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Full-Scale Removal of Arsenate and Chromate from Water Using a Limestone and Ochreous Sludge Mixture as a Low-Cost Sorbent Material

Karin Cederkvist^{1,2*}, Peter E. Holm¹, Marina B. Jensen²

ABSTRACT: The oxyanions arsenate (AsO_4^{3-}) and chromate (CrO_4^{2-}) are major freshwater contaminants. Arsenate is a problematic contaminant in drinking water reservoirs, and chromate limits the use of urban stormwater runoff. High-capacity, low-cost, energy-efficient treatment technologies are required for the removal of these toxic anions from freshwater sources. Using a 50-m-long dual porosity filter, with limestone as filtering grains, treating stormwater runoff from Copenhagen, Denmark, we tested if addition of the waste product ochreous sludge can improve the removal of arsenate (As) and chromate (Cr) without compromising the calcite's removal affinity towards metallic cations. Upon on-site embedding of the ochreous sludge, removal of arsenic and chromium was improved greatly, and copper (Cu) removal remained high. Steady-state effluent concentrations were reduced from 31 to 2 $\mu\text{g As/L}$, 127 to 1.5 $\mu\text{g Cr/L}$, and 18 to 9.6 $\mu\text{g Cu/L}$ upon mixing with the ochreous sludge. Limestone-ochreous sludge represents a promising low-cost oxyanion and cation sorbent operating at neutral pH without pH control. *Water Environ. Res.*, **82**, 401 (2010).

KEYWORDS: arsenate, chromate, dual porosity filtration, limestone, ochreous sludge, water treatment.

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Introduction

Clean freshwater is one of the most precious resources on Earth, increasingly in demand in both developed and developing countries. Lowering of water quality by toxic substances occurs globally. In regions experiencing strong urbanization or suffering from droughts, the use of secondary low-quality water sources for essential supply purposes is becoming more prevalent (Binning et al., 2006). Further, in high-income regions, citizens express rising expectations regarding the quality of domestic drinking water and water in the urban environment (i.e., park lakes, streams, and rivers).

Techniques capable of transforming large volumes of low-quality water to a quality adequate for sensitive supply purposes are needed all over the world. With reverse osmosis and membrane filtration, even wastewater can be turned into drinking

water; however, in many regions, the associated costs disqualify such advanced and relatively high-tech techniques. Thus, there is a market for low-cost treatment techniques. The challenge is to identify the appropriate sorbents and ensure a high hydraulic capacity.

Arsenic (As) and chromium (Cr) are two of the potentially most toxic inorganic contaminants in water. They cause severe health effects to humans and damage ecosystems. Under oxidizing conditions, they exist primarily as As(V) and Cr(VI), which form the negatively charged oxyanions arsenate (AsO_4^{3-}) and chromate (CrO_4^{2-}), respectively. All arsenic species are toxic, while only the hexavalent form of chromium is toxic. Since the 1980s, evidence has unfolded gradually that arsenic is present in elevated concentrations in part of tapped groundwater resources; the World Health Organization (Geneva, Switzerland) drinking-water standard is 10 $\mu\text{g As/L}$ (World Health Organization, 2004). The 10- $\mu\text{g As/L}$ level is difficult to meet for a number of waterworks in Denmark, where the standard recently has been lowered, to 5 $\mu\text{g As/L}$ (Danish EPA, 2005). Chromium is mainly a problem in urban stormwater runoff, especially in road runoff, where it originates from chromium-plating of screens and rims on cars, and in effluent from industries—especially galvanizing industries.

Established treatment processes for arsenic- and chromium-contaminated water include chemical precipitation, membrane filtration, ion exchange, and sorption processes (e.g., Bissen and Frimmel, 2003). These methods typically rely on chemical addition and are energy-intensive (Bailey et al., 1999; O'Connell et al., 2008). It is desirable to identify more sustainable water-treatment solutions, introducing reuse of waste products and other low-cost and energy-efficient materials with good sorption capacity.

Dual porosity filtration (DPF) is a novel water-treatment technology targeting suspended solids in the particle size range 1 to 100 μm and dissolved contaminants. Currently, the authors are testing this technique in a pilot plant in Oerestad, which is a new urban district in Copenhagen, Denmark. Hydraulically, DPF is mimicking water flow in fractured soil, with high-porosity compartments (mimicking fractures) for support of convective flow of water through the filter, and low-porosity compartments (mimicking matrix soil) with stagnant or slowly flowing water for retention of contaminants. Flow is oriented horizontally and solely gravity-driven. After each storm event, the pilot plant drains off and stays aerated, until the next runoff event. The unit-removal mechanisms are sedimentation, adsorption, and biodegradation.

