

Dynamic adsorption of trinitrotoluene on granular activated carbon

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Abstract

The effects of trinitrotoluene (TNT) dynamic adsorption on granular activated carbon produced by 'Miloje Zakic', Serbia, are presented. The main task was to determine the conditions for TNT dynamic adsorption in order to remove the dissolved TNT from wastewater. The effects of temperature, concentration and flow rate in the chromatographic system were examined. Flow rates between 1 and 4 dm³/h were used. The heights of activated carbon in the columns were 70 and 135 mm while the diameter was 12 mm. The experiments were conducted at different temperatures (10–60 °C) and TNT influent concentrations ranging from 32.76 to 171 mg/dm³ were used. The adsorption capacity of the activated carbon increased with increasing temperature, but it decreased with increasing input concentration and flow rate. The results obtained indicate that the influence of temperature is greater than was expected and the bed height and the amount of GAC used could be significantly lowered by increasing the temperature. The possibility of desorbing TNT from saturated activated carbon was also investigated. The amount of TNT adsorbed per mass unit of adsorbent was calculated using a model that optimally agreed with the experimental data.

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1. Introduction

There has been increasing concern in recent years regarding the removal of trinitrotoluene (TNT) from wastewater as environmental regulations have steadily become more stringent. Special treatment is required for wastewater streams, which contain not only suspended, but also dissolved TNT. These procedures should be safe and efficient and should yield non-toxic effluents.

There are various methods for the separation of dissolved TNT from wastewater. They can be divided into concentration and destruction methods. Concentration methods mainly include procedures such as carbon adsorption [1–3] and solvent extraction [4]. Destruction methods comprise procedures for destroying TNT by catalytic and advanced oxidation employing UV and hydrogen peroxide [5,6], biodegradation [7] and incineration [8].

Wastewater and groundwater containing TNT are very difficult to treat and with the more rigorous restrictions being planned, new processes will be necessary. Currently TNT contaminated water is treated by granular activated carbon (GAC) adsorption and pilot scale plants based on this technique are operational in some of US military establishments [9–12]. However, GAC is a transfer technology and the regeneration of GAC may be an issue depending on the amount of TNT adsorbed. Researchers are exploring numerous chemical and biochemical treatments, or their combination, to fully regenerate and reuse the activated carbon [13–16].

A GAC system can be operated in a variety of ways and the choice of operating modes can have a significant impact on service life, chemical loading on the GAC at exhaustion and GAC utilization rates [11]. Hinshaw et al. [12] investigated competitive adsorption of HMX, RDX, TNT and 2,4-DNT on different GACs. Other effects from temperature, actual versus synthetic pink water, and acetone stripping were also evaluated in this study and are also presented and explained in some references [13].

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Dynamic studies on the adsorption of TNT from aqueous solutions on GAC (producer Miloje Zakic, Serbia) in columns were carried out to generate data for the design of pilot plants and possible application for the continuous treatment of explosives from explosive manufacturing plants. The influence of parameters such as feed concentration, flow rate and temperature was investigated. The possibility of stripping TNT from activated carbon by acetone was also examined.

2. Experimental

2.1. Materials

In all the experiments, coconut granular activated carbon type K-81/B was used as supplied by 'Miloje Zakic', Krusevac, Serbia. The characteristics and properties of the carbon are listed in Table 1. All the investigations were carried out with solutions of TNT (from industrial production) in distilled water.

2.2. Analysis

The analytical technique usually used to determine the concentration of TNT is reversed phase high performance liquid chromatography (RPHPLC) [17,18]. This method was chosen because of a sufficiently low detection limit, satisfying accuracy and reproducibility, simplicity, as well as the possibility of analyzing samples of small volumes up to about 400 μ l. The HPLC measurements were carried out with a Hewlett Packard 1081 series HPLC system with UV detection at 254 nm. The stationary phase was an Eurospher RP-18, 250 mm \times 4.6 mm i.d. cartridge packed with 5 μ m particles (Fa. Knauer, Berlin, Germany). The column was kept at 30 °C. A mobile phase consisting of 50% water, 38% methanol and 12% acetonitrile (vol.%) was used at a flow rate of 1.5 ml/min. For the external calibration, at least three replications were performed for each standard concentration. The mean was then used for calibration curve.

