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Adsorption of multi-heavy metals onto water treatment residuals: sorption capacities and applications

Yi Wai Chiang ^{a,*}, Karel Ghyselbrecht ^b, Rafael M. Santos ^c, Johan A. Martens ^a, Rudy Swennen ^d, Valérie Cappuyns ^{d,e}, Boudewijn Meesschaert ^{a,b}

^a Department of Microbial and Molecular Systems, KU Leuven, Kasteelpark Arenberg 23, B-3001 Heverlee, Belgium

^b Faculty of Industrial Engineering Sciences and Technology, Katholieke Hogeschool Brugge-Oostende, Zeedijk 101, B-8400 Oostende, Belgium

^c Department of Chemical Engineering, KU Leuven, Willem de Croylaan 46, B-3001 Heverlee, Belgium

^d Department of Geology, KU Leuven, Celestijnenlaan 200E, B-3001 Heverlee, Belgium

^e Faculty of Economics and Management, Hogeschool-Universiteit Brussel, Warmoesberg 26, B-1000 Brussels, Belgium

*Corresponding author

Email addresses: yiwai.chiang@biw.kuleuven.be (Y.W. Chiang), boudewijn.meesschaert@biw.kuleuven.be (B. Meesschaert).

ABSTRACT

Inherently formed iron-based water treatment residuals (WTRs) were tested as alternative sorbents for multi-heavy metal removal from synthetic solutions, contaminated sediments, and surface waters. The WTRs were mainly composed of iron (hydr)oxides and had a high BET surface area (170.7 m²/g), due to the presence of micro- and mesopores. The sorption capacity of

WTRs for As(V), Cd²⁺, Pb²⁺ and Zn²⁺ from synthetic solutions surpassed that of a commercially available goethite by 100-400% for single contaminant tests, and by 240% for total sorption in multi contaminant tests. The maximum sorption capacity of WTRs towards As(V), Pb²⁺ and Zn²⁺ was estimated by Langmuir equation fitting to range between 0.5 to 0.6 mmol/g, and their maximum sorption capacity for Cd was 0.19 mmol/g. WTRs performed significantly better than goethite for adsorption of cationic contaminants (Cd, Co, Ni, Pb, Zn) in the sediment tests, independent of the dosage or sediment sample. At the highest WTRs dosage (250 mg/g), concentrations of the cationic contaminants decreased by at least 80%, while approximately 40% removal was obtained with 50 mg/g dosage. Sorbent mixtures composed of WTRs with goethite, and with a clinoptilolite natural zeolite were used to reduce As leaching. The sorbent mixtures delivered the desired performance, with the natural zeolite performing better than the goethite as an amendment to WTRs. In addition, up to 90% removal of surface water contaminants was achieved with both fresh WTRs and the WTRs regenerated using 0.01 M EDTA.

Keywords: Water treatment residuals; Adsorption; Heavy metals; Sediment; Surface water; Remediation; Iron (hydr)oxides

1. Introduction

Growing awareness of the risks posed by heavy metals in the environment has recently been driving the search for sustainable technologies for the treatment of contaminated sites (e.g. Brown et al. [1]). Soils, groundwater, sediments and rivers at many locations in Europe have been exposed to intense pollution from historical mining and metallurgical activities. Whilst the

industry has improved practices over time, the accumulated pollutants persist in the affected areas, posing local (at the source or sink) and peripheral (due to contaminant mobility) environmental risks [2-4]. The redistribution of heavy metals can adversely affect water resources and endanger the health of surrounding ecosystems and human populations; as such, cost effective and ecological remediation of these sites is essential. The application of sorbents with high affinity for heavy metals, and in particular those derived from low cost waste materials, is a promising and attractive remediation route [5].

Water treatment residuals (WTRs) are waste products generated by certain drinking-water treatment processes, for which no sustainable application has been found to date, resulting in their disposal predominantly by landfilling [6]. These materials are primarily composed of amorphous masses of iron and aluminum hydroxides (respectively producing Fe-WTRs and Al-WTRs); they also contain sediment and humic substances removed from the raw water and traces of coagulating agents used in the water treatment process [7]. WTRs have a large surface area and are highly reactive, which gives them several potential applications as sorbents [8]. A distinction can also be made between the WTRs formed by addition of alum and ferric chloride as coagulants in the water treatment process, which make up the vast majority of WTRs studies to date; and those formed inherently by oxidation of iron and manganese contained in groundwater during water treatment [9, 10].

Researches on the valorization of the coagulated WTRs as sorbent materials have been focused primarily on the adsorption of phosphate [11-14] and arsenic [15-19]. Makris et al. [20] explained that the sorption capacity of these WTRs with respect to phosphate is related to their microporosity rather than due to surface precipitation, based on the even distribution of P within WTRs particles. Arsenic sorption mechanism has been attributed to the inner-sphere

complexation between As and surface hydroxyls in the WTRs [21]. Efforts to assess the use of the coagulated Al-WTRs for heavy metal adsorption have been less concerted and include investigations on B [22], Cr [23], Hg [24], Se [25] and Pb [23, 26]. Hardy et al. [27] studied the sorption of Cu, Pb and Zn onto both coagulated Al- and Fe-based WTRs from simulated acid mine drainage.

Heavy metal adsorption by inherently formed Fe-WTRs has been seldom studied. Nielsen et al. [10] investigated the addition of these types of WTRs as amendments to soils contaminated with oxyanionic arsenic and chromium; leaching was reduced by 91% for Cr and 98% for As. The mineral composition of these WTRs, consisting mainly of ferrihydrite [10], could also be suitable for adsorption of cationic heavy metals. Qian et al. [28] tested the adsorption of a range of metals (Cd, Cu, Ni, Pb and Zn) onto ferrihydrite/apatite composite additives and attributed it to the formation of inner-sphere sorption complexes or co-precipitation.

In the present work, inherently formed Fe-WTRs are utilized as sorbents for remediation of multi heavy metal contaminated sediments and surface waters originating from fluvial systems exposed to historical pollution from non-ferrous metallurgical activities in Belgium. Contamination levels and the mobility of the contaminants are determined in sediment and surface water samples. The sorption capacity of WTRs towards individual heavy metal and metalloid contaminants is investigated by determining sorption isotherms at fixed pH. Batch and column adsorption tests are conducted to determine sediment and surface water treatment performance, required sorbent dosage, and assess their potential as a sorbent amendment or filter material for field application. The performance of WTRs is compared against goethite, a sorbent material with a similar chemical composition as WTRs (i.e. iron (hydr)oxides) that is widely

applied in industry). Sorbent mixtures consisting of WTRs, goethite and clinoptilolite natural zeolite are also tested to provide optimized remediation performance.

