Polyphenols recovery from wastewater by adsorption on polymeric resins

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This work reports an experimental investigation on the recovery of polyphenols from aqueous solution by means of adsorption on polymeric resins. The target of this study is the development of a process to recover the polyphenolic compounds contained in olive mill wastewaters. The adsorption kinetics and equilibrium where investigated in a batch mixed adsorber and in a bench scale column. The desorption in alcoholic solutions was proven to be feasible. A phenomenological model of the process was implemented and the accordance between experiments and simulations is satisfactory.

1. Introduction

Polyphenols have antioxidants characteristics with potential health benefits. They may reduce the risk of cardiovascular disease and cancer. Since synthetic antioxidant compounds may be dangerous for human health, there has been a growing interest in the use of alternative natural antioxidants: polyphenols are among the major plant compounds with antioxidant activity (Aehle et al. 2004).

In this context, the interest of the scientific community has been focussed on the extraction of antioxidant compounds from inexpensive or residual sources from agricultural industries, such as tomato wastes and olive vegetation wastewaters (Moure et al., 2001). Moreover, the removal of polyphenols is needed for the disposal of the wastewater, since phenolic compounds inhibit the biological degradation of its organic matter (Otero et al., 2005).

This work reports an experimental investigation on the removal of a specific polyphenol from aqueous solutions by adsorption on a polymeric resin. The examined process was the recovery of 4-methylchatecol ("4MC") from aqueous solutions by using the resin Amberlite XAD16 , a polystyrene-based material with a high surface area.

First of all, the adsorption equilibrium and kinetics were investigated at isothermal conditions by using a stirred vessel. The concentration of 4MC was measured by a spectrophotometer.

Adsorption experiments were, then, performed in a fixed bed column in order to determine breakthrough curves at different operating conditions. The desorption was accomplished by washing the adsorption bed by alcoholic solutions.

Finally, a simulation model of the adsorption process was implemented in gPROMS environment. On the basis of the equilibrium and kinetic parameters, previously determined, a good agreement between the experimental and simulated results was obtained.

2. Experimental

2.1 Experimental apparatus and procedures

The first series of experiments were carried out in batch mode by using a thermostated vessel fitted with a magnetic stirrer. The experimental procedure was as follows. An aqueous solution of 4MC, at a fixed concentration, was maintained under a strong agitation in the thermostated vessel until the required temperature was attained. Then the adsorbent particles were added and the 4MC concentration was measured at fixed interval of time.

The second series of experiments concerned the use of a fixed bed column. The experimental setup is shown in Fig. 1: it consisted of a Perspex column, 190 mm in height and 40 mm in diameter, filled with adsorbent particles, 0.6 mm in size. Some glass spheres were put over the adsorbent bed, both to compact the bed and to uniformly distribute the feed stream. Nevertheless a good compacting was not achieved: in fact the bed void fraction ε was quite high, i.e. approximately 0.51.
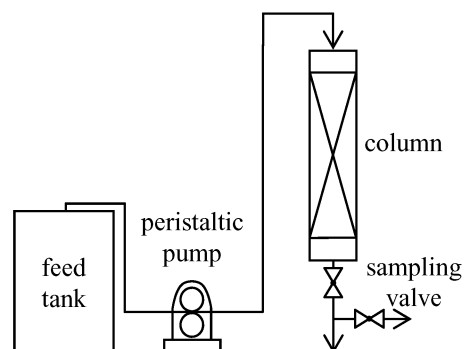

Figure 1: The fixed column apparatus.

A peristaltic pump assured a constant flow rate of the feed, whereas a valve after the bed exit allowed the sampling of the outlet stream.

The adopted procedure was as follows. Before the run start, a 4MC solution, at a fixed composition, was charged in the feed tank; at the same time the bed outlet valve was closed and the bed was filled with distilled water. Then, the pump was switched on, the outlet valve was open and the run started. The samples of the outlet streams were withdrawn at fixed intervals of time and the 4MC concentration was measured by a spectrometer model DU-65 supplied by Beckman. This analysis was performed by using a light wavelength of 280 nm.

2.2 Experimental results

2.2.1 Batch experiments

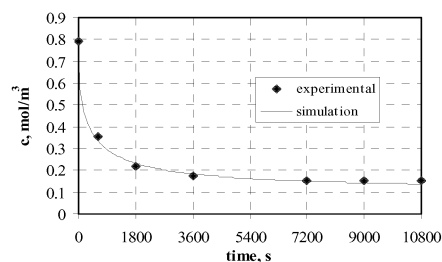Figure 2 shows the trend of the solution concentration for a typical batch run.

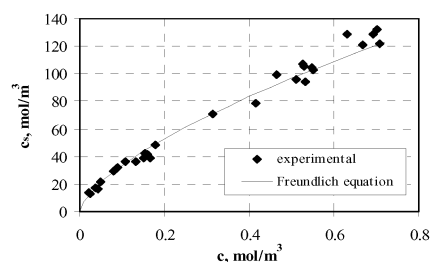*Figure 2: Dynamics of the adsorption: c vs time for ε = 0.984.*

Figure 3: Equilibrium of the adsorption.

