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Pollution of Water Sources from Agricultural and Industrial Effluents: Special Attention to NO_3^- , Cr(VI) , and Cu(II)

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Abstract

One of the most important challenges facing humanity today is to conserve and sustain water resources (either surface water or groundwater). This challenge became more pronounced with the increase of urban, agricultural, and industrial activities that discharge a considerable amount of wastewater. Therefore, the preservation of water sources from pollutants is a major concern, shared by all, public, industrial, scientific, researchers, and decision-makers. This chapter analyzes in more detail the pollution and pollutants caused by agricultural and industrial activities. Particular attention is given to pollution via nitrogen and heavy metals (NO_3^- , Cr(VI) , and Cu(II)) in either international or national level. The effect of these pollutants on human health and environment, their standards/regulations, and the different current methods used for their detection and treatment are all discussed in the chapter.

Keywords: water chemistry, pollution, pollutants, nitrate, copper, chromium, detection methods, treatment methods

1. Introduction

One of the most important challenges facing humanity today is to conserve and sustain natural resources, including water, in order to increase economic and social development along with environment protection. However, urban and industrial sectors not only use the available water but also discharge a considerable amount of wastewater. The impact of these effluents on living organisms may be harmful due to the direct or chronic toxicity of these substances or the products of their degradation. Significant efforts are being made to control the use and spread of these substances. These topics are addressed more thoroughly in this chapter. Particular attention is given to pollution via NO_3^- and heavy metals. Besides the various activities that lead to the pollution of our freshwater bodies and the effect of these pollutants on human health and environment, the chapter also discusses the different methods used for water pollutant detection, standards/regulations, and some of the used treatment methods to protect water bodies.

2. Water quality

Water availability not only depends on the quantity of water, but also on the water quality, the physical structures, laws, regulations, and socioeconomic factors that control its demand and use [1]. The quality of water is defined by a set of general parameters, such as dissolved oxygen (DO), alkalinity, pH, hardness, conductivity, salinity, turbidity, etc. These properties are mostly linked to the geological and ecological characteristics of the water body basin, and although they have a large spatial variability, they are maintained within certain ranges in each specific water body [2, 3]. In fact, degradation in quality of water bodies (surface or underground) has become more apparent because of the increase of economic activity as well as the insufficiency of proper sanitation. This increase is generating a significant number of pollutants.

2.1 Water pollution and pollutants

Water pollution happens when the amounts of pollutants (chemical, physical, or biological) discharged into the water body can no longer be contained by the natural ecosystem. Furthermore, two types of water pollution can be identified: (i) accidental pollution that is punctual and often of large scale and (ii) chronic pollution corresponding to the discharge of permanent pollutants with low doses. The European water framework directive (2000/60/EC) has defined “pollutant” as any artificial substance made by man and dispersed in environment and which is likely able to generate an impact [4]. In addition, water pollutants are those that make water unfit for consumption or degrade some of its properties [5, 6]. However, it seems difficult to define “pollutant” while knowing that the environmental fate of numerous chemicals reveals that most are causing severe to moderate health hazards and are significantly harmful to the environment [26].

2.1.1 Classification of water pollutant

Water pollutants are divided into various categories; each category of pollutants has its own proper means of entering the environment and its own particular hazards. In general, pollutants present in water/wastewater are dissolved or undissolved substances (as illustrated in **Figure 1**). Dissolved pollutants are all substances that are dissociable and transformed into cations and anions. These pollutants are divided in two categories, organic and inorganic substances, while undissolved pollutants are precipitated components, suspended solids (SS), colloidal materials, floating materials, oil, grease, foams, clay minerals, and others.

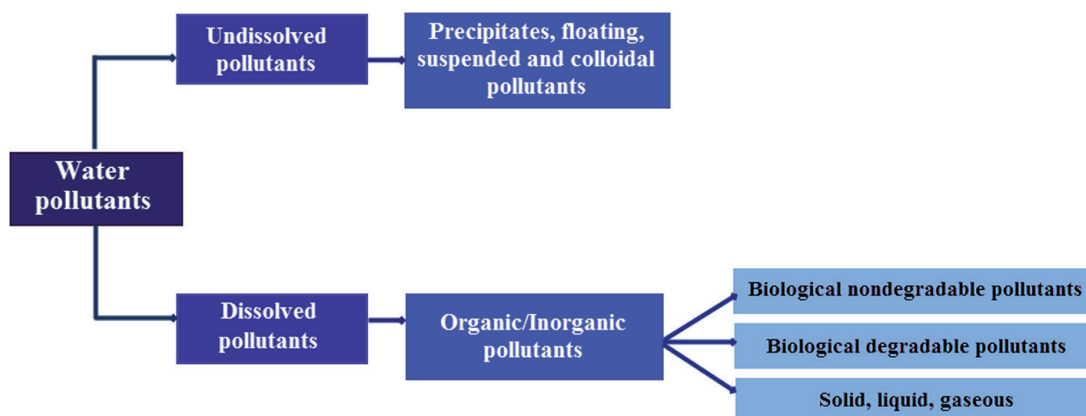


Figure 1.
Classification of water pollutants as dissolved and undissolved substances.

2.1.1.1 Organic pollutants

Organic compounds accommodate carbon and commonly other elements such as hydrogen, oxygen, nitrogen, sulfur, and others. Diverse organic matters occur naturally in water or from anthropogenic sources. These organic compounds may be considered contaminants if their concentrations adversely affect an aquatic system [7]. Furthermore, the organic matter is divided into two types (dissolved and particulate organic matter) depending on their origin and solubility [8]. Organic pollutants can be further divided into (i) oxygen-demanding contaminants, (ii) synthetic organic contaminants, and (iii) crude oil and various petroleum products.

2.1.1.2 Inorganic pollutants

Inorganic contaminants (IOCs) are non-biodegradable pollutants and persist in the environment. IOCs in waters can as well be classified into categories according to nature (as demonstrated in **Figure 2**). The toxicity of a pollutant is directly proportional to its concentration and the presence of other compounds. Metals in high concentration can be toxic which is aggravated when reacting with organic compounds to form organometallic compounds.

2.1.1.3 Suspended solids and sediments

SS appear in the water via the runoff of surface and through municipal sewers. Moreover, the presence of SS in hydrosphere can block the sunlight penetration in water, which is necessary for the vegetation photosynthesis. In addition, if the deposited solids are organic in nature, they increase the growth of anaerobic conditions [10].

2.2 Water pollutants according to activity

As already mentioned, human activities threaten water quality by generating a wild variety of pollutants based on the type of industrial activity. Some of these activities have occurred over several generations, and some have started more recently. In the following section, urban, agricultural, and industrial activities in relation to specific contaminants, their sources, and their effects on water quality in the environment are discussed.

