Proc. Estonian Acad. Sci. Chem., 2001, **50**, 4, 205–216

XYLIDINE-POLLUTED GROUNDWATER PURIFICATION
Adsorption experiments and breakthrough calculations

Janek REINIK[a], Andres VIIROJA[a], and Juha KALLAS[b]

[a] Department of Chemical Engineering, Tallinn Technical University, Ehitajate tee 5, 19086 Tallinn, Estonia; jreinik@hot.ee
[b] Department of Chemical Technology, Lappeenranta University of Technology, P.O. Box 20, FIN-53851 Lappeenranta, Finland

Abstract. 2,4-Xylidine is a carcinogenic component originating from missile fuel, and it often dominates in polluted groundwater in the areas of abandoned Soviet missile bases in Eastern Europe. One of the possible processes for its removal is adsorption onto granulated activated carbon. However, the corresponding equilibrium relationships as well as information on the process kinetics are not available. In this work Langmuir's and Freundlich's isotherm parameters were obtained from batch adsorption equilibrium tests. Initial concentration of 2,4-xylidine was varied in the range of 200–300 mg/L in the experiments. The solid phase diffusion coefficient was obtained from the batch kinetic runs. The breakthrough curves were measured during dynamic experiments in two packed bed columns with diameters of 16 and 26 mm. The obtained experimental curves were compared to those calculated by the Thomas and Rice methods. In some cases a satisfactory fit was achieved, but in several cases more advanced modelling methods should be used for better prediction of the xylidine-contaminated groundwater breakthrough profiles in a packed bed reactor.

Key words: 2,4-xylidine, adsorption isotherm, kinetics, dynamics, packed bed adsorber design, breakthrough curves.

INTRODUCTION

Xylidine-polluted groundwater can be found in sites of former Soviet military missile bases due to spills of a xylidine-based missile fuel. The two-component missile fuel consists of triethylamine (50%) and xylidine (45%) [1]. According to analyses [2] in an abandoned Soviet missile base at Keila-Joa (Northwest Estonia), the polluted groundwater contains components that originate from missile fuel – 2,4-xylidine (210 mg/L), triethylamine (125 mg/L), *p*-toluidine (10 mg/L), and aniline (5 mg/L). More precise analyses [3] showed also the

presence of xylene, ethylaniline, trimethylaniline, dimethylnitrobenzene, form- and acetamidexylidine, and trimethylholine in small amounts. Similar contamination of groundwater can be found at former military bases in Barta and Tasi, West Latvia [4].

Triethylamine is an easily volatile component and therefore the treatment of xylidine, as the main toxic component, was in the focus of this work. The limiting concentration for aromatic amines (incl. xylidines) in groundwater is 0.1 μg/L according to Estonian legislation [5]. There is a high risk for exposure of the groundwater contaminated with carcinogenic xylidine to the drinking water wells with the resultant impacts on human health.

Several investigations have been carried out on the purification of water contaminated with aromatic amines, including xylidines. Avontis et al. [4] developed a treatment process for xylidine-contaminated soil and water in abandoned military bases in Latvia. For groundwater remediation, research was done using steam stripping for concentrating xylidine. The residual xylidine in the stream of column bottoms was destroyed using advanced oxidation processes with UV photolysis, UV/hydrogen peroxide, photo-Fenton's reaction, and dark Fenton's reaction. According to the results of photolysis research, oxidation of 2,4-xylidine requires a prohibitively long residence time to reach undetectable concentration levels. Results of UV/hydrogen peroxide experiments indicated a trend of decreasing exposure time required to achieve undetectable levels of xylidine with increasing hydrogen peroxide concentrations. Research into Fenton's reagent indicated the enhancement of Fenton's reagent with UV light and faster oxidation of xylidine with increasing Fe^{2+} ion concentration. The best results were achieved with UV/hydrogen peroxide and photo-Fenton's reaction.

Preis et al. [6] developed a treatment process for aromatic amino compounds from rocket fuel residues by photocatalysis over UV-irradiated titanium dioxide in solar reactors of shallow pond configuration. The immobilized photocatalyst enabled wastewater to be treated without the expense of constant stirring, necessary for the slurry type reactors. This would also avoid complications concerning the catalyst separation after treatment. Despite good purification efficiency, the process is time consuming as it was observed by Avontis et al. [4].

