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КИНЕТИКА АДСОРБЦИИ ФОРМАЛЬДЕГИДА ИЗ ВОДНЫХ РАСТВОРОВ УГЛЕРОДНЫМИ ПОРИСТЫМИ МАТЕРИАЛАМИ В ПРИСУТСТВИИ ФОСФОРНОЙ КИСЛОТЫ

Рассмотрена кинетика адсорбции углеродными пористыми материалами формальдегида из водных растворов в присутствии фосфорной кислоты. Рассчитаны значения коэффициентов внешнего массопереноса и внутренней диффузии. Выявлено влияние вклада внешнего массопереноса и внутренней диффузии в процессе адсорбции формальдегида. Определено время установления сорбционного равновесия.

Ключевые слова: формальдегид, углеродные нанотрубки, стеклоуглерод, кинетика адсорбции

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ADSORPTION KINETICS OF FORMALDEHYDE FROM AQUEOUS SOLUTIONS BY CARBON POROUS MATERIALS IN PRESENCE OF PHOSPHORIC ACID

In this paper we studied the adsorption kinetics of formaldehyde on porous carbon nanotubes and glassy carbon from aqueous solutions in the presence of phosphoric acid. The values of the external and internal mass transfer diffusion coefficients were obtained. We found the influence of the contribution of external mass transfer and internal diffusion on the process of formaldehyde adsorption. The time of establishment of sorption equilibrium was determined.

Key words: formaldehyde, carbon nanotubes, glass carbon, adsorption kinetics

INTRODUCTION

It is known that 4,4-dimethyl-1,3-dioxane is a key intermediate for the industrial synthesis of isoprene [1]. It is obtained by condensation of the aqueous solution of formaldehyde with 2-methylpropene in the presence of phosphoric acid. In the last decade, a porous materials has been used for the above process [2].

However, in this work were not considered features of interaction of reagents and products of Prins reaction with porous materials. Therefore, the aim of this work was to study the adsorption of formaldehyde from aqueous solutions by carbon nanotubes and glassy carbon in the presence of phosphoric acid.

EXPERIMENTAL

We have used carbon nanotubes with a diameter 7-11Å ("Tomsk Catalyst Plant", Tomsk) and glassy carbon as sorbents [3, 4].

Adsorption of formaldehyde from aqueous solutions was investigated at (75±1) °C from a limited volume under constant agitation (laboratory mechanical stirrer, 17 rps).

Samples of a porous carbon sorbent [in the case used of nanotubes their weight was (0.10±0.01) g, and in the case of glassy – (0.84±0.01) g] were introduced into the solutions containing 50 mL of aqueous formaldehyde with the initial concentrations of 5.85-7.07 mol/l and 2.5 ml of 81% phosphoric acid. The contact time of the solution with samples of sorbents ranged from 120 to 3600 s. The formaldehyde contentration in solution was determined by the sulfite method [5].

RESULTS AND DISCUSSION

Adsorption of formaldehyde (a) from aqueous solutions by porous carbon material was evaluated according to the equation (1) [6]:

$$a = [(c_0–c_t)\cdot V]/m, \quad (1)$$

V – volume of solution, l; m – sorbent mass, mg; c_t – adsorbate concentration at various time points, mol/l; c_0 – adsorbate concentration at the initial time, mol/l.

Relative approach of the adsorption to equilibrium (γ) was calculated according to the equation (2) [6]:

$$\gamma = a / a_{max}, \quad (2)$$

a_{max} – adsorption at equilibrium, mg/g.

Changing adsorbed formaldehyde (T) at different times was calculated according to the equation (3) [6]:

$$T = - \ln(1-\gamma) \quad (3)$$

External diffusion mass transfer coefficients (βn) and internal diffusion from an aqueous formaldehyde solution were calculated using the equation (4) [4]:

$$\beta_n = tg\alpha / T, \quad (4)$$

tgα – the tangent linear portion of the graph according to the inclination angle T = *f*(t).

For the considered porous material there is a high rate of adsorption of formaldehyde in the initial period: for carbon nanotubes up to 120, and glassy – 600 s. Adsorption rate decreases significantly with the increase of contact time. Time adsorption equilibrium for the carbon nanotubes is 120, and glassy – up to 600 s.

Experimental formaldehyde adsorption kinetic curves from aqueous solutions by carbon nanotube are shown in Fig. 1.

