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SORPTION OF PHENOLS DERIVATIVES ON MACROPOROUS 2,3-EPOXYPROPYLMETHACRYLATE-N-VYNILPYRROLIDINE-ETHYLENEDIMETHACRYLATE COPOLYMERS

The adsorption process of phenols derivatives onto macroporous copolymers with different contents of two monomers from water solutions has been investigated. The rows of phenols input onto six copolymers have been established.

Introduction

In our previous work we described the sorption of aromatic compounds from water by methacrylate and functionalized methacrylate [1—3] and styrene-divinylbenzene [4] macroporous copolymers. To understand the mechanisms of polymer-adsorbate interaction the effect of chemical structure of adsorbate was investigated.

2. Experimental

2.1. Materials

Copolymers synthesis

The copolymers were prepared by employing the same procedure as before [5]. The copolymers denoted so that the first number relates to the content of 2, 3-epoxypropyl methacrylate (GMA), and the second number relates to the content of N-vinylpyrrolidone (VP) in wt.%. The content of the crosslinking agent (ethylene dimethacrylate) was 40 wt.% in any case.

2.2. Methods

Characterization of adsorbents

The retention of water and cyclohexane by copolymers was determined by the centrifugation technique, the specific surface area of dry membranes was determined by the thermal desorption of nitrogen.

Sorption properties

Macroporous copolymers (0.01—0.03 g) was suspended in citrate-phosphate buffer pH 6.6 (5 ml) containing 0.25, 0.5, 1.25, 2.5, or 5.0 mg of phenol compound/ml and shuttled for 72 h. Then the water phase was analysed for the content of phenols spectrophotometrically on spectrophotometer Specord M-40. The content of adsorbate was determined at following wavelengths: Phenol 270, hydroquinone 237, p-nitrophenol 322, o-nitrophenol 273, and p-chlorophenol at 280 nm.

Buffer was prepared by mixing solutions of 0.1 M citric acid and 0.2 M sodium orthophosphate mono H to pH 2.2, 3.6, 5.0, 6.6, and 8.0.

The equilibrium sorption capacity of the adsorbent was calculated by the following eq.:

$$m = (c - c_p) \times V/g,$$

where c is the starting solution concentration, c_p is the equilibrium solution concentration (mg/ml), V is the solution volume (ml) and g is the weight of the adsorbent.

The coefficients of the Langmuir isotherm were calculated according following eq.:

$$1/m = 1/m_c + 1/(m_c K)*1/c_p$$

where m is the sorption capacity of adsorbent, c_p is the equilibrium concentration of phenol in solution, m_c is the calculated equilibrium sorption capacity and K is calculated coefficient.

3. Results and discussion

Sorption of different phenol derivatives on macroporous copolymers of GMA-VP-EDMA and aminolyzed copolymers were studied to understand the effect of the adsorbate on sorption. Three copolymers were prepared with a rising amount of vinylpyrolidone, 0,30 and 55 %, and a constant amount of crosslinker, 40 %. Properties of this copolymers as pore volume, specific surface area and mean pore radius are shown in table 1.

As follows from the fig. 1 the sorption on G60, a mean polar adsorbent of the II type according to the Kiselev classification, the phenol derivatives are sorbed in the following row

Phenol < Hydroquinone < p-Chlorophenol < < p-Nitrophenol

On the GP30—30 (fig. 2) one can see the following input legitimacy:

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Table 1

Composition and porous structure characteristics of methacrylate sorbents

Sorbent	% N	Solvent regain ml/g		S_g	r
		Water	Cyclohexane	m^2/g	nm
G60	—	2.08	1.40	60	69.3
G60-NH_2	2.32	1.39	1.07	48	57.9
GP30-30	2.16	1.66	0.64	54.7	60.7
GP30-30-NH_2	3.75	1.81	0.91	73.6	48.2
GP5-55	4.42	2.33	0.022	13.4	347.8
GP5-55-NH_2	5.13	2.62	0.19	10.5	493.0