Waters containing low concentrations of hazardous organic molecules are difficult to treat by conventional methods without significant process costs. Treatment of xylidine-polluted groundwater with the traditional distillation method turned out to be economically not feasible in the mathematical modelling stage [7].

Direct biological treatment of groundwater requires selection of proper enzymes and regimes. Aerobic biological treatability was demonstrated for the selected compounds of wastewater by Lowhorn et al. [8]. Phenol, methylethylketone, aniline, and 4-methylpyridine were selected in the work as model pollutants because of their high concentration and relative toxicity. Experiments with batch biological reactors demonstrated that phenol, methylethylketone, and aniline were biologically metabolized only when each compound was the sole

source of carbon. Because of low concentration of xylidine in groundwater, the effectiveness of the biodegradation process is questionable.

Nyssen et al. [9] effectively removed aromatic amines, including 4-(*n*-butyl)-aniline and 2,6-xylidine from water by foam flotation with the anionic surfactant sodium dodecylsulphate. With initial amine concentrations of 10 mg/L or less, residual amine concentrations of less than 0.1 mg/L were generally obtained after 10–30 min of flotation. The sodium dodecylsulphate concentration and flotation time are directly related to the amount of amine removed. Amine removal is the most efficient at pH values low enough (usually about 3) so that the amine is protonated and at low ionic strength.

In the study of Nyström [10] experiments with aniline and azobenzene were carried out by extraction of the organic molecules from the aqueous phase into the oil phase of an oil/water emulsion and by subsequent ultrafiltration of the emulsion.

The removal of aromatic amines from water could be conducted using active chlorine. In general, amines can be expected to produce soluble chloro-substituted compounds. Since chlorinated aromatic derivatives are known to be toxic, chlorination of aromatic amines, investigated by Jenkins et al. [11], does not appear to be a suitable removal process.

This work concerns the purification of contaminated groundwater by means of granulated activated carbon in a packed bed adsorber.

ADSORPTION THEORY

The design of packed bed adsorber involves mainly the calculation of the breakthrough curve. This requires availability of the adsorption isotherms and the solid phase diffusivity.

Adsorption equilibrium

Traditional adsorption equilibrium isotherms of Langmuir and Freundlich as well as the linear isotherm were used for fitting the experimental data.

$$q = \frac{bc}{1+bc} q_{\max}, \quad q = K_{\mathrm{f}} c^{n_{\mathrm{f}}}, \text{ and } q = Kc, \tag{1}$$

where b is the component's Langmuir coefficient, $q_{\max}$ is the maximum amount of the adsorbed component at a given temperature, K_{f} and n_{f} are Freundlich's constant and exponent for the component respectively, K is the slope of the linear isotherm, and c is the concentration of the solute.

Adsorption in the particle

For a well-stirred batch reactor where external mass transfer is relatively fast the governing equation for adsorption can be described by the following mass balance equation [12]:

$$\frac{\delta q}{\delta t} = D_s \frac{1\delta}{r^2 \delta r}\left(r^2 \frac{\delta q}{\delta r}\right), \tag{2}$$

where r is the radial position, D_s is the solid phase effective diffusion coefficient, which describes the diffusion in the pores of activated carbon, and t is time. Equation 2 has many analytical solutions [13–18] depending upon the initial and boundary conditions.

In order to solve Eq. 2 Crank's method [19] was used in this work assuming that the concentration of the solute at the surface remains constant ("infinite bath") and the external film resistance is negligible. For small times, or more precisely, for $\bar{q}/q_\infty < 0.3$, the equation to determine D_s may be written as:

$$\frac{\bar{q}}{q_\infty} = 6\left(\frac{D_s t}{R^2}\right)^{1/2}\left[\pi^{-1/2} + B\right], \tag{3}$$

where $\bar{q}$ is the average concentration in the solid at any given time, q_∞ is the average concentration in the solid at infinite time, R is the particle radius, and B is constant. Thus, a plot of $\bar{q}/q_\infty$ versus the square root of time gives a straight line of slope $6(D_s/\pi r^2)^{1/2}$ [20].

