged waters vary widely, and often only focus on limiting discharge in areas susceptible to eutrophication. However, legislation throughout the world is shifting to stricter guidelines (Preisner *et al.*, 2020). Despite the relatively low presence (by mass) of other substances, such as heavy metals and emerging contaminants in industrial wastewater, their potency and significant impacts on human health and the environment still render them very problematic.

The following section will highlight the main characteristics of a few major industries, focusing on what differentiates them from one another, given the great variability found in industrial wastewater composition.

Table 2.1 Major contaminants found in industrial wastewaters and their primary industrial sources.

Substance Type	Substance	Major Sources
Nutrients	Nitrogen (N)	Most sectors
	Phosphorus (P)	
	Sulfur (S)	
	Potassium (K)	
Heavy metals	Arsenic (Ar)	Metal and glass manufacturing, energy, car repair, tanneries
	Cadmium (Cd)	
	Chromium (Cr)	
	Copper (Cu)	
	Lead (Pb)	
	Mercury (Hg)	
	Nickel (Ni)	
	Zinc (Zn)	
Organic matter	Biochemical/chemical oxygen demand (BOD/COD)	Food industry, pulp and paper, wood preservation
	Suspended solids (SS)	
Organic substances	Chlorinated organics	Chemical manufacturing, pulp and paper, wood preservation
	Benzene	Most sectors
	Di(2-ethylhexyl)phthalate (DEHP)	
	Halogenated organics (AOX)	
	Linear alkylbenzene sulfonates (LAS)	
	Naphthalene	
	Nonylphenol and ethoxylates (NPE)	
	Organotin compounds	
	Phenols	
	Polycyclic aromatic hydrocarbons (PAH)	
	Toluene	
	Xylenes	
Inorganic substances	Chlorides	Energy, iron and steel production, chemical manufacturing
	Cyanides	
	Fluorides	
	Brominated diphenyl ethers (PBDES)	Flame retardants (textile, furnishing and electrical insulation manufacturing)
	Chlorinated paraffin	Plastic manufacturing, flame retardant, sealants, paints
	Pharmaceutical compounds	Pharmaceutical industries
	Polydimethylsiloxanes (PDMS)	Lubricants, electrical insulators and antifoam production
Emerging contaminants	Per – and Polyfluoroalkyl substances (PFAS)	Flame retardants, cleaning products, stain-resistant products, paints, automotive, construction, electronics

2.3.1 Food and beverage industries

The food production and processing sector encompasses a large variety of industries, including animal production, animal processing, fruit and vegetable washing, general food processing (fruit, vegetable, meat, dairy), bottling and packaging, and so on. A common characteristic of wastewater generated in these industries is high organic matter content, notably high biochemical oxygen demand (BOD) and high total suspended solids (TSS). There are also additional contaminants that are more industry and process specific. For example, wastewater from animal industries may contain blood, tissue/body residues, and often high amounts of oil and grease, while wastewater from fruit and vegetable industries may contain pesticides. Salts, surfactants, flavoring compounds, pathogens, and nutrients are also present in variable concentrations.

Given the role of organic compounds in the food and beverage sector – such as organic acids used to regulate pH, act as preservatives, and enhance flavors (Quitmann *et al.*, 2013; Valta *et al.*, 2015) – they are one of the primary contributors to the release of non-chlorinated organic substances (EEA, 2019). An overview of wastewater production and associated BOD and total nitrogen (TN) concentrations from food and beverage production and processing is presented in Table 2.2.

The largest wastewater producer in the food and beverage sector is the dairy industry, which is characterized by wastewaters with high BOD, COD, and salt contents. Between 50 and 80% of

Table 2.2 Wastewater characteristics from select sectors of the food and drink industries.

Sector	Water Production (m^3/Unit)	BOD (mg/L)	BOD/TN (–)[a]	Unit of Production
Fruits and vegetables				
Sugar cane	0.5–10	250–5000	25–60	1 t produced
Canning (fruit/vegetables)	4–50	600–7500	27–37	1 t processed
Pea processing	13–18	300–1350		1 t processed
Tomato processing	4–8	450–1600		1 t processed
Carrot processing	11	800–1900		1 t processed
Potato processing	7.5–16	1300–3300	5–14	1 t processed
Citrus processing	9	320	27–37	1 t processed
Animal industries				
Fish farming[b]	0.5–1.5	0.4–300	1–20	1 t produced
Dairy (without cheese)	1–10	300–5000	3–14	1000 L milk
Dairy (with cheese)	2–10	500–8000		1000 L milk
Chicken processing	15–60	100–2400	3–10	1 t produced
Beef processing	10–16	200–6000		1 t processed
Fish processing	5–35	2700–3500	7–43	1 t processed
Slaughterhouse	0.5–3	150–8500	–	1 cattle/2.5 pigs
Beverage and confectionary				
Sweets/candies	5–25	200–1000	–	1 t produced
Margarine	20	1500	–	1 t processed
Yeast production	150	7500	–	1 t produced
Alcohol distillation	60	3500	30–100	1 t cane processed
Brewery	5–20	500–4000	7–43	1 m^3 produced
Soft drinks	2–5	600–2000	5–200	1 m^3 produced
Wine	5	–	–	1 m^3 produced

Various sources from practice.

Table 2.3 Wastewater characteristics from some dairy industries effluents.

Process Effluent	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	TN (mg/L)	TP (mg/L)	pH
Butter	220–2650	8900	700–5070	–	–	12.1
Cheese	590–5000	1000–63500	190–3400	18–830	5–280	3.3–9.5
Fluid milk	500–1300	950–2400	90–450	–	–	5–9.5
Ice cream	2500	5200	3100	–	14	5–7
Mixed dairy	240–5900	500–10400	60–5800	10–660	0–600	4–11
Whey	9500–60 000	50 000–100 000	1250–22 150	200–2000	120–530	3.9–6.5
Whey processing	590–1200	1070–2180	80–440	–	–	5–9

Adapted from Kolev Slavov (2017).

the water used by the dairy industry becomes contaminated, with estimates placing the volume of wastewater generated at 2.5 times the volume of processed milk (Kolev Slavov, 2017), which would result in over 2 billion m^3 of wastewater generated yearly. The most polluted waters stem from equipment cleaning, sanitary waters, and manufacturing by-products. These wastewaters are high in organic matter and solids, with whey being one of the primary pollutants, while sanitary waters are an important source of nitrogen (Kolev Slavov, 2017). Currently, multiple processes are used to treat dairy wastewaters, including mechanical, physicochemical, chemical, and biological treatment approaches, as will be discussed in section 2.4.

Table 2.3 provides an overview of the composition of wastewaters from dairy industries, adapted from the work of Kolev Slavov (2017). As noted, these wastewater streams remain highly variable, even for the same process effluent, given the great variability in processes applied throughout industries. We will explore the potential to recover resources from wastewater in section 2.5, but we can already note that the high level of organic contaminants (BOD and COD) can be targeted, while nitrogen and phosphorus could potentially be recovered from certain waste flows (notably those associated with cheese and whey). Indeed, the use of on-site anaerobic digesters has been growing quickly in recent years as a strategy to recover energy for many dairy industries.

