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A study on the kinetics of olive mill wastewater (OMWW) polyphenols adsorption on the commercial XAD4 macroporous resin

Konstantinos B. Petrotos*, Paschalis E. Gkoutsidis, Maria I. Kokkora, Konstantia G. Giankidou, Andreas G. Tsagkarelis

Department of Biosystems Engineering, Laboratory of Food and Environmental Process Engineering, Technological Educational Institute of Larissa, TEI Campus, Larissa 41100, Greece
Tel. +30 2410 684524; Fax: +30 2410 613158; email: petrotos@teilar.gr

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ABSTRACT

The commercially available macroporous resin XAD4 was evaluated for its capacity to adsorb the polyphenols contained in olive mill wastewater (OMWW). The adsorption was performed in the mode of fixed packed bed contactor. The effects of OMWW flow rate, temperature, dilution and pH on the resin adsorption capacity were investigated. Polyphenols concentration decreased with time. The pattern of the total polyphenols concentration dependence on time was found similar in all cases. The pattern included a very steep section for roughly the first 2 h of the operation, followed by a second section of decreasing gradient down to a final asymptotic equilibrium limit. Neither the time required for approaching the equilibrium nor the magnitude of the equilibrium concentration was substantially affected by the OMWW temperature. The increase of OMWW flow rate affected markedly the speed of approaching the equilibrium but not its position. The variation of the total polyphenols concentration showed that higher concentrations yielded more rapid kinetics at the initial section, but no apparent differentiation of the time was required to approach equilibrium. Acidic pH appeared to be favourable for the adsorption. Finally, a novel modelling approach was developed to simulate the adsorption process kinetics.

Keywords: Olive mill wastewater (OMWW); Dephenolization; Adsorption; Macroporous resins; Mathematical modelling

1. Introduction

The cultivation of olive trees and the production and use of olive oil is a well known and established practice in the Mediterranean region for more than 7,000 years now. The consumption of olive oil is rapidly increasing worldwide, due to its high dietetic and nutritional value. The production of olive oil increased from 1.85 million tons in 1984 to 3.17 million tons in 2003 (70% increase) [1]. Along with the production of olive oil, the olive mill produces a stream of wastewater known as olive mill wastewater (OMWW), which constitutes a major and still unsolved problem with a major environmental impact. The annual world OMWW production is estimated from 7 to over 30 million m^3. Although the quantity of the waste produced is much smaller than other types of waste (i.e. domestic sewage) and its production is seasonal, the contribution of OMWW to environmental pollution is important, because of some "peculiarities" of the case,

*Corresponding author.

which have to be used with both the chemical synthesis of the waste and some aspects of the current situation in the olive oil sector.

The phytotoxic and antimicrobial properties of OMWW are mainly attributed to its phenolic content and also to some organic acids, such as acetic and formic acid, which are accumulated as microbial metabolites during storage. Its direct application to plants inhibits the germination of different seeds and early plant growth of different vegetable species and may cause leaf and fruit abscission as well. Different kinds of crops show different reactions to OMWW spreading and some of them may tolerate a certain amount of OMWW during early growing stages [2]. As far as its antimicrobial activity is concerned, catechol, 4-methylcatechol and hydroxytyrosol are its most active compounds against a number of bacteria and fungi. Several authors have reported OMWW activity against soil Gram (+) spore bacteria like *Bacillus megaterium* ATCC 33085, Geotrichum, Rhizopus, Rhizoctonia, *Bactrocera oleae* and *Pseudomonas syringe* [3].

These biotoxic properties of phenols in OMWW constitute a significant inhibitor to the biological processes, which take place in common wastewater treatment plants. Thus, the dephenolization of OMWW is a major step, which has to be taken in order to facilitate potential treatment and/or disposal of this waste stream in the environment in a proper way. On the other hand, hydroxytyrosol, 2-hydroxytyrosol, tyrosol, oleanolic acid and maslinic acid, flavonoids, anthocyanins and tannins, which are found in OMWW, are considered as natural antioxidants with considerable commercial and economic interest. The most interesting one appears to be hydroxytyrosol, a compound of high added value, due to its antioxidant and potentially beneficial properties to human health. Results of *in vitro* research demonstrate that hydroxytyrosol inhibits human LDL oxidation, scavenges free radicals, inhibits platelet aggregation and the production of leucotriene for human neutrofils and confers cell protection. It also acts against both Gram (+) and Gram (−) bacteria. Research has also shown that hydroxytyrosol could be effectively used as food preservative, for the protection of olive trees in agriculture, and also in the cosmetics industry for anti-aging products [4,5].