Breakthrough curve

The mass balance for infinite length of the bed, dZ, can be presented as follows:

$$\varepsilon dL\frac{\partial c}{\partial t} + (1-\varepsilon)dZ\rho_p \frac{\partial \bar{q}}{\partial t} = u_0 c - u_0(c+dc), \tag{4}$$

where ρ_p is the particle density, ε is interstitial space, and u_0 is superficial velocity of fluid in empty column $(u_0 = v/\varepsilon)$. The solutions for the adsorption systems are generally given in terms of the Goldstein function in the form $c/c_0 = J(\xi,\tau)$:

$$J(\xi,\tau) = 1 - \int_0^\xi e^{(-\xi-\tau)} I_0(\sqrt{4\tau\xi})d\xi, \tag{5}$$

where I_0 is the hyperbolic zero-order Bessel function of the first kind, ξ is a dimensionless distance equal to $L(K_L a/\varepsilon v)$, and τ is a dimensionless time equal to $[K_L a/K(1-\varepsilon)][t-(L/v)]$, where L is the overall column length, v is the average axial velocity of the flowing fluid in the void spaces, and $K_L a$ is the volumetric mass transfer coefficient.

Rice [21] proved that the Goldstein function solution is exact for systems that can be characterized by a combination of an individual film transfer coefficient k_L and a diffusivity in the pores of the adsorbent, D_s, assuming that the concentration profile inside the particle is parabolic and the adsorption isotherm is linear. The overall mass transfer coefficient, K_L, in the Goldstein function model is determined from the relation $\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{Kk_s}$, where $k_s = 5\,D_s / R$ and $k_L = 1.15\,\mathrm{Re}^{-0.5}\,Sc^{-2/3}v$.

Thomas [22] uses for the calculation of the breakthrough curve instead of the linear isotherm constant the Langmuir equation constants for equilibrium.

EXPERIMENTAL

Granulated activated carbon (GAC) NORIT RB 1 was chosen as adsorbent. Literature survey showed that no information is available on 2,4-xylidine adsorption isotherms and solid phase diffusion coefficient. These values cannot be calculated theoretically but have to be determined experimentally.

The adsorbent NORIT RB 1 is made in The Netherlands with the following properties: particle diameter $d = 1.0 \times 10^{-3}$ m, density of adsorbent ρ_{bulk} = 724.1 kg/m^3 [23]. The 2,4-xylidine (TY 6-09-05-656-77) used in our experiments was from the Voikovo factory (Russia).

During the pre-treatment the adsorbent was boiled in distilled water and periodically washed with distilled water until the water was free from any suspended impurities. The carbon was then dried in an oven at 110 °C and stored in a calcium chloride dessicator.

Analyses to determine the 2,4-xylidine concentration were in all experiments performed with an HP diode-array spectrophotometer at wavelengths between 284 and 288 nm.

Equilibrium experiment

The adsorption equilibrium experiments were carried out with various initial concentrations of 2,4-xylidine (100 to 310 mg/L) and GAC (0.01–3.5 g/L). The solutions were properly mixed. The duration of the equilibrium runs was 48 h. The results are presented in Fig. 1.

The constants for adsorption isotherms were obtained from equilibrium data:

– Langmuir isotherm: $q[\mathrm{mg/g}] = \frac{bc}{1+bc} q_{max} = \frac{0.45c}{1+0.45c} 200.0$ $\qquad R^2 = 0.7944$

– Freundlich isotherm: $q[\mathrm{mg/g}] = K_f c^{n_f} = 77.4c^{0.202}$ $\qquad R^2 = 0.9409$

– Linear isotherm: $q[\mathrm{mg/g}] = Kc = 1.66c$ $\qquad R^2 < 0.2$

The Freundlich isotherm describes the equilibrium situation better than the Langmuir isotherm.

