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**REMOVAL OF ORGANIC DYES
FROM AQUEOUS SOLUTIONS BY POWDERED
ACTIVATED CARBON ADSORPTION COMBINED
WITH MEMBRANE MICROFILTRATION**

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This contribution deals with study of the combined adsorption–membrane process for organic dye removal. Adsorption equilibrium and kinetics of Egacid Red sorption on powdered activated carbon (PAC) were studied in batch experiments. From the experimental data the parameters of Langmuir adsorption isotherm and rate constants were determined. During the combined hollow fibre membrane microfiltration operated in dead-end mode it was found that membrane was effective for removal of PAC particles from water suspensions, and PAC tendency for irreversible membrane fouling was extremely low. The presented combined adsorption-membrane process has a potential application for organic dye removal.

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Introduction

Wastewater reclamation and reuse is an essential and urgent issue in the world. Textile dye wastewater are usually complex, variable and highly coloured. They are toxic and make a serious health risk to humans.

During the last years, several physical, chemical and biological decolorization methods have been reported [1]. All of them have their advantages and drawbacks. Amongst the numerous techniques of dye removal, adsorption is the procedure of choice and gives the best results as it can be used to remove different types of dyes and organic pollutants [1,2,3].

However, 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 [3].

Recent studies of the activated carbon adsorption process have been focused on combination of powdered activated carbon (PAC) adsorption with low pressure membrane separation process, i.e. microfiltration or ultrafiltration [3,4,6]. 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 dye and soluble organics which are adsorbed on the powdered activated carbon.

This contribution deals with 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.

Theory

Equilibrium Data

Adsorption properties and equilibrium data, commonly known as adsorption isotherms, describe how adsorbed amount of pollutant in equilibrium depends on its concentration in solution. There are several isotherm forms used for analysis of experimental sorption equilibrium data; however, the two most common types are the Langmuir and the Freundlich isotherms.

In the Langmuir isotherm, the relation between adsorbed a_e [mg g^{-1}] and fluid phase c_e [mg l^{-1}] solute concentration in equilibrium is given by

$$a_e = \frac{a_\infty k_L c_e}{1 + k_L c_e} \quad (1)$$

Here a_e is the equilibrium mass of solute adsorbed per unit mass of PAC, a_∞ [mg g⁻¹] and k_L [l mg⁻¹] are model parameters.

Freundlich isotherm

$$a_e = K_f c_e^{1/n} \quad (2)$$

(K_f [l g⁻¹] and n are model parameters) is basically empirical, and it is especially useful for the description of adsorption onto adsorbent surfaces with heterogeneous energy distribution.

Kinetic Data

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 most often [2,5,7].

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 v_a [mg s⁻¹] can be expressed as

$$v_a = k'_A (1 - \theta) A c \quad (3)$$

where θ is the fraction of carbon surface occupied by adsorbed solute, k'_A [L m⁻² s⁻¹] is the adsorption rate constant which depends on adsorbent affinity and temperature, and A [m²] is the total surface of PAC.

For the desorption rate an analogous equation can be written:

$$v_D = k'_D \theta A \quad (4)$$

in which k'_D [mg m⁻² s⁻¹] is the desorption rate constant.

The fraction θ for one-layer adsorption can be expressed using adsorbed amount a [mg g⁻¹]

$$\theta = \frac{a}{a_\infty} \quad (0 \leq \theta \leq 1) \quad (5)$$

$$\frac{da}{d\tau} = \frac{v_A - v_D}{m_{PAC}} = k_A \left(1 - \frac{a}{a_\infty}\right) c - k_D \frac{a}{a_\infty} \quad (6)$$

$$k_A = k'_A \sigma \quad [l \text{ g}^{-1} \text{ s}^{-1}] \quad k_D = k'_D \sigma \quad [\text{mg g}^{-1} \text{ s}^{-1}] \quad (7)$$

where $\sigma = A/m_{PAC}$ [$\text{m}^2 \text{g}^{-1}$] is specific surface of PAC.

At equilibrium state, $da/d\tau = 0$ and Eq. (1) can be rearranged to obtain Langmuir isotherm

$$a = \frac{a_\infty k_A c}{k_D + k_A c} = \frac{a_\infty k_L c}{1 + k_L c} \quad (8)$$

where $k_L = k_A/k_D$.

