

Testing of potential reactive materials for removal of heavy metals from contaminated water

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One of the most important environmental problems of the last decade is water (groundwater, surface water) contamination, which poses a significant ecological risk to the environment and human health. Permeable reactive barrier (PRB) is an efficient technology for remediating contaminated water on industrial and mining sites. The PRB technology is based on an emplacement of a reactive material in the subsurface designed to intercept a contaminated groundwater plume. The contaminated plume flows through the reactive material where the contaminants are transformed into environmentally acceptable species. The aim of the present study was to test experimentally caustic calcined magnesite, limestone, dolomite and blast furnace slag as potential reactive materials for the PRB technology. The effects of the chemical composition of contaminated water and water-to-reactive material weight ratio on the efficiency of heavy metals removal were investigated. The results have shown that caustic calcined magnesite (CCM-KK) was the most suitable reactive material for removal of cations Fe³⁺, Al³⁺, Cu²⁺, Zn²⁺, Ni²⁺, and Mn²⁺. This reactive material was able to increase the pH of the contaminated water to the value of about 10 and the efficiency of selected cations removal up to 100 % was observed.

Key words: contaminated water, heavy metals, removal, reactive materials

Introduction

At the present time, industrial waters and acid mine drainage (AMD) are considered as the main sources of water pollution in many countries (Akcil and Koldas, 2006, Blais et al, 2008). These waters contain heavy metals and are characterized by low pH. Heavy metals such as copper, zinc and nickel are commonly found in wastewaters emanating from mining activities, metal finishing industry, refining and smelting of metals and metallurgical processes. Wastewaters from these industries generally contain large amounts of Fe³⁺, Al³⁺, Cu²⁺, Ni²⁺ and Zn²⁺ ions (Vhahangwele, 2015). Because of their high solubility in the aquatic environments, heavy metals can be absorbed by living organisms. This results in serious environmental problems and causes negative effects to the eco-systems and human life's (Barakat, 2011, Kurniawan et al., 2006). The water contaminants come from two categories of sources: (a) point sources and (b) diffuse sources. Diffuse contamination may have greater environmental impacts because much larger volumes of water are affected. Point sources of groundwater contamination include abandoned mines, dumps, tailings or areas of old metallurgical, chemical, manufacturing and other industrial plants. The contaminants interact with the moving groundwater and spread out to form a plume moving in the same direction as the groundwater. The resulting groundwater contamination plume may extend several hundred meters or even further away from the source of contamination. Groundwater can also be contaminated over a wide area by diffuse sources such as households, sewer systems or agriculture (due to the use of fertilisers and pesticides). Contaminations from point sources are generally related to urban development, while diffuse sources are generally rural in nature (Thiruvengkatachari et al., 2008, Hashim et al., 2011). Compared to other technologies, permeable reactive barriers (PRB) are the representatives of so called passive treatment systems (Obiri-Nyarko et al., 2014) and have become more competitive and economical for the contaminated water remediation (Liu, et al. 2015). PRBs use the natural hydraulic gradient of the groundwater plume to move the contaminants through the reactive barrier (wall), filled with a suitable reactive material and placed perpendicularly in the flow path of a contaminated groundwater plume (Philips, 2009). The contaminated groundwater flows through the reactive material, and contaminants are removed by precipitation, ion exchange, adsorption, redox reaction or biological treatment, and having been transformed into environmentally acceptable form (Blowes et al., 2000, Chen, et al., Hashim et al., 2011, Obiri-Nyarko et al., 2014, Thiruvengkatachari et al., 2008). Most PRB technologies have been installed in industrial, mining and agricultural sites and have been successfully applied to remove a variety of contaminants including heavy metals, volatile organic compounds and radionuclides (Philips, 2009).