2.3.2 Textile industries and leather production

Textile manufacturing and leather production are two other primary generators of industrial wastewaters. As highlighted in Figure 2.3, in China, the textile industry is responsible for the third highest industrial wastewater discharge and the highest COD discharge. Indeed, wastewaters from textile processes are high in volume and generally contain very high amounts of BOD, COD, and TSS, though lower amounts of nutrients. The pH is a key parameter that varies between industries. This is significant as pH corrections may be required to enable some treatment or resource recovery technologies. The general characteristics from various textile manufacturing processes are presented in Table 2.4.

Beyond these general properties, textile industries are also characterized by the abundance of certain compounds (Bisschops & Spanjers, 2003; Yaseen and Scholz, 2019). For example, due to the frequent and heavy use of dyes within many of these industries, flows often have highly variable tinctorial characteristics. Additionally, reactive dyeing processes use large quantities of sodium chloride, leading to wastewaters reaching up to 6000 mg Cl$^-$/L and 7000 mg Na$^+$/L (Yaseen & Scholz, 2019). Oil and grease (lipids) are also very common, often being by-products or reagents for certain treatment/manufacturing steps. For example, wool scouring (washing) produces high amounts of oil and grease, while oils and fats are important additives for fiber spinning and fabric manufacturing. Metals can also be present throughout these wastewaters, notably from dyes, many of which contain chromium, cadmium, lead, zinc, copper, or cobalt (Bisschops & Spaniers, 2003; Halimoon and Yin,

Table 2.4 Wastewater characteristics from textile manufacturing processes (bisschops & spanjers, 2003; bond & straub, 1974; von Sperling, 2007).

Process	Water Production (m^3/unit)	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	pH	Unit of Production
Cotton	120–750	200–1500	400–1800	200	8–12	1 t produced
Wool	500–600	500–600	–	–	–	1 t produced
Rayon	25–60	500–1200	–	–	–	1 t produced
Nylon	100–150	350	–	–	–	1 t produced
Polyester	60–130	1500–3000	–	–	–	1 t produced
Cotton desizing	–	–	950–20 000	1000–26 200	8.8–9.2	–
Wool scouring	20–70	2000–60 000	2000–90 000	1000–30 000	7.6–11	1 t produced
Cotton scouring	–	100–2900	8000	184–17 00	7.2–13	–
Synthetic scouring	–	–	500–2800	600–3300	8–10	–
Wool dyeing	20–60	400–5000	620–7920	900	4.6–8	1 t produced
Cotton dyeing	–	970–1460	1115–4585	130–25 000	9.2–10.1	–
Textile bleaching	–	250–300	288–13500		6–13.5	–
Tanning[a]	20–40	600–4000	2000–11200	600–3000	11–12	1 t hide processed
Laundry	–	1600	2700	250–500	8–9	–
Leather[b]	–	2000	2340–7180	–	4.1–4.7	–
Shoes	5	3000	–	–	–	1000 pairs produced

[a]Kannaujiya *et al.* (2019); [b]Ramasamy (2019).

2010). Indeed, in dyeing wastewater, heavy metal concentrations can be as high as 12.1 mg Cu/L, 2.7 mg Cr/L, 7.5 mg Cd/L, and 3.4 mg Zn/L (Bisschops & Spaniers, 2003), while the effluent from tanneries can reach up to 391 mg/L of Cr and 268 mg/L of Mg (Sahinkaya *et al.*, 2017). Another class of substance used in high quantities in textile manufacturing that ends up in wastewaters is surfactants, notably anionic and non-ionic surfactants, with concentrations ranging from 15 mg/L in silk and lycra printing plants up to 2000 mg/L for desizing wastewaters (Bisschops & Spaniers, 2003). Nutrients such as nitrogen, phosphorus, and sulphates are also present, as in most wastewaters, often ranging between 70 and 80 mg/L for total Kjeldahl nitrogen (TKN), between 0 and 300 mg/L of phosphate, and between 0 and 2250 mg/L of sulphates, depending on the process (Yaseen & Scholz, 2019). Regarding nutrients, sulfur and/or phosphorus recovery could be of particular interest for some of these textile waste streams, given the potential for high concentrations.

Wastewaters from the leather industry are also characterized by very high COD and BOD, as observed in Table 2.4 (leather; tanning). Beyond high organic loads, tanneries discharge a significant amount of chromium, due to the prevalence of the chrome-tanning process throughout the world. Wastewaters from plants using the chrome process have been reported to contain chromium (Cr) concentrations of over 500 mg/L (Kannaujiya *et al.*, 2019). Sulfides are also prevalent, ranging between 50 and 900 mg/L (Kannaujiya *et al.*, 2019). A variety of resources can be targeted for recovery from leather and tanning wastewaters, including sodium sulfide and fats (Sawalha *et al.*, 2020).

2.3.3 Wood-related industries

Pulp and paper industries generally produce waste effluents with high levels of organic material, such as BOD, COD, and suspended solids, while generating significant volumes of wastewater (around 70 m^3 per ton of paper produced) (Hubbe *et al.*, 2016), alongside important chlorinated organics, methanol, and sulfur concentrations. Indeed, processes that involve further wood treatment, such

Table 2.5 Wastewater characteristics from processes used throughout pulp and paper industries.

Process	BOD (mg/L)	COD (mg/L)	TSS (mg/L)	N (mg/L)	P (mg/L)	S (mg/L)	MeOH (mg/L)	pH
Thermomechanical pulping whitewater	1541	2713	127	7	–	–	–	4.6
Thermomechanical pulping	2800	5600–7210	383–810	12	2.3	72	25	4.2
Chemi-thermomechanical pulping	3000–4000	6000–9000	500	–	–	167	1500	6.2
Kraft mill	2000–10 700	4000–16 000	3620	306–600	1–2	6–375	421–8500	8.2
Bleach Kraft mill	128–184	1124–1738	37–74	2	–	–	40–76	10.1
Sulfite mill	2000–5110	4000–27 100	–	–	–	800–1270	–	2.5–5.9
Bleached pulp mill	1566	2572	1133	–	–	–	–	7.5
Wood preparation	250	–	600	–	–	–	–	–
Paper making	330–27 000	610–5020	760–800	11	0.6	97	9	7.8
Newsprint mill	–	3500	250	–				–
Chip wash	12 000	20 000	6095	86	36	315	70	–
Digester house	13 088	38 588	23 319	–				11.6
Spent liquor	13 300	39 800	253	55	10	868	90	–

Adapted from Bajpai (2000) and Ashrafi *et al.* (2015).

as bleaching, can generate organic substances, notably chlorinated organics like trichloromethane (chloroform). Wood processing and preserving industries also tend to have waste flows with high levels of organic materials, while also using many toxic compounds such as heavy metals (arsenic, copper, chromium) and organic substances (phenols, oils). Overall, wood-related industries are the second most important contributors to the release of organic substances in Europe, as well as the most important source of chlorinated organics (EEA, 2019). General wastewater characteristics from pulp and paper processes are presented in Table 2.5.

