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Removal of tetracycline from polluted water by chitosan-olive pomace adsorbing films

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ABSTRACT

This paper focuses on the removal of tetracycline from polluted water by chitosan-olive pomace adsorbing films. More specifically, both raw olive solid wastes (olive pomace) and the olive solid wastes/chitosan composite were compared and used for this purpose. Adsorption capacities values of 16 mg×g^{-1} and 1.6 mg×g^{-1} were obtained for the two adsorbents respectively. However, chitosan/olive pomace is proposed as suitable for environmental applications avoiding the dispersion of the pomace blocked inside the chitosan film. To detail the adsorption process, the effect of several experimental parameters such as the pH values, ionic strength, amount of adsorbent and pollutant and temperature values was investigated. The results showed that the adsorption process improved increasing the pH values, with a maximum at pH 8, and it was negatively affected by the presence of salts that retarded the adsorption. Indeed, the desorption of tetracycline was obtained in a $MgCl_2$ 2M solution. So, a low-cost and cleaner approach, fundamental for the pollutant recovery and for an adsorbent safe reuse, for several cycles of adsorption/desorption, transforming a waste in resource is presented. The kinetics, isotherms models of adsorption and the thermodynamic parameters ($\Delta G°$, $\Delta H°$ and $\Delta S°$) were also evaluated observing that the physisorption of the pollutant occurred with and an endothermic character ($\Delta H°>0$) with $\Delta G°<0$ and $\Delta S°>0$. The use of Advanced Oxidation Processes was proposed as possible alternative to the tetracycline recovery, obtaining its degradation after the desorption. With the present paper, the alternative reuse of olive pomace is reported avoiding its disposal in the environment claiming its potential in the removal/recover of emerging contaminants from water.

KEYWORDS: olive mill solid wastes; chitosan; tetracycline adsorption and removal; photodegradation; TiO_2

1. INTRODUCTION

In the last years, the number of publications regarding the detection and the removal of pharmaceuticals and personal care products from aquatic environment, is enormously increased (Sophia and Lima, 2018), stressing the emergency related to their removal from water, due to the insufficiency of the common wastewater treatment plants in removing these contaminants (Egea-Corbacho et al., 2019; Lopez-Serna et al., 2019; Yang et al., 2017; Naidu et al., 2016; Eggen et al., 2010). These substances have been called “emerging contaminants” (EPs), and are present in treated and untreated wastewater (UNESCO, 2011). In this regard, among the different sources of water contamination, antibiotics in general, and tetracycline in particular, are worth mentioning (Dehghan et al., 2019; Wen et al., 2019). Indeed, Tetracycline (TC), a broad-spectrum antibiotic, usually applied in human and veterinary medicine (Chen et al., 2016), is frequently found in wastewater (Yeşilova et al., 2018; Safari et al., 2015; Martins et al., 2015; Zhu et al., 2014). Although TC is considered easily degradable, only a small portion of TC can be degraded to inactive products through metabolic reactions, such as basification, dissociation, and glucuronidation (Dai et al., 2019; Lin et al., 2013), obtaining a lower mineralization rate and detecting low amounts of total organic carbon, indicative of the presence of intermediate compounds, probably more toxic than the original one (Dai et al., 2019; Daghrir and Drogui, 2013; Lin et al., 2013). Daghrir and Drogui (2013) reported that the removal of tetracycline through wastewater treatments is not complete. So, the wastewater treatment plants are unable to completely remove this pollutant that induces adverse effects on ecosystems and human health. As a result, with the increasing concern for water quality and public health, the development of efficient platforms for TC removal from water is highly desirable, by applying new efficient, sustainable and low-cost wastewater treatment technologies. Among various approaches, the adsorption methods are considered suitable for this purpose, avoiding the release of other pollutants usually arisen from chemical treatments (Martins et al., 2015), and are efficient and low-cost approaches for managing pollutants (Ahmed and Hameed, 2018; Martins et al., 2015). For the TC removal is interesting the use of MOF (Zhou et al., 2018), cryogels (Yeşilova et al., 2018), zeolite-hydroxyapatite-activated oil palm ash composite, active carbon and pumice (Khandaya and Hameed, 2018; Selmi et al., 2018; Fan et al., 2016; Guler and Sarioglu, 2014). The importance of the TC removal arises mainly from the very recent publications reported by Dai et al. (2019), Dehghan et al. (2019) and Wen et al. (2019) that described the use of ground spent coffee, zeolitic imidazolate frameworks and bentonite-derived mesoporous materials for its removal. Other information are reported in the works of Ahsan et al. (2018), Qin. et al. (2018), Zhang et al. (2018), Ma et al. (2017), Sayğılı and Güzel (2016), Zhang et al. (2015) and Gao et al. (2012). Although the mentioned works reported a highly efficient removal of TC from water, dispendious conditions of work are described to obtain the adsorbent. Further, among these adsorbents, the possibility of recovering and reusing the adsorbent for several cycles, by using green methods, inhibiting the formation of secondary pollutants, is not considered (a detailed description is reported at the end of the paper). On this base, the present work reports the first example about the development of an approach to a cleaner production/pollution prevention (Belayutham et al., 2016) by using agricultural wastes for removing and recovering TC from water with a simple and eco-sustainable technology. Indeed, in the growing interest towards the development of eco-friendly procedures in several application fields (Gubitosa et. al., 2018; Lu et al., 2018; Rizzi et al., 2018a, 2018b, 2016a, 2016b; Zilouei et al., 2018; Petrella et al., 2016, 2012, 2010) including the environmental one, the use of agricultural/food wastes appear very interesting for this purpose (Zilouei et al., 2018; Rizzi et al., 2017a, 2014; Semeraro et al., 2017; Liu et al., 2012). The olive pomace (OP) usage, as agricultural waste, if compared with the aforementioned works, could be considered a way for reducing the overall environmental impact of food by-products through a virtuous life-cycle (Muscolo et al., 2019; Hens et al., 2018; Morali et al., 2016; Kurk and Eagan, 2008; Finnveden et al., 2005). About this, it is noteworthy that OP was previously used to remove textile dyes and metals from water (Petrella et al., 2018; Petrella et al., 2017; Rizzi et al., 2017a, 2017b, 2017c), demonstrating its wide-range application with respect to different class of pollutants and the previous literature.