The choice of a suitable reactive material is generally determined by numerous factors, including the reactive material reactivity, contaminants (type, concentrations and removal mechanisms), hydraulic performance, stable and environmentally compatible by-products, availability and price (Gavaskar et al., 2000, Obiri-Nyarko et al., 2014). The suitable reactive material should be able to remove the contaminants (heavy

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metals) within an acceptable residence time. Selection of the particle size of the reactive material should take into account the trade-off between reactivity and hydraulic conductivity. The selected reactive material should be able to retain its reactivity and hydraulic conductivity over time. This consideration is governed by the potential for precipitate formation and depends on how quickly the selected reactive material is able to react with the contaminants. The by-products generated during the water treatment process should not have harmful and toxic effects on the environment. An important consideration in selecting a suitable reactive material is a waste production and possibilities of disposal of the used material after exhausting its capacity. The selected reactive material should be easily available in large quantities at a reasonable price (Gavaskar et al., 2000). At the present, zero valent iron is the reactive material mostly used in PRB due to the successful removal of organic and inorganic contaminants, such as chlorinated volatile organic compounds (VOCs), hydrocarbons, chromium, and arsenic (Gavaskar et al., 2000, Obiri-Nyarko et al., 2014, The Interstate Technology&Regulatory Council, 2005). Recently, the use of natural and waste materials for remediation has received attention as they provide cheaper alternatives (Wantanaphong et al., 2005). There are many types of materials that may provide treatment of, contaminated water, such as organic materials, complexing agents, phosphate minerals, hydroxyapatite, and biological apatite, zeolite, clay, limestone, metal oxides, microorganisms and polymers (Obiri-Nyarko et al., 2014, The Interstate Technology&Regulatory Council, 2005). The use of natural and waste materials may be more appropriate because of their (a) great ability to remove contaminants and (b) lower cost (The Interstate Technology&Regulatory Council, 2005).

Limestone (calcite), hydrated lime (Ca(OH)_2), and dolomite ($\text{CaMg(CO}_3)_2$) are alkaline materials used particularly for the treatment of groundwater contaminated with heavy metals (Chen, et al., Hashim et al., 2011). The application of these materials adjusts the pH of the contaminated water to a point where the solubility of metals is reduced to allow their precipitation. There are two major problems relating to the use of these materials: (a) clogging the barrier by the precipitates formed and reduction of its hydraulic performance, and (b) loss of the efficiency of the system because of coating the alkaline particles with precipitates. Furthermore, large doses of alkaline materials may result in remobilization of heavy metals, because the actual pH value can be higher than the optimal one required for the precipitation. Therefore, since these materials work by pH adjustment, it is imperative to ensure that the ideal pH conditions are maintained within the barriers during their use (Obiri-Nyarko et al., 2014, Thiruvengkatachari et al., 2008). Limestone and dolomite are the most commonly employed alkaline reactive materials due to their availability and low-cost in most countries (Barakat, 2011). As an alternative to limestone, the use of caustic calcined magnesia (CCM) has been employed in recent years (Lin et al., 2005, Rötting et al., 2008). CCM (MgO) is used in environmental control technology and compared to the most commonly used alkalis (limestone, hydrated lime or dolomite) it presents some essential advantages (Lin et al., 2005). Theoretically, the pH of a saturated Mg(OH)_2 slurry is about 10, but in reality, buffer solutions can be formed with pH of 9-9,5 (Ayora et al., 2013, Caraballo et al., 2009, Cortina et al., 2003, Rötting et al., 2008). Due to the milder basic character and low solubility of Mg(OH)_2 , CCM as a reactive material in passive remediation systems is very useful due to its relatively low environmental impact, and the safety of its transportation and use, as well (Cortina et al., 2003, Navarro et al., 2006). Blast furnace slag is a by-product of iron making, widely used for road base construction and other products. Being an industrial by-product, slag has the advantage of being very inexpensive, especially when a local source is available. Major components include SiO_2 , Al_2O_3 , CaO ; MgO , FeO and sulphides in the form of CaS , MnS and FeS are minor components. (Václavík et al., 2012, The Interstate Technology&Regulatory Council, 2005). In PRB technology, it can also be used as a reactive material for the removal of heavy metals and other contaminants. The removal of heavy metals using slag is likely to occur through sorption and precipitation of metal hydroxides under high-pH conditions, due to the high lime content. Slag usually buffers the pH of groundwater around 12 (The Interstate Technology&Regulatory Council, 2005).

