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Sorption Activity of Nanosized Powders of SnO_2 and $CoFe_2O_4$

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Abstract

Nanosized powders of the oxides SnO_2 and $CoFe_2O_4$ with the specific surface of 130 and 160 m^2/g, respectively, were obtained by means of mechanochemical synthesis from the salt systems of the corresponding reagents. The physicochemical characteristics of the powders and their absorption ability with respect to microorganisms and organic pollutants were studied. It was established that the sorption of bacterial cells *Micrococcus albus* and *Pseudomonas putida* during filtration of the microbial oil-polluted suspension through the columns filled with the nanosorbents under investigation is 99.999–100 %. Due to the developed specific surface, the nanosorbents can be used for high-quality purification of drinking water from microorganisms and organic pollutants, which is important in the efforts to decrease the infectious morbidity of the population.

Key words: nanosorbents, specific surface, microorganisms, sorption activity

INTRODUCTION

Nanoparticles of various oxides are used in diverse processes of adsorption-based purification, in the separation of gases and liquids. Increased interest to these nanoparticles is determined by a set of physical and chemical characteristics and their unusual magnetic properties. These features include the dimension factor of nanoparticles, ensuring their highly developed surface (130–160 m^2/g) [1, 2]. The presence of functional groups on the surface of nanoparticles enhances their adsorption properties and allows considering them as highly efficient sorbents with respect to microorganisms, enzymes, proteins and other biological objects [3, 4].

It is interesting and important to investigate the absorption capacity of SnO_2 and $CoFe_2O_4$ nanoparticles with respect to microorganisms. It is known that the number of bacteria adsorbed on the surface of a certain mass of sorbent depends on the surface charge of nanoparticles, its degree of dispersion and specific surface area: the smaller is particle size, the larger is their total surface [5]. It should be noted that the phenomenon of microorganism adsorption is specific and has profound biological sense, for example, in the case of phage adsorption on host cells or sorption of bacteria on a solid substrate, and also in the case if sorbents are used to treat intestinal diseases in order to remove pathogenic microflora from the organism [6].

The goal of the present work was to study the sorption activity of mechanochemically synthesized nanosized SnO_2 and $CoFe_2O_4$ powders with respect to microorganisms and oil pollutants.

METHODS AND MATERIALS

Nanosorbents SnO_2 and $CoFe_2O_4$ obtained by means of mechanochemical synthesis from the salt systems of the corresponding reagents were the object of investigation. The synthesis was carried out in a MPV planetary mill for 30 min, with the ratio of balls to reagent powder mass equal to 20 : 1 [2]. A mixture of the reagents, of "kh. ch." (chemically pure) reagent grade, dried preliminarily at 120 °C, was diluted with sodium chloride and sealed in steel cylinders with the balls 5 mm in diameter, made of ShKh 15 steel. The resulting product was washed with distilled water until complete removal of salts, centrifuged in a centrifuge (MPW Med. Instruments, Poland) and dried at room temperature.

The phase composition, particle size and structure of the resulting nanosized powders were determined on a Shimadzu XRD-6000 setup (Japan) and by means of transmission electron microscopy using the EM-125 instrument (Elektron Plant, Ukraine). Investigation of the magnetic properties of synthesized nanosorbents was performed using the analysis of the temperature dependence of initial magnetic permeability at a frequency of 1 kHz, as well as magnetization curves and their derivatives obtained in pulsed magnetic fields with strength up to 3 T. The specific surface area (S_{sp}) of the samples was determined by means of the thermal desorption of nitrogen with a Sorbi N 4.1 instrument (Russia). Infrared spectra were recorded with a Nicolet 5700 FT-IR spectrometer (France). The wavenumber measuring range was 400–4000 cm^{-1}, with a diffuse reflection attachment.

The sorption activity of the obtained nanosorbents was studied under the static and dynamic conditions with respect to the collection strains of aerobic microorganisms: *Micrococcus albus* and *Pseudomonas putida*, obtained from the Department of Collection of Microorganisms, SSC Vektor (Koltsovo settlement, Novosibirsk Region, Russia). Bacteria were grown at 30 °C in Raymond's liquid mineral medium, which has the following composition, g/L: Na_2CO_3 0.1, $NaSO_4 \cdot 5H_2O$ 0.02, Na_2HPO_4 0.7, KH_2PO_4 0.5, $MgSO_4$ 0.2, $CaCl_2 \cdot 6H_2O$ 0.01, NH_4Cl 2.0, NaCl 2.0. We added 1 mL of the solution of microelements prepared according to Pfennig [7] to the mineral medium. Hexadecane 0.5 % was introduced into the medium as an organic additive.

