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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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Y. S. Yu^a; K. Kondo^a; K. Takemoto^a

^a Department of Applied Fine Chemistry, Faculty of Engineering Osaka University Suita, Osaka, Japan

To cite this Article Yu, Y. S. , Kondo, K. and Takemoto, K.(1987) 'Functional Monomers and Polymers. Cxli Adsorption of Biomedical Organic Compounds on Activated Carbons', *Journal of Macromolecular Science, Part A*, 24: 1, 85 — 92

To link to this Article: DOI: 10.1080/00222338708058511

URL: <http://dx.doi.org/10.1080/00222338708058511>

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FUNCTIONAL MONOMERS AND POLYMERS. CXLI.* ADSORPTION OF BIOMEDICAL ORGANIC COMPOUNDS ON ACTIVATED CARBONS

Y. S. YU, K. KONDO, and K. TAKEMOTO

Department of Applied Fine Chemistry
Faculty of Engineering
Osaka University
Suita, Osaka, Japan

ABSTRACT

The adsorption of various biology-related organic compounds, including nucleic acid bases, nucleosides, nucleotides, creatinine, uric acid, and vitamin B₁₂, was studied by using activated carbons having micro- and macropores of different sizes and volumes. An activated carbon made of coconut shell was found to show good adsorption for a number of compounds and selective adsorption for nucleic acid bases, nucleosides, and nucleotides. The selectivity depended on the molecular weight: The higher the molecular weight, the less the compound was adsorbed. Carbonaceous adsorbents having different porosity distributions were made from synthetic polymers. These adsorbents showed selectivity of adsorption, particularly for creatinine, uric acid, and vitamin B₁₂. The selectivity was explained by the diameters and volumes of the pores in the adsorbents.

*For Part CXL of this series, see Ref. 3.

INTRODUCTION

Activated carbon has long been known as a good adsorbent due to its excellent micropore structure and good chemical stability. The activated carbon made from coconut shell has shown better adsorption for many biomedical organic compounds than that obtained from other natural materials, such as wood, bone, or pitch. For this reason the activated carbon made from coconut shell is a useful material for clearing blood poisoned by some biomedical compounds by means of direct hemoperfusion (DHP) [1]. Various activated carbons made from natural materials have a good capacity of adsorption, but their mechanical strength is low, and they do not have good selectivity because of their wide distribution of pore diameters.

Because of their significance for applications in the medical and technological fields, synthetic polymers were carbonized to obtain carbonaceous adsorbents having excellent micropore structure and narrow distribution of pore diameters. Compared with the activated carbon made from natural materials, the carbonaceous adsorbents have a better mechanical strength and selectivity of adsorption.

This paper describes the adsorption behavior of some biomedical organic compounds, including nucleic acid bases, nucleosides, nucleotides, creatinine, uric acid, and vitamin B₁₂, as well as other purine derivatives, on activated carbon made from coconut shell. In addition, the synthesis and carbonization of poly(styrene-*co*-divinylbenzene), poly(vinylidene chloride), and polyacrylonitrile to prepare carbonaceous adsorbents of different distributions of pore diameters, as well as the selectivity of adsorption for creatinine, uric acid, and vitamin B₁₂, are described.

EXPERIMENTAL

Materials Used as Adsorbents

Adsorbents 1 to 6

Styrene-divinylbenzene copolymer beads of 40% crosslinking were obtained from the Chemical Plant of Nankai University, China. The beads were at first swelled with 1,2-dichloroethane and then sulfonated with concentrated sulfuric acid at 80°C for 2 h, further at 170°C for 5 h. The sulfonated beads were pyrolyzed in a quartz tube (inner diameter 35 mm, length 100 cm) fixed in a cracking furnace. A nitrogen flow carrying a trace amount of air was passed over the pyrolyzing beads by a quartz conduit. The pyrolysis was carried out at differ-

ent high temperatures from 300 to 800°C for 0.5 h; then the products were cooled to room temperature for 4-8 h. Carbonaceous Adsorbents 1 to 6 thus obtained were spherical and 0.6-0.8 mm in diameter.

Adsorbent 7

Adsorbent 7 was a spherical carbonaceous adsorbent (diameter 0.6-0.8 mm) which was obtained commercially (BAC-Mu; made in Japan).

