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Organic dye removal by combined adsorption–membrane separation process

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ABSTRACT

Wastewater reuse is one of the principal tasks of modern industry. For this purpose several physical, chemical and combined methods have been used. This contribution deals with the study of combined adsorption–membrane separation process in water treatment. The hollow fiber membrane microfiltration dead-end process combined with adsorption on powdered activated carbon (PAC) was used to separate organic dye from water solutions. Adsorption characteristics of organic dye Egacid Red G200 on PAC were studied in batch experiments. From the experimental data the parameters of Langmuir, Freundlich and Sips adsorption isotherms were evaluated. The Langmuir type kinetic model was investigated to find the best-fitted model for the experimental data obtained. During the submerged hollow fibre membrane microfiltration operated in dead-end mode it was found that the membrane was effective for removal of PAC particles from water suspensions. Only limited membrane fouling was observed in the range of variables tested. From this study it is evident that the combined membrane process has a potential application for organic dye removal.

Keywords: Membrane microfiltration; Wastewater; Organic dye; Adsorption; Activated carbon

1. Introduction

Low pressure membrane processes (i.e. microfiltration and ultrafiltration) have been widely used in water treatment industry. They are very useful at turbidity and microorganisms rejection, however they do not remove dissolved organic compounds. Then, at the present time, a single process is not capable of adequate treatment, mainly due to the complex nature of effluents. In practice, a combination of different processes is often used to achieve desired water quality in the most economical way [1,2].

Activated carbon adsorption processes have been successfully employed to control effectively problems related to organic substances (including dyes) in both natural water and wastewaters. Recent studies of the activated carbon adsorption process have been focused on combination of powdered activated carbon (PAC) adsorption with microfiltration or ultrafiltration [1–4].

Membranes provide a positive barrier to biological impurities as well as high concentrations of both natural solids and PAC, which are suspended in wastewater. 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.

This contribution deals with the study of the combined adsorption–membrane process for organic dye removal. Adsorption equilibrium and kinetics data are evaluated and a simple mathematical model describing sorptive process in microfiltration system is presented and discussed.

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2. Theory

2.1. Adsorption equilibrium isotherm

The equilibrium isotherm is fundamental in describing the interactive behaviour between the solutes and adsorbent. Three of the most commonly used isotherms are the Langmuir, Freundlich and Sips models [5–8]. 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 amount a^* and fluid phase solute concentration c is given by:

$$a^* = \frac{a_\infty k_L c}{1 + k_L c} \tag{1}$$

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

$$a^* = a_\infty k_L c = b\,c \tag{2}$$

The Freundlich isotherm

$$a^* = K_f . c^{1/n} \tag{3}$$

(K_f and n are model parameters) is basically empirical. The Freundlich model considers monomolecular layer coverage of solute by the adsorbent. It also assumes that the adsorbent has energetically heterogeneous surface.

The Sips isotherm can be considered as a combination of the Langmuir and Freundlich models and it can be expressed as:

$$a^* = \frac{a_{\max}(B.c)^{1/n}}{1 + (B.c)^{1/n}} \tag{4}$$

where $a_{\max}$ is maximum amount of solute uptaken per unit mass of PAC, B and $1/n$ are the Sips model parameters. If the value for $1/n$ is less than one, it indicates that it is a heterogeneous adsorbent, while values closer to or even equal to one indicate that the adsorbent has relatively homogeneous binding sites [5].

2.2. Adsorption kinetics

In order to investigate the mechanism of sorption, several kinetic models have been proposed in the literature for sorption processes. Among them, the pseudo-first-order kinetic model, pseudo-second-order kinetic model and intraparticle diffusion model have been used the most often [6,7,9,10]. The pseudo kinetic models are not based on any physical concept of the adsorption process but they are simply mathematical models which describe the course of the process in time. The parameters of the pseudo models which are estimated from experimental data depend not only on the mechanism of adsorption process but also on the particular conditions of the experiment such as initial concentration of adsorbed species. Generalization of these models to different types of process is not possible. The simplest model based on some physical insight into the process of adsorption is the Langmuir kinetic model.

