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Cattle Wastewater Treatment by Almond Hull and Cherry Pit Coagulation-Flocculation Process †

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Abstract: Cattle wastewater (CW) is a potential source of several environmental problems. The high pollutant load of CW and the lack of adequate treatments contribute to the entrance of different contaminants into the ecosystems. In this work, CW was treated by a coagulation-flocculation (CF) process. This work aimed to optimise the CF process with the application of almond hull (AH) and cherry pit (CP) as coagulants to treat CW. The results showed that it was possible to achieve a chemical oxygen demand (COD), turbidity and total suspended solids (TSS) removal of 39.1, 38.3 and 52.9%, respectively, for AH (pH 3.0 and 0.1 g/L) and 42.4, 88.8 and 22.3%, respectively, for CP (pH 3.0 and 0.1 g/L). It can be concluded that treating CW via the CF process with the application of AH and CP as coagulants is a sustainable and clean process. Also, the valorisation of food by-products through wastewater treatment is effective in promoting sustainable cattle production.

Keywords: livestock wastewater treatment; by-products; sustainable production.

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1. Introduction

The livestock industry has been increasing globally. Despite being an important protein source for many communities, the lack of a sustainable management system causes a significant environmental impact. Cattle wastewater (CW) is characterized by high organic matter, suspended solids, faecal coliforms, different drugs (antibiotics, parasiticides and steroid hormones) and nutrients. The lack of proper CW treatment represents several environmental issues including depletion of dissolved oxygen, increase of turbidity and suspended solids [1]. Therefore, the application of an adequate treatment process is important to ensure adequate discharge into the environment.

The coagulation-flocculation (CF) process is widely used for the treatment of different wastewater, including CW. This treatment consists of removing the colloidal material, such as suspended solids and organic material that causes the intense colour and turbidity of CW [2]. Different chemical coagulants proved to be effective, such as aluminium sulphate, ferric chloride and ferric sulphate. However, previous studies have demonstrated the possible negative effects on human health when exposed to these substances for a long period of time [3]. The sludge produced during the CF process and its disposal in regular landfills or reuse for agricultural activities may be a possible pathway for chemical coagulants to enter ecosystems [4]. Plant-based coagulants have emerged as a solution to this ecological issue. Previous studies have demonstrated the ability of plant-based coagulants to achieve significant results in wastewater treatment [5]. Thus, the aim of this work is to optimise the CF process using almond hull (AH) and cherry pit (CP) as coagulants to treat CW. The influence of pH and coagulant concentrations is studied in the removal of chemical oxygen demand (COD), total suspended solids (TSS) and turbidity. The utilization of plant-based coagulants may represent a future alternative towards sustainable wastewater treatment. Moreover, its application during the CF process allows the valorisation of almond and cherry by-products.

2. Material and Methods

2.1. Cattle wastewater sampling

The cattle wastewater (CW) was collected from a cowshed located in the Douro region, North of Portugal. The samples were stored in plastic containers, transported to the laboratory and kept at - 40°C until used.

2.2. Analytical techniques

Different physical-chemical parameters were determined to characterise the CW, such as turbidity, total suspended solids (TSS), chemical oxygen demand (COD), biochemical oxygen demand (BOD_5) and biodegradability (BOD_5/COD). The characteristics of CW are described in Table 1.

Table 1. Cattle wastewater characterisation.

Parameters	Value
pH	7.7 ± 0.1
Electrical conductivity (μS/cm)	103 ± 5
Turbidity (NTU)	7207 ± 17
Total suspended solids – TSS (mg/L)	6930 ± 78
Chemical oxygen demand – COD (mg O_2/L)	21 178 ± 25
Biochemical oxygen demand – BOD_5 (mg O_2/L)	4929 ± 103
Nitrates (ppm)	2876 ± 75
Phosphate (mg P_2O_5/L)	2956 ± 34
Biodegradability – BOD_5/COD	0.23

2.3. Coagulants preparation and characterisation

Almond (*Prunus dulcis*) and cherry (*Prunus avium*) were chosen as plant-based coagulants due to their intensive production and generation of by-products in the Douro region, north of Portugal. The samples were obtained directly from producers located in this region and transported to the laboratory. The hull from the almond and the pit from the cherry were washed and dried in an oven at 70°C for 24 h. Each natural coagulant was ground into powder using a groundnut miller, left to cool and stored in a tightly closed plastic jar.