Several attempts have been recorded to extract the useful polyphenol fraction from OMWW. The most widely used are solvent extraction (both liquid–liquid and solid–liquid extraction) [6–8] and adsorption in adsorbent resins [9]. For the purification and separation of these substances from the mixture of antioxidants extracted from OMWW, chromatographic methods are used. Liquid–liquid extraction is a simple and convenient alternative for this purpose. Polar solvents are best for the extraction of polyphenols from OMWW and the yield of extraction increases with increasing polarity of the solvent. Among various polar solvents tested, such as methyl isobutyl ketone, methyl ethyl ketone, diethyl ether and ethyl acetate, the latter is considered the most suitable. Apart from the type of solvent used, other factors affecting the process efficiency are the pH of OMWW (better when acidic), the ratio of solvent/waste and the number of theoretical steps in batch systems [4,5]. Mathematical modelling of the kinetics of adsorption and desorption of the polyphenols from OMWW is necessary in order to obtain the necessary design tools for industrial-scale application.

Adsorption is the attachment of dissolved compounds (adsorbate) from polluted waters to a solid substance (adsorbent) as a result of attractive interaction of the molecules of the adsorbate with micropores or macropores of the adsorbent having comparable dimensions to that of the molecules. In the case of OMWW, adsorbates are polyphenols and tannins. The most widely used adsorbents for this purpose are activated carbon, activated clay and superabsorbent polymers.

Activated carbons adsorption installations [10,11] are associated with extremely high costs, resulting from both the high initial cost of the material and also from the subsequent high operational costs. A possible solution to this economic burden could be the use of activated carbons produced by olive stone and solvent extracted live pulp, inexpensive by-products of the olive oil industry. In this way, the volume of solid waste could also be reduced [12]. The use of activated clay is another cheap alternative with maximum removal of polyphenols about 81 and 71% for organic matter [13]. Furthermore, low cost unselective solid phases were employed; interestingly, most of them were organic by-products applied as biosorbents, such as olive pomace [14], banana peel [15], dried biomass from the aquatic fern Azolla [16] and sawdust [17]. Sand [18] was also employed as the adsorbing phase. However, no effective phenol extraction and purification is possible from such complex and heterogeneous matrices, which have to be disposed as solid waste or can eventually combusted for energy production [17]. The use of macroporous resins [19,20], however, offers significant advantages over many other conventional methods, including a minimum of a 10-fold increase in sample loading capacity, higher selectivity, easier desorption, lower solvent consumption, absence of chemical residues in the product, better mechanical strength and ability to reuse and also improved cost efficiency [21–24].

The pH of the solution constitutes a parameter that strongly influences the adsorption capacity of a macroporous resin, due to its influence on the adsorption mechanisms. It remains under discussion as to what exactly is the influence of pH on the adsorption of polyphenols by macroporous resins [23]. Adsorption kinetics describes how the sorption process evolves in time, until equilibrium is reached. The sorption process consists of both mass and heat transport [24]. Hence, the influence of solution temperature, flow rate and dilution also needs to be evaluated in order to find the optimum conditions for polyphenols adsorption to macroporous resins.

The objectives of this study were: (i) to evaluate the effects of temperature, pH, flow rate and dilution on the adsorption and desorption of OMWW poly phenols to XAD4 macroporous resin and (ii) to develop a mathematical model to describe the kinetics of polyphenols adsorption to XAD4 resin.

2. Materials and methods

2.1. Olive mill wastewater

Samples of OMWW were taken from the cooperative olive mill at Gonnoi village, Larissa, central Greece, in November 2008. The samples were taken directly from the output stream of the decanter centrifugal of the olive mill and they were stored in fourteen 25 L plastic bottles at a temperature of 275 K.

