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Research article

# Valorization of treated wastewater from the soaking of baby alpaca skin fur

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ABSTRACT

Baby alpaca fur industry generates considerable wastewater during the soaking process, which contains high levels of total suspended solids (TSSs), proteins, and salts, among other components. The valorization of wastewater after precipitation, coagulation–flocculation, and aeration treatments was evaluated for use in irrigation water, fertigation, groundwater recharge, concrete construction, and disposal. The precipitation treatment sludge and the coagulation–flocculation treatment were evaluated as a protein source, soil quality improvement, and disposal. The treatment system included evaluations of nine pH levels, seven coagulant doses, and seven aeration times. The contents of TSSs, chemical oxygen demand (COD), total Kjeldalh nitrogen (TKN), ammonia nitrogen ($N–NH_3$), and oils and fats (O&G), among other parameters, were determined in the treated and untreated wastewater. Before entering the treatment system, the physicochemical characterization of the wastewater showed a high concentration of parameters related to organic matter and dust, such as O&G, five-day biological oxygen demand ($BOD_5$), COD, TSSs, TKN, and $N–NH_3$. The optimal removal parameters were pH 12 for the chemical precipitation of proteins, a dose of 480 mg/L $FeCl_3$ as a coagulant for TSSs removal, and 150 min of aeration; removal efficiencies of 99.02 %, 77.49 %, 79.93 %, and 64.62 % for TSSs, Cod, TKN, and $N–NH_3$, respectively, were obtained. The wastewater after treatment can be used for groundwater recharge and concrete construction, and the wastewater with 2 % dilution can be used for irrigation water and fertigation. The sludge after precipitation is rich in protein and can be used as a protein source or soil quality improver.

## 1. Introduction

The baby alpaca fur industry in Peru has developed in an artisanal manner. According to Alpaca Collections, the supply of alpaca skin undergoing fur processing in the fur industry in 2023 was 400,000 skins.

Alpaca skin fur processing includes ribera (soaking and fleshing), tanning, post-tanning, and finishing stages. The soaking substage comprises washing the skins with water [1,2]. Through washing, dirt is removed from the skin; rehydration is provided, and nonstructural proteins are removed [3]. Chowdhury et al. [4], reported that the soaking substage is the most polluting of the leather

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**Abbreviations**

| | |
|---|---|
| ARR | Soaking wastewater |
| ARR-T | Treated soaking wastewater |
| P-ARR | Precipitate from chemical precipitation treatment |
| S-ARR | Supernatant from chemical precipitation treatment |
| SCF-ARR | Supernatant from coagulation–flocculation treatment |
| T | Temperature |
| EC | Electric conductivity |
| TSSs | Total suspended solids |
| COD | Chemical oxygen demand |
| TKN | Total Kjeldalh nitrogen |
| $N–NH_3$ | Ammonia nitrogen |
| $BOD_5$ | Five-day biochemical oxygen demand |
| O&G | Oils and fats |
| TOC | Total organic carbon |
| C/N | Carbon to nitrogen ratio |
| $FeCl_3$ | Ferric chloride |
| KOH | Potassium hydroxide |
| HCl | Hydrochloride acid |
| SAR | Sodium absorption ratio |
| Na | Sodium |
| Ca | Calcium |
| Mg | Magnesium |
| P | Phosphorus |
| K | Potassium |
| Al | Aluminum |
| Cr | Chrome |

tanning process, corresponding to 50%–55 % of the total pollution.

The soaking wastewater (ARR) is characterized by high organic load expressed as total suspended solids (TSSs) (2100–6080 mg/L), chemical oxygen demand (COD) (6350–10560 mg $O_2$/L), five-day biochemical oxygen demand ($BOD_5$) (1200–1785 mg $O_2$/L), oils and fats (O&G) (50–334 mg/L), chlorides (5000–16559 mg/L), and nitrogenous compounds such as proteins expressed as the total Kjeldahl nitrogen (TKN) (482–1200 mg/L) [4–8] and ammonia nitrogen ($N–NH_3$) (17–206 mg/L) protein degradation products [8,9].

The high concentration of salts in the ARR makes it challenging to apply conventional biological treatments [5]. Therefore, chemical treatments, such as protein precipitation, coagulation–flocculation, and oxidation by aeration, are chosen [8,10]. The removal of proteins eliminates a large percentage of suspended solids and nitrogenous organic compounds such as TKN between 59.3% and 61.8 % [11] and $N–NH_3$ between 45% and 97 % [12], depending on the state of skin preservation [12,13]. Proteins have a wide range of isoelectric points that can take pH values from 3 to 12 [10,11,14,15]. Therefore, the protein removal treatment refers to the pH where the protein has a double electric charge (isoelectric point). These proteins tend to precipitate because there is no repulsion between the other molecules. Treatment by coagulation–flocculation of ARR removes the TSSs by removing the electrical double layer, achieving efficiencies of 74.8%–93.5 % [11,16]. The oxidative treatment by aeration removes $N–NH_3$ by oxidation and release at high pH achieving up to 92.6 % removal rates [12,17].

The valorization of treated soaking wastewater (ARR-T) includes its use in irrigation water, fertigation, groundwater recharge, and concrete construction. Simultaneously, sludge can be valorized as a protein source or soil quality improver. The water classification for irrigation considers the analysis of Na, Ca, and Mg ions, along with electrical conductivity values, which can be represented by the Wilcox diagram [18,19] as well as the comparison of related national and international standards [20–24]. Fertigation valorization includes utilizing nutrients such as proteins, amino acids, and other nitrogenous compounds that can be included in irrigation water. According to Phocaides [25], 50–200 mg/L of N, 12–60 mg/L of P, and 15–250 mg/L of K are required for different types of crops. Conversely, Wada et al. [26] suggested a TKN demand of 130 mg/L for a Lactuca sativa crop. In addition, sludge from precipitated proteins and coagulation–flocculation treatment from soaking water can be used as a protein source for formulated food [27], a soil quality improver.

The research objective was to valorize wastewater from soaking baby alpaca skins treated using chemical precipitation, coagulation–flocculation, and aeration for potential use as irrigation water, fertigation, and groundwater recharge as well as assess the valorization of sludge as a protein source for animal food or soil quality improvement.

## 2. Methodology

### 2.1. Sampling and characterization of soaking wastewater

Between September 2016 and March 2023, at a point before discharge to the sewer, six samples of ARR were taken from a fur micro-industry located south of the city of Lima in Peru that processes baby alpaca skins in an artisanal manner (five skins per week). Water quality tests were performed using the methods suggested by SMEWW-APHA-EF 23rd Ed.2017, O&G method 5520 B, 5-day $BOD_5$ method 5210 B, COD method 5220 D, TSS method 2540 D, sulfides method 4500-S2-D, N–$NH_3$ method 4500-$NH_3$-D, TKN method 4500-Norg-B, EC method 2510-B, sulfates and chlorides using EPA method 300.1 Rev 1.0, 1997, and total metals EPA method 200.8 Rev 5.4, 1994.