Sorption of microorganisms was studied in the dynamic mode during the filtration of pure and oily bacterial suspensions through a glass column packed with nanosorbent. The concentration of oil pollution was 2 %, column diameter 1.0 cm, height 30 cm. To prepare bacterial suspensions, we used daily cultures of microorganisms grown on meat peptone agar (MPA). During the studies of sorption processes in the dynamic mode, we took into account the mass and height of the sorbent layer in the column, the rate of filtration, the volume and the number of microorganisms in the initial bacterial suspension and after filtration. The number of sorbed microbial cells per 1 g of nanosorbent and the percentage of sorption (A) of microbial cells were calculated using the formula

$A = 100N_f/N_{in}$

Here N_f and N_{in} are the numbers of cells after filtration and in the initial suspension, respectively.

To assess the sorption capacity towards organic pollutants into the liquid phase sampled after filtering the oily bacterial suspension, we added chloroform, thoroughly shook the mixture, separated the chloroform extract from the aqueous phase. Chloroform was removed using the rotary evaporator; the residue was investigated by means of IR spectroscopy.

In the static mode, the sorption activity of nanosorbent with respect to microorganisms was studied using the method proposed by E. V. Dianova and A. A. Voroshilov. For this purpose, 1 g of sorbent and 1 mL of the cell suspension of microorganisms under study were placed into a large test tube, then 9 mL of sterile saline was added. After stirring for 10 min and settling (20 min), bacterial inoculation was performed from the upper layer onto the agar medium in order to account for the number of microorganisms after sorption. The tubes with culture were mounted on 3 × 2 cm magnets to achieve more complete precipitation of adsorbed cell. The initial number was determined using the same method but without the addition of sorbent.

RESULTS AND DISCUSSION

Preparation and properties of nanosized oxides

To obtain SnO_2 and $CoFe_2O_4$ nanosorbent powderы, reactant mixture with an inert diluent (NaCl) at a mass ratio equal to 1 : 2 was sealed in steel cylinders with quenched balls. In this case, chemical reactions take place at the interfaces that are continuously renewed during mechanical activation and grinding reactants, such as chlorides and carbonates, in the presence of an inert diluent (NaCl). Heat released during the reaction is dissipated in the diluent, as a result, mechanochemical synthesis proceeds in a quiet mode without heating, and the final products are nanoparticles dispersed in a soluble salt matrix. The following reagents were used for the synthesis of nanosorbents: $SnCl_2$ ("ch." reagent grade), Na_2CO_3 ("ch. d. a."), NaCl ("kh. ch."), $FeCl_3$ ("kh. ch."), $CoCl_2$ ("kh. ch."). Cobalt, iron and tin chlorides were crystal hydrates.

The synthesis of tin dioxide and cobalt ferrite was carried out according to reactions

$$SnCl_2 + Na_2CO_3 + 0.5O_2 = SnO_2 + 2NaCl + CO_2\uparrow \quad (1)$$

$$2FeCl_3 + CoCl_2 + 4Na_2CO_3 = CoFe_2O_4 + 8NaCl + 4CO_2\uparrow \quad (2)$$

According to the electron microscopic results, the synthesized $CoFe_2O_4$ powder is composed of the agglomerates (265±15) nm in size, consisting of weakly interconnected nanoscale particles with a diameter 3 to 15 nm. The fraction of particles 4–8 nm in size was about 65 % (Fig. 1, *a*).

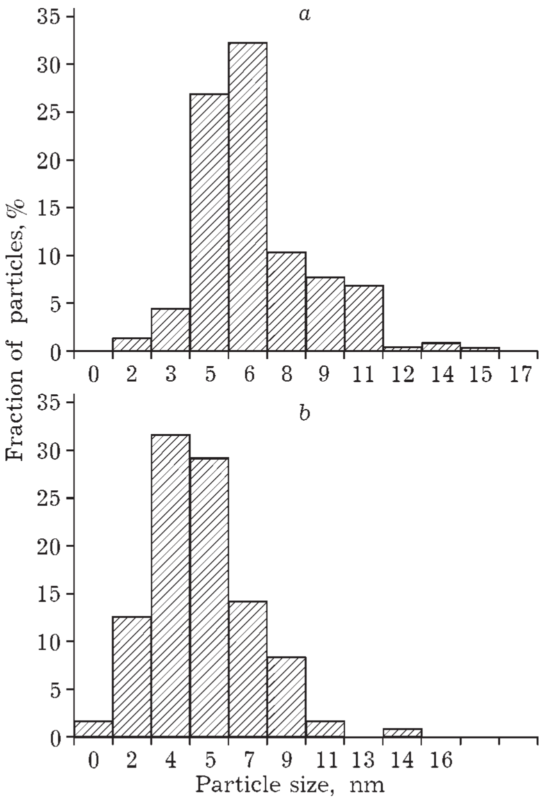

Fig. 1. Histograms of the synthesized $CoFe_2O_4$ (*a*) and SnO_2 (*b*) nanopowders.

