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# Combined membrane process at waste water treatment

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## Abstract

This contribution deals with the study of hollow fibre membrane dead-end microfiltration combined with powdered activated carbon sorption used in removing of organic dyes from wastewater. Adsorption characteristics of model reactive dye OSTAZIN RED on powdered activated carbon were studied. Adsorption isotherms and kinetics were measured from which followed, that adsorption of this dye on activated carbon is favourable, however the time to reach an equilibrium is around 7 days. From hybrid separation process characteristics measurements it resulted that the activated carbon does not foul this type of membrane and the permeate flux is recovered after membrane backflush. A simple mathematical model describing dynamic sorptive process in microfiltration system is presented and discussed.

*Keywords:* membrane microfiltration, waste water, hollow fibre, activated carbon

## 1. Introduction

Wastewater discharges from textile dye houses are usually complex, variable, and highly coloured. These are toxic to some aquatic organisms and are of serious health risk to human beings. Conventional treatment processes presently in use at waste water treatment works do not usually achieve satisfactory colour removal, resulting in coloured effluent being discharged from the treatment plants [1]. Consequently, downstream use of the treated water is limited, and the highly visible nature of the pollution source often gives rise to public concern. Thus, there is a constant need to have an effective process that can efficiently remove these dyes from wastewater. During the last years, several physical, chemical and biological decolorization methods have been reported [2,3]. Because of the high cost and disposal problems, many of these conventional methods for treating dye wastewater have not been widely applied. Effluent treatment normally includes neutralization, flocculation, coagulation, settling, carbon adsorption, detoxification of organics by oxidation (using ultraviolet systems or peroxide solutions), and biological treatment.

Activated carbon adsorption processes have been successfully employed to control effectively problems related to organic substances (including dyes) in both natural water and wastewaters. The structural characteristics (total surface area, size, shape and volume of pores) and chemical characteristics (charge, type and number of surface groups, impurities) of the activated carbon will influence the adsorption behaviour of any solute. Other factors affecting adsorption are good contact between the activated carbon and the water being treated and sufficient contact time.

Two standard types of liquid phase carbon adsorption are the fixed-bed and moving-bed systems. The fixed-bed system is used primarily for low-flow waste water streams with contact times around 15 minutes, and it is a batch operation.

Moving-bed carbon adsorption systems operate continuously with waste water typically being introduced from the bottom of the column and regenerated carbon from the top (countercurrent flow) [1,4]. Recent studies of the activated carbon adsorption process are

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focused on combination of powdered activated carbon (PAC) adsorption with low pressure membrane separation process, i.e. microfiltration or ultrafiltration [5,6]. With this vacuum/suction driven process, hollow fibre membranes are directly immersed in wastewater with dosed PAC. The membranes provide a positive barrier to biological impurities as well as high concentrations of both natural solids and PAC, which are suspended in the wastewater. For smaller diameter of PAC particles adsorption kinetics is enhanced. Thus, in addition to turbidity reduction, the process can also be optimized for reduction of soluble organics which are adsorbed on the powdered activated carbon.

The performance of this membrane-adsorption process depends on system configuration, operating modes, carbon dose, carbon adsorptive characteristics and influent characteristics [1,5,8,10]. In order to investigate the mechanism of adsorption in combined system, the several kinetic models have been used in the literature for sorption processes. The internal particle diffusion was usually considered to be the rate limiting steps in adsorption process.

The objective of this study is to evaluate the achievement of adsorption and membrane microfiltration processes individually in the removal of reactive dye and then study the performance of the combined adsorption–microfiltration process. The first order and pseudo second-order models were used for adsorption kinetics description.

