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Treatment of Agro-Industrial Wastewaters by Coagulation-Flocculation-Decantation and Advanced Oxidation Processes – A literature Review †

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† Presented at the 1st International Electronic Conference on Processes: Processes System Innovation, 17–31 May 2022; Available online: https://ecp2022.sciforum.net.

Abstract: The agro-industry has increased over the years, as a necessity to supply the needs of the population for food and drinking. This increase led to a significant production of agro-industrial wastewaters characterized by high content in organic matter, polyphenols, suspended solids and turbidity, making these wastewaters danger if released to the environment without proper treatment. In this work, it was collected and reviewed recent findings aiming the feasibility of coagulation-flocculation-decantation (CFD) and advanced oxidation processes (AOPs) for the treatment of agro-industrial wastewaters. More specifically, mechanisms, limitations, operational conditions and relevance of the different treatment processes for wastewater treatment and reuse are discussed. As a result, it is concluded that CFD process an AOPs can be performed separated or combined to achieve high efficiency in agro-industrial wastewater treatment.

Keywords: advanced oxidation processes (AOPs); coagulation-flocculation-decantation (CFD); photo-fenton; sulfate radical-based AOP; ozone-based AOP.

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Proceedings* **2022**, *69*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Published: date

1. Introduction

One of the world's largest source of pollution is the agroindustry, which can be defined as a set of economic activities, including production, processing or industrialization and commercialization of agricultural and forestry products, either for food or non-food purposes [1,2]. In Mediterranean countries, most of the agroindustry in centered in the production of olive oil and wine, however, several other productions are of worthy mention: coffee, dairy, palm oil and pulp mill. These activities are the biggest soil, water and energy consumers in the agro-industrial sector, generating significant volumes of solid materials and wastewaters with important polluting characteristics [2,3]. Considering the high volumes generated and the high organic content that these wastewaters have, it is necessary to apply technologies that are effective. Most studies focus their research on single compounds which are easier to degrade, however, these types of wastewaters are much harder to treat. Therefore, the main goal of this review is to summarize and discuss recent methodologies designed to reduce the organic carbon and polyphenols from agro-industrial wastewaters. The most relevant scientific articles used for this review were selected using Web of Science, Scopus and Google Scholar databases.

2. Coagulation-Flocculation-Decantation Process

To treat the agro-industrial wastewater, the physical-chemical process of coagulation-flocculation-decantation (CFD) can be applied. In the coagulation process, small suspended colloids in water are destabilized after diminishing their surface charges by the addition of coagulants with an opposite charge; then, the destabilized particles aggregate and settle down, accelerate particle aggregation further and improve settlement efficiency (Figure 1). Polymeric flocculants with flexible long chain conformation are sometimes fed after coagulation as coagulant aids. These polymeric flocculants act as bridges that adsorb and connect various colloidal particles in water to form large flocs that can be effectively removed by sedimentation [4]. In accordance to Howe *et al*., [5], to obtain particle destabilization, several mechanisms are applied: (1) compression of the electrical double layer, in which if ions are added into the solution, then the electroneutrality can be achieved in a shorter distance; (2) adsorption and charge neutralization, in which particles are destabilized by adsorption of ions or polymers with opposed charge; (3) adsorption and interparticle bridging, in which the polymer remains extended into the solution and continuously adsorbs on remaining surface sites of other particles, and therefore creating a ‘‘bridge’’ between particle surfaces that originates a larger particle that can settle more efficiently; (4) enmeshment in a precipitate, or "sweep floc", which occurs when large concentrations of coagulant are applied. The iron and aluminum generates precipitates that are insoluble and the particles become entrapped in the amorphous precipitates.

In order to attain a more economically sustainable, environmentally friendly and viable production, research interest has been directed towards the evaluation and use of unconventional protein sources, particularly from plant products such as seeds, leaves and other agricultural by-products. In the work of Dkhissi *et al*., [6], a plant-based coagulant was applied for the treatment of vegetable oil refinery wastewater, achieving a high removal of turbidity, chemical oxygen demand (COD) and color.

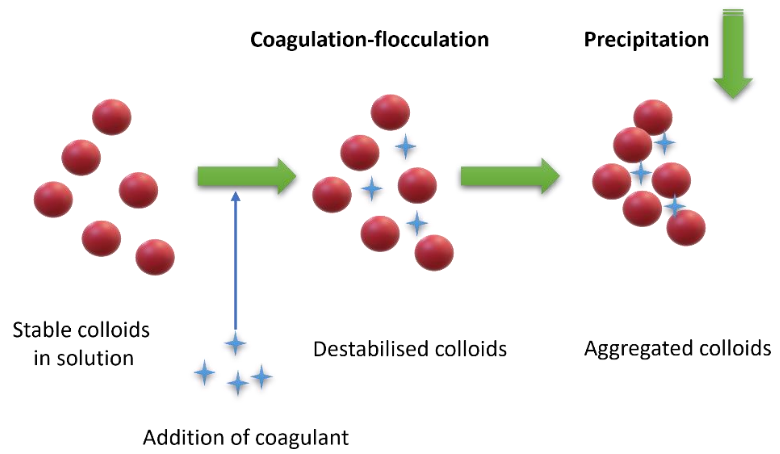

Figure 1. Coagulation-flocculation-decantation scheme.

