IRIS - Archivio Istituzionale dell'Università degli Studi di Sassari

Copper(II) and lead(II) removal from aqueous solution by water treatment residues

Questa è la versione Post print del seguente articolo:

Original
Copper(II) and lead(II) removal from aqueous solution by water treatment residues / Castaldi, P., Silvetti, M., Garau, G., Demurtas, D., Deiana, S.A.. - In: JOURNAL OF HAZARDOUS MATERIALS. - ISSN 0304-3894. - 283:(2015), pp. 140-147. [10.1016/j.jhazmat.2014.09.019]

Availability:
This version is available at: 11388/60850 since: 2022-05-23T13:37:57Z

Publisher:

Published
DOI:10.1016/j.jhazmat.2014.09.019

Terms of use:

Chiunque può accedere liberamente al full text dei lavori resi disponibili come “Open Access”.

Publisher copyright

note finali coverpage

(Article begins on next page)

11 September 2026

COPPER(II) AND LEAD(II) REMOVAL FROM AQUEOUS SOLUTION BY WATER TREATMENT RESIDUES

Journal of Hazardous Materials 283 (2015) 140–147

http://dx.doi.org/10.1016/j.jhazmat.2014.09.019

0304-3894/© 2014 Elsevier B.V. All rights reserved.

Accepted Manuscript (post-print)

Paola Castaldi*, Margherita Silvetti, Giovanni Garau, Daniela Demurtas, and Salvatore Deiana

Dipartimento di Agraria, Sezione di Scienze e Tecnologie Ambientali e Alimentari, University of Sassari, Viale Italia 39, 07100 Sassari, Italy

*Corresponding author. Tel.: +39079229214; fax: +39079229276. E-mail address: castaldi@uniss.it (P. Castaldi).

Abstract

In this study we investigated the ability of Fe- and Al-based water treatment residues (Fe- and Al-WTR) to accumulate Pb(II) and Cu(II) at pH 4.5. The role of the inorganic and organic fractions of WTRs in metals sorption was also assessed. Sorption isotherms showed a higher sorption of Pb(II) by both WTRs with respect to Cu(II) (e.g. 0.105 and 0.089 $mmol \cdot g^{-1}$ of Pb(II) and Cu(II) respectively sorbed by Fe-WTR). Fe-WTR

revealed a stronger sorbent for both metals than Al-WTR. The amount of Pb(II) and Cu(II) sorbed by Fe-WTR was about the 69% and 63% higher than that sorbed by the Al-WTR. The organic matter of Fe- and Al-WTR contributed to about 26% and 8.5% respectively in the sorption of both metals. The sequential extraction procedure showed that the greatest amount of metals sorbed by both WTRs were tightly bound and not extractable, and this was particularly apparent for Cu(II). The FT-IR spectra indicated the formation of inner-sphere complexes between the Fe(Al)–O nucleus and Pb(II) and Cu(II). Moreover, the FT-IR spectra also suggested that the humic fraction of WTRs interacted, through the carboxylate groups, with Cu(II) and Pb(II) by forming mainly monodentate and bidentate complexes, respectively.

Keywords: Fe- and Al-WTR; Pb(II) and Cu(II); Sorption isotherms; Sequential extraction; FT-IR spectroscopy

1. Introduction

Trace metal cations, such as Pb(II), Cu(II), Cd(II), and Zn(II), are toxic inorganic pollutants, whose presence in soil can be of natural or anthropogenic origin [1]. Several agricultural practices, such as the application of fertilizers, sewage sludge, the disposal of effluent and mining activities can increase the trace metals content in soils [2]. This in turn can have negative consequences on soil fertility, biology and functionally [3-5]. In this regard, the mobile and bioavailable metal fractions are certainly the most impacting from an environmental point of view [6]. The abundance of these fractions in soil mainly depends on the sorption-desorption equilibria that govern the partition of

pollutant between soil solution and soil solids [2,5,7]. Indeed sorption is the major process responsible for accumulation of trace metals [1], where "sorption" encompasses adsorption, surface precipitation and fixation reactions [5,8-9].

The most important soil constituents involved in trace metal sorption are predominantly inorganic colloids such as clays, Fe, Al and Mn (oxy)hydroxides, and organic colloidal matter (particularly humic substances). All these constituents can play an important role in limiting trace metals mobility and toxicity in soil [1,4,10-11].

Many techniques based on the use of various sorbents (e.g. zerovalent Fe, compost, phosphate, lime, red muds, zeolites and clay minerals) have been proposed for the remediation of trace metals polluted soils [12-15]. However, all these approaches could be further attractive if the sorbent is inexpensive and does not require complicated pre-treatment or regeneration. In this regard, the drinking-water treatment residuals (WTRs), the waste material resulting from the treatment of surface-, or ground-water with Al and Fe salts, seems to meet these requirements [16-18]. In the conventional treatment of coagulation-filtration, suspended solids, natural organic matter, dyes, contaminants, etc., are removed from the raw water supply by the addition of aluminum, iron or calcium salts as coagulants, resulting in the production of water treatment residuals (WTRs) [16-22]. WTRs generally contain activated carbon, organic polymers, natural organic matter (above all humic substances), $CaCO_3$ and mainly Fe or Al (oxy)hydroxides [16-23]. The simultaneous presence of these constituents makes WTRs as suitable candidates for reducing trace metal mobility in polluted soil and waters through different sorption processes.

Many studies showed that WTRs are able to accumulate As(V) and P(V) anions and that such ability is closely related to the pH of the system [18-21,23]. However, few

studies addressed the affinity of WTRs towards trace metals [22] and their potential effectiveness at decreasing the solubility of divalent metal cations such as Cu(II) or Pb(II) in contaminated soils is unknown. Likewise, it is unknown the role of the inorganic and organic fractions of WTRs in the adsorption processes of metal(loid)s.

The objective of this paper was therefore: i) to determine the ability of a Fe- and an Al-based WTR, to accumulate Pb(II) and Cu(II) cations at pH 4.5; ii) to ascertain the role of the inorganic and organic fractions of WTRs in the sorption processes, and iii) to understand the mechanisms which regulate the sorption of both metals.

