Nordic Energy Research Programme   Norwegian U. of Science and Technology

Adsorption of 2,4-Xylidine on Granulated Activated Carbon in a Packed Bed Absorber

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1. Introduction

A removal of carcinogenic 2,4-Xylidine from aqueous solution using packed bed adsorber was carried out. The component has been detected in the groundwater of the abandoned Soviet missile bases in Eastern Europe. The pollutant originates from the Xylidine-based missile fuel, SAMIN. The purpose of the work was to predict, in the first approximation, the breakthrough profiles of Xylidine in the packed bed adsorber.

The concentration limit for aromatic amines (both aniline and xlidine) in groundwater is 0.1 µg/l according to Estonian legislation.[1] So the groundwater must be purified below that level.

Experiments with photocatalytical oxidation shows good purification effectiveness,[2] but the process is time consuming. Attempt to treat the groundwater with the distillation method is economically not feasible.[3] Therefore it was decided to investigate another way to treat the groundwater – the granulated activated carbon (GAC) adsorption in packed-bed reactor.

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. In order to calculate the breakthrough curve of the adsorption, the adsorption equilibrium and kinetic experiments were carried out. Distilled water was used as a solute and NORIT RB1 granulated activated carbon was used as an absorbent.

2. Adsorption Equilibrium

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

$$q = \frac{bc}{1+bc} q_{max} \ , q = K_f c^{n_f} \quad \text{and} \quad q = Kc \qquad [1]$$

The adsorption experiments were carried out for the component xylidine, with different initial concentrations (100 to 300 mg/l), in 100-ml flasks at the temperature 17 ^{o}C, with an equilibrium time of 48 hours. The TEA is an easily evaporating compound and was not included in the adsorption experiments. The dosage of GAC in the flasks varied between 0.01–3.5 g/l. The solutions were properly mixed. Water analysis was carried out with a Hewlett-Packard 8452A Diode-Array Spectrophotometer. Equilibrium isotherms had the same constants at given temperatures.
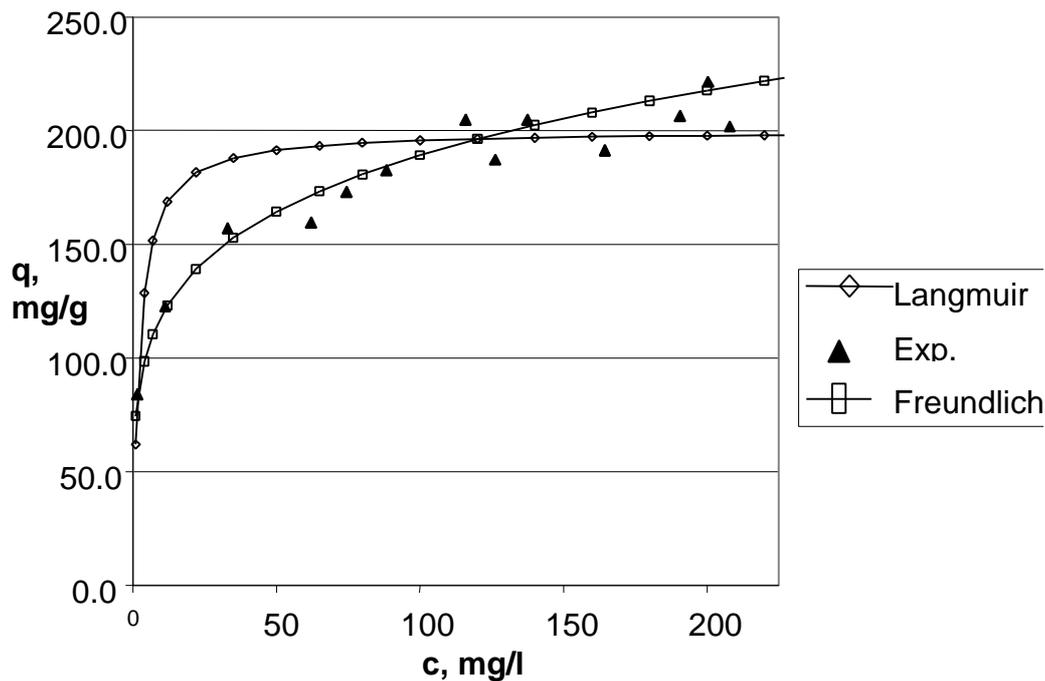
Figure 1. Comparison of 2,4-Xylidine equilibrium data to Langmuir and Freundlich isotherm equations (T=17°C).