### 2.2. Soaking wastewater treatment

The soaking wastewater was treated using a sequence of partial treatments comprising the precipitation of solids and proteins at the isoelectric point, followed by the coagulation–flocculation treatment for removing suspended solids, and finally by an aeration treatment to remove N–$NH_3$ (Fig. 1).

#### 2.2.1. Chemical precipitation treatment

The chemical precipitation of soaking residual water (ARR) proteins as a function of the isoelectric point was evaluated at pH 2–13 [10,11,14,15] using a potentiometer (SI Analytics, Lab 850); the control was the original pH 6.8 sample. Precipitation was performed using 1 M HCl and 1 M KOH solution. After treatment, the TSSs, COD, TKN, and N–$NH_3$ parameters were analyzed in the supernatant S-ARR. S-ARR was used for the coagulation–flocculation treatment, while the P-ARR precipitate was separated using decantation and characterized.

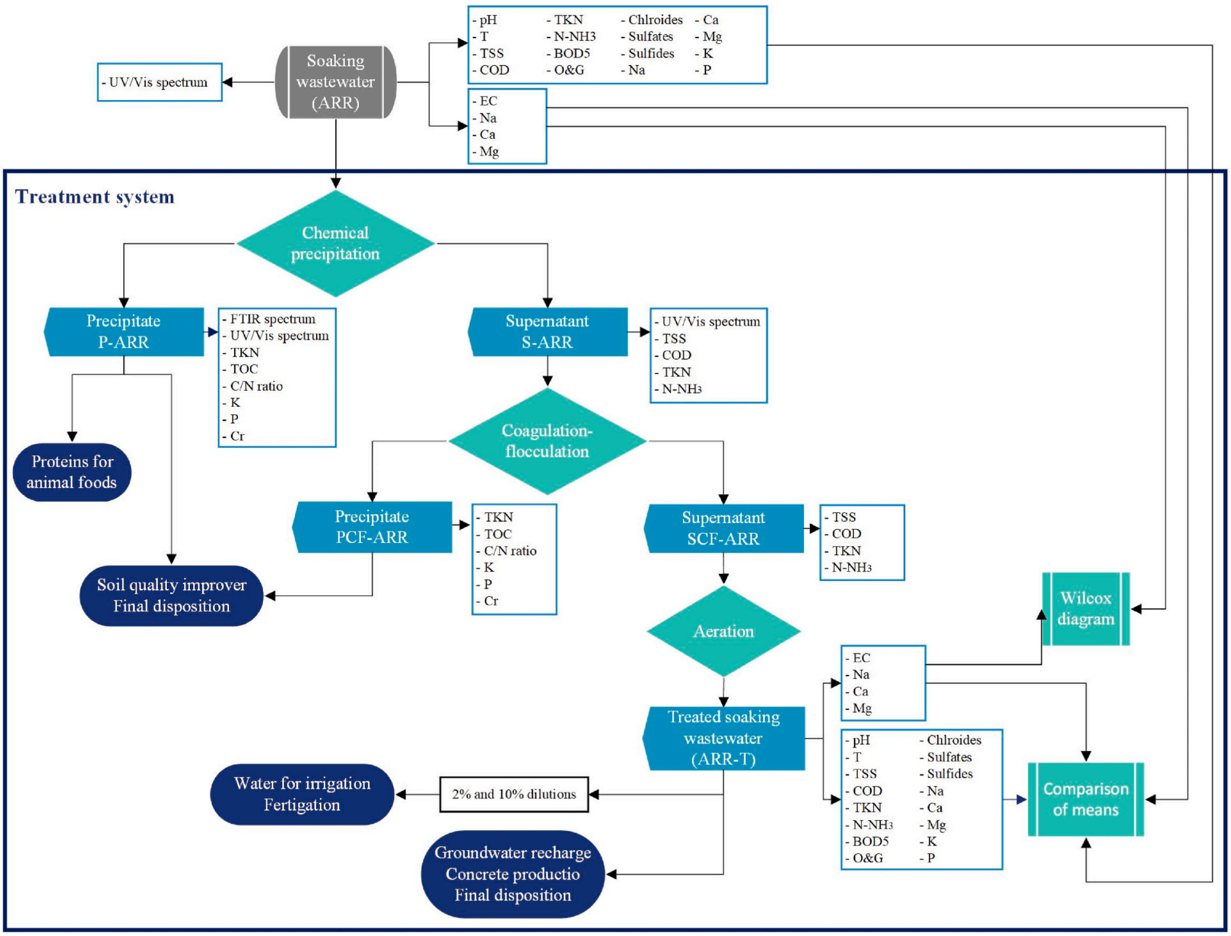


**Fig. 1.** Flowchart of the recovery of residual water from soaking baby alpaca skins.

#### *2.2.2. Coagulation–flocculation treatment*

The S-ARR was used by adjusting the pH to 7. The tests were performed in a 1 L capacity jar tester (Phipps & Bird 7790-900B) with rapid mixing at 240 rpm for 1 min and slow mixing at 50 rpm for 20 min. Doses of 0, 80, 160, 240, 320, 400, and 480 mg/L $FeCl_3$ were evaluated and allowed to settle for 30 min. The TSSs, COD, TKN, and $N–NH_3$ parameters of the SCF-ARR supernatant were analyzed to determine the treatment efficiency. SCF-ARR was used for the aeration treatment.

#### *2.2.3. Aeration treatment*

The SCF-ARR supernatant was adjusted to a pH of 11.5 to remove the dissolved $N–NH_3$ from the water [28]. In total, 5 L of wastewater from the previous treatment was placed in a 100 L capacity vessel and aerated using a 50 L lubricated Truper brand air compressor rated at 2.5 HP. The aeration tests were conducted for 25, 50, 75, 100, 125, and 150 min with an airflow of 67.7 L/min at 90 psi. The control was the wastewater from the previous treatment at pH 11.5 without aeration during the 150 min of treatment. The TSSs, COD, TKN, and $N–NH_3$ parameters of the treated soaking wastewater (ARR-T) were analyzed to determine the treatment efficiency.