2.2. OMWW pre-treatment

Due to the high total suspended solids content of OMWW, the OMWW samples were filtered through a muslin cloth prior to use to facilitate the subsequent ultrafiltration and to protect the ultrafiltration component of any blockage.

The second step of the pre-treatment process involved the ultrafiltration of the filtered OMWW. For the ultrafiltration, a set of 18 commercially available membranes (PCI MEMBRANES-FP 100) having a molecular weight cut-off of 100,000 Daltons was used. Initially, a "cleaning" process took place, which involved the use of 15 L distilled water at a temperature of 308–313 K and a maximum flow rate (zero pressure). After the membranes were cleaned, the filtered OMWW samples were ultrafiltered. In this case, the operating pressure was 4 bar and the temperature was 333 K [25]. The concentrate stream was flowed back to feed vessel, while permeate stream was being collected separately. The ultrafiltration process continued till approximately 80% of the initial volume was collected as permeates.

2.3. Macroporous resin XAD4: adsorption and desorption of polyphenols

Polyphenol adsorption was performed in the mode of fixed packed bed contactor in order to apply adsorption and desorption without removing the resin and furthermore take advantage of convection movement which facilitates the mass transfer in both steps (adsorption and desorption). Pre-treated OMWW (5 L) was circulated using a peristaltic pump (Watson–Marlow 620 Du), through a XAD4 resin column. The XAD4 resin has the ability to retain selectively the polyphenols. The duration of the adsorption process was 8.5 h (510 min). An overview of the experimental set up is presented in Fig. 1.

The experimental conditions were: (a) the treated OMWW was circulated through the resin using a flow rate of 100 mL min^{-1}at three temperatures of 293, 213 and 333 K, (b) the treated OMWW was circulated through the resin at a steady temperature of 313 K at three different flow rates of 50, 100 and 200 mL min^{-1}, (c) dilutions of treated OMWW with deionized water at rates of 1/2, 1/5 and 1/10 at temperature of 313 K and flow rate of 100 mL min^{-1} and (d) at pH of 3.1, 4.9 and 7.0, at temperature of 313 K and flow rate of 100 mL min^{-1}. The pH value of 4.9 constitutes the pH of the OMWW. The OMWW pH was adjusted to 3.1 by the addition of H_2SO_4 and to 7.0 by the addition of NaOH.

Samples were taken in 1-h basis, starting at $t = 0$ (before the beginning of OMWW circulation through the resin column), when the initial concentration of polyphenols was determined in the sample used. A total of 10 samples were collected throughout the experiment. The concentration of total phenols in the collected samples was determined via the Folin–Ciocalteu method.

At the end of each experiment described above, polyphenols desorption occurred by eluting the column with 10 L of water–ethanol solution (50% v/v) in order to clean and regenerate the column. During the desorption process, samples were collected every 15 min for a total of 105 min. The concentration of total phenols in the collected samples was again determined via the Folin–Ciocalteu method.

2.4. Kinetic model

Mathematical modelling of the kinetics of the polyphenols adsorption by the macroporous resin XAD4 was carried out by the use of the XLSTAT 2010 software, in order to simulate the adsorption against time. Constants were determined experimentally by multiple variable non-linear regression analysis, using the NLREG software.

