



## Adsorption of catecholamines from their aqueous solutions on hypercrosslinked polystyrene

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### ABSTRACT

Hypercrosslinked polystyrene Diapak P-3 was investigated as a high-capacity adsorbent for catecholamines (i.e. epinephrine, norepinephrine and dopamine). Morphological data for the sorbent were evaluated by scanning electron microscopy and nitrogen adsorption–desorption method. The results showed that Diapak P-3 possesses high microporous surface area of  $1132 \text{ m}^2 \text{ g}^{-1}$  and a bimodal pore size distribution. Batch adsorption studies were performed to evaluate effect of pH and contact time on catecholamines uptake. The molecular forms of catecholamines are favorable for the adsorption, best results (maximum adsorption capacity) were found at pH 7–9. The adsorption kinetic properties were obtained by application of the pseudo-first order kinetic model. From adsorption isotherms, the two-site Langmuir model showed the best fit and total adsorption capacity of 86, 68, and  $52 \text{ mg g}^{-1}$  for dopamine, epinephrine, and norepinephrine, respectively. From the obtained results, the hypercrosslinked polystyrene Diapak P-3 has showed good adsorptive characteristic for catecholamines.

### 1. Introduction

Catecholamines (CAs) represents a group of biogenic amines, among which epinephrine (E), norepinephrine (NE) and dopamine (DA) are very well known as neurotransmitters or hormones [1]. These compounds play significant role in maintaining normal physical activity of the body including heart rate, blood pressure and the reactions of the sympathetic nervous system [2]. As a result, CAs can serve as biomarkers for the diagnosis, therapy and prognosis of several cardiovascular and neurological disorders [3–5]. For instance, NE and E act as biomarkers in studying heart disease, diabetes and anxiety. The deficiency of DA neurotransmission has been proved to be associated with Parkinson diseases and Schizophrenia [6, 7]. For these reasons, the measurement of CAs in several biological fluids is of great importance [8, 9]. Traditionally, high performance liquid chromatography is applied with electrochemical, fluorimetric or mass-spectrometric detection [10–14].

Because of the low concentration levels of CAs in biological fluids and their high tendency to spontaneous oxidation a procedure of their extraction from a sample and enrichment is critical to develop a more sensitive and selective assay. Adsorption has been widely used in the most popular sample preparation methods based on solid-phase

extraction (SPE). Alumina [15, 16], cation exchange cartridges [17], silica-C18 [18–20] and hydrophilic–lipophilic balance (HLB) Oasis cartridges [21–23] are the typical solid phase extraction materials for sorption of CAs. Activated aluminum oxide usually needs alkaline media leading to low recovery (60–80%) due to instability of catecholamine in the alkaline conditions. In addition, because of high polarity of CAs their preconcentration on conventional reverse-phases also has low efficiency. Comparison of various sorbents for isolation of catecholamines from biological fluids showed that the best results were obtained with a polymeric Oasis HLB adsorbent [13]. The search for new adsorbents making possible quantitative isolation of CAs is important.

In recent years, hypercrosslinked polystyrenes (HCPs), first synthesized by V.A. Davankov et al. [24], have gained increasing attention in the fields of adsorption, separation and purification [25, 26]; at present, HCPs are manufactured by several companies. Hypercrosslinked polystyrenes owe their surprising and practically useful properties to the unusual structure which is determined by conditions of the polymer network formation. HCPs are usually obtained by intensive cross-linking of polystyrene chains in solution or in swollen state with conformationally rigid bridges. Such rigid bridges of diphenylmethane type are formed on solvated polystyrene chains with

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monochlorodimethyl ether [27, 28].

The HCPs adsorbents have a number of new unique physicochemical properties, including the high specific surface, mechanical and hydrolytic stability, the combination of hydrophobicity of the surface with water wettability, the exceptionally high rigidity of the polymer structure, and the pronounced affinity for polar organic compounds. These basically important properties, in their turn, are conditioned upon specific physical structure of the polymers. Hypercrosslinked polystyrene is a highly porous material but its porosity differs from the porosity of traditional macroporous poly(styrene–divinylbenzene) sorbents, activated carbons, silica gels, porous glasses, etc. [29]. Furthermore, HCP is a “restricted access material”. The pores of HCP with the diameter of 15–30 Å are available for most low molecular weight substances but are not available for such macro molecules as proteins and polysaccharides [30]. As it was shown earlier, HCP effectively absorbs from water solutions such polar compounds as primary aliphatic amines [31], various phenols [32–37], dyes [37, 38], methomyl pesticide [39], phenylhydrazine derivatives [40], methylxanthines [31–43], sulfonamides [44, 45], tetracyclines [46–48], salicylic acid [49, 50], and benzene [51]. Our literature survey shows that HCP was not used for sorption of catecholamines. Meanwhile, this adsorbent is very promising for preconcentration of CAs. Due to its size selectivity one can expect its usefulness for isolation of low molecular weight substances from complex matrices such as blood, urine and other biological liquids. High mechanical stability of HCP makes it promising for flow-based preconcentration/separation systems. All this indicates importance of an in-depth physicochemical investigation of sorption properties of HCP regarding CAs to assess and govern effectivity and selectivity of this adsorbent.

The present work aimed at investigation of the adsorption behavior of catecholamines: dopamine, epinephrine and norepinephrine from their aqueous solutions on hypercrosslinked polystyrene. Effects of different factors on the adsorption were evaluated. Mechanisms for strong adsorption of these catecholamines on HCP were deduced from fitting adsorption isotherms and by studying the effect of pH.

