Research article

# Impact of carboxymethyl cellulose coating on iron sulphide nanoparticles stability, transport, and mobilization potential of trace metals present in soils and sediment

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Frederik Van Koetsem [*], Lynn Van Havere, Gijs Du Laing

*Laboratory of Analytical Chemistry and Applied Ecochemistry, Department of Applied Analytical and Physical Chemistry, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent, Belgium*

## A B S T R A C T

The stability and transport behaviour of carboxymethyl cellulose (CMC) stabilized iron sulphide (FeS) engineered nanoparticles (ENPs) as well as their concurrent scavenging and mobilization of trace metal contaminants from field-contaminated soils and sediment was studied through a series of batch and column experiments. The synthesized CMC-FeS ENPs were shown to have a hydrodynamic diameter of $154.5 \pm 5.8$ nm and remained stable in suspension for a prolonged period of time (several weeks) when kept under anaerobic conditions. In the absence of CMC, much larger FeS particles were formed, which quickly aggregated and precipitated within minutes. Batch experiments indicated that the CMC-FeS ENPs have a high affinity for metal contaminants (*e.g.*, Cd, Cr, Cu, Hg, Ni, Pb, and Zn), as high amounts of these trace metals could be retrieved in the aqueous phase after treatment of the soils with the nanoparticles (*i.e.*, up to 29 times more compared to the water-leachable metal contents). Furthermore, batch retention of the nanoparticles by the solid soil phase was low (<37%), also suggesting a high stability and potential mobility. Nanoparticle treatment of the soils also affected the $CaCl_2$-, TCLP-, and SPLP-leachability of trace metals, although no clear trend could be observed and metal leaching appeared to depend on the specific element under consideration, the type of extraction liquid, as well as on soil properties. Column breakthrough tests demonstrated that the CMC-FeS ENPs were highly mobile in the tested soil, even without the use of an external pressure (*i.e.*, just via gravitational percolation). Maximal breakthrough of the nanoparticles was observed after approximately 10 or 16 pore volumes (PVs) for 83.3 or 500 mg $L^{-1}$ CMC-FeS ENPs, respectively, and only about 7% of the nanoparticles were retained by the soil after 22.7 PVs. Simultaneous elution of trace elements showed that up to 19, 8.7, or 11% of the respective Cd, Pb, or Zn content originally present in the soil was extracted after 22.7 PVs, with initial peaking occurring during the first 5 PVs. Moreover, filtration of the percolates over 0.10 μm (which was shown to be able to retain *ca.* 98% of the CMC-FeS ENPs) indicated that the vast majority of these extracted metals were associated with the nanoparticles and thus did not occur as "dissolved" species. Therefore, the high affinity of CMC-FeS ENPs for metals together with their high stability and mobility, suggests that association of trace metals with the nanoparticles could potentially lead to particle-facilitated contaminant transport in the environment, in case conditions favouring colloidal transport are prevailing.

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## 1. Introduction

Contamination of water bodies, sediments, and soils with heavy metals (or metalloids) such as As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Zn is considered to be a worldwide problem, primarily originating from anthropogenic activities (*e.g.*, ore mining and processing, fossil fuel combustion, industrial waste disposal, or usage of pesticides, paints, fertilizer, and sewage sludge), although geogenic processes (*e.g.*, natural geological weathering) could also lead to elevated trace metal concentrations (Du Laing et al., 2009; Frohne et al., 2014; Hou et al., 2013; Plathe et al., 2010, 2013). Whatever the source, heavy metals are known to induce toxicological responses in humans and organisms and are believed to be hazardous to

public health and ecosystems, even at trace levels (Hua et al., 2012; Plathe et al., 2013). For instance, As, Pb, Hg, and Cd were ranked 1st, 2nd, 3rd, and 7th, respectively, in the 2013 Priority List of Hazardous Substances reported by the Agency for Toxic Substances and Disease Registry (ATSDR, 2013).

As major environmental compartments, sediments and soils are considered to be a large sink for metal contaminants, and opposed to organic pollutants, most metals are not readily susceptible to microbial or chemical degradation to non-toxic end products *in situ* and will therefore persist in the environment (Hou et al., 2013; Kostal et al., 2005; Wuana and Okieimen, 2011). Alterations in their physicochemical appearance potentially affecting metal mobility, bioavailability, and toxicity are however possible, and depending on the environmental conditions, the metals could for instance be re-suspended and transported via pore water and end up in ground- or surface water causing a secondary contamination zone, and thus soils and sediments can act both as a sink and a source of prolonged metal contamination in the aquatic environment (Hou et al., 2013; Wuana and Okieimen, 2011). Effective and sustainable remediation options are therefore required in order to adequately restore and protect contaminated aquatic and terrestrial ecosystems (Wuana and Okieimen, 2011).

