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PHYSICO-CHEMICAL AND SORPTIVE PROPERTIES OF NANOCOMPOSITES BASED ON ZIRCONIUM(IV) OXIDE

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Abstract. Nanocomposites "activated carbon–zirconium(IV) oxide" were synthesized by homogeneous precipitation. The obtained samples were characterized by X-ray analysis and electron microscopy. The chemical composition of the nanocomposites was determined by the thermal analysis. Sorption properties were determined. The degree of phosphate ions removal was almost 97 %.

Keywords: nanocomposites, zirconium(IV) oxide, activated carbon, homogeneous precipitation, sorption, regeneration.

1. Introduction

Powders of ZrO_2 have many uses because of their high viscosity, mechanical stability, radiation and corrosion resistance, hardness, melting point, fireproofing, electrical conductivity and low thermal conductivity at low temperatures [1]. They are applied in production of substrates for fluorescent and photosensitive materials [1-3], ceramic materials, and new materials with high service characteristics, bioceramics [4-10], chemically resistant and high-strength nanoceramics [11-20]. Zirconium(IV) oxide of cubic modification is used as a solid electrolyte in solid oxide fuel cells [21, 22] and a protective anti-rust coating steel [23]. Tetragonal and monoclinic modifications are used as catalysts (due to the activity of acid sites on the surface), ceramics [24, 25] and carriers for catalysts (due to the high thermal resistance) [26, 27]. In addition, ZrO_2 materials can be used as inorganic sorbents [28] through its sorption activity to anions and cations. This allows considering ZrO_2 and materials based on it as a tool to improve the ecological environment.

Particularity of using ZrO_2 as a sorbent is due to its high selectivity to multivalent anions (chromates, borates, sulfates, phosphates, arsenates, *etc*.). Zirconium(IV) oxide can be used at high temperatures without losing its effectiveness. The greatest sorption capacity is observed for hydrated zirconium(IV) oxide (in its amorphous state) [29, 30].

Unfortunately, the use of ZrO_2 as a sorbent is limited because of its high cost. To reduce the cost of these sorbents the zirconium(IV) oxide can be synthesized in a nanodispersed state on various carriers with high-developed surface. Silica, activated carbon, carbon nanotubes, *etc*. can be used as carriers. In terms of cost and technology the most accessible carriers are silica gel and activated carbon. However, activated carbon is characterized by more developed specific surface area (compared to the listed carriers) and a variety of sorption properties. This makes it most appealing for these purposes.

Thus, the aim of this work is synthesis of nanocomposites "activated carbon–zirconium(IV) oxide" and determination of their sorption characteristics for using them as sorbents.

2. Experimental

2.1. Materials

The reagents $ZrOCl_2 \cdot 8H_2O$ (chemically pure), urea (chemically pure), activated carbon were used as materials. Activated carbon was pre-crushed and sieved to remove fractions of more than 63 microns and dried at the temperature of 383 K for 2 h to remove water.

2.2. Methods

The nanocomposites "activated carbon–zirconium(IV) oxide" were synthesized by the method of homogeneous precipitation according to the procedure given in [31]. The necessary mass fraction of ZrO_2 in the nanocomposites was prepared by adding various amounts of $ZrOCl_2$ (thus received samples 1–4). Synthesis of nanocomposites was carried out at 368–373 K. During the synthesis the following reactions occurred:

$$(NH_2)_2CO + 3H_2O = 2NH_4OH + CO_2 \qquad (1)$$
$$ZrOCl_2 + 2NH_4OH \rightarrow ZrO(OH)_2 + 2NH_4Cl \qquad (2)$$

The precipitate was separated, washed and dried. Further the products were separated and treated at the temperatures of 573, 623, 673 and 723 K according to the reaction:

$$ZrO(OH)_2 \rightarrow ZrO_2 \cdot H_2O \qquad (3)$$
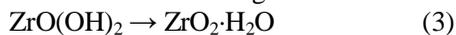
These samples of nanocomposites were investigated by the methods of X-ray analysis (DRON-3M) and electron microscopy (scanning electron microscope MIRA3 TESCAN).