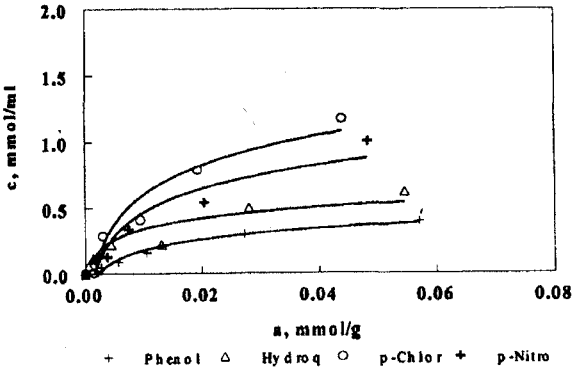

Fig. 1. Sorption isotherms of Phenols on G60

Hydroquinone < Phenol < p-Nitrophenol < < p-Chlorophenol

Finally, on the GP5-55 (fig. 3) the following picture can be seen:

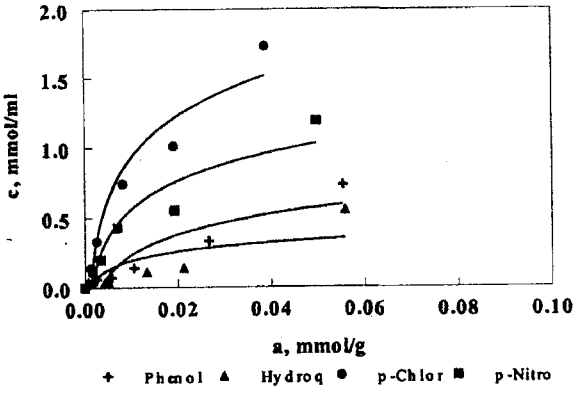

Fig. 2. Sorption isotherms of Phenols on GP30-30

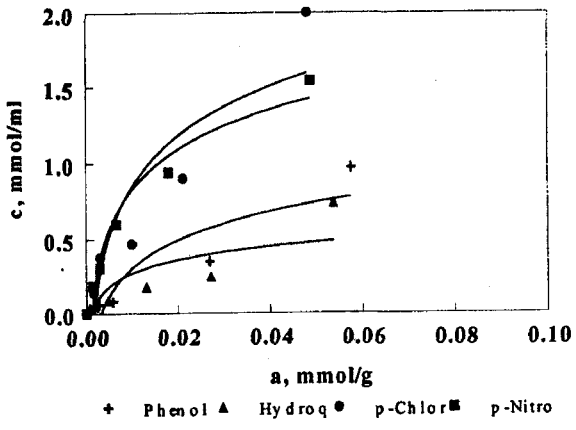

Fig. 3. Sorption isotherms of Phenols on GP5-55

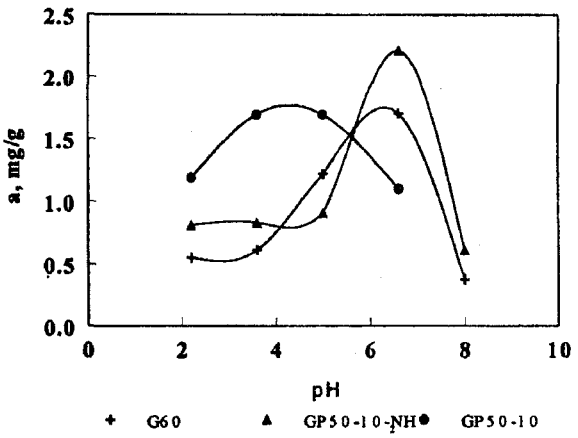

Fig. 4. pH Dependence on Phenol Sorption for Phenols

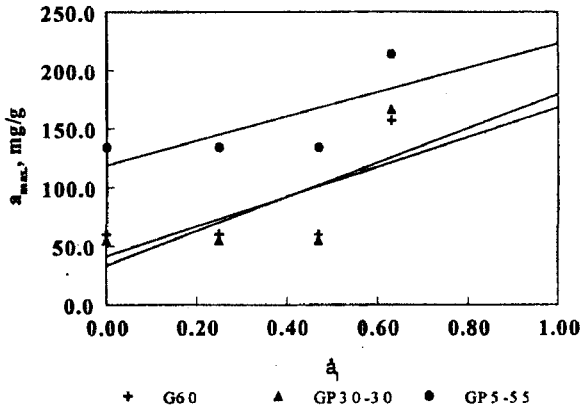

Fig. 5. Correlation of a_{max} with $\mathring{a}_1$ for Phenols

Hydroquinone < Phenol < p-Chlorophenol < < p-Nitrophenol

The determined row is in principal in agreement with the electro-negativity of the phenol substitutent (fig. 5). The sorbed amount of phenols rise with the value of the Taft σ_I constant, which for H–, HO–, Cl–, NO_3– groups are 0.00, 0.25, 0.47, and 0.67, respectively. There is a very high effect especially of nitro-group on sorption.

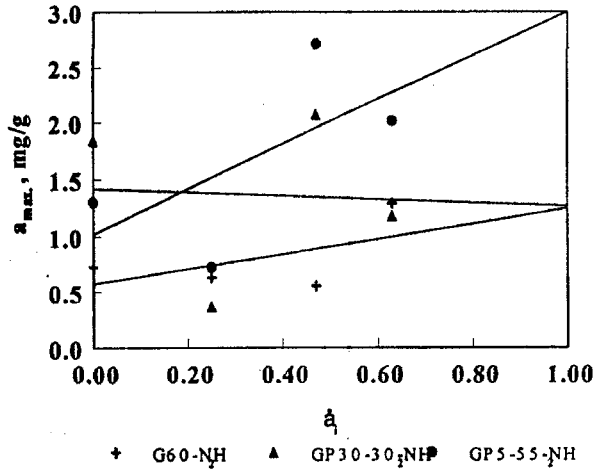

Fig. 6. Correlation of a_{max} with $\mathring{a}_1$ for Phenols

In the case of amino derivatives of G60-NH_2, understandable. Because of the ionization of the GP30—30—NH_2, and GP5—55—NH, there is not weak basic NH_2-groups the mechanism of sorption the effect of substitution so simple and proceed through the ionic bond and therefore the