For the batch experiment ($V [l] = \text{const.}$, $c_{PAC} [\text{g l}^{-1}] = \text{const.}$) mass balance gives

$$c = c_0 - c_{PAC} a \quad (9)$$

Equation (6) together with Eq. (9) and initial conditions $c(\tau = 0) = c_0$, $a(\tau = 0) = 0$ can be integrated which leads to

$$a = a_1 a_2 \frac{\exp\left(\frac{\tau}{t}\right) - 1}{a_1 \exp\left(\frac{\tau}{t}\right) - a_2} \quad (10)$$

$$\text{where } t = \frac{a_\infty}{k_A c_{PAC} \sqrt{D}} \quad (11)$$

$$a_1 = \frac{\beta + \sqrt{\beta^2 - 4\gamma}}{2}, \quad a_2 = \frac{\beta - \sqrt{\beta^2 - 4\gamma}}{2} \quad (12)$$

$$D = \beta^2 - 4\gamma, \quad \beta = \frac{c_0}{c_{PAC}} + a_\infty + \frac{1}{k_L c_{PAC}}, \quad \gamma = \frac{a_\infty c_0}{c_{PAC}} \quad (13)$$

Mathematical Model of Combined Separation Process

In the combined process a tank of volume V was filled with wastewater containing dyestuff (with initial concentration of dye c_0). The tank was equipped with

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

$$\frac{dV}{d\tau} = 0 \quad (14)$$

$$\frac{dm_{PAC}}{d\tau} = 0 \quad (15)$$

and dye mass balance is

$$\dot{V}c_0 - \dot{V}c = \frac{d(Vc)}{d\tau} + \frac{d(am_{PAC})}{d\tau} \quad (16)$$

Here m_{PAC} is total mass of PAC in tank, \dot{V} is a volumetric permeate flow, V is tank volume, c is dye concentration and τ is time. After differentiation Eq. (16) takes the form

$$\dot{V}c_0 - \dot{V}c = c \frac{dV}{d\tau} + V \frac{dc}{d\tau} + a \frac{dm_{PAC}}{d\tau} + m_{PAC} \frac{da}{d\tau} \quad (17)$$

It can be simplified using Eq. (14) and (15) to

$$\frac{dc}{d\tau} = \frac{1}{t}(c_0 - c) - c_{PAC} \frac{da}{d\tau} \quad (18)$$

where $t = V/\dot{V}$. Differential equations (6) and (18) can be solved with the initial conditions $\tau = 0$: $c = c_0$, $a = 0$.

Here, the Runge–Kutta method of the 4th order was used for numerical integration of the system.

Materials and Methods

The experiments were carried out using aqueous solutions of Egacid Red (Ostacolor, the Czech Republic), C.I. Acid Violet 7,18055. The dye concentration in solutions was determined spectrophotometrically at a wavelength of 544 nm. In

most cases, a proper dilution was necessary to obtain a well measurable absorption. Powdered activated carbon CW20 was obtained from Silcarbon, its specific surface area was $1300 \text{ m}^2 \text{ g}^{-1}$. The particle size fulfilled DIN 19 603 (i.e. 85 % particles were $< 40 \text{ }\mu\text{m}$, and 5 % $> 80 \text{ }\mu\text{m}$).

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

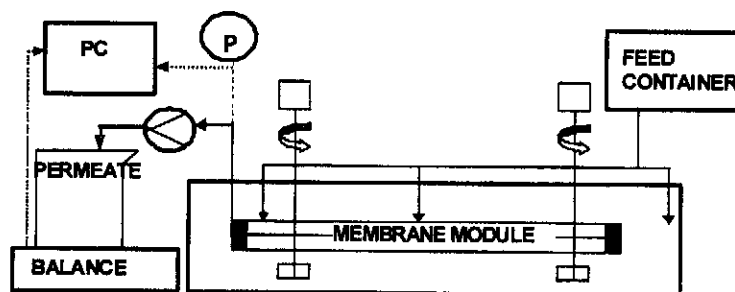


Fig. 1 Experimental set-up of dead-end microfiltration unit

The apparatus consisted of a 15-litre feed container, a gear pump, membrane module, valves at the module outlet and prefilter ($5 \text{ }\mu\text{m}$). 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) provides constant output flowrate regardless of changes in pressure and can easily be used for membrane backflushing (reversing flow direction).