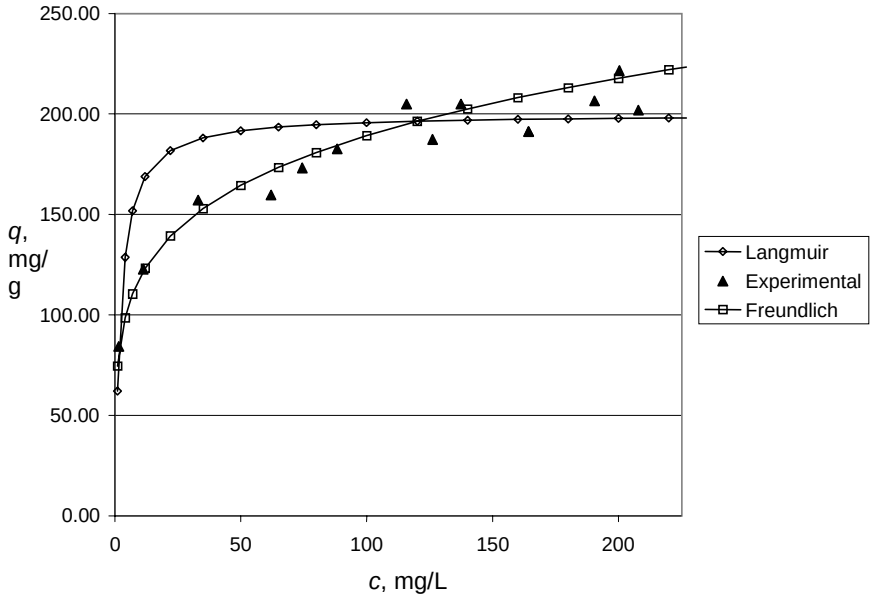

Fig. 1. Comparison of experimental 2,4-xylidine equilibrium data to Langmuir and Freundlich isotherms (t = 17 °C).

Kinetic experiments

The kinetic runs were carried out in a 0.016 m^3 vessel (diameter 0.27 m) at 17 °C. The reaction mixture was properly and continuously mixed with a six-ladder turbine propeller with a diameter of 0.15 m. To improve the mixing of the adsorbent, additionally four flow resistance plates were installed inside the vessel. The initial concentration of 2,4-xylidine was 205 mg/L and GAC concentration was 0.67 g/L.

The samples were taken off from the reactor with a syringe and filtrated through syringe filters (pore size 0.2 μm) before analysing. The results of the kinetic runs are presented in Fig. 2.

The solid phase diffusion coefficient is according to Crank [19] $D_s = 2.32\times10^{-12}$ m^2/s; Vermulen et al. [cited in 24], $D_s = 1.5\times10^{-10}$ m^2/s; and Huang & Li [14], $D_s = 1.23\times10^{-13}$ m^2/s.

Dynamic experiments

Dynamic experiments were carried out in order to compare the experimentally obtained profiles to the theoretical breakthrough curves. The experiments were carried out with two separate columns of *Pharmacia Biothech* with diameters of 16 and 26 mm at 17 °C. The bed height varied between 8 and 30 cm and hydraulic loading from 1.7 to 40 cm/min. The results of four runs of similar superficial fluid velocities are presented in Fig. 3.