2 Materials and Methods

2.1 Samples description

Two different water treatment residues (WTRs) were studied: one, identified as Al-WTR, was obtained from the drinking-water treatment plant of Abbanoa industry in Truncu Reale Sassari (Italy), whereas the other, identified as Fe-WTR, derived from the Bidighinzu plant of the same industry. The WTRs were sampled from stockpiles that were formed within 1 year of production. WTR samples were air-dried overnight at 105°C and finely grounded. The chemico-physical characteristics of the WTRs samples are reported in Table 1 (for a full description of the carried analytical methods applied see Castaldi et al. [23]). Particularly to determine the content of humic substances (Na-HS) the method reported by Ciavatta et al. [24] was used.

The dissolution measurements of WTRs were performed by the acid dissolution batch method previously described [25]. Briefly, 250 mg of both WTRs were titrated

(902 Titrando-Metrohm equipped with software Tiamo 2.3) with solutions containing different amount and concentration of HCl (0.01, 0.1 or 1.0 M) or NaOH 0.01 M, until the pH values of 7.0, 5.5, 4.5, and 3.5 were stable, into a final volume of 200 mL. After the samples were shaken at 300 rpm on a horizontal shaker at 20 °C for 24 h, the water extracts were recovered by centrifugation and filtered through a 0.22-gm Millipore filter. The filtered solutions were analysed for total Fe, Al, and Mn content using a Perkin Elmer Analyst 600 flame atomic absorption spectrometer (FAAS) equipped with a HGA graphite furnace. The content of dissolved organic carbon (DOC) in the filtered solutions was also determined according to Brandstetter et al. [26].

For sorption trials, Fe- and Al-WTR samples were brought to pH 4.5 with either 0.01 or 0.1 M HCl solutions. The chemical characteristics of the acidified WTRs are reported in Table 2.

Each experiment was conducted in triplicate and mean values±standard deviations are reported.

2.2 Sorption kinetics of Pb(II) and Cu(II) on WTRs at pH 4.5

All chemicals were of analytical grade and used without further purification. For kinetic studies, polyethylene bottles containing 0.1 g of each WTR at pH 4.5 were filled with 25 mL of a solution containing 20.0 µmol of $Pb(NO_3)_2$ or $Cu(NO_3)_2$ (0.8 mM, the concentration of the last point of the sorption isotherm).

At different times (5, 10, 15, 30, 60, 180, 360, 900, and 1440 min) the samples were centrifuged at 8000 rpm for 10 min and filtered with 0.2 µm cellulose acetate filter to separate the liquid and solid phases. An aliquot of the supernatant was taken and Pb(II)

and Cu(II) were quantified by using a Perkin Elmer Analyst 600 flame atomic absorption spectrometer (FAAS) equipped with a HGA graphite furnace.

Each point of the sorption kinetics was carried out on three independent samples and mean values±standard deviations are reported.

2.3 Sorption isotherms of Pb(II) and Cu(II) on WTRs at pH 4.5

Fe- and Al-WTR samples were artificially and separately polluted with monometallic solutions containing increasing concentrations of Pb(II) and Cu(II) derived from their nitrate salts. Batch experiments were prepared for Fe-WTR and Al-WTR at pH 4.5 and at constant temperature (25±1 °C). This pH value was chosen because of at pH 4.5 and at the maxima concentration of $Pb(NO_3)_2$ and $Cu(NO_3)_2$ used (0.8 mM) any fraction of both metals precipitates as oxide or hydroxide, as highlighted by the distribution diagrams of MEDUSA (Figures not shown).Polyethylene bottles containing 0.1 g of WTR were filled with 25 mL of separated metal-enriched solutions. Ten different metal concentrations were used (from 0.04 to 0.8 mM corresponding to 1.0 and 20.0 µmol 25 mL^{-1} respectively). Sodium chloride (NaCl) at different concentrations (i.e. 0.5, 1.0 and 2.0 mM) was used to study the effects of ionic strength on metal ions sorption.

The mixtures (0.1:25 ratio of WTR/metal solution) were shaken for 24 h at constant temperature (25±1 °C). After equilibrium, the samples were centrifuged at 7000 rpm for 10 min and filtered with 0.2 µm cellulose acetate filter to separate the liquid and solid phases. Supernatant aliquots were taken and Pb(II) and Cu(II) quantified using a Perkin Elmer Analyst 600 flame atomic absorption spectrometer, as previously described.

In order to investigate the role of the WTR organic matter in the metal sorption, the total extractable carbon (TEC) was separated from the remaining WTR phases using the protocol proposed by Ciavatta et al. [24]. Polyethylene bottles containing 0.1 g of WTRs at pH 4.5, following the TEC solubilisation ($WTR_{w/o}TEC$), were filled with 25 mL of 0.8 mM Pb(II) and Cu(II) solutions. The mixtures were shaken for 24 h at constant temperature (25±1 °C) and then centrifuged, filtered and analyzed as above.

Each determination was carried out on three independent samples and mean values±standard deviations are reported.

2.4 Sequential extraction of Pb(II) and Cu(II) sorbed by WTRs at pH 4.5

Before the sequential extraction, Fe- and Al-WTR samples (0.1 g) saturated with Pb(II) or Cu(II) at pH 4.5 (i.e. those deriving from the last point of the isotherms) were washed with 25 ml of distilled water, in order to remove the salts deposited in the sorbents, and shaken for 2 minutes. Washings were repeated three times.

Subsequently solid samples (0.1 g) were placed in 50 ml centrifugation tubes, treated with 25 mL of distilled water and shaken for 2 h at 20°C to extract soluble metal [27]. Samples were then treated with 25 mL of 0.1 N $Ca(NO_3)_2$ to extract the exchangeable phase, and subsequently with 25 mL of 0.02 M EDTA to extract the complexed phase [27]. After each step of the extraction process the samples were centrifuged at 7000 rpm for 10 min, filtered with 0.2 μm cellulose acetate filter to completely separate the liquid and solid phases, and the content of Pb(II) and Cu(II) was analysed as described above. After the third washing, the residual fraction of metals was determined by drying the solid phase overnight at 105 °C and digesting it with 65% HNO_3+ 30% H_2O_2 in a

Microwave Milestone MLS 1200. The trace metal concentrations were analysed as described above.

Each step of the sequential extraction procedure was carried out on three independent samples and the mean values±standard deviations were reported.