More specifically, two adsorbent systems are described in this work: OP in powder, and chitosan membrane (CH) blended with OP powder (CH/OP). CH was used as physical platform to sustain OP avoiding its dispersion in water for a safer environmental application. Differences between OP and CH/OP on the removal of TC were investigated, and CH/OP was selected as the most suitable one, resulting a highly performant low-cost alternative material. Another important aspect of this work is the removal of ketoprofen, diclofenac, and their mixture in presence of TC, evidencing the wide potentiality of CH/OP as adsorbent. The TC recover from the adsorbent was also successfully explored, proposing the recycle of both adsorbent and TC in a virtuous life-cycle. Advanced Oxidation Processes (AOPs) were also proposed as alternative with respect to TC recovery. For this purpose, TiO_2, as photocatalyst, was used both to destroy the desorbed TC in solution and inside the adsorbent (obtaining CH/OP/TiO_2 to perform experiments of solid-state TC photodegradation). The results of this research not only transform the waste in a resource, but also suggest novel approaches for the clearness of wastewater containing TC, that can be of great practical significance. With this alternative use of OP, its disposal, as pollutant, should be avoided, giving it another claim and valorising the agricultural waste. Additionally, the cost associated for its disposal, and usually supported by oil mills, should be lowered. It is worth to mention that the main world producer countries of pomace, as Spain, Italy, Greece, Turkey, Syria and Tunisia, could take advantage with this innovative application. Indeed, olive production across the Mediterranean area has a long past and nowadays the olive oil industries are very important in these countries, both in terms of wealth and tradition.(Rizzi et al., 2017a) Interestingly, Muscolo et al. (2019), recently reports as in the Europe, Italy is the second European oil producer country with the main production in Sicily, Calabria and Puglia. Unfortunately, many oil mills are family enterprises that don't know the risks for the treatment of agricultural wastes, and the more informed companies are generally not inclined to adopt new technologies if the cost is elevated. As a result, these wastes are often disposed untreated into the environment causing serious damage to soil and groundwater. So, the proposed alternative reuse of the OP could be a good solution, reducing the environmental impact.

2. EXPERIMENTAL

2.1 In batch equilibrium experiments. Experiments were carried out to study the behavior of OP and CH/OP respect to the TC adsorption. The adsorption capacities were calculated in terms of q_t (mg×g^{-1}) at time *t* for TC, by applying the following **Equation 1** (Rizzi et al., 2017a, 2017b, 2017c):

$$q_t = \frac{C_0 - C_t}{W} \times V \tag{1}$$

where *V* represents the volume of adsorbed solution (15 mL), *W* is the weight of the dried adsorbent material (g), C_0 and C_t (mg×L^{-1}) represent the concentration of TC at initial and *t* time. In detail, a fixed amount of adsorbent into flasks containing 15 mL of TC solution at different initial concentrations (5.0×10^{-5}M, 2.5×10^{-5}M, 1.25×10^{-5}M, corresponding to 24 mg/L, 12 mg/L and 6 mg/L of TC, respectively) was used. The adsorbents were put in flasks containing TC solutions, under continuous stirring at 250 rpm, and UV-Vis absorption spectra were recorded to evaluate the TC removal efficiency from water. To infer the exact TC concentration, the internal standard calibration method was used. The effect of both solution ionic strength, (by using different salts at 0.1M and 2M of concentration), and changes in pH values, (ranging from 2 to 12), were also investigated. Besides, the effect of adsorbent amount was explored as follows:

a) OP: from 6 mg to 100 mg

b) CH/OP composite films: from 75,14 to 468,87 mg (in detail CH/OP1: 75.14 mg; CH/OP2: 173.72 mg; CH/OP3: 291.94 mg; CH/OP4: 468.87 mg).

2.2 Adsorption kinetics. In order to obtain information related to the kinetics of the adsorption process, both pseudo-first-order and pseudo-second-order kinetic models were adopted and applied to experimental data. The linearized equations for pseudo-first (**Equation 2**) and pseudo-second-order (**Equation 3**) models were adopted (Rizzi et al., 2017a):

$$\ln(q_e - q_t) = \ln(q_e) - K_1 \times t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} \times t \tag{3}$$

where q_e and q_t represent the OP or CH/OP adsorption capacities at equilibrium and at time *t*, respectively ($mg \times g^{-1}$) and k_1 (min^{-1}) and k_2 ($g \times (mg \times min)^{-1}$) are the rate constants of pseudo-first and second order models, respectively.

