

Agro-Industrial Wastewater Treatment using Conventional and Advanced Approaches: A Review

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

Keywords: Coagulation, Fenton Processes, Flocculation, Hydroxyl ions.

1. INTRODUCTION

One of the world's largest sources of pollution is the agroindustry, which can be defined as a set of economic activities, including the 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 is centered on the production of olive oil and wine; however, several other products are worthy of mention: coffee, dairy, palm oil, cassava effluent, 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 pollutants from agro-industrial wastewaters.

2. COAGULATION-FLOCCULATION DECANTATION PROCESS

To treat 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, accelerating particle aggregation further and improving settlement efficiency. Polymeric flocculants with flexible long-chain conformations are sometimes fed after the 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 with [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 generate 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 [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.

3. ADVANCED OXIDATION PROCESSES (AOP)

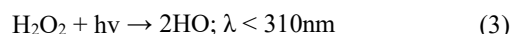
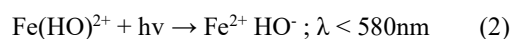
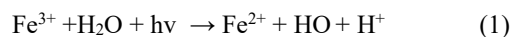
Conventional treatment methods have been reported to be inefficient for agro-industrial wastewater treatment, considering that some contaminants are recalcitrant to

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 ($\text{HO}^\cdot$) radicals that are responsible for the degradation of pollutants in the wastewater. These $\text{HO}^\cdot$ radicals attack the organic molecules rapidly and non-selectively [8]. The AOPs can be divided according 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 the “near-UV to visible region” of light, up to 600 nm, to improve $\text{HO}^\cdot$ radical production (Equation (1)) [9]. Two additional reactions take place in the photo-Fenton process: (1) photo-reduction of Fe^{3+} to Fe^{2+} ions (Equation (2)) [10] and (2) hydrogen peroxide photolysis via shorter wavelengths (Equation (3)) [11], as follows:



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

3.1.2. Ultrasound-Fenton Process

In recent years, some extensive research on the use of the 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, the production of more hydroxyl ions by the degradation of H_2O_2 (Equation (5)) and the regeneration of Fe^{2+} (Equation (6)) can be observed, as follows:

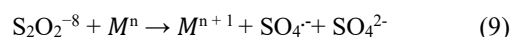


The application of HR-AOPs is a very efficient process for agro-industrial wastewater treatment. In the work of [14], a pilot-scale solar Fenton process was applied to the treatment of winery wastewater in a CPC photocatalytic reactor under natural solar irradiation. The results showed that the photo-Fenton 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 an *A. fischeri* test as toxicity bioassay.

4. 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 ($\text{SO}_4^{\cdot-}$): (1) peroxymonosulphate (HSO_5^- ; PMS), which is the active ingredient of triple potassium salt, $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$, with the 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 the HSO_5^- decomposes to $\text{SO}_4^{\cdot-}$. PMS can be easily dissolved in water, with a solubility of $>250 \text{ g L}^{-1}$. Its water solution is acidic. It has an asymmetrical structure, and the distance of the O–O bond is $1.453 \text{ \AA}$. The bond energy is estimated to be in the range of $140\text{--}213.3 \text{ kJ/mol}$. (2) persulfate (PS), which is a colorless or white crystal and has high stability. It can be easily dissolved in water, with a solubility of 730 g L^{-1} . The water solution of PS is acidic. It has a symmetrical structure, and the distance of the O–O bond is $1.497 \text{ \AA}$, and its bond energy is 140 kJ/mol [16]. Persulfate activation can be achieved by heat, UV radiation, or metal ions, as observed in Equations (7)–(9) [17]:



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

5. 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 the sterilization of polluted water, and after a few years of pilot tests at water treatment plants in Paris, ozone was first used for 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. According to [21], a winery's wastewater was previously treated by the CFD process, achieving a COD removal of 48.0%. With the application of ozonation, the COD removal increased to 60.7%; thus, the combination of CFD with ozonation was shown to be synergistic.

6. CONCLUSION

The agro-industry has been shown to be very important for the development of populations and must be capable of responding to the need to provide food and to develop the economy of the countries. However, it is concluded that the increase in these industries leads to the production of large volumes of wastewater with a high content of 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.

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