New functions for old porous and layered nanocomposites

Sridhar Komarneni

Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, USA

Here we show that the as-prepared organoclays and organosilicas are multi-functional materials for environmental applications. Different organic surfactants were used to prepare MCM-41 materials while cetyltrimethylammonium bromide (CTMAB) was used to synthesize MCM-48. Toluene sorption properties of all organosilicas and organoclays were investigated. Among organosilicas, MCM-48 exhibited the highest distribution coefficient (K_d) for toluene (95±9 L/Kg). An organoclay, prepared with montmorillonite and CTMAB showed the maximum K_d (345±22 L/Kg) for toluene among all the organosilicas and organoclays. The organoclays were found to be superior to as-prepared organosilicas for toluene uptake. Organoclays and organosilicas removed toluene by partitioning rather than adsorption.

The perchlorate and nitrate uptake of surfactant modified layered clay minerals and organosilicas were tested. Octadecyltrimethylammonium (ODTMA), Dodecyltrimethylammonium (DoDTMA), and hexadecyltrimethylammonium (HDTMA) exchanged montmorillonite from Wyoming removed perchlorate in the range of 0.025 to 0.071 meq/g from a 2mM perchlorate solution. Synthetic HDTMA (5.0 CEC) Na-1-mica exhibited the highest exchange of perchlorate with 0.348±0.011 meq/g, while DoDTMA montmorillonite had the lowest exchange with 0.025±0.009 meq/g. A commercially available organoclay, Cloisite® 10A exchanged 0.280±0.003 and 0.359±0.003 meq/g of perchlorate and nitrate, respectively. A variety of oraganosilicas such as MCM-41, MCM-48 and MCM-50 were tested. Organo-clays procured from two commercial sources were also investigated for their perchlorate exchange. Among the MCM-41 materials, the sample prepared from octadecyltrimethylammonium (ODTMA) chloride showed the highest perchlorate uptake capacity of 0.227±0.006 meq/g while MCM-48 showed the highest perchlorate uptake capacity of 0.437± 0.011 meq/g among all the oraganosilica and organo-clay nanocomposites tested. Kinetics studies showed that the adsorption followed pseudo-second-order kinetics model. The good fit of the experimental data and the values of correlation coefficients (R^2) indicated the applicability of Langmuir model to perchlorate exchange in the present study. Tested under the same conditions, a surfactant modified carbon showed a perchlorate uptake of 0.303±0.005 meq/g and this carbon is currently being used for filtration of drinking water. The synthetic organosilica materials, in addition to a commercially available organoclay, Cloisite® 10A, were also tested with the occluded surfactant as sorbents for nitrate. The results showed that the highest nitrate uptake capacities were achieved with Cloisite® 10A (0.359±0.003 meq/g) followed by a layered organosilica (0.287±0.008 meq/g). MCM-48 and MCM-41 silica exchanged 0.096±0.002 and 0.157±0.005 meq/g of nitrate, respectively. Kinetics studies showed that the exchange followed pseudo-second-order kinetic model. Layered organosilica gave a good fit to the Langmuir model among all the studied samples with correlation coefficient (R^2) close to unity (0.99). The exchange of anions such as perchlorate and nitrate by organosilicas and organo-clays is attributed to entrapped neutral template located in the mesopores of organosilicas and interlayers of organo-clays. Positively charged surfactant ions balance the negative charge on the inorganic host while the chloride ions of the entrapped neutral surfactant templates are responsible for anion exchange with perchlorate and nitrate. A simple hybrid method for the synthesis of SBA-15 nanorod arrays inside the commercially available porous alumina membrane was developed and these may be useful in nanodevice fabrication and bio-macromolecule separation.