According to the IR spectroscopic data, there were carbonate (absorption bands at 1620, 1465, 1447, 1341, 876 cm^{-1}) and hydroxyl functional group (absorption bands at 876, 586 cm^{-1}) on the surface of cobalt ferrite (Fig. 2).

According to X-ray diffraction (XRD) data, processed using the full profile analysis programme ROWDER CELL 2.5, the powder of $CoFe_2O_4$ nanosorbent contains 90.8 vol. % of cobalt ferrite, 3.3 vol. % of magnetite and 6 vol. % of unidentified amorphous phase. According to the data of X-ray structural analysis, the lattice parameter of cobalt ferrite spinel (*a*) is 8.372 Å. The coherent length (*L*) is 9.2 nm; the specific surface of nanosized cobalt ferrite is 160 m^2/g. The physical properties of nanosized $CoFe_2O_4$ powders were described in detail in [1].

According to the electron microscopic analysis, nanoscale particles of tin dioxide SnO_2 can be divided into two dimensional levels. The first one includes spherical particles with a size ranging from 3 to 11 nm, this is so-called light fraction; its content in the sample is about 40 % (see Fig. 1, *b*). The second level includes poorly aggregated spherical particles with a size 40–80 nm. In addition, the composition includes separate particles with a size 100–120 nm and aggregates with a size up to 200 nm.

The X-ray structural analysis showed that the major tin oxide phase formed during mechanochemical synthesis is SnO_2 with the tetragonal lattice. We detected also the SnO_2 phase with orthorhombic lattice, which is the high-

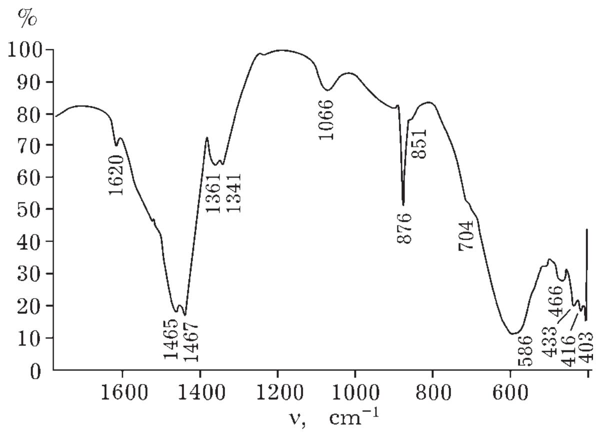

Fig. 2. IR spectrum of nanosized particles of cobalt ferrite ($CoFe_2O_4$).

pressure phase, which is characteristic of the particles several nanometres in size, as the authors noted for the first time [7, 8]. The resulting nanosized tin oxide powder contains about 2 vol. % magnetite, which explains its weak magnetic properties. The specific surface area of nanosized tin oxide is 130 m^2/g. According to the IR spectroscopic data, adsorbed and crystal water is present in tin dioxide.

Sorption activity of SnO_2 and $CoFe_2O_4$ nanosorbents with respect to microorganisms under static and dynamic conditions

Static conditions. Sorption of the fixed spherical cells of *Micrococcus albus* strain and rod-like mobile *Pseudomonas putida* was performed with different concentrations of microbial cells in the medium with pH 4.5, 7.2 and 9.0. The mass of nanosorbent added in all the versions of the experiment was 1 g (Table 1).

The action of the sorbent on microorganisms depends on the specific experimental conditions, including pH of the medium and the number of microorganisms in the initial suspension. Specific sorption of micrococcus for the initial number equal to 64 million cells, depending on pH, using $CoFe_2O_4$ was 62.07–63.90 million cells/g, the amount of sorption was 99.98–99.84 %. For the case of SnO_2 as a sorbent, the value of sorption of *Micrococcus* does not exceed 99.6 % (see Table 1). As follows from the data shown in Table 1, the maximum sorption for the *Micrococcus strain* in both versions is observed at pH 7.2.

The sorption of microorganisms of *Pseudomonas* genus was studied in two versions of experiments with different concentrations of bacterial cells in the initial bacterial suspension (see Table 1). One can see that the sorption capacity of nanoparticles and the sorption of mobile cells of *Pseudomonas* increases in direct proportion to an increase in the number of cells in the initial suspension; the maximum was detected at pH 7.2, too. Sorption of microbial cells on SnO_2 nanoparticles with a specific surface of 130 m^2/g was 99.75 %, for $CoFe_2O_4$ with specific surface area 160 m^2/g it was 99.99 %.

