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Low biosorption of PVA coated engineered magnetic nanoparticles in granular sludge assessed by magnetic susceptibility

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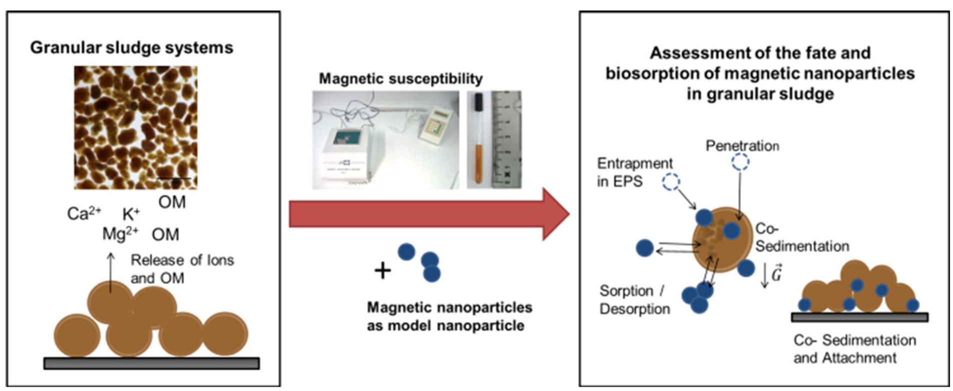
HIGHLIGHTS

- Magnetic susceptibility is used to elucidate the fate of EMNP in WWT systems.
- 5–35% removal of PVA coated EMNP indicates low interaction with granular sludge.
- Mass balance proves low and reversible bioaccumulation of PVA coated EMNP.
- Physical co-sedimentation is more dominant than sorption processes.

GRAPHICAL ABSTRACT



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ABSTRACT

When engineered nanoparticles (ENP) enter into wastewater treatment plants (WWTP) their removal from the water phase is driven by the interactions with the biomass in the biological treatment step. While studies focus on the interactions with activated flocculent sludge, investigations on the detailed distribution of ENP in other types of biomass, such as granulated sludge, are needed to assess their potential environmental pollution. This study employed engineered magnetic nanoparticles (EMNP) coated with polyvinyl alcohol (PVA) as model nanoparticles to trace their fate in granular sludge from WWT. For the first time, magnetic susceptibility was used as a simple approach for the in-situ quantification of EMNP with a high precision (error $<2\%$). Compared to other analytical methods, the magnetic susceptibility requires no sample preparation and enabled direct quantification of EMNP in both the aqueous phase and the granular sludge. In batch experiments granular sludge was exposed to EMNP suspensions for 18 h. The results revealed that the removal of EMNP from the water phase (5–35%) and biosorption in the granular sludge were rather low. Less than 2.4% of the initially added EMNP were associated with the biomass. Loosely bounded to the granular sludge, desorption of EMNP occurred. Consequently, the removal of EMNP was mainly driven by physical co-sedimentation with the biomass instead of sorption processes. A mass balance elucidated that the majority of EMNP were stabilized by particulate organic matter in the water phase and can therefore likely be transported further. The magnetic susceptibility enabled tracing EMNP in complex matrices and thus improves the understanding of the general distribution of ENP in technical as well as environmental systems.

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1. Introduction

The increasing number of potential applications of engineered nanoparticles (ENP) is likely contributing to their release into the global water cycle. The real fate of ENP transported into the environment is difficult to evaluate (Delay and Frimmel, 2012; Gottschalk et al., 2013; Gottschalk and Nowack, 2011; Schaumann et al., 2014). Compared to other chemical compounds (e.g. inorganic or organic pollutants), there is only a limited database regarding the concentrations and distribution of ENP in the environment (Mueller and Nowack, 2008). Among other technically relevant ENP, magnetic ENP (EMNP) are applied in medical diagnostics and drug delivery (Mahmoudi et al., 2011), catalysis (Kang et al., 2011), soil remediation (Johnson et al., 2009) or wastewater treatment (WWT) (Hu et al., 2006; Xu et al., 2012). After their release, ENP are primarily found in receiving water bodies with wastewater treatment plants (WWTP) as main point sources (Nowack and Bucheli, 2007). It is widely known that ENP are partly removed from wastewater by interactions with the biomass without any special treatment step (Gomez-Rivera et al., 2012; Kiser et al., 2010; Park et al., 2013; Wang et al., 2012). Recent publications on silver nanoparticles (Ag-NP) revealed that interactions and transformations in WWTP significantly influence their fate, highlighting the complexity of the system (Kaegi et al., 2011, 2013). Various known particle-particle (e.g. transport, homo-agglomeration, sedimentation) as well as particle-biomass interactions (e.g. entrapment in biomass, sorption, desorption, penetration, co-sedimentation) are expected to happen during WWT (Brar et al., 2010; Jin et al., 2014; Liu et al., 2014; Westerhoff et al., 2013). However, the separate evaluation of the impact of these processes on the removal of ENP is still a major challenge. Besides the mentioned impacts, biomass properties (such as e.g. extracellular polymeric substances (EPS) content) were found to be key factors for the removal and biosorption of ENP in biomass (Kiser et al., 2010). Biomass from WWT can be e.g. flocculent sludge with an open filamentous structures or granular sludge with a more compact structure. Granular sludge can be defined as biomass aggregates which settle significantly faster than flocculent sludge (de Kreuk et al., 2007). Comparative studies revealed that granular sludge is biologically more resistant to toxic ENP, like Ag-NP or Ce-NP, than to flocculent sludge due to its protective dense EPS. Moreover, granular sludge removed ENP significantly less efficient compared to flocculent sludge, which emphasizes the importance to investigate different kinds of biomass in this context (Gu et al., 2014; Ma et al., 2013).

