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ORIGINAL PAPER

Potential of anthracite, dolomite, limestone and pozzolan as reactive media for de-icing salt removal from road runoff

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Abstract De-icing salt (NaCl) application is a common practice during winter road maintenance in northern countries, compromising ecosystem services. Ecoengineering facilities, including reactive filter beds, are becoming an effective strategy for road runoff management. Different materials (anthracite coal, dolomite, limestone, and pozzolan) were tested as reactive media of filter beds. Characterization showed that dolomite has the best physical properties (resistance to fragmentation, porosity) for filter bed construction and maintenance, followed by limestone. NaCl removal efficiency was investigated in batch at different concentrations (150–5000 mg L^{-1} Cl). Removal efficiency substantially varied depending on the element (Cl or Na), the material, and the added NaCl concentration. At the lowest NaCl concentration, Cl removal was higher onto anthracite (48 %) and dolomite (59 %); but greater Na removal was reached onto limestone (54 %) and pozzolan (67 %). At higher concentrations, Cl removal was similar (anthracite), decreased (dolomite), or increased (limestone, pozzolan); and Na removal increased (anthracite) or decreased (dolomite, limestone, pozzolan). Parallel experiments at 4 °C showed lower NaCl removal, anthracite being the most efficient. Practical applicability was evaluated in columns using synthetic runoff solution (NaCl and metals). NaCl removal efficiency was much lower in column assays with respect to batch. The highest NaCl removal was reached onto dolomite, followed by limestone. Metals were successfully removed, generally remaining over time in a wide range (41–89 % Cd, 78–97 % Ni, 44–88 % Cu, and 3–83 % Zn) depending on the material, being pozzolan the least efficient. Further studies including a combination of materials would be of high interest.

Keywords Adsorption · Filter beds · Geomaterials · Highway pollution · NaCl · Surface water · Trace metals

Introduction

Anthropogenic salinity is a global and growing threat causing severe biodiversity losses and compromising the ecosystem goods and services provided by freshwater and soil. The application of de-icing salts, primarily NaCl, has become a common practice in northern countries in order to carry out winter road maintenance. Most of the salts are transported by projection and splash, nebulization, wind transport, and/or runoff during rainfall events and snow melting periods (Blomqvist 2001), affecting: surface water (density, electrical conductivity), groundwater (polluting potential drinking water sources), soil (aggregate stability, organic matter dispersion, infiltration), and biodiversity (Green et al. 2008; Dai et al. 2012). There is also the additional risk of increasing the mobility of other pollutants found in roadside soils, such as trace metals primarily by the formation of chlorocomplexes (Bäckström et al. 2004; Rasa et al. 2006).

Ecoengineering facilities are becoming a widespread practice for road runoff pollution management. These facilities employ and amplify natural processes for

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removing pollutants (de-icing salts, trace metals, hydrocarbons) through a treatment chain consisting of several units including constructed wetlands (CW), detention basins (DB), and underground reactive filter beds (FB). They have proved to be techno-economically feasible, energy efficient, and environmentally sensitive (Jiang et al. 2014). Nonetheless, while most of the studies on road runoff treatment are aimed at removing metals and polycyclic aromatic hydrocarbons (PAH) (Tromp et al. 2012), those targeted to the removal of de-icing salts are remarkably scarce (Rémi et al. 2013). In Quebec, a treatment chain consisting of a free water surface-flow CW (multiculture planting) in parallel to an underground reactive FB (80 % limestone, 20 % dolomite), and preceded by a DB, was constructed with the aim of treating de-icing salted runoff from A40 Highway (Morteau et al. 2008; Guesdon et al. 2013; Galvez-Cloutier et al. 2014). The authors showed that: (1) the global system successfully removed high NaCl amounts from collected road runoff; (2) NaCl was successfully removed by the CW during summer season, while removal rates decrease after storm events; and (3) NaCl was efficiently removed by the FB during and after medium and high precipitations. Hence, results proved the seasonal improvement of using FB as a first or second line to CW for de-icing salted runoff entering the treatment chain.

Reactive media of FB include material(s) ideally fulfilling one or more of the following characteristics: natural, unmodified, locally available, economic (low cost), physicochemically stable, resistant to fragmentation and dissolution, and efficient for removing a wide range of salts often present in road runoff (primarily de-icers and metals) (Morteau et al. 2008; Barral et al. 2014). Different materials have been proposed (alone or in combination) to remove from road runoff: PAHs and trace metals including gravel, sand, zeolite, vermiculite, granular activated carbon, and peat (Fuerhacker et al. 2011); and de-icing salts including limestone and dolomite (Galvez-Cloutier et al. 2014). Given the limited number of studies aiming at de-icing salt removal, sorption experiments comparing different candidate materials are required. Among coals, anthracite is interesting for its abundance and microporous structure (Kim et al. 2003). It is a hard and compact material with lesser impurities than other similar mineral coals and has recently showed high removal efficiency of pollutants such as nitrobenzene and its derivatives (Parham and Saeed 2013). Carbonate rocks such as dolomite and limestone have been reported as effective candidate materials for removing a wide range of pollutants (both cations and anions): trace metals (Albadarin et al. 2012; Sdiri et al. 2012), iron (Aziz et al. 2004), phosphorus (Karaca et al. 2004; Mateus et al. 2012) and sulphate (Silva et al. 2012). Natural pozzolan is a black or red igneous rock whose porosity and cellular texture confers a high potential retention capacity. Pozzolan has been traditionally employed as building material (in cement and concrete), but it has revealed high suitability for removing Cl ions (Al-Rawajfeh et al. 2013) and chlorinated benzenes (Cottin and Merlin 2010).

The aim of this study was to comparatively analyse the NaCl removal capacity of four candidate materials (anthracite coal, dolomite, limestone, and pozzolan). The sorption of Cl and Na onto materials from aqueous solution was investigated in batch experiments. Some experiments were also carried out at 4 °C. The practical applicability was experimentally tested under dynamic conditions in columns using a synthetic runoff solution including NaCl and trace metals (Cd, Cu, Ni, and Zn). The potential displacement of trace metals by NaCl was specifically discussed.

This research is part of a larger project conducted from 2011 to 2014. The selection and characterization of materials were performed from autumn 2012 to summer 2013 at Laval University (Canada), in collaboration with Autoroute du Sud de la France Company (France). The sorption experiments, in batch and columns, were conducted between autumn 2013 and summer 2014 on laboratory scale at Laval University.

