Science of the Total Environment 544 (2016) 722–729

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Short and long term biosorption of silica-coated iron oxide nanoparticles in heterotrophic biofilms

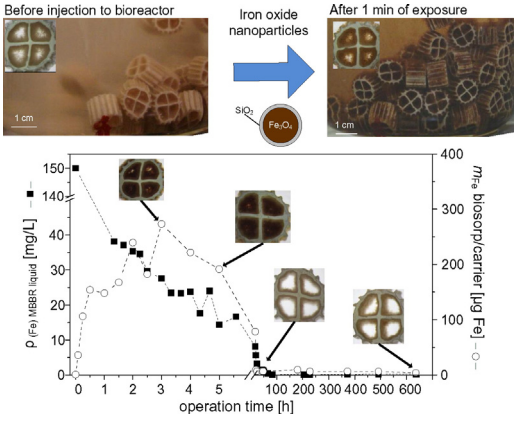
Maria P. Herrling [a], Susanne Lackner [a,b], Oleg Tatti [a], Gisela Guthausen [c], Markus Delay [a], Matthias Franzreb [d], Harald Horn [a,e,*]

[a] Engler-Bunte-Institut, Chair of Water Chemistry and Water Technology, Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany
[b] Urban Bioengineering for Resource Recovery, Bauhaus-Institute for Infrastructure Solutions, Bauhaus-Universität Weimar, Coudraystraße 7, 99423 Weimar, Germany
[c] Pro²NMR, Institute for Biological Interfaces 4 and Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Adenauerring 20b, 76131 Karlsruhe, Germany
[d] Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
[e] DVGW Research Laboratories for Water Chemistry and Water Technology, Engler-Bunte-Ring 1, 76131 Karlsruhe, Germany

HIGHLIGHTS

- $scFe_3O_4$-NP mainly attach to the outer biofilm layers and biofilm detachment occurs.
- Biosorption of $scFe_3O_4$-NP onto biofilms happens quickly, but is rather low.
- Transport of $scFe_3O_4$-NP in the liquid is more dominant than sorption to biofilms.
- 57% of input $scFe_3O_4$-NP exits the MBBR, indicating low retention capacity.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 October 2015
Received in revised form 29 November 2015
Accepted 30 November 2015
Available online xxxx

Editor: D. Barcelo

Keywords:
Magnetic nanoparticles
Wastewater treatment
Magnetic susceptibility

ABSTRACT

The increased application of engineered nanoparticles (ENP) in industrial processes and consumer products has raised concerns about their impact on health and environmental safety. When ENP enter the global water cycle by e.g. wastewater streams, wastewater treatment plants (WWTP) represent potential sinks for ENP. During biological WWT, the attachment of ENP to biofilms is responsible for the desired removal of ENP from the water phase avoiding their release into the aquatic environment. However, the fundamental mechanisms guiding the interactions between ENP and biofilms are not yet fully understood. Therefore, this study investigates the behavior and biosorption of inorganic ENP, here magnetic iron oxide nanoparticles coated with silica ($scFe_3O_4$-NP), with heterotrophic biofilms at different time scales. Their magnetic properties enable to follow $scFe_3O_4$-NP in the biofilm system by a magnetic susceptibility balance and magnetic resonance imaging. Biofilms were exposed to $scFe_3O_4$-NP at short contact times (5 min) in flow cells and complementary, $scFe_3O_4$-NP were introduced into a moving bed biofilm reactor (MBBR) to be observed for 27 d. Mass balances revealed that $scFe_3O_4$-NP sorbed to the biofilm within a few minutes, but that the total biosorption was rather low (3.2 µg Fe/mg TSS). $scFe_3O_4$-NP

* Corresponding author: Engler-Bunte-Institut, Chair of Water Chemistry and Water Technology, Karlsruhe Institute of Technology (KIT), Engler-Bunte-Ring 9, 76131 Karlsruhe, Germany.
E-mail address: harald.horn@kit.edu (H. Horn).

http://dx.doi.org/10.1016/j.scitotenv.2015.11.174

Biomass
Mass balance

mainly sorbed to the biofilm surface inducing the detachment of outer biofilm parts starting after an exposure time of 3 h in the MBBR. The biosorption depended on the exposure concentration of $scFe_3O_4$-NP, but less on the contact time. Most $scFe_3O_4$-NP exited the flow cell (up to 65%) and the MBBR (57%) via the effluent. This effect was favored by the stabilization of $scFe_3O_4$-NP in the bulk liquid by organic matter leading to a low retention capacity of the MBBR system. The results contribute to improve our understanding about the fate of ENP in environmental and in technical biofilm systems and give indications for future investigations needed.

