

Evaluation of Zn, Cu and Pb sorption-desorption phenomena in kaolinite-sand media filtration pilot scale installation

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Abstract

The retention of Zn, Cu and Pb from highway runoff with reactive filter media was studied. Besides the physical retention of traditional filter beds, a reactive filter bed enhances the dissolved heavy metals retention processes due to sorption and precipitation, transferring pollutants from the dissolved form to the media matrix. A synthetic effluent was used to simulate highway runoff and, for filter bed media, sand and kaolinite were used. Results obtained for those three heavy metals show a very high reactive filter media retention capacity and a very high resistance to desorption processes.

Introduction

A large number of heavy metals and organic micro pollutants in highway runoff appear as a result from automobile traffic. Cu, Pb, Zn and Cd – sometimes Ni and Cr – are considered the most important heavy metals associated with both mobile and stationary sources [1]. These metals are either dissolved in the storm water or bound to particulates [2, 3].

Unlike organics and xenobiotic compounds, metal elements are not degraded in the environment. As a consequence metal elements exert both a short-term toxicity impact, characterized by concentration or activity, and a long-term toxicity impact, characterized by mass accumulation [4].

Previous studies with highway runoff have shown that Zn, Cd, Ni and Cu are predominately dissolved; Pb and Cr are equally distributed between dissolved and particulate-bound phases, while Fe and Al are predominately bound to particles [4].

Strategies for highways runoff contaminants control, such as infiltration methods, detention methods, vegetated filter strips and wetlands have been proposed.

Using infiltration ponds particles can be retained in pond bottom layers, but dissolved heavy metals might contaminate aquifers. Even with detention ponds, where particles could settle, small particles and dissolved heavy metals can contribute to groundwater contamination.

A decision with regard to the effectiveness of filtration or sedimentation is balanced by particle size gradation and density characteristics as well as loading characteristics and specific site constraints.

Since filtration media are mainly designed for mechanical retention removal, they only contribute to the removal of heavy metals in the particulate form. The use of a reactive bed for the filter media will enhance the dissolved heavy metals retention processes due to sorption and precipitation, transferring pollutants from the dissolved form to the media matrix. This will contribute to the control of receiving waters (surface and groundwater) pollution due to highway runoff. Therefore, the immobilization of dissolved metal complexes and particulate-bound metal elements through reactive filtration mechanisms can induce the development of an innovative “in-situ” retention technique, characterized by high heavy metal retention efficiency and simple operational procedures.

In developing an effective treatment practice, feasibility must be evaluated based on characteristics of the runoff loading and the physicochemical mechanisms that can be utilized given the site [5]. The development of an “in-situ” retention technique, applying current construction materials with low variability properties, could help to develop a prototype technical solution for the reduction of heavy metal pollution from highway runoff.

Experimental studies with different filter bed types have been developed at a laboratorial scale: iron-oxide-coated sand, natural zeolites and granular activated carbon [3].

The use of minerals in the constitution of reactive filter bed may enhance the feasibility of this technical effluent at a real scale installation. However, the behaviour of the immobilized heavy metals by desorption must be known, since by this way the retained heavy metals can return to the dissolved form. Therefore, the heavy metals desorption behaviour is relevant.

Laboratory experiments are necessary in order to evaluate infiltration data and sorption-desorption phenomena in a reactive-filtration pilot-scale installation.

A research program was developed to study those data and related processes and phenomena. Previous work has reported the heavy metals partitioning, the hydraulic behaviour, physicochemical control parameters and the efficiency of dissolved heavy metal removal involved in the dual-

media reactive filter, with a sand and kaolinite filter bed, over a one year experimental study [6].

This paper reports Zn, Cu and Pb mass retention in the filter media layers and the immobilized heavy metals behaviour by desorption procedures.

Experimental details

The experimental installation consists of two reservoirs and three equal diameter cylindrical columns of transparent polyethylene. The layout of the installation is depicted in Fig. 1.

