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Review

A Critical Review of Systems for Bioremediation of Tannery Effluent with a Focus on Nitrogenous and Sulfurous Species Removal and Resource Recovery

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Abstract: Tanneries generate copious amounts of potentially toxic sludge and effluent from the processing of skins and hides to leather. The effluent requires remediation before discharge to protect the receiving environment. A range of physicochemical methods are used for pre- and post-treatment, but biological secondary remediation remains the most popular choice for the reduction of the organic and macronutrient fraction of tannery effluent. This review provides an update and critical discussion of biological systems used to remediate tannery effluent. While the conventional activated sludge process and similar technologies are widely used by tanneries, they have inherent problems related to poor sludge settling, low removal efficiencies, and high energy requirements. Treatment wetlands are recommended for the passive polishing step of beamhouse effluent. Hybrid systems that incorporate anoxic and/or anaerobic zones with sludge and/or effluent recycling have been shown to be effective for the removal of organics and nitrogenous species at laboratory scale, and some have been piloted. Novel systems have also been proposed for the removal and recovery of elemental sulfur and/or energy and/or process water in support of a circular economy. Full-scale studies showing successful long-term operation of such systems are now required to convince tanneries to modernize and invest in new infrastructure.

Keywords: activated sludge; aeration; anaerobic digestion; beamhouse; hybrid; macronutrient; membrane bioreactor; tanning; treatment wetland; wastewater

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Abbreviations

AD = anaerobic digestion; AS = activated sludge; BAF = biological aerated filter; BOD_5 = 5-day biological oxygen demand; BNR = biological nutrient removal; BSO = biological sulfide oxidation; BSR = biological sulfate reduction; CAS = convectional activated sludge; COD = chemical oxygen demand; CW = constructed wetland; DO = dissolved oxygen; EO = electrochemical oxidation; HA = hydrolysis and acidification; HLFCR = hybrid linear flow channel reactor; HRT = hydraulic retention time; HSSF = horizontal subsurface flow; MBBR = moving bed bioreactor; MBR = membrane bioreactors; ML = mixed liquor; MLVSS = mixed liquor volatile suspended solids; OLR = organic loading rate; OUR = oxygen utilization rate; RAS = return activated sludge; RO = reverse osmosis; SBR = sequencing batch reactor; SOB = sulfur oxidizing bacteria; SRT = solids retention time; STR = stirred tank reactor; SWWS = secondary wastewater sludge, TAN = total ammonia nitrogen; TDS = total dissolved solids; TKN = total Kjeldahl nitrogen; TN = total nitrogen; TOC = total organic carbon; TW = treatment wetland; TSS = total suspended solids; TWW = tannery wastewater; TWWTP = tannery wastewater treatment plant; UASB = upflow anaerobic sludge blanket; VOA = volatile organic acids; WAS = waste activated sludge; WWTP = wastewater treatment plant.

1. Introduction

Despite the emergence of alternative materials, the durability, flexibility, and aesthetic appeal of leather have led to a sustained increase in the demand for this product [1]. However, there are significant environmental concerns due to inadequate waste management by many tanning and leather-finishing facilities [2,3]. Among other concerns, high volumes of toxic tannery wastewater (TWW) are disseminated to the environment through larger tanneries and thousands of artisanal (micro-) tanneries [4–6]. Traditional and unsustainable tanning methods are still widely practiced, especially in micro-tanneries [4]. It has been shown that the improper discharge of tannery wastewater (TWW) has negatively impacted the quality of soil and ground and surface water in India and Pakistan [5]. For example, high concentrations of toxic metals, including chromium (Cr), were measured in an area in India that had historically been irrigated with TWW [6]. Consequently, tanneries worldwide face mounting pressure to embrace more sustainable practices.

Tannery wastewater is usually highly saline and contains varying concentrations of total suspended solids (TSS), organics, metals, and inorganics from beamhouse and tanyard operations, which is discussed in more detail in Section 2 [7]. Tanneries are water-intensive. In a study conducted in Bangladesh, it was calculated that the wet processes in tanneries accounted for 97% of the total water footprint of leather, which also includes drinking water and irrigation water for the feed crops of the animals [8]. Studies suggest that TWW from some processes can be successfully re-used in other tannery processes, thereby reducing the amount of TWW being discharged [7,9]. Irrespective of the volume, it is imperative that TWW is treated to comply with local discharge regulations [5,6] and that the industry at large adopts more modern, effective, and sustainable processes and TWW treatment methods [4,10].

In most larger tanneries, the quality of TWW is improved via a combination of primary and tertiary physicochemical and biological processes before discharge. Physicochemical treatment processes are important for the holistic remediation of TWW. These include coagulation/flocculation, flotation, electrocoagulation, advanced oxidation processes, membrane separation, absorption, photocatalytic treatment, ozonation, wet air oxidation, and thermal catalysis [11–16]. An example of how primary and secondary (biological) processes are typically combined in a conventional TWW treatment facility is shown in Figure 1.

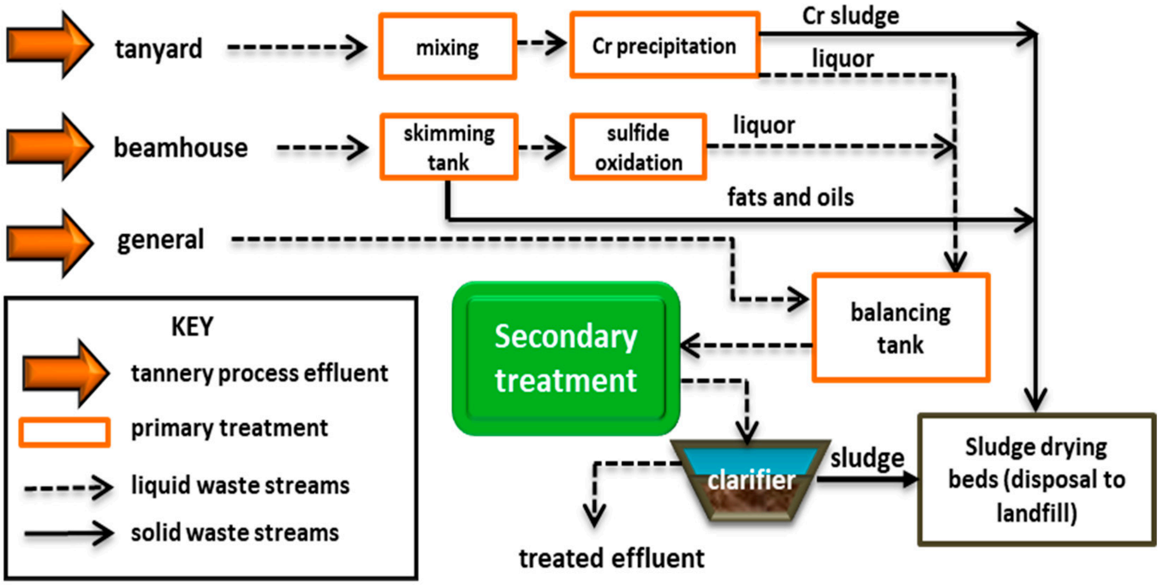

Figure 1. Set-up of a typical wastewater treatment plant at a tannery that employs wet-blue tanning (adapted from [2]).

Recent reviews on the topic of TWW treatment include descriptions of primary, secondary, and tertiary treatment technologies [11–13]. Due to the all-encompassing nature of these reviews, they contain limited information on the biological remediation of TWW. A more comprehensive and up-to-date appraisal of biological TWW treatment systems is, therefore, warranted as the subject was last reviewed in 2011 [14]. This manuscript includes (i) a short explanation of TWW from beamhouse and tanning operations, including both wet-blue and vegetable tanning; (ii) a comprehensive evaluation of the operation and performance of secondary TWW remediation systems, with a focus on the removal of organics, nitrogenous, and sulfurous compounds; and (iii) discussions on opportunities for using biological systems for recovering resources from TWW in support of a bio-circular economy.

