

Development of an on-site Fe⁰ process for treatment of copper- and zinc- contaminated roof runoff

Développement d'un procédé Fe⁰ sur site pour le traitement du cuivre et du zinc dans les eaux de ruissellement de toitures

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RÉSUMÉ

L'objectif de ce projet est le développement d'un procédé Fe⁰ comme système de prétraitement de ruissellements de toitures chargés en métaux. Des analyses de rupture, de cinétique et de grands flux ont été effectuées dans des conditions d'écoulement en laboratoire avec simulation réaliste de ruissellements de toitures, en faisant varier les paramètres de qualité des eaux. Des modèles de diffusion surface-pores et des modèles Phreeqc d'équilibre thermodynamique ont été utilisés pour prédire et comprendre les comportements des processus d'élimination des métaux dans des colonnes Fe⁰. Du carbonate de calcium (CaCO₃), de la dolomite (CaCO₃MgCO₃) et de la magnésite (MgCO₃) ont été combinés au système de fer pour améliorer l'élimination des métaux. Enfin, la configuration la plus prometteuse a été installée sur site pour le traitement des ruissellements de toitures chargés en zinc et en cuivre. Le système était composé d'une spirale de Fe₀ suivie d'une aération sur un filtre à lit fixe de pumicite et dolomite.

ABSTRACT

The objective of the present work was to develop the Fe⁰ process as a pre-treatment system of the metal-contaminated roof runoff. Breakthrough, kinetics and mass flow analyses were performed under laboratory flow-through condition using realistic roof runoffs, varying in the water quality parameters. The pore-surface-diffusion based (PSDM) and thermodynamically-equilibrium Phreeqc models were used to predict and empathise the behaviors of the metal removal in the Fe⁰ columns. To enhance of the removal of metals, calcium carbonate (CaCO₃), dolomite (CaCO₃MgCO₃) and magnesite (MgCO₃) were combined into the iron system. Finally, the most promising configuration was installed on-site for treatment of copper and zinc roof runoff. This system consisted of a spiral shape of Fe⁰ followed by aeration and a fixed-bed pumice/dolomite filter.

KEYWORDS

Column study, heavy metals; modeling; roof runoff; zero-valent iron barrier.

1 INTRODUCTION

Infiltration of roof, street and highway runoffs is among the recent ideas of urban water management that is of increasing interest. The infiltration of the stormwater naturally reduces flooding potential, whereas the filtrate also sustains the declining groundwater resource. In the infiltration practices, roof runoff is traditionally considered to be an advantage over the street and highway runoffs, in that it generally contains less organic and inorganic particulates, which may result in rapid clogging of the infiltration layer. In some particular cases, when the runoffs are originated from the roofs made from metals, however, the runoff can be highly contaminated with dissolved compounds, specifically with the toxic heavy metals such as copper and zinc (Zobrist et al, 2000; Gromaire et al, 2001; Boller and Steiner, 2002). An arising problem, when these contaminated waters are infiltrated for groundwater recharge, is a potential cause of deterioration of drinking water resource.

The objective of this work was to develop the Fe⁰ system for treatment of metal-contaminated roof runoff under close to- or realistic conditions elucidated in relation with previous batch test (Rangsviek and Jekel, 2005). The experimental works were separated into two parts. Firstly, the particle Fe⁰ impregnated with pumice was studied under flow-through conditions in the laboratory. The kinetics, breakthrough and mass flow analyses were performed using a realistic roof runoff. An attempt was also made to predict the breakthrough curves and to elucidate the dominant mechanisms involved in the treatment processes for further up-scaling of the processes. In the second part, the Fe⁰ treatment configuration was optimized. The most promising treatment process was installed and tested on-site for the treatment of copper and zinc roof runoffs.