The aim of this paper was to test four selected reactive materials (caustic calcined magnesia, limestone, dolomite and blast furnace slag) and choose the most suitable one for heavy metals removal from given contaminated water.

Theoretical background

Chemical precipitation is the most widely used process for heavy metals removal from contaminated waters, because it is relatively simple and inexpensive to operate (Fu and Wang, 2011, Kurniawan et al., 2006). Precipitation is a physical-chemical process, in which dissolved ions of heavy metals are converted to relatively insoluble compounds of heavy metals (precipitates) by the addition of a precipitating agent. Metals can be removed by precipitation as insoluble metal hydroxides, sulfides, carbonates, and phosphates. Typically, when an alkaline reactive material is used in a PRB, metals are precipitated from the solution in the form of hydroxide according to Eq. (1) (Kurniawan et al., 2006, Blais et al., 2008):



Tab. 2. The chemical composition of real contaminated water.

Real contaminated water	pH	Concentrations of metals [mg/l]						Organic compounds
		Fe	Mn	Cu	Zn	Ni	Al	
D HPV (long-term average)	1.9	997	14.8	20.5	8.7	0.6		Present
D HPV (sample used in the present study)	2.1	1369	11.7	28.8	15.9	0.34	170.0	Present

Model contaminated water was prepared by dissolving chemicals - the sulphates of Cu^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Al^{3+} , and Fe^{3+} in distilled water. The chemical composition of the model contaminated water was adjusted to represent a long-term average of the results obtained in the given industrial area. Since the total concentration of dissolved cations of metals was up to 50-times higher than the concentration of H^+ ions at pH=2, model contaminated water with pH=3.2 (i.e. with approx. 10-times lower concentration of H^+ ions) was used to test a potential effect of initial pH of the water tested. The concentrations of individual components in the synthetic contaminated water were determined by inductively coupled plasma (ICP) method and are shown in Table 3.

Tab. 3. The chemical composition of model contaminated water.

Model contaminated water	pH	concentrations of metals [mg/l]						Organic compounds
		Fe	Mn	Cu	Zn	Ni	Al	
DB	3.2	882.9	15.0	20.7	29.5	0.9	0.7	absent

Laboratory batch tests

In each test, a defined amount (0.4 or 0.8 g) of reactive material was added to 40 ml of contaminated water (synthetic or real one) in a glass tube. The tube's content was intensively mechanically mixed at room temperature for 2 hours. Then the slurry was filtered, pH of the filtrate was measured, the filtrate was acidified by concentrated HNO_3 to decrease the pH and stabilize the solution before chemical analysis and, finally, analysed by the ICP method. The efficiency (E) of individual metals removal was calculated using Eq. 2:

$$E = \frac{c_0 - c_r}{c_0} \cdot 100 \quad (2)$$

where: c_0 is the initial concentration [mg/L] and c_r is the final concentration [mg/L] of Cu^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Fe^{3+} or Al^{3+} .

Results and discussion

In this study, the effects of the pH, reactive material used and S:L (i.e., reactive material – to – water) ratio (1:100 and 1:50) on the efficiency of heavy metals (Cu, Zn, Ni, and Mn) removal from the contaminated waters were studied. The pH values measured in distilled water after an addition of individual reactive materials (CCM-JE, CCM-KK, BFS, L, D) are compared in Fig. 2. The samples CCM-JE and BFS have reached the highest pH values, followed by CCM-KK. Limestone and dolomite gave lower pH values than CCM-KK. The differences in pH values probably resulted from different contents of lime (CaO), reactive magnesium oxide (MgO), and calcium and magnesium carbonates (CaCO_3 , MgCO_3) in the reactive materials used. There was only a little difference in pH observed for individual reactive materials at different S:L ratios.