In this study, the Langmuir type kinetic model (supposing one-layer adsorption) was investigated to find the best-fitted model for the experimental data obtained.

According to this theory the adsorption rate ν_A [mg/s] can be expressed as

$$\nu_A = k'_A.(1-\theta).A.c \tag{5}$$

where θ [-] is the fraction of carbon surface occupied by adsorbed solute, k'_A [L/(m^2.s)] is the adsorption rate constant which depends on adsorbent affinity and temperature and A [m^2] is the total surface of PAC.

For the desorption rate an analogical equation can be written:

$$\nu_D = k'_D.\theta.A \tag{6}$$

in which k'_D [mg/(m^2.s)] is the desorption rate constant. The fraction θ for one-layer adsorption can be expressed using adsorbed amount a [mg/g]

$$\theta = \frac{a}{a_\infty} \qquad (0 \le \theta \le 1) \tag{7}$$

Net adsorption rate per unit of PAC (m_{PAC}) mass is as follows

$$\frac{da}{d\tau} = \frac{v_A - v_D}{m_{\text{PAC}}} = k_A(1 - a/a_\infty)c - k_D.a/a_\infty \tag{8}$$

where τ is time and new rate constants

$$k_A = k'_A\sigma \quad [\text{L/(g.s)}] \qquad k_D = k'_D\sigma \quad [\text{mg/(g.s)}] \tag{9}$$

and $\sigma = A/m_{\text{PAC}}$ [m^2/g] is specific surface of PAC.

At equilibrium state, $da/d\tau = 0$ and Eq. (8) can be rearranged to obtain the Langmuir isotherm:

$$a^* = \frac{a_\infty k_A c}{k_D + k_A c} = \frac{a_\infty k_L c}{1 + k_L c} \tag{10}$$

where $k_L = k_A/k_D$.

For the batch experiment (V [L] = const., c_{PAC} [g/L] = const.) mass balance gives

$$c = c_0 - c_{\text{PAC}}.a \tag{11}$$

where c_0 is the initial dye concentration.

Eq. (8) together with Eq. (11) and initial conditions $c\,(\tau = 0)$, $a\,(\tau = 0)$ can be integrated which leads to

$$a = a_1 a_2 \frac{\exp(\tau/\tau_0) - 1}{a_1 \exp(\tau/\tau_0) - a_2} \tag{12}$$

where

$$\tau_0 = \frac{a_\infty}{k_A c_{PAC}\sqrt{D}} \tag{13}$$

$$a_1 = \frac{\beta + \sqrt{D}}{2}, \quad a_2 = \frac{\beta - \sqrt{D}}{2} \tag{14}$$

$$D = \beta^2 - 4\gamma, \quad \beta = \frac{c_0}{c_{PAC}} + a_\infty + \frac{1}{k_L c_{PAC}}, \quad \gamma = \frac{a_\infty c_0}{c_{PAC}} \tag{15}$$

2.3. Mathematical model of combined separation process

At the combined process a tank was filled with wastewater (volume V) containing dyestuff (with initial concentration of dye c_0). The tank was equipped with a submerged hollow fibre membrane module. At the time $\tau = 0$ the mass m_{PAC} of powdered activated carbon was dosed into the system and constant permeate flow was preselected. The water removed by permeation was replaced with feed wastewater (concentration c_0) 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

$$\frac{dV}{d\tau} = 0 \tag{16}$$

$$\frac{dm_{PAC}}{d\tau} = 0 \tag{17}$$

and dye mass balance is

$$\dot{V}c_0 - \dot{V}c = \frac{d(V.c)}{d\tau} + \frac{d(a.m_{\text{PAC}})}{d\tau} \tag{18}$$

Here m_{PAC} is total mass of PAC in tank, $\dot{V}$ is a volumetric permeate flow, c is dye concentration. After differentiation Eq. (18) takes the form:

$$\dot{V}c_0 - \dot{V}c = c\frac{dV}{d\tau} + V\frac{dc}{d\tau} + a\frac{dm_{\text{PAC}}}{d\tau} + m_{\text{PAC}}\frac{da}{d\tau} \tag{19}$$

It can be simplified using Eqs. (16) and (17) to

$$\frac{dc}{d\tau} = \frac{1}{t}(c_0 - c) - c_{\text{PAC}}\frac{da}{d\tau} \tag{20}$$

where $t = V/\dot{V}$. Differential Eqs. (8) and (20) can be solved with initial conditions $\tau = 0 : c = c_0, a = 0$. Here, Runge–Kutta method of the 4th order was used for numerical integration of differential equations.

