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Depot effect of bioactive components in experimental membrane filtrations

D Mitev[1], D Peshev[2], G Peev[2] and L Peeva[3]

[1] REGPOT-2012-2013-1 NMP INERA Project, Institute of Solid State Physics-BAS, 72 Tzarigradsko Chaussee Blvd., 1784 Sofia, BULGARIA
[2] University of Chemical Technology and Metallurgy, Department of Chemical Engineering, 8 Kl. Ohridsky Blvd., 1756 Sofia, Bulgaria
[3] Chemical Engineering and Chemical Technology, Imperial College London, Exhibition Road, London SW7 2AZ, U.K.

Email: dpmitev@yahoo.com

Abstract. Depot effects were found to be accompanying phenomena of membrane separation processes. Accumulation of target species in the membrane matrix during feasibility tests can hamper proper conclusions or compromise the filtration results. Therefore, we investigated the effects of delayed membrane release of chlorogenic acid and caffeine, considered as key compounds of interest in spent coffee products' recovery treatment. Permeate fluxes and key components release were studied in course of 24 hours via nanofiltration of pure solvent, both immediately after the mock solution filtration and after idle stay. Conclusions are drawn and recommendations advised for proper analysis of experimental data on membrane screening.

1. Introduction

Adsorptive depot effects have drawn significant attention in the field of membrane filtration, especially when small scale experiments were involved. Ideally, no part of the analytes or the compounds of interest should be retained in the membrane matrix. However, in real applications, considerable amount of the filtered solutes can be adsorbed during the initial filtration stages, predetermined by the membrane (material, presence/absence of wetting agents, pore size and distribution), solute type, pH, ionic strength, and even filtration flow rate [1]. A range of separations have been studied in the scope of this phenomenon: from individual compounds such as toluidine blue [1], benzalkonium chloride, chlorhexidine acetate, phenylmercuric nitrate and phenylethyl alcohol [2-3], estrogen 17β-estradiol [4], triethanolamine and sodium benzoate [5], a gamut of sixteen neutral, acidic and basic compounds [6], surfactants [7], to viruses [8] and bovine serum albumin (BSA) [9] and other peptides (luteinizing hormone releasing hormone, gamma globulin and BSA) [10], monoclonal antibodies and surfactant influence thereon [11]; with membranes of different materials being mainly of microfiltration types (sterilising grade) though.

This research reveals the depot effects accompanying nanofiltration of standard caffeine (CAF) and chlorogenic acid (CGA) solutions, aimed at modeling of spent coffee ground recovery via membrane filtration.

2. Experimental part

2.1. Materials

All reagents used were of analytical grade quality: chlorogenic acid (Sigma-Aldrich Chemie GmbH, Steinheim, Germany), caffeine (Chimspectar, Sofia, Bulgaria). Distilled water (water still GFL Typ 2004, Burgwedel, Germany) was used throughout the work.

2.2. Instruments

Following instrumentation was used throughout the work:

Membrane filtration. "Dead-end" filtration cell of type "METcell" (Membrane Extraction Technology Ltd., London, UK), fitted with 0.0054 m^2 nanofiltration membrane "Microdyn Nadir" NP 030 P (Microdyn-Nadir GmbH, Wiesbaden, Germany); operating pressure up to 60 bar (compressed nitrogen) under internal stirring 1000 min^{-1}.

Spectrophotometry. An S-22 UV/Vis type of spectrophotometer (Boeco, Germany) was used for determination of the maximal spectral absorption at wavelengths of 275 and 330 nm.

2.3. Preparation of the standard solutions

Feed solutions of 497.01 mg kg^{-1} caffeine and 495.70 mg kg^{-1} chlorogenic acid were prepared with distilled water. Given concentrations correspond to the spectrophotometric evaluation of the final solutions, according to the standard curves represented on figure 1 (a-b).