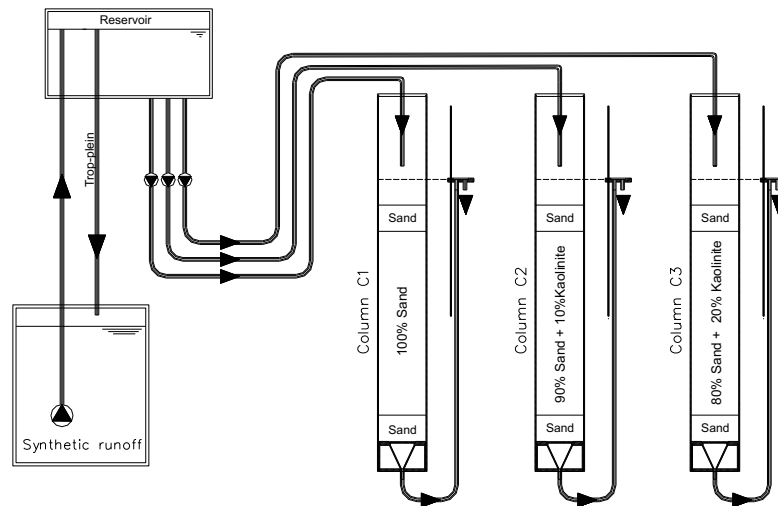


Fig. 1. Experimental layout.

The inner diameter of the columns is 172 mm. The bottom structure was constructed in order to allow a sliding movement at the end of the experiment.

Downstream head control was established by means of a weir in order to easily measure the head loss through the filter media.

In each column, different adsorptive filtration beds with 70 cm height were installed: a single sand medium in column C1; a dual media of 10% of kaolinite and 90% of sand in column C2; a dual media of 20% kaolinite and 80% sand in column C3. For mechanical protection, a 10 cm sand layer was applied to the top and to the bottom of the filter bed. The filter media composition was defined in previous pilot scale studies based on their hydraulic conductivity behaviour.

Each column was fed with a synthetic highway runoff by regulated flow pumps. This synthetic solution was obtained from the dilution of Zinc acetate dehydrate ($(\text{CH}_3\text{COO})_2 \text{Zn} \times 2\text{H}_2\text{O}$), Copper (II) acetate monohydrate ($(\text{OOCCH}_3)_2 \text{Cu} \times \text{H}_2\text{O}$) and Lead (II) acetate trihydrate ($(\text{CH}_3\text{COO})_2 \text{Pb} \times 3\text{H}_2\text{O}$). The maximum solubility values for these reagents, at 20°C, are: 430 g L⁻¹, 72 g L⁻¹, and 410 g L⁻¹, respectively.

Laboratory analyses were carried out according to Standard Methods [7]. Reagent grade chemical products and ultra-pure water were used. All glassware coming in contact with the samples was washed with Nitric Acid and rinsed with de-ionized water.

After the samples were collected, the physicochemical parameters (pH, conductivity and temperature) as well as the hydraulic head were measured immediately. The sample was then filtered on a 0.45 µm porosity membrane, and acidified to pH less than 2 with HNO₃. All the samples were then preserved at 4°C. Pb was analyzed by Graphite Furnace Atomic Absorption Spectrometry (GFAAS), while Zn was analyzed by Inductive Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Cu was analyzed by GFAAS or ICP. Detection limits were of 0.001 mg L⁻¹ (GFAAS) and 0.01 mg L⁻¹ (ICP-AES) for Cu, 0.002 mg L⁻¹ (GFAAS) for Pb and 0.01 mg L⁻¹ (ICP-AES) for Zn. Materials and experimental details are presented in [6].

Operational Procedures

Synthetic effluent with a constant flow rate of 10 L d⁻¹ was applied with different metal concentrations: 8.0 mg Zn L⁻¹, 1.0 mg Cu L⁻¹ and 0.4 mg Pb L⁻¹. After Zinc breakthrough (at 156th day), Cu and Pb concentrations were doubled. The hydraulic load was 0.43 m d⁻¹ (157 m year⁻¹).

The Total Organic Carbon (TOC) concentration related to the acetate, in the original concentration, was 6.72 mg C L⁻¹, with the following contribution: Zn-5.870 mg C L⁻¹ (87.38 %); Cu-0.7553 mg C L⁻¹ (11.24 %) and Pb-0.09266 mg C L⁻¹ (1.38%).