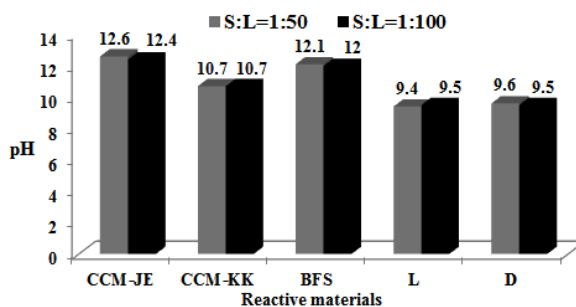


Fig. 2. pH values measured in distilled water after adding reactive materials.

The comparison of the final pH values measured in the model and real contaminated water after the precipitation of hydroxides is illustrated by Fig. 3 and 4. The initial pH values of the model and real contaminated water were 3.2 and 2.1, respectively.

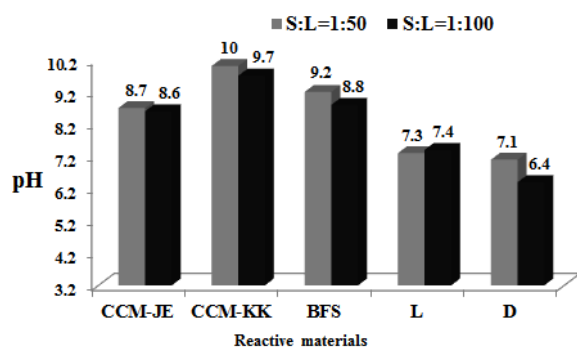


Fig. 3. Comparison of the final pH values in contaminated water DB.

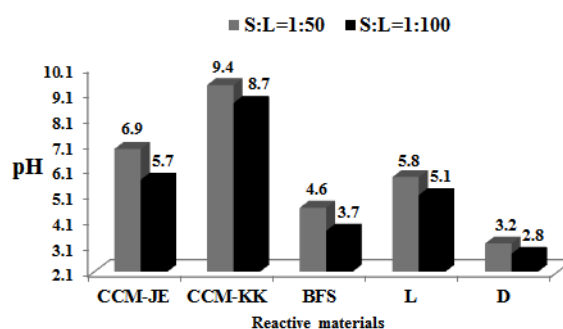


Fig. 4. Comparison of the final pH values in contaminated water D HPV.

It can be seen from Fig. 3 and 4 that in both cases (i.e., in the model and real contaminated water), reactive material CCM-KK has reached the highest pH values. The high pH is likely to be caused by the high content of the reactive magnesium oxide (MgO) due to optimal thermal treatment of the raw magnesite used. In the case of model contaminated water DB, the samples BFS and CCM-JE have reached slightly lower pH values than CCM-KK. Limestone and dolomite have reached the lowest pH values. In the case of real contaminated water D HPV, the sample CCM-KK was more effective in raising the pH than other reactive materials used. CCM-JE has practically achieved neutral pH, while other materials have achieved much lower pH values. Different final pH values measured in the model and real contaminated water were probably caused by the differences in the initial water acidity, concentrations of iron and aluminium, and presence/absence of organic compounds. In the contaminated water sample DB, only a smaller part of added reactive materials was consumed to increase the initial pH value and the reactive materials were mostly used to remove monitored heavy metals. It can be concluded that in contaminated water with higher iron and aluminium content (D HPV), the major part of added reactive materials was consumed to reduce the concentration of iron and aluminium and only a residual part of the reactive materials was used to precipitate the monitored heavy metals. Another important factor was the presence or absence of soluble organic substances, which might influence the heavy metals removal. No soluble organic substances were present in the model contaminated water DB, while the real contaminated water D HPV contained soluble organic substances.

