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A comprehensive study on the kinetics of olive mill wastewater (OMWW) polyphenols adsorption on macroporous resins. Part II. The case of Amberlite FPX66 commercial resin

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ABSTRACT

The commercially available macroporous resin Amberlite FPX66 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 to be similar in all cases. The pattern included a very steep section for roughly the first hour of the operation, followed by a second section of decreasing gradient down to a final asymptotic equilibrium limit. Regarding the time required for approaching the equilibrium, this was found to be unaffected by the temperature. On the contrary, the magnitude of the equilibrium concentration was substantially affected by the OMWW temperature presenting an optimum at 40˚C. The increase in the OMWW flow rate affected markedly the speed of approaching the equilibrium but not its position. The variation of the total polyphenols concentration with time showed that higher concentrations yielded more rapid kinetics at the initial section, but there was no apparent differentiation of the time required to approach the 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; Amberlite FPX66

1. Introduction

Olive oil consumption is increasing worldwide due to its high dietetic and nutritional value. The production of olive oil increased from 1.42 million tons in 1990/91 to 3.25 million tons in 2011/12 (128.9% increase) [1]. Olive oil extraction results in the production of a wastewater stream, which constitutes a major environmental concern. The annual world olive mill wastewater (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

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waste (i.e. domestic sewage) and its production is seasonal, OMWW constitutes a serious environmental threat due to its high organic load and phytotoxic and antibacterial properties.

These phytotoxic and antimicrobial properties of OMWW are mainly attributed to its phenolic content and also to some organic acids, which are accumulated as microbial metabolites during storage. OMWW direct application to plants inhibits the germination of different seeds and early plant growth of different vegetable species and may cause leaf and fruit abscissions as well. Different kinds of crops show different reactions to OMWW 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-methyl-catechol and hydroxytyrosol are its most active compounds against a number of bacteria and fungi [3].

Dephenolization of OMWW is necessary in order to facilitate potential utilization in other sectors (e.g. agriculture) or disposal to the environment in a proper way. On the other hand, polyphenols, which are found in OMWW, are considered as natural antioxidants with considerable commercial and economic interest. Macroporous resins are often used for efficient separation and purification of polyphenols from a solution [4–7].

The adsorption process refers to the attachment of dissolved compounds (adsorbate) from polluted waters to a solid substance (adsorbent) as a result of attractive interaction between 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. One of the most widely used adsorbents for this purpose is superabsorbent polymers. The use of macroporous resins offers significant advantages over many other conventional methods, including a minimum of tenfold increase in the 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 [4,8–10].

The kinetics of the adsorption describes how the sorption process evolves in time until the equilibrium is reached. The sorption process consists of both mass and heat transport [10]. 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 pH of the solution containing the polyphenols also 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 [9]. Furthermore, 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 applications.

The objectives of this study, which are complementary to a previous study regarding the use of XAD4 commercial resin [11], were: (i) to evaluate the effects of temperature, pH, flow rate and dilution on the adsorption and desorption of OMWW polyphenols to FPX66 macroporous resin, (ii) to develop a mathematical model to describe the kinetics of polyphenols adsorption to FPX66 resin and (iii) to compare the effectiveness of the two alternative resins XAD4 and FPX66 on the isolation of OMWW polyphenols.

2. Materials and methods

2.1. Olive mill wastewater

Samples of OMWW were taken from the co-operative olive mill at Pournari village, Larissa, central Greece, in November 2014. The samples were taken directly from the output stream of the decanter centrifuge of the olive mill, and they were stored in 14 25-L plastic bottles at a temperature of 2˚C.

2.2. OMWW pretreatment

Due to the high total suspended solids content of OMWW, the OMWW samples, prior to use, were passed through a centrifugal finisher equipped with a stainless steel screen with openings of 150-μm diameter, to facilitate the subsequent microfiltration and protect the microfiltration component of blockage problems.

The second step of the pretreatment process involved the microfiltration of the centrifuged OMWW. A tubular module with a ceramic membrane of total area of 0.23 m^2 and pore size of 0.2 μm was used. The microfiltration process lasted until approximately 80% of the initial volume was collected as permeate.

2.3. Resin FPX66: adsorption and desorption of polyphenols

Polyphenol adsorption was performed in the mode of fixed packed-bed contactor. About 5 L of microfiltered OMWW (MF-OMWW) was circulated using a peristaltic pump (Watson–Marlow 620 Du), through a column filled with the FPX66 resin. The commercially available FPX66 resin (Amberlite FPX66, Rohm and

Haas) is a food-grade adsorbent resin, which has the ability to retain high-value materials. The adsorption process lasted for 8 h (480 min).