2.2.1 Urban pollution

Population growth and urbanization do have important roles in enhancing water pollution. Urbanization generally leads to higher phosphorus and NO₃

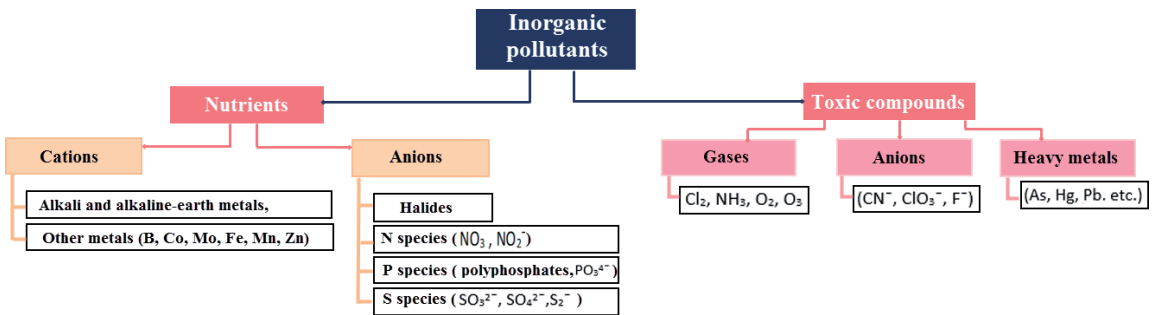


Figure 2.
Classification of inorganic pollutants [9].

concentrations in urban catchments [11, 12]. Urban runoff is the greatest cause of surface water pollutants in numerous parts of the world; according to Singh and Gupta [13], urbanization is second to agriculture as the primary cause of water degradation.

2.2.2 Agricultural pollution

Agriculture is perchance the primeval contribution of man for the survival and prosperity of human kind [14]. Just as agriculture has comprehensively changed the face of the Earth, its impacts have equally profoundly re-wrought the nature of its waters (by degrading both surface and groundwater resources) [15]. These impacts implicate effects on water chemistry, alteration of the hydrological cycles, suspended loads from soil erosion, biocide leaching, and others. Indeed, agriculture can be both cause and victim of water pollution. Since 1990, the connection that exists between land and water use in the agricultural activity is recognized by the Food and Agriculture Organization (FAO) of the United Nations, by its clear requirement “appropriate steps must be taken to ensure that agricultural activities do not adversely affect water quality so that subsequent uses of water for different purposes are not impaired” [16]. The sources of agricultural pollutants could be “point” or “nonpoint” [11, 14, 17, 18]. In fact, water pollution caused by agricultural sources, as nonpoint sources, are hard to supervise and regulate, giving the diffusive nature of agricultural sources. According to Chen et al. [17] the nonpoint source water pollution from agriculture has exceeded that from industry and has become the largest source of nonpoint pollution in China.

2.2.2.1 General information on agricultural pollutants

In 2011, pollutant emissions from the different agricultural sources were firstly considered in the Chinese national wastewater pollutant inventory [6]. These pollutants are organic and/or inorganic coming from large quantities of agrochemicals products, such as insecticides, pesticides, herbicides, fungicides, fertilizers, and veterinary products. According to the Chinese Ministry of Environmental Protection (CMEP) [19], agricultural sources were found to release a total of 11.86 million tons of chemical oxygen demand (COD), accounting for 47.4% of the total COD wastewater from all sources in 2011. Meanwhile, a total of 0.83 million tons of NH_4^+ -N was also released from agricultural sources, which represents 31.8% of the total NH_4^+ -N wastewater from all sources. In general, agriculture is responsible for the release of four categories of water pollutants into the water environment as follows: (i) nutrients, (ii) pathogens, (iii) pesticides, and (iv) silts.

2.2.2.1.1 Nutrients

Animal wastes and chemical fertilizers are applied to soil to provide the nitrogen, phosphorus, and trace elements necessary for crop growth. When applied, these fertilizers are either taken up by crops, remain in the soil, or enter the aquatic environments. Nitrogen (N) compounds can accumulate in soil crust and vadose zone for years. Furthermore, N in the presence of oxygen is transformed either to N gases, nitrite (NO_2^-), or NO_3^- . The fundamental paths of N cycle include nitrogen fixation, nitrification, denitrification, ammonification, volatilization, and atmospheric deposition. In addition to the natural complexity of the N cycle, N fluxes continue to be substantially modified by human activities especially by agriculture and burning of fossil fuels [20]. **Figure 3** shows a simplified N cycle diagram of nitrogen [21].

2.2.2.1.1.2 Nitrate sources

One of the main sources of NO_3^- is the intensive use of fertilizers in agriculture activity, as already mentioned [23, 24]. It is worth mentioning that in some cases, especially in aquifers of arid and semiarid areas, agricultural and domestic wastes are commonly found mixed together and they both contribute in increasing NO_3^- concentration [25]. According to Paschke et al. [26], an increase in NO_3^- concentration after a 10-year period (1990–2000) is simultaneously related with a decrease of the herbicide atrazine and its degradation product desethylatrazine. NO_3^- has a high mobility and low affinity for adsorbing onto clay particles, which facilitates its passage into groundwater [27]. However, despite its high solubility, it is not distributed homogeneously within the aquifer [28]. Indeed, Zhang et al. [29] confirmed the distinctively higher concentration in shallow depths compared with deeper parts of an aquifer. Gutiérrez et al. [21] identified some of the groundwater of aquifers with NO_3^- contamination depending on the type of area, aquifers of semiarid, arid and hyperarid areas (**Table 1**).

The impact of NO_3^- pollution on surface water and groundwater has been the focus of several studies on many sites all over Morocco. According to Menkouchi et al. [30] the pollution of the groundwater by NO_3^- affects nearly all the Moroccan territory with approximately 6% of resources having NO_3^- content more than the national standard. Furthermore, Menkouchi demonstrated the contamination of Boujaad center with NO_3^- (exceeded 80 mg/L). According to the spatial distribution of NO_3^- contents made by Tagma et al. [31], the groundwater in Souss plain is less polluted than Chtouka-Massa plain. In fact, 36% of Chtouka-Massa's wells exceed the regulatory NO_3^- limit while only 7% in Souss plain. Maria Calvache et al. [32] confirmed the highly presence of NO_3^- in Chtouka Ait Baha, Massa, and Tiznit. Recently, Malki et al. [33] has studied and confirmed the NO_3^- contamination of Belfaa and the irrigated area along Massa River. Hydrogeochemical results on groundwater samples collected in 2010 show that the Bou-Areg aquifer is vulnerable to NO_3^- contamination [34]. The contamination of the Loukkos basin, Essaouira, and the basin of Triffa plain in northeast Morocco was confirmed.

2.2.2.1.1.3 Nitrate effects on human health and environment

Results of many studies suggest that ingestion of relatively high levels of NO_3^- could cause health problems. The toxic action of NO_3^- exposure, through diet or drinking water, can be divided into acute (short-term) effects and chronic (long-term) effects [35]. The main concern of an acute toxicity is the capacity of NO_3^- to cause methemoglobinemia (known as blue baby disorder) after oral ingestion. In fact, in the gastrointestinal tract, the ingested NO_3^- is reduced to NO_2^- that binds to hemoglobin to form methemoglobin. In the case of infants, it only takes a 10 mg/L N- NO_3^- to cause methemoglobinemia [21, 36]. For chronic toxicity, the consumption of NO_3^- at levels higher than 50 ppm has been associated with (i) increased thyroid volume and subclinical thyroid disorders, (ii) increased incidence of goiter in children, (iii) carcinogenicity due to the conversion of NO_3^- to NO_2^- and formation of genotoxic/carcinogenic N-nitroso compounds, such as N-nitrosamines and N-nitrosamides, some of which are known carcinogens [23, 35].