The mass fraction of ZrO_2 in the synthesized nanocomposites was determined by thermogravimetric methods. The specific surface area of samples was measured by desiccator method of benzene vapor adsorption. The value specific surface area (S_{spe}, m^2/g) of the nanocomposites was calculated using the formula:

$$S_{spe} = a_m \cdot N_A \cdot S_0 \qquad (4)$$

where a_m – molar adsorption, mol/g, N_A – Avogadro constant ($6.02 \cdot 10^{23}$ mol^{-1}), S_0 – surface area occupied by one molecule of benzene ($39 \cdot 10^{-20}$ m^2).

Full static exchange capacity was determined as follows. The dried sample with weight 2.0 ± 0.2 g was placed to Erlenmeyer flask (250 cm^3) and 100 cm^3 of NaOH solution (0.1 mol/l) was added. The flask was tightly closed by cork and mixed for 24 h. After mixing the solution was poured in a dry flask. Then it was titrated by HCl solution (0.1 mol/l) with methyl orange indicator. Full static exchange capacity (SEC, mg-eq./g) was calculated by the formula:

$$SEC = \frac{(V \cdot K_1 - K \cdot V_1 \cdot K_2)}{m \cdot (100 - W)} \cdot c \qquad (5)$$

where V – volume of NaOH solution, ml, K – coefficient equal to the ratio of volume of working solution to the volume of solution taken for titration; V_1 – volume of solution used to titrate the sample solution after interaction with the sample, ml; m – sample mass, g; W – moisture content, mas %; c – the concentration of NaOH and HCl solutions, mol/l, K_1 and K_2 – correction factors of NaOH and HCl solutions, mol/l, respectively.

Sorption properties of composites samples were studied on the model solution ($KH_2PO_4 \cdot 2H_2O$) with the concentration of 100 mg/l in terms of P_2O_5. The final phosphate content was determined by the standard photometric method with the yellow vanadium-molybdenum complex. The regenerate ability of sorbent samples was evaluated by the method presented in [32].

3. Results and Discussion

Fig. 1 shows X-ray diffractions analysis of sample 1 treated at the temperatures of 573, 623, 673 and 723 K.

Amorphous ZrO_2 ("halo" in the range $2\theta = 30–40°$) is formed at heat treatment at 573 and 623 K (according to

X-ray diffractorgrams represented in Fig. 1). At the temperatures higher than 673 K crystalline ZrO_2 of tetragonal modification (peaks at $2\theta = 30, 35, 50$ and $60°$) is formed. For samples 2-4 X-ray diffractograms are similar. Thus, to obtain conditioned composites based on amorphous ZrO_2 the final temperature must be up to 673 K. It should be also noted that the formation of ZrO_2 tetragonal modification in nanocomposites is associated with the stabilizing effect of the activated carbon.
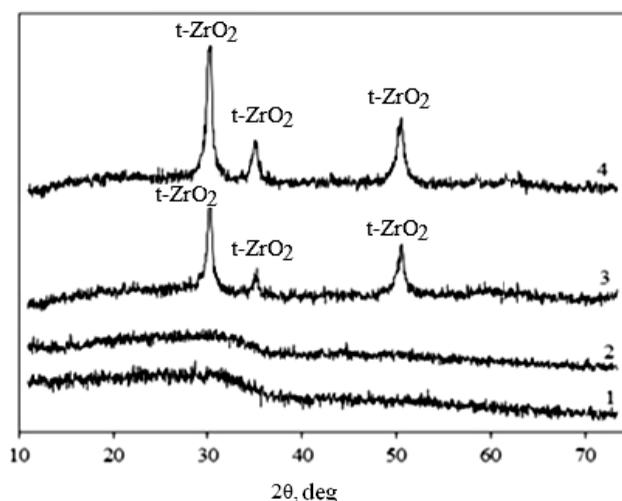
**Fig. 1.** X-ray diffractions of sample 1 treated at different temperatures, K: 573 (1); 623 (2); 673 (3) and 723 (4). t-ZrO_2 – tetragonal phase of zirconium(IV) oxide

Fig. 2 shows SEM images of sample 1. It can be seen that the aggregates of zirconium(IV) oxide particles are distributed concerning activated carbon more or less evenly.

The chemical composition and specific surface area of the synthesized nanocomposites samples 1–4 are presented in Table 1. According to the data presented in Table 1 the specific surface area of samples 1–4 is decreased with increasing content of ZrO_2. It indicates partial blocking of activated carbon pores. However, the decrease of samples specific surface area from the original activated carbon carrier is insignificant and the smallest of its value is still high (in Sample 4 – 342.8 m^2/g).