3. Materials and methods

The experiments were carried out using aqueous solutions of Egacid Red G 200 (Ostacolor, Czech Republic). The chemical formula of Egacid Red is depicted in Fig. 1. Dye concentration in solutions was determined by VIS spectrophotometry at a wavelength of 518 nm. Powdered activated carbon CW20 was obtained from Silcarbon, its specific surface area was 1300 m^2/g. The particle size fulfilled DIN 19,603, i.e. most of particles were < 40 μm.

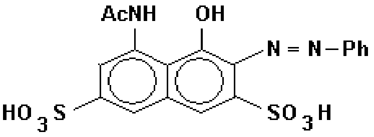

Fig. 1. The chemical structure of Egacid Red G 200.

3.1. Batch adsorption experiments

For determination of equilibrium and kinetic data batch adsorption experiments were conducted by adding different amounts of PAC (0.5 g/L or 1 g/L) into the Erlenmeyer flask containing model wastewater prepared by dissolution of powdered dye in distilled water. After mixing at constant temperature (25°C) for 4 h samples were taken from the flask and filtered through 0.8 μm membrane filter. The dye final concentrations were determined by VIS spectrophotometry. Kinetic experiments were conducted at constant temperature of 25°C, the pH of 4.9 and magnetic stirrer was used for mixing. To obtain concentration curves as a function of time samples were withdrawn at timed intervals, filtered, and dye concentration in filtrate was determined.

Using obtained concentration data the adsorption capacity $a = \frac{(c_0 - c)}{m_{PAC}}V$ was calculated.

3.2. Combined adsorption/microfiltration experiments

The continuous adsorption/microfiltration experiments have been performed using a stirred system as shown in Fig. 2. The apparatus consisted of 15-l feed container, a gear pump, membrane module, valves at the module outlet and prefilter (5 mm). 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) provided constant output flowrate regardless of changes in pressure and could easily be used for membrane backflushing (reversing flow direction).

The membrane used in the filtration experiments was a hollow fibre polypropylene membrane module (Eidos, Czech Republic). PP fibres were characterised by inside diameter 0.24 mm and outside diameter 0.31 mm. The pores were of slit shape with characteristic dimensions 0.1 × 0.7 mm. The structure of hollow fibres can be seen from Fig. 3. The active module area was 0.94 m^2.

Hollow-fibre membrane modules may operate in either an "inside–out" or "outside–in" mode. In the in-

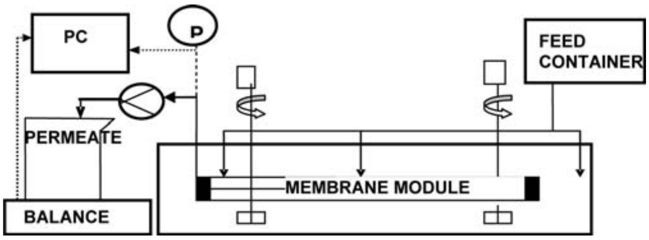

Fig. 2. Experimental set-up of dead-end microfiltration.

