engineering proceedings

Proceeding Paper

Cattle Wastewater Treatment Using Almond Hull and Cherry Pit as Coagulants–Flocculants †

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† Presented at the 4th International Electronic Conference on Applied Sciences, 27 October–10 November 2023; Available online: https://asec2023.sciforum.net/.

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 ecosystems. In this work, CW was treated using a coagulation–flocculation (CF) process. This work aimed to optimise the CF process with the application of almond hulls (AHs) and cherry pits (CPs) as coagulants to treat CW. The results showed that it was possible to achieve chemical oxygen demand (COD), turbidity and total suspended solids (TSS) removal of 39.1, 38.3 and 52.9%, respectively, for AHs (pH 3.0 and 0.1 g/L) and 42.4, 88.8 and 22.3%, respectively, for CPs (pH 3.0 and 0.1 g/L). It can be concluded that treating CW via the CF process with the application of AHs and CPs 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

Citation: Gomes, A.; Jorge, N.; Teixeira, A.; Peres, J.A.; Lucas, M.S. Cattle Wastewater Treatment Using Almond Hull and Cherry Pit as Coagulants–Flocculants. *Eng. Proc.* **2023**, *56*, 222. https://doi.org/10.3390/ASEC2023-15494

Academic Editor: Simeone Chianese

Published: 31 October 2023

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 characterised by high levels of organic matter, suspended solids, faecal coliforms, different drugs (antibiotics, parasiticides and steroid hormones) and nutrients. The lack of proper CW treatment leads to several environmental issues, including the depletion of dissolved oxygen and increases in 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 types of 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 have proven 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 its 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 hulls (AHs) and cherry pits (CPs) as coagulants to treat CW. The influence of pH and the coagulant concentrations on the removal of chemical oxygen demand (COD), total suspended solids (TSS) and turbidity was studied. The utilisation of plant-based coagulants may represent a future alternative for 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

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 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. Coagulant 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 hulls from the almonds and the pits from the cherries 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). Infrared spectra in transmission mode were recorded in the 4000–400 cm^{-1} frequency region. Microstructural characterisation was carried out using 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 AHs and CPs were mixed separately with the CW samples using a fast mix at 150 rpm/3 min and a slow mix at 20 rpm/20 min at ambient temperature (25 °C). Four pH values (3.0, 6.0, natural and 9.0) and coagulant concentrations (0.1, 0.5, 1.0 and 2.0 g/L) were tested. The samples were left to sediment overnight and were subsequently collected for analysis.

2.5. Statistical Analysis

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

3. Results and Discussion

3.1. Coagulant Characterisation

Figure 1 shows the Fourier transform infrared spectroscopy (FTIR) spectra of the almond hulls (AHs) and cherry pits (CPs). 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 of the presence of phenolic hydroxyl groups, proteins, carbohydrates and lignin. Asymmetric C-H and C=O valence vibrations are presented in the 2980–2820 cm^{-1} and 1750–1700 cm^{-1} regions, respectively. Aliphatic compounds are typical of these regions. The asymmetric C=C vibrations of the aromatic ring are represented between the 1650 cm^{-1} and 1400 cm^{-1} regions. The peaks at 1018.41 cm^{-1} and 1022.23 cm^{-1} of the AHs and CPs, respectively, are associated with asymmetric C-O valence vibrations. The 900–700 cm^{-1} region of the spectrum represents the =CH vibrations of 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.

