








Review

# Chromium Remediation from Tannery Wastewater in Arequipa, Peru: Local Experiences and Prospects for Sustainable Solutions

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**Abstract:** The release of tannery wastewater contributes to chromium (Cr) pollution globally. Herein, we conduct a novel consolidation of research from the Arequipa region of southern Peru that integrates university theses written in Spanish alongside peer-reviewed journal articles. The objective is to provide a place-based complement to existing research in English scientific journals focused on effective tools for Cr treatment from tannery wastewater. Our consolidation categorized a total of 75 publications (70 theses and five peer-reviewed) into five distinct strategies for Cr treatment: adsorption (twenty-three studies), phytoremediation (eighteen studies), bioremediation (thirteen studies), electrocoagulation (five studies), and other techniques (fifteen studies). This synthesis highlighted potentially promising approaches that could be sustainably tailored to regional resources and waste products. This includes sorptive materials derived from food waste such as native achiote peels (*B. orellana*) and avocado seeds (*P. americana*) either used directly or as a feedstock for biochar. Other technologies include phytoremediation using microalgae and resident vascular plants and microbial bioremediation that capitalizes on indigenous bacteria and fungi. Promise was also discerned in studies that incorporated a combination of abiotic and biotic mechanisms tailored toward the region, such as infiltration using selective and bioactive materials, wetlands, solar distillation, iron-based coagulation and flocculation, and bioreactors. These findings provide a sustainable complement to prior global investigations for effective attenuation strategies by adding novel materials and techniques that could be further explored to assess the viability of implementation at pilot and larger scales. These promising technologies and the ability to tailor sustainable treatments toward local resources highlight the opportunity to prioritize the treatment of tannery wastewater to ensure a cleaner environment by informing policy makers, academics, and industry on technologies that could be adopted for implementation in the region.



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## 1. Introduction

Toxicity associated with chromium (Cr) contamination in surface waters is a global challenge [1]. While natural processes contribute to the presence of Cr in water bodies, anthropogenic activities are of particular concern. An example of industrial release is the leather tanning process [2], which relies heavily on Cr salts. When not properly treated, the discharge of tannery wastewater results in elevated levels of Cr in the receiving waters [3]. These point sources of contamination present meaningful opportunities for in-depth studies focused on the development and implementation of efficient Cr remediation and removal techniques. Mitigating the detrimental impact of tannery wastewater discharge on aquatic ecosystems requires a comprehensive exploration of innovative treatment methodologies.

The mobility and toxicological impact of Cr is influenced by the oxidation state. Although considered less toxic, short-term human exposure to trivalent chromium (Cr(III)) causes irritation of the eyes and respiratory tract [4]. It can also be oxidized to the more toxic hexavalent chromium (Cr(VI)) phase in the presence of organic matter under mildly acidic conditions. Exposure to Cr(VI) in humans has been associated with allergic dermal reactions; when inhaled, it causes respiratory complications, irritation, bleeding from the nose, and potentially lung cancer. Cr(VI) ingestion can cause ulcers, weakening of the immune system, damage to the kidneys and liver, and genetic mutations [5]. Chromium can also damage aquatic ecosystems and decrease soil fertility where analogous oxidative and DNA damage can increase mortality in Cr-sensitive microorganisms. Chromium also affects plant enzyme activity and photosynthesis, causing hindered growth and reduced yields [6], and bioaccumulates in animal tissues and organs [7].

Chromium pollution is widespread globally [8–13], with a prominence in Latin American countries [4,14–19]. The country of Peru is a clear example of documented anthropogenically sourced Cr contamination, with an unfortunate wealth of studies that have reported surface water pollution in rivers situated throughout the country (Table 1). Arequipa is the largest leather-producing territory in Peru [20]. In 2010, there were 96 tanning companies in the Arequipa Region, of which 67 were located at the Rio Seco Industrial Park (RSIP), in the Cerro Colorado District (Regional Ordinance 121). However, more than 400 companies (small, medium, and large) were listed and grouped into 60 associations in 2017, of which nearly 100 operated at RSIP by 2023, generating over 3000 jobs [21].

**Table 1.** Examples of total Cr-related studies in water and sediments from different Peruvian rivers (BD: Below detection).

River	Administrative Region	Cr Concentration		Source
		Water (mg/L)	Sediments (mg/kg)	
Ichu	Huancavelica	0.02		[22]
Opamayo and Sicra	Huancavelica	0.05		[23]
Zaña	Lambayeque	BD		[24]
Quiroz	Piura	1.3		[25]
Ramis	Puno	0.008		[26]
Chili	Arequipa	0.004		[27]
Chili	Arequipa	BD		[28]
RSIP effluents	Arequipa	4.3–7.7		[29]
Añashuayco	Arequipa		3750–9220	[30]
Coata	Puno		4–28	[31]
Apurimac	Caylloma and Arequipa		1–3	[32]
RSIP effluents	Arequipa		10.4	[33]

Both Moran [27] and Luque [28] reported some degree of Cr pollution in the Chili River, which crosses the city of Arequipa. In querying a potential source, Salazar-Pinto et al. [29] and Tejada-Meza et al. [33] analyzed samples in a tributary to the Chili River that transits through the RSIP. These source waters exceeded Peru's maximum contaminant limits (MCLs) of 0.5 mg/L [34], which were established for surface water effluents from industrial sectors such as materials manufacturing, beverage industries, and tanneries. Similarly, Vilca and Gordillo [30] investigated Arequipa's RSIP and the Aashuayco Ravine for a period of three months, finding Cr associated sediments that were well in excess of the 1000 mg/kg Peruvian MCL [35].

In April 2023, our research team observed RSIP effluent downstream of processing activities. This tributary to the Chili River (Figure 1) is a small unlined surface water course that changed colors over time (from green to brown, most likely a reflection of upstream industrial dumping), with an unpleasant smell. As reported by Tejada-Meza et al. [33], the average total Cr content in this effluent was above 10 mg/L, with a flow estimate of 31 L/s at the time of the visit. While lower than the values reported by Aboulhassan et al. [36] in wastewaters from Moroccan tanneries, this exceeded the Peruvian MCL of 0.5 mg/L for total Cr. While speciation was not documented in that analysis, the chromium MCL is further extended to 0.1 mg/L for Cr(VI) [34], leading to the conclusion that the discharge of inadequately treated tannery wastewater by companies in RSIP has exacerbated this environmental challenge and efforts to mitigate the Cr content of RSIP wastewater have been insufficient. Tejada-Meza et al.'s [33] recent findings on the adverse effects of RSIP's tannery wastewaters on bioindicator species reinforce these concerns.



**Figure 1.** View of surface water flow (31 L/s) impaired by RSIP wastewater effluent. This tributary undergoes insufficient treatment and subsequently enters the Chili River. Photo taken in April 2023 by and featuring paper authors.

While international literature reviews on Cr contamination, its negative health and environmental impacts, and remediation strategies are available [13,37,38], understanding Cr contamination challenges and identifying technological and sustainable solutions requires an approach that integrates local knowledge, societal acceptance of solutions [39], and the unique power of place-based inquiries. This manuscript summarizes and contextualizes research on Cr remediation, particularly as it relates to wastewater produced at RSIP. The