1. Introduction

The increasing application of products implementing nanotechnology contributes to the release of engineered nanoparticles (ENP) into the aquatic environment (Delay and Frimmel, 2012; Gottschalk and Nowack, 2011; Klaine et al., 2008). The distribution and fate of ENP in the environment has been the focus of many experimental and modeling studies to evaluate potential negative impacts on ecosystems and human health (Gottschalk et al., 2013a; Schaumann et al., 2015; Sun et al., 2014). With respect to the distribution of ENP in the environment, their interactions with biofilms have a major impact on mass flows and bioavailability (Fabrega et al., 2011; Westerhoff et al., 2013). As in most environments microorganisms preferentially exist in form of biofilms, a fundamental understanding of the interactions of ENP with biofilms is critical to understand the fate of ENP in environmental and technical systems (Ikuma et al., 2015). When ENP enter the water cycle by e.g. wastewater streams, ENP will potentially end up in wastewater treatment plants (WWTP) which represent sinks for ENP. Therefore, it is crucial to investigate the behavior of ENP in WWTP, not least for reasons of pollution control. The biological treatment step, in particular, contributes to the removal of ENP from the wastewater (WW) through interactions of ENP with the biomass, such as attachment by sorption processes (Brar et al., 2010; Kiser et al., 2010). Estimated concentrations of various ENP in WWTP effluents are in the concentration range of a few ng/L to 5 μg/L as summarized in Gottschalk et al. (2013b). For example, measured concentrations were reported to be <12 ng/L for Ag-NP (Li et al., 2013) and <5 to 15 μg/L for TiO_2-NP (Kiser et al., 2009). Compared to conventional activated sludge systems, technical systems employing biofilms, such as moving bed biofilm reactors (MBBR), in which biofilms are attached to plastic carrier materials (McQuarrie and Boltz, 2011; Odegaard et al., 1994; Wessman et al., 2004) are an only little investigated regarding their removal of ENP. Recent studies show that the removal of various ENP during WWT is influenced by a complex framework of parameters, i.e. biofilm properties (e.g. biofilm compactness) (Gu et al., 2014), particle properties (e.g. particle size and surface properties) (Peulen and Wilkinson, 2011) and water matrix (Battin et al., 2009; Fabrega et al., 2011). Furthermore, the experimental setup as the type of bioreactor (e.g. batch experiments (Kaegi et al., 2013; Rottman et al., 2012), sequencing batch reactors (Wang et al., 2012; Yang et al., 2015), membrane bioreactors (Tan et al., 2015) or pilot WWTP (Hou et al., 2013; Kaegi et al., 2011)) plays a key role. This leads to a high variability of the removal efficiency for different kinds of ENP in WWT, which can between 10 and 90% in laboratory scale up to field-scale systems (Westerhoff et al., 2013). So far, the term "biosorption" is commonly used in WWT to summarize the total chemical and physical sorption mechanisms of ENP to the biomass by sorption to the cells and extra cellular polymeric substances (EPS) as well as bio-uptake (Kiser et al., 2010). In this context, it has recently been stated that biofilms generally serve as efficient "sponges" for ENP, but efforts to elucidate the fundamental mechanisms driving the interactions of ENP and biofilms are still at an early stage (Ikuma et al., 2015). Especially for newer WWT technologies employing biofilms, such as MBBR systems, research is needed to evaluate if the mentioned "sponge-like" behavior for ENP can be transferred to all biofilms. Information gained about the sorption of ENP to the biofilm is relevant to estimate their mass flows in the aquatic environment in short and long term. To the authors' knowledge, there is no study about the fate of ENP in MBBR based biofilm systems under complex hydrodynamic conditions. The behavior of ENP entering MBBR systems is still uncertain and needs to be investigated to evaluate the MBBR's risk potential for the release of ENP at different time scales.

To meet this gap, the pathways and interactions of silica-coated iron oxide nanoparticles ($scFe_3O_4$-NP) with biofilms in MBBR systems were assessed. $scFe_3O_4$-NP (particle core made of Fe_3O_4) were utilized as tracer nanoparticle. Their magnetic properties enable their sensitive quantification via a magnetic susceptibility balance and their in-situ and *non-invasive* visualization within the biofilm matrix using magnetic resonance imaging (MRI). The experimental approach has been demonstrated and evaluated in a previous study (Herrling et al., 2015a).

The main goals of this work were to:

(1) Investigate the biosorption of $scFe_3O_4$-NP onto biofilm carriers in flow cell experiments at short contact times.
(2) Asses the removal and behavior of $scFe_3O_4$-NP during continuous MBBR operation.
(3) Establish mass balances for $scFe_3O_4$-NP to get insights into the time and concentration dependent biosorption onto the biofilm.
(4) Visualize the biosorption of $scFe_3O_4$-NP within the biofilm matrix using MRI.

2. Materials and methods

2.1. MBBR operation and biofilm characterization

A laboratory scale MBBR (V_{MBBR} = 700 ml) filled with K1 polyethylene carrier material (diameter: 9 mm, AnoxKaldnes AB, Sweden) with a filling ratio of 25% using 110 plastic carriers was operated for 6 months (Fig. 1 A). The cylindrical carrier material (Fig. 1B) had a specific surface area of 500 m^2/m^3. The reactor was fed with acetate for the cultivation of heterotrophic biofilms (substrate composition in Supporting information Table SI 1). The hydraulic retention time (HTR) for the cultivation of the biofilm (3 months) was set to 15 h to minimize washout of the bacteria and was then stepwise reduced to 5 h for the $scFe_3O_4$-NP exposure experiments. Thorough mixing and oxygen saturation was guaranteed by aeration with pressurized air. The pH value was set to 8–9 by dosing acidic water (0.014% HCl solution). The electrical conductivity (~1500 μS/cm) remained stable over the whole experiment. During the reactor operation, the soluble chemical oxygen demand (COD, filtered with 0.45 μm filter) was monitored using tests kits (LCK 414, HACH LANGE GmbH, Düsseldorf, Germany). The amount of biomass attached to the carriers was quantified by determining the total suspended solid content (TSS) using 5 carriers. Biofilms were imaged using a stereomicroscope (Stereomicroscope SMT, Rathenow, Germany).

2.2. $scFe_3O_4$-NP: preparation and characterization

Silica coated iron oxide nanoparticles ($scFe_3O_4$-NP) (MagPrep25 silica magnetic nanoparticles, ρ_{stock}(Fe) = 35 g/L, Merck KGaA, Darmstadt, Germany) with a primary particle size of 25 nm were used. $scFe_3O_4$-NP consisted of a magnetite core (Fe_3O_4) and a silica shell (SiO_2) which