Conventional and innovative processes for neutral mine drainage treatment and reuse of residuals

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Abstract Characterization and treatment of neutral mine drainage (NMD) from three mines located in the "Colline Metallifere" park near Grosseto (Tuscany, Italy) is the main objective of this research. As a consequence of NMDs characteristics, the first study focused on an 'active' coagulation-flocculation-sedimentation process with jar-tests and settleability in column tests. In the second term the objective of laboratory scale trials was the treatment of NMD by slow filtration with several nonwoven fabrics. Finally, exhausted nonwoven fabric were used in slow filtration tests to verify the sorbent potential of metallic (oxy-)hydroxides for As removal from contaminated groundwater.

Key Words neutral mine drainage, coagulation-flocculation-sedimentation, slow filtration, nonwoven fabric, As removal.

Introduction

In literature there are frequent references to 'passive treatments' like alkaline producing systems, settling ponds and constructed wetlands as a viable treatment for mine drainage (MD). Because of frequent occurrence and longevity of discharge of water from mines in consequence of mineral excavation, 'passive techniques' seem to be cost-effective with respect to 'active systems'. At the same time it is necessary to respect some quite stringent design criteria (Skousen *et al.* 1998, Hedin *et al.* 1994) to passively treat MD. An often employed figure for the sizing of aerobic settling ponds and wetlands is 10 g m^{-2} d^{-1} and in the present case it seemed immediately difficult the respect of such a value because of drainages characteristics and the absence of large areas. A promising technique for the 'passive treatment' of neutral mine drainage (NMD) seems to be the vertical flow reactor designed by Sapsford *et al.* (2009). This type of reactor consist of a low footprint slow filter where the accreting ochre cake on a gravel bed perform a self-filtration and an autocatalytic effect on oxidation/precipitation of iron and manganese.

On the other hand, 'active systems' are better suited to treat large volumes of MD. These systems often require the use of large quantities of chemicals such as lime, hydrogen peroxide and sodium hydroxide to neutralize MD and promote the precipitation of metals in the form of oxides and hydroxides. Moreover, in the case of coagulation-flocculation-sedimentation process should also be dosed flocculant to facilitate the aggregation of metal (oxy-)hydroxides and the subsequent removal of flocs in sedimentation tanks. The use of these chemicals results in a significant increase of operational costs for chemicals and quantity of waste sludge produced, which in turn requires high costs for transportation and disposal in landfills.

Another concern about mining activity is the storage of waste materials from mineral processing. It often happens that scraps from sulfides processing are disposed of in piles on land and, as a consequence of tailings weathering, the aquifer is contaminated by metals and various compounds.

This study concerns the experimental activities conducted for characterization and treatment of NMD discharged from Niccioleta, Boccheggiano and Gavorrano mines located in the 'Colline Metallifere' park near Grosseto in Tuscany, Italy (Tesser *et al.* 2011). At the initial stage, experimental activities focused on the optimization of chemical dosing and reaction time to reduce costs and sludge production in the coagulation-flocculation-sedimentation process. In the second term the objective of laboratory scale trials was the NMD treatment by a modified vertical flow reactor where the filtering layer consisted of nonwoven fabrics. This device permitted to reuse exhausted nonwoven fabrics in slow filtration tests to verify the arsenic removal capacity of ferric (oxy-)hydroxides of Gavorrano NMD in the treatment of contaminated groundwater in Scarlino town near Gavorrano.

Materials and Methods

Sites and neutral mine drainages characterization

Characteristics of all sites investigated and of respective NMDs are presented in table 1. Values are average of data collected from monitoring activity of NMDs over a period of six years (from 2005 to nowadays) carried out by regional agency for environmental protection (ARPAT), Tuscany Region and Syndial Spa. Concentration of metals and sulfate exceed always or occasionally Italian regulatory limits set for reclaimed wastewater disposal