2. Methodology

2.1. Materials sampling and characterization

Water treatment residuals (WTRs) were collected from an integrated drinking water/wastewater treatment plant in West Flanders, Belgium [9]. The WTRs are produced as a result of cascade aeration of groundwater seepage captured from an unconfined dune aquifer that is recharged with treated wastewater, the primary purpose of which is reduction in the iron and manganese contents of the water. Precipitation of iron-rich colloids is aided by dosage of a minor quantity of organic flocculent (PDADMAC). The WTRs are collected in a sand filter and back flushed to a storage bin prior to disposal. Freshly-generated WTRs were collected directly from the discharge of the water treatment plant. Prior to characterization and utilization as a sorbent, these samples were oven dried at 105 °C for 24 hours. Goethite (Fe(OH)O) (Sigma Aldrich, Belgium) and a natural zeolite (ZEOCEM, Slovakia), predominantly consisting of clinoptilolite, were also acquired for comparison of performance as single sorbents and in sorbent mixtures.

Sediment samples used in this study originate from areas affected by historical pollution due to metallurgical activities in north-eastern Belgium [29], which have contaminated soil, groundwater and sediments in small brooks that discharge into larger fluvial systems. In the study area, chemical precipitates derived from groundwater-associated Fe²⁺ seeping into the overlying surface water significantly contribute to the composition, concentration, and fluxes of

suspended sediments [30]. These Fe^{2+} -enriched groundwaters originate from subsurface water percolation through glauconite bearing Tertiary sands. Three sampling points (A, B, C) were chosen at locations that were exposed to seepage of contaminated groundwater. Sediment samples were collected from the upper 10 cm of the submersed river bed, and surface water samples were also collected from the river. Sediment samples were stored in water-filled air-tight sealed plastic containers and refrigerated to minimize physicochemical and biologically driven changes. Prior to use, sediments were filtered through a 3.15 mm sieve to remove organic and inorganic debris. For collection of porewater (mechanically entrained water), a portion of the sediments was centrifuged and filtered immediately after the sampling. Surface water was collected immediately downstream from the sediment collection points.

Mineralogical analysis was conducted by X-ray Diffraction (XRD) (Philips PW1830), equipped with a graphite monochromator and a gas proportional detector, using $\text{Cu K}\alpha$ radiation at 30 mA and 45 kV, step size of $0.02^\circ 2\theta$ and counting time 2 s per step, over 5 to $70^\circ 2\theta$ range; mineral identification was done in DiffracPlus EVA (Bruker) software. BET nitrogen adsorption–desorption isotherms were performed on a Micromeritics TriStar 3000 apparatus. Particle size analysis was performed by Laser Diffraction (LD) (Malvern Mastersizer S). Chemical composition of solid samples was determined by X-ray Fluorescence (XRF, Panalytical PW2400). Morphological assessment was performed by imaging with a Scanning Electron Microscope (SEM) (Philips XL30 FEG). Aqueous samples were analyzed for heavy metal and metalloid concentrations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Thermo Electron X Series), with a detection limit (DL) of $1 \mu\text{g/L}$, and Atomic Absorption Spectroscopy (AAS) (Varian), with a detection limit of 1 mg/L .

2.2. Leaching experimental methodology

Batch leaching tests were performed on WTRs and sediment samples to determine the heavy metal and metalloid leaching behavior in aqueous solution at their natural pH values (without sorbent addition). The tests were carried out according to standard procedure DIN 38414 [31], in sealed plastic containers over 24 hours with a liquid to solid ratio (L/S) of ten (10 g solids in 100 ml dilute salt solution (0.01 M CaCl₂)), agitated at 160 rpm on a vibration table (Gerhardt Laboshake). The solution was filtered using a 0.45 µm membrane filter prior to dilution and acidification (2% nitric acid) for ICP-MS and AAS measurements (in triplicate). The following elements were analyzed: As, Cd, Co, Ni and Pb by ICP-MS, and Zn by AAS. WTRs leachate (without acidification) was also analyzed by Ion Chromatography (IC) (DIONEX series 4500i) for anions (Cl⁻, NO₃⁻, PO₄³⁻ and SO₄²⁻).

2.3. Sorption isotherms experimental methodology

Experiments were carried out with sorbents in aqueous solutions of varying concentrations (5, 20 and 100 mg/L) of each heavy metals of interest at pH = 5.5, to determine the equilibrium heavy metal concentrations (adsorbed and in solution) and the adsorption isotherms. A fixed pH close to the pH of the sediment and porewater samples was chosen since heavy metal solubility is significantly influenced by pH and since the sorbents are expected to have pH buffering (or acid neutralization) capacity, which could significantly alter (increase) the equilibrium pH. Standard analysis solutions of each heavy metal (As(V), Cd²⁺, Pb²⁺ and Zn²⁺), based in nitric acid, were used to make up the test solutions. Sorbent dosage of 1 g/L was used.

Solutions were shaken at 160 rpm over 48 hours, filtered (0.45 μm membrane filter), and analyzed by ICP-MS (for As, Cd and Pb) and AAS (for Zn) in triplicates. The pH of the test solutions was maintained by adjustment with 5M HNO_3 . To assess competition for adsorption sites, multi-element solutions were also prepared and tested; solutions containing equal amounts of the four heavy metals were prepared (ranging from 5 to 100 mg/L individually) and mixed with 4 g/L sorbent over 48 hours.

2.4. Sediment treatment experimental design

Batch sorption tests were performed with collected sediments to assess the performance of WTRs as an amendment to the sediment for immobilization of heavy metal and metalloid contaminants. Sorption tests consisted in mixing porewater solution with untreated sediment at a fixed L/S ratio of five (20 g sediment in 100 ml solution), together with varying amounts of single sorbents (5, 10 and 50 g/L). Sorbent to sediment dosages were accordingly 25, 50 and 250 mg/g. The mixtures were shaken for seven days. The pH was measured at completion to assess the sorbent pH-buffering effect. Aqueous filtered (0.45 μm membrane filter) samples from the sorption tests were tested in triplicates by ICP-MS and AAS to determine equilibrium contaminant concentrations in solution. These results were used to calculate percentage removal sorption performance by comparison with original porewater values. Sorbent mixtures were also composed with the three sorbent materials studied, in order to enhance contaminant stabilization performance. The experimental design was analogous to single sorbent tests. Mixture composition and dosage are detailed in section 3.3.2.