Zn was the most mobile metal with retention efficiency values decreasing to less than 50% in a 15, 70 and 110 day period, for columns C1, C2 and C3, respectively.

The evolution of dissolved heavy metal removal efficiencies in the three experimental columns with time can be found in [6].

For Cu and Pb, and after 260 days, the retention efficiencies obtained were above 70% and 40%, respectively, in Column C1, and above 90% in the sand and kaolinite media columns.

The different retention efficiencies of Zn observed in the three columns suggest a direct relation to the filter bed characteristics, since the breakthrough period in column C2, with a 10% kaolinite filter bed, was almost

half the breakthrough period in column C3, with a 20% kaolinite filter bed. Although other processes may occur, these results indicate that the Cation Exchange Capacity is relevant and therefore sorption processes are the major phenomena.

Desorption Procedures

At the end of the experiment, and for each column, the filtration media were separated in 6 layers and numbered from the bottom to the top. Representative samples of each layer were submitted to chemical desorption.

The desorption experiment was carried out in a 24 hour period, using a solution of: 2.5 mL of 0.1 M NaNO₃, 2.5 g air dried filter media and 247.5 mL deionised water.

For each layer, two desorption procedures were applied. The first resulting from a 24 hour mixing at 55 rpm of the effluent (labelled pH6), and the second with the same procedure but acidified at pH=2 with HNO₃, (labelled pH2). The pH evolution with time was monitored.

Although other methods are available, in this work the total metals retained in each layer will be evaluated by the values obtained by desorption at pH2.

The samples obtained after a 24 hour mixing were filtered in a 0.45 µm membrane, acidified with HNO₃ to pH less than 2 and kept at 4° C before the analytical analysis.

An electronic microscope observation was carried out in order to evaluate the particulate heavy metal retention in the filtration membrane.

Results for desorption at pH2 and pH6 for columns C1, C2 and C3, respectively, are presented in Tables 1, 2 and 3.

Retention efficiencies and desorption results obtained can be used for estimating the fraction of heavy metals that can be desorbed.

Table 1. Column C1: Zn, Cu and Pb concentrations in the desorption experiment.

Layer	Zn (mg/L)		Cu (mg/L)		Pb (mg/L)	
	pH2	pH6	pH2	pH6	pH2	pH6
C1-1	0.86	0.40	0.52	0.21	0.252	0.064
C1-2	0.65	0.49	0.58	0.36	0.199	0.087
C1-3	0.65	0.58	0.54	0.45	0.192	0.111
C1-4	0.68	0.63	0.64	0.62	0.199	0.184
C1-5	0.73	0.64	0.76	0.69	0.249	0.191
C1-6	0.61	0.60	1.28	1.26	0.287	0.291

Table 2. Column C2: Zn, Cu and Pb concentrations in the desorption experiment.

Layer	Zn (mg/L)		Cu (mg/L)		Pb (mg/L)	
	pH2	pH6	pH2	pH6	pH2	pH6

C2-1	1.15	0.62	0.39	0.091	0.327	0.063
C2-2	4.49	0.59	0.23	0.006	0.128	0.004
C2-3	4.47	0.59	0.32	0.008	0.189	0.004
C2-4	4.87	0.64	1.19	0.036	0.703	0.021
C2-5	5.87	0.69	5.06	0.051	1.37	0.058
C2-6	2.00	0.70	3.38	0.23	0.876	0.078

Table 3. Column C3: Zn, Cu and Pb concentrations in the desorption experiment.

Layer	Zn (mg/L)		Cu (mg/L)		Pb (mg/L)	
	pH2	pH6	pH2	pH6	pH2	pH6
C3-1	0.86	0.40	0.52	0.21	0.252	0.064
C3-2	0.65	0.49	0.58	0.36	0.1999	0.087
C3-3	0.65	0.58	0.54	0.45	0.192	0.111
C3-4	0.68	0.63	0.64	0.62	0.1999	0.184
C3-5	0.73	0.64	0.76	0.69	0.249	0.191
C3-6	0.61	0.60	1.28	1.26	0.287	0.291

Hereafter, the values obtained for Zn, Cu and Pb, in the three columns and at the different layers are compared and discussed.