Additionally, when N is present in overabundance of the requirements of the biological system, it increase NO_3^- leaching which results in water eutrophication and acidification of sensitive soils [36]. This acidification involves changes in river and lake chemistry that produces secondary changes in the aquatic biota. The United States Environmental Protection Agency (USEPA) identifies eutrophication as the critical problem in those US surface waters with impaired water quality,

Areas	Region	Land use, crops	% >50, N	Range of NO ₃ ⁻ values
Semiarid	Gaza Strip, Palestine	U, recovery	58%, N = 12	2–185
Semiarid	Rio Grande Valley, USA	A, U	6%, N = 587	0.1–61
Semiarid	Basin and Range, USA	A, U	8%, N = 3539	0.1–130
Semiarid	Andhra Pradesh, India	A, U, sweet lime, cotton	18%, N = 496	0.1–896
Semiarid	North China Plain	A, wheat, maize	9.5%, N = 295	Ave. 45.3
Semiarid	Dakar, Senegal	U	61%, N = 36	0.3–1390
Semiarid	Southwest Niger	Land clearing	25%, N = 28	0.2–176
Semiarid	Seville, Spain	A, cotton, potato	~70%, N = 16	35–630
Semiarid	La Mancha, Spain	A, corn, wheat, barley	18%, N = 684	<0.5–125
	Chihuahua, Mexico	A, U, alfalfa	40%, N = 45	2.2–266
Semiarid	Livermore CA, USA	A, L, vineyard	17%, N = 35	5.2–60.2
Semiarid	Osona, Spain	L, pigs	82%, N = 60	10–529
Semiarid	South Platte River, USA	A, G, corn	47%, N = 30	0.7–229
Semiarid	Grombalia, Tunisia	A, U, citrus trees	Shallow 73%, N = 26 40%, N = 25	0.5–514 2–231
Semiarid	Arava Valley, Israel	A, U, flowers, palms, vine	30%, N = 53	1–330
Arid/hyperarid	Monte Desert, Argentina	G	0%, N = 29	0.3–49.2
Arid/hyperarid	NW China	G, subsistence farming	32%, N = 52	<0.1–113
Arid/hyperarid	Central Iran	U, A, almonds, alfalfa	0%, N = 120	5–40
Arid/hyperarid	Southern Iran	A, wheat	5.9%, N = 34	1.5–70.7
Major land use: A = agricultural, L = livestock, G = grazing, U = urban. With N = number of samples exceeding 50 mg(NO ₃ ⁻)/L [21]				

Table 1.
NO₃⁻ concentration (mg(NO₃⁻)/L) and % samples exceeding 50 mg(NO₃⁻)/L in some aquifers from semiarid, arid, and hyperarid areas.

whereas the United Nations Environment Programme (UNEP) states that eutrophication is “probably the most pervasive water quality problem on a global scale” (UNEP 1991). High NO₃⁻ concentrations are known to stimulate heavy blue-green algal growth (such as *Cyanobacteria*), which produce poisonous toxins to fish and mammals simultaneously.

2.2.2.1.1.4 Standards and regulations for nitrates

In order to restore the quality of water and deter hazards to humankind, various approaches have been targeted in terms of standards and legislation. In many countries, there are strict limits on the permissible concentration of NO₃⁻ in

drinking water and in many surface waters. The USEPA [37] has set an enforceable standard called maximum contaminant level (MCL) in water for NO_3^- at 10 parts per million (ppm) (10 mg/L) and for NO_2^- at 1 ppm (1 mg/L), [59] and this is for all public water supplies. A summary of water quality guidelines for N- NO_3^- , made by the USEPA, is reported in **Table 2** [39]. Furthermore, the intake limits for NO_3^- in foods were set by the joint expert committee on food additives of the FAO/WHO and the European commission's scientific committee on food, at an acceptable daily intake for NO_3^- of 0–3.7 mg (NO_3^-)/kilogram (kg) body weight [40]. The same goes for Canada that set a MCL at 10 mg/L for NO_3^- as N and 1 mg/L for NO_3^- as N. For Morocco, the quality limits imposed by Order No. 1277-01 of 10 Shaaban 1423 (17 October 2002) setting quality standards for surface water used for the production of drinking water, has also set a MCL at 50 mg/L for NO_3^- [41].

2.2.2.1.1.5 Nitrate detection methods

NO_3^- ions can be detected through laboratory-based methods or in situ sensor-based methods. In general, they are two techniques for NO_3^- detection, direct and indirect methods. While comparing the two methods, the major disadvantage of using a direct method is measurement errors due to interference from other contaminants [38, 42, 43]. Many methods are currently available to the laboratory technicians for the detection and analysis of NO_3^- in a variety of sample matrices. The most commonly used techniques are (i) spectroscopic detection, (ii) electrochemical detection, and (iii) chromatography detection.

2.2.2.1.1.6 Nitrate removal techniques

There are a number of popular and conventional treatment methods available for reduction or removal of NO_3^- in water bodies. In addition, several technologies are being investigated or proposed as denitrification methods. **Figure 4** presents an overview of some of the techniques used for NO_3^- removal from water [23]. Reverse osmosis (RO) is considered as an ex situ and in situ application for the reduction of NO_3^- from water. The efficiency of the process depends on the used pressure; this later should be sufficient to overcome the osmotic pressure [44]. According to Harries et al. [47], RO works well with NO_3^- and NO_2^- . Rejection of 96–98% was

Water use	NO_3^- mg/L as nitrogen	NO_2^- mg/L as nitrogen
Drinking water	10 (maximum)	1 (maximum)
Freshwater aquatic life—acute	32.8 (maximum)	0.06 (maximum) when the chloride is less than or equal to 2
Freshwater aquatic life—chronic	3.0 (30-d average)	0.02 (30-d average) when the chloride is less than or equal to 2
Marine aquatic life—acute	None proposed	None proposed
Marine aquatic life—chronic	3.7 (30-d average)	None proposed
Livestock watering	100 (maximum)	10 (maximum)
Wildlife	100 (maximum)	10 (maximum)
Recreation and esthetics	10 (maximum)	1 (maximum)

Table 2.
Summary of water quality guidelines for nitrogen.

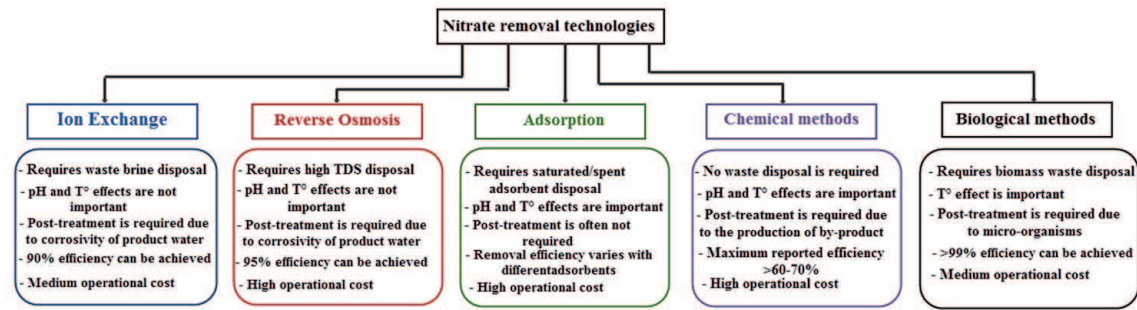
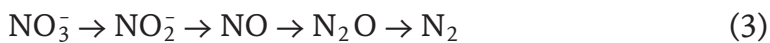


Figure 4.
Nitrate removal techniques.

found for monovalent ions, while 98–99% was found for divalent ions. In addition, ion exchange membranes (IEMs) have great potential in water denitrification. In fact, ion exchange is a reversible reaction between an electrolyte and a complex, where NO_3^- and NO_2^- , which have a negative ionic charge, will bind to the positively charged sites on the anion exchange beads of IEMs [44, 45]. For electrodialysis (ED), according to Mohsenipour et al. [46], the feed water supplied should have a turbidity that is lower than 2.0 nephelometric turbidity units. Furthermore, the concentration of free chlorine in water should be less than 0.5 mg/L, while these of hydrogen sulfide and manganese levels should be lower than 0.3 mg L. With electrodialysis systems about 70–85% of the water that is supplied to the system is available for use as low NO_3^- water [47].

