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ADSORPTION KINETICS STUDY OF PAC-ORGANIC DYE SYSTEM

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This paper deals with the study of organic dye adsorption from aqueous phase on powdered activated carbon. Theoretical part summarises the kinetic models mostly used for description of adsorption on powdered activated carbon. Sorptive capacity and adsorption kinetics were studied in experimental part.The rate constants of studied system Ostazine orange on PAC were estimated.

Introduction

Industrial wastewaters from dyestuffs production and utilization belong to one of possible sources of environmental pollution. Large amounts of dyes are annually produced and applied in many different industries, including the textile, cosmetic, paper, leather, pharmaceutical, and food industries. The presence of even trace concentrations of dyes in effluent is highly visible and undesirable, the typical

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wastewaters contain several miligrams of dye per litre.

Dyes in wastewater undergo chemical as well as biological changes, consume dissolved oxygen, and destroy aquatic life. The dyestuffs are classified according to their solubility, colouring properties, and chemical structure. After colouring is completed, the waste ought not to be discharged into the environment without purification. Among several chemical and physical methods, the adsorption has often been found to be superior compared to other techniques for wastewater treatment.

Adsorption is a relatively cheap and well established process which can be combined with other separation techniques. Dissolved dye is separated from the liquid with the use of a solid adsorbent which can consequently be separated by microfiltration from the liquid phase. The design of an adsorption-microfiltration unit depends on thorough understanding of solid-liquid phase equlibria as well as kinetics behaviour of the system.

Theoretical

The equilibrium isotherm is fundamental in describing the interactive behaviour between the solutes and adsorbent. Two of the most commonly used isotherms are the Langmuir and Freundlich models [1-3]. The Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface and the energy of adsorption is constant. The relation between adsorbed amount, q_e, and fluid phase solute concentration, c_e, at equilibrium is given by

$$q_e = \frac{q_\infty k_L c_e}{1 + k_L c_e} \tag{1}$$

Here q_e is the equilibrium mass of solute adsorbed per unit mass of PAC, q_∞ and k_L are model parameters.
The Freundlich isotherm

$$q_e = K_f c_e^{1/n} \tag{2}$$

(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.

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 [3-6]. 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 pseudo first-order kinetic model is the simplest relation describing sorptive kinetics

$$\frac{dq_t}{dt} = k_f\left(\hat{q}_e - q_t\right) \tag{3}$$

Integration of equation (3) for initial condition ($t = 0$, $q_t = 0$) gives

$$\ln\left(\hat{q}_e - q_t\right) = \ln\hat{q}_e - k_f t \tag{4}$$

or

$$q_t = \hat{q}_e\left(1 - e^{-k_f t}\right) \tag{5}$$

where q_t is an adsorbed amount at time t, $\hat{q}_e$ is the sorptive capacity at equilibrium state, and k_f is the kinetic constant of pseudo first-order model. $\hat{q}_e$ is an independent parameter which is not calculated from adsorption isotherm but is determined from kinetics only.

For sorptive kinetics evaluation many authors used the pseudo second-order model based on equation

$$\frac{dq_t}{dt} = k_s\left(\bar{q}_e - q_t\right)^2 \tag{6}$$

and its integrated form

$$q_t = \frac{\bar{q}_e^2 k_s t}{1 + \bar{q}_e k_s t} \tag{7}$$

where k_s is kinetic constant of pseudo second-order model. The parameters k_s and $\bar{q}_e$ can be obtained from the plot of t/q_t vs. t which is a straight line

$$\frac{t}{q_t} = \frac{t}{\bar{q}_e} + \frac{1}{k_s \bar{q}_e^2} \tag{8}$$

$\bar{q}_e$ is an independent parameter which is not calculated from adsorption isotherm but is determined from kinetics only.

The pseudo second-order model was successfully used by many authors [4-8] to describe adsorption on PAC.

The adsorption mechanism of adsorbate onto adsorbent follows three steps: film diffusion, pore diffusion and intra-particle transport. The slowest of these three steps controls the overall rate of the process. Intraparticle diffusion model is based on assumption that the rate determining step of adsorption is diffusion in adsorbent pores. The relation between adsorbed amount, q_t, and time, t, is given by

$$q_t = k_d t^{0.5} \tag{9}$$

where k_d is kinetic constant of the model. The slope of the linear part of the curve (q_t vs. $t^{0.5}$), gives the rate of the adsorption controlled by intraparticle diffusion.

Materials and Methods

The experiments were carried out using aqueous solutions of Egacid Orange H-R (Synthesia, the Czech Republic), C.I. Reactive orange 12, A4339. The dye concentration in solutions was determined spectrophotometrically at a wavelength of 415 nm. In most cases, a proper dilution was necessary to obtain a well measurable absorption. Specific surface area of powdered activated carbon CW20 (Silcarbon) was 1300 $m^2 g^{-1}$. The 85 % portion of particles were < 40 μm, and 5 % > 80 μm. The initial dye concentration varied from 280 mg l^{-1} to 1300 mg l^{-1}.

