Advanced Powder Technology 25 (2014) 695–703

Contents lists available at ScienceDirect

Advanced Powder Technology

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

Original Research Paper

A novel method of combination of Kraft lignin with synthetic mineral support

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ARTICLE INFO

Article history:
Received 27 June 2013
Received in revised form 27 September 2013
Accepted 25 October 2013
Available online 9 November 2013

Keywords:
Inorganic mineral support
Kraft lignin
Biosorbents
Thermal and electro-kinetic stability
Porous structure

ABSTRACT

The main goal of this research was to produce and to give a full physicochemical description of a new group of products obtained by combining a commercially available Kraft lignin with the synthetic inorganic support $MgO{\cdot}SiO_2$. Hybrid systems of this type may have a wide range of applications, particularly considering the variety of functional groups present in the structure of lignin, as well as the large surface area presented by the inorganic oxide system. These features allow the products to be classed as effective adsorption materials, with a broad range of users connected with protection of the environment. The lignin was combined with the surface of the synthetic mineral support by way of initial activation of the lignin, followed by its reaction with the precipitated oxide system $MgO{\cdot}SiO_2$. The materials (biosorbents) thus obtained were subjected to thorough physicochemical analysis, including evaluation of their dispersive–morphological character, thermal and electro-kinetic stability, and porous structure parameters. Additionally, to confirm the effectiveness of the combining operation, the FT-IR spectra were analyzed and the elemental composition of this new group of hybrid biosorbents was determined.

1. Introduction

Over recent years a great deal of research has been carried out using materials of biological origin to prepare hybrid products with specific physicochemical and utility properties. The materials used include in particular lignin, chitin and chitosan [1–6]. The combining of materials of this type, offering unique properties, with other materials such as inorganic mineral substances makes it possible to obtain systems with very interesting parameters and a wide range of applications. Such systems can be successfully used as relatively cheap polymer fillers or as selective biosorbents of certain inorganic/organic pollutants [7–10]. The need to protect the environment, along with economic factors, has made it a very important objective to develop innovative biosorbents, which may in the near future come to replace the sorption materials that are currently in general use.

The unique properties of lignin, including the presence of functional groups such as hydroxyl, ether and carbonyl, enable it to be combined relatively easily with mineral supports. Such supports include co-precipitated inorganic oxides, which are characterized by large specific surface area, a high degree of homogeneity, thermal stability, and defined electro-kinetic properties [11–14]. The presence of hydroxyl groups on the surface of such systems is a determining factor in their reactivity and facilitates their combination with numerous compounds, including lignin [15–18].

Many scientific investigations have been carried out to evaluate organic/inorganic systems, and it is believed likely that work on such materials will bring useful results, since these composites offer very good properties and significant functionality [19–21].

The paper [22] presents a process for obtaining a silica–lignin xerogel. The researchers first obtained a silica material (using the sol–gel method) and then modified the silica using lignin. It was found that an increase in the quantity of lignin used causes significant changes in the parameters of the porous structure. The introduction of lignin into the mineral matrix causes an increase in specific surface area, as well as a decrease in pore volume. Similar results were obtained when a hybrid biosorbent was prepared using rice husks as a precursor for both lignin and silica [23].

The synthesis of a hybrid biocomposite based on lignin and hydrated silica is described in [15]. The system was prepared by way of initial precipitation of silica in a polar medium, its surface modification using aminosilane, followed by combination with activated Kraft lignin. A silica/lignin hybrid was obtained with very large specific surface area and optimum dispersive–morphological parameters. It was also shown that the properties of the hybrid material are determined chiefly by the quantity (by weight) of lignin used in the process and by the initial functionalization of the mineral support with alkoxysilane. In [24] a comparison was made of lignin-derived hybrid biocomposites obtained using silicas

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http://dx.doi.org/10.1016/j.apt.2013.10.016

produced in polar and non-polar media and by the Stöber process. The results indicate clearly the effectiveness of the proposed method for combining lignin with a mineral support. The best physicochemical parameters, including primarily the defined electro-kinetic stability, were obtained for the biocomposites based on Stöber silica. The effectiveness of the process was confirmed by XPS, FT-IR and elemental analysis.

In view of the dynamic development of industry and continuing need for new multifunctional materials, an attempt was made to produce a new group of hybrid systems based on lignin and an inorganic mineral support, with defined physicochemical properties, including above all specified porous structure parameters. The materials obtained in this manner may constitute a new group of functional biosorbents.

2. Experimental

2.1. Materials

The synthetic mineral oxide system was obtained in a process of precipitation from aqueous solutions of sodium silicate and magnesium sulfate, as described in previous work [25–26]. As a result of this process, an oxide system characterized by micrometer-sized particles (dominant particle diameter 7.8 μm), amorphous structure and a relatively large BET surface area (514 m^2/g) was obtained. In the combination process, Kraft lignin (Sigma–Aldrich) was used in quantities of 3, 5, 10, 20, 30, 40 and 50 parts by weight (samples TS 1.1–7.1) relative to the $MgO{\cdot}SiO_2$.