2.3 Adsorption Isotherms. Among the reported models, the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm equations (Rizzi et al., 2018b; Sayğılı and Güzel 2016) were applied to analyze the sorption process of TC on the presented adsorbents. If the Langmuir model describes the experimental data, it suggests that the adsorption occurs onto homogeneous surfaces with uniformly energetic adsorption sites and a monolayer coverage. **Equation 4** reports the adopted linear form of the Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L\,Q_0} + \frac{C_e}{Q_0} \tag{4}$$

where q_e (mg×g^{-1}) is the adsorbed amount of TC at equilibrium, C_e is the equilibrium concentration of the TC (mg×L^{-1}) in solution, K_L is Langmuir equilibrium constant (L×mg^{-1}) and Q_0 the maximum adsorption capacity (mg×g^{-1}). The Freundlich isotherm was also applied. The assumption of the model is that the surface of the adsorbent is heterogeneous and adsorption sites having different energy of adsorption are contemplated. The energy of adsorption varies as a function of the surface coverage. **Equation 5** reports the linear form of this equation.

$$\log(q_e) = \log(K_F) + \frac{1}{n}\log(C_e) \tag{5}$$

where K_F (L×mg^{-1}) is the Freundlich constant and n is the heterogeneity factor. K_F is related to the adsorption capacity, whereas the 1/n value indicates if the isotherm is irreversible (1/n=0), favorable (0<1/n<1) or unfavorable (1/n>1). When the Temkin model in its linear form was adopted, the **Equation 6** was used.

$$q_e = B_1 ln(K_T) + B_1 ln(C_e) \tag{6}$$

The isotherm constants B_1 and K_T can be determined from the slope and the intercept of **Equation 6**, respectively. K_T is the equilibrium binding constant (L×mol^{-1}) corresponding to the maximum binding energy and B_1 is related to the heat of adsorption. In this case, if the model well fit the experimental data it indicates that the heat of adsorption during the adsorption process linearly decreases with the coverage due to adsorbent–adsorbate interactions. The adsorption is characterized by a uniform distribution of binding energies.

With regard the Dubinin–Radushkevich isotherm (D-R), it is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. **Equation 7** represents the linear form of the model:

$$\boldsymbol{ln q_e = ln(Q_0) - K_{D-R}} \times \varepsilon^2 \qquad \textbf{(7)}$$

where q_e, Q_o, $K_{D\text{-}R}$ are the adsorption capacity at equilibrium (mg/g), the theoretical isotherm saturation capacity (mg/g) and the Dubinin–Radushkevich isotherm constant (mol^2/J^2), respectively. ε is the Polanyi potential and it is described by **Equation 8**:

$$\varepsilon = \boldsymbol{RT ln}(\mathbf{1} + \frac{\mathbf{1}}{\boldsymbol{C_e}}) \qquad \textbf{(8)}$$

where R, T and C_e represent the gas constant (8.314 J/mol K), absolute temperature (K) and adsorbate equilibrium concentration (mg/L), respectively.

The approach is usually applied to distinguish the physical and chemical adsorption with its mean free energy, E, that can be inferred by the following relation (**Equation 9**):

$$\boldsymbol{E} = \frac{\mathbf{1}}{\sqrt{\mathbf{2}\boldsymbol{K_{D-R}}}} \qquad \textbf{(9)}$$

From the value of E, information about the adsorption nature can be deduced. Indeed, if the value of E is between 8 and 16 kJ/mol, the adsorption process is supposed to proceed via chemisorption, while for values of E<8 kJ/mol, the adsorption process is of physical nature.

2.4 Thermodynamic studies. Free energy (*ΔG°*), entropy (*ΔS°*), and enthalpy (*ΔH°*) were determined (Selmi et al., 2018; Chen et al., 2016) for the TC adsorption on CH/OP (or CH/OP/TiO_2) at the three selected temperatures, 298, 288 and 278 K. In particular, the change in free energy (ΔG°) was estimated from **Equation 10**:

$$\mathbf{\Delta G° = -RT}\ \boldsymbol{Ln}\ \mathbf{K_{eq}} \qquad \textbf{(10)}$$

in which R is the universal gas constant (8.314 J/mol K), T is the temperature (K) and K_{eq} represents the equilibrium constant. So, the values of $\Delta H°$ and $\Delta S°$ were inferred combining **Equation 10** with **Equation 11** obtaining **Equation 12**.

$$\Delta G° = \Delta H° - T\Delta S° \qquad \textbf{(11)}$$

$$\ln K_{eq} = -\frac{\Delta H^{0}}{RT} + \frac{\Delta S^{0}}{R} \qquad \textbf{(12)}$$

See ESI for more experimental information.