2.3. Column operation

A scheme of the column system used for TNT dynamic adsorption is given in Fig. 1.

Table 1

Activated carbon properties

Ash (%)	5.5
Apparent density (kg/m ³)	440
Iodine number (mg/g)	1200
Pore volume (cm ³ /g)	0.9
Surface area BET-N ₂ (m ² /g)	1200
Particle size, mean diameter (mm)	0.9
Sieve analysis (DIN 4188) (mm) (%)	>1.6 mm; 2.8 0.426–1.6 mm; 96.5 <0.425 mm; 0.5 <0.355 mm; 0.2

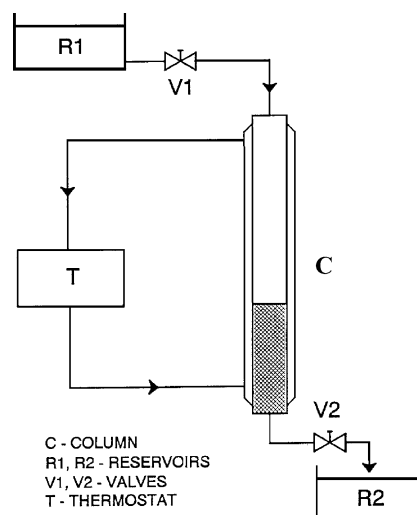


Fig. 1. Experimental set-up for column studies.

The experimental apparatus constructed at the Faculty of Technology and Metallurgy (Belgrade, Serbia and Montenegro) consisted of a Pyrex glass jacketed column (C), which had been partially filled with granular activated carbon. The length of the column was 0.5 m and the internal diameter was 12 mm. Gravity flow was obtained through the column from the top of the reservoir (R1) to the bottom of the reservoir (R2). The flow-rate was manually maintained at a constant value, by means of valves V1 and V2. Isothermal conditions in the column were obtained by passing hot or cold water through the column jacket. The same column was used to examine the possibility of activated carbon desorption.

2.4. Procedure

Experimental examinations of TNT dynamic adsorption were carried out under isothermal conditions at various temperatures, flow rates, influent concentrations and adsorbent bed heights. Fifteen experiments were carried out in order to study the effect of each of the four operating variables.

In the dynamic experiments, the responses of the column (TNT effluent concentrations as a function of time) on step changes of the input concentration were obtained. Column effluent samples were collected from the effluent line discharging from the bottom of the GAC column. Samples for TNT analysis were collected in 5 ml vials. The effluent concentrations were measured by the RPHPLC technique. The pH of the solutions was about 6.4 and did not significantly change before and after adsorption. Table 2 lists all the adsorption experiments and gives an overview of the experimental conditions. The heights of activated carbon in the columns were 70 and 135 mm while the diameter was 12 mm. The experiments were conducted at different temperatures (10–60 °C) and TNT influent concentrations ranging from 32.76 to 171 mg/dm³ were used. Preliminary experiments were conducted at flow rates between 1 and 4 dm³/h. Based on these experiments flow rates of 1, 2 and 4 dm³/h were used

Table 2
Experimental conditions in dynamic adsorption experiments

Experiment	θ ($^{\circ}\text{C}$)	m (g)	L (mm)	F (dm^3/h)	C_0 (mg/dm^3)
E-1	20	3.0	70	2	64.00
E-2	30	3.0	70	2	64.00
E-3	60	6.0	135	2	42.50
E-4	20	6.0	13.5	2	42.50
E-5	15	6.0	135	2	52.00
E-6	2	6.0	135	2	32.76
E-7	60	3.0	70	1	39.00
E-8	60	3.0	70	2	36.00
E-9	60	3.0	70	4	45.00
E-10	60	3.0	70	2	48.00
E-11	60	3.0	70	2	59.00
E-12	60	3.0	70	2	54.40
E-13	60	3.0	70	2	165.00
E-14	60	3.0	70	4	167.50
E-15	60	3.0	70	4	171.00

θ : temperature; m : activated carbon mass; L : adsorbent bed height; F : flow rate; C_0 : TNT input concentration.

for further studies at 60°C while all experiments at lower temperatures were performed at flow rate of $2\text{ dm}^3/\text{h}$.