2.5. Surface water treatment experimental design

Column sorption tests were performed with collected surface water to assess the performance of WTRs as a filtration-type adsorbent for heavy metal and metalloid contaminants. A TitroCol7343 apparatus (Cornelius Consult, Germany) was used as described in Cappuyns and Swennen [32]. Test conditions were: upflow percolation with a flow rate of 6.25 ml/min, dry sorbent thickness of 1.5 cm (17 g), residence time of five minutes, and three liters of surface water were passed through the column. Samples of the water that passed through the column were collected every 375 ml percolated, and their pH was measured. Aqueous filtered (0.45 μm membrane) samples from the column tests were tested in triplicates by ICP-MS and AAS to determine equilibrium contaminant concentrations in solution. These results were used to calculate percentage removal sorption performance by comparison with original contaminated surface water values. The spent sorbent was regenerated by mixing in 500 ml of 0.01 M EDTA (ethylenediaminetetraacetic acid) solution for six days and re-tested to assess its performance.

3. Results and Discussion

3.1. Characterization results

The elemental composition of all sorbent and sediment materials is reported in Table 1. All the materials are primarily iron based. The goethite is inferred to contain 64 wt% $\text{FeO}(\text{OH})$; modest quantities of silica (SiO_2) and alumina (Al_2O_3) are present. It also contains trace concentrations of four heavy metals, namely Co, Ni, Pb and Zn, ranging from 200 to

1,300 mg/kg, likely adsorbed contamination acquired during industrial manufacturing. The high iron content of the WTRs material is in agreement with its expected ferrihydrite (a metastable ferric hydroxide) content [10]. Assuming all Fe (61%) is present as ferrihydrite, the proportion of this mineral in the material can be calculated to be approximately 87 wt%. Coagulant based Fe-WTRs have reportedly lower Fe content ranging from 17 to 53% [11, 17, 18]. The inherently formed WTRs also contain moderate quantities of Ca, Si and P, as well as two heavy metals: As (1,200 mg/kg) and Zn (300 mg/kg).

The three sediment samples collected contain varying amounts of As, Cd, Co, Ni, Pb and Zn. Zinc is the principal contaminant in sediments A and B, at 4.3 and 2.8 wt%, respectively. Sediments A and B also contain large amounts of As (9,000 and 1,100 mg/kg) and Cd (21,000 and 1,400 mg/kg, respectively). Sediment C contains significant quantities of Zn (4,700 mg/kg) and As (6,000 mg/kg). Lead is present in all three sediments, at levels of 1,200, 300 and 200 mg/kg for samples A, B and C, respectively. Cobalt and nickel are present only in sediment A at amounts below the XRF detection limit (defined as approximately below 200 mg/kg). The main matrix element of all sediment samples is Fe; however sediments B and C contain significantly more Fe than sediment A. This likely indicates varying levels of Fe-(hydr)oxides, clay minerals and organic matter between the samples, whose presence in sediments have been correlated with heavy metal content [33]. These differences may account for sediment A containing higher quantities of all six heavy metals than the other two sediments.

The crystallographic composition of the sorbent and sediment materials inferred from the XRD analysis is presented in Fig. 1. The goethite material was confirmed to contain goethite (FeO(OH)) as well as quartz (SiO₂), which is also consistent with its chemical composition (Table 1). The fresh WTRs material was found to be highly amorphous, displaying only a small

peak for quartz. The amorphous nature of WTRs is also visible by inspection of SEM images (Fig. 2). All sediments clearly contain quartz, but they also exhibit the characteristic poorly crystalline scattering bands that can be attributed to hydrous ferric oxides such as ferrihydrite [34].

Sorbent and sediment materials show bimodal particle size distributions (Fig. SC-1 in Supplementary Content). WTRs and sediment samples have a main peak ranging from 10 to 200 μm , and a secondary peak below 1 μm . Their average particle size values are similar, reported as volume mean diameter ($D(v,0.5)$), ranging from 30 to 43 μm , volume moment mean diameter ($D[4,3]$), ranging from 39 to 66 μm , and surface area moment mean diameter ($D[3,2]$), ranging from 2.3 to 3.3 μm . Goethite consists mainly of smaller particles, with its main peak at 0.2 to 0.6 μm , and a secondary peak at 10 to 200 μm . The resulting average particle sizes are much smaller than the other materials, ranging from 0.7 μm for $D[3,2]$ to 6.3 μm for the $D[4,3]$. The $D[3,2]$ values are indicative of the active surface area of the materials, therefore based on these results it would seem appropriate to consider goethite as having better sorption potential than WTRs.

The specific surface areas of the materials, however, contradict the LD results. Fresh WTRs were found to possess significantly greater surface area than the goethite, 170.7 m^2/g compared to 28.5 m^2/g for the latter. Coagulant based Fe-WTRs have reportedly lower surface area, 27.5 m^2/g [19] and 76.8 m^2/g [14], while Neilsen et al. [10] reported comparable surface areas of 181 and 231 m^2/g for two inherently formed WTRs. The nitrogen adsorption/desorption isotherms (Fig. SC-2 in Supplementary Content) infer that fresh WTRs contains significantly more micropores (due to high adsorption capacity of low relative pressure (i.e. $P/P_0 < 0.01$)), mesopores (due to the greater inflection in the relative pressure range $0.1 < P/P_0 < 0.4$), and

macropores (due to the larger hysteresis loop at the relative pressure range $P/P_0 > 0.4$) than the goethite sample. These features are not detectable by LD. Hence, the potential for WTRs to act as a sorbent is strengthened by the nitrogen adsorption results.

The utilization of materials in the environment requires that these materials meet certain environmental regulations. Given WTRs are waste residues from an industrial process, it is of particular importance to assess its leaching behavior towards regulated metals and anions. The leaching results of fresh WTRs material are given in Table 2. All values conform to the Belgian regulations on use of non-structured building materials in the environment [31]. Anion analysis showed that, although the present sample contained a significant amount of P (2.5 wt %) in the solid phase, no phosphate leaching was detected. The WTRs material was also found to be slightly alkaline (pH = 8.1), while coagulant based Fe-WTRs are reportedly slightly acidic in nature (e.g. pH = 5.4 [17], 6.0 [11]). It should be noted that upon mixing the WTRs with sediments or surface waters, the pH can shift, potentially causing solubilization of certain components of WTRs, arsenic (present at 0.12 wt%) being of particular concern. This will be elucidated in the sorbent test results (section 3.3).

Table 2 also presents batch leaching values of the sediment samples. Comparing to the regulatory limits for the non-structured building materials [31], it is clear that the sediments pose serious risk to the environment. These sediment samples would be classified as Class 4 (considerable risk for the environment) according to the evaluation system for alluvial soils proposed by Cappuyns and Swennen [4]. Zinc concentrations exceed the limits for all sediments, cadmium concentrations are problematic for two of the sediments, and cobalt is exceeded in sediment A. Arsenic and lead leaching values are low, despite their significant presence in the sediment solids. This indicates that these elements have either good affinity for sorption sites on

the sediments, or that they are present in the sediment in less soluble species than the other contaminants, or that at the natural pH of the sediments solubilization of these elements is less favorable than for the other elements. Nickel leaching is not high, in accordance with low nickel content of the solids. The contaminant mobility observed confirms that the sediments are capable of resupplying heavy metals to solution upon dilution, which in a fluvial system is of particular concern as these sediments will be re-suspended by incoming groundwater, surface water and rainfall, and will be carried downstream to larger and less contaminated water bodies. Hence their amendment with sorbents to immobilize the contaminants is a recommended remediation option.

