

A Review on Processes for Olive Mill Waste Water Treatment

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ABSTRACT

The olive mill waste water (OMWW) are effluents issued from the extraction of olive oil, these effluents are cloudy-looking liquids with a reddish-brown color, their pH varies from 4 to 5. They are very rich in polyphenols, which causes many environmental problems, such as water pollution. Currently, on an industrial scale, there is no reliable, efficient, and less expensive technique for OMWW treatment. OMWW are evaporated in watertight basins or discharged into watercourses. Several techniques have been studied to treat these industrial effluents. The objective of this work was to compare these studies to formulate the recommendations that can be adopted for an effective and cheaper treatment of these effluents which constitute a major environmental problem for water resources. Indeed, it can be concluded that it is very difficult to treat OMWW by conventional methods due to its non-biodegradability and high cost of others methods like distillation and oxidation. In the end, it was concluded that for a better OMWW treatment, it is necessary to start firstly by the adsorption of phenolic compounds which are responsible for the non-biodegradability of OMWW while using cheaper adsorbents namely clays, bio-adsorbents or apatites, then dilute the OMWW with domestic wastewater. The dilution of OMWW by urban wastewater leads to good mineralization of organic matter by enriching the medium with microorganisms, which facilitates the elimination of the organic load and then we use the usual techniques as a plant filter or active sludge for mixture treatment.

Keywords: OMWW, phenolic compounds; organic matter; treatment; adsorption.

INTRODUCTION

The olive tree has been cultivated for thousands of years in Mediterranean countries where it occupies a capital place in tree production. It is a tree rustic and well adapted to dry climate and poor soils. The olive industry is a very important activity in these countries. Olive oil can be extracted by simple pressure or centrifugation, using a 2 or 3 phase system. Due to the increase in demand from the olive oil market, the olive industry is constantly growing worldwide and especially in Mediterranean countries. In this context, the olive oil producing countries are faced with serious environmental problems due to

inadequate management solutions of discharges from the olive industry. Indeed, the by-products of oil mills are essentially olive mill waste water (OMWW). The consumption of large quantities of water for the extraction of olive oil leads to a production of large quantities of OMWW. Due to their acidity, which results from to the presence of organic acids, including phenolic acids, fatty acids, etc. (Achak et al. 2009a), and high organic load, notably polyphenols compounds (Davies et al. 2004; Solomakouet al. 2021), in some producing countries it is forbidden to discharge these effluents into the natural environment and public sewerage systems. The discharge of these liquid effluents without treatment prerequisite generates

environmental disasters at all levels (Boukhoubza et al. 2007; Lidija 2015; Comegna et al. 2022).

These considerations have led several researchers to study applications for the treatment and recovery of effluents olive oil mills (Achak et al. 2009a; Martins et al. 2015; Gholamzadeh et al. 2016; Benaddi et al. 2022b). Studies carried out on the treatment of OMWW by physico-chemical methods, namely oxidation (Sami et al. 1995; Uğurlu et al. 2007; Celalettinet al. 2010), distillation (Ben Othman et al. 2022), Ozonation (Olivier et al. 2009; Martins et al. 2015), membrane technology (De Almeida et al. 2018; Wassem et al. 2019), electrochemistry (Chokri et al. 2013), and liquid-liquid extraction (Martins et al. 2021) have given encouraging results, but the high cost of these techniques limits their use, whether due to the cost of solvents or energy. Other techniques, such as coagulation, infiltration have also been also studied (Achak et al. 2009a; Achak et al. 2019). Biological processes have been studied by other authors (Tsioulpas et al. 2002). However, these methods did not give good results due to the high organic load, salinity and the high value of phenolic compounds that inhibit biological treatment. This guided researchers to focus on the adsorption of these compounds; several studies have been conducted and have given good results (Sunil et al. 2013; N. N. Nassar et al. 2014; Víctor-Ortega et al. 2016; Ali et al. 2018; Sellaoui et al. 2019, Papaoikonomou et al. 2021). The high cost of adsorbents pushes researchers to study the effectiveness of less expensive and abundant adsorbents (Girish and Rachamandra 2012; Ali et al. 2012; Giusy et al. 2016) such as bioadsorbents (Achak et al. 2009b; Gupta et al. 2013, Benaddi et al. 2022b; Haydari et al. 2022) or apatites (Bahdod et al. 2009; Bouyarmane et al. 2010; Bouyarmane et al. 2014). In particular, these adsorbents have shown good results for other pollutants (Saoiabi et al. 2016; Oumani et al. 2019). Another problem of the adsorption technique is that their particles are finely divided and cause separation difficulties vis-à-vis the treated water. The encapsulation within the beads of biopolymers makes it possible to overcome this problem while maintaining their adsorption properties after use and saturation. Alginate is one of the polymers that have been the subject of numerous studies, due to its high ability to fix a wide range of metal pollutants in aqueous solutions (Escudero et al, 2017). A study was carried out