Table 1 *Site and NMDs characteristics at the points of discharge.*

Site	Niccioleta	Boccheggiano	Gavorrano
Extracted mineral	pyrite	pyrite + various sulfides	pyrite
Flow ($l\ s^{-1}$)	280	80	70
pH	6.6	7.4	6.77
ORP (mV)	102.7	247.8	-26.49
DO ($mg\ l^{-1}$)	5.5	9.0	3.61
T (°C)	16.4	17.8	33.3
Al ($mg\ l^{-1}$)	1.6	1.7	0.08
B ($mg\ l^{-1}$)	0.3	0.2	0.1
Cu ($mg\ l^{-1}$)	0.01	0.04	0.01
Fe ($mg\ l^{-1}$)	17.4	15.6	14.94
Mn ($mg\ l^{-1}$)	0.4	0.2	2.9
Sulfate ($mg\ l^{-1}$)	1082	1067.1	1457
Zn ($mg\ l^{-1}$)	0.4	1.3	0.25
Turbidity (NTU)	< 20	25 - 250	25 - 100
Colour at	none	ochre	yellow

on land or in surface water bodies.

It is important to stress that while in NMDs from Boccheggiano and Gavorrano mines flocs of ferric (oxy-)hydroxides are already formed (colour of samples are typically yellow or ochre), Niccioleta NMD is characterized by pH/ORP values which allow the iron to remain dissolved as ferrous ion Fe^{2+}. As a consequence, at the sampling time, Niccioleta NMD occurs slightly turbid and colourless and under quiescent conditions formation of (oxy-)hydroxides takes 12—24 h. This aspect was properly taken into account in carrying out laboratory scale tests.

Laboratory scale tests on physical-chemical treatment of NMD

At an initial stage, experimental activity focused on the treatment of NMD with coagulation-flocculation-sedimentation process. Several jar-test experiments were carried out using a multiple stirrer jar-test apparatus from VELP and were conducted with different concentration of flocculants and lime (this latter only for Niccioleta NMD), and different duration of coagulation, flocculation and sedimentation steps. Results of the jar-tests were evaluated in terms of turbidity, total suspended solids, iron and manganese removal. Experiments were operated at a circum-neutral pH lower than that corresponding to the zero point of charge (pH_{ZPC}), which is usually in the range 7.9 – 8.5 (Dzombak and Morel 1990, Ajmal *et al.* 1993). When $pH<pH_{ZPC}$, ferric oxides present primarily a cationic surface charge; for this reason, jar-tests were conducted using two commercial anionic polyelectrolytes (Dryfloc 203/PT and Reinflock EA 70; Tab. 2).

Table 2 *Operational conditions tested in jar-tests.*

Parameter	Unit	Range
Polyelectrolytes concentration	$mg\ l^{-1}$	0 - 10
Lime dose	$mg\ l^{-1}$	0 - 85
Duration of coagulation	min	0 - 1
Duration of flocculation	min	10 - 30
Duration of sedimentation	min	5 - 30

Once defined the best operational conditions in terms of chemicals dose and duration of coagulation/flocculation steps, some settleability tests were conducted in a plexiglass column (h=2 m, d_i=10.5 cm) fed at the bottom with flocculated NMDs using a peristaltic pump. Settleability tests were conducted with overflow velocity in the range 0.55 – 3.19 $m\ h^{-1}$.

Laboratory scale tests on NMD filtration using nonwoven fabrics

Nonwoven fabrics of mean pore size: 10, 15, 50 and 80 mm are made of high density polypropylene (PP) while nonwoven fabric of mean pore size 20 mm is made of polyester (PES). Both materials are suitable for NMD/AMD filtration because they have a degradation temperature greater than 400 °C and negligible changes in weight, strength and structure after a prolonged exposure to acidic conditions (HNO3, 1M @ pH < 2, 60 °C, 16 h). PP and PES can adsorb respectively 66.11 %wt and 76.91 %wt of water. Geotextiles can be distinguished on the basis of their structure as reported in fig. 1. While PP10, PP15 and PP50 are constituted by a thin layer coupled to a backing layer, PES20 and PP80 consist of a single coarse layer with pronounced roughness.

