Removal of contaminants from aqueous solutions by beds made of rejects of the lightweight aggregates production

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Abstract

This work describes the attempt to reuse rejected sieved fractions from the lightweight expanded clay aggregates production, as filter bed, used in the removal of some water contaminants, namely nickel, lead and suspended particles, as an alternative to land filling deposition.

Expanded clay fractions and materials used for efficiency comparison were first characterised, by means of physical, chemical and mineralogical tests, in such a way that possible factors, on which removal depends, could be determined.

Besides the classical purpose of suspended particles' removal, assay on the removal of heavy metals were also performed through the filtration in fixed beds. Experiments were performed at different contaminant concentrations and by testing several operational conditions.

The performance is better for all the studied contaminants using beds made of smaller sieved fractions, 0/0.5 mm, showing higher packing density values (straining is favored), and for lower filtration rates which improve contact time between pollutants and filtration material. Pb(II) removal was higher than Ni(II) one. When comparing with the traditional filtration materials, lightweight aggregates rejects demonstrate their good performance, once it was more effective than sand, considering suspended particles' removal, and for heavy metal removal, efficiencies were similar or higher than those found for granular activated carbon (GAC).

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1. Introduction

Growing concern on the need of treatment, elimination or valorisation of wastes is a current consequence of the increasing conscience of the community towards issues involving the safety of the environment. Increase on consumption levels and consequent increase of industrial production has led to a fast decrease of the available natural resources and, at the same time, a high volume of production of wastes or sub-products are being generated. Lightweight aggregates, that have many applications in building processes and building materials, are then graded and applied according to the particle size [1]. Nevertheless, there is still a considerable amount of generated lightweight aggregates with a size less than 2–3 mm, which are regarded as wastes from the traditional applications point of view.

The objective of this study is to investigate the performance of rejected sieved fractions from lightweight clay aggregates production (LCA) in the turbidity removal, and in a novel utilization: removal of heavy metal species from aqueous solutions. If well succeeded, this might constitute a reuse way that is alternative to the common land filling practice.

Sorption of metal ions from aqueous solutions has been studied by numerous researchers [2–4]. Activated carbon is undoubtedly, the most used and studied sorbent material, but due to its high price, like the ion exchange resins one, some waste products from agricultural, forestry and industrial operations may have potential as inexpensive sorbents [5–7].

Depth bed filtration, by means of granular media, is traditionally used for water turbidity removal [8,9]. Operating conditions and removal performance are strongly dependent on the design of a granular-medium filter, involving the consideration of the type of medium, size and depth, filtration rate, pressure available for driving force10, and method of filter operation [10–17].

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Natural clay is already considered as a low cost sorbent [18,19]. However, clay particles are too fine and have flaky shapes resulting in very low bed porosity filter and limited grain resistance to attrition. By contrast, rejects of light-weight clay aggregates production are large and hard enough since they were processed at reasonably high temperature [1], but their sorption capabilities might be lower. There are not many reports on this, but Johansson [20] describes the use light expanded clay aggregates for the removal of phosphorous from aqueous solutions, apparently with very good indicators.

2. Experimental

2.1. Adsorbate solutions and suspensions

All chemicals used to prepare the contaminant solutions were of analytical grade. Stock Ni(II) and Pb(II) solutions (1000 ppm) were prepared from nickel(II) nitrate hexahydrate (Merck[R]) and lead nitrate (Merck[R]), respectively, and these solutions were used to prepare the other working solutions (100 and 10 ppm).

For turbidity removal tests several suspensions were prepared using clay. For each test it was prepared 2 l of deionised water, with approximately 0.1486 g of clay sieved under 75 μm. By this mean, each prepared suspension was in the range of 37/57.5 NTU. For highly concentrated solutions, suspensions were prepared with a variable quantity of clay.

2.2. Sorbents preparation and characterisation

Average chemical composition of the LCA rejects was determined by XRF (Philips X'UNIQUE II). Their miner-alogical composition was also determined by XRD (Rigaku Geigerflex D/max Series). Reasonable constancy along the time was observed after several checks in consecutive months.