Materials and methods

Materials tested

The reactive media we tested (hereafter referred as materials) were chosen based on five criteria: (1) potentially efficiency for removing NaCl and trace metals, (2) availability for sale, (3) economic (low cost), (4) physicochemically stable with a minor impact on ecosystems, and (5) natural and unmodified. Materials were supplied by Autoroute du Sud de la France Company and included: anthracite coal (Baldoyra coal, Eastern Pyrenees, France), dolomite (SRC, Gard, France), limestone (SMW Delorme, Orgon, Bouches-du-Rhône, France), and pozzolan (Ardechoise quarry, Ardèche, France) (Fig. 1). Materials (~20 kg each, 20–50 mm) were washed in abundant tap water to remove fine particles after which they were air-dried (7 days) in all cases, and further oven-dried (105 °C, 24 h) in the case of pozzolan. Then, each material was well homogenized and characterized (resistance to fragmentation, porosity, surface area, point of zero salt effect, and cation and anion exchange capacity), and sorption experiments in batch and columns were performed. Mineralogical composition of materials has been previously described (Guesdon and Galvez 2012). Briefly, materials showed a high purity: anthracite coal (95 % $C_{240}H_{90}O_4NS$; 5 %

Fig. 1 Materials tested as reactive media: anthracite coal (**a**), pozzolan (**b**), dolomite (**c**), and limestone (**d**)

ankerite Ca(Fe, Mg, Mn)$(CO_3)_2$), dolomite (98 % $CaMg(CO_3)_2$), and limestone (100 % $CaCO_3$). In the case of pozzolan, 44 % augite, (Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)$_2$O$_6$, 20 % olivine, (Mg, Fe)$_2$SiO$_4$, 19 % nepheline, (Na, K)AlSiO$_4$, and 9 % anorthite, (Ca, Na)(Al, Si)$_2$Si$_2$O$_8$, were predominant.

Sorption experiments

The use of fine particle size often generates big issues of hydraulic obstruction and clogging (Vohla et al. 2011). Hence, to simulate more realistic conditions extrapolated to full-scale FB systems, a 20–50-mm particle size was used for sorption experiments.

Sorption curves: batch assays

Isotherm assays were carried out in batch with NaCl as sorbate and the four materials (anthracite coal, dolomite, limestone, and pozzolan) as sorbents. All of the experiments were carried out in duplicate. Each material (200 g) was placed in 1000 mL-polypropylene bottles with 500 mL (1:2.5 w/v) of NaCl aqueous solution containing 0 (control), 150 (C_1), 1500 (C_2), 3000 (C_3), or 5000 (C_4) mg L^{-1} of Cl. The bottles were shaken in a Mid-Range Reciprocal Shaker for 4 h (Eberbach Shaker) at 260 ± 13 oscillations per minute (opm) at a temperature of 22 °C, according to previous studies (Galvez-Cloutier and Michaux 2013). Supplementary isotherm assays were performed in a cold chamber at a constant temperature of 4 °C with anthracite coal and dolomite, considering their greater potential based on the results at 22 °C and the characterization assays. Both the materials and the solutions were placed in the cold chamber 24 h before the experiment. At the end of the mixing period, the solutions were filtered under vacuum (0.45-µm-pore-size cellulose ester membrane filter, Advantec Inc.). The filtrate was: (1) frozen for Cl quantification; or (2) acidified to pH 2 by adding the necessary volume of concentrated HNO_3 and kept at 4 °C for Na quantification.

Removal efficiencies (%) were calculated by the following Eq. 1:

$$\text{Removal} = \left(\frac{C_i - C_e}{C_i}\right) \times 100 \tag{1}$$

where C_i and C_e are the initial (before removal) and equilibrium (after removal) Cl or Na concentrations in solution (mg L^{-1}), respectively.

Sorbed Cl and Na concentrations (q_e; mg g^{-1}) were calculated by the following mass balance relationship (Eq. 2):

$$q_e = V\frac{C_i - C_e}{W} \tag{2}$$

where C_i and C_e are the initial and equilibrium Cl or Na concentrations in solution (mg L^{-1}), respectively, V is the volume of the solution (L), and W is the mass (g) of the material. The equilibrium sorption data were fitted into the isotherm models of Langmuir (Eqs. 3 and 4) and Freundlich (Eq. 5), represented, respectively, by the following equations:

$$\frac{q_{\mathrm{e}}}{q_{\mathrm{e}}^{0}} = \frac{K_{\mathrm{L}}}{1 + K_{\mathrm{L}} C_{\mathrm{e}}} \tag{3}$$

$$R_{\mathrm{L}} = \frac{1}{1 + \left(1 + K_{\mathrm{L}} q_{\mathrm{e}}^{0}\right)} \tag{4}$$

$$q_{\mathrm{e}} = K_{\mathrm{F}} C_{\mathrm{e}}^{\frac{1}{n}} \tag{5}$$

where K_{L} and K_{F} are constants that depend on the type of material and the chemical species; q_{e}^{0} is the maximum sorption capacity (mg g^{-1}) of the solid in the Langmuir model (Barral et al. 2014); $1/n$ is a heterogeneity parameter in function of the strength of the sorption process.

Nonlinear regression was performed using a trial and error method with the help of solver add-in functions of Microsoft Excel software. In the trial error procedure, isotherm parameters were determined by maximizing the values of the coefficient of determination (Karadag et al. 2007).

Multipollution scenario: column assays

Duplicate transparent vertical *Plexiglas* columns (12 cm internal diameter; 32 cm long) were packed with each of the four materials to a height of 12.5 cm. In order to simulate the filling process that would occur in a FB in the field, the materials were released from the top of the column at one time until reaching 12.5 cm height. Vertical columns were fed upwards from their base with synthetic runoff solution at a 4.5 mL $\min^{-1}$ continuous up-flow maintained by a peristaltic pump (Model. 7553-80, Cole-Parmer Instrument Company, IL, USA) in closed atmosphere. The flow rate of 4.5 mL $\min^{-1}$ allowed a retention time of about 2.5 h (Galvez-Cloutier and Michaux 2013), in line with the 2-h minimum retention time recommended for FBs (Morteau et al. 2008). The synthetic solution included NaCl at 150 mg Cl L^{-1} (C_1 level) and a mixture of trace metals (Cd, Cu, Ni, and Zn). Metals were added using chloride ($CdCl_2$) or sulphate salts ($CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 6H_2O$, $ZnSO_4 \cdot 7H_2O$) in aqueous solution at 2 Cd, 20 Cu, 3 Ni, and 300 Zn μg L^{-1} in order to simulate a multipollution scenario as typically reported in road runoff (Wong et al. 2000; Galvez-Cloutier and Michaux 2013). At different time intervals (0, 15, 30, 60, 90, 120, 180, 240, 360 min, 1, 2, 3, 5, 7, 10, and 20 days), 50 mL of both the input (reservoir) and the output solutions (top of the column) was recovered. The collected solutions were filtered under vacuum (0.45-μm-pore-size filter, Swinnex 25, Millipore Inc.) and treated for storing until analysis as described above. For each time, pH values and concentrations of Na, trace metals (Cd, Cu, Ni, and Zn), and major anions (Cl^-, HCO_3^-, CO_3^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) were measured. Visual Minteq v.3.0 computer program (Gustafsson 2011) was used to predict chemical speciation in the solutions. The database that comes by default in the Visual Minteq program was used. The pH values and concentrations (mg L^{-1}) of Na, trace metals, and major anions were used as input data, simultaneously entered into the code for each individual solution.