by Benaddi et al. (2022b), which was aimed at investigating the efficiency of hydroxyapatite-sodium alginate composite (HA/SA) for the adsorption of phenolic compounds, which are contained in OMWW, it showed promising results in reducing the phenol compounds and organic matter by 60% and 64%, respectively. In this work the authors discussed the steps of production of OMWW, their composition including phenolic compounds, their negative impact on water, health and environment. Moreover, a general comparison between the different treatment techniques was carried out to formulate an effective recommendation for OMWW treatment.

PRODUCTION OF OMWW

Traditional units

In these units, the olives are crushed and kneaded using animal-drawn crushers, comprising one or two rotating wheels. The dough obtained is distributed manually in bags or scourtins which are then stacked under presses with wooden lever or with two screws and nuts in wood or metal. This results in a solid residue called raw pomace and an oily mash made up of liquid effluents and oil. The recovery of the oil is obtained by decantation. The oils issues from these units are of poor quality for the following reasons:

- absence of washing and leaf stripping of olives;
- a lack of washing of the scourtins;
- prolonged contact time between oil and OMWW.

Industrial units use three extraction systems

Three-phase discontinuous system

The olives are stored and washed in the courtyard of the olive mill and then crushed in a stone mill. The paste obtained is pressed. Pressure is subdivided into 4 types:

- stone or metal crusher units with manual press;
- stone or metal crusher units with electric press without centrifugation;
- stone or metal crusher units with electric press with centrifugation;
- stone or metal crusher units with electric super press with centrifugation.

This discontinuous operation has three stages: filling the mats with paste, pressing with hydraulic presses, and then cleaning the mats. The liquid

resulting from the pressure is sent to natural settling tanks to separate liquid effluents from the oily phase.

Three-phase continuous system

This continuous extraction method requires prior grinding carried out in hammer or disc mills. The paste obtained is kneaded in compartments heated to a temperature less than or equal to 35°C. During kneading, the paste is diluted with hot water to facilitate the extraction and grouping of oil droplets. Using a pump, the paste is sent to a horizontal centrifuge, which performs a separation of its three phases; oil, liquid effluent and pomace. This three-phase system consumes more water than the press system and therefore generates more liquid effluent, on average 1 m³ per ton of crushed olives.

Two-phase continuous system

The pollution generated by the three-phase process and the scarcity of water resources are the basis of the research into a new, less polluting technology. The new process, from the last decade, makes it possible to obtain good quality oil and moist olive cake with low production of liquid effluent. This is why this technology is called the continuous “ecological” process or the continuous two-phase process.