Table 3 presents analytical results of the porewater of the three sediment samples and the surface water sample. In accordance with the sediment leaching tests, the primary contaminant in the porewaters and surface water is zinc, with concentrations ranging from 6.2 to 778 mg/L. Cadmium values are also very significant, exceeding 3.2 mg/L in two cases. The high concentrations for these two heavy metals are in agreement with their large quantities in the solid phase. Arsenic values in the porewater are rather low compared to the rather high solid phase values. This is likely related to the pH values of the porewater and the leaching solution, which range from 3.9 to 5.9, and the oxidation state of the arsenic. At this pH range, As(III) is expected to be predominantly insoluble, in contrast with As(V) and the other cationic heavy metals detected [35]. Nickel and cobalt were essentially undetectable in the solid phase by XRF analysis; however they are present in significant quantities in the liquid phase, both in porewaters and surface water. This suggests that these metals have low affinity for the sediment materials, and their presence in solution is predominantly controlled by pH. Under pH 6.5, and in the absence of adsorption sites or co-precipitation mechanisms, these metals are theoretically highly

soluble [35]. In the case of lead, sediments A and B and the surface water have pH values at which Pb is not expected to be soluble; in the case of sediment C, though the pH was comparatively low, Pb concentration was also rather low. It is possible that lead has greater affinity for the sediment materials than the other more mobile heavy metals, or that it is present as a less soluble species.

3.2. Sorption isotherms

The sorption affinity of the WTRs and the goethite to the four main sediment contaminants (As, Cd, Pb and Zn) was first assessed using synthetic solutions of the respective heavy metals to generate sorption isotherm data. The isotherms were fitted using the well established Langmuir equation (1), where c is the solute concentration in solution (mmol/L); D is the solute uptake onto the sorbent (mmol/g); D_m is the empirically derived maximum sorption capacity (mmol/g); and k is an empirically derived constant (L/mmol). All experiments were performed at a constant pH of 5.5, which ensures the heavy metals in question are fully soluble as verified by Visual MINTEQ modeling [35], and thus their removal from solution can be solely attributed to adsorption rather than precipitation mechanism.

$$D = \frac{D_m kc}{1 + kc} \quad (1)$$

The constructed adsorption isotherms for goethite and fresh WTRs are presented in Fig. 3. The respective Langmuir equation coefficients, obtained by least squares fitting are provided in Table 4. Sorption capacities (D_m) of WTRs for all four heavy metals are significantly higher (100–

400%) than those for goethite, both in the single and the multiple element cases. Sorption capacity of WTRs for As(V), Pb²⁺ and Zn²⁺ are similar, at approximately 0.5-0.6 mmol/g, in comparison, goethite capacity for these elements ranges from 0.12 to 0.25 mmol/g. Both sorbents have lower sorption capacity for Cd²⁺, yet WTRs reaches 0.19 mmol/g compared to 0.06 mmol/g for goethite.

In the case of multiple element adsorption, sorption capacities for Cd²⁺ and Zn²⁺ decrease by 40% to 75%, indicating competition for adsorption sites, while for As(V) and Pb²⁺ remain relatively constant ($\pm 20\%$), indicating these elements have preferential affinity for adsorption sites, are immobilized by different mechanisms, and/or are less stable in soluble state at pH 5.5. The total sorption capacity of WTRs in the case of multiple element adsorption is 240% higher than for goethite.

The sorption similarities between goethite and WTRs are in agreement with their similar chemical and mineralogical compositions; the stronger capacities of WTRs can be attributed to its enhanced specific surface area. These results prove WTRs' potential as remediation sorbents under laboratory conditions. Adsorption isotherms are useful for gaining insight into adsorption affinity and mechanisms, and the results are used to estimate sorbent dosage in remediation applications. However, these tests were performed under controlled conditions, with synthetically pure solutions, and in a two-phase (sorbent-solution) system; therefore their performance in real remediation application cannot be accurately predicted. To this purpose, in sections 3.3 and 3.4 the sorbents are tested with real contaminated sediments and surface water to assess their true treatment performance.

3.3. Sediment treatment

3.3.1. Single sorbent sediment treatment

Results for batch sorption tests of goethite and WTRs mixed with each sediment sample at different dosages are shown in Fig. 4; the values are compared to porewater concentrations (i.e. 0 mg/g sorbent dosage). The final equilibrium pH of the solutions is also presented in Fig. 4.

WTRs exceed the performance of goethite for Cd, Co, Ni, Pb and Zn almost invariably, irrespective of sorbent dosage or sediment type. Moreover the performance of WTRs steadily improves with increasing sorbent dosage for most cases, while goethite performance is often stagnant with increasing dosage. At the highest dosage of 250 mg/g, WTRs achieves an average removal of more than 80% for Cd, Ni, Pb and Zn. At one fifth of this dosage, 50 mg/g, its application results in an average removal of 40%. Goethite only proves efficient for lead removal in all three sediments, for arsenic in the case of sediment A and B, and for nickel in the case of sediment B. As such, the two most mobile contaminants, cadmium and zinc, are not efficiently remediated by goethite. It should be noted that although cadmium mobility was increased with WTRs addition to sediment B, the concentrations of cadmium for this sample were much lower than for the other two sediments. Furthermore, the use of goethite resulted in increased cadmium mobility for the other two sediments as well, in contrast with satisfactory removal by WTRs.

The efficacious performance of WTRs is in agreement with its superior sorption capacities determined by isotherm testing. Moreover, the equilibrium pH (Fig. 4) suggest that the acid neutralization capacity (i.e. pH buffering) positively contributes to the performance of WTRs. Goethite addition has essentially no effect on solution pH, with values very similar to those measured from sediment porewaters and natural pH sediment leaching tests. Addition of

WTRs to the sediments, on the other hand, increases the equilibrium pH by up to one pH unit compared to porewater values. This shift in pH, which was found to be proportional to WTRs dosage, can result in lower solubility of the cationic contaminants due to changes in chemical speciation and affinity for adsorption sites [35]. The pH values reached, however, are in theory (according to geochemical modeling) not sufficient to induce direct contaminant precipitation, therefore adsorption mechanisms should be attributed to the performance achieved.