The membrane unit operated in outside-in dead-end filtration configuration. In order to prevent the continuous accumulation of solids on the membrane surface the membrane was occasionally backflushed by permeate, when concentration of PAC was higher than 5 g l^{-1} . 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.

For determination of equilibrium and kinetic data, the batch adsorption experiments were conducted by adding different amounts of PAC (0.5 g l^{-1} or 1 g l^{-1}) into the Erlenmeyer flask containing model wastewater. After mixing at constant temperature ($25 \text{ }^\circ\text{C}$) for 4 hours samples were taken from the flask and filtered through $0.8 \text{ }\mu\text{m}$ membrane filter. Then the filtrate was measured for the dye concentration. Kinetic experiments were conducted at constant temperature of $25 \text{ }^\circ\text{C}$ and at good mixing conditions (magnetic stirrer). To obtain concentration

decay curves as a function of time, samples were withdrawn at definite intervals, filtered, and the dye concentration in the filtrate was determined.

Results and Discussion

Sorptive Ability of PAC

From the adsorption capacity measurements the parameters of Langmuir isotherm were determined according to Eq. (1) – see Fig. 2. The fact that Langmuir isotherm fits the experimental data very well confirms the monolayer coverage of dye onto particles and also the homogenous distribution of active sites on the PAC material. The maximum sorptive capacity of PAC achieved for *Egacid Red* was 392 mg g^{-1} .

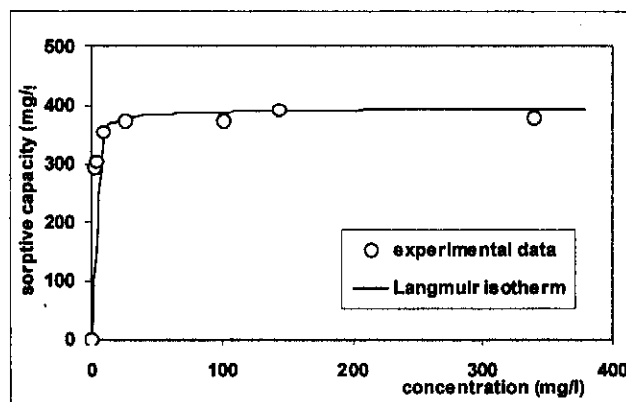


Fig. 2 Adsorption isotherm of *Egacid Red* on PAC at $25 \text{ }^\circ\text{C}$, $c_{\text{PAC}} = 0.5 \text{ g l}^{-1}$, parameters of Langmuir isotherm: $a_{\infty} = 392 \text{ mg g}^{-1}$, $k_L = 0.97705 \text{ l mg}^{-1}$

Adsorption Kinetics

Effect of contact time on removal of reactive dye from solutions for different initial concentrations was also studied. The equilibrium period required for the maximum removal was around 4 hours.

The example of results of kinetic measurements is shown in Fig. 3, where the experimental data are compared with the theoretical plot calculated according to Eq. (10).

The kinetic parameters of the model evaluated by non-linear regression of experimental data were $k_A = 0.2488 \text{ l g}^{-1} \text{ min}^{-1}$, and $k_D = 0.2546 \text{ mg g}^{-1} \text{ min}^{-1}$.

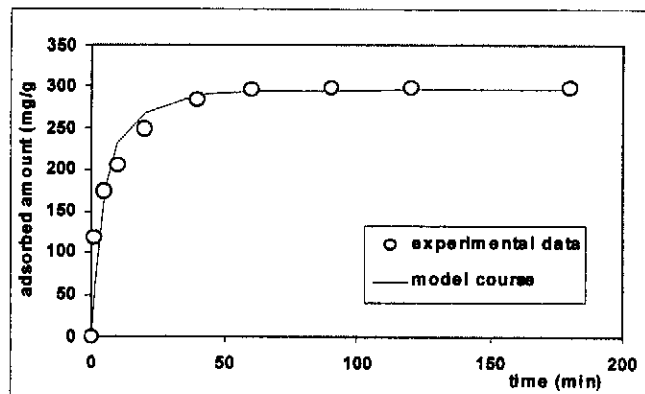


Fig. 3 Adsorption kinetics of *Egacid Red*, $c_0 = 300 \text{ mg l}^{-1}$, $c_{PAC} = 1 \text{ g l}^{-1}$, $k_A = 0.2488 \text{ l g}^{-1} \text{ min}^{-1}$, $k_D = 0.2546 \text{ mg g}^{-1} \text{ min}^{-1}$

