Interaction of natural organic matter (NOM) and the Fe0 process for treatment of copper - and zinc-contaminated roof runoff

Interactions des matières organiques naturelles avec le fer (Fe0) pour le traitement des eaux de ruissellement chargées en métaux

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RÉSUMÉ

La barrière de Fe0 est une technologie prometteuse de traitement des ruissellements de toitures chargés en cuivre et zinc. Toutefois, des études récentes montrent que ces procédés échouent dans certaines conditions de fonctionnement où les matières organiques naturelles (MON) sont des facteurs essentiels de perte significative d'efficacité du traitement. Dans ce projet les mécanismes d'interaction MON/procédés Fe0 pour le traitement des métaux sont étudiés. Une caractérisation poussée des échantillons d'eau de ruissellement contenant des MON a été effectuée au moyen de diverses méthodes y compris les résines d'adsorption XAD 4/8, la complexation du cuivre, la capacité acidique et la chromatographie en phase liquide avec détection en ligne du carbone (LC-OCD). Les résultats ont été utilisés pour décrire l'élimination du Cu^{2+} et Zn^{2+} au cours des études de cinétique et des configurations d'écoulement.

ABSTRACT

Fe^0 barrier is a promising technology for the treatment of copper and zinc contaminated roof runoff. However, recent findings showed that Fe^0 processes fell at some operational conditions, in which natural organic matter (NOM) is among the crucial factors contributing to a significant decrease in the treatment efficiency. The present work assesses the mechanisms involved in the interaction of NOM and the Fe^0 processes for treatment of metals. Extensive characterization of NOM containing roof runoff samples have been carried out employing various methods including XAD-4/8 adsorption resins, copper complexation, acidic capacity and liquid chromatography with online carbon detection (LC-OCD). The characterized results were used to describe the removal of Cu^{2+} and Zn^{2+} during the kinetic batch and during the flow-through configurations.

KEYWORDS

Characterization, Fe^0, metals, natural organic matter, stormwater runoff.

1   INTRODUCTION

Natural organic matter (NOM) is a complex mixture of a variety of polyfunctional organic ligands; ranging from simple to more complex compounds of humic and fulvic acids. It is highly heterogeneous, containing a mixture of two major types of functional groups, carboxylic and phenolic compounds, in which the pK_a values are estimated to be 4.5 and 10 respectively (Perdue, 1985). It is well known that NOM plays a crucial role in facilitating the transport of metals in the aquatic environment. In conventional treatment processes of drinking water, NOM can reduce the treatment efficiency of the targeted compounds.

In a batch investigation of Fe^0 treatment of metal-contaminated stormwater runoff, Rangsivek and Jekel (2005; paper no.145 NOVATECH) showed that the NOM significantly inhibited the depletion rates of Zn^{2+}. In addition, the presence of NOM in the runoff caused immediate breakthroughs of both copper and zinc under flow-through configuration at a relatively low concentration of NOM, i.e., 9 mg DOC L^{-1}. The mechanism by which NOM contributes to an adverse effect was still unclear. It was, however, found that the competition of humic fractions of NOM for adsorption on freshly precipitated iron oxides is a relevant process. NOM may also retard the rate of iron oxidation during Fe^0 system (Rangsivek and Jekel, 2005).

The objective of the present work was to elucidate the mechanisms involved in the interaction of NOM and the Fe^0 treatment process of copper and zinc under stormwater runoff conditions. In the investigation, the runoffs were characterized according to the XAD-resin adsorption method coupled with acid-base titration and copper complexation, as well as chromatography with online carbon detection (LC-OCD) analyses. The characterization results were subsequently used for describing the behavior of copper and zinc removal in the batch and column systems containing Fe^0 medium.

