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Review

Integrated Process of Immediate One-Step Lime Precipitation, Atmospheric Carbonation, Constructed Wetlands, or Adsorption for Industrial Wastewater Treatment: A Review

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Abstract: The transition from the linear economy paradigm to the circular economy in industrial wastewater treatment systems is on the global agenda. The search for new simple, eco-innovative, and low-cost processes for treating industrial wastewater, which can also be used by small and medium-sized industries, has been a constant challenge especially when environmental sustainability is considered. So, a new integrated industrial wastewater treatment system has been developed that includes the immediate one-step lime precipitation process (IOSLM) and atmospheric carbonation (AC), followed by constructed wetlands (CWs) or adsorption. The current review provides an overview of industrial wastewater treatment strategies for high- and low-biodegradable wastewater. A background on functionality, applicability, advantages and disadvantages, operating variables, removal mechanisms, main challenges, and recent advances are carried out for each process that makes up the IOSLM+AC+CW/adsorption integrated system. The prospects of the IOSLM+AC+CW/adsorption integrated system are also discussed. Not neglecting the improvements that still need to be made in the integrated treatment system as well as its application to various types of industrial wastewater, this review highlights that this treatment system is promising in industrial wastewater treatment and consequent by-product recovery. The IOSLM+AC integrated system showed that it can remove high amounts of organic matter, total suspended solids, oils and fats, phosphorus, and ammonium nitrogen from industrial effluents. On the other hand, constructed wetlands/adsorption can be alternatives for refining effluents still containing organic matter and nitrogen that were not possible to remove in the previous steps.

Keywords: integrated wastewater treatment; lime precipitation; high-biodegradability wastewaters; low-biodegradability wastewaters; C/N ratio; organic matter; nitrogen

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1. Introduction

Industries are of great importance in society as they meet the daily needs of consumers. However, due to cleaning operations, cooling water, and manufacturing in industry, wastewater is generated. The produced wastewater volume and the industrial wastewater characteristics are different from industry to industry as different raw materials are used. Some industrial wastewaters, such as winery wastewater and brewery wastewater, have a wide pH range of around 3 to 12 [1,2]. Other effluents, such as rubber processing wastewater (pH 3.7 to 5.5, [3]), distillery industry wastewater (pH 3.8 to 4.4, [4]), and olive mill wastewater (pH 4 to 6, [5]) are acidic. High values of chemical oxygen demand (COD), biological oxygen demand (BOD), and total suspended solids

(TSS) have been found in some industrial effluents (Table 1), such as dairy wastewater (COD at 1900 to 2700 mg O_2 L^{-1}, BOD at 1200 to 1800 mg O_2 L^{-1} and TSS at 500 to 740 mg L^{-1}, [6]), brewery wastewater (COD at 2000 to 6000 mg O_2 L^{-1}, BOD at 1200 to 3.600 mg O_2 L^{-1} and TSS at 2901 to 3000 mg L^{-1}, [2]), distillery industry wastewater (COD at 70,000 to 98,000 mg O_2 L^{-1}, BOD at 45,600 to 60,000 mg O_2 L^{-1} and TSS at 2000 to 14,000 mg L^{-1}, [4]), winery wastewater (COD at 320 to 296,119 mg O_2 L^{-1}, BOD at 125 to 130,000 mg O_2 L^{-1} and TSS at 0 to 30,300 mg L^{-1}, [1]), and among others. Regarding total nitrogen (TN), rubber processing (200 to 1800 mg N L^{-1}), and distillery industry (1000 to 1200 mg N L^{-1}) wastewaters have higher concentrations (Table 1). For ammonia (Table 1), higher values were found for seafood processing wastewater (3.2 to 1059 mg N L^{-1}), swine wastewater (321 to 1129 mg N L^{-1}), and tannery wastewater (100 to 300 mg N L^{-1}). Greater total phosphorus (TP) concentrations have been found for swine (148 to 1039 mg L^{-1}) and slaughterhouse (25 to 200 mg L^{-1}) wastewaters (Table 1). On the other hand, higher concentrations of heavy metals (e.g., Fe^{3+}, Pb^{2+}, and Cu^{2+}) are expected to be found in battery manufacturing wastewater [7]. Some industrial wastewaters, such as textile industry wastewater, paper mill wastewater, tannery wastewater, explosives wastewater (e.g., TNT, RDX, and HMX), petrochemical wastewaters, and others, are poorly biodegradable. The wide range of contamination levels observed in many industrial effluents is justified by changes in the industrial process (e.g., production volume, changes in the manufacturing process, and degree of cleaning performed).

Generally, the contaminant levels in industrial effluents are quite high compared with contaminant levels in domestic wastewater [8]. According to Metcalf and Eddy [8], a typical untreated domestic wastewater can have a COD of 250 to 800 mg O_2 L^{-1}, a BOD of 110 to 350 mg O_2 L^{-1}, a TSS of 120 to 400 mg L^{-1}, a TN of 20 to 70 mg N L^{-1}, the absence of nitrates, trace concentrations of heavy metals, ammonia of 12 to 45 mg N L^{-1}, and a TP of 4 to 12 mg L^{-1}, depending on the wastewater flowrate. These values are much lower than those found in many industrial wastewaters, as mentioned above and found in Table 1. Thus, compared to domestic wastewater, industrial wastewater presents a greater challenge in its treatment, given the high concentration of pollutants present, the high variability of its composition, and consequently the high damage that it can cause to the environment if there is no treatment or if the treatment is inappropriate.

Unfortunately, the lack of treatment or inappropriate treatment of industrial wastewater has been a source of pollution of groundwater, lakes, and rivers [9,10]. For example, eutrophication is one of the problems associated with the discharge of nutrients (especially nitrogen and phosphorus) and organic matter into the receiving watercourse, which leads to a marked oxygen depletion due to bacterial decomposition of organic matter and high turbidity, with severe consequences for the natural fauna and flora [11,12]. On the other hand, the presence of toxic products in industrial effluents is another factor that, in addition to being lethal for many organisms, can, in some cases, lead to the accumulation of these compounds in the food chain, making them unfit for consumption [13]. In addition, industrial effluents (rich in organic matter) are often released into public sewage networks without prior treatment, which causes problems in urban wastewater treatment systems since these systems have a limited treatment capacity. Therefore, the installation of industrial wastewater treatment plants in industries is essential to producing effluents with characteristics that can be discharged into water or the domestic sewage system.

This review article discusses industrial wastewater treatment strategies, with a special focus on the immediate one-step lime precipitation process (IOSLM), atmospheric carbonation (AC), constructed wetlands (CWs), and adsorption. The applicability, operating variables, removal mechanisms, advantages and disadvantages, main challenges, and recent advances are discussed for the referred technologies.

Table 1. Typical characteristics of different industrial wastewaters.

Types of Industrial Effluent	**pH**	**COD ($mg O_2 L^{-1}$)**	**BOD ($mg O_2 L^{-1}$)**	**TSS ($mg L^{-1}$)**	**TN ($mg N L^{-1}$)**	**NH_3 ($mg N L^{-1}$)**	**TKN ($mg N L^{-1}$)**	**TP ($mg P L^{-1}$)**	**Reference**
Winery wastewater	3–12	320–296,119	125–130,000	0–30,300	NR	NR	NR	NR	[1]
Brewery wastewater	3–12	2000–6000	1200–3600	2901–3000	NR	NR	25–80	NR	[2]
Rubber processing wastewater	3.7–5.5	3500–14,000	1500–7000	200–700	200–1800	NR	NR	NR	[3]
Distillery industry wastewater	3.8–4.4	70,000–98,000	45,000–60,000	2000–14,000	1000–1200	NR	NR	NR	[4]
Olive mill wastewater	4–6	40,000–220,000	35,000–110,000	NR	NR	NR	NR	NR	[5]
Dairy wastewater	7.2–8.8	1900–2700	1200–1800	500–740	NR	NR	NR	NR	[6]
Textile industry wastewater	5.5–10.5	350–700	150–350	200–1100	NR	NR	NR	NR	[14]
Seafood processing wastewater	6.1–7.1	1147–8313	463–4569	324–3150	21–471	3.2–1059	NR	13–47	[15]
Swine wastewater	7.4–7.9	2050–33,860	287–5820	1000–27,800	NR	321–1129	483–2502	148–1039	[16]
Pulp and paper mill wastewater	3.9–8.2	1314–4100	480–1353	83–605	NR	NR	NR	NR	[17]
Slaughterhouse wastewater	4.9–8.1	1250–15,900	610–4635	300–2800	50–841	NR	NR	25–200	[18]
Tannery wastewater	7–8.5	3000–6000	1200–2700	2000–3000	NR	100–300	250–400	NR	[19]
Pharmaceutical wastewater	6.7–7.2	616–4750	322–2440	120–354	NR	NR	24.6–82.7	1.2–3.4	[20]
Petroleum refinery wastewater	7.5–9.4	744–1673	205–448	280–340	NR	40–45	82–95	1.67–1.73	[21]

Note: NR—not reported.