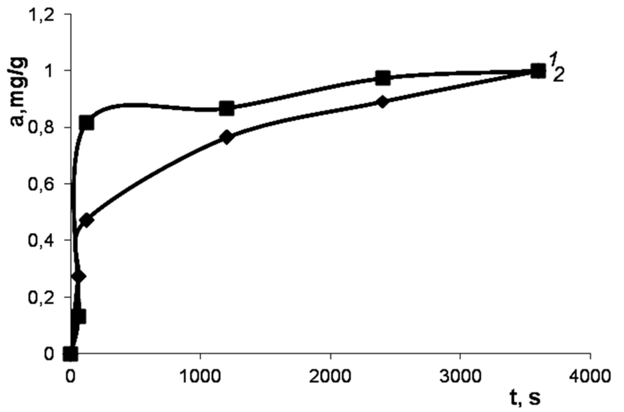

Fig. 1. Kinetic curves of formaldehyde adsorption from aqueous solutions with the concentration of 5.85-7.07 mol/l in the presence of phosphoric acid by carbon porous materials at 75 °C. (1 - carbon nanotubes, 2 – glassy carbon)

Рис. 1. Кинетические кривые адсорбции формальдегида из водных растворов в диапазоне концентраций 5,85-7,07 моль/л в присутствии фосфорной кислоты углеродными пористыми материалами при температуре 75 °С. 1 – Углеродные нанотрубки, 2 – стеклообразный углерод

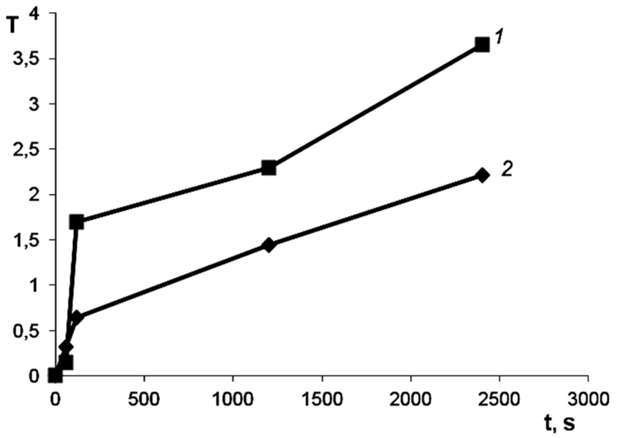

Fig. 2. Change in a quantity the adsorbed substance during adsorption from aqueous formaldehyde solution with concentration of 5.85-7.07 mol/l in the presence of phosphoric acid by carbone porous materials at 75 °C. 1 - Carbon nanotubes, 2 – glassy

Рис. 2. Изменение количества адсорбированного вещества при адсорбции формальдегида из водного раствора с концентрацией 5,85-7,07 моль/л в присутствии фосфорной кислоты углеродными пористыми материалами при температуре 75 °С. 1 – Углеродные нанотрубки, 2 – стеклообразный углерод

In the initial period (in seconds to 120 for a carbon nanotubes and to 600 s for a glassy) for these porous carbon materials kinetic data (R = 0.991-0.998) are described by first-order kinetics (Fig. 2) i.e. adsorption rate depends only on the concentration of formaldehyde in the solution (Fig. 2). A further deviation from a straight line shows an increase in internal diffusion effect on the formaldehyde adsorption rate. Mass transfer coefficient of external and internal diffusion were calculated by equations (3) and (4) (Table).

Table

Kinetic parameters of formaldehyde adsorption from aqueous solutions in the concentration range of 5.85-7.07 mol/l by carbone porous materials in the presence of phosphoric acid at 75 °C

***Таблица*. Кинетические параметры адсорбции формальдегида из водных растворов в диапазоне концентраций 5,85-7,07 моль/л углеродными пористыми материалами в присутствии фосфорной кислоты при температуре 75 °С**

Sorbent	Equilibrium time, s	External mass transfer coefficient (β_n), s^{-1}	Coefficient of internal diffusion, s^{-1}
Carbon nanotubes	120	$8.3\cdot10^{-3}$	$7.1\cdot10^{-4}$
Glassy carbon	600	$1.4\cdot10^{-3}$	$1.1\cdot10^{-4}$

CONCLUSIONS

We have found that formaldehyde adsorption process both for a carbon nanotube, and for a glassy carbon from the aqueous solution in the presence of phosphoric acid has been determined by influence of the external mass transfer and internal diffusion. It is shown that time of achievement equilibrium sorption in the system formaldehyde – water – phosphoric acid in the case of carbon nanotubes 120 s, and glassy carbon – 600 s.

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