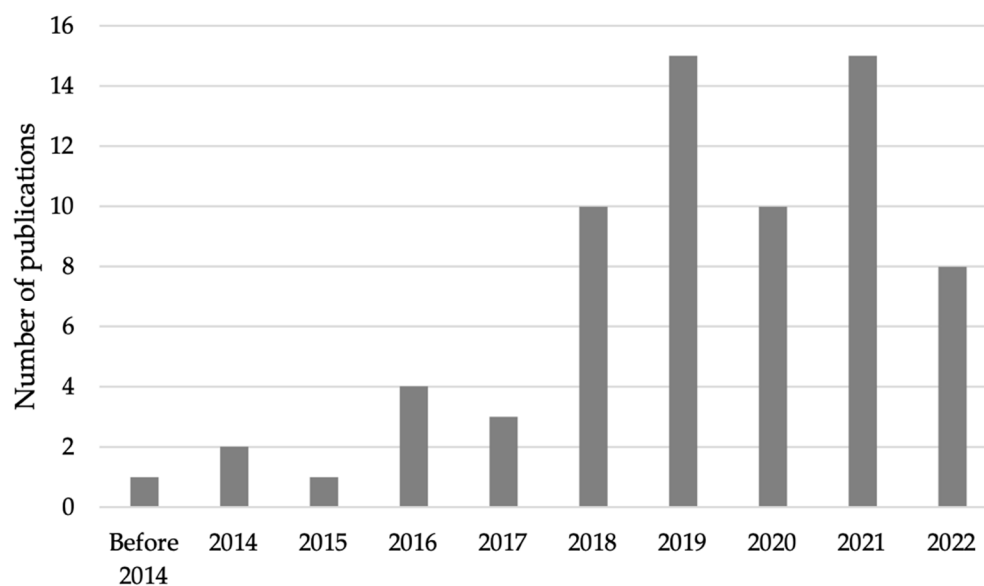
analysis draws on Peruvian undergraduate and graduate theses from local academic institutions in Arequipa, alongside topical peer-reviewed articles identified through Google Scholar, Scopus, and Web of Science. Special emphasis is placed on Spanish-language publications, which have received limited international visibility, creating an opportunity to increase global understanding of place-based approaches toward the treatment of Cr from tannery wastewaters and foster mechanisms for local adoption.

## 2. Cr Removal Techniques Evaluated in the Arequipa Region

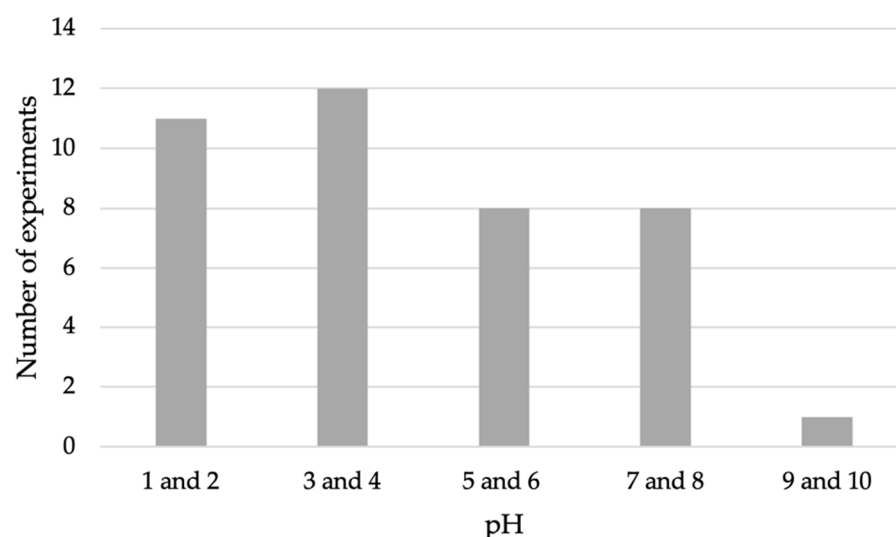
Although several authors have published international articles on Cr-contaminated soils in Arequipa [39–42], domestic investigations into the treatment of more complex tannery wastewater are relevant to this regional challenge. For example, Zapana et al. [42] used a pilot-scale constructed wetland system to treat RSIP's tannery wastewater. Treatment was achieved primarily through bioaccumulation in macrophytes *I. cernua* and *N. aquaticum*, achieving ~98% removal for this industrial wastewater. Another investigation, Herrera-Yari et al. [43], used a solar parabolic cylindrical concentrator on synthetic RSIP tannery effluents, reducing 173 mg/L Cr(VI) to ~26 mg/L Cr(VI) (i.e., 85%) to less toxic Cr(III) through photocatalytic degradation. Zapana-Huarache and colleagues [44] designed and tested the application of the filamentous fungus *P. citrinum*, which removed 80% of influent Cr(VI). Finally, Bejarano-Meza et al. [45] used magnetic iron-based nanoparticles synthesized with *O. europea* bone extract to remove nearly all detectable Cr(VI) from RSIP's tannery effluents. In addition to these peer-reviewed research articles written in English, Roque et al. [46] (Spanish) used the native bacterium *C. aquaticus* to attenuate 89% of the total chromium (34.8 to 3.82 mg/L) in the RSIP tannery wastewater of which ~70% was and remained Cr(III) (24.2 to 2.66 mg/L).

Of the total number of publications found in this synthesis (75), 38 experiments focused on treating total Cr (CrT), 48 on Cr(VI), and 12 on Cr(III) (98 experiments in total, as some studies analyzed more than one Cr species). However, the peer-reviewed publications about Cr removal from tannery wastewater in Arequipa summarized above are derived mostly from English journals. There is however a wealth of additional knowledge contained within 70 Spanish-written graduate (9) or undergraduate (61) theses focusing on Cr removal in the Arequipa Region. A large portion of the theses came from the faculties of Chemistry and Chemical Engineering (21%) and Environmental Engineering (25%), followed by Biology (15%), Biotechnology (11%), and Pharmacy (8%). The published university theses related to Cr removal applied to wastewater from tanneries increased in number within the last decade with a potential lull during and after the COVID-19 pandemic (Figure 2). More recent 2023 and 2024 publications (four and one, respectively) are not formally tallied because their numbers do not reflect the reality of publications, due to issues of time lapse between thesis completion and availability in online repositories.

Numerous techniques to remove or remediate the residual Cr content of tannery wastewaters were found in this synthesis. These techniques were categorized into five main groups: adsorption, phytoremediation, bioremediation, electrocoagulation, and a catch-all collection of other methods. Notably, there was no consistent approach across studies regarding key parameters such as pH, temperature, or treatment time. As a result, direct comparisons of Cr removal efficiency and rates are challenging. Additionally, studies from Arequipa indicate that the acidity of treated tannery wastewater from RSIP can vary, likely due to a combination of upstream dumping practices combined with specific adjustments for treatment methods, which can alter pH levels to differing extents (Figure 3). Building on these findings, the following sections describe the progress made in Cr removal research in Arequipa across different methodological approaches.



**Figure 2.** Temporal evolution of the number publications (peer-reviewed and theses) related to Cr treatment conducted in the Arequipa Region of southern Peru. Though four publications for 2023 and one for 2024 were identified, a terminus of 2022 was selected to account for a time lapse between thesis completion and availability in online repositories.



**Figure 3.** pH values documented at experiments done in Arequipa, showing that, in general, the acidity of treated tannery wastewaters is not constant in all treatment approaches evaluated.

### 2.1. Adsorption

A total of 23 publications focused on the application of different adsorbents to remove Cr from tannery wastewaters were found in the Arequipa Region. In terms of adsorption techniques, various plant adsorbents (leaves, fruits, seeds, tubers, shells, etc.) with a variety of porous sizes ranging from 75 to 350  $\mu\text{m}$  were found with the capacities to absorb Cr. The extent of removal ranged from a low of 12% (lemon pectin) to removal rendering Cr non-detectable (achiote peel, avocado seed, and pea pods). Promising results (at least 95% removal) were obtained using materials such as sawdust, Peruvian potatoes, corn crown, rice peel, and olive pits (see Table 2). Moreover, considering both treatment times and Cr elimination, adsorption is feasible for large-scale projects. The results suggest that large amounts of Cr can be removed in short periods. For local waste materials, there are further potential economic advantages with respect to material acquisition and transport. For example, Deza and Salinas [47] eliminated 99% of Cr(VI) in 30 min using olive seed,

while Pacheco [48] and Herrera and Sosa [49] were able to remove the majority of Cr(VI) in the same amount of time using corn crown and potatoes, respectively. Achiote peels [50] seem to be particularly efficient, with rapid removal of detectable Cr(VI) in only 5 min, while avocado seeds [51] were used to eliminate detectable Cr(VI) in 15 min. The latter two materials represent sustainable options, where common local food waste materials could be applied in Arequipa. However, while the use of waste products could be economically compelling, the associated costs of transporting and the application of these materials are currently unknown. While other materials performed relatively well, they either took hours to reach an adsorption peak or did not specify treatment times; for example, Paz [52] removed total Cr (CrT) to BD in 16 h using pea pods.

