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Original Research

Glass and cellulose acetate fibers-supported boehmite nanosheets for bacteria adsorption

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ABSTRACT

In this work, *in situ* method of producing hybrid fibrous adsorbents in which boehmite nanosheets with high sorption properties formed on the surface of hydrophilic microfibres, such as cellulose acetate and glass fibre, was described. The boehmite nanosheets were fabricated by the reaction of composite AlN/Al nanoparticles with water at 60 °C. The synthesized samples were characterized by X-ray diffractometer, scanning, transmission electron microscopy, Fourier transform infrared spectrometer (FT-IR), zeta-potential and specific surface area analyzers. The introduction of microfibres into a diluted aqueous suspension of nanopowders causes heteroadagulation of the nanoparticles and accelerates their further transformation. This effect is most substantial with the glass microfibre, which is thought to have a higher concentration of surface groups capable of generating hydrogen bonds that act as heteroadagulation and nucleation centres. The experimental results showed that the morphology of the resultant hybrid fibrous adsorbents differed accordingly: the nanosheets were attached on-edge to the glass microfibre surface, while on the surface of the cellulose acetate microfibre, they were secured in the form of spherical “nanoflowers” of agglomerated nanosheets. The effect of the morphology of hybrid fibrous adsorbents on adsorption bacteria *Escherichia coli* was also investigated.

1. Introduction

At present, the modification of fibrous materials with nanoparticles for uses in adsorption of inorganic [1] and organic [2] molecules, electrochemical cells [3] and bactericidal materials [4] is an actively developing scientific field at the interface of physical chemistry and nanotechnology. One challenging aspect is the development of new hybrids of polymers and inorganic fibrous adsorbents, comprising fibres of natural or synthetic polymers bearing surface-bound, inorganic nanoparticles [5]. Such materials combine the attractive properties of a polymer matrix, *i.e.*, mechanical stability, chemical resistance [6], high porosity [7], and low hydrodynamic drag, with the unique sorption properties resulting from the high specific surface area [8] and chemical activity of a nanodimensional inorganic component [9]. Particles comprised of nanosheets [10] or nanopetals [11] are of special interest, due to their large specific surface area [12] and open-pore structure [13]. Strong adsorption properties (rate, capacity and selectivity) are not only demonstrated by graphene [9], a classic nanosheet material, but also by boron nitride nanosheets [14], zinc oxide [15] nanosheets and ferrous oxide nanopetals [16]. Flower-shaped boehmite AlOOH nanopetals are produced using a self-assembly method [17] usually under hydrothermal conditions [18]. In research [19], a simple hydrothermal method has been employed and a self-assembled flower-like hierarchical γ-boehmite is self-assembled. Cai at al. [20] have synthesized boehmite flower-like structures under hydrothermal conditions. This work is the first report on the evolution of boehmite morphology from nanoplates to flower-like structures.

At present, many methods of fastening nanoparticles to polymer fibres have been developed. The simplest method is impregnation of the finished fibrous material with a suspension of nanoparticles [21]. Nanoparticulate adhesion can be improved by pre-modification of the fibre surface *via* a chemical or plasma treatment [22]. A complicated, multi-stage processes, found in the literature, involves monomer polymerization in the presence of a nanoparticle precursor and electrospinning of the resultant polymer into fibres, followed by a thermal treatment of the fibres, in which the fibre is carbonized, restoring the precursor in nanoparticulate formation [23]. A relatively simple and inexpensive production method is the production of nanoparticles *in situ*, so that the nanoparticles are formed directly on the flax [24], viscose [25], wool [26], polymer [27] fibres surface. An *in*

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situ process of producing aluminum oxyhydroxide nanofibres with diameters of approximately 5 µm from aluminum powder on the surface of glass microfibres resulted in an electropositive bacterial adsorbent [28]. Hydroxide nanosheets and nanofibres as well as aluminum oxyhydroxide nanosheets and nanofibres are also formed by the interaction of aluminum nitride AlN with water [29]. Interest to these structures is due to their high ability of adsorbing bacteria, viruses, DNA/RNA, proteins, endotoxins, and antigens [30]. The morphology of these particles depends on the size and shape of the original AlN particles, as well as on the reaction conditions. The size of the original particles determines the reaction rate and the degree of conversion: large particles react slowly and incompletely, as the oxyhydroxide layer builds up on the surface of the particle, obstructing the diffusion and inhibiting continuation of the reaction. Smaller particles react completely; furthermore, as the reaction zone is limited by the volume of the precursor particle, the shape of the products will replicate the shape of the precursor, taking into account the growth in size resulting from the greater porosity of the product. Earlier, we produced aluminum boehmite nanopetals using Al nanopowder composed of 70–120 nm spherical particles [31] and composite AlN/Al nanoparticles with polyhedral (faceted) particles smaller than 50–90 nm [32]. The nanopowders were produced using a method of electrical explosion of an aluminum wire in argon or nitrogen. The two nanopowders are practically identical when synthesized in extreme excess of water and under mild conditions (*i.e.*, 50–70 °C, atmospheric pressure and a pH of 6–10). This makes it possible to introduce various microfibres into the reaction medium and use this reaction to produce hybrid fibrous adsorbents *in situ*.