3. RESULTS AND DISCUSSION

The proposed adsorbents were preliminary investigated from the morphological point of view, through macroscopic and microscopic analyses (see ESI for a detailed description). **Figure S1A** reports as chitosan film appeared without further modification, while **Figures S1B** and **C** show OP in powder and blended inside chitosan film (CH/OP), respectively. The microscopic observation (**Figures S1D, E**) of the CH/OP composite film, from two images related to different regions of the same adsorbent, indicated the irregular surface morphology of our sample. The presence of irregular structures on the adsorbent external surface are important key features for the adsorption of pollutants (Rizzi et al., 2017a). X-ray map images of the adsorbent were also acquired. As expected, given the nature of chitosan films and the main components of pomace (cellulose, hemicelluloses, lignin, amino acids and/or proteins, see ESI for the detailed composition of the pomace), the main presence of nitrogen and oxygen atoms was observed (**Figures S1F-G**). When the adsorbent CH/OP was enriched with TiO_2, the catalyst appeared uniformly distributed, as confirmed by results relative to the different investigated film regions (**Figures S1F-G**). The porous nature of the OP was also confirmed by measuring both the density and the pore diameters (see ESI for experimental details). The density of the used material was estimated to be 1.5240±0.0020 g/cm^3. While the average pore radius of the adsorbent was 15.649 Å with a pore diameter ranging from 20 to 500 Å. The calculated BET total surface area was greater than 0.324 m^2/g, and the total volume and surface area of pores were 0.002 cm^3/g and 0.225 m^2/g, respectively.

3.1 Adsorption of TC from water by OP and hybrid CH/OP adsorbents

In agreement with literature (Abdel-Ghani et al., 2016; Abdulghani et al., 2013), TC showed a characteristic UV-Vis absorption spectrum with two main absorption bands in the UV region, corresponding to $\pi \rightarrow \pi^*$ transitions. These bands can be considered diagnostic for spectrophotometrically following the TC removal, by the pomace, from water. Chitosan represents only a physical support for OP, because TC is not adsorbed by chitosan (*data not shown*). Starting from OP powder, fixing the TC concentration at 2.50×10^{-5}M, a significative removal was obtained when the amount of the adsorbent was ≥25 mg (**Figure 1A**). By choosing 1h as contact time, the adsorbed TC percentage increased by increasing the OP amount from 25 mg to 100 mg. At 100 mg of OP, about the 75% of the TC was removed, and, by extending the contact time, the adsorption was almost complete. On the other hand, when the OP amount was set at 25 mg, while changing the TC amount (**Figure 1B**), the results indicated as, by diluting the TC solution, the adsorbed TC percentage increased. The same results were obtained when OP was blended with chitosan forming CH/OP (**Figures 1C, D**). More specifically, different CH/OP films with different weights were used and indicated by numbering them consecutively as CH/OP1, CH/OP2, CH/OP3 and CH/OP4, as function of film mass increasing. According to results obtained for OP, maintaining constant, in this case, the contact time at 2h, the adsorption percentage increased with the adsorbent weight (**Figure 1C**). Indeed, from CH/OP1 to CH/OP4, the removed TC percentage increased from about 25% to 75%. By diluting the TC solution, using the previous experimental condition and the CH/OP3 sample, the percentage of the TC removal from water increased (**Figure 1D**). Overall, these observations suggested that TC adsorption depends on the free sites on the adsorbing surface. In particular, as the initial TC concentration decreased or the amount of adsorbent increased, multiple active sites resulted available to host the TC molecules, increasing the pollutant amount adsorbed (Rizzi et al., 2019, 2018b). However, as arise from the contact time length and from the weights of the used films, the CH/OP composite material showed a lower rate of adsorption, in comparison with OP, due to the presence of the chitosan matrix that delayed, as a whole, the process. To get more details about the adsorption process and to evidence the adsorption capacities of both the adsorbents, the q_t values were calculated (**Equation 1**) and compared, checking the best kinetic model able to fit the experimental data. **Figures 2A** and **B** show the q_t values for OP (**Figure 2A**) and CH/OP (**Figure 2B**), respectively, changing the adsorbent amounts. Interestingly, the q_t evolution of CH/OP tended to become linear in comparison with the results arisen from the use of OP. More specifically, TC adsorption onto OP at the beginning of the process was rapid (**Figure 2A**), becoming gradually slower as approaching the equilibrium (plateau of the curve), due to the free site saturation. Indeed, at the beginning of adsorption, many free active sites were available for TC, but with elapsing the time, they got occupied slowing down the adsorption process (Rizzi et al., 2019; Khanday and Hameed, 2018). Further, the initial concentration gradient contributed to enhance the driving forces due to pressure gradient, which results in movement of TC molecules towards the adsorbent surface (Dai et al., 2019; Khanday and Hameed, 2018). At the plateau region, another effect that can be considered was the arising of repulsive forces between TC molecules in solution and those adsorbed onto the adsorbent, contributing in slowing down the adsorption process (Chen et al., 2016). Regarding the CH/OP system, the initial rapid change of the q_t values was absent (**Figure 2B**). Since chitosan films without OP are unable in adsorbing the TC, this result indicated that the presence of the polysaccharide limited the TC uptake, overall hindering its removal from water. However, also in this case, with elapsing the contact time, the q_t values tend to level off. Further, when blocked inside CH, the OP was present as aggregates and not as fine powder contributing in reducing the adsorbent surface area. It is noteworthy that for both the adsorbents, by increasing their amount, the relative adsorption of TC molecules increased (see the plateau region beginning that was quickly reached in presence of the largest amount of the adsorbent); on the other hand, the adsorption capacity decreased. This result, in agreement with literature (Rizzi et al., 2018b, 2019), can be explained considering that, using a large amount of adsorbent, the adsorption sites partially remained unsaturated during the adsorption process, reducing as a whole the q_t values, nonetheless the TC removal was quite complete.

