Reusable organo-mineral nanostructured materials with immobilized chelating ligands for selective water purification from toxic and radioactive metals

Volodymyr Zaitsev*, Olena Artiushenko, Luidmila S. Kostenko, Iryna Tomashchuk, Nataliya G. Kobylinska

Pontifical Catholic University of Rio de Janeiro, Taras Shevchenko National University of Kyiv, Ukraine, Université de Bourgogne, France

Here we report the results of application of nanostructured hybrid organo-mineral adsorbents with covalently immobilized strong complexing agents for water purification from toxic and radioactive metals. We developed procedures for preparation of the adsorbents having layer of chelating agents. These agents react with certain groups of metal ions and extract them from contaminated water. Then the adsorbed metals can be re-extracted and concentrate for further utilization and the material can be reused. Selectivity of immobilized ligands towards certain metal ions ensures the assure adsorption selectivity. Covalent immobilization ensures stability of the adsorbents. Currently we developed procedure of immobilization and studied a wide range of strong chelation ligands. Some of them have selectivity to most of heavy metals (for example 2,6-pyridinedicarboxylic acid (PdCA), and ethylenediaminetriacetic acid (EDTA)), others have selectivity to rare earth elements (REEs) and trans-uranium elements (for example hydroxamic acid (BPHA) and aminomethylphosphonic acid (ADPA). Several nanomaterials were studied as prospective supports for ligand immobilization. Mainly these are nanostructured materials such as silica gel (SiO_2) and natural diatomites; layered materials, such as clay (bentonites): and magnetic nanomaterials (Fe_3O_4/SiO_2).

Metal adsorption selectivity, capacity and kinetics were studied in dynamic (solid-phase extraction, SPE) and static (dispersive solid phase extraction, DSPE) conditions for different type of surface water (natural and industrial). Also, some adsorbents were studied for REEs pre-concentration and separation as prospective substitution for solvent extraction of REEs form recyclable sources such as e-waste. It has been demonstrated that, for example SiO2-BPHA can be successfully used as adsorbent for removal of REE ions from aqueous solution with pH > 2.5 within 10 min. Essential (more than 100 times) growth of distribution coefficient with atomic number of REE is observed for multielement solution. In optimal conditions selectivity factor is about 80 of pares Lu/La and Yb/La, and about 60 for pare Tm/La, which indicates high potential of SiO2-BPHA in REEs separation.

Bentonite with immobilized fragments of ADPA is tested for purification of contaminated river-water samples in bulk and in dynamic filtration modes. The Bnt-ADPA chemisorbs up to 0.19 mmol g-1 of metal ions such as Pb, Cu, Zn, Fe (III) in 15 minutes. These cations can be quantitatively removed from contaminated water with pH > 6.5. The adsorption/desorption process on Bnt-ADPA is completely reversible and allows multiple utilization of the adsorbent for water purification. It is demonstrated that simple filtration of samples through Bnt-ADPA filter resulted in complete (>97%) elimination of Pb(II) and significant decrease of concentration (59-65%) of Cu (II) and Zn (II).

Core-shell superparamagnetic nanoparticles with covalently immobilized derivatives of ethylenediaminetriacetic acid (MNP@SiO2-TMS-EDTA). Due to superparamagnetic properties MNP@SiO2-TMS-EDTA can be used for magnetic solid phase extraction of heavy metals from water. It has been demonstrated that Fe(III, II), Ni, Cu, Hg (II) and Cd ions can be rapidly, within 7 min, removed from water with pH ≥ 5.5 and then quantitively desorbed by 0.1 M HNO3. The sorbent capacity reached 69.4, 36.7, and 19.0 mg g-1 for Pb(II), Cd(II) and Cu(II), respectively. High affinity of metals toward MNP@SiO2-TMS-EDTA and its reusability allow multiple application of the magnetic adsorbent for analysis of polluted environmental water.