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APPLICATION OF SORPTION AND MEMBRANE METHODS IN THE PROCESS OF WATER PURIFICATION FROM DICLOFENAC

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The results of experimental investigation in water purification from pharmaceuticals by the example of diclofenac by means of activated carbon adsorption and using nanofilter membranes are presented. High efficiency of application of these processes in water purification is shown.

Introduction

One of the new areas of ecological chemistry is connected with the appearance of pharmaceutical active compounds in aqueous medium. Investigations in this problem were carried out in many countries – in Austria, Brazil, Canada, Croatia, Great Britain, Germany, Greece, Italy, Spain, Switzerland, the Netherlands and the USA. They showed that more than 80 different compounds, pharmaceuticals and a number of metabolites are present in aqueous medium. Some pharmaceuticals of different categories were found in sewage water at concentration to several ml/g and also in some surface water situated downstream from sewage water reprocessing stations. The investigations show that some pharmaceuticals are not completely removed at sewage disposal plants. In some cases they were found in drinking water samples at the level of minimally detectable concentration [1–8].

The given paper includes the results of investigations in water purification from pharmaceuticals, particularly (specifically) from widespread analgesic–diclofenac.

The experiments were carried out in the laboratories of the university in Karlsruhe (Germany) – water purification from diclofenac by means of activated carbon adsorption and using of nanofilter membranes. Purification by the mentioned methods was carried out both with humic substances (HS) in aqueous medium and without them.

Materials and methods

The experiments were carried out using diclofenac sodium ($C_{14}H_{10}Cl_2NNaO_2$). For carrying out the experiments with humic substances water with their high content from Holo lake (Black forest, Germany) was used. Water was of brownish color with dissolved organic carbon concentration in a sample equals 25 mg/l. For determining diclofenac concentration the spectrophotometer Cary 50 with measurement wavelength 275 nm was used. Analyzing samples 1sm quartz cell was used.

For determining organic substances concentration the analyzer Sievers 820 of total organic carbon was used. Diclofenac concentration in the presence of impurities (in this case – humic substances) was determined by means of high-performance liquid chromatography at chromatograph Agilent 1100. Carrying out measurements UV detector and two columns N24 Purospher RP-18 with parameters (length, inner diameter) 125×4 mm and N25 Purospher RP-18 250×4 was used. Diclofenac was found at wavelength 230 nm within time intervals – 19,5 and 12,5 min in the first and the second columns respectively. Phosphate buffer with concentration 9,8 мM KH_2PO_4 and 8,8 мM H_3PO_4, pH 3,1; flow rate 1 ml/l, introduced sample volume 10 microliter were used for all columns. Membranes NF90 and NF200 of FilmTec company [9], applying in roll nanofiltration elements manufacturing were used for carrying out nanofiltration, table 1.

Table 1. *Main characteristics of membranes NF90 and NF200*

Characteristics	NF 90	NF200
Selectivity, %	–	–
NaCl	85...95	–
$MgSO_4$	>97	97
$CaCl_2$	–	35...50
Atrazine	–	95
Type of a membrane	Polyamide thin-film composite	
Maximal working temperature, °C	45	
Maximal working pressure, bar	41	
Maximal pressure drop, bar	1,0	
pH range, continuous exposure	3...10	
pH range, short-time purification (30 min)	1...12	
Maximal feeding flow, m^3/h	15,9	

Activated carbon Norit SA UF produced by Norit company [10] was used for carrying out adsorption, table 2. The mentioned sorbent has high clinical characteristics because of hyperfine structure of its particles. Norit SA UF has high adsorptive capacitance for a number of compounds; it is especially widely applied in drinking water purification. Dimineralized water was used when preparing all solutions. pH magnitude in studied solutions was maintained equal to 7±0,2.

Table 2. *Sorbent Norit SA UF specifications*

Producer	Norit
Name	Norit SA U
Specific surface area, m^2/g	1200
Particles mean diameter, micrometers	7
Particle size >180 mkm, max. % of total mass	0,1
>400 mkm	0,0
Packed density, kg/m^3	160
Humidity, max., %	5

Experimental investigations on adsorption activated carbons diclofenac and humic substances

Series of experiments was carried out to study diclofenac sorption on activated carbon. Calibration curves for diclofenac have been plotted at spectrophotometer and chromatographer beforehand. Maximal degree of absorption of diclofenac by activated carbon (AC), rate of sorption were determined. Then HS were added into initial solutions and the experiments were carried out in their presence. Influence of HS on sorption in various conditions was studied. Freundlich model was applied for sorption isotherms plotting. As a result, sorption curve which shows that maximal charge of AC is obtained at high concentration of diclofenac was plotted and it amounted a specific value of the order of 0,25...0,28 (diclofenac/sorbent).Humic substances having appreciably larger size of molecules were absorbed in significantly less degree than diclofenac. Therefore their presence did not influence significantly maximal charge of AC, their absorption was minimal.

