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Simultaneous removal of CU^{II}, NI^{II} and ZN^{II} by a granular mixture of zero-valent iron and pumice in column systems

S. Bilardi, P.S. Calabró*, N. Moraci

Department of Civil, Energy, Environmental and Materials Engineering (DICEAM), Mediterranea University of Reggio Calabria, Via Graziella, Loc. Feo di Vito, Reggio Calabria 89122, Italy, emails: stefania.bilardi@unirc.it (S. Bilardi), paolo.calabro@unirc.it (P.S. Calabró), nicola.moraci@unirc.it (N. Moraci)

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ABSTRACT

The granular mixtures between zero-valent iron (ZVI) and other materials (e.g. sand, pumice) have been recently proposed to overcome the problems (e.g. clogging) related to the use of ZVI alone in treatment systems such as permeable reactive barriers or individual potabilisation systems. This paper presents the results of the research activity, carried out by column tests, aimed at comparing the performance of a granular mixture between ZVI and pumice (weight ratio 30:70) and of pure ZVI for the individual and combined removal of Cu^{II}, Ni^{II} and Zn^{II}. The specific objective was to verify the occurrence of phenomena of mutual interaction and/or competition among contaminants. In fact, although metal removal by ZVI has been extensively documented in the past, the great majority of studies examined either very simple systems (i.e. single metal solutions) or very complicated ones (e.g. real acid mine drainage). In both cases, and for different reasons, the occurrence of mutual interactions (positive or negative) among the chemical species present in water is impossible to detect. For these reasons, this paper compares column experiments carried out in similar conditions using both monocontaminant and pluricontaminant solutions. The concentration values used for the three contaminants were of 500 or 50 mg/l for Cu^{II} and 50 mg/l for Ni^{II} and Zn^{II}. In monocontaminant systems, in both reactive media the removal sequence observed is $Cu > Zn > Ni$. In pluricontaminant solutions, Cu^{II} removal is unaffected by the presence of the other metals while the removal efficiencies of Ni and Zn decrease in respect to monocontaminant tests. In the mixture ZVI/pumice, the long-term removal efficiency reduction is higher for Zn (about 58% in respect to the experiment carried out with the solution containing Zn only) than for Ni (reduction of about 33%), leading to the removal sequence $Cu > Ni > Zn$ for the test with the highest Cu^{II} concentration. This behaviour has been explained, hypothesising the possible spontaneous formation of a bimetallic system between ZVI and Cu capable of enhancing Ni removal especially in the short term.

Keywords: Copper; Bimetallic system; Hydraulic conductivity; Nickel; Pumice; Zero-valent iron; Zinc

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*Corresponding author.

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1. Introduction

Zero-valent iron (ZVI) is a widely used reactive medium for water treatment (e.g. contaminated groundwater remediation by permeable reactive barriers (PRBs), stormwater runoff treatment and potabilisation systems at household level). ZVI has been studied in depth to verify its suitability for the removal of dissolved metals from groundwater by PRBs [1] and in particular from groundwater impacted by mine drainage [2–4] containing redox-sensitive metals such as hexavalent chromium [5–7] and uranium [8] or metalloids such as arsenic [9,10]. Its use for runoff treatment [11] or for drinking water systems at household level [12] is more recent.

From previous research it is now clear that ZVI can also activate additional removal mechanisms different from oxidation–reduction, allowing the removal of metals that cannot be reduced by ZVI (e.g. Zn), by co-precipitation and sorption. Reduction may be driven by four different reaction paths: Fe^0 (direct reduction), reduction by aqueous Fe^{II}, reduction by adsorbed or structural Fe^{II} reduction by molecular (H_2) or atomic (H) hydrogen [13].

Despite the high removal efficiency, the major issue related to the use of ZVI is its long-term behaviour. In several published cases the hydraulic conductivity and removal efficiency were progressively reduced during operation, potentially compromising the functionality of the system [14,15]. The granular mixtures between ZVI and other materials (e.g. sand, pumice) are now an established way to overcome these problems [16–21].

In this study, the individual removal and combined removal of copper, nickel and zinc were evaluated through column tests using, respectively, a granular mixture of ZVI and pumice in weight ratio 30:70 and ZVI alone.

The current literature is dominated by studies on the use of ZVI to remove Cu from acid mine drainage [3,4,22], from stormwater runoff [23] or from synthetic monocontaminant solutions [20,24]. Cu removal is mainly attributed to the cementation process that involves the reduction of the oxidised form of the contaminant, Cu^{II}, and the subsequent deposition of Cu^0 onto the iron surface but also to adsorption and co-precipitation on iron corrosion products.

