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Removal of nickel from aqueous solutions by clay-based beds

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Abstract

The use of spray-dried natural clays for the removal of nickel ions in aqueous solution is discussed in this paper. Two different clays were tested and their mineralogical composition and physical characteristics related to efficiency of nickel removal. In particular, relevant parameters including flow rate and overall removal efficiency were evaluated for 4.8 cm depth filters. The removal efficiency of the tested clays was generally similar or greater than that of granular activated carbon (GAC). The mineralogical composition of the clays, particularly the presence of montmorilonite, might explain this behaviour. Higher cation exchange capacity and development of surface negative charge on clay particles in contact with water also contribute to this promising performance, despite the lower available specific surface area of the spray-dried grains in comparison with granular activated carbon. The calcination of pressed pellets made of contaminated filter grains gives consolidated ceramic bodies that can be used in the fabrication of common products like wall or floor tiles, where nickel ions remain firmly attached and inertized.

Keywords: Filtration; Clay beds; Nickel removal

1. Introduction

Filtration is the process by which suspended or dissolved impurities in a liquid are removed by attachment to the grains of a filter medium. Granular bed filters are widely used in potable water or wastewater treatments, with sand [1] and activated carbon materials [2,3] being the most common filtration materials. Operating conditions and removal performance are strongly dependent on the design of a granular-medium filter, involving the consideration of the type of medium [4,5], size and depth [6,7], filtration rate [8,9], pressure available for driving force [10], and method of filter operation [11]. Rich smectite/kaolinite natural clays are known for their high adsorbent and cationic exchange potential [12,13], and have been used in filtration operations [14]. The low price and abundance make these clays attractive candidates for filtration purposes, however their very small sizes and flaky shapes result in very low bed porosity filter and limited grain resistance to attrition. Therefore, a spray-drying technique was developed to increase the average particle size and hardness [15]. Promising results for the removal of several metallic-ion and organic species by clay-based filtration beds were reported [16–18]. Their use is now extended for nickel ions. Two different clays are tested and their physical and mineralogical characteristics will be related with removal performances.

2. Experimental

Two Portuguese natural ball-clays named ZA-4 and NC were characterized and processed by spray drying, as described elsewhere [19]. Collected grains were then calcined at 600 °C for 2 h and sieved by using the following series: 1000–500–420–355–212 μm. These different sized grains (≈60 g) were used as a filtration bed of small filters (4.8 cm depth), as shown in Fig. 1. The filtration rate was evaluated from head loss measurements (water gauge) through the filter and was related to the average grain size of the particles and packing density of the forming beds. A simple relationship (calibration curve) between both parameters was obtained and then used to establish controlled operating conditions. The performance of ZA-4 and NC filters for nickel removal

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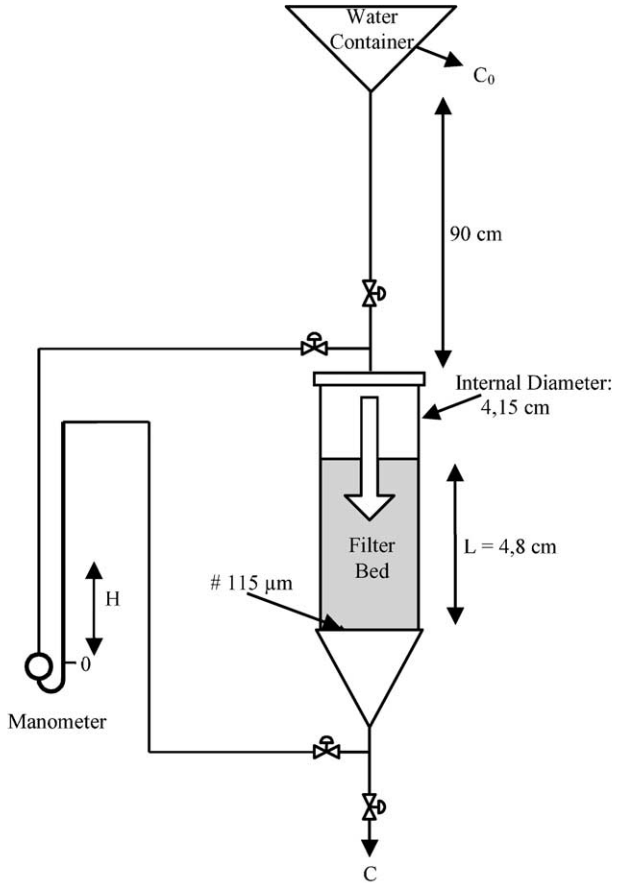

Fig. 1. Schematic representation of the filtration apparatus.