2   MATERIALS AND METHODS

The runoff solutions originated from two roof types, a copper roof (UDK) and a bitument roof with zinc gutter (TU) (Rangsivek and Jekel, 2005; paper no.145 NOVATECH07). The roof areas are located in the same catchments (approx. 100 m distances), near the city center of Berlin-Zoologischergarten. The runoff samples were collected from the reservoirs installed onsite. TU-FF and TU-SW are representatives of the TU roof and considered as a first flush volume from the beginning of Summer and the late Summer, year 2005, respectively. The Cu-R sample was collected from the copper roof in Autumn, operationally defined as an event mean volume. After collection, the runoff samples were pre-filtrated using 0.45 µm cellulose nitrate membrane filter (Satoerius, Germany) and kept at 4°C. In addition to that, Suwannee River natural organic matter (SR-NOM, IHSS, USA) was also employed as a referent standard. It was diluted in deionised water and then adjusted to have a similar characteristic to the realistic runoff solutions. Detailed characterization of the source waters employed in this study is demonstrated in Table 1.

2.1   Characterization techniques of NOM

Isolation of NOM was performed according to the method described by Aiken et al. (1992). In the fractionation procedures, Amberlite XAD-8 and XAD-4 resin adsorption chromatography were employed, for which three fractions including hydrophobic,

hydrophilic and transphilic fractions were obtained from the procedures. Because a smaller amount of isolated fraction was obtained at each step of fractionation, only bulk runoffs and their corresponding hydrophobic fractions were further characterized for copper complexation and acidity.

The complexation of copper was carried out by means of measuring the free copper against the Ion Selective Electrode (ISE, Neolab, Germany) in an equilibrated solution, the Cu^{2+} concentration of which was increased by a stepwise adding of a Cu^{2+} stock solution. To evaluate the charge interaction between runoff NOM and the reactive surfaces in Fe^0 system, the carboxylic and phenolic acid density of runoff NOM was performed by a potentiometrix titration, in which the carboxylic acidic group is defined by consumption of NaOH from pH 3 to 8. The phenolic group required twice the amount of titrant as an estimation. Additionally, an online liquid chromatography with organic carbon detector (LC-OCD) was employed for an advanced characterization of NOM (Huber and Frimmel, 1996). The method divided the bulk NOM into different compositions based on molecular sizes. With the addition of the XAD adsorption method, in the present work the impact of NOM was additionally evaluated based on hydrophobic characteristic of NOM.

Source*	pH	Condc.	DOC	UVA$_{254}$	SUVA	HPO	HPI	TPI
		$\mu S\ cm^{-1}$	mg L$^-$	m^{-1}	m^{-1} mg^{-1} L	%	%	%
TU-SW	6.0	134	36	104	2.88	64.8	17.1	18.1
TU-FF	5.0	19	9.9	16.5	1.67	7.6	70.1	22.4
CU-R	6.4	148	9.8	29.9	3.07	45.3	27.5	27.2
SR-NOM	5.0	300	4.3	24.1	5.64	93.4	1.70	4.90

*Prefiltrated using 0.45 µm cellulose nitrate filter; HPO hydrophobic fraction; HPI hydrophilic fraction and TPI transphilic fraction

1. TU-SW: Bitumen roof runoff with zinc gutter at TU Berlin collected during Autumn

2. TU-FF : 1 to 30 dilution of the first flush of TU-SW after long drought period in the beginning of the Summer

3. CU-R: Copper roof runoff at the university of art in Berlin (UDK)

4. SR-NOM: prepared using Suwannee River NOM in deionized water (DI)

Table 1. Characteristics of source waters

2.2 Kinetic batch and column experiments

All runoff solutions were adjusted to have a constant pH and conductivity of 300 µS cm^{-1} using NaOH and HNO$_3$. The concentrations of Cu^{2+} and Zn^{2+} were brought to 5 mg L^{-1} at two initial pH, e.g, 2.5 and 5.0. The batch tests were carried out by means of equilibrating the 50 mL of the runoff solutions with a 0.5 g L^{-1} of Fe^0 (cal. 0.186 m^2 L^{-1} Fe^0) for 200 h. This Fe^0 has been characterized and used in previous investigations (Rangsivek and Jekel, 2005; Rangsivek and Jekel, paper no.145). The pH was allowed to vary over the course of the run. The experiment was carried out at pH 2.5 even though this is not typical for roof runoff conditions. At this highly acidic pH, the evaluation of mechanisms associated NOM impact in the Fe^0 system could be observed in a clearer manner. In addition, the final pH was ranged under the typical runoff condition.