The experiments aimed at evaluating Ni removal by ZVI [20,22,25], underlining that the possibility of a spontaneous electrochemical cementation process between Ni and ZVI is less favoured than in the case of Cu because the standard redox potential of the couple Ni^{II}/Ni^0 is only slightly higher than that of Fe^{II}/Fe^0, consequently attribute quantitative Ni removal to adsorption, co-precipitation and adsorptive size-exclusion.

Regarding Zn, reduction by ZVI is excluded since the standard redox potential of the couple Zn^{II}/Zn^0 is lower than that of Fe^{II}/Fe^0 and therefore its removal is due to the other mechanisms activated by ZVI [22,26].

2. Materials and methods

2.1. Materials and contaminated solutions

The ZVI used in the experiments is of the type FERBLAST RI 850/3.5, distributed by Pometon S.p.A., Mestre – Italy. The material contains mainly Fe (>99.74%), with identified impurities including Mn (0.26%) and traces of O, S and C. The pumice comes from the quarries of Lipari (Aeolian Islands, Sicily, Italy), and its mineralogical composition is determined as follows: SiO_2: 71.75%; Al_2O_3: 12.33%; K_2O: 4.47%; Na_2O: 3.59% and Fe_2O_3: 1.98%; moreover it contains about 4% of bound water trapped in the pumice structure during the sudden cooling of magma and traces of other compounds (e.g. CaO, SO_3, MgO, TiO_2, FeO, MnO and P_2O_5). The two materials are characterised by uniform grain size distribution; the coefficient of uniformity (U) (i.e. the ratio between the diameters corresponding to 60 and 10% finer grain size distribution) is 2 and 1.4 for the Fe^0 and pumice, respectively. The mean grain size (d_{50}) (i.e. the diameters corresponding to 50% finer grain size distribution) is approximately 0.5 and 0.3 mm for ZVI and pumice, respectively.

The solutions used to feed the columns were obtained by dissolving, individually or in combination, copper nitrate, nickel nitrate and zinc nitrate in distilled water. Copper(II) nitrate hydrate (purity 99.999), nickel(II) nitrate hexahydrate (purity 99.999) and zinc(II) nitrate hexahydrate (purity 99.0) were obtained from Sigma-Aldrich. The concentration values used for the three contaminants were of 500 mg/l or 50 mg/l for Cu and 50 mg/l for Ni and Zn.

2.2. Column tests

Polymethyl methacrylate (Plexiglas) columns, 50 cm long with 5 cm internal diameter, equipped with several sampling ports, were used in this study. Ten column tests, five with columns containing a granular mixture ZVI/pumice with a weight ratio 30:70 and five containing pure ZVI, were carried out using solutions contaminated by either Cu, Ni or Zn, or solutions where the three metals were simultaneously present (Table 1). To allow a direct comparison of the different column tests, the ZVI amount was set at

240 g. In the columns where ZVI was used alone, since it did not fill all the space available (in fact the reactive layer was of about 3 cm), washed quartz gravel was used as filling material.

The solution was pumped, in an up-flow mode, from a single PE bottle for each solution using a precision peristaltic pump (Ismatec, ISM930), and the flow rate was maintained constant at a value of 0.5 ml/min (Darcy velocity equal to 0.38 m/day). In order to evaluate the evolution of the clogging for the ZVI/pumice mixture and for ZVI alone, during column tests the hydraulic conductivity was measured using either constant-head ($k > 10^6$ m/s) or variable-head ($k < 10^{-6}$ m/s) permeability methods [27].

In order to characterise tested systems for contaminant removal, the removal efficiency (E) and the specific removal were calculated using Eqs. (1) and 2:

$$E = M_{\text{rem}}/M_{\text{in}} \times 100 \quad [\%] \tag{1}$$

$$E_s = M_{\text{rem}}/M_{\text{ZVI}} \times 100 \quad [\%] \tag{2}$$

where M_{in} is the mass of contaminant that has flowed into the column, M_{rem} is the mass of contaminant removed and M_{ZVI} is the mass of ZVI present in the column.

2.3. Analytical method

The aqueous concentrations of Cu^{II}, Ni^{II} and Zn^{II} were measured by Atomic Absorption Spectrophotometry (AAS – Shimadzu AA – 6701F) using conventional Standard Methods [28]. All chemicals used for experiments and analysis were of analytical grade.

