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SORPTION OF PHENOL BY SIMPLE AND MODIFY 2, 3-EPOXIPROPYLMETHACRYLATE-VINYLPYRROLIDONE COPOLYMERS

The sorption of phenol under the static and dynamic conditions onto GMA- VP-EDMA copolymers with different chemical compositions has been investigated. It has been established sorption of phenol rises with the amount of the vynilpyrrolidone in the copolymer increasing. The influence of pH and different conditions onto sorption processes has been explored.

Introduction

Carbonaceous adsorbents are preferentially used as sorbents for organic compounds [1] as e. g. phenols [2,3]. The interaction between carbon and phenol occurs due to physical adsorption and in the small amount also by H-bond forming with the surface hydroxyl groups of the adsorbent. The interaction with Lewis acids, which are somewhere on the surface, is also possible. The acid groups in the intense of Brönstedt theory were not on the active carbon surface detected. The organic compounds are adsorbed very strongly and therefore desorption is impossible in some cases.

The synthetic polymeric porous materials, is a group of adsorbents, which were first time synthesized in the end of 50ies. It is possible to vary the porous structure of polymeric adsorbents of the same chemical composition in the large interval. Using an inert solvent in a mixture with reagents forms the porous structure. The solvent should be a good solvent of monomers, and practically should not solve the polymers. In the role of the inert solvent paraffins are more advantageous. It is possible to change the chemical structure of polymeric adsorbents in wide polarities. By varying of the starting monomers by the synthesis of porous polymers it is possible to obtain adsorbents, with prevailing hydrophobic or hydrophilic properties. Mostly hydrophobic are the styrene-divinylbenzene copolymers; methylmethacrylate and vinylpyridine copolymers are more polar and therefore are behave of properties for sorption of the polar compounds from water solutions.

Polymeric adsorbents are used for adsorption of aliphatic and aromatic nitro and chloro derivatives. From the great row of polymeric adsorbents

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for sorption of phenols were recommended preferentially the macroporous styrene-divinylbenzene copolymers [4—5] and also more polar acrylic or methacrylic acid with divinylbenzene [6].

The absolute value of the Gibbs standard molar energy of p-chloroaniline adsorption by styrene-divinylbenzene copolymers lowers that of active coals [7]. As follows from the Table the values $-\Delta G^\circ$ of p-chloroaniline adsorption by styrene-divinylbenzene copolymers are between 16.9 and 21.4 kJ/mol. The last value was determined on copolymer with the narrow pore distribution. On opposite the values $-\Delta G^\circ$ of p-chloroaniline adsorption by microporous active carbon KAD and active antracene is equal 23.4 kJ/mol.

One of reasons for explanation of the lower adsorption energy of styrene-divinylbenzene copolymers in comparison with active carbons is shading of the carbon atoms of the polymeric chains by the hydrogen atoms in the matrix of styrene-divinylbenzene copolymer. The hydrogen preserves such narrow contact between the carbon atoms of the polymer and the adsorbate to such distance, which is achieved on the carbonaceous materials. And the dispersion forces decreases very intensively with the increasing distance.

Secondly, in the pores of styrene-divinylbenzene copolymers is not the loading effect of adsorption potentials in narrow micropores, amount of which is in styrene-divinylbenzene copolymers very low. In the Polisorb 40/100 this value did not dwarf 6 % of the pore sum.

This difference between polymeric adsorbents and carbonaceous is employed in the technology. Because of the lower adsorption energy it is easier to desorb the adsorbed compound by the solvent or vapour from polymer, than from active coal. And therefore also the regeneration of polymeric

adsorbents by solvents is more economical in comparison with the regeneration by same method of microporous adsorbents, which included mainly carbonaceous adsorbents.

But also desorption from styrene-divinylbenzene copolymers didn't proceed quantitatively.

The sorption of phenols by macroporous copolymers is affected also by diffusion in the mass of polymer. The diffusion coefficient depends preferentially on the primary particle size, which forms the primary structure of the porous polymer and on the ratio of effective diffusion coefficient and of the molar diffusivity of the adsórbate, which the function of the mean value of the slope working curve at different temperatures. This constant is independent on the adsórbate but depends on the physical properties of the adsorbent.

For the sorption of phenol the macroporous vinylpyridine [8] copolymers and gel-like poly-vinylacetate copolymers with silanes [9] were recommended. The last are exhibit a unbelievable high sorption of 4-chlorophenol (1033 mg/g of dry polymer), but it is necessary to take into a account that the interaction with the last copolymer proceeds by a different mechanism. Absorption with the volume swelling and volume changes of the copolymer hindrances the following desorption.

The sorption of phenols were studied on methacrylate copolymers in the form of spherical beads and compared with sorption on styrene-divinylbenzene copolymers. By using the linear free energy relationship the ionic mechanism of sorption was confirmed on the aminoderivatives of metha-crylate copolymers.