2.5 FT-IR spectroscopy

The FT-IR spectra of the WTRs and $WTR_{w/o}TEC$ samples doped with Pb(II) or Cu(II) at pH 4.5, relative to the last point of the isotherms, were recorded at room temperature using a Nicolet 380 FT-IR spectrometer equipped with EZ Omnic software. The FT-IR spectra were recorded in the 2000 to 400 cm^{-1} range, and were collected after 320 scans at 4 cm^{-1} resolution. The KBr disc technique was used for sample preparation. The KBr (FT-IR grade, Fluka) was dried at 200°C for 24 h. To prepare KBr pellets, 4 mg of Fe- or Al-WTR, was ground (for 1-2 minutes) together with 196 mg of KBr. The preparation of pellets has been comprehensively described in Castaldi et al. [23].

3. Results and Discussion

The main goal of our research was to determine the ability of Fe- and Al-WTR to act as sequestering agents for Pb(II) and Cu(II) in acidic conditions. In particular, all sorption experiments were performed at pH 4.5 because at this pH value, and at the highest concentration of Pb(II) and Cu(II) used (i.e. 0.8 mM), no metal precipitation occurs. On the contrary, metal precipitation as oxide or hydroxide becomes significant (especially for Pb) at higher pH values. Besides, as most of the mining soils polluted by

trace metals are very often strongly acidic, we studied the sorbing properties of WTRs at pH 4.5 in preparation for their possible use as amendments in such polluted environments.

As a first step of the study, we investigated the sorption capacities of Fe- and Al-WTRs towards the two metal ions. Subsequently, we evaluated the contribution of the inorganic and organic fractions of WTRs in the sorption process. Finally, we attempted to elucidate the mechanisms which regulate the sorption of both metals through a sequential extraction procedure and FT-IR spectroscopy.

3.1 Chemico-physical properties of WTRs

The chemico-physical properties of untreated Fe- and Al-WTR are reported in Table 1, and were previously discussed in Castaldi et al. [23]. X-ray diffraction analysis revealed no crystalline Al or Fe (oxy)hydroxides components, indicating that both materials were amorphous and particles poorly ordered [23]. The dissolution of both WTRs was taken into account in order to identify a possible solubilisation of WTRs phases (organic matter, Fe, Al and Mn (oxi)hydroxides) at different pH values (Table 2). The highest release of DOC was observed at pH 5.5 and 4.5 in the Fe and Al-WTR respectively, while the highest solubilisation of Fe, Al and Mn was detected at strongly acidic conditions (i.e. pH 3.5). These results should be taken into considerations as WTR dissolution in acidic environment could (re)-mobilise metals previously sorbed.

The Fe-WTR at pH 4.5 showed an increase of dissolved organic carbon (~0.40 vs 0.10 $mg \cdot g^{-1}$ d.m. in the untreated Fe-WTR). Finally the content of humic substances

essentially remained unchanged in the Al-WTR, while decreased in the Fe-WTR samples (Table 3).

3.2 Sorption kinetics of Pb(II) and Cu(II) on WTRs at pH 4.5

The kinetic tests, carried out at pH 4.5 by dispersing, at different contact times, 0.1 g of WTR in solutions containing Pb(II) or Cu(II) 0.8 mM, showed that Pb(II) sorption by the Fe- and Al-WTR was biphasic, highlighting an initially fast sorption (first 60 min), followed by a slower Pb(II) sorption rate; a similar behavior was observed for Cu(II) sorption (Fig. 1). The sorption of Pb(II) was faster than that of Cu(II) in both WTRs, indeed after the first hour more than 72% and 85% of Pb(II) was sorbed by Fe- and Al-WTR respectively, while the amount of Cu(II) sorbed was about 60% of the total copper sorbed after 24 h. The biphasic pattern of Pb(II) and Cu(II) sorption suggests that the initial fast rate could be due to the retention of both cations on readily accessible surface sites [28]. The slow sorption step may be due to the presence of sites not immediately accessible and/or with poor affinity for Pb(II) and Cu(II) [1].

3.3 Sorption isotherms of Pb(II) and Cu(II) on WTRs at pH 4.5

Sorption experiments were performed at different ionic strength of the background electrolyte (0.5, 1.0 and 2.0 mM NaCl) (data showed in the Supplementary Fig. 1), in order to assess if different Na(I) concentrations can cause a decrease of Pb(II) or Cu(II) sorption by the WTRs. However the different ionic strength did not influence significantly the amount of trace metals sorbed, indicating that Na(I) was unable to

compete with Pb(II) or Cu(II) ions for surface sorption sites. Besides, the effect of NaCl concentration on trace metals sorption was similar for Cu(II) and Pb(II) (Supplementary Fig. 1). Consequently, only the results from sorption experiments performed with 1.0 mM ionic strength were discussed here (Fig. 2). Sorption isotherms showed a higher sorption of Pb(II) by Fe- and Al-WTR with respect to Cu(II) (Fig. 2a). Moreover, Fe-WTR was more effective than Al-WTR in the sorption of both metal ions. The maximum amount of Pb(II) sorbed by Fe-WTR [0.105 mmol Pb(II) g^{-1}] was about 1.2 times higher than that of Cu(II) [0.089 mmol Cu(II) g^{-1}] while negligible differences were observed for Al-WTR (Fig. 2a). Similar results have been observed by other authors, which showed higher sorption of Pb(II) than Cu(II) by Fe and Mn (oxy)hydroxides [10,29]. Both Cu(II) and Pb(II)-isotherms reached a plateau, so showing a saturation of WTRs Pb- and Cu-binding sites at a final concentration of 0.8 mM.

The amount of Pb(II) and Cu(II) sorbed by Fe-WTR was about the 69% and 63% higher than that sorbed by the Al-WTR. This could be mainly related to the physical and chemical characteristics of the WTRs (surface area, CEC and pH_{pzc}), and to the amount and chemical properties of the OM present in WTRs (Table 3). Besides, the higher content of Fe and Mn in the Fe-WTR, with respect to Al-WTR, could have contributed to the higher affinity of Fe-WTR towards Pb(II) and Cu(II) (Table 3).

