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### GAC-ADSORPTION OF 5-METHYLRESORCINOL

The oil-shale mining and chemical industry, based mainly on the oil-shale thermal and chemical treatment, are the important branches of industry in the Republic of Estonia. Waste waters from these activities contain several toxic compounds, mostly phenols, resorcinols and their alkylderivatives. Up to present time limits for concentrations were established only for common phenols, not for resorcinols, that's why there are only a few papers [1, 2] concerning their removal from industrial effluents. At the same time the toxicity (measured as LD<sub>50</sub> for white mice) of the volatile phenols is only twice higher than for resorcinols.

According to rough estimates for the Kohtla-Järve Oil Shale Processing Plant waste waters the total content of phenols is 100 mg/l. From these total phenols over 95% are nonvolatile (resorcinols) and among resorcinols the 5-methylresorcinol (5MR) can be taken as a representative component as its concentration prevails.

It is known, that for phenolic waste waters treatment good results can be obtained with GAC-adsorption. From these considerations the task of this work arises - investigation of the possibilities of GAC-adsorption for purification resorcinols-containing waste waters.

In order to estimate the adsorption efficiency, the classical adsorption equilibrium, kinetics and dynamics studies were carried out using 5MR solutions and three component model solutions of 5MR, phenol and *p*-cresol. As an adsorbing matter GAC RB-1 (cylindrical granules of 0.97 mm in diameter with an average length of 2.7 mm) was used. 5MR concentration in the water was measured with spectrophotometer Hewlett-Packard 8452A (270 nm). The model solution was analyzed also with HPLC VARIAN 500.

Equilibrium tests were conducted at room temperature in cylindrical bulbs 100 ml in volume put on the magnetic mixer with waste water portions of 50 ml. Equilibrium experimental results are presented as adsorption isotherms and integral adsorption equilibrium curves (IAEC). Experimental isotherms were fitted in Freundlich

$$q = K c^n \quad (1)$$

and Langmuir isotherm equations

$$q = q_{max} \frac{c}{1/k + c} \quad (2)$$

where the coefficients  $K$ ,  $n$ ,  $q_{max}$  and  $k$  were calculated.

Fitting error for isotherms was found as

$$\delta = \frac{\sum |q_{exp} - q_{calc}|}{\sum q_{calc}} 100 . \quad (3)$$

From IAEC data the parameters for the characteristic distribution curve (CDC), according to the paper by Okazaki et al. [3] were determined, using equation

$$c_{calc} = \int_{x_{min}}^{x_{max}} \frac{(1 + k c_{exp}) c(x, 0)}{1 + k c_{exp} + k c_s x} dx , \quad (4)$$

where the initial concentration distribution of the solute was described as parabolic

$$c(x, 0) = A(x - B)(x - C) . \quad (5)$$

CDC parameter fitting was performed with the SMIN program [4], the objective function was evaluated as a sum of the square differences between experimental and calculated IAEC values. IAEC fitting error, presented here in Tables 1 and 2, was calculated as in the Okazaki's paper

$$E = \sum \frac{|1.0 - c_{calc}/c_{exp}|}{N_{exp}} 100 . \quad (6)$$

Obtained CDC were later used for calculating breakthrough curves (BC) accordingly [1].

Equilibrium experiments for 5MR solutions were performed in three runs, test conditions and calculated results are listed in Table 1 and presented in Figs. 1-3. Reason for the bigger contact time than usually (2 days) was, that we could expect the adsorption of resorcinols worse than for phenols. Test run I was therefore performed with twice longer contact time, run II after another week and run III continued two more weeks for studying the time factor influence.

Equilibrium experiments for the model solutions are presented in Table 2 and Figs. 4-6. Two different data sets are obtained via different equipment used for determining concentrations in the water.