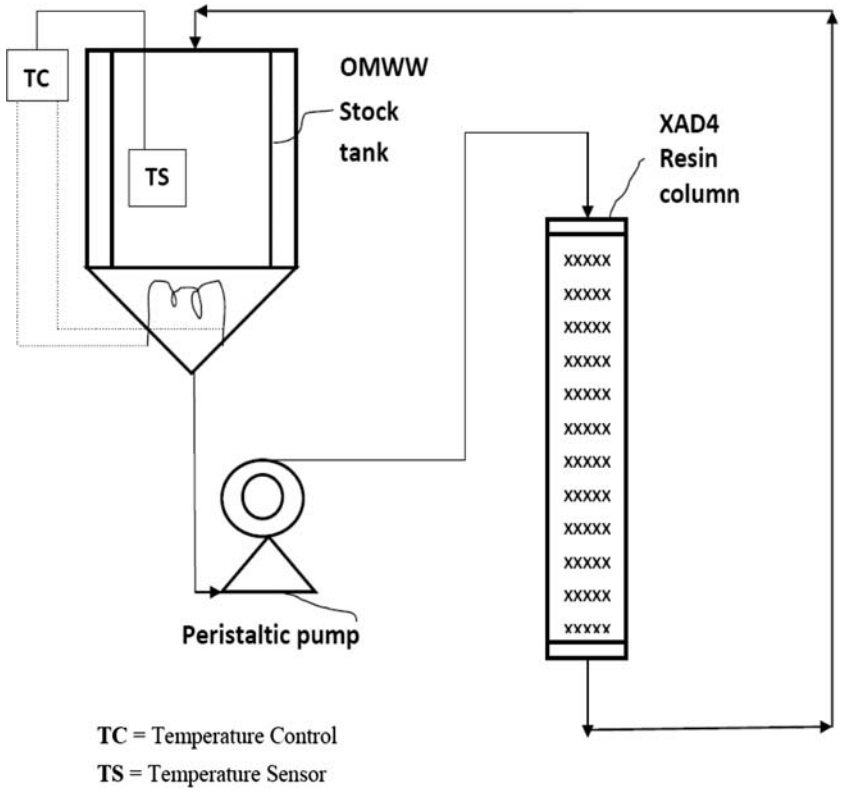

Fig. 1. The experimental set-up overview.

3. Results and discussion

3.1. The effect of the OMWW pH

Polyphenols adsorption to XAD4 resin was more effective in the acidic pH (Fig. 2). At neutral pH, the adsorption capacity of the resin decreased by a factor of 1.6 in comparison to the pH of 4.9, which is the pH of the OMWW before any adjustment. No significant differences were observed between the adsorption capacity of XAD4 between pH of 3.1 and 4.9, indicating that the resin is effective in strongly acidic pH. This may be explained by the fact that polyphenols are not oxidized in acidic pH and therefore they are better preserved. Under acidic pH, the equilibrium was reached after approximately 180 min.

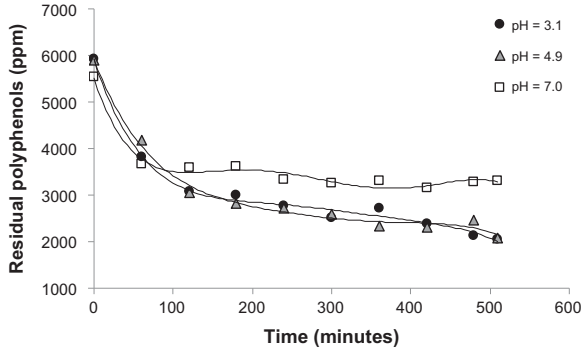

Fig. 2. The effect of the pH of the OMWW on the residual concentration of total polyphenols as a function of time. The OMWW flow rate was 0.1 L min^{-1} and the temperature was 313 K.

3.2. The effect of temperature

The effect of temperature on the capability of the XAD4 macroporous resin to adsorb polyphenols as a function of time is presented in Fig. 3. The concentration of residual total polyphenols decreases with time, which indicates the effectiveness of XAD4 resin to adsorb the polyphenols. However, temperature had no significant effect neither on the kinetics of the adsorption nor on the final amount of polyphenols adsorbed. Temperature increase, however, facilitated the permeation of the OMWW through the resin column and ensured a higher flow rate, which is a desirable effect, as it implies higher yield. As shown in Fig. 3, equilibrium was reached after approximately 180 min.