The specific surface areas (S_{spe}) and full static exchange capacities (SEC) were determined for two samples of activated carbon which were ground to particle size less than 63 µm. The first sample of activated carbon was without additional heat treatment (C1). The second sample was treated at 573 K for 1 h (C2). The third sample (nanocomposite) was Sample 1 (Table 2, heat treatment temperature is 573 K). Table 2 shows that in the pre-heat treated activated carbon sample, unlike similar not treated, the specific surface area and SEC are higher. It

a)   b)
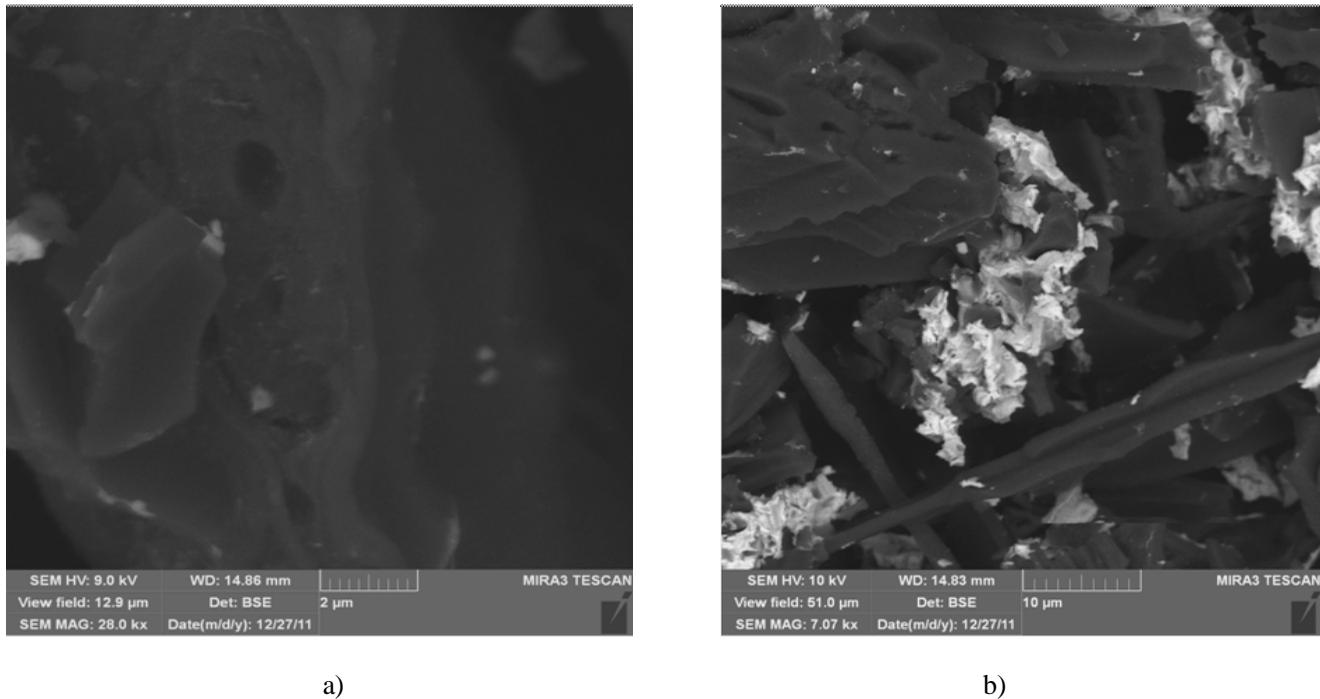
Fig. 2. SEM images of sample 1 treated at $T = 723$ K: magnification of 28000x (a) and 7070x (b)

Table 1

**Chemical composition and specific surface areas
of nanocomposite samples 1–4 ($T = 723$ K)**

Nanocomposites samples	Experimentally determined ZrO_2 mass content in nanocomposites, %	Theoretically calculated ZrO_2 mass content in nanocomposites, %	The specific surface area, m^2/g
Sample 1	27.1	28.6	342.8
Sample 2	15.8	16.0	406.3
Sample 3	6.9	7.1	469.7
Sample 4	3.4	3.7	490.1

Note: the specific surface area of activated carbon is 528 m^2/g

associated perhaps with the removal of residual volatile hydrocarbons. The nanocomposite sample has less specific surface area, but a high intrinsic (as in Sample C2) full static exchange capacity.