### *2.3. Valorization of treated soaking wastewater and sludge*

The valorization of the ARR-T was evaluated as irrigation water, fertigation, groundwater recharge, concrete construction, and disposal. The sludge formed by the P-ARR and PFC-ARR precipitate was assessed as a protein source, soil quality improver, and disposal. The sodium absorption ratio of ARR and ARR-T was determined. The Wilcox diagram was elaborated using the electrical conductivity values to classify the water according to its salinization and its utility as irrigation water. In addition, a comparison was made with national and international standards. The TKN and $N–NH_3$ nutrient contents were compared with fertigation water. P-ARR valorization was evaluated by identifying the removed proteins by Fourier-transform infrared (FTIR, Nicolet iS10, Thermo Fisher Scientific) spectrophotometry and spectral scanning with the UV–Vis spectrophotometer (Genesys 150, Thermo Scientific) OECD 101 method. P-ARR and PCF-ARR sludge were valorized. The TKN, total organic carbon (TOC), and C/N ratio, ash, and EC were determined using the BGB1.II 292–2001 method. The P, K, and Cr levels were measured using the EPA 3050-B SW-846 METHOD EPA 6010D method.

### *2.4. Statistical analysis*

The treatment trials were conducted in triplicate. The percentage removal for each treatment is presented in a box-and-whisker plot. The normal distribution of the values was performed using the Shapiro–Wilk test. Analysis of variance was performed to determine if the treatments influenced the parameters analyzed. A Tukey's test was used to determine the significant differences between treatments and between the ionic composition and nutrients of ARR and ARR-T. XLSTAT software version 2023.2.1414 (Addinsoft, NY, USA) was used, with a significance level of 5 % in all cases.

## 3. Results and discussion

### *3.1. Physicochemical characterization*

The mean of TSSs, COD, $BOD_5$, TKN, and $N–NH_3$ parameters in the ARR (Table 1) varied widely because of the nature, origin, and conservation of the skins [8,12,29,30]. The TSSs concentration was 2533 ± 295 mg/L, which was within the range of 460–24460 mg/L for tannery wastewater in general [4,8,11,12,31], lower than the range of 3069–10800 mg/L for bovine hide soaking wastewater [4,11,29,30], lower than 11000 mg/L obtained in the liming and de-liming process [4], and lower than 24406 mg/L obtained during leather finishing [12,32]. Nevertheless, it was greater than 460 mg/L obtained in sedimentation treatment for tannery wastewater in general [33]. High TSSs values were obtained due to the soiling of hides, dust, dung, hair, and blood, which depend on the nature and quality of the hides [8,12,29,30].

The COD concentration was 8900 ± 1043 mg $O_2$/L. This value was within the range of 638–71040 mg $O_2$/L for tannery wastewater in general [4,8,11,12,31], greater than the range of 2200–7188 mg $O_2$/L, and lower than 10560 mg $O_2$/L for bovine hide soaking wastewater [4,11,29,30]. Similarly, the value obtained was lower than 25300 mg $O_2$/L from the liming and de-liming process [34], lower than 49000 mg $O_2$/L from the pickling and Cr plating process, and lower than 71040 mg $O_2$/L from the dyeing and re-tanning process [4]. Furthermore, it was greater than the range of 638–1785 mg $O_2$/L from sedimentation and biological treatment for tannery wastewater in general [33,35]. High COD values were obtained from the soiling of skin, hair, blood, and fat; the fat percentage of alpaca skin was within the range of 5.0%–12.5 % [36].

The $BOD_5$ concentration was 7839 ± 1989 mg $O_2$/L. This value was higher than the range of 205–5240 mg $O_2$/L for tannery wastewater in general [4,8,11,12,31] and greater than the range of 908–1700 mg $O_2$/L for bovine hide soaking wastewater [4,11,31], when the content of oils and fats was between 225 and 324 mg $O_2$/L [11]. In addition, it was greater than the range of 1625–1710 mg $O_2$/L from the liming and de-liming process [31], greater than 2400 mg $O_2$/L from the dyeing and re-tanning process, greater than 1900 mg $O_2$/L from the oiling and storing process [4], and lower than 10850 mg $O_2$/L from the liming process [34]. In addition, it was higher than the range of 205–732 mg/L with sedimentation or equalization treatment for tannery wastewater in general [35,37]. The $BOD_5$ concentration was greater than those reported in other studies because of the greater fat concentration in alpaca skins [36], dirt in the skins (soil and manure), and proteins.

**Table 1**

Nutrient and ion concentrations of soakaway wastewater (ARR), treated soakaway wastewater (ARR-T), and 2 % diluted treated soakaway wastewater (ARR-T D2%). Data are presented using mean ± standard deviation format, based on three replicates.

| | Parameters | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | pH | T (°C) | EC (μS/cm) | TSSs (mg/L) | COD ($mgO_2/L$) | TKN (mg/L) | $N–NH_3$ (mg/L) | $BOD_5$ ($mgO_2/L$) | O&G (mg/L) | Chlorides (mg/L) | Sulfates (mg/L) | Sulfides (mg/L) | Na (mg/L) | Ca (mg/L) | Mg (mg/L) | K (mg/L) | P (mg/L) |
| ARR | 6.78 ± 0.08[b] | 24.2 ± 0.5[b] | 5775 ± 135[b] | 2533 ± 295[a] | 8900.1 ± 1043.2[a] | 171.9 ± 21.9[a] | 79.7 ± 11.7[a] | 7838.5 ± 1988.5[a] | 1837.5 ± 137.5[a] | 212 ± 56[b] | 220.6 ± 46.4[a] | 1.53 ± 1.18[a] | 1442.5 ± 298.5[a] | 149.5 ± 29.9[a] | 18.3 ± 4.9[a] | 45.9 ± 29.1[b] | <0.055[a] |
| ARR-T | 8.49 ± 0.12[a] | 25.6 ± 0.6[a] | 7225 ± 15[a] | 24.9 ± 4.4[b] | 2003.5 ± 95.5[b] | 34.5 ± 8.5[b] | 28.2 ± 6.2[b] | 1071 ± 121[b] | 98.9 ± 1.2[b] | 746.5 ± 23.5[a] | 0.5 ± 0.0[b] | 0.28 ± 0.22[a] | 777.4 ± 217.4[b] | 24.4 ± 0.85[b] | 2.1 ± 0.2[b] | 718.1 ± 5.5[a] | <0.055[a] |
| ARR-T D2% | – | – | 144.5 | 0.498 | 40.07 | 0.69 | 0.564 | 21.42 | 1.978 | 14.93 | 0.01 | 0.0056 | 15.548 | 0.488 | 0.042 | 14.362 | <0.055 |
| Sewage discharge[c] | 6 a 9 | <35 | – | 500 | 1000 | – | 80 | 500 | 100 | – | 1000 | 5 | – | – | – | – | – |
| Discharge to water body[d] | 5 a 9 | <40 | – | – | – | – | 20 | – | 50 | – | – | – | – | – | – | – | – |
| Vegetable irrigation[e] | 6.5–8.5 | – | 2500 | – | 40 | – | – | 15 | 5 | 500 | 1000 | – | – | – | – | – | – |
| No restriction[f] | 6.5–8.4 | – | 700 | – | – | – | – | – | – | <142 | – | – | – | – | – | – | – |
| Moderate restriction[f] | 6.5–8.4 | – | 700–3000 | – | – | – | – | – | – | 142–355 | – | – | – | – | – | – | – |
| Severe restriction[f] | 6.5–8.4 | – | > 3000 | – | – | – | – | – | – | > 355 | – | – | – | – | – | – | – |
| Ornamental irrigation[g] | – | – | – | ≤140 | – | – | – | ≤240 | – | – | – | – | – | – | – | – | – |
| Irrigation of uncooked vegetables[g] | – | – | – | ≤20 | – | – | – | ≤20 | – | – | – | – | – | – | – | – | – |
| Cleaning of toilets[g] | – | – | – | ≤10 | – | – | – | ≤10 | – | – | – | – | – | – | – | – | – |
| Discharge to water bodies[h] | 6.0–9.0 | – | – | – | 150 | 70 | – | 60 | 8 | 350 | 300 | – | 200 | 200 | 60 | – | 15 |
| Groundwater recharge[h] | 6.0–9.0 | – | – | – | 50 | 45 | 5 | 15 | – | 350 | 300 | – | 200 | 200 | 60 | – | 15 |

