

PL-12**DIRECTED DESIGN OF NOVEL ADSORBENTS BASED ON HALLOYSITE MINERAL**

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Abstract. We carried out a comprehensive study of the effect of various conditions for the reactions of modification of nanotube-galloisite material (Halloysite nanoclay) (SigmaAldrich) and natural halloysite (Starocheremshanskoe ore, Chelyabinsk region, Russia) (type and amount of solvent, reaction time and temperature, use of the Brensted weak base catalyst, halloysite: silane: solvent) molar ratio on the degree of hydrolysis and the degree of functionalization. For functionalization purposes, 3-aminopropyltriethoxysilane (APTES), N- (2-aminoethyl) -3-aminopropyltrimethoxysilane (AEAPTMS), (3-mercaptopropyl) trimethoxysilane (MPTMS), (3-chloropropyl) trimethoxysilane (3PTMS) and 3-chloropropyl) trimethoxysilane (GOPTMS) were used. Toluene, dioxane-1,4, butanol, acetonitrile and tetrahydrofuran, hexane were used as solvents. In the case of using (3-aminopropyl) triethoxysilane and (3- (2-aminoethylamino) propyl) triethoxysilane, a degree of modification equal to 25% was achieved, and in the case of using (3-mercaptopropyl) trimethoxysilane and (3-chloropropyl) trimethoxysilane and (3-glycidyoxypropyl) trimethoxysilane the degree of modification which is 50-55%, has been done.¹ The use of water during APTES functionalization leads to an increase in degree of functionalization in the case of widely used solvents such as toluene (up to 86%), acetonitrile, and tetrahydrofuran (THF). In the case of functionalization with AEAPTMS, the use of water leads to an increase in degree of functionalization in the case of THF (up to 46%), which was used in experiments. Modified halloysite materials with the highest degree of functionalization achieved are further supposed to be functionalized with complexing functional groups. It was established that the halloysite surface functionalization with (3- (2-aminoethylamino) propyl) triethoxysilane and (3-mercaptopropyl) trimethoxysilane leads to a significant increase in the affinity of the material with respect to the Irving-Williams series ions, such as Zn(II), Cu(II), Ni(II), Co(II). Surface modification of the halloysite nanotube material with 3-chloropropyltriethoxysilane does not significantly affect the acidity of the medium near the surface, however, reduces the number of titrable functional groups of halloysite. In the case of functionalization with 3-glycidyoxypropyltrimethoxysilane, APTES and AEAPTMS, a decrease in the acidity of the medium near the surface of halloysite nanotubes is observed. Also, when titrating these samples, titration of surface functional groups has not been observed due to the complete interaction with silanes. The most significant changes are observed when modifying the surface of halloysite using APTES. All the results obtained will be further used to study the effects of pH of the external solution, pH_{loc} inside halloysite tubes, surface electrostatic potential (SEP) on the processes of sorption of metal ions and catalytic transformations at the phase boundary.

References

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