3. Advanced Oxidation Processes (AOP)

Conventional treatment methods have been reported to be inefficient for agro-industrial wastewater treatment, considering that some contaminants are recalcitrant to some degree [7]. Advanced oxidation processes (AOP) can be applied as an alternative or a complement treatment to degrade these recalcitrant compounds. The AOPs generate extremely reactive hydroxyl radicals ($HO^{\bullet}$) radicals that are responsible for the degradation of pollutants in the wastewater. These $HO^{\bullet}$ radicals attack the organic molecules rapidly and non-selectively [8]. The AOPs can be divided in accordance to the oxidant used:

hydroxyl radical based AOP (HR-AOP), sulfate radical based AOP (SR-AOP) and ozone based AOP.

3.1. HR-AOPs

3.1.1. Photo-Fenton Process

The photo-Fenton process is an improvement of the Fenton process, due to the application of "near-UV to visible region" of light, up to 600 nm to improve the $HO^{\bullet}$ radical production (Equation 1) [9]. Two additional reactions take place in the photo-Fenton process: (1) photoreduction of Fe^{3+} to Fe^{2+} ions (Equation 2) [10] and (2) hydrogen peroxide photolysis via shorter wavelengths (Equation 3) [11], as follows:

$$Fe^{3+} + H_2O + hv \rightarrow Fe^{2+} + HO^{\bullet} + H^{+} \quad (1)$$

$$Fe(HO)^{2+} + hv \rightarrow Fe^{2+}\ HO^{\bullet};\ \lambda < 580\ \text{nm} \quad (2)$$

$$H_2O_2 + hv \rightarrow 2HO^{\bullet};\ \lambda < 310\ \text{nm} \quad (3)$$

Conventional UV-C lamps (which are mainly mercury lamps) present several problems: overheating, short lifetime, low photonic efficiency and environmentally unfriendly properties. LED lights appeared has a viable alternative since they present longer lifetimes, lower energy consumption, high efficiency, they do not overheat and are less harmful to the environment [12].

3.1.2. Ultrasound-Fenton Process

In recent years, some extensive researches on the use of ultrasound-Fenton (US-Fenton) process for the treatment of water and wastewater has been performed. With the application of ultrasound, a lot of microscopic bubbles that are called cavities are produced. They are formed among water molecules while they gradually become greater. Next, with severe destruction, an application of pressure, and a high temperature, according to Equation 4, water molecules are broken apart, and consequently, hydroxyl radicals are produced [13]. By combining the US with Fenton processes, it is observed the production of more hydroxyl ions by degradation of H_2O_2 (Equation 5) and the regeneration of Fe^{2+} (Equation 6), as follows:

$$H_2O + US \rightarrow HO^{\bullet} + HO^{-} \quad (4)$$

$$H_2O_2 + US \rightarrow 2HO^{\bullet} \quad (5)$$

$$FeHO_2^{2+} + US \rightarrow Fe^{2+} + HO_2^{\bullet} \quad (6)$$

The application of HR-AOPs are a very efficient process for agro-industrial wastewater treatment. In the work of Velegraki and Mantzavinos [14], a pilot-scale solar Fenton process was applied for the treatment of winery wastewater in a CPC photocatalytic reactor under natural solar irradiation. The results showed that the photo-Fenton process utilizing solar energy is highly efficient in the mineralization and detoxification of real winery wastewater, and the final wastewater exhibited very low toxicity using *A. fischeri* test as toxicity bioassay.