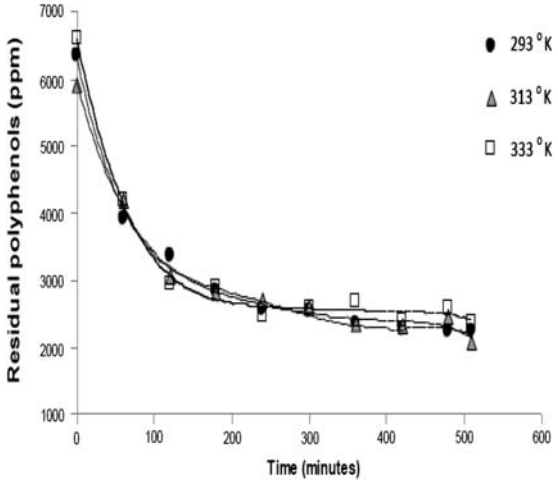

Fig. 3. The effect of temperature on the residual concentration of total polyphenols, as a function of time. OMWW flow rate was 0.1 L min^{-1}.

3.3. The effect of flow rate

Although the flow rate of OMWW did not influence the final equilibrium point, Fig. 4 shows that the higher the flow rate, the quicker the equilibrium was achieved. In the case of OMWW flow rate at 0.2 L min^{-1}, the residual polyphenols concentration was half the initial one in the first 60 min. The equilibrium was achieved within the first 180 min for all flow rates tested and at that point residual polyphenols concentration was approximately half the initial concentration. This finding indicates that it is better to use higher flow rates, as higher amount of polyphenols will be adsorbed in less time, leading to production profit in industry.

3.4. The effect of dilution

The difference in the initial polyphenols concentration of the OMWW resulted in different amounts of residual polyphenols at the equilibrium (Fig. 5). The kinetics of the adsorption is quicker in higher concentrations. In all cases, at the equilibrium point (at 180 min), the residual polyphenols concentration is approximately half the initial concentration. This finding indicates that the pre-treatment step of the ultrafiltration was effective and no procedure, such as dilution, was necessary for the efficient removal of the polyphenols using the XAD4 resin.

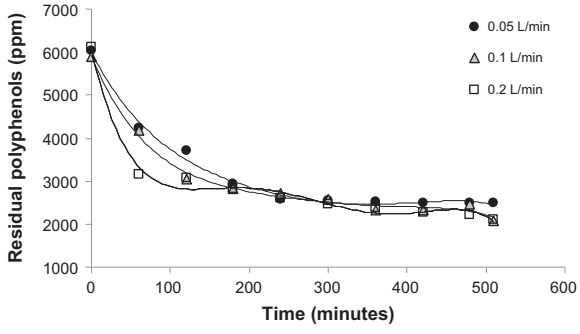

Fig. 4. The effect of OMWW flow rate on the residual concentration of total polyphenols, as a function of time. The OMWW temperature was 313 K.

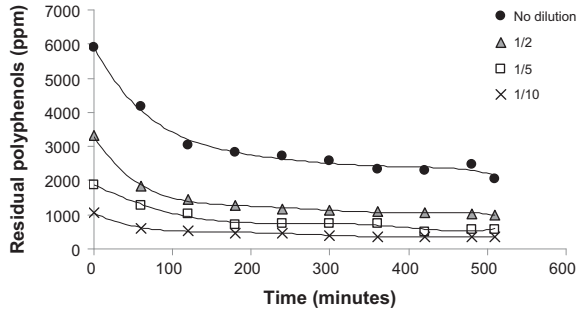

Fig. 5. The effect of OMWW dilution on the residual concentration of total polyphenols, as a function of time. The OMWW solution flow rate was 0.1 L min^{-1} and the temperature was 313 K.

3.5. Desorption

As illustrated in Fig. 6 indicatively for three of the above-described experiments, it takes an hour of washing with the ethanol solution (50% v/v) to achieve the desorption of the polyphenols adsorbed to the XAD4 resin. Considering a washing time of 1 h and an ethanol flow rate of 0.1 L min^{-1}, the necessary volume of ethanol solution is 3.46 times the volume of the resin column. This relationship may be used as a standard for industrial application.