2.2. Process of combination of Kraft lignin with mineral support

The preliminarily obtained mineral support – $MgO{\cdot}SiO_2$ – was used in the process of combination with Kraft lignin. A technological diagram of this process is shown in Fig. 1. First, two solutions were made. Solution 1 was made of lignin dissolved in a mixture of dioxane:water (9:1, v/v). Solution 2 (oxidizing) was made of sodium periodate (Sigma–Aldrich) dissolved in water. Then solution 2 was dosed into solution 1 at a rate of 1.1 cm^3/min, in the dark. To the mixture of the two solutions the mineral support was added, and the whole of the content was stirred for 1 h. Finally the solvent was removed in a vacuum evaporator, and the product was subjected to convection drying at 105 °C for 24 h.

2.3. Evaluation of physicochemical properties of the hybrid material

The dispersive characteristics of the $MgO{\cdot}SiO_2$/lignin hybrid material were determined with a Mastersizer 2000 apparatus (Malvern Instruments Ltd.), using the laser diffraction method and measuring particles of sizes from 0.2 to 2000 μm. The morphology and microstructure of the materials obtained were analyzed using a Zeiss EVO40 scanning electron microscope. The observations enabled evaluation of the degree of dispersion, the structure of particles and their tendency towards aggregation or agglomeration. With regard to the color of the Kraft lignin and its presence in the mineral support structure after combination, colorimetric analysis was performed using a colorimeter (Specbos 4000, JETI Technische Instrumente GmbH). Daylight (D65) was used as a standard light source. The instrument evaluated the color in terms of the CIE $L^*a^*b^*$ color space system. In this color space, L^* represents the brightness, and a^* and b^* are appropriate color coordinates. Using a Zetasizer Nano ZS (based on the non-invasive back scattering light method) it was also possible to measure the electrophoretic mobility using laser Doppler velocimetry (LDV), and indirectly the zeta potential (the Zetasizer Nano ZS software provides the ability to convert electrophoretic mobility values to zeta potential based on the Henry equation). The electro-kinetic potential was measured over the whole pH range in the presence of 0.001 M NaCl electrolyte, which made it possible to determine the electro-kinetic curves. The hybrid material was also subjected to thermal stability analysis with the use of STA 449F3 apparatus (Netzsch GmbH). The tests were carried out in a nitrogen atmosphere, with the temperature varying within a range of 30–1000 °C. The specific surface area A_{BET} (BET method) was calculated based on data measured by low-temperature adsorption of nitrogen. The isotherms of nitrogen adsorption/desorption were measured at 77 K using an ASAP 2020 apparatus (Micromeritics Instrument Co.). With regard to the high accuracy of the instrument used (±0.0001 m^2/g) the surface area values were rounded

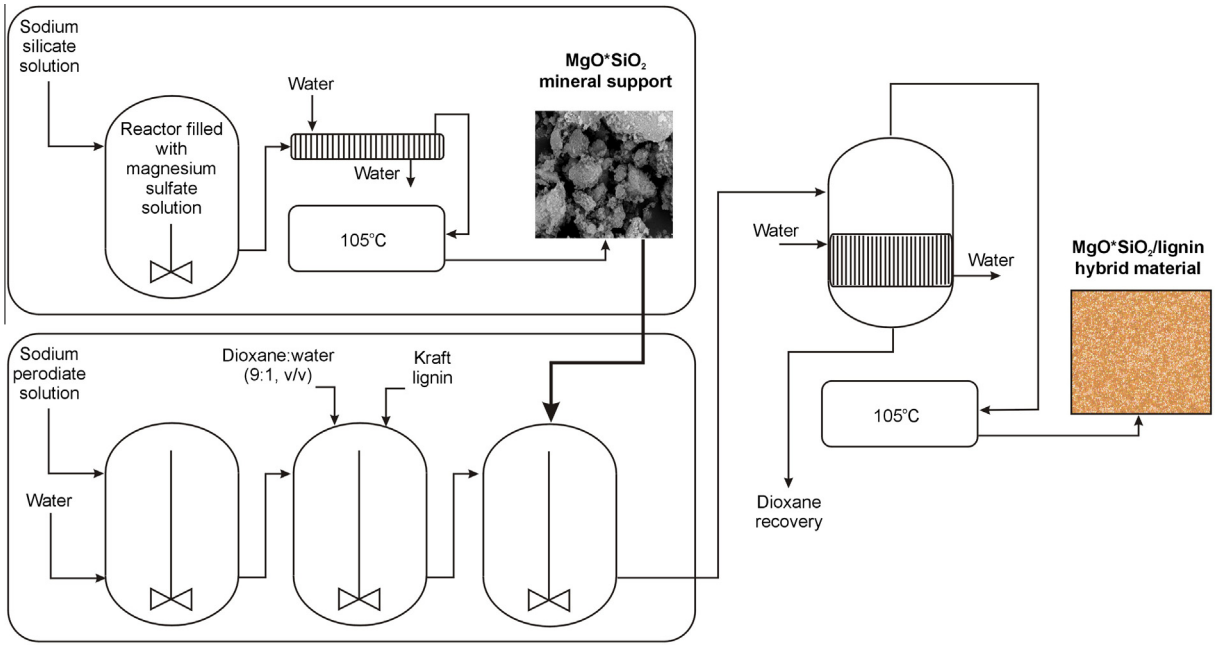

Fig. 1. Technological diagram of the production of a lignin-based hybrid material.