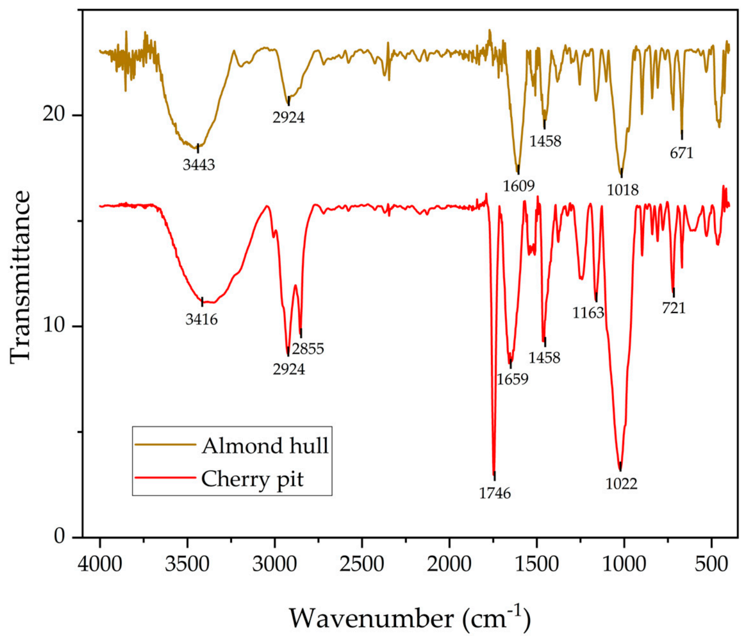
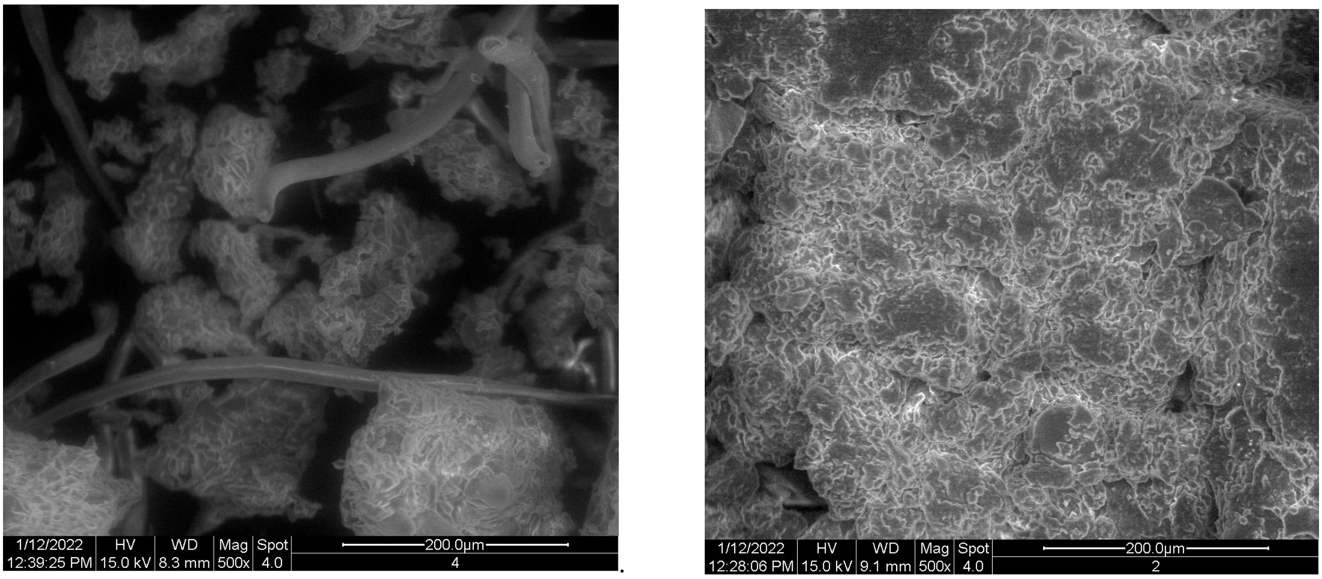


Figure 1. Fourier transform infrared spectroscopy (FTIR) analysis of almond hulls and cherry pits.

Figure 2 presents the scanning electron microscopy (SEM) images of AHs and CPs. 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 pores as AH. Although the literature reports conflicting results, highly porous surface areas may be associated with higher adsorption capacities, which are important for treating hazardous wastewater [9].

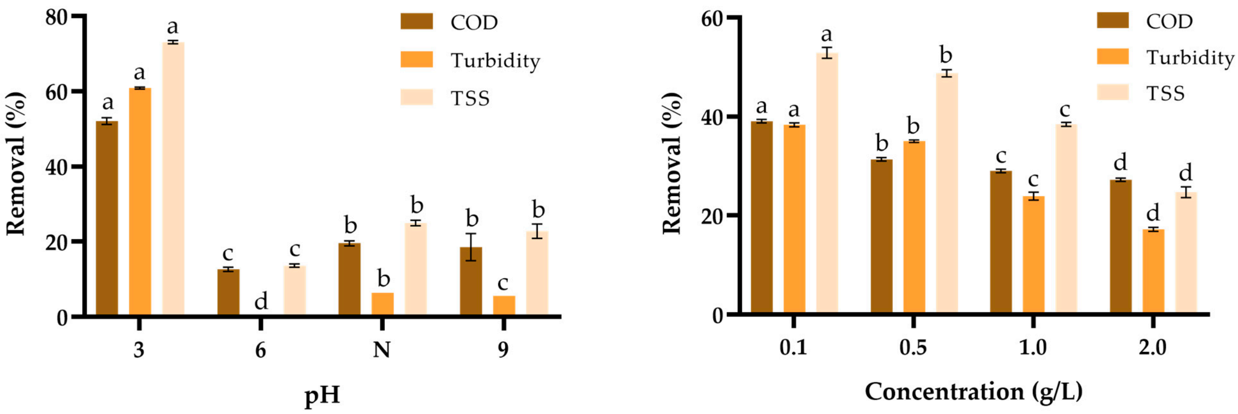


(**a**) (**b**)

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

3.2. Coagulation–Flocculation Experiments

The coagulation–flocculation (CF) process using AHs and CPs as coagulants was optimised. Different levels of pH were tested (3.0, 6.0, natural and 9.0). Thus, different coagulant 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 the AH coagulant, the results showed the 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 AHs 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 AHs 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 statistically significant differences ($p < 0.05$).