The sorption data are well represented in the whole region studied, and this confirmed that it is appropriate to use the Langmuir kinetic model to predict the sorption kinetics of *Egacid Red*.

Combined Separation Process

Figure 4 shows typical permeate dye concentration decay curve at PAC dose of 1 g l^{-1} 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 flows to and from the tank were maintained using pumps. The wastewater in the tank was kept at the constant level. The addition of the PAC resulted in an immediate decrease in effluent concentration. The 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 was found to be a function of the ratio of the total mass of PAC in the tank to the influent flow rate. During the combined separation process membrane fouling was not observed, because only low concentration of PAC was used, so membrane backflushing was not necessary.

The comparison of experimental data and theoretical plot is made in Fig.4. It can be seen that the kinetic model used (6) is quite suitable for the description of the process kinetics and predicts dynamic behaviour of the experiment well. There are, however, some discrepancies between measured data and model course, especially in the second stage of experiment which could be explained by non-ideal mixing conditions.

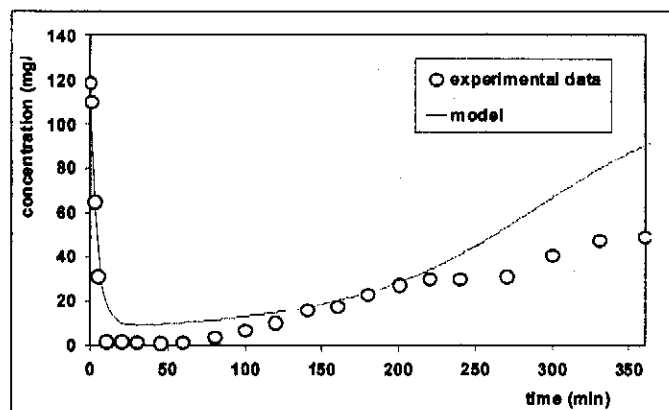


Fig.4 Sorptive ability of PAC for *Egacid Red* in combined process, $c_0 = 119 \text{ mg l}^{-1}$, $c_{PAC} = 1 \text{ g l}^{-1}$, permeate flux = $10 \text{ l m}^{-2} \text{ h}^{-1}$

Conclusion

Parameters of Langmuir adsorption isotherm and rate constant were determined for *Egacid Red* sorption proces on PAC. During the submerged hollow fibre membrane microfiltration operated in dead-end mode it was found out, that membrane was effective for removal of PAC particles from water suspensions. Only limited membrane fouling was observed in the range of variables tested, so 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. The experimental results indicate that complete removal of dye was achieved even in the case of very low PAC dose. Also, the treated water may be reused because of high water quality. There are, however, some problems which should be solved including PAC dose and regeneration.

A simple mathematical model describing dynamic sorptive process in microfiltration system is presented and discussed.

Acknowledgements

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References

- [1] Crini G.: *Bioresour. Technol.* **97**, 1061 (2006).
- [2] Bhatnagar A., Jain A.K.: *J. Colloid Interf. Sci.* **281**, 49 (2005).
- [3] Mallevialle J., Odendaal P. E., Wiesner M. R.: *Water Treatment Membrane Processes; McGraw-Hill*, 1996.
- [4] Zhang J., Giorno L., Drioli E.: *Desalination* **194**,101 (2006).
- [5] Crini G., Peindy H.N., Gimbert F. and Capucine R.: *Sep. Purif. Technol.* **53**, 97 (2007).
- [6] Jirankova H., Cakl J., Markvartova O., Dolecek P.: *2nd European Conference on Filtration and Separation, France*, 2006.
- [7] Inbaraj S., Chien J.T., Ho G.B., Yang J., Chen B.H.: *Biochem. Eng. J.* **31**, 204 (2006).