The Fourier-transform infrared spectroscopy (FTIR) spectra of the almond hull (AH) and cherry pit (CP) coagulants were obtained through the mixing of coagulant powder with KBr as previously described by Jorge *et al.* (2023) [6]. Likewise, a transparent pellet was obtained and analysed for each sample using an IRAffinity-1S Fourier Transform Infrared spectrometer (Shimadzu, Kyoto, Japan). The infrared spectra in transmission mode were recorded in the 4000–400 cm^{-1} frequency region. The microstructural characterisation was carried out with scanning electron microscopy (FEI QUANTA 400 SEM/ESEM, Fei Quanta, Hillsboro, WA, USA).

2.4. Coagulation-flocculation experimental set-up

The coagulation-flocculation (CF) process was performed in a Jar-test device (ISCO JF-4, Louisville, KY, USA), with four mechanical agitators powered by a regulated speed engine. The AH and CP were mixed, separately, with the CW samples under a fast mix of 150 rpm/3 min and a slow mix of 20 rpm/20 min, at ambient temperature (25°C). Were tested four pH (3.0, 6.0, natural and 9.0) and coagulant concentrations (0.1, 0.5, 1.0 and 2.0 g/L). The samples remained in sedimentation overnight and were subsequently collected for analysis.

2.5. Statistical analysis

The data was checked for normality using the Shapiro-Wilk test and the equal population variances using the Brown-Forsythe test. One-way analysis of variance (ANOVA) with Tukey's post-hoc multiple comparisons was used for normal data and findings were presented as mean and standard deviation (GraphPadPrism version 9.0). P-values were considered significant when $p < 0.05$.

3. Results and discussion

3.1. Coagulants characterisation

Figure 1 shows the Fourier-transform infrared spectroscopy (FTIR) spectrum of the almond hull (AH) and the cherry pit (CP). The area between 4000 and 400 cm^{-1} was analysed. The peaks inserted in the 3450-3050 cm^{-1} region indicate asymmetric valence O-H vibrations which are typical for the presence of phenolic hydroxyl groups, proteins, carbohydrates and lignin. The asymmetric C-H and C=O valence vibrations are presented in the 2980-2820 cm^{-1} and 1750-1700 cm^{-1} regions, respectively. The aliphatic compounds are typical of these regions. The asymmetric C=C vibrations of the aromatic ring are represented between 1650 cm^{-1} to 1400 cm^{-1} region. The peaks 1018.41 cm^{-1} and 1022.23 cm^{-1} of the AH and CP, respectively, are associated with the asymmetric C-O valence vibrations. The 900-700 cm^{-1} region of the spectrum represents the =CH vibrations of the aromatic hydrocarbons [5, 7]. The presence of several hydroxyl groups may contribute to the efficient degradation of several organic compounds due to the high oxidative potential of these groups.