For filtration tests, sieved fractions 0/0.5, 0/3 and 0.5/3 mm were chosen. Their direct use in the as-produced condition was not possible, since the amount of fines (dust) is very significant and easy clogging of filtration beds might occur. Moreover, the level of turbidity is unacceptable and previous washing (deionized water) + drying (at 110 °C, for 1 h) steps are needed.

Several materials were also used, for efficiency comparison: sand (sieved to obtain 250/500 μm fraction), granular activated carbon (Merck[R]) (sieved to obtain 75/500 μm and 0.5/1 mm fractions) and ZA-4 clay (natural Portuguese clay) prepared elsewhere [2,18]. Sieved fractions 500/1000 and 212/355 μm were calcinated at 600 °C for 2 h.

Dependence of electrokinectic potential on pH values, for granular activated carbon (GAC) and LCA 0/0.5 mm was determined.

Specific surface of LCA was obtained by BET technique. Packing density (ρ_e) was obtained using a 250 ml graduated test tube, full of aggregates, following packed until constant volume (V). Mass (m) was registered. Packing density is given by $\rho_e = m/V$ (g/cm^3).
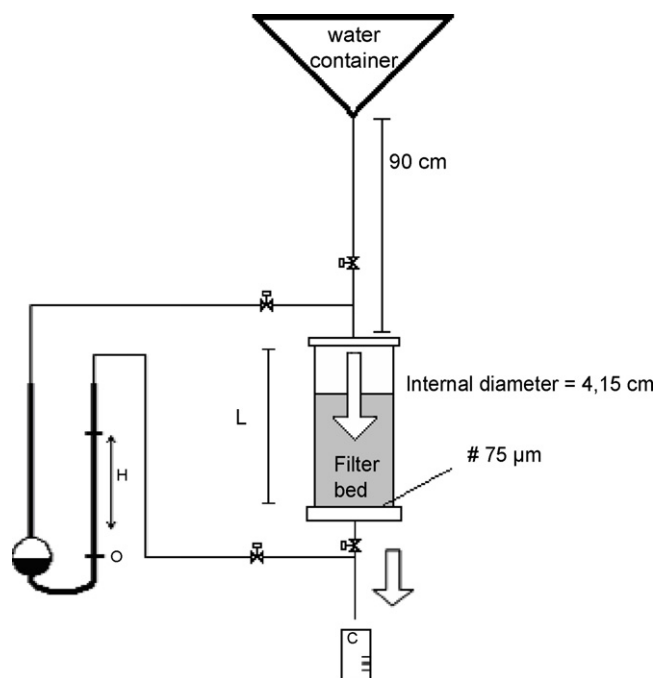

Fig. 1. Experimental setup used in the removal experiments.

2.3. Filtration tests

Fig. 1 shows the experimental setup used in filtration tests, for heavy metals and turbidity removal. Small-depth filters bed (L = 9.5 cm) made with the three sieved fractions already described was used for heavy metal removal. Other tested variables included: (i) the effect of filtration regime (rates of 4.43 and 0.44 m/h); (ii) the initial heavy metals concentration (C_0).

Initial (C_0) and final (C) nickel and lead concentrations were estimated by Induced Couple Plasma (ICP-Jobin Yvon 70 Plus). Each test involved 1 l solution of Ni(II) or Pb(II), and samples for removal measurements were taken in each 100 ml. Before ICP analysis, they were acidified with 0.2 ml nitric acid 65%.

The removal performance was evaluated by the ratio $(C_0 - C)/C_0$ (here named removal efficiency) or by the weight ratio between the amount of contaminant (μg) per g of filtration material used in the filter bed. In general, maximum errors estimated on % removal are less than 5%.

For turbidity removal tests, it was varied the filter depht (L = 9.5, 30 or 45.5 cm), the filtration material (LCA, ZA-4 and sand), and filtration rate (4.43 and 0.44 m/h). Each 100 ml sample taken after filtration, as also the initial suspension, was acidified with 0.2 ml nitric acid 65%, and turbidity (NTU) was measured my the means of AquaLytic[R] PCcompact[R] Turbidimeter. The removal performance was evaluated by the ratio $(T_0 - T)/T_0$.