The equilibrium experiments for 5MR proved that achieving the equilibrium conditions is a time-consuming process and the equilibrium adsorptivity is increasing with longer contact time considerably. With such as long contact time as in the run III, some biological oxidation possibly took place because the water turned turbid. Equilibrium test data on model solution give about 1.5 times greater adsorptivities when HPLC is used for concentration measurements than in the case with

Table 1. Experimental conditions and results for 5MR adsorption equilibrium tests.

Parameters	Run		
	I	II	III
Initial concentration of 5MR, mg/l	403	403	167
Number of test points	12	12	14
Contact time, day	4	11	25
Freundlich equation coefficients:			
$K$ , l/g	22.13	28.98	29.70
$n$	0.3378	0.3651	0.4313
Fitting error $\delta$ , %	4.38	5.04	7.53
Langmuir equation coefficients:			
$q_{max}$ , mg/g	145.16	193.72	269.93
$k$ , l/mg	0.0300	0.0416	0.0414
Fitting error $\delta$ , %	6.89	4.28	7.53
CDC parameters:			
$A$	$-1.0552 \cdot 10^{-4}$	$-2.6069 \cdot 10^{-5}$	$-6.1293 \cdot 10^{-6}$
$B$	1.9987	-4.9992	0.001644
$C$	298.74	494.445	559.220
$k$ , l/mg	0.111832	0.081161	0.083922
$x_{min}$ , mg/g	9.9974	19.9979	0.00176
$x_{max}$ , mg/g	236.524	332.6385	464.543
Fitting error $E$ , %	7.63	5.37	13.86

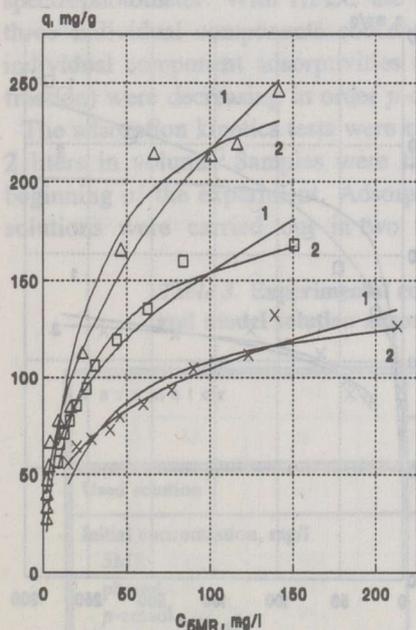


Fig. 1. The experimental ( $\times$  - run I;  $\square$  - run II;  $\Delta$  - run III) and calculated equilibrium isotherms (1 - Freundlich; 2 - Langmuir) for the 5MR

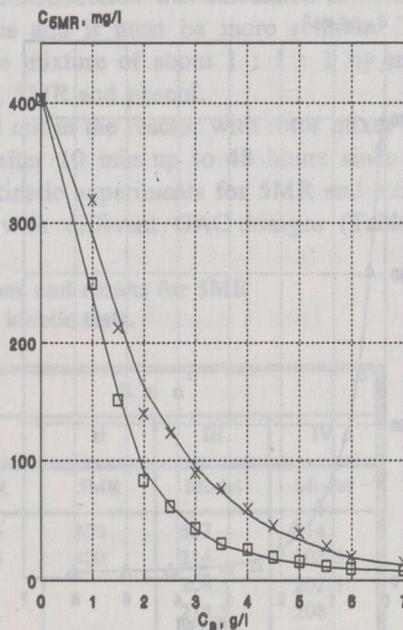


Fig. 2. The experimental ( $\times$  - run I;  $\square$  - run II) and calculated IAEC-s for the 5MR

Table 2. Experimental conditions and results for the model solution adsorption equilibrium test