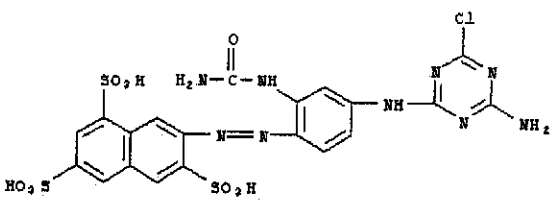

Fig. 1 Chemical structure of Egacid Orange H-R

For determination of equilibrium and kinetic data, batch adsorption experiments were conducted by adding various amounts of PAC (1 g l^{-1} or 2 g l^{-1}) into the Erlenmeyer flask containing model wastewater. After mixing at constant temperature (22 °C), samples were taken at definite time intervals and filtered through 0.8 μm membrane filter. The dye concentrations were determined by means of aVIS spectrophotometer.

The kinetic experiments were conducted at constant temperature of 22 °C, the pH of 6.5 and at good mixing conditions (magnetic stirrer). To obtain concentration decay curves as a function of time, the samples were withdrawn at definite time intervals, filtered, and the dye concentration in filtrate was determined. The overall time of the experiments was about 7 days.

Results and Discussion

Adsorption Isotherms

The sorptive capacity of PAC for Egacid Orange has been calculated using mass balance equation

$$q_e = \frac{V(c_0 - c_e)}{m_{PAC}} \tag{10}$$

where c_0 and c_e are initial and equilibrium dye concentrations. From the adsorption capacity measurements the parameters of the Langmuir and Freundlich isotherms were determined according to equations (1) and (2), respectively — see Table I and Fig. 2.

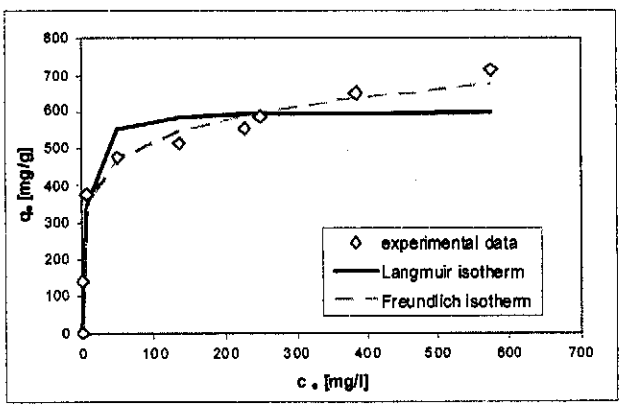

Fig. 2 Adsorption isotherms of Egacid Orange on PAC at 22 °C, $c_{PAC} = 1$ g l^{-1}

For lower dye concentrations the Langmuir isotherm fits the experimental data well, however, for higher concentrations the Freundlich isotherm yielded a much better fit than the Langmuir model. Table I shows the constants of the models mentioned. Parameter a_∞ of Langmuir isotherm suggests the maximum sorptive capacity of 605 mg g^{-1}, while the Freundlich model indicates a higher value.

Table I Parameters of Langmuir and Freundlich isotherms

Model	Langmuir		Freundlich	
	q_∞, mg g^{-1}	k_L, l mg^{-1}	K_F, mg g^{-1} (l mg^{-1})$^{1/n}$	$1/n$
Parameters	604.7	0.2202	39942	0.147

The effect of contact time on removal of reactive dye from solutions with various initial concentrations was evaluated using both pseudo first-order and pseudo second-order models. Integrated forms, Eqs. (5) and (7), were used.

The mass balance equation for batch experiments can be written as

$$\frac{\mathrm{d}(Vc)}{\mathrm{d}t} = -m_{PAC}\frac{\mathrm{d}q_t}{\mathrm{d}t} \tag{11}$$

and its integration for initial conditions $c(0) = c_0$, $q_t(0) = 0$ at V = const. gives

$$c = c_0 - c_{PAC}q_t \tag{12}$$

where

$$c_{PAC} = \frac{m_{PAC}}{V} \tag{13}$$

Then, the concentration-time dependence can be obtained by combination of equations (12) and (5) or (7).

Table II The parameters of kinetic model studied

Experiment	Initial dye conc. mg l^{-1}	Pseudo first-order		Pseudo second-order	
		k_f, min^{-1}	$\hat{q}_e$, mg g^{-1}	k_s, g mg^{-1} min^{-1}	$\bar{q}_e$, mg g^{-1}
1	280	7.04×10^{-2}	128.8	6.85×10^{-4}	141.0
2	380	6.07×10^{-3}	358.2	2.67×10^{-5}	372.9
3	650	5.00×10^{-3}	444.2	1.65×10^{-5}	467.6
4	837	5.44×10^{-3}	492.6	1.66×10^{-5}	517.5

The curves of the adsorbed amount of dye versus contact time are shown in Figs 3-5. The initial dye concentration decreased rapidly during initial period and this confirmed strong interactions between the dye and the adsorbent. After that, the concentration of dye in the liquid phase remained almost constant. In Figs 3-5 the experimental data are compared with theoretical values calculated according to Eqs (10) and (11).