Table 1. Constants for adsorption isotherms obtained from equilibrium data.

Isotherm	Isotherm equation	R^2
Langmuir	$q[mg/g] = \dfrac{bc}{1+bc}q_{max} = \dfrac{0.45c}{1+0.45c}200.0$	0.7944
Freundlich	$q[mg/g] = K_f c^{1/n_f} = 77.4c^{0.202}$	0.9409

The equilibrium isotherm is presented in Figure 1, and the values of the Langmuir and Freundlich isotherms are presented in Table 1. The Freundlich isotherm describes the equilibrium situation better than the Langmuir isotherm.

3. 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:[4]

$$\frac{dq}{dt} = D_s \frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dq}{dr} \right) \qquad [2]$$

where r is the radial position, D_s is the solid phase diffusion coefficient and t is time.

In order to solve equation (2) Crank's method[5] 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, the equation to determine D_s may be written as:

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

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15-16 May 2001, NTNU, Trondheim, Norway
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where 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 a constant. Thus, a plot of q/q_∞ *versus* the square root of time gives a straight line of slope $6(D_s/pr^2)^{1/2}$.

The kinetic experiments were carried out in a 16 m³ vessel (diameter 0.27 m) at the temperature 17 °C during four days. The reactor was properly mixed and samples were analysed with the Hewlett-Packard 8452A Diode-Array Spectrophotometer. The initial concentration of xylidine was 205 mg/l and GAC concentration was 0.67 g/l. The result of the kinetic run is shown in Figure 2.

The solid phase diffusion coefficient calculated by Crank's method[5] is $D_s = 7.41 \times 10^{-12}$ [m²/s]. According to Vermulen *et al*.[6] $D_s = 1.5 \times 10^{-10}$ m²/s and Huang *et al*.[7] $D_s = 1.23 \times 10^{-13}$ m²/s.

4. Breakthrough Curves and Conclusion

The isotherm parameters and diffusion coefficients obtained from equilibrium and kinetic run were included in the breakthrough curve calculation models of Rice[8] and Thomas.[9] Values of the input parameters are presented in Table 2.

The breakthrough curves were calculated utilising Thomas and Rice methods, and profiles were compared with laboratory experimental curves. Breakthrough curve predictions showed a satisfactory fit in some cases but more advanced methods should be used in order to predict the Xylidine contaminated groundwater breakthrough profiles in a packed bed adsorber.