[a,b] Different letters of the same parameter imply statistically significant differences ($p < 0.05$) as determined by Tukey's test.
[c]D.S. 010-2009-VIVIENDA [23].
[d]CONAMA 430 [24].
[e]D.S. 004-2017-MINAM [20].
[f]FAO [21].
[g]WHO-EM/CEH/106/E [22].
[h]JS: 893/2002 [67].

The TKN concentration was 171.9 ± 21.9 mg/L, which was lower than the range of 2701–388.6 mg/L for tannery wastewater in general [11,12]. This result was lower than 270–388.6 mg/L for cowhide soaking wastewater [11,29] and greater than the range of 31.18–115.7 mg/L from the liming, de-liming, and tanning processes [9]. In addition, the result was greater than the range of 110–115 mg/L with sedimentation and activated sludge treatment for tannery wastewater in general [33,38]. This concentration was attributed to the protein content present in blood and meat debris [39].

The N–$NH_3$ concentration was 79.7 ± 11.7 mg/L, which was within the range of 6.8–923 mg/L for tannery wastewater in general [8,12]. This result was lower than the range of 84.7–150 mg/L for bovine hide soaking wastewater [11,29] and greater than the range of 16.80–68.75 mg/L from the liming, de-liming and tanning processes [9]. Furthermore, it was lower than 85–223.4 mg/L with sedimentation treatment for tannery wastewater in general [33,40] and much lower than 923 mg/L for supernatant from a settling tank [41] but greater than 6.8 mg/L in an effluent did not include the hair removal process [42]. Skins provide a low N–$NH_3$ content when they are well-preserved [13]. In contrast, the presence of weevils and skin decomposition due to bacteria occurs when there are problems with the preservation of alpaca skins. These bacteria produce bacterial enzymes that break down collagen proteins into amino acids. Simultaneously, these enzymes fractionate amino acids into amines, organic acids, alcohols, and carbohydrates. Bacterial enzymes continue the decomposition process by attacking the amines to finally break them down into hydrogen, carbon dioxide, and ammonia [43]. This also occurs when wastewater is stored for treatment by sedimentation or some other process. Another factor was the use of bactericides, as stated by Wang et al. [13].

The O&G concentration was 1837.5 ± 137.5 mg/L, which is greater than the range of 11.4–780 mg/L for tannery wastewater in general [8,11]. This result was greater than the range of 224.5–323.4 mg/L for beef hide soaking wastewater [11], greater than 185 mg/L from liming process [34], greater than 11.4 mg/L with sedimentation treatment for general tanning wastewater [44], and greater than 334–780 mg/L for general tanning wastewater for cattle and swine [45,46]. The differences could be attributed to variations in the fat content of the hides used in different studies. Naffa et al. [36] reported a 5.0%–12.5 % fat content in alpaca skin, while Rasulova [47] reported that cattle skins typically contain 3%–10 % fat [36]. In that sense, the fat content of the skin influences the O&G concentration in the residual soaking water.