COMPOSITION OF OMWW

The chemical composition of OMWW is very variable. It depends on several factors, such as the production area, the variety and the degree of maturation of the crushed olives, the crushing process and practices as well as the settling time. Electrical conductivity of OMWW varies from 8 to 20 ms/cm for modern units and can reach up to 60 ms/cm for traditional olive mills. This mineralization is due to the presence of Na⁺, Cl⁻ and Ca²⁺ ions, which come from the salts added for the conservation of olives before their crushing as well as the salts existing in the olives (Belaqziz et al. 2016). Results also show that OMWW contains mineral compounds such as nitrates, phosphates and certain heavy metals, such as iron (Neffa et al. 2014). It also contains several organic compounds, such as proteins and sugars (Boukhoubza et al. 2007). The richness in organic matter, expressed in COD is generally high, it varies according to the mode of extraction of

the olives, it is relatively low in the OMWW produced by the modern oil mill (from 70 to 170 mg/L) and can reach up to 600 mg/L for the traditional olive mills. OMWW also contains large amounts of polyphenols; in fact, its concentration varies from 0.1 to 17.5 g/L depending on the trituration method (Davies et al. 2004; El Ghadraoui et al. 2020 Solomakou et al. 2021). This difference is due to the dilution effect linked to the large quantity of water used in the case of modern olive mills. Polyphenols represent about 20% of the organic matter of OMWW. Using the technique of analysis by chromatography coupled with mass spectrometry, several phenolic compounds were identified in OMWW. The best-known phenolic alcohols are tyrosol (4-hydroxyphenylethanol), hydroxytyrosol (3,4-dihydroxyphenylethanol) and Catechol (Allouche al. 2004; Achak et al., 2009a, El Ghadraoui et al. 2020; Benaddi et al. 2022b), Several phenolic acids have been identified in OMWW, namely caffeic, protocatechuic, p-hydroxybenzoic, veratric, ferulic, syringic, gallic and sinapic, vanillic, p-coumaric (El Ghadraoui et al. 2020; Martins et al. 2021; Benaddi et al. 2022b). Flavonoid compounds are represented by catechins, various dihydroxychalcones and antocyanins. Figure 1 illustrates the structure of different polyphenols existing in OMWW (Torrecilla, 2010).

IMPACT OF OMWW ON THE ENVIRONMENT AND THE ECONOMY

Phenolic compounds in OMWW cause serious pollution problems. Their major danger comes from their toxicity even at low concentrations and their strong recalcitrance to biodegradation. Certain structures of the phenolic compounds contained in the OMWW are highly toxic and linked to the inhibition of the OMWW biodegradation (Sayadi and Ellouz, 1993; Sayadi and Ellouz, 1995).

The effect on health

Phenolic compounds are probably the organic compounds that cause organoleptic problems, at low concentrations cause odor problems and bad taste due to the formation of chlorophenols, and at high concentrations phenols affect the health of human beings by denaturing proteins and destroying cells (Lidija 2015).

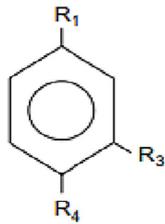
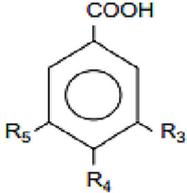
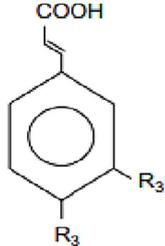
Tyrosol related	R₁	R₃	R₄	
	Et-OH	H	OH	Tyrosol
	Et-OH	OH	OH	Hydroxytyrosol
	Et-COOH	H	OH	<i>p</i> -Hydroxyphenylacetic
Benzoic acid	R₃	R₄	R₅	
	H	H	H	Benzoic acid
	H	OMe	OMe	<i>p</i> -Hydroxybenzoic acid
	OH	OMe	OMe	Protocatechuic acid
	OMe	OMe	OMe	Vanillic acid
	OMe	OMe	OMe	Veratric acid
	OH	OMe	OMe	Gallic acid
	OMe	OMe	OMe	Syringic acid
Cinnamic acid	R₃	R₄		
	H	H		Cinnamic acid
	H	OH		<i>p</i> -Coumaric acid
	OH	OH		Caffeic acid
	OMe	OH	OH	Ferulic acid