The point of zero charge (pH_{PZC}) of the Fe- and Al-WTR is equal to 7.50 and 6.85 respectively, therefore at pH 4.5 the surfaces of both WTRs are positively charged. Consequently, the sorption of Pb(II) and Cu(II), affected by apparent Coulombic repulsion, could be mainly regulated by the formation of chemical bonds between Pb(II) and Cu(II) and the surface OH/OH_2 groups of the Fe/Al and Mn (oxy)hydroxides) with

the consequent release of H^+ in solution. Such a mechanism typically occurs with pure iron or aluminum (oxy)hydroxides [i.e. 30-35].

The presence of organic matter within the WTRs could also play an important role in Pb(II) and Cu(II) sorption. Organic matter, particularly the humic substances may immobilize Pb(II) and Cu(II) via specific adsorption reactions [1]. According to HSAB (hard and soft acids and bases) theory, Cu(II) and Pb(II) ions can react with humic substances via O and N atoms to form stable complexes [36]. On the other hand, dissolved organic matter or fulvic acids could contribute to mobilization of Pb(II) and Cu(II) through complexation reactions [1].

In order to better clarify the role of the organic matter in the sorption of the two metals, we conducted sorption experiments after the removal of the extractable organic carbon in alkaline solutions ($WTR_{w/o}TEC$). Particularly, we added 0.1 g of $WTR_{w/o}TEC$ to 25 mL of 0.8 mM $Pb(NO_3)_2$ or $Cu(NO_3)_2$ solutions (0.1:25 w/v ratio) rebalanced at pH 4.5. The amount of metals sorbed by $WTR_{w/o}TEC$ decreased substantially with respect to untreated WTR (Fig. 2b). The decrease of Pb(II) and Cu(II) sorbed by Fe-$WTR_{w/o}TEC$ was higher than 26% with respect to untreated control, while the decrease of Pb(II) and Cu(II) sorbed by Al-$WTR_{w/o}TEC$ was of 13% and 8.5% respectively. The lower sorption of both metals by $WTR_{w/o}TEC$ (particularly evident for Fe-$WTR_{w/o}TEC$) could be due to the loss of high-affinity binding sites for Pb(II) and Cu(II) [4], as well as to an alteration of the WTRs surficial charge. For instance, it has been reported that humic acids may still carry a negative charge even at pH 2.0 [36].

In order to describe the sorption of metal ions by WTRs, two types of models, i.e. Langmuir and Freundlich isotherms, were applied to describe the equilibrium sorption of Pb(II) and Cu(II) from liquid solution.

The Langmuir equation, which is the simplest and most common model assuming monolayer adsorption, was applied for adsorption equilibrium as follows:

$$x/m = KbC/(1+KC);$$

where *b* is the maximum monolayer coverage capacity of the sorbent (mg g^{-1}) and *K* (dm^3 mg^{-1}) is a constant related to the energy of sorption which quantitatively reflects the affinity between the sorbent and the sorbate.

The Freundlich model is an empirical equation employed to describe heterogeneous systems. The Freundlich isotherm can be expressed as:

$$x/m = K_F C^{1/n}$$

were K_F and *n* are the Freundlich exponent.

The sorption constants and correlation coefficients obtained from the fitting of Langmuir and Freundlich models to the batch data are listed in Table 4. Comparison between isotherms models showed that the Freundlich isotherm represents the adsorption process better than the Langmuir isotherm, so indicating the presence in the WTRs of heterogeneous sites for Pb(II) and Cu(II) adsorption.

Nevertheless, the maximum Pb(II) and Cu(II) sorption capacity of the Fe- and Al-WTR, as determined by the Langmuir equation, agreed with the experimental results (Table 4). Particularly, the coefficient *b* confirms the higher sorption of Pb(II) than Cu(II) by both WTRs.

The Freundlich *Kf*, which can be related to the affinity of Fe- and Al-WTR for metal ions, was higher for Pb(II) than Cu(II). Moreover, the *n* value, which was greater than 1 indicates that the sorption of Pb(II) and Cu(II) by the Fe- and Al-WTR can be described as favorable [21].

Taken together, these results indicate that: (i) Pb(II) and Cu(II), at the pH value considered, have a different affinity towards the tested WTRs, (ii) Pb(II) and Cu(II) are likely involved in different sorption mechanisms with the WTRs surfaces, (iii) Fe-WTR showed a greater Pb(II) and Cu(II) sorption capacity compared to Al-WTR, (iv) extractable organic matter in WTRs is fundamental in conditioning metals sorption and this was particularly evident for Fe-WTR.

3.4 Sequential extraction of Pb(II) and Cu(II) sorbed by WTRs at pH 4.5

WTRs samples containing Pb(II) or Cu(II) were subjected to sequential extraction following the procedure proposed by Basta and Gradwohl [25] in order to determine the nature of the interactions established between the metal ions and the surfaces of WTRs (Fig 3a). The sequential extraction procedure applied permits to determine the fraction of the metal ion water-soluble, exchangeable and adsorbed, allowing to determine the metal availability for plants and microorganisms [12-13].

The amount of Pb(II) and Cu(II) soluble in H_2O (i.e. metals readily leachable and bioavailable in the environment) was about 13% and 16% in Fe-WTR, respectively. An amount equal to ~10% of both the metal ions was found in Al-WTR (Fig. 3a). The H_2O soluble fractions, higher in Fe-WTR in line with the DOC values, could be originated following the formation of soluble complexes between dissolved organic matter and Pb(II) and Cu(II), as hypothesized by several author [e.g. 1]. The fractions of Pb(II) and Cu(II) extracted with $Ca(NO_3)_2$ (i.e. the relatively labile and potentially bio-available exchangeable fractions) were always lower than 4% of total metals sorbed (Fig. 3a).

Such pattern seems governed by the tendency of Pb(II) and Cu(II) to form inner sphere complexes with Fe(Al) (oxy)hydroxides and organic matter [37].

The metal fractions extracted with EDTA (i.e. the relatively immobile and not readily bio-available or leachable metal [27]) was higher for Pb(II) (49.7% and 52.6% in Fe- and Al-WTR respectively) than Cu(II) (34.2% and 37.0% in Fe- and Al-WTR respectively), anyway highlighting the ability of Pb(II) and Cu(II) to form inner sphere complexes with the surface sites of both WTRs.

