Materials Research Bulletin 60 (2014) 516–523

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Carboxyl-rich carbon microspheres prepared from pentosan with high adsorption capacity for heavy metal ions

Qiong Wu, Wei Li, Shouxin Liu *

Key Laboratory of Bio-based Materials Science and Technology of Ministry of Education, Northeast Forestry University, Harbin, Heilongjiang 150040, PR China

ARTICLE INFO

Article history:
Received 30 January 2014
Received in revised form 1 September 2014
Accepted 5 September 2014
Available online 6 September 2014

Keywords:
A. carbides
B. solvothermal
C. electron microscopy
Thermogravimetric analysis (TGA)

ABSTRACT

Carboxyl-rich carbon microspheres (CSp) were synthesized through hydrothermal carbonization of hemicellulose-derived by-products of pulp refining with no other additives. Characterization of the products revealed that CSp rich in oxygen-containing groups with good dispersion and thermal stability can be obtained. Because of the abundant surface oxygen-containing functional groups, the prepared CSp exhibited excellent adsorption capacities for Pb(II) and Cd(II) from aqueous solution, with highest adsorption capacities of 380.1 and 100.8 mg/g for Pb(II) and Cd(II), respectively. Following metal ion adsorption, the content of carboxyl groups decreased from 39.1% to 6.8% for CSp–Pb and to 9.8% for CSp–Cd. Freundlich and Langmuir model isotherms were used to determine the equilibrium uptakes of the two heavy metal ions, revealing that both Pb(II) and Cd(II) were chemically adsorbed as multilayers on CSp.

1. Introduction

Removal of hazardous metal ions, especially in low concentrations, from industrial effluent is of great interest because of the large quantity of materials processed. Metal ions of lead (Pb) and cadmium (Cd) have a harmful effect on human physiology and other biological systems [1]. Several methods including membrane separation, adsorption, neutralization and sedimentation have been studied for the treatment of wastewater containing Pb and Cd compounds [2,3]. Among these methods, adsorbent adsorption is effective and widely used [4]. Porous carbon in either powder or granular form can allow relatively efficient removal of these metals. The adsorption of metal ions from aqueous solution onto porous carbon is generally assumed to be induced by the oxygen-containing functional groups of carbon [5,6], although other factors such as coordination with defect sites and van der Waals interactions may also contribute to the adsorption process. The surface chemistry of carbon materials provides an unlimited yet simple tool to face new environmental challenges. By tailoring the surface chemistry of carbon materials, many current industrial challenges in fields such as catalysis, water remediation and energy storage may be overcome [7,8].

Hydrothermal carbonization of hexoses such as glucose, fructose and starch has proved to be an effective and environmentally friendly way to produce functional carbonaceous materials with abundant oxygen-containing groups and certain porous structures that show great potential in the fields of catalysis, adsorbents, energy storage and CO_2 sequestration [6,9]. Li and Sun [10] prepared colloidal carbon spheres with a large amount of carbonyl, condensed benzene rings and large reactive/hydrophilic oxygen functionalities by hydrothermal carbonization of glucose; they proposed that the reaction pathway involved dehydration and aromatization. We previously prepared carbon sphere-activated carbon hybrid carbon materials from glucose and commercially activated carbon by hydrothermal carbonization [11]. The abundant surface oxygen-containing functional groups in these materials contributed to their high specific adsorption capacity for Cr(VI). Titirici [12] compared the reaction routes of hexose and pentose. They detected different intermediates of 5-hydroxymethylfurfural (5-HMF) and furfural for hexose and pentose, respectively. The carbon material derived from pentose showed higher aromaticity, yield and more oxygen-containing functional groups than that of hexose. This implies pentose may be more suitable than hexose for the preparation of high-value adsorbents [13], but this knowledge has found very limited use so far.