Figure 1. Chemical structure of some phenol derivatives commonly found in OMWW (Torrecilla, 2010)

Impact on soil and water resources

Even if the OMWW bring organic matter to the soil, the richness of this material in toxic phenolic compounds reduces its biodegradability whereas the viscous nature of OMWW and their richness in oils lead to the formation of an impermeable deposit on the soil and causes its asphyxiation (Belaqziz et al. 2016). The level of groundwater contamination by OMWW storage basins depends on several factors, namely the nature of the soil, the depth of the water table and its flow rate (Boukhoubza et al. 2007) as well as contact time between OMWW and soil (Comegna et al. 2022).

The dumping of OMWW in the soil and in watercourses as well as the evaporation of OMWW in non-watertight basins promotes their infiltration into the groundwater. These effluents, highly loaded with organic acids, induce an increase in the acidity of the groundwater, a considerable reduction in the dissolved oxygen content as well as an enrichment of the environment in organic and phenolic compounds, in this case also the biological compartment of underground aquatic ecosystem. Stygobia species react first. When the groundwater is contaminated, they

can completely disappear in the event of major pollution. For this reason and in relation to their sensitivity to mineral and organic pollutants, the stygobia population could be used as an indicator of olive oil pollution. It would thus constitute a complementary tool to physico-chemical analyses, useful for assessing the quality of groundwater (Boukhoubza et al. 2007). The probability of groundwater contamination can be reduced by prohibiting the discharge of OMWW into watercourses and into the ground by the application of the laws in force, as well as the design of a well-sealed storage basin for OMWW.

Economic impact

When OMWW is discharged directly into the public sewers, this generates an increase in the values of organic matter, acidity, heavy metals etc., with a reduction in the efficiency of the purification of public stations of wastewater treatment and a considerable increase in treatment costs (additional investment to be adapted at the level of wastewater treatment plants, frequent maintenance and replacement of equipment, increase in energy bills, etc.). In Morocco, to better

preserve the environment and in particular water resources, the olive crushing units have been classified among the projects subject to impact studies (Law N° 12-03 relating to environmental impact studies). Limit values for certain pollution indicator parameters have also been applied to the discharge of OMWW.

OMWW processing techniques

Thermal processes

Natural evaporation

Olive oil mill effluents are placed in 0.7 to 1.5 m deep evaporation basins or ponds and are waterproofed by a 1.5 mm thick layer of geomembrane. The depth of the basins is chosen to ensure total evaporation before the next olive growing season. After drying, olive oil mill effluents are either incinerated or used as organic fertilizer or as additives in composting for their high potassium and phosphorus content. Self-purification during evaporation is done by the microorganisms present in the effluents of olive oil mills. During their stay in the evaporation ponds, the OMWW undergo changes in their composition as a result of aerobic or anaerobic fermentations (Jarboui et al. 2008). The agents responsible for this degradation are bacteria and yeasts present in the OMWW (Ben Sassi et al. 2008).

Forced evaporation

To promote the evaporation of effluents from olive oil mills, the exchange surface with the air is increased. Evaporator panels are introduced into the storage basins of the olive oil mill effluents; the latter are pumped from storage basins, then projected by sprinklers onto juxtaposed panels, having a large exchange surface with air. The disadvantages of this method include the release of bad odors and the importance of the cost of energy spent.

Biological processes

These processes consist of using microorganisms to degrade the organic compounds of OMWW. They are subdivided into aerobic and anaerobic processes.