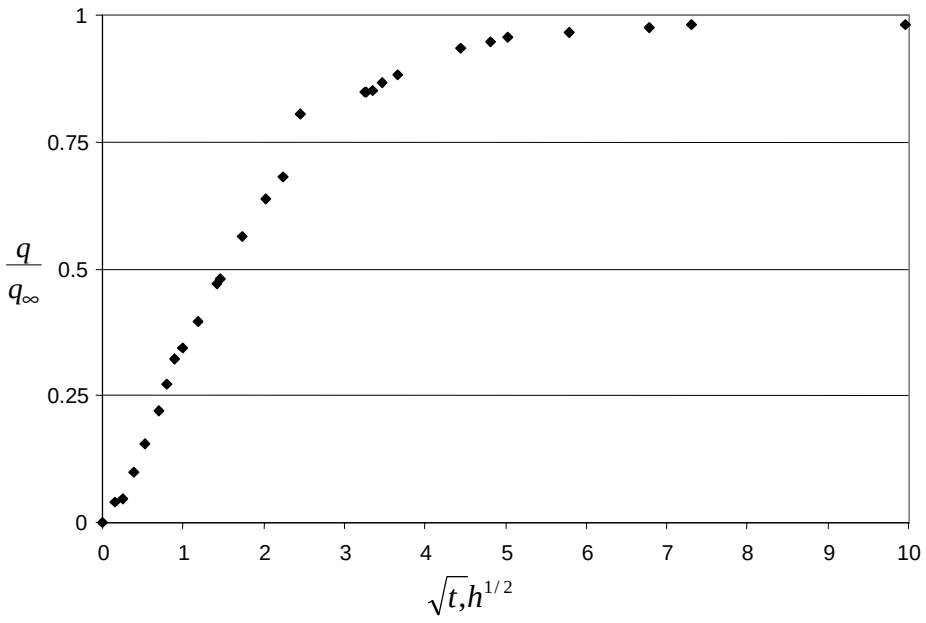

Fig. 2. 2,4-Xylidine kinetic run at 17 °C . The plot of $\bar{q}/q_\infty$ versus the square root of time.

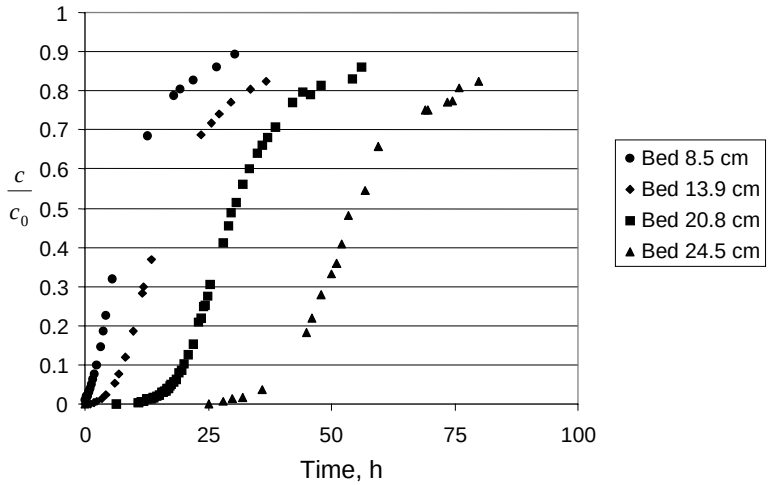

Fig. 3. Breakthrough curves for four different bed depths. Liquid superficial velocity in empty column: u_0 = 4.4 cm/min. Interstices: $\varepsilon_{8.5}$ = 0.233, $\varepsilon_{13.9}$ = 0.258, $\varepsilon_{20.8}$ = 0.406, $\varepsilon_{24.5}$ = 0.361.

Input parameters to the Thomas and Rice calculation methods are presented in Table 1.

Table 1. Input parameters of the Thomas and Rice calculation methods

Parameter	Unit	Value
Linear isotherm constant (Rice method)[a], K	m^3 liq/m^3 solid	897–1426
Maximum adsorbable concentration on solid adsorbent (Thomas method)[a], q_{max}	kg/m^3	144.8
Langmuir isotherm constant (Thomas method)[a], b	m^3/kg	450.5
Solid phase diffusion coefficient[a], D_s	m^2/s	2.32×10^{-12}
Liquid phase diffusion [25], D_f	m^2/s	8.9×10^{-10}
Liquid phase viscosity [26], μ	Pa*s	9.47×10^{-4}
Liquid density, ρ	kg/m^3	988
Empty column superficial velocity[b], u_0	m/s	2.6×10^{-4}–6.8×10^{-3}
Initial concentration[b], c_0	kg/m^3	0.19–0.32
Height of the bed[b], L	m	0.2–0.6
Void fraction in the bed[b], ε	m^3 fl/m^3 bed	0.23–0.42

[a] determined experimentally;
[b] individual to each experiment.

The results of dynamic experiments compared with theoretical curves are shown in Fig. 4. The experiments were carried out with different bed heights, velocities, and void spaces.

RESULTS AND DISCUSSION

The Freundlich isotherm describes the 2,4-xylidine equilibrium situation on GAC better than the Langmuir isotherm. The maximum adsorbable amount of 2,4-xylidine on GAC NORIT RB 1 is according to the Langmuir isotherm 200 mg/g (with an initial concentration of 250 mg/L). The adsorption capacity at the residual (equilibrium) concentration $c_e = 1$ mg/L is 77.4 mg/g according to the Freundlich isotherm.