3. Results and discussion

3.1. Removal efficiency of Ni^{II}, Cu^{II} and Zn^{II}

Fig. 1 shows the normalised concentration (C/C_0) of the contaminants for the column tests carried out using single metal solutions, where C is the effluent concentration measured at the outlet and C_0 is the influent concentration. The experiments carried out using Cu solution (Tests A and A1) demonstrate that this metal is easily removed by both the granular mixture and ZVI, already the first sampling port (3 cm from inlet, data not shown) and for the whole duration of the test without any sign of medium exhaustion. Ni removal (Tests B and B1) is significantly less effective especially if ZVI alone is used, a fact that has been attributed [29] to a slower reaction kinetic requiring a higher residence time (contact time between contaminant and reactive medium) or equivalent barrier thickness. This is better guaranteed in the system containing the ZVI/pumice mixture (14.6 h of residence time in 50 cm of reactive medium) in respect to the pure ZVI (0.7 h of residence time in 3 cm of reactive medium) using the same amount of ZVI (240 g) in both systems.

Zn removal (Tests C and C1) is more effective than that of Ni, although breakthrough is nevertheless quite fast. The better removal of Zn in respect to Ni is attributable to higher sorption affinity that iron oxides have for Zn than for Ni [30,31]. Therefore, in mono-contaminant systems, using either the granular mixture between ZVI and Pumice or just ZVI, the removal sequence is Cu > Zn > Ni.

Fig. 2 shows Ni and Zn breakthrough curves (concentration versus time profile) for column tests with the granular mixture ZVI/Pumice and three-contaminant solutions (Test D and E) at sampling

Table 1
Experimental conditions of column tests

ID	Reactive medium	ZVI (g)	Pumice (g)	Contaminant/concentration (mg/l)	Test duration (h)
A	ZVI/pumice 30:70	240	560	Cu/500	1,694
B	ZVI/pumice 30:70	240	560	Ni/50	1,694
C	ZVI/pumice 30:70	240	560	Zn/50	2,088
D	ZVI/pumice 30:70	240	560	Cu/500–Ni/50–Zn/50	2,088
E	ZVI/pumice 30:70	240	560	Cu/50–Ni/50–Zn/50	1,488
A1	ZVI	240	–	Cu/500	1,404*
B1	ZVI	240	–	Ni/50	1,694
C1	ZVI	240	–	Zn/50	2,016*
D1	ZVI	240	–	Cu/500–Ni/50–Zn/50	600*
E1	ZVI	240	–	Cu/50–Ni/50–Zn/50	432*

*Test stopped after column clogging.

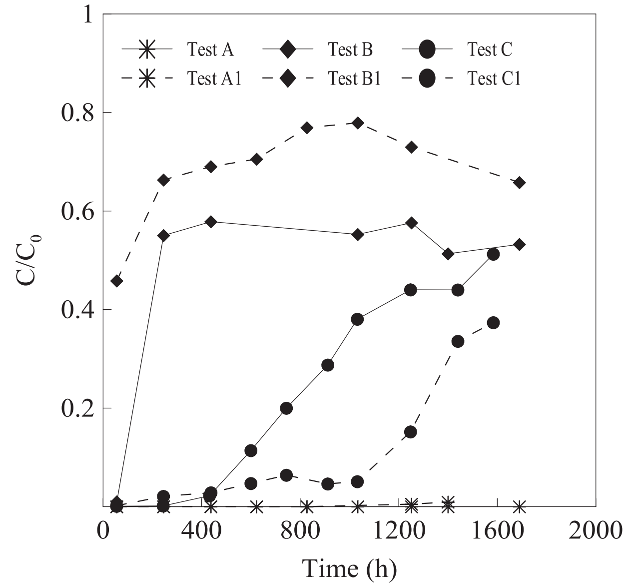

Fig. 1. Breakthrough curve at the outlet for tests A, B, C, A1, B1 and C1.

ports located, respectively, at 3 and 50 cm from inlet.

Cu data have not been reported since the breakthrough was observed only in Test D and up to the sampling port at 8 cm from inlet, instead already at 18 cm of column length at which the metal concentration is always below the concentration limit (1 mg/l) allowed by Italian regulations [32]. For Test E, Cu concentration is always below the concentration limit (1 mg/l) already at 3 cm sampling port.

As observed for single-metal solutions, Ni needs a longer residence time to be removed and breakthrough occurs already at the first sampling (Fig. 2(a) and (b)). In particular, Ni is never removed below the concentration limit (0.02 mg/l) allowed by Italian regulations. Zn is removed below the concentration limit (3 mg/l) allowed by Italian regulations only at the first sampling (after 55 h of column experiment).