Although highly efficient towards the cationic contaminants, WTRs performance for arsenic removal was less satisfactory. At the highest sorbent dosage a consistent increase in arsenic concentrations was found in all sediments; at lower dosages this did not occur. The source of arsenic could be from the sediment itself, due to pH shift inducing As(III) mobility [35], however it is also possible that the WTRs itself releases arsenic into solution. In either case, for application of WTRs in a remediation application, it appears ideal to amend WTRs with an arsenic-specific sorbent to contain this problem. Goethite itself is a potential candidate as it showed satisfactory arsenic removal performance with sediments A and B (sediment C porewater did not contain arsenic). Another candidate is natural zeolite of the clinoptilolite variety [35].

3.3.2. Sorbent mixture sediment treatment

To improve the single sorbent tests results, sorbent mixtures consisting of fresh WTRs with goethite (M1) and with natural zeolite (M2) were prepared. Characterization, isotherms, and single sorbent performance of the natural zeolite material have been previously reported in Chiang et al. [35]. The sorbent mixture dosages ($Q_{mixture}$, expressed in units of grams sorbent

mixture per 100 ml solution per 10 g sediment) and compositions (i.e. individual sorbent dosages ($Q_{sorbent}$)) were determined based on an in-house developed methodology [5], which is illustrated by equation (2) and is summarized as follows:

A desired remediation target, expressed as a percentage reduction in sediment porewater contaminant concentration (φ) is chosen as 90%.

The sorption capacity of each sorbent (i) for each contaminant (j) at the final equilibrium concentration of the contaminant applying the desired removal percentage ($D_{j,eq}$) is calculated using the obtained Langmuir isotherm equations.

The total amount of each contaminant that must be adsorbed is estimated as the sum of their sediment porewater concentration ($c_{j,pw}$) and their leaching concentration at pH 4 ($c_{j,pH4}$) (Table SC-1 in Supplementary Content), multiplied by a scaling factor (λ), which here is equal to 0.1 (to reflect the 100 ml volume of solution in batch sorption tests).

A percentage adsorption contribution of each sorbent to the required total contaminant adsorption amount (η_i) is specified (details given in Chiang et al. [5]); here goethite and natural zeolite contributions are attributed a value of 28% and WTRs contribution is attributed a value of 72% (these values are proportional to the superior overall performance of WTRs determined by single sorbent testing).

$$Q_{mixture} = \sum_{i=1}^s Q_{sorbent,i} = \sum_{i=1}^s \left\{ \eta_i \cdot \sum_{j=1}^e \left[\frac{\varphi \cdot (c_{j,pH4} + c_{j,pw}) \cdot \lambda}{D_{j,eq}} \right] \right\} \quad (2)$$

Results of batch sorption tests conducted using the sorbent dosages and compositions given in Table 5 are displayed in Fig. 5. Zinc removal targets were achieved with both sorbent

mixtures for all three sediments. Mixture M2 was more successful for lead removal, and mixture M1 achieved slightly better results for cadmium. As had been the case with single sorbents, cadmium was also slightly mobilized from sediment B, but the final concentrations are again rather small ($\leq 5 \mu\text{g/L}$). There was an improvement with respect to arsenic removal. In three of the six test cases there was reduction in arsenic concentration in solution, two of these using mixture M2 (i.e. with natural zeolite). Of the other three test cases, only one exceeded $10 \mu\text{g/L}$ As: mixture M1 with sediment A, yielding a final value of $31 \mu\text{g/L}$ As. Therefore natural zeolite is concluded to be the most beneficial amendment to WTRs sorbent for heavy metal immobilization in sediments. Furthermore the sorbent mixture concept, and the sorbent dosages and compositions determined by the aforementioned methodology, are shown to be successful for the development of sediment remediation solutions.

3.4. Surface water treatment

Column sorption tests were conducted with fresh WTRs to gain insight on sorption kinetics, contaminant removal extent, and sorbent exhaustion towards surface water treatment. The concentration of four contaminants (Cd, Co, Ni, and Zn) over time is shown in Fig. 6a, together with the pH of the percolate. Percent removal of cadmium is most extensive throughout the test, followed by zinc, cobalt and nickel. It should be noted that in terms of mass quantities, zinc removal is by far the highest. Arsenic and lead concentrations were consistently below detection limits, indicating no detrimental effect of the use of WTRs with respect to As and Pb. The sorption kinetics are essentially identical for the four heavy metals tracked; up to the third sampling the concentrations of the contaminants steadily decrease, followed by an immediate

increase and finally leveling off to constant removal values (between 25% to 75%). This trend indicates that the rate of adsorption at the beginning is faster than the rate of solution diffusion through the sorbent bed, thus the concentrations in the effluent gradually decreases. Once the rate of adsorption drops, the concentration in the effluent solution increases. After percolation of 2200 ml surface water, an equilibrium level is reached, indicating that the sorbent is saturated. However as can be seen (Fig. 6), the equilibrium concentrations of the contaminants in the effluent indicate continuous removal from the surface water. These constant removal values may be attributed to the pH of the solution, which is buffered by the sorbent throughout the test to approximately 7.2, and thus is able to induce partial precipitation of the contaminants even though sorption sites become saturated. Eventually, after significantly greater percolation volumes, it can be expected that the acid neutralization capacity of the sorbent should decrease and removal values should fall to near zero.

One of the potential limitations of the use of WTRs is their availability/accessibility. For remediation projects that require continuous supply and/or large quantities of fresh WTRs applications, the local WTRs supply could be easily out-strip [7]. A solution to this limitation, coupled with application of the material as a filter sorbent (as described in this section) rather than as an in-situ sediment amendment (as applied in section 3.3), would be the regeneration of the sorbent by means of, for instance, chemical treatment. Zhou and Haynes [23] used 0.1 N HNO_3 solution to desorb Pb(II) and Cr(III) from spent Al-WTRs, and found that satisfactory performance of the sorbent remained for up to eight successive sorption/desorption cycles. In this study EDTA was chosen as an extractant as it has shown great affinity for binding cationic heavy metals by chelation, including Cd, Ni, Pb and Zn [4, 36, 37]. Fig. 6b presents the sorption performance of the regenerated WTRs for surface water treatment. Compared to the fresh WTRs,

the regenerated WTRs performed equally well for Zn and Cd in terms of peak performance, but it remained at that performance level for nearly the entire length of the test, whereas fresh WTRs performance declined over time (and volume of percolated water). Cobalt and nickel removal performance was poorer during the first 1 L treated water compared to fresh WTRs, but it also remained nearly constant during the entire test. The slight improvement in the overall performance of the regenerated WTRs may be due to the liberation of additional sorption sites by the EDTA that had been occupied in the original material, and/or due to sorption activity of adsorbed EDTA on the regenerated WTRs.

These results are encouraging for the application of WTRs at large scale as their regenerability overcomes possible supply shortage. Further optimization of this remediation methodology, by varying sorbent dosages, flow velocities and residence times, may lead to better results, such as the prolongation of the sorption controlled stage and enhanced and more leveled removal performance. Still, the proof of concept for this remediation approach utilizing WTRs is here confirmed.