The kinetic experiments showed the diffusion coefficient in solid phase for 2,4-xylidine to be $D_s = 2.32 \times 10^{-12}$ m^2/s (calculated according to the "infinite bath" method), which is in the same order of magnitude as for phenol on Calgon Filtrasorb 400 adsorbent ($D_s = 7.75 - 9.01 \times 10^{-12}$ m^2/s) [27].

Comparison of the experimental breakthrough curves to the breakthrough profiles calculated by Rice [28] and Thomas methods [29] did not show a satisfactory fit. A possible explanation is that the xylidine adsorption equilibrium follows the Freundlich isotherm while the Rice method uses the linear isotherm and the Thomas method uses the Langmuir isotherm equation. More precise numerical methods [e.g. 30, 31] should be used to calculate more accurate breakthrough profiles. The Thomas and Rice methods were satisfactorily accurate in predicting in the first approximation the breakpoint time (in our case the minimum detectable concentration) for our environmental engineering purposes.

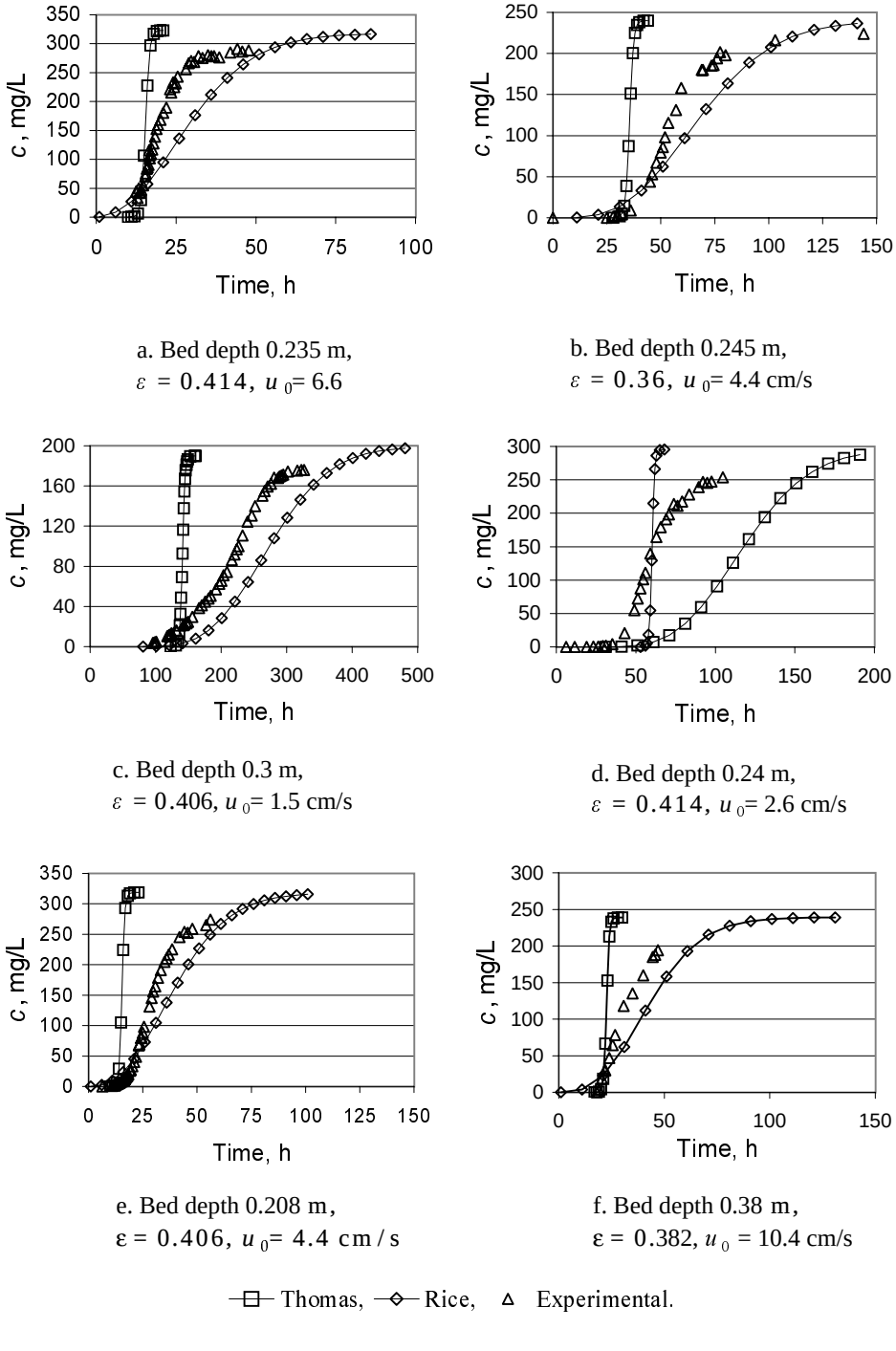

Fig. 4. Results of dynamic experiments versus theoretical curves.

CONCLUSIONS

The adsorption equilibrium and the diffusion coefficient of 2,4-xylidine were estimated on granulated activated carbon from experimental data. Experimental breakthrough curves were compared to those calculated by the Thomas and Rice methods. Experimental breakthrough curves lie between the two calculated curves. For better prediction the mathematical model of breakthrough curve needs further development.

ACKNOWLEDGEMENTS

The work was carried out in Lappeenranta University of Technology and financially supported by the Nordic Energy Research Programme and the Centre of International Mobility.

REFERENCES

1. Raukas, A. (ed.) *Endise Nõukogude Liidu sõjaväe jääkreostus ja selle likvideerimine*. EV Keskkonnaministeerium, Tallinn, 1999.
2. Keila Geoloogia Ltd. Environmental pollution investigations, Keila-Joa military missile base. Report, 1993 (unpublished).