from aqueous solutions was then estimated, and compared with a commercial standard material (granulated activated carbon—GAC). The different solutions were prepared by dissolving $NiSO_4.6H_2O$ in distilled water and initial (C_0) and final (C) nickel concentrations were estimated by Induced Couple Plasma (ICP—Jobin Yvon 70 Plus). The removal performance was evaluated by the ratio $(C_0{-}C)/C_0$ (hereby named removal efficiency) or by using the weight ratio between the amount of retained contaminant (µg) and the filtration material (g). As an attempt to clarify the relevance of the cation exchange process in the overall removal performance, ICP measurements of other existing cations, such as iron, calcium, sodium, potassium, etc., where also made. In addition to nickel-contaminated solutions, reference filtration tests with pure and acidified (0.1 N HCl) distilled water were performed. The filtration rate during tests was maintained constant (4.4 or 0.44 m/h).

After removal operations, some powder (4 g) was dried and then unidirectionally pressed. Pellets of about 30 mm diameter for 2 mm height were obtained and calcinated at a maximum temperature of 1140 and 1050 °C for 4 h, for ZA-4 and NC materials, respectively. This operation simulates the fabrication of common ceramic products like tiles, in which those clays are currently used. At the same time, reactions occurring during firing should promote the inertization of retained Ni species. In order to evaluate the inertization degree, leaching tests with strongly acidified solutions ($HCl + HNO_3$, 1:1.5) were performed and nickel concentration was then measured by ICP. The volatile nature of nickel required an estimation of loss levels upon firing. For that purpose, calcined pellets were totally destroyed by dissolution in very strong acidic solutions ($HF + HNO_3 + HCl$, 2.5:1.5:1) and the Ni concentration was then measured.

3. Results

The effect of different variables, including material characteristics (nature, size and shape) and operation parameters, on filtration performance are discussed in the following sections. In most cases [Ni^{2+} in µg]/g vs. filtrate volume was used, since it gives a sensitive view of removal performance.

3.1. Initial concentration of contaminant

To study the effect of the initial concentration of Ni^{2+} in solution (C_0) in the removal efficiency of the clay bed, several starting solutions were used (99.4, 524, and 1051 ppm). The results for ZA-4 clay beds are shown in Fig. 2. Removal efficiency is almost independent of the contaminant concentration and is greater than 80% until approximately 1000–1500 µg of Ni^{2+} per gram of clay was retained. The efficiency of the filter decreases quickly after this point, until the saturation limit of about 4000 µg Ni^{2+}/g is reached. The anticipated filter lifetime will be increased when highly concentrated solutions are used.

3.2. Average grain size of the filtration material

The effect of different sized ZA-4 clay fractions (355–212, 420–355, 500–420 and 1000–500 µm) on nickel removal efficiency is outlined in Fig. 3. The filtration performance decreases as grain size increases, possibly because of the decreasing number of grains per unit volume and concomitant decreasing of the available contact area for filtration. This effect is stronger for faster filtration regimes. As grain size increases, more porous and open is the filter itself and more quick is the removal operation, leading to less efficient results. Furthermore, these coarser particles are made of agglomerates of small grains and the access to their central cavity and internal porosity is more difficult (see Fig. 4A), thus disabling the removal of Ni^{2+} inside the grain [15]. This situation is more perceptible by comparing individual grains (Fig. 4B) with agglomerates (Fig. 4C).

3.3. Flow rate

This study required an adjustment of the relevant operation parameters so that a relationship could be made between average size of filter grains and their implication in flow rate, for a constant head loss of about 981 Pa (see Table 1). As expected, the filtration rate tends to decrease for finer-grained beds, due to decreasing porosity of the bed (higher packing density).

Two different filtration rates (4.43 and 0.44 m/h) were utilised during these tests and the results are provided in Fig. 3. Removal efficiency of nickel tends to increase with decreasing filtration rate, being the differences more obvious when using coarser particles. This anticipated behaviour is due to the increasing interaction/contact time between the solution and filtration material. A compromise between speed and performance is necessary because shorter contact times are desirable to