It can be seen that, after the first 2 hours, the concentration in the solution does not significantly decreases any longer thus, for practical purposes, the equilibrium is attained. In Fig. 3 the so measured equilibrium points are plotted for all the performed batch runs. The concentration of the 4MC in the adsorbent mass, i.e. the adsorbed load c_s, was calculated from the following mass balance:

$$c_s = \frac{\varepsilon}{1-\varepsilon} \cdot (c_0 - c_f) \qquad (1)$$

where c_0 and c_f are the solute concentration at the beginning and at the end of each run, respectively.

2.2.2 Fixed bed column experiments

Four different runs were performed by using the fixed bed apparatus. The main operating conditions are reported in Tab. 1. The outlet stream concentrations vs time for the 4 runs are plotted in Fig. 4.

Table 1: Main operating conditions for the fixed bed column runs.

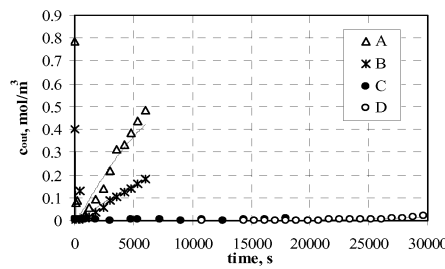| run ID	c_{in} mol/m^3	τ s	run time s
A	0.81	24	6000
B	0.40	24	6000
C	0.40	140	18000
D	0.39	140	29700

Figure 4: c_{out} vs time for the 4 runs.

2.3 Preliminary investigation on the desorption process

Ethanol containing 5% of water was adopted as recovery solvent. Desorption was carried out at the end of each run by discharging the exhausted resin particles into a vessel filled with ethanol. The desorption took place by stirring the suspension for a fixed period of time. The volumetric ratio between the solvent and the original solution was rather low down to 0.1. The solute concentration in the alcoholic was measures at fixed interval of time. The desorption process was proven to be faster than the adsorption one: the equilibrium was attained after few minutes. For all the runs, the quantity of 4MC who was left in the resin was lower than the measuring accuracy and could not be quantified.

3. Simulation model

3.1 Diffusion and adsorption model in a spherical particle

When the diffusivity in the pore is independent of the adsorbate concentration, c_p, the 4MC mass balance inside an adsorbent particle may be written as follows:

$$\frac{2 \cdot D_P}{r} \frac{\partial c_P(r,t)}{\partial r} + D_P \frac{\partial^2 c_P(r,t)}{\partial r^2} = \frac{\partial c_P(r,t)}{\partial t} + \frac{1}{\varepsilon_P} \frac{\partial c_S(r,t)}{\partial t} \qquad (2)$$

where D_p is the diffusivity inside the pore and ε_p is the particle porosity.
The diffusion inside the pores is generally very slow when compared to the surface adsorption step, thus the concentration of the adsorbate in the pore, c_p, can be considered in equilibrium with the adsorbent load, c_s. If Freundlich equation holds:

$$c_S(r,t) = k_{eq} \cdot [c_P(r,t)]^\gamma \qquad (3)$$

The initial condition for eq. (2) is:

$$c_p(r,t_0) = 0 \qquad (4)$$

and the boundary conditions are the following:

$$\frac{\partial c_P(r=0,t)}{\partial r} = 0 \qquad (5)$$

$$k \cdot [c(t) - c_P(r=r_P,t)] = D_P \cdot \frac{\partial c_P(r=r_P,t)}{\partial r} \qquad (6)$$

Where k is the mass transfer coefficient within the boundary layer of the particle.

3.2 Adsorption in the stirred vessel
In a well-stirred suspension, as was the case for the performed batch runs, the mass transfer resistance in the particle boundary layer is negligible and eq. (6) is reduced to

$$c_p(r=r_p,t) = c(t) \qquad (6b)$$

For a batch suspension the solute mass balance has the following expression:

$$c(t) + \frac{(1-\varepsilon)}{\varepsilon} \cdot \frac{\int_0^{r_p} (\varepsilon_p \cdot c_p + c_s) \cdot 4 \cdot \pi \cdot r^2 dr}{\frac{4}{3} \cdot \pi \cdot r_p^3} = c(t_0) \qquad (7)$$

The model for the adsorption batch process consists of the set of eqs. (2)-(5), (6b) and (7). The batch experiments where used to estimate the adjusting parameters k_{eq} and γ in eq. (3) and the pore diffusion, D_p in eq. (2).