To determine the removal rate of metals, water samples of 1 or 2 ml were taken at regular intervals. The samples were subsequently filtrated using a glass filter. They were made up to 10 mL with 5% HNO$_3$ solution and kept cool at 4°C before analysis of metals including Cu^{2+}, Zn^{2+} and Fe^{2+}. pH, UV$_{254}$, UV$_{436}$ and LC-OCD were analyzed

for bulk NOM at the initial and at the final samples. Based on the analysis of the 200 h-samples, membrane filtration using 0.45 μm cellulose or grass filter gave no significant difference both are defined by the dissolved substances.

In addition to the kinetic batch test, the results of the column investigations for determination of the impact of NOM on the removal of metals in Fe^0 system is evaluated in this present paper. The experimental work and the results have been described in details elsewhere (Rangsivek and Jekel, paper no.145). Briefly, TU roof
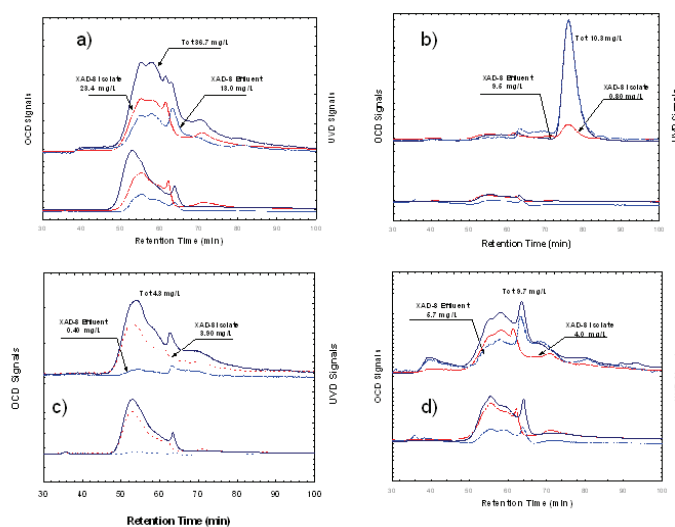

Figure 1 LC-OCD of bulk NOM and its corresponding XAD-8 isolated fractions of a) TU-SW b) TU-FF c) SR-NOM and d) Cu-R runoffs

runoff spiked with heavy metals were fed into the column containing Fe^0 supported with pumice, which is insignificantly reactive toward metals. The columns were run in an up-flow mode at either 5 or 20 min empty bed contact time (EBCT) and the concentrations of NOM in the feeding solutions were varied in order to examine the impact of EBCT and NOM concentration on the treatment processes, respectively. The water samples were taken before and after passing through the columns in which they were analyzed for the total concentrations of copper, zinc and iron. The differences in measured concentrations are attributed to the removal rates as a result of reaction with Fe^0. A preliminary study showed that total metals (Cu, Zn and Fe) remain relatively dissolved in the runoff solution and, hence, bulk concentrations were defined as the dissolved compounds.

3   RESULTS AND DISCUSSION

3.1   Characterization of NOM

3.1.1   Hydrophobicity and molecular size

A comparison between LC-OCD chromatograms of the roof runoffs used in this study shows that the NOM from the same sources of roof or catchment have distinctly different characteristics (Figure 1). The TU-SW and Cu-R are comprised mainly of humic substances and building blocks that have a strong UV absorption, most likely derived from the decomposition of the plants. In addition to that, a minor content of polysaccharides has also been detected. Fulvic acid is the main part of SR-NOM and

the obtained LC-OCD diagram is similar to its corresponding fulvic fraction as determined in previous work (Rangsivek and Jekel, 2005). In all of these runoff samples, humic substances are found in significant proportion, all of which have a prevailing hydrophobic characteristic. The water samples also appear to be highly aromatic as demonstrated by the value of SUVA (Table 1).