The effect of four operating conditions on the adsorption capacity of the FPX66 resin was evaluated. The parameters tested were: temperature (20, 40 and 60°C), flow rate (100, 200 and 300 mL min^{-1}), pH (3.1, 4.9 and 7.0) and dilution (1/1, 1/2, 1/5 and 1/10). The pH value of the MF-OMWW was 4.9. MF-OMWW pH was adjusted to 3.1 by the addition of H_2SO_4, and 7.0 by the addition of NaOH.

Samples were taken every twenty minutes within the first hour of operation, starting at $t = 0$ (before the beginning of OMWW circulation through the resin column), and in one-hour-basis afterwards. At $t = 0$, the initial concentration of polyphenols [$C(0)$] was determined. A total of eleven samples were collected throughout each run. At each sampling time, three samples were collected and analysed for the concentration of total phenols using the Folin–Ciocalteu method.

At the end of each experiment described above, polyphenols desorption occurred by eluting the column with water–ethanol solution (50% v/v), in order to clean and regenerate the column. During the desorption process, samples were collected every 10 min for a total of 60 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 FPX66 was carried out by the use of NLREG software (NLREG version 6.0, 1992–2003, Phillip H. Sherrod), in order to simulate the adsorption against time. Constants were determined experimentally by multiple variable non-linear regression analysis using the NLREG software. Analysis of variance (ANOVA) was carried out at 5% probability level.

3. Results and discussion

3.1. The effect of the OMWW pH

Polyphenols adsorption to FPX66 resin was more effective in acidic pH (Fig. 1). At neutral pH, the adsorption capacity of the resin decreased by a factor of 1.1, in comparison to the pH 4.9, which is the pH of the MF-OMWW before any adjustment. Comparing the two acidic pH values of 3.0 and 4.9, it was shown that the adsorption capacity of FPX66 was higher at the more acidic pH, indicating that the resin is more

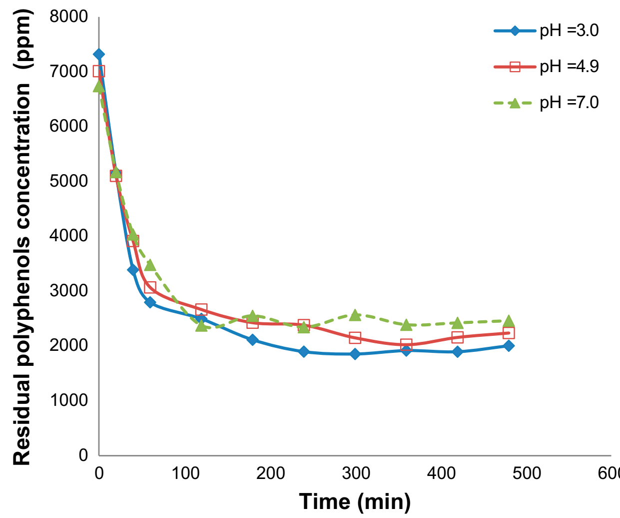

Fig. 1. The effect of the OMWW pH on the residual concentration of total polyphenols as a function of time. The OMWW flow rate was 0.1 L min^{-1} and the temperature was 40°C.

effective in strongly acidic pH. Although the differences between the treatments appear limited towards the end of the process, pH did influence polyphenols adsorption, as it can be seen also from the data shown in Fig. 5, which show that polyphenols recovery was higher for the acidic pH 3.0.

3.2. The effect of temperature

The effect of temperature on the capability of the FPX66 macroporous resin to adsorb polyphenols as a function of time is presented in Fig. 2. The concentration of residual total polyphenols decreased with time, which indicates the effectiveness of the resin to adsorb the polyphenols. The operation temperature had no significant effect on the time required to reach the equilibrium. It significantly affected, however, the total amount of polyphenols adsorbed by the resin at the equilibrium point. As shown in Fig. 2, the equilibrium, at any temperature, was reached after approximately 60 min. The optimum temperature, which corresponds to the temperature resulting in the highest amount of polyphenols adsorbed by the resin at the state of equilibrium, was 40°C.