The pulp and paper industry already implements significant resource recovery to recover many of the chemicals used throughout the various processes. One notable example is the recovery boiler, applied with most Kraft processes, alongside some sulfide processes. These boilers are employed to recover the chemicals used during the pulping process from the wastewater, known as black liquor, through a variety of steps, alongside energy through combustion (Vakkilainen, 2005). From this process, black liquors are used to generate heat, reduce emissions of inorganic sulfur, produce sodium carbonate and sodium sulfide (both of which are used as reagents during pulping), and recover inorganic chemicals. While recovery boilers have been a staple of the pulp and paper industry since the 1930s, significant progress has been made in recent years regarding resource recovery, leading to a constant reevaluation of recovery alternatives in the field. Generally, energy is the primary resource targeted for recovery, due to the vast quantities of organic residues arising from the processes. Though alternatives such as incineration, gasification, and pyrolysis can be of interest for the liquors from pulping processes (sulfite and kraft mills), as will be discussed in sections 2.4 and 2.5, some recovery processes can face significant challenges. For example, pulp and paper wastewaters typically contain very low nutrient concentrations, with the exception of sulfur. Therefore, if biological recovery processes such as anaerobic digestion are sought, additional nutrients are required to enable the biological pathways. Furthermore, compounds such as chlorine and its reactive byproducts are plentiful, leading to hundreds of different chlorinated hydrocarbons, including chlorinated lignosulfonic acids, chlorinated resin acids, chlorinated phenols, guaiacols, catechols, benzaldehydes, vanillins, syringovanillins, and chloropropioguaiacols, as well as products of lignin degradation, notably chlorolignins (Hubbe *et al.*, 2016), many of which can be detrimental to biological processes through toxicity (Chen *et al.*, 2014; Yin *et al.*, 2001).

As mentioned, most nutrients in pulp and paper wastewaters tend to be low. The exception to this is sulfur, which can be very high in wastewaters from certain pulp and paper processes. This is notably the case for chemical pulping, which is either undertaken through sulfite or sulfate (Kraft) pathways. Both processes are pulping processes that seek to extract almost pure cellulose from wood. The first (sulfite) process achieves this extraction through a reaction of aqueous sulfur dioxide (SO_2) with a base (calcium, sodium, magnesium or ammonium). The second, and more popular, (Kraft) process generally uses sodium hydroxide (NaOH) and sodium sulfide (Na_2S) to produce wood pulp. Consequently, a significant amount of sulfur ends up in various process effluents, as shown in Table 2.5, with concentrations potentially ranging above 1000 mg L^{-1}. As mentioned, recovery boilers already seek to recover a portion of this sulfur, but a significant portion of sulfur still leaves pulp and paper mills as waste and could be valorized.

Methanol is another by-product of pulp mills that could be targeted for resource recovery, as it is generated in massive amounts and is generally considered as a waste product. Indeed, the Kraft process typically produces around 5 kg of methanol per ton of dry pulp, ranging upwards to 15 kg per dry ton (Joyce, 1979; Zhu *et al.*, 2000). Given its volatile nature, the condensate from Kraft evaporators is particularly rich in methanol, with concentrations ranging between 1000 and 46 000 mg/L, representing between 80 and 96% of total COD for this effluent (Badshah *et al.*, 2012). Another area of complexity that must be addressed when treating wastewaters from pulp and paper plants are the variable wood extracts that are hydrophobic and soluble in neutral solvents. These compounds include resin acids, fatty acids, sterols, diterpene alcohols, and tannins. They are among the main contributors to pulp mill effluent toxicity but are also resistant to chemical degradation (Hubbe *et al.*, 2016).

2.3.4 Metal and mining industries

As noted previously, the mining industry is among the main contributors to wastewater use and discharge throughout the world. Many processes involved in mining and refining of metals and ore lead to significant wastewater generation, with mining alone being responsible for 800 million m^3 of wastewater annually throughout Europe (WWAP, 2017). These waters can stem from a variety of sources, including water intensive processes such as electroplating, flotation, and cooling. However, given the 'open' nature of many of these processes, rain waters are also an important source of wastewater, washing exposed surfaces, transporting, and leaching various substances, both from the rock surfaces and from industrial equipment (oils and grease, hydraulic fluids, etc.). Indeed, the recovery and refining of metals and ores lead to the contamination of process water with the metals, any other elements found alongside the desired product, and the chemicals used in these processes. For example, a significant amount of arsenic tends to be found in gold deposits (Straskraba & Moran, 1990), leading to the release of arsenic, cyanide, and very fine particles of gold following the commonly applied cyanide leaching (cyanidation) process (Straskraba & Moran, 1990). Similarly, gold also tends to naturally form with sulfide-type ores (Welham, 2001). Following extraction of the desired elements, the sulfur inevitably ends up forming sulfuric acid in acid mine drainage, that is acid solutions rich in heavy metals (Druschel *et al.*, 2004). Another common extraction and recovery process is flotation. Flotation is the most popular mineral processing method and therefore the greatest consumer of water in mineral processing plants (Li *et al.*, 2019). These waters tend to be heavily contaminated with (non-organic) suspended solids, organic flotation reagents, and heavy metal ions (Li *et al.*, 2019).

Coolant water also tends to be a major source of contaminated water. Indeed, during refining, notably of iron and steel, water is used as a coolant for the high temperature reduction reactions used in these processes. As such, the water comes in contact with a variety of contaminants, notably ammonia, sulfides, and cyanide, alongside a variety of organic compounds (Biswas, 2013). There is also

Table 2.6 Wastewater characteristics from processes used throughout the metal and mining industry.

Compound	Blast Furnace Gas Cleaning	Slag Crushing	Rolling Mills	Cooling of Pig Iron	Pickling Wastewater	Flotation and Enrichment of Lead and Zinc Ores
TSS (mg/L)	330–670	500–600	1000–1500	500–3500	–	20 000–140 000
TDS (mg/L)	800–4000	450–550	400–500	500–2000	–	–
Cyanide (mg/L)	0.6–1.3	Negligible	–	–	–	2–5
Thiocyamates (mg/L)	0–17	3–4	–	–	–	2–5
Iron (mg/L)	140–1180	–	–	–	80–600	–
Chloride (mg/L)	–	–	–	30–300	–	–
Sulfate (mg/L)	–	100–150	100–150	20–650	200–2000	–
Calcium (mg/L)	–	–	–	–	50–200	–
Aluminium (mg/L)	–	–	–	–	0–50	–
Lead (mg/L)	–	–	–	–	–	5–10
Zinc (mg/L)	–	–	–	–	–	0.1–10
Copper (mg/L)	–	–	–	–	–	0.4–8
pH	7–9	–	–	7–8	1.5–4.5	–

Adapted from Jørgensen (1979).

a major source of acidic wastewater from the conversion of iron to steel that is further contaminated by ferrous salts. Given the role of metals in this sector, mining and refining industries are the most important direct source of heavy metals and are nearly on-par with the chemical manufacturing industry for overall (direct and indirect) release of these substances (EEA, 2019). Table 2.6 presents a general overview of wastewater composition of some of the major processes involved in metal and mining industries, while Table 2.7 highlights some of the metals that can be present in various metal and mining waters. It is important to note that the compositions in Table 2.7 are extracted from a limited sample of works and are only intended to highlight the presence of the different metals and their variability.