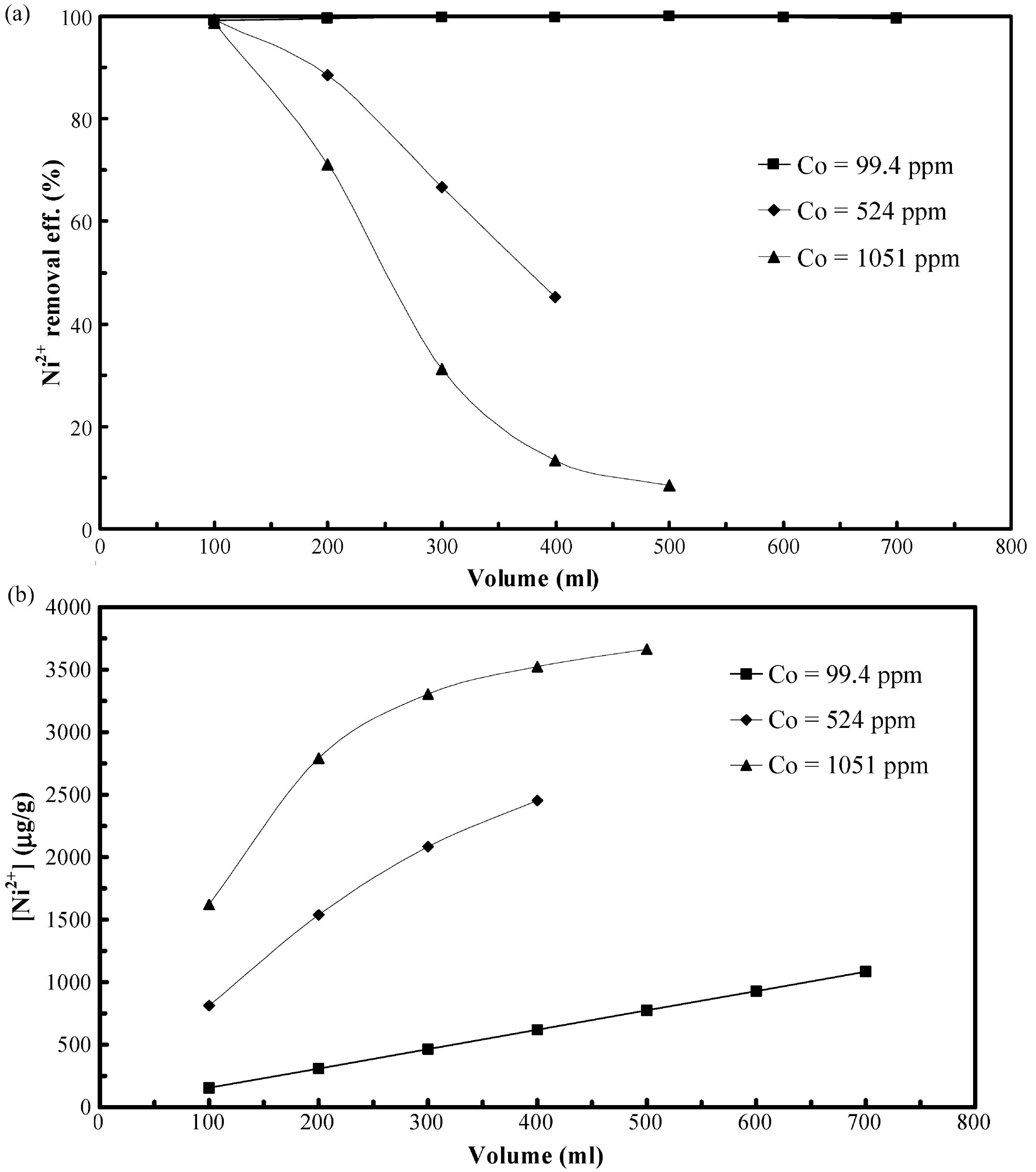

Fig. 2. Ni^{2+} removal by ZA-4 clay beds made of 355–212 μm sieved grains as a function of the initial concentration of the contaminant (C_0). The flow rate was kept constant (4.43 m/h) and two different representations were used: (A) (C_0–C)/C_0% removal efficiency vs. filtrate volume; (B) cumulative concentration of retained Ni/per gram vs. filtrate volume.