## 2. Theory

### Equilibrium data

The Langmuir and Freundlich models are considered to describe satisfactory the experimental data. Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. The relation between adsorbed  $a^*$  and fluid phase  $c$  solute concentration is given by

$$a^* = \frac{a_{\infty} k_L c}{1 + k_L c} \quad (1)$$

Here  $a^*$  is the equilibrium mass of solute adsorbed per unit mass of PAC,  $a_{\infty}$  and  $k_L$  are model parameters. For low adsorbate concentrations linear approximation of Langmuir isotherm can also be used in the form

$$a^* = a_{\infty} k_L c = b c. \quad (2)$$

Freundlich isotherm

$$a^* = K_f \cdot c^{\frac{1}{n}} \quad (3)$$

( $K_f$  and  $n$  are model parameters) is basically empirical. It is especially useful for the description of adsorption onto adsorbent surfaces with heterogeneous energy distribution, when the energy term  $k_L$  of the Langmuir Eq. (1) varies as a function of the surface coverage strictly due to variations in the heat of adsorption.

### Kinetic data

In order to investigate the mechanism of sorption several kinetic models have been proposed in the literature for dye adsorption processes [4,9]. In this work simple relationship

$$\frac{da}{d\tau} = k_1 (a_1^* - a) \quad (4)$$

was chosen to analyze and simulate concentration decay curves in the constant volume batch adsorption experiment. Here  $k_1$  is first-order rate constant of sorption,  $a$  is the amount of dye adsorbed at time  $\tau$  and  $a_1^*$  is the adsorbed amount, which would be in equilibrium with actual

solute concentration  $c$ . Using Eq. (2) to express  $a_1^*$  in combination with dye mass balance integration of Eq. (4) gives

$$a = \frac{bc_0}{bc_{PAC} + 1} \left[ 1 - e^{-k_1(bc_{PAC} + 1)\tau} \right] \quad (5)$$

Here  $c_0$  is initial dye concentration and  $c_{PAC}$  is powdered activated carbon concentration. Another model for the analysis of sorption kinetics is pseudo-second-order model given by

$$\frac{da}{d\tau} = k_2(a_2^* - a)^2, \quad (6)$$

where  $k_2$  is the pseudo-second-order rate constant of sorption and  $a_2^*$  is a constant which is related to the adsorbed amount, which would be in equilibrium with solute concentration reached at steady state of a batch experiment. Integrating Eq (6) for boundary conditions  $\tau = 0$  to  $\tau = \tau$  and  $a = 0$  to  $a = a$  and rearranging into linear form we obtain

$$\frac{\tau}{a} = \frac{\tau}{a_2^*} + \frac{1}{k_2(a_2^*)^2} \quad (7)$$

#### Mathematical model of combined separation process

Let us consider a tank of volume  $V$  filled with wastewater containing dyestuff. Tank is equipped with submerged hollow fibre membrane module. Initial concentration of dye is  $c_0$ . At the time  $\tau = 0$  the mass  $m_{PAC}$  of powdered activated carbon is dosed into the system and constant permeate flow is preselected. The water removed by permeation is replaced with feed wastewater to maintain a constant level in the tank. Assuming ideal mixing of the fluid phase and taking into account complete PAC rejection, the mass balance equations for the system can be written as

$$\frac{dV}{d\tau} = 0, \quad (8)$$

$$\frac{dm_{PAC}}{d\tau} = 0, \quad (9)$$

and dye mass balance is

$$\dot{V}c_0 - \dot{V}c = \frac{d(V.c)}{d\tau} + \frac{d(a.m_{PAC})}{d\tau}. \quad (10)$$

Here  $m_{PAC}$  is a total mass of PAC in a tank,  $\dot{V}$  is a volumetric permeate flow,  $V$  is a tank volume,  $c$  is a dye concentration and  $\tau$  is time.