Analytical methods

Resistance to material fragmentation at two particle sizes (6.3–10 and 10–14 mm) was determined following the norm NF P 18-574 (AFNOR 1990), and dynamic fragmentation coefficient (DF) was calculated. Porosity was measured by gas pycnometry: envelope and skeletal volumes were obtained by means of a powder and helium pycnometers, respectively (Quantachrome Inc.). Surface area was determined by the methylene blue method (Santamarina et al. 2002). Bulk density was measured by dipping M g of material in a known volume of water (V ml) and was expressed as the M-to-final V ratio. Materials were ground (Fritsch Pulverisette) and passed through a 400-μm sieve. Then, point of zero salt effect test (PZSE) and cation (CEC) and anion exchange (AEC) capacities were determined by long equilibrium time method and 0.5 mol L^{-1} ammonium nitrate methods, respectively (Pansu and Gautheyrou 2006).

In the solutions collected from batch and column assays, concentration of anions (Cl^-, HCO_3^-, CO_3^{2-}, NO_2^-, NO_3^-, PO_4^{3-}, and SO_4^{2-}) was quantified by high-performance liquid chromatography-HPLC (1525 Binary HPLC Pump System, Waters Inc.); Na by flame emission atomic spectroscopy-EAS; Zn by flame absorption atomic spectroscopy-AAS (AA240FS, Varian Inc.); and Cd, Cu, and Ni by graphite furnace AAS with Zeeman background correction (AA240Z, Varian Inc.). Detection limit in μg L^{-1} was: Cd = 0.01, Pb = 0.2, Na = 2, Ni = 0.24, Zn = 10, Cl = 25, HCO_3 = 50, CO_3 = 50, NO_2 = 50, NO_3 = 75, SO_4 = 75, PO_4 = 125. All chemicals and reagents were analytic grade from Fisher Scientific Inc. (Canada) and EMD Chemicals Inc. (USA). All glassware used was rinsed with nanopure water (Ultrapure Water System, Barnstead Nanopure).

Statistical analyses

Significance of differences of Cl and Na removal efficiency by materials among NaCl levels (C_1, C_2, C_3, and C_4) was investigated by means of one-way analysis of variance (ANOVA) using a post hoc test (Tukey). Before performing the ANOVA test, a Levene's test was performed to analyse the homogeneity of variance. These analyses were made using the Statistical Package for the Social Sciences v.17 (SPSS Inc.) software. Graphics were created using GraphPad Prism v. 6.01 software (GraphPad Inc.).

Results and discussion

Characterization of materials

Ensuring the resistance of materials is essential to maximize its effectiveness during underground reactive FB construction and maintenance (transport, installation, compaction, and replacement of materials). Resistance of materials to fragmentation gives an idea of its sensitivity to changes in its particle size, which could lead to clogging and then losses in filtering properties. In this regard, dynamic fragmentation coefficient (DF) is a good indicator of the material sensitivity to a mechanical impact, the lower DF the greater resistance to fragmentation. As shown in Table 1, similar DFs were obtained for dolomite, limestone and pozzolan (~28 %). Anthracite coal showed the highest DF (about twice) which evidences its lower fragmentation resistance. Higher material porosity provides greater hydraulic conductivity but also determines the amount of water that can be retained by materials. Hence, increased porosity may enhance fragmentation in the medium and long term during hot–cold, wet–dry and freeze–thaw cycles. Pozzolan showed the largest porosity (57 %), consistent to previously reported (Cottin and Merlin 2010), followed by limestone (22 %), and ultimately by dolomite (4 %). So it can be inferred that dolomite presents the best physical properties for minimizing fragmentation processes, followed by limestone. Anthracite coal porosity could not be measured, but it is expected to be quite high, ~50 % (Wang et al. 2009).

Porosity was positively related to the surface area and negatively to bulk density (Table 1), as often observed (Prochaska and Zouboulis 2006). Hence, anthracite coal showed the highest surface area, according to literature (Jiang et al. 2014), followed by pozzolan, suggesting a greater sorption capacity. Surface area values per unit of mass of material were lower than those obtained by other authors (Toprak and Kopac 2011). Most studies employ a particle size far below, between 0.02 and 10 mm (Vohla et al. 2011). The low surface area of materials in the present study is consistent with the selected larger particle size (20–50 mm). This may involve that some of the interior pores could be unapproachable by the Cl and Na ions (Albadarin et al. 2012) and thus lower removal efficiency than in other studies is expected. Surface area and porosity were positively related to cation exchange capacity (CEC). CEC determines ion sorption ability by complexation, ion exchange, and precipitation (Bradl 2004). The highest CEC was measured in pozzolan, followed by anthracite coal; being five and three times more, respectively, than the lowest (dolomite). Anion exchange capacity (AEC) was very low for anthracite coal and lower than the quantification limit (0.05 cmol_ kg^{-1}) for dolomite, limestone, and pozzolan, maybe due to the fact that the method used in this study is rather conceived for soils (Pansu and Gautheyrou 2006). Indeed, according to the point of zero salt effect (PZSE) test, material surfaces have an acidic character (Table 1) which confers AEC, higher in the cases of dolomite and anthracite coal.

NaCl removal efficiency

As shown in Fig. 2, removal efficiency substantially varied depending on the nature of the element (Cl or Na), the material (anthracite coal, dolomite, limestone, and pozzolan) and the added NaCl concentration ($C_1 = 150$; $C_2 = 1500$; $C_3 = 3000$; and $C_4 = 5000$ mg L^{-1} Cl).