3.3 Adsorption in the fixed bed column

When the plug flow assumption within the adsorption column holds, the adsorbate mass balance in the fixed bed may be written as:

$$u_E \cdot \frac{\partial c(z,t)}{\partial z} + \frac{\partial c(z,t)}{\partial t} - D_L \cdot \frac{\partial^2 c(z,t)}{\partial z^2} + \frac{a}{\varepsilon} \cdot k \cdot [c(z,t) - c_P(z, r = r_P, t)] = 0 \qquad (8)$$

where u_E is the effective velocity of the solution thought the bed, D_L the axial dispersion coefficient, ε the bed void fraction and z is the axial coordinate ranging from 0 and H, at the top and bottom of the bed, respectively. The boundary condition for eq. (8) are:

$$c(z = 0, t) = c_{in} \qquad (9)$$

$$\frac{\partial c(z = H, t)}{\partial z} = 0 \qquad (10)$$

Both the mass transfer coefficient, k, and the axial dispersion coefficient, D_L, can be estimated on the basis of the operating conditions and the physical characteristics of the solution (Wilson and Geankoplis, 1966, Langer et al. 1978).

The model consisted of the set of eqs. (1)-(6), (8)-(10) and of the above mentioned correlations to determine D_L and k. The concentrations c, c_p and c_s in eqs. (1)-(6) depends only on the axial coordinate, z, because of the plug flow hypothesis. Since the measurement error of the bed void fraction was quite high, it was used as adjusting parameter.

4. Results and discussion

The estimated values for the parameters D_p, k_{eq} and γ are reported in Tab. 2. As expected, the estimated pore diffusivity is lower than the one predicted for the diffusivity in the solution bulk by means of the correlation of Wilke and Chang (1955), equal to $1.9 \cdot 10^{-9}$ $m^2 \cdot s^{-1}$.

Table 2: Estimated parameters.

Parameter	value	dimensions
D_p	$6.8 \cdot 10^{-10}$	$m^2 \cdot s^{-1}$
k_{eq}	153	$(mol \cdot m^{-3})^{(1-\gamma)}$
γ	0.66	#

The estimated equilibrium curve, plotted in Fig. 3, properly fits the experimental data. In Fig. 5 the 95% confidence ellipsoids for the estimated parameters are plotted: the cross correlation between them is low and their statistical significance is satisfactory.
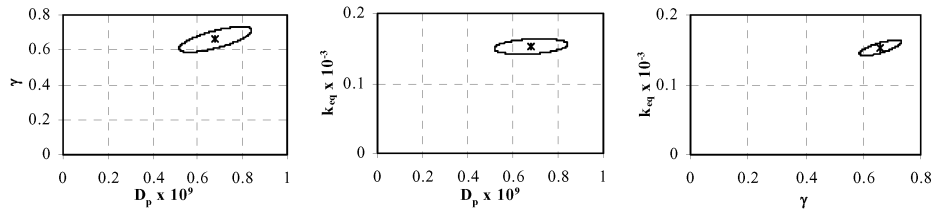

Figure 5: 95% confidence ellipsoids for the three estimated parameters D_p, k_{eq} and γ.

Concerning the fixed bed column runs, the simulated trends of the outlet stream concentration, reported in Fig. 4, show a good agreement with the experimental ones: The value of the adjusting parameter, i.e. the bed void fraction, resulted equal to 0.59, that is higher than the measured value equal to 0.51. This deviation is reasonable and can be justified by either a not complete exposure of the adsorbent particles to the solution or some simplifications of the model.

5. Conclusion

This preliminary work on a particular polyphenol shows that the adsorption on polymeric resins can satisfactorily remove polyphenolic compounds from aqueous solutions when a rather high residence time is adopted. The desorption in alcoholic solvents takes place in a very short period of time.

The adsorption kinetics and equilibrium were described and the modelling of the column apparatus gave satisfactory results.

On the basis of the achieved results, future work will be devoted to investigate the removal of polyphenolic compounds from the real olive mill wastewater.

7. List of Symbols

a specific external surface of the adsorbent in the bed, $m^2 \cdot m^{-3}$.

c concentration of 4MC in the solution bulk, $mol \cdot m^{-3}$.

c_P concentration of 4MC adsorbate, $mol \cdot m^{-3}$.

c_S concentration of the adsorbed 4MC, $mol \cdot m^{-3}$ of resin.

D_L axial dispersion coefficient, $m^2 \cdot s^{-1}$.

D_P pore diffusivity, $m^2 \cdot s^{-1}$.

H bed height, m.

k mass transfer coefficient, $m \cdot s^{-1}$.

k_{eq} Freundlich equation parameter, $(mol \cdot m^{-3})^{(1-\gamma)}$.

γ Freundlich equation parameter, dim.less.

r particles radial coordinate, m.

r_P particles external radius, m.

u_E effective velocity of the solution thought the bed, $m \cdot s^{-1}$.

z axial coordinate in the bed m.

ε void fraction of the adsorber.

ε_P porosity of the resin.

τ resident time in the column, s.

additional under script:

0   initial

f   final

in   inlet

out   outlet

8. References

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