In order of directly comparing the contaminants' removal for all the experiments carried out (monocontaminant and three contaminant solutions, ZVI/pumice granular mixture and pure ZVI), Figs. 3 and 4 show Ni and Zn concentrations vs. time measured at the outlet of the column for all the investigated systems. Cu data have not been reported since, as already mentioned, this metal is practically always removed below instrument's detection limit.

For tests carried out using the three contaminant solutions, the trends are similar: when using the solution containing 500 mg/l Cu, Zn removal is similar to that of Ni in the short and medium term, while using the 50 mg/l Cu one, Zn removal is higher.

In order to make a direct comparison of the long-term performance possible, Table 2 reports the removal efficiency and the contaminants mass removed calculated after 1,440 h from the beginning of the experiments for tests A-E and B1-C1, although for test A1 the presented data refer to the last sampling available (1,404 h), and experiments D1 and E1 have not been reported due to their limited duration. Table 3 presents the removal efficiency and the contaminants mass removed calculated after 432 h from the beginning of the experiment in order to have an equal amount of contaminants in input to all the columns.

For 1,440 h duration (Table 2), in the tests carried out using a three contaminant solution and a granular mixture of ZVI and pumice (tests D and E), Cu removal is unaffected by the presence of the other metals while the removal efficiencies of Ni and Zn decrease in respect to monocontaminant tests. It is nevertheless interesting that the removal efficiency reduction is higher for Zn (about 58% in respect to the experiment carried out with the solution containing Zn only) than for Ni (reduction of about 33%), thus leading to very similar removal efficiencies for Ni and Zn and for test D, to a change in the sequence that in this case is Cu > Ni > Zn.

Data presented in Table 3 confirm that Ni removal is enhanced in three contaminant systems. In fact, in three out of four cases the removal of this metal is higher than in corresponding monocontaminant ones. In the short term, experiments carried out with ZVI (experiments D1 and E1) maintain the sequence Cu > Zn > Ni, but in these cases the removal efficiencies for Ni did not diminish but increased by about 40%. Zn removal efficiencies are reduced in respect to the experiments carried out with monocontaminated solutions.

Tables 4 and 5 present the values of long-term specific removal (Es) after 432 and 1,440 h from the beginning of the experiments for all the tests and for tests A–E, respectively. Moreover, the same tables show the minimum thickness of the reactive medium (granular mixture of ZVI and pumice in weight ratio 30:70) required to reach a removal efficiency greater than 95% for Ni and Zn and greater than 99% for Cu, which is more easily removed. For Ni and Zn, the required removal level is reached with thicknesses greater than 50 cm, therefore the calculation has been made under the hypothesis that specific removal is constant along the column.

The simultaneous removal of the three contaminants (Zn 100 mg/l, Cu 50 mg/l and Ni 50 mg/l) was studied [21,22] by column experiments aimed at the treatment of artificial acid mine drainage solutions