After differentiation Eq. (10) takes form

$$\dot{V}c_0 - \dot{V}c = c \frac{dV}{d\tau} + V \frac{dc}{d\tau} + a \frac{dm_{PAC}}{d\tau} + m_{PAC} \frac{da}{d\tau}. \quad (11)$$

It can be simplified using Eq. (8) and (9) to

$$\frac{dc}{d\tau} = \frac{1}{t}(c_0 - c) - c_{PAC} \frac{da}{d\tau} \quad (12)$$

where  $t$  is

$$t = \frac{V}{\dot{V}}. \quad (13)$$

The differential equation (12) combined with appropriate sorption kinetic model (i.e. Eq. (4) or (6)) can be solved with initial conditions  $\tau = 0 : c = c_0, a = 0$ . The numerical Runge-Kutta method of the 4<sup>th</sup> order [7] can be employed for determination of concentration-time dependency in the permeate flow. The general process parameters required for solving of the model are PAC dosage ( $m_{PAC}, c_{PAC}$ ), the hydrodynamic retention time ( $t$ ), the adsorption isotherm relationship (i.e. the parameters of Langmuir isotherm  $a_\infty$  and  $k_L$ ) and the adsorption kinetic parameters (i.e. the rate constants of sorption  $k_1$  or  $k_2$ ).

The isotherm parameters can be obtained directly from batch adsorption experiments. The kinetic parameters can be determined using data from batch adsorption studies by the least squares residuals technique. For the pseudo-second-order adsorption model the constant  $a_2^*$  must additionally be determined for each time interval of the numerical procedure used. An approximate approach to such a process is to consider it as a fictitious batch system in which adsorption starts at the actual solute concentration  $c$  and it is finished in equilibrium, where solute concentration is  $c_e$ . Combining the material balance of this fictitious batch system with the adsorption isotherm (i.e. Eq. (1)) the constant  $a_2^*$  for the actual solute concentration can be determined from quadratic equation

$$k_L c_e (a_2^*)^2 - (1 + k_L c + k_L c_e a + k_L c_e a_\infty) a_2^* + k_L c a_\infty + k_L c_e a a_\infty = 0 \quad (14)$$

### 3. Materials and methods

The experiments were carried out using aqueous solutions of reactive dye OSTAZIN RED HB (OSTACOLOR, Czech Republic), i.e. disodium salt of 1-amino-2-sulpho-4-[3-(2-sulphoethylsulphonylanilino)] anthraquinone, C.I. Reactive Red E 5241. Concentration of dye was measured by spectrophotometer at a wavelength of 536 nm. Coal based powdered activated carbon CW20 was obtained from SILCARBON. The particle size fulfilled DIN 19 603 (i.e. 85 % particles were  $< 40 \mu\text{m}$ , and 5%  $> 80 \mu\text{m}$ ).

Microfiltration experiments were performed on hollow fibre polypropylene membrane module (Eidos, Czech Republic). PP fibres were characterised by inside diameter 0.24 mm and mean pore size  $0.1 \times 0.7 \mu\text{m}$ . The active module area was  $0.94 \text{ m}^2$ . Schematic drawing of the experimental system is given in Fig.1.

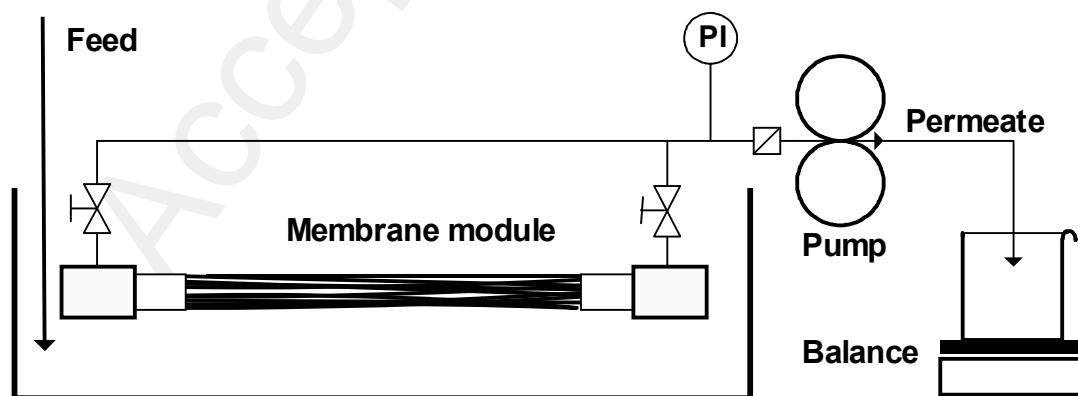


Fig. 1. Experimental set-up of dead-end microfiltration unit

Apparatus consisted of 15-litre feed container, a gear pump, membrane module, valves at the module outlet and prefilter (5  $\mu\text{m}$ ). The permeate was collected in a flask placed on an electronic balance, which was connected to a personal computer. The apparatus was also equipped with a pressure monitoring system.