One of the common and promising purification methods is the biological treatment of wastewaters operated by denitrifying bacteria. The idea of using this process to remove NO_3^- from drinking water has gained ground, especially in Europe [44]. Biological denitrification is mostly advised for the removal of relatively low concentration of N components. Furthermore, NO_3^- are efficiently removed when an external organic carbon source, generally methanol, ethanol, or acetic acid, is added [48]. The rate of denitrification also depends on the type and concentration of carbon as well as carbon to nitrogen (C/N) ratio. The reduction of NO_3^- to nitrogen is done in four steps as shown in Eq. (3).



Mohsenipour et al. [46] also reported the efficiency of NO_3^- removal by a biological denitrification method using *Pseudomonas* bacteria and carbon source (starch of 1%) for initial NO_3^- concentrations of 500 and 460 mg/L; the denitrification rates were respectively equal to 86 and 89% [49]. Furthermore, various conventional and nonconventional materials from different origins have been studied and conceived, as adsorbents, to limit the harmful effects of NO_3^- [23]. Huang and Cheng [50] used powdered activated carbon (PAC) and carbon nanotubes (CNTs) for pollution reduction of NO_3^- and demonstrated that the adsorption capacity of CNTs was found to be higher than PAC and decreased for pH higher than 5. Bamboo powder charcoal and nonactivated granular carbon (from coconut shells activated with zinc chloride) demonstrate good removal efficiency in NO_3^- removal [51]. Natural adsorbents such as clay, zeolite, bentonite, and others were also studied [46, 52]. The effect of various variables such as pH, temperature, adsorbent dosage, other ions, and the amount of surfactant was tested on NO_3^- removal, and it been demonstrated that except pH and temperature, the other variables are found to have a marked effect on NO_3^- removal. It should be noted that the removal of NO_3^- has been conducted using modified and unmodified agricultural waste [74]. Mizuta [51] summarized the various sorbents which have been used so far

for the elimination of NO_3^- and demonstrated that hydrotalcite-type compounds/layered double hydroxides and chemically modified adsorbents are found promising sorbents for enhanced removal of NO_3^- from water. Tyagi et al. [53] made a summary of relevant published data with some of the latest important findings on the use of nanomaterials as NO_3^- adsorbents. These nanoparticles can be metallic, semiconductor, or polymeric. **Table 3** reports some of the different nanomaterials used for NO_3^- removal along with their experimental working parameters such as pH, adsorbent dose, initial NO_3^- concentration, and temperature.

2.2.3 Industrial pollution

Industrial wastewater is a generic term involving a wide array of wastewater discharged out of various industries [54]. Indeed, there are many kinds of industrial wastewater, with complex composition, because water fulfills several roles and functions in all types of industries. Measurements of parameters like biochemical oxygen demand (BOD), COD, pH, and alkalinity can allow to classify industrial pollution [55]. Indeed, industrial effluents can be classified according to the dominant nature of pollution, and it may be characterized by a high concentration of organic/inorganic compounds [56]. It should be noted that among the industries generating waste, certain of the most dangerous wastewater comes from sectors such as refineries, mining, tanneries, pharmaceuticals, pulp mills, and sugar production/distillery [57]. The food and agriculture industries generate wastewaters with high BOD, which is estimated to 0.6–20 m³ wastewater/ton of product (such as bread/butter/milk or fruit juice). For instance, the conventional process in distillery industry generates ~15 L of wastewater per liter of alcohol with a BOD level of about 90,000 mg/L [57]. The most important contributor of wastewater volume (18%), COD (23%), and a major source of NH_4^+-N is the paper and paper products industry, while the raw chemical material and chemical products industry is the dominant source of NH_4^+-N (35.3%) and an important source of COD and petroleum hydrocarbons [59]. Around 80% of the heavy metal discharges into water sources come from four industries, namely, the nonferrous metal manufacturing and processing industry (27.5%), the fur and leather products manufacturing industry (19.4%), the metal product manufacturing industry (17.7%), and the nonferrous metal ore mining industry (14.0%). This is also true for the Moroccan industrial activities and its discharges. According to the Moroccan federation of metallurgical, mechanical, and electromechanical industries, this industrial sector includes more than 1000 companies divided into four main sub-sectors, including iron and steel, metal transformation, coating, surface treatment, and services related to the metallurgical, mechanical, and electromechanical industries.

2.2.3.1 General information on metal pollutants

Although metals are natural components of the Earth's crust and contribute in various physiological processes of living organisms, their elevated concentrations (above the level of homeostatic regulation) produced by industrial activity [58] can be toxic to human and ecological receptors. The majority of elemental metals and their compounds and complexes are extremely stable in the environment [59]. Most metals are extremely soluble in circumneutral waters (as in **Figure 5**) [60].

Furthermore, metals are excellent conductors of electricity and mostly enter chemical reactions as positive ions. These metals are often involved in electron transfer reactions involving oxygen and leads to the formation of toxic oxyradicals [61]. The metals' fate and toxicity are highly dependent on their speciation or the form in which they exist in a given aquatic system [7]. An example of the importance

Nanomaterial	Type	Modification	Initial NO ₃ ⁻ concentration	pH	Nanomaterial dose	T°	Contact Time	NO ₃ ⁻ removal efficiency
Nanoparticles	Iron (Fe0) (nanoscale zero valent iron (NZVI))	Coated with graphene oxide (GO)	5 mg/L	6.9	1 g/L	—	8 h	90%
	Iron (Fe0) (NZVI)		100 mg/L		5 g/L	Room	30 min	>96.5%
	Iron (Fe0) (NZVI)	Pd-Cu deposited on NZVI	100 mg/L		0.25 g	Room	1 h	78%
	Iron (Fe0) (NZVI)	Fresh NZVI coated with nickel	1 mg/ml		0.1 g/10 ml	20 °C	2 min	100%
	TiO ₂ /Fe0	—	10 mg/L	3	1:10 ratio of TiO ₂ /Fe0		30 min	95%
	Nano-alumina	—	40 mg/g	4.4	1 g/L	25 ± 2 °C	70 min	4 mg/g
Nanotubes	CNTs	Oxidized	50–600 mg/L	7	50 mg	25 °C	50 h	70%
	CNTs	Iron oxide nanoparticle immobilized	2.5–100 mg/L		5 mg	25 °C	90 min	91.75%
Nanofibers	Chitosan	Microalgae immobilized	30 mg/L	6.5–7.0	—	—	16 days	87 ± 4%
		Chitosan nanofibers	30 mg/L	6.5–7.0	—	—	16 days	32 ± 3%
Nanoshell	SiO ₂ -FeOOH-Fe core shell	NZVI	64 mg/L	3	—	—	120 min	99.84%
Nanocluster	Spherical NZVI	—	80 mg/L	3–7	4 mg/L	—	60 min	95%
Nanocomposites	Carbon-silicon	—	50 mg/L		100 mg	—	60 min	44.89%,11.34 mg/g
	Iron/chitosan/zirconium composite	—	1–1000 mg/L	3	—	—		89.3 mg/g
	Magnetic graphene	Nanosized lanthanum hydrous	20 mg/L	6–8	40 mg	293–313 K	30 min	138.88 mg/g

Nanomaterial	Type	Modification	Initial NO ₃ ⁻ concentration	pH	Nanomaterial dose	T°	Contact Time	NO ₃ ⁻ removal efficiency
	Nanocomposite	Doped composite	20 mg/L	6–8	50 mg	293–313 K	30 min	83%
	Chitosan/Zeolite/nano ZrO ₂	—	20 mg/L	3	0.02 g	35 °C	60 min	23.58 mg/g

Table 3.
Comparison of NO₃⁻ removal by different nanomaterials [53].