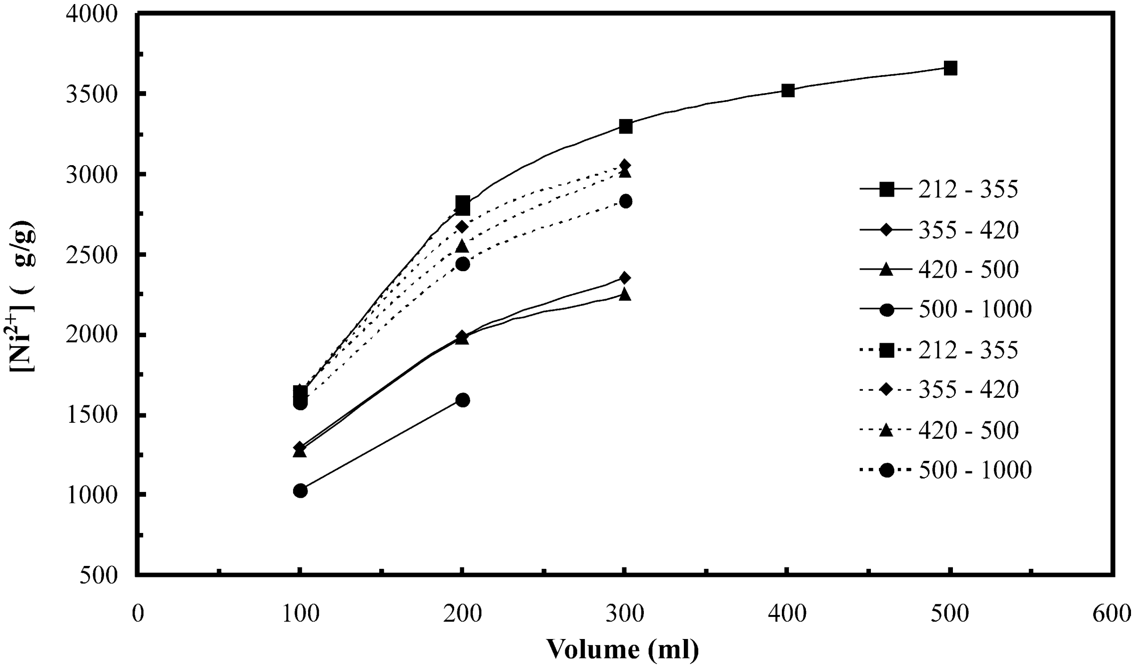

Fig. 3. Ni^{2+} retention of ZA-4 clay beds made by several sieved fractions operating at two different flow rates: (i) solid lines (4.43 m/h); (ii) dashed lines (0.44 m/h).

process larger volumes of water. It should be noted that the removal efficiency of the finest-grained beds (355–212 μm) is less dependent on the filtration rate, probably because these structures are less porous and the contact with the filtered solution is always very high.

3.4. Nature of the filtration material

Comparative tests involving two different clay grains (ZA-4 and NC—sieved fraction 355–212 μm) and one of the clay (ZA-4) and activated carbon (sieved fraction 420–355 μm) were also performed. Comparison with a standard filtration material (activated carbon) is useful for evaluating the potential of the clays.

All these tests were conducted with highly concentrated solutions (C_0 around 1000 ppm) to quickly detect performance differences (Figs. 5 and 6). ZA-4 clay exhibits a lower retention capacity than NC, especially for high retention levels where an abrupt performance decline is observed and saturation is noticed. This difference is probably related to mineralogical and compositional differences between the two clays, in particular the amount of smectite, prevalent in NC clay [18].

Table 1
Typical flow rates obtained by the use of different sieved fractions of ZA-4 clay grains, under a constant head loss of 981 Pa (between the entrance and the exit of the filter)

Sieved fraction (μm)	Rate (m/h)
355–212	1.79
420–355	3.28
500–420	6.49

Comparing the filtration performance of ZA-4 clay with GAC (Figs. 6A and B), some apparently contradictory results are obtained using the current representation (μg/g vs. volume). This is due to the significant differences in packing densities (0.842 and 0.457 g/cm^3 for ZA-4 and GAC, respectively). For a fixed filter volume, a smaller weight of GAC is necessary and the direct comparison with the clay results is misleading. A better approach for comparing the filtration performances of these materials is obtained by representing the volume of filtration material instead of its weight (Fig. 6B). With volume comparison, the clay seems to exhibit slightly better efficiency than the standard filtration material in the Ni^{2+} removal process. This behaviour is not predicted from the known values of specific surface areas (22.0 and 849.1 m^2/g, respectively for ZA-4 clay and GAC), but might be related with differences in the electrokinetic potential of particles in aqueous suspension, as shown in Fig. 7.

The stronger removal capacity of positive species shown by clay materials might be partly explained by the development of larger electronegative potential of suspended particles in the explored pH region, as it was referenced earlier in this paper. Table 2 gives the average values of filtered solution as a function of Ni^{2+} concentration, denoting an acidification tendency with increasing nickel content. The majority of tests were done with nickel concentrations around 1000 ppm (corresponding to pH values near 3.7) and in these conditions electronegative potentials of different materials are ordered as follows (in absolute value): NC > ZA-4 > GAC. This sequence might help to explain the comparative filtration performance of different beds.

3.5. Filter lifetime in continuous operation

By knowing the typical removal performances of the clay-based filters, mostly expressed in Figs. 2 and 3, is now possible to estimate the average lifetime under a continuous filtration regime. For a cubic filter of 10 m^3 in volume and taking in account of the value of 0.9–1 g/cm^3 for the packing density of clay grains [15], this results in about 10 t of clay being needed (420–355 μm). For a strongly polluted solution ($C_0 = 1$ g/l) and assuming the Portuguese legal permitted levels (50 ppm) for nickel concentration (Law no. 236/98, 1998) the removal efficiency of the filter should be higher than 95%. Fig. 2 shows that this filtration performance is maintained until about 1500 μg/g has been removed, corresponding to 15 kg of attached nickel in total for the actual filter. Assuming now a filtration rate near the lower level of the fast regime (5 m/h), the rate of nickel removal reaches 5 kg/h and a fully operational lifetime of about 3 h is estimated under a continuous regime. For a less polluted solution ($C_0 = 100$ ppm) 10 times longer lifetime is predicted, which seems to be much more suitable for monitoring. However, these data indicate that, in reality, there will be few pollution practical applications that will be solvable using this technique, unless suitable co-adjuvant pre-treatment operations has been also applied.