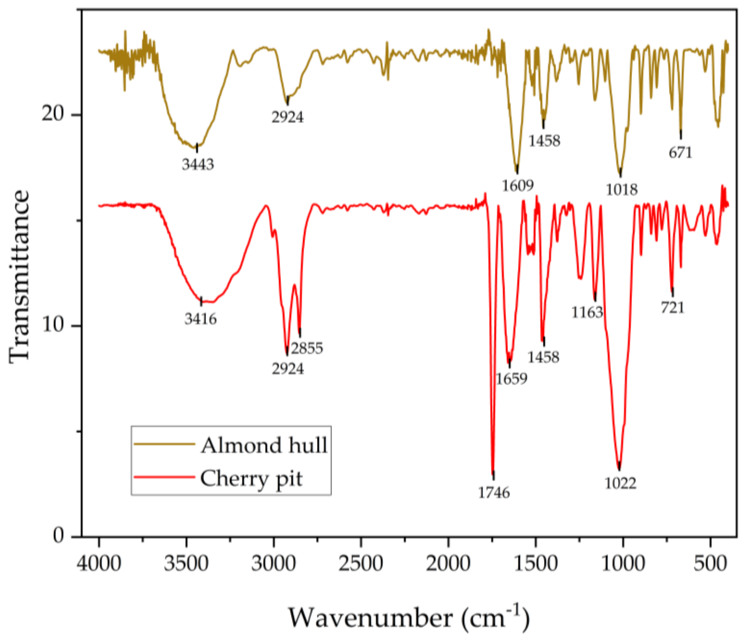
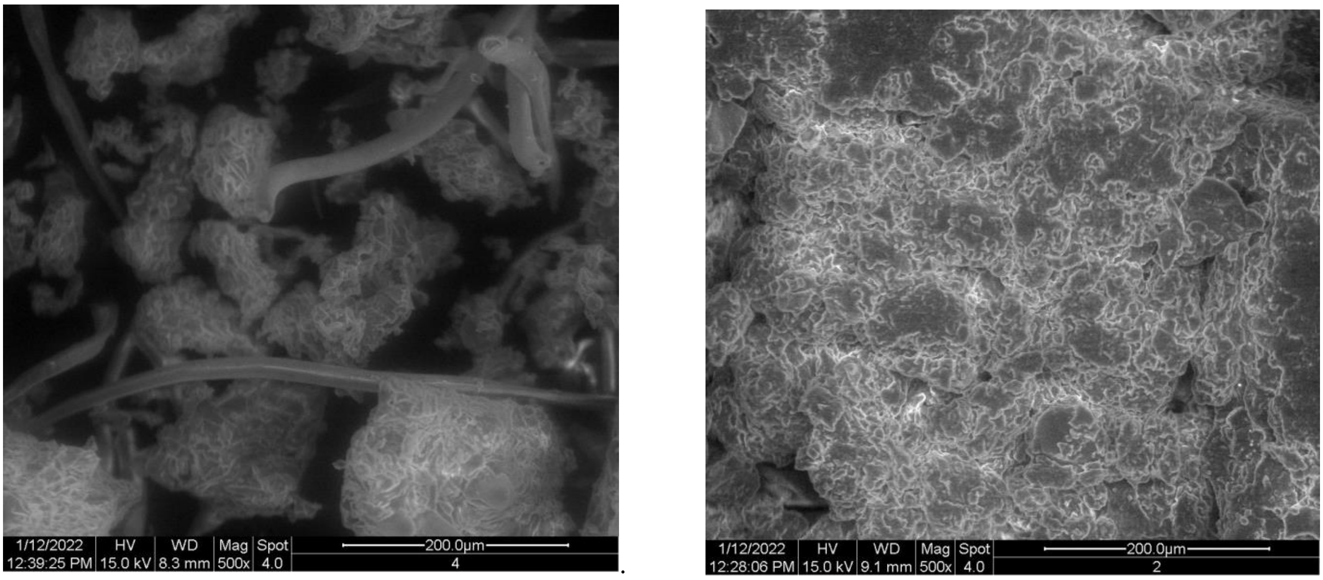


Figure 1. Fourier-transform infrared spectroscopy (FTIR) analysis of almond hull and cherry pit.

Figure 2 presents the scanning electron microscope (SEM) images of AH and CP. The AH powder presents a highly porous surface (Figure 2a), similar to those previously found in studies using plant-based materials [8]. On the other hand, the CP powder does not present as many porous as AH. Despite the literature reported conflicting results, highly porous surface areas may be associated with higher adsorption capacities being important to treat hazardous wastewater [9].