Gear pump Heidolph 5025 provides relatively constant output flowrate regardless of changes in pressure and can easily be used for membrane backflushing (reversing flow direction).

The membrane unit was operated in outside-in dead-end filtration configuration. In order to prevent the continuous accumulation of solids on the membrane surface the membrane was backflushed by permeate. Backflushing was initiated manually after preselected period of filtration. In the system PAC adsorption and membrane separation were carried out simultaneously. Specific amount of PAC dose was added once at the beginning of the experimental run. Both the permeate volume and the pressure were monitored in order to calculate basic process characteristics - permeate flux as well as pressure drop.

For determination of equilibrium and kinetic data batch adsorption experiments were conducted by adding different amounts of PAC into the Erlenmeyer flask containing model wastewater. After mixing at constant temperature (25 $^{\circ}$  C) for 7 days samples were taken from the flask and filtered through 0.1  $\mu\text{m}$  membrane filter. Then the filtrate was measured for the dye concentration. Kinetic experiments were conducted at constant temperature of 25 $^{\circ}$  C and at good mixing conditions (magnetic stirrer). To obtain concentration decay curves as a function of time samples were withdrawn at timed intervals, filtered, and dye concentration in filtrate was determined.

#### 4. Results and discussion

##### Sorptive ability of PAC

The adsorption capacity depends on the properties of adsorbate and adsorbent. Figure 2 shows the adsorption isotherm of the system studied.

