Removal of Dissolved Metals from Road Runoff Using Zeolite PRBs

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Nowadays, the network of roads and road infrastructure as petrol station, road drainage system etc. exemplify key sources of environmental pollution. Therefore, to ensure the acceptable quality of groundwater, a proper protection system is required. Recently, in this purpose the permeable reactive barrier (PRB) systems are commonly used. In order to examine the effectiveness of zeolite, medium filling PRBs, for removal of heavy metals (Cu, Zn, Pb, Ni, Cd) from road runoff (aqueous solution) comprehensive laboratory investigations were undertaken in Department of Geotechnical Engineering Warsaw University of Life Sciences - SGGW. The program of investigations consists of the kinetic and equilibrium tests with artificial solutions. To predict the kinetic constants of sorption for tested cations the first and second order kinetics equations were used. The chemical equilibrium of metal concentrations was reached after 24 h. The tests results indicate that the occurrence of competitive cations in solution reduced lead and copper concentrations. The percentage removal of particular heavy metals from aqueous solution was as follows: Cd – 54 %, Cu – 31 %, Ni – 48 %, Zn – 92 % and Pb – 70 %. The test results obtained demonstrate that zeolite could be a promising medium for removal of metal cations from road runoff.

1. Introduction

Pollution of ground water by heavy metals causes great public anxiety because of serious threats to natural environment and human health. The heavy metals are infiltrate towards groundwater in numerous ways e.g. waste effluents from industries, mine drainage, road infrastructure and transport (Weng and Wu, 2012). Contrary to organic pollutants, heavy metals are not degradable. The emission of these contaminants into the environment is high and out of control, especially in the vicinity of roads. Snow melt and water runoffs from roads are mixture of pollutants such as heavy metals, organic compounds, deicing agents and suspension. In practice, to protect groundwater environment along the routes the infiltration lagoons, reservoirs for rainwater runoff retention, facilities for collection and separation of oily substances are used (Marsalek et al., 2001). In the last two decades new technology called Permeable Reactive Barriers (PRBs) has been developed and proposed for environmental protection (Gavaskar 1999). The PRBs are an in situ treatment zones that passively capture a plume of contaminants and remove or break down the contaminants during contact with reactive materials, releasing uncontaminated water. This technology based on natural attenuation processes e.g. sorption has been widely used for the removal of metal ions (Wang and Peng, 2010; Inglezakis et al., 2005). Zeolite is one of reactive material that could be used as an adsorbent in PRBs in vicinity of roads due to its selectivity for several cations particularly for heavy metals (Balintova et al. 2012; Fronczyk et al., 2012; Wyszkowski and Radziemska 2010).
The aim of this paper is to examine the zeolite ability to treat road runoffs from heavy metal ions: Pb, Cu, Zn, Cg and Ni. In this paper kinetic and equilibrium sorption test results are presented.

2. Materials and test method

Adsorbent

Zeolite used in the tests was obtained from Bystré in the Slovakia (Zeocem a.s.) (Figure 1). The mineral composition of the Slovak zeolite is as follows: $(Ca; K_2; Na_2; Mg)_4 Al_8Si_{40}O_{96} \cdot 24\ H_2O$.The tested material, in 84 % natural clinoptilolite, contains the following additions: cristobalite 8 %, illite 4 %, feldspar rock mineral group 4 %, carbonaceous rock <0.5 % and minute quantities of quartz. Its particle size and surface area were 0.50–1.00 mm and 32.4 m^2/g, respectively. Prior to the batch adsorption experiments, zeolite was treated with 2 M (5 %) NaCl solution at 21 °C by shaking for a period of 24 h to activate the zeolite pores. Subsequently, it was washed with distilled water and dried in an oven at 105 °C.

Figure 1: Zeolite from Bystré (Slovakia) used in the research

Adsorbates

All batch tests were performed using a dilute solutions simulated the road runoff. The solutions used in batch tests were prepared by dissolving in 5 mL of distilled water required quantity of analytical reagent grade of cadmium, copper, nickel, lead and zinc (6.7 mL for kinetic tests and 2.5, 5.0, 7.5, 9.0, 110 mL for equilibrium tests) and then diluted to 100 mL with distilled water.