4. Conclusions

Inherently formed iron-based water treatment residuals (WTRs) were utilized for the remediation of sediments and surface water originating from heavy metal contaminated brooks in the Campine region of Belgium. The sorption and remediation performances of WTRs were compared to goethite. It was found that WTRs possess significantly higher specific surface area than goethite ($170.7 \text{ m}^2/\text{g}$ compared to $28.5 \text{ m}^2/\text{g}$, respectively), which contributes to its better

heavy metal sorption performance towards single contaminants (100-400% higher capacities) and multiple contaminants (240% higher total sorption capacity) measured from isotherm tests.

During batch sorption tests with contaminated sediments, WTRs performed on average significantly better than goethite for adsorption of cationic contaminants (Cd, Co, Ni, Pb, Zn). Arsenic leaching, however, was proportional to WTRs dosage, indicating mobility of arsenic present in the WTRs. To overcome this problem, sorbent mixtures composed of WTRs with goethite, and with clinoptilolite natural zeolite were tested. Natural zeolite performance was found to be better than goethite as an amendment to WTRs; the optimized sorbent mixture delivered the desired performance towards stabilization of all sediment contaminants. This strategy ensures the applicability of the WTRs in the field as inexpensive alternatives to commercial sorbents.

The WTRs were also used as a sorbent filter material to treat contaminated surface water. Column sorption tests indicated this approach to be feasible, with fresh WTRs achieving up to 90% removal of surface water contaminants. Regeneration of the sorbent material also proved possible using EDTA; performance of the regenerated sorbent was similar to that of the fresh sorbent. This approach allows utilization of WTRs in large scale, continuous and/or remote applications, where sorbent supply could be a potential barrier for the use of these materials. It also reduces the risks of applying waste materials in the open environment by eliminating the need for monitoring their fate and possible long term effects on the environment.

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Fig. 1. Crystallographic composition of (a) goethite and fresh WTRs, and (b) sediments, determined by X-ray Diffraction (XRD).

Fig. 2. Morphology of WTRs acquired by Scanning Electron Microscopy (SEM): a. 1000x magnification, b. 5000x magnification.

Fig. 3. Single element and multi-element adsorption isotherms of fresh WTRs and goethite for As(V), Cd²⁺, Pb²⁺, Zn²⁺ at pH 5.5.

Fig. 4. Batch sorption tests with goethite and WTRs: solution equilibrium concentrations of As, Cd, Co, Ni, Pb and Zn, and pH as a function of sorbent dosage (25 to 250 mg/g) for sediments A (a), B (b), C (c) and d. When interpreting and comparing data, note different scales of logarithmic y-axes.

Fig. 5. Batch sorption tests with sorbent mixtures M1 and M2: porewater (pw) and solution equilibrium concentrations of As, Cd, Pb and Zn for sediments A, B and C. When interpreting and comparing data, note different scales of logarithmic y-axes.

Fig. 6. Surface water treatment by WTRs: column leachate concentrations of Cd, Co, Ni, and Zn over time (volume percolated) for fresh (a) and regenerated (b) WTRs.

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Table 1

Elemental composition, average particle sizes and BET surface area of fresh WTRs, goethite, and sediment samples

Element	Fresh WTRs (wt%)	Goethite (wt%)	Sediment A (wt%)	Sediment B (wt%)	Sediment C (wt%)
Al	1.0	4.5	4.5	2.1	0.5
As	0.12	-	0.9	0.11	0.6
Ca	6.8	-	-	-	-
Cd	-	<DL	2.1	0.14	<DL
Cl	0.15	<DL	0.11	0.06	0.04
Co	-	0.02	<DL	-	-
Fe	61	40	30	66	70
K	0.3	1.8	1.0	0.4	0.07
Mg	0.25	0.6	0.14	0.15	0.09
Mn	0.8	2.3	0.03	<DL	0.02
Ni	-	0.03	<DL	-	-
P	2.5	-	-	-	-
Pb	<DL	0.02	0.12	0.03	0.02
S	0.3	-	5.2	1.9	5.1
Si	5.0	12.7	11.7	5.1	2.2
Ti	0.03	0.21	0.13	0.07	0.02
W	0.09	<DL	<DL	0.13	0.10
Zn	0.03	0.13	4.3	2.8	0.47
Balance (O, H, C...)	21.6	37.7	39.8	21.0	20.8
D[4,3]	38.6	6.3	66.0	45.0	59.6
D[3,2]	2.3	0.7	3.3	2.5	2.6
D(v,0.5)	29.9	1.5	43.3	27.8	32.1
BET Surface area (m ² /g)	170.7	28.5	-	-	-

Detection limit (DL) defined as below 0.02 wt%.

Table 2

Batch leaching values (in mg/kg dry matter) for fresh WTRs and sediment samples at natural pH, determined by ICP-MS, AAS and IC.

	pH	As mg/kg	Cd mg/kg	Co mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg	Cl ⁻ mg/kg	NO ₃ ⁻ mg/kg	PO ₄ ³⁻ mg/kg	SO ₄ ²⁻ mg/kg
WTRs	8.1	0.38	0.13	0.02	0.31	0.03	4.0	520	80	< DL	730
Sed A	5.3	0.05	36	3.1	1.4	< DL	2,160	nd	nd	nd	nd
Sed B	5.4	0.04	0.05	0.41	0.29	< DL	137	nd	nd	nd	nd
Sed C	4.0	0.04	9.6	0.63	1.1	< DL	3,301	nd	nd	nd	nd
Limit ^a	7-12	1.00	1.00	1.00	2.00	2.00	9.00	5,000	-	-	10,000

^a Arrêté du Gouvernement wallon favorisant la valorisation de certains déchets (M.B. 10.07.2001 - err. 18.07.2001) [31].

DL = 0.01 mg/kg; nd = not detected.