3.3. The effect of flow rate

Although the flow rate of OMWW did not influence the final asymptotic equilibrium point, Fig. 3 shows that increasing the flow rate from 0.1 to 0.2 L min^{-1}, the equilibrium was achieved quicker. In

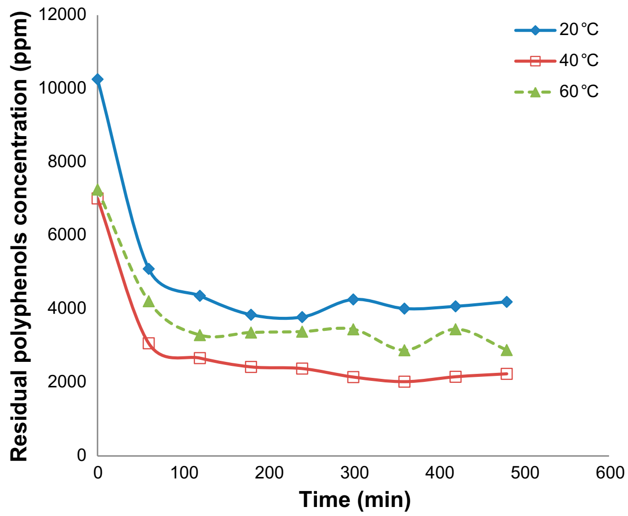

Fig. 2. The effect of OMWW temperature on the residual concentration of total polyphenols as a function of time. The OMWW flow rate was 0.1 L min^{-1} and the dilution was 1/1.

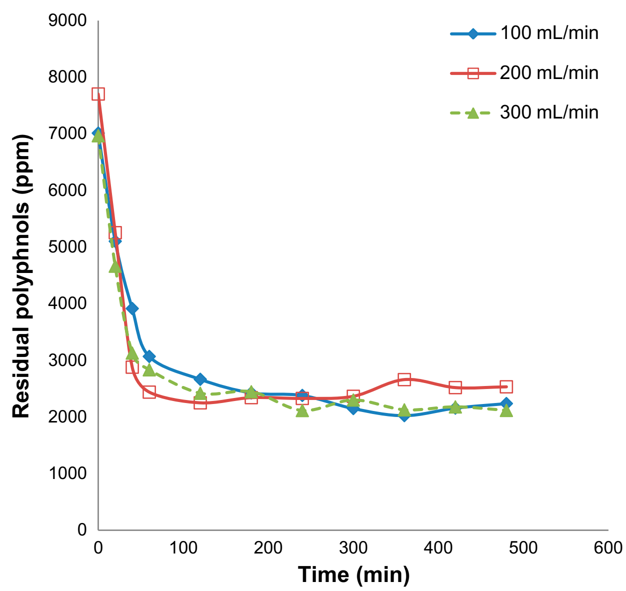

Fig. 3. The effect of OMWW flow rate on the residual concentration of total polyphenols as a function of time. The OMWW temperature was 40°C and the dilution was 1/1.

the case of OMWW flow rate at 0.2 L min^{-1}, the residual polyphenols concentration was the optimum (approx 32% of the initial concentration), and it was achieved within approximately 60 min. This finding indicates that it is better to use higher flow rates, as a higher amount of polyphenols will be adsorbed in less time, leading to production profit for the industry, provided the higher cost related to the higher circulation speed is not counterbalancing the operational benefit. On the other hand, increasing the flow rate from 0.2 to 0.3 L min^{-1} resulted in a reduction in the performance suggesting that 0.2 L min^{-1} was the operational optimum value.

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. 4). Equilibrium was achieved at approximately 60 min from the beginning of the experimental run (the breaking point of the kinetics curve is shown in Fig. 4). By calculating the percentage of the adsorption of OMWW at the time of 60 min for various dilutions using Eq. (1), it was observed that the highest % adsorption was achieved at a dilution of 1:2 (Table 1), which marks the optimum performance regarding the dilution ratio:

$$\text{OMWW polyphenols adsorption } (\%) = \frac{C(0) - C(60\,\text{min})}{C(0)} \quad (1)$$

3.5. Desorption

Fig. 5 illustrates indicatively for one of the above-described experiments the kinetics of the