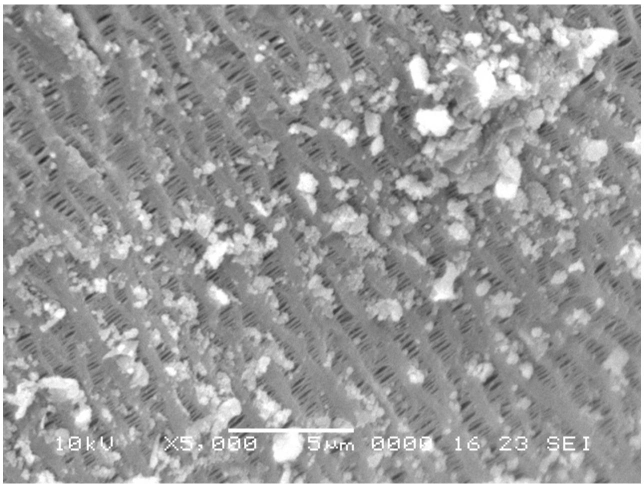

Fig. 3. SEM picture of hollow fiber surface covered by PAC, magnification 5000×.

side–out mode, the feed water enters the fibre lumen and is filtered radially through the fibre wall. The filtrate is then collected from outside of the fibre. During outside–in operation, the feed water passes from outside the fibre through the fibre wall to the inside, where the filtrate is collected in the lumen.

The membrane unit was operated in outside–in dead-end filtration configuration. In the system PAC adsorption and membrane separation were carried out simultaneously. Both the permeate volume and the pressure were monitored in order to calculate basic process characteristics — permeate flux as well as pressure drop.

4. Results and discussion

4.1. Adsorption equilibrium isotherms

Adsorption isotherms describe how pollutants interact with sorbent materials and so it is important to establish the most appropriate correlation for the equilibrium curve. In the present study, the adsorption of dye on the adsorbent at equilibrium has been expressed using the Langmuir, the Freundlich and Sips isotherms.

Fig. 4 shows the Freundlich, Langmuir and Sips curves for Egacid Red G200 onto PAC at a constant solution temperature of 25°C along with the experimental data. The curves were generated using Eqs. (1), (3) and (4).The parameters of isotherms are listed in Table 1.

For lower dye concentration all three isotherms fit the experimental data well, however for higher concentrations the Sips and Freundlich isotherms yielded a much better fit than the Langmuir model.

Table 1 shows the constants of the models mentioned. Parameter a_∞ of the Langmuir isotherm suggests the maximum sorptive capacity is 323 mg/g while Sips constant $a_{\max}$ indicates much higher value, 816 mg/g. But since the maximum experimental value of equilibrium dye concentration is only about 300 mg/l and adsorbed amount about 350 mg/g, we cannot conclude from the experiments that the high value of amax for Sips model is quite reliable. The Freundlich isotherm in the range of concentrations fits experimental data well but it predicts unlimited absorbed amount with increasing concentration in the solution.

4.2. Adsorption kinetics

The curves of the adsorbed amount of dye versus contact time are shown in Fig. 4. The initial dye concentration decreased rapidly during initiative period and

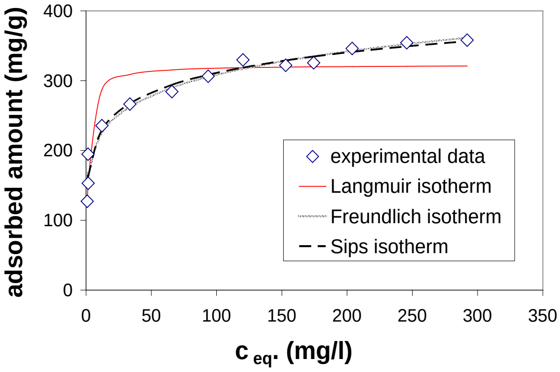

Fig. 4. Adsorption isotherms of Egacid red G 200 on PAC at 25°C.