2.3.5 Oil and gas production and refining

Another major contributor to global wastewater generation, the oil and gas sector generates more than 3 billion m^3 of wastewater annually (Saunders, 2017). Oil and gas production generates two main kinds of wastewaters: process water and produced water. Process water is the result of the various chemical processes used to produce petrochemicals, often leading to waters rich in hydrocarbons, organic acids and compounds, and inorganic substances (Allen, 2008). Produced water arises from salt water trapped in underground formations that surfaces during extraction. This water contains high quantities of hydrocarbons and metals, as well as spent caustics and salt that can be a burden to treatment equipment (Wei *et al.*, 2019), and is the largest source of wastewater (by volume) of oil and gas extraction, with ratios of produced water to oil potentially ranging upwards of 100:1 (EPA, 2019). An overview of a variety of these wastewaters is provided in Table 2.8, while Table 2.9 provides general characteristics from petroleum refineries and petrochemical plant wastewaters.

2.3.6 Chemical industry

Chemical manufacturing is the main source of inorganic substances in industrial wastewaters, as well as an important contributor to heavy metal release (EEA, 2019). The substances found in these wastewaters are dependent on the chemicals being used and manufactured, but are generally comprised

Table 2.7 Some examples of heavy metal loads of various flows emanating from the metal and mining industries.

Type of Metal	Electroplating[a,b,c]	Basic Mine Water[d]	Acid Mine Drainage[e]	Mine-impacted Groundwater[f]	Smelting Wastewater[f]	Scrap Leachate[g]
Magnesium (mg/L)	–	74.6	342	1950	–	–
Aluminium (mg/L)	–	0.022–0.024	54.3	–	–	166
Vanadium (mg/L)	–	–	–	–	–	–
Chromium (mg/L)	34–225	–	0.12	–	2.3	44
Manganese (mg/L)	–	0.001–0.003	6.05	–	–	–
Iron (mg/L)	2.6–8.55	–	391	675	88	244
Cobalt (mg/L)	–	–	8.9	–	0.04	–
Nickel (mg/L)	28–190	–	3.78	–	12	642
Copper (mg/L)	0.92–36.5	–	44.9	60	164.48	12 293
Zinc (mg/L)	24–239	–	5.9	65	455.6	4375
Palladium (mg/L)	–	–	–	–	–	183.1
Silver (mg/L)	–	–	–	–	–	10.9
Cadmium (mg/L)	–	–	0.01	–	76.05	–
Platinum (mg/L)	–	–	–	–	–	20.9
Gold (mg/L)	–	–	–	–	–	11
Lead (mg/L)	2.5	–	6.9	–	4.6	111
Bismuth (mg/L)	–	–	–	–	85	–
Indium (mg/L)	–	–	–	–	–	1008
Tin (mg/L)	–	–	–	–	–	122

[a]Chang and Kim (2007); [b]Sankararamakrishnan *et al.* (2008); [c]Kumar *et al.* (2011); [d]Nordstrom *et al.* (2015); [e]Sahinkaya *et al.* (2017); [f]Weijma *et al.* (2002); [g]Umeda *et al.* (2011).

of unreacted reagents, co or intermediary products, end products, acids or bases used to control pH, as well as heavy metals that are often employed in a variety of processes. A range of sectors fall within this industry, such as chemicals, petrochemicals, polymers, fertilizers, pharmaceuticals, cosmetics, and many other consumer products. Wastewater characteristics from some of these industries are presented in the tables below, highlighting how variable these streams can be between industries. Indeed, Table 2.10 presents wastewater characteristics from the pharmaceutical industry, in which we note extremely variable ranges for compounds and properties such as TSS, total dissolved solids (TDS), COD, BOD, and pH, while having relatively high levels of heavy metals, chlorides, sodium, and oil and grease. Table 2.11 presents the interesting case of wastewater generated from the plastic recycling industry during pre-washing and washing, demonstrating a wide variety of contaminants due to the nature of their use, being in contact with an array of different compounds.

2.4 CURRENT PRACTICE IN INDUSTRIAL WASTEWATER TREATMENT

Given the wide range of substances found in industrial wastewaters, as highlighted in section 2.3, treatment processes are also as variable. Table 2.12 presents an overview of conventional treatment processes used to treat industrial wastewaters. These processes are divided into mechanical, physical, chemical, biological, and thermal processes. The first two are mainly separation processes, with mechanical and physical treatments using physical properties, such as particle size, solubility, density, boiling point, and so on., to drive separation. Chemical treatments can be either focused on separation

Table 2.8 Wastewater characteristics from oil and gas production wastewater (EPA, 2018).

Compound	Drilling Wastewater	Produced Water	Process Wastewater	Flue Gas Desulfurization[a,b]
TSS (mg/L)	168–47 300	57–353	–	–
TDS (mg/L)	557–39 500	2861–226 733	191.9–151 713	–
BOD (mg/L)	79.8–1119	244–2120	–	–
COD (mg/L)	153–9270	1360–3070	–	–
Aluminium (mg/L)	1.7–6916	–	–	0.147
Ammonia (mg/L)	0.98–34.98	–	0.147–2.86	–
Barium (mg/L)	2.55–471	0.963–787	0.05–6.86	–
Benzene (mg/L)	–	0.0015–1.7	–	–
Bromide (mg/L)	–	270–798	14.71	–
Chloride (mg/L)	158–23 469	698–141 200	5–74 975	–
Mercury (mg/L)	–	–	–	0.066–0.289
Potassium (mg/L)	–	0–2190	–	–
Selenium (mg/L)	–	–	–	1.24–3.13
Sodium (mg/L)	167–15 726	733–63 284	–	–
Strontium (mg/L)	1.8–663	nd–4370	0.11–149.35	–
Sulfate (mg/L)	nd–1568	nd–3350	13.06–16.32	–

[a] Staicu *et al.* (2017); [b] Gingerich *et al.* (2018).

Table 2.9 General wastewater characteristics from petroleum refineries and petrochemical plants.