3.6. Industrial application

To achieve satisfactory polyphenols removal from the OMWW, however, it is necessary to decrease the

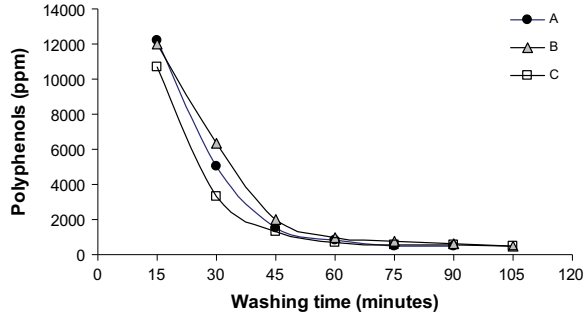

Fig. 6. Polyphenols desorption from the XAD4 macroporous resin, as a function of washing time. The ethanol solution (50% v/v) flow rate was 0.1 L min^{-1} and the temperature was 293 K.

polyphenols concentration in the final solution at least to the 10% of the initial concentration. The experimental data obtained from all the above-mentioned experimentation indicate that this is an achievable goal. As it is illustrated in Fig. 7, using three adsorption stages of 2-h duration each, followed by 1-h washing of the resin with a 50% v/v ethanol solution can lead to reducing the initial polyphenol concentration to the desirable level, namely from approximately 6,000 to 600 ppm. This procedure exploits the fact that the adsorption kinetics is more rapid during the first 2 h, when the equilibrium is approached. After that, adsorption kinetics was too slow and therefore it is not time efficient to continue the adsorption process till the achievement of the desirable polyphenol concentration.

Working temperature may be room temperature, since OMWW temperature was shown not to affect adsorption, and suggested OMWW flow rate may be $0.1\,\mathrm{L\,min^{-1}}$, which is efficient rate for industrial application.

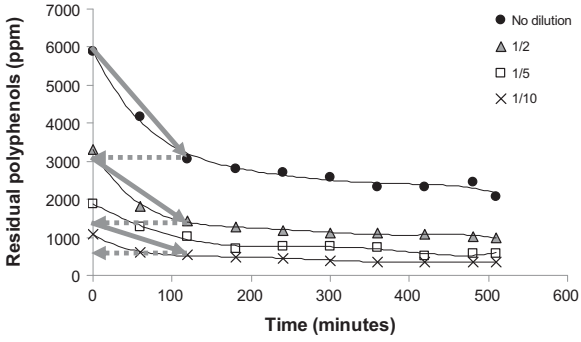

Fig. 7. Schematic illustration of the suggested system for the polyphenols removal from the OMWW, till polyphenol reduction to the 10% of the initial concentration is achieved through three adsorption–desorption stages.

This procedure may be executed using only one resin column, with consecutive adsorption and desorption circles. Alternatively, two resin columns may be used. In the later case, when one column will be used for adsorption, the other will be cleaned and vice versa, thus being more time efficient.

Also, especially noteworthy is the fact that the use of the XAD4 resin resulted in complete removal of the odour of the OMWW and also improved the colour of the OMWW, from dark brown to clear light brown–yellow.

3.7. Kinetic model

The mathematical model, which better simulated the kinetics of the polyphenols adsorption, was in the form shown in Eq. (1), where $C(t)$ is the polyphenols concentration at any time t (min) since the beginning of the adsorption, $C(0)$ is the initial polyphenols concentration at time = 0 min and pr1, pr2 and pr3 are parameters which depend on OMWW characteristics (temperature, flow rate and dilution).

$$C(t) = \frac{C(0) \times \mathrm{pr1}}{t^{\mathrm{pr2}} + \mathrm{pr3}} \tag{1}$$

The model was tested for all the experimental conditions used and the parameters pr1, pr2 and pr3 were determined. A synopsis of the experimental conditions, results (parameter values) and the goodness of statistics are given in Table 1. As suggested by the coefficient of determination (R^2), in all cases the data predicted by the model were very close to the actual measured ones. Indicatively, the relationship between the predicted and the measured values is shown in Fig. 8 for the case of OMWW temperature = 313 K, flow rate = $0.1\,\mathrm{L\,min^{-1}}$ and dilution factor = 1/2.

