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Introduction

Oxide nanomaterials are attractive due to their ability to sorb both cations and anions depending on the solution acidity. They are attractive for sorption of U(VI) compounds, which are in cationic or anionic forms depending on the solution composition. In order to expend the pH interval, where different ionic forms are sorbed, oxides can be modified with selective components

Experimental

Hydrated titanium dioxide (HTD) was modified with $Co_2[Fe(CN)_6]$ nanoparticles. The first step of HTD obtaining was electrodialysis of the TiCl₄ solution, sol was synthesized by this manner. Further hydrogel granules were precipitated using a special gelling agent. During azeotropic drying, large grains of hydrated titanium dioxide (HTD) were formed. This sample (I) contained mainly regular nanopores, a size of which was about 3 nm. These pores performed a function of nanoreactors, where $Co_2[Fe(CN)_6]$ nanoparticles are synthesized (sample II). At last, the sample III was coprecipitated with $Co_2[Fe(CN)_6]$.



TEM images Sample II

Results and discussion



HTD nanofibers are formed during azeotrop drying (sample I). Nanoparticles of $\text{Co}_2[\text{Fe}(\text{CN})_6]$ are synthesized in nanoreactors (voids between fibers). During coprecipitation, lower content of the selective component has been found.



Regarding the sample I, narrow mesopores (r=1-2 nm) are related to voids between nanofibers. The isotherm shows no hysteresis loop indicating sufficient contribution of microporosity to the total pore volume.

Formation of $Co_2[Fe(CN)_6]$ nanoparticles between HDT nanofibers (sample II) results in increase of mesoporosity evidently due to partial dissolution of HDT. Small mesoporosity has been found for the sample III.

Uranium(VI) sorption

Solutions of following composition (mol/dm³) were used: U(VI) (1×10^{-4}) , H₂SO₄ (0.02). Anionic complexes of U(VI) are in the solutions of this composition.



The optimal dose is lower for sample II and U(VI) removal degree is higher comparing with unmodified HTD. The sorption rate is higher despite the presence of selective constituent. The model of pseudosecond order

 $t/A = 1/(K_2 \cdot A_{eq}^2) + t/A_{eq}$ was applied for sorption kinetics (table).

Table. Uranium(VI) sorption kinetics

Sorbent	A _{eq} ·10 ⁴ , mol/g (<i>experimental</i>)	A _{eq} ·10 ⁴ , mol/g (calculated)	K ₂ , g/(mol·s)	R ²
Sample I	1.26	1.29	621.4	0.99
Sample II	1.58	1.59	2365.9	0.99

Conclusions

Sample III shows weak adsorption of U(VI) due to small amount of $Co_2[Fe(CN)_6]$ in HTD. Incorporation of $Co_2[Fe(CN)_6]$ to previously formed nanofibrous HTD (sample II) allows us to obtain the nanoparticles of selective constituent. Developed mesoporosity increases sorption rate in 3 times comparing with unmodified HTD (sample I).

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