The fraction of Pb(II) and Cu(II) non extractable from WTRs (i.e. metal pools not readily bioavailable in the short-term) was higher than 32% for both systems, reaching the highest values for Cu(II) (the residual Cu(II) was higher than 48% of total copper sorbed by Fe- and Al-WTR) (Fig. 3a). The high capacity of WTRs to retain the two metal ions could be related to different interaction mechanisms involving both inorganic and organic components of WTRs. The organic components may participate in the retention of the two metal ions through complexation reactions occurring on both the external surfaces of organic matter as well as within the macro and/or micropores. Inside the macro-micropores, the interaction between the two metal ions and organic structures such as humic acids can give rise to the formation of poorly soluble aggregates. Besides, the occlusion of the micro -and macropores of WTRs by metal-organic aggregates could prevent Cu(II) and Pb(II) ions from reacting to other molecules such as EDTA, thereby making them non bioavailable [i.e. 12]. Moreover, the complexation of two metal ions by organic matter in the form of fulvic acids can give rise to the formation of rather soluble aggregates, which can directly determine the release of Pb(II) and Cu(II) (as highlighted by the extraction with H_2O) [1]. Nevertheless, the irreversible Pb(II) and Cu(II) fixation into the micropores of the

inorganic fraction of WTR, i.e. Fe and Al phases, could certainly contribute to metal retention by WTRs [1,38].

To determine the contribution of the organic fraction on the WTRs retention capacity the sequential extraction was also applied to WTRs [doped with Pb(II) or Cu(II)] after the removal of TEC (i.e. $WTRs_{w/o}TEC$) (Fig. 3b). The more striking differences between WTRs and $WTRs_{w/o}TEC$ were related to the decrease of water-soluble Pb(II) and Cu(II) and to the increase of exchangeable metal [extraction with $Ca(NO_3)_2$] in the latter. The decrease of water-soluble fraction in the $WTRs_{w/o}TEC$ was higher than 70% with respect to WTRs, so confirming the formation of soluble Cu(II) or Pb(II) organic complexes, as reported above. The increase of the metal exchangeable fraction, higher for Cu(II) than Pb(II), can be explained by considering that the extraction of the organic matter has made available a number of inorganic sites which can interact electrostatically with both metal ions. The residual fraction of the metals was higher than 40% in $WTRs_{w/o}TEC$, so confirming a strong retention of Pb(II) and Cu(II) into the internal micropores of Fe and Al phases. Finally the residual Cu(II) was higher than residual of Pb(II), supporting the statements above reported for the residual fraction found in the WTRs.

Globally, these results show that the specific sorption of both cations seems to play a more important role than nonspecific adsorption. In particular, the Cu(II), even if less sorbed, was more strongly retained than Pb(II) by the colloidal component of WTRs.

3.5 FT-IR Spectroscopy

To assess the involvement of the organic and inorganic components of the WTRs in the sorption process of the two metal ions, untreated WTRs and $WTRs_{w/o}TEC$, polluted and not polluted with Cu(II) and Pb(II), were analyzed, together with humic substances (Na-HS) extracted by the sorbents, through FT-IR spectroscopy.

The FT-IR spectra of WTRs (Figures 4 and 5) showed a broad band in the 1770-1500 cm^{-1} region which could likely be the result of the superposition of several bands deriving from the heterogeneity of WTRs that, as final residues of the waste water treatment, incorporate organic and inorganic substances. This broad band, as deduced from the FT-IR spectra of the humic substances (Na-HS) and $WTR_{w/o}TEC$ (Figures 4 and 5), can be considered as the result of the overlapping of the following bands: a band at ~1720 cm^{-1} (C=O stretching of carboxylic, aldehydes, ketones, amide and quinone moieties [39]), a band at ~1660 cm^{-1} (OH bending mode of H_2O associated to the Fe and Al surfaces [23]), another at ~1600 cm^{-1} (asymmetric stretching vibration of the carboxylate group (ν_{asCOO^-}) [40]), and a final one at ~1540 cm^{-1} (not conjugated carbonylic C=O, the N–H deformation of the amide (band II of the amide) and stretching of C=N). The observed band at 1450 cm^{-1} could be assigned to C–O stretching of phenolic OH, C–H deformation of CH_2 and CH_3 groups [41], and the band at ~1415 cm^{-1} to the symmetric stretching vibration of the carboxylate group (ν_{sCOO^-}) [40]. Finally the band at ~1040 cm^{-1} could be assigned to the stretching vibrations of Fe(Al)–O nucleus [42]. These finding were supported by the FT-IR spectra registered on the humic substances extracted from WTRs and brought to pH 4.5 (Na-HS) (Figures 4 and 5) which, in addition to the peaks reported above for the WTRs, showed a peak at ~1150 cm^{-1} due to C−O vibrations associated with polysaccharide structures and at 990 cm^{-1} ascribable to methylene groups. Finally, the peaks at 615 cm^{-1}, characteristic of

Si−O stretching vibrations, and at 500 cm^{-1}, typical of Si−O bending vibrations [41], could prove the presence of silicate as impurities.

The FT-IR spectra of WTRs doped with Pb(II) and Cu(II) showed a shift and an increase of the intensity of bands in the ~1600-1580 cm^{-1} and 1420-1390 cm^{-1} range attributable respectively to the asymmetric and symmetric stretching of the carboxylate group of the humic fraction as reported above [40,43-44]. The difference between the frequencies of $\nu_{as}COO^-$ and ν_sCOO^- ($\Delta\nu$) gives useful information about the type of interaction of the carboxylate groups with metal ions [40,43-44]. If the $\Delta\nu$ value of the complex is lower than that recorded for the Na-Humate (Na-HS) a bidentate chelating mode can be assumed, while a monodentate chelating mode is proposed if the $\Delta\nu$ (COO^-) of the complex is higher than that of the Na-HS [40,43-44]. A $\Delta\nu$ value of 203 (and 200) and 175 (and 173) is measured for the spectra of Fe (and Al)-WTR doped with Cu(II) and Pb(II) respectively and of 187 for Na-HS extracted. These $\Delta\nu$ values suggest a monodentate and a bidentate chelating mode for Cu(II) and Pb(II) with the carboxylate groups of the HS, respectively. Further, these data support the results obtained in the sorption experiments (paragraph 3.2), which suggested that the sorption of Cu(II) and Pb(II) by WTRS was regulated by different interaction mechanisms.