Dynamic experiments were carried out with two separate *Pharmacia Biotech* columns (D = 16 and 26 mm). The results of the dynamic runs with data fitting are presented in figures 3 through 8.
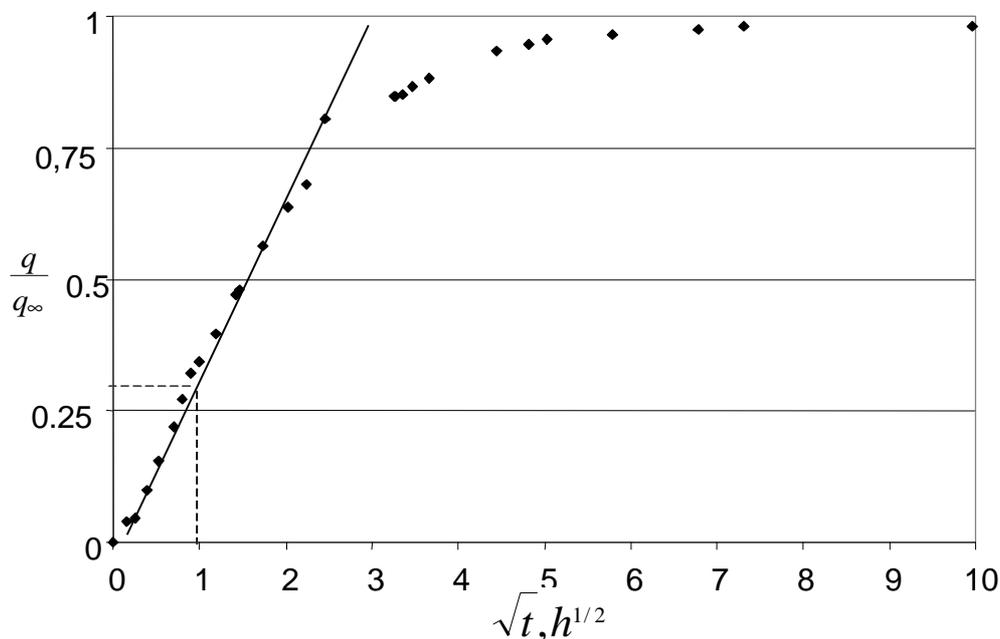
Figure 2. The 2,4-Xylidine kinetic run at a temperature of 17°C. The plot of $\bar{q}/q_\infty$ *versus* the square root of time.