Numerous techniques have been developed and employed in order to remediate water or soil systems contaminated with heavy metals both *in* and *ex situ*, including but not limited to immobilization, soil washing, chemical extraction, membrane filtration, and phytoremediation technologies (Hua et al., 2012; Huang et al., 2011; Mallampati et al., 2013; Wuana and Okieimen, 2011). Moreover, with the advances in nanotechnology over the recent years, nanomaterial-based techniques have also been proposed as promising and even more efficient, durable, and cost-effective remediation options compared to traditional technologies (Cundy et al., 2008; Hua et al., 2012; Karn et al., 2009; Liu and Lal, 2012; Sánchez et al., 2011). The two main advantages nanomaterials possess over traditional remediation options, which stem from their exceptionally small dimensions (typically <100 nm), are a higher specific surface area and reactivity, and an enhanced deliverability of the small-sized particles in the subsurface of porous media such as soils or sediments (Hua et al., 2012; Liu and Lal, 2012). Examples of nanomaterials showing great potential for treatment of heavy metal-contaminated aqueous or terrestrial systems include nanosized zeolites, zerovalent iron (ZVI), iron oxides, aluminium oxides, manganese oxides, titanium oxides, cerium oxides, phosphates, iron sulphides, and carbon nanotubes. Remediation is generally based immobilization and/or reduction of the metal contaminants (Hua et al., 2012; Liu and Lal, 2012). For instance, ZVI engineered nanoparticles (ENPs) have been used to reduce aqueous Cr(VI) and $Pb^{2+}$ to $Cr^{3+}$ and $Pb^0$, respectively, thereby decreasing the solubility/mobility and toxicity of those metals (Cao and Zhang, 2006; Ponder et al., 2000). ZVI ENPs have also been shown to be able to treat other potentially toxic elements such as Ag, As, Cd, Hg, and Ni in aqueous and soil media, whereby the decontamination mechanisms again included reduction of the metal ions on the ZVI surface and/or adsorption of the metals on the ZVI shell, consisting of a layer of iron oxides (Alidokht et al., 2011; Kanel et al., 2005, 2006; Li and Zhang, 2006; Li and Zhang, 2007; Liu and Lal, 2012).

According to previous reports, injection of iron sulphide (FeS) nanoparticles into soils and sediments can be applied to immobilize heavy metal contaminants (*e.g.*, As and Hg) and hence render them unavailable to organisms and plants (Gong et al., 2012; Xiong et al., 2009; Zhang et al., 2010). However, as the particle size is reduced from the microscale to the nanoscale, the particle surface energy increases, and thus nanoparticles are inherently less stable and more prone to aggregation due to inter-particle interactions

(*e.g.*, Van der Waals forces). Consequently, the high chemical reactivity, sorption capacity, and mobility of the particles rapidly diminishes or even vanishes due to the formation of larger clusters, and hence the particles are not particularly suitable for *in situ* delivery in the subsurface (He et al., 2007; Hua et al., 2012). Therefore, stabilizing surface coatings (*e.g.*, thiols, carboxylic acids, surfactants, or polymers) are often used in order to enhance nanoparticle dispersibility and reduce aggregation, either through electrostatic repulsion, by providing steric hindrance, or via a combination of both (He et al., 2007). As being a low-cost and environmentally friendly "green" product, carboxymethyl cellulose (CMC) has been proposed as a potential suitable stabilizing agent (He and Zhao, 2007; He et al., 2007; Xu and Zhao, 2007), and CMC-stabilized FeS ENPs have already been demonstrated to display a much greater physical stability, soil deliverability, and reactivity compared to non-stabilized particles (Gong et al., 2012; Xiong et al., 2009).

However, the greatly amplified stability and mobility of such CMC-coated particles, together with their high sorption capacity of metal contaminants could potentially also lead to enhanced contaminant extraction and/or particle-facilitated contaminant transport in the environment instead of immobilization of the pollutants. Such well-dispersed nanoparticles could thus impart an elevated environmental risk as they may persist longer in the environment and be transported more easily over longer distances, which might result in an expansion of the contaminated area (Fang et al., 2009; Plathe et al., 2010, 2013). For example, As, Cr, Cu, Pb, and Zn have already been demonstrated to bind with natural Fe- and Ti-containing nanoparticles or small aggregates of them, which could remain suspended and highly mobile in surface water (*e.g.*, through (electro)steric stabilization by natural organic matter) (Plathe et al., 2010, 2013). Thus, the stability and transport behaviour of nanoparticles in complex environmental matrices are key factors not only governing their own ultimate fate, but also the fate, mobility, and potential bioavailability and toxicity of trace metal contaminants (Gimbert et al., 2007; Liu et al., 2012; Plathe et al., 2013).

This study primarily aimed at investigating the stability and transport of CMC-coated FeS ENPs as well as their concurrent impact on trace metal scavenging and mobility in field-contaminated soils and sediment, in order to contribute to the knowledge on their behaviour and fate in aqueous and terrestrial environments and invoke awareness on potential environmental risks associated with the use of such nanoparticles, *e.g.*, as an *in situ* environmental remediation option. Therefore, bare and CMC-stabilized FeS particles were synthesized and thoroughly characterized to examine the effect of CMC. Afterwards, batch and column experiments were set up to study CMC-FeS ENPs affinity for trace metal contaminants present in soils and sediment, and to investigate their transport behaviour. Finally, the effect of the nanoparticles on batch-leachability of trace metals was also explored.

## 2. Materials and methods

### 2.1. Synthesis of CMC-stabilized FeS ENPs

CMC-stabilized FeS ENPs were synthesized based on a method developed by Xiong et al. (2009). Firstly, a 1 wt% CMC solution was prepared by dissolving carboxymethyl cellulose sodium salt (VWR International, LLC, Radnor, PA, USA) in ultrapure water (18.2 MΩ cm$^{-1}$) (Milli-Q®, EMD Millipore Corp., Billerica, MA, USA) using an ultrasonic bath (Sonorex Super RK103H, Bandelin electronic GmbH, Berlin, Germany). A 7.5 mL aliquot from this CMC solution was added to 112.5 mL $N_2$-purged Milli-Q® water, and the solution was further purged with $N_2$ for 20 min to eliminate