Removal of Cl

Anthracite coal and dolomite removed Cl more efficiently (48 and 59 %, respectively) than the other materials (Fig. 2a) at the lowest added NaCl concentration (C_1 level), consistent with their higher PZSE (anthracite and dolomite) and AEC values (anthracite) (Table 1). At higher added NaCl concentrations, it was observed that Cl sorption capability of materials was not always related to the measured material properties (the same observation was done for Na sorption). In such conditions, NaCl sorption is likely to be modulated by the combined action of the material properties and experimental factors (NaCl initial concentration, temperature, etc.).

Table 1 Characteristics of materials

Material	DF (%)		Porosity	Surface area	Bulk density	PZSE	CEC	AEC
	6.3–10 mm	10–14 mm	%	(10^4) $\mathrm{m^2\ g^{-1}}$	$\mathrm{g\ cm^{-3}}$		$\mathrm{cmol_+\ kg^{-1}}$	$\mathrm{cmol_-\ kg^{-1}}$
Anthracite coal	54	50	NM	1.67	1.56	9.04	1.38	0.08
Dolomite	28	27	4	0.85	3.08	9.19	0.41	<0.05
Limestone	27	31	22	0.92	2.84	8.72	0.54	<0.05
Pozzolan	26	28	57	1.19	2.19	8.61	2.25	<0.05

DF Dynamic fragmentation coefficient, *PZSE* point of zero salt effect, *CEC* cation exchange capacity; *AEC* anion exchange capacity, *NM* not measured

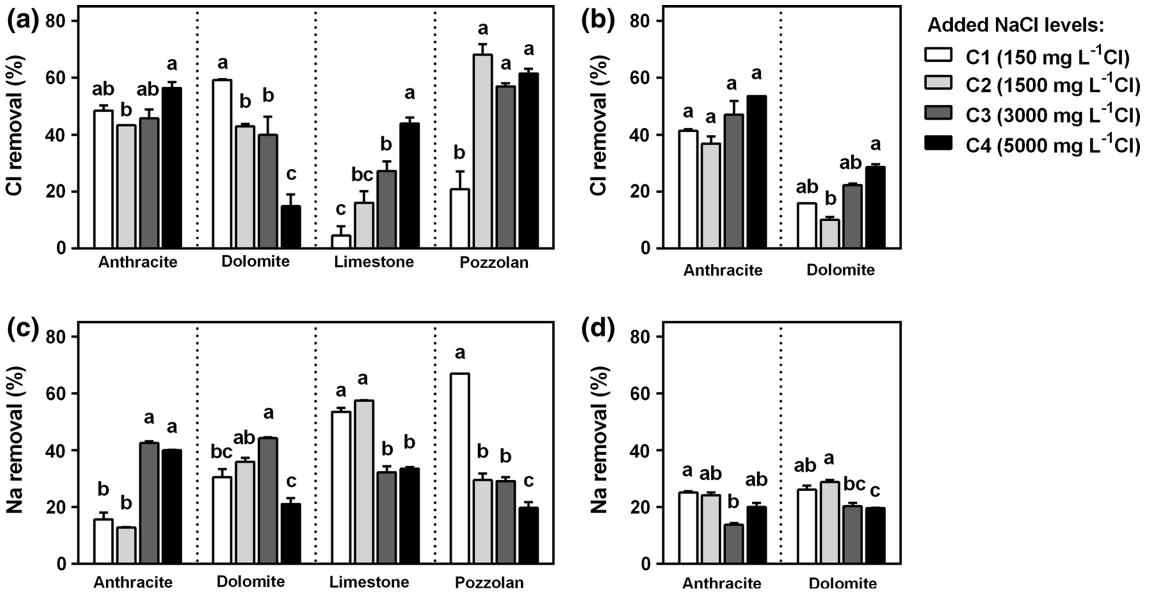

Fig. 2 Removal efficiency of Cl (**a**, **b**) and Na (**c**, **d**) in batch assays onto anthracite coal, dolomite, limestone, and pozzolan from aqueous solution at C_1, C_2, C_3, and C_4 levels (150, 1500, 3000, and 5000 mg L^{-1} Cl, respectively) at 22 °C (**a**, **c**) and 4 °C (**b**, **d**). *Different letters indicate* significant differences among levels at $p < 0.05$ after one-way ANOVA

At C_2, C_3, and C_4 levels, Cl removal onto anthracite coal remained almost constant (ranging from 43 to 56 %) and showed no linear relation to the added NaCl level. This may confer a good efficiency following pulses of high salinity often occurring during storm events. In the case of dolomite, Cl removal efficiency was satisfactory but negatively related to the added NaCl level: 59 % (C_1) > 43 % (C_2) = 40 % (C_3) > 15 % (C_4). At 4 °C (Fig. 2b), and lower efficiency was found on dolomite (ranging from 10 to 29 %) with respect to that observed at 22 °C while was similar on anthracite coal (37–54 %). So it can be inferred that effectiveness of dolomite for Cl removal may be reduced during winter season, but satisfactory in the case of anthracite coal. Low and very low Cl percentages were removed onto pozzolan (21 %) and limestone (4 %) at C_1 level. Nonetheless, removal efficiency increased with rising the added NaCl concentration. Thus, at C_2 to C_4 levels pozzolan showed the highest Cl removal efficiency (from 61 to 68 %), with values consistent to those previously reported (Al-Rawajfeh et al. 2013), followed by limestone (from 16 to 45 %). Al-Rawajfeh et al. (2013), studying Cl sorption onto pozzolan, argued that at low added NaCl concentrations, Cl sorption may be independent of the added NaCl concentration because of number-of-ions to available-surface-area ratio is low. However, at higher added NaCl concentrations the available sorption sites decreases, which may explain the Cl sorption becomes dependent on the initial concentration.