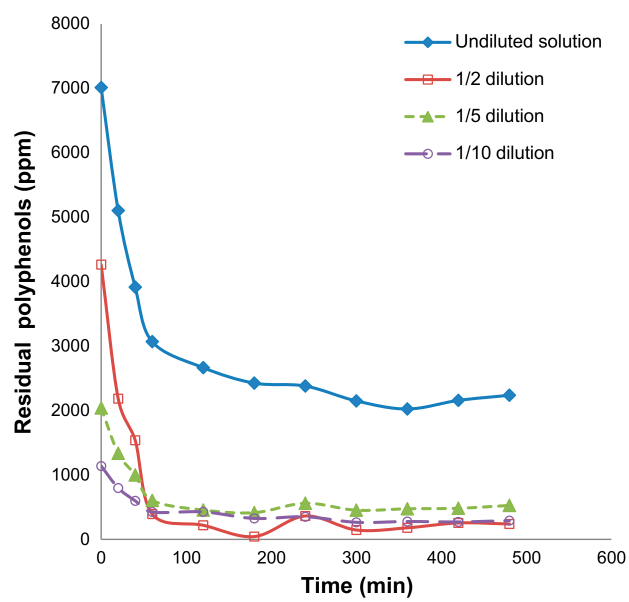

Fig. 4. The effect of OMWW dilution on the residual concentration of total polyphenols as a function of time. The OMWW temperature was 40°C and the flow rate was 0.1 L min^{-1}.

Table 1
Calculated values of % OMWW polyphenols adsorption for various dilutions at the time point of 60 min

	Undiluted	Dilution 1/2	Dilution 1/5	Dilution 1/10
OMWW polyphenols adsorption (%)	0.56	0.91	0.70	0.63

OMWW elution from the FPX66 resin at three pH values. As shown in Fig. 5, it took an hour of washing with the ethanol solution (50% v/v) to achieve the desorption of the polyphenols adsorbed to the FPX66 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 polyphenols concentration in the final solution at least to 10% of the initial concentration. The experimental data obtained from all the above-mentioned experimentation indicate that this is an achievable goal. Using two adsorption stages of one-hour duration each, followed by one-hour washing of the resin with a 50% v/v ethanol solution can lead to a reduction in the initial polyphenol concentration to the desirable level, namely from approximately 7,000 ppm to less than 700 ppm. This procedure exploits the fact that the adsorption kinetics is more rapid during the first 1 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 40˚C, since this OMWW temperature value was shown to optimize the adsorption, and the suggested OMWW flow rate may be 0.2 L min^{-1}, which is an efficient rate for industrial application.

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 latter 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 FPX66 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.

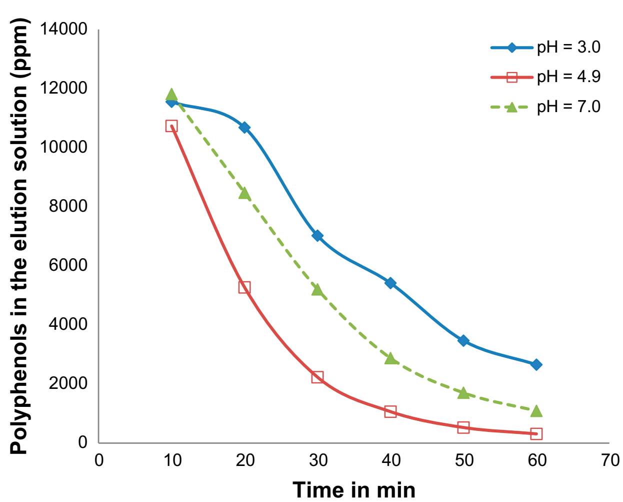

Fig. 5. Polyphenols desorption from the FPX66 macroporous resin as a function of washing time. The ethanol solution (50% v/v) flow rate was 0.1 L min^{-1} and the temperature was 20˚C.

3.7. Kinetic model

The mathematical model that better simulated the kinetics of the polyphenols adsorption was in the form shown in Eq. (2). $C(t)$ is the polyphenols concentration at any time t (minutes) since the beginning of the adsorption, $C(0)$ is the initial polyphenols concentration at time = 0 min, and $pr1$, $pr2$, $pr3$ and $pr4$ are parameters, which depended on OMWW characteristics (temperature, flow rate, dilution):

$$C(t) = C(0) \times \frac{pr1 \times t + pr2 \times t^2 + 1}{pr3 \times t + pr4 \times t^2 + 1} \qquad (2)$$

The model was tested for all the experimental conditions used, and parameters $pr1$, $pr2$, $pr3$ and $pr4$ were determined. A synopsis of the results (parameter values) and the goodness of statistics are given in Table 2 for some of the tested experimental conditions. As suggested by the coefficient of determination (R^2), in all the cases, the data predicted by the model were very close to the actual measured values. Indicatively,