The kinetic models well agree with these findings. In particular, by using the q_t values reported in **Figures 2A** and **B**, the results reported in **Figures 2C-F**, applying the pseudo-first (**Equations 2)** and pseudo-second (**Equations 3)** order kinetic models, were obtained. The calculated R^2 values and the correspondence between the adsorption capacity at equilibrium, $q_{e,cal}$ (calculated from the kinetic elaboration), and $q_{e,exp}$ (experimentally inferred form **Figures 2A** and **B**) indicated that the TC adsorption on OP followed a pseudo-second order kinetic (R^2>0.99), while on CH/OP, a pseudo-first order one (R^2>0.99). Both for OP in powder and CH/OP, the kinetic constants are reported in **Table S1**. On the other hand, when CH/OP was taken into account the influence of other factors should be considered more important and the TC diffusion inside the adsorbent could play a key role, due to the presence of chitosan network that hindered the TC adsorption. To gain more insights into the delayed TC adsorption process on CH/OP, the TC concentration was changed observing how the adsorption modifies on the CH/OP film. In detail, whereas the adsorption efficiency decreased at increasing the TC amount (**Figures 3A**), the adsorption capacities of the adsorbent (q_e) increased from 0.1 to 0.5

mg/g. The high TC concentration induced a greater mass transfer, increasing the adsorption capacity indicating the important role of diffusion. So, the Weber equation $q_t=K_i t^{1/2}$ was applied, by varying the amount of TC, and a linear trend was observed (**Figure 3B**). The kinetic constants related to the intra-domain diffusion rate in mg/(g×min$^{0.5}$) were calculated. Increasing the TC concentration, the following K_i values were obtained: 0.02 mg/(g×min$^{0.5}$), 0.03 mg/(g×min$^{0.5}$) and 0.07 mg/(g×min$^{0.5}$). So, when CH/OP adsorbent was used, the intra-domain diffusion can be considered the main mechanism controlling the sorption process (Moussavi and Khosravi,2011).

3.2 Salts and pH effects on TC adsorption onto OP.

Due to the main role of the OP in the TC removal from water in comparison with the CH film, a deep insight study about the effect of ionic strength and pH on the TC adsorption process on OP was performed.

The molecular structure of TC (**Figure 4A**) is characterized by three dissociation constants (Dong et al., 2018). In particular, TC exists as cation (TCH_3^+) at pH<3.3 (pKa_1), as zwitterion ($TCH_2^{\pm}$) in the range of pH 3.3–7.7 (pKa_2), and as TCH^- and TC^{2-} anionic forms at pH>7.7 (the latter anion for $pH>pKa_3=9.7$) (Chen et al., 2016). In order to better investigate the process, the TC adsorption onto pomace was studied at several pH values. More specifically, a small amount of pomace, *i.e.* 25 mg, was used, fixing the contact time at 1h. The percentages of TC adsorption were evaluated and reported in **Figure 4B**. Interestingly, a very low TC adsorption was observed at pH 2, while, increasing the pH values, the TC adsorption increased. On this base, the pH_{PZC} of the OP-based adsorbent was experimentally measured (**Figure 4C**) by using the drift method (Rizzi et al., 2018b), and a pH_{PZC} around pH 8 was obtained, indicating that the pomace was positively charged below pH_{PZC}, while is negatively charged at $pH>pH_{PZC}$. So, the low adsorption capacity observed at pH<4, suggested the presence of repulsive forces between TCH_3^+ and the positively charged surface of the adsorbent. On the other hand, the increment of TC adsorption observed in the 7-10 pH range (**Figure 4B**), exactly around the pKa_3 of TC ($pKa_3=9.7$), where the charge on the absorbent drops to zero, could indicate better interaction between $TCH_2^{\pm}$, TCH^{-} and the neutral surface of the adsorbent. At pH>10, when the TC is mainly present in its dianionic form (TC^{2-}), there is again a slight electrostatic repulsion with the negatively charged surface of OP, determining, as a result, the slight reduction of the antibiotic adsorption. Overall, these observations can be interpreted considering the importance of electrostatic interactions between TC and the pomace surface (Peiris et al., 2017; Rivera-Utrilla et al., 2013; Rivera-Utrilla and Sanchez-Polo, 2002). However, since the adsorption was observed at each pH value, in particular when the charge of the adsorbent surface was zero, it is possible to hypothesize that, besides the electrostatic interactions, the TC adsorption could involve the hydrogen bonds formation, between the TC phenolic groups and the oxygenated groups of OP (Rivera-Utrilla et al., 2013), and Van der Waals forces.

To better detail the process, some experiments were performed in presence of different electrolytes (NaCl, NaI, KCl, LiCl, $MgCl_2$, $CaCl_2$ at 0.1M), using 25 mg of pomace, at pH 6, and 1h, as contact time (**Figures S2A**).