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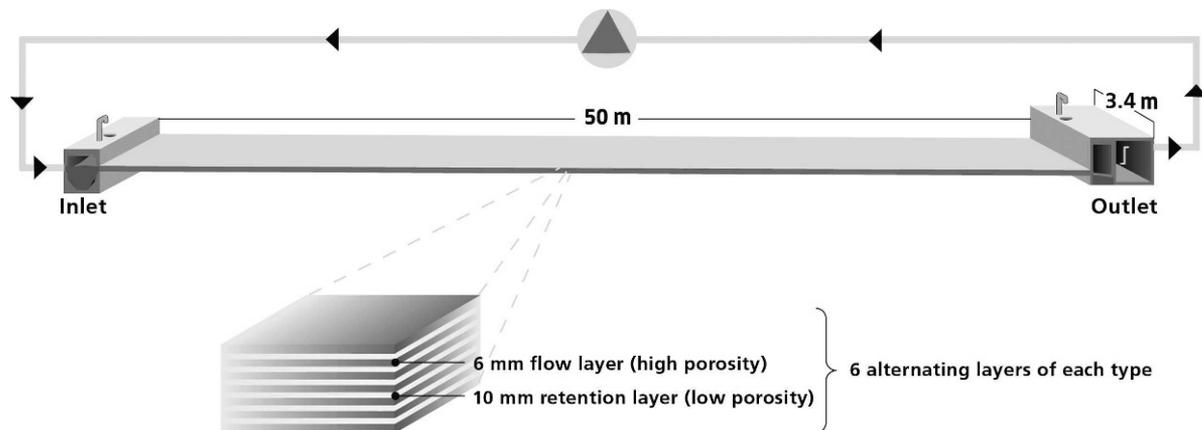


Figure 1—Illustration of the DPF pilot plant. The arrows from the outlet to the inlet illustrate the experimental conditions in this experiment, where recirculation of the water was obtained by using a centrifugal pump.

The DPF facility is used for treatment of stormwater runoff from roads in Oerestad. The DPF technique is under development, and, if successful, the treated road runoff will be used to supply a 10-km-long canal system that serves amenity purposes in the district. The Municipality of Copenhagen permits direct discharge of road runoff to the district canals of Oerestad, if the runoff can meet the following quality requirements: suspended solids <25 mg/L, total zinc (Zn_{tot}) <110 $\mu\text{g/L}$, total copper (Cu_{tot}) <12 $\mu\text{g/L}$, total chromium (Cr_{tot}) <10 $\mu\text{g/L}$, total lead (Pb_{tot}) <3.2 $\mu\text{g/L}$, and total phosphorus (P_{tot}) <100 $\mu\text{g/L}$. So far, the DPF facility has shown to effectively retain suspended solids and cationic metals, such as zinc (Zn), lead (Pb), and copper (Cu), but it fails to meet the local Cr_{tot} permits of 10 $\mu\text{g/L}$ (Jensen, 2007). Presumably, chromium is present mainly as the negatively charged chromate, CrO_4^{2-} , with only weak sorption ability to calcite (Yolcubal and Akyol, 2007). Therefore, a modification of the filter matrix is necessary to improve chromate removal efficiency.

In natural terrestrial and aquatic environments, geosorbents, such as the iron oxides, are known to constitute the primary sorbents of oxyanions. They have affinity towards arsenate and chromate ions, even at neutral and alkaline pH. This is because of their relatively high point of zero charge pH (pH_{pzc}), large surface area, and ability to form inner-sphere surface complexes with the oxyanions (e.g., Fendorf et al., 1997). The sorptive properties of iron oxides have been investigated already in relation to water treatment processes for arsenate and chromate. Granular ferric hydroxide (Asgari et al., 2008), zero-valent iron, goethite (Mohan and Pittman, 2007), and different types of sorbent materials, such as sand, cement, and polymeric materials coated with iron oxides (Benjamin et al., 1996; Genc-Fuhrman et al., 2007; Katsoyiannis and Zouboulis, 2002; Khaodhiar et al., 2000; Kundu and Gupta, 2005) are among the iron-based sorbents that are being examined. Ochreous sludge, a byproduct of groundwater treatment, is a potential low-cost alternative source for iron. Ochreous sludge is being generated continuously at water-supply facilities, when groundwater is aerated, to oxidize and precipitate its content of reduced iron, Fe(II), as Fe(III). The resulting Fe(III) oxides are primarily in the form of amorphous ferrihydrite, with a surface area of 100 to 350 m^2/g (Georgaki et al., 2004; Jambor and Dutrizac, 1998). The sludge is highly hydrous, and the sludge dry matter consists of approximately 30 to 40% iron and sizeable concentrations of calcium, organic matter, silicic acid, phosphate,

and quantities of trace elements representative for the groundwater source of origin (Aktor, 1990; Georgaki et al., 2004).