2. Industrial Wastewater Treatment Strategies

Different physical, chemical, and biological methods have been combined to remove/reduce nutrients (e.g., ammonium, nitrate, and phosphorus), organic matter, total suspended solids, and other compounds from industrial wastewater. Since each industrial effluent has its own characteristics, the combined treatments will have to be specific to that wastewater. The option of physicochemical treatments or biological treatments to remove a given contaminant from the effluent has been questioned [22,23]. Although biological treatments seem to be more interesting processes in ecological terms than physicochemical treatments, some characteristics of industrial wastewater, such as the low biodegradability of the effluent, may condition their use [24–26]. For example, activated sludge is not viable for treating poorly biodegradable wastewater [27]. Mixing low-biodegradability effluents with highly biodegradable effluents or adding biodegradable organic matter to the effluent could be examples of solutions to improve the biodegradability of wastewater for use in biological treatment; however, the latter solution entails costs [28]. Recently, several pretreatment technologies have been evaluated to treat and improve the biodegradability of industrial wastewater for suitable biological treatment. Some examples of wastewater treatment technologies that improve the biodegradability of wastewater include advanced oxidation processes (AOP) and electrochemical treatments [29–32], and constructed wetlands [28]. AOP (e.g., ozonation, UV/O_3, ozonation coupled with H_2O_2, O_3/UV/H_2O_2, sonification, photocatalytic oxidation, Fenton, and other processes) are effective in the treatment of various wastewaters. However, they have the disadvantages of generating sludge, are a complex technology, and some reagents (e.g., hydrogen peroxide) are costly [33]. Electrochemical treatments (e.g., electrocoagulation, electrodialysis, electrochemical oxidation, among others) are fast and effective processes for certain metals, do not need chemicals, and have low sludge production. However, these processes have high energy consumption costs [34,35]. Compared to these processes, the adsorption process and constructed wetlands are recognized for their low-cost wastewater treatment [36], eco-friendly treatment, and treatment of various types of industrial wastewaters, including low biodegradable wastewater (e.g., pulp and paper wastewater, petrochemical wastewater, pharmaceutical wastewater, and others) [37–40]. However, the adsorption process can be less efficient than in constructed wetlands [41]. Constructed wetlands can also improve the biodegradability of effluents, since in these systems, the exudates produced by plants are highly biodegradable and can stimulate the cometabolism of contaminants in the rhizosphere [28]. Mangkoedihardjo [28] investigated the performance of low-biodegradable wastewater using phytotreatment before the biological oxidation process. The author observed that hyacinth plants were able to increase the BOD/COD ratio of industrial wastewater from 0.05–0.11 to 0.30–0.52, with simultaneous high-significant COD removals. However, for better efficiency of constructed wetlands, pretreatment of wastewater is necessary to remove various contaminants (e.g., TSS) and thus reduce the potential risk of system clogging [42]. The precipitation of nondegradable pollutants on the substrate surface is also one of the reasons for clogging [43]. According to Karungamye [44], the effluents to be treated in constructed wetlands should not exceed a suspended solids concentration of 100 mg L^{-1}. Thus, the effluent must undergo a primary treatment to reduce the solid load. Primary decanters and coagulation-flocculation processes have been used as pretreatment methods to reduce the contaminant load of constructed wetlands [45]. Recently, a combined treatment consisting of an immediate one-step lime precipitation process (or lime precipitation) followed by atmospheric carbonation has been considered an efficient pretreatment of industrial wastewaters [46], leachate [47], and urban wastewaters [48] in the removal of COD, TSS, oils and fats, phosphorus, and ammonium nitrogen. However, despite the high removals obtained by the combined treatment, the final effluent still needs to be refined. Although there are few reported cases, recent research has shown that constructed wetlands or adsorption processes can act as low-cost refining processes for industrial wastewater treated by the IOSLM and AC integrated processes, regardless of the biodegradability index of the effluent to be treated [49,50]. In fact, IOSLM contributes to reducing the C/N ratio and removing organic matter and TSS from biodegradable or poorly biodegradable effluents [51,52]. However, a decrease in the biodegradability index has also been observed with the application of IOSLM, making the wastewater non-biodegradable, as observed by Luz et al. [46] and Ramalho et al. [47]. On the other hand, atmospheric carbonation contributes to lowering the pH of highly alkaline wastewater as well as increasing the C/N ratio by removing ammonia [51,52]. In this way, the removal of organic matter and ammonia during pre-treatment will contribute to better efficiency of the CW and the adsorption process, which would not be possible with the coagulation-flocculation process as it does not favor the removal of ammonia from the effluent. Thus, IOSLM+AC+CW/adsorption could be a low-cost and ecological treatment solution for low and high C/N ratio effluents and poorly biodegradable wastewater. Although the adsorption process is interesting to apply when the areas on the ground are limited for the implementation of CWs, this process is limited in the removal of nitrates, in which case the solution would be to obtain a nutrient solution of nitrates to reuse.

IOSLM+AC+CW/adsorption can be considered an eco-innovative wastewater treatment system. In fact, eco-innovative wastewater treatment technologies refer to the application of environmentally sustainable technologies and approaches in treating wastewater to minimize their negative impacts (e.g., minimizing greenhouse gas emissions) on the environment while also maximizing their potential benefits. Typically, these technologies are energy-efficient and resource-efficient processes that minimize the use of chemicals and other inputs and may incorporate renewable energy sources and closed-loop systems to reduce the overall environmental footprint [53]. So, some eco-innovative aspects have been found in this integrated process, namely [47,48,54]: (i) The IOSLM process (or lime precipitation) uses a single reagent (hydrated lime) of low cost and high availability; the sludge produced is stabilized, is rich in nutrients, has the potential to be used in acid soils, and is less harmful than iron/alum sludge obtained by conventional coagulation-flocculation processes (the iron/alum sludges can contaminate groundwater by leaching iron and aluminum salts in acidic soils [55] and limit plant growth due to lower nutrient availability [56,57]; the destination of iron/alum sludges is landfilling disposal); (ii) The atmospheric carbonation process contributes to atmospheric CO_2 mitigation since in this process atmospheric CO_2 is used to neutralize alkaline effluent to values around neutrality, therefore, no consumption of acids and the problems associated with them occurs; (iii) Constructed wetlands are eco-friendly, and mimic natural processes that already occur in nature; and (iv) Many wastes that could end up in landfills can be used as adsorbents in industrial wastewater treatment through the adsorption process.

To the best of our knowledge, no review article was found that included a detailed and joint review of the potential of each of these processes. More information regarding the operation, potentialities, and limitations of each of these treatment processes in industrial wastewater treatment are described in the following sections.

3. Immediate One-Step Lime Precipitation Process

3.1. Theory and Applications

The immediate one-step lime precipitation process (or lime precipitation) aims to change the solubility of the substances, converting the soluble substances into insoluble substances, by adding lime to the wastewater. A scheme of the lime precipitation process is presented in Figure 1. Lime precipitation is a process where rapid and slow mixing takes place. Rapid mixing for a good mixture between the precipitating agent and the wastewater to form precipitates. Slow mixing is necessary for the agglomeration of particles to increase their sedimentation (Figure 1). In immediate one-step lime precipitation, the flocculation step does not exist since it uses high lime dosages to immediately produce large amounts of precipitates that settle in the mantle, dragging many particles with them [51,54].

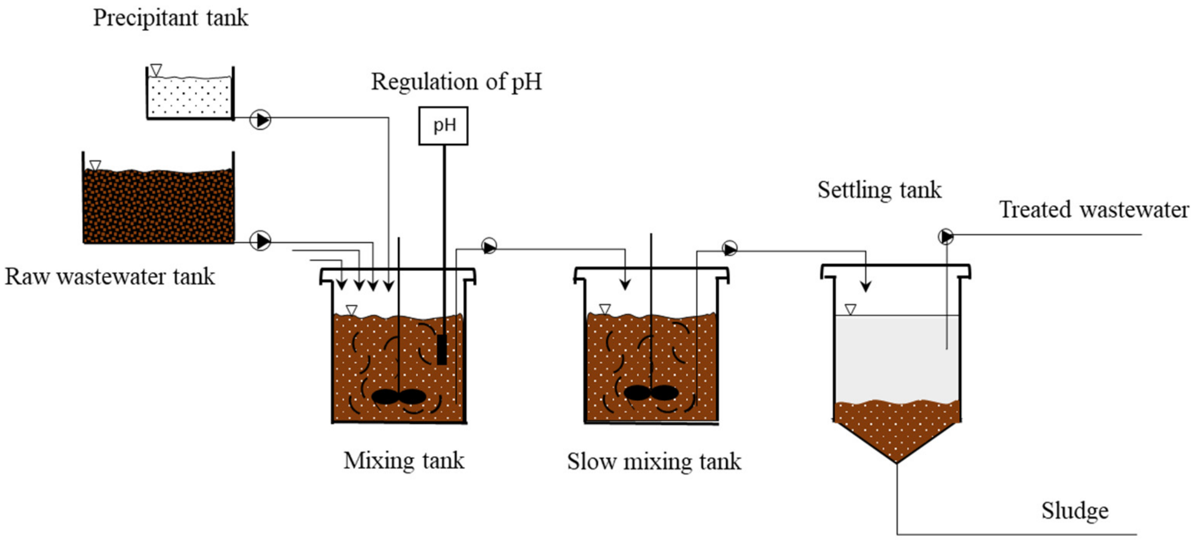

Figure 1. Lime precipitation process.

Quicklime (CaO) and hydrated lime ($Ca(OH)_2$) are the two forms of lime mostly used in wastewater treatment. CaO is the result of the calcination of $CaCO_3$ at high temperatures (Equation (1)). Hydrated lime results from the hydration of CaO with water (Equation (2)). The solubility of $Ca(OH)_2$ decreases with increasing temperature [58].

$$CaCO_3\ (s) \rightarrow CaO + CO_2\ (g) \tag{1}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{2}$$

Lime is cheaper than other chemicals and can easily be purchased anywhere [59,60]. Lime has been used for pH control [61,62], urban wastewater treatment [48], stabilized leachates [63], and treatment of industrial wastewaters such as plywood industry wastewater [64], cotton textile wastewater [65], tannery wastewater [66,67], olive mill wastewater [68], explosive wastewaters [51], slaughterhouse wastewater [52], and others.

3.2. Operating Variables and Removal Mechanisms

High removals of COD, BOD, color, total phosphorus, total coliforms, heavy metals, turbidity, and organic nitrogen have been observed in the IOSLM process/lime treatment of various types of wastewaters (Table 2). The amount of hydrated lime required for optimal effluent clarification varies with the type of wastewater to be treated, more specifically with the composition of the water, for example, alkalinity, total hardness, and ammonium concentration [69]. Sometimes the dosages used are higher than theoretically foreseeable since hydrated lime partially dissolves [60]. Boukhoubza et al. [68] tested different concentrations of hydrated lime (10 to 150 g L^{-1}) to treat 1 L of olive mill wastewater at pH 12. The authors observed that small concentrations of hydrated lime contributed to a greater effluent dilution effect than the effect of coagulation. Increasing concentrations of lime decreased the volume of solution added, and, in this case, the recorded reductions could be related to the coagulation effect rather than dilution. High concentrations of hydrated lime or CaO solution (e.g., 200 g L^{-1}) have been used in the literature [46,47,63,70]. Ramalho et al. [47] observed that stirring time in the immediate one-step lime precipitation process has a small influence on organic load and NH_4^+ removal.

The effect of effluent composition buoyancy on the effectiveness of the lime precipitation process has been scarcely documented in the literature [71]. Prazeres et al. [54] applied IOSLM to treat different high-strength cheese whey wastewaters (without cheese whey recovery, 60% cheese whey recovery, and 80% cheese whey recovery). The authors observed that cheese whey recovery significantly influenced the characteristics of the wastewater to be treated and, consequently, the removal of various parameters.