In contrast with other samples, a low molecular weight acid was mainly detected for TU-FF and as a result the water demonstrates a hydrophilic characteristic (70.1%). This might come about because a large part of NOM in the water are amphiphilics and neutrals that posses a low organic functional group (Figure 1; Table 1). The result is well consistent with the lowest values of an index of aromaticity as compared with other runoffs.

3.1. 2   Acidity of source water

	Carboxylic (mmol/g-C)	Phenolic (mmol/g-C)	Total acidity (mmol/g-C)	Overall acidity (mmol/L)
TU-SW	1.81	0.91	2.72	49.0
TU-FF	3.84	1.92	5.76	28.5
SR-NOM	9.07	4.54	13.61	29.3
Cu-R	6.43	3.22	9.65	47.3

Table 2 Esimated contents of carboxyl and phenolic groups

A calculation of the acidic naturalizing capacity of the NOM in different runoff samples is shown in Table 2. According to these results, the content of carboxylic and phenolic compounds for SR-NOM, Cu-R, TU-FF and TU-SW are decreasing in order of carboxylic compounds: 9.07, 6.43, 3.84, 1.81 mmol g^{-1} C; and 4.54, 3.22, 1.92, 0.91 mmol g^{-1} C for phenolic compounds, respectively. TU runoff from the same source shows a relatively low organic content, although they exhibit different compositions. The generally low ligand content in TU-FF solution could reasonably be attributed to its composition from hydrophilic compounds. The organic content in TU-SW is low because the calculation took into account the total mass of organic compounds. However, the TU-SW has the highest overall acidity content of 49 mmol/L. In other samples of SR-NOM and CU-R, the water consisted mainly of humic substances per mass and thus demonstrated relatively high organic functional groups. In comparison, the carboxyl and phenolic content obtained from this study are within the same range (Lu and Allen, 2002).

3.1.3   Copper complexation capacity

According to the titration curve, the NOM capacity for copper complexation prevails significantly only for the TU-SW runoff (not shown). This could be explained because the water has the highest total acidity content (Table 2). Similarly, the Cu-R might also process high complex of copper but this could not be determined because complexation seems to be dominated at a relatively low concentration range (~ mg CiL-1) and the original copper concentration was already high (~ mg CiL-1). Similar results were obtained in the titration of the hydrophobic fractions of the runoff NOMs. The acidity of the runoff NOM in the present work can be considered to be relatively low, probably due to a low pH at 5.5 being employed. In an alkaline pH solution, the NOM-complexation of metals is significantly greater. A 10 fold copper complexation increase per pH was reported by Lu and Allen (2002).

3.2 Influence and interaction of NOM on the removal of Cu^{2+}, Zn^{2+} and DOC

3.2.1 Batch kinetic study

Under both pH conditions, Cu^{2+} depletion rate takes place rapidly and a complete removal was achieved within 18 hours run regardless of initial pH. The rates of copper removal were in the range of 2.90-9.56 h^{-1} comparable with the results in the previous study (Rangsivek and Jekel, 2005).

Removal rate of Zn^{2+} is lower than that of Cu^{2+} and shows a strong dependence on the pH (Figure 2a and 2c). The reactions in pH_i 5.0 solution (pH_f 6-10) proceed at higher rates than the reactions at pH_i 2.5 (pH_f 5-6) for all of the tested runoff solutions, 14.1-40.8 h^{-1} and 87.7-267 h^{-1}, respectively. A higher removal rate with respect to pH values could be reasonably explained by the larger number of negative surfaces coordinated on iron oxides that favor the adsorption processes of Zn^{2+} (Rangsivek and Jekel, 2005). It is noteworthy that the final pH in this batch test is much higher as compared with the results obtained in the previous work. Such an increase in pH might have been due to a longer contact time between the iron and the solution that allowed rate-limiting reactions to take place. Thus, beside the adsorption processes an increase in pH during the reaction will also influence the rate of precipitation of iron oxides (Rangsivek and Jekel, 2005). Furthermore, in an alkaline pH, the precipitation of metal hydroxide becomes more significant and therefore this process must be taken into consideration.