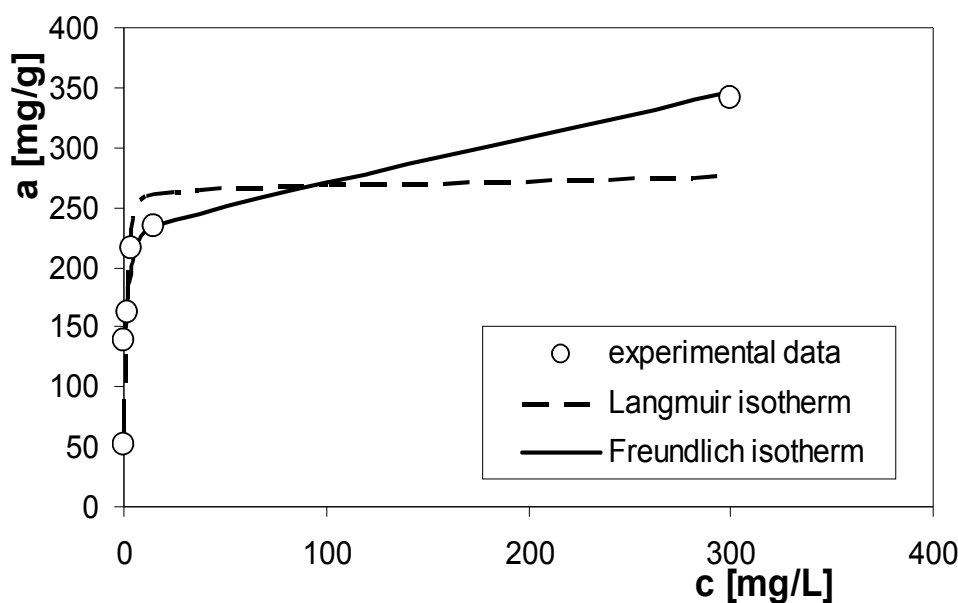


Fig. 2. Adsorption isotherm of OSTAZIN RED HB on PAC at 25 $^{\circ}$ C

Langmuir and Freundlich models were not found to satisfactorily describe the adsorption of the reactive dye studied. Langmuir isotherm fits the experimental data better for lower dye concentrations. On the other hand, theoretical plots of Freundlich isotherm approximate experimental data successfully for higher concentrations. The determined isotherm parameters for dye used and PAC are listed in Table 1. The maximum sorption capacity was estimated to be 289.9 mg/g, indicating moderate capacity of PAC to remove OSTAZIN RED HB from wastewater. This behaviour might be ascribed to the fact that the large size of dye molecules impedes sorption process.

Langmuir isotherm		Freundlich isotherm	
$a_{\infty}$ [mg/g]	$k_L$ [L/mg]	$K_f$ [L/g]	$n$ [-]
289.9	1.1485	163.91	7.60

Table 1. Langmuir and Freundlich model parameters for OSTAZIN RED HB at 25°C

Effect of contact time on removal of reactive dye from solutions for different initial concentrations was also studied. The equilibrium period required for maximum removal was around 7 days; however, the sorption half-time was below 100 min in all cases. The example of results of kinetic measurements is shown in Figure 3, where the experimental data are compared with the theoretical ones calculated according to the first-order kinetic relation (Eq. (5)) and pseudo-second-order kinetics (Eq.(7)). It can be seen that two phases are included in the kinetics - a rapid dye sorption stage and a subsequently much slower stage - before the equilibrium was established.

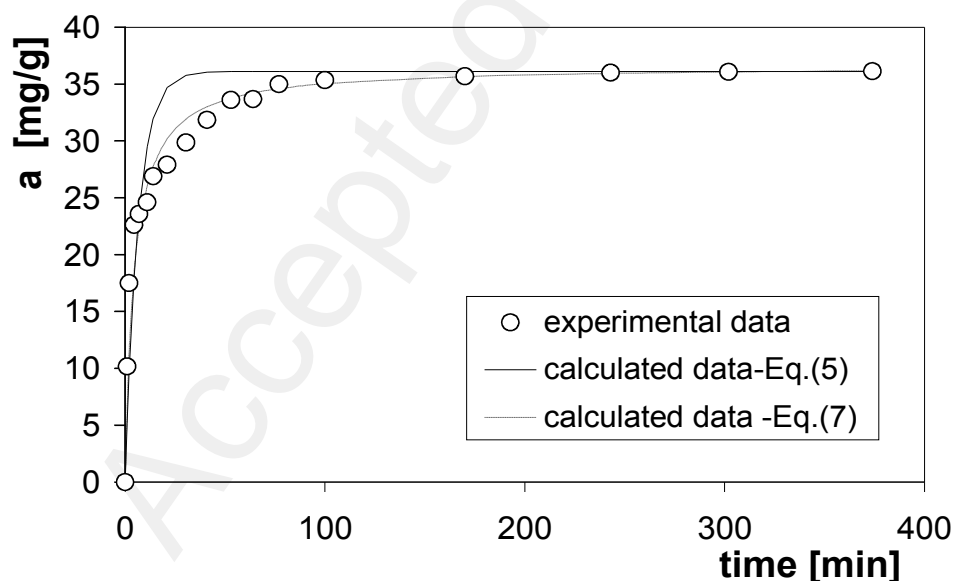


Fig. 3. Adsorption kinetic of OSTAZIN RED HB on PAC at 25°C (initial concentration of dye 108 mg L<sup>-1</sup>; PAC concentration 3 g L<sup>-1</sup>),  $k_1 = 0.0001543 \text{ min}^{-1}$ ,  $k_2 = 0.00612 \text{ g} \cdot (\text{mg} \cdot \text{min})^{-1}$ ,  $a_2^* = 36.6 \text{ mg} \cdot \text{g}^{-1}$

The results indicate that the pseudo-second-order kinetic model provides better correlation with experimental results.