Compound	Range	Average
TSS (mg/L)	20–930	120
TDS (mg/L)	270–87 810	2900
BOD (mg/L)	1–14 230	110
COD (mg/L)	75–265 100	610
Ammonia (mg/L)	20–65	30
BTEX (mg/L)	0.005–1290	10
Heavy metals (mg/L)	0.01–100	6
Oil and grease (mg/L)	3.5–2990	60
Phenol (mg/L)	0.2–210	50
Sulfate (mg/L)	1.5–100	25
Sulfide (mg/L)	18–870	25

Adapted from Jain *et al.* (2020).

or transformation, while potentially allowing for both simultaneously. Regardless of whether the goal is transformation or separation, chemical reactions are the driving factor. The last two treatment types (biological and thermal), tend to be used to breakdown and transform problematic contaminants into more manageable or less hazardous forms. Biological treatments involve the use of microorganisms to undertake biochemical reactions, notably to treat organic matter and some organic and inorganic substances. In some cases, especially when there are significant quantities of heavy metals and

Table 2.10 General wastewater characteristics from pharmaceutical industry wastes.

Compound	Range	Metal	Range
TSS (mg/L)	30–1200	Cadmium (mg/L)	0.036–0.56
TDS (mg/L)	135–4000	Chromium (mg/L)	0.01–1.11
BOD (mg/L)	20–15 660	Copper (mg/L)	0.02–1.67
COD (mg/L)	130–38 640	Iron (mg/L)	0.02–2.35
TN (mg/L)	80–500	Lead (mg/L)	0.03–6.53
TAN (mg/L)	74–116	Nickel (mg/L)	8.5–10.8
TP (mg/L)	18–47	Manganese (mg/L)	6.41–8.47
Chloride (mg/L)	200–2800	Zinc (mg/L)	0.2–1.3
Sodium (mg/L)	155–2000		
Potassium (mg/L	128–140		
Sulfate (mg/L)	80–360		
Sulfide (mg/L)	40–100		
Oil and grease (mg/L)	0.5–3965		
pH	3.9–8.5		

Adapted from Rana *et al.* (2017).

emerging contaminants, thermal processes can be applied to ensure the destruction (or at least concentration to facilitate safe disposal) of these compounds at high temperature.

2.5 WHICH RESOURCES CAN BE RECOVERED FROM INDUSTRIAL WASTEWATER TREATMENT?

Though some of the substances contaminating industrial wastewaters are generally undesirable, many of them have some value and can be reused in other circumstances. Of the contaminants highlighted in section 2.3, the following can be of interest to recover and reuse: inorganic/organic compounds (nutrients, metals, chemical compounds, stabilized organic biosolids), water and energy. Recovery pathways are presented in Figure 2.5 and briefly described below.

Table 2.11 General wastewater characteristics from plastics recycling.

	Polyethylene Terephthalate		High Density Polyethylene: Polypropylene	
Compound	Pre-washing	Washing	Pre-washing	Washing
TS (mg/L)	660–1310	5180–5455	650–1090	7810–8090
TSS (mg/L)	345–634	732–1136	450–876	211–466
COD (mg/L)	315–684	750–983	340–581	100–267
Oil and grease (mg/L)	23–122	20–96	156–266	70–130
Cadmium (mg/L)	–	–	–	0.04–0.06
Iron (mg/L)	4.75–8.06	6.73–7.86	7.13–12.90	3.03–6.06
Lead (mg/L)	0.06–0.14	0.8–1.84	–	0.80–1.35
Manganese (mg/L)	0.08–0.11	0.07–0.08	0.09–0.15	0.06–0.11
pH	7	11.9	7	12.4

Adapted from Santos *et al.* (2005).

Table 2.12 Conventional processes applied to industrial wastewater treatment and the main potential recoverable resources.

Process Type	Process	Description	Main Potential Recoverable Resources
Mechanical treatment	Centrifugation	Separation of particles through centrifugal force based on their size, density and viscosity	Organic solids, nutrients
	Filtration	Separation of particles based on size. Undertaken with membranes (reversed osmosis, ultra- and microfiltration)	Organic solids, high-quality water (if reversed osmosis)
	Flotation	Separation of particles based on their hydrophobic/philic nature (can be controlled by chemical additives)	Organic solids, nutrients, metals
	Sedimentation	Separation of particles due to gravity	Organic solids, nutrients, metals
Physical treatment	Adsorption	Separation of certain substances by physically immobilizing them onto an adsorbent	Nutrients, chemical compounds, metals
	Coagulation and flocculation	Agglomeration of particles into flocs to facilitate their separation	Organic solids, nutrients, metals
	Distillation	Separation of substances based on boiling points	Chemical compounds
	Evaporation	Separation by surface vaporization of liquids below their boiling point	Organic solids, nutrients
	Extraction	Separation of substances based on their relative solubility in different immiscible liquids	Nutrients, metals, chemical compounds
	Irradiation	Disinfection method to kill off pathogens using ultraviolet rays	Potential high-quality water
	Precipitation	Formation of a solid precipitate due to a change in physical conditions (temperature, concentration)	Nutrients, metals, chemical compounds
	Freeze concentration	Freezing (crystallizing) water to facilitate the removal of other compounds	Organic solids, nutrients
	Stripping	Separation of volatile components from a liquid stream to a vapor stream	Nutrients, chemical compounds
	Absorption	Separation of certain compounds by uptake into another	Nutrients, metals, chemical compounds
Chemical treatment	Electrolysis	Separation of ions using membranes and direct electric current	Nutrients, metals, chemical compounds
	Ion-exchange	Removal of dissolved ions from a solution by replacing them with ions of similar charge	Nutrients, metals, chemical compounds
	Oxidation/reduction	Removal of organic and inorganic substances through oxidation reactions	Potential high-quality water
	Precipitation	Formation of a solid precipitate due to chemical reactions	Nutrients, metals, chemical compounds
	Scrubbing	Removal of substances from a gas stream using a liquid solution. Often applied following stripping	Nutrients, chemical compounds

(*Continued*)

Table 2.12 Conventional processes applied to industrial wastewater treatment and the main potential recoverable resources. (*Continued*)

Process Type	Process	Description	Main Potential Recoverable Resources
Biological treatment	Aerobic treatment	Breaking down of organic contaminants and conversion of nutrients by aerobic microorganisms	Organic solids, nutrients
	Anaerobic treatment	Breaking down of organic contaminants and conversion of nutrients by anaerobic microorganisms	Energy, organic solids, nutrients
	Nitrification/ denitrification	Conversion of ammonia-nitrogen and nitrate-nitrogen to dinitrogen gas using anoxic and aerobic systems operated in series	Organic solids
Thermal treatment	Gasification	Thermal degradation with a controlled amount of oxygen. No combustion	Energy, chemical compounds, organic solids, nutrients
	Incineration	Combustion of organic substances	Energy, inorganic solids (ash), nutrients, metals
	Pyrolysis	Thermal degradation in the absence of oxygen. No combustion	Energy, chemical compounds, organic solids, nutrients
	Thermal hydrolysis	Thermal treatment at high temperature and pressure to improve organic matter for anaerobic digestion	Organic solids, nutrients