Parameters	Data obtained with	
	Spectrophotometer	HPLC
Initial concentration, mg/l:	635.2	635.2
5MR		213.4
phenol		208.0
p-cresol		218.5
Number of test points	9	13
Contact time, day	3	3
Freundlich equation coefficients:		
$K$ , l/g	51.62	69.56
$n$	0.1528	0.2033
Fitting error $\delta$ , %	4.12	3.59
Langmuir equation coefficients:		
$q_{max}$ , mg/g	122.26	187.40
$k$ , l/mg	0.07102	0.2058
Fitting error $\delta$ , %	2.90	14.4
CDC parameters:		
$A$	$-1.1230 \cdot 10^{-4}$	$-1.7820 \cdot 10^{-5}$
$B$	-4.9994	-3.9364
$C$	349.96	667.96
$k$ , l/mg	0.2662	0.11648
$x_{min}$ , mg/g	$2.597 \cdot 10^{-3}$	$8.598 \cdot 10^{-5}$
$x_{max}$ , mg/g	240.003	427.528
Fitting error $E$ , %	4.13	29.3

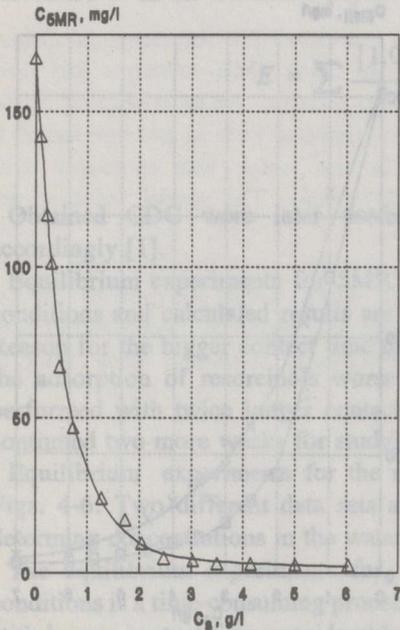


Fig. 3. The experimental ( $\Delta$ ) and calculated IAEC for the 5MR in test run III

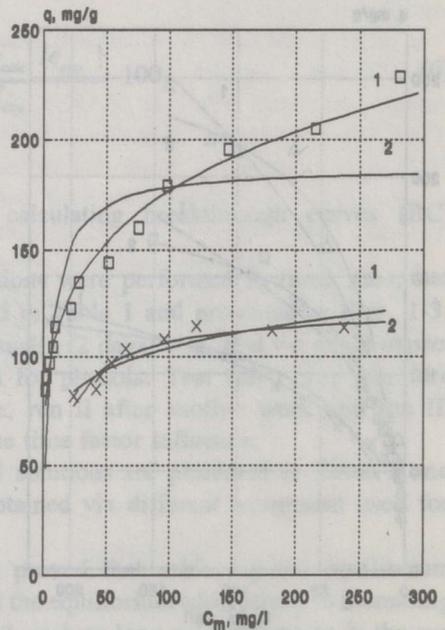


Fig. 4. The experimental ( $\times$  - spectrophotometer;  $\square$  - HPLC) and calculated equilibrium isotherms (1 - Freundlich; 2 - Langmuir) for the model solution

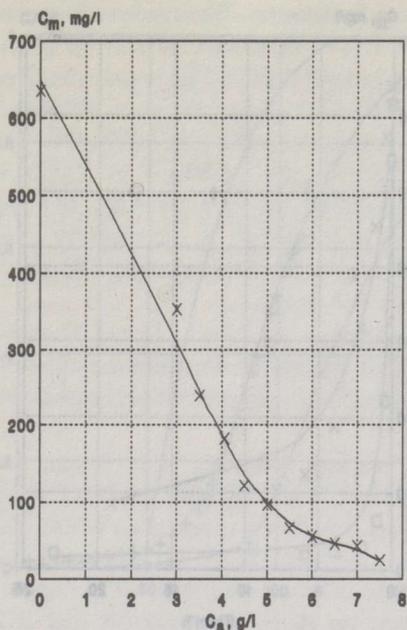


Fig. 5. The experimental (x) and calculated IAEC for the model solution by the spectrophotometer data

