Removal of Pesticides and Their Ionic Degradates by Adsorptive Processes [Project #4022]

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OBJECTIVES:
The objectives of this research project were to

1. evaluate the adsorbability of polar/ionic pesticides and ionic degradates on activated carbon,
2. determine polar/ionic pesticide and ionic degrade breakthrough behavior in granular activated carbon (GAC) adsorbers,
3. develop recommendations for drinking water utilities regarding GAC adsorber design and operation parameters, and
4. evaluate different adsorption test methods in relation to direct conclusions for water utilities (GAC selection and removability of new compounds).

BACKGROUND:
Recent studies have shown that polar/ionic pesticides and ionic degradates are detected in several surface and groundwaters in the United States and Europe. While a wide range of pesticides such as atrazine and bromacil can be effectively removed by activated carbon adsorption during drinking water treatment, in contrast, more polar pesticides and ionic degradates are expected to be less adsorbable. Therefore, an evaluation of the adsorption treatment steps for the removal of such compounds was needed.

APPROACH:
Based on a literature search, a range of polar/ionic pesticides and ionic degradates in water supplies were selected for the fundamental adsorption tests in this research project. Due to high use rates, a high detection frequency was found for the ionic chlorophenoxy herbicides and the non-ionic chloracetanilides. For the chloroacetanilides, the ionic degradates (ethane sulfonic acids [ESA] and oxanilic acids [OA]) are detectable as well. Thus, the ionic pesticides bentazone, mecoprop, and 2,4-D and the ionic degradates metolachlor ESA, metolachlor OA, metazachlor ESA, metazachlor OA, acetochlor ESA, and acetochlor OA were used for the fundamental adsorption tests.

A standardized small column test was applied for the evaluation of adsorbability of the ionic pesticides and degradates that allowed the determination of breakthrough curves within a few days. The small column test results were used to conclude if the compounds are likely to be removed by GAC adsorption in full scale plants.

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Detailed results for ionic pesticide and degradate removal were discovered by operating a GAC pilot plant under practical conditions. Service time of GAC adsorbers for ionic pesticide removal were determined, depending on different factors such as empty bed contact time (EBCT) and GAC type.

Fundamental adsorption tests (single solute and coadsorption isotherms, isotherms at different pH and on preloaded carbons) were carried out in order to complete the fundamental assessment of ionic pesticides and degradate adsorption. The results from these different adsorption test methods were then compared and evaluated in relation to their practical application for water treatment plants, both as a suitable (rapid) test for GAC selection and for their potential to evaluate the possibility of removing a new compound in the GAC adsorber.

RESULTS/CONCLUSIONS:
One of the widely used classes of agricultural herbicides is the chloroacetanilides, with chemical agents such as acetochlor, metazachlor, or metolachlor. Due to progress in analytical methods, the detection frequency of pesticide degradates has increased. In addition to the precursor compounds, ionic degradates (-ESA and -OA) can also be detected in water supplies up to concentrations in the range of a few µg/L.

Worldwide, in many water utilities, GAC adsorption is implemented for the elimination of micropollutants. For this challenge, GAC adsorbers are generally operated to about 30,000 bed volumes (BV) to 75,000 BV depending on several factors such as adsorbability and the concentration of the trace organic compound, the maximum concentration level in the filter effluent (standards and regulations), and the organic background. In general, GAC adsorption is considered as an economical treatment step if the GAC replacement is not required before 15,000 BV, which corresponds to a GAC demand of about 33 g GAC per m³ treated water.

The implementation of small column tests provided breakthrough curves for the ionic pesticides and degradates used in this research project. Due to the definition of small column test results, compounds with a 10% breakthrough (1) after 15,000 BV are considered strongly adsorbable and can be removed in GAC adsorbers, and (2) before 15,000 BV compounds are considered weakly adsorbable and not removable by GAC.

From the small column test results the adsorbability of the pesticides and ionic degradates were determined as follows:

- weakly adsorbable: metolachlor ESA, metazachlor OA, metazachlor ESA
- strongly adsorbable: mecoprop, 2,4-D, metolachlor, metazachlor, acetochlor, 2,4-dichlorophenol
GAC pilot plant experiments confirmed the small column test results. In the GAC adsorbers (GAC Bed depth: 1.5 m; EBCT: 9 minutes), the 10% breakthrough of metolachlor ESA was observed before 15,000 BV. Within short GAC layers of 0.5 m (EBCT: 3 minutes), metolachlor ESA could not be removed completely. From coadsorption isotherms and preloading studies it could be concluded that the adsorption behavior of the weakly adsorbable ionic metolachlor ESA is significantly affected by competitive adsorption and preloading by natural organic substances. Therefore, a complete removal of such ionic degradates in GAC adsorbers is possible when fresh (or perhaps freshly reactivated) GAC was placed into service just prior to the contamination.

Using bituminous coal based GAC types (agglomerates), the non polar precursor metolachlor and the herbicides mecoprop and 2,4-D could be removed with a 90%-elimination rate to at least 37,000 BV. Bentazone was a borderline compound in the pilot plant studies as well, with a 10%-breakthrough of 18,000 BV.