Table 2
Experimental conditions (*T*: temperature, *F*: flow rate, *d*: dilution) and statistical simulation of parameters *pr*1, *pr*2, *pr*3 and *pr*4 of Eq. (2)

Experimental conditions			Parameter values				Statistics		
T (°C)	*F* (mL min^{-1})	*d*	*pr*1	*pr*2	*pr*3	*pr*4	R^2	DF[a]	Prob. (*F*)
20	100	1/1	0.005852	3.31E-005	0.028991	5.65E-005	0.994	10	<0.01
40	100	1/1	0.027409	0.000635	0.029175	0.002216	0.996	10	<0.01
60	100	1/1	0.017681	0.001121	0.010927	0.002639	0.974	10	<0.01
40	200	1/1	−0.02375	0.000563	−0.02756	0.001631	0.998	10	<0.01
40	300	1/1	0.012015	0.001096	0.004853	0.003588	0.997	10	<0.01
40	100	1/2	−0.0107	4.20E-005	0.017743	0.000329	0.985	10	<0.01
40	100	1/5	−0.00776	0.0001018	0.009247	0.000329	0.990	10	<0.01
40	100	1/10	0.077940	0.0010811	0.065940	0.004910	0.987	10	<0.01

[a]Degrees of freedom.

Fig. 6 presents the predicted and measured values for the case of OMWW temperature of 40°C, flow rate of 0.1 L min^{-1} and dilution factor of 1.

The proposed model is not a theoretical model aiming to describe the basic phenomena that can be involved in the adsorption process. It is a simulation model, which can be utilized for designing purposes in the industry, as it gives a very good estimate (proximity almost equal to one), and therefore can be used to estimate design parameters.

The same methodology (Eq. (2)) was applied successfully to describe the kinetics of the polyphenols adsorption by the XAD4 resin, achieving R^2 values of 99% and *F*-values lower than 0.01. Table 3 includes indicatively the parameter values and the goodness of statistics in the case of XAD4 resin for certain experimental conditions (pH 7, temperature: 40°C, flow rate: 100 mL min^{-1} and dilution: 1/1). The data concerning the XAD4 resin were extracted from the literature [11].

As a second step, the four coefficients *pr*1, *pr*2, *pr*3 and *pr*4 were predicted as functions of temperature, flow rate and dilution using Eq. (3). In Eq. (3), $i = 1$–4, T = temperature in °C, F = flow rate (mL min^{-1}) and d = dilution factor:

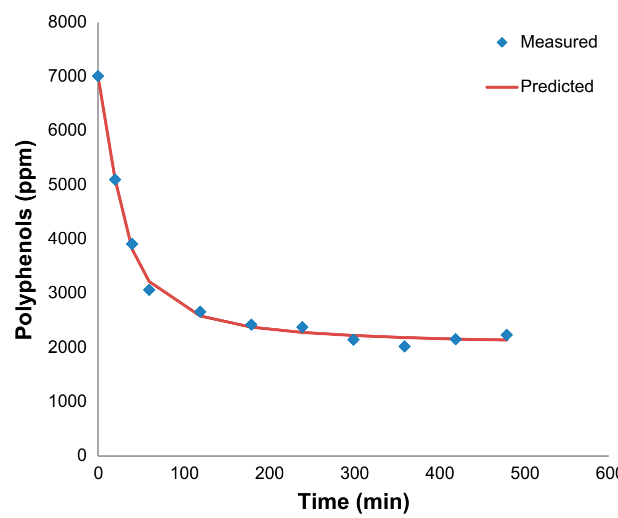

Fig. 6. Predicted (Eq. (2)) and experimental values of polyphenols concentration (OMWW temperature: 40°C, flow rate: 0.1 L min^{-1} and dilution: 1/1).

$$pr(i) = \frac{k1(i)}{k2(i) + k3(i) \times T + k4(i) \times T^2 + k5(i) \times F + k6(i) \times F^2 + k7(i) \times d + k8(i) \times d^2} \quad (3)$$

In Table 4, the values of the eight coefficients, for each one of the four parameters *pr*1, *pr*2, *pr*3 and *pr*4, are presented along with the correlation R^2 values which are very close to unity, which implies a perfect correlation.