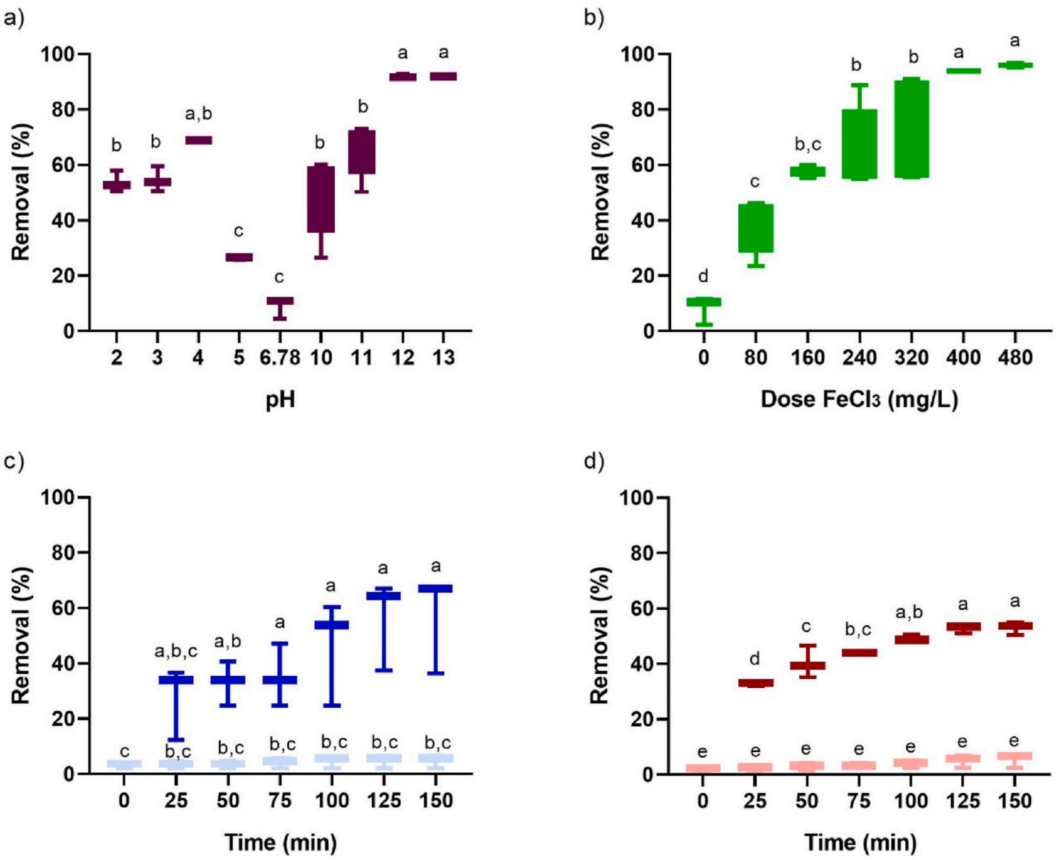


**Fig. 2.** Removal percentage of a) Total suspended solids (TSSs) as a function of pH, b) TSSs as a function of the $FeCl_3$ dose, c) Total Kjeldahl nitrogen as a function of aeration times, and d) Ammonia nitrogen as a function of aeration times.

### 3.2. Treatment system

#### 3.2.1. Chemical precipitation treatment

Owing to the high TKN concentration in the ARR, protein precipitation was performed at its isoelectric point by indirectly measuring the TSSs content in the S-ARR supernatant. The TSSs removal percentages ranged from 8.87 % ± 3.66 % at pH 6.78 (control) to 92.13 % ± 0.75 % at pH 12 (Fig. 2a). The mean TSSs removal percentage at pH 12 was considerably greater than the treatments at different pH, including the control, except at pH 4 y 13, and was within the range of 70.5%–81.3 % at pH 10 with NaOH [11]. Conversely, the percentage of TSSs removal was greater than the range of 39%–67 % at pH 5.5 obtained by electrocoagulation treatment [37], and greater than 68 % at pH 3 by photo-Fenton-electrocoagulation [32], and greater than 76.1 % by sedimentation [8] but lower than 96 % of pH 7–9 by electrocoagulation [37,46], lower than 98 % by ozone-activated sludge, lower than 92 % by SBR treatment for 5 days, and lower than 97 % by coagulation–flocculation with alumina and cationic polymer [8,16,29]. The COD removal was 25.10 % ± 0.28 % with the treatment at pH 12. This value was lower than 50 % when using lime, lower than 59.4 % with $Ca(OH)_2$ at pH ≥ 10 for general tanning process wastewater, lower than 60.99 % with commercial lime at pH 9 for general tanning process wastewater, lower than 43.20 % with KOH, and lower than 52.36 % at pH 10 with NaOH [11,48]. Moreover, the results obtained were lower than the range of 40%–97.9 % obtained using the electrocoagulation treatment [30,32,34,37,46,49] and lower than the range of 40%–99 % by the activated sludge biological treatment, membrane bioreactor or SBR [5,8,12,29,38,41,42]; the results were also lower than 93.5 % by coagulation–flocculation with alumina and cationic polymer, but greater than 20 % by treatment by ozonation for 30 min [33]. The differences in removal were attributed to the characteristics of the soaking wastewater that presented high COD and chloride concentrations. Treatment by precipitation at the protein isoelectric point was aimed at separating the proteins and being able to reuse them; COD removal was complimentary. TKN removal was 29.33 % ± 1.34 %, which is similar to 26.42 % reported by Castañeda et al. [11], achieving protein precipitation at its isoelectric point because the amino acid functional groups (carboxylic and amino) were ionized, thus forming an internal salt. This result was lower than the range of 36%–96 % obtained by the membrane bioreactor and biological treatments [12,29,41], where protein oxidation was observed and lower than 62 % at pH 7–9 and 95.7 % at pH 10 by electrocoagulation [30,46], where higher removal was observed at higher pH via the precipitation of proteins near the isoelectric point. By contrast, it was higher than the 1.4%–9.6 % range obtained with wetlands by nitrogen assimilation in plants [50]. N–$NH_3$ removal with KOH was 7.78 % ± 3.20 %, which was lower than 28.33 % with lime reported by Castañeda et al. [11]. This difference was attributed to the poor solubility of lime, which is a weaker base than KOH, thus reducing the degradation of free amino acids [51]. The result was lower than the range of 45.6%–92.0 % by the activated sludge treatment with and without subsequent oxidation or membrane bioreactor [8,12,38] as well as by electrocoagulation (43.1 %) [49] because a higher level of N–$NH_3$ oxidation to oxidized species occurs with these treatments.

#### 3.2.2. Coagulation–flocculation treatment

TSSs coagulation and flocculation were performed because of the high TSSs concentration in the S-ARR supernatant. The effectiveness of two coagulants $Al_2(SO_4)_3$ and $FeCl_3$ with a dose of 80 mg/mL for both was compared, obtaining TSSs removal of 42.69 % ± 1.49 %, and 39.47 % ± 10.77 %, respectively, without finding differences between the two coagulants. Therefore, $FeCl_3$ was used because of its lower toxicity than $Al_2(SO_4)_3$. The sludge formed after treatment with $Al_2(SO_4)_3$ is classified as hazardous because it contaminates water bodies, affecting the physical and chemical properties of aquatic ecosystems. In addition, it adversely affects the life cycle of different aquatic species, contributes to water acidification, and affects soil quality and fertility. Furthermore, it irritates mucous membranes such as the eyes and respiratory tract because of the particle size of ≤2.5 μm of the sludge generated with $Al_2(SO_4)_3$ [52].

TSSs removal ranged from 8.12 % ± 5.09 %–96.05 % ± 0.58 % with doses of 0 (control) and 480 mg/L $FeCl_3$, respectively (Fig. 2b), after applying the coagulation–flocculation treatment. All treatments were considerably higher than the control (0 mg/L $FeCl_3$). TSSs removal at a dose of 480 mg/L $FeCl_3$ was considerably higher than at 80 mg/L $FeCl_3$, which was similar to that reported by Castañeda et al. [11] (96.8 % with $Al_2(SO_4)_3$) and higher than the values reported by Song et al. [53] (25%–45 % with $FeCl_3$). TSSs removal obtained with $FeCl_3$ was higher than the range of 39%–68 % at pH 3–5.5 by electrocoagulation treatment [32,37], higher than 76.1 % by sedimentation [8], and similar to 96 % at pH 7–9 by electrocoagulation [37,46] or 97 % by coagulation–flocculation with alumina and a cationic polymer [16]. The COD removal was 43.32 % ± 0.08 % under the same coagulant dosage and within the 40%–70 % range with 100–2000 mg/L $FeCl_3$ reported by Lofrano et al. [54]. Hence, a high Cl ions concentration positively influences the COD removal efficiency. This removal rate was within the range of 40%–68 % by electrocoagulation treatment [37,49] when having large amounts of Cl ions, lower than the 91.5%–97.9 % range at high pH with additional oxidation by electrocoagulation [30,32,46], and lower than 93.5 % by coagulation–flocculation with alumina and a cationic polymer [16]. Oxidative processes, such as electro-persulfate and electro-Fenton [55], showed better yields in COD reduction but required longer treatment times. This is not very convenient for an artisanal baby alpaca skin tanning system because of the type of infrastructure and the level of sophistication required.