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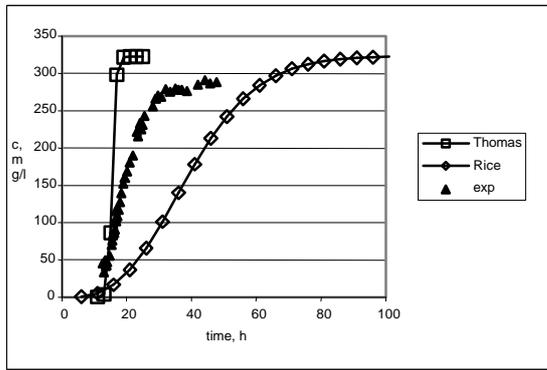
Figure 3. Bed depth is 0.235 m,
e= 0.414, u_0 = 6.6 cm/s
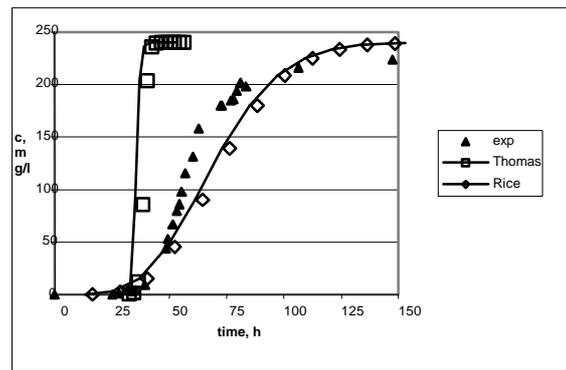
Figure 4. Bed depth is 0.245 m,
e= 0.36, u_0 = 4.4 cm/s
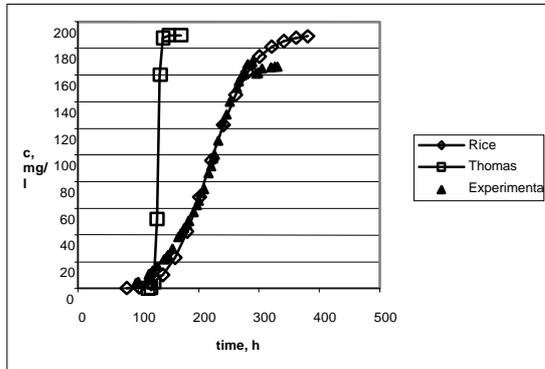
Figure 5. Bed depth is 0.3 mm,
e= 0.406, u_0 = 1.5 cm/s
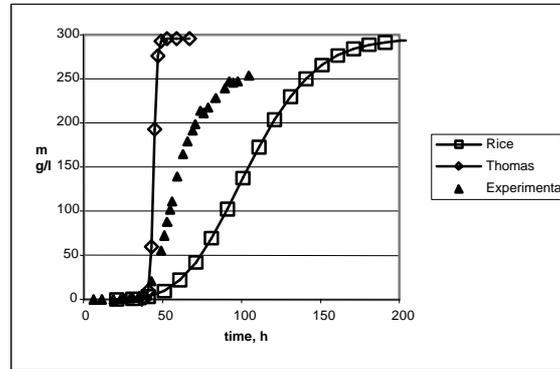
Figure 6. Bed depth is 0.24 m,
e= 0.414, u_0 = 2.6 cm/s
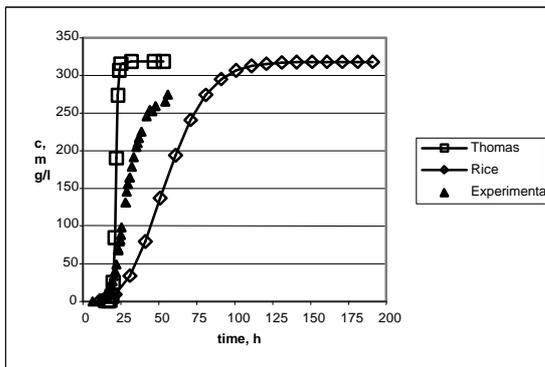
Figure 7. Bed depth is 0.208 m,
e= 0.406, u_0 = 4.4 cm/s
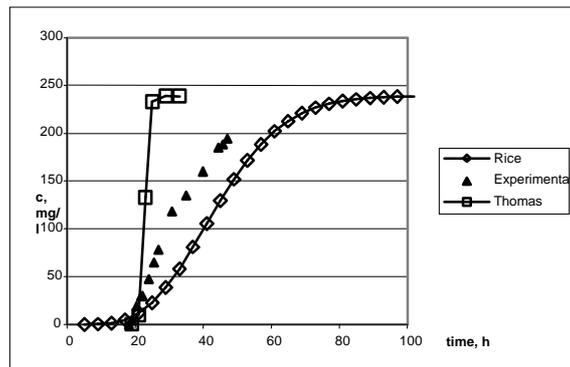
Figure 8. Bed depth is 0.38 m,
e= 0.382, u_0 = 10.4 cm/s

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Table 2. Input parameters for the Thomas and Rice calculation methods.

Parameter	Unit	Value
Average linear isotherm constant (for the Rice method), K (initial concentration 250 mg/l)	[m^3 liq / m^3 solid]	1090
Maximum adsorbable concentration on solid adsorbent (for the Thomas method), q_{max}	[kg/m^3]	145
Langmuir isotherm constant (for the Thomas method), b	[m^3/kg]	450
Solid phase diffusion coefficient,[4] D_s	[m^2/s]	$7.4 \cdot 10^{-12}$
Liquid phase diffusion,[10] D_f	[m^2/s]	$8.9 \cdot 10^{-10}$
Liquid phase viscosity,[11] μ	[Pa*s]	$9.47 \cdot 10^{-4}$
Liquid density, $?$	[kg/m^3]	988
Empty column superficial velocity, u_0	[m/s]	$2.6 \cdot 10^{-4} - 6.8 \cdot 10^{-3}$
Initial concentration, c_0	[kg/m^3]	0.19 – 0.32
Height of the bed, L	[m]	0.2 – 0.6
Void fraction in the bed, e	[m^3 fl/ m^3 bed]	0.23 – 0.42

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