2. Characteristics of Tannery Effluent

Tannery operations generate significant volumes of TWW, characterized by high concentrations of various pollutants. While the volume and character of TWW varies from tannery to tannery, it has been estimated that a metric ton of raw hide/skin yields 450–730 kg of solid waste, approximately 500 kg of wet sludge, and 20–40 m^3 of complex effluent containing residual processing chemicals [2,7]. Beamhouse operations consist of processes that pre-treat the skins or hides before tanning, namely, soaking, liming, unhairing, fleshing, deliming and bating, and pickling (Figure 2). Salt is used to preserve skins and hides, but if green (unsalted) hides are processed, the effluent is less saline. The solids consist of organic as well as inorganic matter, with most of the organics consisting of fats and proteins removed from the hides and skins during unhairing and fleshing [2,7]. The exact nature of the TSS in the beamhouse effluent depends on the types of skins or hides that are processed and seasonal factors [2,7].

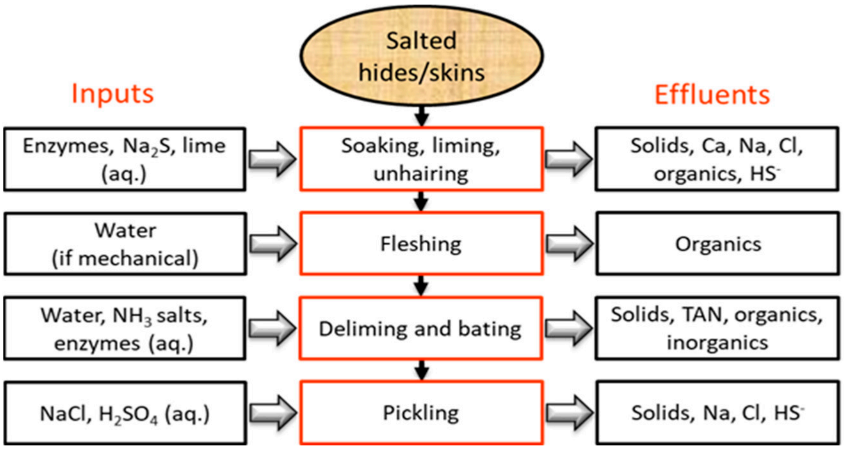

Figure 2. Schematic showing conventional inputs and main effluent constituents from beamhouse unit operations. TAN = total ammonia nitrogen.

Conventional wet-blue tanning employs Cr, which can be converted into the highly carcinogenic hexavalent form Cr(VI) in the environment. Although tannery wastewater treatment plants (TWWTPs) usually precipitate and recycle Cr, it may persist in the final effluent, sometimes in high concentrations (Table 1). The effluents from non-Cr tanning processes (e.g., wet-white tanning with glutaraldehyde and vegetable tanning) areis, therefore, perceived as less toxic [15]. However, wet-blue tanning is still widely applied because it produces consistently high-quality leather products. Fortunately, alternative processes that can equal wet-blue in terms of leather quality are slowly gaining industry traction [15,16].

Overall, beamhouse operations account for over 80% of the organic load, up to 70% of the total ammonia nitrogen (TAN), and most of the salinity of mixed TWW [3,7,17,18]. Tanyard effluent contains dyes, higher amounts of SO_4^{2-} than beamhouse effluent [3], and high concentrations of Cr or tannins emanate from wet-blue and vegetable tanning, respectively. Tannin concentrations as high as 19.7 g/L have been measured in effluent from vegetable tanning [19].

The effluent from each beamhouse and tanning unit operation has been characterized [20]. While this is important to confirm the etiology of each pollutant, in the 'real world', the streams from the beamhouse are typically combined, as are those from tanning. The beamhouse and tanning effluent may later be blended into a general effluent stream after some form of physicochemical treatment (Figure 1). Most tanneries limit the number of parameters that are routinely measured in the general TWW to those required for legislative purposes [2,7]. These include temperature, pH, TSS, biological oxygen demand (BOD) and/or COD, sulfate (SO_4^{2-}) sulfide (S^2), Cr((VI) and/or (III)), Cl, and ammonia nitrogen (NH_3-N) [11]. Academic studies typically report remediation efficiencies obtained from combined TWW effluent streams [7], but a few studies have focused on the treatment of beamhouse or tanning effluent as separate streams (Table 1). Considerable inter-tannery TWW variations occur in both, which is clear from the tabulated results. It is also well accepted that there are daily and seasonal intra-tannery variations in the quality and quantity of TWW [7].

Table 1. Selected parameters (measured averages) in beamhouse and tanning effluents.

pH Units	**TSS g/L**	**COD g/L**	**BOD_5 g/L**	**TKN mg/L**	**NH_3 mg/L**	**SO_4^{2-} g/L**	**Na mg/L**	**Cl^- mg/L**	**Cr g/L**	**Country**	**Reference**
					Beamhouse effluent						
6.4	0.03	-	-	268	96	-	-	-	-	Spain	[18]
12.0	4.32	40.3	-	3570	-	5.53	5683	-	-	Morocco	[21]
-	1.06	1.15	-	109	-	0.87	-	1700	-	Spain	[22]
					Chrome tanning effluent						
4.1	0.46	0.39	0.12	-	-	0.05	-	-	2.00	Brazil	[23]
3.6	0.04	4.19	0.02	-	-	0.25	-	-	2.13	Egypt	[24]
3.5	2.00	1.70	0.65	-	-	-	-	-	-	Sudan	[25]
					Vegetable tanning effluent						
3.5	3.30	25.5	4.05	-	-	7.40	-	-	-	India	[19]
7.1	5.30	7.63	3.04	-	860	0.02	-	741	-	Cameroon	[26]
4.5	1.85	27.0	-	-	-	3.93	-	-	-	India	[27]
6.0	3.21	24.3	2.80	37.2	16.8	0.03	259	751	-	Ghana	[28]

Total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); chemical oxygen demand (COD); 5-day biological oxygen demand (BOD_5); total Kjeldahl nitrogen (TKN); ammonia (NH_3), sulfate (SO_4^{2-}), sodium (Na), chloride (Cl^-), chromium (Cr).

3. Bioremediation of Tannery Wastewater

3.1. Introduction

In comparison to most physicochemical TWW treatment methods, biological treatment methods require little or no chemical inputs, are more economical, and generate less potentially toxic sludge [29]. All biological remediation strategies are designed to reduce the organic load in TWW and ammonia (NH_3) in the case of aerated systems. More recently, biological removal of S species has also been advocated [30,31]. Nutrient cycling is complex, and there are an exhaustive number of chemical reactions that can occur involving carbon (C), sulfur (S), nitrogen (N), and phosphorus (P) in wastewater treatment plants (WWTPs) [32–35]. Tannery effluents only contain negligible amounts of phosphorus (P), so in contrast to domestic and many other forms of industrial effluents, there is little focus on the secondary removal of this macronutrient [26,33]. On the contrary, P is sometimes added to balance microbial nutrient requirements [33]. The removal of P is, therefore, not considered in this review, which focusses on the most common reactions involving N and S cycling shown in Figure 3.