Kinetic and equilibrium tests

Batch kinetic experiments for 67 mg/L mixed metal solution were conducted to evaluate the uptake rates and contact times needed to achieve equilibrium. For data interpretation two kinetic models were used - first and second order kinetics models. The first order kinetic equation is as follows:

$$C_s = C_{so} \cdot \exp(-k_1 \cdot t)$$

(1)

The second order kinetic equation is:

$$C_s = \frac{1}{(\frac{k_2.t}{C_{so}})}$$

(2)

where C_s - the amounts of solute adsorbed per unit adsorbent at time t (mg/g), C_{so} - the initial concentration of solute adsorbates (mg/L), k_1 - the first order rate constant (1/h), k_2 - the second order rate constant $(1/(mg \cdot L^{-1}) \cdot h)$.

The equilibrium tests were carried out using 2 g of zeolite. The initial concentrations of metals were varied from 0 to 110 mg/L. Aqueous solutions without adsorbates were used as control samples. The double-blind tests and the other aqueous solutions containing mixtures of Cd, Cu, Ni, Pb, Zn and zeolite were placed into 250 mL bottle made of PE. Before tests, the values of pH, temperature and electrical conductivity were measured using a portable instrument pH/conductivity meter (SCHOTT, Germany). The samples were then placed into rotary shaker set at 15 rpm for 24 h, after which pH, temperature and conductivity values were measured. The tests were performed in duplex at laboratory temperature of 20 - 22 ºC.

The final concentrations of the heavy metal ions in the solution were measured by plasma – atomic absorption spectroscopy, ICP – AAS (Thermo Scientific, USA). The removal ratio R (%) from the aqueous solutions was calculated by the mass balance in equation:

$$R(\%) = \frac{(C_0 - C_C)}{m} \cdot 100\%$$

(3)

where C_o and C are the initial and final metal concentrations (mg/L), m is mass of adsorbent (mg).

3. Results and discussion

In order to examine the possible mechanism of the sorption the kinetic test data were further analyzed with two kinetic models – first and second order kinetics. In table 1 the parameters of adsorption kinetics for Pb: calculated rate constants (k_1 and k_2), adsorbed amount of metals (Cs), and correlation coefficient of linear regression (R^2) were showed. The adsorption kinetics of Cd, Cu, Ni and Zn were not express properly (R^2 lower than 0.5) using the first and second order kinetics equation.

Table 1: Kinetic data calculated for metal ions exchange on zeolite

Metal	First order kinetic model			Second order kinetic model		
	Cs (mg/L)	k_1 (min^{-1})	R^2	Cs (mg/L)	k_2 (min^{-1})	R^2
Pb (II)	7.89	0.520823	0.57	7.89	0.014332	0.91

The figure 1 demonstrates the effect of contact time on the metal ions adsorption onto zeolite. The initial ion concentration in solution was 67 mg/L, pH was 4.5 and temperature 20 ^{o}C. According to the correlation coefficient ($R^2 = 0.91$), the second order kinetics equation is the most appropriate for Pb adsorption. In figure 2, at first step of the reaction concentrations of reagents retreating quickly and then change slowly with small concentrations of substrates remain for longer periods of time.
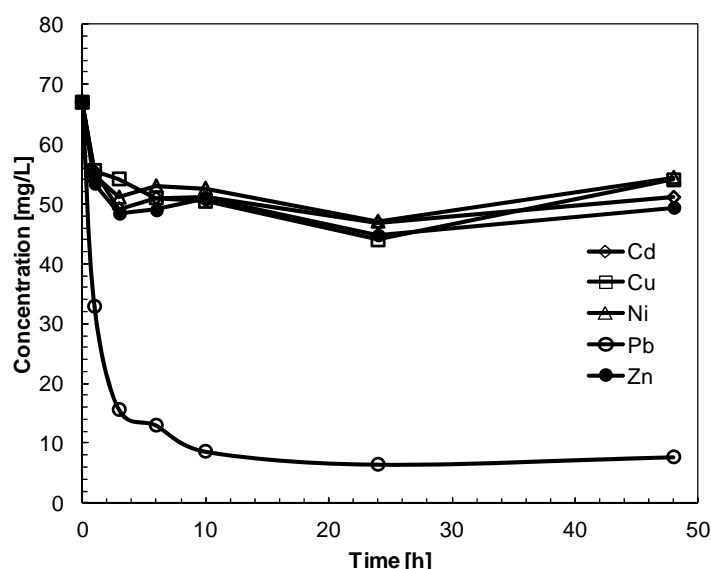