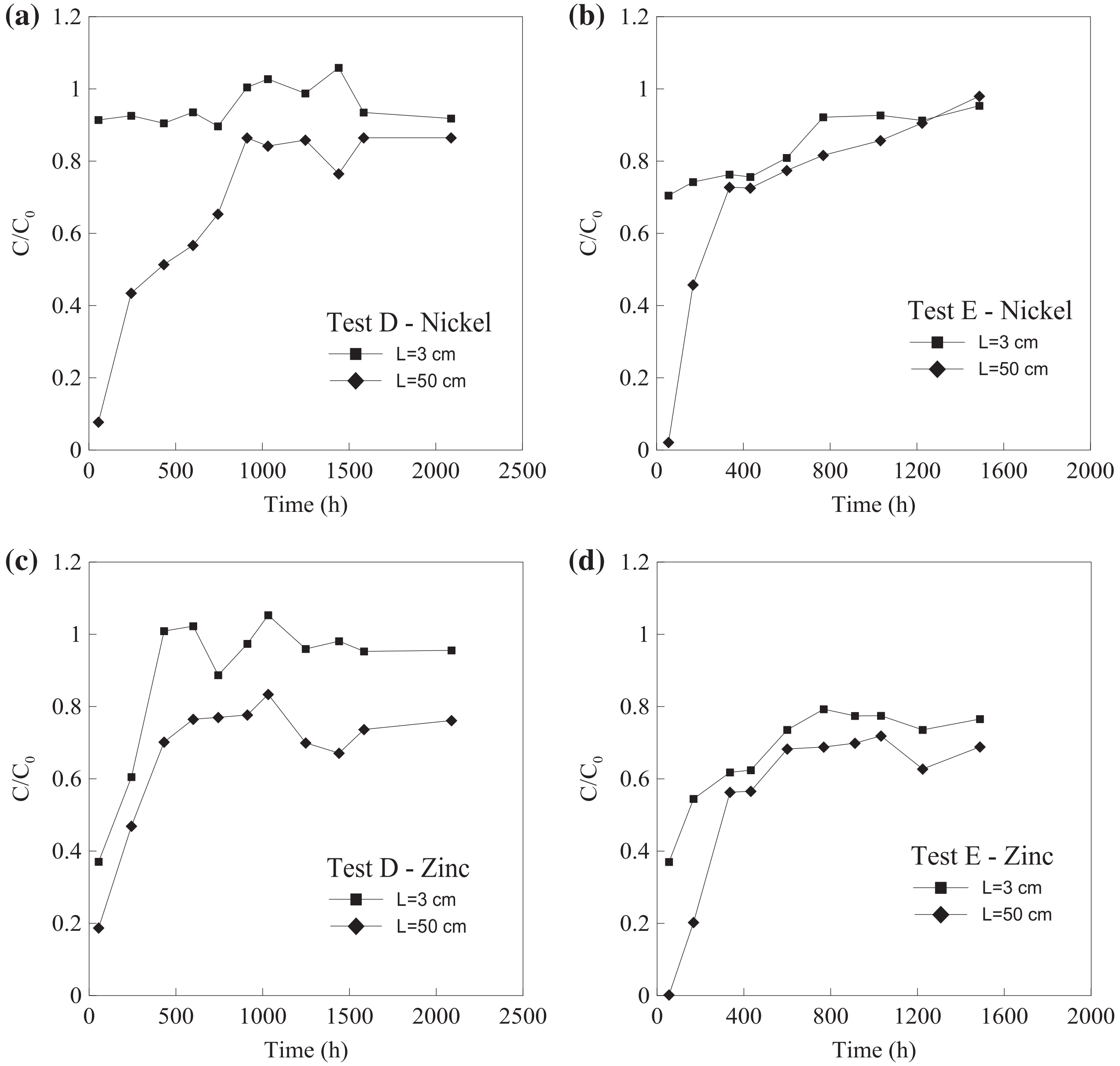

Fig. 2. Breakthrough curve versus time at sampling ports at 3 cm and 50 cm from inlet for Ni in (a) Test D, (b) Test E, and for Zn in (c) Test D and (d) Test E.

(other compounds were also present in the column's influent). In these studies, column test results basically confirmed the findings of the experiments presented in this paper for Cu and Ni but showed better Zn removal, which could be related to the different test conditions (e.g. flow rate).

The removal efficiency of Cu and Zn observed in tests D and E (Table 3) is comparable to the results obtained by [23] during their study on the removal of these metals from roof runoff. Finally, the higher Zn removal efficiency in respect to Ni is further confirmed by the results of another research carried out by batch tests [33].

The comparison of the performance in Ni removal for the column systems D–E and D1–E1 proves that the presence of Cu positively influences Ni removal, and it is possible that, especially at the beginning of the test when more virgin ZVI was available, the enrichment of the column medium in Cu due to the fast cementation of this latter [34] leads to the formation of a bimetallic system between ZVI and Cu that enhances Ni removal.