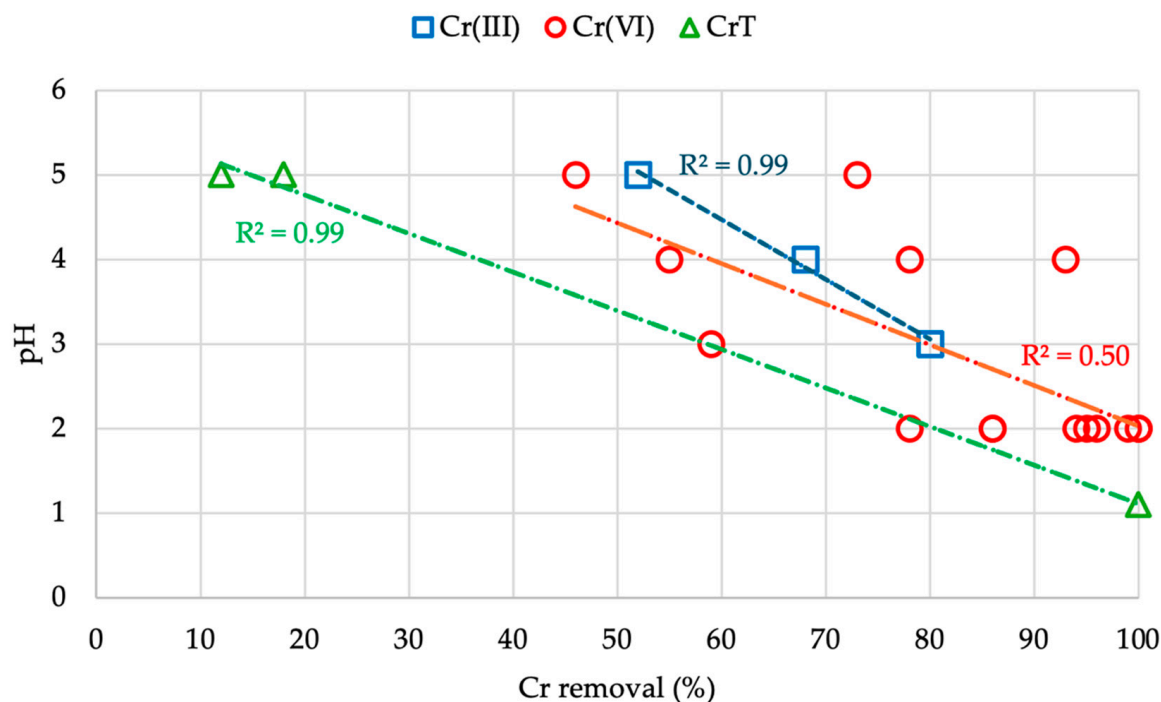
**Table 2.** Locally derived and inexpensive materials/waste tested for Cr adsorption capacity from tannery wastewaters in Arequipa, southern Peru.

Adsorbent	Species	Removal		pH	T (°C)	Time (min.)	Particle Size	Source
		(%)	(mg/g)					
Pea pods ( <i>Pisum sativum</i> ) *	CrT	BD	NA	1.1	RT	960	NA	[52]
Orange pectine ( <i>Citrus × sinensis</i> ) *	CrT	18	NA	5	RT	15	180–250 µm	[53]
Lemon pectine ( <i>Citrus limon</i> ) *	CrT	12	NA	5	RT	15	180–250 µm	[53]
Arequipan papaya seed ( <i>Vasconcellea pubescens</i> ) *	Cr(III)	80	NA	3	25	NA	NA	[54]
Olive seed ( <i>Olea europaea</i> ) *	Cr(III)	68	NA	4	RT	9	250 µm	[55]
Shrimp skeleton ( <i>Palaemon serratus</i> ) *	Cr(III)	52	NA	5	19	NA	NA	[56]
Achiote peel ( <i>Bixa orellana</i> ) *	Cr(VI)	BD	NA	2	RT	5	75–150 µm	[50]
Avocado seed ( <i>Persea americana</i> ) *	Cr(VI)	BD	NA	2	NA	15	75–150 µm	[51]
Olive seed ( <i>Olea europaea</i> ) *	Cr(VI)	99	NA	2	RT	30	70–160 nm	[47]
Potato varieties ( <i>Solanum tuberosum</i> Var. <i>Canchan</i> , <i>Unica</i> , <i>Peruanita</i> , and <i>Perricholi</i> )	Cr(VI)	96	NA	2	25	30	150–850 µm	[49]
Sawdust *	Cr(VI)	95	2.2	NA	60	180	0.35 mm	[57]
Corn crown ( <i>Zea mays</i> ) and rice husk ( <i>Oryza sativa</i> ) *	Cr(VI)	95	NA	2	RT	30	Less than 0.42 mm	[48]
Coffee seed's endocarp ( <i>Coffea arabica</i> ) *	Cr(VI)	94	NA	2	RT	120	75–150 µm	[58]
Metallic iron nanoparticles using <i>Eucalyptus</i> sp. Leaves *	Cr(VI)	93	NA	3 to 5	RT	60	180 nm	[59]
Wheat ( <i>Triticum</i> sp.)	Cr(VI)	86	NA	2	45	180	200 µm and 125 µm	[60]
Potato peel ( <i>Solanum tuberosum</i> ) *	Cr(VI)	86	NA	2	NA	50	<250 mm	[61]
Arequipan papaya seed ( <i>Vasconcellea pubescens</i> ) *	Cr(VI)	78	NA	2	25	NA	NA	[54]
Olive fruit ( <i>Olea europaea</i> )	Cr(VI)	78	NA	2 to 6	RT	NA	250 µm	[62]
Egg shells *	Cr(VI)	73	NA	5	RT	15	NA	[63]
Sancayo peel ( <i>Corryocactus brevistylus</i> ) *	Cr(VI)	59	NA	3	30	30	NA	[64]
Quinoa ( <i>Chenopodium quinoa</i> )	Cr(VI)	55	NA	"Acid"	20	NA	450–250 µm	[65]
Shrimp skeleton ( <i>Palaemon serratus</i> ) *	Cr(VI)	46	NA	5	19	NA	NA	[56]
Activated charcoal from rice husk ( <i>Oryza sativa</i> ) *	Cr(VI)	NA	53	2	20	240	Surface area 690 m <sup>2</sup> /g	[66]

(\*) Waste products. NA, not available; BD, below detection; RT, room temperature.

Finally, it is worth noting that all these adsorption experiments were conducted under acidic conditions with a pH between 1.1 and 6), which is lower than what was found using other treatment methods, or than reported by other studies conducted with RSIP tannery effluents [31]). Figure 4 presents a synthesis of these regional studies. While these studies were not explicitly designed to explore the strength of these trends (e.g., sorption isotherms) and rather were conducted at different pH values for different studies, this synthesis supports a trend toward more effective sorption under acidic conditions. Hence, future investigations of promising materials should quantify pH optima with consideration

of sorption isotherms, synergy with effluent pH, and/or costs associated with chemical pH adjustments to better understand application viability.



**Figure 4.** Synthesis of results of Cr species removal from aqueous solution as a function of pH as compiled from adsorption-based studies herein. This analysis demonstrates that more effective attenuation generally relates to lower pH conditions for CrT ( $R^2 = 0.99$ ), Cr(VI) ( $R^2 = 0.50$ ), and Cr(III) ( $R^2 = 0.99$ ), agreeing with the existing literature.