Anaerobic treatments

It is a biochemical fermentation process in which organic substances, such as proteins, lipids

or carbohydrates, are degraded by fermentation into intermediate products, mainly acids and alcohols. Anaerobic digestions for the treatment of olive mill wastewaters (OMW) are reviewed by Hamdi (1996). A major limitation of the anaerobic digestion of OMW is inhibition of methanogenic bacteria by simple phenolic compounds, certain organic acids and polyphenols. Pretreatment methods that modify or remove these natural inhibitors improve the digestion of OMW. These anaerobic treatments make it possible to reduce energy consumption, thus the anaerobic bacteria have the ability to transform most of the organic substances present into methane, and there are no bad odors. On the other hand, this technique generates a large quantity of sludge and seems to be unstable because of the inhibiting effect of polyphenols, the ammonia deficit and the low alkalinity of OMWW.

Aerobic treatments

Aerobic purification is carried out in two successive phases: biodegradation of biodegradable organic matter which requires the supply of oxygen and nutrients (phosphoric acid and urea), followed by solid liquid separation with the aim of separating biological sludge from purified water. The effluents from olive oil mills being highly loaded with organic matter; they cannot be treated directly by aerobic means. As a result, several authors have recommended diluting them before processing. A study carried out by El Hajjouji et al. (2014) showed that the anaerobic treatment of diluted OMWW during 45 days can degrade up to 76% of phenolic compounds. The major drawback of aerobic treatment is the high consumption of oxygen.

Physical processes

Distillation

Effluents discharged from olive oil mills can be concentrated using a distiller. This process reduces the volume of these effluents by 70% and the residue can be used as fuel to heat the distiller or as fertilizer in agriculture. Condensed water can be reused in olive mill processes. The great problem with this technique is the high cost of energy. Ben Othman et al. (2022) have studied the treatment of OMWW by the distillation technique; the results obtained showed a reduction of phenolic compounds that exceeds 95% by applying a cylindrical-parabolic solar collector as a source of clean

energy which allows them to improve the productivity of the system compared to the traditional solar distillate. The distillate after its neutralization with lime can be reused in the field of irrigation.

Filtration

Achak et al. (2009a) studied the treatment of OMWW by an experimental treatment pilot which consists of two columns filled to a thickness of 10 cm with gravel at the top and bottom and 60 cm with sand. One column is fed with raw OMWW, the other with OMWW diluted to 50% with urban wastewater with a daily tank of 2 cm/day (1.5 l/day). After percolation through the filter, the OMWW is collected by a drain at the system outlet. The dilution of OMWW by urban wastewater ensures a significant elimination of the organic load. Their enrichment by micro-organisms makes it possible to have a strong mineralization of the organic matter. At the sixth week, for diluted OMWW, the reduction rate of crude COD (75%), dissolved COD (91%) and polyphenols (90%), is much greater compared to raw OMWW, crude COD (36%), dissolved COD (33%) and polyphenols (53%).

Membrane treatment

Ultrafiltration is a physical process of solute/solvent separation on a membrane which applies to aqueous solutions, under the action of a hydrostatic force generally not exceeding a few bars. This pressure difference ensures the sorting of the various solutes, by molecular sieving. The size of the molecules retained by ultrafiltration ranges from 0.002 μm to 0.1 μm , depending on the membrane chosen. The biodegradation of OMWW in a membrane bio-reactor (MRB) with an external ceramic membrane, using an acclimatization phase was studied by JAOUAD et al. (2016). The biomass, despite the low respiratory activity of the order of 3.2 $\text{mgO}_2\text{g MLVSS}^{-1}\text{h}^{-1}$ due to the stressful conditions of the surrounding environment, showed significant treatment performance up to a mass composition of OMWW comprising 40% OMWW/ 60% glucose. The COD and polyphenol reduction rates thus obtained reached 90% and 65%, respectively.

Physicochemical techniques

Oxidation

One of the techniques available for the treatment of OMWW is the use of so-called “Advanced

Oxidation Processes” (AOP) systems. These systems are based on the generation of the hydroxyl radical ($\text{OH}\cdot$) which is a highly reactive intermediate with a high oxidation potential and capable of reacting non-selectively with most organic and inorganic substances. The hydroxyl radical is unstable and must be continuously generated in situ by chemical reactions involving ozone, hydrogen peroxide, UV radiation, titanium or a mixture of these different systems.