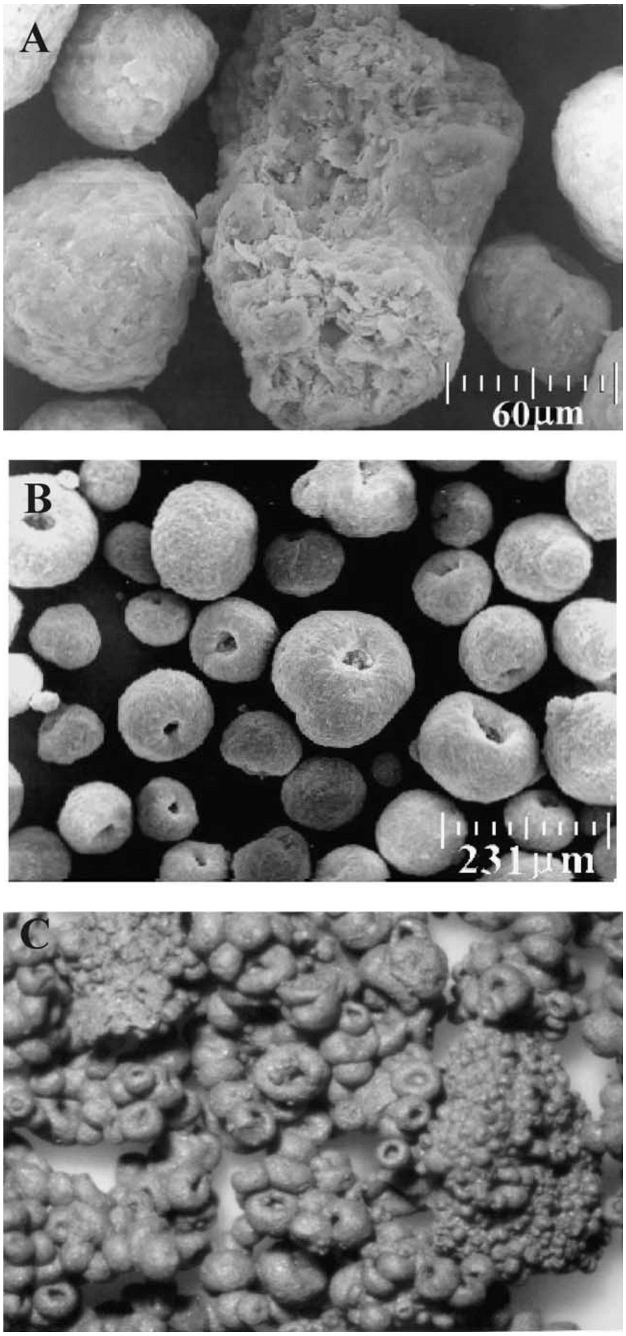

Fig. 4. Morphological aspects of ZA-4 clay grains: (A) detail of the inner part of a grain; (B) several individual grains; (C) formation of agglomerates from small grains.

3.6. Removal mechanism

To clarify the dominant removal mechanism of metallic ions in the clay particles, complementary ICP analyses were made by determining the concentration of all the probable existing ions in filtered solutions. This procedure helps to clarify the relevance of the cationic exchange process. In this study, only 355–212 μm sieved grains were used.

Table 3 gives the chemical analysis of the distilled water before and after passing through the filter clay grains. The enrichment in calcium, sodium and potassium shows that both materials tend to release these species, as predicted from their weakly bonded character.

On using Ni-containing solutions, two different situations were observed depending on the initial concentration of contaminant. For C_0 levels of about 10 ppm, the amount of retained nickel is lower than the concentration of released cations. On contrary, by using strongly Ni concentrated solutions (99.4 and 1051 ppm) retention values overcome the overall concentration of

Table 2
pH evolution of the filtered solution as a function of Ni^{2+} concentration (C_0)

C_0 (ppm)	pH
10	5.25
100	4.51
500	4.00
1000	3.67

all released species, which might indicate the occurrence of an ion exchange mechanism. For example, the seventh consecutive run C_0 of 99.4 ppm produces the removal of 3.37 meg/l of nickel balanced by the release of 3.41 meg/l of other cations. This should be strong evidence that the function of the clay is in cation exchange. However, it should be noted that the clay might contain some free $CaCO_3$, which is strongly dissolved at low pH values. To confirm this suggestion, a moderately acidified solution (HCl 0.1 N) was also passed thought the filter. Results in Table 4 confirm the occurrence of a significant dissolution of calcium carbonate.