Experimental data (expressed in mg g^{-1}) at 22 °C were described using Langmuir and Freundlich sorption isotherm models (Fig. 3). Isotherm constants and regression coefficients, obtained by nonlinear regression, are reported in Table 2. Freundlich was the model that best fit the sorption data on anthracite coal, limestone, and pozzolan, but Langmuir on dolomite (Table 2). The goodness of fit (expressed by the coefficient of determination, R^2) was generally satisfactory, being poor for dolomite. The two models, Freundlich and Langmuir, fit well in the case of Cl sorption onto anthracite coal and pozzolan. The Freundlich $1/n$ parameter indicates the strength of the sorption process. Values of $1/n$ for Cl showed that on anthracite coal, limestone, and pozzolan a cooperative sorption is likely to occur, revealed by S-isotherms, in which solute–solute forces are stronger than those between solute and substrate (Giles et al. 1974). Values of the R_L Langmuir equilibrium parameter were in the range of $0 < R_L < 1$ which indicates a favourable sorption process. The Langmuir parameter of q_e^0 is the upper limit for q_e and represents the maximum sorption of the ion determined by the number of reactive surface sorption sites (Bradl 2004). The q_e^0 values for anthracite coal, limestone, and pozzolan were in the range of 55 and 98 mg g^{-1}, in agreement with the literature (Lv et al. 2009).

Removal of Na

Anthracite coal showed the lowest Na removal efficiency at C_1 and C_2 levels (~15 %) (Fig. 2c), contrary to what was expected by its high CEC (Table 1), but increasing up to 43 % at C_3 and C_4 levels. Conversely, Na removal efficiency onto dolomite, limestone, and pozzolan was generally lower when rising the added NaCl concentration.

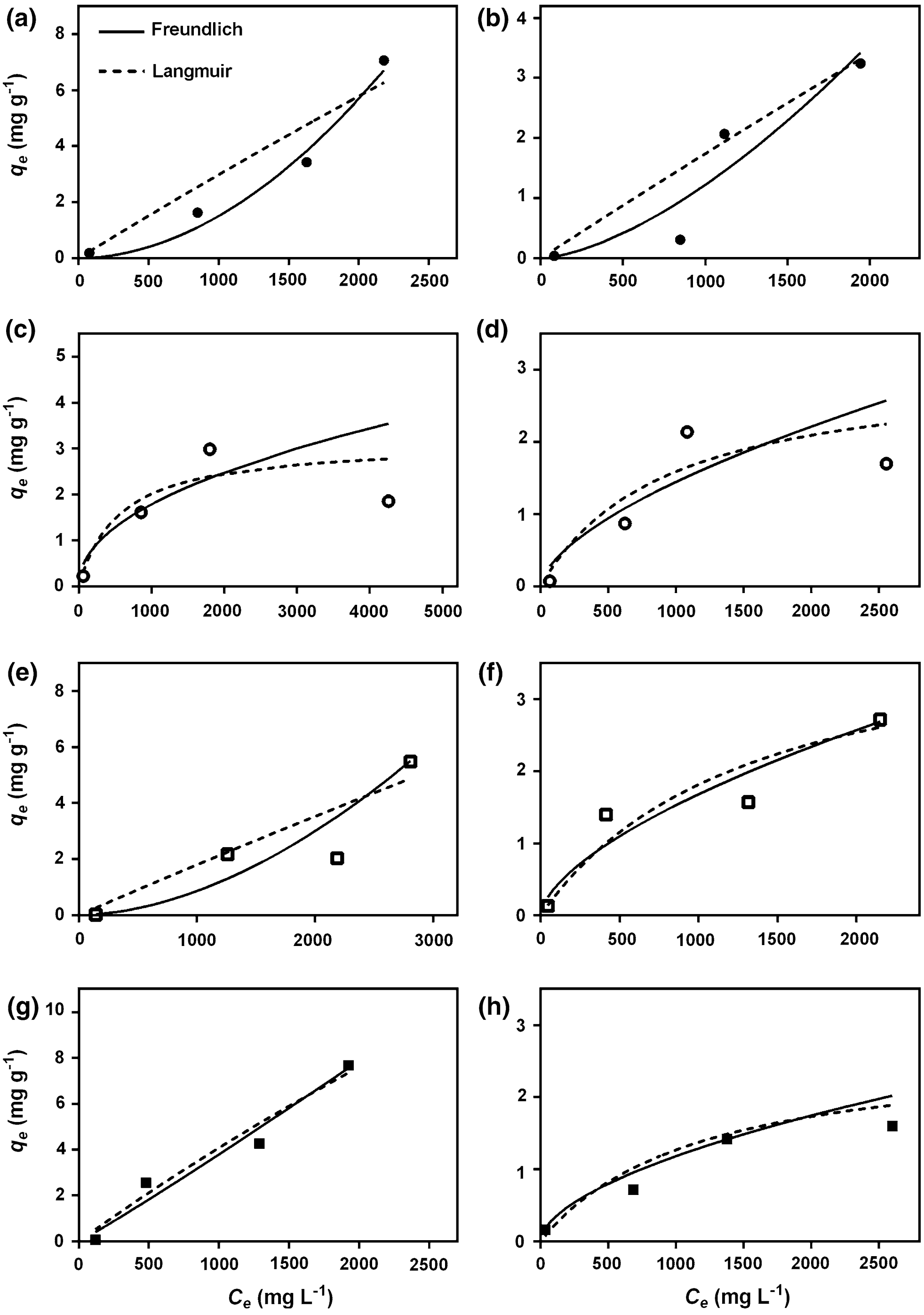

Fig. 3 Freundlich and Langmuir sorption isotherm modelling of Cl (**a**, **c**, **e**, **g**) and Na (**b**, **d**, **f**, **h**) onto anthracite coal (**a**, **b**), dolomite (**c**, **d**), limestone (**e**, **f**), and pozzolan (**g**, **h**) at 22 °C using nonlinear regression analysis. *Symbols* show the experimental data for each material: anthracite coal (*filled circle*), dolomite (*circle*), limestone (*square*) and pozzolan (*filled square*)

Thus, although Na was successfully removed onto pozzolan at C_1 level (67 %), Na removal decreased up to threefold at C_4 level (20 %). Regarding dolomite, 31–44 % of Na removal efficiency was accounted at C_1, C_2, and C_3 levels, decreasing to 21 % at C_4 level. About 55 % of Na was removed onto limestone at C_1 and C_2 levels for then decreasing by half at C_3 and C_4 levels (~33 %). Dissolution processes due to stirring of materials with NaCl solution in batch are likely to occur which involves the partial destruction of mineral networks and the dissolution of some ions present in minerals (Barral et al. 2014). This would allow Na ions to be more strongly sorbed, probably by coprecipitation processes (Okumura and Kitano 1986). At very high added NaCl concentrations (as in C_4 level), Na removal efficiency may be highly affected due to the possible saturation of sorption sites and electrostatic repulsion which deserves further study. At 4 °C (Fig. 2d), the Na removal efficiency onto anthracite coal and