3. Results and discussion

3.1. Characterisation of lightweight rejects

Table 1 shows the average chemical composition of the as-received rejects. As expected, Si, Al, and Fe are the main

Table 1
Average chemical composition (XRF) of the as-received rejects, concerning major elements/oxides (>0.1 wt. %)

Na_2O	MgO	Al_2O_3	SiO_2	P	SO_4	K_2O	CaO	Mn	Fe_2O_3	TiO_2
0.248	3.97	19.7	52.7	0.125	0.221	5.26	4.61	0.105	11.6	1.29

Table 2
Packing density, ρ_e, and specific surface of selected lightweight aggregates sieved fractions

Material (mm)	Specific surface (m^2/g)	ρ_e (g/cm^3)
0/0.5	2.40	0.75
0/3	1.55	0.60
0.5/3	2.76	0.56

Fig. 3. Dependence of electrokinectic potential on pH values, for granular activated carbon (GAC) and LCA 0/0.5 mm.

elements. XRD results show that quartz is clearly dominant. Calcite ($CaCO_3$), Portlandite ($Ca(OH)_2$) Anorthite ($CaAl_2Si_2O_8$) and Hercynite (($Fe_{0.803}Al_{0.197}$)($Al_{1.803}Fe_{0.197}$)O_4) are also detected, confirming the clayish nature of the material. We should mention that a reasonable constancy was observed from tests conducted in consecutive months.

It is important to quantify the amount of carbonates and hydroxides, since they tend to complex metal ions in solution, compromising its correct analytical determination. We should remind that a reasonable constancy was observed from tests conducted in consecutive months.

Since physical parameters of formed beds are expectably relevant in the removal efficiency, some determinations were made. Table 2 gives the packing densities of beds made of several sieved fractions and the corresponding specific surface.

As expected, closed beds are formed when smaller grains are used. The effect of the finer particles is easily observable by comparing 0/3 and 0.5/3 mm fractions. In addition to the size, particles shape is another morphological relevant parameter. Larger grains are normally less spherical and their compactness is expectably lower. Fig. 2 shows the three sieved fractions used in this study. Particles from 0.5/3 mm fractions have more assorted shapes and are apparently less spherical.

LCA and GAC differences in the electrokinectic potential of particles in aqueous suspension are shown in Fig. 3.

Although, LCA does not have stronger removal capacity of positive species as clay has, in relation to GAC [2,18], for the pH region verified in this study (optimal efficiency is reached at pH ~13), LCA have the expected ability to remove cations on its surface, by adsorption.
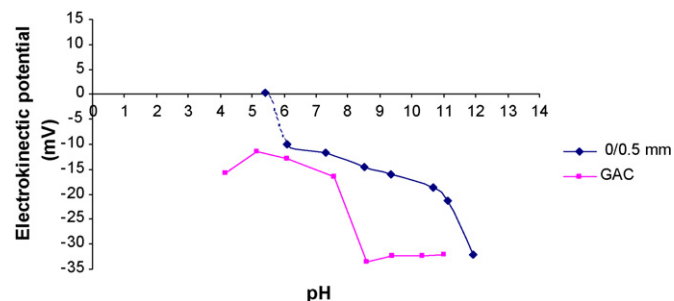
3.2. Filtration

3.2.1. Heavy metal removal

The effect of initial concentration (C_0) of Ni(II) and Pb(II) contaminants in the removal efficiency was studied by using three different levels: 10, 100 and 1000 ppm (ICP analysis gives the exact values). As it was expected, higher removal efficiencies are obtained for less contaminated solutions (Figs. 4 and 5).

Removal of lead is more effective than nickel, as can be easily seen by comparing results for 1000 ppm solutions which are closer to the saturation. This difference should be related with differential chemical affinity of both ions to the LCA. Differences in the ionic radii (Pb^{2+} is bigger) should also be important. In both cases, however, no decreasing performance is noticed, even after 10 runs (1 l).

The effect of different sized LCA fractions (0/0.5, 0/3 and 0.5/3 mm) on Ni(II) and Pb(II) removal is outlined in Figs. 6 and 7.

Ni(II) and Pb(II) removal is better for the smallest fraction 0/0.5 mm, what seems to be due to physical entrapping, resulted from the higher packing density. 0/3 mm fraction does not have the lower ρ_e value, but shows the lowest specific surface amongst all materials. For coarser materials, specific surface seems to determine the removal process.