Experimental   Part

Copolymerization

The solution of monomers and initiator in inert solvent (see table 1) was deoxygenated with a flow of nitrogen and than degassed under the vakuum for 10 minutes and ultrasonic stirred. Then the solution was injected into the form, which consists from heated desks (10x10 cm) covered by a polypropylene foil and silicone distance packing (thickness 1 mm). The polymerization was provided at 70 °C for 9 hours. The obtained membrane was decanted during a week by 3 x 250 ml of ethanol, mixture ethanol-water (1:1) and on the end by distilled water.

Modification **with ammonia**

The 2,3-epoxipropyl methacrylate — vinyl-pyrrolidone copolymers were suspended in aqueous ammonia (27wt.%) and heated for 3 hours at 70 °C. Then the polymer was washed out with distilled water to the pH 7. Modified polymers we used for the further sorption measurements.

The sorption of phenol was investigated under the static and dynamic conditions.

Under the static conditions were the wet copolymer (0.1 g) was mixed and stirred with 5 ml of the buffered phenol solution of different concentration for 24 hours at 25 °C. The adsorbed amount of phenol was evaluated determined from the difference of phenol concentration before and after sorption by spectrophotometric measurement according to the band at 280 nm.

Under the dynamic condition the phenol sorption was investigated by flow of the phenol solution (5 mmol/1, pH 7) by the flow rate 0.2 ml/min through the column or the cell with the membrane of diameter 2 cm and thickness 1 mm. The desorp-tion was provided by water flow at flow rate 1 ml/min. The concentration of phenol behind the column was detected by the refractometer Waters 401. From the brahe-through curves and flow rate values the sorption capacity was evaluate.

Results   and   Discussion
Sorption of Phenol

Poly(N-vinylpyrrolidone) form complexes with phenols [10], therefore the complexis stability constants exhibit relatively high values we used macroporous polymers of vinylpyrrolidone in the form of particles or beads for sorption of phenols from water. The sorption of phenol rise (table 3) with the amount of the vinylpyrrolidone in the copolymer. The low sorption of G60 confirms our earlier experience. The macroporous copolymer G5 sorb in the batch method 0.34 to 0.53 mmol phe-nol/g. The sorption of macroporous copolymers derivatives under dynamic conditions was similar and the values are changed in the interval from 0.1 to 0.5 mmol/g of dry polymer.

Under the dynamic conditions (table 5) the highest sorption was observed with GP30−30 copolymer. This is the copolymer with the highest internal specific surface area and therefore also with the highest amount of micropores.
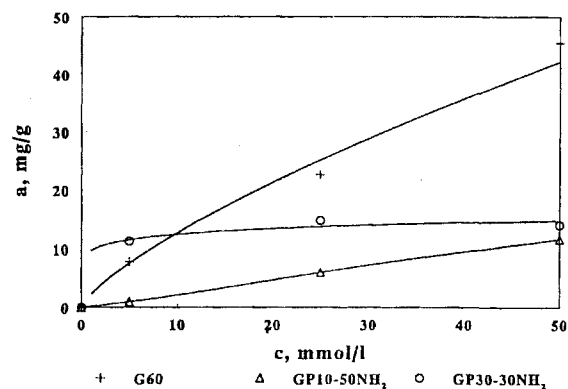

Fig. Sorption isotherms of phenol on GMA-VP-EDMA membranes and membranes modified with ammonia

The determined sorption isotherm (fig.) confirms the adsorption mechanism of sorption in the case of copolymers without functional groups because of linearity of the isotherm. In the case of derivatives saturation occurs what shows the sorption according to the ionic bonds.

The desorbed amount of phenol in the limits of experimental errors confirms that the membranes are fully regenerable by using pure water only,

Table 1

Composition between monomeric mixture and of copolymers

Copolymer	GP-5-55	GP-10-50	GP-30-30	GP-50-10
Composition of monomeric mixture				
GMA, ml	0.3	0.6	1.8	3
VP, ml	3.3	3	1.8	0.6
EDMA, ml	2.4	2.4	2.4	2.4
Solvent	9	9	9	9
ABIBN, g	0.06	0.06	0.06	0.06
Composition of polymers				
% C	58.61	60.22	59.09	59.36
	58.57	59.90	59.13	59.10
% H	8.18	8.04	7.74	7.46
	8.13	7.99	7.79	7.55
% N	4.40	4.00	2.13	0.82
	4.45	4.00	2.19	0.83

Table 2

Pore radius of GMA- VP-EDMA Membranes and Membranes Modified with Ammonia in Dry and Swollen state

Membrane	Starting membrane		Ammonia modified	
	a*	b**	a	b
GP-5-55-NH_2	347	0.6	499	14.7
GP-10-50-NH_2	266	3.6	146	16.0
GP-30-30-NH_2	60.7	6.8	49.2	24.5
GP-50-10-NH_2	67.3	10.5	48.9	30.8
G-60-NH_2	43.7	65.0	58.0	54.6

a — in the swollen state.