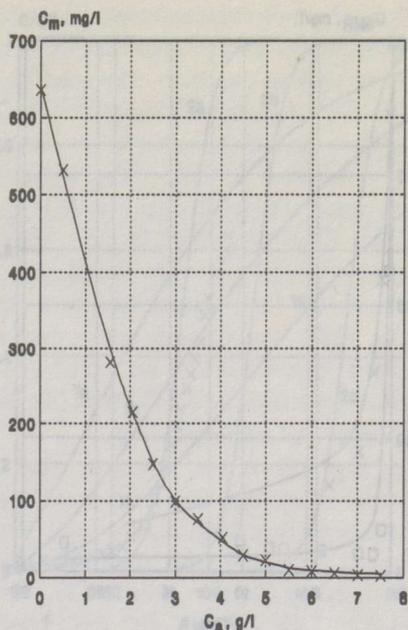


Fig. 6. The experimental (x) and calculated IAEC for the model solution by the HPLC data

spectrophotometer. With HPLC the total concentration was calculated as sum of three individual components concentrations and it must be more reliable. The individual component adsorptivities (in the mixture of about 1 : 1 : 1 by mass fraction) were decreasing in order *p*-cresol, 5MR and phenol.

The adsorption kinetics tests were carried out in the reactor with rotor mixer and 2 liters in volume. Samples were taken after 10 min up to 48 hours since the beginning of the experiment. Adsorption kinetic experiments for 5MR and model solutions were carried out in two runs with different GAC dosages (Table 3,

Table 3. Experimental conditions and results for 5MR and model solution adsorption kinetic tests.

Parameter	Run			
	I	II	III	IV
Used solution	5MR	5MR	Model	Model
Initial concentration, mg/l	398.5	400	637	614
5MR	398.5	400	214	203.5
phenol			204.5	202.5
<i>p</i> -cresol			218.5	208
GAC dosage, g/l	6.667	13.33	6.667	13.33
$D_s \cdot 10^{-12}$ , m <sup>2</sup> /s	0.094	0.295	0.0441	0.0472
$k_p$ , mg/(h <sup>1/2</sup> ·g)	26.91	28.45	35.57	35.42
$t^{1/2}$ , h <sup>1/2</sup>	0.968	0.510	1.17	0.629

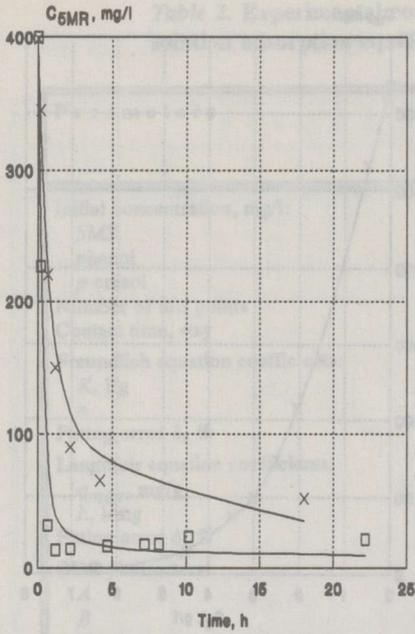


Fig. 7. The experimental ( $\times$  - run I;  $\square$  - run II) and calculated adsorption kinetics for the 5MR

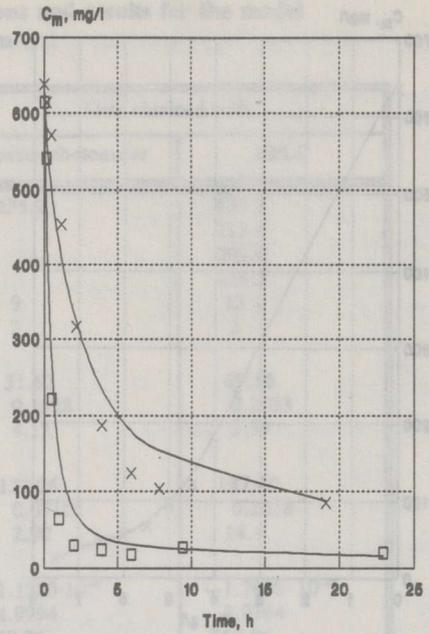


Fig. 8. The experimental ( $\times$  - run III;  $\square$  - run IV) and calculated adsorption kinetics for the model solution