3.8. Comparison of FPX66 and XAD4 resins on the basis of their performance for isolation of OMWW polyphenols

FPX66 resin resulted in a lower polyphenols concentration in the final solution, hence a higher

Table 3
Statistical simulation of parameters *pr*1, *pr*2, *pr*3 and *pr*4 of Eq. (2), for the case of the XAD4 resin

Parameter values				Statistics		
*pr*1	*pr*2	*pr*3	*pr*4	R^2	DF[a]	Prob. (*F*)
556.2288	6.3860	194.0660	18.9196	0.991	9	<0.01

[a]Degrees of Freedom

Table 4
Statistical simulation of parameters *k*1*i*, *k*2*i*, *k*3*i*, *k*4*i*, *k*5*i*, *k*6*i*, *k*7*i* and *k*8*i* (Eq. (3).) for the FPX66 resin

	i = 1 (*pr*1)	*i* = 2 (*pr*2)	*i* = 3 (*pr*3)	*i* = 4 (*pr*4)
*k*1*i*	−4.17327687	0.00158856473	−26.2276506	0.0035929962
*k*2*i*	−3,580.23626	117.135919	−10,291.5399	173.723128
*k*3*i*	76.3675386	−5.60505615	113.907291	−7.72697987
*k*4*i*	−0.805499144	0.05550827	−1.89120927	0.0771399102
*k*5*i*	16.0495494	0.0285809958	141.536419	0.0325648361
*k*6*i*	−0.0425608074	−8.46057238E-005	−0.410196469	−8.9161E-005
*k*7*i*	6,407.04912	194.700131	−18,528.268	113.192225
*k*8*i*	−5,924.44684	−175.9574	16,341.7862	−102.003616
R^2	0.992	1.00	0.969	0.999
Prob. (*F*)	<0.01	<0.01	<0.01	<0.01

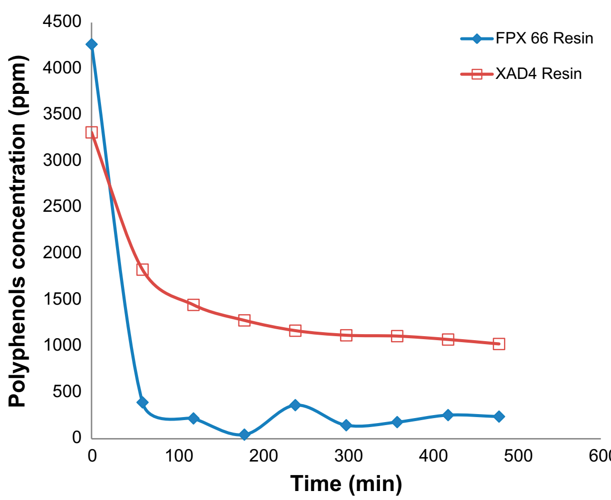

Fig. 7. Comparison of XAD4 and FPX66 macroporous resins for their capability to adsorb OMWW polyphenols (OMWW temperature: 40˚C, flow rate: 0.1 L/min, dilution: 1/2).

adsorption of OMWW polyphenols, as clearly presented in Fig. 7. The data in Fig. 7 also clearly show that FPX66 resin resulted in a faster approach of the equilibrium than XAD4, and much higher amount of adsorbed polyphenols per unit of resin mass at the equilibrium point. The data of Fig. 7 constitute only a typical example, as the same trend was confirmed for all the tested conditions of the present experimental work. The data concerning the XAD4 resin which are used to compare this resin with the FPX66 resin were extracted from the literature [11].

4. Conclusions

Commercially available macroporous resin FPX66 can be used effectively for the removal of polyphenols from OMWW. At the same time, it removes completely the odour and improves the colour of the OMWW. The OMWW operation temperature had no significant effect on the time required to reach the equilibrium, but it significantly affected the total amount of polyphenols adsorbed by the resin at the equilibrium point. The optimum temperature, which corresponded to the maximum amount of polyphenols adsorbed by the resin at the state of equilibrium, was 40˚C. Although the flow rate of OMWW did not influence the final equilibrium point, the flow rate of 0.2 L min^{-1} resulted in reaching the equilibrium point quicker. OMWW solution pH should be acidic for better yield. The optimum dilution ratio for OMWW solution was found to be 1:2. The suggested kinetics model simulated the polyphenols adsorption to the FPX66 resin efficiently and can be utilized for designing purposes in an industrial scale. A comparison of FPX66 to XAD4 resin revealed a substantially better performance for the FPX66 resin.

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