As shown, the OP adsorption capacity, in presence of electrolytes, was quite lower than in absence of salt (**Figure S2A**). In particular, by increasing the cation size, in the series $Li^+<Na^+<K^+$, the adsorption reduced (passing from 50 to 30% in the presence of salts), suggesting that the electrolytes hinder the attractive electrostatic interactions between TC and OP (Peiris et al., 2017). In particular, as usually reported in similar studies (Zhang et al., 2019), the salts could occupy the sites on the adsorbent, competing with TC molecules for the adsorption. This changes the TC affinity and reduces the adsorption efficiency. Interesting results were observed when salts containing bivalent ions, as Ca^{2+} and Mg^{2+} (**Figure S2A**), were investigated: the use of Mg^{2+} more affected the adsorption process, significantly decreasing the TC removal from water. In literature, Ca^{2+} and Mg^{2+} ions are

indicated as inhibitor of the TC adsorption due to the formation of particular complexes (Zhao et al., 2011; Lambs et al., 1988). So, the observed results can be interpreted considering that the formation of a complex between TC and Ca^{2+}/Mg^{2+}, reduces the affinity of the TC for the adsorbent surface (Punamiya et al., 2015). Therefore, summarizing, while in the case of electrolytes containing monovalent cations, it was possible to affirm that the OP adsorption capacity decreased due to an enhanced screening effect of the OP surface charges, with a reduction of the affinity between OP surface sites and TC (Rivera-Utrilla et al., 2013); on the other hand, regarding the Mg^{2+} effect, the TC adsorption resulted inhibited due the formation of TC-Mg^{2+} complexes through the coordination of the TC ketoenolate moiety that stabilized the zwitterionic conformation of TC, as well documented in literature (Palm et al., 2008; Wessels et al., 1998). As a result, it is possible to hypothesize that the TC ketoenolate moiety could be also involved during the adsorption process. Finally, since the behavior exhibited by NaCl, NaI, KCl and LiCl was the same, NaCl was selected among them for studying the effect of monovalent electrolyte concentration, by increasing its concentration from 0.1M to 2M. Moreover, also the bivalent cation concentration effect was explored, increasing the concentration by comparing two Mg^{2+}-based salts, $MgCl_2$ and $MgSO_4$ (**Figure S2B**). From a general observation, increasing the electrolyte concentration in the medium, it is evident that the adsorbed TC percentage was further reduced. In particular, independently by the counter-ion (Cl^- or SO_4^{2-}), in presence of high Mg^{2+} amounts, the TC adsorption failed, indicating the so far suggested important role of the cation Mg^{2+}.

3.3 Release of TC: adsorbent recycle.

CH/OP composite film appeared to be the best candidate for a real wastewater treatment due to the manageability of chitosan film with respect to OP powder; so, it was subjected to adsorption consecutive experiments, with the aim of evaluating its loading capacity. CH/OP was put in contact with a TC solution (2.50×10^{-5}M), and, after its cleaning, that solution was substituted with a fresh one. UV-Vis spectra were acquired at appropriate contact times for evaluating the adsorbed TC percentage (**Table S2**). So, under our experimental conditions, the CH/OP film was very performant for the TC removal from water, also after 8 consecutive cycles of adsorption. These results emphasized the use of this ecofriendly and low-cost approach for wastewater treatments (Fresner, 1998), even though the contact time, necessary to obtain adsorption efficiencies greater than 50%, raised from 7h to 64h, at the increasing of the adsorption cycles number. The release of the total amount of the adsorbed TC was also attempted, obtaining a release of 95%.

Moreover, the ability to adsorb and desorb the pollutant for several consecutive adsorption/desorption cycles was investigated. CH/OP was dipped in the TC solution (2.50×10^{-5}M); then, after 2 h (this time can be also increased for increasing the adsorbed TC amount), the film was removed from the TC solution and dipped again in a 2M $MgCl_2$ solution, selected as the best salt to induce the TC recovery, for other 2h, obtaining the TC release (**Table S3**). Three cycles of adsorption/desorption were accomplished, and, after each cycle, the film was washed with fresh water for removing the electrolyte excess, that otherwise could slow down the subsequent TC adsorption. After three cycles, the very good performance of the CH/OP composite is evident (**Table S3**), suggesting that more than 3 cycles can be performed.

3.4 Isotherm of adsorption.

A comprehensive investigation of the adsorbate/adsorbent equilibrium relationship on CH/OP (**Figures 5**) was carried out by means of the Langmuir, Temkin, Freundlich and D-R isotherm models (**Equations 4-9**). The obtained results suggested that the process can be well described by Langmuir, Temkin and Freundlich isotherm models suggesting the heterogeneous character of the adsorption process. (Jang et al., 2018). See **Table S4** for the isotherm parameters calculated also at different temperature values. Interestingly, the favorable character of the adsorption process was also evidenced by the *n* values arisen from the Freundlich equation. Indeed, $n>1$, in the range 1.45-1.53, were obtained during this study by changing the temperature values. The increase of the constant isotherm values with the temperature indicated the endothermic character of the process. Although the D-R model fitted not well the experimental data, the correspondent parameters were also inferred and reported in **Table S4**. The Q_0 values well agree with the correspondent ones obtained by applying the Langmuir model, on the other hand the E values <8 KJ/mol suggested that the adsorption nature of TC onto the adsorbent was the physisorption (Sayğılı and Güzel, 2016).