Filtration tests were carried out in plexiglass columns (h=2 m, d_i=8 cm) fed by peristaltic pumps. Nonwoven fabrics were placed at the bot-

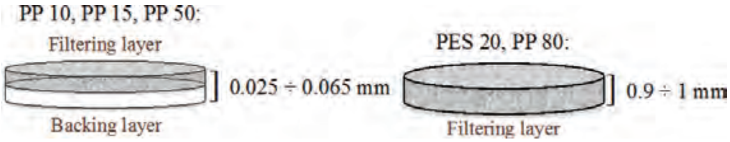

Figure 1 Nonwoven fabrics: structure and thickness.

tom of columns and filtration tests were operated in down-flow mode at a constant filtration rate (≈ 2 m d^{-1}) and variable hydraulic head difference (up to ≈ 1.5 m). At this stage, in order to shorten the duration of tests, columns were fed with a synthetic solution containing on average 56 mgFe L^{-1}, 19mgMn L^{-1}, 180 mgTSS L^{-1} and turbidity of 240 NTU, which are concentrations 4- or 5-fold higher than those of Gavorrano NMD. Feeding solution was prepared using Gavorrano NMD added with particulate matter sampled in the settling pond which collects Gavorrano NMD.

In cases of nonwoven fabrics with mean pore size of 10 and 15 µm, As removal capacity of accumulated (oxy-)hydroxides was tested. Once the maximum hydraulic head difference was reached, columns were drained and then fed with a synthetic solution with 200 µgAs(V) L^{-1}. In order to evaluate the As removal capacity of (oxy-)hydroxides, columns effluent was regularly monitored for As concentration over time.

Water sampling and analyses

Measurements of pH, ORP and temperature were carried out using a WTW pH 3310 and relative probes. Turbidity was measured using a portable Hach-Lange 2100P. Total suspended solids were evaluated according to the IRSA-CNR method (Capri *et al.* 2004). Water samples were monitored for both 'total' and 'dissolved' (after filtration at 0.45 µm through cellulose nitrate filter) concentration of metals (Fe, Mn and As). Samples were collected and acidified, and then analysed for total metals on an ICP-OES (Perkin Elmer Optima 2000 Oes DV). Permeability calculations for the ochre/nonwoven fabric bed was done by using the Darcy law.

(Oxy-)Hydroxides sampling and analyses

(Oxy-)Hydroxide samples were characterized by X-ray diffraction (XRD Bruker D8 Advance), X-ray fluorescence (WD-XRF Rigaku PrimusII) and BET (Coulter SA-3100) methods. Samples in XRD analysis were X-rayed using Cu-Kα radiation from 10° to 80° 2θ with a step size of 0.05° and a time step of 1 s or from 18° to 60° 2θ with a step size of 0.03° and a time step of 2 s. X-ray diffractograms were interpreted by comparing the 2θ-values with: reference spectra from previous studies (Das *et al.* 2011), JCPDS database and a free mineralogy database (webmineral.com). X-ray fluorescence analysis used a Rh radiation (4 kW) to conduct a standardless semiquantitative analysis (SQX-XRF) and determine the chemical percentage composition of particulate matter. Surface area measurements were determined by nitrogen adsorption fitted to the BET equation.

Results

Coagulation-flocculation-sedimentation tests

The addition of chemicals in jar-tests showed to greatly improve the removal of Fe, TSS and turbidity as jar-tests carried out with raw NMDs without chemicals addition showed no coagulation of ferric (oxy-)hydroxides. Low dosages of 0.25 – 1 mg L^{-1} (of active substance) of anionic polyelectrolyte and a flocculation time of 30 minutes allowed satisfactory iron removal rates in all studied NMDs. After 30 minutes sedimentation, drainages resulted clear and colourless and was achieved a 90 % turbidity removal and a 95 % total iron/TSS removal. In cases of Boccheggiano and Gavorrano NMDs, the best efficiency removal was achieved with the following conditions: no coagulation, 30 minutes of flocculation with 0.5 mg L^{-1} of flocculant and 30 minutes of sedimentation. Nevertheless to achieve the previous results with Niccioleta NMD, it was necessary to pre-treat samples with the addition of 80 mg L^{-1} of lime before 1 minute of rapid mixing (coagulation step) or with a fine-bubble aeration (0.3 l_{air} min^{-1} $l_{NMD}{}^{-1}$) for 1 h; in this way pH and ORP values resulted respectively equal to 8.7 and 210 mV. Sedimentation tests in column confirmed these results with comparable removal rates. Trials at fixed overflow velocity of 0.5 m h^{-1} removed ≈ 99 % of total iron and turbidity, while tests at fixed overflow velocity of 3.2 m h^{-1} removed 96 % of total iron and 87 % of turbidity on average. This suggests the coagulation-flocculation-sedimentation process as a viable treatment for investigated NMDs.