Table 2

Phenol Sorption on Macropous Copolymers of N-vinylpyrrolidone
Conditions: Sortent 0.01-0.03g, nitrate-phosphate puffer pH6,6 5ml.

G-60		G60-NH_2		GP30-30		GP30-30-NH_2		GP5-55		GP5-55-NH_2	
c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g
0	0	0	0	0	0	0	0	0	0	0	0
0.0027	0.05	0.002	0.06	0.003	0.06	0.003	0.04	0.0027	0.06	0.0027	0.05
0.0057	0.09	0.006	0.09	0.006	0.07	0.006	0.07	0.0058	0.08	0.0059	0.05
0.0106	0.16	0.011	0.16	0.011	0.14	0.011	0.16	0.0269	0.35	0.0106	0.15
0.0273	0.30	0.028	0.34	0.027	0.33	0.026	0.35	0.0575	0.45	0.0266	0.39
0.0571	0.40	0.058	0.45	0.055	0.50	0.056	0.50			0.055	0.60

Table 3

p-Chlorophenol Sorption on Macropous Copolymers of N-vinylpyrrolidone

G-60		G60-NH_2		GP30-30		GP30-30-NH_2		GP5-55		GP5-55-NH_2	
c mmol/ml	A mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g
0	0	0	0	0	0	0	0	0	0	0	0
0.0015	0.1	0.002	0.09	0.001	0.14	0.002	0.14	0.0016	0.14	0.0012	0.12
0.003	0.29	0.003	0.2	0.003	0.33	0.004	0.14	0.0031	0.38	0.0024	0.28
0.0095	0.41	0.011	0.28	0.008	0.74	0.003	0.38	0.0100	0.47	0.0078	0.57
0.0193	0.79	0.021	0.35	0.019	1.01	0.01	0.47	0.0211	0.90	0.0165	1.05
0.0439	1.17	0.045	0.51	0.039	1.30	0.021	0.90	0.0480	1.30	0.0375	1.30
						0.048	1.20				

