



Ordered mesoporous carbons as effective sorbents for removal of heavy metal ions



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ABSTRACT

Herein, we report the systematic study on adsorption of heavy metal ions by ordered mesoporous carbon CMK-3. This sorbent has been obtained by hard templating using SBA-15 and subsequently, oxidized (by treatment with $(\text{NH}_4)_2\text{S}_2\text{O}_8/\text{H}_2\text{SO}_4$) and amino-functionalized (by treatment with N-(3-trimethoxysilylpropyl)diethylenetriamine). Pristine, oxidized and amino-functionalized carbons have been characterized by nitrogen sorption, X-ray diffractometry, X-ray photoelectron spectroscopy, scanning and transmission electron microscopy and tested for their ability to adsorb heavy metal ions (Pb, Zn, Cu, Cd) from the aqueous solutions. The observed static sorption capacities are very high up to 0.8 mmol/g and were at least twice higher than the values corresponding to the commercial activated carbon Norit[®] SX2. Adsorption kinetics is also very fast – for majority of the systems ~90–95% of the equilibrium amount is adsorbed after several minutes. Desorption efficiencies of the adsorbed heavy metals vary from 41% (for Zn) to 99% (for Pb).

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1. Introduction

Nowadays, the increasing amounts of anthropogenic pollutants in the aqueous environment impose hazard for human health. Thus, there is emergent expectation and demand for developing efficient protocols for controlling the industrial emissions to avoid their release to the environment [1]. Heavy metals represent one of the most important environmental problems due to their toxic effects and growing accumulation throughout the food chain. The main sources of heavy metal pollution include metallurgical, tannery, chemical manufacturing, mining, battery manufacturing, painting and surface treatment industries [2]. The pollution of water resources due to the indiscriminate disposal of heavy metals has been causing worldwide concern for the last few decades. It is well known that majority of heavy metals can have toxic or harmful effects on human beings and ecological environments. It, therefore, becomes necessary to remove these pollutants from these wastewaters by an appropriate treatment [3]. There are many methods

used for removal of heavy metal ions from wastewater and sewage [4], however, they are not always successful.

Among them, processes based on adsorption, are particularly promising [5] because of their easy operations, high efficiency, cost efficiency, versatility as well as availability of different adsorbents [6–8]. It should be clearly pointed out here that the development and application of adsorption processes cannot be considered separately from the development of technology of new adsorbents applied both on the laboratory and industrial scales [9]. As far as classical sorbents are concerned, the activated carbon is the most widely applied. It possesses a highly-developed surface area and chemical inertness, but the dominance of micropores (<2 nm) in the structure hinders diffusion of many species into the pores. Therefore, recently much attention has been devoted to other types of carbon-based materials such as carbon nanotubes, carbon aerogels and ordered mesoporous carbons.

Ordered mesoporous carbons (OMCs) can be synthesized via two routes based on template carbonization allowing for the preparation of carbon materials with controlled architecture and relatively narrow pore size distribution [10]. The first one is called the ‘hard-templating’ or ‘nanocasting’ method. In this multi-step route an ordered mesoporous silica serves as a hard template: it is impregnated with an appropriate carbon precursor (e.g. sucrose, furfuryl alcohol), carbonized and finally removed by dissolving in

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NaOH or HF. Such treatment results in porous carbon material being the reverse replica of silica template [11–13]. The template must exhibit three-dimensional pore structure to be suitable for the synthesis of OMCs, otherwise disordered microporous carbon is formed [6]. The second method called ‘soft-templating’ is a simple, one-step method where triblock copolymers are applied as the template. Due to the interactions between triblock copolymer and polymeric carbon precursor and further heating, resulting in degradation of sensitive copolymer molecules, the ordered mesoporous carbon can be obtained [14–16]. There is also another method involving the use of colloidal silica. In this method, particles of colloidal silica penetrate the carbon precursor (usually liquid crystal pitch) at higher temperature assuring sufficient softening of the carbon precursor. The obtained carbon-silica composite is carbonized and finally the colloidal silica particles are removed by NaOH or HF [17,18]. In the case of this method, the final carbon material is porous but not ordered.

The properties of OMC are very interesting: they show chemical inertness and good mechanical and thermal stabilities [19]. One of the most important advantages of OMC (as well as other carbon materials) is that their surface is hydrophobic which makes the sorption of long-chain organic molecule very effective. Another advantage is the possibility of functionalization of the carbon surface which is achieved mainly via post-synthesis oxidation. It provides an easy way to create desired functionalities such as carbonyl, carboxyl or hydroxyl groups, which can serve as adsorption centers or grafting points for other species (usually achieved via covalent bonding).

Many functional groups can be covalently attached in this way to the surface of OMC [20], including basic and acid functionalities [21–23]. In this way, it is possible to obtain materials with targeted surface chemistry, which is very often crucial in the adsorption applications. The enhanced sorption properties onto oxidized/functionalized carbon materials, are frequently described in the literature [24–26]. This is aimed at improving the hydrophilic properties of the carbon surface [27]. The most popular reagents which are used for oxidation/functionalization of carbon surface are: nitric acid [28–30], ammonium persulfate [31], amino-propyltriethoxysilane [32], ethylenediamine [33].

