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Effect of inorganic and organic ligands on the sorption/desorption of arsenate on/from Al-Mg and Fe-Mg layered double hydroxides

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In recent decades, a class of anionic clays known as layered double hydroxides (LDHs) has attracted substantial attention due to the potential use in many applications, such as photochemistry, electrochemistry, polymerization, magnetization and biomedical science. There has also been considerable interest in using LDHs as adsorbents to remove environmental contaminants due to their large surface area, high anion exchange capacity and good thermal stability.

We studied the sorption of arsenate on Al-Mg and Fe-Mg layered double hydroxides (easily reproducible at low-cost) as affected by pH and varying concentrations of inorganic (nitrate, nitrite, phosphate, selenite and sulphate) and organic (oxalate and tartrate) ligands, ii) the effect of residence time on the arsenate desorption by these ligands, and iii) the kinetics of arsenate desorption by phosphate.

The Fe-Mg-LDH sorbed nearly twice the amount of arsenate compared to the Al-Mg-LDH, due, in part, to its greater surface area and lower degree of crystallinity. Moreover, the Fe-Mg-LDH sorbed more arsenate than phosphate, in contrast to the Al-Mg-LDH, which adsorbed more phosphate than arsenate, probably because of the greater affinity of arsenate than phosphate for Fe sites and, vice versa, the greater affinity of phosphate than arsenate for Al sites.

Arsenate sorption onto samples decreased by increasing pH, due, maybe, to the high affinity of hydroxyl ions for LDHs and/or to the value of zero point charge of two sorbents. The rate of decline in the amount of arsenate sorbed was, however, relatively constant, decreasing the fastest for the Fe-Mg-LDH compared to the Al-Mg-LDH.

The capacity of ligands to inhibit the fixation of arsenate followed the sequence: nitrate < nitrite < sulphate < selenite < tartrate < oxalate « phosphate on Al-Mg-LDH and nitrate < sulphate $\approx$ nitrite < tartrate < oxalate < selenite « phosphate on Fe-Mg-LDH. The inhibition of arsenate sorption increased by increasing the initial ligand concentration and was greater on Al-Mg-LDH than on Fe-Mg-LDH, evidently because arsenate anions have a stronger affinity for Fe than Al and for the presence in Fe-Mg-LDH of short-range-ordered materials on which arsenate forms very strong inner-sphere complexes not easily desorbable by competing ligands.

The longer the arsenate residence time on the LDH surfaces the less effective the competing ligands were in desorbing arsenate from sorbents. The effect of increasing residence time on desorbing arsenate was similar for all ligands. However, for Al-Mg-LDH systems with phosphate, tartrate and oxalate, more arsenate was desorbed compared to Fe-Mg-LDH systems, at the same residence time. The amounts of arsenate desorbed by phosphate from LDHs increased with time, being characterized by an initially very fast desorption reaction followed by a much slower desorption reaction until a plateau was reached. A greater percentage of arsenate was removed by phosphate from Al-Mg-LDH than from Fe-Mg-LDH, suggesting that the main difference between two LDHs was in the amount of more easily desorbable arsenate.

The implementation of decontamination systems of As-contaminated sources by providing for LDHs use would be able to combine the lower costs of remediation and effective removal of As from them.