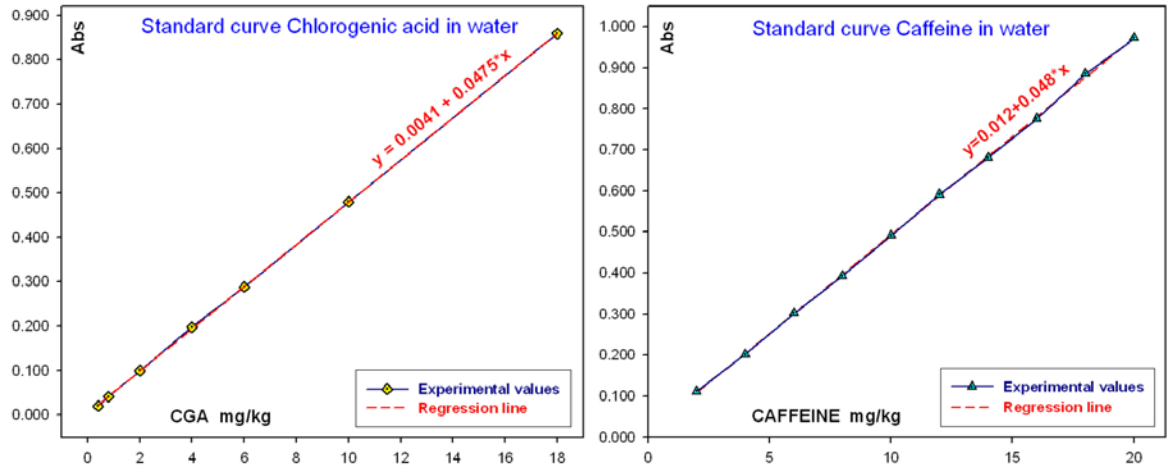

Figure 1. (a) Standard spectrophotometric curves for chlorogenic acid at 330 nm (Rsqr = 0.9999) and (b) caffeine at 275 nm (Rsqr = 0.9998).

2.4. Nanomembrane conditioning

Prior to nanofiltration runs with standard mock solutions, each coupon of the used membrane of type "Microdyn Nadir" NP 030 P was conditioned by a filtration of distilled water until 200 ml of permeate was collected at 40 bars transmembrane pressure difference (figure 2 a-b). Spectrophotometric assay showed negligible, though noticeable response background absorptions at both wavelengths (retentate/total permeate): 0.015/0.011 AU at 330 nm; and 0.021/0.011 AU at 275 nm, which would correspond to ±0.229/±0.251 mg kg^{-1} CGA; and ±0.188/±0.375 mg kg^{-1} CAF respectively if they were really present.

Corresponding response of the NP 030 P nanomembrane shows up at different pressures during the water conditioning step. Conditioned at lower pressure membranes express higher permeate fluxes, which are fully reversible after moderate pressure changes, as shown by the 5 to 10-bars plot on figure 2(b). A preliminary conditioning at 40 bars immediately before 10 bars water filtration lowers the flux's plateau to ~4.5 LMH/bar though; this in turn might be an indicator of structure transformations

of the membrane after the high pressure treatment. Despite these differences it must be noted that all permeate fluxes obeyed the manufacturers specification of >1 LMH/bar.