Figure 4 shows typical permeate dye concentration decay curve based on absorbance data at PAC dose of 3 g/L for the combined system. The membrane was submerged in a tank containing wastewater. A known dose of PAC was added to the tank. An agitator was used to keep the PAC in suspension. The influent and effluent flows to and from the tank were maintained using pumps. The wastewater in the tank was kept at the constant level. When dye wastewater alone was fed into the membrane system without PAC, it was evident that membrane alone was not effective in the retention of the dye (the concentration of dye in permeate was the same as in the feeding stream).

The addition of the PAC resulted in an immediate decrease in effluent concentration. Complete removal of dye was achieved for some period in which the colour was no longer visible (concentration less than  $1 \text{ mg L}^{-1}$ ). Then the concentration of the effluent started to increase with time. The beginning of this process was found to be a function of the ratio of the total mass of PAC in the tank to the influent flow rate.

Fig. 4 also shows the values predicted by the theoretical model for the first-order and the pseudo second-order kinetics, respectively. It can be seen that the pseudo second-order kinetic model fits the experimental data better. This result is consistent with the batch experiments mentioned above. Nevertheless, the values of effluent concentration predicted by both models are higher than experimental data. The higher degree of removal achieved in the initial part of experiments compared to the model predictions could be caused by the presence of PAC filter cake on the membrane surface, in which better contact between the activated carbon and the water being treated can be expected.

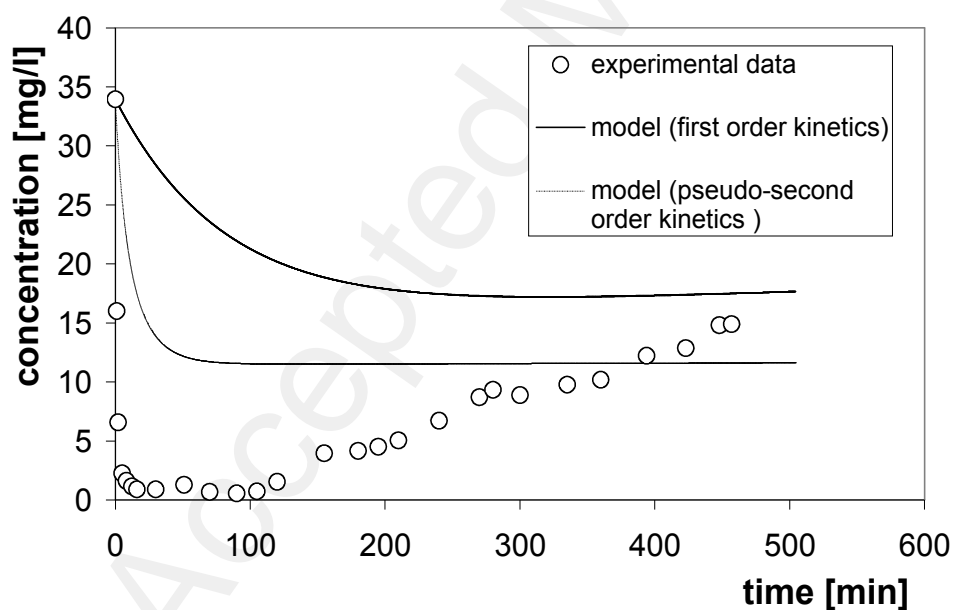


Fig. 4. Effect of PAC dose on the removal efficiency of reactive dyes in the combined process (initial dye conc.:  $34 \text{ mg L}^{-1}$ , PAC conc.:  $3 \text{ gL}^{-1}$ , permeate flux:  $10 \text{ Lm}^{-2}\text{hr}^{-1}$ , tank volume: 14 L)



## 4.2. Membrane fouling

A major advantage of hollow fibre membrane modules is the high membrane surface area to footprint ratio compared to other configurations of membranes. However, this may lead to a greater tendency to fouling, i.e. the loss of permeability due to irreversible deposition on or within the membrane (pore closure or restriction, cake formation) [11].