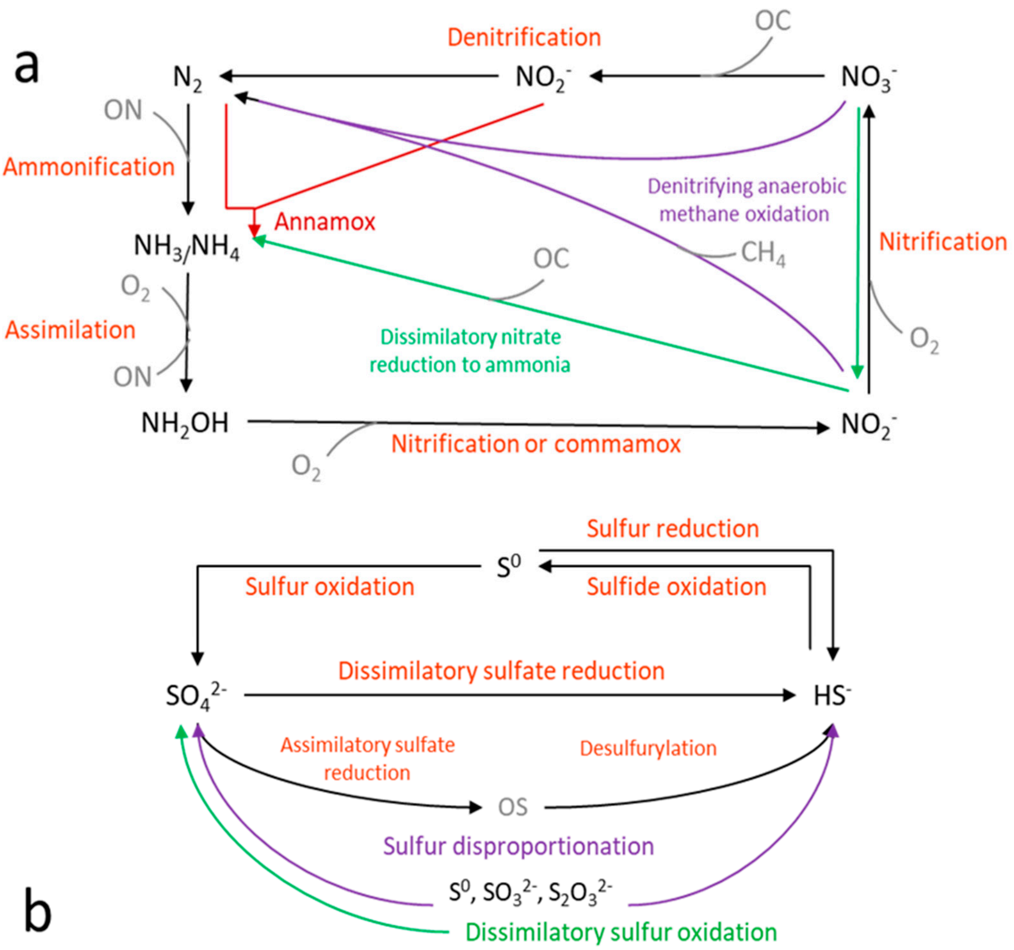

Figure 3. Major biological nitrogen (**a**) and sulfur (**b**) cycling pathways taking place in wastewater treatment plants. Adapted from Meng et al. [32] and Lin et al. [34]. OC = organic carbon, ON = organic nitrogen, OS = organic sulfur.

Under anaerobic/anoxic conditions, TWW particulates are typically broken down more effectively than under aerobic conditions, and denitrification can take place in the absence of oxygen (O_2). Apart from nitrification and denitrification, other pathways for N conversions exist in WWTPS, including anaerobic ammonium oxidation (ANNAMOX) and denitrifying anaerobic methane oxidation (DAMO), shown in Figure 3. The denitrification of TWW is theoretically not limited by the lack of organic electron donors, which is roughly determined by the COD to TN ratio, with a reported threshold of >3.5 [36]. The ratios measured in fourteen studies reviewed by Mpofu et al. [7] ranged from as low as 5 to as high as 1980, all above the threshold. However, there are drawbacks associated with a lack of O_2. Biological sulfate reduction (BSR) is promoted, and SO_4^{2-} is converted to toxic hydrogen sulfides (HS^-/H_2S) that can pollute the atmosphere [30,37]. Secondly, some organic molecules, such as aromatics from TWW, may be recalcitrant in anaerobic/anoxic environments [30,37], although others, including tannins from vegetable tanning, may be more biodegradable under anaerobic conditions [38]. Given that aerobic and anaerobic/anoxic systems have advantages and disadvantages for the remediation of TWW, there is a move towards adopting hybrid biological technologies to maximize TWW bioremediation. Apart from improving removal efficiencies, new TWW bioremediation strategies seek to recycle water and nutrients and/or produce energy or value-added products [31]. This step toward a circular bioeconomy offers economic and environmental benefits for the modern era [39,40].

Biological systems such as conventional activated sludge (CAS) and its variants [41], anaerobic digestion (AD), membrane bioreactors (MBR), and treatment wetlands (TWs) have been applied in the bioremediation of TWW and are critically discussed in Section 3.

3.2. Conventional and Hybrid Activated Sludge

3.2.1. Conventional Activated Sludge Systems

In CAS systems, influent wastewater continuously enters an aerated reactor and is remediated as it flows in a linear manner (plug flow) through the reactor. The mixed liquor (ML) from CAS reactors flows to clarifiers, where the solids settle out gravitationally from the clarified effluent. The settled sludge contains functional microbial species in flocs, and a portion of the sludge, known as the return activated sludge (RAS), is fed back to the reactor while the rest is wasted (waste-activated sludge, WAS). Recycling ratios of ML and RAS are important operational parameters that require periodic adjustments to maximize system performance.

The CAS process is widely applied in TWWTPs across the globe, but the systems generate significant quantities of secondary wastewater sludge (SWWS), are energy intensive, and contribute to global warming. It is estimated that 1000 W/hour of electricity is required for aeration to remove ~106 mg of BOD with a generation of 106 mg of CO_2 [42]. In addition, issues with filamentous overgrowth, poor removal efficiencies, and poor floc settling in clarifiers treating TWW have been reported [2,43]. Ultimately, these drawbacks, coupled with limited potential for resource recovery, make reliance on CAS increasingly unsustainable for tanneries in the context of modern environmental concerns [44,45].

Nonetheless, attempts have been made to improve the efficiency of the CAS process. In one study, a full-scale 2-stage CAS system treating TWW combined with domestic wastewater was bioaugmented with ‘beneficial’ microorganisms [40]. Good COD, S^{2-}, and TN removal efficiencies, with 99% removal of NH_3, were reported (Table 2), but the system lacked comparison with a non-augmented system. Although nitrates/nitrites (NO_3^-/NO_2^-) were not measured, it was assumed that denitrification was limited by the high concentrations (1–5 mg/L) of dissolved oxygen (DO) of and the residual N (14.6 mg/L) was due to the presence of NO_3^-/NO_2^-. Under the high-DO conditions, 99% removal of 2.8 ± 0.3 mg HS^-/L was achieved, but the influent and effluent SO_4^{2-} concentrations were not measured, so it was not clear whether removal was due to oxidation and/or atmospheric losses and/or precipitation as metal S^{2-} as previously described [46].

De Gisi et al. [47] conducted a pilot study using CAS as a pre-treatment step to specifically reduce the organic fraction of highly saline and sulfurous re-tanning TWW before reverse osmosis (RO). Flocculation and sand filtration were incorporated after CAS to enhance process efficiency. The authors did not report on N and S removal from the CAS reactor, but 54 to 74% COD removal was achieved (Table 2). Despite the energy-intensive nature of the overall process, the membranes functioned well, removing almost all the SO_4^2, NH_4^+, and NO_3^-. The RO permeate was suitable for reuse, which is particularly advantageous in regions facing water scarcity.