3.2. SR-AOPs

The interest in persulfate began in earnest around 2000–2002, when work on persulfate began to appear regularly in conference proceedings and in presentations at major remediation meetings [15]. There are two types of sources to obtain the sulfate radical ($SO_4^{\bullet-}$): (1) peroxymonosulphate (HSO_5^{-}; PMS), which is the active ingredient of a triple potassium salt, $2KHSO_5{\bullet}KHSO_4{\bullet}K_2SO_4$, with an appearance of a white solid powder. It is stable when the pH is less than 6 or 12. When the pH is 9, it shows poor stability where half of HSO_5^{-} decomposes to SO_5^{2-}. PMS can be easily dissolved in water, with the solubility of > 250 g L^{-1}. Its water solution is acidic. It has asymmetrical structure, the distance of O-O bond is 1.453 Å. The bond energy is estimated to be in the range of 140–213.3 kJ/mol. (2) persulfate (PS), which is a colorless or white crystal and has high stability. It can be easily dissolved in water, with the solubility of 730 g L^{-1}. The water solution of PS is acidic. It has symmetrical structure, the distance of O-O bond is 1.497 Å, and its bond energy is 140 kJ/mol [16]. Persulfate activation can be achieved by heat, UV radiation or metal ions, as observed in Equation 7 – 9 [17]:

$$S_2O_8^{2-} \rightarrow 2SO_4^{\bullet -} \quad (7)$$

$$S_2O_8^{2-} + hv \rightarrow 2SO_4^{\bullet -} \quad (8)$$

$$S_2O_8^{2-} + M^{n} \rightarrow M^{n+1} + SO_4^{\bullet -} + SO_4^{2-} \quad (9)$$

The application of SR-AOPs showed to be very effective in the treatment of agro-industrial wastewaters. For example, in the work of Domingues *et al*., [18], the application of PS/Fe^{2+} in the treatment of OMW achieved a total polyphenols removal of 63%.

3.3. Ozone-Based AOPs

In 1840, Schönbein discovered ozone and by 1872 the chemical structure of ozone (O_3) was finally confirmed as a triatomic oxygen molecule. Later in 1886, de Meritens found that ozone could be used as a germicide for sterilization of polluted water and after a few years of pilot tests at water treatment plants in Paris, ozone was firstly used in water treatment (and used continuously) in Nice, France in 1906 for drinking water disinfection [19]. Ozone is an unstable gas with a characteristic penetrating odor, which is partially soluble in water. Ozone is also a powerful oxidant with a redox potential of 2.07 V in an alkaline solution. Therefore, O_3 is able to oxidize a lot of inorganic and organic substances [20]. The application of ozone has proven to be effective for agro-industrial wastewater treatment. In the work of Jorge *et al*., [21], a winery wastewater was previously treated by CFD process achieving a COD removal of 48.0%. With application of ozonation, the COD removal increase to 60.7%, thus the combination of CFD with ozonation showed to be synergistic.

4. Conclusions

The agro-industry has shown to be very important for the development of the populations, been capable to respond to the need to provide food and to develop the economy of the countries. However, it is concluded that the increase of these industries leads to a production of large volumes of wastewater with a high content in organic matter, total polyphenols and suspended solids. Therefore, to guarantee the safety of the environment and its ecosystems, it is necessary to apply the necessary treatment processes. Following the literature indications, it can be stated that the coagulation-flocculation-decantation and advanced oxidation processes can be applied singly or combined to achieve maximum efficiency in wastewater treatment. Thus, it is concluded:

1. The CFD process employs coagulants of different origin (metallic, oenology or plant-based) and employs different mechanisms in simultaneous. Several reviews show that application of plant-based coagulants have similar efficiency than metallic coagulants, with lower costs and reduced environmental contamination;

2. The HR-AOPs are dependent of parameters, such as concentration of H_2O_2, Fe^{2+} and pH. It is concluded that application of UV radiation and ultrasound increases the efficiency of the Fenton process. The literature review shows that HR-AOPs are effective in the removal of organic matter from agro-industrial wastewater, reducing the toxicity to lower levels;

3. The SR-AOPs are activated by several mechanisms (thermal activation, alkaline activation, radiation activation and transition metal ions and metal oxide activation). The literature review shows that PMS and PS have similar effect in the removal of organic matter from agro-industrial wastewater. The results also show a high efficiency of SR-AOPs, for the removal of total polyphenols;

4. The ozonation process is enhanced under different conditions (alkaline solution, addition of H_2O_2, radiation and catalyst), with production of $HO^{\bullet}$ radicals. The literature

review shows that application of ozonation process have a high efficiency in the removal of organic carbon and total polyphenols from agro-industrial wastewater.

In summary, the CFD process and AOPs show great potential for the treatment of agro-industrial wastewater treatment, with further research directed for the reuse of the wastewater for irrigation purposes.

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

Funding: This research was funded by the North Regional Operational Program (NORTE 2020) and the European Regional Development Fund (ERDF) and express their appreciation for the financial support of the Project AgriFood XXI, operation nº NORTE-01-0145-FEDER-000041, and to the Fundação para a Ciência e a Tecnologia (FCT) for the financial support provided to CQVR through UIDB/00616/2020. Ana R. Teixeira also thanks the FCT for the financial support provided through the doctoral scholarship UI/BD/150847/2020.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

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

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