## 2.2. Phytoremediation

A total of 18 phytoremediation-associated studies were found for the Arequipa Region. Both microalgae (Table 3a) and vascular plants (Table 3b) showed a high propensity to remove Cr from polluted tannery wastewater. Promising examples included the microalgae *D. quadricauda* [67], *Chlorella* sp., and *Espirulina* sp. [68], and the vascular plants *I. cernua* and *N. aquaticum* [40,67]. Of these, *I. cernua* was particularly promising, with 98% removal of Cr(VI) in only 5 days [42]. While other species performed well, they took weeks or months to reach results, making them less attractive for further large-scale sustainable applications. Moreover, since only six phytoremediation-based studies found in this synthesis documented both Cr removal (%) and pH, no clear pattern was identified in terms of removal capacity and pH values ( $R^2 = 0.14$  for CrT). Furthermore, it is pertinent to note that the pH values tested, when available, correspond to neutral conditions, which may facilitate plant growth [69].

**Table 3.** (a) Phytoremediation survey of different microalgal species as applied toward polluted tannery wastewaters in Arequipa, southern Peru. (b) Phytoremediation survey of different vascular plant species as applied toward polluted tannery wastewaters in Arequipa, southern Peru.

(a)							
Species	Cr Species	Cr Removal (%)	Cr Removal (Other Units)	pH	Time (Days)	Incubator Type	Source
<i>Chlorella</i> sp.	CrT	96	NA	NA	10	Inoculum	[68]
<i>Espirulina</i> sp.	CrT	95	NA	NA	10	Inoculum	[68]
<i>Acutodesmus dimorphus</i>	CrT	75	NA	>7.5	15	Batch	[70]
<i>Arthrospira platensis</i>	CrT	33	NA	>7.5	15	Batch	[70]
<i>Desmodesmus quadricauda</i>	Cr (VI)	94	1.7 mg/L	NA	9	Flow through	[67]
(b)							
Species	Cr Species	Cr Removal		pH	Time (Days)	Source	
		(%)	(Other Units)				
<i>Eichhornia crassipes</i> root	CrT	99	NA	NA	25	[71]	
<i>Isolepis cernua</i> and <i>Nasturtium aquaticum</i>	CrT	99	NA	7	70	[72]	
<i>Eichhornia crassipes</i> leaves and stems	CrT	94	NA	NA	25	[71]	
<i>Eichhornia crassipes</i> and <i>Lemna minuta</i>	CrT	92	NA	7	32	[73]	
<i>Hydrangea macrophylla</i>	CrT	88	NA	NA	90	[74]	
<i>Eichhornia crassipes</i>	CrT	49	NA	NA	45	[75]	
<i>Buddleja</i> sp.	CrT	41	NA	NA	90	[41]	
<i>Eichhornia crassipes</i>	CrT	35	NA	7	45	[76]	
<i>Ficus carica</i> (fruits)	CrT	NA	0.1 mg/kg	NA	180	[77]	
<i>Eleocharis montevidensis</i> (stem)	CrT	NA	17.4 mg/kg	NA	15	[78]	
<i>Tagetes</i> sp.	CrT	NA	560 mg/kg	7.3–8.6	60	[79]	
<i>Ficus carica</i> (estate)	CrT	NA	3.1 mg/kg	NA	180	[77]	
<i>Medicago sativa</i>	CrT	NA	0.8 mg/kg	NA	90	[80]	
<i>Eleocharis montevidensis</i> (leave)	CrT	NA	22.7 mg/kg	NA	15	[78]	
<i>Eleocharis montevidensis</i> (root)	CrT	NA	504 mg/kg	NA	15	[78]	
<i>Eleocharis montevidensis</i>	Cr(III)	23	41.2 µg/gps	NA	20	[81]	
<i>Baccharis salicifolia</i>	Cr(III)	12	27.1 µg/gps	NA	20	[81]	
<i>Tessaria integrifolia</i>	Cr(III)	7	18.9 µg/gps	NA	20	[81]	
<i>Chenopodium murale</i>	Cr(III)	5	27.1 µg/gps	NA	20	[81]	
<i>Croton ruizianus</i>	Cr(III)	NA	17.3 mg/kg	NA	34	[82]	
<i>Isolepis cernua</i> and <i>Nasturtium aquaticum</i>	Cr(VI)	98	NA	NA	5	[42] *	
<i>Eichhornia crassipes</i> and <i>Lemna gibba</i>	Cr(VI)	93	NA	7	32	[73]	

NA: Not available. (\*): Peer-reviewed.

### 2.3. Bioremediation

A total of 13 studies focused on microbial bioremediation (fungi and bacteria) for the treatment of Cr species from tannery wastewaters were found in Arequipa (Table 4a,b). While mechanisms may also include bioaccumulation and sorption, microbial reduction of Cr(IV) to Cr(III), potentially in association of the respiration of other electron acceptors such as sulfate, seemed particularly promising. Loaiza [83] isolated and cultivated a sulfate-reducing bacterial consortium using a Cr<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solution followed by cultivation in a bioreactor containing RSIP tannery effluents, eliminating most detectable Cr(VI). Additional studies on bacterial potential for Cr removal (Table 4a) included *C. aquaticus* and *Streptococcus* sp. [84], and *K. oxycata* [85], with 94% (CrT) and 92% (Cr(VI)) removal (from solution), respectively. Similarly, 89% of Cr(VI) was removed using the bacterium *P. mirabilis* [86].



**Table 4.** (a) Bioremediation with live bacteria from polluted tannery wastewaters in Arequipa, southern Peru. (b) Bioremediation with fungi from polluted tannery wastewaters in Arequipa, southern Peru.

(a)							
Species	Cr Species	Cr Removal (%)	Cr Removal (Other Units)	pH	Temp. (°C)	Time (Days)	Source
<i>Corynebacterium aquaticus</i>	CrT	94	NA	NA	32	5	[84]
<i>Streptococcus</i> sp.	CrT	94	NA	NA	32	5	[84]
<i>Corynebacterium aquaticus</i>	CrT	89	NA	7.3	25	3.2	[46] *
<i>Pseudomonas</i> sp.	CrT	NA	1040 mg/L	NA	NA	24	[87]
<i>Corynebacterium aquaticus</i>	Cr(III)	89	NA	7.3	25	3.2	[46] *
Sulfate-Reducing Bacteria	Cr(VI)	BD	NA	7.7	RT	11	[83]
<i>Klebsiella oxycata</i>	Cr(VI)	92	NA	NA	RT	10	[85]
<i>Proteus mirabilis</i>	Cr(VI)	89	NA	NA	RT	1.5	[86]
<i>Bacillus subtilis</i>	Cr(VI)	74	NA	NA	RT	10	[85]
<i>Streptococcus</i> spp.	Cr(VI)	68	NA	NA	32	5	[84]
<i>Escherichia coli</i>	Cr(VI)	63	NA	NA	RT	10	[85]
<i>Bacillus pumilus</i>	Cr(VI)	46	NA	NA	RT	1.5	[86]
<i>Streptococcus</i> sp.	Cr(VI)	44	NA	NA	32	3	[84]
<i>Corynebacterium aquaticus</i>	Cr(VI)	40	NA	NA	32	3	[84]
<i>Enterobacter cloacae</i>	Cr(VI)	37	NA	NA	RT	10	[85]
<i>Halomonas campaniensis</i>	Cr(VI)	37	NA	NA	RT	1.5	[86]
<i>Pseudomona aeruginosa</i>	Cr(VI)	22	NA	NA	RT	10	[85]
<i>Pseudomonas</i> sp.	Cr(VI)	NA	<0.005 mg/L	NA	NA	24	[87]

(b)							
Species	Cr Species	Cr Removal (%)	Cr Removal (Other Units)	pH	Temp. (°C)	Time (Days)	Source
<i>Aspergillus niger</i>	CrT	97	48 mg/g	NA	RT	21	[88]
Filamentous fungi and activated charcoal	CrT	97	NA	4	RT	16	[89]
Filamentous fungi	CrT	83	NA	4	RT	16	[89]
<i>Penicillium</i> sp.	Cr(III)	96	NA	NA	NA	10	[90]
<i>Saccharomyces cerevisiae</i>	Cr(VI)	87	NA	NA	37	2	[91]
<i>Fusarium petrophilum</i>	Cr(VI)	87	NA	4.3	RT	16	[92]
<i>Penicillium citrinum</i>	Cr(VI)	80	NA	4.5–5.2	RT	21	[93]
<i>Penicillium citrinum</i>	Cr(VI)	80	NA	NA	RT	5	[44] *
<i>Trichoderma viride</i>	Cr(VI)	20	NA	NA	RT	5	[44] *

NA, not available; BD, below detection; RT, room temperature; (\*), peer-reviewed.