This paper investigates the *in situ* formation of boehmite nanosheets on the surface of hydrophilic microfibres of various chemical compositions. The effect of the morphology of hybrid fibrous adsorbents on adsorption bacteria *Escherichia coli* was also investigated.

2. Materials and experimental methods

2.1. Materials

Composite AlN/Al nanoparticles of the investigation were produced by a method of electrical explosion of an aluminum wire in the atmosphere of nitrogen ("Advanced Powder Technologies Company", Tomsk, Russia, website: www.nanosized-powders.com). The nanop owder consists of, by weight percent, 60% aluminum nitride, and 40% aluminum. These particles constitute a composite with a core-shell structure, where the core is the metallic aluminum and the shell is the aluminum nitride. The composition and properties of hydrophilous microfibre materials are given in the Table below (Table 1).

2.2. In situ *synthesis of hybrid fibrous adsorbents*

A 0.5 g sample of composite AlN/Al nanoparticles (1% of mass) was added to 50 ml of distilled water under continuous stirring. A 0.5 g sample of cellulose acetate microfibres was added to the suspension, which was then heated from 25 to 60 °C for 60 min, long enough to complete the reaction. The glass microfibres well-dispersed in water, were then filtered using a 250 µm mesh sieve and rinsed with distilled water. Cellulose acetate, a nonwoven material that preserve their shape in the reaction medium, was extracted from the reaction vessel with pinchers and washed by dipping in the distilled water. The samples were dried at 105 °C until a constant mass was attained. The preparation procedure of hybrid fibrous adsorbents is schematically illustrated in Fig. 1.

To estimate the mass of aluminum oxyhydroxide in the hybrid fibrous adsorbents they were pre-annealed for 2 h at 900 °C. The ash content in the cellulose acetate fibre specimens amounts to less than 0.0001 g; consequently, the residue after annealing is equal to the mass of Al_2O_3. The percentage of the mass fraction of boehmite μ, was calculated based on the following formula (1)

$$\mu = (1.42m_2)/(m_1 + m_2)\cdot 100\% \quad (1)$$

where μ is the mass fraction of boehmite in the specimen, m_1 is the microfibre mass (g), m_2 is Al_2O_3 mass (g), and 1.42 is the ratio between the molar masses and boehmite, with hyper-stoichiometric water ($Al_2O_3\cdot 2.4H_2O$) and aluminum oxide (Al_2O_3) factored out.

For the glass microfibre specimens, the mass fraction of boehmite was calculated based on the following formula (2)

$$\mu = (1.42m_3 - m_1)/m_3\cdot 100\% \quad (2)$$

where m_3 is the specimen mass after annealing.

2.3. Characterisation

The specific surface area of specimens was determined using a method of thermal desorption of nitrogen and was calculated according to the BET method (Sorptometer M, Katakon, Russia). The phase composition of specimens was defined by a method of X-ray phase analysis with CuK_α-emission, using the PCPDFWIN data base (XRD-6000, Shimadzu, Japan). The specimen morphology was studied *via* transmission (JEM 21000, JEOL, Japan) and scanning (LEO EVO 50, Zeiss, Germany) electron microscopy. For assessing of nanoparticle size distributions were used automated TEM-image capture, automated particle analysis and statistical evaluation of the data (3000 nanoparticles). The size of composite AlN/Al nanoparticles agglomerates in aqueous suspension was defined by a method of sedimentation density gradient centrifugation (CPS 24000, CPS Instrument, USA). FT-IR spectra were recorded using a Nikolet 5700 spectrometer (Thermo Electron, USA) at the wave-number range of 4000–500 cm^{-1} under ambient conditions. Composite AlN/Al nanoparticles transformation kinetics in water was monitored by the change in pH of the reaction medium (multitest pH-, ion-meter, Semiko, Russia).

2.4. Adsorption of bacteria by hybrid fibrous adsorbents

The adsorptions for *E. coli* on hybrid fibrous adsorbents was measured using bacteria *Escherichia coli* K-12 (Russian National Collection of Industrial Microorganisms). The fibrous adsorbents (5000 ± 0001 mg) was added to 10 ml of bacterial suspension. The value of bacterial suspension pH was 7.2. The initial inoculum concentration of bacteria *E. coli* was 10^7 cells ml^{-1}. The mixture was agitated at 200 rpm and 25 °C for 1 h. Isolation of unattached bacteria was accomplished by injecting 3 ml of sucrose solution (60% by wt.)

Table 1
Basic characteristics of microfibrous matrices.

Material grade, manufacturer	Fibre composition, elementary unit of polymer	Specific surface area, m^2/g	Mean diameter of fibre, µ	Density, g/cm^3	Production method, form of specimen
FPA-15-2,0 Esfil Tehno, Estonia http://www.esfiltehno.ee	Cellulose acetate, $[-C_6H_7O_2(OCOCH_3)_3-]_n$	3	1.5	1.28	Electric spinning nonwoven material
Glass microfibre B-06-F Lausha Fibre International, USA http://lfifiber.com	Borosilicate *glass* [≡Si-O-]	5	0.6	2.23	Melt blow molding, cotton wool