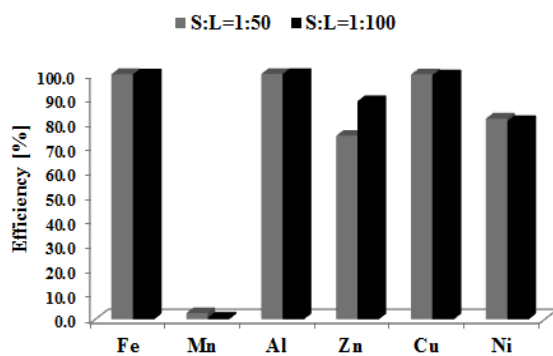


Fig. 5. The efficiency of metals removal from DB using dolomite.

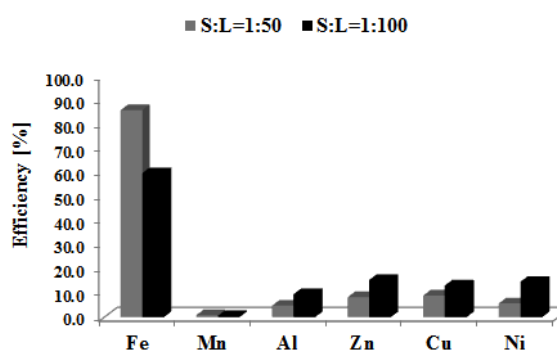


Fig. 6. The efficiency of metals removal from D HPV using dolomite.

The values of the efficiency of the heavy metals removal from water samples DB and D HPV using an addition of individual reactive materials tested in the present study are compared in Fig. 5 - 14. Fig. 5 and 6 illustrate the situation after an addition of dolomite (D). The final pH values 6.4 and 7.1 were observed in contaminated water DB at the S:L ratio 1:100 and 1:50, respectively. At the S:L ratio 1:50 and S:L=1:100 Fe, Al, and Cu were completely removed. The efficiency of Ni removal for both S:L ratios was almost the same (approximately 80 %). At the S:L ratio = 1:100, zinc has been removed to 89 %, while at the S:L ratio = 1:50, the efficiency decreased to 75 %. No manganese has been removed. The final pH values for the water sample D HPV were 3.2 and 2.8 at the S:L ratio = 1:50 and 1:100, respectively. In this case, Fe has been removed only to 86 % and 60 % at the S:L ratio = 1:50 and 1:100, respectively. The efficiency for other metals was lower than

15 %. In the case of the contaminated water DB, iron, aluminium, and copper were completely removed, while zinc, nickel, and manganese remained partly dissolved. The observed efficiency of nickel removal was higher than that for zinc, although zinc is expected to precipitate at a lower pH than nickel - however, the concentration of nickel was significantly lower than that of zinc. It can be concluded that in contaminated water D HPV, a significant part of added dolomite was consumed to increase pH and to reduce iron concentration, and only a residual part of dolomite was used to remove the heavy metals. The final pH values measured at both S:L ratios were far from optimal pH values for monitored metals removal.

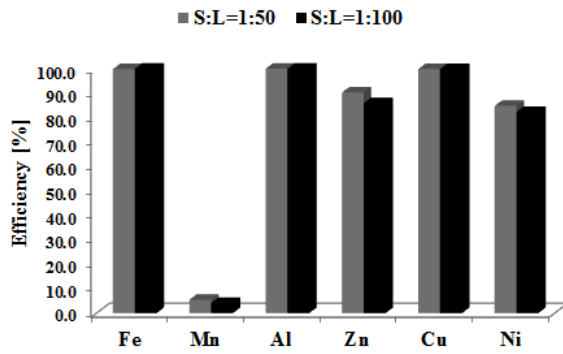


Fig. 7. The efficiency of heavy metals removal by using limestone in DB

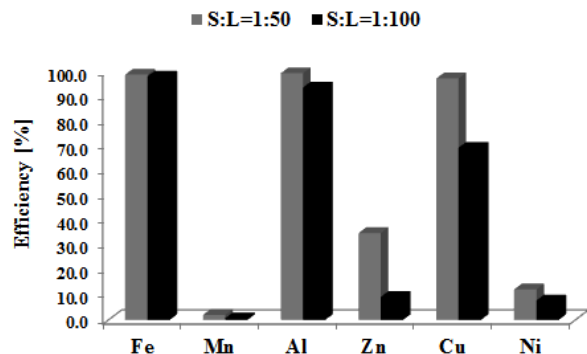


Fig. 8. The efficiency of heavy metals removal by using limestone in D HPV.