Near-complete removal of Cr was also obtained using a system approach that integrated fungi with adsorption-based technologies (Table 4b). Solis [90] treated RSIP's tannery wastewater with the fungus *Penicillium* sp. (2.2 g/L) under completely mixed conditions to remove 96% of Cr(III). When further combined with the microalga *Acutodesmus dimorphus*, zeolite, and activated carbon, the system achieved 99% removal. Similarly, the application of the fungus *A. niger* by Aymara [88] and the combination of native fungi and activated charcoal by Quina [89] resulted in 97% CrT removal.

While overall reduction/removal was laudable, many of these bacteria- and fungi-based studies required extended treatment times to obtain efficient results, rendering them less attractive techniques for removing Cr species from tannery wastewater. The most promising results, when considering both removal extent and treatment time, were obtained using the bacterium *P. mirabilis* [86] or the fungus *S. cerevisiae* [91], which eliminated nearly 90% of Cr(VI) in 36 and 48 h, respectively. Unlike in the sorptive studies, a clear correlation between Cr removal species and pH was harder to discern because of the limited number of experiments documenting both variables and a presumed requisite of appropriate and likely circumneutral pH constraints for effective microbial growth.

#### 2.4. Electrocoagulation

Five studies in the Arequipa Region evaluated electrocoagulation (see Table 5), in which the authors applied electrical current with voltages between 0 and 40 volts and intensities between 0 and 60 amps to treat different Cr species from tannery wastewaters. Most experiments obtained high removal yields in all Cr species, except for Alvarez and Vilca [94], who applied a graphite anode and nickel-covered metal cathode, resulting in low treatment capacity for CrT. However, the authors obtained their results in a shorter time (only five minutes), compared to the rest of the experiments. Laura and Salinas [95] removed Cr(III) to BD in 30 min and no clear effects from voltage, intensity, or time on pollutant removal capacity were detected. This limited number of studies was conducted across a range of acidic pH values, which made it difficult to discern if there were any patterns between Cr removal and pH.

**Table 5.** Electrocoagulation to treat polluted tannery wastewaters in Arequipa, southern Peru.

Cr Species	Cr Removal (%)	Optimum Conditions	pH	Voltage (V)	Intensity (A)	Time (min.)	Source
CrT	99	Aluminum electrodes	3.2	NA	0.095	44	[96]
CrT	23	Graphite anode and nickel-covered metal cathode	2	9	3	5	[94]
Cr(III)	BD	Iron anodes and aluminum cathodes	5	3–20	0–60	90	[97]
Cr(III)	BD	Aluminum electrodes	4	0–12	0–50	30	[96]
Cr(VI)	99	Aluminum electrodes	5.9	40	14	45	[98]

NA, not available; BD, below detection.

#### 2.5. Other Cr Removal Techniques

Fifteen additional studies implemented technologies that are less clearly linked into the above classifications (Table 6). In some cases, nature-inspired approaches, such as biofilters, infiltration strategies, and wetlands, likely operated with a synergy of biological and/or abiotic reduction, bioaccumulation, and sorption-based mechanisms. Particular highlights for Cr removal included solar distillation [99], magnetic iron nanoparticles [100], artificial wetlands [101], iron-based coagulation-incorporating polymers [102], and infiltration systems [30,103,104]. Similar to the study already mentioned by Almiron et al. [41], Huillca [78] used a wetland system colonized with the plant species *E. montevidensis* to remove Cr from polluted waters, with a bioaccumulation factor of 13.9 and 22.0 through aerial and root systems, respectively.

Considering only studies with sufficient additional information beyond removal extent, and besides the already mentioned peer-review studies done by Herrera-Yari et al. [43] and Bejarano-Meza et al. [45], particularly promising results were obtained using infiltration approaches. For example, Leguía and Puma [104] used a bio-sand filter to remove 99% of CrT in 46 min. Similarly, Rendón [103] used sodium bentonite filters to remove 94% of Cr(VI) in 30 min, while Paye and Gomez [105] attenuated CrT to below detection in eight hours using a mixture of zeolite and perlite. Unlike applied sorptive technologies, these studies tended toward increased efficiency at higher pH values ( $R^2 = 0.20$  and  $0.94$  for Cr(VI) and CrT, respectively), suggesting a potential interaction between multiple attenuation mechanisms.

**Table 6.** Other techniques to treat polluted tannery wastewaters in Arequipa, southern Peru.

Cr Species	Treatment	Cr Removal (%)	Cr Removal (Other Units)	pH	Time	Source
CrT	Zeolite and perlite	BD	NA	“Basic”	8 h	[105]
CrT	Bio-sand filter	99	NA	8–9	46 min	[104]
CrT	Artificial wetlands with <i>S. americanus</i> , <i>E. montevidensis</i> , and <i>H. bonariensis</i>	99	NA	7–9	6 days	[101]
CrT	Constructed wetlands with <i>Eleocharis palustris</i>	96	2.5 g/kg	NA	NA	[106]
CrT	Sandy-loam soil filter	NA	9220 mg/kg	6.9–7.2	NA	[30]
CrT	Diatoms coated with FeCl <sub>3</sub>	NA	125 mg/g	6	4.5 h	[107]
CrT	Shrimp cephalothorax biofilter ( <i>C. caementarius</i> )	NA	0.7–0.9 mg/kg	Acid	NA	[108]
Cr(VI)	Solar distillation	BD	NA	NA	3 days	[99]
Cr(VI)	Magnetite nanoparticles	BD	NA	NA	3 weeks	[100]
Cr(VI)	Magnetic iron-based nanoparticles	100	NA	2	30 min	[45] *
Cr(VI)	Polymer (Floerger AN 910) and FeCl <sub>3</sub> coagulant	96	NA	6	NA	[102]
Cr(VI)	Sodium bentonite filters	94	NA	4	30 min	[103]
Cr(VI)	Ionic exchange resins	93	0.15 mg/L	3	30 min	[47]
Cr(VI)	Ionic exchange resins	93	NA	3–5	30 min	[109]
Cr(VI)	Cu nanoparticles and copper oxide	NA	15 mg/L	2	NA	[110]
Cr(VI)	Photovoltaic reduction UV/TiO <sub>2</sub>	85	NA	3.8	4 h	[43] *

NA: Not available. BD: Below detection. (\*): Peer-reviewed.

### 3. Discussion

#### 3.1. General Analysis

Several global reviews on how different techniques are used to treat CrT, Cr(III), and/or Cr(VI) from tannery wastewaters already exist [111–116]. When compared to these international efforts, the techniques applied in Arequipa to remove Cr species from tannery wastewaters feature place-based adaptations that could be applied sustainably in the region. The socioeconomic status of southern Peru favors practical treatment strategies for the removal of Cr from tannery wastewater that rely on inexpensive and easily available materials and techniques. Nanotechnology, for example, is a common method used to treat Cr from wastewater [113,117,118], but only two studies [100,110] used this technique in Arequipa. Similarly, authors have used chemical precipitation of Cr (VI) worldwide in tannery wastewater [119,120], but no Arequipa-specific studies were found using this method. However, Portada [121] demonstrated 74% Cr(III) removal from tannery wastewaters through chemical precipitation in only 30 min in Puno (southern Peru). Another common method not found is the use of dry (and presumably limited biological activity) microbial bacterial biomass for Cr adsorption, as achieved by Rizvi et al. [122] in India, who used desiccated biomass comprised of *P. aeruginosa*, *B. subtilis*, and *A. chroococcum* to remove Cr and other metals and highlighted 96% removal by *B. subtilis*. While not directly explored, this highlights a potential synergy in sorption with biological processes for live microbial cells. International studies provide a strong precedent for the need to further evaluate various treatment methods for tannery wastewaters, including coagulation and flocculation, electrochemical treatments such as electro-flotation and electro-oxidation (distinct from electrocoagulation presented herein), ion exchange, membrane filtration, electrodialysis, photocatalysis, and biological treatments (e.g., trickling filters and aerated lagoons) [111–120]. While these methods have been studied in various contexts, Arequipa presents a relevant test case for assessing their applicability to local tannery wastewater conditions.