Fig. 2. View of lightweight clay aggregates sieved fractions (from left to right): 0/3 mm, 0.5/3 mm, 0/0.5 mm.
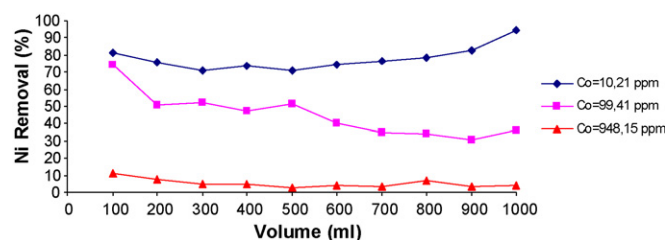
Fig. 4. Effect of initial Ni^{2+} concentration on the metal removal efficiency of filtration through a 0/3 mm sieved bed; flow rate = 4.43 m/h.

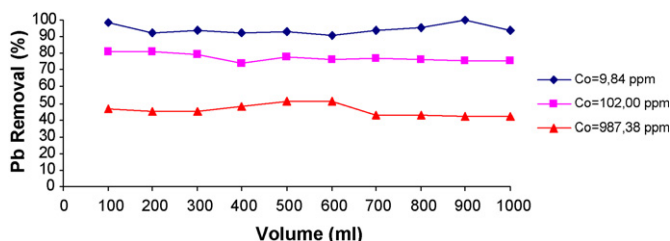Fig. 5. Effect of initial Pb^{2+} concentration on metal removal efficiency of filtration through a 0/3 mm sieved bed; flow rate = 4.43 m/h.
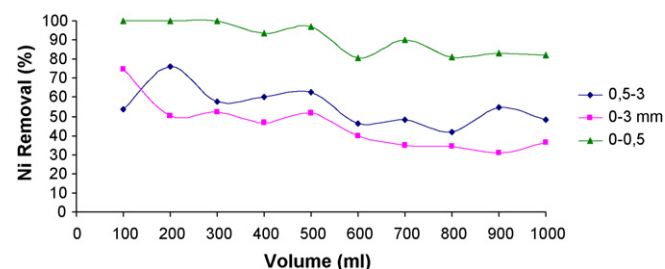

Fig. 6. Ni^{2+} removal efficiency through filtration beds made of different sieved fractions: $C_0 = 100$ ppm; flow rate = 4.43 m/h.

Fig. 8. Effect of the flow rate on Ni^{2+} ($C_0 = 100$ ppm) removal through several beds: 4.43 m/h (solid lines); 0.44 m/h (dashed lines).

Fig. 9. Effect of the flow rate on Pb^{2+} ($C_0 = 100$ ppm) removal through several beds: 4.43 m/h (solid lines); 0.44 m/h (dashed lines).

0.5 mm fractions, the advantage of using lower flow regimes in the removal of both metals is less significant. This kind of representation (μg/g vs. volume) apparently contradicts the conclusions depicted from Figs. 6 and 7, since they show 0/3 mm fraction as the material with better removal performance. This is due to differences in packing density (0.60 and 0.75 g/cm³ for 0/3 and 0/0.5 mm, respectively), i.e., for a fixed filter volume, a higher amount of 0/3 mm fraction is necessary.

In order to compare efficiency removal of LCA with other material, two GAC sieved fractions were tested in the removal of Ni(II) and Pb(II) (Fig. 10).

These results were compared with the ones obtained for LCA at 0.44 m/h and for $C_0 = 1000$ ppm. GAC filtration beds have better efficiency than 0.5/3 and 0/3 mm in the beginning of Ni(II) removal, but they have a tendency to show earlier saturation. For Pb(II) removal both materials have similar efficiencies.