2 MATERIALS AND METHODS

The model runoff (TU-SW) originated from a Bitumen roof with zinc gutter at Technical University of Berlin (TU-Berlin). Zero-Valent Iron (ZVI, Fe⁰) was prepared as scrape iron particles (0.70-1.25 mm) with surface area of 0.348 m² BET g⁻¹ (Rangsviek and Jekel, 2005). For field investigation, the iron was also prepared in a spiral shape. Granulate pumice (PM) was obtained from Raab group (Germany). For optimization of the Fe⁰ barrier, a pure calcium carbonate (CaCO₃) (Akdolit, Germany), a mixed mineral of Ca and Mg carbonate (CaMg(CO₃)₂) (Akdolit, Germany) and a pure Mg carbonate (MgCO₃) (Magnesia, Germany) were employed. In addition, granular activated carbon (Chemron, Germany) and Granular Ferric Hydroxide (Wasserchemie, Germany) were also trialled. The media were sieved to have a similar size as Fe⁰ and used with no further treatment.

2.1 Laboratory and field experiments

The breakthrough experiments were conducted as a set of comparative tests usually consisting of 4-6 columns in each run. Unless otherwise stated, a column (2.5 cm diameter, 25 cm length) containing particle Fe⁰ (15 g) homogeneously mixed with PM (20 g) (~10% Fe⁰ v/v) was employed as a standard criteria. There were two sampling ports with Teflon sieves at the inlet and the outlet ends of the column. The media were supported by glass beads (diameter 2 mm) at both ends. To begin a set of breakthrough experiments, a pump (Ismatec, Ecoline, Germany) drove the runoff up into the columns with a Tygon tube (diameter 2.79 mm) in an up-flow mode, while the other pump incrementally injected the prepared-metal stock solution into the flowing stream (Figure 1) giving a distinctly different characteristic of water quality parameters. The runoff solutions were filled up daily and thus source variation of stormwater could not be prevented. Investigation in a set of experiments using

realistic runoff, other qualities of the runoff might also contribute an effect on the breakthrough results. However, since the runoff is originated from the same reservoir, the differences in the obtained results from the comparative columns can thus be attributed to the varying water quality parameters. The samples were analyzed for copper, zinc and iron using a GBC atomic adsorption spectrophotometer (GBC 906AA, Australia). A comparison of un-filtrated and filtrated samples (0.45 μm) revealed that the total concentration of copper and zinc was sufficient dedicating to its corresponding dissolved value. The prediction of the breakthrough curves for the purpose of up-scaling was performed using pore surface diffusion model (PSDM.). For evaluation of the mechanisms that involved the removal of copper and zinc within the column test, Phreeqc equilibrium model (Prakhurst, 1999) was employed.

For the kinetic and on-site investigations, the columns were prepared using a plexi-glass column 3.5 cm in diameter and 56 cm in length. The columns consisted of 7 ports along the side wall with an equal distance of 7 cm for determination of metals after elapsed time along the flow. The kinetic column test was carried out under the same conditions as the breakthrough system for evaluation of up-scaling. Due to high consumption of water and a severe plugging of the flow, only primary results of breakthrough from larger columns have been obtained.

In order to evaluate the Fe^0 treatment barrier under realistic conditions, large columns were installed on-site for treatment of roof runoff originating from copper and zinc roofs. The on-site systems received realistic rain events. In the first experimental periods, columns containing particle Fe^0 with pumice and other dolomitic materials were tried but it was found that the columns were clogged after a few rain events. After successful optimization of the column test was established in the laboratory, spiral iron showed the most promising result. The on-site columns were filled only with spiral shape iron without any other media, followed by an aeration and post-filtration systems of pumice and dolomite, homogenously mixed within the same fixed filtration. Detailed investigation of onsite-treatment is described elsewhere.

3 RESULTS AND DISCUSSION

3.1 Impact of water quality on the breakthrough of metals in Fe^0 columns

3.1.1 Effect of pH

As compared with the previous batch investigation (Rangsivek and Jekel, 2005), in the present work the treatability of metals by Fe^0 influenced by runoff quality parameters has been evaluated in a fixed-bed system, i.e., in the system that is closer to realistic field conditions. This study has advantages not, only to study the influence of hydraulic and water characteristics on a short-term basis, but also to evaluate the performance of the Fe^0 barrier in the long-term period.