Figure 2: Effect of agitation time on heavy metals concentration

However, the removal of other heavy metals (Cd, Cu, Ni, Zn) by zeolite was very difficult for graphic interpretation. The results showed that the lead presence in aqueous concern of metal ions solution had negative effect for removal efficiency of other metal ions. The metal ions removal ratio R was as fallows, for Ni R = 20.4 %, Cd R =22.4 %, Cu R = 21.9 %, Zn R = 24.3 % and Pb R= 79.0 %. This effect could be caused by competition for reactive surface sites between the reagents. The typical sequence of selectivity ion exchange for zeolite is (Zamzow, 1990):
$Pb^{2+}>Cd^{2+}>Cu^{2+}>Co^{2+}>Cr^{2+}>Zn^{2+}>Ni^{2+}>Hg^{2+}$, which is corresponded to test results obtained.
The sorption of metal ions from multielement solution was carried out for initial concentrations as fallows, 25, 50, 75, 90, 110 mg/L. The adsorption on zeolite was determinate by the sorption capacity of the reactive material and the selectivity of the zeolite for different heavy metal ions. In the equilibrium study the same ions competition effect was observed. It was concluded that Pb, Zn and Cd are preferred by zeolite. In figure 3 the removal ratio R (%) from the aqueous solution for different initial concentrations were presented.
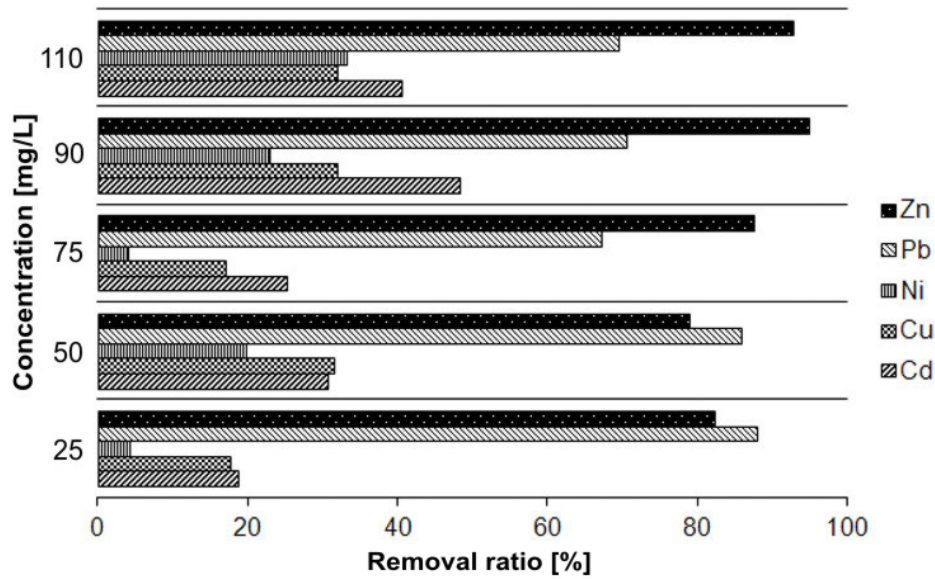
Figure 3: The metal ions removal ratio R (%) from aqueous solutions of different initial concentrations

The isotherm analysis model including adsorption capacity was applied only for Pb and Cu. Certainly, it has been assumed to be caused by metals competition and by low level of initial pH. The experimental data obtained for Pb were fitted to the Freundlich and pseudo-Langmuir adsorption isotherm (Figure 4) applied to equilibrium adsorption assuming heterogeneous adsorption onto a surface, which is not restricted to the formation of monolayer. The linear Freundlich adsorption isotherm is expressed by the following equation:

$$log(x/m) = logK_F + N_F \cdot logC \tag{4}$$

and pseudo-Langmuir isotherm:

$$x/m = \frac{Q_m K_1 C}{(1 - K_2 C)[1 + (K_1 - K_2)C]} \tag{5}$$

However, also the Cu ions were fitted to the Henry's isotherm (Figure 5), which is represented as:

$$x/m = K \cdot C \tag{6}$$

where x/m is the adsorption capacity of zeolite at equilibrium (mg), C is the concentration of metal ions in equilibrium solution (mg/L) Q_m is a single-layer adsorbed density (mg/g), K_F and K are Freundlich and Henry's constants respectively, N_F is the heterogeneity factor, K_1 and K_2 are the equilibrium adsorption constant of the first and the second layer (L/mg).