Table 1
Statistical simulation of parameters pr1, pr2 and pr3 (Eq. (1))

Experimental conditions			Parameter values			Statistics	
T (K)	F (mL/min)	d	pr1	pr2	pr3	R^2	DF[a]
293	100	1/1	11,297	0.500	10,957	0.996	7
313	100	1/1	13,077	0.500	12,636	0.975	7
333	100	1/1	11,211	0.500	10,948	0.965	7
313	50	1/1	13,773	0.500	13,457	0.970	7
313	200	1/1	11,169	0.500	11,065	0.976	7
313	100	1/2	8,923	0.500	8,629	0.995	7
313	100	1/5	10,401	0.500	9,894	0.953	7
313	100	1/10	10,226	0.500	9,910	0.997	7

[a]Degrees of freedom.

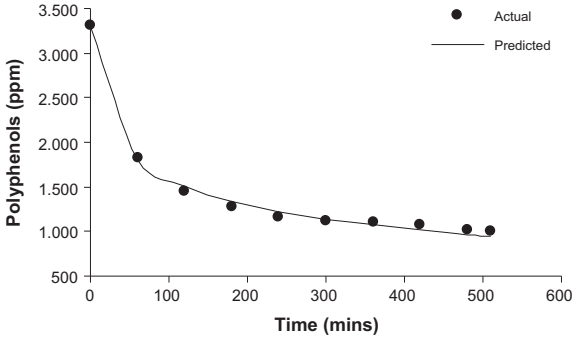

Fig. 8. The relationship between the predicted (Eq. (1)) and the measured values of polyphenols concentration for the case of OMWW temperature = 313 K, flow rate = 0.1 L min^{-1} and dilution factor = 1/2.

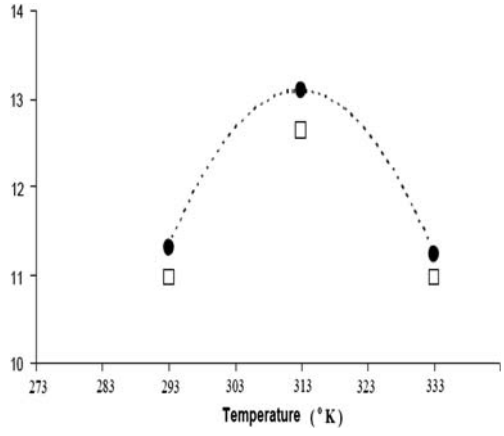

Fig. 9. Dependence of parameters pr1 and pr3 (Eq. (1)) on OMWW temperature, at experimental conditions of 0.1 L min^{-1} flow rate and with no OMWW dilution (●: pr1 and □: pr3).

As it is evident from Table 1, pr2 is equal to 0.5 in all cases, whereas pr1 and pr3 depend on OMWW temperature, flow rate and dilution factor. Moreover, it can be seen that pr3/pr1 ≈ 1. This last finding leads to model simplification. More specifically, dividing both the numerator and the denominator of the fraction shown in Eq. (1) by pr1 and assuming that pr3/pr1 is equal to 1, results to Eq. (2), where $k = 1/\text{pr1}$. The influence of temperature, flow rate and dilution on pr1 and pr3 are presented in Figs. 9–11, respectively. It may be suggested from Figs. 9–11 that there is a linear relationship between flow rate and both pr1 and pr3, a second-degree polynomial relationship between temperature and both pr1 and pr3 and

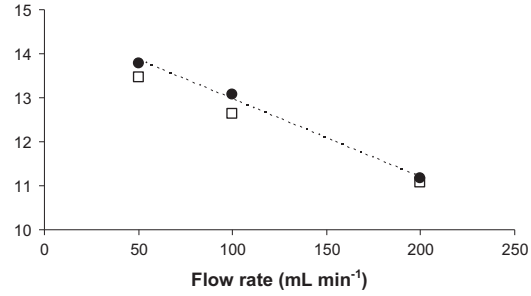

Fig. 10. Dependence of parameters pr1 and pr3 (Eq. (1)) on OMWW flow rate, at experimental conditions of 313 K temperature and with no OMWW dilution (●: pr1 and □: pr3).