The FT-IR spectra of WTRs and $WTR_{w/o}TEC$, which were very similar to those of amorphous Fe and Al hydroxides [42], were characterized by two broad bands centered at ~1640 and 1040 cm^{-1}, assigned to the water O–H groups bending mode associated to the Fe and Al surfaces and to the stretching vibrations of Fe(Al)–O nucleus, respectively [23,42]. The strong band at 1040 cm^{-1} shifted to lower frequencies (~1027 and 1035 cm^{-1}) after the Cu(II) or Pb(II) sorption, suggesting the involvement of the Fe(Al)–O sites in the coordination of Cu(II) or Pb(II).

4. Conclusions

In this study we showed for the first time that WTRs are able to act as accumulators of Pb(II) and Cu(II) ions from acidic aqueous solutions. In our analytical conditions, Fe-WTR revealed a higher affinity for both metals than Al-WTR. The greater specific surface area and CEC of Fe-WTR could explain its higher affinity for both metals compared to Al-WTR.

The mechanism which regulated the sorption of Cu(II) and Pb(II) by the WTRs could be the result of chemical interactions that gave rise to the formation of inner-sphere surface complexes. It is important to underline that a strong contribution to this adsorption mechanism is derived from the organic matter incorporated in the WTRs

The sequential extraction procedure showed that low concentrations of the Pb(II) and Cu(II) sorbed by WTRs were in the form of water-soluble and exchangeable fractions, while the greatest concentrations of the metals sorbed were tightly bound and would not be expected to be readily released under natural conditions.

The FT-IR spectra of WTRs doped with Pb(II) and Cu(II) suggest a predominant monodentate chelating mode for Cu(II) and a prevalent bidentate chelating mode for Pb(II) with the carboxylate groups of the humic substances. Moreover, the formation of inner sphere complexes between Cu(II) or Pb(II) and the inorganic Fe(Al)–O was also highlighted.

Taken together the results obtained suggest that different interaction mechanisms can be hypothesized to explain lead and copper sorption by both WTRs at acidic pH: i) ligand exchange with superficial H^+ (relevant for both organic and inorganic WTRs

fractions) and ii) strong retention of Pb(II) and Cu(II) into Fe and Al (oxy)hydroxides micropores (particularly relevant for copper). These findings suggest that WTRs can be a valuable resource as metal-immobilizing agents in acidic soils and waters polluted by Pb(II) and Cu(II).

Acknowledgements

The financial support of Regione Sardegna (L.R. 7/2007 Progetti di ricerca di base-Bando 2012) is gratefully acknowledged.

References

[1] H.B. Bradl, Adsorption of heavy metal ions on soils and soils constituents, J. Colloid Interf. Sci. 277 (2004) 1-18.

[2] B.J. Alloway, Heavy Metals in Soils, Blackie Academic & Professional, London, 1995.

[3] M. Nachtegaal, D.L. Sparks, Effect of iron oxide coatings on zinc sorption mechanisms at the clay-mineral/water interface, J. Colloid Interf. Sci. 276 (2004) 13-23.

[4] E.F. Covelo, F.A. Vega, M.L. Andrade, Competitive sorption and desorption of heavy metals by individual soil components, J. Hazard. Mater. 140 (2007) 308-315.

[5] E.F. Covelo, F.A. Vega, M.L. Andrade, Sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by a Fibric Histosol and its organo-mineral fraction, J. Hazard. Mater. 159 (2008) 342-347.

[6] P. Castaldi, P. Melis, M. Silvetti, P. Deiana, G. Garau, Influence of pea and wheat growth on Pb, Cd, and Zn mobility and soil biological status in a polluted amended soil, Geoderma 151 (2009) 241-248.

[7] D.L. Sparks, A.M. Scheidegger, D.G. Strawn, K.G. Scheckel, Kinetics and mechanisms of metal sorption at the mineral–water interface, in: D.L. Sparks, T.J. Grundl (Eds.), Mineral–Water Interfacial Reactions, ACS Symposium Series 715, Washington, DC, American Chemical Society, 1999, pp. 108-135.

[8] R. Apak, in: A. Hubbard (Ed.), Encyclopedia of Surface and Colloid Science, Dekker, New York, 2002.

[9] G. Sposito, The Surface Chemistry of Soils, Oxford University Press, New York, 1984.

[10] L. Della Puppa, M. Komarek, F. Bordas, J.C. Bollinger, E. Joussein, Adsorption of copper, cadmium, lead and zinc onto a synthetic manganese oxide, J. Colloid Interf. Sci. 399 (2013) 99-106.

[11] P. Castaldi, G. Garau, A. Palma, S. Deiana, Formation of biopolymers owing to the oxidation of esculetine by Cu(II) ions in a Ca-polygalacturonate network, J. Inorg. Biochem. 108 (2012) 30-35.

[12] P. Janoš, L. Herzogová, J. Rejnek, J. Hodslavská, Assessment of heavy metals leachability from metallo-organic sorbent—iron humate—with the aid of sequential extraction test, Talanta 62 (2004) 497-501.

[13] G. Garau, P. Castaldi, L. Santona, P. Deiana, P. Melis, Influence of red mud, zeolite and lime on heavy metal immobilization, culturable heterotrophic microbial populations and enzyme activities in a contaminated soil, Geoderma 142 (2007) 45-57.

[14] P. Castaldi, M. Silvetti, E. Mele, G. Garau, S. Deiana, Arsenic mobilization by citrate and malate from a red mud–treated contaminated soil, J. Environ. Qual. 42 (2013) 774-781.

[15] M. Silvetti, P. Castaldi, P.E. Holm, S. Deiana, E. Lombi, Leachability, bioaccessibility and plant availability of trace elements in contaminated soils treated with industrial by-products and subjected to oxidative/reductive conditions, Geoderma 214–215 (2014) 204-212.

[16] K.C. Makris, W.G. Harris, Time dependency and irreversibility of water desorption by drinking-water treatment residuals: Implications for sorption mechanisms, J. Colloid Interf. Sci. 294 (2006) 151-154.

[17] R. Nagar, D. Sarkar, K.C. Makris, R. Datta, V.L. Sylvia, Bioavailability and bioaccessibility of arsenic in a soil amended with drinking-water treatment residuals, Arch. Environ. Contam. Toxicol. 57 (2009) 755-766.