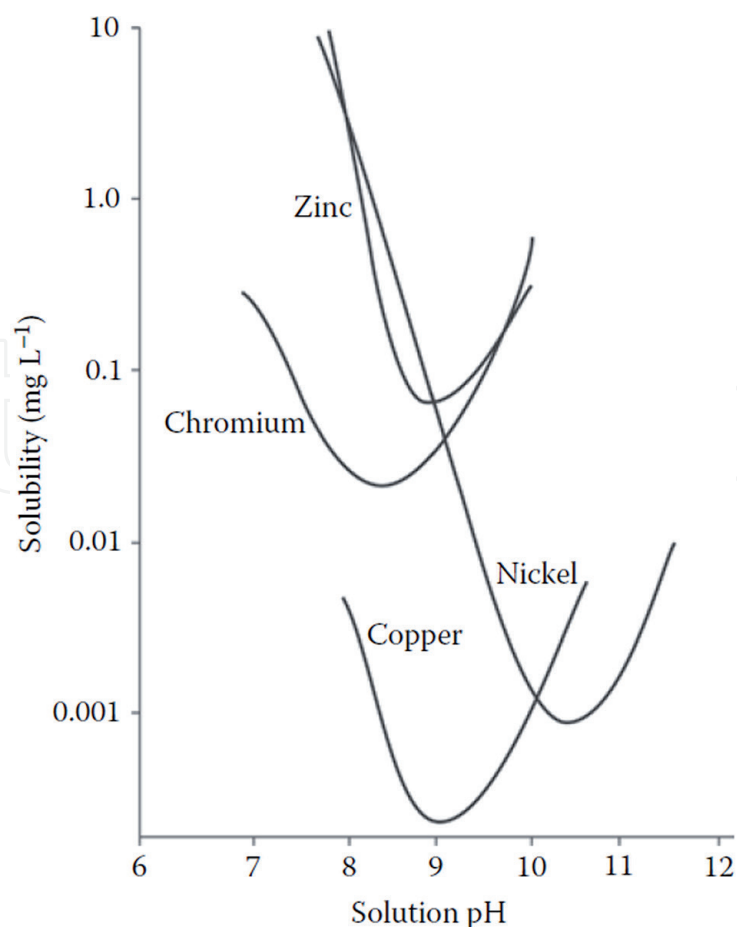


Figure 5.
 Solubility curves for common metals in freshwater with pH [60].

of metal speciation and redox conditions is hexavalent chromium (Cr(VI)). Many of metals are transition metals (such as cadmium and Cu) or heavy metals (such as lead and silver) that can form metalloids which bond to organic compounds to form lipophilic substances that are often highly toxic. Metals are also lost from solution by precipitation as the pH changes [7, 60, 61]. **Table 4** shows the ranking of these metals according to their toxicity through biological and carcinogenicity tests [62].

2.2.3.1.1 Heavy metal pollutants

Any metallic element with relatively high density as compared to water and toxic even at low concentrations is termed as “heavy metal” [63, 64]. Among these metals, Cr is one of the top 16 major toxic contaminants that have detrimental effects on human health [64, 65]. Besides Cr, Cu is generally considered as a highly harmful metal at high concentration [66]. Accordingly, the following section discusses and summarizes relevant information about Cr and Cu.

Cr as a metallic element was first discovered and isolated in 1797 by the French chemist Nicolas-Louis Vauquelin [35, 67]. The world resources of Cr exceed 10.9 billion metric tons of shipping-grade chromite [67]. Ferric chromite (FeCr_2O_4) is the principal Cr ore, found mostly (with 96% of the world’s reserves) in South Africa. Minor common sources include chrome ochre (Cr_2O_3), and crocoite (PbCrO_4) are also present [58]. Cr is widely used in engineering and chemical industries because of its durability and esthetic quality. The principal uses for Cr are metallurgical (67%), refractories (18%), and chemical (15%). In addition, Cr exists in three stable forms in the environment with different oxidation states and ionic nature [65]. The physicochemical properties of Cr are presented in **Table 5** [67].

Bioaccumulative character	Chemical elements
Very bioaccumulative	Pb, Zn, Cu
Relatively bioaccumulative	Hg, Ni, Cd
Slightly bioaccumulative	As, Cr
Carcinogenicity	
Strong carcinogenicity	As, Pb
Non-carcinogenic	Cr, Ni, Cd, Zn, Cu
Toxicity	
Group of highly toxic elements	Cd, Hg
Relatively toxic elements	Pb, Ni, As, Cu, Cr(VI)
Slightly toxic elements	Cr(III), Zn

Table 4.
Classification of metals according to their toxicity [62].

Physical and chemical properties of Cr	
Atomic number	24
Atomic mass	51.996
Atomic radius (pm)	185
Main oxidation state(s)	+2, +3, +6
Ionic radius (pm)	87–94 (+2), 75.5 (+3), 55–69 (+4), 48.5–71 (+5), 40–58 (+6)
Electronegativity (pauling)	1.66
Density (g/cm ³)	7.19
Melting/boiling point (°C)	1.907/2.671
Isotopes	4 stable + 17 unstable
Acid/base of oxide	Strong acid
State (st 27 °C, 1 atm)	Solid
Metallic character	Metal
Element group(s)	Transition element
Affinity	Lithophile

Table 5.
Physical and chemical properties of Cr [67].

The oxidation states of Cr can go from −2 to +6; however, only the +6 and +3 oxidation states are commonly encountered in the environment. Cr(III) is highly insoluble, relatively immobile, and most thermodynamically stable [58], while Cr(VI) has high water mobility and solubility and can be easily reduced. Cr(VI) is recognized to be more poisonous (100 times more toxic than Cr(III)), mutagenic, and carcinogenic in nature [68].

2.2.3.1.1.1 Chromium VI sources

To date, naturally occurring Cr(VI) in groundwater has been detected in the following geologic environments: (i) chromite ore bodies, (ii) arid alluvial basins in the southwest United States, (iii) saline brines in evaporate basins, and (iv)

serpentinite ultramafic terrains [67], while the major industrial source of Cr(VI) emissions are (i) chemical manufacturing industry, (ii) metal finishing industry, (iii) manufacturers of pharmaceuticals, (iv) electrical and aircraft manufacturers, (v) cement-producing plants (as cement contains Cr), and (vi) production of wood, stone, glass, and clay products. Owlad et al. [69] reported the concentration of Cr(VI) in the wastewater of several industries (as in **Table 6**) and estimated the concentration of Cr(VI) in wastewater caused by industries between 0.1 and 200 mg/L.

2.2.3.1.1.2 Speciation of Cr(VI)

In aqueous solution, Cr(VI) may exist in a variety of oxospecies (viz., dichromates ($\text{Cr}_2\text{O}_7^{2-}$), chromates (CrO_4^{2-}), H_2CrO_4 , and acid chromates (HCrO_4^-)) depending on pH of the solution, total Cr concentration, the presence of oxidizing and reducing compounds, the redox potential, and kinetics of the redox reactions [64, 70]. At $\text{pH} < 1$, the predominant species is H_2CrO_4 , while as the pH is raised from pH 2 to 6, the HCrO_4^- and $\text{Cr}_2\text{O}_7^{2-}$ anions prevail.