The overall aim of this study was to develop a low-cost sorbent for the removal of arsenate and chromate, which simultaneously holds affinity towards cations and supports large-scale production of supply water from low-grade reservoirs or wastewaters. The specific aim was to document if embedding of iron oxides in the form of ochreous sludge could improve the sorption affinity of a limestone-based filter matrix and thereby the removal efficiency of the oxyanions chromate and arsenate, without comprising the high affinity of limestone towards the cationic contaminants (i.e., Cu^{2+} , in this case).

Materials and Methods

Dual Porosity Filtration Pilot Plant. The field experiment was conducted in a DPF pilot plant in Oerestad (Figure 1), Copenhagen. In a normal drift situation, the water passes through the plant from the inlet to the outlet chamber, mainly flowing through the high-porosity compartments, which support a horizontal sheet-like flow. The high-porosity compartments overlie mattresses containing a filtering and sediment storage material. Contaminants are carried with convective flow in the high-porosity compartments into the plant. The contaminants are transferred to the low-porosity compartments by gravity and diffusion, where they are retained.

The plant shown in Figure 1 is 50 m long, 3.4 m wide, and 0.1 m deep. It is comprised of 6 horizontal layers, each made up of a high-porosity compartment overlying a low-porosity compartment. The high-porosity compartment supports the convective flow of water through the filter. It has a height (slit width) of 6 mm, width of 3.4 m, length of 50 m, and is made from a rigid polyethylene. The low-porosity compartment is a 3.4-m-wide and 50-m-long mattress, is 10 mm thick, and is made from two geotextiles, the upper with a mesh size of $0.6 \text{ mm} \times 0.6 \text{ mm}$, and the lower with a mesh size of $0.3 \text{ mm} \times 0.3 \text{ mm}$. The mattress is filled with a filtering material—in this case, limestone grains (see details below). The lower geo-textile prevents suspended solids accumulated in the low-porosity compartments from migrating downward to the high-porosity compartment underneath. The water flow through the DPF plant is gravity-driven. In an operating situation, stormwater runoff is led to the inlet chamber, where it builds up, until a hydraulic gradient of 1% is achieved.

This corresponds to a +0.5 m water level difference between inlet and outlet. After each rain event, the DPF plant is drained and, in this way, aerated.

The filter is equipped with built-in microtubes (1.4-mm inner diameter), which are distributed along the filter (1, 10, 20, 30, 40, and 49 m) for sampling of water from the high-porosity compartments numbers 2 and 4 during treatment.

The pH is measured daily in the inlet chamber by a built-in pH meter (pHix Compact, MJK, Naerum, Denmark).

Materials and Chemicals. The original filter matrix of the low-flow compartments in the filter consists of mined bryozoan limestone, originating from Faxø Limestone Quarry, Denmark, with diameter range of 1 to 3 mm, bulk weight of 1250 kg/m³, and bulk porosity of 54%. The total amount of limestone in the DPF plant is approximately 13 000 kg. Because the DPF plant was tested for 1 year before this experiment, withheld suspended solids and dissolved metals and other contaminants were present already in the filter material.

The added ochreous sludge originated from Sjaelsoe Waterwork (Hoersholm, Denmark). Dry matter content, trace element composition, and total organic carbon (TOC) content were analyzed.

To test the treatment efficiency of the filter with (1) the original filter matrix and (2) embedded ochreous sludge, identical pulses (pulses 1 and 2) containing 2.5 g As as Na₂HAsO₄ in 0.5 L of distilled water, 2.5 g Cr as K₂Cr₂O₇ in 0.5 L of distilled water, and 6.4 g Cu as CuSO₄·5H₂O in 0.5 L of distilled water was added. Each pulse additionally contained 250 g Br as KBr in 1 L of distilled water, with bromide functioning as a conservative tracer. All chemicals used were analytical-grade. Arsenic and chromium were added in their anion forms, and, consequently, when arsenic and chromium are referred to hereafter, it is assumed that the majority remained in the oxidized anionic form as the oxyanions arsenate and chromate.

Initialization of the Filter. To initialize conditions in the DPF pilot plant, the system was filled with stormwater runoff. After this, inlets and outlets were shut off, and the closed volume of water was set to recirculate from the outlet chamber back to the inlet chamber, by use of a screw centrifugal pump with frequency converter from Hidrostat (Hidrostat AG, Neunkirch, Switzerland) and a connecting pipeline. The flowrate was 4.1 to 4.3 m³/h, as measured with a magnetic flowmeter (MagFlux 7200 Sensor DN65, MJK). The aim of the initialization period was to remove the suspended solids and dissolved pollutants from the recirculating water. After the initialization, the composition of the water is somewhat different from stormwater runoff and should be considered as solids-free water, which is ready to be spiked with pulses of arsenate and chromate.

Test of Original Filter Matrix. The removal efficiency of the original filter matrix for arsenate, chromate, and copper was tested under steady conditions of recirculating flow of 4.1 to 4.3 m³/h, by adding pulse 1 to the approximately 6 m³ of water in the inlet chamber.