Fig. 3 shows the results of phosphate ions sorption from model solutions by nanocomposites samples. The maximum removal level is achieved in all cases for the sorption duration of 120 min (96.8; 90.4; 86.7 and 79.9 %, respectively) (Figs. 3a–d). Thus, sorption of phosphate decreases with decreasing of ZrO_2 content in nanocomposites. Removal of phosphate from water by activated carbon does not exceed 27 %.

The final temperature of heat treatment also affects the sorption properties of nanocomposites. The removal of phosphate ions from aqueous solutions decreases with increasing of the final temperature of nanocomposites processing (Fig. 3).

Table 2

**The specific surface areas and *SEC*s
of activated carbon samples**

Samples	S_{spe}, m^2/g	*SEC*, mg-eq./g
C1	528	0.173
C2	567.4	0.284
Sample 1	419.6	0.278

Fig. 4 shows the ion exchange and regeneration curves of sorbent (Sample 1, synthesized by treating at 573 K). Ion exchange curve has two jumps. The first one corresponds to pH = 7, and the second one – to pH = 5. This indicates that the sorption of Cl^- ions probably occurs on the surface activated carbon and on the surface of ZrO_2. Thus, according to Fig. 4, the sample can be regenerated and reused in cycles of sorption purification.
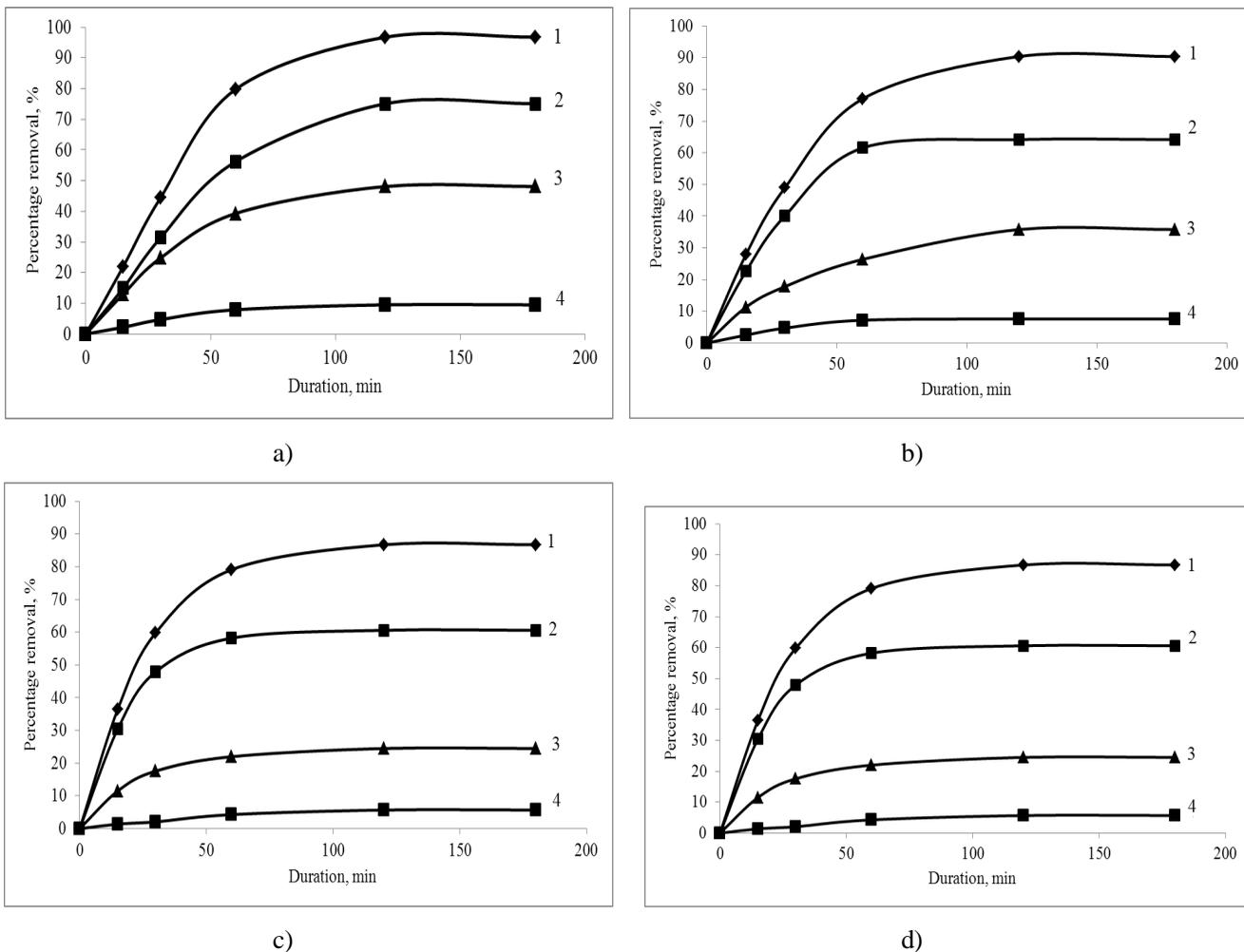
Fig. 3. The removal phosphates degree on the duration of sorption
at different final temperatures treatment (K) of nanocomposites: 573 (1); 623 (2); 673 (3) and 723 (4).
Sample 1 (a); Sample 2 (b); Sample 3 (c) and Sample 4 (d). Degree of phosphates sorption by crushed
activated carbon at 120 min is 26.9 %
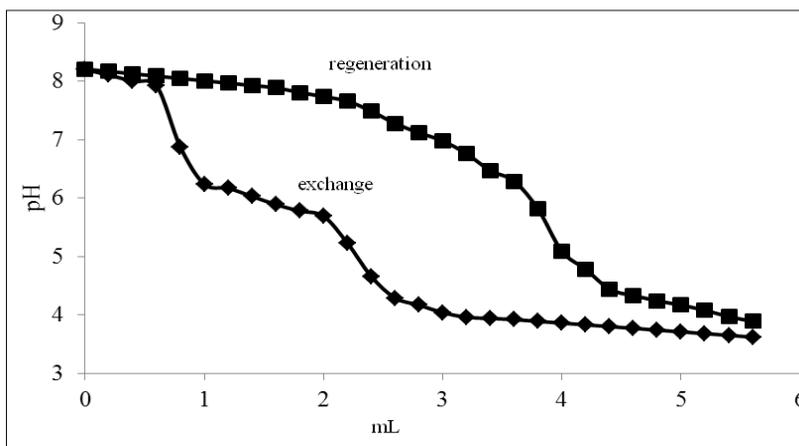
Fig. 4. Ion exchange and regeneration curves of nanocomposite Sample 1
synthesized by thermal treatment at 573 K