Figure 1 illustrated the results of experimental determination of the influences of pH on the removal of copper and zinc in Fe^0 barrier. Under the conditions studied, a fraction of dissolved copper and zinc (\sim total concentration) could not be treated and immediately eluted out from the columns ($c/c_0 = 0.1$ for copper and 0.3-0.5 for zinc). The breakthrough curves (BTCs) of copper and zinc at pH 4.2 and 5.8 follow similar patterns. At a throughput of 500-1,000 BV, the concentrations of copper and zinc slightly dropped before continuously stepping-up again until exhaustion (\sim 4000 BV). This lag period of Cu^{2+} and Zn^{2+} removal was most likely due to the formation of iron oxides resulting from the iron corrosion reaction.

The BTCs of copper and zinc at pH 6.5 demonstrated a distinctly different characteristic, showing a steep concentration increase in the first 500-800 BV followed by a much declining breakthrough shape. In addition, while the other two columns reached exhaustion at about the 4000 BV throughput, the column operating at more alkaline pH did not, suggesting a more sustainable removal of metals is achieved. An abruptly shift off of the breakthrough at 4000 BV for both copper and zinc is most likely due to an increase in NOM by source variation (c.f. NOM effect). NOM has been reported exhibiting a retard effect on Fe^0 system (Rangsivek and Jekel, 2005).

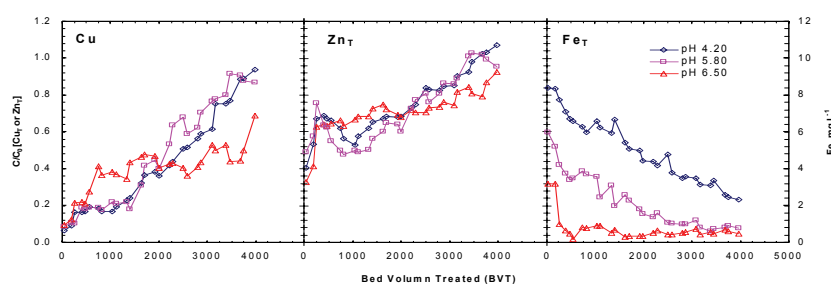


Figure 1 Breakthrough curves of copper and zinc in concomitant with the release of iron from the column operated at pH 4.2, 5.8 and 6.5 [Cu^{2+} 5 mg L⁻¹, Zn^{2+} 5 mg L⁻¹, 5 min EBCT, 20°C, 30-50 $\mu\text{S cm}^{-1}$, 10% particle Fe^0 (v/v) with pumice]

In comparison with the columns operating at pH 4.2 and 5.8, the lower amount of dissolved iron dissipated out of the column at pH 6.5 implied that more iron oxides precipitated inside the column, thus, serving as adsorption sites for the metals. The equilibrium calculations, i.e., which assume the reaction of metals with incrementally increasing amount of Fe^0 , demonstrated that both adsorption and cementation processes are taking place inside the Fe^0 column. These processes result in a precipitation of copper metal or oxides and other iron precipitates, the dominant species are depending on thermodynamically favour of the solution, which is agreed well with the experimental results. Nevertheless, it is noteworthy that only qualitative interpretation may be determined from these equilibrium calculations, since exact quantitative analysis has not been performed. Furthermore, other impacts involving the removal processes should also have been taken into consideration.