Figs.7,8). In these tests concentration was measured only with spectrophotometer. For expression of the adsorption rate the effective (apparent) diffusion coefficients  $D_s$  of 5MR at infinite contact time [5] as well as the rate constant  $k_r$  of adsorbed 5MR concentration reduction and so called half life period  $t^{1/2}$  [6] were calculated. For  $k_r$  and  $t^{1/2}$  the assumption that relation between the concentration of adsorbed matter and square root from the contact time is linear at the starting period of adsorption was used.

Modeling of 5MR adsorption kinetics gives quite large dispersion of calculated effective diffusion coefficients.

Table 4. Experimental conditions for adsorption dynamic tests

Parameter	Run		
	I	II	III
Used solution	5MR	Model	Model
Initial concentration, mg/l:	155.7	578.1	571.8
5MR	155.7	189.0	189.8
phenol		190.1	189.3
p-cresol		199.0	192.7
Superficial velocity, cm/s	4.24	4.25	4.03
GAC bed height, cm	49	51.5	51.6
Bed voidage	0.437	0.449	0.45

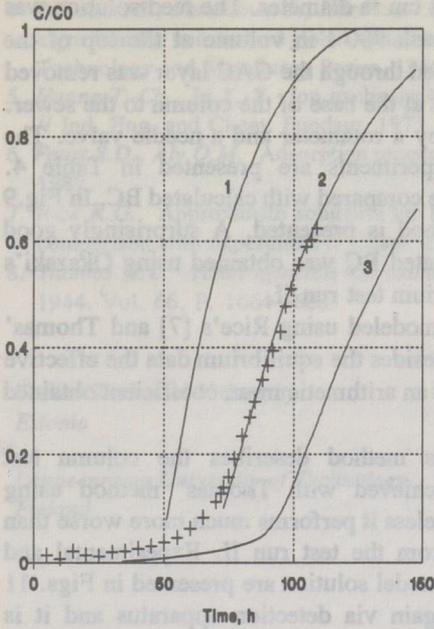


Fig. 9. The experimental (+) and calculated by the Okazaki's method BC-s for the 5MR (1 - CDC parameters from test run I; 2 - from test run II; 3 - from test run III)

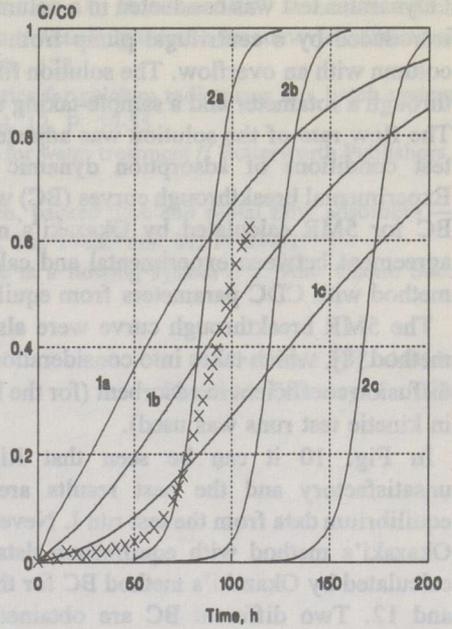


Fig. 10. The experimental (x) and calculated by the Rice's (1) and Thomas' (2) method BC-s for the 5MR (a - equilibrium data from test run I; b - run II; c - run III).

