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- Recycling
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Database

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Title

Verhalten von Nanosilber in Kläranlagen und dessen Einfluss auf die Nitrifikationsleistung in Belebtschlamm.
Behavior of nanosilver in wastewater treatment plants and influence on the nitrification performance of activated sludge.

Descriptors

Abwasserbelastung; antibakterielles Ausrüstungsmittel; Ausflocken; Belebtschlamm; Emissionsminderung; Kläranlage; Nanoteilchen; Nitrifikation; Schwermetallentfernung; Silber; Silberchlorid; Silbersulfid; Stoffbilanz; Überprüfung; Untersuchungsmethode

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Abstract
In der vorliegenden Studie wurde der Weg des Nanosilbers auf folgende Weise nachvollzogen: Feststellung verminderter Nitrifikationsleistung im Belebtschlamm einer Kläranlage, Erstellung einer Massenbilanz für Nanosilber in einer Pilotkläranlage und Verifizierung der Bilanz durch eine Untersuchung in einer realen kommunalen Kläranlage, in die durch einen Indirekteinleiter partikuläres Silber eingetragen wurde. Der Einfluss von vier marktüblichen Nanosilberadditiven auf die Ammoniumoxidation im Belebtschlamm wurde in Batchreaktoren untersucht. In einer Pilotkläranlage wurde partikuläres Silberchlorid und metallisches Nanosilber jeweils für die Dauer zweier Schlammalter (25 Tage) dosiert und weitere zwei Schlammalter bilanziert. Die Zugabe von 1 mg/L Ag in Form von Silbernitrat, metallischem Nanosilber, partikulärem Silberchlorid und Mikrokomposit-Silber blieb ohne Wirkung auf die Nitrifikationsleistung. Dagegen resultierten 100 mg/L Ag für alle Silberformen in einer Hemmung, welche zwischen 100% für Silbernitrat und 20-30% für kolloidales Nanosilber lag. In der Massenbilanzstudie wird deutlich, dass nach Zugabe von partikulärem Silberchlorid 96 % des Silbers mit dem Schlamm und 4% über das Nachklärbecken - also das gereinigte Abwasser - ausgetragen werden. Die Massenbilanz für metallisches Nanosilber fällt ähnlich aus. Die Bilanzen aus der Pilotkläranlage decken sich mit derjenigen von einer realen Kläranlage. Der Silberaustrag korreliert mit dem Feststoffaustrag im Schlammabzug und Nachklärbeckenablauf. Die Jahresfracht zum Vorfluter dürfte bei 4 bis 40 mg/a Ag pro Einwohnerwert liegen. Mit Elektronenmikroskopie lässt sich zeigen, dass das Nanosilber in und an die Belebtschlammflocken gebunden vorliegt. Chlorid ist im Abwasser in größeren Mengen verfügbar, sodass Silberionen praktisch vollständig zu Silberchlorid ausfallen. Silberionen binden auch an organischen Komplexbildnern und reduzierten Schwefelgruppen. Die Massenbilanz über die Kläranlage unterstreicht, dass Nanosilber sehr gut an Partikeln bindet und effizient aus dem Abwasser eliminiert wird. Mit der Reduktion der ungelösten Stoffe (GUS) lässt sich auch die Silberfracht im Ablauf vermindern. Wenn nötig, kann die Nanosilberfracht bei der Abwassernachbehandlung (Raumfiltration oder Flächenfiltration) weiter reduziert werden. Der Schlamm stellt die wichtigste Senke für Nanosilber dar. Silberpartikel über 100 nm Größe binden weniger gut als Nanosilber im engeren Sinne. Alle analysierten Silberpartikel im Zulauf, Ablauf und Schlamm deuten darauf hin, dass das Silber vor allem sulfidisch (als Ag2S) die Kläranlage verlässt. Aufgrund der vernachlässigbaren Wasserlöslichkeit dieser Silberform werden keine Silberionen freigesetzt. Die Forschung ist auf Prozessmechanismen und die Oberflächenmodifikation von Nanosilber zu konzentrieren, die die Speziierung und das Bindungsvermögen unter Umweltbedingungen beeinflussen. Maßnahmen zur Emissionsminderung sollten dem Vorsorgeprinzip folgend entwickelt werden.

The authors studied the impact of nanosilver on the nitrification of sewage sludge, quantified the mass flow of nanosilver in a pilot-plant, and verified the mass balance in a full-scale municipal wastewater treatment plant where nanosilver was introduced to the municipal plant by an indirect discharger. The addition of four different nanosilver additives on ammonia oxidation in activated sludge has been studied in batch-reactors. The pilot-plant treating domestic wastewater was operated with a 12 day sludge age. Nanosilver was applied to the activated

sludge tank within two sludge ages. Influent, effluent and sludge were also sampled on a fullscale plant and analyzed for silver. Silver nitrate, metallic nanosilver, nano-scaled silver chloride and microcomposite silver did not show any effect on ammonia oxidation after the addition of 1 mg/L Ag to the activated sludge. In contrast, 100 mg/L Ag inhibited the nitrification process by 100 % after the addition of silver nitrate and 20 to 30% after addition of colloidal polymer-coated nanosilver. A complete mass balance of the pilot-plant, a steady-state system with known fluxes, demonstrates significant enrichment of silver in the sewage sludge (96 %) after the addition of silver chloride to the plant and small losses of silver into the secondary effluent (4 %). The mass fluxes were similar to metallic colloidal nanosilver investigated under the same conditions. Overall, it is estimated that from public wastewater treatment plants about 4 to 40 mg/a Ag per inhabitant equivalent are discharged annually to the receiving water. The analysis by SEM-EDX demonstrates adsorption and incorporation of nanosilver on biological floes. This method yields first insight into complex building and transformation of silver associated with sulfide after adding metallic nanosilver and silver chloride to wastewater. Silver ions released from nanosilver react immediately with large amounts of chloride present in wastewater to form silver chloride. Silver ions may react with organic ligands or sulfide groups additionally. The mass balance reflects the excellent attachment of nanosilver to activated sludge and biological floes. Therefore, the main elimination process of nanosilver is attachment to the activated sludge. The major fraction of nanosilver is removed from the system by the excess sludge withdrawal. Nonetheless, the efficiency may be further improved by a tertiary filtration step. All analyses of influent, effluent and sludge confirmed that silver exists as silver sulfide. Nanosilver research should be driven to the identification of transformation processes in real environmental matrices and the influence of coatings on the adsorption behavior, and source control measures following the precautionary principle should be performed.

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