Upon rapid mixing using a long-stick brush, single samples were obtained at time zero from the inlet chamber, the outlet chamber (effluent), and from each of the 6 microtube sampling sites along the filter. Sampling was repeated after approximately 0.5, 1.25, 1.75, and 3.5 hours of recirculated flow. Hereafter, a fraction collector (ISCO 3700, Lincoln, Nebraska) was set to continue collection of effluent samples from the outlet chamber for another 62 hours, with sampling intervals of 6 hours.

Embedding of Ochreous Sludge and Test of Calcite-Ochreous Sludge Matrix. Approximately 60 hours after the addition of pulse 1, a volume of 1 m³ of ochreous sludge with a dry matter content of approximately 8%, corresponding to an ochreous sludge:limestone ratio of approximately 0.006, was added to the circulating volume of water, by pouring the sludge into the inlet chamber. To keep the sludge suspended in the inlet chamber, a stirring pump was lowered to the bottom of the chamber. After 3 days of continued recirculation, the water body was clear, with only a slight reddish color. During these 3 days, samples for the turbidity measurement were obtained from the inlet chamber every hour by the ISCO sampler, to follow the embedding of ochreous sludge in the calcite matrix in the low-porosity compartments.

Hereafter, pulse 2 was added, and a sampling regime identical to that used for pulse 1 was followed, with a sampling period of 47 hours.

In summary, the filter initialization lasted 15 days, after which, pulse 1 was introduced, and sampling was performed for 65.5 hours. Following this, ochreous sludge was introduced to the system and recirculated for 3 days. Finally, pulse 2 was introduced, and sampling was performed for 47 hours.

Chemical Analyses. To quantify the trace element composition of the ochreous sludge, dried sludge was digested in strong acid, according to U.S. Environmental Protection Agency (Washington, D.C.) (U.S. EPA) method 3052 (U.S. EPA, 2007b), and analyzed by inductively coupled plasma mass spectroscopy using an Agilent 7500c ICP-MS (Agilent Technologies, Tokyo, Japan) equipped with an octopole reaction system. Check analysis on Standard Reference Material from the National Institute of Standards and Technology (Gaithersburg, Maryland) (NIST) 2709 was included. Total organic carbon in the dried ochreous sludge was found by dry combustion with TOC ELTRA CS 500 (ELTRA GmbH, Neuss, Germany) combustion at 1300°C on triplicate tests.

The dry matter content of the ochreous sludge was estimated by filtration through a glass-fiber filter, with drying and weighing according to DS/EN 872:2005.

Turbidity measurements to follow embedding of ochreous sludge were obtained indirectly by using a Hach Lange Xion500 field spectrophotometer (Hach Lange GmbH, Dusseldorf, Germany), measuring light absorption at 860 nm.

The bromide (Br⁻) concentration in the water samples was analyzed with an ion selective bromide electrode type 500, with a solid-state crystal membrane, and a reference electrode R503/P and bridging electrolyte ELY/BR/503 (WTW, Weilheim, Germany). The limit of detection for bromide was 2 mg/L.

The arsenic, chromium, and copper were analyzed on acidified water samples on a Perkin Elmer 5100 atomic absorption spectrophotometer, with Zeeman 5100 background correction; HGA-600 graphite furnace; and an AS-60 auto sampler, with argon as the internal gas (PerkinElmer, Wellesley, Massachusetts). Duplicate analyses were performed on each sample and, within batch precision, expressed as the relative standard deviation (RSD%), which was less than 5% or 0.003 absorbance. The limits of detection for arsenic, chromium, and copper were 0.4, 0.3, and 0.14 µg/L. To test for matrix interferences on the measurements, standard addition was performed, and no significant matrix interferences were seen.

Because the water was slightly turbid after the embedding of ochreous sludge, samples from the pulse 2 experiment were

Table 1—Characterization of ochreous sludge by ICP-MS (the determination of lead should be considered semi-quantitative only).

Metal	Concentration ($\mu\text{g/g dw}$)	RSD (%)	Recovery of certified reference material (NIST) (%)
Arsenic	24	0.06	98
Chromium	11	0.7	86
Copper	18	3.6	88
Cobalt	0.99	1.6	91
Lead	4.4	59	92
Aluminum	92	1.7	95
Vanadium	18	0.6	98
Molybdenum	1.3	1.6	107

filtered through a 0.45- μm cellulose acetate filter (Sartorius, Minisart, Aubagne, France). Unfiltered samples were sent to a certified external laboratory, where they were digested in 7 M HNO_3 at 120°C for 30 minutes in a microwave oven, following U.S. EPA method 3051A (U.S. EPA, 2007a) and analyzed by ICP-MS according to ISO17294-2 (ISO, 2004). Because of no significant difference in concentration between the filtered and unfiltered samples, it was concluded that the filtered samples analyzed by graphite furnace atomic absorption spectrometry are representative of the total concentrations in the effluent.