3.1.2 Effect of DO and IS

In principal it is expected that higher IS and DO will increase the removal rates of copper and zinc because more iron oxides may be produced (Rangsivek and Jekel, 2005). However, according to the experimental results from flow-through columns, the removal rate of Cu^{2+} were inhibited by the increasing IS and DO. This could probably be due to a greater effect of the passivation layer of iron oxides on Fe^0 under column condition. In comparison with the batch tests, the flow-through system is characterized by a system operating under a significantly higher metal flux per unit mass of Fe^0 . For this reason, an increase in DO and IS can stimulate the rates of deposition of a non-conductive layer of cuprite and iron oxides on the surface of the iron. Besides the load of solid precipitation, it is very likely that a thick non-porous layer of oxides was formed because of a relatively low flow and low ionic strength of

the solution. Contrary to this, the layer of oxides can easily dissipate out into the solution under the batch system which leads to a spontaneous corrosion of iron.

3.1.3 Effect of Temperature, NOM and EBCT

Determination of the temperature impact on the removal of metals in Fe^0 system was performed using runoff collected in the Summer, which is characterized by its high turbidity and concentrations of inorganic ions. It differed significantly from the aforementioned investigations of pH, DO and IS, which are spring-originated (a dilute solution). The runoff samples from the summer period possessed NOM content of about $9\text{--}70\text{ mg L}^{-1}$ which was much higher than the sample from the spring ($\sim 9\text{ mg L}^{-1}$ DOC). Investigation using this runoff for determining the temperature effect shows that the breakthrough of metals occurred immediately after initiating the solution (not shown). A very low rate of metal removal was observed in the column test and the temperature effect could not be distinguished from the comparative columns. In order to improve the assessment of temperature effect, the feeding runoff was substituted by deionized water (DI) adjusted to have a similar characteristic to the runoff water, e.g., range of conductivity, metal concentrations and pH, except that the NOM remains zero. Subsequently, a higher removal rate of metals was attained with respect to increasing temperature, consistent with the previous batch investigations (Rangsivek and Jekel, 2005). Therefore, it was concluded that the results from the first 3900 BV were influenced by the NOM concentration in the runoff solution.

In an attempt to elucidate the impact of runoff NOM and EBCT on the treatment

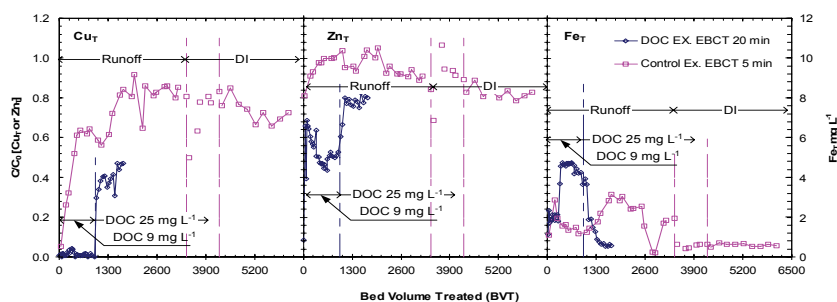


Figure 2 Breakthrough curves of copper and zinc in concomitant with the release of iron from the column operated at varying EBCT and NOM concentration [Cu_i^{2+} 5 mg L^{-1} , Zn_i^{2+} 5 mg L^{-1} , pH, 5-6, 5 or 20 min EBCT, 10% particle Fe^0 (v/v) with pumice]

of copper and zinc under flow-through conditions, a comparative set of experiments has been performed at varying EBCT and NOM concentrations (Figure 2). The results demonstrated the improved removal rates at a higher retention time. An increase in contact time from 5 to 20 min allowed up to a 50 % better immobility of zinc. For further evaluation on the impact of NOM, the fed runoff in the column with 20 min EBCT was substituted with 25 mg L^{-1} NOM containing runoff solution (formerly $\sim 9\text{ mg L}^{-1}$ NOM). Immediately, both copper and zinc at the outlet substantially increase. This happened in concomitant with the reducing rate of iron releasing, suggesting that the NOM has had a significant influence on the corrosion of iron. It is, therefore, clear that NOM has a great impact on the removal rate of metals and also that the

breakthroughs in the previous section of temperature effect have probably come about due to the surface blockage of iron influenced by the presence of NOM.