[18] R. Nagar, D. Sarkar, K.C. Makris, R. Datta, Effect of solution chemistry on arsenic sorption by Fe- and Al-based drinking-water treatment residuals, Chemosphere 78 (2010) 1028-1035.

[19] M.K. Gibbons, G.A. Gagnon, Understanding removal of phosphate or arsenate onto water treatment residual solids, J. Hazard. Mater. 186 (2011) 1916–1923.

[20] J.A. Ippolito, K.A. Barbarick, H.A. Elliott, Drinking Water Treatment Residuals: A Review of Recent Uses, J. Environ. Qual. 40 (2011) 1-12.

[21] A.O. Babatunde, Y.Q. Zhao, A.M. Burke, M.A. Morris, J.P. Hanrahan, Characterization of aluminium-based water treatment residual for potential phosphorus removal in engineered wetlands, Environ. Pollut. 157 (2009) 2830-2836.

[22] Y.W. Chiang, K. Ghyselbrecht, R.M. Santos, J.A. Martens, R. Swennen, V. Cappuyns, B. Meesschaert, Adsorption of multi-heavy metals onto water treatment residuals: Sorption capacities and applications, Chem. Eng. J. 200-202 (2012) 405-415

[23] P. Castaldi, E. Mele, M. Silvetti, G. Garau, S. Deiana, Water treatment residues as accumulators of oxoanions in soil. Sorption of arsenate and phosphate anions from an aqueous solution, J. Hazard. Mater. 264 (2014) 144-152.

[24] C. Ciavatta, M. Govi, L. Vittori Antisari, P. Sequi, Characterization of humified compounds by extraction and fractionation on solid polyvinylpyrrolidone, J. Chromatogr. 509 (1990) 141-146.

[25] D. Ketrot, A. Suddhiprakarn, I. Kheoruenromne, B. Singh, Association of trace elements and dissolution rates of soil iron oxides, Soil Res. 52 (2014) 1-12.

[26] A. Brandstetter, R.S. Sletten, A. Mentler, W.W. Wenzel, Estimating dissolved organic carbon in natural waters by UV absorbance (254 nm), Z. Pflanzenernähr. Bodenk 159 (1996) 605-607.

[27] N. Basta, R. Gradwohl, Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure, J. Soil Contam. 9 (2000) 149-164.

[28] D.G. Strawn, A.M. Scheidegger, D.L. Sparks, Kinetics and mechanisms of PbII sorption and desorption at the aluminum oxide water interface, Environ. Sci. Technol. 32 (1998) 2596-2601.

[29] Christl, R. Kretzschmar, Competitive sorption of copper and lead at the oxide-water interface: implications for surface site density, Geochim. Cosmochim. Ac. 63 (1999) 2929-2938.

[30] J.R. Bargar, G.E. Brown, G.A. Parks, Surface complexation of Pb(II) at oxide-water interfaces: I. XAFS and bond-valence determination of mononuclear and polynuclear Pb(II) sorption products on aluminum oxides, Geochim. Cosmochim. Acta 61 (1997) 2617-2638.

[31] J.R. Bargar, G.E. Brown, G.A. Parks, Surface complexation of Pb(II) at oxide water interfaces: II. XAFS and bond-valence determination of mononuclear Pb(II)

sorption products and surface functional groups on iron oxides, Geochim. Cosmochim. Acta 61 (1997) 2639-2652.

[32] D.G. Strawn, D.L. Sparks, The use of XAFS to distinguish between inner- and outer-sphere lead adsorption complexes on montmorillonite, J. Colloid Interf. Sci. 216 (1999) 257-269.

[33] C.L. Peacock, D.M. Sherman, Copper(II) sorption on goethite, hematite and lepidocrocite: a surface complexation model based on ab initio molecular geometries and EXAFS spectroscopy, Geochim. Cosmochim. Acta 68, (2004) 2623-2637.

[34] J. Zhu, V. Cozzolino, M. Pigna, Q. Huang, A.G. Caporale, A. Violante, Sorption of Cu, Pb and Cr on Na-montmorillonite: competition and effect of major elements, Chemosphere 84 (2011) 484-489.

[35] C. Tiberg, C. Sjöstedt, I. Persson, J.P. Gustafsson, Phosphate effects on copper(II) and lead(II) sorption to ferrihydrite, Geochim. Cosmochim. Ac. 120 (2013) 140-157.

[36] J. Hizal, R. Apak, Modeling of copper(II) and lead(II) adsorption on kaolinite-based clay minerals individually and in the presence of humic acid, J. Colloid Interf. Sci. 295 (2006) 1-13.

[37] G. Garau, M. Silvetti, P. Castaldi, E. Mele, P. Deiana, S. Deiana, Stabilising metal(loid)s in soil with iron and aluminium-based products: microbial, biochemical and plant growth impact, J. Environ. Manage. 139 (2014) 146-153.

[38] L. Axe, P. Trivedi, Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe and Mn oxides, J. Colloid Interf. Sci. 247 (2002) 259-265.

[39] T.J.F. Cunha, E.H. Novotny, B.E. Madari, L. Martin-Neto, M.O. de O Rezende, L.P. Canelas, V. de M. Benites, Spectroscopy characterization of humic acids isolated from amazonian dark earth soils (Terra Preta de Índio), in: W.I. Woods, W.G. Teixeira, J. Lehman, C. Steiner, A. Winklerprins, L. Rebellato (Eds.), Amazonian dark earths: wim sombroek's vision, Berlin: Springer, 2009, pp. 363-372.

[40] P. Castaldi, G. Lauro, C. Senette, S. Deiana, Role of the Ca-pectates on the accumulation of heavy metals in the root apoplasm, Plant Physiol. Bioch. 48 (2010) 1008-1014.

[41] M. Izquierdo, P. Marzal, C. Gabaldón, M. Silvetti, P. Castaldi, Study of the interaction mechanism in the biosorption of copper(II) ions onto Posidonia oceanica and peat, Clean-Soil Air Water 40 (2012) 428-437.

[42] S. Goldberg, C.T. Johnston, Mechanisms of arsenic adsorption on amorphous oxides evaluated using macroscopic measurements, vibrational spectroscopy, and surface complexation modeling, J. Colloid Interf. Sci. 234 (2001) 204-216.

[43] K. Nakamoto, Infrared and raman spectra of inorganic and coordinating compounds, John Wiley & Sons, New York, 1978.