2.5.1 Nutrients

As noted in section 2.3, inorganic substances, notably nutrients, are among the main contaminants of industrial wastewaters. These nutrients, such as nitrogen (N), phosphorus (P), and potassium (K), are the major plant nutrients used as fertilizers throughout agriculture to stimulate plant growth. Given the vast amount of the nutrients used as fertilizer, it is evident that recovery of this type of products is absolutely necessary to ensure global food production without further disrupting the worldwide ecosystem. Benefits are not only derived from alternative production of N and P, diminishing the impact associated to fossil resource use on climate change, but also from lessening dependence on the limited supply of certain commodities and increasing food security, all of which warrant maximum resource recovery. Indeed, the global supply of some nutrients such as potassium and phosphorus is mainly produced in a few countries (China, Morocco, USA, Canada, Russia, Belarus) (USGS, 2020), requiring extensive exportation to international markets. The ability to recover these nutrients at a local level can therefore be of extreme benefit, both to the environment and in creating a local and sustainable nutrient supply chain.

Beyond the three major macronutrients (N, P and K), industrial wastewaters can also be rich in three other important macronutrients that can serve as fertilizers: sulfur, calcium and magnesium. A specific hot spot is regeneration of water softening or reverse osmosis brines. Common processes used to recover nutrients include absorption, adsorption, electrolysis, extraction, ion-exchange, precipitation, and scrubbing (Table 2.12). Furthermore, processes such as anaerobic digestion, composting, gasification, pyrolysis, and incineration can be used to recycle certain nutrients, allowing for their recovery in downstream processes (Walling *et al.*, 2019). For example, phosphorus can be

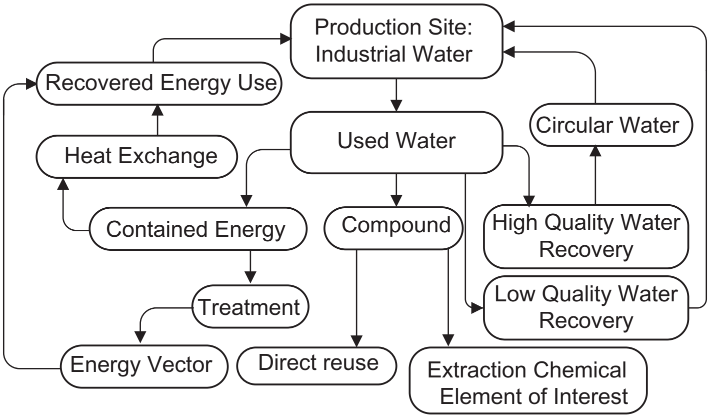

Figure 2.5 Three main recovery applications for industrial wastewater.

recovered from incineration ash through chemical extraction, while nitrogen can be recovered from the remaining liquid (digestate) after anaerobic digestion through stripping and scrubbing (Walling *et al*., 2019).

2.5.2 Metals

A number of used water flows from the metal processing or metals finishing industries will contain an array of different metals and heavy metals that, up until now, are processed towards disposal of the metals after a chemical treatment converting the soluble metals to a sludge separated from the treated used water. Alternative techniques such as extraction, adsorption, or ion exchange, could be applied to recover these metals.

Indeed, as is the case for phosphorus, some metals can be recovered from incineration ash (Šyc *et al*., 2020). There is also a growing interest in metal recovery from various industrial wastewaters, especially mining and metal processing wastewaters (section 2.3.4). This has mainly been explored through a combination of biological, membrane (filtration), and precipitation processes, with particular focus on the biological sulfate-reduction process (Gómez & Lens, 2017; Huisman *et al*., 2006; Kumar & Pakshirajan, 2021; Weijma *et al*., 2002). This process uses microorganisms to reduce sulfate to sulfide, producing sulfidic metal precipitates along the way, and has currently been applied at full scale to recover metals such as copper (Cu), nickel (Ni), and Zinc (Zn) (Gómez & Lens, 2017). Further processes that have been implemented or are being developed for metal recovery include: hybrid membrane technologies, electrocoagulation, ion exchange, and solvent extraction (Brooks, 2018; Parga *et al*., 2009). Recently, interest in recovering lithium (Li) has also been growing, especially with regard to its recovery from the brine in wastewaters, either through sorption or evaporation. Oil and gas and mining wastewaters are of particular interest, as well as wastewaters from battery recycling (Kim *et al*., 2018; Kumar *et al*., 2019; Park *et al*., 2015).

2.5.3 Chemical compounds

Depending on the industry, there can be an interest in extracting molecules such as hydrocarbons and organic acids from wastewater, often using extractive or transformative processes. A classic example of a transformative pathway is fermentation (anaerobic biological process), which is commonly used to obtain acids or alcohols from organic matter, notably ethanol and lactic acid. The process can also be used to obtain lipids, proteins, and/or biopolymers. Ethanol can serve as a chemical precursor or reagent for many processes, or as a source of clean energy, while lactic acid is used throughout food, cosmetic, and pharmaceutical industries in a wide variety of roles (Walling *et al.*, 2019). To generate good yields of ethanol or lactic acid, substrates with high sugar or starch concentrations are needed. Therefore, food processing industries can be of particular interest, given the sugars and starch found in fruit and vegetable residues. Corn and potato starch wastewaters are good examples of flows that have been targeted for fermentation, while other products, such as bioplastics and lipids, can also be targeted (Xue *et al.*, 2010). Pulp and paper wastewaters can also be rich in starch, but the presence of complex molecules such as cellulose, hemicellulose, and lignin can require pretreatment to render these complex sugars accessible before fermentation.

If fermentation is not viable, either for technical or economic reasons, processes such as gasification and pyrolysis can be used to obtain a variety of compounds. Beyond applying these technologies to recover energy through hydrogen (H_2) and methane (CH_4) generation (alongside a large variety of energetic co/by-products), organic compounds can be formed through the thermal transformation pathways. One such example is the use of gasification to produce dimethyl ether and/or methanol from black liquor (Kraft wastewater, discussed in section 2.3.3) (Ekbom *et al.*, 2003; Naqvi *et al.*, 2010b). Furthermore, a portion of the significant sulfur found in black liquors can be converted to hydrogen sulfide (H_2S), which can then be sent to a Claus process for desulfurization and recovery of elemental sulfur (and carbon dioxide). The sulfur can then be reused in the pulping process. However, work still remains before gasification can be used as a reliable recovery technique for sulfur recovery from pulp and paper liquors (Hruška *et al.*, 2020; Naqvi *et al.*, 2010a).