A direct comparison is unfortunately hindered by the preference of Arequipa authors to express their results in terms of percent removal as opposed to benchmarks against

material mass (e.g., mg/kg) and the establishment of adsorption isotherms, making it difficult to develop a global comparative analysis. Expressing results in material-relevant units that capture mass treatment capability, isotherms, and normalization or optimization of treatment conditions such as pH, temperature, and treatment times, as previously discussed by Garcia-Chevesich et al. [123], would facilitate benchmarking regional treatment strategies against the global literature to increase this contribution. Nevertheless, this compilation of place-based studies holds significant value. Rather, this unique place-based compilation of otherwise not visible research provides trajectories and opportunities that build on local understanding and acceptance of potential materials and technologies that could be appropriate for local solutions to this wastewater quality challenge.

Tanning industries (such as those operating in RSIP in Arequipa) generate effluents that can have highly variable pH values (between 2 and 9) due to the chemical processes involved in transforming animal hides into leather, which include the use of acids, bases, and other chemicals [124]. Analogous variability was confirmed in our place-based analysis across sites in the region. While Tejada-Meza et al. [33] reported that the pH of the RSIP's tannery effluents was  $8.2 \pm 0.4$  during their analysis window, this may not be constant because of the changing quality (color/smell) of the surface water effluent observed by our team during the field visit (see Section 1 for details), most likely a result of upstream dumping. The potential variability of tannery wastewater requires effluent-specific analysis of parameters, such as pH, ionic strength, organic and inorganic concentrations, temporal variability, and flow, to most effectively select and optimize treatment technologies (and potential multistage or adaptable approaches) that help achieve environmental discharge standards.

### 3.2. Promising Strategies for Cr Attenuation in Arequipa

#### 3.2.1. Adsorption

Adsorption is a frequently applied technique in the treatment of Cr-contaminated water. In the specific case of treating Cr-contaminated tannery wastewater, adsorption is used to eliminate Cr ions by binding them to a solid adsorbent material [125]. Sorption applications that rely on water contact are straightforward to implement and can be applied toward the removal of a diverse array of heavy metals, even at trace concentrations [126–130]. They can be further tailored toward specific metals with the capability for recovery, regeneration, and reuse, which can contribute to cost-effectiveness and provide a more environmentally benign alternative to chemical dosing [127–131]. However, as sorbents have a finite supply of active sites, analyses such as sorption isotherms should be quantified to understand attenuation capacity and then extended to explore the viability of pilot-scale applications with complex effluent matrices.

With these considerations as well as related investigations into cost-benefit and life-cycle analysis, adsorption materials could be applied to the region because they can be derived from locally abundant food waste products or be used as feedstocks for biochar, supporting broader sustainability themes. With the caveat of limited context to establish isotherms and equilibrium kinetics, the most promising adsorption results (>95% removal) were documented for plant materials (achiote peels, avocado seed, pea pods, sawdust, potatoes, corn crown and rice peel, and olive pits) that are present and, in most cases, waste products in the Arequipa Region of southern Peru (see Table 2 for details). Achiote peels [50] and avocado seeds [51] were particularly promising in terms of percent removal and time. This synergy of locally abundant waste materials and effective attenuation suggests an opportunity to further explore applications at scale to better ascertain potential sustainability.

As previously discussed in Section 3.1 and depicted in Figure 4, the results collectively suggest that more acidic waters tend to eliminate more Cr (in all forms) during sorption applications, agreeing with studies developed for wastewaters in other parts of the world [132]. Unfortunately, only one author [66] mentions surface treatment area ( $690 \text{ m}^2/\text{g}$ ), while the rest simply report particle diameter (75–850  $\mu\text{m}$ ). Despite the limitations of the units previously discussed and in considering the available information (i.e., % removal most commonly), some results listed in Table 2 appear to be competitive with other Peruvian and international studies that have focused on testing different materials to remove Cr from tannery wastewaters using adsorption-based approaches. Studies within other regions of Peru identified adsorption onto materials such as wood ash [133], moringa seeds [134], *Eucalyptus* sp. leaves [135], and lemon peel [136] as efficient methods to remediate Cr in water.

Similarly, these Arequipa-centric results are analogous to results obtained in other countries. For example, similar to Mollinedo and Huanca [51] in Arequipa, Hernandez et al. [137] were able to achieve Cr(VI) removal to BD levels using avocado waste biomass in Bolivia, while Boeykens et al. [138] removed 80% of Cr(VI) using avocado seeds from polluted waters in Argentina. Bansal et al. [139] and Sivakumar [140] achieved 77% and 88% Cr(VI) removal, respectively, from polluted tannery wastewaters in India using rice husk, which compares favorably to the 95% Cr(VI) removed by Pacheco [48] in Arequipa using this material. Mass-normalized removal from Arequipa included 2.2 mg/g with sawdust [57] and 4.3 mg/g with banana peel [141].

As is true for many pollutants, activated carbon and related products such as waste-derived biochar (when originated from organic matter) are particularly appropriate for Cr attenuation. This could also limit the ancillary release of nutrients and soluble organics associated with otherwise unprocessed food waste. Fahim et al. [142] applied activated carbon to remove up to 99% Cr(III) from Egyptian tannery wastewater and Payel and Sarker [143] removed 99.8% of CrT from these toxic industrial fluids using banana flower stalk (rachis) biochar in Bangladesh. A study in Arequipa reported 52 mg/g achieved with biochar from rice husk [66]. This compares favorably to what Mohan et al. [144] achieved in India using low-cost biochar derived from agricultural waste materials and cloth-like deployment, with a 22 mg/g Cr(VI) removal capacity from tannery wastewaters. Moreover, Estrella [145] used a composite of activated carbon impregnated with multiwalled carbon nanotubes in Ecuador to remove 28 mg/g of the contaminant in 90 min.

Our local place-based synthesis identified adsorption materials not previously described in the Peruvian and international literature, such as Arequipan papaya seed, sancayo cacti peel, Peruvian potato varieties, and quinoa (see Table 2). Of these, the former two materials are considered agricultural waste, whereas the latter two have commercial value as agricultural products. The most promising materials identified in this synthesis (achiote peels and avocado seeds) add a local novel feedstock for Cr treatment from tannery wastewater as they are considered waste in Arequipa; although avocado seeds have been used to treat other types of polluted waters by Mahmoud et al. [146] in Egypt and Boeykens et al. [138] in Argentina, their application to tannery wastewaters is novel. Another effective waste product identified in this synthesis is olive seed. In building upon this theme, Malkoc et al. [147] removed 12.2 mg/g of Cr(VI) in Turkey using pomace (an industrial olive oil waste product which contains 59–74% olive seed and pulp); even more promising, El-Aassar et al. [148] removed 137.7 mg/g of Cr(VI) using a blend of olive seed waste, anthracite, and chitosan. Though shrimp carapace waste material has been studied for metal removal in India and Saudi Arabia [149,150], our synthesis adds locally abundant freshwater river shrimp (*P. serratus*) to this body of knowledge. Indeed, grounded

shrimp skeleton was shown to be more effective at removing Cr species than commercial chitin/chitosan, as concluded by Fabbicino and Gallo [151] in Italy.