Table 3

Sediment porewaters and surface water contaminant values, determined by ICP-MS and AAS

	pH	As μg/L	Cd μg/L	Co μg/L	Ni μg/L	Pb μg/L	Zn μg/L
Sediment A porewater	5.2	18	3,252	597	215	13	272,000
Sediment B porewater	5.6	6	1	47	32	2	6,200
Sediment C porewater	3.9	< DL	131	312	256	8	778,000
Surface water	5.9	< DL	3,212	232	84	< DL	131,000

DL = 1 μg/L

Table 4

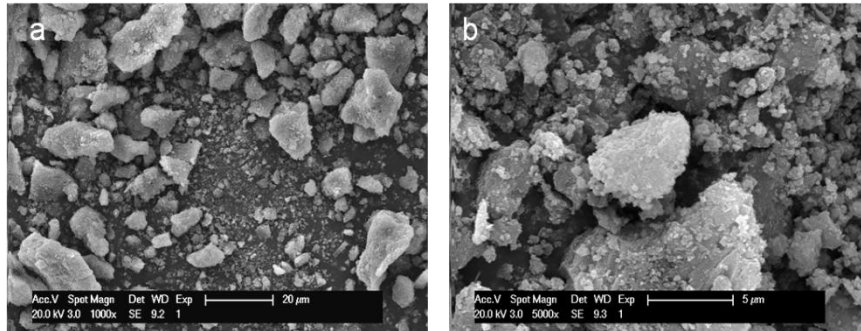
Langmuir equation parameters of fresh WTRs and goethite for four heavy metals (As(V), Cd²⁺, Pb²⁺, Zn²⁺)

Element	Sorbent	D_m (mmol/g)	k	Element	Sorbent	D_m (mmol/g)	k
As(V)	WTRs Single	0.534	4.49	Cd ²⁺	WTRs Single	0.187	13.5
	Goethite Single	0.254	0.75		Goethite Single	0.058	10.1
	WTRs Multiple	0.668	3.75		WTRs Multiple	0.098	14.6
	Goethite Multiple	0.200	0.64		Goethite Multiple	0.018	2.81
Pb ²⁺	WTRs Single	0.579	103.6	Zn ²⁺	WTRs Single	0.612	0.98
	Goethite Single	0.125	62.2		Goethite Single	0.122	1.31
	WTRs Multiple	0.483	41.0		WTRs Multiple	0.153	7.80
	Goethite Multiple	0.121	10.4		Goethite Multiple	0.076	1.05

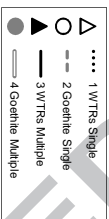
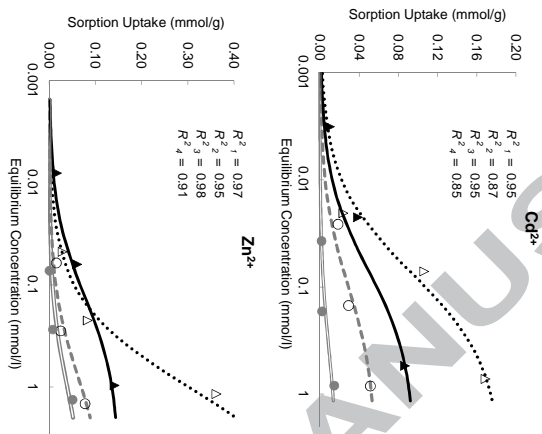
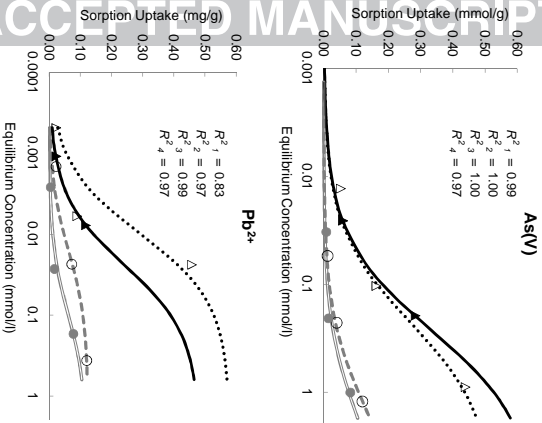
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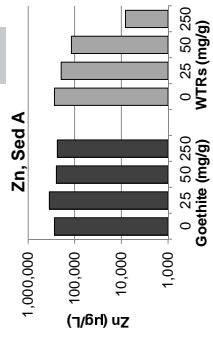
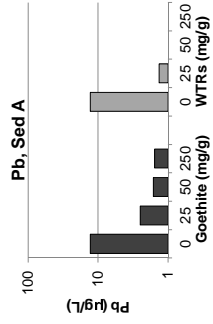
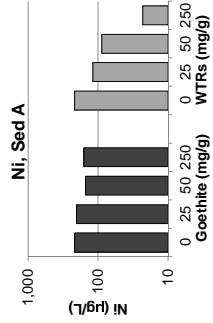
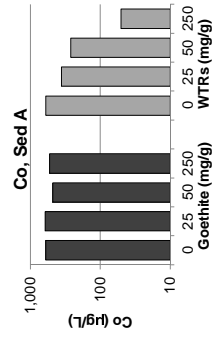
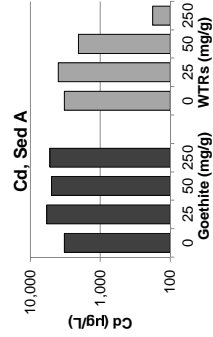
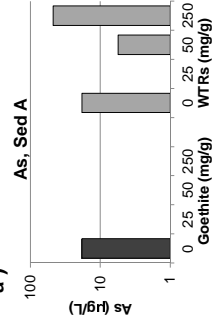
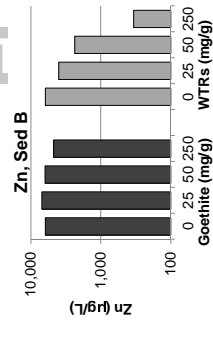
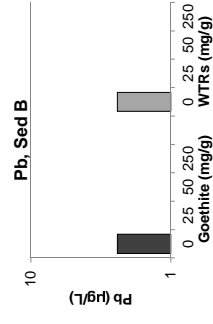
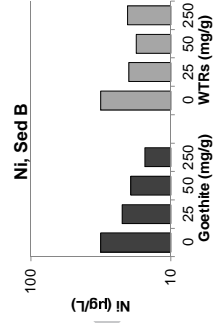
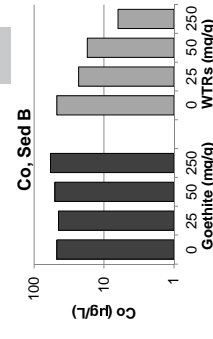
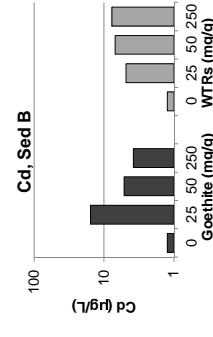
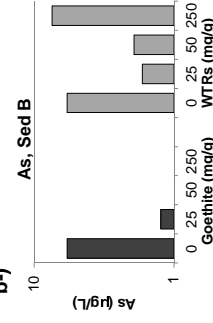
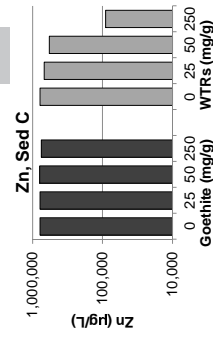
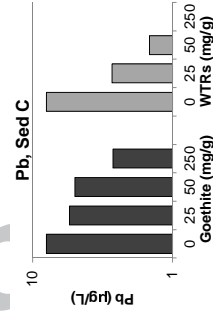
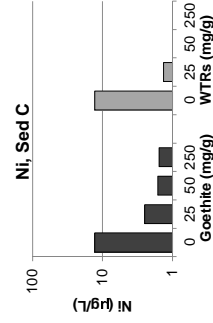
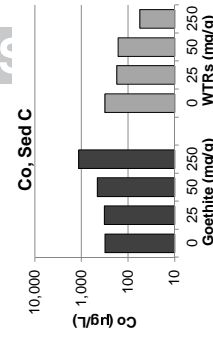
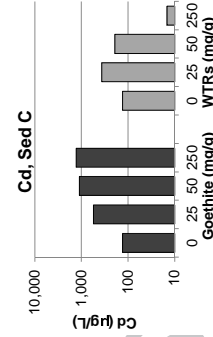
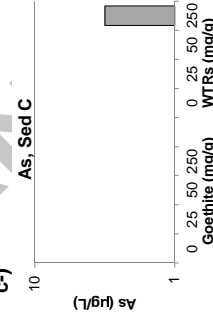
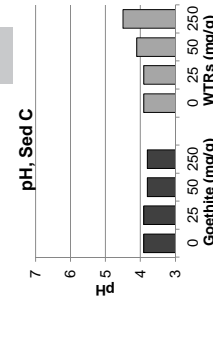
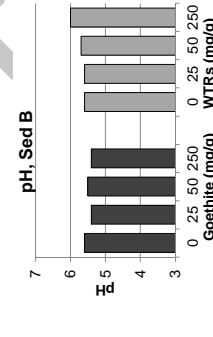
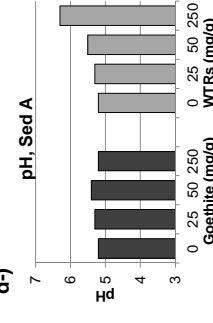
Composition (in terms of individual sorbent dosages required to treat 10 g contaminated sediments in 100 ml solution) of sorbent mixtures M1 and M2, and final equilibrium pH values after batch sorption tests