All non-disposable glass and plasticware used for stock solutions and analytical determinations were double acid-washed.

Results and Discussion

Characterization of Ochreous Sludge. Table 1 shows the composition of trace elements in the ochreous sludge.

All analytical recoveries of the NIST-certified reference material were in the range 86 to 107% of the certified values, which is acceptable. However, the lead determination had a very high relative standard deviation (RSD), and the determination

should be considered only semi-quantitative. The results show that the ochreous sludge is enriched with metals and metalloids, although the concentrations of cobalt, lead, and molybdenum are low compared with typical levels found in soil, sediments, and sludges. The concentration of arsenic exceeds the Danish Soil Quality Criterion of 20 mg/kg (20 ppm) for clean soil and inorganic waste residues. Mobilization of arsenic and other harmful elements in the sludge is critical to the use of the sludge as a filtering material. It is important that the treatment system remains in an oxidized state, and controlled aeration needs to be incorporated.

The content of TOC was found to constitute 4.1 to 4.2% of the ochreous sludge, and the dry weight was approximately 8% (results not shown).

Flow Patterns for Pulses 1 and 2. A breakthrough curve (BTC) was obtained for each pulse, by plotting the bromide effluent concentration versus time, with time zero corresponding to pulse addition (Figure 2).

In both cases, steady bromide concentrations in the effluent were observed approximately 5 hours after the pulse addition (Figure 2). From Figure 2, it can be seen that a residual bromide concentration of 8 mg/L already is present in the water before the introduction of pulse 1. Because of the recirculation of a closed volume of water, the concentration of bromide increased to a higher level upon addition of pulse 2. Accordingly, bromide was first observed in the effluent at a distance of 50 m from the inlet after 1.4 hours of flow, which corresponds to a traveling velocity of 0.6 m/min and displacement of 6 m^3 of water, or 1 m^3 per dual porosity layer. A volume of 1 m^3 corresponds well with the expected volume of mobile water, which should equal the geometric volume of the high-porosity layer, which is 0.006 m \times 3.6 m \times 50 m = 1.08 m^3 . Peak bromide concentrations for both pulses were observed 3.5 hours after the pulse addition. A higher peak concentration could have occurred between 3.5 and 5 hours, when no samples were taken. The simultaneous microtube sampling from the high-flow compartments 2 and 4 showed similar bromide concentrations in the two layers, indicating that

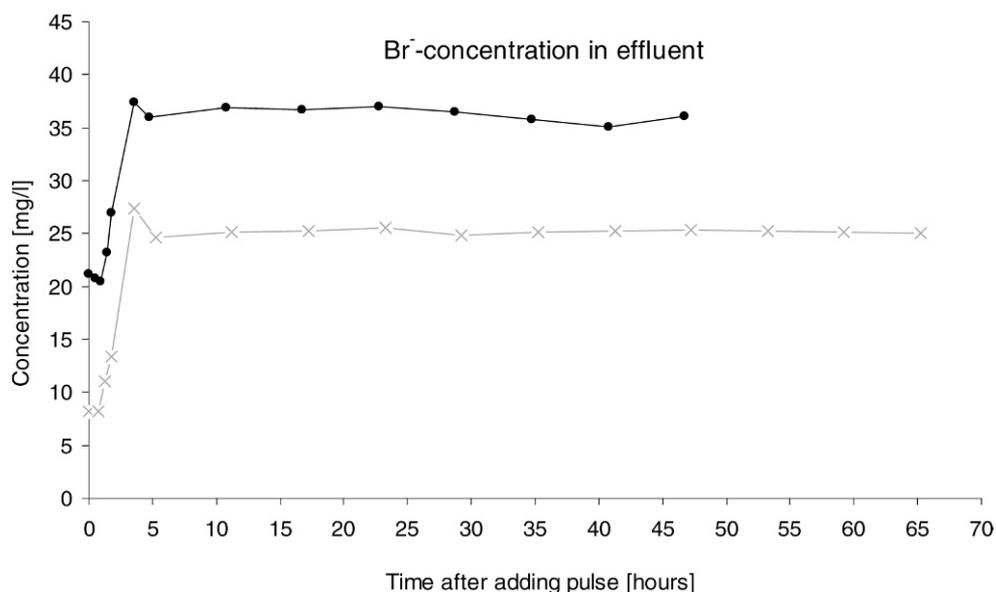


Figure 2—Bromide concentrations in the effluent after addition of pulse 1 (x) and pulse 2 (●) at time zero to the recirculating influent in the inlet chamber.

