

Transformation of phosphonates during activated carbon filtration

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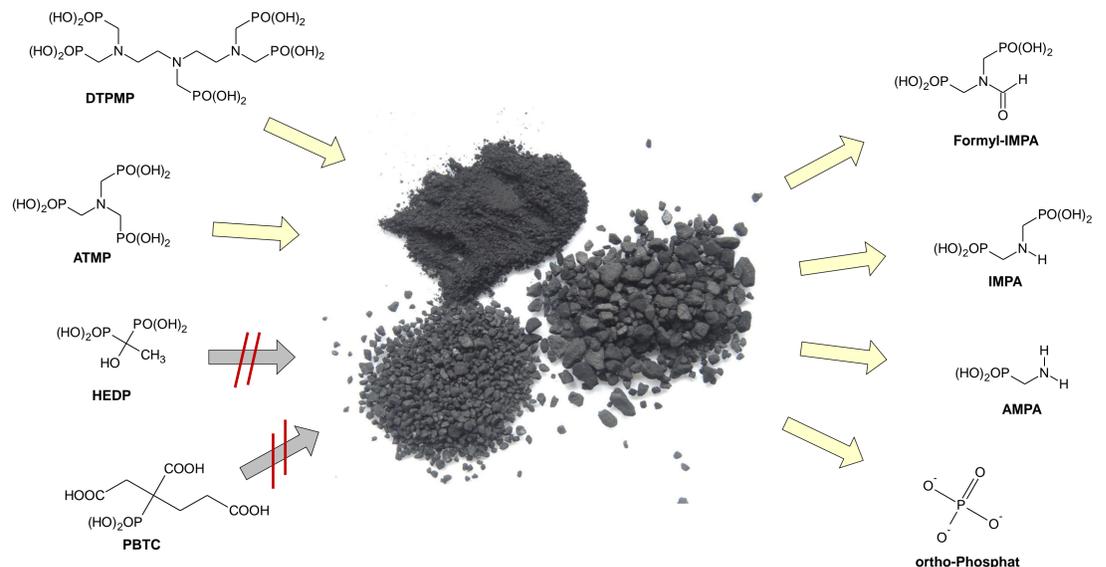
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Introduction

This recent observation has hitherto not been described in literature: Some phosphonates can undergo chemical transformation during activated carbon filtration. Currently it is commonly assumed that phosphonates are persistent and cannot be retained by sorption on activated carbon due to their ionic nature.

These surprising findings indicate the need for a more refined definition of the term "persistence". Publications dealing with the subject of "phosphonates and activated carbon" should be critically re-read. Analogous reactions are also to be expected during steps in wastewater treatment plants involving activated carbon.

The transformation of phosphonates on activated carbon can be an important topic from a technical, analytical, toxicological and legal point of view and should therefore also be considered in the future.



Transformation during full scale treatment

During the KonTriSol research project, RO membrane concentrate treatment procedures were investigated. Depletion of DTPMP was observed after a granular activated carbon filtration step applied by a water supplier. Throughout multiple samplings, it was demonstrated that the DTPMP concentration in the filter effluent was strongly lowered, while the orthophosphate concentration simultaneously increased (fig. 1).

It was also possible to detect IMPA and AMPA in the filter effluent.

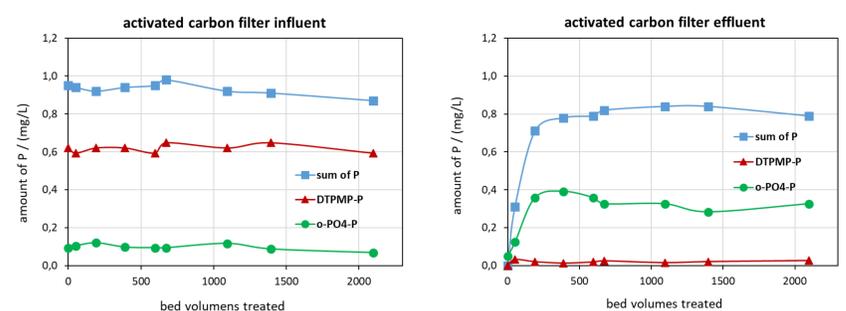


Figure 1: Monitoring of a full scale activated carbon filter over 9 weeks with a treated volume of 42000 m³