Table 2 Langmuir and Freundlich nonlinear isotherm constants and regression coefficients for Cl and Na (NaCl levels from 150 to 5000 mg L^{-1} Cl) onto anthracite coal, dolomite, limestone, and pozzolan

Element	Model	Parameter	Anthracite coal	Dolomite	Limestone	Pozzolan
Cl	Langmuir	q_e^0 (mg g^{-1})	98.559	3.139	93.795	55.153
		K_L (L mg^{-1})	$3.11 \cdot 10^{-5}$	0.0018	$1.95 \cdot 10^{-5}$	$7.98 \cdot 10^{-5}$
		R_L	0.997	0.994	0.998	0.996
		R^2	0.869	0.740	0.775	0.955
	Freundlich	K_F (L mg^{-1})	$2.6 \cdot 10^{-6}$	$6.79 \cdot 10^{-2}$	$3.51 \cdot 10^{-6}$	$2.62 \cdot 10^{-3}$
		$1/n$	1.920	0.473	1.797	1.053
		n	0.521	2.113	0.561	0.949
		R^2	0.979	0.621	0.858	0.962
Na	Langmuir	q_e^0 (mg g^{-1})	79.18	3.068	4.222	2.724
		K_L (L mg^{-1})	$2.25 \cdot 10^{-5}$	$1.08 \cdot 10^{-3}$	$7.52 \cdot 10^{-4}$	$8.70 \cdot 10^{-4}$
		R_L	0.998	0.997	0.997	0.998
		R^2	0.796	0.769	0.891	0.910
	Freundlich	K_F (L mg^{-1})	$2.7 \cdot 10^{-5}$	0.021	0.024	0.024
		$1/n$	1.549	0.615	0.614	0.563
		n	0.646	1.052	1.320	1.729
		R^2	0.883	0.698	0.904	0.891

dolomite was moderate (24–29 %) with a slight trend to decrease (14–20 %) with rising the added NaCl concentration. As for Cl, Freundlich was the model that best fit Na sorption data on anthracite coal, limestone and pozzolan, while Langmuir on dolomite (Fig. 3; Table 2). The $1/n$ and n values indicated a favourable sorption onto dolomite, limestone, and pozzolan ($1/n < 1$, $n = 1$–10). Values of the R_L were in the range of $0 < R_L < 1$, indicating a favourable sorption process. The q_e^0 values ranged from 3 to 4 mg g^{-1} (except pozzolan, 79 mg g^{-1}), consistent with those observed by others authors (~2–6 mg Na^+ g^{-1}) studying Na sorption on calcite (Ishikawa and Ichikuni 1984).

Multipollution scenario: NaCl and trace metal removal

In order to evaluate on laboratory the practical applicability of the materials as reactive media in field installations (FB), a synthetic runoff solution (NaCl and metals) was passed through columns filled with each of the materials for 20 days. The removal efficiency of Cl, Na, Cd, Cu, Ni, and Zn onto the materials at the C_1 level (150 mg L^{-1} Cl) over the 20 days of column assay is shown in Fig. 4 and the pH values in the Table 3. Chloride and Na removal efficiency was greatly reduced in column assays with respect to that observed in batch. Overall, the highest Cl and Na removal efficiency was reached onto dolomite, followed by limestone, and ultimately anthracite coal and pozzolan as follows: (1) <1, 1–30, <1–20 and <1–1 % removed Cl; and (2) 1–8, 2–9, 2–7 and <1–3 % removed Na (anthracite coal, dolomite, limestone, and pozzolan, respectively). Indeed, dissimilarities between static (batch assays) and dynamic conditions (column assays) are expected. This is due to the fact that the pollutant solution-phase concentration (NaCl and metals) is continuously increasing in the column system (Goel et al. 2005), so the equilibrium is never achieved. In fact, this behaviour is expected to occur in a field installation (filter bed) that continuously receives road runoff. As shown in Fig. 4, NaCl removal stabilizes within the studied time, generally before 3 days. Considering the high solubility of NaCl in water, we believe that the results are very encouraging.

One of the challenges of active underground FBs is not only the removal of de-icing salts from road runoff but also trace metals, considering the interaction among them. A competitive binding of metal ions (included into the synthetic runoff solution) to the reactive surface sorption sites may explain the observed differences in the present study between batch (static, only NaCl) and column assays (dynamic, NaCl and trace metals). Also, the formation of soluble chlorocomplexes with metals may account for the highly decrease on Cl removal. The role played by other anions besides Cl^- on metal complexation was not considered as its presence in the solutions was very low (or even lower than the detection limit): (1) 5.5 mg L^{-1} or 15.6 mg L^{-1} SO_4^{2-} at day 0 (solutions in contact with anthracite coal and dolomite, respectively) decreasing to 0.2 mg L^{-1} at day 1; (2) HCO_3^- up to 2 mg L^{-1} (limestone); and (3) NO_2^- up to 0.4 mg L^{-1} (limestone). A combination of materials should be investigated for improving the removal efficiency of NaCl and trace metals simultaneously, as previously proposed for mixtures of pollutants (Reddy et al. 2014).

Trace metal removal efficiency was generally high, as usually reported (Reddy et al. 2014), although large