4. Conclusions

The obtained results lead to the following conclusions. The use of homogeneous deposition method to synthesize "activated carbon–zirconium(IV) oxide" nanocomposites produces samples with uniform distribution of nanoparticles ZrO_2 on the activated carbon surface. The sorption properties of obtained nanocomposite at 573 K are following: SEC = 0.278 mg-eq./g, S_{spe} = = 419.6 m^2/g. These values are similar to the corresponding values of industrial activated carbon samples. The removal degree of phosphate anions from aqueous solutions by nanocomposites is higher by 3–4 times compared with activated carbon. Nanocomposite "activated carbon–zirconium(IV) oxide" can be regenerated and reused in cycles of anions sorption purification.

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ФІЗИКО-ХІМІЧНІ І СОРБЦІЙНІ ВЛАСТИВОСТІ НАНОКОМПОЗИТІВ НА ОСНОВІ ЦИРКОНІЙ(IV) ОКСИДУ

Анотація. *Синтезовано нанокомпозити «цирконій(IV) оксид–активоване вугілля» методом гомогенного осадження. Отримані зразки охарактеризовані ренгенофазовим аналізом і електронною мікроскопією. За даними термічного аналізу встановлено хімічний склад нанокомпозитів. Досліджені сорбційні характеристики, за якими ступінь вилучення фосфат-йонів становила біля 97 %.*

Ключові слова: *нанокомпозити, цирконій(IV) оксид, активоване вугілля, гомогенне осадження, сорбція, регенерація.*