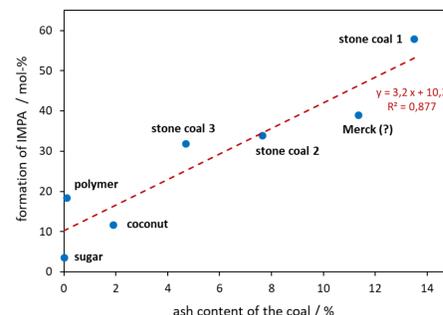
Laboratory scale treatment tests

Comparative measurements in laboratory tests showed rapid transformation of the nitrogen-containing phosphonates DTPMP and ATMP. No comparable reaction was observed with HEDP and PBTC.

The tests showed that the transformation was not triggered by biological processes: Chemical and thermal sterilization of the activated carbon from the full scale filter did not stop the reaction.

The transformation was further confirmed with a set of fresh commercial activated carbons (charcoals derived from stone coal, coconut, synthetic polymer, and sugar) and different particle sizes (powdered carbon or granular activated carbon), whereby variations in the rate of conversion were found. In these batch experiments a correlation between the reaction rate and the ash content was observed (fig. 2). The influence of the elemental composition of the coal for finding stronger correlations and an exploration of the chemical pathway is subject of ongoing research.

One stone coal was chosen for a set of small scale column tests to evaluate the influence of temperature and contact time on the transformation of ATMP (fig. 3a and 3b). At elevated temperatures, Formyl-IMP was formed as a further transformation product. The molecular formula was confirmed by IC-ESI-TOF measurements.



Coal type	Coal ash / %	ATMP o-PO4 / %	DTPMP o-PO4 / %	HEDP o-PO4 / %	PBTC o-PO4 / %
stone coal 1	13,5	58	44	-	-
Merck (?)	11,4	39	24	-	-
stone coal 2	7,7	34	24	-	-
stone coal 3	4,7	32	44	-	-
coconut	1,9	12	15	-	-
polymer	0,1	18	14	-	-
sugar	0,0	4	14	-	-

Figure 2: Batch experiments with different types of coal - correlation of IMPA and phosphate formation (mol-%) vs. ash content (% w/w)

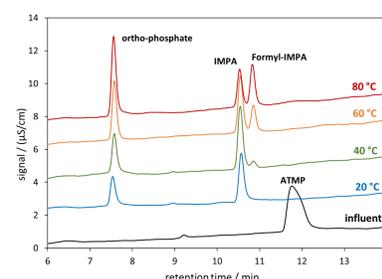


Figure 3a: Small scale column tests: influence of the column temperature on the reaction

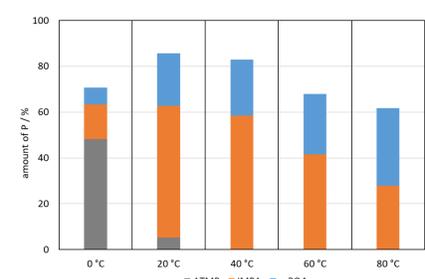


Figure 3b: Small scale column tests: influence of flow rate on the reaction

Conclusion and Outlook

Laboratory tests have clearly demonstrated the chemical reaction pathway. It is therefore assumed that chemical reactions are also the responsible factor in the full scale treatment. The nitrogen-containing antiscalants ATMP and DTPMP reacted with various carbons. A comparable reaction was not found with PBTC and HEDP.

It was found that the ash content of the coals investigated correlates with the reaction intensity. AMPA was only detected in very low concentrations. Further investigations are currently being carried out, including determination of heavy metals by ICP-MS and reactions with other phosphorus containing antiscalants.

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