Fig. 7 and 8 illustrate the efficiency of monitored metals removal after an addition of limestone (L). The final pH values 7.4 and 7.3 were observed in contaminated water DB at the S:L ratio 1:100 and 1:50, respectively. At the S:L ratio 1:50 and S:L=1:100, Fe, Al, and Cu were completely removed. The efficiency of removal was 90% for zinc and 85 % for a nickel at the S:L ratio =1:50, but at the S:L ratio = 1:100 the efficiency was decreased to 85 % for zinc and 82 % for nickel. Manganese has been removed only to 5 % at both ratios. The final pH values for the water sample D HPV were 5.8 and 5.1 at the S:L ratio = 1:50 and 1:100, respectively. In the case of contaminated water D HPV, only Fe, and Al were completely removed. The efficiency of copper removal was 97 % and 70 % at the S:L ratio = 1:50 and 1:100, respectively. At the S:L ratio = 1:50, zinc has been removed only to 35 %, and at the S:L ratio = 1: 100, the efficiency was decreased to 9 %. The efficiency of nickel removal was only 12 % and 8 % at the S:L ratio = 1:50 and 1:100. No manganese has been removed using limestone. In the case of contaminated water DB, iron, aluminium and copper were completely removed, while the removal of zinc, nickel, and manganese was not complete. The optimal pH values which are needed to remove zinc, nickel and manganese have not been reached in this case. It can be assumed that in contaminated water D HPV, a significant part of added limestone was consumed to increase pH and to reduce iron and aluminium contents, and only a residual part of added limestone was consumed to remove copper, zinc, nickel, and manganese.

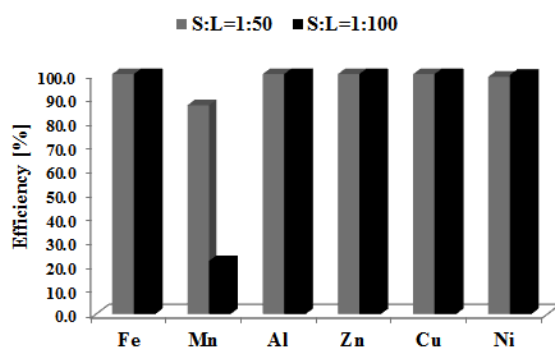


Fig. 9. The efficiency of metals removal from DB using blast furnace slag.

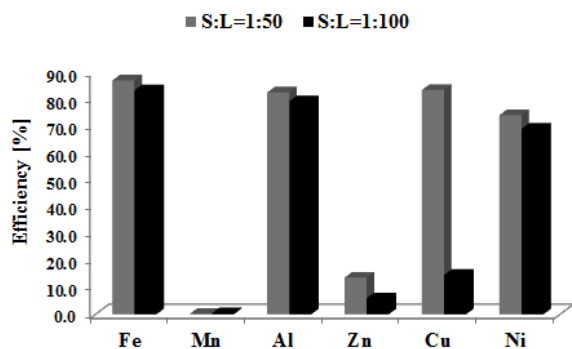


Fig. 10. The efficiency of metals removal from D HPV using blast furnace slag.

Fig. 9 and 10 illustrate the efficiency of heavy metals removal after the addition of blast furnace slag (BFS). The final pH values 8.8 and 9.2 were observed in contaminated water DB at the S:L ratio 1:100 and 1:50, respectively. It can be seen that in the case of contaminated water DB, the S:L ratio has not affected the efficiency of Fe, Al, Zn, Cu, and Ni removal and these heavy metals were completely removed. The only exception was manganese - the efficiency of manganese removal was 87 % and 22 % at the S:L ratio = 1:50 and 1:100, respectively. The final pH values for the water sample D HPV were 4.6 and 3.7 at the S:L ratio = 1:50 and 1:100, respectively. In the case of contaminated water D HPV, the S:L ratio affected the efficiency of the heavy

