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Institute for Sanitary Engineering, Water Quality and Solid Wastemanagement | ISWA

**Studies on the removal of phosphonates and ortho-phosphate from wastewater using metal-containing filter materials**

The considerable efforts to reduce the nutrient inputs into surface waters, which will become necessary in the context of the implementation of the European Water Framework Directive, will require a more detailed consideration of the phosphorus emissions, as this is the only way to achieve the water management objectives with the greatest possible efficiency. The substance group of phosphonates, which are used in many industries such as the textile and paper industries, as bleaching stabilizers in drinking water treatment as antiscalant or for the hardening stabilization of cooling water, is quantitatively relevant. Phosphonates are stable in a wide pH range and very persistent against thermal and biological decomposition.

Phosphonates are suspected of contributing to the long-term eutrophication of water bodies. For example, the possibility of a continuous decomposition to microbiologically available phosphates exists by UV radiation from sunlight. The oversupply of phosphate is an essential characteristic of ecologically unbalanced waters. Phosphate is therefore an important target substance for the sustainable improvement of the environmental condition of water.

Phosphonates can be removed from wastewater by flocculation when iron salts are used. The principle here is the transfer of the metal into hardly soluble iron hydroxides. These polar flocks with a relatively large specific surface serve as adsorbents for the negatively charged phospho-nates. The flocculation process can have essentially two disadvantages. Depending on the wastewater, a sludge volume of up to 30% of the sample volume can occur (own investigations). This sludge must be elaborately separated, further treated and disposed of in a further sedimentation or filtration stage. In addition, phosphonates, especially in wastewaters with low water hardness, can complex the added iron and thus prevent flock formation. This effect can be compensated by increased flocculant dosage concentrations, but this leads to increased β-values (molar ratio of dosed flocculant to phosphorus in wastewater). For phosphonate-containing paper machine wastewater, even a flocculant threshold value was found in our own experiments which was so high that it could not be attributed to the inhibitory effect of complexation by the phosphonate itself. The latter observation shows that due to the complex wastewater matrix, therefore, only a very difficult control over the optimal flocculant dosage can be present.

One possible alternative, which exploits the relatively high adsorption affinity of phosphonates on metal-containing surfaces, could be the use of metal-containing filters. Such filters can consist of pure metal oxides, which are often available as fine powders. To avoid the use of such powders in wastewater treatment, various methods have been developed to coat, for example, sand with metal oxide surfaces. These methods are essentially based on the suspension of thoroughly washed sand in an Fe(III) solution with the possible addition of NaOH. This suspension is heated at high temperature for several hours and then washed several times. Furthermore, iron hydroxide filters are commercially available (e.g. FerroSorp® from HegoBiotec), which are already used in the treatment of sewage and raw water, as well as examinations by Nowack and Stone (1999a, 1999b, 2006) about the removal of phosphonates at goethite are known.

The objective of this project is to investigate previously neglected filter materials for the removal of environmentally relevant phosphorus-containing compounds from wastewater. These include in particular ortho-phosphate and the most important phosphonates PBTC, HEDP, NTMP, EDTMP and DTPMP. With the previous project with the title “Development of technical methods for the removal of phosphonates, taking into account the specific wastewater matrix” sponsored by the Willy-Hager-Foundation (also at ISWA) there will be an almost complete spectrum of possible methods (precipitation / flocculation, (Photo-)Fenton, UV/Fe(II), filtration) for the removal of these compounds, taking into account the different conditions from several industries.

In addition to the adsorption capacity for the environmentally relevant phosphorus compounds, the technical applicability of filter materials depends very much on their abrasion resistance, reactivation and regenerability, i.e., their property as a long-lasting adsorbent. In the experiments, therefore, the amount of loading capacity of the filters in relation to the compounds mentioned is tested not only by means of adsorption isotherms. Long-term tests are also carried out in laboratory-scale and pilot-scale experiments with continuously operating, circulating filter columns with regular backflushing events, applied to real wastewater.

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