In addressing potential applications, it is recommended that the most efficient materials mentioned above, in synergy with local abundance as easily acquired waste products as well as considerations of novelty, be further investigated to explore their ability to remove Cr and other metals from tannery wastewaters at larger scales, their conversion and analysis of resultant biochar, and with considerations of transportation, implementation, and disposal costs and impacts. Similarly, other materials already tested for Cr removal (e.g., passionfruit by Campos-Flores et al. [152] in Trujillo, Peru, or clay pellets to increase adsorption in Cameroon [153]) or for the local treatment of other metals (see Garcia-Chevesich et al. [123] for details) should also be tested in Arequipa for Cr removal from tannery wastewaters. The place-based investigations would also benefit from exploration of emerging adsorbent-based techniques applied toward analogous wastewaters elsewhere, such as nanobiocomposite spheres [117] and polymer-based adsorbents (e.g., Chavez and Alpaca [102]). Finally, a techno-economic and sustainability evaluation should complement the feasibility of using promising materials directly and as feedstocks for biochar to further explore their applicability toward larger-scale tannery wastewater treatment applications.

### 3.2.2. Phytoremediation

Phytoremediation is an eco-technological method based on the ability of algae or larger plants to adsorb, bioaccumulate, and/or degrade aqueous pollutants [154,155]. It offers the potential for an inexpensive method that does not rely on skilled labor for implementation [156]. The efficacy of Cr removal via phytoremediation depends on various factors including plant or algal species, the initial concentration of Cr in the treated water, environmental conditions, and the duration of exposure [155]. While phytoremediation presents a sustainable and economically favorable approach for the extraction of metals from contaminated waters, its application is constrained by slower treatment timeframes, limited capacity, liabilities with resultant bioaccumulation, and reliance on environmental conditions [157].

Based on percent removal, promising results from Arequipa (Table 3a,b) were achieved with *I. cernua* and *N. aquaticum* [72], and *D. quadricauda* [67], with further promise in other Peruvian regions that are using *P. persica* [158]. The international community has studied *Typha* spp. [159] in the USA, *C. alternifolius*, *T. domingensis*, *P. karaka*, and *B. aethiopicum* [160], *P. coccineum*, *B. mutica*, and *C. papyrus* [161] in Ethiopia, and *Trichoderma* sp. [162] in India, with lesser efficiency for *E. craassipes* in Bangladesh [163].

While most Arequipan reports focused on percent removal, Flores [79] documented removal of 560 mg/kg using *Tagetes* sp. The locally cultivated microalga species *D. quadricauda* [67] was not previously documented in the international literature for this application, as summarized in the literature review on microalgal applications toward contaminant remediation by Jácome-Pilco et al. [164]. The Arequipa studies identified other vascular plant species not previously studied for Cr removal from tannery wastewaters, including *Buddleja* sp., *I. cernua*, *N. aquaticum*, *H. macrophylla*, *C. murale*, *E. montevidensis*, *B. salicifolia*, *T. integrifolia*, *C. ruizianus*, and *I. cernua*. However, as previously discussed, the species that seems to be the most promising and should be further explored is *I. cernua*, a native species from southern Peru that is novel in the field of Cr removal from tannery wastewater. In embracing a theme of utilizing a combination of different mechanisms and technologies, *I. cernua* could be incorporated in constructed wetland-based treatment systems as reported by Morales-Paredes et al. [165]. However, the implementation of larger-scale phytoremediation-based treatment systems in Arequipa is accompanied by environmental and practical constraints such as the need to harvest and dispose of plants that bioaccumu-

late this toxic metal. Furthermore, Arequipa has an arid climate, which could constrain water availability. However, recent climate change and anthropogenic projections [166] suggest that surface water resource availability is expected to increase in the region and hence could mitigate this concern.

### 3.2.3. Bioremediation

Bioremediation employs live microorganisms (including bacteria or fungi) to attenuate metal contaminants from polluted waters through mechanisms such as redox cycling, precipitation, indirect complexation (e.g., with associated iron oxyhydroxides), and bioaccumulation [167,168]. Microorganisms are pivotal in bioremediation as they leverage contaminants as a resource for energy or nutrients [169] or through fortuitous biotransformation reactions that are more cometabolic in nature with less obvious benefit to metabolic processes [170,171]. Of particular relevance to bioremediation is the reduction of Cr(VI) to Cr(III) to limit mobility and toxicity [172] (see details in Section 1). Investigations focusing on enzymatic processes are of great interest for chromate bioremediation, as they represent detoxification processes in inherently Cr-resistant microorganisms [173].

The utilization of nature-based solutions that incorporate bioremediation for the treatment of pollutants such as Cr offers an efficient and sustainable alternative. Bioremediation can be more cost-effective than engineered applications, such as chemical precipitation or membrane filtration, with lower material, operational, and waste costs [174,175]. Despite these benefits, bioremediation can harbor kinetic limitations, potentially requiring weeks or even months and larger physical treatment footprints when contrasted with some of the more rapid technologies explored herein and elsewhere [176]. Extended treatment durations may diminish the efficiency of systems designed for large-scale or continuous-flow operations, particularly in contexts necessitating larger flows and swift remediation. This issue is particularly pronounced in scenarios involving industrial effluents from RSIP, where prompt interventions are essential to avert further contamination [177]. Moreover, these processes necessitate additional resources such as energy, nutrients, and other substrates, thereby escalating operational costs and constraining the scalability of these systems [166,178]. Microbial or fungal colonies may also be adversely impacted by environmental stressors, the environmental variability of introduced tannery wastewaters, and the depletion of metabolic resources during prolonged operations, consequently undermining long-term efficacy and the system resilience [176]. Bioremediation can also yield toxic or more mobile by-products, potentially exacerbating pollution or adversely affecting ecosystems [178]. Moreover, the accumulation of heavy metals in resultant biomass can necessitate effective removal or disposal strategies [174]. Temporal complexities further necessitate system optimization and continuous monitoring to maintain stability and effectiveness in treatment processes [179,180]. These are all surmountable considerations that should be kept in mind to optimize bioremediation systems and tailor them toward local conditions to ensure that overall sustainability metrics are achieved.

Promising results within the Arequipa-specific literature to remove Cr species through bioremediation (Table 4a,b) came from the use of unspecified sulfate-reducing bacteria [83], the fungi *Penicillium* sp. [90] and *A. niger* [88], and the combination of filamentous fungi with activated charcoal [89]. These results entailing greater than 97% attenuation of Cr species from tannery wastewater can be compared with other Peruvian and international research. At the national level, similar results were obtained using *A. niger* [181] and *Pseudomonas* sp. [123,182]. Internationally speaking, similar results were obtained using *A. niger* in Mexico [183] and *Pseudomonas* sp. in Ecuador [184], and *E. coli* and *Pseudomonas* sp. in Argentina [185] and China [186]. The Arequipan author Aymara [88] attained 48 mg/g of Cr removal with *A. niger*, while Chen et al. [187] exceeded this capacity by applying a

hydroxyl-functionalized magnetic fungal nanocomposite in China. In addition, sulfate-reducing bacteria (SRB) have been applied more widely to remove challenging heavy metals through the formation of metal sulfides, with a powerful precedent in treating mining-impacted waters [188–190]. Besides Cr, Cu, and Zn, Lloyd et al. [191] used SRB to eliminate Tc(VII), Cr(VI), Se(IV), and Te(IV) from polluted solutions. The implementation of sulfate reduction and other bioremediation strategies likely necessitates the construction and maintenance of an actively managed or passive bioreactor [189,190], while phytoplankton can work with less infrastructure demand to treat Cr-contaminated tannery wastewater in the Arequipa Region. A bioremediation application would have to consider footprint, flow constraints, and potential fouling for optimal removal to be effective.

Furthermore, though some microorganisms used in Arequipa to remove Cr species from tannery wastewater are not found in the international literature, the results revealed that the bacterium *P. mirabilis* [86] and the fungus *S. cerevisiae* [91] were particularly promising for further exploration into treatment-relevant investigations that address long-term viability and large-scale applications. Though the former species has been applied to remove Cr from polluted waters [192], we are not aware of its application toward tannery wastewaters outside of these Arequipa-specific studies. *S. cerevisiae*, as documented by Benazir et al. [193] in Indian tannery effluents, attained similar results to those obtained in Arequipa and improved overall treatment through mixed consortia, which is an approach that should be explored in southern Peru.