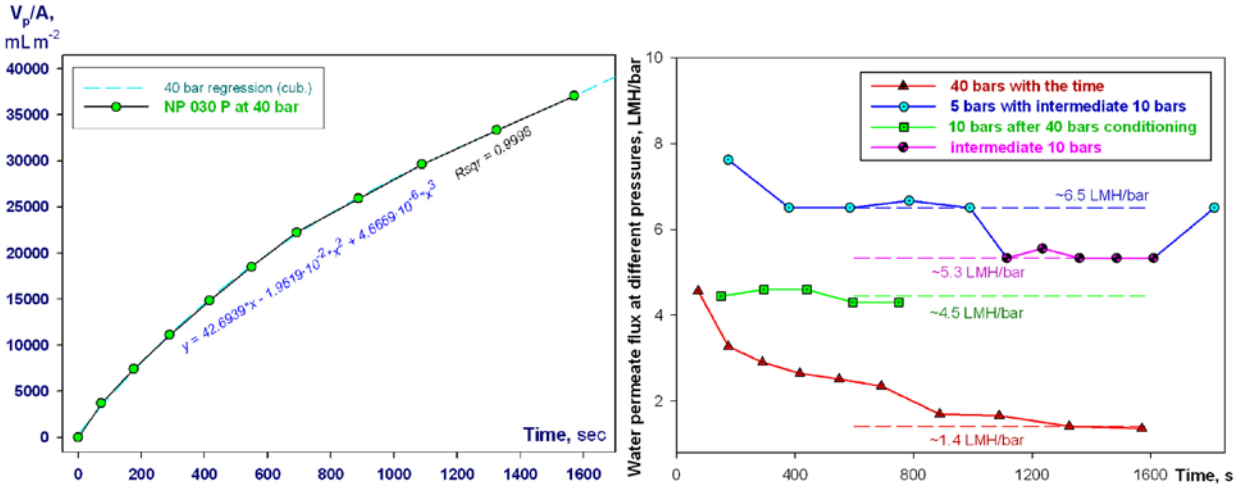

Figure 2. Kinetics of the NP 030 P nanofiltration conditioning: (a) cumulative permeate volume per unit membrane area versus time at 40 bars; (b) water permeate fluxes of NP 030 P at different pressures versus time.

2.5. Nanomembrane filration

100 ml of the standard solutions were subjected to nanofiltration at temperature of 298.15 K and pressure of 30 bar. The membrane separation continued until 51 ml of permeate (P) were isolated for CGA and 52 ml for CAF; with retentate (R) being the rest.

3. Results and Discussion

The aim of this research is to establish the separation performance in terms of permeate flux and solute rejection of the nanomembrane in water solutions of CGA and CAF, while accounting for and quantifying the related depot-effects in the NP 030 P membrane.

3.1. Nanomembrane filtration of standard solutions

Nanofiltration runs of both standard solutions were performed in "dead-end" filtration mode, under intensive mixing provided by internal magnetic stirrer as described in Section 2. Furthermore, four subsequent filtrations of 100 ml distilled water each one were done in both cases. At every filtration 50 ml of permeate were collected, followed by additional 3 ml permeate for estimation of C_{pe} (permeate concentration at the end of nanofiltration; mg kg^{-1}). The output kinetics of both the filtration procedures and "depot" adsorption values are shown in table 1 and figure 3 (a-b).

"Microdyn Nadir NP 030 P" is a commercial nanofiltration membrane (30 % retention for NaCl and 80-95 % for Na_2SO_4; MWCO ~400 Da); with polyethersulfone (PES) active membrane layer on PE/PP support [12]. During the filtrations considerable rejection was registered for CGA (molecular weight 354.31 Da), where a quadratic regression was the best fit for the nanofiltration kinetics (figure 3(a)). The membrane rejection in regard to the CGA contents of the standard solution was calculated according to [13]:

$$R_{CGA} = (lg(C_r / C_f) / lg(V_f / V_r)) \,.\, 100 = 75.7\ \% \qquad (1)$$

Table 1. Kinetics of separating filtration (T), membrane washings (t_i) and concentration of the respective fractions.

Permeate, ml	**Filtration time CGA**, sec.					**Filtration time CAF**, sec.				
	T_{Fcga}	t_{1cga}	t_{2cga}	t_{3cga}	t_{4cga}	T_{Fcaf}	t_{1caf}	t_{2caf}	t_{3caf}	t_{4caf}
10	540	450	424	333	330	146	152	130	135	134
20	1130	835	805	669	640	273	284	260	280	300
30	1780	1248	1196	1017	965	404	410	390	410	470
40	2430	1668	1580	1390	1275	550	547	540	555	665
50	3145	2110	1966	1765	1600	704	693	689	705	863
	Active concentrations CGA, mg kg^{-1}					**Active concentrations CAF**, mg kg^{-1}				
Permeate C_p	58.95	25.35	2.39	0.88	0.31	440.48	59.45	25.60	0.21	0.60
Permeate C_{pe}	-	3.93	0.84	0.38	0.04	-	1.98	0.08	0.06	0.35
Retentate	850.49	6.10	0.61	1.26	0 (neg.)	504.19	0.67	0.08	0 (neg.)	0.50

The obtained rejection value shows moderate capability of the membrane to retain CGA and related compounds, present in spent coffee residues. As far as in terms of molecular weight CGA represents the lower limit amongst the antioxidant constituents in coffee raw material [14], one shall expect even higher efficiency of the investigated membrane in concentration of antioxidant liquid extracts from coffee.