3.2.2. Hybrid Activated Sludge Systems

While CAS systems can achieve high nitrification rates unless anoxic zones are created within the systems for denitrification and/or DAMO, TN removal rates are poor, and high concentrations of NO_3^- and some NO_2^- are found in effluents [32]. Biological nutrient removal (BNR) WWTP configurations achieve higher TN removal by nitrification–denitrification (aerobic–anoxic) or denitrification–nitrification (anoxic–aerobic). The latter always necessitates recycling of ML from the aerobic to the anoxic zone. Simple configurations consist of two zones (e.g., modified Ludzack–Ettinger) or three zones (e.g., University of Cape Town, 3-stage Bardenpho process configurations) [32,48]. Additional anaerobic zones are incorporated in others, such as the 5-stage Bardenpho configuration, especially when an anaerobic zone is required for the removal of P. However, enhanced biological P removal is not relevant for TWW for reasons alluded to in Section 3.1.

To reduce energy consumption for aeration, enhance the biodegradability of TWW and/or improve removal of total nitrogen (TN), pilot and laboratory-scale studies have been conducted on hybrid systems that incorporate anoxic and/or anaerobic reactors up-front of CAS reactors (Table 2). Some of the complex organics found in TWW can be quite recalcitrant, which led a group of researchers to investigate whether the addition of an upstream anaerobic hydrolysis and acidification (HA) reactor would improve the biodegradability of the CAS influent [43]. They did not report on CAS removal efficiencies per se but found that low temperatures significantly reduced the COD removal efficiency of the HA reactor (from 30 to 40% at temperatures between 15 °C and 25 °C to <15% at temperatures < 10 °C). Others also employed AD before CAS to treat high-strength raw TWW without physicochemical intervention [49]. The clarified CAS effluent was then polished in a series of TWs, but the individual performances of the different units were not evaluated. There was also no apparent recycling of RAS or ML needed to retain functional and acclimated microbial communities. Nonetheless, the integrated system (including the TWs) achieved high overall COD removal rates (97%, influent: 12.5 ± 3.9 g/L), nitrification, and SO_4^{2-} removal (Table 2), but the average TN (62 mg/L) in the TW effluent was still marginally above the stipulated discharge limit of 60 mg/L.

A hybrid anoxic–aerobic system focused on COD and TN removal by incorporating an upstream anoxic reactor for pre-denitrification was piloted [50]. To allow for nitrification, the ML from the CAS reactor and clarifier sludge were recycled to the head of the anoxic reactor at rates of 100–200% and 100–150%, respectively. It was found that high organic loading rates (OLR) and low DO levels (2 mg/L) hindered nitrification but that when operational parameters were adjusted (OLR 0.72 $\text{kgCOD/m}^3\cdot\text{day}^{-1}$), the system functioned effectively in removing 95–98% COD (influent: 5.5 ± 1.2 g/L) and 95% NH_3. Of interest, the authors found that the presence of Cr (23.3–42.5 mg/L) did not adversely affect nitrification rates.

Other studies by Sodhi et al. [51–53] on hybrid CAS systems have been conducted at laboratory-scale (Table 2). Although outcomes require validation at pilot scale, some promising results were obtained. The first "MANODOX" system consisted of four sequentially operated biological reactors, namely an aerobic moving bed bioreactor (MBBR), followed by AD, anoxic, and CAS reactors with RAS sent to the anoxic, CAS, and MBBR reactors [51,53]. The performance of the system was compared to a stand-alone CAS system run in parallel, and significantly higher N removal rates were achieved due to denitrification in the MANODOX system. The main focus of the 320-day study was to reduce the volume of SWWS and a notable 72% reduction was achieved when compared to the stand-alone CAS. The authors later determined that removal efficiency in the MANODOX system was not significantly affected by variable OLR within the range tested (1.47–2.01 $\text{kgCOD/m}^3\cdot\text{day}^{-1}$) and that the accumulation of exopolysaccaharides (EPS) was three times lower in the SWWS from the MANODOX system than single stage CAS [53]. Although the MANADOX system showed promising results, the overall process consisted of many unit operations that may not be feasible at scale. The same authors studied and compared two simpler hybrid system configurations with stand-alone CAS, which also mainly focused on SWWS volume reduction [52]. The first consisted of an anoxic zone followed by CAS (An-CAS), while the second consisted of upstream CAS followed by AD and oxic reactors (CAS-OSA). The effect of OLR (up to 1.89 $\text{kgCOD/m}^3\cdot\text{day}^{-1}$) was studied [52]. When compared to CAS, the systems were more resistant to shock loading, and the SWWS volume was reduced by 21% and 52%, respectively, by the An-CAS and CAS-OSA configurations. While this was less than the 72% achieved by the MANADOX system, running such systems in tanneries would incur far lower operational and maintenance costs, which merits piloting the technologies with a view to full-scale implementation [52].

Table 2. Summary of studies on treatment of tannery wastewater using conventional and hybrid activated sludge systems.

TWW	Pre-Treatment	Anaerobic/Anoxic	Selected Operational Parameters (CAS)	Selected Influent Parameters	Removal Efficiency	Country [Ref]
Full-scale system						
70% TWW 30% DWW	"Semi-finished"	None	2-stage CAS HRT: 2.5 and 0.4 days DO: 1–5 mg/L	COD: 2.08 ± 0.52 g/L TN: 61.9 ± 25.1 mg/L NH_3-N: 54.2 ± 22.3 mg/L HS^-: 2.8 ± 0.3 mg/L	95% COD removal 76% TN removal 98% NH_3-N removal 99% HS^- removal	China [40]
Pilot scale systems						
Re-tanning TWW	Screening → equalization → pH adjustment	None	HRT: 30 hrs DO: 4.0–4.9 F/M: 0.37–0.75 kgCOD/kgMLVSS·day^{-1}	COD: 5.5 ± 1.2 g/L NH_3-N: 80–160 mg/L $NO_3{}^-$: 200–510 mg/L $SO_4{}^{2-}$: 0.9–2.3 g/L Cl^-: 1.2–2.1 g/L	54–74% COD removal	Italy [47]
Raw TWW	Biological	Stirred anoxic reactor	HRT: 40 hrs DO: 2.2–5.8 mg/L OLR: 0.72–1.13 1.9 kgCODm^{-3}·day^{-1}	COD: 5.5 ± 1.2 g/L NH_3-N: 80–160 mg/L $SO_4{}^2$: 0.36–0.68 g/L	95–98% COD removal 46–95% NH_3-N removal	Ethiopia [50]
Raw TWW	Screening → Biological	AD	HRT: 24 hrs	COD: 12.5 ± 3.9 g/L TN: 125–258 mg/L NH_3-N: 287 ± 178 mg/L $SO_4{}^2$: 0.80–0.51 g/L	97% COD removal 70% TN removal 85% NH_3-N removal 96% $SO_4{}^{2-}$ removal	Ethiopia [49]
Laboratory studies						
Raw TWW	Equalization → C&F→ Biological	MBBR, AD, anoxic	HRT: 30 hrs DO: 1.8–2.5 mg/L SRT: 11–19 days	COD: 1.6 ± 2.2 g/L (range: 1.6–2.3 g/L)	Effluent COD: <0.2 g/L	India [51]
Raw TWW	Equalization → C&F → Biological	(1) Anoxic (2) AD, oxic	HRT: 30 hrs DO: 1.5–2.5 mg/L SRT: (1) 26–34 days, (2) 21–26 days	COD: 1.9 ± 0.1 g/L (range: 1.7–2.1 g/L)	Effluent COD: 1) 0.25 ± 0.44 g/L 2) 0.16 ± 0.29 g/L	India [52]

CAS = conventional activated sludge; COD = chemical oxygen demand; C&F = coagulation and flocculation; DO = dissolved oxygen; DWW = domestic wastewater; HRT = hydraulic retention time; MBBR = moving bed bioreactor; OLR = organic loading rate; SRT = solids retention time; TN = total nitrogen.