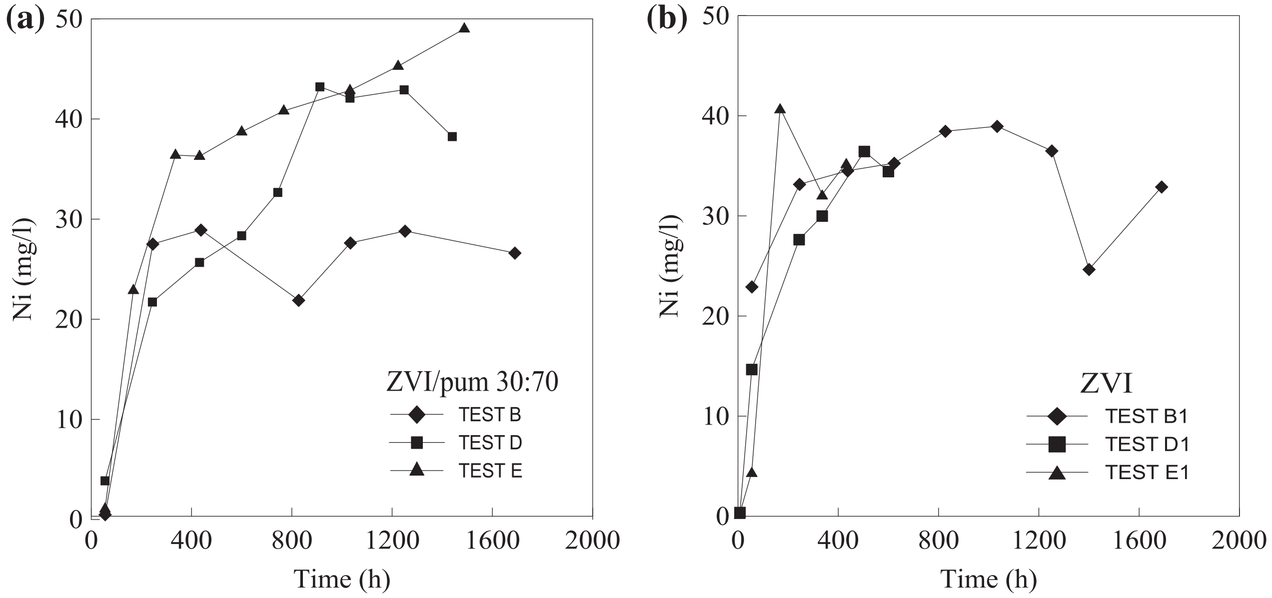

Fig. 3. Time-dependant evolution of Ni concentration in the column effluent for (a) test B-D-E and (b) B1-D1-E1.

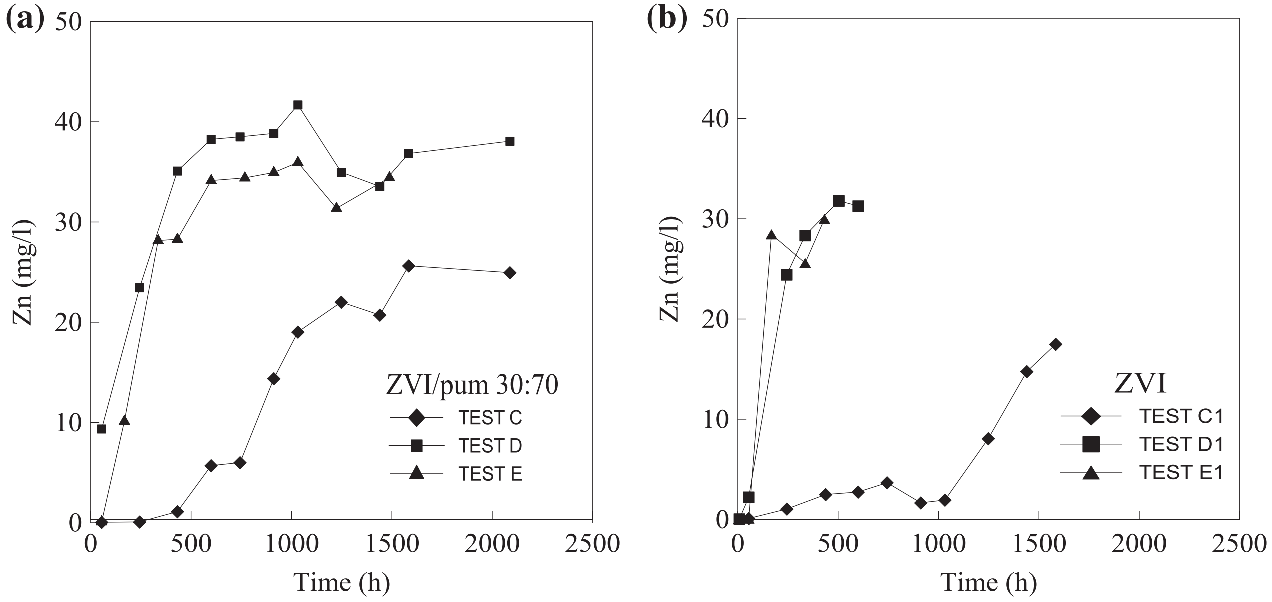

Fig. 4. Time-dependant evolution of Zn concentration in the column effluent for (a) test C-D-E and (b) C1-D1-E1.