Therefore, under the static conditions at pH 7.2 the highest sorption was detected; its value is proportional to the number of cells in the initial suspension and the specific surface of the nanosorbent. Under the acidic (pH 4.5) and alkaline (pH 9.0) medium, the sorption activity decreases in all versions of the experiment (see Table 1). Due to the presence of functional groups on the surface of nanoparticles (hydroxyl, carboxyl, and carbonyl) and magnetite, the nanosized $CoFe_2O_4$ and SnO_2 powder appears to be the materials with excellent absorption properties.

For the extraction of emulsified oil with the sorbent under static conditions, the equilibrium in the system gets established within 45 min, and the extent of oil extraction (if its initial concentration was 20 g/dm^3 and mass of sorbent 10 g/dm^3) reaches 96 %.

TABLE 1

Effect of pH of the medium on the sorption capacity of $CoFe_2O_4$ and SnO_2 nanosorbents with respect to microorganisms under the static conditions

Bacteria, genus	pH	Initial number	Sorption capacity, million cells/g		Sorption, %	
	of medium	of cells, million cells	SnO_2	$CoFe_2O_4$	SnO_2	$CoFe_2O_4$
Micrococcus	4.5	64	61.5 7	62.07	96.2	96.98
	7.2		63.74	63.90	99.6	99.84
	9.0		61.95	62.24	96.8	97.65
Pseudomonas	4.5	96	92.44	93.27	96.3	97.15
	7.2		95.23	95.42	99.2	99.48
	9.0		93.12	93.72	97.0	97.63
	4.5	124	120.77	121.82	97.4	98.34
	7.2		123.69	123.98	99.75	99.99
	9.0		121.52	122.01	98.0	98.40

TABLE 2

Sorption of microbial cells and polluting oil under dynamic conditions

Bacteria, genus	Initial microbial suspension		After filtration through a column with nanosorbent*	
	Number of cells, million	Concentration of oil, %	Sorption, %	Concentration of oil, %
Pseudomonas	102	2.0	99.999/100	0/0
Micrococcus	85	2.0	100/100	0/0

* The first value is for SnO_2, the second for $CoFe_2O_4$.

Dynamic conditions. Sorption under dynamical conditions was studied during the filtration of pure bacterial suspension and the suspension contaminated with oil in the concentration of 2 %. Oil from the Sovetskoye deposit in West Siberia was used in the experiments; its viscosity was 9.14 mPa · s and density 0.861 g/cm^3 at 20 °C. Oily and pure suspensions of *Micrococcus* and *Pseudomonas* with the initial number of cells 85 and 102 million, respectively, were filtered through the columns filled with $CoFe_2O_4$ and SnO_2 (Table 2). In both versions of the experiments, the height of the sorbent layer was 4 cm, column diameter was 1.2 cm, the volume of the initial suspension was 8 cm^3, and filtration rate was 1.4–1.5 cm^3/h. During the filtration of pure suspension, the microbes are fully extracted with the nanosorbents. In this case the value of sorption for *Micrococcus* and *Pseudomonas* is 100 %. The data obtained during the filtration of oily bacterial suspension are given in Table 2.

The aqueous phase completely purified from oily components was obtained at the outlet of the column. Hydrocarbons in the liquid phase at the outlet of the column were controlled using IR spectroscopic methods. For filtering the oily bacterial suspension containing movable cells of *Pseudomonas* through the column with SnO_2, cell sorption was 99.999 %, and in the case of nanosorbent $CoFe_2O_4$ sorption was 100 %. Fixed spherical cells of *Micrococcus* were absorbed from oily medium on nanosorbents by 100 % (see Table 2).

The addition of nanosorbents into oily culture medium provides simultaneous adsorption of hydrocarbons and bacterial cells of oil-consuming microorganisms. Such a combination of the hydrocarbon substrate and the agents of its utilization in one volume contributes to the accumulation of biomass and stimulates the oxygenase activity of microorganisms.

CONCLUSION

Comparative analysis of the data suggests that the static and dynamic sorption capacity of $CoFe_2O_4$ nanoparticles was slightly higher compared to SnO_2. This difference (hundredths and thousandths of a percent) was apparently determined by their specific surface, magnetic properties and the active sites on the surface of the sorbent.

The high sorption activity of $CoFe_2O_4$ and SnO_2 nanopowders towards organic compounds and microorganisms with different morphological features (*Micrococcus albus* and *Pseudomonas putida*) implies the development of special cartridges for simultaneous profound purification of water from organic pollutants and microorganisms.

In addition to high adsorption properties, $CoFe_2O_4$ and SnO_2 nanopowders have high chemical stability and mechanical strength.

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