## 2. Experimental

### 2.1. Materials

Analytical grade epinephrine hydrochloride, norepinephrine hydrochloride and dopamine hydrochloride were purchased from Sigma–Aldrich. Sodium hydroxide (NaOH), hydrochloric acid (HCl), sodium metabisulfite ( $\text{Na}_2\text{S}_2\text{O}_5$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), octane-1-sulfonic acid sodium salt, acetonitrile, methanol and other reagents were supplied by Sigma. Commercial HCP (Diapak P-3, particle size – 50–100 µm, pore diameter – 10–1000 Å) was obtained from Bio-KhimMak (Russia). The polymeric adsorbent HCP was activated with methanol prior to use. Deionized water was prepared using Milli-Q water purification system (Millipore, France).

Stock solutions (1 mg mL<sup>-1</sup>) of E, NE and DA were prepared by dissolving 20 mg of a pure substance in 20 mL of deionized water. Working standard solutions of CAs were prepared daily by diluting the primary stock solutions with deionized water in the presence of 0.8 mM sodium metabisulfite.  $\text{Na}_2\text{S}_2\text{O}_5$  was used as an antioxidant to avoid oxidization of CAs, as described in the literature [52]. All of the above solutions were stored at –20 °C before use.

### 2.2. Characterization of hypercrosslinked polystyrene Diapak P-3

The porous structure parameters of HCP were determined from nitrogen adsorption isotherms measured at 77 K. Before analyses, the samples were outgassed at 373 K. The BET surface area was calculated from desorption isotherms using the standard Brunauer–Emmert–Teller equation. The mesoporous pore size distribution was determined from desorption isotherms using the Barrett, Joyner and Halenda (BJH)

method. All calculations were performed automatically by an Accelerated Surface Area and Porosimeter system (ASAP 2010, Micromeritics, USA). The zeta potentials were determined using a Malvern Instruments Zetasizer Nano ZS. (Malvern Ltd., U.K.). The microstructure of the sorbent was studied on a LEO SUPRA 50 VP scanning electron microscope (Carl Zeiss, Germany) with a field emission source.

### 2.3. Adsorption experiments

Adsorption of CAs from aqueous solution was performed at 22 °C (295 K) in a batch mode. The HCP were conditioned in methanol before the adsorption experiments. In each experiment, 20 mg of adsorbent was added into 25 mL of water solution containing 2 mg L<sup>-1</sup> of CAs for a kinetic study and 1.5–110 mg L<sup>-1</sup> for measuring the isotherms in the presence of 0.8 mM sodium metabisulfite as an antioxidant. After stirring for 1–30 min for kinetic study and 30 min for measuring isotherms, the sorbent was separated by centrifugation. The concentration of each solute remaining in the water phase was analyzed by high-performance liquid chromatography with electrochemical detection (HPLC–ED). Uniform shaking speed was maintained for all the experiments. All the adsorption experiments were conducted in duplicate. The equilibrium adsorption capacity of CAs,  $q$  (mg g<sup>-1</sup>), was calculated according to the following equation:

$$q = (c_0 - c_{eq}) \times V/w \quad (1)$$

here  $V$  is the volume of the aqueous solution (mL),  $w$  is the weight of dry adsorbent (g),  $c_0$  and  $c_{eq}$  is the initial and the equilibrium concentration (mg L<sup>-1</sup>) of CAs in solution respectively.

To study effect of pH on adsorption, the initial pH of CAs solutions was adjusted from 2 to 10 using NaOH or HCl aqueous solution. Effect of contact time was studied based on batch assays performed for periods of time ranging from 1 to 30 min. The adsorption isotherms were determined at pH 8 ± 0.5 without adding any buffer to avoid the presence of an electrolyte in the system.

### 2.4. Chromatographic conditions

HPLC–ED analysis was performed using a Tswett-Yauza-04 liquid chromatograph (NPO Khimavtomatika, Russia) with an amperometric detector ( $E = 0.8$  V, glassy carbon electrode). The separation was performed on a Luna 5u C18(2) column (150 × 3.0 mm, 5 µm) produced by Phenomenex (USA). The mobile phase consisted of acetonitrile and 0.1%  $\text{H}_3\text{PO}_4$  in water (10:90, v/v) with addition of sodium octanesulfonate (0.3 mM). The flow rate was 0.4 mL min<sup>-1</sup>. The eluent was degassed in a Bransonic 1510R-DTH ultrasonic bath (USA).

## 3. Results and discussion

### 3.1. Characteristics of the hypercrosslinked polystyrene Diapak P-3

The nitrogen adsorption and desorption isotherms of the HCP Diapak P-3 are shown in Fig. 1(a). It can be seen that the N<sub>2</sub> adsorption isotherm seem close to type-II classification. At the initial part of the adsorption isotherm with a relative pressure below 0.05, the N<sub>2</sub> adsorption capacity increases sharply with increasing the relative pressure, proving that micropores are existent. The visible hysteresis loop of the desorption isotherm indicate that mesopores are also present. The parameters of the HCP, as determined by the nitrogen adsorption-desorption method, are listed in Table 1. It is clearly seen from Table 1 that HCP Diapak P-3 is a kind of typical microporous adsorbent with high surface area of 1132 m<sup>2</sup> g<sup>-1</sup> and a bimodal pore distribution. According to Table 1 the micro- and mesoporosities of HCP are around 53% and 42%, respectively. The combination of two pore ranges: the micropore range and the meso-macropore range of HCP suggests that it would be a good adsorbent for adsorption of CAs from aqueous solution.

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