Some reaction mechanisms of the IOSLM process/lime treatment in wastewater treatment have been observed, namely:

Effluent pH increases since the dissolution of hydrated lime in wastewater provides hydroxyl ions (OH^-) (Equation (3)) [63,65].

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \tag{3}$$

Carbonate and hydroxide anions can react with a wide range of cations, leading to the formation of highly insoluble precipitates [72]. For example, the instantaneous conversion of calcium bicarbonates and magnesium bicarbonates into precipitated calcium carbonates (Equation (4)) and magnesium carbonates (Equation (5)), as well as the transformation of magnesium carbonates into precipitated magnesium hydroxides (Equation (6)) [60,63]. In fact, these compounds have low solubility product values (i.e., 4.7×10^{-9} for $CaCO_3$ and 8.9×10^{-12} for $Mg(OH)_2$, respectively), and the minimum solubility of calcium carbonate and magnesium hydroxide occurs at pH 9.1–9.5 and around 11, respectively [73].

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightleftarrows 2CaCO_3\ (s) + 2H_2O \tag{4}$$

$$Ca(OH)_2 + Mg(HCO_3)_2 \rightleftarrows MgCO_3 + CaCO_3\ (s) + 2H_2O \tag{5}$$

$$Ca(OH)_2 + MgCO_3 \rightleftarrows Mg(OH)_2\ (s) + CaCO_3\ (s) \tag{6}$$

Neutralization of suspended impurities results in the destabilization of charged particles and their aggregation [64]. The formed calcium carbonate and magnesium hydroxide can act as coagulants [74]. Furthermore, colloidal particles can be trapped during the formation of calcium carbonate precipitates [75].

Total phosphorus removal (Equations (7) and (8)) occurs in the pH range of 8–12 [75]. The degree of phosphorus removal by the IOSLM process/lime treatment is a function of the following factors: initial phosphorus concentration, lime concentration, the concentration of other anions competing with phosphorus for precipitating cations, and wastewater pH [76]. The phosphate precipitation rate is influenced by the presence of carbonates, as the latter compete with the phosphate ions for calcium ions [77,78].

$$3Ca(OH)_2 + 2PO_4{}^{3-} \rightarrow Ca_3(PO_4)_2\downarrow + 6\ OH^- \tag{7}$$

$$4Ca(OH)_2 + 3PO_4{}^{3-} + H_2O \rightarrow Ca_4H(PO_4)_3\downarrow + 9\ OH^- \tag{8}$$

Disinfection of the effluent is due to the exposure of microorganisms/viruses to high pH under a certain contact time, as well as the occurrence of the adsorption of microorganisms to the formed precipitates [46,60].

Organic matter removal by surface adsorption, co-precipitation, precipitation, coagulation-flocculation, or chemical reaction [63].

Removal of heavy metals (e.g., Ni, Zn, Fe, Cr, and others) in the form of precipitated hydroxides (Equations (9) to (12)) or carbonates, as well as their adsorption on calcium carbonate. Metal hydroxide precipitation is highly dependent on pH [67,71,72,79].

$$C_r(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3\downarrow + 3CaSO_4\downarrow \tag{9}$$

$$NiSO_4 + Ca(OH)_2 \rightarrow Ni(OH)_2\downarrow + CaSO_4\downarrow \tag{10}$$

$$ZnSO_4 + Ca(OH)_2 \rightarrow Zn(OH)_2\downarrow + CaSO_4\downarrow \tag{11}$$

$$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2\downarrow + CaSO_4\downarrow \tag{12}$$

Table 2. Application of lime precipitation/IOSLM in the treatment of industrial wastewater, landfill leachate, and urban wastewater.

Type of Wastewater	Reagent and Applied Dose/pH	Operation Mode	Optimum Removal Efficiency	Reference
Landfill leachates	Lime (4 g L^{-1}), pH 11.85	Rapid mixing (300 rpm) for 5 min, slow mixing (30 rpm) for 30 min, followed by settling for 30 min.	COD (25.5%), Ca^{2+} (93.5%), Mg^{2+} (98.5%), NH_4^+ (56.2%), total alkalinity (87.7%), and Fe (75.4%).	[63]
	Lime (2.0 g L^{-1}), pH = 11.20		COD (18.0%), Ca^{2+} (65.0%), Mg^{2+} (65.0%), NH_4^+ (29.7%), and total alkalinity (80.0%).	
	Lime (6.0 g L^{-1}), pH 10, 40		COD (0.4%), Ca^{2+} (91.5%), Mg^{2+} (95.5%), NH_4^+ (24.7%), and total alkalinity (90.9%).	
	CaO (27.6 g L^{-1})	300 rpm stirring speed for 2–60 min, followed by settling for 2 h.	Stirring time has a small influence on organic load and NH_4^+ removal.	[47]
	CaO (18.2–33.3 g L^{-1})	300 rpm stirring speed for 40 min, followed by settling for 2 h.	COD (64%) at 27.6 g L^{-1} of CaO.	
Plywood industry wastewater	Lime (1.5 g L^{-1})	Rapid mixing and settling for 2 h.	COD (40%), TSS (36.8%), phenol (41%), and TKN (48.1%).	[64]
Olive mill wastewater	Lime (10 g L^{-1}), pH 12	Rapid mixing (200 rpm) for 5 min, slow mixing (60 rpm) for 10 min, and filtration (11 μm) after a resting period.	COD (72%), TSS (73%), and Phenol (60%).	[68]
Textile wastewater	Lime (0.8 g L^{-1}), pH 13–13.5	Rapid mixing for 1–2 min, slow mixing for 15–20 min, followed by settling for 45 min.	COD (50–60%) and color (70–90%).	[65]
Tannery wastewater	CaO and $Ca(OH)_2$ (0.3 to 3.2 g alkali/g Cr^{3+})	10 min of vigorous stirring, 200 rpm, and a settling time of 24 h.	Cr (99.8%), SO_4^{2-} (66.9%), $ZnSO_4$ (99.6%), $FeSO_4$ (21.4%), CN^{-1} (70.9%), $NiSO_4$ (52.8%), and $Fe_2[Fe(CN)_6]$ (76.4%) for CaO, Cr (99.8%), SO_4^{2-} (61.6%), $ZnSO_4$ (99.9%), $FeSO_4$ (7.1%), CN^{-1} (84.0%), $NiSO_4$ (54.4%), and $Fe_2[Fe(CN)_6]$ (90.5%) for $Ca(OH)_2$	[67]
Cheese whey wastewater	Lime, pH 6 to 13	700–800 rpm for 1 min, 300–400 rpm for 1 min, followed by settling for 24 h.	The highest COD removal (29.7%) was obtained at pH 11.0. Total phosphorus (61.9–95.6%) only occurred at pH $\geq$ 8.0. Highest total phenols removals (63.2–65.5%) at pH 12.0 and 13.0.	[78]

Table 2. *Cont.*

Type of Wastewater	Reagent and Applied Dose/pH	Operation Mode	Optimum Removal Efficiency	Reference
	$Ca(OH)_2$, pH 8.57 to 12.37	Vigorous agitation. Then the agitation system was switched off.	Under optimum conditions: COD (90%), turbidity (99.8%), TSS (98–99%), oils and fats (82–96%), phosphorus (98–99%), potassium (96–97%), and total coliforms (100%) for 80% cheese whey recovery and lime application.	[54]
Vinasse wastewater	$Ca(OH)_2$ (12–100 g L^{-1}), pH 10.14–12.49.	Rapid agitation.	COD (51%), absorbances, magnesium, nitrogen, and phosphorus had depletions ($\geq$70%) at pH 12.13 and 12.49.	[70]
Olive oil mill wastewater	$Ca(OH)_2$, pH 11.0 to 12.75.	Rapid agitation followed a settling time of 24 h.	COD (11.4–17.8%), total phosphorus (23.6–42.2%), turbidity (60.9–100%), total phenols (25.9–48.0%), and absorbances at 220 nm (10.3–33.5%), 254 nm (18.5–45.9%), 410 nm (34.2–81.6%), and 600 nm (22.1–77.3%).	[80]
Winery wastewater	Quicklime, slaked lime, Calcium hydroxide, using 1–50 mL L^{-1} for slaked lime and calcium hydroxide, and 5–40 mL L^{-1} for the quicklime.	Vigorous stirring for 2 min followed by a settling time of 1 h.	High removal levels of BOD_5 (77.9%), turbidity (98.7%), total phosphorus (87.1%), total phenols (99.9%), fecal coliforms, and Enterococcus (100%) at 25 mL L^{-1} of slaked lime.	[46]
Urban wastewater	Hydrated lime, reagent-grade $Ca(OH)_2$ and quick lime, pH 9.5 to 12.5.	Vigorous mechanical stirring (magnetically agitated, rotation speed of 300 rpm) followed by a settling time of 120 min.	COD (88%), BOD_5 (86%), TP (89%), N-organic (75%), and total coliform count (100%) at 0.7 g L^{-1} (reaction pH of 11.5) of hydrated lime.	[48]
Explosives wastewater	$Ca(OH)_2$ (2–19 g L^{-1}), pH 9–12.	Rapid mixing (3 s^{-1}) for 1 min, followed by settling for 46 min.	COD (92.1%), oils and fats (98.2%), organic nitrogen (100%) at 7.76 g L^{-1} (reaction pH of 10) of hydrated lime.	[51]
Slaughterhouse wastewater	$Ca(OH)_2$, pH 9.5–12.	Rapid mixing (3 s^{-1}) for 1 min, followed by settling for 60 min.	COD (7–91%), BOD_5 (80–86%), TP (98–99%), TSS (52–99%), 254 nm (87–96%), 410 nm (83–96%), oils and fats (47–92%), turbidity (62–97%) at reaction pH of 12.	[52]
	Lime (100–600 mg L^{-1})	Stirring at 100 rpm for 1 min, slow mixing at 40 rpm for 30 min, followed by a settling time of 30 min.	TSS (41.9%), BOD (38.9%), and COD (36.1%) at 400 mg L^{-1} of lime.	[81]