[44] E.G. Palacios, G. Juarez-Lopez, A.J. Monhemius, Infrared spectroscopy of metal carboxylates II. Analysis of Fe(III), Ni and Zn carboxylate solutions, Hydrometallurgy 72 (2004) 139-148.

Table 1

Properties of the Fe- and Al-WTR samples used in the study

Chemical parameters	Fe-WTR	Al-WTR
pH	7.88±0.06	6.45±0.01
EC ($mS \cdot cm^{-1}$)	3.01±0.06	5.69±0.13
Ashes (% d.m.)	46.86±0.29	43.00±0.95
S_{BET} ($m^2 \cdot g^{-1}$)	35	28
pH_{PCZ}	7.50±0.11	6.85±0.13
Cation Exchange Capacity (CEC: $cmol_{(+)} \cdot kg^{-1}$ d.m.)	75.02±1.78	66.76±2.03
Organic matter (% d.m.)	24.47±0.13	23.17±0.16
Humic and Fulvic acids (HA+FA) (% d.m.)	2.43±0.14	2.26±0.20
DOC ($mg \cdot g^{-1}$ d.m.)	0.10±0.00	0.11±0.00
Total N ($mg \cdot g^{-1}$ d.m.)	8.04±0.64	8.68±0.58
Total P ($mg \cdot g^{-1}$ d.m.)	0.68±0.03	0.89±0.01
P Ass ($\mu g \cdot g^{-1}$ d.m.)	n.d.	0.71±0.02
mg kg^{-1} d.m.		
Total Fe	245,480±44	17,437±37
Total Al	19,320±24	138,520±18
Total Mn	31,636±37	8,645±12
Total Ca	89.34±2.32	11,027±15
Total Mg	69.54±3.24	2,032±13
Total Na	32.15±1.24	156.46±4.81
Total K	99.48±2.35	3,827±10

Table 2

DOC content and Fe, Al e Mn released following WTR dissolution at different pH values

	DOC ($mg \cdot L^{-1}$)	Fe ($mg \cdot L^{-1}$)	Al ($mg \cdot L^{-1}$)	Mn ($mg \cdot L^{-1}$)
Fe-WTR				
pH 7.0	0.125±0.00	n.d.	3.14±0.26	12.68±1.03
pH 5.5	0.563±0.01	61.99±3.02	9.43±0.84	13.04±1.15
pH 4.5	0.504±0.01	99.96±6.24	9.84±0.92	144.19±7.33
pH 3.5	0.502±0.00	125.49±8.04	9.97±0.88	148.32±8.483
Al-WTR				
pH 7.0	0.138±0.00	n.d	n.d	n.d
pH 5.5	0.175±0.00	2.18±0.20	68.83±3.36	7.45±1.55
pH 4.5	0.238±0.00	21.45±1.33	70.51±3.82	7.90±1.71
pH 3.5	0.221±0.00	27.49±2.05	70.88±2.97	8.11±1.87

Table 3

Properties of the Fe-WTR and Al-WTR samples at pH 4.5 used in the study

Chemical parameters	Fe-WTR	Al-WTR
Organic matter (% d.m.)	24.96±0.16	22.76±0.11
CEC ($cmol_{(+)} \cdot kg^{-1}$ d.m.)	61.98±1.33	55.45±1.46
DOC ($mg \cdot g^{-1}$ d.m.)	0.40±0.00	0.19±0.00
Total extractable carbon (% d.m.)	8.41±0.25	8.02±0.28
Humic and Fulvic acids (HA+FA) (% d.m.)	1.72±0.13	2.17±0.15
Total Fe (*mg g^{-1} d.m.*)	145.51±4.22	13.15±1.26
Total Al (*mg g^{-1} d.m.*)	11.45±1.08	82.11±3.64
Total Mn (*mg g^{-1} d.m.*)	11.21±0.94	2.33±0.08

Table 4

The Langmuir and Freundlich parameters relating to the Pb(II) and Cu(II) sorption into Fe and Al-WTRs samples

Model	Parameters		
Langmuir isotherm	*b (mmol g^{-1})*	*K (L $mmol^{-1}$)*	R^2
Fe-WTR Pb(II)	0.194	3.36	0.84
Fe-WTR Cu(II)	0.106	3.33	0.81
Al-WTR Pb(II)	0.073	3.07	0.82
Al-WTR Cu(II)	0.065	3.06	0.82
Freundlich isotherm	K_F *(mmol g^{-1})*	*n*	R^2
Fe-WTR Pb(II)	0.642	1.784	0.86
Fe-WTR Cu(II)	0.506	1.183	0.96
Al-WTR Pb(II)	0.485	1.945	0.97
Al-WTR Cu(II)	0.467	1.398	0.96

Figure Captions

Fig. 1. Pb(II) and Cu(II) sorption kinetics on Fe- (a) and Al-WTR (b) at pH 4.5*.

*±standard deviations (error bars) were between ±0.01 and 0.068.

Fig. 2. Sorption isotherms of Pb(II) and Cu(II) on Fe- and Al-WTR at pH 4.5 and at ionic strength 1.0 mM NaCl (a). Sorption of Pb(II) and Cu(II) after the removal of the extractable organic carbon ($WTR_{w/o}TEC$) (b).

*±standard deviations (error bars) were between ±0.01 and 0.087.

Fig. 3. Percentage of Pb(II) and Cu(II) extracted with H_2O; $Ca(NO_3)_2$; EDTA; and not extracted from WTR (a) and $WTR_{w/o}TEC$ (b)*.

*±standard deviations (error bars) were between ±0.9 and 1.5%.

Fig. 4. FT-IR spectra of Fe-WTR and Fe-$WTRs_{w/o}TEC$ polluted and not polluted with Cu(II) and Pb(II) at pH 4.5.

Fig. 5. FT-IR spectra of Al-WTR and Al-$WTRs_{w/o}TEC$ polluted and not polluted with Cu(II) and Pb(II) at pH 4.5.

Supplementary Figure 1

Sorption isotherms of Pb(II) and Cu(II) on Fe- and Al-WTR at pH 4.5 and at ionic strength 0.5 mM (a), 1.0 mM (b) and 2.0 mM (c) NaCl.

*±standard deviations (error bars) were between ±0.01 and 0.094.