Table 4

Hydrochinone Sorption on Macropous Copolymers of N-vinylpyrrolidone

G-60		G60-NH_2		GP30-30		GP30-30-NH_2		GP5-55		GP5-55-NH_2	
c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	C mmol/ml	a mmol/g	c mmol/ml	a mmol/g
0	0	0	0	0	0	0	0	0	0	0	0
0.0006	0.06	0.003	0.05	7E-04	0.04	8E-04	0.02	0.0007	0.04	0.0006	0.05
0.0014	0.12	0.011	0.13	0.002	0.05	0.002	0.02	0.0017	0.05	0.0016	0.05
0.0045	0.22	0.058	0.25	0.005	0.04	0.005	0.01	0.0048	0.09	0.0046	0.15
0.0131	0.22	0.058	0.35	0.013	0.11	0.014	0.12	0.0132	0.18	0.0130	0.39
0.0281	0.50			0.021	0.14	0.028	0.16	0.0272	0.25	0.0261	0.50
0.0546	0.62			0.056	0.30	0.056	0.25	0.0537	0.35	0.0548	0.56
										0.0543	0.65

Table 5

p-Nitrophenol Sorption on Macropous Copolymers of N-vinylpyrrolidone

G-60		G60-NH_2		GP30-30		GP30-30-NH_2		GP5-55		GP5-55-NH_2	
c mmol/ml	A mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	A mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g
0	0	0	0	0	0	0	0	0	0	0	0
0,0016	0,11	2E-04	0,12	0,002	0,12	0,002	0,13	0,0014	0,19	0,0014	0,14
0,0038	0,13	0,003	0,2	0,003	0,2	0,004	0,17	0,003	0,31	0,0031	0,24
0,0075	0,34	0,007	0,43	0,007	0,43	0,008	0,39	0,0066	0,60	0,0065	0,50
0,0204	0,54	0,019	0,55	0,019	0,55	0,02	0,53	0,018	0,94	0,0172	0,93
0,0483	1,00	0,05	0,80	0,05	1,00	0,05	0,85	0,0487	1,30	0,046	1.15

Table 6

o-Nitrophenol Sorption on Macropous Copolymers of N-vinylpyrrolidone

G-60		G60-NH_2		GP30-30		GP30-30-NH_2		GP5-55		GP5-55-NH_2	
c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g	c mmol/ml	a mmol/g
0	0	0	0	0	0	0	0	0	0	0	0
0.0005	0.05	8E-04	0.03	6E-04	0.03	6E-04	0.02	0.0004	0.05	0.0006	0.02
0.0012	0.08	0.001	0.09	0.002	0.04	9E-04	0.15	0.0012	0.05	0.0012	0.05
0.0018	0.13	0.002	0.24	0.002	0.09	0.001	0.03	0.0016	0.09	0.0017	0.08
0.0034	0.19	0.004	0.25	0.005	0.16	0.001	0.25	0.0032	0.24	0.0036	0.16
0.0067	0.9	0.01	1.32	0.007	0.46	0.006	0.11	0.0064	0.44	0.007	0.35
						0.004	0.14				
						0.007	0.42				
						0.007	0.44				

Table 7

pH Dependence of Phenol Sorption

G60		GP50-10-NH_2		GP50-10	
PH	a mg/g	pH	a mg/g	PH	a mg/g
2.2	0.55	2.23	0.81	2.18	119
3.6	0.61	3.59	0.82	4.99	1.69
5.0	1.22	5	0.91	6.58	1.69
6.6	1.7	6.59	2.1	8.04	1.1
8.0	3.75	8.018	0.61		

Table 8

Constants of Langmuir Equation

Sorbent	Phenol			p-Chlorophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	60	0.34	0.991	60	0.34	0.991
GP30-30	55	0.45	0.989	55	0.45	0.989
GP5-55	134	0.16	0.995	134	0.16	0.995
G60-NH2	197	0.27	0.996	197	0.27	0.996
GP30-30-NH2	134	0.11	0.994	134	0.11	0.994
GP5-55-NH2	50	0.33	0.999	50	0.33	0.999