3.3. Main Challenges and Recent Advances

Although IOSLM is a simple operation, fast (i.e., high precipitation speed), low-cost (chemical cost and energy requirements) [82,83], and does not contribute to an increase in salinity (unlike some salts used, such as iron and alum [60]) or the formation of toxic secondary pollutants [72], this process leaves the effluent with a high pH [79], the NH_4^+ removal is limited [84], and it produces large amounts of sludge [60]. Effluent with a high pH is unsuitable for some sequence treatment processes within a wastewater treatment plant, and calcium carbonate precipitation may occur in the distribution pipelines [79]. The first two disadvantages mentioned above can be minimized by the atmospheric carbonation process since this process contributes to lowering the pH and removing ammonia [51,52] (See Section 4). Despite the large volume of sludge produced by the IOSLM process, when compared to coagulation processes using ferric chloride or alum chloride as coagulants, the sludges possess superior thickening and dewatering characteristics and are suitable for filter pressing at a lower cost [54,60]. Furthermore, the sludge does not need the addition of polymers or more lime to dewater it, which results in savings in chemical reagents, unlike the iron and alum sludge obtained by the coagulation process, which still needs to be conditioned [60]. The sludge is chemically stabilized due to the high pH applied, does not decompose quickly, causes few odor problems, and has recycling potential [60,74]. Finding economically viable and ecological solutions is important to minimize the impact of increased sludge production. The reuse of lime sludge from landfill leachate treatment by the IOSLM process to cover landfills has been considered an eco-innovative solution [85]. Some sludge resulting from the treatment of cheese whey wastewater by the IOSLM process has potential application in agriculture as a fertilizer since it contains many nutrients such as calcium, phosphorus, potassium, magnesium, and others, although with some limitations due to its saline nature (i.e., high NaCl content) [54]. On the other hand, the reuse of lime sludge from the IOSLM process/lime precipitation to treat industrial wastewater has been rarely reported. Ayeche [75] used hydrated lime sludge (with a purity of 67.03%) produced in the manufacture of acetylene to treat dairy wastewater, and the author observed substantial removals of suspended solids, organic matter, nitrogen, and phosphorus. The use of thermal treatment (calcination process) can also be a solution to recover the hydrated lime from the sludge and use it again as a reagent. Bal Krishna et al. [86] investigate the effectiveness of pre-treated lime sludge from a groundwater treatment plant through heat treatment in removing phosphorus from an aqueous solution. The authors observed that calcination of the sludge at 700 °C greatly improved the phosphorus removal from the aqueous solution compared to if it were applied to dry lime sludge at 105 °C. Recently, Madeira et al. [87] evaluated the reuse of sludge from the IOSLM process in wet or calcined form and as a coagulant or adjuvant coagulant to treat slaughterhouse effluents with different characteristics. These authors observed that the use of lime sludge as a coagulant aid and with heat treatment contributed to greater removals of COD from 3 to 91%, TP 98%, turbidity from 99 to 100%, *E. coli* 100%, and TKN from 3 to 62%, depending on the characteristics of the wastewater of the slaughterhouse treated. Subsequently, the authors carried out successive reuses of sludge, using lime sludge as a coagulant aid and with heat treatment. The results showed that the quality of the effluent did not change after each reuse (except for phosphorus, which increased). In addition, after each reuse, there were savings in terms of the dose of hydrated lime applied in the IOSLM process, and the sludge was more compacted and stabilized with a high pH value after three sludge reuses. The sludge obtained is rich in nutrients and may have a potential application in nutrient-poor and acidic soils.

4. Atmospheric Carbonation

4.1. Theory and Applications

Atmospheric carbonation (or atmospheric CO_2 sequestration) is a process that aims to reduce the pH of an alkaline effluent using atmospheric CO_2. Basically, this process consists of leaving the alkaline effluent exposed to the atmosphere over time at rest and at room temperature (Figure 2).

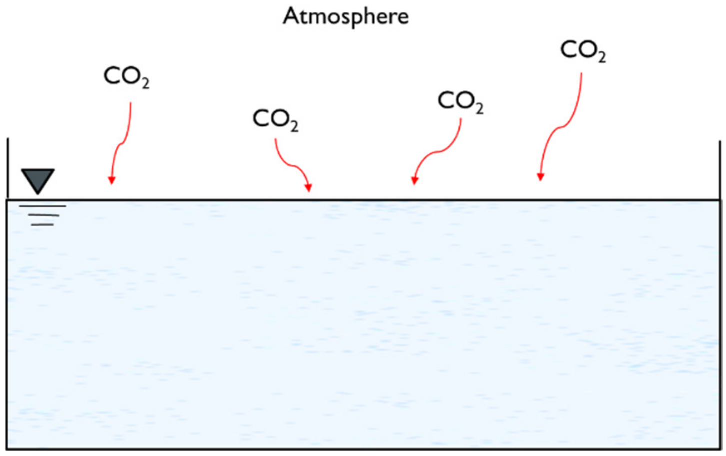

Figure 2. Atmospheric carbonation process.

The atmospheric carbonation process has recently been used to neutralize industrial wastewater (e.g., vinasse from the sugarcane ethanol industry [70], winery wastewater [46], explosive wastewaters [51], slaughterhouse wastewater [52], and cheese whey wastewater [54]), urban wastewater [48], and landfill leachate [47], resulting from the lime precipitation process.

4.2. Operating Variables and Removal Mechanisms

Reductions in pH, conductivity, calcium concentration, magnesium concentration, ammonia concentration, phenolphthalein alkalinity, and total alkalinity have been observed over the carbonation time for most wastewater treated by the IOSLM process/lime precipitation (Table 3).

Time, the absence/presence of precipitates from the IOSLM process/lime precipitation, and the injection of atmospheric air have been the factors analyzed in the carbonation process. Time has been the main factor analyzed by the authors, as it is the factor that regulates the continuity of carbonation reactions between the supernatant and the atmosphere. This factor is dependent on the operational variables applied (e.g., air injection or absence/presence of sludge) [48,70] and on the initial characteristics of the alkaline wastewater (e.g., pH, temperature, and others) [88]. Correia et al. [48] observed that the injection of atmospheric air contributes to a shorter carbonation time. On the other hand, Prazeres et al. [70] found that the presence of sludge from lime precipitation contributes to an increase in the carbonation time to reach a pH around neutrality. Madeira et al. [51] also observed that the presence of IOSLM sludge contributes to an increase in the carbonation time since the sludge slows down the effluent pH drop. This brings advantages that include the use of one less sludge/effluent separation step, since during atmospheric carbonation, precipitates of calcium carbonate are formed, as well as the great removal of ammonia since high pH values will remain longer for ammonia volatilization. On the other hand, Madeira et al. [52] observed that the application of higher reactor area/volume (A/V) ratios contributes to greater contact of the effluent with the atmospheric air, thus allowing a greater transfer of atmospheric CO_2 to the effluent and consequently a rapid pH reduction of the effluent. Despite the rapid decrease in pH, ammonia removal is not diminished by increasing the A/V ratio. Increasing the A/V ratio of the reactor contributes to the need for larger areas of the site, which may be a disadvantage for sites limited in area. The authors also observed that regardless of the reaction pH chosen from the range of 9.5 to 12, the same carbonation time would be necessary to reach pH 8. However, this does not happen when a pH of 9.5 is desired, where higher reaction pHs require longer carbonation times [52].

Table 3. Summary of a literature review about the neutralization of alkaline wastewater treated by lime precipitation through the carbonation of atmospheric CO_2.

Type of Effluent	Operating Conditions	Initial Physicochemical Characteristics	Final Physicochemical Characteristics	References
Vinasse from the sugarcane ethanol industry	$V = 2.6$ L $A = 162$ cm^2 Room temperature = 16.8 ± 2.3 °C Without agitation, air injection, and reagent addition With or without precipitate	Without precipitate: pH = 10.6 Conductivity ≈ 10 mS cm^{-1} Ca ≈ 2400 mg L^{-1}	After 15 days: pH ≈ 8 Conductivity ≈ 10.8 mS cm^{-1} Ca ≈ 2400 mg L^{-1}	[70]
		With precipitate: pH = 12.34	After 20 days: pH ≈ 8	
		Without precipitate: pH = 12.05	After 9.2 days: pH ≈ 8	
Winery wastewater	$V = 1$ L Without agitation, air injection, and reagent addition Without precipitate	pH =12.4 Conductivity = 6.5 mS cm^{-1} Ca = 499.8 mg L^{-1} Mg = 179.9 mg L^{-1}	After 15 days: pH = 7.46 Conductivity = 1.805 mS cm^{-1} Ca = 426.5 mg L^{-1} Mg = 6.6 mg L^{-1}	[46]
Cheese whey wastewater	$V = 3.5$ L $A = 162$ cm^2 Without agitation, air injection, and reagent addition Without precipitate	pH ≈ 12 Conductivity ≈ 4.75 mS cm^{-1} Ca ≈ 300 mg L^{-1} Mg ≈ 13 mg L^{-1}	After 7.3 days: pH ≈ 8 Conductivity ≈ 4 mS cm^{-1} Ca ≈ 200 mg L^{-1} Mg ≈ 2 mg L^{-1}	[54]
Landfill leachate	$V = 3$ to 4 L $A = 200$ cm^2 Without agitation, air injection, and reagent addition Without precipitate	pH = 12.5 NH_4^+ = 889 mg N L^{-1} Conductivity = 23.1 mS cm^{-1} Calcium Hardness = 490 mg $CaCO_3$ L^{-1} P. alkalinity = 6600 mg $CaCO_3$ L^{-1} Total alkalinity = 7530 mg $CaCO_3$ L^{-1} COD = 460 mg O_2 L^{-1}	After 32 days: pH = 10.10 NH_4^+ < 0.1 mg N L^{-1} Conductivity = 15.0 mS cm^{-1} Calcium Hardness < 0.1 mg $CaCO_3$ L^{-1} P. alkalinity = 2350 mg $CaCO_3$ L^{-1} Total alkalinity = 4480 mg $CaCO_3$ L^{-1} COD = 474 mg O_2 L^{-1}	[47]
Urban wastewater	$V = 4$ L $A = 200$ cm^2 Without agitation and reagent addition With precipitate With or without air injection	Without air injection: pH ≈ 11.5 Conductivity = 1.144 mS cm^{-1}	After 9.2 days: pH = 8.4 Conductivity ≈ 1.050 mS cm^{-1}	[48]
		With air injection (85 L h^{-1}): pH ≈ 11.5 Conductivity ≈ 1.300 mS cm^{-1}	After 4.2 days: pH ≈ 8 Conductivity ≈ 1.170 mS cm^{-1}	