#### 3.2.4. Electrocoagulation

Electrocoagulation has been applied in industrial wastewater treatment facilities for discharge or recycling. This technique entails applying an electric current to the water, prompting the coagulation and precipitation of suspended and dissolved contaminants [194]. Most of the surveyed experiments employing electrocoagulation resulted in nearly complete Cr removal (Table 5). A highlight was led by Laura and Salinas [95], who applied aluminum electrodes (locally the most common method) to remove all Cr species to below detection limits from tannery wastewater in only 30 min. Juarez and Osorio [97] achieved similar results using iron anodes and aluminum cathodes. However, lower Cr removal was documented by Alvarez and Vilca [94] using a graphite anode and nickel-covered metal cathodes, while near complete Cr removal was achieved in other Peruvian regions applying aluminum cathodes/anodes pairs [195–199], as well as copper cathodes and lead anodes [195]. Among competitive international results, Gao et al. [200] and Aoudj et al. [201] combined electrocoagulation and electroflotation to remove Cr in Hong Kong and Algeria, respectively, both decreasing Cr concentrations below national standards.

Electrocoagulation presents several advantages for metal extraction from contaminated waters, notably high efficiency, and rapid removal [202]. The technology requires readily available electrical equipment and minimal chemical additives [202]. It is capable of treating a wide variety of water types and pollutants [202], thereby making it suitable for diverse industrial wastewaters such as RSIP effluents. However, electrocoagulation requires disproportionately high energy inputs when contrasted with other engineered treatment technologies, can be less efficient in highly saline or acidic waters, produces a waste sludge that necessitates dewatering and potentially hazardous disposal, and electrodes rapidly corrode, with a need for frequent replacement [203]. Hence, despite the promise of nearly complete removal in relatively short periods of time, electrocoagulation is expensive compared to other approaches due to infrastructure, energy, and other operational costs [204]. Therefore, analysis to evaluate the economic feasibility of this technique for pilot and large-scale treatment of tannery wastewater in Arequipa may best be used as



a benchmark when exploring potentially more sustainable treatment technologies such as those outlined prior to this section.

### 3.2.5. Other Cr Removal Techniques

The high solar radiation present in Arequipa lends promise toward solar distillation, which uses solar energy to evaporate water from a polluted source to be later condensed into a clean container. However, much like membrane-based exclusion, evaporative applications result in a concentrated waste stream that necessitates further treatment or disposal and could present a barrier to sustainable implementation [205]. In addition to extensive removal as documented by Herrera-Yari et al. [43] (Table 6), Anahua and Pacheco [99] were able to eliminate CrT to BD using solar distillation. However, those implementations took days to weeks, which provides a temporal constraint for adoption. While treatment time is a potential barrier to implementation, novel strategies such as the utilization of materials with high thermal absorption capacity (e.g., black copper, carbon-based nanomaterials, specialized coatings) can accelerate the evaporation process. Further gains can be achieved by optimizing the evaporation surface area, incorporating simple and portable photothermal evaporation structures [206], or possible integration with other technologies explored herein.

Promising Arequipa results were also obtained using infiltration-type strategies in geomedia such as biosand filters (99% of CrT in 46 min), sodium bentonite filters (94% Cr(VI) in 30 min), and zeolite with perlite (CrT to BD in eight hours), as listed in Table 6. This is consistent with the findings of others; for example, Kocaman et al. [207] used biosand filters (among other treatments) to eliminate 0.19 ppm of Cr from industrial wastewaters in Turkey, and Ruiz [100] eliminated CrT to BD using magnetite nanoparticles.

The application of constructed wetlands (as also documented by Arizábal [106] in Arequipa) can bring a series of environmental and social benefits to this arid region while also helping to address the alarming reduction in and need for protection of wetland ecosystems in Peru, as recently reported by Romero-Mariscal et al. [208]. In our synthesis, Lima [101] removed 99% of Cr using constructed wetlands in Arequipa; this is analogous but superior to the 85% removal obtained by Kong et al. [209] in constructed wetlands in China. Similarly, Rojas [107] used diatoms in wetlands to obtain an impressive 125 mg/g Cr removal in Arequipa. Wetlands also provide a synergy in promising phytoremediation technologies, as highlighted earlier, along with additional biogeochemical processes that could reduce and bind soluble Cr in sediments. However, while wetlands show promise to remove Cr, further studies are needed to understand the fate and bioavailability of Cr complexes and species once sequestered in wetland systems and how to best manage sequestration to limit long-term environmental liabilities.

## 4. Conclusions and Recommendations

As Cr pollution from tannery wastewater is a problem in the Arequipa Region of southern Peru, this place-based synthesis represents an important contribution to the state of the art on how to remove this dangerous metal from contaminated waters, with the purpose of having a cleaner environment and a more sustainable leather production. In this literature review, a total of 75 (70 theses and five peer-reviewed, most of them in Spanish) studies evaluating different techniques to remove Cr species from polluted tannery wastewaters were found for the Arequipa Region. The main technical approaches evaluated were adsorption (twenty-three studies), phytoremediation (eighteen studies), microbial bioremediation (thirteen studies), electrocoagulation (five studies), and a broader catch-all category, often combining multiple attenuation mechanisms, which did not cleanly fall into those other categories (fifteen studies).

Numerous studies identified in this synthesis were able to remove the majority of detectable Cr from polluted tannery wastewater. Moreover, efficient techniques explored in the region were identified and were consistent with findings elsewhere using similar materials. Promising place-based solutions included adsorption materials originated from local food waste, such as native achiote peels (*B. orellana*) and avocado seeds (*P. americana*). The use of agricultural waste, such as unprocessed adsorbents or via conversion to biochar, emerged more broadly as a promising approach for large-scale applications in the region due to local availability and rapid treatment times. However, with only 23 studies, and considering the long list of widely available local organic waste materials found by Garcia-Chevesich et al. [123], further exploration into this category toward its applicability in removing Cr from tannery wastewaters could yield further insights. Importantly, these subsequent studies should incorporate the variables needed to understand the adsorption isotherms to enable system predictions and optimization, as well as explore the costs and carbon footprints associated with their adoption.

Other locally promising technologies included phytoremediation using certain microalgae and vascular plants, and bioremediation using bacteria and fungi. At scale, bioremediation applications could be implemented using more holistic strategies that capitalize on both biotic and abiotic mechanisms such as constructed wetlands and sulfate-reducing bioreactors. Additionally, a variety of infiltration strategies employing applicable geomedia and solar distillation in this arid and sunlight-intense region could offer favorable benefits for local applications. These could be enhanced with focused investigations and benchmarks against proven technologies to help develop sustainable and locally tailored technologies to more effectively treat this point source of pollution in Arequipa. In exploring these potential technologies, additional analyses should quantify overall sustainability metrics such as cost, availability, transportation, social benefits, carbon footprint, and feasibility at larger scales.

Future investigations should also focus on collaborative efforts between research institutions and the private sector to achieve common treatment goals while also combining treatment approaches (e.g., using *I. cernua* in constructed wetlands or hybrid approaches that integrate engineered and nature-based solutions). Equally important is to highlight the need to explore the application of proven and emerging treatment technologies not tested in the region, such as chemical precipitation, ion exchange, membrane filtration, trickling filters, and nanocomposite spheres. Moreover, investigations need to better discern attenuation mechanisms, develop process-specific understanding (e.g., sorption isotherms), provide critical comparisons of effectiveness against proven technology benchmarks, and provide cost-benefit and lifecycle analyses to help prioritize feasible solutions.

Despite an abundance of societal interest and documented efforts from local scientists to remove Cr from tannery wastewaters at RSIP, it is evident that those or other initiatives have not been adopted to address ongoing, industry-sourced Cr pollution in Arequipa. This synthesis could provide inspiration for the further exploration and adoption of sustainable approaches that could be used by local authorities, policy makers, and the private sector as they develop mitigation strategies for tannery wastewater treatment that better protect human and environmental health.

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