

Investigation of adsorption properties of alumina produced by vacuum spray method

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Abstract. In this paper nanopowders obtained by vacuum spray method were studied. The phase composition of the obtained powders is $\gamma - \text{Al}_2\text{O}_3$. Obtained nanopowders have specific surface area about $200 \text{ m}^2/\text{g}$. Adsorptive properties of these powders were studied by static adsorption from solutions. The anionic dye eosin was selected as adsorbate. It has been found that the powders obtained by vacuum spray method have significant capacity to adsorb eosin.

1. Introduction

Nowadays nanopowders of aluminium oxide and system based on it are widespread in various branches of technology. These nanopowders are used as adsorbents, catalysts and a raw for nanoceramics. A structure of these nanopowders provides their unique mechanical and physical-chemical properties, which appear as individually as when interacting with other substances.

There are a lot of methods for producing alumina ($\gamma - \text{Al}_2\text{O}_3$), method of dispersing and hydrothermal treatment of the alumina trihydrate for example. It should be noted that this method is a time-consuming and energy-intensive, because it consists of many stages [1]. Furthermore nanopowders of alumina are produced by combustion of large particles of alumina with a binder component. At the high temperature the binder burns down and it leads to obtaining of porous active alumina [2]. But this method has disadvantages too; the essential is nonreproducibility of results.

In this paper the vacuum spray method was used for obtaining of alumina. This technique is a three stage process: preparing a suspension, spraying the suspension on a vacuum spray drying system NanoSprayDryerB-90 and heat treatment of the samples.

In contrast to existing methods of producing active alumina, this method is simple to implement, provides reproducible results and is promising for use in many areas of production, for producing sorbents for example.

Nowadays humanity has a problem of rational use of water resources. There are new adsorption technologies for water treatment against various contaminants: oil products, phenol substances, microbiological objects. Adsorption of microbiological objects which have negative charge in aqueous media occurs most effectively at the surfaces, which are characterized by a positive charge as alumina surface. Therefore the searching and development of this type of adsorbents for water treatment technologies is actual scientific problem now [3].

Alumina produced by NanoSprayDryerB-90 has significant specific surface and positive zeta potential in aqueous solutions [4], so such an alumina is perfect material for sorbents. In this work our study was focused on producing of $\gamma - \text{Al}_2\text{O}_3$ by vacuum spray method and investigation of its adsorption properties.



2. Experimental

2.1. Sample preparation

Vacuum spray drying method (NanoSprayDryerB-90, NSD-method). A 0.5 M aqueous solution of 9-aqueous aluminum nitrate was prepared, after preparation solution was heated at 70 °C for one day. Obtaining of the Al(OH)₃ suspension was produced from anaqueous solution by chemical deposition. Chemical deposition was carried out using aqueous 25% solution of NH₄OH. The resulting Al(OH)₃ suspension was washed by distilled water to remove excess of ammonia. Then the suspension was fed to Nano Spray Dryer B-90 (Switzerland). The following parameters were used in the experiment: air flow rate 140 l/min, the relative intensity of dispersion is 60 – 63%, T = 60 – 80°C, P = 120 Pa, nozzle size 7 nm. The product was divided into pieces, and these pieces were annealed at temperatures 550 °C, 600 °C and 700 °C for 4 hours respectively.

Chemical deposition (CD-method). Also for comparison samples of alumina were prepared by chemical deposition without vacuum spraying. Produced precipitate was filtered and washed with distilled water. After all operations precipitate was dried for 3 days at 60 °C, divided into three pieces and annealed at temperatures of 550 °C, 600 °C, 700 °C for 4 hours respectively.

2.2. Adsorption tests

Static sorption method from the aqua solutions was performed for studying the adsorption properties of alumina. Adsorption was carried out at room temperature. Anionic dye eosin (C₂₀H₆O₅Br₄K₂) with maximum of light adsorption at 490 nm was selected as model adsorbate. The initial and the equilibrium concentration of adsorbate were determined photometrically by spectrophotometer (Pd Spectrophotometer, Japan) [5]. Initial concentration of eosin in aqueous solutions is presented in Table 1.

Table 1. Initial concentration of eosin in aqueous solutions

Number of solution	Eosin concentration(mg/l)
1	4
2	8
3	12

Alumina powders were placed in eosin solutions #1 – 3 (Table 1), were sonicated for 3 min and transmittance of solutions was measured after 1, 2, 3 and 4 hours. Before transmittances measuring the deposition of alumina powder from solutions was carried out by centrifugation at 15000 rpm by Centrifuge CM-50.