One of the AOP reactions is based on the decomposition reaction of H_2O_2 catalyzed by iron or another metal called Fenton’s reagent. Kallel et al. (2009) have studied the effect of pH, concentration of organic matter and the dose of pyroxide on the treatment of OMWW by the oxidation technique, hydroxyl radicals were generated by iron and hydrogen peroxide at zero value. The results found showed a reduction of phenolic compounds by 50% with only 3h of reaction. They also showed that the acidic medium and a dose of peroxide equal 9.5 M are the optimal conditions for better processing efficiency. Celalettin et al. (2010) treated OMWW by the advanced oxidation method based on the system (H_2O_2 Fenton). The result found showed a reduction of 62% of phenolic compounds and 84% of chemical demand on oxygen. Martins et al. 2021 investigated the extraction of several phenolic compounds from two types of OMWW, one from one unit per press and the other from a two-phase unit, while using a technique coupling liquid liquid extraction with Fenton processes. Several phenolic compounds have been identified, namely syringic acid, tyrosol, oleic acid. Which allows them both to recover antioxidants, to increase the biodegradability of OMWW and to decrease their toxicity; they have also shown that the OMWW from two-phase units have higher phytotoxicity. There is another technique called ozonation which consists of the use of ozone O_3 as an oxidation product which allows the destruction of a large number of micropollutants and the improvement of odors. Olivier et al. (2009) eliminated the polyphenols issue from the OMWW of Sfax (Tunisia) very quickly and achieved an 80% reduction in polyphenols. The reduction of pollution by this process is very limited and the reagents are very expensive.

Coagulation

The principle of coagulation is based on the destabilization of colloidal particles in suspension

in the effluents by adding a coagulating agent, thus facilitating their agglomeration. The main coagulation agents used are based on aluminum salt and iron. This process is always followed by flocculation to promote contact between the destabilized particles which clump together to form a floc that can be easily removed by settling and filtration. Achak et al. (2008) treated OMWW issue from a modern olive mill by coagulation-flocculation method with lime and aluminum sulfate. The results obtained showed a decrease in the organic load of COD and polyphenols. The best treatment was recorded with lime alone at a dose of 20 g/l as well as the combination of 1.5 g/l of aluminum sulfate and 20 g/l of lime. The treatment with lime alone results in reductions of 75%, 50%, 43% and 50% respectively for polyphenols, suspended solids, COD and discoloration with a production of 35 g/l of sludge. When applying this process, they encountered many constraints including the production of large quantities of sludge and the difficulty of regenerating coagulants for the purpose of their reuse, which requires additional costs. Other authors have adopted the technique of biocoagulation / flocculation as a pretreatment of OMWW, using cactus juice as a coagulating agent, the main objective was to achieve a pretreatment that minimizes the colloidal charge present in the OMWW without affecting the concentration of polyphenols too much. The study showed that the best yields are obtained with a coagulant dose of 10% at pH₁₀. Significant amounts of COD (74%), polyphenols (40%), MES (89%) and turbidity (93%) are removed. Referring to the analysis of the IR-TF spectra of the freeze-dried sludge obtained after pretreatment, they found that the cactus juice of the *Opuntia* species operates mainly by a double mechanism: the destabilization of colloids via Fe²⁺, Ca²⁺ and Mg²⁺ ions (bridging) and the adsorption of dissolved pollutants (polyphenols and dye) on these aggregates (Neffa et al. 2014).