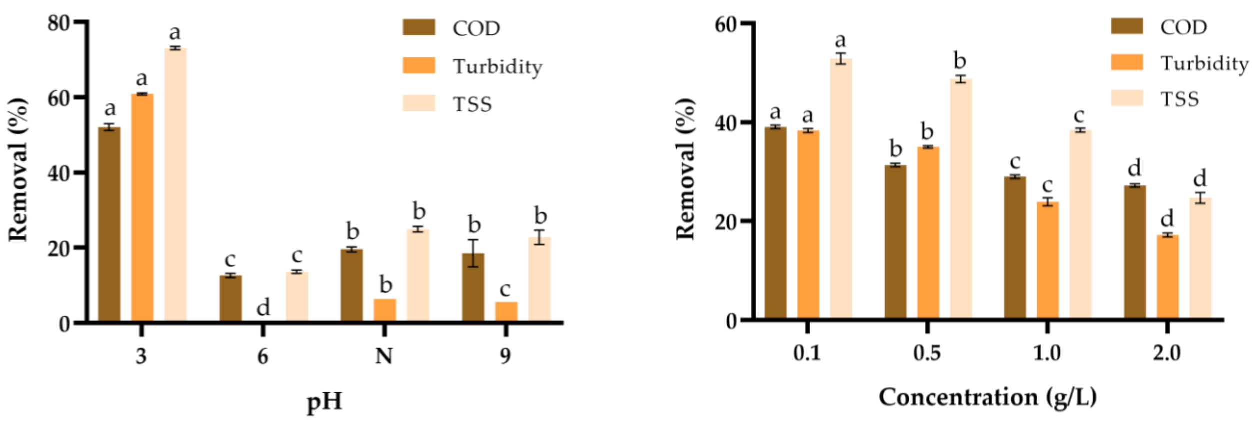


(**a**) (**b**)

Figure 2. Scanning electron microscopy (SEM) images of (**a**) almond hull and (**b**) cherry pit.

3.2. Coagulation-flocculation experiments

The coagulation-flocculation (CF) process using AH and CP as coagulants was optimised. Different levels of pH were tested (3.0, 6.0, natural and 9.0). Thus, different coagulants concentrations were tested (0.1, 0.5, 1.0 and 2.0 g/L) using the pH level that achieved the best removal percentages. Regarding AH coagulant, the results showed a significant removal of chemical oxygen demand (COD), turbidity and total suspended solids (TSS) (52.1, 60.8 and 73.1%, respectively) with the application of pH 3.0 (Figure 3a). It was noted that the efficiency of the cattle wastewater (CW) treatment decreased as the pH level increased. Thus, pH 3.0 was chosen to test the different AH concentrations (Figure 3b). The application of 0.1 g/L of AH allowed the significant removal of COD, turbidity and TSS (39.1, 38.3 and 52.9%, respectively).

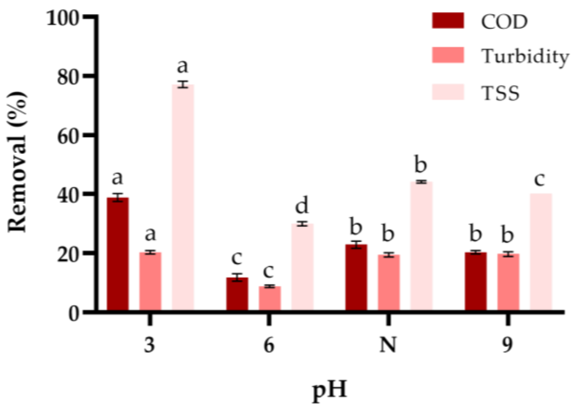


(**a**) (**b**)