Slow filtration tests and (oxy-)hydroxides characterization

Particulate matter generated by drainage in a month and the aged one in the settling pond (in use by many years) have been characterized. XRD analysis permitted to identify amorphous 2-line ferrihydrite and more crystalline goethite/hematite respectively and consistently with previous studies (Das *et al.* 2011, Park *et al.* 2005). Chemical percentage composition of ferrihydrite (56.9 %wt Fe, 0.2 %wt Mn, 34.9 %wt O, 5.01 %wt Si, 0.045 %wt Al) resulted very similar to the one of the 'aged'

Table 3 *Fe and Mn speciation (mean values) and removal rates in slow filtration with PP15.*

	Fe				Mn		
(mg l^{-1})	IN	OUT	Removal rate (%)	(mg l^{-1})	IN	OUT	Removal rate (%)
Dissolved	0.25	0.03	87	Dissolved	10	1.44	85.6
Particulate	50.35	0.0	100	Particulate	7.8	0.01	99.9
Total	50.6	0.03	99.9	Total	17.8	1.45	91.9

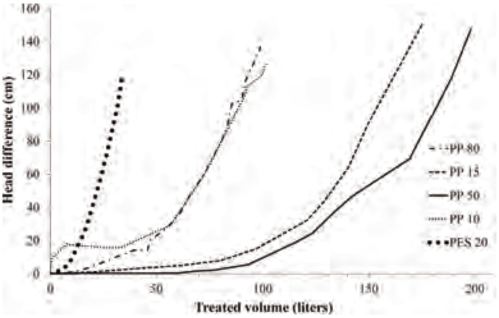

Figure 2: *Head difference vs treated volume in slow nonwoven fabric filtration tests.*

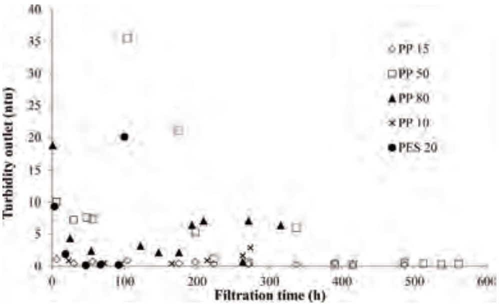

Figure 3: *Turbidity at the outlet vs filtration time in slow nonwoven fabric filtration tests.*

particulate (57.9 %wt Fe, 0.31 %wt Mn, 31.1 %wt O, 5.8 %wt Si, 1.51 %wt Al) in term of Fe and O. Whereas considering Al and Si there was a difference probably caused by contamination from clay along the influent channel to the settling pond. This fact can also explain results of BET analysis which showed that 'young' ferrihydrite has a specific surface area lower than that of 'aged' particulate (237.88 and 316.85 m^2 g^{-1} respectively). Normally amorphous 2-line ferrihydrite is expected to have a larger specific surface area (200 – 400 m^2 g^{-1}, Das *et al.* 2011) than more crystalline goethite/hematite (up to 200 m^2 g^{-1}, Cornell *et al.* 2003). However this is useful for reuse of exhausted geotextiles in As removal (Yiran *et al.* 2010).

Considering the structures of geotextiles (fig. 1), the coarse and highly rough frame of PES20 and PP80 showed the capability to incorporate hydroxides leading to a fast clogging of the filtration layer (fig. 2). Also the duration of PP10 test was limited and equal to 300 h, suggesting that the mean and most representative size of ferric (oxy-)hydroxide crystallites inside of the settling basin was closed to 10 µm. This has been confirmed by turbidity of effluent discharged which was usually closed to 0.6 NTU and anyway lower than 3 NTU (fig. 3). PP50 allowed to filter enriched Gavorrano NMD for 560 h but it has been noticed a fluctuation of turbidity and TSS at the outlet with 6.5 NTU and 1.7 mgTSS L^{-1} on average. As a consequence of these observations, it's possible to state that the best nonwoven fabric to slow filter NMD is PP15, which permitted to remove more than 99 % of turbidity, TSS and iron in a period of 486 h equal to approximately 3 months if used in situ (considering 4.5 as multiplicative factor, par. 2.3). Detailed iron and manganese removal rates are reported in table 3.