According to Palmer and Puls [71] under pH 6.5, HCrO_4^- dominates when the Cr(VI) concentrations are low (< 30 mM), but $\text{Cr}_2\text{O}_7^{2-}$ becomes significant when concentrations are greater than 1 mM, or it may even dominate when the total Cr(VI) concentrations are greater than 30 mM. At a $\text{pH} > 8$ only the yellow ion CrO_2^- exists. $\text{Cr}_2\text{O}_7^{2-}$ dominates in acidic solution at Cr(VI) concentration above 0.01 M, while CrO_4^{2-} dominates in basic solutions independently of Cr(VI) concentration, and H_2CrO_4 is a very strong acid [70]. The chemical equilibria which are involved for Cr(VI) dissociation are as in Eqs. (4)–(6):



2.2.3.1.1.3 Cr(VI) effects on human health and environment

Ingesting large quantity of Cr(VI), either by human or animal, can be corrosive to the skin and eyes and causes stomach upsets and ulcers, convulsions, kidney and liver damage [72, 73]. Allergic reactions consisting of severe redness and swelling of the skin have been noted. Some evidence on animal studies show that Cr(VI) compounds can cause cancer in various tissues due to the low water insolubility [35, 67, 72]. Indeed, due to the fact that Cr(VI) is unstable in the body, easy to diffuse across the membrane, and is reduced intracellularly, it can provide very reactive pentavalent Cr and trivalent Cr which can alter DNA. Ingestion of 1.0–5.0 g of Cr(VI) as chromate results in severe acute gastrointestinal disorders, hemorrhagic diathesis, and convulsions [74]. In 1998, Dartsch et al. [75] noticed that 5 mmol/L Cr(VI) resulted in 50% cell death.

Furthermore, Cr(VI) compounds at high concentration are extremely toxic to plants and retard their growth. Cr and Cr(VI) compounds can cause severe phytotoxicity which may result in reduction of seed germination, nutrient imbalance, degradation of pigments, decrease of antioxidant and enzyme concentration, and oxidative stress [76]. Indeed, Rout et al. [77] demonstrated a 25% reduction in seed germination in the presence of 200 μM Cr(VI). According to Davies et al. [78] Cr

Industry	Cr(VI) concentration (mg/L)
Hardware factory	60.0
Chrome tanning plant	3.7
Electroplating plant	1.0
Electropolishing plant	42.8
Tannery plant	3950.0
Tannery plant	100.0
Tannery plant	1770.0
Tannery plant	8.3
Electroplating plant	20.7
Electroplating plant	75.4

Table 6.
Industrial wastewater containing Cr(VI) [69].

is mostly toxic to higher plants at 100 µg/kg dry weights. Sinha et al. [79] reported that Cr is toxic for most agronomic plants at a concentration of about 0.5–5.0 mg/L in nutrient media and of 5–100 mg/g under soil condition. The Cr toxicity in plants affects photosynthesis in terms of CO₂ fixation, photophosphorylation, electron transport, and enzyme activities as reported by H. Oliveira [76, 80].

2.2.3.1.1.4 Cr(VI) detection methods

Given the different chemistries and malignity of Cr(III) and Cr(VI) complexes, the concentration determination of each chemical speciation rather than the total Cr concentration is often desired [81]. Indeed, Cr(VI) is mainly analyzed, and various methods to prevent its reduction have been developed. There are two main groups of Cr speciation methods: off- and online techniques [82]. The off-line methods use pretreatment techniques for separation and concentration of specific Cr species (in the samples) before its insertion into detection instruments. These pretreatment techniques can be (i) colored complex formation methods, (ii) soluble membrane filter techniques, (iii) chromatographic methods, (iv) electrochemical methods, (v) coprecipitation techniques, (vi) ion exchange techniques, (vii) separation using chelating resins, and (viii) solvent extraction. In the online methods, the separation system is coupled with detection system. These methods include (i) flow injection analysis, and (ii) high-performance liquid chromatography (HPLC) that includes ion chromatography (IC), (iii) ion pair chromatography (IPC), and (iv) reversed-phase chromatography.

The globally acknowledged standard methods for selective Cr(VI) detection are spectroscopic techniques using diphenyl carbazide (DPC) method with a limit of detection (LOD) of 0.12 mg/L [83]. In general, the DPC spectrophotometric determination is an inexpensive and sensitive procedure that also permits the speciation of Cr. It is worth mentioning that de Andrade et al. [84, 85] have employed DPC for the flow injection spectrophotometric determination of Cr(VI). In this work, the authors combined the spectrophotometric procedure with the column preconcentration procedure. New reagents are used for Cr(VI) spectrophotometric determination. Andrle and Broekaert [86] suggested the selective determination of Cr(VI) based upon the formation of a complex between ammonium pyrrolidinedithiocarbamate and Cr(VI). To overcome ion interferences, Pyrzynska [83] proposed a new analysis based on the reaction of Cr(VI) with chromotropic acid (in acidic

medium) along with the presence of NaF as a masking agent for iron. In fact, Bu et al. [87] indirectly determined Cr(VI) by the use of carbimazole based on the redox reaction of carbimazole with Cr(VI). In the same path, Fan et al. [88] developed a new method for Cr(VI) determination based on the reaction of Cr(VI) and ABTS (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate)). Moreover, the selective detection of Cr(VI) is relatively easier based on electrochemical techniques due to the different reduction potentials of Cr(VI) and Cr(III) [89]. Electrochemically cleaned Au electrode is useful for the detection of Cr. Polymer-based electrochemical sensor are also used for Cr(VI) detection. In 2013, Susan and Aziz reported a screen-printed carbon electrode modified with quercetin to detect Cr(VI) in the water, while Welch et al. [90] studied and confirmed the electrochemical detection of hexavalent Cr species at Au, glassy carbon electrode, and boron-doped diamond electrodes. Chen et al. [91] realized trace detection of Cr(VI) in aqueous mediums using electro-adsorption-assisted laser-induced breakdown spectroscopy.

2.2.3.1.1.5 Standards and regulations for Cr(VI)

According to the USEPA water standards, the maximum limit of Cr in drinking water is 0.1 mg/L which is based on the total Cr (EPA, 1990) [92]. Also, the allowable concentration of dischargeable Cr(VI) into surface water is below 0.05 mg/L; however, the permissible concentration of total Cr (Cr(VI), Cr(III) and other forms) is equal to 2 mg/L [93]. The American conference of governmental industrial hygienists' threshold limit time-weighted averages for Cr(VI) is 0.01 mg/m³. In addition, the Canadian guidelines has indicated a limit of 0.05 mg/L for total Cr concentration in drinking water [94]. Krishnani et al. [95] reported that the maximum permissible limits of Cr(VI) to discharge into potable water, in land surface water, and industrial wastewater are 0.05, 0.1, and 0.25 mg/L, respectively. According to the Moroccan official bulletin (NM 03.7.001), the Russian federation [73], and the Indian standard [65, 94], the maximum allowable limits for Cr in drinking and domestic water are 0.05 and 0.5 mg/L for Cr(VI) and Cr(III), respectively.

2.2.3.1.2 Copper

From the most common heavy metals that are often present in industrial wastewater, Cu is usually found at high concentrations in industrial discharges (**Figure 6**) [96]. Cu is an abundant trace element found in a variety of rocks and minerals. Over 90% of modern industrial enterprises need Cu products.