Figs. 8 and 9 summarize the effect of the flow rate on the removal efficiency through several sieved fractions. Results are now represented as the amount of contaminant (μg) kept per g of filtration material. It seems that there is a combined influence of packing density and time for removal (lower flow rate corresponds to increasing contact time). For 0/3 mm fraction, the use of lower flow rate has more obvious benefits, since this material has a lower specific surface value. For 0.5/3 and 0/
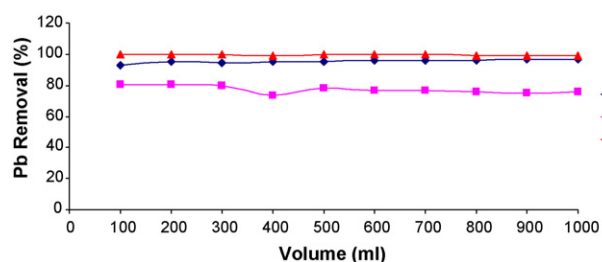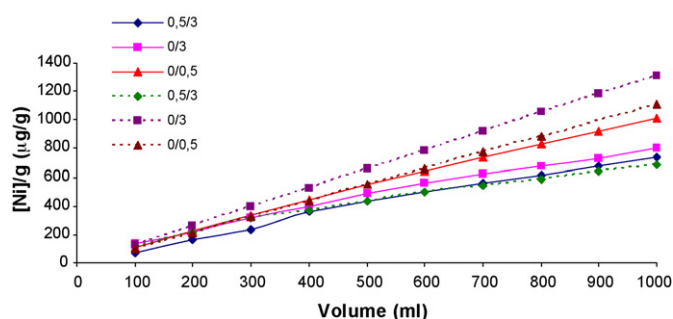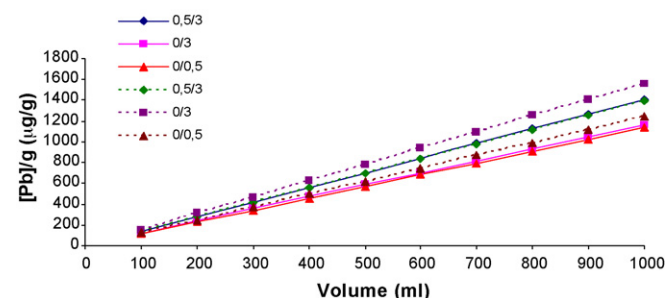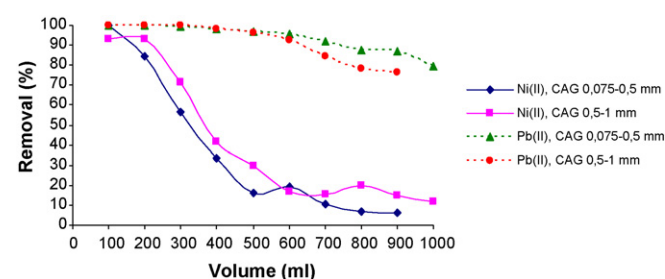

Fig. 7. Pb^{2+} removal efficiency through filtration beds made of different sieved fractions: $C_0 = 100$ ppm; flow rate = 4.43 m/h.

Fig. 10. Ni^{2+} and Pb^{2+} removal efficiency through filtration beds made of CAG different sieved fractions: $C_0 = 1000$ ppm; flow rate <0.44 m/h.
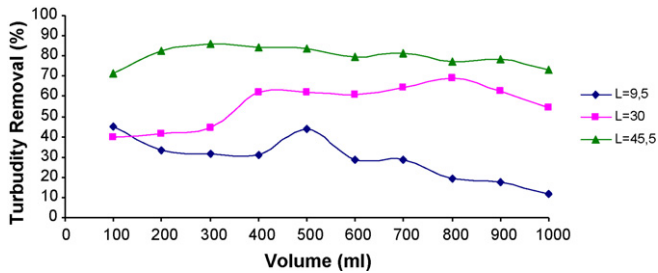
Fig. 11. Turbidity removal efficiency through filtration beds made of LCA 0.5/3 mm sieved fraction and variable depth (L): $C_0 = 42$–44.7 NTU, flow rate = 4.43 m/h.

Fig. 14. Turbidity removal efficiency through filtration beds made of different LCA sieved fraction with depth (L) = 45.5 cm and comparison with sand: $C_0 = 199.7$–438.7 NTU, variable flow rate.
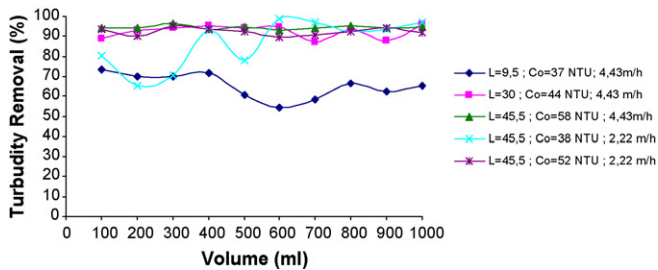

Fig. 12. Turbidity removal efficiency through filtration beds made of LCA 0/3 mm sieved fraction and variable depth (L): $C_0 = 37$–58 NTU, variable flow rate.