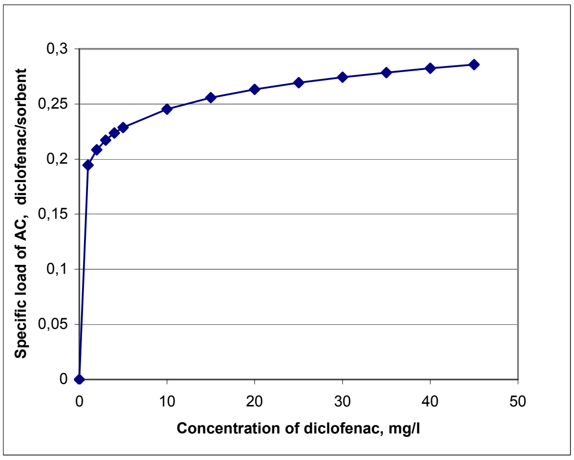

Fig. 1. *Experimental isotherm of diclofenac adsorption with Norit SA UF activated carbon*

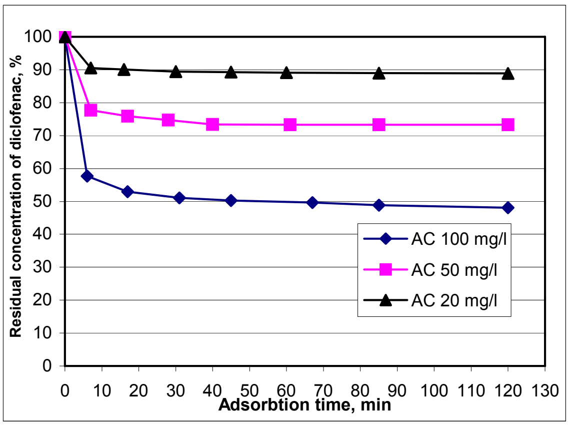

Fig. 2. *Dependence of diclofenac content in solution on adsorption time with Norit SA UF activated carbon*

Application of nanofilter membranes for water purification from diclofenac

Studying of filtration processes with membranes using was the second area of investigations in diclofenac absorption from solutions. Flat-channel experimental setup (fig. 3) was used for carrying out the experiments in filtration. Membranes which find an application in roll module was used in this setup which itself is an analog of roll module for carrying out experimental investigations.

The flat-channel experimental setup operates in the following way. Tank – 1 is filled up with initial solution, arriving at a pump – 3 for generating increased pressure. By means of valves – 2 values of pressure and flow supplied to membrane module – 6, registered on manometer – 5 and rotameter – 4 is controlled. In the membrane module a portion of flow goes through the membrane and the rest portion of flow returns into the tank and cycle repeats. The tank is provided with a thermostating device – 7 for supporting temperature conditions.

Data of changing of diclofenac concentration and membranes selectivity within the time of experiment are presented in table 3.

Table 3. *Concentration of diclofenac, dissolved organic carbon and membrane selectivity during the process of filtration*

Time, h	Diclofenac concentration (without HS), mg/l	Selectivity with respect to diclofenac (without HS), %	Concentration, mg/l		Selectivity with respect to	
			Diclofenac with HS	Dissolved organic carbon	diclofenac (with HS), %	HS, %
NF90						
0,5	<0,02	>99,61	–	–	–	–
1	<0,02	>99,61	<0,02	0,66	>99,61	72,27
2	<0,02	>99,61	<0,02	0,43	>99,61	82,94
17	0,023	99,49	<0,02	0,26	>99,61	89,31
66	–	–	<0,02	0,08	99,62	97,11
NF200						
0,5	0,071	98,43	0,09	0,34	98,03	85,37
1	0,082	98,19	0,11	0,29	97,63	87,67
2	0,085	98,14	0,13	0,71	97,06	72,32
17	0,143	96,90	0,19	0,62	95,91	74,69
66	–	–	0,16	0,18	96,57	93,37

During the whole experiment diclofenac concentration in permeats flow membrane selectivity increases and decreases step-by-step. It is especially appreciable on the membrane NF200. Identical tendency is observed with HS in the initial solution. Concentration in permeats starts stabilizing at experimental time equal to 17 hours. This fact can be explained by diclofenac adsorption on a membrane during the first hours of the experiment. After that membrane saturation to the maximal value constant in time occurs. To trace the same tendency on the membrane NF90 is not possible because of sufficiently low diclofenac concentration in permeats flow. The pattern of change of membrane selectivity with HS is rather difficult. During the first 17 hours selectivity decreases step – by – step and to 66 hours it sharply increases.