3. Hingst, G., Ahrens, H., Otsa, E. & Mueller, S. Gefährdungsabschätzung für die Liegenschaft Raketenbasis Keila-Joa. *Industrieanlagen Betriebsgesellschaft mbH*, Niederlassung Berlin, Estnisches Umweltuntersuchungslabor, Tallinn, 1994, 118.
4. Avontis, J., Kokars, V., Malers, I., Valtere, S., Whittaker, H., Cooper, D. & Whittaker, R. Contamination and environmental remediation of former missile sites near Liepaja. *Crit. Rev. Anal. Chem.*, 1998, **28**, 97–100.
5. EV Valitsuse määrus nr. 174. Ajutised saasteainete kontrollarvud pinnases ja põhjavees. 11.04.1995.
6. Preis, S., Krichevskaya, M. & Kharchenko, A. Photocatalytic oxidation of aromatic amino-compounds in aqueous solutions and groundwater from abandoned military bases. *Wat. Sci. Tech*., 1997, **35**, 265–272.
7. Reinik, J. Past pollution of the former Soviet Army in Estonia and its liquidation. Distillation method. Presentation in Nordic Energy Forum, 2000, Gothenburg, 21–22.06.
8. Lowhorn, R. W., Bustamante, R. B. & Bonner, W. P. Biological treatability of selected organic constituents of PFH liquid waste. *Fuel*, 1994, **73**, 1476–1480.
9. Nyssen, G. A., White, J. S., Bibring, P. & Wilson, D. Removal of trace levels of aromatic amines from aqueous solutions by foam flotation. *Sep. Sci. Technol.*, 1990, **25**, 809–824.
10. Nyström, M. Concentration by UF of hazardous effluents extracted into emulsions from water solutions; examples with aniline and azobenzene. *Desalination*, 1991, **81**, 117–127.
11. Jenkins, R. L., Haskins, J. E., Carmona, L. G. & Baird, R. B. Chlorination of benzidine and other aromatic amines in aqueous environments. *Arch. Environ. Contam. Toxicol*., 1978, **7**, 301–316.
12. Do, D. D. Sorption rate of bimodal microporous solids with an irreversible isotherm. *Chem. Eng. Sci.*, 1989, **44**, 1707–1713.
13. Changtong, A. & Massoth, F. E. Restrictive diffusion in aluminas. *AIChE J.*, 1983, **29**, 725–731.