2.4.1. Examination of the possibility of activated carbon desorption

The possibility of saturated activated carbon desorption with acetone was investigated. The adsorbent was previously saturated with TNT at 60°C in a dynamic system (Fig. 1) by passing the solution of a given concentration of TNT through the activated carbon bed. Acetone was chosen because some authors [12,13] have used it for spiking TNT from GAC, and also the solubility of TNT in acetone is high.

Saturated activated carbon was washed with distilled water, valve V2 was then closed and 10 ml of acetone was poured into the column. The temperature was maintained at 20°C . Sixty minutes later valve V2 was opened and the acetone collected in the bottom reservoir R2. Afterwards, the adsorbent bed was rinsed twice with 5 ml of acetone (10 ml altogether) and this amount was also collected in the bottom reservoir R2.

All waste materials including acetone were placed in appropriate containers and stored short-term until they were properly disposed of or recycled at a licensed hazardous waste facility or recycling center.

3. Results and discussion

Although a large volume of data has been collected on the dynamic adsorptive behavior of TNT on GAC, only the results confirmed by three or more repeated cycles under the same conditions are presented in detail.

In the experimental examination of TNT activated carbon adsorption under equilibrium conditions, the mechanism of TNT adsorption was determined. It was found that the activated carbon capacity for TNT depended considerably on the temperature (Fig. 2).

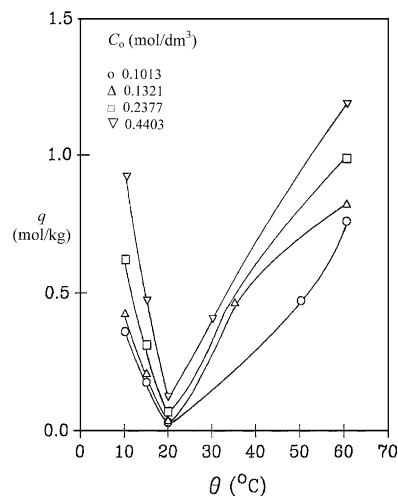


Fig. 2. Adsorption capacity vs. temperature.

An important criterion for the distinction between physical adsorption and chemisorption is the rate of adsorption. Chemisorption, being a chemical process, frequently requires activation energy and so proceeds at a limited rate, which increases rapidly with rising temperature. Furthermore, the rate becomes measurable only above some temperature minimum. Therefore, one often encounters the anomaly that the amount chemisorbed may increase with rise in temperature [19].

All the curves of the TNT amount adsorbed at a given concentration, plotted against temperature have a minimum at 20°C (Fig. 2). At temperatures up to 20°C physical adsorption predominates and the equilibrium curves show that the adsorption rate decreases steadily with increasing temperature. The rate of chemisorption is so low that the amount taken up within the period of each measurement is negligible. At 20°C this rate becomes large enough to produce an appreciable contribution to the total measured adsorption. The contribution of chemisorption becomes increasingly large within temperature region from 20 to 60°C because of the positive temperature coefficient of the rate of chemisorption.

The adsorption capacity during continuous column operation can be estimated by making use of the breakthrough curve; breakthrough being defined as the point when a specified amount of the adsorbate is detected in the effluent. A breakthrough of 10% occurs when the concentration of the effluent is 10% of the influent concentration and 50% breakthrough occur when the concentration of the effluent is 50% of the influent concentration. The area between the ordinate and the breakthrough curve gives the amount of adsorbate removed over the test time. The amount of adsorbate removed per gram of adsorbent is obtained by dividing the total amount of adsorbate removed by the mass of the adsorbent in the column.