Adsorbent 8

The monomer (acrylonitrile), crosslinking agent (divinylbenzene), and initiator (AIBN) were stirred in toluene at room temperature to give a homogeneous solution. The weight of AIBN was 1% of the monomer, and the acrylonitrile/toluene ratio was 3/2 (wt/wt). The mixture was added to aqueous gelatin (1 wt%) and stirred to form a homogeneous suspension. The suspension polymerization was carried out at 65°C for 4 h to give polymer beads 0.8-1.2 mm in diameter and with 10% crosslinking. The beads were treated at 180°C and then 230°C, each for 0.5 h, under a nitrogen flow carrying a trace amount of oxygen. The product was then pyrolyzed under nitrogen at 750°C for 0.5 h in a quartz tube (inner diameter 35 mm, length 100 cm) fixed in a cracking furnace. The beads obtained were activated by steam at 750°C for 0.5 h to give spherical Adsorbent 8, 0.4-0.8 mm in diameter.

Adsorbent 9

Adsorbent 9, a commercially available product (4-10 mesh), was a granular activated carbon made from coconut shells.

Adsorbent 10

Diatomaceous earth (0.25 wt%) was suspended in distilled water with stirring. To the suspension was added a solution of vinylidene chloride (VDC) (bp 32-34°C and diisopropyl peroxydicarbonate (DPO) at -5°C. The VDC/DPO ratio was 100/1 (wt/wt). The mixture was stirred at -5°C for 8 h to give stable drops of VDC with DPO. The suspension polymerization was carried out at room temperature for 24 h without stirring. The polymer beads obtained were washed with water and dried. The polymer beads were decomposed at 185°C for 2 h under nitrogen, then pyrolyzed at 750°C for 5 h in a quartz tube (inner diameter 35 mm, length 100 cm) fixed in a cracking furnace to give spherical Adsorbent 10, 0.6-0.8 mm in diameter.

Measurement of Mechanical Strength

The mechanical strength was determined from the pressure required to make the bead break. The data were averaged for 10 measurements.

Measurement of the Distribution of Pore Diameters

The distribution of pore diameters over 3.6 nm was measured with a USA Quantachrome Scanning porosimeter (mercury pressure method).

Measurement of Adsorption

An adsorbent (1 g) was added to 20 mL of an aqueous solution (the vitamin B₁₂ concentration was 50 mg/L, and all others were 200 mg/L). The mixture was shaken at 36-37°C for 1 h. The adsorption is the percentage of the solute adsorbed under these conditions. The adsorption was determined spectrometrically from the optical density at the maximum adsorption wavelength.

RESULTS AND DISCUSSION

It is known that adsorption depends not only on the surface area of the adsorbent but also on the distribution of pore diameters and on the type of solutes to be adsorbed.

Table 1 shows the results of the adsorption experiments of various biomedical organic compounds using the granular activated carbon (Adsorbent 9). The activated carbon showed good adsorption for the compounds studied, as shown in Table 1, particularly for creatinine and uric acid, as well as for vitamin B₁₂. The adsorption of the adsorbent for nucleic acid derivatives was in the order nucleic acid bases > nucleosides > nucleotides. Note that the activated carbon showed the best adsorption for AMP among the different nucleotides tested. This may be attributed to the difference in the affinity of AMP to water as compared to the other nucleotides. Creatinine, uric acid, and vitamin B₁₂ were adsorbed almost quantitatively, and this result is expected to open a way for application to blood purification.

The activated carbon 9 shows a good microporous structure (surface area 1200-1300 m²/g), and the diameters of the macropores are concentrated at about 358 nm in the distribution (Fig. 1). It is generally understood that, for micropores, there exists an optimum range of pore diameters for adsorbing organic compounds [2], while for macropores that we are concerned with, it is assumed that they would provide favorable inner pathways for diffusing the

TABLE 1. Adsorption on Activated Carbon^a

Solutes	Adsorption, %
Adenine	87
Adenosine	87
AMP	84
Uracil	89
Uridine	84
UMP	66
Thymine	89
TMP	65
Cytosine	86
Cytidine	81
CMP	57
Guanosine	81
GMP	54
Hypoxanthine	87
Inosine	72
IMP	50
Theobromine	86
Caffeine	87
Theophylline	83
Purine	89
Creatinine	99.6
Uric acid	99.8
Vitamin B ₁₂	>95

^aAdsorbent 9, 4-10 mesh.