Electrocoagulation

The principle of electrocoagulation consists in generating in situ in the electrolysis cell, the ions likely to cause the coagulation of colloidal particles by dissolving soluble anodes under the action of a current in order to eliminate pollution. The cations from the anode react systematically with water to give soluble polymerized hydroxyl complexes depending on the pH of the medium. These species play the role of coagulant allowing first of all

the destabilization of the colloidal particles to be eliminated by compression of the double electrochemical layer, then its flocculation. In this case, electrocoagulation occurs. The flocs formed can be transported by the gas formed during electrolysis by electroflotation. If the electrolysis continues towards basic pH, the flocs can be adsorbed on the hydroxides formed by precipitation of the soluble hydroxylated polymers. This is called electroprecipitation. Hanafi et al. (2009) treated the OMWW by the electrocoagulation technique using aluminum electrodes. They reduced color (96–99%), chemical oxygen demand (80–85%), polyphenols (75–80%), orthophosphates (94–99%), ammonium (80–85%), zinc (70–75%) and iron (71–76%) for OMWW diluted five times and an electrolysis time of 15 minutes, without pH adjustment, which constitutes a saving for the neutralization stage. The efficiency of the treatment is strongly influenced by the current density, the electrical voltage and the electrolysis time.

Adsorption

Adsorption is a surface phenomenon by which atoms, ions or molecules (adsorbates) attach themselves to a solid surface (adsorbent). The opposite phenomenon, by which molecules adsorbed on a surface detach from it, is called desorption. The use of adsorption technology for phenolic compounds removal from water is very effective from trace amounts to high concentrations, depending on the recycling of the adsorbent. Many studies have been conducted to study the OMWW treatment by several types of adsorbents:

Charcoal

Activated carbon is a black powder consisting essentially of carbonaceous material with a microporous structure. Activated carbons are considered good adsorbents (Jia and Lua, 2008). It can be obtained from a large number of carbonyl materials (wood, coal, coconut, oil residues, etc.). Following carbonization processes followed by duly controlled activation processes. Activated carbon is part of a range of solids with very high porosity and a large specific surface area ranging from 500 to 1500 m²/g, good pore size distribution and high mechanical strength. For this reason, several studies have been carried out to understand the mechanisms of adsorption of phenol by activated carbons, including models of adsorption kinetics and isotherms involved (Sunil et

al. 2013; Sellaoui et al. 2019). The adsorption of phenolic compounds from OMWW on a series of activated carbons prepared by a two-stage steam activation of olive stone and solvent-extracted olive pulp was studied by Galiatsatou et al. 2002. The results obtained showed that isothermal adsorption data were fitted to the Langmuir model, while adsorption kinetics were evaluated by applying the Lagergren model.

Clays

Clays are aluminosilicates. They consist of a basic mineral component (kaolinite, montmorillonite, etc.) and impurities such as quartz, cristobalite, calcite and organic matter. A study was carried out on the treatment of OMWW issues from a semi-modern unit in the Chefchaouen region in Morocco using the clay adsorption technique. The results found show that the time required to reach equilibrium is 5h for all concentrations of caffeic acid and tannic acid, the adsorption power of thermally activated bentonite reaches the maximum at the activation temperature of 200°C. Indeed, the elimination rate can reach about 95% for caffeic acid and tannic acid. This can be explained by the filling of the sites released by the water molecules evaporated from the surface and the interfoliar sites of the bentonite during activation. The adsorption isotherms of caffeic acid and tannic acid on bentonite have been studied. The results show that the isotherms are of L type in the case of caffeic acid and tannic acid, which means that the adsorption decreases as the sites are occupied. The experimental results of this study are compatible with the Freundlich and Langmuir models (Jeddi et al. 2016).