Table 1
Evaluated parameters of isotherms

Langmuir isotherm		Freundlich isotherm		Sips isotherm		
a_∞ (mg/g)	k_L (L/mg)	Kf ($L^{1/n}mg^{1-1/n}$/g)	n	B (L/mg)	n	$a_{\max}$ (mg/g)
322.6	0.6682	155.6	6.734	0.7269	4.634	816.2

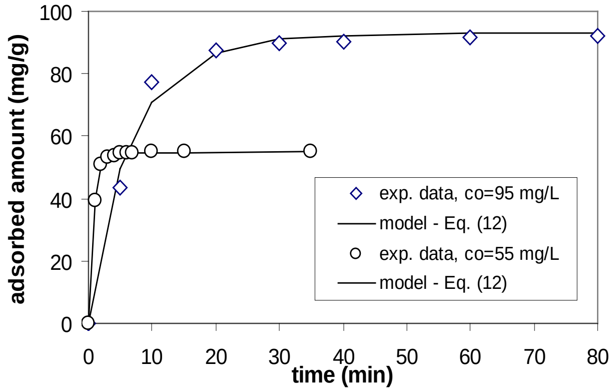

Fig. 5. Adsorption kinetics of Egacid Red on PAC at 25°C.

Table 2
Kinetic parameters determined according to Eq. (12)

Initial concentration, mg/L	55	95
k_A, L.(g.min)$^{-1}$	1.3834	0.1657
k_D, mg.(g.min)$^{-1}$	2.0704	0.2480

this confirmed strong interactions between the dye and the adsorbent. After that, the concentration of dye in the liquid phase remained almost constant. In Fig. 5 the experimental data are compared with theoretical values calculated according to Eq. (12).

The kinetic parameters of the model evaluated by non-linear regression of experimental data are listed in Table 2. The sorption data are well represented by Langmuir isotherm in the studied region of small concentrations and absorbed amount which suggests that for low dye concentration it is appropriate to use the Langmuir kinetic model to predict the sorption kinetics of Egacid Red G 200.

4.3. Combined separation process

Fig. 6 shows typical permeate dye concentration curve at PAC dose of 1 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. The influent and effluent flow rates to and from the tank were maintained using pumps. The wastewater in the tank was kept at constant level. The addition of the PAC resulted in an immediate decrease in effluent concentration. For the initial dye concentration c_0 = 54 mg/L complete removal of dye was achieved for some period in which the colour was no visible (concentration less than 1 mg.L^{-1}). Then the concentration of the effluent started to increase with time. The beginning of this process depended on the ratio of the total mass of PAC in the tank to the influent flow rate. During the course of filtration PAC can cause membrane fouling which can be restored through backwashing [11]. Because only low concentration of PAC was used, the combined separation process did not suffer by membrane fouling, so membrane backwashing was not necessary.

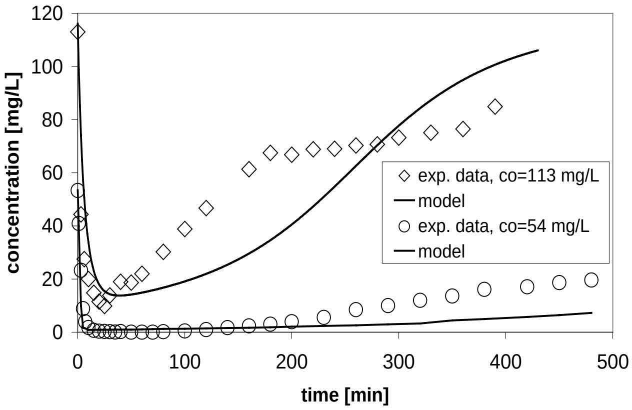

Fig. 6. Dynamic experiments — sorptive ability of PAC for Egacid Red G 200, c_{PAC} = 1 g/L, permeate flux = 5 L.(m^2.h)$^{-1}$.

The comparison of experimental data with numerically integrated values is presented in Fig. 6. In the first stage of the combined process the agreement of experimental and model data is fairly good. After substantial saturation of PAC the dye concentration increases with time. At this stage the PAC concentration has the greatest influence on the model course. It is probable that PAC is not distributed homogeneously throughout the system as the consequence of non-ideal mixing and sedimentation of PAC particles.

4.4. Membrane fouling

A major advantage of hollow fibre membrane modules is the high membrane surface area to volume 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, cake formation) [12].