Oxidation, precipitation and subsequent physical removal of metals by the ochre bed are evident by the decrease of dissolved metals as reported in table 3. This phenomena permitted to meet Italian regulatory limits to discharge in surface water body (2 mgFe L^{-1}, 2 mgMn L^{-1}) but not the ones to discharge on land (2 mgFe L^{-1}, 0.2 mgMn L^{-1}) because of dissolved manganese. Other treated NMDs showed comparable final concentrations equal to 1.35 – 1.63 mg L^{-1} of total Mn which correspond to variable removal rates from 27.6 % to 86 % of dissolved manganese.

Analyzing data in table 4 is possible to point out the influence of (oxy-)hydroxides in slow filtration process. Calculations with clean water (K_0) and after NMD treatment (K_f) permitted to show the correlation between accumulated ochre on nonwoven fabrics and the change in permeability (K). All final permeabilities resulted of the same order of magnitude apart the one of PP20, because a massive release of entrapped solids limited the test duration.

Arsenic removal test

Column operations were carried out by passing arsenic solution with a flow rate of 5.8 ml min^{-1} (2 m^3 m^{-2} d^{-1}) by a peristaltic pump. Feeding solution was provided for 2 cycles up to the maximum storage capacity of the column and the break-

Table 4 *Permeability of nonwoven fabrics before (K_0) and after NMD treatment (K_f).*

Nonwoven fabric	PP10	PP15	PP20	PP50	PP80
K_0 (mm min^{-1})	-	0.787	5.18	1.29	7.71
K_f (mm min^{-1})	6,61E-04	2,41E-04	1,14E-03	5,59E-04	9,49E-04

through curve (Fig. 4) was obtained by plotting C/C_0 against bed volumes (BVs). It was observed that PP15 capacity is ≈ 600 BVs less than the PP10 capacity, this may be due to larger size of pores and/or different composition of collected (oxy-)hydroxides. Arsenic concentrations in the PP10 effluent never rise up to significant values: for instance, As(V) remains below 20 µg L^{-1} for longer than 1600 BVs treated.

Conclusions

Laboratory tests permitted to identify the coagulation-flocculation-sedimentation process with the addition of anionic polyelectrolyte as a viable treatment for neutral mine drainages with high flow rates and large amounts of iron. However a further research at pilot plant scale is needed to verify the high removal rate of iron and total suspended solids in general.

Slow filtration of neutral mine drainages with nonwoven fabrics showed interesting capabilities in capturing ferric (oxy-)hydroxides. The accreting ochre bed on the top of the geotextile catalysed oxidation/precipitation of dissolved iron and manganese and permitted a consequent physical removal of the two metals. This treatment can be used alone or to refine the metals abatement showed by coagulation-flocculation-sedimentation process.

After NMDs filtration, ferric (oxy-)hydroxides (primarily goethite and hematite) on exhausted nonwoven fabrics showed the capability to remove arsenic from contaminated waters through adsorption in slow filtration treatment. Further research is required to investigate the sorbent potential in a pressure filter.

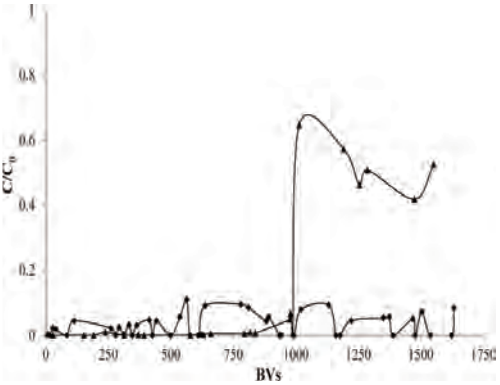

Figure 4 *Breakthrough curves of As(V) on exhausted geotextiles: PP15(triangle), PP10 (square).*

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