For the examined systems the ratio of the effluent concentration (C) to the influent concentration (C_0) was plotted against time in order to obtain the breakthrough curves. The

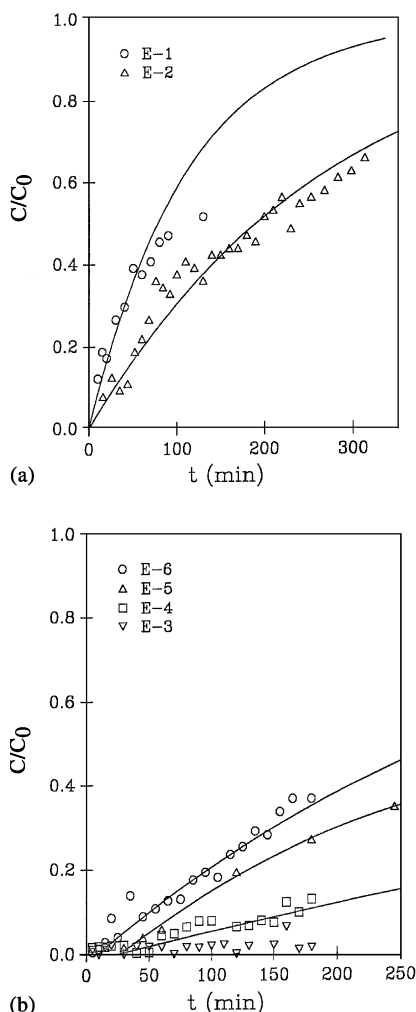


Fig. 3. TNT breakthrough curves for various temperatures: (a) adsorbent bed height 7 cm [$\theta = 20^\circ\text{C}$ (E-1); $\theta = 30^\circ\text{C}$ (E-2)], (b) adsorbent bed height 13.5 cm [$\theta = 60^\circ\text{C}$ (E-3); $\theta = 20^\circ\text{C}$ (E-4); $\theta = 15^\circ\text{C}$ (E-5) and $\theta = 2^\circ\text{C}$ (E-6)].

influence of temperature on the breakthrough curve and adsorption capacity in a dynamic system was examined for a flow rate of $2\text{ dm}^3/\text{h}$ and for two activated carbon bed heights (7 and 13.5 cm).

The results of the influence of temperature for an adsorbent bed height of 7 cm are presented in Fig. 3a and for a bed height of 13.5 cm in Fig. 3b.

It is obvious from Fig. 3 that the defined breakthrough point, the slope of the response curve, and the adsorption capacity (which is larger for higher temperatures) are highly dependent on the bed temperature. As the temperature increases, the TNT effluent concentration in the observed time interval decreases. Also, since the chemisorption also takes place, besides physical adsorption, the behavior of the system can be explained by the fact that the coefficient of diffusion and the constant of chemisorption rate increase with increasing temperature.

The effect of the input concentration of the TNT aqueous solution on the breakthrough curve is presented in Fig. 4. The effect is appreciable, however, only for lower flow rates.

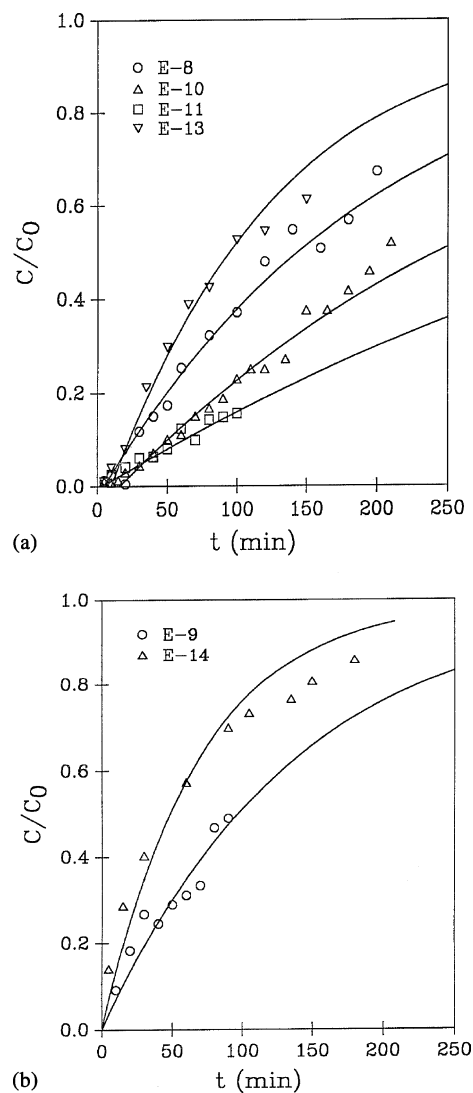


Fig. 4. TNT breakthrough curves for various feed concentrations: (a) flow rate $2\text{ dm}^3/\text{h}$ [$C_0 = 36\text{ mg}/\text{dm}^3$ (E-8); $C_0 = 48\text{ mg}/\text{dm}^3$ (E-10); $C_0 = 59\text{ mg}/\text{dm}^3$ (E-11) and $C_0 = 165\text{ mg}/\text{dm}^3$ (E-13)], (b) flow rate $4\text{ dm}^3/\text{h}$ [$C_0 = 45\text{ mg}/\text{dm}^3$ (E-9); $C_0 = 167.5\text{ mg}/\text{dm}^3$ (E-14)].