3.3. Laboratory Sequencing Batch Reactors and Other Hybrid Systems

Aerobic sequencing batch reactors (SBRs) combine the aeration tank and clarifier in one unit, operating in feed, react, settle, and decant cycles (Figure 4). The react step is aerated and mixed, and the duration of each step, as well as the amount of ML that is retained between cycles, can be manipulated to achieve optimal performance [54]. Similar to CAS systems, settling problems due to poor floc formation may be experienced in SBR systems treating TWW, and interventions such as the addition of polyelectrolytes or TWW dilution may be needed to reduce settling times to practical levels [55]. To the best of our knowledge, only laboratory-based SBR systems treating TWW have been described in the literature, suggesting that they may not perform well when scaled up. One study employed synthetic TWW only. Although a wide range of operational parameters were tested and good sludge granulation and removal efficiencies were reported, the synthetic TWW consisted mostly of milk powder and ammonium sulfate ($(NH_4)_2SO_4$) [56], so it is difficult to extrapolate the results to real TWW given the complexity of this waste stream. Another study used a temperature controlled (30 °C) and bioaugmented system, which would not be practical or economical to operate in the 'real world' [14].

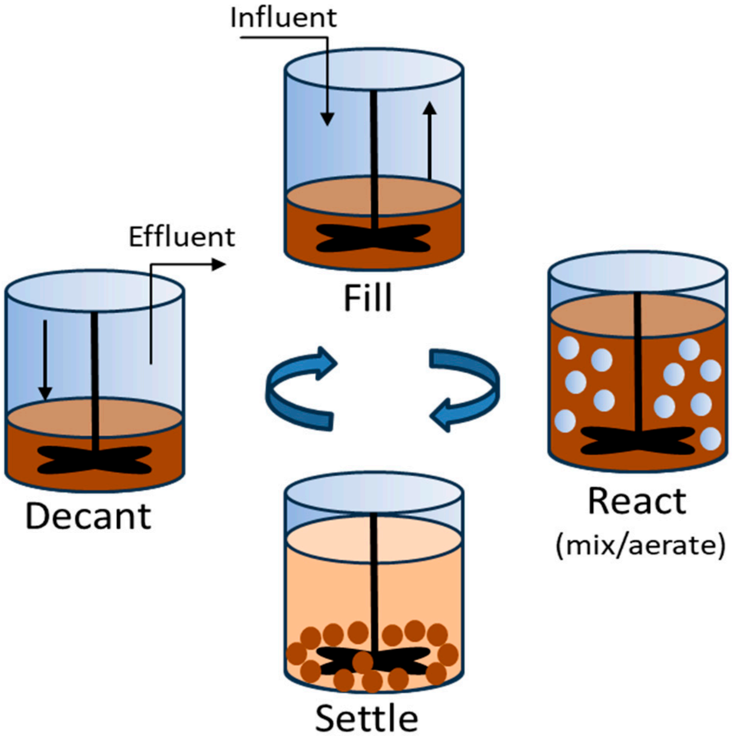

Figure 4. Schematic of the four cycles of simple aerobic sequencing batch reactors.

Studies reporting on the performance of stand-alone SBRs or hybrid SBR systems for bioremediation of real TWW under different operational conditions are presented in Table 3. Good organic removal rates were achieved in all. The most comprehensive study was conducted by Liu et al. [57] using an integrated system comprised of an upflow anaerobic sludge blanket (UASB) reactor followed by an SBR, electrochemical oxidation (EO), and a biological aerated filter (BAF), with equalization tanks between [57]. The system achieved 99% COD removal (influent 4.20–4.80 g/L), with the UASB contributing 50% and the SBR 38% to the overall removal. As with hybrid CAS systems, the results clearly demonstrated the effectiveness of combining different biological processes, and the final effluent complied with the discharge standards of the Chinese leather industry [57]. Most notably, the authors found that (i) a considerable portion of the readily biodegradable organics was removed in the UASB operated at optimal OLR of 4.56 ± 0.20 g/L and hydraulic retention time

(HRT) of 48 hr, (ii) the biodegradability of the TWW improved within the UASB, similar to the findings of Wang et al. [43] with a CAS system with upstream anaerobic HA reactor, (iii) the SBR was useful for additional removal of organics and nitrification, and (iv) UASB treatment led to more stable nitrification in the SBR. In addition, 78.3 ± 1.6% 81.5 ± 2.2% of the $SO_4{}^{2-}$ (influent 334–428 mg/L) and S^- (influent 42–65 mg/L) were removed in the UASB, which would likely have a positive impact on downstream microbial activities in the SBR. It was found that the S^{2-} was immobilized as highly insoluble precipitates of metal salts in the anaerobic sludge.

A study using combined effluent from 128 tanneries in India demonstrated the practical implications of measuring the oxygen utilization rate (OUR) via a respirometer. This parameter was robust for assessing the activity of functional microbial consortia involved in metabolizing organics in TWW [54]. The system achieved 83–99% NH_3-N and 80–82% COD removal. The OUR showed a strong correlation with total COD removal rates and provided better insights into COD removal compared to measurements of different COD fractions (soluble, particulate, total) [54]. In a subsequent study, the same authors investigated nitrification–denitrification in SBRs using synthetic and real TWW [58]. They observed that nitrification occurred within the first 5 h of the mixed and aerated 'react' cycle but was unstable, possibly due to inhibitors in the TWW. In contrast, denitrification was stable during the static anoxic 4 h feed and 1 h settle/decant periods. The system achieved optimum nitrification and denitrification of 6.9 mg NH_4- N/g mixed liquor volatile suspended solids (MLVSS)·h^{-1} and 6.24 mg NO_3-N/gMLVSS·h^{-1}, respectively.

Denitrification has also been reported in other systems, including hybrid linear channel reactors (HLFCRs) that function on the principle that anoxic conditions exist in the bottom layers of the reactors, while more oxygenic conditions exist in the upper layer of the bulk liquid [31]. The authors reported an average 71% reduction in $NO_3{}^-$ (influent: 11.5 ± 0.9 mg/L) and 89% reduction in $NO_2{}^-$ (influent: 4.5 ± 1.2 mg/L) from partially treated mixed TWW. Other researchers studying the denitrification of TWW used fixed film reactors containing polymer balls operated in series [59]. The first two reactors were mixed and were operated to achieve HA of particulates, while the third was anoxic and unmixed for denitrification of TWW pre-treated by coagulation, precipitation, and biological desulfurization. At HRT of 3–6 hrs, 56–69% of the total organic N was converted to NH_3. The abundance of electron donors from HA of endogenous organic matter ensured complete denitrification, reaching a rate of 76.3 mg/L·hr^{-1}. Although the free NH_3 may have contributed to buffering in the denitrification reactor, the concentrations in the final effluent were high (up to 900 mg/L), so additional remediation would be required for nitrification–denitrification to improve the removal of TN.