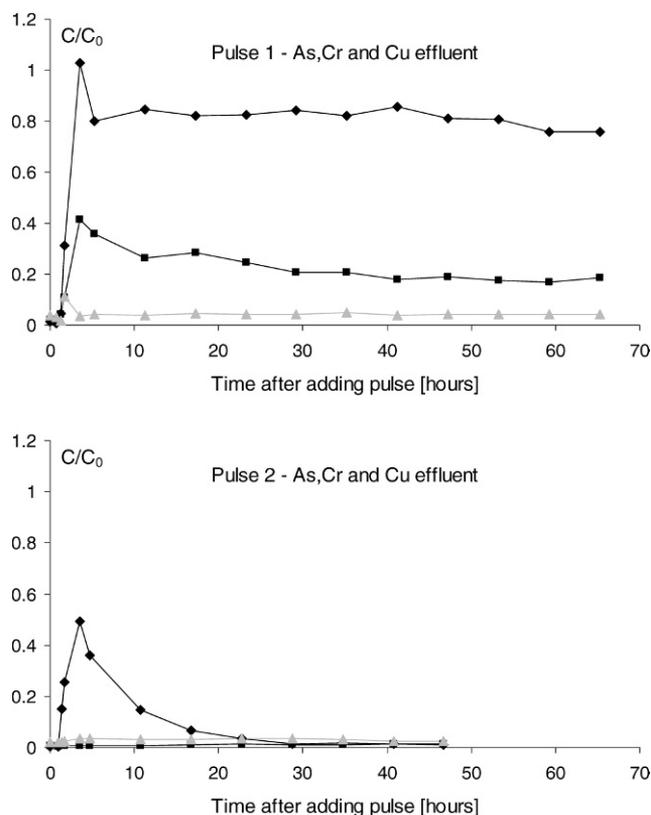


Figure 3—Relative effluent concentrations in the outlet chamber after adding pulses to the inlet chamber at 0 hours. C_0 = pulses 1 and 2 being completely mixed in 15 and 16 m³; ■ = arsenic, ◆ = chromium, and ▲ = copper.

the water was moving at approximately the same rate in all high-porosity compartments. The similarity in BTC curves (Figure 2) demonstrates that no clogging had occurred upon amendment with the ochreous sludge, which also is supported by the fact that the flowrate remained unchanged throughout the experimental period.

From the dilution of the bromide pulses upon complete mixing, the volume of water in the DPF pilot plant was estimated to be 15 m³ for pulse 1 and 16 m³ for pulse 2. The extra volume for pulse 2 is equivalent to the addition of approximately 1 m³ of ochreous sludge.

Retention of Pulses 1 and 2. The pH of the recirculating water was stable, at approximately 7.5 (results not shown) during the entire experimental period.

If the arsenate or chromate added with each pulse were mixed completely in the entire volume of water in the DPF plant (15 m³ pulse 1, 16 m³ pulse 2), and the As or Cr were not retained in the filter, the concentration, denoted C_0 , would be expected in the effluent. Further decreases are assumed to be the result of sorption. The relative concentration in the effluent is plotted in Figure 3.

The plots of the relative concentrations in the effluent (Figure 3) showed that the observed decreases in the concentrations of arsenate, chromate, and copper were not solely the result of dilution, but also the result of removal from the water phase by sorption to calcite and/or ochreous sludge.

The absolute effluent concentration levels of arsenic (as arsenate), chromium (as chromate), and copper are presented in Table 2.

After adding pulse 1, arsenate was first observed after 1.25 hours, and the peak concentration was 69 µg/L after 3.6 hours. Thereafter, the arsenate concentration decreased and stabilized at approximately 30 µg/L after 40 hours. Because the water was recirculated, a constant concentration in the effluent indicated that sorption equilibrium had been reached. Chromate was first observed after 1.25 hours. The peak concentration of 172 µg/L was observed after 3.6 hours, after which, the chromate concentration reached a constant level at approximately 127 µg/L. Assuming a pore volume of 15 m³, this suggests that only a small amount of the added chromate was sorbed. For pulse 1, copper was first observed and peaked at approximately 49 µg/L after 1.7 hours. Thereafter, a steep decrease to a constant value of approximately 18 µg/L was observed. After adding pulse 1 to the original filter, none of the arsenate, chromate, and copper outlet concentrations reached levels below their respective threshold limits for drinking water and freshwater ecosystems.

Figure 3 illustrates that the addition of ochreous sludge significantly improved the overall retention capacity of the filter. Pulse 2 was added to the recirculating water, which could contain remnant concentrations of arsenate, chromate, and copper from pulse 1. The concentration in the outlet before adding pulse 2 was below 1 µg/L for arsenate and chromate and 8 µg/L for copper (data not shown). This indicates that the ochreous sludge mixed into the filter had sorbed most of the remnants of metals and metalloids introduced with pulse 1.

Furthermore, after the addition of ochreous sludge, no peak concentration of arsenate was observed in the outlet for pulse 2.

Table 2—Absolute concentration levels in the effluent. C_0 = the theoretical effluent concentration if the pulse is completely mixed in the entire volume and is conservative.