3.5 Thermodynamic analysis for CH/OP.

Three temperature values were explored, i.e. 278, 288 and 298 K by using CH/OP3 and TC solution with a concentration of 2.5×10^{-5}M. At first glance the results reported in **Figure 6A** indicated as increasing the temperature values, increasing the percentage of TC adsorption from water. At 298 K, after 6h of contact time, the removal was almost complete. The endothermic character of the adsorption process was easily inferred. In order to obtain the thermodynamic parameters, the K_{eq} values were calculated at each temperature (**Table S5**) and by using **Equations 10** and **11**, the ΔG° values were inferred. Subsequently, by using **Equation 12**, ΔH° and ΔS° were obtained (**Table S5**) by plotting $ln(K_{eq})$ *vs.* $1/T$ (**Figure 6B**). The process occurred with a $\Delta G°_{298K}=-13.20$ KJ/mol and $\Delta H°=+50.00$ KJ/mol indicating the spontaneity and confirming the endothermic character of the process, respectively. The positive value of $\Delta S°=+210$ J/mol K suggested as the randomness at the surface of the adsorbent increased. (Tanhaei et al., 2019)

3.6 Degradation of TC free in solution after the desorption from CH/OP.

It is worth to mention that the TC photodegradation is well-known since several years and various information are reported in literature (Jiang et al., 2018; López-Peñalver et al., 2010). The adsorbent reuse could be gained also by photodegrading the adsorbed pollutant, exploiting the photocatalytic features of the well-known photocatalyst TiO_2 to

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be able to induce the formation of •OH under irradiations and by means of Advanced Oxidation Processes (AOPs). In particular, for forming the hydroxyl radical (•OH) in water (Jiang et al., 2018) the attention was focused on the synergistic use of UV, H_2O_2, and Fe(II), through the following combinations: UV-TiO_2, UV/H_2O_2/TiO_2, UV/H_2O_2/Fe/TiO_2. As indicated by Vega et al. (2018), •OH is one of the most important radical species produced by AOPs, being highly reactive and non-selective, with high organic reaction rate constants. Safari et al. (2015) and references therein, suggested that the addition of H_2O_2 (and Fe^{2+}) to TiO_2 under irradiation improved the TC degradation. Indeed, additional •OH are produced under this condition due to the photolysis of the peroxidic bond (–O–O–). The synergistic activity of Fe^{2+} and H_2O_2 under Fenton condition was thus exploited triggering the oxidation process with the further production of •OH (Huang et al., 2017).

On this ground, as first step, CH/OP/TiO_2 was used. After the adsorption of TC, the adsorbent was irradiated with a UV lamp at different times, namely 1, 2, 4 and 8h. Further, the experiments were performed on wet (15 mL or 30 mL of water) and dried CH/OP/TiO_2. In all examined conditions of work, the adsorbed TC was poorly and very slowly degraded, also extending the contact time. This result, nonetheless the presence of TiO_2, could be attributed to the presence of phenols from the pomace, whose antioxidant activity along with their high absorbance in the UV-Vis region is well-known and able to inhibit the TC degradation, acting as UV filter. For example, in **Figure 7A,** the UV-Vis spectrum of the phenols purposely desorbed by the used pomace is reported, highlighting the absorption band of the antioxidants at λ<300 nm able of shielding the UV radiation. In order to overcome this problem, the irradiation with UV light was attempted by swelling the adsorbents loaded with TC in a $MgCl_2$ solution (2M). Under this condition, the release of TC should increase its photodegradation. However, by comparing the results obtained from CH/OP and CH/OP/TiO_2, it was observed how the use of only UV light was enough for photodegrading the outcoming TC. The synergic action of TiO_2 and UV did not take place. Indeed, after 4h of irradiation time, about the 70% of the adsorbed TC was destroyed in both cases. Due to these results, the photodegradation was performed after the TC release from CH/OP avoiding, for the moment, the use of the CH/OP/TiO_2 adsorbent.

In a subsequent experiment, the TiO_2 was added as suspension in the solution containing the released TC. More specifically, CH/OP3 was swollen in a TC solution with a concentration of 2.5×10^{-5}M, and after the almost complete removal of the TC, the release in $MgCl_2$ was carried out. As seen in **Figure 7B**, a very low TC degradation was observed if the TC solution was irradiated with UV light (λ=254 nm) in absence of TiO_2, indicating that the TC molecule is photochemically resistant. Indeed, 6h were necessary to degrade about the 80% of the pollutant (condition 1, in **Figure 7B**).

This finding could be attributed to a small amount of •OH formed in the bulk solution under these conditions. On the other hand, in presence of the TiO_2 as photocatalyst, purposely added to the solution, the TC degradation and inactivation was observed within 1h (condition 2 in **Figure 7B**). In the presence of TiO_2, the production of active species such as •OH, hole and superoxide ions makes the process very efficient (Vega and Valdes, 2018). The H_2O_2 addition to TiO_2 suspensions improved (Safari et al.,2015) the process obtaining the 100% of TC degradation in short time, practically the process occurred accomplished after 1h (condition 3). As previously explained, additional •OH are produced under this condition. Indeed, the synergistic use of UV/H_2O_2, H_2O_2/O_3, Fenton, electro-Fenton, and photo-Fenton showed a good performance for the removal of TC from an aquatic environment. Exploring various combination of UV light, H_2O_2 and Fe as photodegrading agents, as reported in **Figure 7B** (condition 4), when the system H_2O_2/UV was considered, the TC degradation was completed in 1h. By comparing this experimental condition with the use of the only UV light that required ~6h for 80% of the

TC degradation, it was clear that the UV/H_2O_2 treatment was more effective in the pollutant degradation. If the Fenton process was considered (**Figure 7B**, condition 5), the degradation occurred slightly retarded (in 2h), but by adding the UV irradiation, the time necessary for a complete degradation was halved (**Figure 7B**, condition 6). The production of hydroxyl radicals that occurred during the decomposition of H_2O_2 in the presence of ferrous ions, increased in presence of UV–Vis irradiation, thanks to the regeneration of ferrous ions, thus forming additional •OH (Rossi Bautitz and Nogueira., 2007). Overall, during this work different method for photodegrading the TC were presented in order to demonstrate as the antibiotic adsorption process on CH/OP and/or OP could be considered a very fashionable approach to treat wastewater, recovering and/or photodegrading TC.