TKN removal was 28.30 % ± 0.95 % due to the release of ammonia and protein precipitation. This result was lower than the 62%–95.7 % range by electrocoagulation [30,46], where higher removal was observed at a higher pH because of the precipitation of proteins near the isoelectric point. N–$NH_3$ removal was 10.97 % ± 0.65 % due to its release as gas. This result was lower than 43.1 % by an electrocoagulation treatment [49] because of the higher oxidation of N–$NH_3$ to oxidized species.

#### 3.2.3. Aeration treatment

Aeration was performed on the SCF-ARR supernatant because of the high concentration of remaining N–$NH_3$. After applying the aeration treatment, the TSSs content increased slightly, yielding values of 7.10 % ± 3.75 % because of the transformation of water-soluble substances to insoluble forms [56], such as the formation of sulfates that precipitate due to decreasing sulfide content by oxidation (2.7–0.052 mg/L). TKN removal was 56.90 % ± 17.67 % with 150 min of aeration and was significantly higher than the 150 min without aeration control (4.80 % ± 2.46 %) (Fig. 2c), similar to that obtained by Cotman and ZagorcKončan [57] of 43.33 % with 24 h of aeration and an airflow of 120 L/h. Ammonia release and the oxidation of nitrogenous organic matter influenced total nitrogen removal. The TKN result was lower than the 84%–96 % range by membrane and biological bioreactor treatments [12,29], where protein oxidation is favored, and lower than 62%–95.7 % by electrocoagulation [30,46] by protein precipitation. By contrast, it was higher than the 1.4%–9.6 % range by wetlands [50] through nitrogen assimilation in plants.

The N–$NH_3$ removal percentages ranged from 9.76 % ± 7.13 %–53.02 % ± 2.33 % with 0 min and 150 min of aeration, respectively (Fig. 3d). All treatments were considerably higher than their respective controls, without aeration. The N–$NH_3$ removal percentage obtained at 150 min (53.02 %) was significantly higher than the other treatments of 25, 50, and 75 min and higher than that reported by Castañeda et al. [11] (50.6 % during 4 h of aeration). Furthermore, the ammonia range obtained was 27.7%–84.3 %, as reported by Segatto et al. [58]. Increasing the pH to 10.8–11.5 induces equilibrium between ammonia and ammonium ions, forming aqueous ammonia. During ammonia stripping, this aqueous ammonia is converted to gas and released with the injected air [59]. The efficiencies declined below pH 11 and showed no significant increase beyond pH 11.5 during ammonia stripping [58]. The N–$NH_3$ result obtained at 150 min was higher than 43.1 % by electrocoagulation [49] but lower than the range of 92%–95.6 % by biological N–$NH_3$ oxidation treatments [8,38].

COD removal was 44.8 % ± 9.86 %, which was lower than the value reported by Kothiyal et al. of 82.58 % [60], with 7 h of pure oxygen injection at a rate of 0.5 L/min and $MnSO_4$ at 98 %. COD removal was attributed to the oxidation of organic matter, the removal of sulfides, and the removal of N–$NH_3$ as gaseous ammonia.

### 3.2.4. Integrated treatment system

The proposed treatment system achieved high removal efficiencies of 99.02 % TSSs, 77.49 % COD, 79.93 % TKN, and 64.62 % N–$NH_3$. Table 1 lists the concentrations of nutrients and ions in the soaking wastewater before and after treatment. The TKN, TSSs, COD, and O&G content decreased due to the precipitation of proteins and the saponification of fats at pH 12, which were also removed in the flocculation of polymeric extracellular substances [11,27]. A significant increase in the electrical conductivity and K and Cl ion contents was also observed because KOH was used in the chemical precipitation treatment and $FeCl_3$ in coagulation–flocculation; this increase in salts must be removed before protein reuse. In addition, Ca and Mg ion concentrations decreased because of the formation of insoluble substances such as $Mg(OH)_2$ and $CaCO_3$ at pH 12 [61]. The sulfide concentrations decreased because of the oxidation of sulfides to thiosulfate, sulfite, and sulfates [62].

The protein precipitation treatment at the isoelectric point, coagulation–flocculation, and aeration involve operating costs of energy consumption for agitation of the precipitation tank, coagulation–flocculation tank, and aeration compressor. They also involve the consumption of reagents, such as $FeCl_3$ and KOH, which would have an operating cost of \$2.72 per $m^3$ of treated wastewater. This cost was much higher than \$0.07 per $m^3$ when using $Al_2(SO_4)_3$ with cationic polymer [16], higher than \$0.34–\$2.09 per $m^3$ when performing electrocoagulation with low COD effluent [32,46], but lower than \$3.96 per $m^3$ when using electrocoagulation processes with high COD wastewater [44], and lower than \$18.02–\$64.13 $m^3$ in oxidative Fenton or ElectroFenton type processes [32,44].

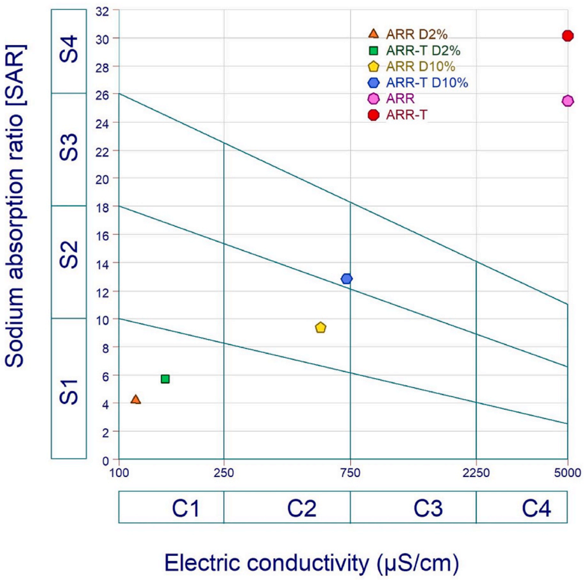


**Fig. 3.** Wilcox diagram of soaking wastewater (ARR) diluted to 10 % (ARR D10 %) and 2 % (ARR D2%), and treated soaking wastewater (ARR-T), diluted to 10 % (ARR-T D10 %) and 2 % (ARR-T D2%).