metals removal. The efficiency was 85 % for Fe, 80 % for Al, and 70 % for Ni at both S:L ratios. At the S:L ratio = 1:50, copper has been removed to 83 %, while at the S:L ratio = 1: 100, the efficiency was decreased to 15 %. Zinc has been removed only to 14 % and 6 % at the S:L ratio 1:50 and 1:100. No manganese has been removed at both ratios. It can be concluded that in contaminated water D HPV, a significant part of the added blast furnace slag was consumed to increase pH and to reduce iron and aluminium, and only a residual part of the added blast furnace slag was used to remove zinc, copper, nickel, and manganese. Thus, the optimal pH values which are needed to remove zinc, nickel, copper and manganese have not been reached.

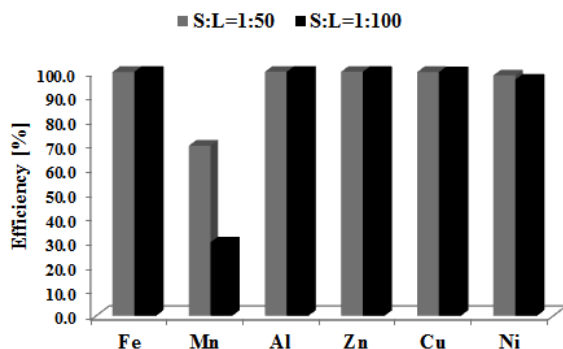


Fig. 11. The efficiency of metals removal from DB using CCM-JE.

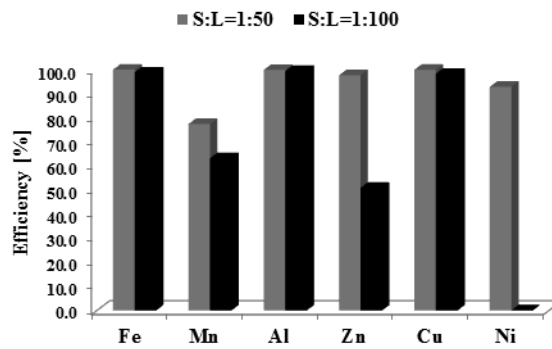


Fig. 12. The efficiency of metals removal from D HPV using CCM-JE.

Fig. 11 and 12 illustrate the efficiency of heavy metals removal after an addition of caustic calcined magnesia CMM-JE. The final pH values 8.7 and 8.6 were observed in the contaminated water sample DB at the S:L ratio = 1:50 and 1:100, respectively. It can be seen that in the case of contaminated water DB, the S:L ratio had not affected the efficiency of Fe, Al, Zn, Cu, and Ni removal and these metals were practically completely removed. Only manganese has not been completely removed: at the S:L ratio = 1:50, the efficiency of approximately 70 % was observed and at the S:L ratio = 1:100, the efficiency was decreased to 30 %. In water sample D HPV, the final pH values were 6.9 and 5.7 at the S:L ratio =1:50 and 1:100, respectively. In the case of contaminated water D HPV, the efficiency of Fe, Al, and Cu removal has not been affected by the value of S:L ratio and the monitored metals were completely removed. At the S:L ratio=1:50, the efficiency of manganese removal was 77 %, and it was decreased to 63 % at the S:L ratio = 1:100. While at the S:L ratio = 1:50, the efficiency was 97 % for zinc and 93 % for nickel, at the S:L ratio = 1:100 the efficiency of zinc was much lower (50 %) and practically no nickel has been removed. It can be concluded that in contaminated water D HPV, a significant part of CCM-JE was consumed to increase pH and to reduce iron, aluminium and copper and only a residual part of added CCM-JE was used to remove zinc, nickel, and manganese. Thus, the optimal pH values which are needed to remove zinc, nickel, and manganese have not been reached.