Biosorbents

Biomaterials have developed owing to their low preparation cost and the possibility of production from renewable feedstocks. The term bioadsorbent refers to a large number of products of biological or plant origin that trap organic or inorganic pollutants without prior transformation (Rocher et al. 2008). Achak et al. studied the adsorption kinetics of hydroxytyrosol and tyrosol on banana peel and wheat bran. The results obtained showed that the quantity adsorbed increases with the pH and that the reaction kinetics are very fast (96% reduction after 3 hours of reaction for the banana and 85% reduction after 4 hours of reaction for the bran of wheat). The results showed that the

banana peel adsorption equilibrium is well described by the two models, Langmuir and Freundlich while the wheat bran adsorption equilibrium is described by the Freundlich model. The results obtained also show that the adsorption kinetics of polyphenols on banana peel or on wheat bran fit to a second-order process (Achak et al. 2009b).

Nanomaterials

Other authors have studied the capacity of nanoparticles based on iron oxide for the treatment of OMWW in the batch and continuous system (Nassar et al. 2014). The result found showed rapid adsorption kinetics and reached equilibrium in less than 30 minutes. The adsorption mechanism fits very well with second-order kinetics and the Brunauer–Emmett–Teller (BET) model indicating multilayer adsorption. The result found also showed the adsorption of mineral salts. The use of these nanoparticles in a column mixed with sand showed a significant reduction in polyphenols and organic matter.

Apatites

Several studies have been carried out to examine the power of apatites for the removal of heavy metals (Bailliez, et al. 2004; Saoiabi et al. 2016); however, the use of apatites for the removal of phenolic compounds is very low (Bouyarmane et al. 2014; benaddi et al. 2020). Treatment studies of OMWW using as an adsorbent and apatite synthesized from Moroccan phosphate was carried out by Benaddi et al. (2020); the results showed that a phenol value reduced by 30% and COD by 38%.

Alginate beads

In recent years, different types of materials have been encapsulated with polymers, including alginates, for application in the field of water treatment (AKSU ET AL. 1998; ABU AL-RUB ET AL. 2004). Biocomposites tested by Duarte et al. (2012) show great potential for application as tertiary treatment of OMWW in terms of removal of color, COD, total phenol content and organic compounds. Treatment with active *T. versicolor* biocomposites was slightly more effective in reducing toxicity in OMWW. Moreover, the biocomposites proved to be reusable for more than 29 days of treatment. A study was carried out by Benaddi et al. (2022b), which involved investigation of the efficiency of hydroxyapatite-Sodium alginate composite (HA/SA) for the adsorption

of phenolic compounds, which are contained in OMWW, it showed promising results in reducing the phenol compounds and organic matter by 60% and 64%, respectively, as well as the disappearance of Hydroxytyrosol and the reduction of Tyrosol by 38%, which are the most predominant polyphenols in OMWW.

As recommendation, it can be concluded that for a better OMWW treatment, it is necessary to start firstly with the adsorption of phenolic compounds which are responsible for the non-biodegradability of OMWW while using cheaper adsorbents namely clays, bioadsorbents or apatites then dilute the OMWW with domestic wastewater. The dilution of OMWW by urban wastewater leads to good mineralization of organic matter by enriching the medium with microorganisms, which facilitates the elimination of the organic load and then use the usual techniques that does not require energy, in particular, many studies carried out have shown the feasibility of treatment of a mixture of OMWW and MWW by conventional techniques like a new design of pilot scale vertical flow constructed wetland (PS-VFCW) (El Ghadraoui et al. 2020). Other authors have even proposed and studied the use of this mixture (OMWW urban water) after treatment in irrigation and they found good results (Ahmali et al. 2020)

CONCLUSIONS

As it was shown, there are several techniques for OMWW treatment, comprising biological and physico-chemical processes, but up to this moment, no strategy is available that can be adopted in a global scale. In the end, the authors concluded that for a better OMWW treatment, it is necessary to start first with the adsorption of phenolic compounds which are responsible for the non-biodegradability of OMWW while using cheaper adsorbents, namely clays, bioadsorbents or apatites then dilute the OMWW with domestic wastewater and then use the usual techniques as a plant filter or active sludge for mixture treatment.

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