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Research area: General aims

Environmental technology // Water

Key words:

Effluents, paper production, metal converting, AOX

TITLE:

Improving the AOX measurement of aqueous samples and raw materials to avoid faulty results

Background/Problem area

Organic halogen compounds (AOX) adsorbable on activated carbon are among the parameters for which monitoring is legally required in many industrial wastewaters. Standard measuring methods for the AOX content of aqueous samples have been available for many years, but various disturbances lead to measurement fluctuations in the range of several 100 %. This is the case in sectors like metal production/working/processing, papermaking, textile production and –cleaning etc. Main disturbances include chloride, DOC (dissolved organic carbon), surfactants and hydrocarbons contained in the wastewater, as well as filterable solids and conductivity. Papermaking pulps, for example, can introduce considerable amounts of AOX into the circuit water and, thus, wastewater of paper mills. PTS method RH 11/91 can be used to estimate the amounts of AOX introduced under standard conditions. In balancing applications, however, the method was found to give incorrectly high values. The measuring technique of AOX must therefore be improved to enable safe and reliable wastewater monitoring and more accurate AOX balances.

Objectives/Research results

Prime objective of the research project is to minimize influences distorting the analytical results of AOX measurements in various industrial wastewaters. Reliable and comparable measurements are to be ensured by the development of wastewater-specific analysis methods and definition of a standard measurement procedure.

The AOX determination of aqueous samples will be improved by VDEh-Betriebsforschungsinstitut (BFI), the research institute in charge of the project IGF17207N; the PTS method will be adapted by the co-operating research institute Papiertechnische Stiftung (PTS).

The variation range of samples from the steel- and metalworking sectors was determined, and the influence of dilution on analytical results investigated. The results showed no effect of dilution on analytical results. Synthetic samples were used for first studies into the effects of chloride contents at different initial AOX concentrations and nitrate rinsing volumes, and to compare the methods of DIN 38409-H14 (AOX) and DIN 38409-H22 (AOX-SPE). The tests have shown that for initial AOX concentrations of 250µg/l and 1,000 µg/l as well as chloride concentrations of 100 mg/l and 1,000 mg/l, the results of AOX analyses differed by maximally 4 % and 6 %, respectively. The analytical results were reproducible. The initial findings suggest that recovery rates cannot be improved by using twice as much nitrate for rinsing. Investigations on different parameters like load and washing flow or volume respectively, Na_2SO_3 dosage, humidity of activated carbon and its storage in chloride containing lab air showed that all results are within the DIN tolerance range. Too high AOX values were found in samples with high chloride and high DOC concentrations. The SPE-AOX method shows lower deviations but cannot be applied to all type of samples, e. g. False low results were received for water samples of pulp mills and in general for samples with high DOC concentrations.

PTS scientists used statistical experimental design to develop and implement a screening plan varying the sample preparation conditions of the AOX release method. The following parameters were varied: soaking time t_E = 0 or 120 min, disintegration time t_A measured as total number of revolutions in the laboratory disintegrator = 25,000 and 75,000, disintegration consistency S_A = 0.6 and 4 %, dilution consistency S_V = 0.1, 0.6 and 4 %, stirring time t_R after dilution = 5 or 60 min, and temperature T = 20 or 40 °C. By means of statistical experimental design and by defining two settings for each of the six parameters, the number of tests could be reduced from several thousand to 27. Looked at individually, the parameters S_A and S_V constitute the most important influences. Interactions between S_V*T, S_A*S_V, t_E*S_V and t_E*S_A were identified as further significant influences by multi-factorial analysis. The results of the screening plan - order and strength of the influential parameters mentioned above - were confirmed by further trials based on three surface response plans comprising 10, 12 and 3 trials. The revised PTS method RH 11/91 probably will have following settings: t_E = 0 min,, t_A = 25.000 revolutions, S_A = 5.5 % and S_V = S_A. A final proof of the new settings will be performed by semi-technical trials.

Application/Economic benefits

Faulty measurements during AOX analysis resulting in levels that seem to exceed the respective limit value must be avoided by all means. Otherwise, the already high cost pressure on small and medium enterprises of the above mentioned sectors could be further increased by unnecessarily high chemical dosing in AOX treatment units, higher (i.e. the loss of reduced) discharge fees for AOX, and extra costs for the dimensioning and operation of treatment stages for AOX reduction. Moreover, the urgency of the subject dealt with in the project was confirmed by the proposed revision of DIN EN ISO 9562 “Determination of adsorbable organically bound halogens (AOX)“ in spring 2012.

Period of time: 01.09.2011 – 31.12.2013

Remarks

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