DOC depletion load is dependent on the pH values (Figure 2b and 2d) indicating that an adsorption process is governed by its removal. In the adsorption of NOM, the H_2O or OH^- groups on the hydroxylated iron oxide surface are replaced by anionic functional groups of NOM (Gu et al., 1994, 1995). This could explain why better removals of NOM for TU-SW, CU-R and SR-NOM than for the TU-FF were attained (Figure 2b and 2d). TU-FF is hydrophobic and consists mainly of a smaller size range of organic compounds (see also in LC-OCD characterization).

Because of the adsorption of NOM on iron oxides, a ternary complex of metal-NOM-iron oxides could be formed. This was evident during the batch test at pH_i 2.5 in which a higher uptake load of zinc could be attained. Fundamentally, the metals are merely adsorbed onto iron oxide surfaces under this condition. Consistent with this assumption, it could be seen from Figure 2b that, except TU-SW, the removal of zinc was generally well correlated with the removal load of NOM. The DOC depletion load in TU-SW solution was about 30 mg DOC L^{-1}, a little higher than that of CU-R. However, the removal of Zn^{2+} was smaller indicating that an inhibition occurs at a higher adsorption of NOM. Other processes might also be relevant.

When the kinetic removal of Zn^{2+} in TU-SW (pH_i 2.5) was observed, it could be seen that the removal rate of Zn^{2+} showed a leveling off over time. This might be because of the residual DOC of TU-SW that could form a metal-ligand complex in the solution and subsequently reduced its removal in the TU-SW solution. In accordance with this batch investigation, Rangsivek and Jekel (2005) have also found that the dissolved iron in the NOM-containing solution remained relatively persistent. A ligand-complex between NOM and dissolved iron was explained.
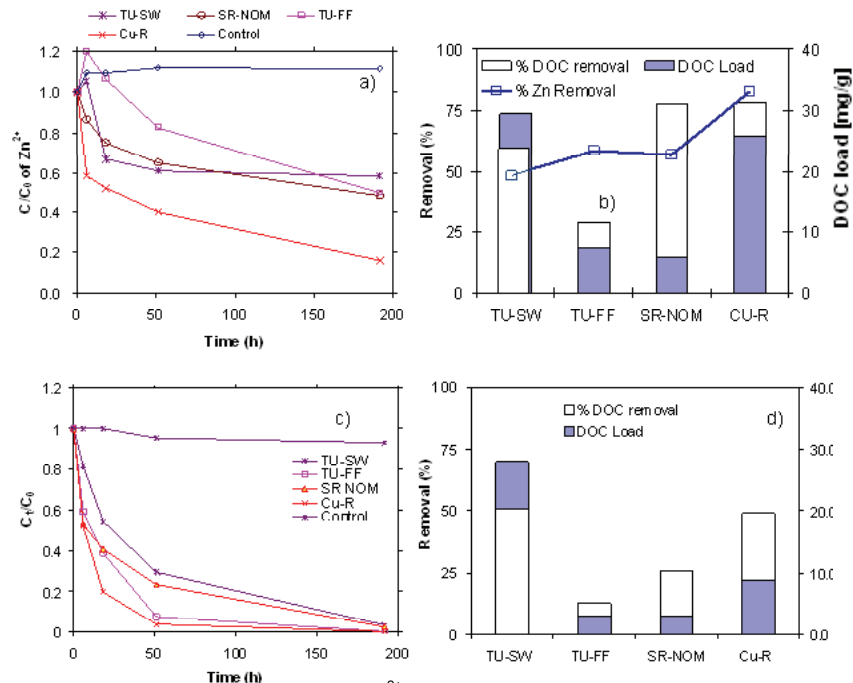
Figure 2 a) and c) the kinetic removal of Zn^{2+} in TU-SW, TUFF, SR-NOM and Cu-R runoff solutions carried out in the batch test at initial pH 2.5 (pH_f 5-6) and 5.0 (pH_f 6-10), respectively, and b) and d) a comparison of its corresponding DOC removal in correlation with removal of Zn^{2+} [Cu_i^{2+} 5 mg L^{-1}, Zn^{2+} 5.0 mg L^{-1}, 0.5 g Fe^0 L^{-1}, well mixed and at room temperature]