14. Huang, T. C. & Li, K. Y. Ion-exchange kinetics for calcium radiotracer in a batch system. *Ind. Eng. Chem. Fund.*, 1973, **12**, 50–55.
15. Suzuki, M. & Kawazoe, K. Batch measurement of adsorption rate in an agitated tank. *J. Chem. Eng. Jap.*, 1974, **7**, 346–350.
16. Nerentnieks, I. Analysis of some adsorption experiments with activated carbon. *Chem. Eng. Sci.*, 1976, **31**, 1029–1035.
17. Palosaari, S. M., Reunanen, J. & Kaipanen, E. Adsorption experiments into a porous sphere. *Acta Polyt. Scand., Chem. Technol. Met*., Ser. 185, 1988.
18. Suzuki, M. & Kawazoe, K. Effective surface diffusion coefficients of volatile organics on activated carbon during adsorption from aqueous solution. *J. Chem. Eng. Jap.*, 1975, **8**, 379–382.
19. Crank, J. *Mathematics of Diffusion*. Oxford at the Clarendon Press, London, 1956.
20. Cooney, D. O. *Adsorption Design for Wastewater Treatment*. CRC Press LLC, 1999.
21. Rice, R. G. Approximate solutions for batch, packed bed tube, and radial flow adsorbers – comparison with experiments. *Chem. Eng. Sci.*, 1982, **37**, 83.
22. Thomas, H. Heterogeneous ion exchange in a flowing system. *J. Amer. Chem. Soc.*, 1944, **66**, 1664–1666.
23. Laari, A. Kaksikomponenttiadsorption läpäisykäyrien mittaus. LTTK, Kemian laitetekniikan laboratorio, 1988 (unpublished).
24. Perry, R. H. & Chilton, C. H. *Chemical Engineers' Handbook*, 5th edn. McGraw-Hill, New York, 1973.
25. Reid, R. C., Prausnitz, J. M. & Poling, B. E. *The Properties of Gases and Liquids*, 4th edn. McGraw-Hill, New York, 1986.
26. Keskinen, K. I. & Aittamaa, J. Flowbat – General Flowsheet Program. Helsinki University of Technology, 1997 (unpublished).
27. Peel, R. G., Benedek, A. & Growe, C. M. A branched pore kinetic model for activated carbon adsorption. *AIChE J.*, 1981, **27**, 26.
28. Reunanen, J., Kaipanen, E. & Palosaari, S. Adsorption läpäisykäyrän laskenta – Ricen ratkaisu. Lappeenranta University of Technology, Kemiantekniikan laitos, Lappeenranta, 1988 (unpublished).
29. Reunanen, J., Kaipanen, E. & Palosaari, S. Adsorption läpäisykäyrän laskenta – Thomasin ratkaisu. Lappeenranta University of Technology, Kemiantekniikan laitos, Lappeenranta, 1987 (unpublished).
30. Michaels, A. S. Simplified method for interpreting data in fixed-bed ion exchange. *Ind. Eng. Chem.*, 1952, **44**, 1922.
31. Okazaki, M., Kage, H., Tsubota, J. & Toei, R. Prediction of breakthrough curve of packed bed adsorber used for treatment of unknown multi-solute waste water. In *Proc. 3rd Chem. Eng. Conf.*, Seoul, 1983, Vol. 4, 277.

KSÜLIDIINIGA REOSTATUD PÕHJAVEE PUHASTAMINE
Adsorbeerimiseksperimendid ja läbilöögikõvera arvutused

Janek REINIK, Andres VIIROJA ja Juha KALLAS

On uuritud kantserogeense ksülidiiniga reostatud vee puhastamist granuleeritud aktiivsöega. Niimoodi saastunud põhjavett leidub endises Keila-Joa raketibaasis. Langmuir' ja Freundlichi isotermi parameetrid määrati tasakaalu katsetest, difusioonikoefitsient adsorbendi poorides aga kineetilisest katsest. Läbilöögikõverad arvutati matemaatiliselt Thomase ja Rice'i meetodiga ning neid võrreldi kolonnikatsete omadega. Katselist läbilöögikõvera profiili ei olnud või-

malik rahuldava täpsusega ennustada eespool mainitud arvutusmeetoditega – kõver asetub Thomase ja Rice'i arvutatud kõverate vahele. Paremate tulemuste saavutamiseks tuleb läbilöögikõvera arvutamisel kasutada täiustatumaid mudeleid. See on uurimistöö järgmine ülesanne.