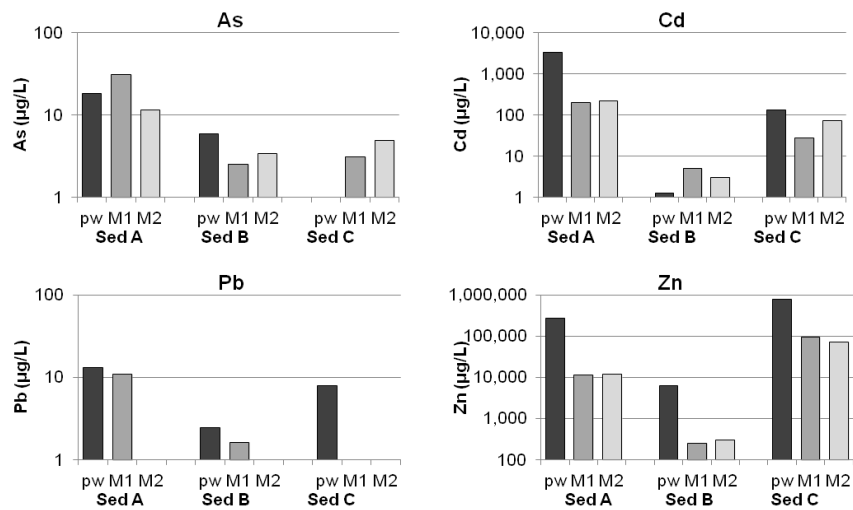
	Sediment A		Sediment B		Sediment C	
	M1	M2	M1	M2	M1	M2
Goethite	5.6 g	-	3.8 g	-	7.5 g	-
Natural Zeolite	-	7.2 g	-	5.1 g	-	11.7 g
Fresh WTRs	3.0 g	3.0 g	2.0 g	2.0 g	3.9 g	3.9 g
Final pH	6.5	6.5	6.7	6.7	5.6	5.6

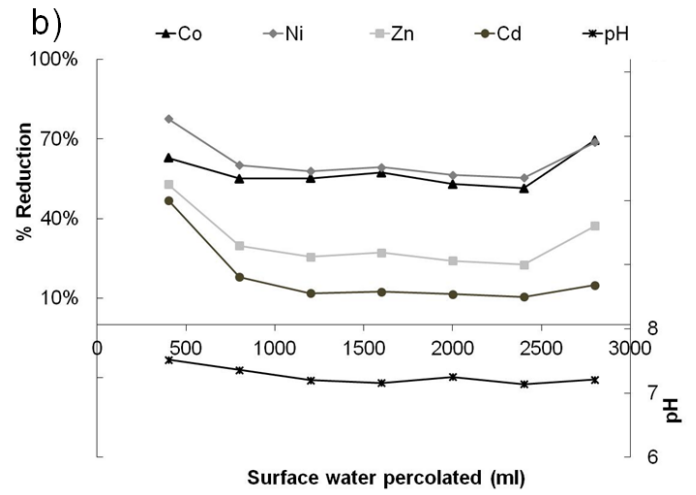
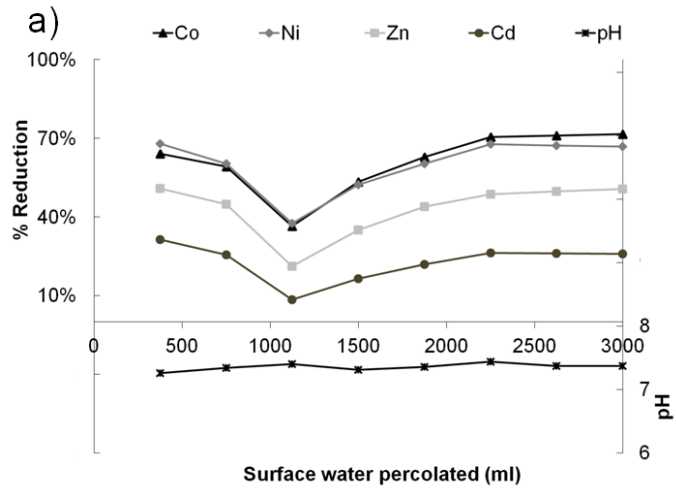


ACCEPTED MANUSCRIPT



a-**b-****c-****d-**





ACCEPTED MANUSCRIPT

WTRs and goethite adsorption performance for As, Cd, Co, Ni, Pb and Zn are compared.

The sorption capacities of the WTRs surpassed that of goethite by 100-400%.

At 250 mg/g WTRs dosage, sediment porewater cationic contaminants decreased by $\geq 80\%$.

Sorbent mixtures of WTRs with clinoptilolite natural zeolite prevent As leaching.

Fresh and regenerated WTRs reduce surface water contaminants by up to 90%.