Column C1

The desorption results obtained for column C1 with a sand filter bed demonstrated small variations of the results from pH2 and pH6. Zn values have small differences through the different layers, while the results obtained for Cu and Pb denote higher values at the bottom layer, but increasing as the layer depth decreases.

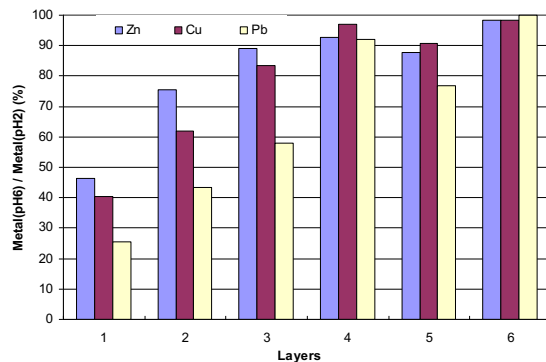


Fig. 2. Column C1: Metal Mass Ratio.

These results suggest that although heavy metals are retained in the sand layers, a very high percentage of these metals are release from the filter media at pH6, as presented in Fig. 2.

The relevance of each layer in the overall retention of Zn, Cu and Pb, at pH2 and pH6, for column C1 is depicted in Fig. 3.

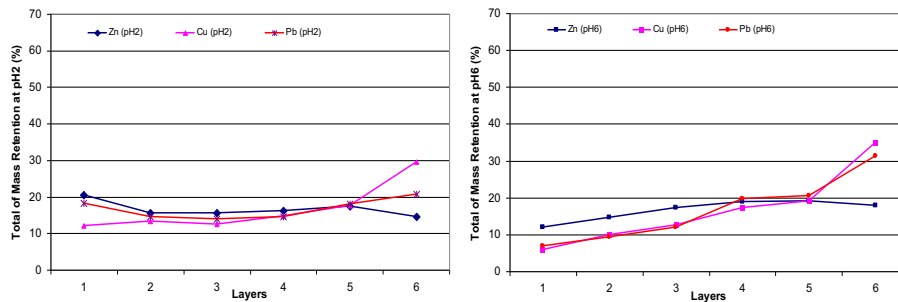


Fig. 3. Layer relevance in overall heavy metal retention at pH2 and pH6.

At pH2 all the reactive layers are equally relevant. At pH6 the retained heavy metals decrease for higher depths. High retention of Cu and Pb in the top layer suggests the occurrence of precipitation and particulate retention, favourable conditions in terms of groundwater protection.

Column C2

In this column, with the reactive layers with 5% of kaolinite and 95% of sand, the heavy metals retained were considerably higher than those in column C1. In the reactive layers heavy metals retention, at pH6, vary from 12% for Zn to less than 5% for Cu and Pb, when compared with the correspondent values at pH2. In the top sand layer, higher heavy metals retention values of Zn and Pb were obtained.

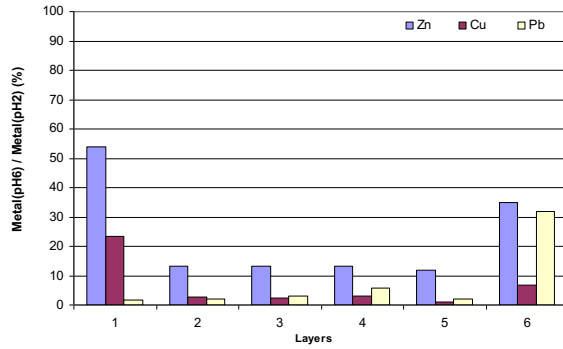


Fig. 4. Column C2: Metal Mass Ratio.

For Zn, the layer relevance in the overall retention is similar at pH2 and pH6, which is possibly due to the verified Zn breakthrough. For Cu and Pb, higher retention relevance is verified in the upper reactive layers as shown in Fig. 5.