As expected, the breakthrough curves were steeper and the breakthrough times shorter at higher concentrations for both flow rates.

Fig. 5 shows the results of experiments obtained at different flow rates. All the experiments were conducted using a 70 mm bed height for a mass of activated carbon of 3 g at 60°C .

Fig. 5a shows the breakthrough curves for experiments E-7, E-8 and E-9. The breakthrough curves are very nearly parallel and, as expected, a higher flow rate leads to a higher effluent TNT concentration.

The breakthrough curves for higher TNT concentrations, $165\text{ mg}/\text{dm}^3$ (E-13) and $167\text{ mg}/\text{dm}^3$ (E-14) are given in Fig. 5b for the flow rates 2 and $4\text{ dm}^3/\text{h}$, respectively. The adsorption capacity and the adsorption rate are nearly independent of the flow rate.

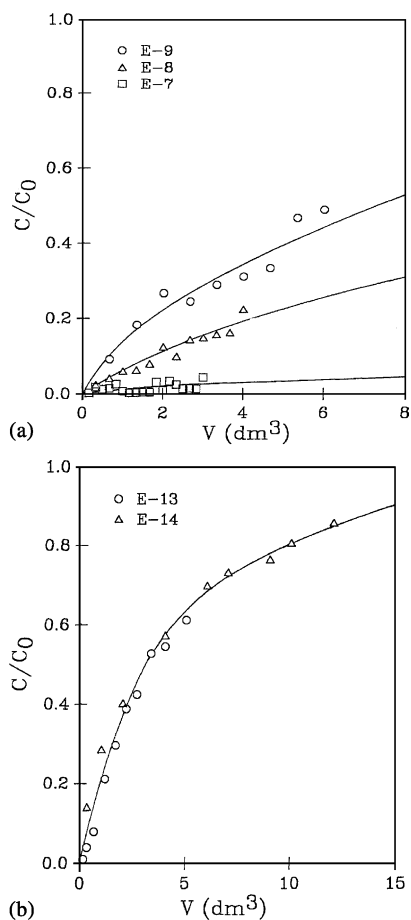


Fig. 5. TNT breakthrough curves at varying flow rate: (a) lower feed concentration [$F = 1 \text{ dm}^3/\text{h}$ (E-7); $F = 2 \text{ dm}^3/\text{h}$ (E-8) and $F = 4 \text{ dm}^3/\text{h}$ (E-9)], (b) higher feed concentration [$F = 2 \text{ dm}^3/\text{h}$ (E-13); $F = 4 \text{ dm}^3/\text{h}$ (E-14)].

The behavior of the system at lower concentrations is in accordance with the influence of the flow rate on the height equivalent of theoretical plates (HETP). The rates used during the experiments (interstitial fluid velocities of 0.006, 0.012 and 0.024 m/s) were comparatively high rates for a chromatographic type of system. For these rates the main resistance to mass transfer is due to pore diffusion and it increases, together with the HETP, with increasing rate; therefore, the efficiency of the column decreases. When the input concentration is high, crystallization and polymerization probably take place. Therefore, the pores of the carbon are clogged and the pore diffusion mass transfer resistance is very high and independent of flow rate.