	C_0 (µg/L)	First arrival (hours)	Peak arrival (hours)	Peak concentration (µg/L)	Time until steady-state (hours)	Steady-state concentration (µg/L)
Pulse 1						
Arsenic	167	1.25	3.6	69	41	30
Chromium	167	1.25	3.6	172	5.3	127
Copper	427	1.7	1.7	49	4	18
Pulse 2						
Arsenic	156	None	None	None	-	2
Chromium	156	1.4	3.6	83	>47	1.5
Copper	400	1.7	4.7	13.5	>47	9.6

The arsenate effluent concentration never exceeded 2 µg/L. For copper, a low peak concentration of 13.5 µg/L was observed after 4.7 hours. Thereafter, it continued to decrease, and, after 47 hours, it was 9.6 µg/L. Chromate peaked at 83 µg/L after 3.6 hours. Subsequently, it decreased to 1.5 µg/L after 47 hours.

Sorption Mechanisms. The first plot in Figure 3 illustrates that arsenate more readily sorbs to calcite grains compared with chromate. Sørensen et al. (2008) found that arsenate sorbs strongly to calcite, with the sorption increasing with decreasing alkalinity, and also is affected by ionic strength. Alexandratos et al. (2007) showed that this could be the result of both adsorption and co-precipitation. Despite the arsenate removal in the filter, the final arsenate concentration of 30 µg/L remained above threshold limits. In the case of chromate, the limestone caused almost no retention, which is in agreement with the low retardation factor and the K_d value (K_d = sorbed metal/metal in solution) for chromate in calcareous soil observed by Yolcubal and Akyol (2007).

It was concluded that the improved retention capacity after the addition of ochreous sludge towards both arsenate and chromate must be a result of the oxyanions sorption to the iron oxides from the ochreous sludge embedded in the low-flow compartments.

Because anions are sorbed more easily to iron oxides at $\text{pH} < 7$, as a result of electrostatic forces, most other arsenate and chromate sorption experiments have been carried out at low pH values. In a literature review, Mohan and Pittman (2006) concluded that no sorbent was efficient for Cr(VI) removal at high pH values. Adsorption of arsenic also may be less effective at higher pH values (Mohan and Pittman, 2007). Because stormwater runoff has a neutral pH (Göbel et al., 2007) and because of the calcite basis of the DPF filter, the pH in the water remained at 7.5 during the entire experimental period. It is worth noting that, even at this pH, it is possible to remove arsenate and chromate.

Although both chromate and arsenate form inner-sphere surface complexes with iron oxides, the plots indicate that the sorption of arsenate was faster than for chromate. Arsenate is a triprotic acid, while chromate is a diprotic acid. Triprotic acids have a broader adsorption edge over a wider pH range. Furthermore, arsenate appears to form stronger associations with iron oxide surfaces; while chromate forms a combination of mono- and bidentate surface complexes, arsenate forms bidentate surface complexes (Grossl et al., 1997).

In addition to the contribution from the formation of the inner-sphere surface complexes, the increased chromate retention observed after the addition of ochreous sludge may be attributed to a reduction of Cr(VI) to Cr(III) by organic matter or by Fe(II) added with the ochreous sludge, followed by sorption of cationic Cr(III) (Deng et al., 1996). This reduction process is slower than the sorption process, but may play a significant role in the final effluent concentration.

Copper was added as a model cation, to test if the addition of ochreous sludge would affect the already good retention of the original filter matrix towards cations. As seen in Figure 3, the addition of ochreous sludge improved the retention capacity of copper also. Copper sorbs to iron oxides by inner-sphere sorption, and the sorption increases with increasing pH; furthermore, copper also forms strong complexes with organic matter (e.g., Brandt et al., 2008), which also is present in small amounts in the ochreous sludge.

The effluent concentration of copper for pulse 1 remained above the threshold limit, whereas, after pulse 2, the concentration was kept below the threshold limit. Notably, the concentration of copper was more than double that of arsenate and chromate. Hence, the original filter and modified filter have a strong retention capacity for divalent copper.

Transfer of Test Results to Full-Scale Applications. After the addition of ochreous sludge, the filter effluent concentration of arsenic never exceeded 2 µg/L. For chromate, a significant effect of ochreous sludge embedded in the filter also was observed, but a peak concentration of 80 µg/L was observed in the effluent, and it took approximately 1 day to reach near-equilibrium conditions and a concentration level below the threshold limit (1.5 µg/L). In a normal operating situation, where water passes through the filter only once, it is not acceptable that concentrations in the effluent are above threshold limits at any time. The field experiment was carried out to test the capacity of the filter before and after the embedding of ochreous sludge. This does not necessarily resemble a realistic situation. Very rarely, a momentary pulse of such high concentrations will be led to the filter. Therefore, high peak outlet concentrations might not be present in a realistic scenario. In road runoff, chromium will not solely be Cr(VI), as in the conducted experiments. The Cr(III), which is sorbed strongly to calcite, organic matter, and iron oxides, also is present (Fendorf, 1995).