Recently, OMCs have found an increasing number of applications in many areas including catalysis [34–36], adsorption [31,37,38], separation [39,40], sensing [41,42], energy storage [43], supercapacitors and electrochemistry [44,45]. Possibility of kilogram-scale synthesis of high-quality OMC [46] coupled with the use of cheap, green precursors [46,47] can make these materials affordable for all the above-mentioned applications. It should be clearly mentioned here that as far as adsorption is concerned, the OMC are not so broadly exploited as ordered mesoporous silicas (OMS). A significant development was achieved during last years. In particular, applications coupling sorption and sensing functions have been shown to be extremely interesting for simultaneous detection and removal of heavy metal ions such as lead [48–50], copper [51–57] and zinc [58]. Other very interesting sensing applications using functional mesoporous materials (also in the form of layers or films deposited on sensing devices) are also possible [59–61] making those materials a real source of advance.

OMCs also draw appreciable attention to their successful environmental applications connected with the removal of contaminants from waters and wastewaters. The range of contaminants tested up to day is very large including dyes [6,62,63], small biomolecules [64], heavy metal ions [31]. Having many attractive features such as developed specific surface area, high pore volume, tunable pore size, good stability and easy surface modification, OMC can render as the next generation of adsorbents [1]. Despite this fact, there is only one comprehensive paper devoted to the study of adsorption of different

heavy metal ions by OMCs [31]. Other publications usually deal with single metal [47], however, they do not include all the adsorption/desorption data (i.e. effect of pH, contact time, initial concentration, desorption efficiency). Only analyzing all these data together, it is possible to judge possible adsorption application.

The aim of this study was to synthesize and characterize the three CMK-3 mesoporous carbons (pristine, oxidized and amine-functionalized) and to test their performance as adsorbents in removal of bivalent heavy metal ions (Pb, Cd, Zn, Cu) from aqueous solutions. We investigated the mesostructural stability, pore evolution, morphology and surface chemistry of the CMK-3 material. All three materials (i.e. pristine, oxidized and functionalized CMK-3) were used as highly efficient sorbents of above-mentioned metal ions. The effect of pH, contact time and initial concentration on heavy metals uptake was studied. Desorption studies were also performed. The sorption properties of these CMK-3 sorbents were compared with the commercial activated carbon Norit® SX2. The sorption capacities with respect to heavy metal ions studied are significantly larger than those found in the literature for other adsorbents.

2. Experimental

2.1. Reagents

The following compounds were used: tetraethyl orthosilicate (TEOS, 98% Sigma–Aldrich), Pluronic 123 (P123, Sigma–Aldrich), sulfuric acid (H₂SO₄, 98% POCH), hydrochloric acid (HCl, 36% POCH), nitric acid (HNO₃, 63% POCH), anhydrous ethanol (EtOH, 99.8% POCH), sucrose (Polish Sugar Company), sulfuric acid (H₂SO₄, 98% POCH), sodium hydroxide (NaOH, POCH), ammonium persulfate (APS, 97%, Chempur), N-(3-trimethoxysilylpropyl)diethylenetriamine (TMPET, 97% ABCR), n-butylamine (NBA, 99%, POCH), toluene (99.5% POCH), deionized water (resistivity 18.2 MOhm-cm). All chemicals were used as received, without further purification. The activated carbon Norit® SX2 was purchased from POCH.

2.2. Synthesis, oxidation and functionalization of CMK-3 materials

Synthesis of Ordered Mesoporous Silica SBA-15. The mesoporous silica was according to [65–67]. In a typical synthesis 2 g of P123 were dissolved in 60 mL of 2 M HCl and 12 mL of deionized water under vigorous stirring at 40 °C. After complete dissolution of P123, 20 mmol TEOS was added dropwise under vigorous stirring. The mixture was stirred for 24 h, transferred into the autoclave and aged for 24 h at 100 °C. After hydrothermal treatment the solid material was recovered by filtration and calcinated at 550 °C.

Synthesis of Ordered Mesoporous Carbon CMK-3. 2.5 g of sucrose was dissolved in 10 mL of water containing 160 µL of the conc. H₂SO₄. Next, 4 g of SBA-15 was added. The mixture was heated at 100 °C for 6 h. After that, the temperature was raised to 160 °C. The impregnation was repeated by using the solution of sucrose in water and 0.1 mL of conc. H₂SO₄. Once again, the mixture was kept at 100 °C for 6 h and at 160 °C for another 6 h. The obtained composite was carbonized at 900 °C for 3 h under nitrogen flow. SBA-15 template was removed by shaking with 1 M EtOH/water solution (volume ratio 1:1). The obtained CMK-3 carbon was thoroughly washed with water and ethanol and finally dried at 80 °C overnight. This not modified sample is abbreviated as P-CMK-3 in the text.

Oxidation of CMK-3. Pristine CMK-3 (1 g) was put into the reactor filled with 1.75 M solution of APS in 2 M sulfuric acid (VI) (50 mL) and stirred for 24 h in RT. After that, the mixture was filtrated and washed with water and ethanol. Black solid was dried at 80 °C overnight. This oxidized sample is abbreviated as O-CMK-3 in the text.

Amine-functionalization of CMK-3. Oxidized CMK-3 (0.5 g) was put into round-bottomed flask filled with toluene (50 mL), 30 µL of

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