Sorbent	Hydrochinone			p-Nitrophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	60	0.34	0.991	157	0.48	0.995
GP30-30	55	0.45	0.989	167	0.51	0.997
GP5-55	134	0.16	0.995	214	0.75	0.997
G60-NH2	197	0.27	0.996	175	0.25	0.995
GP30-30-NH2	134	0.11	0.994	140	0.64	0.995
GP5-55-NH2	50	0.33	0.999	293	0.35	0.999

Продовження табл. 8

Sorbent	Phenol			p-Chlorophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	0.511	50 580	0.912	1.450	5 489	0.893
GP30-30	0.825	27 150	0.729	1.493	10 540	0.968
GP5-55	0.590	47 540	0.876	1.524	6 461	0.923
G60-NH_2	0.567	50 150	0.893	0.552	10 840	0.964
GP30-30-NH_2	0.825	23 590	0.695	1.556	4 656	0.843
GP5-55-NH_2	1.302	13 110	0.405	1.607	7 840	0.936
Sorbent	Hydroquinone			p-Nitrophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	0.664	87820	0.981	1.281	4691	0.844
GP30-30	0.342	35090	0.806	1.173	7123	0.931
GP5-55	0.385	6039	0.957	1.472	11290	0.978
G60-NH_2	0.424	38020	0.923	0.849	16330	0.977
GP30-30-NH_2	0.372	25950	0.831	0.980	8105	0.947
GP5-55-NH_2	0.725	51030	0.959	1.371	9590	0.961

Constants of Freundlich Equation.

Sorbent	Phenol			p-Chlorophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	1.307	0.496	0.968	1.732	0.325	0.808
GP30-30	1.406	0.515	0.947	1.493	0.269	0.758
GP5-55	1.349	0.495	0.956	1.674	0.279	0.782
G60-NH_2	1.302	0.472	0.968	1.205	0.346	0.948
GP30-30-NH_2	1.540	0.546	0.933	1.377	0.292	0.791
GP5-55-NH_2	1.621	0.553	0.909	1.854	0.294	0.760
Sorbent	Hydroquinone			p-Nitrophenol		
	m, mg/g	*K*, ml/g	*r*	*m*, mg/g	*K*, ml/g	*r*
G60	1.472	0.378	0.957	1.609	0.398	0.872
GP30-30	0.866	0.454	0.954	1.535	0.323	0.859
GP5-55	1.184	0.468	0.992	1.634	0.249	0.783
G60-NH_2	1.216	0.502	0.978	1.385	0.288	0.934
GP30-30-NH_2	1.192	0.591	0.988	1.450	0.328	0.896
GP5-55-NH_2	1.846	0.467	0.931	1.693	0.293	0.798

polarity effect of the phenol substituent is not so important.

The effect of pH was determined on G60, GP50—10 and GP50—10—NH, copolymers. On G60 and GP50—10—NH, maximal value of sorption at pH 6.5 were observed. On GP50—10 the maximal value of sorption was at pH 4. See table 7 and fig. 4.

The determined values of phenols sorption on glycidylmethacrylete-vinylpyrrolidone copolymers were tested with Langmuir and Freundlich isotherms, respectively (table 8 and 9). It is hardly to distinguish the better fulfilling of the isotherm. For the data in the figs. 1—3, the model of Freundlich isotherm was used.

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СОРБЦІЯ ФЕНОЛІВ НА МАКРОПОРИСТИХ СОПОЛІМЕРАХ 2,3-ЕПОКСИПРОШЛМЕТАКРИЛАТ-N-ВІНІЛПІРРОЛІДИНІ ЕТИЛЕНДІМЕТАКРИЛАТІ

Досліджено процес адсорбції фенолів з водного розчину на макропористих сополімерах з рівним вмістом двох мономерів. Адсорбція фенолів досліджена на шести сополімерах різного складу.