3. Results and discussion

3.1 XRD and TEM analyses

X-ray analysis was carried out for determining the phase composition and the region of coherent scattering of samples; results are shown in Table 2. Phase composition of ceramics supports was studied using XRD - 7000S Shimadzu diffractometer with CuK α irradiation ($\lambda = 1.5406 \text{ \AA}$). Analysis of phase composition was performed according to ASTM database.

According to the data of Table 2, all the samples content only crystalline phase in form of γ - Al₂O₃. Significant differences in the region of coherent scattering of samples prepared as NSD and CD have not been found.

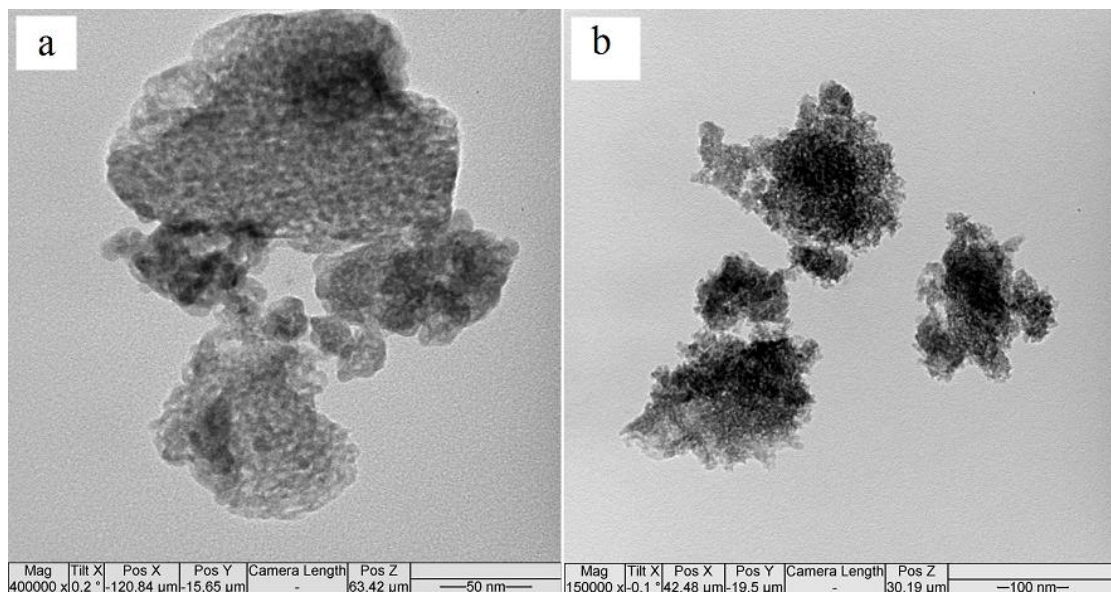
Samples have a considerable surface area (Table 2) up to the largest one – 216 m² / g for the sample #1. Specific surface area slightly decreased with the increasing of temperature treatment for all the samples.

Table 2. Parameters and characteristics of the samples

Number of samples	Method of producing	Temperature of annealing (°C)	Size of CSR ^a (nm)	Phase composition	Specific surface (m ² /g)
1	NSD ^b	550	9,48	$\gamma - \text{Al}_2\text{O}_3$	216
2	CD ^c	550	9,49	$\gamma - \text{Al}_2\text{O}_3$	204
3	NSD	600	9,49	$\gamma - \text{Al}_2\text{O}_3$	177
4	CD	600	9,49	$\gamma - \text{Al}_2\text{O}_3$	200
5	NSD	700	9,19	$\gamma - \text{Al}_2\text{O}_3$	161
6	CD	700	9,46	$\gamma - \text{Al}_2\text{O}_3$	158

^aCoherent Scattering Region^bNano Spray Dryer^cChemical Deposition

Investigation of the samples structure was carried out by transmission electron microscopy (JEM 2100, JEOL) and scanning electron microscopy (NeoScope JCM-6000). Bright field images of the sample obtained by the NSD shown, that the particles have irregular shape, close to the distorted spherical (Figures 1, 2). The medium size of particles was ~ 110 nm. The particles had a uniform grain structure and were partly agglomerated and consisted from the smaller ones. Particles had nanoscale unit at least on one dimension (Figures 1, 2).