Table 3. *Cont.*

Type of Effluent	Operating Conditions	Initial Physicochemical Characteristics	Final Physicochemical Characteristics	References
Explosives wastewater	V = 5 L A = 189 cm^2 Room temperature = 24.5 ± 2.0 °C Without agitation, air injection, and reagent addition With precipitate	pH = 10.3 NH_4^+ = 1505 mg N L^{-1} Conductivity = 9 mS cm^{-1} Ca = 1500 mg L^{-1} Mg = 52.5 mg L^{-1} P. alkalinity = 3674 mg $CaCO_3$ L^{-1} Total alkalinity = 3923 mg $CaCO_3$ L^{-1}	After 10 days: pH = 8 NH_4^+ = 578 mg N L^{-1} Conductivity = 10.3 mS cm^{-1} Ca = 1626 mg L^{-1} Mg = 36.2 mg L^{-1} P. Alkalinity = 62 mg $CaCO_3$ L^{-1} Total alkalinity = 125 mg $CaCO_3$ L^{-1}	[51]
Slaughterhouse wastewater	A/V ratio = 5 and 155.4 m^2/m^3 Without agitation, air injection, and reagent addition Without precipitate	With A/V = 5 m^2/m^3: pH = 11.9 Conductivity = 3.12 mS cm^{-1} Ca = 297.6 mg L^{-1} Mg = 43.3 mg L^{-1} NH_4^+ = 69 mg N L^{-1}	After 13 days: pH = 7.9 Conductivity = 2.46 mS cm^{-1} Ca = 130.9 mg L^{-1} Mg = 20.2 mg L^{-1} NH_4^+ = 22 mg N L^{-1}	[52]
		With A/V = 155.4 m^2/m^3: pH = 11.9 Conductivity = 3.12 mS cm^{-1} Ca = 297.6 mg L^{-1} Mg = 43.3 mg L^{-1} NH_4^+ = 69 mg N L^{-1}	After 1 day: pH = 8.2 Conductivity = 2.40 mS cm^{-1} Ca = 60.2 mg L^{-1} Mg = 31.4 mg L^{-1} NH_4^+ = 12 mg N L^{-}	

The minimum and maximum atmospheric carbonation times reported in the literature were 1 [52] to 20 days [70] to reach pH $\approx$ 8. On the other hand, a non-completion of the carbonation process at pH 8 has been observed by some authors, such as Ramalho et al. [47] who observed that the effluent still had a pH of 10.10 after 32 days of carbonation (Table 3). Prazeres et al. [54] also found that the time required for natural carbonation depends on effluent characteristics.

The decrease in pH of the effluent during the atmospheric carbonation process follows the same reaction mechanisms (Equations (13) to (16)) that lead to ocean acidification caused by increased CO_2 emissions into the atmosphere from anthropogenic sources [89].

$$CO_2\ (g) \rightleftarrows CO_2\ (aq) \tag{13}$$

$$CO_2\ (aq) + H_2O\ (l) \rightleftarrows H_2CO_3\ (aq) \tag{14}$$

$$H_2CO_3 \rightleftarrows H^+ + HCO_3{}^- \tag{15}$$

$$HCO_3{}^- \rightleftarrows H^+ + CO_3{}^{2-} \tag{16}$$

In fact, the effluents from the IOSLM process/lime precipitation are quite alkaline, and consequently, the free CO_2 in the effluent is unavailable, which causes a chemical imbalance of CO_2 between the effluent and the atmosphere with considerable concentrations of CO_2. As a way of counteracting this imbalance, the CO_2 present in the atmosphere tends to dissolve in the water through the water-air interface until it reaches equilibrium (Equation (13)). After dissolution in the water, the dissolved CO_2 is subjected to a hydration reaction through a reaction with water to form H_2CO_3 (Equation (14)). As H_2CO_3 is a weak acid, it dissociates in two steps: the first step (Equation (15)) is the formation of $HCO_3{}^-$ and H^+ ions, and the second step (Equation (16)) is the formation of $CO_3{}^{2-}$ and H^+ ions from $HCO_3{}^-$. The production of H^+ ions leads to a decrease in the pH of the effluent. During atmospheric CO_2 sequestration, H^+ ions are attracted by opposite charges, namely by hydroxide ions forming water molecules. $CO_3{}^{2-}$ ions are attracted by positive charges, namely calcium or magnesium ions, to form precipitated calcium carbonate and magnesium carbonate. In addition to the decrease in pH, water stabilization also occurs during atmospheric CO_2 sequestration, since carbonates tend to be converted into bicarbonates ($HCO_3{}^-$), reaching a maximum in the pH range of 8.4 to 8.6. At this pH range, precipitation of carbonates ($CO_3{}^{2-}$) does not occur since the fraction of carbonates in this pH range is practically zero [90].

During atmospheric carbonation, ammonia can be released into the atmosphere [47]. However, as the pH decreases, ammonia removal becomes more difficult as ammonia is converted to ammonium ions (Equation (17)), reaching 50% ammonia and 50% ammonium ions at pH 9.25 [91,92]. Since air stripping of wastewater with a low ammonia concentration (less than 2 g L^{-1}) is not economically sustainable [93], the atmospheric carbonation process could be an alternative solution.

$$NH_3 + H_2O \rightleftarrows NH_4{}^+ + OH^- \tag{17}$$

COD removal is not expected during the atmospheric carbonation process [47].

4.3. Main Challenges and Recent Advances

The use of atmospheric CO_2 as a neutralizing agent in wastewater treatment is an innovative, low-cost, and environmentally friendly technology. It is easy to apply, does not require reagents or energy (if not using atmospheric air injection), and produces stable wastewater concerning $CaCO_3$, preventing precipitation of $CaCO_3$ in distribution systems. Furthermore, this process contributes to the mitigation of greenhouse gases, is an alternative to the use of acids (e.g., H_2SO_4 or HCl) or CO_2 injection, and consequently reduces costs of reagents, corrosion of equipment by acids, and costs of transport/storage of CO_2 to the treatment site. However, the main challenges of the AC process are its contribution to the release of ammonia into the atmosphere if it is present in the effluent and its high carbonation time [54]. Although increasing the A/V ratio contributes to a significant reduction in carbonation time, such a solution requires a large disposal area that industries often do not have available. So, new approaches to atmospheric carbonation will need to be investigated to minimize the current disadvantages. Recently, Madeira et al. [94] developed a closed-system carbonation process that consists of moving (by gravity) the alkaline effluent treated by the IOSLM process under a capillary (in a staggered manner) that is in contact with injected atmospheric air. The injected air is then collected in an acidic solution to remove the volatilized ammonia. The authors observed that the atmospheric carbonation process developed contributed to a very significant reduction in carbonation time and an effective capture of volatilized ammonia with potential for reuse.

5. Constructed Wetlands

5.1. Theory and Applications

In recent years, constructed wetlands have gained popularity, as an emerging green technology for the treatment of industrial wastewaters [95,96]. Constructed wetlands are artificial wetlands that mimic a set of biological, physicochemical, and chemical processes that occur in natural wetlands to treat industrial wastewater, urban wastewater, and landfill leachate. These processes result from the interaction between the different elements that make up the system (Figure 3), namely: water, plants, microorganisms, and substrate [97]. Plant roots and the substrate act as a barrier to intercept coarse particles that the effluent may contain, while the microorganisms and plants break down and absorb pollutants from the effluent, which makes the constructed wetlands a filtration and purification system for effluents [98]. Generally, the resulting effluents can be discharged into surface waterways or reused for different purposes.

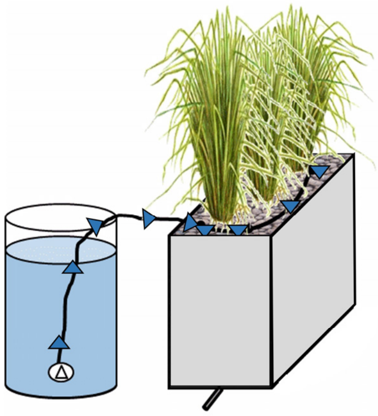

Figure 3. Schematic representation of the constructed wetland.

Constructed wetlands have been used as a secondary treatment (on a small scale, in isolated areas) for BOD removal or as a tertiary treatment (on a large scale, in developed countries) for wastewater refinement (BOD, solids, and nutrients) [99].

5.2. Operating Variables and Removal Mechanisms

Different types and combinations of plants, substrates, and constructed wetlands configurations have been reported in the literature for various types of industrial wastewater to determine the higher efficiency of the removal of pollutants from wastewater.

Biological media (e.g., bagasse, biochar, coal, and oyster shell), construction materials media (e.g., recycled brick, mortar, gravel, and sand), artificial media (e.g., activated carbon, compost, and lightweight aggregates), and industrial by-products (e.g., slag and fly ash) have been used as adhesion materials for biofilms or external sources of organic matter (in the case of biological media) [100,101]. Light-expanded clay aggregates (LECA) have also been widely used as a substrate as they can remove phosphates, have good mechanical strength and hydraulic conductivity, and are a good support structure for the growth of biofilms and plant roots [102].

In terms of wastewater flow regime, different designs have been used, namely, traditionally constructed wetlands (e.g., free water flow constructed wetlands (FWSCWs) and subsurface flow constructed wetlands (SFCWs) (i.e., horizontal flow constructed wetlands (HFCWs) and vertical flow constructed wetlands (VFCWs)), hybrid constructed wetlands (e.g., two-stage constructed wetlands and multi-stage constructed wetlands), and innovative constructed wetlands (e.g., aerated CW, circular flow corridor CW, baffled flow CW, and others) [103]. Each of these systems has its advantages, disadvantages, and applications. FWSCWs have lower construction and operating costs than SFCWs; however, odor issues may occur and it features lower contaminant removal ratios per unit area (which requires a larger area of land) than SFCWs [104]. Compared to FWSCWs, SFCWs tolerate cold weather, have fewer odor problems, and have greater sorption and exchange sites; however, they have higher costs, are subject to clogging of the media, and use small flows [105]. VFCWs have been applied to promote greater aerobic degradation of pollutants since they have a good oxygen supply and require a smaller land area compared to HFCWs; however, the flow distances are short, and they present poor denitrification [106]. HFCWs have long flow distances that allow for more complete degradation of pollutants and enable nitrification and denitrification; however, they require larger land areas and therefore a higher capital cost [107]. To overcome the disadvantages in removing pollutants by each wetland alone, hybrid constructed wetlands (e.g., VFCW-HFCW, VFCW-HFCW-VFCW, and other combinations) have also been applied to reach higher treatment efficiency [36,108]. The denitrification capacity of VFCWs have also been studied with the application of flood levels [109]. Different types of constructed wetlands have been applied to treat different types of industrial wastewater; however, most of the cases reviewed by Vymazal [110] used FWSCWs or HFCWs to treat industrial wastewater.