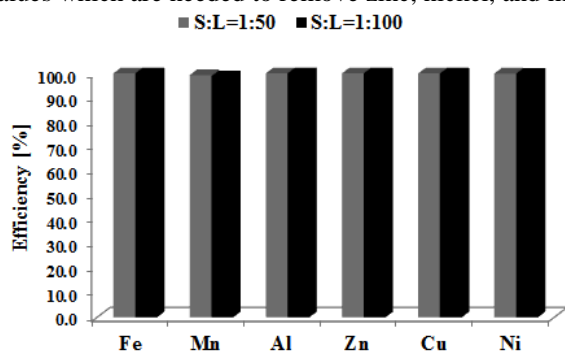


Fig. 13. The efficiency of metals removal from DB using CCM-KK.

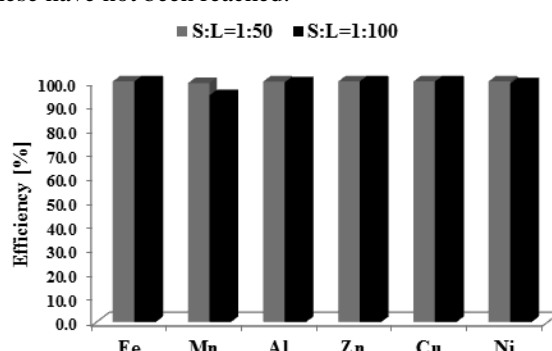


Fig. 14. The efficiency of heavy metals removal from D HPV using CCM-KK.

Fig. 13 and 14 illustrate the efficiency of heavy metals removal after an addition of caustic calcined magnesia CCM-KK. The final pH values were 10.0 and 9.7 at the S:L ratio =1:50 ratio and 1:100, respectively. In Fig. 13, the efficiency values for the model contaminated water DB are shown, while the results for the real water D HPV are summarised in Fig. 14. The final pH values at the S:L=1:50 ratio and S:L=1:100 ratio were 9.4 and 8.7. Practically all the monitored heavy metals were completely removed from both model and real contaminated water at both S:L ratios. It can be concluded that CCM-KK was the best reactive material because it provided the final pH values which are needed to remove heavy metals.

The theoretical prediction of the optimum pH for precipitation of the hydroxides of the monitored metals results from Fig. 1 and from the related text. As can be seen from the accompanying text to Figs. 2-14, a very

good correlation between the obtained results and literature was observed: as the pH was increased, the Fe(III) was precipitated as the first, followed by aluminium, copper, zinc, nickel, and the last was manganese.

Conclusion

In this study, dolomite, limestone, blast furnace slag and two types of CCM (CCM-JE, CCM-KK) were tested as potential reactive materials for the removal of heavy metals from contaminated waters. The effects of the pH and S:L (reactive material: wastewater) ratio on the efficiency of individual heavy metals removal from the model and real contaminated waters were investigated. The performance of the reactive materials used was controlled by the contents of available reactive alkaline components (lime and/or magnesium oxide). Based on the present results, it can be concluded that:

- Dolomite is an unsuitable reactive material because it is unable to increase pH to the optimal value required for the removal of heavy metals from contaminated water.
- Limestone, blast furnace slag, and CCM-JE are suitable reactive materials for the removal of iron, aluminium and copper, but they do not provide sufficiently high final pH value to remove zinc, nickel, and manganese. It was concluded that in iron- and aluminium- rich waters (similar to the tested water sample D HPV), a significant part of added reactive materials (L, BFS, CCM-JE) is consumed to reduce the concentration of iron and aluminium, and to increase the pH and only a residual part of added reactive materials is consumed as a precipitating agent to remove divalent cations of Zn, Ni and Mn.
- The reactive material CCM-KK exhibited a superior reactivity and capacity and was able to remove the monitored heavy metals completely.

CCM-KK prepared and tested in the present study was characterised by a high content of reactive MgO due to the optimal calcination temperature and time applied. This reactive material is capable of neutralizing the acidity in the treated water and removing all heavy metals, without any release of toxins into the environment during its performance.

Acknowledgements

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