Regarding the CP coagulant, the results showed the 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 that as the pH increased, the efficiency of 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 percentages of COD, turbidity and TSS (42.4, 88.8 and 22.3%, respectively).

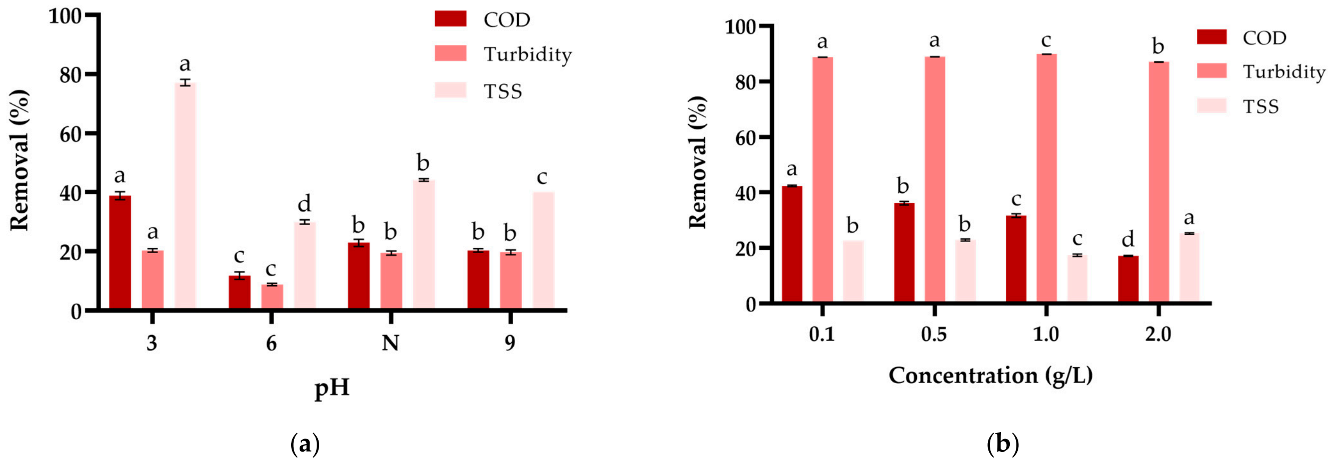


Figure 4. Coagulation–flocculation experiments using CP as coagulant. (**a**) Optimisation of pH (3.0, 6.0, natural (N) and 9.0) under the following conditions: [CP] = 1.0 g/L; fast mix = 150 rpm/3 min; slow mix = 20 rpm/20 min; sedimentation = overnight. (**b**) Optimisation of CP concentration (0.1, 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 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 that contain positive charges. These charges bind to the negatively charged particles in CW that cause turbidity. At lower pH levels, this adsorption process may accelerate, 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 by the bio-compounds in the AH and CP coagulants [11]. The application of plant-based coagulants is a highly competitive approach to wastewater treatment. These coagulants may be a solution to the adverse effects that result from the use of chemical coagulants [3]. Furthermore, they are renewable sources, making this an eco-friendly and sustainable wastewater treatment. Further studies should consider the integration of plant-based coagulants into different treatment processes and their implementation at a larger scale.

4. Conclusions

The cattle wastewater (CW) generated by livestock production contains high organic matter content and suspended solids, which represent a serious environmental problem if discharged without 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. The utilisation of pH 3.0 and 0.1 g/L almond hulls achieved the highest COD, turbidity and TSS removal of 39.1, 38.3 and 52.9%, respectively. Moreover, the application of pH 3.0 and 0.1 g/L cherry pits allowed the highest removal of COD, turbidity and TSS, respectively, with values of 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 the treatment of wastewater.

Author Contributions: Conceptualisation, A.G., N.J. and A.T.; methodology, A.G., N.J. and A.T.; software, A.G.; validation, A.G., N.J. and A.T.; formal analysis, A.G.; investigation, A.G.; resources, A.G. and M.S.L.; data curation, A.G.; writing—original draft preparation, A.G.; writing—review and editing, A.G., J.A.P. and M.S.L.; visualisation, A.G., J.A.P. and M.S.L.; supervision, M.S.L.; project administration, J.A.P. and M.S.L.; funding acquisition, M.S.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are grateful for the financial support of the project OBTain-Objective Building Sustainability (NORTE-01-0145 FEDER-000084).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Data are contained within the article.

Acknowledgments: The authors are grateful for the support of Fundação para a Ciência e a Tecnologia (FCT) to CQVR (UIDB/00616/2020) and the Unidade de Microscopia Eletronica (UME) of UTAD.

Conflicts of Interest: The authors declare no conflicts of interest.

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