The kinetic parameters of the model evaluated by non-linear regression of experimental data are listed in Table II.

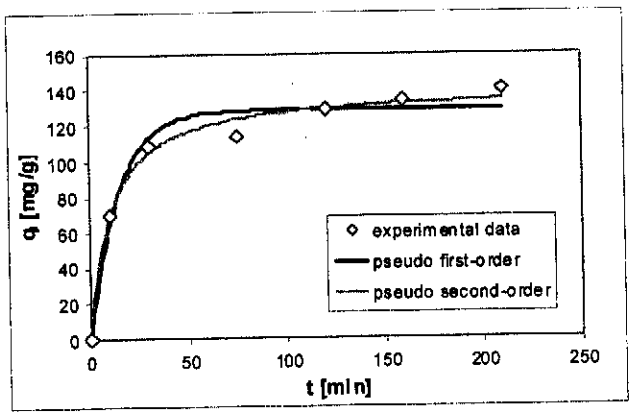

Fig. 3 Kinetic experiment 1, comparison of experimental and theoretical plots, $c_0 = 280$ mg l^{-1}, $c_{PAC} = 1$g l^{-1}

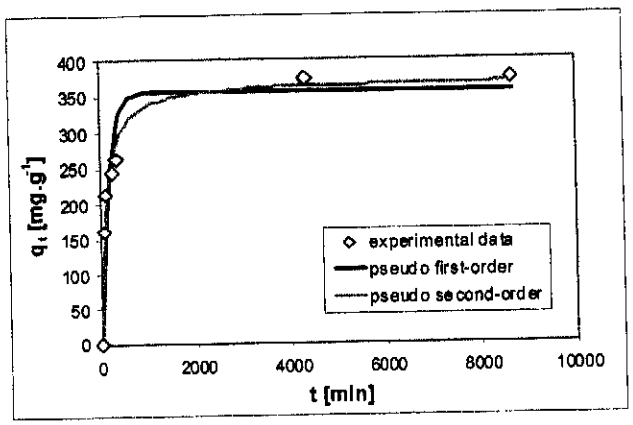

Fig. 4 Kinetic experiment 2, comparison of experimental and theoretical plots, $c_0 = 380$ mg l^{-1}, $c_{PAC} = 1$g l^{-1}

In many cases, the first-order equation does not fit well to the whole range of contact time [2,5,8]. It would only be applicable over the initial stage of the adsorption process.

From the figures it can be seen, that pseudo second-order model is more likely to predict the behaviour of the kinetic experiments of adsorption than pseudo first-order model, in which chemisorption is the rate controlling mechanism. Both the pseudo-first and pseudo-second order kinetics models could not identify the diffusion mechanism and so further experiments are necessary to study the effects of external and intraparticle diffusion.

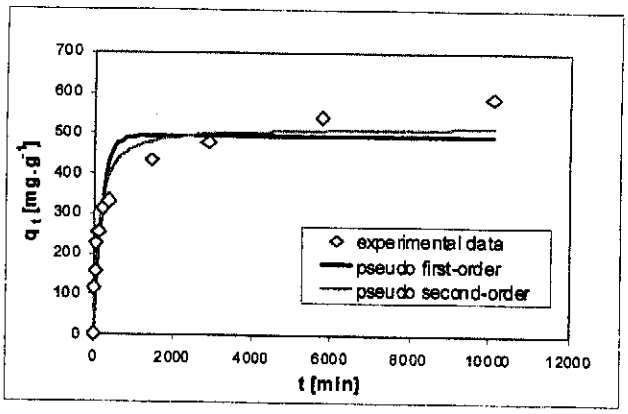

Fig. 5 Kinetic experiment 4, comparison of experimental and theoretical plots, c_0 = 837 mg l^{-1}, c_{PAC} = 1g l^{-1}

Conclusion

The present study shows that the PAC can be used as a potential adsorbent for the removal of organic dyes from their aqueous solutions. The amount of dye sorbed was found to vary with increasing initial dye concentration and PAC dosage. Equilibrium data of Egacid Orange adsorption on PAC was found to follow the Freundlich isotherm. The Freundlich isotherm indicates a higher value of the maximum sorptive capacity than the Langmuir model.

From the experimental data it can be seen that the pseudo second-order model is more likely to predict the behaviour of the kinetic experiments of adsorption than the pseudo first-order model.

Acknowledgements

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