Fig. 15. Turbidity removal efficiency through filtration beds made of ZA4 clay different sieved fractions: $C_0 = 338$–551.77 NTU, variable depth (L), variable flow rate.

3.2.2. Turbidity removal

The first batch of turbidity removal tests had the following purposes: studying the influence of depth bed, for a certain sieved fraction (Figs. 11–13), and flow rate.

The higher depth bed, 45.5 cm, revealed to be the most effective, once, as the superficial area grows it is possible to retain more suspended material. For $L = 30$ cm an high removal efficiency was found for LCA 0/3 mm, and it could occur for 0/0.5 mm sieved fraction if it did not take place the abrupt decreasing on the efficiency removal for 500 ml of filtrated solution (Fig. 13). This reveals the possible particle detachment formerly retained in the filter, or a new free "path" found by contaminated solution.

So, considering $L = 45.5$ cm the removal efficiency varies between 80 and 100%, according to the used sieved fraction. Smaller sieved fractions (0/0.5 and 0/3 mm) are more effective than coarser ones (0.5/3 mm) on the turbidity removal, due to the more effective packing.
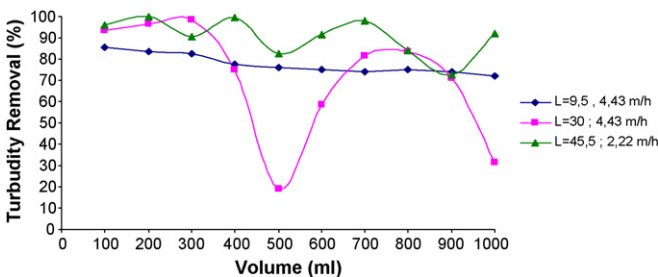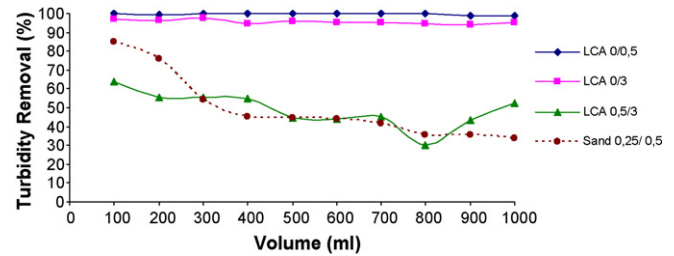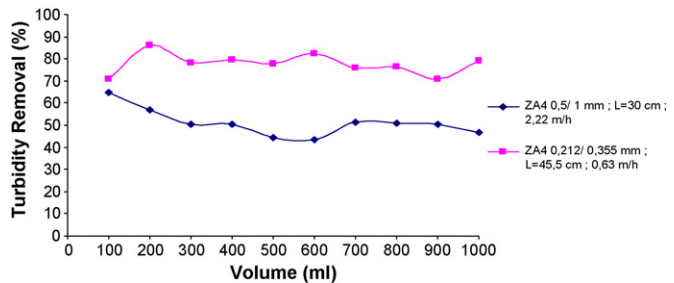

Fig. 13. Turbidity removal efficiency through filtration beds made of LCA 0/0.5 mm sieved fraction with variable depth (L): $C_0 = 37$–48.3 NTU, variable flow rate.

Fig. 12 shows that different studied flow rates (4.43 and 2.22 m/h), for equal L and C_0, were not of great relevance for results. However, Farizoglu et al. [9] testing 7.64–22.91 m/h found lower removal efficiencies when using higher flow rates. Due to practical issues, was not possible, in the present work, testing so high and distinctive flow rate values.

The second batch of turbidity removal tests, when the optimal parameters were already studied, was conducted in order to study the initial particle concentration in solution. Results for high initial concentration tests (Figs. 14 and 15) should be compared with the ones from Figs. 11–13.