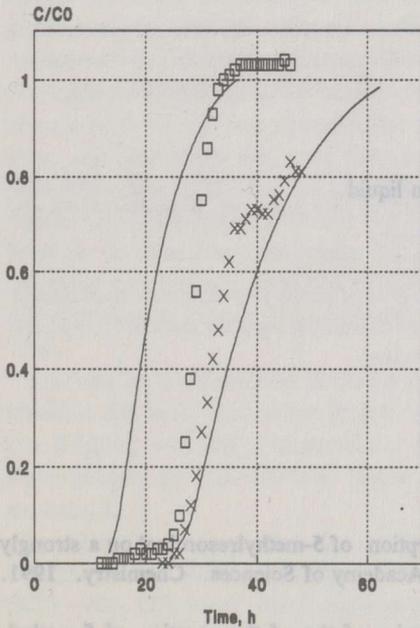


Fig. 11. The experimental (□ - spectrophotometer; x - HPLC) and calculated by Okazaki's method BC-s for the model solution in the dynamic test run II

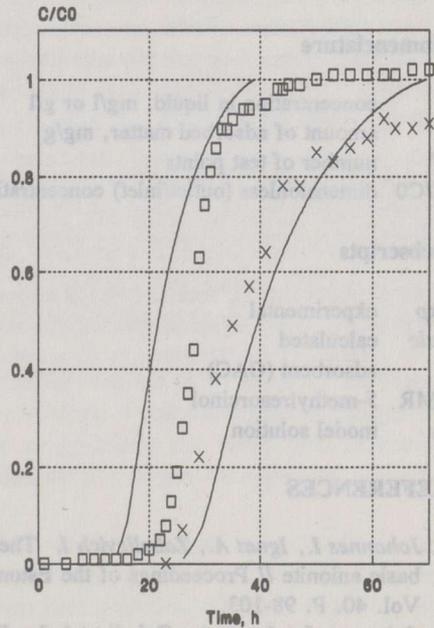


Fig. 12. The experimental (□ - spectrophotometer; x - HPLC) and calculated by Okazaki's method BC-s for the model solution in the dynamic test run III

Dynamics test was conducted in a column 4 cm in diameter. The feed solution was introduced by a centrifugal pump from a tank 900 l in volume at the top of the column with an overflow. The solution filtered through the GAC layer was removed through a rotameter and a sample-taking unit at the base of the column to the sewer. The flow rate of the solution was adjusted by a rotameter and a needle valve. The test conditions of adsorption dynamic experiments are presented in Table 4. Experimental breakthrough curves (BC) were compared with calculated BC. In Fig. 9 BC for 5MR calculated by Okazaki's method is presented. A surprisingly good agreement between experimental and calculated BC was obtained using Okazaki's method with CDC parameters from equilibrium test run II.

The 5MR breakthrough curve were also modeled using Rice's [7] and Thomas' method [8], which takes into consideration besides the equilibrium data the effective diffusion coefficient in adsorbent (for the last an arithmetic mean coefficient obtained in kinetic test runs was used).

In Fig. 10 it can be seen that Rice's method describes the column test unsatisfactory and the best results are achieved with Thomas' method using equilibrium data from the test run I. Nevertheless it performs much more worse than Okazaki's method with equilibrium data from the test run II. Experimental and calculated by Okazaki's method BC for the model solution are presented in Figs. 11 and 12. Two different BC are obtained again via detection apparatus and it is obvious that the HPLC data give better agreement between experimental and calculated results. The Rice's and Thomas' methods were worked out for calculating BC in one-component systems and the model solution was not modelled with these methods. The Okazaki's method predicts with sufficient accuracy the behaviour of the adsorption column in operation with resorcinols containing waste waters.

### Nomenclature

$c$	concentration in liquid, mg/l or g/l
$q$	amount of adsorbed matter, mg/g
$N$	number of test points
$C/C_0$	dimensionless (outlet/inlet) concentration in liquid

### Subscripts

$exp$	experimental
$calc$	calculated
$s$	adsorbent (GAC)
5MR	5-methylresorcinol
$m$	model solution

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