The Cu reserves and production (mines and concentrates) in major countries in 2014 are reported in **Table 7** [97]. Cu is involved in reduction, oxidation processes, adsorption/desorption, and dissolution processes which lead to many changes in its speciation. Cu is a transitional metal and appears in nature in four oxidation states: elemental copper Cu(0) (solid metal), Cu(I) cuprous ion, Cu(II) cupric ion, and rarely Cu(III). However in natural water systems, Cu can exist only in two different oxidation states, Cu(I) and Cu(II) [87]. The oxidation states of Cu depend on the concentration of oxygen.

In its oxidation state, Cu forms very stable complexes with both organic and inorganic ligands. The toxicity of serine and citrate is enhanced in case of estuarine bacteria, while Cu-amino acid and Cu-citrate are enhanced in case of *Daphnia* and algae, respectively [99]. In its pure form, Cu has outstanding criteria such as electrical and thermal conductivity, strong chemical stability, good corrosion resistance, and high plasticity and malleability, which makes it so attractive for industries.

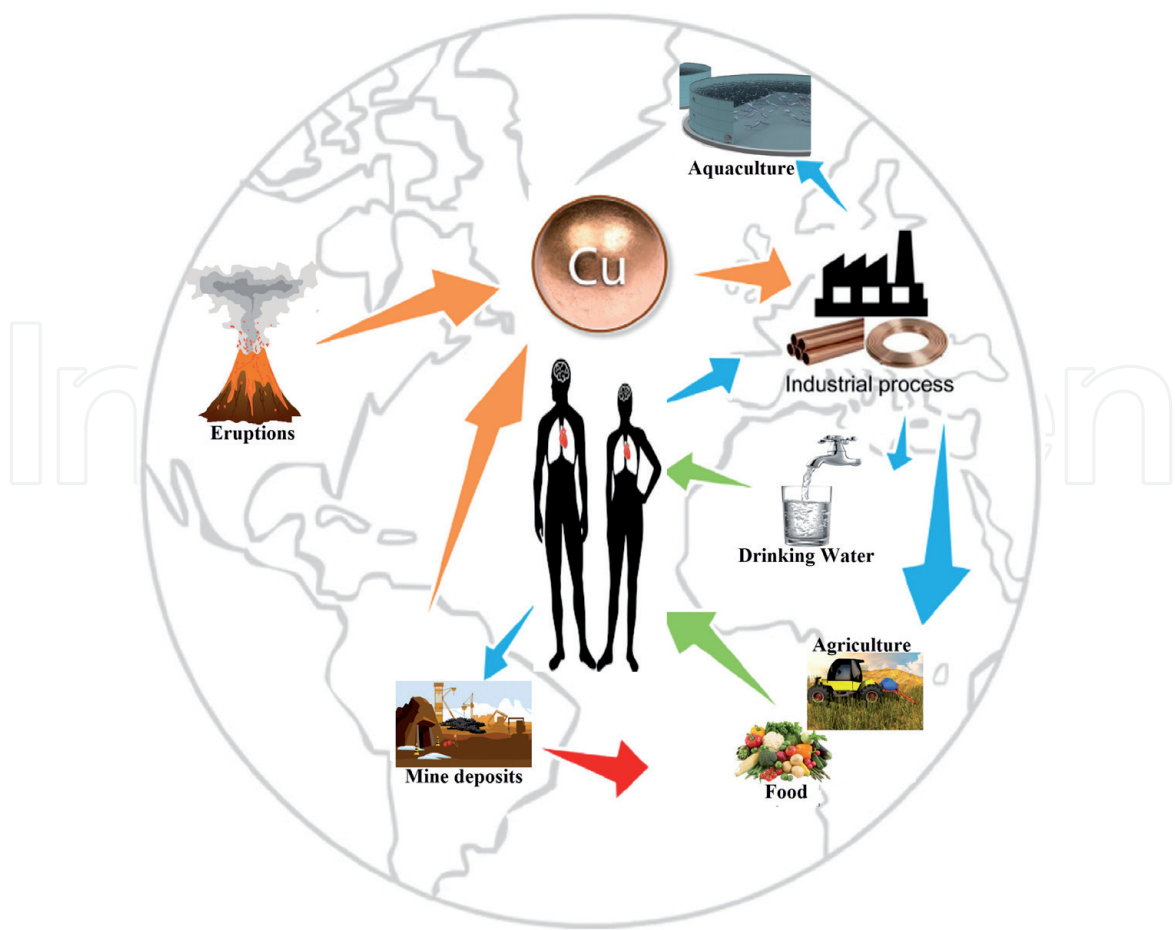


Figure 6. Ecology of Cu. Colored arrows represent various aspects, namely, orange, elemental Cu fluxes; blue, human Cu interventions; green, human Cu intake; red, contamination [96].

Country	Reserves/ (ten thousand tons)	Percentage of global reserves/(%)	Cu mine production /(ten thousand tons)	Cu concentrate production /(ten thousand tons)
Chile	20,900	29.86	575.0	274.7
Australia	9300	13.29	97.0	
Peru	6800	9.71	138.0	
Mexico	3800	5.43	51.4	
The United States	3500	5.00	138.3	108.6
Russia	3000	5.00	72.0	87.4
China	3000	4.29	192.3	764.9
Poland	2800	4.00		
Indonesia	2500	3.58		
Zambia	2000	2.58	75.6	70.9

Table 7. Cu reserves and production (mines and concentrates) in major countries [97].

2.2.3.1.2.1 Copper (II)

As stated before, Cu is a redox-active element meaning it can easily go back and forth between the oxidized Cu(II) state and the reduced Cu(I) state [100]. The following Eqs. (7)–(9) represent the reduction processes for Cu ions:



Cu(II) is suggested to be the primary species in nearly all natural waters. In this oxidation state, Cu forms very stable complexes with both organic and inorganic ligands [101]. $\text{Cu}_2(\text{OH})_2^{2+}$ is believed to be the principal cationic hydrolysis product. In contrast, Cu(I) is unstable in aqueous solution and tends to change rapidly to Cu(II). Cu(II) forms strong complexes with the electron donor groups in organic compounds (O, N, and S) [102].

2.2.3.1.2.2 Cu(II) effects on human health and environment

Many studies confirmed that an increased concentration of Cu(II) in the body leads to serious health problems [96, 98, 103]. Cu and Cu(II) is absorbed in the intestine and then transported to the liver and binds to albumin [96]. Due to its catalytic role, Cu can reduce human immunodeficiency and leads to symptoms of anemia, vomiting, neutropenia, hypopigmentation, bone abnormalities, and growth disorders. It was also related to abnormalities in the metabolism of glucose and cholesterol. Brewer et al. [100] also studied the many roles of Cu in human metabolisms and explained properly the different genetic diseases caused by this metal, namely, Wilson's disease, Menkes disease, and Alzheimer's disease. From an environmental point of view, the high concentration of Cu with an extreme acidity inhibits the ordinary development of plants and animals, reduce the biodiversity, contaminate water reservoirs, and even corrode infrastructure. Generally, sheep suffer plenty from Cu poisoning, because of the effects of Cu that manifest at fairly low concentrations [103].