3.2 MODELLING

3.2.1 Model prediction of the breakthrough curves

The model prediction of the breakthrough curves of the Fe^0 system was investigated by employing a pore surface diffusion model (PSDM), which assumes the transport of contaminants to the reactive surface governed by film diffusion, intra-particle or pore and surface diffusion and internal surface diffusion. In the modeling procedures, the equilibrium parameters such as K_F and n , and kinetic parameter such as film (k_F) and surface/pore diffusion (D_s) coefficients were estimated from the existing study of metal removal in system containing iron medium, e.g., from Smith (1998) and Rangsviek and Jekel (2005). The parameters take into account the adsorption and cementation (for copper) processes as a single constant (Table 1).

The PSDM can adequately predict the breakthrough data from the experiment under varying runoff conditions (data not shown). The data from the determination of temperature and NOM effect were not taken into account since it was clear that the model poorly predict the curves. For other experimental data, some variance from the simulated and experimental data exists. In the case of alkaline conditions, an over-prediction curve of the model was attained. Improvement of the prediction can be made by varying the both kinetic and equilibrium parameters, e.g., by varying the K_F , k_F and D_s values. An example of sensitivity results is illustrated in Figure 3. Accordingly, K_F is shown to be the most sensitive parameter, whereas, changing in the kinetic parameters (k_F and D_s) does not catch much of the results. In this case, it is recommended that the K_F must be assessed based on the available data at different sites as they can vary significantly (Rangsviek and Jekel, 2005).

	NOM content mg L^{-1}	K_F $\text{L}^n \text{mg mg}^{-n} \text{g}^{-1}$	$1/n$	$k_F \times 10^{-3}$ cm s^{-1}	$D_s \times 10^{-10}$ $\text{cm}^2 \text{s}^{-1}$
Copper- Fe^0	0	20.0	0.60	9.00	1.00
Copper- Fe^0	4-9	20.0	0.60	9.00	1.00
Copper- Fe^0	9-70	100.0	0.40	9.00	1.00
Zinc- Fe^0	0	10.0	1.00	0.20	3.50
Zinc- Fe^0	4-9	10.0	1.00	0.20	3.50

Table 1 A comparison of the equilibrium and kinetic parameters for modelling of copper and zinc breakthrough curves [Cu_i^{2+} 5 mg L^{-1} , Zn_i^{2+} 5 mg L^{-1} , pH_i 5-6, 5 min EBCT, 10% particle Fe^0 (v/v) with pumice]

3.2.2 Up-scaling of the treatment processes

For the purpose of up-scaling of the treatment unit, the kinetic experiments were carried out using larger columns, in which the samples were taken from the sampling ports along the column. Figure 3 illustrates the data from the first and second ports of the kinetic column test fitted with the model results employing identical kinetic and equilibrium parameters as the breakthrough column. It could be seen that the model can predict the breakthrough (point) of copper very well (full line), which is similar to the removal of zinc (not shown). Furthermore, the model can easily capture the experimental data from the experiment that was performed using different iron ratios, i.e., 50 % of iron (data not shown).

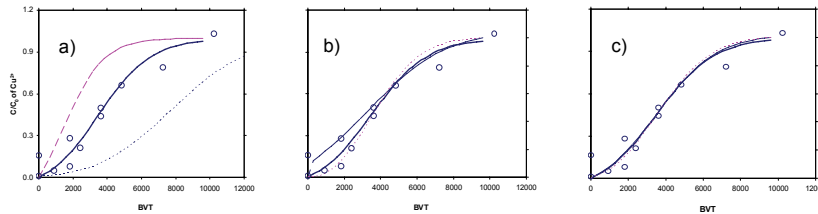


Figure 3 Sensitivity analysis of the breakthrough of copper obtained from a kinetic column test a) k_F were based on table 1, b and c) k_F and D_S varied 25%.