3.1. Desorption of the saturated activated carbon

The whole amount of TNT, which was desorbed from activated carbon was 85.3 mg, measured gravimetrically. That was only 36.7% of the whole amount of adsorbed TNT (232.4 mg), which was obtained from the material balance for adsorption (experiment E-11). Similar results were obtained for the extraction of TNT from activated carbon by

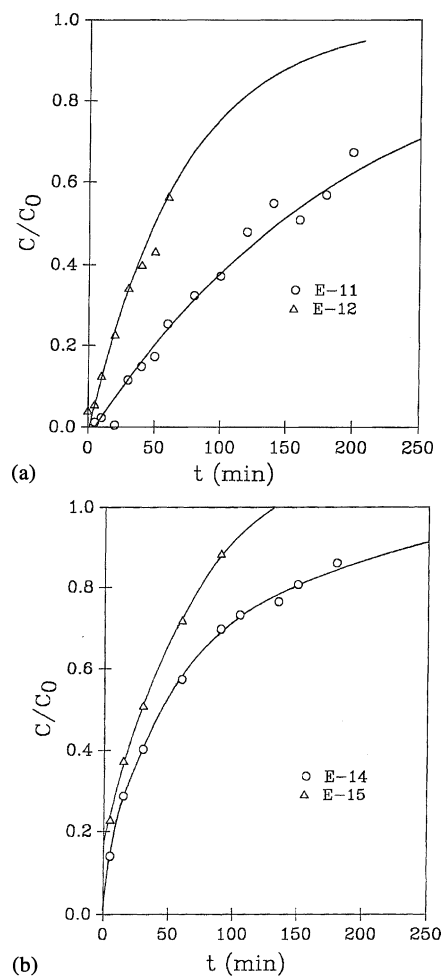


Fig. 6. Breakthrough curves for TNT adsorption on: (a) fresh activated carbon (E-11) and regenerated activated carbon (E-12), (b) fresh activated carbon (E-14) and activated carbon regenerated in a Soxlet extractor (E-15).

acetonitrile, where up to 62% of the added TNT was strongly bound to the carbon and was not extractable with acetonitrile [20]. The low efficiency of activated carbon regeneration was confirmed, in comparison with the breakthrough curve of adsorption of regenerated activated carbon (experiment E-12).

The breakthrough curves for fresh and regenerated GAC are presented in Fig. 6a. Obviously, the defined breakthrough degree was achieved earlier and the slope of the breakthrough curve was steeper for adsorption I than for adsorption II. This can be explained by the fact that during adsorption at 60°C , part of the TNT was irreversibly bound to the adsorbent surface through chemisorption and the sites for adsorption remained occupied.

The same results were obtained by the regeneration of activated carbon in a Soxlet extractor with acetone. The breakthrough curve of adsorption of the fresh adsorbent (experiment E-14) and breakthrough curve of adsorption of the regenerated adsorbent (experiment E-15) are presented in Fig. 6b.

The experimental results of activated carbon desorption showed that the regeneration of activated carbon, previously

saturated with TNT by adsorption at 60 °C, would not be economical because of the low degree of desorption.

4. Modeling of dynamic adsorption

Three models were applied to describe the experimental results of the dynamic adsorption of TNT by activated carbon.

- 1 Model of normal distribution [21];
- 2 Model of a first order system with dead time [22,23];
- 3 Model based on gas adsorption kinetics [24,25].

The estimated parameters were based on the minimum value of the absolute deviation of the experimental values from the theoretical curve. The points of $C/C_0 < 0.05$ were not considered because of system unsteadiness at the start.

The response of the system (effluent fluid concentrations as a function of time) on step changes of the input concentration is given by the following equations:

1. Model I—a model of normal distribution

$$\frac{C(t)}{C_0} = \frac{1}{2} \left[1 + \operatorname{erf} \frac{t - t_c}{\sqrt{2}\tau_c} \right] \tag{1}$$

the error function $\operatorname{erf}(x)$ is

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x \exp(-T^2) dt \tag{2}$$

and

$$T = \frac{t - t' - t_c}{\sqrt{2}\tau_c} \tag{3}$$

where t' is the interval of the time (min); t_c the average value of the distribution (min); τ_c the standard deviation of the distribution (min^2).

2. Model II—a model of a first order system with dead time

$$\frac{C(t)}{C_0} = K_t \left[1 + \exp \frac{t - D'}{\tau} \right] \tag{4}$$

where the characteristic points are $C(0)/C_0 = 0$; $C(\infty)/C_0 = K_t$; $C(\tau)/C_0 = 0.632$; where K_t is a constant; τ the time constant of the system; D' the dead time

3. Model III—Yoon–Nelson’s model

$$\frac{C(t)}{C_0} = 1 + \exp \left[\frac{-2.1972(t_{50} - t)}{t_{50}t_{10}} \right]^{-1} \tag{5}$$

where t_{50} is the time of 50% breakthrough; t_{10} the time of 10% breakthrough.