2.2.3.1.2.3 Cu detection methods

The development of analytical methods for the selective detection and visualization of Cu(II) is significant. The common methods for the detection of Cu(II), as for Cr(VI), include liquid chromatography, electrochemical detection, spectrophotometry, solid-phase extraction coupled with atomic absorption spectroscopy, potentiometric techniques, X-ray fluorescence, atomic emission spectroscopy, and inductively coupled plasma mass spectrometry [104, 105]. According to Ramanjaneyulu et al. [106, 107], the existing reagents for the photometric determination of Cu permit the detection of 0.025–30 $\mu\text{g/mL}$ Cu. For instance, the diethyldithiocarbamate reagent is considered one of the most frequently used reagents for Cu(II) determination with a LOD of 0.1 $\mu\text{g/L}$. Zagurskaya et al. [107] developed a spectrophotometric method of determination of Cu(II) with a ligand for a new coordination compound, the sodium salt of 4-phenylsemicarbazone 1,2-naphthoquinone-4-sulfonic acid (L). The formation of this new complex is accompanied by a color change and LOD of 0.012 mg/L .

2.2.3.1.2.4 Standards and regulations for Cu and its derivative

The maximum permissible limits (MPL) for Cu in water are listed in **Table 8**. Furthermore, the USEPA has set a MPL for Cu discharges either in the soil or in wastewater. The MPL in the soil is equal to 100 mg/L , while the limit for wastewater

International standard organizations								
	WHO	USEPA	ISI	CPCB	ICMR	BIS	EU	NM
Cu permissible limit (mg/L)	1.0	1.3	0.05	1.5	1.5	1.3	2	2

**WHO; USEPA, United States Environmental Protection Agency; ISI, Indian Standard Institution; CPCB, Central Pollution Control Board; ICMR, Indian Council of Medical Research; BIS, Bureau of Indian Standards; EU, European limits via Directive 98/83/EC on the quality of water intended for human consumption; NM, the Moroccan official bulletin (NM 03.7.001).*

Table 8.
Permissible limits of drinking water quality [104, 105, 109].

that can be discharged into the public sewage system is 1 and 0.1 mg/L, respectively, for wastewater that can be discharged into public wastewater and which can be discharged into the recipient (surface and groundwater) [108].

2.2.3.1.2.5 Heavy metal (namely Cr and Cu) removal techniques

Faced with more and more stringent regulations, nowadays heavy metals are the environmental priority pollutants. In this regard, a wide range of removal technologies, such as chemical precipitation, ion exchange, adsorption, membrane filtration, and electrochemical, have been the subject of research nowadays.

In precipitation processes, chemicals react with heavy metal ions to form insoluble precipitates (such as hydroxide, sulfide, carbonates, etc.) by pH adjustment. The forming precipitates can be removed by physical means such as sedimentation, flotation, or filtration. **Table 9** reports some of the recent research in Cu(II) and Cr(VI) removal by chemical precipitation. It should be mentioned that Davarnejad and Panahi [110] reported that the adsorption method is considered to be the most common process used to remove different Cu ions from industrial wastewater. The efficiency of adsorption depends on many parameters; high surface area, pore size distribution, functional groups, and the polarity of the adsorbent determines the efficiency of adsorption process [66].

Many different cheap adsorbents have been developed and used for the removal of both Cu and Cr ions from metal-contaminated wastewater. Recently, activated carbons, agriculture byproducts, zeolites, and industrial wastes are widely employed to remove Cr(VI) from waters and industrial wastewaters [113]. Iftikhar et al. [114] investigated the use of rose waste biomass in Cr(III) and Cu(II) removal. In this study, the capacity of adsorption of Cu(II) and Cr(III) by rose biomass varies with temperature, and the maximum adsorption capacities of 55.79 and 67.34 mg/g, respectively, for Cu(II) and Cr(III) were found at 303 ± 1 K, with adsorption over 98% of Cu(II) and Cr(III). Natural zeolites are the most studied natural materials for the adsorption of heavy metals [115]. Ali and Yaşar [116] show the zeolite’s high selectivity for Cu ions. In the same context, Barakat [117] studied the effect of pH on Cu adsorption and demonstrate that A4 zeolite is efficiently used to adsorb Cu(II), at natural and alkaline pH. At the same time, Francis et al. [115, 118] studied activated phosphate, zirconium phosphate, and calcined phosphate at 900°C, as net adsorbents to remove Cu(II). In addition, many researchers have reported that electrocoagulation (EC) is a suitable technology for heavy metal removal. The efficiency of this method in removing Cr(VI), Cu(II), and Ni from wastewater of an electroplating plant was investigated by Akbal and Camcidotless [119]. These authors achieved 100% Cu, 100% Cr, and 100% Ni removal at an EC time of 20 min with the use of Fe-Al electrode pair. **Table 10** resumes some of the electrochemical studies on Cr(VI) removal.

Species	Initial metal concentration	Precipitant	Optimum pH	Removal efficiency (%)
Cu(II), Zn(II), Cr(III), Pb(II)	100 mg/L	CaO	7–11	99.37–99.6
Cu(II), Zn(II), Pb(II)	0.018, 1.34, 2.3 mM	H ₂ S	3.0	100, >94, >92
Cr(III)	5363 mg/L	CaO and MgO	8.0	>99
Cr(VI)	30 mg/L	FeSO ₄	8.7	>99
Cu(II), ZN	100 mg/L	Lime (Ca(OH) ₂), Soda ash (Na ₂ CO ₃), Sodium sulfide (Na ₂ S)	10–11	>99

Table 9.
Heavy metal removal using chemical precipitation [111, 112].

	Concentration	pH	Anode-cathode	Removal	Reference
Electrocoagulation Cr(VI)	5 mg/L	7.0	Al alloy-Fe	98.2%	[113]
	1,000 mg/L	1.2	Carbon steel	100%	[113]
	100 mg/L	2	Fe-Cu	100%	[113]
	1,000 mg/L	4.5	Fe	100%	[113]
	—	4	Al–Al	99%	[113]
Electrochemical Cr(VI)	Concentration	pH	Electrodes	Removal	
	3–50 mg/L	2	Carbon felt	100%	[113]
	12 mg/L	3	CNTs	96%	[113]
	50 mg/L	0.5	Polyaniline	~70%	[113]
	350 mg/L	0.7	Polypyrrole-coated Al ₃	100%	[113]
	20 mg/L	11	Au nanoparticle-decorated TiO ₂ nanotube array	100%	[113]
	1470 mg/L	1.84	Stainless steel	100	[112]
	8 mg/L	2.0	Carbon aerogel	98.5	[69]

Table 10.
Cu(II) and Cr(VI) removal electrochemical methods.

3. Conclusion

Widespread pollution of surface and underground water resulted largely from increased pollutant discharges from industrial (specially the heavy metals), municipal, and agricultural sources (nutriments such as N and P), excessive water abstraction from the environment, and poor water resource management and enforcement of pollution control regulations. The preservation of water sources from pollutants, NO₃[−], Cr and Cu, is a major concern, shared by all, public, industrial, scientific, researchers, and decision-makers. Over the past two decades, environmental regulations have become more stringent and require an improved quality of the treated effluents. Consequently, wide ranges of treatment technologies have been developed to remove agricultural and industrial pollutants. The

set of methods presented in this chapter is certainly not exhaustive, but its main objective is to show the diversity of techniques used for NO_3^- and heavy metal (Cu(II) and Cr(VI)) removal. The choice of one technique over the others depends on several factors such as the cost of processing, ease of reproducing, and the added value, along with the mode of use of the obtained treated water and the occurrence, or lack thereof, of harmful side products. Consequently, the development of new treatment methods is always a topical research topic.

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Conflict of interest

The authors declare no conflict of interest.

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