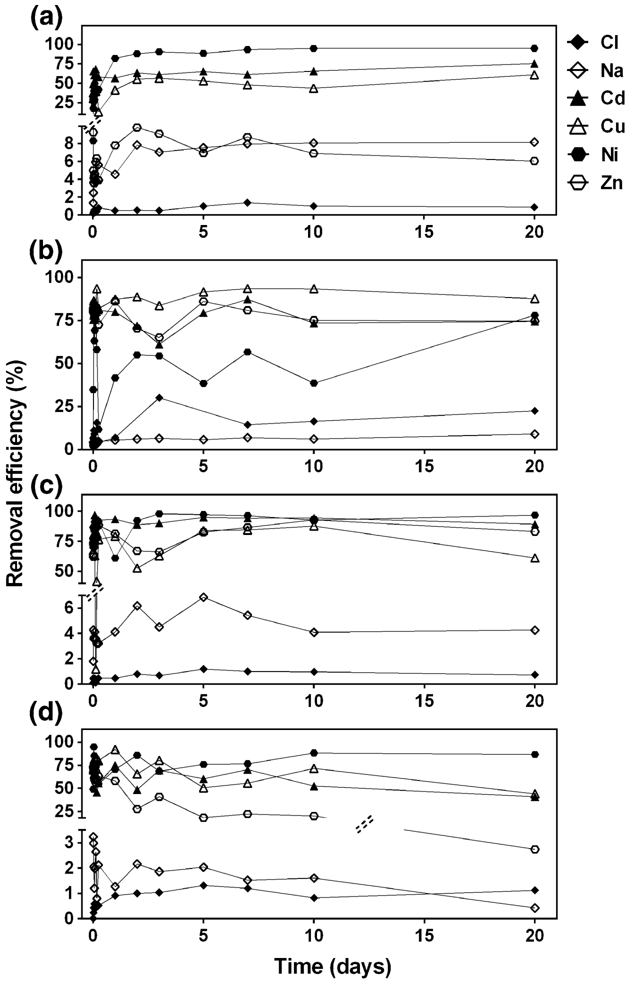

Fig. 4 Removal efficiency of Cl, Na, Cd, Cu, Ni, and Zn over time (up to 20 days) in column assays performed with a synthetic runoff solution with NaCl (C_1 level = 150 mg L^{-1} Cl) and trace metals (2 Cd, 20 Cu, 3 Ni, and 300 Zn μg L^{-1}) onto anthracite coal (**a**), dolomite (**b**), limestone (**c**), and pozzolan (**d**)

differences were observed depending on the material. As shown in Table 3, higher pH values in the solutions collected from the column system with dolomite were found (from 7.7 to 8.2), followed by limestone (from 6.8 to 7.3), pozzolan (from 6.7 to 5.8), and anthracite coal (from 4.6 to 5.7). From these data, the highest trace metal removal efficiency onto dolomite and limestone is expected. Indeed, at day 20 the sequence of metal removal efficiency was as follows: (1) Ni (95 %) > Cd (75 %) > Cu (61 %) ≫ Zn (6 %) onto anthracite coal; (2) Cu (88 %) > Ni (78 %) > Zn (75 %) ~ Cd (74 %) onto dolomite; (3) Ni (97 %) > Cd (89 %) > Zn (83 %) > Cu (61 %) onto limestone; and (4) Ni (87 %) > Cu (44 %) > Cd (41 %) ≫ Zn (3 %) onto pozzolan. A criterion in the material choice should be to show an adequate metallic removal efficiency that remains over time. In this regard, the values of metal removal efficiency followed a general trend towards equilibrium from 2 to 5 days of contact time (Fig. 4) except the case of pozzolan. At the end of the experiment (day 20), the removal efficiency of Ni, Cd, and Cu onto anthracite coal was 11.5, 2.0, and 1.5-fold, respectively, higher than at the beginning (day 0) (Fig. 4a). A moderate decline was noted in the case of Zn. Similar patterns were observed in the case of dolomite (Fig. 4b), although with a much smaller increase for Ni at day 20 of the experiment (2.2-fold) without reaching equilibrium during the experienced time. In the case of limestone (Fig. 4c), metal removal efficiency was higher (case of Cd, Ni, and Zn) at the end of the experiment; Cu removal remaining constant over time. While in general the removal efficiency onto anthracite coal, dolomite, and limestone shows an upward trend (or remains constant) over time, metal removal efficiency onto pozzolan declined progressively. Thus, a very high decrease on Na, Cd, Cu, and Zn removal efficiency onto pozzolan (up to 0.04-fold) was observed over time (Fig. 4d). The progressive decrease observed in the pH values in the solutions in contact with pozzolan over time (Table 3) may account for this result. This makes pozzolan should not be considered as a suitable candidate material for the purpose of the present study.

Table 3 pH values of the individual solutions collected at different times in the column assays performed with a synthetic runoff solution with NaCl (C_1 level = 150 mg L^{-1} Cl) and trace metals (2 Cd, 20 Cu, 3 Ni, and 300 Zn μg L^{-1}) for each of the four selected materials (anthracite coal, dolomite, limestone, and pozzolan)

Time (days)	Anthracite coal	Dolomite	Limestone	Pozzolan
0	4.6	7.7	6.8	6.7
0.01	4.2	7.9	7.0	6.7
0.02	4.2	8.1	7.1	7.0
0.04	4.1	8.1	7.2	7.1
0.06	4.1	8.2	7.2	6.7
0.08	4.1	8.1	7.2	6.6
0.13	4.2	8.2	7.4	6.7
0.17	4.3	8.3	7.2	6.7
0.25	4.3	8.3	7.3	6.7
1	4.8	8.4	7.2	6.6
2	5.1	8.3	7.3	6.8
3	5.3	8.3	7.1	6.5
5	5.5	8.3	7.3	6.6
7	5.6	8.2	7.3	6.3
10	5.5	8.3	7.2	6.3
20	5.7	8.3	7.3	5.8

As indicated, pH plays a key role in removal efficiency. The surface charge of materials becomes more negative with increasing pH and attracts metal cations for sorption. Moreover, with increasing pH the proportion of hydrolyzed metal species rises, which are more strongly sorbed than

Table 4 Predicted percentages with Visual Minteq of the different chemical species of Cl, Na, Cd, Cu, Ni, and Zn in the individual solutions collected at 0, 1, and 20 days in the column assays performed with a synthetic runoff solution with NaCl (C_1 level = 150 mg L^{-1} Cl) and trace metals (2 Cd, 20 Cu, 3 Ni, and 300 Zn µg L^{-1}) for each of the four selected materials (anthracite coal, dolomite, limestone, and pozzolan)