The effect of filtration flux on membrane fouling was studied by varying the filtration flux in the range from  $7 \text{ Lm}^{-2}\text{hr}^{-1}$  to  $94 \text{ Lm}^{-2}\text{hr}^{-1}$ . When the filtration period was finished (after 30 minutes) the membrane was backflushed by permeate and consequently the operation at higher permeate flux was set. As expected, the lower filtration flux led to the lower transmembrane pressure development and the highest dye removal. It was also found, that PAC tendency for irreversible membrane fouling is extremely low and membrane backflushing is effective in restoring the permeate flux (or pressure difference) back to the initial values in the whole range of experiments – see Figure 5.

The filtration cake resistance was also investigated and it was observed that there is negligible resistance caused by the cake, as the PAC cake was quite loosely adhered to the membrane surface. For the submerged system, it is apparent that the process will benefit from a high PAC dosage as long as the high concentration of PAC does not lead to a significant increase of membrane fouling.

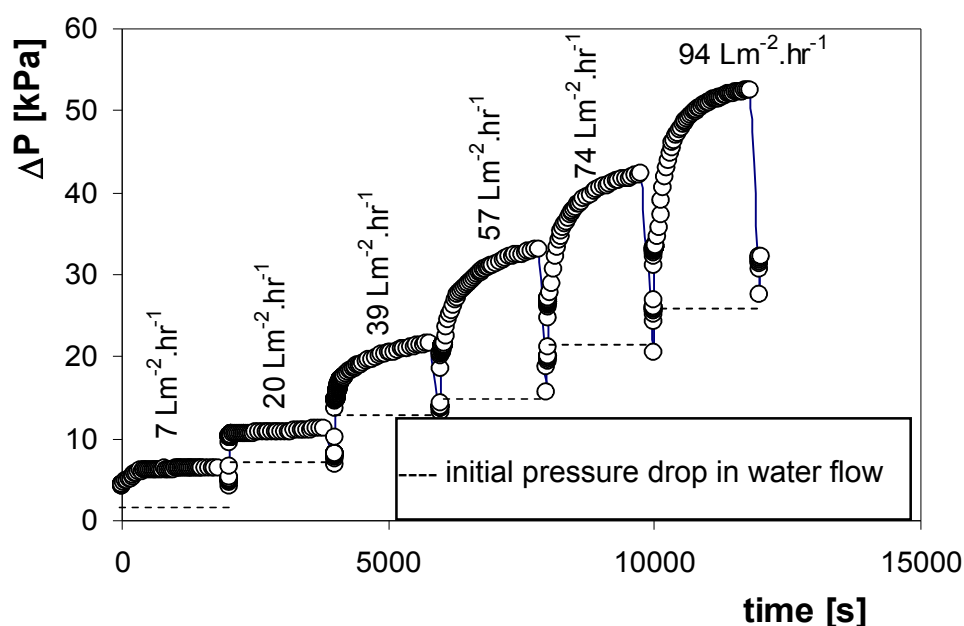


Fig. 5. Pressure drop-time dependency for microfiltration of PAC water suspension, concentration of PAC  $20 \text{ g L}^{-1}$ , backflush duration 2 minutes

## Conclusions

Adsorption isotherms and rate constants were determined from which followed, that adsorption of the reactive dye OSTAZIN RED HB on activated carbon is favourable, however the time to reach an equilibrium is around 7 days. During the submerged hollow fibre membrane microfiltration operated in dead-end mode it was found out, that polypropylene membrane was effective for removal of PAC particles from water suspensions. Only limited membrane fouling was observed in the range of variables tested. Membrane backflushing was effective in restoring the permeate flux back to the initial values. From this study it is evident

that the combined membrane process has a potential application for reactive dye removal. The experimental results indicate that complete removal of dye was achieved (less than  $1 \text{ mg L}^{-1}$ ) even in the case of very low PAC dose. Also, the treated water may be reused because of high water quality. A simple mathematical model describing dynamic sorptive process in microfiltration system is also presented and discussed.

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