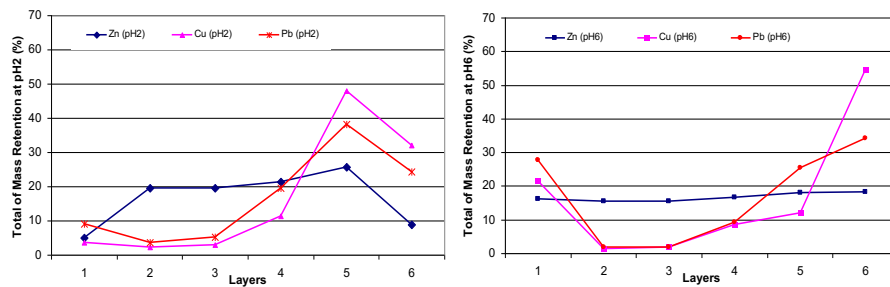


Fig. 5. Layer relevance in overall retention of Cu at pH2 and pH6.

Column C3

The results obtained in Column C3 are similar to those obtained in Column C2. The metals released at pH6 were slightly higher for Zn, than those verified in column C2, with about 15%, and almost the same values for Cu and Pb, near 5%.

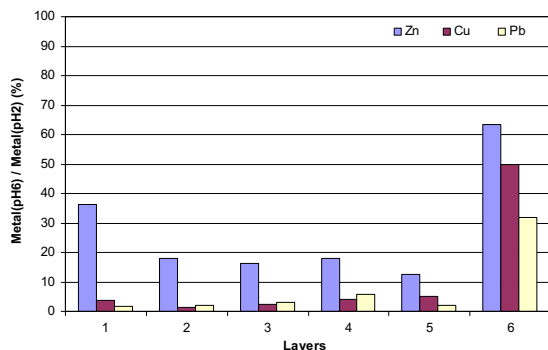


Fig. 6. Column C3: Metal Mass Ratio.

The top layer of the reactive filter demonstrates higher retention than the lower layers, possibly due to the absence of a breakthrough occurrence. Higher resistance to desorption of heavy metals present in the reactive layers is verified. Heavy metals released at pH6 are lower in the bottom layers, which is a favourable result when looking for groundwater protection.

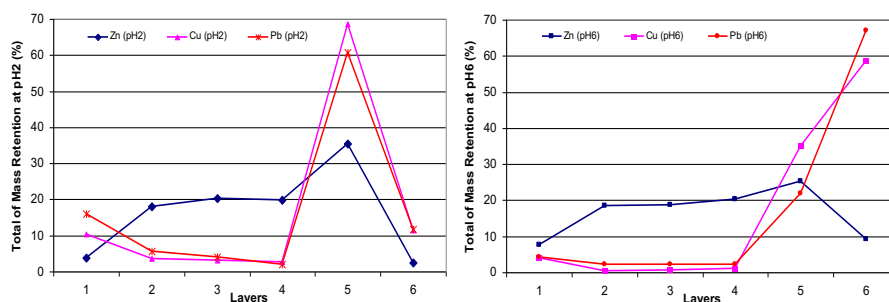


Fig. 7. Layer relevance in overall retention of Pb at pH2 and pH6.

Conclusion

Results obtained for chemical desorption allow evaluation of the heavy metals retention in each layer and their environmental availability at pH6.

In column C1, with a sand filter medium, a significant amount of retained metals is released at pH6.

In columns C2 and C3 with reactive filter media, high retention efficiencies were found, since the environmental availability results obtained were 12% - 18% for Zn and lower than 5% for the Cu and Pb.

After a one year experimental period, the retention efficiencies verified in column C1 for the dissolved Cu and Pb were 70% and 40%, respectively, and above 90% in the columns C2 and C3. This demonstrates the high longevity of filter media in these experimental conditions.

A direct link of reactive layers and a high retention efficiency of dissolved heavy metals can be established. Moreover a strong resistance to chemical desorption of previously retained heavy metals in those reactive layers was also found.

The results obtained in this research project encourage the development of innovative engineering solutions for retention of heavy metals in highway runoff, and thus contributing for surface and groundwater protection.

References

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