Further relationships and consequences for the operation of GAC adsorbers could be derived from the pilot plant studies. With increasing bed depth the breakthrough curves for all the ionic compounds became flatter due to kinetic effects. Consequently, the activated carbon efficiency increased with increasing bed depth. From the pilot plant studies it could be concluded that within short GAC layers of 1 m or less (corresponding to EBCT of < 6 minutes at a filter velocity of 10 m/h), the saturation of GAC adsorption capacity was low and an early micropollutant breakthrough was observed. For an effective removal of ionic compounds such as mecoprop, bentazone, or the ionic degradates the GAC bed depth in the adsorber should be at least 1.5 m corresponding to EBCT of 9 minutes. For bentazone, for example, increasing the bed depth from 0.5 m to 1.5 m increased throughput to a 10%-breakthrough by a factor of 3.

Furthermore, the operation time of GAC adsorbers and the specific costs depend on the GAC type. Currently, the GAC market changes fast, and the selection and evaluation of a GAC type becomes more and more important. A lot of new products, especially bituminous coal based GAC types from Asia, are offered as well as coconut shell (CC) based GAC with different activation grades. The results showed that, so far, only pilot plant studies allow an evaluation of GAC type for the removal of ionic pesticides and degradates. The pilot adsorbers (EBCT: 9 minutes) with three different bituminous coal based GAC types showed that the operation time to 10% breakthrough for metolachlor ESA, metolachlor, and bentazone decreased in the following order: F 300 (most effective), GAC 1240 EN, Hydrafaffin XC 30 (least effective).

This ranking could not be correlated to product specification data such as iodine number or BET. It is assumed that macropores and mesopores are more important for micropollutant adsorption than supposed so far. Furthermore, the Hydrafaffin XC 30 was not suitable for the ionic pesticide and ionic degradate removal, which could not have been anticipated from product specification or isotherm data. Hydrafaffin XC 30 is
produced by directactivation. In contrast, GAC 1240 EN and F 300 were agglomerated activated carbons. For general conclusions, if directactivated GAC might not be applied for ionic pesticide and degradate removal, more investigations with different directactivates are required.

Single solute isotherm data are fundamental for adsorption modeling so far. However, the results showed that neither the ranking of adsorbability of different micropollutants nor GAC selection agree with adsorber results. The ranking of adsorbability in single solute and coadsorption studies differed. These observations do not conform to the conventional adsorption theory that the impact of competitive adsorption increases with decreasing adsorbability of the target compound. Therefore, besides competitive adsorption, other effects might be responsible for the capacity reduction, e.g., interactions between humic substances and micropollutants or competitive adsorption kinetics.

Based on the findings from this research project, GAC selection is not possible by isotherms or the product specification data such as BET or iodine numbers. Consequently, more parameters have to be taken into account for GAC selection. Isotherm tests are carried out with pulverized GAC, without consideration of adsorption kinetics. However, initial basket stirrer apparatus experiments indicated that kinetic experiments might be a better method for GAC selection. Correlations between kinetic properties of trace organic pollutants and pore size distribution are required to evaluate GAC characteristics for micropollutant adsorption in natural water.

APPLICATIONS/RECOMMENDATIONS:
GAC adsorbers for the removal of micropollutants are generally operated to about 30,000 BV to 75,000 BV. Polar/ionic pesticides and ionic degradates can be removed by GAC adsorption in fixed bed adsorbers. However, with decreasing adsorbability of the micropollutant, an earlier replacement of the GAC might be required. By removing the weakly adsorbable ionic chloracetanilides degradates such as -OA and -ESA metabolites, to a large extent, the operation time of GAC adsorbers will be lower than 15,000 BV. In GAC adsorbers for DBP control, a complete removal of such compounds might be possible.

In short, for GAC layers of 0.5 m (corresponding to EBCT of 3 minutes), a complete removal of ionic pesticides and degradates is not possible. By increasing the bed depth of the GAC layer from 0.5 m to 1.5 m, the specific throughput can be increased, e.g., by a factor of 3 for bentazone. Thus GAC adsorbers should be designed with a GAC bed depth of at least 1.5 m corresponding to EBCT of 9 minutes at a flow rate of 10 m/h. With increasing bed depth, the GAC efficiency increases as well and the specific costs for GAC decrease. A variation of flow rate was not carried out in this project. Therefore, investigations with different EBCTs and different flow rates allow the optimization of GAC adsorber design and operation parameters and the minimization of operation costs.

The evaluation of adsorbabilty of micropollutants and the selection of an activated carbon are essential factors for water utilities. It is important to get this information within a short time, with low costs and preferably by batch experiments. Small column tests meet
these demands for evaluating the adsorbability of new micropollutants. In contrast, only pilot plant studies allow the selection of an optimal GAC type for the micropollutant removal. Pilot studies require operation times of several months.

Due to the fact that, for micropollutant removal, GAC adsorbers were not operated to a complete micropollutant breakthrough, the initial breakthrough is the determining factor, not the equilibrium adsorption capacity, which is determined in isotherm tests. Therefore, future research should focus on the development of a rapid test that takes into account adsorption kinetics. The application of the original GAC particle size fraction and realistic micropollutant concentrations are basic requirements. Pore size distribution, especially macro- and mesopores, are supposed to be important for micropollutant adsorption out of natural water. Fundamental research on diffusion processes dependent on pore size distribution is required.

**RESEARCH PARTNER:**
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