3.7 Comparison of Q_{max} values obtained in literature for removal of TC from water by using different adsorbent materials.

Table 1 reports the comparison of Q_{max} values (the maximum adsorption capacity) of the studied adsorbents. Many papers are reported in literature about the TC removal and for this purpose the most representative have been selected, from 2012 to nowadays, proposing the comparison of different typology of adsorbents. It is worth to mention that, in the most cases, different temperature and pH values, and different experimental conditions were adopted. If compared with our results, the showed data indicate that very high adsorption capacities were obtained for composite cryogel, KOH-activated carbon or active carbon from tomato. The use of sulfonated tea waste and ground spent coffee, as more greener production approaches, occurred more interesting for our aim; however, if the production of the former required very hard conditions of work (Authors reported the use of high temperature and H_2SO_4 for 4h), on the other hand the latter adsorbent was held in a thermostatic chamber at 60°C for 48 h. So, beside the high adsorption capacities under optimized condition of work, all of listed adsorbents required pre-treatment (increasing the associated costs) if compared with our work, or in same case hard acid condition of work far for cleaner and sustainable production technologies. On the other hand, a greener approach is presented, for the first time, in this paper avoiding the use of additional treatments and hard condition of work proposing agricultural wastes as resources. Indeed, in the work of Dai et al. (2019) the use of ground spent coffee did not investigated the possibility to recover the pollutant or perform consecutive cycles of adsorption and/or desorption. So, all of the adsorbents reported in **Table 1** could be considered secondary pollutant and should be removed from the environment. On the other hand, with our work, the olive wastes are removed from the environment and used to clean water from pollutants. The latter is recovered proposing safe ecofriendly adsorbents, and as alternative the TC can be photodegraded far from water after the recover avoiding the production of more toxic metabolites in water. So, nonetheless, during this study the obtained Q_{max}, arisen from the Langmuir isotherm, are lower than values reported for other materials, several consecutive cycle of adsorptions (or adsorption/desorption) are proposed increasing the adsorption capacities showing other advantages, as the reuse of safe adsorbents, overpassing this drawback.

Overall, avoiding the use of chitosan, the Q_{max} can be increased to 16 $mg \times g^{-1}$ and to much more greater values considering the adsorption/desorption approaches.

Moreover, the economic impact of the proposed technology can be beneficial for real applications. Indeed, the associated costs are very low: 0.00031€ per gram of row olive pomace and 1€ per gram of chitosan. Further, in agreement with the principles of circular economy and green chemistry, the use of salts for the desorption can be a positive aspect, considering that the associated cost of $MgCl_2 \cdot 6H_2O$ is approximately 35 € per 100 g. Overall, the main costs of the process can be attributed to the desorption process;

however, it should be considered that the price reported by Sigma Aldrich for the pollutant is about 200€/100g, obtaining a net gain in the recovery of the TC. In conclusion, comparing this paper with the works in **Table 1**, we avoid hard conditions of work by adopting green and safer technologies with a particular highlight to the experimental conditions for the adsorption and desorption processes, the contact time and the absence of particular expensive pre-treatment of the adsorbents. Moreover, as described in the following, the proposed adsorbents exhibit another advantage: they are able to remove other pollutants, and their mixture, showing their wide-ranging applications potentiality, useful for industrial applications (see ESI for the removal of Ketoprofen and Diclofenac and their mixture in presence of TC).

4. CONCLUSIONS

During this work the first use of olive solid waste, exhausted olive pomace (OP), as adsorbent, to remove the antibiotic tetracycline (TC) from water is presented. More specifically, the OP was studied both in powder (as received) and blended inside a chitosan membrane, which acted as physical platform, for OP obtaining chitosan/OP (CH/OP) films, avoiding the dispersion of the waste in water as secondary pollutants. To photodegrade the adsorbed TC, the use of TiO_2 is proposed also mixing the photocatalyst inside the film (obtaining CH/OP/TiO_2). However, this approach occurred not useful and the TC photodegradation was obtained after its release in $MgCl_2$ from the adsorbent by using AOPs. Subsequently, the use of CH/OP was evaluated if the TC removal occurred in presence of EPs as ketoprofen and diclofenac showing as the adsorption of TC was not affected. Further, ketoprofen and diclofenac were also removed from water highlighting the high performance of CH/OP for environmentally friendly applications. A comprehensive investigation about the use of these adsorbents is therefore presented in the paper evaluating the adsorption capacities, the kinetic, the thermodynamic and the isotherms of the adsorption processes adopting TC as model pollutant. The possibility to use and re-use the adsorbent for consecutive cycles of adsorption/desorption, recovering also the TC, is presented with the future perspective to remove a largest class of pollutants.

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