Although literature on ZVI–Cu bimetallic systems for metal removal is scarce (the papers dealing with the removal of chlorinated solvents are more abundant), relevant information can nevertheless be found. It is reported [35] that Cu-coated ZVI (mass ratio Cu to ZVI in the range 2.5–10%) nanoparticles were more efficient in Cr(VI) removal because the self-inhibitory effect due to the formation on the ZVI surface of insulating Fe(III)–Cr(III) (oxy)hydroxide film was greatly reduced. It was also reported that coating Cu onto the surface of ZVI not only increases the deepness of the oxidation film but also increases the oxidation state of iron in the film. These results were basically confirmed by the batch experiment results reported by a different research group [36].

In the experiments presented in this paper, with reference to the tests carried out using the three contaminant solution with 500 mg/l Cu and ZVI only, the

Table 2
Removal efficiency (E) calculated for a fixed value of mass of contaminant in input into the columns (equivalent to 1,404 h of operation for test A1 and 1,440 h for tests A-E and B1-C1)

	m_i (g)			E			Mass removed (mol)			
ID	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	∑Ni+Zn
A	21.6	–	–	99.9%	–	–	3.30E−01	–	–	–
B	–	2.16	–	–	55.6%	–	–	2.05E−02	–	2.05E−02
C	–	–	2.16	–	–	80.3%	–	–	2.65E−02	2.65E−02
D	21.6	2.16	2.16	99.7%	37.2%	33.8%	3.30E−01	1.37E−02	1.12E−02	2.49E−02
E	2.16	2.16	2.16	99.8%	26.0%	43.2%	3.30E−01	9.57E−03	1.43E−02	2.38E−02
A1	21.0	–	–	99.2%	–	–	3.28E−01	–	–	–
B1	–	2.16	–	–	31.8%	–	–	1.17E−02	–	1.17E−02
C1	–	–	2.16	–	–	95.0%	–	–	3.14E−02	3.14E−02

Table 3
Removal efficiency (E) calculated at equal contaminant mass in input to the columns (equivalent to 432 h of operation)

	m_i (g)			E			Mass removed (mol)			
ID	Cu	Ni	Zn	Cu	Ni	Zn	Cu	Ni	Zn	∑Ni+Zn
A	6.5	–	–	99.9%	–	–	1.02E−01	–	–	–
B	–	0.65	–	–	60.6%	–	–	6.74E−03	–	6.74E−03
C	–	–	0.65	–	–	98.7%	–	–	9.81E−03	9.81E−03
D	6.5	0.65	0.65	99.6%	64.7%	54.9%	1.02E−01	7.16E−03	5.46E−03	1.26E−02
E	0.65	0.65	0.65	99.7%	51.3%	67.5%		5.68E−03	6.71E−03	1.24E−02
A1	6.5	–	–	99.9%	–	–	1.02E−01	–	–	–
B1	–	0.65	–	–	39.9%	–	–	4.42E−03	–	4.42E−03
C1	–	–	0.65	–	–	97.8%	–	–	9.72E−03	9.72E−03
D1	6.5	0.65	0.65	99.8%	44.1%	59.0%	1.02E−01	4.88E−03	5.86E−03	1.07E−02
E1	0.65	0.65	0.65	99.6%	49.5%	65.3%	1.02E−01	5.48E−03	6.49E−03	1.20E−02

Table 4
Specific removal (Es), calculated after 432 h of operation and corresponding minimum thickness values required to reach a removal efficiency >95% for Ni and Zn and >99% for Cu

	Es ($g_{\mathrm{cont}}/g_{\mathrm{ZVI}}$)			Barrier thickness (cm)		
ID	Cu	Ni	Zn	Cu	Ni	Zn
A	4.51E−01*			<3.0		
B		1.64E−03			78.4	
C			2.67E−03			48.1
D	1.69E−01**	1.75E−03	1.49E−03	<8.0	73.4	86.5
E	4.50E−02*	1.39E−03	1.83E−03	<3.0	92.6	70.4
A1	2.71E−02			<3.0		
B1		1.08E−03			7.1	
C1			2.65E−03			<3.0
D1	2.70E−02	1.19E−03	1.60E−03	<3.0	6.5	4.8
E1	2.70E−03	1.34E−03	1.77E−03	<3.0	5.8	4.4

*Calculated considering the mass of ZVI present in 3 cm of column length (in this experiment Cu removal is higher than 99.5% at 3 cm sampling port).

**Calculated considering the mass of ZVI present in 8 cm of column length (in this experiment Cu removal is higher than 99.5% at 8 cm sampling port).