Despite the fact that arsenate and chromate are both oxyanions, some differences were observed in their removal patterns. The treatment of arsenate-contaminated water by iron oxides and calcite grains appears to be more stable and effective than for chromate-contaminated water. An optimal filter for the treatment of arsenate-contaminated drinking water might be different than an optimal filter for chromate-contaminated stormwater runoff.

As the arsenate concentration found in the effluent is below the drinking-water threshold value, it seems justified to advocate for further exploitation of the use of a DPF filter with embedded ochreous sludge for the remediation of arsenate-contaminated water.

To ensure proper removal of chromate from stormwater runoff, while maintaining the benefits of the calcite matrix towards other contaminants, one option could be to build a pre- or post-treatment chamber, with a slightly acidic pH and an iron-coated sorbent different from calcite.

In addition to initial concentrations, the sorption of the metals in the filter will depend on contact time with the filter matrix. In the DPF plant, the retention time of the water is constant, as a result of the construction of the facility. To evaluate whether the optimized sorbents could be used in the treatment for chromate and arsenate-contaminated water, further experiments, simulating more realistic field conditions, should be conducted, to test whether effluent peak concentrations above threshold level will occur.

Use of the Residual Product Ochreous Sludge. The addition of a small quantity of ochreous sludge significantly improves the retention capacity of the limestone-based DPF filter towards arsenate, chromate, and copper and, as such, represents a waste product with an interesting potential. As shown in Table 1, ochreous sludge contains a relatively high concentration of arsenic, chromium, copper, and other metals. In case of arsenic, the content exceeds the Danish Soil Quality Criterion of 20 mg/kg. Consequently, the use of ochreous sludge as a source for iron oxides for water treatment purposes may be questioned. However, it is expected that the trace metals are bound strongly or

incorporated to the iron oxides in the ochreous sludge and will remain so if redox instability and desorption mechanisms can be suppressed. The sorption capacity of the ferrihydrite can be altered; that is, the iron oxide can dissolve, as a result of a reducing environment or because of acidic conditions. Because the filter drains after each storm event and stays aerated until the next runoff event, the risk of longer-lasting reducing conditions inside the filter is diminished. Similarly, controlled aeration steps should be ensured if used for the removal of arsenic from drinking water. In the DPF plant, the buffering capacity of the calcite ensures no significant variation in pH; thus, no acidic dissolution of the iron oxides and subsequent desorption may be feared. However, with time, the amorphous ferrihydrite can recrystallize to more crystalline iron oxides with lower surface area—and thereby desorption could happen (Jambor and Dutrizac, 1998). This should be taken into consideration when evaluating the risks of leaching from the ochreous–calcite matrix.

Upon saturation with sorbates, the limestone–ochreous sludge sorbent matrix needs to be replaced and deposited as hazardous waste. Considering the calcareous basis of the deposited filter material, this will be stabilized already, and the risk of contaminant leaching will be low.

Conclusion

An experimental investigation was carried out on a limestone-based DPF plant, to test if a modification of the limestone with the waste product ochreous sludge would improve the retention capacity towards the oxyanions arsenate and chromate, without compromising the removal of cationic metal ions, in this case represented by Cu^{2+} .

The investigation shows that calcite grains with less than 1% embedded ochreous sludge effectively remove arsenate, chromate, and Cu^{2+} . The reaction rates for arsenate and Cu^{2+} are fast, with no or barely visible breakthroughs, while the reaction rate for chromate is slower, with clear breakthroughs and approximately 2 days of contact before a steady-state effluent concentration is observed.

First, it is concluded that ochreous-sludge-modified limestone represents a promising low-cost sorbent for the treatment of wastewater having an anion–cation mixed contaminant profile. The treatment requires no acidification or other pH control, as the sorption processes take place at neutral pH.

Second, it is concluded that the on-site addition of ochreous sludge to the DPF plant did not change the flow pattern of the water, as documented by the bromide BTC obtained before and after sludge embedding, indicating that ochreous sludge did not clog the filter. Further, this points to the advantage of the gravity-driven DPF technology for removal of fine particles from wastewater.

More studies are needed to investigate the long-term sorption capacity of the ochreous sludge–limestone filter matrix.

The better retention of arsenate compared with chromate indicates that, despite oxyanion similarities, their sorption mechanisms differ. To ensure the proper removal of chromate from stormwater runoff, while maintaining the benefits of the calcite matrix towards other contaminants, one option could be to build a pre- or post-treatment chamber with a slightly acidic pH and use an iron-oxide-based sorbent.

The high concentration of trace elements in ochreous sludge can be problematic, as a result of the risk of desorption. However,

when present with calcite, the risk of desorption to acidic dissolution is minimal, and desorbed cationic metals from recrystallizing iron oxides can be sorbed by calcite.

Credits

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