3.4. Systems for Biological Sulfate Reduction and/or Sulfide Oxidation and Sulfur Recovery

It is important to understand the status of S species in TWW during remediation. Under anaerobic conditions, $SO_4{}^{2-}$ is converted into the poisonous, corrosive, and flammable H_2S, which may be in solution, volatilized as a toxic air pollutant, or dissolved as highly corrosive HS^-/S^{2-} [46]. Even after aerobic TWW treatment, toxic H_2S gas can be re-formed in the environment or municipal sewage systems after discharge. Dissolved and total S has been measured in four spatial areas from sewers receiving effluent from tanneries [46]. Values ranged from 97.6 ± 170 mg/L to 135 ± 210 mg/L (total S) and 1.2 ± 2.6 mg/L to 40.4 ± 82.8 with an upper limit of 360 mg/L for dissolved S [46]. Concentrations of H_2S in the sewer headspace up to 3 g/L were measured, all values far exceeding the literature values for municipal sewers [46]. The authors proposed S^{2-} ppt. with iron (Fe) salts as a mitigation measure to prevent the build-up of H_2S gas and to protect the sewage system from corrosion [46].

Table 3. Performance of laboratory sequencing batch reactors treating tannery wastewater.

TWW Origination	PRE-Treatment	Selected Operational Parameters	Relevant Influent Parameters	Optimal Performance	Country [Ref]
* TWW	Polyelectrolytes, TWW dilution	6 L SBR HRT: 48 hr MLVSS/MLSS: 0.85	$COD_{soluble}$: 1.5–4.0 g/L BOD: 0.48–1.23 g/L	75–80% COD removal	Italy [55]
* TWW	No details provided	10 L SBR at 30 °C pH 7 Bioaugmented HRT: 5-days	COD: 6.24 g/L OLR: 2 $kgCOD/m^3 \cdot day^{-1}$	75% COD removal	India [14]
TWW combined from 128 tanneries	Coagulation, Cr ppt.	8 L SBR 12 hr cycle	COD: 1.91 ± 0.17 g/L NH_3-N: 120 ± 15 mg/L OLR: 1.9 $kgCODm^{-3} \cdot day^{-1}$	80–82% COD removal 83–99% NH_3-N removal	India [54]
TWW combined from 90 tanneries (wet-blue to finished leather)	Coagulation	6 L SBR 12 hr cycle 4:7:1 (feed:react:decant) 50% ML retained	COD: 1.64 ± 0.21 g/L NH_3-N: 132 ± 16 mg/L OLR: 1.9 $kgCODm^{-3} \cdot day^{-1}$	Nitrification: 6.9 mg NH_4-N/gMLVSS·h^{-1} Denitrification: 6.24 mg NO_3-N/g VSS h^{-1}	India [58]
* TWW	Screening (coarse and fine) UASB	React 8–20 hr, Settle 0.5 hr SRT: 30-day MLSS: 4 g/L	COD: 4.20–4.70 g/L NH_3-N: 274–317 mg/L	38% COD removal (SBR) 99% COD removal (system) 84% NH_3-N removal	China [59]

* TWW = tannery wastewater (no details provided); BOD = biological oxygen demand; COD = chemical oxygen demand; DOC = dissolved organic carbon; HRT = hydraulic retention time; MLVSS = mixed liquor volatile suspended solids; MLSS = mixed liquor suspended solids; NH_3-N = ammonia as nitrogen; OLR = organic loading rate; SBR = sequencing batch reactor; UASB = upflow anaerobic sludge blanket.

The first study to understand BSR during remediation TWW was conducted in 1996 [60]. The authors used pilot systems consisting of stirred tank reactors (STRs) followed by suspended fixed film bed reactors operated in upflow mode to compare the BSR of TWW from three different tanneries. Using multiple regression analysis, they found no significant differences in the origin of the TWW on BSR rates, indicating that the results could be extrapolated to other tanneries. However, this was not the case with COD removal, which differed in the TWW from different origins. The pH had a notable effect on BSR in the STR (Table 4). A similar study was performed to ascertain whether TWW would be a relevant carbon source for BSR in acid mine drainage [61]. The authors compared the performance of a UASB and a STR operated with sludge recycling from a small clarifier. The systems were operated at OLRs of 0.4–1.0 gCOD/L·day^{-1} and 0.2–10 gCOD/L·day^{-1}, respectively, and the highest BSR rates were obtained in the UASB (Table 4). The S^{2-} concentration in the influent was high (average 1.3 g/L), with 7–8% in the form of H_2S. Neither of these studies determined whether S^{2-} was removed via volatilization or precipitation into the solids fraction.

Another group of researchers found that sulfate-reducing bacteria (SRB) out-competed methanogens in a UASB-treating TWW with a low COD:$SO_4{}^{2-}$ ratio of 1.4 (range 1.1–4.6) [62]. Half-inhibition constants of NH_3 and $SO_4{}^{2-}$ of 180 mg/L and 480 mg/L, respectively, were calculated for BSR [62]. In contrast to other studies, the authors found that anaerobic treatment did not increase the biodegradability of the TWW. Competition between sulfidogens and methanogens during the remediation of TWW has also been studied in terms of electron flows diverted to each group in an advanced facultative pond [63]. It was found that the relative electron flow towards BSR (59–83%) was higher than the flow towards methanogenesis (17–41%), and the flow of electrons towards SRB increased when the $SO_4{}^{2-}$ increased and/or the COD:$SO_4{}^{2-}$ ratio decreased. Other studies have shown that although sulfidogens and methanogens require organic substrates, both processes can take place simultaneously with high CH_4 yields provided there are sufficient electron donors and the $SO_4{}^{2-}$ concentration in the substrate is not too high [44,64]. For example, it was found that methanogenesis was only inhibited with TWW $SO_4{}^{2-}$ concentrations $\geq$1.96 g/L during AD of secondary TWW sludge from a CAS reactor [64]. In this instance, the concentration of total organic carbon (TOC) was the most significant driver of the BSR bacterial and methanogenic archaeal community structures in anaerobic sequencing batch reactors (ASBRs) [65].

Recovery of S species from TWW has been advocated in support of a circular economy. For example, $SO_4{}^{2-}$ (22.5 g/L) from TWW has been crystallized into gypsum using Ca compounds as initiators [66]. Physicochemical conversions such as these are energy- and resource-intensive as they typically require numerous unit operations, and ancillary waste streams are inevitable. It has been proposed that biological sulfide oxidation (BSO) can be utilized as a cheaper and more environmentally friendly alternative [18,19,63,67,68]. It was found that much of the S^{2-} from BSR was converted to elemental S (S^0) in an advanced facultative pond by an abundance of pink photosynthetic sulfur bacteria in the upper layer of the pond, and the authors suggested that this could be harvested [63]. Biological sulfide oxidation was also studied in a laboratory-aerated STR inoculated with sludge from a tannery WWTP and fed with sodium sulfide (Na_2S) supplemented with macronutrients. The authors focused on the molecular identification of relevant bacterial species by cloning and sequencing 16S rRNA gene amplicons and verifying these using fluorescent in situ hybridization. They also used culture-dependent techniques to isolate sulfur-oxidizing bacteria (SOB) and found that different species of the saline-tolerant genus Halothiobacillus dominated the SOB population.