The model parameters are given in Table 3.

The calculated response curves with parameters from Table 3 as the function of dimensionless time are shown in Figs. 7–9.

In order to compare the models, the absolute deviations of the experimental values from the theoretical ones are given in Table 4.

Table 3
Model parameters

Experiment	Model I		Model II		Model III	
	t_c (min)	τ_c (min^2)	τ (min)	D' (min)	t_{50} (min)	t_{10} (min)
E-1	90	80	113	0	90	0
E-2	198	160	276	0	198	1
E-3	410	150	400	24	400	170
E-6	206	121	397	9	206	50
E-8	230	128	555	4	230	70
E-9	92	75	140	0	92	1
E-10	203	121	327	16	203	48
E-11	132	88	200	5	132	16
E-12	49	33	70	1	49	5
E-13	95	69	122	10	95	3
E-14	66	51	70	0	66	1
E-15	29	29	42	0	29	1

t_c : average value of distribution; τ_c : standard deviation of distribution; τ : time constant of the system; D' : dead time; t_{50} : 50% breakthrough time; t_{10} : 10% breakthrough time.

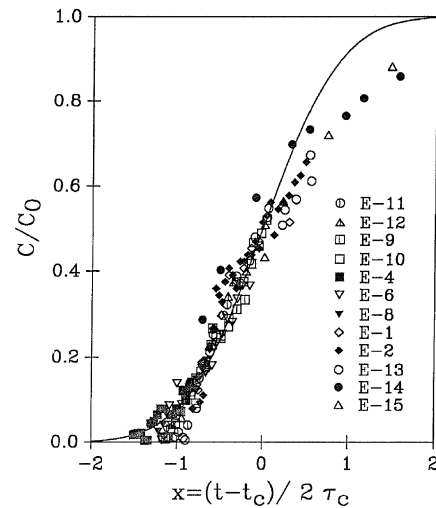


Fig. 7. Comparison of experimental data with calculated response curve according to model I.

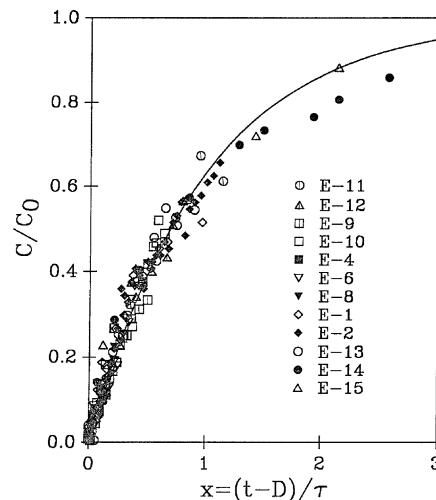


Fig. 8. Comparison of experimental data with calculated response curve according to model II.

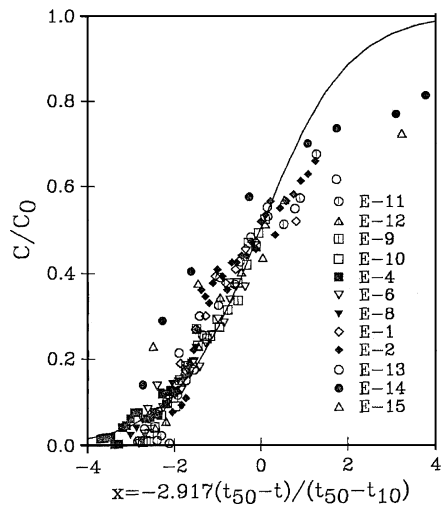


Fig. 9. Comparison of experimental data with calculated response curve to model III.

As can be seen from Table 4 and Figs. 7–9, the best agreement of the calculated and experimental values is obtained for model II, and this model was used for the calculation of the total saturation capacity of the activated carbon (g TNT/charge):

$$Q_{\text{tot}} = \frac{1}{m} \int_0^{\infty} F(C - C_0) dt = FC_0 \int_0^{\infty} \left(1 - \frac{C}{C_0}\right) dt \quad (6)$$

By introducing the expression for C/C_0 , according to Eq. (4) into Eq. (6), one obtains:

$$Q_{\text{tot}} = \frac{1}{m} FC_0 \tau \exp(D'/\tau) \quad (7)$$

The calculated values of the total saturation capacity, Q_{tot} , are given in Table 5.