Non-transformative pathways can also be used to recover compounds already present in wastewaters through a variety of chemical or physical processes (Table 2.12). As discussed in section 2.3.5, wastewaters from the oil and gas sector contain high levels of organics and sodium, making them strong targets for compound recovery through processes such as evaporation for sodium, or extraction, filtration, and distillation for hydrocarbon recovery. Chemical recovery from black liquor is also of interest. We previously discussed the potential to recover energy and methanol from these pulping wastewaters (section 2.3.3), and many other recovery alternatives exist. One such example is the recovery of lignin from pulp and paper liquors. The lignin can then be available to use as an energy source, while current research is also exploring the prospects of using lignin to produce carbon fiber (Akpan, 2019).

2.5.4 Stabilized organic biosolids

To maintain a healthy and arable soil, maintaining soil organic matter content is crucial. Intensive agriculture tends to deprive arable soils of this essential component. Processed organics, such as biosolids from anaerobic digestion and composting, have a high added value in providing the necessary stable carbon to build up soil organic matter. These processed organics are obtained following all mechanical processes, given that these generally aim at separating solid and liquid phases, as well as certain physical processes, such as evaporation and freeze concentration, which leave behind solid organic fractions. However, to be able to apply these solids to land as soil amendments and organic fertilizers, these biosolids must meet specific criteria regarding pathogen elimination and heavy metal and toxic compound limitations. As such, the solids obtained from the above-mentioned processes are often further processed through biological or thermal pathways to meet regulatory restrictions. These treatments can involve aerobic processes (such as activated sludge treatments and composting), anaerobic processes (such as fermentation and anaerobic digestion), and/or thermal processes, as detailed in Table 2.12.

2.5.5 Water

Water is an extremely valuable resource, representing a major cost for both acquisition and proper disposal. Therefore, water recovery is an important part to any industrial process design. Water can be reused at different levels depending on the required level of quality. A major distinction can be made between reuse after partial purification by either degrading or extracting pollutants from the used water, which would account for a low-grade quality reuse. High grade quality reuse typically uses reverse osmosis as a final treatment step to generate circular water that can be reintroduced in the main production process.

2.5.6 Energy

The final major resource is energy. Energy recovery form industrial wastewaters can take two main forms: (1) indirect recovery of the calorific potential from the substances found in the waste streams, and (2) direct recovery of energy from the flow through heat transfer. Indirect energy recovery from the substances in the waste is related to the transfer of energy rich chemically reduced equivalents, contained in the organic substances, towards a uniform energy vector with different possible applications. Multiple processes can be used to recover this energy, including incineration, anaerobic digestion, fermentation, gasification and pyrolysis, while emerging technologies are continually being investigated and deployed to further recover energy rich compounds. One such example is the recovery of fat from sludges through air flotation, providing a great substrate for heating or as a co-substrate for anaerobic digestion (Fields *et al.*, 2020). The alternative of direct energy recovery by heat transfer (e.g. using heat exchangers) is a well-known field with technology and design considerations that are common knowledge.

2.5.7 Symbiotic resource recovery

Finally, it must be remarked that, with regard to resource recovery, the operational spectrum should not focus strictly on reuse for a given individual company. The exchange of recovered resources between different companies within each other's vicinity is also a viable model, which can constantly be adapted to the alternating needs of the companies involved. One such example is the Kalundborg Symbiosis, which is a major project in Kalundborg, Denmark, involving 12 different companies constantly exchanging resources, including energy, chemicals, and waters of various qualities.

This more holistic approach to resource recovery is extremely important. It requires going beyond a focus on a specific part of a process or even the whole process chain itself. Instead, it looks further to work toward optimizing resource flows across the local surroundings. A solution that is optimal for one plant can be completely unfeasible for another, despite apparent similarities. For example, ammonium sulfate, which is often recovered via stripping and absorption with sulfuric acid with the intention to be used as a fertilizer, could possibly be of more interest locally as a chemical reagent, depending on the situation. Indeed, ammonium sulfate is used in a variety of industries, including the manufacture of chemicals, dyes, flame retardants, and laboratory chemicals. Therefore, one could imagine an industrial park where one plant is seeking to recover its nitrogen. Agricultural lands are far away, meaning that transporting ammonium sulfate as a fertilizer would be costly, as it would either require inefficiently transporting a large amount of liquid over long distances or the crystallization of the ammonium sulfate. However, a nearby chemical manufacturer requires large quantities of ammonium sulfate, presenting a fantastic avenue for local recovery and valorization. Further symbiosis and local integration could be achieved if another local industry generates sulfuric acid, given that it is a common industrial byproduct. Indeed, flue-gas desulfurization is often used to generate high quality sulfuric acid from gas emanating from the combustion of fossil fuels or wastes. Furthermore, recovering nitrogen through the pathway of stripping and scrubbing is not only limited to the production of ammonium sulfate, but can be used to produce a variety of ammonium salts, depending on the acid used in the scrubbing process. Therefore, there can be flexibility in developing a resource recovery process. This flexibility was also highlighted earlier when discussing the opportunities of transformative technologies such as fermentation and gasification.

2.6 CHAPTER SUMMARY

In this chapter, we have explored the sources of industrial wastewater, the contaminants that are found within these waters, and the value and potential of recovering some of these contaminants as resources. Particular detail was given to select industries, highlighting how process and sector dependent these waste flows are. Examples include high organic matter contents generated by the food and beverage sector, the presence of tinctorial compounds and associated heavy metals in the textile industry, the massive wastewater generation and dissolved solid and ions from oil and gas production, and the dominance of chemical manufacturing in inorganics release, among many others. Following this, a plethora of wastewater treatment processes were presented, with notable emphasis on the recovery of resources, including nutrients, energy, chemical compounds, organic matter, metals, and water itself.

Overall, the takeaway message of this chapter is that industrial processes are a major contributor to global water consumption and wastewater generation, and their proper management is therefore critical. These wastewater flows represent a rich and valuable source of resources that should be targeted for recovery. It is important to remember, however, that the compositions of these flows are as unique as the processes that make them, as highlighted throughout this chapter. Therefore, when exploring, developing, and implementing industrial resource recovery processes, it is important to know the characteristics of the flows being assessed, given that they can render certain alternatives completely infeasible, while making others more attractive. Resource recovery from industrial wastewaters is a paradigm: resources can be found in any waste flow, and the key to the development and implementation of appropriate recovery approaches relies on openness, creativity, and awareness of the tools and techniques (processes) that are available. Indeed, what can seem farfetched to someone in one field or industry can be commonly known and applied in another, strengthening the need to learn and share to build a more sustainable future.

Following this chapter, you should have developed an understanding of the interest in recovering resources in industry, both from an economic and environmental perspective, and you should be able to answer the following:

- How important is industrial wastewater generation throughout the world?
- What industries primarily contribute to this generation?
- How and why is the generation of industrial wastewater variable from region to region?
- What contaminants are found in industrial wastewaters?
- How do wastewaters from various industries compare to one another?
- What is the reason for differences in wastewater composition within and between industries?
- What resources can be recovered from industrial wastewaters?
- Why recover resources from industrial wastewaters?
- What processes can be used to recover resources from industrial wastewaters?