Many studies have indicated that pollutant removal efficiencies depend on the type of plant species used in the constructed wetland [111]. Therefore, the choice of the appropriate plant is an important factor in phytoremediation processes [112]. Plants have been classified as emergent, submerged, or floating, and their use depends on the type of constructed wetlands [113]. Plants that have been applied in constructed wetlands for industrial wastewater treatment, include: *Typha latifólia* e.g., for distillery wastewater [114], slaughterhouse wastewater [115], petroleum refinery wastewater [116] and floriculture wastewater [117]; *Phragmites karka* e.g., for distillery wastewater [114]; *Juncus effusus* e.g., for winery wastewater [118]; *Cyperus immensus* e.g., for paper and pulp wastewater [119]; *Phragmites australis* e.g., for slaughterhouse wastewater [115], dye wastewater [120], textile wastewater [121], cork boiling wastewater [122], fish farm wastewater [123] and olive mil wastewater [124]; *Brachiaria mútica* e.g., for textile wastewater [120]; *Typha domingensis* e.g., for paper and pulp wastewater [119]; *Canna indica* e.g., for mixed wastewater from steel mill, paper and dyeing factory [125]; *Pampas grass* e.g., for glass industry wastewater [126]; *Eichhornia crassipes* e.g., for petrochemical wastewater [127]; *Typha augustifolia* e.g., for seafood processing wastewater [128]; *Canna lilies* e.g., for floriculture wastewater [117]; *Pennisetum purpureum* e.g., for swine wastewater [129]; *Cyperus papyrus* e.g., for sugar mill wastewater [130]; *Phalaris arundinácea* e.g., for tile drainage [131] and among others.

Several environmental factors and operational conditions can affect nitrogen and organics removal, such as pH, temperature, availability of oxygen, availability of organic carbon sources, hydraulic load and retention time, the mode of influent feed (i.e., continuous, intermittent, batch, tidal, and step feed modes), nitrogen and organics loading, recirculation, bed depth, and plant harvesting [132,133]. In addition, the removal of nutrients and organic matter in constructed wetlands can be inhibited by the harmful effects of the presence of heavy metals on plants and microorganisms. Removal of metals in constructed wetlands can occur by precipitation, plant uptake, and microbial metabolism, but it depends on substrate type, plant species, and wastewater composition [134]. Removal of heavy metals (e.g., Pb, Cd, Cu, and Zn) (>85%) present in mixed domestic-industrial wastewater has been observed using recirculating standing hybrid-constructed wetlands planted by *Canna indica* L. and filled with lava rock and gravel [135]. According to Zhang et al. [135], these systems require a smaller area, allow a rapid co-precipitation of heavy metals, and consequently a decrease in toxicity in plants and microorganisms, as well as a consistent and effective removal of total nitrogen, total phosphorus, and organic matter.

Substantial removals of pollutants have been observed in the treatment of different industrial wastewaters by constructed wetlands (Table 4). The removal of pollutants from constructed wetlands is quite complex and involves a set of removal mechanisms, including physical (sedimentation and filtration), chemical (e.g., sorption, complexation, and precipitation), and biological (biodegradation, microbial transformation, and microbial/plant assimilation) processes that can occur simultaneously [136]. According to Vymazal [137], the nitrogen transformation mechanisms involved in constructed wetlands are ammonia volatilization, ammonification, nitrification, denitrification, fixation, absorption, and assimilation by plants, ammonium ion adsorption, and anammox. Removal of organic matter in constructed wetlands is associated with both aerobic and anaerobic degradation [138]. The plant also plays an important role in the phytoremediation of industrial effluents, and many mechanisms may occur, namely: degradation (rhizodegradation, phytodegradation), accumulation (phytoextraction, rhizofiltration), dissipation (phytovolatilization), and immobilization (phytostabilization) to degrade, remove, or immobilize contaminants [139].

Table 4. Pollutant removal efficiencies obtained in constructed wetlands for different industrial wastewaters.

Wastewater Types	Removals	Reference
Seafood wastewater	BOD (91–99%), TSS (52–90%), TN (72–92%), and TP (72–77%)	[140]
Winery wastewater	BOD (70%), COD (71%), TSS (87%), TKN (52%), and PO_4^{3-} (17%)	[118]
Tannery wastewater	BOD (98%), COD (98%), TSS (55%), TP (87%), and NH_4^+ (86%)	[141]
Steel industry wastewater	COD (77%), NH_4^+ (77%), Fe (94%), and Mn (81%)	[142]
Refinery wastewater	COD (80%), oil (93%), BOD (88%), and TKN (86%)	[143]
Aquaculture wastewater	COD (27%), TSS (66%), TN (67%), TP (24%), and NO_3^- (59%)	[144]
Textile wastewater	Cr (40–50%)	[145]
Abattoir wastewater	BOD (97%), COD (97%), TSS (94%), TN (74%), and NH_4^+ (99%)	[146]
Distillery wastewater	BOD (85%), COD (80%), TKN (75%), NO_3^- (57%), NH_4^+ (2–10%), and SO_4^{2-} (69%)	[147]
Brewery wastewater	TSS (89%), COD (92%), TN (83.6%), NH_4^+ (92.9%), TP (74.4%), and PO_4^{3-} (79.5%)	[148]
Cheese wastewater	BOD (55%), COD (72%), TSS (60%), TP (30%), and TN (50%)	[149]
Olive mill wastewater	COD (85%), TSS (90%), TP (83%), TKN (83%), Phenol (80%), NH_4^+ (54%), and NO_3^- (46%)	[124]
Pulp and paper wastewater	COD (88%), color (96%), BOD (93%), and chlorophenols (90%)	[150]
Mixed industrial wastewater	BOD (66%), COD (67%), NH_4^+ (24%), organic-N (83%), and PO_4^{3-} (62%)	[151]

5.3. Main Challenges and Recent Advances

Although CWs are recognized for easy operation and maintenance, a low carbon footprint, lower maintenance (with little external energy input), and lower capital construction costs [113,152–154], these systems have higher land area requirements and retention times than conventional systems [106,113,155,156]. The search for new plants to consistently comply with the permit requirements for removing pollutants has been a real challenge. In recent years, *Chrysopogon zizanioides* (L.) Roberty (formerly known as *Vetiveria zizanioides* (Linn.) Nash) has instigated the interest of several researchers in the phytoremediation process due to its characteristics, namely its strong resistance and survival to extreme climatic and edaphic conditions (e.g., drought and flooding, high concentration of pollutants (i.e., nutrients, heavy metals, and persistent organic matter), pH 3 to 10.5, salinity until 47.5 dS m^{-1}, temperatures ranging from -9 to 55 °C), as well as its roots quite long that allow greater absorption of pollutants and a greater supply of oxygen for aerobic bacteria to develop [157–161]. In addition, this plant also has economic value since it serves as a raw material to produce perfumes and cosmetics [162]. This plant has shown similar potential and sometimes more effectiveness in removing contaminants from industrial wastewater than some commonly used plant species, such as Cyperus species, Phragmites species, and Typha species [163]. *Vetiveria zizanioides* has been applied to remove organic matter from contaminated surface water [111,164], treat landfill leachate [47] and urban wastewater [165–167], rehabilitation and soil stabilization of sites contaminated with high levels of heavy metals [168–170], and treat industrial wastewater, e.g., aquaculture wastewater [171], piggery effluent [172,173], pinora effluent, palm oil mill effluent, biogas effluent [174], textile wastewater [175], olive mill wastewater [160], milk factory wastewater [176], tofu wastewater [161], paperboard mill wastewater [177], high explosives from munition industry wastewater [178] and others. High COD, BOD, and TSS removal efficiencies have been observed in some poorly biodegradable water from industrial wastewater (e.g., biogas wastewater [174] and tofu wastewater [161]) when *Vetiveria zizanioides* is used (Table 5); however, the same did not occur for some wastewater that was not very biodegradable, such as palm oil mill wastewater [174] and textile wastewater [175]. The use of constructed wetlands to treat poorly biodegradable industrial wastewater is a challenge since the effluent can influence the growth of microorganisms as well as the associated removal mechanisms [125]. Most investigations have been carried out with FWSCWs, requiring a long hydraulic retention time (1 to 120 days) when using *Vetiveria zizanioides* (Table 5). These systems require mosquito control [156].

Although several investigations have been registered on the potential of vetiver in wastewater treatment, studies on its efficacy in treating industrial effluents with high nitrate content are limited. Panja et al. [178] evaluate the phytoremediation potential of *Vetiveria zizanioides* in removing explosive compounds and nitrates from wastewater effluents generated in an industrial munition facility. The authors observed high removal efficiencies of nitroguanidine (79%), nitrates (95%), dinitroanisole (96%), RDX (100%), and HMX (100%); however, this was only possible with the use of four successive batches (except for RDX and HMX, which was one batch) once the vetiver plants started to show visible symptoms of stress, such as chlorosis and fallen leaves, and died within the first few days, returning to be replaced by a new batch of vetiver plants. These results show that further research is needed. Almeida et al. [109] evaluate the potential of phytoremediation of *Vetiveria zizanioides* for nitrate and organic matter removal from synthetic wastewater in subsurface vertical flow-constructed wetland systems. The authors observed that the ratio of COD/NO_3^--N in wastewater affected the efficiency of NO_3^--N removal and that a low hydraulic load and a high COD/NO_3^--N ratio ensure good effects of nitrate and organic matter removal. The authors did not observe obvious symptoms of toxicity signals during the experimental tests. Thus, *Vetiveria zizanioides* has good phytoremediation potential in the fields of nitrate nitrogen and organic substance removal. For the heterotrophic denitrification process to occur, highly concentrated nitrate wastewaters require a certain amount of organic matter, which sometimes they do not have [179].

Table 5. Application cases of phytoremediation of industrial wastewater using *Vetiveria zizanioides*.