More recently, HLFCRs have been proposed as passive systems for simultaneous partial organic remediation and removal and recapture of S species [30,31]. The reactors are operated in plug-flow mode that promotes BSR in anoxic conditions in the bulk liquid and partial S^{2-}/HS^- oxidation to S^0 in the interface between the bulk liquid and the atmosphere once a floating S biofilm (FSB) has been established [30,31]. It was shown that functional SRB and SOB endogenous to the TWW used in the study were selected over those from saline-adapted inocula from sulfidogenic estuaries, obviating the need for bioaugmentation [68]. The FSB can be periodically harvested as a bio-S product that contains organic C and has superior qualities to highly leachable inorganic fertilizer equivalents [30]. Near-complete S^{2-}/HS^{-} removal can be achieved in HLFCRs, and the treated effluent is amenable to AD because it is less toxic but still contains sufficient organic substrate [30]. In a later study, a pilot hybrid HLFCR–anaerobic SBR system recovered 21% of the inlet S in the FSB and 238 mL $CH_4/gCOD_{added}$. It was calculated that a medium-sized tannery treating 2258 m^3 beamhouse effluent could generate 3420 m^3CH_4, 50 m^3 irrigation water, and 31 tons of biofertilizer, promoting a circular bioeconomy and net positive tannery operations [31]. Methanogenic archaea were not active in the HLFCRs, but both SRB and methanogens were active in the anaerobic SBRs [44].

3.5. Anaerobic Digestion

While AD allows for the recovery of energy in support of a bio-circular economy, it is not widely applied as a stand-alone technology for TWW remediation because sensitive functional microbes are inhibited by inorganic S and N species, volatile organic acids (VOAs), and/or heavy metals in concentrations typically found in TWW [7,31,65,68]. This can be overcome by pre-treatment to reduce the concentration of inhibitors and/or by co-digesting TWW with other substrates [30,69]. In a recent manuscript, researchers [7] advocated for the application of AD integrated with other forms of remediation in TWWTPs in developing countries, offering opportunities to establish biorefineries for resource recovery and the promotion of sustainable economic development. Readers are referred to this review for details of previous studies on AD of TWW, which mostly reported biogas and/or CH_4 yields and COD removal efficiencies. Details of non-methanogenic hybrid bioremediation systems incorporating anaerobic reactors for HA and/or sulfidogenesis are included in Section 3.2–3.4. In terms of N and S removal during AD, 49–85% reduction in SO_4^{2-} while co-digesting ostrich TWW and slaughterhouse wastewater blended at different ratios (%v/v) and inoculum to substrate ratios (2–5) has been reported [64]. When beamhouse and tanning effluent was blended in different ratios (%v/v), 7–81% and 34–85% decreases in NO_3^{2-} and SO_4^{2-} were measured [69].

3.6. Membrane Bioreactors

Membrane bioreactors decouple solids retention time (SRT) and HRT and are not reliant on clarifiers like traditional suspended growth systems. They also have lower spatial footprints, generally operate more stably, and are more conducive to recovery and the reuse of process water when coupled with RO [70–72]. Despite their advantages, MBRs have not been introduced in tanneries ostensibly due to high capex and operational costs, unresolved problems with fouling caused by the high amounts of organic and inorganic suspended solids in TWW, and the need to periodically regenerate the membranes [73,74]. Moktadir et al. [72] recently reviewed laboratory studies on a variety of MBR-based technologies for the remediation of TWW, and readers are referred to this publication for further details. In essence, hybrid MBR technologies provide promising results for COD and N reduction from TWW, and of the different options, the authors advocate that MBBRs have the greatest potential for successful remediation of TWW [72], but the technology still needs to be tested in the field.

Table 4. Systems for biological sulfate reduction and/or sulfide oxidation.

TWW Origination	Reactor/s	Operational Parameters	Relevant Influent Parameters	Optimal Performance	Country [Ref]
Mixed raw TWW 3 tanneries (ABC)	Pilot STR-UFFR Intermittent UFFR 7.9 L	35-day operation Temp: UFFR 34 °C pH: 5.6–7.0 HRT: 3.5 day	COD: 8.20 ± 6.19, 5.97 ± 3.08, 2.99 ± 2.87 g/L (A,B,C) $SO_4{}^{2-}$: 1.00 ± 0.55, 1.25 ± 0.85, 0.75 ± 00.29 g/L (A,B,C)	STR $SO_4{}^{2-}$ removal: 5%, 38%, 45% (pH 5, 6, 7) UFFR $SO_4{}^{2-}$ removal: 43%, 24%, 20% (pH 5, 6, 7)	South Africa [60]
Mixed raw TWW	Pilot UASB, STR Continuous UASB/STR: 1.5 m^3	58-day operation Temp: ambient pH: 7.9–8.2 HRT: 4 days	pH: 7.5 COD: 5.32 g/L $SO_4{}^{2-}$: 3.19 g/L	Removal: UASB SRR: 0.6 g $SO_4{}^{2-}$/L·day^{-1} UASB ORR: 0.5 gCOD$^-$/L·day^{-1}	South Africa [61]
Settled mixed TWW (vegetable tanning)	Pilot UAF Continuous 52 L	160-day operation Temp: 35 °C ± 0.5 pH: 7.3 ± 0.2 HRT: 2.2 ± 0.2 days	COD: 2.53 ± 0.70 g/L $SO_4{}^{2-}$: 1.81 ± 0.60 g/L HS^-: 10 ± 5.5 mg/L	COD removal 42% $SO_4{}^{2-}$ removal 53%	Italy [62]
Synthetic N & P supplemented	Aerated laboratory CSTR Continuous 450 L	53-day operation Temp: 10.7 ± 2.7 °C pH: 2–4 HRT: NG	$SO_4{}^{2-}$: 1.61 ± 0.37 g/L	SOR: 22 mg HS^-/L·day^{-1}	Italy [67]
Mixed raw TWW (wet-blue tanning)	Pilot AFP Continuous 23 m^3	Temp: ambient pH: 8 HRT: 3–8 days	Loading rates $SO_4{}^{2-}$: 6–182 g/m^3·day^{-1} COD: 0.132–2.27 g/m^3·day^{-1}	Removal: $SO_4{}^{2-}$: 0.385–2.65 g/L COD: 0.723–8.22 g/L	Ethiopia [63]
Mixed TWW (wet-blue tanning)	Laboratory HLFCR in series Continuous 4 L working volume	104-day operation Temp: Ambient pH: 7.5 HRT: 4-days	COD: 7.0–27 g/L $SO_4{}^{2-}$: 2.50 g/L HS^-: 0.35 g/L	Removal: $SO_4{}^{2-}$: 80% HS^-: >97%	South Africa [30]
Mixed raw TWW (wet-blue tanning)	Laboratory HLFCR in series Continuous 16.2 L working volume	76-day operation Temp: ambient pH: 7.0–7.7 HRT: 4-days	COD: 22.8 ± 3.7 g/L $SO_4{}^{2-}$: 1.95 ± 0.31 g/L HS^-: 1.12 ± 0.00 g/L	Removal: $SO_4{}^{2-}$: 54% HS^-: 96%	South Africa [31,44]

(C) STR = (continuously) stirred tank reactor; UFFR = upflow fixed film reactor; HRT = hydraulic retention time; COD = chemical oxygen demand; UASB = upflow anaerobic sludge blanket; SRR = sulfate reduction rate; ORR = organic removal rate; UAF = upflow anaerobic filter; SOR = sulfide oxidation rate; NG = not given; AFP = advanced facultative pond; HLFCR = hybrid linear flow channel reactor.

3.7. Treatment Wetlands

Treatment wetlands, formerly known as constructed wetlands (CWs), are passive treatment systems that can 'polish' TWW to meet legislated requirements for discharge to the environment for reuse via irrigation, as evidenced by studies conducted in Ethiopia [75,76], Spain [77], and Peru [78]. A major advantage of well-acclimated TWs is that they can produce effluent of a consistent quality when remediating wastewater, such as TWW, that varies in composition and volume [77]. A few pilot studies have investigated the performance of TWs for tertiary treatment of TWW (Table 5), comparing different factors, including hydraulic retention times (HRT) [75,79,80], OLR [79,81], plant species [78,81,82], and media substrate types [76,78,83–85].