4 OPTIMIZATION OF THE Fe^0 BARRIER SYSTEM

Fe^0 alone (supported with pumice) can barely cope with the standard requirements. To optimize the system, different media have been trialed for the enhancement of the Fe^0 system. When granular activated carbon (GAC) and granular ferric hydroxides (GFH) were employed, no satisfactory results were obtained (results not shown). Therefore, dolomitic materials such as calcite, dolomite and magnesite were combined into the system for accelerating the precipitation processes of the metal hydroxides and facilitating the adsorption processes. A series of experiments performed in the laboratory and in the field shows that the dolomitic material

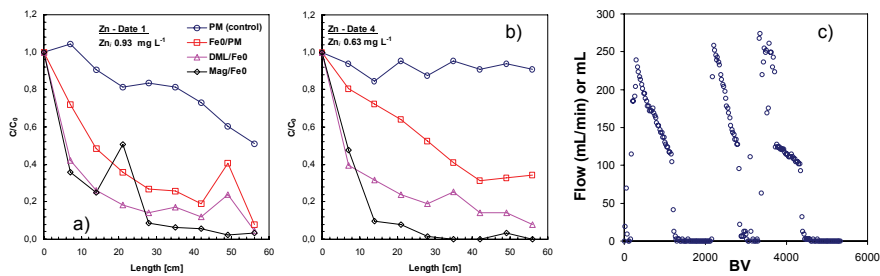


Figure 4 a and b) Removal profile of Zn^{2+} measured from the on-site installation of columns receiving roof runoff on the date 1 and 4, respectively and c) the representative profiles of hydraulic conductivity of the Fe^0 system.

significantly increases the removal rate of metals, specifically at the beginning of the experiment where pH buffering capacity is still high. A Magnesite/ Fe^0 column outperformed dolomite and calcite for removal of the metals, however, is exhibited a higher potential for clogging. Magnesite is thus considered a very problematic medium. Using these materials, the pH was initially maintained at 8-11 in concomitant with the concentration of alkalinity ($CO_3^{2-} + HCO_3^- + OH^-$), Ca^{2+} as well as Mg^{2+} depending on the compositions of the material. At a later stage when the surface of dolomitic materials was passivated, their pH buffering capacity was greatly reduced.

Based on the results demonstrated in the present work, the most suitable treatment processes was comprised of a spiral shape iron in the first column (without pumice), followed by aeration and a fixed-bed system containing pumice and dolomitic materials. The system can efficiently treat the runoff and it also lessens the clogging problem. The system relies on the production of dissolved iron in the Fe^0 column. The iron is subsequently transforms into iron oxides within the Fe^0 column or at the post filter bed of dolomite and pumice that helps facilitating the oxidation rate of iron. In

this case, the metals are additionally immobilized by means of precipitation into metal hydroxide compounds. Figure 4a and 4b show the representative field results of two Fe⁰ system receiving runoff from TU. With this configuration, about 60-100 % of metal concentrations could be removed at EBCT of 5 min and about 30-80 % was achieved with 1 min EBCT. Occasionally, the filter bed must be backwashed to maintain hydraulic loading capacity (figure 4c).

5 CONCLUSION

The study demonstrated that the breakthroughs of copper and zinc treated by Fe⁰ system were either accelerated or hindered under different water characteristics. In most cases, the performance of Fe⁰ impregnated pumice can hardly cope with both short and long term operation of the treatment process, with regarded to an effective treatability and clogging potential. At a very high NOM concentration, i.e., up to 70-300 mg L⁻¹ realistically measurable in the roof runoff, the removal rate of metals dramatically decreases, and subsequently results in an over-prediction of the breakthrough curves. For an enhancement of the removal of metals under these non-favourable conditions, calcium carbonate (CaCO₃), dolomite (CaCO₃MgCO₃) and magnesite (MgCO₃) are combined into the iron system. Finally, the most promising configuration was installed on-site for treatment of copper and zinc roof runoff. This system consisted of a spiral shape of Fe⁰ followed by aeration and a fix-bed pumice/dolomite filter.

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