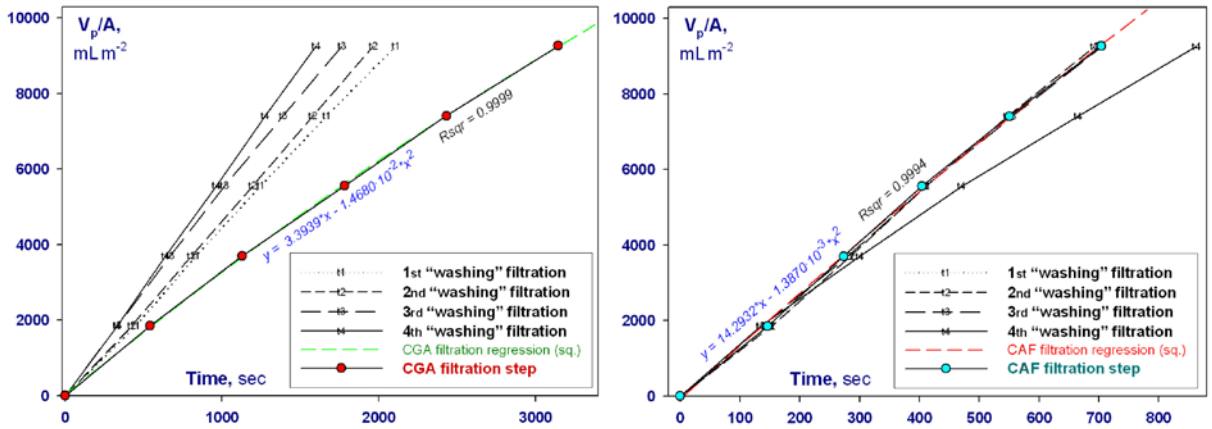

Figure 3 (a) - (b). NP 030 P nanofiltration of CGA and CAF solutions, plus subsequent four pure water (washing) filtrations in each case.

The experimental results showed negligible retention capacity of the membrane with respect to caffeine (molecular weight 194.19 Da; figure 3 (b)):

$$R_{2\,CAF} = (lg(C_r / C_f) / lg(V_f / V_r)) \,.\, 100 \;=\; 2.0\ \% \qquad (2)$$

The combination of high rejection for CGA and higher molecular weight polyphenols with antioxidant activity and negligible rejection for CAF at the same time, demonstrates the membrane applicability in production of caffeine free coffee products as well as for isolation of natural caffeine. According to the material balance 4.9 mg or 9.9 % of the available CGA was adsorbed onto the membrane during the nanofiltration step; respectively 2.6 mg or 5.2 % for the nanofiltration of CAF (table 1). These values indicate the uncertainty in the determination of the membrane rejection values, using laboratory scale batch experiments, especially in case of new “unsaturated” membranes.

3.2. The effect of "washing" filtrations

In the case of CGA, desorption was a relatively slow process and the influence of concentration polarisation was noticeable until the third washing filtration (quadratic regression fit). With the course of washings the process fastened evenly, despite that between the second and third "washing" filtrations an 18-hour-long pause took place (figure 3(a)).

For the CAF nanofiltrations, relatively small molecules did not block the membrane; washing filtrations practically overlap the nanofiltration kinetics. The only deviation here is the course of the last "washing" filtration, made after an 18-hours-long pause as well. Possible reasons for the phenomenon include a relaxation change of the membrane, or a release of dissolved CAF by the membrane polymer after the idle period. Both hypotheses need a further confirmation though

4. Conclusions

Depot effect of CGA and CAF water solutions nanofiltration have been established (those of CGA being significantly stronger), which has to be considered evaluating process characteristics.

A nanofiltration step was suggested, with potential integration in technologies for production of decaffeinated alkaloid beverages, or as a separation method for chlorogenic acid or caffeine from suitable sources.

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