2.7 EXERCISES

Exercise 2.1: A dairy producing industry fabricating 2000 L of milk per week (no cheese) is looking for ways to improve its wastewater management. How much wastewater is produced on average by the company over a year? Assuming that half of this wastewater flow comes from fluid milk processing, how much BOD, COD, and TSS is generated at this site over a year?

Exercise 2.2: Compare and discuss the mass loads of BOD, COD, TN, TP, TS, and pH across the following industries:

(1) Dairy industry
(2) Wood-related industries

(3) Textile and leather
(4) Oil and gas production and refining

Exercise 2.3: What resources could be recovered from pulp and paper industrial sludge? What conventional technologies could be applied that would allow to recover these resources, all while treating the sludge? What compounds could hinder recovery?

Exercise 2.4: Which of the following steps involved in the manufacturing of bleached pulp are responsible for the highest and lowest generation of BOD and TSS: assuming that wood preparation generates 300 L/s of wastewater, pulping produces 150 L/s of wastewater, and bleaching produces 550 L/s (assuming average values for BOD and TSS concentrations).

Exercise 2.5: A citrus processing plant processes 10 tons of citrus per day, how much wastewater would this process generate annually? What would the yearly BOD production be? How much nitrogen could be expected (low and high, yearly, estimates)? Is this process of interest for energy and/or nutrient recovery?

Exercise 2.6: Maximum sulfate levels for discharge of wastewaters vary, ranging up to 1000 mg/L, while the standard for drinking water recommended by the World Health Organization is 250 mg/L. Treatment and recovery processes for sulfate include both chemical and biological pathways, such as precipitation and reduction by sulfate-reducing bacteria. Of the industrial wastewaters presented throughout this chapter, which ones would require consideration of sulfates during their treatment?

Exercise 2.7: Wastewater from an industrial process is characterized by a BOD and COD in the orders of 10^2 and 10^3 mg/L, with a pH ranging from low acidic to slightly alkaline. This wastewater is also noted as having a significant load in sodium, chloride and heavy metals, notably copper and chromium, while nutrient content (TKN and TP) is low. What process does this water stem from?

Exercise 2.8: The major macronutrients recovered from wastewaters for reuse in agriculture are nitrogen, phosphorus, and potassium. What are three other macronutrients that can be recovered from industrial wastewaters and which of the industrial sources and processes presented throughout this chapter could prove interesting for recovery of some of these nutrients?

Exercise 2.9: What compounds, if any, could be of interest to recover in produced water emanating from oil and gas wastewater?

Exercise 2.10: What type(s) (mechanical, physical, chemical, biological, thermal) and process(es) do the following descriptions relate to:

(1) Conversion of COD into energy by microorganisms in conditions without oxygen.
(2) Recovery of water and removal of contaminants by vaporization at ambient temperatures.
(3) Conversion of COD into energy at high temperatures and in the presence of oxygen.
(4) Recovery of particulate matter, such as organic solids, based on size using membranes.
(5) Immobilization of contaminants onto a surface based on their ionic charge.
(6) Separation of compounds based on differences in freezing/boiling points.
(7) Recovery of phosphate and ammonium by addition of magnesium to form struvite ($NH_4MgPO_4 \cdot 6H_2O$).
(8) Recovery of energy, biosolids and biooil at high temperatures without oxygen.
(9) Agglomeration of particles into flocs and separation based on size or density.
(10) Recovery of stripped ammonia (gas) using sulfuric acid (H_2SO_4) to form ammonium sulfate, $(NH_4)_2SO_4$.

2.8 DISCUSSION QUESTIONS

Question 2.1: An industrial park is willing to improve its resource management. The park is composed of 10 industries (four food and drink industry, two mining industry, four power generation), each producing various types of effluents that are currently treated by conventional methods. You are recruited as an engineer to improve the overall resource management of the industrial park, all while reducing conventional treatment costs. What data or information will you collect from each industry? What management approach will you apply? What criteria will your choices be based on?

Question 2.2: A progressive food processing industry driven by environmental regulations wants to improve its overall sustainability. It currently produces significant amounts of solids (sludge) through conventional treatment of its wastewaters. These sludges are currently being landfilled. Nutrients are biologically treated through nitrification-denitrification to transform nitrogen into nitrogen gas that is released into the atmosphere, all while producing biological sludge. Phosphorus is being precipitated as an aluminium phosphate sludge. You are asked to provide a presentation to the board of directors, indicating the current practice and the flows that could potentially be recovered. You are also asked to provide motivations for why resources should be recovered, as well as general considerations that will define the technico-economic feasibility of resource recovery.

Question 2.3: A wood-related industry is willing to install a production site in a dense city with about 900 000 inhabitants. You work as a wastewater engineer for the city and are asked to evaluate the health and environmental risks associated to the installment of such industry in the city. Provide a table with the potential risks and potential solutions to circumvent these risks (if any).

Question 2.4: All of the wastewater characterizations shown throughout this chapter have been variable, sometimes ranging by multiple orders of magnitude for a single compound within a process. As an engineer potentially tasked with conceiving processes around such variability, how would you circumvent or take into account this uncertainty?

Question 2.5: The recycling and recovery of industrial wastewaters within industry has been undertaken for decades now and is an integral part of process design. However, as our society transitions towards circular economies and resource recovery becomes ever more present, recovered resources such as nutrients are now making their way into agricultural fields and residual biomass is being used to produce energy. This can lead to potential issues with adoption of these products due to the lack of social awareness or societal acceptance. What reasons or risks, be they real or perceived, can lead to someone being opposed to the recovery and reuse of products derived from industrial wastewaters? Are these reasons justified?

Question 2.6: Beyond the technical feasibility of recovering resources, what other considerations must be taken into account?

Question 2.7: What industries that you are aware of could potentially present an interesting avenue for resource valorization? What resources could be recovered, how feasible would this be, and how would you go about it?

Question 2.8: Based on Table 2.12, how would you describe, in your own words, the differences between the various types of treatment and recovery processes (mechanical, physical, …)?

Question 2.9: An industrial wastewater treatment process is applying anaerobic digestion to treat their wastewater. During this process, a significant amount of nitrogen in the wastewater is converted to ammonia, which is then sent to an ammonia stripping and scrubbing section to recover ammonium sulfate (H_2SO_4). The ammonium sulfate can either be crystallized and distributed as a solid, or left in solution; what benefits could each alternative offer and how could this ammonium sulfate be valorized?

Question 2.10: You are tasked with conceiving the wastewater treatment process for a mine in a very isolated area. Knowing that access to resources such as chemical reagents can be very costly, given large shipping and storage fees, how would your design take this reality into consideration? Are there any treatment and recovery processes that you might initially be drawn to consider? Why?

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