The Henry isotherm is typical for low surface coverages and the adsorption independents of the coverage - lack of inhomogeneities on the surface. The analysis of equilibrium studies indicate to Pb accumulation in the large available surface and adsorption on the outer surface of zeolite. Consequently, the other heavy metals ions had a lower uptake in comparison with lead. With curves in the Figure 4 demonstrating "S"-type adsorption, multilayer adsorption of Pb can be expected. The effect of pH was observed in many studies for the adsorption of heavy metal ions (Johnson et al. 2000; Nassar, 2010; Tang et al. 2012). High pH increases the adsorption process, the surface of sorbent deprotonation is superior, which indicates forces between the sorbent surface and the metal ions (Nassar 2012). Moreover, Pb sorption equilibrium data were also analyzed using Langmuir, Temkin and Redlich-Petersen models. Unfortunately, the data didn't fit to these modeled isotherms.
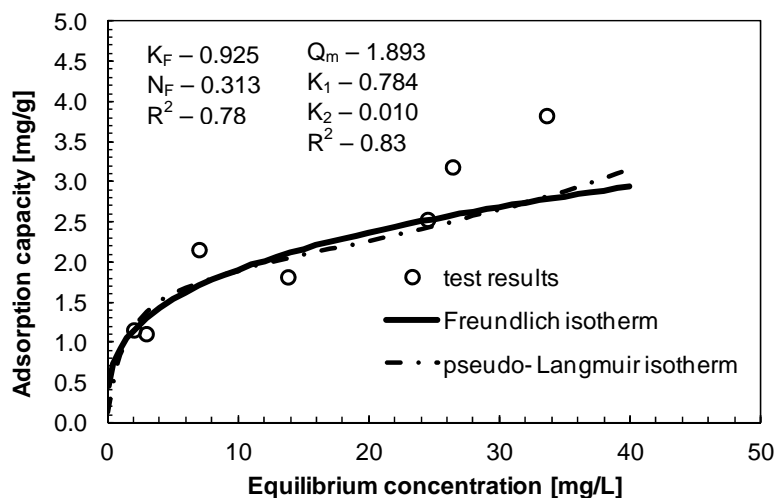
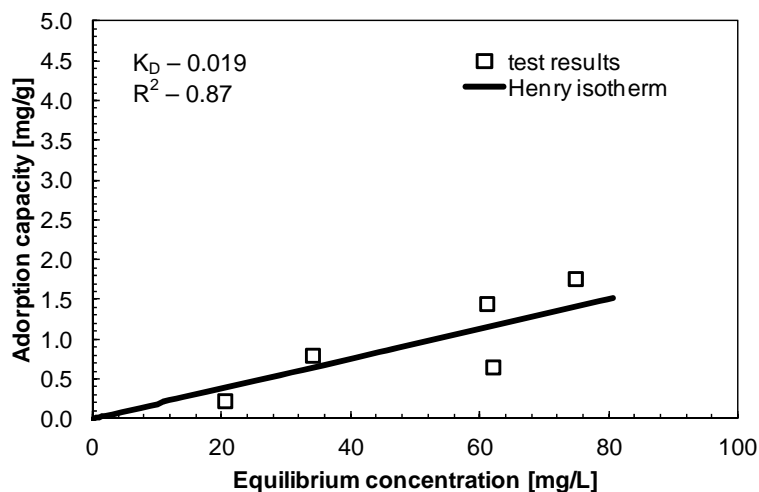*Figure 4: Freundlich isotherm for the sorption of Pb*

Figure 5: Henry's isotherm for the sorption of Cu

4. Conclusions

The present work demonstrated that zeolite is efficient reactive material to prevent migration of heavy metals from road runoff. Based on the test results, the following major conclusions can be drawn:

- The mechanisms of metal uptake differ significantly, depending on the metal species.
- In adsorption kinetics the equilibrium was achieved in time shorter than ten hours.
- During tests the competition of heavy metals was observed, which occupy available exchange sites in the zeolite's structure.
- The largest removal was obtained for lead (from 67 % to 88 % depending on the initial concentration) and the lowest for nickel (from 4 % to 33 %).
- The adsorption isotherms were determined for Cu by Henry and for Pb by Freundlich and pseudo-Langmuir models. Isotherm modelling could be helpful in clarifying the mechanism of sorption process.
- The experimental data obtained for Pb show, that multilayer adsorption could be taken into account.

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