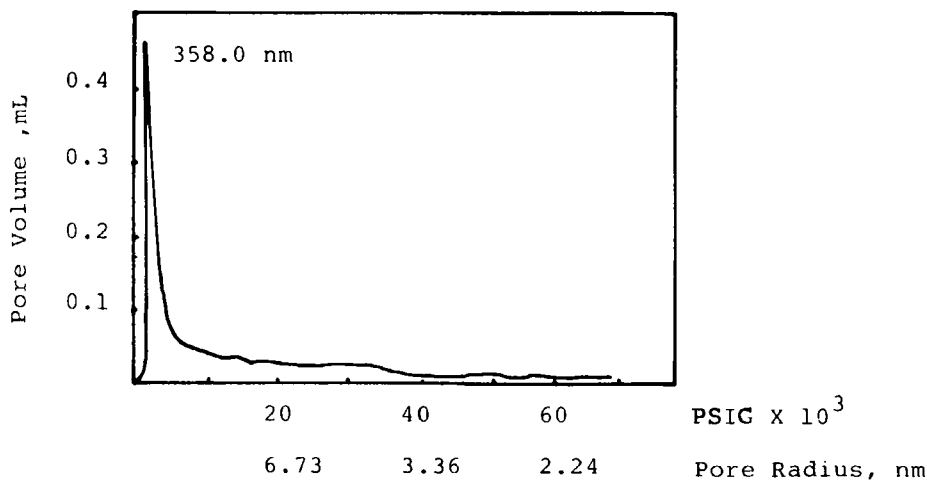


FIG. 1. Distribution of the pore diameters of Adsorbent 1 (carbonaceous coconut shell).

solutes. Although the molecular sizes of creatinine, uric acid, and vitamin B₁₂ are different, the macropores with diameters of approximately 358 nm are large enough so that all three molecules can diffuse rapidly to the internal surface of the adsorbent, and adsorption occurs almost quantitatively. The adsorption of carbonaceous adsorbents, such as 1 to 6, however, seems to be selective for these three compounds (Table 2). These adsorbents, made from synthetic polymer beads, are rich in micropores (surface area 451-1 300 m²/g) and possess various macroporous structures. As shown in Table 2, Adsorbents 1 to 3 showed a selectivity for creatinine, uric acid, and vitamin B₁₂, because such macropore structures seem to be favorable for diffusing creatinine and uric acid, which have smaller molecular sizes than vitamin B₁₂. Adsorbent 1, with macropores of 14 nm and a volume of 0.263 mL/g, clearly showed selective adsorption for creatinine and uric acid, and no adsorption for vitamin B₁₂. It was found that the selectivity of adsorption tends to decrease with increasing volume of macropores; Adsorbent 3 with a macropore volume of 0.323 mL/g seems to show only little selectivity for creatinine and uric acid in spite of the difference in their molecular sizes.

Adsorbents 4, 5, and 6 with macropores of 17 nm still showed no selectivity for creatinine and uric acid. When the macropore size exceeded 107 nm, that is, in the case of Adsorbents 7-10, vitamin B₁₂, which has a much

TABLE 2. Adsorption on Various Carbonaceous Adsorbents

	Adsorbent ^a									
	1	2	3	4	5	6	7	8	9	10
Surface area, m ² /g	451	513	571	506	640	783	1 294	539	1 200-1 300	1 000
Mechanical strength, g/grain	524	424	733	1 104	894	1 021	717	1 700	b	1 470
Diameter of macropores over 3.6 nm, nm	14.0	14.0	14.0	17.0	17.0	17.0	107.6	120.0-200.0	358.0	1 070.0
Volume of macropores over 3.6 nm, mL/g	0.263	0.293	0.323	0.353	0.353	0.380				
Adsorption, %: Creatinine	84	89	90	97	97	98	99	98	99	99
Uric acid	67	79	89	98	98	98	99	98	99	99
Vitamin B ₁₂	0	0	Trace	40	40	60	95	98	98	98

^aAdsorbent 9: 4-10 mesh; others, beads of 0.4-0.8 mm diameter.

^bUnmeasurable because of brittleness.

larger molecular size than creatinine and uric acid, can be adsorbed almost quantitatively. In this sense they can be regarded as excellent adsorbents among those studied here for these three compounds, although selectivity could not be expected.

ACKNOWLEDGMENT

The authors wish to thank Professor B. L. He (P. L. Ho) of Nankai University, China, for his helpful discussion and encouragement.

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