Considering that the process of soaking and obtaining baby alpaca skin is of an artisanal level, the simplicity of the proposed methodology makes its implementation feasible in fur production plants.

The industrial scale-up of the proposed treatment system should consider that the average daily production is 100 baby alpaca skins, with water consumption of 5–7 L per skin in the soaking process, indicating a maximum generation of soaking residual water (ARR) of 0.7 $m^3$/day. This amount of wastewater can be treated on the industrial level using three settling tanks for the precipitation and coagulation–flocculation treatment, and one DAF tank for aeration and ammonia removal, with a capacity of 2 $m^3$ for each tank. The reagent dosing, agitation, and aeration systems must be controlled manually to adjust the required parameters. The tanks used should be connected to an ARR-T storage tank via a piping and pumping system for delivery to the operators in charge of irrigating green areas.

### 3.3. Valorization of treated soaking wastewater and sludge

The valorization of soaking wastewater and sludge was evaluated using a treatment system (Fig. 1). The wastewater after the ARR-T treatment was evaluated for irrigation water, fertigation, groundwater recharge, and concrete construction. The sludge generated after the chemical precipitation treatment (P-ARR precipitate) and coagulation–flocculation treatment (PCF-ARR) were evaluated as a soil quality improver and a protein source for animal feed.

#### 3.3.1. Water for irrigation and other applications

ARR and ARR-T with their respective 10 % (D10 %) and 2 % (D2%) dilutions were evaluated for irrigation water. As shown in the Wilcox diagram (Fig. 3), ARR and ARR-T showed increased values of electrical conductivity (5775 and 7255 μS/cm, respectively), Na (1442.5 and 777.4 mg/L, respectively), Ca (149.5 and 24.4 mg/L, respectively), and Mg (18.3 and 2.1 mg/L, respectively) (Table 1). Therefore, they are classified as C4S4 water of poor quality, while ARR (D10 %) is classified as C2S2 of good quality in terms of the ionic content; however, its organic load as the COD is very high, and ARR-T (D10 %) is classified as C2S3 of medium quality. Conversely, ARR (D2%) and ARR-T (D2%) are classified as C1S1 water of very good quality [63].

The ARR-T (D2%) complies with water quality conditions for irrigation when compared with ECA Category 2, and water for irrigation according to D.S. 004-2017-MINAM [20] complies with irrigation without FAO [21] restrictions and ornamental plant irrigation according to the WHO [22]. In addition, because no Cr is used in the soaking process, it does not represent a risk, being long-term stable and safe use in irrigation activities. Although ARR-T presents some parameters that do not comply with international and national standards, the use of ARR-T (D2%), as determined in the Wilcox diagram (Fig. 3), is a viable solution for irrigation use and

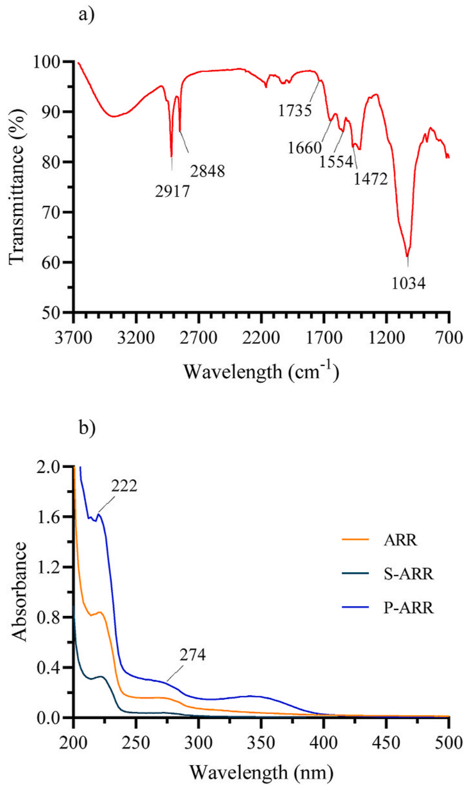


**Fig. 4.** a) FTIR spectrum of the P-ARR precipitate obtained after a chemical precipitation treatment, and b) UV–Vis spectral scanning of the soaking residual water (ARR), S-ARR supernatant, and P-ARR precipitate after a chemical precipitation treatment.

reuse, being sustainable over time. Nevertheless, the salt should be removed manually before applying the treatment system to comply with stricter regulations.

The reuse of ARR-T (D2%) for irrigation helps reduce the demand for drinking water and freshwater sources, which is important in areas of water scarcity [64]. This treated water provides a steady source for crop irrigation [65], even during predicted drought periods [66]. Some potential risks exist because of insufficient nutrients and possible long-term accumulation of contaminants. For this, a continuous monitoring system of water and soil quality, and complementary agricultural practices is recommended to ensure sustainable and efficient management.

The ARR-T exceeds the COD, $BOD_5$, O&G, Cl, Na, and Ca parameters of the maximum allowable values established for the discharge of nondomestic wastewater into the sanitary sewer system (D.S. 010-2009-VIVIENDA) [23], and values established for discharge into water bodies of CONAMA Resolution No. 430 [24] and the Jordanian Standard (JS: 893/2002) [67]. In addition, it exceeds the values of COD, $N–NH_3$, $BOD_5$, Cl, and Na for groundwater recharge according to the Jordanian Standard (JS: 893/2002). Hence, its discharge represents a considerable risk (Table 1).

However, ARR-T can be used in concrete construction that consumes a substantial amount of water, which increases the setting time of the cement paste and the compressive strength without affecting the rheological properties of the fresh concrete or the mechanical properties of the hardened concrete [68].

### 3.3.2. Water for fertigation

The ARR-T, when diluted to 10 % (ARR-T D10 %), can be used in fertigation because its N (3.45 mg/L) and K (71.8 mg/L) contributions meet the requirements for the adequate fertilization of plants with a range for N and K of 50–200 mg/L and 15–250 mg/L, respectively [25]. In addition, it presents an electrical conductivity of 725.5 μS/cm, which is adequate (<2500 μS/cm). However, Al, As, Cd, Cr, Cu, Ni, Pb, and Zn were not detected.