**Figure 1.** TEM microphotographs of sample #3(a), sample #4 (b)

Presumably, the presence of the granular structure shows that the particles consist of smaller crystallites, which is consistent with XRD (CSR is ~ 9 nm). The gaps between crystallites presented the porous structure of the samples.

The powders produced by CD had different morphology. These particles had a jagged irregular shape (Figures 1, 2).

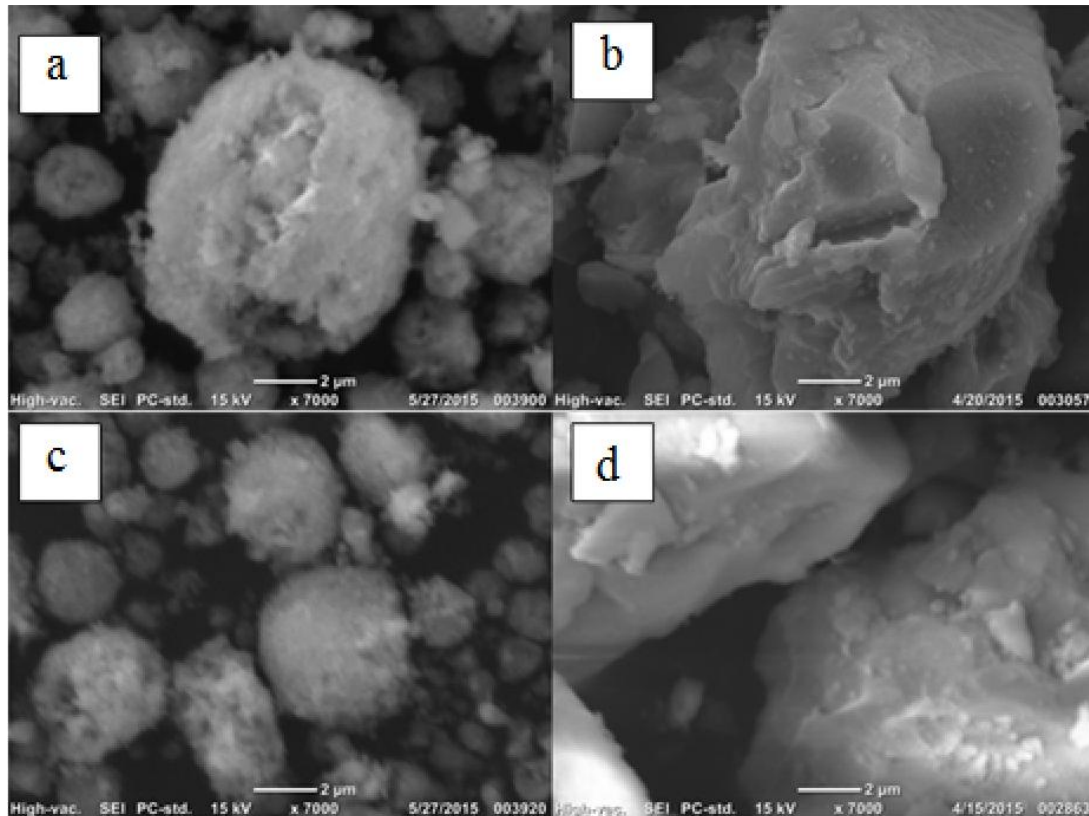


Figure 2. SEM microphotographs of samples: #1 (a), #2 (b), #3 (c), #4 (d)

According to the Figure 2 particles obtained by CD had a smoother surface and a higher agglomeration.

3.2. Sorption properties of samples

All synthesized samples of alumina adsorbed eosin from the aqueous solution. Anionic dye eosin can absorb on positively charged surface, so all the obtained samples of alumina are characterized by a positively charged surface.

Fig. 3 shows that the samples obtained by NSD adsorbed a comparable to CD samples amount of eosin. The samples #3 and #5 obtained by spray dryer and annealed at 600 and 700 °C adsorbed a larger amount of eosin (with initial C 4 mg/l) than similar samples prepared by chemical precipitation (Figure 3, a).

Figure 3, b shows that the sample #6 prepared by CD have the bigger value of adsorption at initial concentration of eosin 8 mg / l. At the initial concentration of eosin 12 mg/l the higher adsorption demonstrate samples #1 (NSD) and #6 (CD).

All samples are characterized by large capacity for adsorption of eosin due to a positively charged surface.