** b — in the dry state.

Table 3

Sorption of Phenol (mg/g) on GMA- VP-EDMA Membranes by Batch Method
Conditions: cca 0.1 g of wet copolymer, 5ml of phenol solution 1 ml buffer, 24 hours, 25°C

Phenol solution conc., mg/l	5.1	6.8	4.3
PH	4	6	8
GP-10-50	6.13 (0.065)	6.83 (0.073)	5.33 (0.062)
GP-30-30	5.37 (0.057)	5.31 (0.056)	5.45 (0.058)
GP-50-10	5.65 (0.060)	6.35 (0.067)	5.77 (0.061)
G-60	4.44 (0.047)	5.00 (0.053)	4.61 (0.049)

In brackets mmol of phenol sorbed/g of wett polymer.

Table 4

Hydrodynamic properties of GMA-VP-EDMA Membranes

Polymer	Starting Copolymer			Modified Copolymer		
	Pressure, atm	r, nm	Permeability, $m/h \cdot 10^5$	Pressure, atm	r, nm	Permeability, $m/h \cdot 10^2$
GP-5-55	0.5	4.3	0.6	2.5	14.7	41.7
	1	4.1	1.3	3	14.1	44.7
	2	3.7	2.0	3.5	15.1	59.5
	3	3.7	3	4	15.0	60.6
	4	3.8	4.1	—	—	—
GP-10-50	0.5	3.6	0.48	3	16	61.7
	1	3.4	0.86	3.5	15	69.7
	2	3.5	1.8	4	15	76.3
	3	3.5	2.6	4.5	15	71.4
	4	3.5	3.6	—	—	—
GP-30-30	0.5	6.8	1.5	2	24.5	81.2
	1	5.9	2.2	2.5	23.8	95.8
	2	5.7	4.1	3	24.0	117
	3	5.7	6.1	4	24	156
	4	5.7	8.3	—	—	—
GP-50-10	0.5	10.5	4.1	1.5	30.8	167
	1	9.7	6.9	2	40.4	245
	2	9.5	13.2	2.5	42.5	339
	3	9.5	20.0	3	41.7	392
	4	9.7	27.7	—	—	—
G-60	0.5	65	167	1.5	54.6	330
	1	54.4	234	2	53.3	420
	2	53.6	456	2.5	53.7	535
	3	53.1	670	3	53.7	639
	4	53.9	921	—	—	—

Table 5

Dynamic sorption capacity of GMA-VP-EDMA Membranes for phenol.
Conditions: 5 mmol/1 Phenole, pH 7, now rate 0.2 ml/min

Copolymer	Adsorption		Desorption	
	mmol/g	mg/g	mmol/g	mg/g
GP-5-55	0.028	2.65	0.038	3.55
GP-10-50	0.027	2.55	0.012	1.17
GP-30-30	0.112	10.53	0.113	10.7
GP-50-10	0.011	1.08	0.025	2.20
G-60	0.083	7.82	0.084	7.92
GP-5-55-NH_2	0.030	2.81	0.020	1.86
GP-10-50-NH_2	0.010	0.94	0.168	15.86
GP-30-30-NH_2	0.120	11.28	0.195	18.34
GP-50-10-NH_2	0.081	7.62	0.085	7.97
G-60-NH_2	0.064	6.00	0.079	7.44

Sorption isotherms of Phenol.
Conditions: pH 7, flow rate 0.2 ml/min

Solution conc., mmol/l	G-60		GP-10-50-NH₂		GP-30-30-NH₂	
	mmol/g	mg/g	mmol/g	mg/g	mmol/g	mg/g
Adsorption						
5	0.083	7.8	0.010	0.94	0.120	11.3
25	0.241	22.6	0.064	6.0	0.157	14.8
50	0.484	45.5	0.125	11.7	0.150	14.1
Desorption						
5	0.084	7.9	0.016	1.5	0.195	18.3
25	0.152	14.3	0.162	15.2	0.705	66.3
50	0.894	84.0	0.893	83.9	0.725	68.1

Mechanical properties   of macroporous   membranes

Polymer	E_s, kPa	E_b, kPa	σ_b, kPa	ε_b, %
GP-5-55	11 300	4 220	150	3.6
GP-10-50	14 720	4 100	29	0.7
GP-30-30	22 020	13 500	283	2.1
GP-50-10	57 530	26 300	1088	4.1
G-60	2 736	1 597	63.4	4.0

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СОРБЦІЯ ФЕНОЛУ ПРОСТИМИ ТА МОДИФІКОВАНИМИ 2,3-ЕПОКСИПРОШЛМЕТАКРИЛАТ-ВШІЛШРРОЛІДОН СОПОЛІМЕРАМИ

Досліджено сорбцію фенолів в статичних та динамічних умовах на GMA-VP-EDMA сополімерах з різним хімічним складом. Встановлено, що сорбція фенолу зростає зі збільшенням вмісту вінілпірролідону в складі сополімеру. Було досліджено вплив pH та інших факторів на процес поглинання.