Wastewater Types	CW Type	Media	HRT (d)	HL (m^3 d^{-1})	Initial Concentrations	Removal Performance (%)	Country	References
Aquaculture Wastewater	FWSCW (2 m × 1 m × 0.5 m)	Coarse sand and corals	1	0.576	NH_3 (0.1–0.2 mg L^{-1}), PO_4^{3-} (6–10 mg L^{-1})	NH_3 (2–67%), PO_4^{3-} (0–75%)	Indonesia	[171]
Piggery Wastewater	FWSCW (1 m × 3 m × 1 m)	Soil	5	0.18	BOD (767.90 mg L^{-1}), COD (1330.25 mg L^{-1}), TKN (158.67 mg L^{-1}), TP (69.90 mg L^{-1})	BOD (74%), COD (70%), TKN (88%), TP (83%)	Thailand	[173]
Pinora Wastewater	FWSCW	-	120	-	TSS (385 mg L^{-1}), BOD (4836 mg L^{-1}), COD (6296 mg L^{-1}), NO_3^- (0.721 mg L^{-1}), NH_3 (9.69 mg L^{-1})	TSS (82%), BOD (94%), COD (86%), NO_3^- (10%), NH_3 (41%)	Ghana	[174]
Palm Oil Mill Wastewater	FWSCW	-	120	-	TSS (278,600 mg L^{-1}), BOD (44,520 mg L^{-1}), COD (128,911 mg L^{-1}), NO_3^- (0.80 mg L^{-1}), NH_3 (20.40 mg L^{-1})	TSS (71%), BOD (51%), COD (10%), NO_3^- (6%), NH_3 (40%)	Ghana	[174]
Biogas Wastewater	FWSCW	-	120	-	TSS (330 mg L^{-1}), BOD (492 mg L^{-1}), COD (1952 mg L^{-1}), NO_3^- (0.122 mg L^{-1}), NH_3 (17.3 mg L^{-1})	TSS (95%), BOD (91%), COD (82%), NO_3^- (99%), NH_3 (42%)	Ghana	[174]
Pig farm Wastewater	FWSCW (50 cm × 38.5 cm × 23 cm)	-	4	-	COD (825 mg L^{-1}), BOD_5 (500 mg L^{-1}), NH_3 (130 mg N L^{-1}), TP (23 mg L^{-1})	COD (64%), BOD (69%), NH_3 (20%), TP (27%)	China	[172]
Olive mill wastewater	FWSCW	-	67	-	TOC (1132 mg L^{-1}), TN (26.6 mg L^{-1})	TOC (85%), TN (93%), TP (39%)	Turkey	[160]
					TOC (3168 mg L^{-1}), TN (72.6 mg L^{-1})	TOC (89%), TN (24%), TP (92%)		
Milk factory wastewater	FWSCW	-	120	-	Mn (0.49 mg L^{-1}), Fe (16.15 mg L^{-1}), Zn (4.09 mg L^{-1}) Pb (0.05 mg L^{-1})	Mn (34%), Fe (28%), Zn (53%), Pb (9%)	Thailand	[176]

Table 5. *Cont.*

Wastewater Types	CW Type	Media	HRT (d)	HL (m^3 d^{-1})	Initial Concentrations	Removal Performance (%)	Country	References
Tofu wastewater	FWSCW	Zeliac	15	-	COD (5759 mg L^{-1}), BOD (580 mg L^{-1}), TSS (552 mg L^{-1})	COD (76%), BOD (72%), TSS (75%)	Indonesia	[161]
Paperboard mill wastewater (raw and treated)	FWSCW	-	40	-	TSS (1000 mg L^{-1}), BOD (156 mg L^{-1}), COD (512 mg L^{-1}), TN (39 mg L^{-1}), TP (9.25 mg L^{-1}), Lead (2.01 mg L^{-1}), cadmium (1.90 mg L^{-1})	TSS (60%), BOD (96%), COD (50%), TN (64%), TP (65%), Lead (51%), cadmium (27%)	India	[177]
					TSS (200 mg L^{-1}), BOD (44 mg L^{-1}), COD (256 mg L^{-1}), TN (25 mg L^{-1}) TP (8.50 mg L^{-1}), Lead (0.96 mg L^{-1}), cadmium (0.42 mg L^{-1})	TSS (75%), BOD (72%), COD (56%), TN (70%), TP (43%), Lead (91%), cadmium (81%)		
Explosives wastewater	VFCW (40 cm × 60 cm × 70 cm) with flooding level at 25%	LECA	-	0.02	COD (361 mg L^{-1}), NO_3^- (145 mg N L^{-1}), NH_4^+ (4.8 mg N L^{-1})	COD (>90%), NO_3^- (55%), NH_4^+ (75%)	Portugal	[50]
Slaughterhouse wastewater	VFCW (40 cm × 60 cm × 70 cm)	LECA	0.29	0.02	COD (2648 mg L^{-1}), NH_4^+ (48.8 mg N L^{-1})	COD (59–83%), NH_4^+ (52–65%)	Portugal	[49]
Textile wastewater	HFCW (1 m × 0.6 m × 0.3 m)	Limestone soil	25	-	TSS (100–120 mg L^{-1}), COD (820–1200 mg L^{-1}), BOD (226–282 mg L^{-1})	TSS (81%), COD (46.2%), Cu (73.6%), color (78.2%)	Tanzania	[175]
Munition industry wastewater	FWSCW	-	100	-	Nitroguanidine (3996 mg L^{-1})	Nitroguanidine (79%)	United States of America	[178]
			100		NO_3^- (352,734 mg N L^{-1})	NO_3^- (95%)		
			100		Dinitroanisole (120 mg L^{-1})	Dinitroanisole (96%)		
			20		RDX (7.8 mg L^{-1}), HMX (12 mg L^{-1})	RDX (100%), HMX (100%)		

Note: HRT—Hydraulic Residence Time; HL—Hydraulic Load.

Studies related to the effect of the C/N ratio on the denitrification of effluents with highly concentrated nitrate are still limited. Low nitrogen removals (28 to 58%) in constructed wetlands have been reported when effluents with low biodegradability (i.e., 0.16 to 0.36) are used [100]. When poor biodegradability is due to a lack of biodegradable carbon in the effluent, some authors have added an external carbon source (e.g., methanol) [180] or used organic substrates [181] to supply carbon to the system and thus increase the biodegradability of the effluent and consequently improve heterotrophic denitrification in constructed wetlands. Saeed and Sun [133] evaluated the constructed wetlands with sugarcane bagasse and sand media for the treatment of textile wastewater. The authors observed that the organic carbon content of sugarcane bagasse facilitated denitrification in the vertical flow-constructed wetlands. Saeed and Khan [100] evaluated the removal of pollutants from a low biodegradable mixed industrial wastewater using two parallel hybrid constructed wetlands composed of two VFCWs (with different combinations of biological (i.e., bagasse, biochar, coal, and oyster shell) and construction (recycled brick, mortar, gravel, and sand) media materials) followed by surface flow constructed wetland, planted by *Phragmites australis*. The authors concluded that higher organics and nitrogen removal percentages were obtained with biological materials than with construction materials, due to carbon leaching. However, high removal percentages of NH_4-N ($\geq$90%), TN ($\geq$86%), P ($\geq$91%), BOD ($\geq$92%), COD ($\geq$85%), and color ($\geq$87%) across both systems were obtained, which reveals that the combination of VFCWs (packed with biological and construction materials) and FWSCWs, can be a solution for the treatment of hardly degradable industrial wastewater.

6. Adsorption

6.1. Theory and Applications

Adsorption is a process that has been widely used to remove organic matter from industrial wastewater. In the adsorption process, there is an accumulation of adsorbates (e.g., organic or inorganic pollutants) on the surface of the adsorbent using intermolecular forces of attraction. This happens when an adsorbent with a highly porous surface structure comes into contact with a solution containing absorbates [182]. Then, the adsorbent is removed from the solution by sedimentation or filtration. Different conventional and nonconventional adsorbents have been used for the removal of pollutants from wastewater. Conventional adsorbents include commercial activated carbons, inorganic materials, and ion-exchange resins. On the other hand, nonconventional adsorbents include natural materials, agricultural wastes, industrial by-products, activated carbons from solid wastes, biosorbents, and miscellaneous adsorbents [183–185].

Commercial activated carbons are the most prevalent and extensively used adsorbents for wastewater treatment [186]. These are produced from the carbonization process of carbon-rich organic materials such as wood, peat, coconut shells, and coals (anthracite, bituminous, lignite, and others). This process occurs under slow heating in the absence of air below 600 °C to remove volatile impurities such as oxygen, hydrogen, nitrogen, and sulfur. Then, a physical activation (using agents such as O_2, CO_2, or steam at high temperatures) or chemical activation (using agents such as H_2SO_4, H_3PO_4, KOH, K_2S, and $ZnCl_2$) is carried out [187,188]. As a result, the activated carbon produced has a porous structure, a large specific surface area, and high surface reactivity [189]. These properties are important in the removal of various types of contaminants such as heavy metals [190], organic matter [191–193], phosphorus [194], and nitrogen [195]. Activated carbon is usually used as a tertiary treatment for persistent pollutant removal after biological treatment [196]. The pore structure is composed of micropores (pore diameter < 2 nm), mesopores (2 nm < pore diameter < 50 nm), and macropores (pore diameter > 50 nm) [197]. Powdered activated carbon (PAC) and granular activated carbon (GAC) are the two forms of activated carbon applied in wastewater treatment (Figure 4), being able to remove pesticides, aromatic and phenolic derivatives, pharmaceutics, volatile organic compounds, hydrocarbons and surfactants, metals, dyes, and others [185].

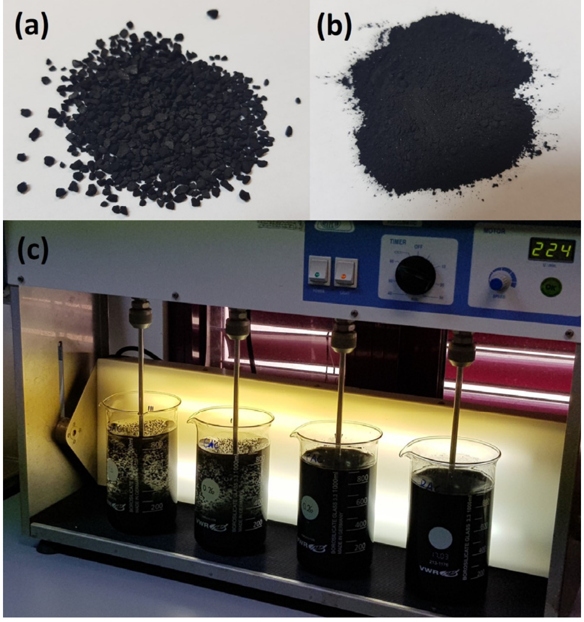

Figure 4. Adsorption process using: (**a**) granular activated carbon adsorbent, (**b**) powdered activated carbon adsorbent, and (**c**) Jar test.