The change of pH values of the influent solution (Table 2) seems to be slightly relevant in determining the removal performance, as shown in Fig. 2. Adsorption and filtration processes are both usually sensitive to pH, but adsorption is more so. A careful control of pH change of the solution as it passed through the columns is needed for evaluating the system performance and was not performed. However, preliminary measurements of the effluent pH give similar values in all the tested conditions, which would account for the equivalent removal efficiency, independent of the influent pH.

3.7. Inertization of removed nickel in clay matrix

Clay-based spray-dried grains are normally used to fabricate wall and floor tiles. In this process, the powder is uniaxially pressed and formed pieces are then consolidated by firing at high temperatures (>1000 °C). Despite the coarser nature of the grains now previously

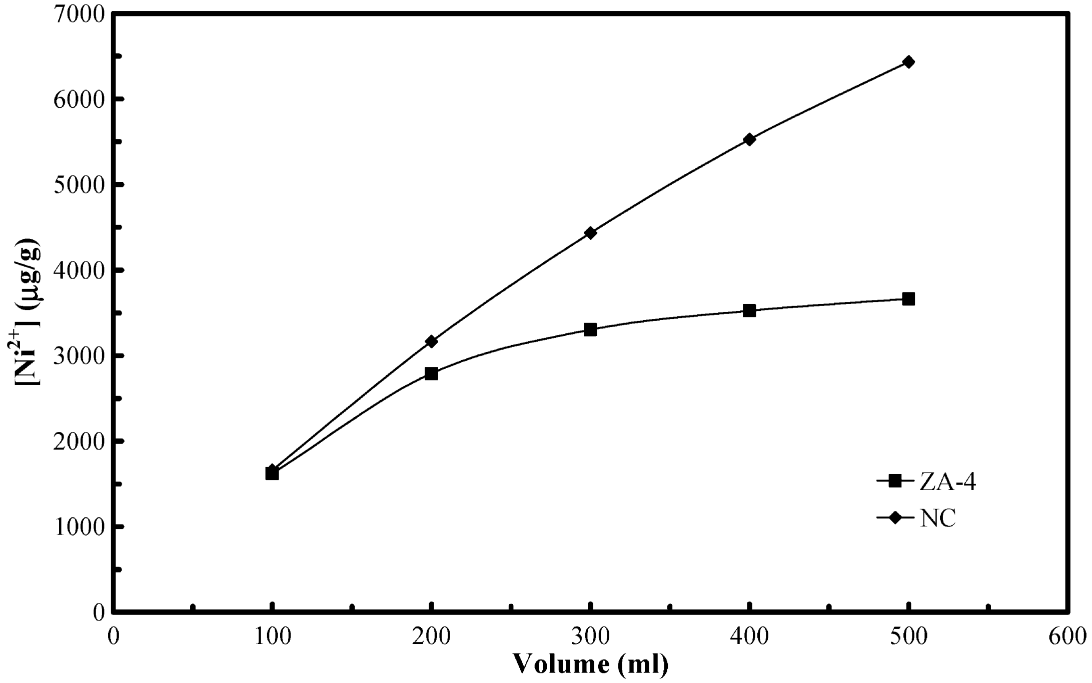

Fig. 5. Ni^{2+} retention of 355–212 µm sieved beds made by ZA-4 and NC clay grains. The flow rate was kept constant (4.43 m/h).

Table 3
Chemical analysis (ICP) of distilled water before and after several removal runs at constant rate (4.43 m/h)[a]

	Al^{3+} (ppm)	Fe^{3+} (ppm)	Mn^{2+} (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	Na^{+} (ppm)	K^{+} (ppm)
Distilled water	<0.025	<0.010	<0.005	<0.005	<0.005	<0.100	<0.100
ZA-4							
1 run	0.278	0.138	<0.005	1.01	19.9	6.04	6.29
4 runs	0.322	0.112	<0.005	0.41	8.6	0.91	3.25
NC							
1 run	1.1	0.37	<0.005	2.45	9.66	126	25.7
2 runs	0.65	0.26	<0.005	0.20	0.17	13.5	3.01
3 runs	0.70	0.28	<0.005	0.20	0.07	4.43	1.14

used as filtration material, its compaction by pressing is still easy to control. Pellets made from saturated filtration grains are easily obtained and the firing process might promote strong fixing reactions of the removed species on to the ceramic grains, giving a final non-toxic and inert material. The incorporation in a normal matrix made of smaller and as-spray-dried grains is also viable as an alternative way to reduce the final relative concentration of removed contaminants in the fired pieces. In this sense, each saturated filtration bed does not constitute a contaminated load that requires special treatments or disposal needs, as normally happens with common filtration materials.