4. Conclusions

Results of the removal efficiency of heavy metals (Pb and Ni) from aqueous solutions through particulated beds made of rejects generated in the production of lightweight aggregates are reported and seem promising. Filtration under slower regime (0.44 m/h) was found optimal amongst all tested conditions (faster filtration and adsorption). The efficiency tends to increase with the use of finer grains, especially for Ni(II) removal. However, differences between tested sieved fractions are not very high and tend to be less significant for lead. This means that as-processed batch can be directly used, apart the needed washing step to remove dusts.

Exhaust beds can potentially be reused in the production of new lightweight aggregates and retained contaminants will be expectably fixed by firing in the clay matrix. Future studies will help to define maximum incorporation levels for this completely residues-free cycle.

References

[1] S. Pinto, M. Almeida, A.M.S. Correia, J.A. Labrincha, V.M. Ferreira, K. Rosenbom, Use of recycled materials in buildings and structures, in: Proceedings of International RILEM Conference on the Use of Recycled Materials in Buildings and Structures, Barcelona, Spain, vol. 2, (2004), pp. 771–777.

[2] G. Márquez, M.J. Ribeiro, J. Ventura, J.A. Labrincha, Removal of nickel from aqueous solutions by clay-based beds, Ceram. Int. 30 (1) (2004) 111–119.

[3] L. Dabek, Sorption of zinc ions from aqueous solutions on regenerated activated carbons, J. Hazard. Mater. B101 (2003) 191–201.

[4] T.K. Budinova, K.M. Gergova, N.V. Petrov, V.N. Minkova, Removal of metal ions from aqueous solution by activated carbons obtained from different raw materials, J. Chem. Tech. Biotechnol. 60 (1994) 177–182.

[5] H. Hasar, Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from almond husk, J. Hazard Mater. B97 (2003) (2003) 49–57.

[6] S. Al-Ashed, Z. Duvnjak, Sorption of cadmium and other heavy metals by pine bark, J. Hazard. Mater. 56 (1997) 35–51.

[7] S. Bailey, T. Olin, R. Bricka, D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (11) (1999) 2469–2479.

[8] J.L. Cleasby, G. Logsdon, Lecho granular y filtration de precapa, in: American Water Works Association (Ed.), Calidad y tratamineto del água. Manual de Sumistros de agua comunitaria, MacGrawHill Professional, 2002, pp. 453–546.

[9] B. Farizoglu, A. Nuhoglu, E. Yildiz, B. Keskinle, The performance of pumice as a filter bed material under rapid filtration conditions, Filtr. Sep. 40 (2003) 41–47.

[10] K.J. Ives, Specifications for granular filter media, Effluent Water Treat. J. 22 (1975) 296–305.

[11] K.J. Ives, Testing of filter media, J. Water SRT Aqua 39 (1990) 144–151.

[12] R. Ben Aim, S. Vigneswaran, H. Prasanthi, V. Jegatheesan, Influence of particle size and size distribution in granular bed filtration and dynamic microfiltration, Water Sci. Technol. 36 (1997) 207–215.

[13] K.J. Ives, C.S. Fitzpatrick, Detachment of deposits from sand grains, Colloids Surf. 39 (1989) 239–253.

[14] J.L. Cleasby, Declining rate filtration, Water Sci. Technol. 27 (1993) 11–18.

[15] K.V. Ellis, M.E. Aydin, A study of three slow sand filters at various flow rates with constant temperature, J. Water SRT Aqua 42 (1993) 88–96.

[16] M.A. Boller, M.C. Kavanaugh, Particle characteristics and headloss increase in granular media filtration, Water Res. 29 (1995) 1139–1149.

[17] S.D. Lambert, N.J. Graham, A comparative evaluation of the effectiveness of potable water filtration processes, J. Water SRT Aqua 44 (1995) 38–51.

[18] M.J. Ribeiro, J.A. Labrincha, Spray-dried calcined clays in water filtration columns used for chromium removal, Colloid Polym. Sci. 276 (1998) 723–729.

[19] S. Hawash, H. El-Abd, M.S. El-Geundi, M.M. Nassar, J.Y. Farah, Useful adsorption equilibriums by means of natural clay, Adsorpt. Sci. Technol. 9 (1992) 231–243.

[20] L. Johansson, The use of leca (light expanded clay aggregates) for the removal of phosphorous from wastewater, Water Sci. Technol. 35 (1997) 87–93.