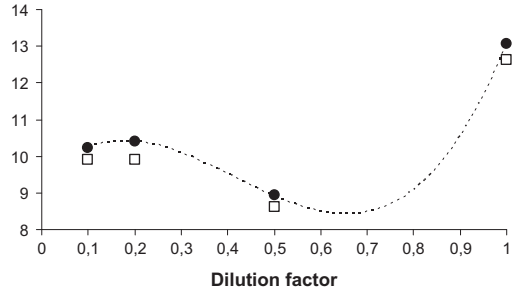

Fig. 11. Dependence of parameters pr1 and pr3 (Eq. (1)) on OMWW dilution factor, at experimental conditions of 313 K temperature and 0.1 L min^{-1} OMWW flow rate (●: pr1 and □: pr3).

finally, a third-degree polynomial relationship between dilution factor and both pr1 and pr3. Thus, k ($k = 1/\text{pr1}$), which is inversely proportional to pr1, is given in Eq. (3).

Consequently, the mathematical simulation of the polyphenols adsorption by the macroporous resin XAD4 against time is presented in the model shown in Eq. (2).

$$C(t) = \frac{C(0)}{k \times t^{0.5} + 1} \tag{2}$$

where $C(t)$ is the polyphenols concentration at any time t (min) since the beginning of the adsorption, $C(0)$ is the initial polyphenols concentration at time = 0 min and k is a parameter, which is depended on OMWW flow rate (F) expressed in mL min^{-1}, temperature (T) in K and dilution factor (d), according to Eq. (3):

$$k = \frac{1}{\text{p1} \times F + \text{p2} \times (T - 273) + \text{p3} \times (T - 273)^2 + \text{p4} \times d + \text{p5} \times d^2 + \text{p6} \times d^3 + \text{p7}} \tag{3}$$

Table 2
Experimentally determined constants used for the estimation of parameter k, as described in Eq. (3). Parameter k is necessary for the simulation of the polyphenols adsorption kinetics to the XAD4 macroporous resin (Eq. (2))

Constant	Final estimate
p1	−0.0176
p2	0.3404
p3	−0.0043
p4	129,937,796
p5	−460,081,068
p6	3,663,138
p7	434,657,782

Constants p1–p7 were determined experimentally by multiple variable non-linear regression analysis and are presented in Table 2.

The above described novel kinetics model provides a very good estimate of the measured values of the adsorption and therefore can be considered as a useful tool for the design of an OMWW treatment plant in industrial scale.

Additionally, a modified version of the above-mentioned model was developed in order to take into account the kinetics of the polyphenol adsorption on the XAD4 incorporating the contribution of the mass of the resin. This model was developed by following the analysis given below.

At the time t from the beginning of the experimental run, the quantity of the polyphenols adsorbed on the resin will be Mr(t), where:

$$\mathrm{Mr}(t) = M(C(0) - C(t)) \tag{4}$$

where M = the mass of the liquid OMWW in kg, $C(0)$ = the initial polyphenols concentration in OMWW liquid at time $t = 0$ (min), $C(t)$ = the polyphenols concentration in OMWW liquid at any time t (min) since the beginning of the adsorption.

If the resin mass is supposed to be symbolized by MR (in kg) then Eq. (4) can be converted to:

$$\mathrm{Mr}(t)/\mathrm{MR} = (M/\mathrm{MR})(C(0) - C(t)) \tag{5}$$

and consequently by substituting the quantity Mr(t)/MR with Cr(t) = concentration of polyphenols adsorbed on the resin mass at time t (min) since the run commenced and $C(t)$ by its value according to Eq. (2) a modified model form is obtained which takes into account the resin mass:

$$\mathrm{Cr}(t) = (M/\mathrm{MR})C(0)(\mathrm{kt}^{0.5}/(\mathrm{kt}^{0.5} + 1)) \tag{6}$$

4. Conclusions

Commercially available macroporous resin XAD4 can be used effectively for the complete removal of polyphenols from OMWW. At the same time, it removes completely the odour and improves the colour of the OMWW. Polyphenols adsorption kinetics and equilibrium point were not influenced by OMWW temperature. Increasing the OMWW flow rate accelerates the kinetics of the adsorption, but with no evident effect on the final equilibrium point. OMWW pH should be acidic for better yield. Equilibrium is achieved within 2–3 h. The suggested kinetics model simulated the polyphenols adsorption to the XAD4 resin efficiently and can be utilized for designing purposes in an industrial scale.

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