### 3.3.3. Sludge valorization

Sludge can be valorized by the content of the proteins recovered from precipitation ARR (P-ARR) primarily comprising collagen, keratins, histones, and others, as observed in the FTIR spectrum (Fig. 4a). The absorption at 3416 $cm^{-1}$ corresponds to the N–H stretching vibration, and the peaks at 2917 and 2848 $cm^{-1}$ were assigned to the methyl and methylene stretching vibrations, respectively. The following peaks were also observed: 1735 $cm^{-1}$ for the residual C=O bond; 1660 $cm^{-1}$ for the amide I group of C=O and N–N stretching vibrations; 1554 $cm^{-1}$ to the amide II group of N–H, C–N, and C–C stretching vibrations; 1472 $cm^{-1}$ to the C–H bending vibration; and 1034 $cm^{-1}$ to the C–O stretching vibration [69]. The spectrum was similar to that reported by de Campos et al. [70] for histones, highly positively charged proteins rich in histidine, lysine, and arginine, with a high isoelectric point found in blood [71].

In the spectra of the ARR, S-ARR, and P-ARR samples, the peaks at 222 nm (Fig. 4b) corresponding to the $\pi \rightarrow \pi^*$ transitions of the aromatic ring of the phenolic group and at 274 nm corresponding to the formation of the hydrogen bridge with the tyrosine hydroxyls of the proteins [72,73] are observed. The protein content in the P-ARR precipitate was higher than that found in the ARR and S-ARR supernatant; which can be reused for animal feed.

The TKN content in the P-ARR precipitate was 2.4 % ± 0.002 %, which was higher than that reported by Chowdhury et al. [4] (0.0022 %) and similar to that reported by Castañeda et al. [11] (2.3%–3.1 %) for tannery soaking process effluents. This difference was because alpaca skin with higher fat contents was used. The TOC content in the sample was 28.3 % ± 0.02 %, which provided a C/N ratio of 12.3 ± 0.006, confirming the presence of nitrogenous organic compounds such as proteins. The C/N ratio of P-ARR is considered stable because it is between 10 and 25 [74,75]. Hence, its application in the crop field will be beneficial as an organic source of nutrients and soil improvers due to the more than 60 % increase in humic substance content [76]. In addition, it will not emit greenhouse gases. Therefore, the impact of sludge use in agriculture is positively significant. In addition, the P-ARR sludge does not contain toxic metallic elements, such as Cr or Al, because only the pH of the solution was increased with KOH (Table 2).

The sludge from the coagulation–flocculation treatment PCF-ARR showed a high C/N ratio of 43.2, but it must be stabilized using a

**Table 2**
Nutrient and ion concentrations in precipitation treatment sludge (P-ARR) and coagulation–flocculation treatment sludge (PCF-ARR). Data are presented using mean ± standard deviation format, based on three replicates.

| Parameters | P-ARR | PCF-ARR | Stabilized biosolid[c] | Compost[d] | General waste[e] |
|---|---|---|---|---|---|
| TOC (%) | 28.30 ± 0.02[a] | 15.00 ± 0.03[b] | 30 (Organic matter 60 %) | – | – |
| TNK (%) | 2.40 ± 0.002[a] | 0.35 ± 0.01[b] | – | 0.3–1.5 | – |
| C/N ratio | 12.30 ± 0.006[b] | 43.20 ± 0.008[a] | – | 10.0–25.0 | – |
| Ash (%) | 51.43 ± 1.50[b] | 74.03 ± 1.45[a] | – | | – |
| EC (dS/m) | 4.50 ± 0.06[b] | 4.67 ± 0.04[a] | – | 5 | – |
| P (%) | 0.90 ± 0.03[a] | 0.16 ± 0.03[b] | – | 0.4–1.0 | – |
| K (%) | 0.42 ± 0.09[b] | 1.17 ± 0.09[a] | – | 0.6–1.5 | – |
| Cr (mg/kg) | <0.05[a] | <0.05[a] | 1200 | 100 | 4000 (Cr VI) |

[a,b] Different letters of the same parameter imply statistically significant differences ($p < 0.05$) as determined by Tukey's test.
[c]D.S. 015–2017 VIVIENDA [78].
[d]NTP-201.207.2020 FERTILIZANTES [79].
[e]NSWEPA [77].

composting-type process. In this way, the C/N ratio will be lower than 20. Therefore, it can be used as a source of nutrients and soil improvers. An important limitation in the use of sludge is its high salt content expressed as its ash content between 51.43 % ± 1.50 % and 74.03 % ± 1.45 % of P-ARR and PCF-ARR sludge, respectively (Table 2), which is represented mainly by Cl ions that could salinize soils.

The sludge generated from the coagulation–flocculation treatment (PCF-ARR) and from chemical precipitation (rich in protein) (P-ARR) are classified as general waste according to NSWEPA [77] because they do not present detectable levels of metals, thereby meeting the criteria of the established pollutant threshold parameters (CT1). Both types of sludge also meet the toxicity and sanitization parameters of D.S. 015-2017-VIVIENDA [78], allowing their reuse for agricultural purposes. Coagulation–flocculation sludge must be stabilized by composting before use. In this way, the sludge obtained after the treatments can be applied safely to the soil, complying with WHO [22] parameters. Thus, the sludge can be applied directly to the soil to enrich it, or safely disposed of in a sanitary landfill.

## 4. Conclusions

The ARR showed high concentrations of the parameters related to organic matter from alpaca skin and dust impregnated in the skin and fiber. The TSSs, COD, $BOD_5$, TKN, $N–NH_3$, and O&G levels in ARR were 2533 mg/L, 8900 mg $O_2$/L, 7838 mg $O_2$/L, 172 mg/L, 79.7 mg/L, and 1838 mg/L, respectively. These levels were considerably higher than those found in ARR-T when chemical precipitation, coagulation–flocculation, and aeration treatments were applied. The optimal protein precipitation was obtained at pH 12, a coagulant dose of 480 mg/L $FeCl_3$, and an aeration time of 150 min. The proposed treatment system achieved high removal efficiencies of 99.02 % TSSs, 77.49 % COD, 79.93 % TKN, and 64.62 % $N–NH_3$. The treated soakaway wastewater (ARR-T) can be valorized for irrigation with a good to moderate quality when diluted to 2 %, while the P-ARR precipitate obtained after chemical treatment, containing nitrogen from a protein origin, can be reused in the production of animal feed and as a soil quality improver.

## Data availability statement

Data will be made available on request.

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## CRediT authorship contribution statement

**Jacqueline Jannet Dioses Morales:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Lena Asunción Téllez Monzón:** Supervision, Methodology, Investigation. **Rodolfo Linares Nieto:** Resources, Project administration, Funding acquisition. **Paola Jorge-Montalvo:** Writing – review & editing, Writing – original draft, Software, Investigation. **Lizardo Visitación-Figueroa:** Writing – review & editing, Writing – original draft, Methodology, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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