Table 5
Specific removal (Es), calculated after 1,440 h of operation and corresponding minimum thickness values required to reach a removal efficiency >95% for Ni and Zn and >99% for Cu

	Es (g_{cont}/g_{ZVI})			Barrier thickness (cm)		
ID	Cu	Ni	Zn	Cu	Ni	Zn
A	1.50E+00*			<3.0*		
B		5.00E−03			85.4	
C			7.23E−03			59.1
D	2.49E−01**	3.35E−03	3.04E−03	18.0**	127.7	140.5
E	1.50E−01*	2.34E−03	3.89E−03	<3.0**	182.7	110.0

*Calculated considering the mass of ZVI present in 3 cm of column length (in this experiment Cu removal is higher than 99.5% at 3 cm sampling port).

**Calculated considering the mass of ZVI present in 18 cm of column length (in this experiment Cu removal is higher than 99.5% at 18 cm sampling port).

Table 6
Hydraulic conductivity determined at the end of column tests for all investigating systems

ID	Time (h)	*k* (cm/s)	ID	Time (h)	*k* (cm/s)
A	1,694	1.6E−02	A1	1,404	5.5E−07
B	1,694	3.1E−02	B1	1,694	9.9E−03
C	2,088	4.4E−02	C1	2,016*	4.7E−07
D	2,088	2.2E−02	D1	432*	2.3E−06
E	1,488	3.2E−02	E1	432*	3.0E−07

*Test stopped after column clogging.

amount of Cu coated onto Fe granules is of about 2.5–3% at the end of the experiment. For the experiment carried out using the same solution and the granular mixture ZVI/pumice, considering that Cu is mainly removed in the first 18 cm of the column (data not shown), the amount of it coated onto Fe granules is about 7–8% at the end of the experiment.

The fact that in systems D1 and E1 the sequence Cu > Zn > Ni was maintained is attributable to the limited duration of the experiments and to the fact, already mentioned, that due to the limited hydraulic residence time, Ni removal is less favoured in ZVI systems in respect to ZVI/pumice ones.

3.2. Hydraulic conductivity

The hydraulic conductivity measured at the beginning of the column tests was between 1.5×10^{-2} and 3.0×10^{-2} cm/s both using ZVI only or the ZVI pumice granular mixtures. With the exception of test B1, all the experiments carried out on column systems containing only ZVI were forcedly interrupted because of tygon tube disconnection due to the excessive pressure caused by the clogging of the reactive medium. Table 6 clearly shows how the granular mixture between ZVI and pumice is far more effective than ZVI alone in maintaining unvaried hydraulic conductivity in the long term [20]. It is also evident (experiments D1 and E1) that the use of the multicontaminant solution significantly accelerates the hydraulic conductivity reduction in the columns filled with only ZVI while negative effects have not been observed in the experiments (D and E) carried out using the ZVI/pumice granular mixture.

4. Conclusions

This paper presents the results of column tests carried out in order to compare the performance of a granular mixture between ZVI and pumice (w.r. 30:70) and of pure ZVI for the individual and combined removal of Cu^{II}, Ni^{II} and Zn^{II}.

Considering single metal solutions, the two reactive media are able to remove Cu, Ni and Zn with the removal sequence Cu > Zn > Ni, and consequently the residence time or barrier thickness in the system strictly necessary to guarantee metal removal decreases with the same sequence.

In pluricontaminant solutions the removal efficiency of Cu is virtually unaffected by the presence of the other metals while Zn and Ni removal decreases from single metal solutions to three contaminant solutions, as observed in the long term (1,404 h). In particular, using the mixture ZVI/pumice, removal efficiency reduction is higher for Zn than Ni and in one particular case where the three contaminant solution containing 500 mg/l of Cu was used, the removal sequence for the mixture ZVI/pumice changes to Cu > Ni > Zn. The use of pluricontaminant solutions significantly accelerates the hydraulic conductivity reduction in the ZVI columns (total test duration prior to column clogging was 600 and 432 h, respectively).

The superior removal of Ni observed in the three contaminant solutions, and especially in the one containing the highest Cu concentration and using the granular mixture as reactive medium, could be due to the enrichment of the reactive material in Cu. In fact, the fast cementation of the latter probably leads to the formation of a bimetallic system between ZVI and Cu that enhances Ni removal. This finding, if further confirmed, is particularly interesting since Ni removal by ZVI is quite problematic. For this reason, a research programme aimed at testing a granular mixture between pumice and copper-coated ZVI for Ni removal is in progress.

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