Therefore, this study used EMNP coated with PVA (polyvinyl alcohol) as model ENP to trace their fate in granular sludge systems. For the first time, EMNP were quantified in-situ, in both the water phase and sorbed to the granular sludge. A simple approach is used: based on their magnetic properties EMNP were quantified by magnetic susceptibility. This approach demonstrates a *non-invasive* way for EMNP quantification compared to other frequently used methods such as emission or mass spectrometry. The main goals of this study were: (1) The demonstration of the applicability and benefits of the magnetic susceptibility for the selective quantification of EMNP in granular sludge. (2) The investigation of the interactions between EMNP and granular sludge originating from WWT with respect to water chemical parameters and impact of different granular sludge size fractions. (3) The quantification of the biosorption of EMNP in the granular sludge by a proper mass balance.

2. Materials and methods

2.1. EMNP: properties, preparation and quantification via magnetic susceptibility balance (MSB)

The synthetic EMNP used (chemagen Technologie GmbH, Baesweiler, Germany ($c_{stock}(\text{Fe}) = 25$ g/L suspended in water)) consisted of superparamagnetic magnetite (Fe_3O_4) cores (~15 nm) coated with polyvinyl alcohol (PVA, $(C_2H_4O)_x$). The organic coating (steric) stabilizes the particles and prevents particle oxidation and iron release. The EMNP particle size and the zeta potential were measured using dynamic light scattering and laser DOPPLER anemometry, respectively (($n = 10$); refractive index for iron oxide: 2.42; adsorption coefficient: 0.01, Zetasizer Nano ZS, Malvern Instruments, Worcestershire, United Kingdom). The prepared EMNP suspensions formed larger agglomerates with a size of 194 ± 13 nm (polydispersity index of 0.17), as it is common in natural and technical water systems (Petosa et al., 2010). The zeta potential was −7 ± 0.3 at pH value of 8. The isoelectric point was at pH ~ 5.5–6 indicating that agglomeration was favorable to happen. Long term stability experiments were conducted for EMNP in suspensions with ultrapure water being stable over 100 h (see supplementary information Fig. SI 1). For preparation prior to the batch experiment, EMNP suspensions were diluted (ratios 1:10 and 1:50) with ultrapure water (Milli-Q, Merck Millipore, Billerica, MA, USA), stirred intensively and settled for 20 h. The decanted supernatant of those suspensions was further diluted to the desired concentration. We used initial EMNP concentrations of $c_0(\text{Fe}) = 100$; 200; 1000 mg/L for our model system to trace the distribution of EMNP in the granular sludge. Chosen concentrations were intentionally higher than environmental relevant concentrations of ENP (Gottschalk et al., 2009) to elucidate the detailed interactions with the biomass. A calibration was performed to correlate the measured magnetic susceptibility (χ_V) with the Fe concentration ($c(\text{Fe})$) of the EMNP (Fig. 1).

The iron concentration for the calibration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian VistaPro, Agilent Technologies, Santa Clara, USA; detection limit for Fe: 10 μg/L) after *aqua regia* digestion (HCl and HNO_3 at 200 °C; CEM Mars V, Kamp-Lintfort, Germany). The measurements were done immediately after sampling to achieve reproducible results. EMNP were also quantified based on their magnetism with the magnetic susceptibility balance (MSB AUTO, Sherwood Scientific, Cambridge, England, range of operation: χ_V of $0.001 \cdot 10^{-7}$ to $1.00 \cdot 10^{-3}$). Without application of an external magnetic field, the elemental magnetic dipoles of the EMNP do not have a permanent alignment (no magnetic behavior). Consequently, no magnetic attraction and agglomeration is expected due to internal magnetic forces. By application of an external magnetic field EMNP experience a strong aligned magnetization and therefore might temporarily agglomerate. However, a direct contact of the magnetic cores of the EMNP used is prevented by surface functionalization e.g. by organic chains creating an interspace between the single particles. This allows the quantification of EMNP concentration via the

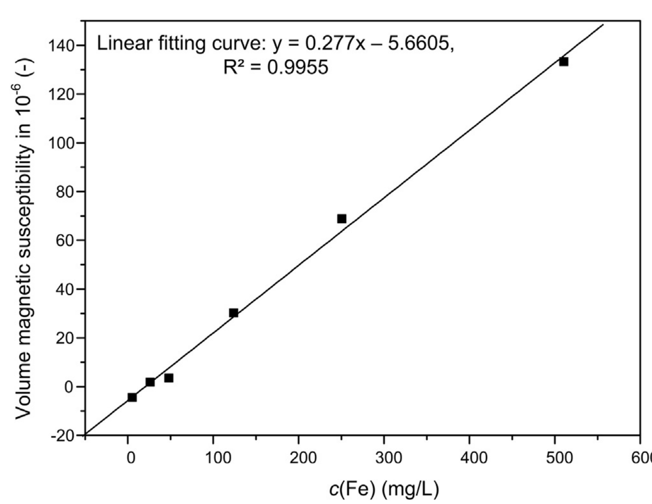

Fig. 1. Calibration curve of the volume magnetic susceptibility χ_v ($n = 3$, y-axis) for EMNP suspensions (Fe_3O_4-core with PVA coating) in ultrapure water and the iron concentration (x-axis) determined by ICP-OES. Standard deviations are too small to be recognized (<10%). The working range of the calibration is between 5.5–511 mg/L Fe.