PAC and GAC differ essentially in terms of the origin of production, grain size, type of equipment used, mode of use, the possibility of regeneration, and production costs [198]. PAC is mainly made from wood, while GAC is made from coconut shells or coal. GAC has a larger particle size than PAC [199]. PAC is used in rapid mix units by batch treatment processes, while the adsorption for GAC is usually continuous on a packed bed [191]. Granular active carbon can be used several times before going through the regeneration process, while PAC is not regenerated, but rather, usually disposed of [200]. The production of powdered activated carbon is less costly than the GAC; however, when used frequently, it has higher operating costs than the GAC [201]. So, GAC is a cost-friendly option for large treatment plants. Contrary to the PAC, which is soon discarded, there is the possibility of bacteria growing in the GAC [202].

6.2. Operating Variables and Removal Mechanisms

The adsorption process is complex and is influenced by several factors, namely the dosage and characteristics of the adsorbent (i.e., specific area, porosity, pore diameter and structure, and granulometry), the characteristics of the solution (i.e., pH, the concentration of the adsorbate, the presence of other species, and temperature), the characteristics of the adsorbate (i.e., polarity, ionic nature, functional groups, solubility, and diameter), and the contact time [13,203]. For example, the pH of the solution plays a very important role in the adsorption process since it can influence the degree of ionization of the substances present in it as well as the surface charge of the adsorbent, which affects the reaction kinetics [204]. Lee et al. [205] observed that an accumulation of calcium (in the form of calcium carbonate) over time on activated carbon deteriorates synthetic organic chemicals' adsorption. It is not expected that the removal of ammonia by adsorption occurs in very alkaline effluents since the ammonia molecule is in neutral form (unlike the NH_4^+ ion) to be adsorbed to carbon [206].

The adsorption capacity of adsorbent materials has been evaluated through adsorption isotherms, which are the ratios between the amount of adsorbate adsorbed per unit mass of adsorbent and the concentration of adsorbate in solution at equilibrium at a constant temperature [207]. From the equilibrium models, it is possible to obtain useful information about the surface properties of the adsorbent, the mechanism of adsorption, and the interaction between the adsorbent and the adsorbate [208]. Thus, different isothermal models have been used to evaluate and interpret experimental adsorption data, namely the Langmuir isotherms (which assume, for example, that the surfaces are homogeneous and that the adsorption occurs chemically in a monolayer), Freundlich isotherms (which assume, for example, that the surfaces are heterogeneous and that the adsorption occurs in multilayers), and other models [209]. On the other hand, the speed with which the adsorbate is retained on the surface of the adsorbent material has been evaluated through adsorption kinetics studies. Kinetics is important as it controls the efficiency of the process. Different models can be fitted to the adsorption process data concerning time; among the most commonly used are pseudo-first-order kinetics and pseudo-second-order kinetics [210]. Other kinetic models, such as the Weber and Morris model, the Bangham model, and the pseudo-n order model, have also been used [211]. The adsorption mechanism can involve four steps: (i) the transport of the adsorbate from the bulk of the solution to the boundary layer surrounding the adsorbent particles; (ii) the transport of the adsorbate by diffusion along the boundary layer to the entrance of the adsorbent pores; (iii) the transport of the adsorbate inside the pores of the particle to the adsorption sites by a combination of molecular diffusion through the liquid contained inside the pores and diffusion along the surface of the adsorbent; and (iv) the attachment of the adsorbate to an available site of the adsorbent involves several mechanisms, such as physical adsorption, chemical adsorption, ion exchange, precipitation, and complexation [212,213].

A small particle size means faster adsorption kinetics. A large volume of micropores generally corresponds to a high surface area and good adsorption capacity for small molecules, while a large volume of mesopores or macropores may indicate a good adsorption capacity for larger molecules [214].

6.3. Main Challenges and Recent Advances

Adsorption is a low-cost, easy-to-operate process with application in a wide pH range, and it has high performance in removing organic and inorganic pollutants [215]. However, this process has low selectivity and produces waste products whose regeneration is expensive [216]. One of the challenges of using conventional adsorbents is separating the adsorbent from the treated wastewater. The use of GAC in a packed bed does not require an additional step to remove the adsorbent from the water; however, the same does not happen with PAC. In most studies, the adsorbent separation is carried out by filtration and centrifugation methods [217]. Separation of the adsorbent by filtration and sedimentation represents an extra cost and time for wastewater purification. Conventional separation processes such as centrifugation, precipitation, filtration, and chromatography are not economically viable [186]. Furthermore, as the PAC has a small particle size, the blockage of filters or the loss of the solid particles could occur [218]. Magnetic separation of the adsorbent is not possible since activated carbon has no magnetic properties. However, the combination of activated carbon with iron oxide nanoparticles (e.g., Fe_3O_4 (magnetite) or Fe_2O_3 (maghemite)) has been studied to achieve a separation of the combined using a magnetic field [219], since magnetic iron oxide nanoparticles have superparamagnetic properties [220]. Borghi and Fabbri [219] compared the percentage of magnetic-activated carbon (MAC) residues obtained using magnetic separation, sedimentation, and filtration. The authors noted that the magnetic separation of MACs would result in a lower percentage of MAC residues in the treated water. Since iron is one of the most abundant metals on Earth and the production of iron oxide nanoparticles (using co-precipitation) is low-cost and easy to synthesize, its incorporation into activated carbon is popular [221–224]. On the other hand, the synthesis of magnetic carbon nanocomposites is considerably cheap and requires low operational energy [225,226]. Moreover, magnetic carbon nanocomposites can be used several times after desorption, making it an environmentally friendly water purification process.

MAC has been extensively applied to remove organic (water-soluble organic dyes, phenolic compounds, humic substances, pharmaceuticals, and others) and inorganic (mercury (II), arsenic (V), gold, phosphate, and others) compounds [227–229]. However, despite the advantages in terms of magnetic separation, some limitations have been observed in terms of the efficiency of contaminant removal in the MAC adsorption process. Lompe et al. [230] evaluated the influence of iron oxide nanoparticles (IONP) upon the adsorption of organic matter on magnetic powdered activated carbon using three magnetic powdered activated carbons (MPAC) with mass fractions of 10%, 38%, and 54% maghemite nanoparticles. The authors observed that maghemite IONP does not contribute significantly to the adsorption of natural organic matter itself and reduces the adsorption capacity of MPAC by blocking the mesopores of the carbon matrix when mass fractions above 38% of maghemite nanoparticles were used. However, improvements in the adsorption capacity with the incorporation of iron oxide nanoparticles in PAC have also been observed by other authors. Park et al. [231] evaluated the simultaneous removal of bisphenol A (BPA) and natural organic matter (NOM) by applying powdered activated carbons impregnated with iron oxide nanoparticles (IONPACs). The authors observed that IONPAC adsorbents had considerably greater sorption capabilities for BPA and NOM compared to native, bare PAC particles. On the other hand, Madeira et al. [49] evaluated the effect of incorporating iron oxide nanoparticles in PAC and GAC on the organic matter adsorption capacity of slaughterhouse wastewater treated by IOSLM and AC. The authors observed that the incorporation of iron oxide nanoparticles into PAC and GAC did not affect the adsorption capacity. Additionally, the authors also observed that there were no significant differences in COD removal after filtration and magnetic separation for both adsorbents with incorporated iron oxide nanoparticles. Vargues et al. [232] used PAC and PAC combined with iron oxide nanoparticles (PACMAG) as adsorbents to remove common pharmaceuticals (ibuprofen and amoxicillin). These authors observed that the kinetic models and the isothermal models were different between PAC and PACMAG for both drugs, which means that the incorporation of iron oxide nanoparticles can influence the adsorption mechanism.

7. Conclusions

In this review, an alternative and integrated strategy for industrial wastewater treatment consisted of immediate one-step lime precipitation and atmospheric carbonation, followed by constructed wetland or adsorption. Each of the processes that make up the integrated IOSLM+AC+CW/adsorption system has been widely addressed for industrial wastewater treatment since these processes are recognized for their low cost, easy operation, environmental advantages, effectiveness, and flexibility.

Using a single low-cost and easily available reagent (i.e., hydrated lime), the IOSLM process is initially applied with the aim of removing a large part of the contamination present in industrial effluents, namely, in terms of organic matter, total suspended solids, oils and fats, and nutrients (such as organic nitrogen and phosphorus). Subsequently, the AC process is used effectively to reduce the pH of the high alkaline wastewaters obtained in the IOSLM process, as well as to reduce the conductivity and concentrations of calcium and ammonia nitrogen through atmospheric carbonation reactions. Atmospheric carbonation can be carried out in an open system or a closed system for ammonia recovery, depending on the amount of ammonia present in the wastewater. Atmospheric carbonation does not require chemicals or specialized maintenance, has low energy consumption, and contributes to the mitigation of atmospheric CO_2. Additionally, CWs or adsorption processes are used as tuning processes to remove contaminants (e.g., organic matter or nitrogen) that were not possible to remove in the previous steps.

Unlike the IOSLM process and the adsorption process, the implementation of atmospheric carbonation and constructed wetlands processes requires large areas of land. However, if adsorption is an alternative process to constructed wetlands, this concern no longer arises. On the other hand, the implementation of a staggered carbonation system or the reuse of gases from industry could be used to reduce the pH, reducing the area to be implemented.

The proposed IOSLM+AC+CW/adsorption integrated treatment system contributes to forming by-products (e.g., sludge, ammonia, and treated effluent) that can be recovered, which contributes to a circular economy. It is important to note that the IOSLM+AC+CW/adsorption integrated treatment system is flexible as it integrates a set of processes and operating variables that can be modified to meet the characteristics of the industrial wastewater to be treated, which makes it a very promising technology in the treatment of industrial wastewater.

Despite the IOSLM+AC+CW/adsorption being a promising system, there are still aspects to consider in future research in each of the processes used or sequence of processes, such as: (i) testing the treatment sequence on a full-scale under different environmental conditions (temperature, CO_2, and others) and other types of industrial wastewater; and (ii) promoting the circularity of by-products obtained in each of the processes. For example, reuse sludge from the IOSLM process as a coagulant (aid) or as an acidity corrector in acidic and/or calcium-deficient soils; valorize ammonia captured in atmospheric carbonation systems (e.g., for green hydrogen production); recover the treated wastewater as nutritional solutions for agricultural purposes; and regenerate adsorbents to be used again.

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