Experimental data of flow changing within experimental time with HS and without it are presented in table 4.

Great difference in permeats flow of the membrane NF200 in two experiments should be noted. It is connected with the fact that membranes were taken from different sets and producer admits such variant in the absence of some kind of changes in other characteristics.

Presence of HS in the experiment results in significant change of flow decrease rate. Influence of HS on a given parameter is explained by membrane contamination [11, 12]. Thus, we may reach a conclusion that HS presence in solution results in decrease of permeats flow.

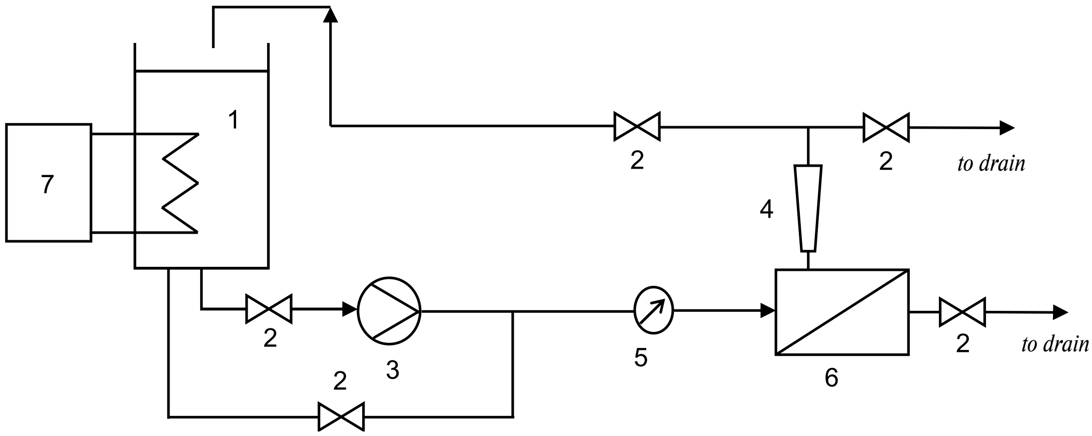

Fig. 3. *Diagram of flat-channel experimental setup: 1) tank with initial solution; 2) valve; 3) pump; 4) rotameter; 5) manometer; 6) membrane module; 7) thermostat*

Table 4. *Change of permeata flow without humic substances and with them*

Time, h	Flow of permeats, ml/min		Permeability, l/(h·m²·bar)		Change of permeability, %	
Without humic substances						
	NF90	NF200	NF90	NF200	NF90	NF200
0,5	6,77	6,85	8,46	8,56	100,00	100,00
1	6,76	6,84	8,45	8,55	99,81	99,88
2	6,69	6,84	8,37	8,55	98,85	99,81
17	6,65	6,82	8,32	8,52	98,29	99,53
With humic substances						
0,5	6,58	3,17	8,22	3,97	100,00	100,00
1	6,56	3,16	8,20	3,95	99,69	99,72
2	6,56	3,16	8,20	3,95	99,76	99,68
17	6,23	3,06	7,78	3,83	94,65	96,47
66	5,95	2,99	7,44	3,74	90,50	94,29

Obtained experimental data are the basis for development of technology of water purification from diclofenac both by sorption and membrane methods. The results of investigations may be also applied to waste solutions purification and to valued component release from them.

Conclusion

1. Series of experiments in adsorption of pharmaceutical by the example of diclofenac and its nanofiltration on membranes of NF90 and NF200 batches (USA) is carried out. It is shown that sorbent load factor on basis of activated carbon at high concentration of diclofenac achieves 0,25...0,28 (diclofenac weight/sorbent weight). Humic substances results in adsorption efficiency decrease, but degree of purification from diclofenac remains sufficiently high.
2. In membrane purification conditions the selectivity in respect of diclofenac remained on sufficiently high level during the whole time of the experiments (more than 99% on the membrane of NF90 batch and more than 95% on NF200 one). HS influence was in step-by-step decrease of permeats flow.

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