Macronutrient and TSS removal are typically the primary foci of studies for the remediation of TWW in TWs. Organics and N and S compounds can theoretically be mineralized, the latter two via nitrification–denitrification and BSR-BSO, respectively [75,86]. The plants and media used in TWs need to be 'fit for purpose'. In line with conventional TWs, different forms of gravel have been employed as the substrate in most pilot TW systems treating TWW (Table 5). In some cases, sand has been added as a top layer to improve plant germination [77,81]. A more expansive approach is to employ hybrid TW systems to maximize functionality. Saaed et al. [84] employed different flow regimes and media in a three-stage pilot TW system (Table 5). The use of coco-peat in the primary vertical flow system created oxygenic conditions for nitrification and aerobic organic biodegradation.

It is preferable to select non-invasive plant species that are resilient to TWW and suited to the prevailing climatic conditions [78]. Phragmites and Typha species are popular choices (Table 5). Arundo donax, Canna indica, Sarcocornia fruticosa, and Stenotaphrum secundatum have also been studied, and Isolepis cernua has been acclimated to pre-treated TWW, while Nasturtium aquaticum was unable to acclimate [78–82]. In another study, four plant species showed varying degrees of stress to raw TWW (Echinochloa pyramidalis > Cyprus latifolius > Typha domingensis > Pennisetum purpureum) but adapted well when TWW was diluted by 50% [76].

Based on the studies conducted to date, the COD concentrations in the diluted or treated TWW used as influent to the TWs ranged from 1.14 ± 0.3 to 1.14 to 11.6 ± 6 g/L [75,84]. The highest COD removal rate (771 kg COD/ha/day) but the lowest COD removal efficiency (53%) was measured in a two-stage horizontal subsurface flow (HSSF) system [85]. In this study, it is possible that the removal efficiency could be improved by increasing the HRT, but it also highlights the fact that readily biodegradable organics are typically removed in upstream secondary treatment systems (in this case, two-stage AD). Anomalous removal rates can, therefore, be found because of the high proportion of more recalcitrant organics in the pre-treated TWW. Four of the studies included data on the removal of TN and/or other forms of N (TKN, NH_4^+, NO_3^-), and in each case, the final effluent met the discharge standards of the country where the study was conducted. Although studies rarely include results on S removal, some results are highly promising [75]. Removal rates of 78% and 93% in influent SO_4^{2-} and S^{2-}, respectively, were obtained in a TW planted with Phragmites karka [75]. Lower SO_4^{2-} removal rates were achieved in systems planted with the grasses Leptochloa fusca (42%) and Brachiara mutica (25%) [87].

Table 5. Tertiary treatment of tannery wastewater in treatment wetlands (leather finishing effluent excluded).

TW Type	TWW	Media	Plants	Influent Parameters	Average Removal Performance	Country [Ref]
Pilot HSSF	50%	Basalt gravel	*Pennisetum purpureum*, *Typha domingensis*, *Cyprus latifolius*, *Echinochloa pyramidalis*	COD: 1.19 ± 0.6 g/L NO_3^-–N: 30 ± 8 mg/L TSS: 427 ± 306 mg/L	79–84% COD (334–355 kg COD/ha/day) 63–71% % NO_3^--N 69–71% TSS	Ethiopia [76]
Pilot HSSF in series	Treated: 2-stage AD	Basalt gravel	*Phragmites karka*	COD: 1.14 ± 0.3 g/L TN: 220 ± 18 mg/L SO_4^{2-}: 433 ± 162 mg/L S^{2-}: 6.6 ± 0.4 mg/L TSS: 427 ± 306 mg/L Cr: 11.7 ± 7.0	93% COD (537 kg COD/ha/day) 78% TN 78% SO_4^{2-} 93% S^{2-} TSS NG 97% Cr	Ethiopia [75]
Pilot HSSF	Treated: PC, DAF	Granitic gravel 5–8 mm	*Typha latifolia*	COD: 2.1 g/L TSS: 208 mg/L Cr: 1.1 mg/L	53% COD (771 kg COD/ha/day) 69% TSS 50% Cr	Argentina [85]
Pilot HSSF batch mode	Treated: PC, secondary	Limestone gravel 23–40 cm, sand (top)	*Phragmites australis*	TKN: 816 ± 12 mg/L Cr: 0.23 ± 0.0 mg/L	10% TKN 48% Cr	Spain [77]
Lab-scale VF → HSSF → VF	"Raw"	Peat → slag 20 mm → pea gravel 1.2–2.3 mm	*Phragmites australis*	COD: 11.6 ± 6 g/L NH_4^+: 111 ± 39 mg/L NO_3^-: 66 ± 35 mg/L TSS: 27.6 ± 10.2 g/L	98% COD (377 kg COD/ha/day) 86% NH_4^+ 50% NO_3^- 55% TSS	Bangladesh [84]
Pilot HSSF → FWSF	Treated: PC	Gravel and sand	*Isolepsis cernua* → *Nasturtium aquaticum*	COD: 2.4 ± 1.3 mg/L TSS: 272 ± 118 mg/L Cr: 8.11 ± 4.86 mg/L	89% COD 90% TSS 100% Cr	Peru [78]

HSSF = horizontal subsurface flow; VF = vertical flow; FWSF = free water surface flow; TWW = tannery wastewater; AD = anaerobic digestion; PC = physicochemical; DAF = dissolved air flotation; COD = chemical oxygen demand; = NO_3^-–N nitrate as nitrogen; TSS = total suspended solids; TN = total nitrogen; SO_4^{2-} = sulfate; S^{2-} = sulfide; TKN = total Kjeldahl nitrogen; NG = not given.

Although Cr can be adsorbed onto the medium or absorbed by plants, and good removal rates can be obtained (Table 5), a major drawback is that the Cr removal functionality can be reversed if adsorption sites are expended and/or if there is a change in redox status that causes desorption, and/or if the plants senesce [86]. Large amounts of ancillary toxic waste may be generated, requiring specialized landfills for disposal. It can, therefore, be contended that while TWs are viable options for polishing beamhouse and general waste streams from tanneries, they should be used with caution for treating streams from wet-blue tanning unless complete physicochemical Cr removal is conducted upstream. Another concern is that none of the published studies have focused on the removal of Na from TWW. Beamhouse effluent can contain high levels of salts from the soaking process (Section 2). Sodium does not partition into the substrate of CWs [86,88] and can cause sodicity in the receiving environment. The use of halophytic plants to remove Na may be an option [86] but would require monitoring and regular plant removal.

The advantages of TWs are that harvested macrophyte biomass can be used as a soil conditioner or green fertilizer, reducing secondary pollution risks [89]. The biomass can also be converted into solid fuel or biogas using low-maintenance technologies [90]. Treated effluent can be used for agricultural irrigation or low-grade process water, addressing increasing water demands.

4. Conclusions and Recommendations

Tanneries are one of the most polluting industries. Biological treatment of TWW forms an important link in ameliorating the negative effect of TWW on the environment. Biological systems can also be used to assist in recovering resources such as energy and S^0 from TWW in support of a circular economy. Promising hybrid systems and other novel systems have been described in the literature, but tanneries still tend to rely on older technologies such as CAS that have inherent problems. There is a need for long-term and credible testing of systems that have proven successful at laboratory and then pilot scale in the ‘real world’ in order to provide evidence that such systems offer environmental and economic benefits. To reduce the financial burden on tanneries for research, government funding agencies should consider co-funding to support this important economic sector.

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