In the batch experiments at pH_i 5 (Figure 2d) a complete removal of Zn^{2+} was obtained. As already mentioned, an increasing pH in an alkaline range would induce several complex reactions which may generate a misleading interpretation of the results. In an alkaline pH the processes of metal-hydroxides precipitation might be dominant over adsorption processes, as previously discussed. In general, however, the removal rate of Zn^{2+} seems to be inhibited in the presence of NOM (c.f., Figure 2c and 2d), in contrast to the result at pH 2.5. For these reasons, it may be concluded that the NOM could cause either an enhanced or an inhibitory effect on the removal of Zn^{2+} within the Fe^0 system. The affect produced depends strongly on the experimental conditions.

3.2.2   Column study

Assessment of NOM impact on the Fe^0 system under flow-through condition was evaluated employing the results from Rangsivek and Jekel (paper no.145). In the experiments for determination of NOM impact, the Fe^0 column operating at 20 min EBCT was firstly fed with TU-SW (9 mg l^{-1} of NOM), in which both copper and zinc are removed under operated conditions to approximately 100% and 55% of initial concentration, respectively. The iron concentration at the outlet was in a range of 6- 8 mg l^{-1}, indicating an extensive corrosion of iron. At approximately 1000 BV, the fed solution was substituted with the 25 mg L^{-1} NOM-containing runoff. Immediately both copper and zinc concentrations from the column were substantially increased concomitantly to the reduction of iron concentration from the column. This decrease in iron concentration suggests that the adsorbed NOM probably has blocked the

reactive surface sites of iron. A competitive adsorption between metals and NOM might also be a governing process.

3.2.3 NOM as analysed by LC-OCD

The LC-OCD chromatograms of TU-SW and TU-FF bulk NOM show that a larger molecular weight compound, specifically the humic substance, is preferentially removed during the reaction with Fe^0. The NOM of TU-FF runoff decreases to only a small extent and the fraction removed is a larger sized fraction. A ligand-exchange mechanism between organic functional groups of humic substances and hydroxyl on iron oxides surface governs the reactions of NOM adsorption (Gu et al., 1995; Rangsivek and Jekel, 2005).

Further elucidation of the adsorption behavior of organic compounds in the Fe^0 system was evaluated based on the hydrophobic characteristics of NOM. In the TU-SW and TU-FF samples, when the molecule is large, a non-humic fraction (XAD-8 effluent) is removed as equally as the hydrophobic fraction (XAD-8 isolate) (not shown). The highly hydrophobic NOM from Suwannee River exhibits almost a complete removal, whereas Cu-R shows a similar result to that of TU-SW. In contrast, the smaller molecular weight fractions of hydrophilic and transphilic substances holding a higher concentration to the bulk NOM concentration of TU-FF are merely adsorbed. Thus, from these findings it is clear that the adsorption of NOM on iron oxide surfaces is more associated with the size of organic molecule than with the hydrophobic characteristic.

4 SUMMARY AND IMPLICATIONS

Based on the results, it was shown that the NOM interacts with metals through several complex processes. NOM not only directly hinders the rate of iron corrosion but also indirectly contributes to a competitive adsorption of the metals on iron oxides. The metal-ligand complexes in the solution prevent the adsorption of metals to take place. In order to enhance the treatment efficiency of the Fe^0 barrier in the presence of NOM, dolomitic materials should be incorporated into the treatment system to induce the precipitation of metal hydroxides and to increase the affinity for adsorption of the metals (Rangsivek and Jekel, paper no. 145).

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