About 400 million tons of paper is produced each year globally. This process consumes a large amount of wood but has a relatively low utilization rate. During pulp refining, considerable amounts of

* Corresponding author. Tel.:+86 451 82191204; fax: 86 451 82191204.
E-mail address: liushouxin@126.com (S. Liu).

http://dx.doi.org/10.1016/j.materresbull.2014.09.015
0025-5408/

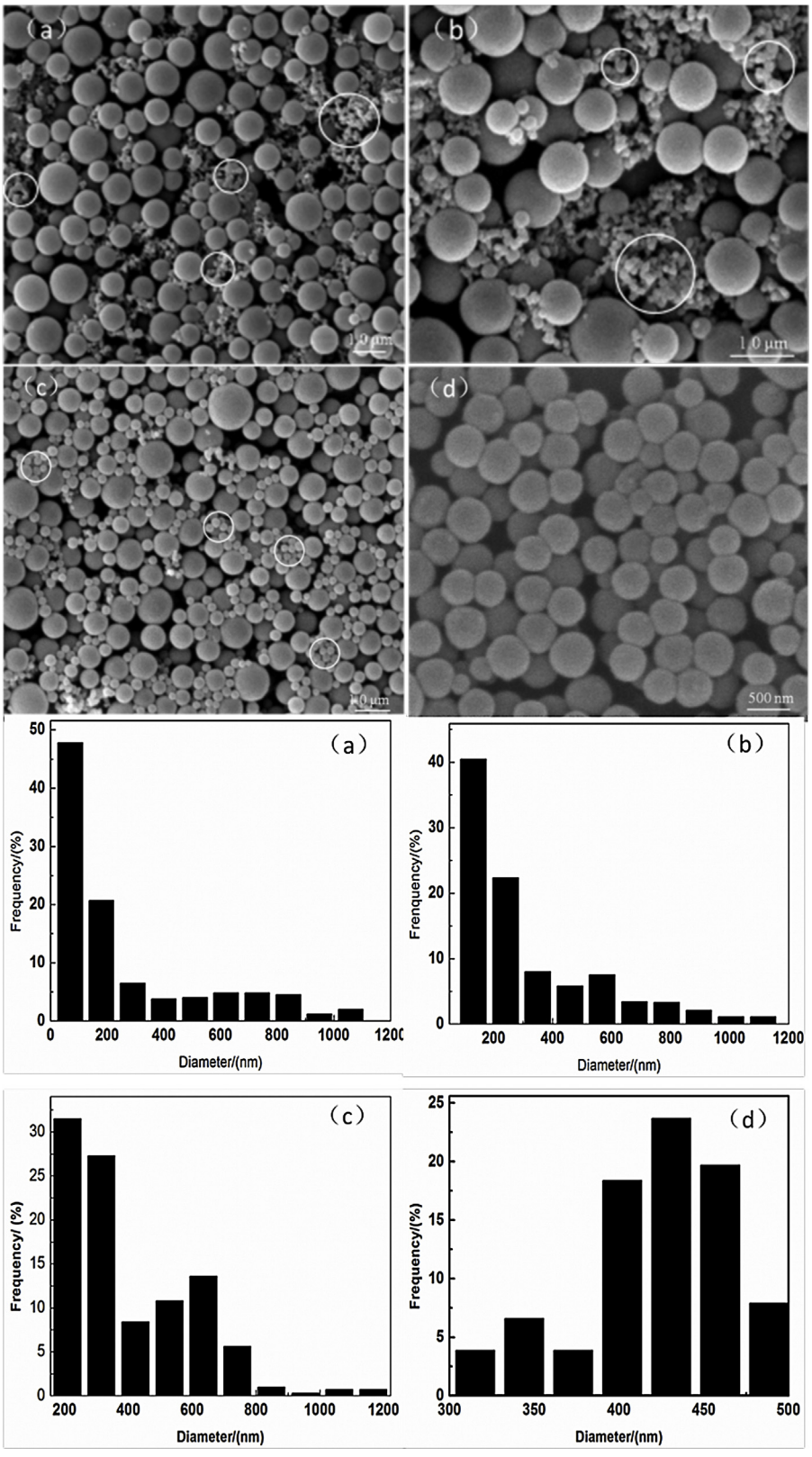

Fig. 1. SEM images and size histograms of (a) CSp-190, (b) CSp-200, (c) CSp-210, and (d) CSg-210.

hemicellulose-derived products such as pentosan are removed to improve the quality of final products, and these by-products are usually discarded with no further use. Making full use of hemicelluloses to produce high-value functional carbon materials will improve the productivity of biomass, which aligns with the strategy of sustainable development and has practical importance.

In the present contribution, pentosan separated from bleach hard kraft pulp (BHKP) as a by-product of pulp refining is used as a