Table 5 shows very promising inertization results of fired pellets after leaching tests with strongly acidic solutions. Differences between both clay materials are

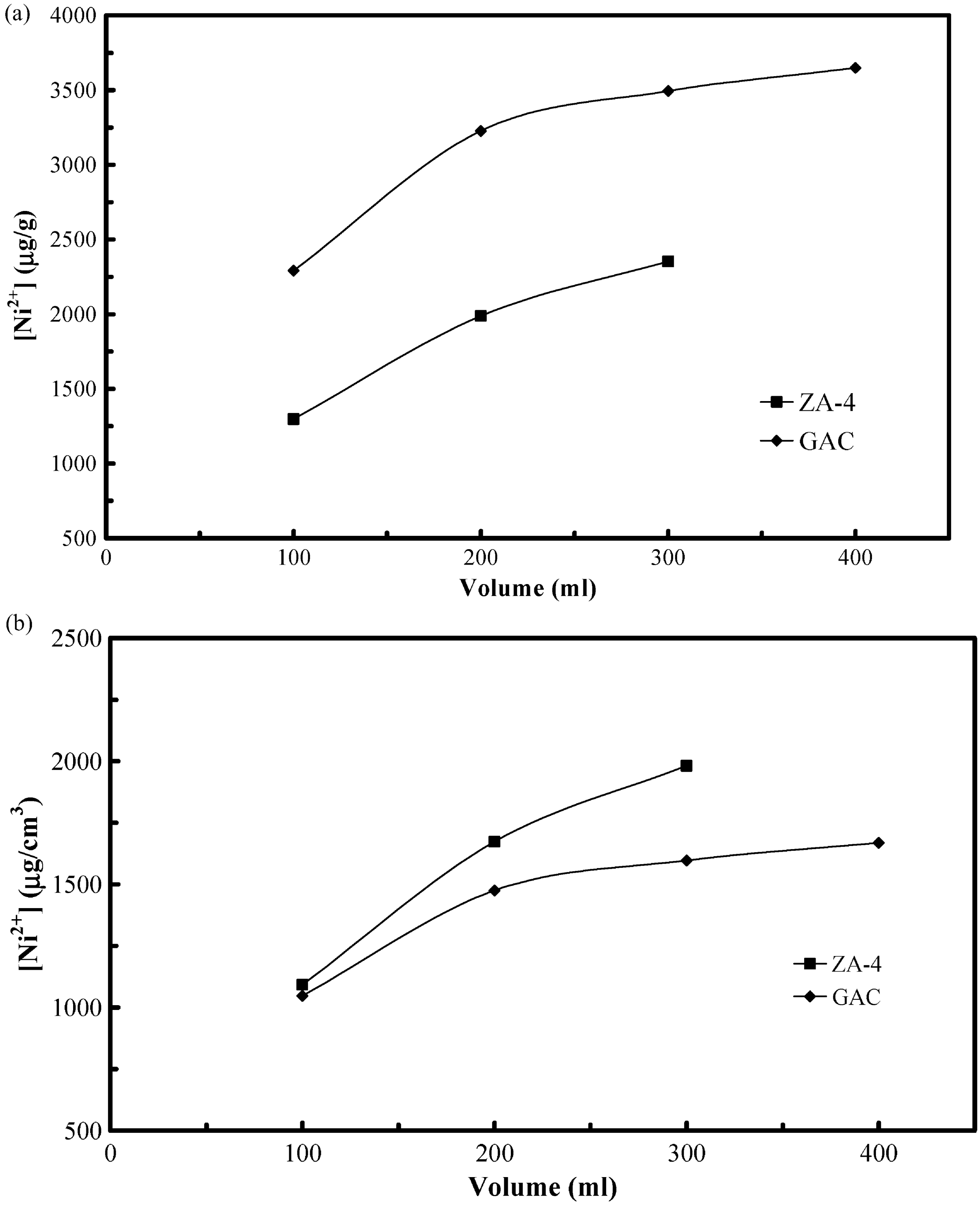

Fig. 6. Ni^{2+} retention of 420–355 μm sieved beds made by ZA-4 clay and activated carbon (GAC) grains. The flow rate was kept constant (4.43 m/h): (A) Usual representation (μg/g vs. volume); (B) new representation (μg/cm^3 vs. volume), that permits a direct comparison of differential dense filtration materials.