Element	Chemical specie	Anthracite coal			Dolomite			Limestone			Pozzolan		
		0	1	20	0	1	20	0	1	20	0	1	20
Cl	Cl^-	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8	99.8
Na	Na^+	99.8	99.8	99.8	99.8	99.8	99.9	99.8	99.8	99.8	99.8	99.8	99.8
	$NaSO_4^-$	1.7	1.6	<0.1	1.7	1.7	<0.1	<0.1	<0.1	<0.1	1.7	<0.1	<0.1
	NaCl (aq)	0.4	0.4	0.4	0.4	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4
	$NaHCO_3$ (aq)	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	0.2	<0.1	<0.1	0.2	<0.1	<0.1
	$NaCO_3^-$	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cd	Cd^{2+}	75.9	76.4	76.4	74.3	77.2	80.3	76.1	76.4	76.4	75.8	76.5	76.6
	$CdOH^+$	<0.1	<0.1	<0.1	1.8	<0.1	<0.1	0.4	<0.1	<0.1	0.7	<0.1	<0.1
	$CdCl^+$	23.0	23.2	23.2	21.8	22.0	19.4	23.1	23.2	23.2	23.1	23.1	23.1
	$CdCl_2$ *(aq)*	0.4	0.4	0.4	0.3	0.3	0.2	0.4	0.4	0.4	0.4	0.4	0.3
	$CdCO_3$ *(aq)*	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	$CdSO_4$ *(aq)*	0.8	<0.1	<0.1	1.6	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cu	Cu^{2+}	81.4	83.1	82.6	5.7	79.5	79.9	27.4	80.3	81.0	18.6	80.5	83.1
	$CuOH^+$	17.0	16.1	16.7	55.3	19.2	19.4	62.1	18.8	18.2	64.8	18.7	16.1
	$Cu(OH)_2$ *(aq)*	0.2	0.2	0.2	36.1	0.3	0.3	9.4	0.3	0.3	15.1	0.3	0.2
	$Cu_2(OH)_2^{2+}$	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	0.2	<0.1	<0.1	0.4	<0.1	<0.1
	$Cu(OH)_3^-$	<0.1	<0.1	<0.1	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1
	$CuCl^+$	0.5	0.5	0.5	<0.1	0.5	0.4	0.2	0.5	0.5	0.1	0.5	0.5
	$CuCO_3$ *(aq)*	<0.1	<0.1	<0.1	2.1	<0.1	<0.1	0.6	<0.1	<0.1	1.0	<0.1	<0.1
	$CuSO_4$ *(aq)*	0.8	<0.1	<0.1	0.1	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	Ni^{2+}	98.9	99.8	99.8	93.3	99.3	99.8	98.9	99.8	99.8	98.3	99.8	99.8
	$NiOH^+$	0.1	0.1	0.1	3.6	0.1	0.1	0.9	0.1	0.1	1.4	0.1	0.1
	$Ni(OH)_2$ *(aq)*	<0.1	<0.1	<0.1	1.0	<0.1	<0.1	0.1	<0.1	<0.1	0.1	<0.1	<0.1
	$NiCl^+$	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	$NiCO_3$ *(aq)*	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	$NiSO_4$ *(aq)*	0.9	<0.1	<0.1	1.7	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn	Zn^{2+}	97.5	98.4	98.4	36.7	97.7	98.4	86.6	98.3	98.3	77.1	98.3	98.4
	$ZnOH^+$	0.6	0.6	0.6	11.3	0.7	0.8	6.2	0.7	0.7	8.5	0.7	0.6
	$Zn(OH)_2$ *(aq)*	0.1	0.1	0.1	50.8	0.1	0.1	6.4	0.1	0.1	13.6	0.1	0.1
	$ZnCl^+$	0.9	0.9	0.9	0.3	0.8	0.7	0.8	0.9	0.9	0.7	0.9	0.9
	$ZnCO_3$ *(aq)*	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	$ZnSO_4$ *(aq)*	1.0	0.1	<0.1	0.7	0.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

the free metal ions. The predicted percentage of the different chemical species of Cl, Na, Cd, Cu, Ni, and Zn in the individual solutions collected at 0, 1, and 20 days from the experimental systems was calculated (Table 4). Intermediate times were not included for reasons of space. Almost 100 % of the Cl and Na species were in the form of free ion (Cl^- and Na^+), and only a minor proportion was as NaCl *(aq)* (∼0.4 %) and $NaSO_4^-$ (up to 2 %), partially explaining the low Cl and Na removal efficiency. About 74–80 % of Cd species were in the form of free ion (Cd^{2+}). At the low added Cd concentration of the present study (2 µg L^{-1}), chemisorption processes (ion exchange) of Cd^{2+} onto materials are likely to occur rather than precipitation ones (Bradl 2004). Besides Cd^{2+}, chlorocomplexes ($CdCl^+$) were also present (∼19–23 %), being less strongly sorbed than Cd^{2+}, which may explain the lower Cd removal than that observed for Cu and Ni. Also, Cd displacement by Cl ions was evidenced (Bäckström et al. 2004). Cu^{2+} was the predominant Cu specie (80–83 %) from the beginning (case of anthracite coal) or from day 1 (dolomite, limestone, and pozzolan). Hydrolyzed species are important at day 0 except in solutions in contact with anthracite coal: 55–65 % $CuOH^+$ (dolomite, limestone, and pozzolan) and 36 % $Cu(OH)_2$ (*aq*) (dolomite). The very high proportion of hydrolyzed Cu species at pH ≥ 8 explains the higher Cu removal onto dolomite. Nearly 100 % of the Ni species were in the form of free ion (Ni^{2+}), and a minor proportion were in a chloro-, sulfo- and hydroxocomplex form (anthracite coal and dolomite, day 0), suggesting non-specific adsorption. Hydrolyzed species of Zn [$ZnOH^+$, $Zn(OH)_2$(*aq*)] appeared from day 1 (dolomite, limestone, and pozzolan), mainly in the case of dolomite [51 % $Zn(OH)_2$ (*aq*)] explaining the higher Zn removal onto this material.

Conclusion

Results showed that dolomite has the best physical properties for minimizing fragmentation processes, essential to maximize filter bed effectiveness during construction and maintenance. Anthracite coal and dolomite were the most efficient in removing Cl ions at the lowest added NaCl concentration (150 mg L^{-1} Cl). At higher levels (1500–5000 mg L^{-1} Cl), Cl removal onto anthracite coal remained constant but decreased onto dolomite. Although low Cl percentage was removed onto pozzolan and limestone at low NaCl concentration, removal efficiency highly increased with rising the added NaCl concentration. Conversely, limestone and pozzolan were the most efficient in Na removal at low added NaCl concentration. With rising the NaCl concentration, Na removal efficiency onto anthracite coal increased, while it decreases onto the other materials. The experiments at 4 °C showed lower Cl and Na removal than at 22 °C, anthracite coal removing NaCl more efficiently than dolomite. In all cases, anthracite coal showed a higher potential effectiveness against salinity pulses and low temperatures. The multipollution scenario showed that NaCl removal efficiency is lower in column assays with respect to batch, attributed to the continuously increase in NaCl concentration, the competitive binding of metals for sorption sites, and the formation of soluble metallic chlorocomplexes. The highest NaCl removal in column assays was reached onto dolomite, followed by limestone, and ultimately by anthracite coal and pozzolan. A very high trace metal removal efficiency was noted and remained over time, except in the case of pozzolan. Further studies could include a combination of materials, taking advantage of their physical properties and multielemental removal efficiency at low or moderate initial concentrations. Also, further studies aiming to material regeneration in field facilities in the medium/long term could be very interesting.

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