The effect of filtration flux on membrane fouling was studied by varying the filtration flux in the range from 5 Lm^{-2}h^{-1} to 55 Lm^{-2}h^{-1}. It was found, that PAC tendency for irreversible membrane fouling is extremely low, so that pressure drop values have been practically constant. An example is given in Fig. 7, where the experimental data are depicted for measurements with PAC concentration of 10 g/L. In Fig. 3 the presence of PAC on the membrane surface is demonstrated as a SEM picture.

5. Conclusions

The combined adsorption-membrane process was studied in this work. Kinetic and equilibrium studies were reported for the adsorption of Egacid Red G 200 from aqueous solutions onto PAC. Experimental data indicated that the adsorption capacity was dependent on operat-

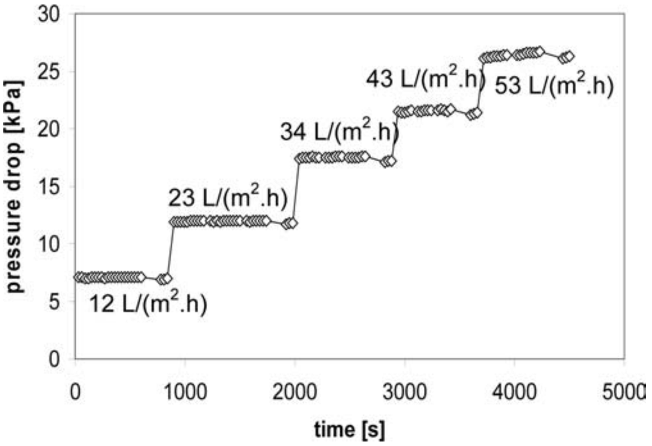

Fig. 7. Pressure drop-time dependency for microfiltration of PAC water suspension, concentration of PAC 10 g L^{-1}.

ing variables such as adsorbent mass, contact time and initial dye concentration. From the kinetic measurements good agreement of experimental data with the Langmuir kinetic model was found. Real adsorption mechanism is expected to be more complicated than simple monolayer homogeneous adsorption with probable contribution of intrapore diffusion. More experiments with organic dye will be carried out to elucidate mechanism of the adsorption.

During the submerged hollow fibre membrane microfiltration operated in dead-end mode it was found that the membrane was effective for removal of PAC particles from water suspensions. Only limited membrane fouling was observed in the range of variables tested so that PAC tendency for irreversible membrane fouling is extremely low. From this study it is evident that the combined membrane process has a potential application for organic dye removal.

Acknowledgements

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Symbols

A — Total surface of PAC, m^2
a — Adsorbed amount per unit weight of sorbent, mg/g
a^* — a in equilibrium, mg/g
a_∞ — Maximum adsorptive capacity, mg/g
$a_{\max}$ — Parameter of the Sips model, mg/g
a_1, a_2 — Parameters in Eqs. (12), (14), mg/g
b — Parameter in Eq. (2), L/g
B — Parameter of Sips model, L/mg
c — Solute concentration, mg/l
c_{eq} — Equilibrium solute concentration, mg/l
c_0 — Initial solute concentration, mg/l
c_{PAC} — Concentration of PAC, g/l
D — Parameter in Eqs. (13)– (15), mg^2/g^2
k'_{A} — Adsorption rate constant, L/(m^2.s)
k'_{D} — Desorption rate constant, mg/(m^2.s)
k_{A} — Modified adsorption rate constant. L/(g.s)
k_{D} — Modified desorption rate constant, mg/(g.s)
k_{L} — Constant of Langmuier isotherm, L/mg
K_{f} — Parameter of Freundlich isotherm, L$^{1/n}$mg$^{(n-1)/n}$/g
m_{PAC} — Mass of PAC, g
n — Parameter of the Freundlich or Sips isotherm
t — Time constant, s
V — Volume, m^3
$\dot{V}$ — Volumetric flow rate, m^3/s

Greek

β — Parameter in Eqs. (14), (15), mg/g
γ — Parameter in Eq. (15), mg^2/g^2
ν_{A}, ν_{D} — Adsorption/desorption rate, mg/s
θ — Coverage fraction
σ — Specific surface of PAC, m^2/g
τ — Time, s

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