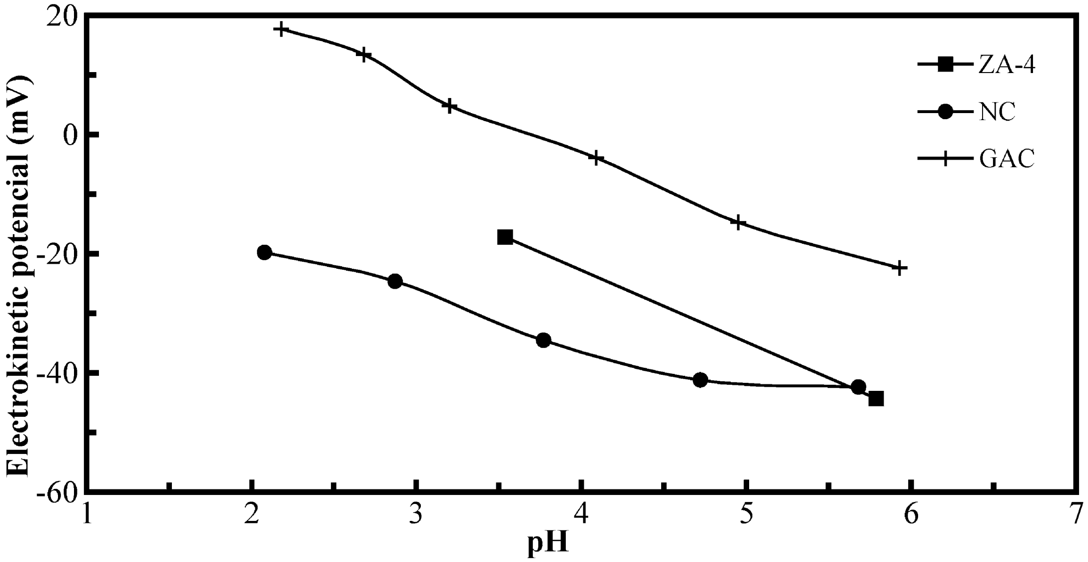

Fig. 7. Dependence of electrokinetic potential on pH values, for ZA-4, NC, and granular activated carbon (GAC) materials.

minor, despite the use of different maturing temperatures. NC clay is much more fusible than ZA-4 and lower firing temperatures are required to obtain fully consolidated structures (maximum densification). Relevant losses due to volatilization of nickel were observed during firing, deserving a careful control and optimization of the firing cycle and advanced cleaning processes of the exhaust gases. Similar results were observed with different volatile contaminants like Pb and Cd[18].

Table 4

Chemical analysis (ICP) of an acidified (0.1 N HCl) solution before and after several removal runs at a constant rate (4.43 m/h) through a ZA-4 clay bed made of 212–355 μm sieved grains[a]

Filtration runs	Al^{3+} (ppm)	Fe^{3+} (ppm)	Mn^{2+} (ppm)	Mg^{2+} (ppm)	Ca^{2+} (ppm)	Na^{+} (ppm)	K^{+} (ppm)
–	<0.05	<0.01	<0.009	0.187	0.033	2.74	0.247
1	<0.05	<0.01	0.232	83.9	1163	41.7	57.4
2	141	6.27	2.06	41.0	1536	16.3	115
3	271	25.1	1.61	24.7	1074	12.2	85.5
4	251	32.4	1.18	18.7	595	10.3	56.4
5	182	30.4	0.864	12.7	292	7.80	37.6

[a] Each run involved 100 ml of a renewed solution having the same initial concentration.

Table 5

Volatilization of nickel upon firing of pressed pellets made of clay grains previously used as filtration beds

Clay	N1	N2	Volatilization (%)	N3
ZA-4	3.663	3.007	18.9	0.002
NC	6.434	5.697	12.1	0.051

N1 and N2 (mg/g) are, respectively, the nickel concentrations retained in clay grains and in pellets fired at 1050 °C (for NC) and 1140 °C (for ZA-4). N3 is the nickel concentration present in strong acidified ($HCl + HNO_3$, 1:1.5) leaching solutions.

4. Conclusions

Operation parameters like filtration rate and concentration of filtered solution logically affect the removal efficiency. In accordance, the filter lifetime is longer for less polluted solutions and removal efficiency increases in slow speed regimes. The nature of the filtration material and its average grain size also affect the removal process. Clay-based materials show similar or higher performance than the activated carbon standard material. Mineralogical characteristics of the clays, namely the presence of good adsorbent phases like some smectite minerals, might explain this behaviour. The development of surface negative charge on suspended clay particles also contributes to this promising performance, despite the lower available specific surface area of the spray-dried grains in comparison with GAC.

Saturated filtration clay-based loads might be directly used as raw material or added as a minor component for the production of ceramic tiles. Firing process promotes strong inertization reactions between different phases, and removed contaminants remain firmly attached to the clay grains in the final and inert product. As it does not require disposal treatments this solution is environmentally interesting.

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