The data given in Table 5 confirmed the previous conclusions about the influence of temperature, concentration and flow rate on TNT adsorption, including the possibility of activated carbon regeneration. Increase of the saturation capacity of activated carbon in the case of extremely high input con-

Table 4
Absolute deviations of the experimental values from the theoretical ones

Experiment	Absolute deviation for $C/C_0 > 0.05$ (%)		
	Model I	Model II	Model III
E-1	13.0	16.0	17.5
E-2	18.6	11.8	19.7
E-4	22.5	23.8	21.2
E-6	12.6	12.1	13.5
E-8	8.8	9.8	10.2
E-9	12.4	13.8	13.4
E-10	7.3	6.3	8.7
E-11	10.5	6.3	11.3
E-12	19.1	5.1	21.0
E-13	20.2	6.2	21.3
E-14	20.4	15.1	21.1
E-15	11.6	15.3	23.5
Total absolute deviation	14.75	11.8	16.86

Table 5
Total saturation capacity of activated carbon calculated according to model II

Experiment	θ (°C)	C_0 (mg/dm ³)	m (g)	L (mm)	F (dm ³ /h)	Q_{tot} (mg/g)
E-1	20	64.00	3	70	2	0.0804
E-2	30	64.00	3	70	2	0.1963
E-4	20	42.50	6	135	2	0.3363
E-6	2	32.76	6	135	2	0.0739
E-8	60	36.00	3	70	2	0.2273
E-9	60	45.00	3	70	4	0.1400
E-10	60	48.00	3	70	2	0.1831
E-11	60	59.00	3	70	2	0.1344
E-12	60	54.40	3	70	2	0.0432
E-13	60	165.00	3	70	2	0.2428
E-14	60	167.50	3	70	4	0.2598
E-15	60	171.00	3	70	4	0.1596

centrations can be explained by crystallization in parts of the apparatus, which were not heated and crystallization on the activated carbon itself.

5. Conclusions

The results of the experimental examination of dynamic adsorption presented in this study show that the adsorption capacity is highly dependent on the bed temperature, input concentration and flow rate. The adsorption capacity of the activated carbon increased with increasing temperature, but it decreased with increasing input concentration and flow rate.

Some authors [1] obtained similar results for TNT adsorption on GAC using a column of 50 mm diameter, a bed height of 800 mm and a feed concentration of 100 mg/dm³ at room temperature. Obviously, the influence of temperature is greater than was expected and the bed height and the amount of GAC used could be significantly lowered by increasing the temperature.

The results of activated carbon desorption indicate that the regeneration of activated carbon, previously saturated with TNT by adsorption at 60 °C, would not be economical because of the low desorption degree. GAC could only be defined as successful if a technology enabled 100% of the activated carbon to be regenerated and reused.

The results obtained by modeling the dynamic adsorption, based on the experimental results, confirmed the previously obtained conclusions.

According to the experimental results, conditions for TNT dynamic adsorption for removing dissolved TNT from wastewater were determined. In order to increase the efficiency of the system, it was recommended that the process be carried out under the following conditions:

- increased temperature (about 60 °C),
- lower flow rate,
- low input concentrations of TNT in the wastewater (less than 60 ppm).

Naturally, the economic effects must also be considered. Concerning increased temperature, there are usually no additional expenditures for heating the column, because the heat of the reactor cooling fluids may be used.

A low flow rate increases the efficiency of the system, but on the other hand it requires large dimensions of the apparatus for achieving a defined capacity. We should therefore balance a decrease of the costs due to increase of the adsorbent efficiency with an increase of costs because of larger dimensions. Increase of the activated carbon capacity by lowering the input concentration could be performed and in that case a thorough primary purification of the wastewater is required.

Further investigations in this area should be directed towards the examination of applying fibrous activated carbon, because of its large sorption capacity and good dynamic properties concerning adsorption and desorption processes.

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