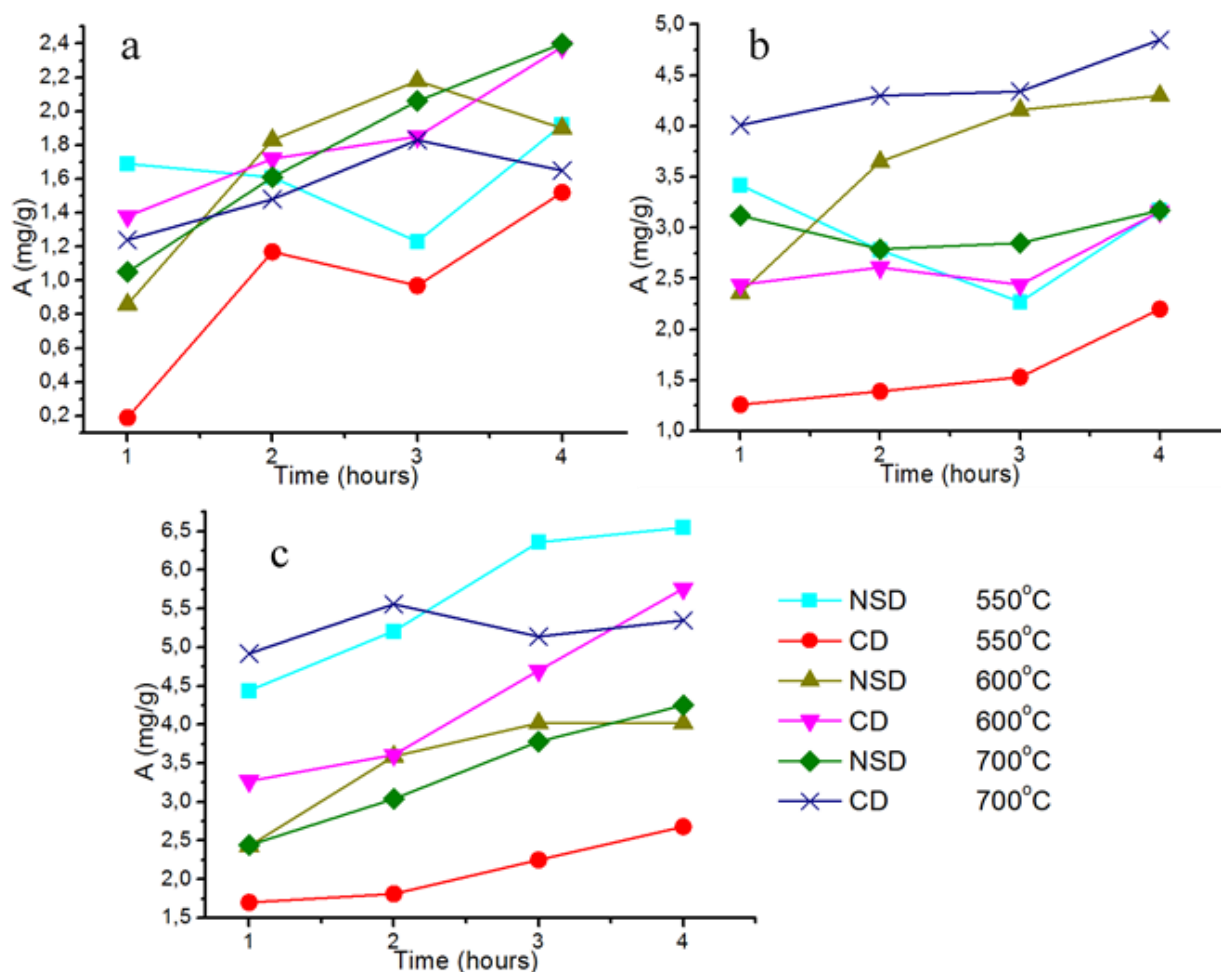


Figure 3. Adsorption of eosin (a – initial concentration of eosin is 4 mg / l; b - 8 mg / l; c – 12 mg / l)

4. Conclusion

The nanosized alumina powders were obtained by NSD method, it should be mentioned that all the samples content only γ - Al_2O_3 phase. The powders had large specific surface area $\sim 200 \text{ m}^2 / \text{g}$. All samples are characterized by large capacity for adsorption of eosin due to a positively charged surface. So it can be used in adsorption of microbiological objects which have negative charge in aqueous media.

References

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