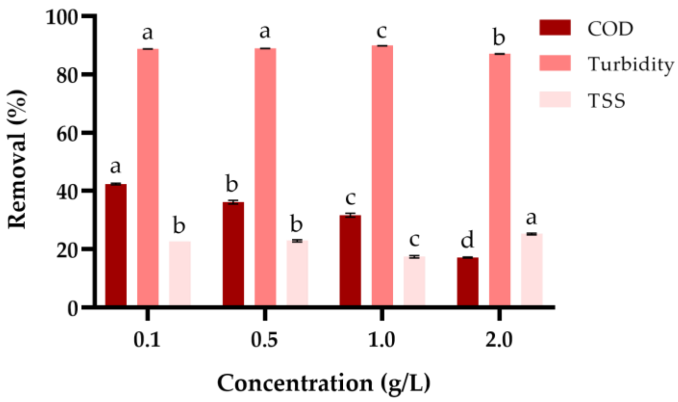
Figure 3. Coagulation-flocculation experiments using AH as coagulant (**a**) optimisation of pH (3.0, 6.0, natural (N) and 9.0) under the following conditions: [AH] = 1.0 g/L; fast mix = 150 rpm/3 min.;

slow mix = 20 rpm/20 min; sedimentation = overnight; (**b**) optimisation of AH concentration (0.1, 0.5, 1.0 and 2.0 g/L) under the following conditions: pH = 3.0; fast mix = 150 rpm/3 min.; slow mix = 20 rpm/20 min; sedimentation = overnight. The different letters represent the statistically significant differences ($p < 0.05$).

Regarding CP coagulant the results showed significant removal of COD, turbidity and TSS with the application of pH 3.0 (38.9, 59.3 and 77.2%, respectively) (Figure 4a). It was observed as the pH increased the efficiency removal decreased. Therefore, pH 3.0 was used to test different CP concentrations (Figure 4b). The concentration of 0.1 g/L showed the highest removal percentage of COD, turbidity and TSS (42.4, 88.8 and 22.3%, respectively).



(**a**)



(**b**)

Figure 4. Coagulation-flocculation experiments using CP as coagulant (**a**) optimisation of pH (3.0, 6.0, natural (N) and 9.0) under the following conditions: [CP] = 1.0 g/L; fast mix = 150 rpm/3 min.; slow mix = 20 rpm/20 min; sedimentation = overnight; (**b**) optimisation of CP concentration (0.1, 0.5, 1.0 and 2.0 g/L) under the following conditions: pH = 3.0; fast mix = 150 rpm/3 min.; slow mix = 20 rpm/20 min; sedimentation = overnight. The different letters represent the statistically significant differences ($p < 0.05$).

It was observed that the CF efficiency decreased as the pH level increased. Plant-based coagulants are water-soluble proteins which contains positive charges. These charges bind with the negative charged particles of CW that causes turbidity. At lower pH levels, these adsorption process may accelerates increasing the CF efficiency [10]. Furthermore, the CF efficiency decreased as the coagulant concentration increased. These results may be due to the higher organic contents added from the bio-compounds of the AH and CP coagulants [11]. The application of plant-based coagulants is a highly competitive approach in wastewater treatment. These coagulants may be a solution to the adverse effects that result from the use of chemical coagulants [3]. Furthermore, are renewable sources, eco-friendly and sustainable wastewater treatment. Further studies should consider the integration of plant-based coagulants in different treatment processes and its implementation at a larger-scale.

4. Conclusions

The cattle wastewater (CW) generated from livestock production presents high organic matter content and suspended solids which represents a serious environmental problem if discharged without a proper treatment. Therefore, in this work, a coagulation-flocculation (CF) process using almond and cherry by-products as coagulants was adopted to treat CW. The results showed that the efficiency of the CF process is dependent on the pH level and coagulant concentration factors. The utilization of a pH 3.0 and 0.1 g/L of almond hull achieved the highest COD, turbidity and TSS removal of 39.1, 38.3 and

52.9%, respectively. Moreover, the application of a pH 3.0 and 0.1 g/L of cherry pit allowed the highest removal of COD, turbidity and TSS, respectively, 42.4, 88.8 and 22.3%. It can be concluded that the utilisation of almond and cherry by-products as coagulants is a sustainable environmental technology for CW treatment. The application of these coagulants allows the valorisation of food industry wastes and treat the wastewater.

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