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REMOVAL OF COPPER(II) IONS FROM GROUNDWATER USING POWDERED DEVONIAN DOLOMITE IN PERMEABLE REACTIVE BARRIERS

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Abstract: Contamination of groundwater by copper has been an environmental issue for a long time. Accordingly, the aim of this study is to investigate the effect of powdered Devonian dolomite on Cu(II) removal from aqueous solution. Experiments were carried out as a function of contact time, dosage, initial concentration, solution pH and competitive ions. The results show that for contact times of up to 60 min the amounts of Cu(II) adsorbed increase by 44 - 62%. Moreover, adsorption increases most intensively in the first 24 hrs of the process. The data is in agreement with the pseudo-second-order kinetic model what indicate that the rate-limiting step in the adsorption of Cu(II) was chemisorption, and that pore diffusion is an important element of the adsorption processes. The Langmuir maximum adsorption capacity of powdered Devonian dolomite in relation to Cu(II) ions is 3.025 mg/g. Moreover, the pH of a initial solution has little effect on the amount of Cu(II) adsorbed by dolomite. The Cu(II) removal percentage in pH ranging from 2.0 ± 0.2 to 8.0 ± 0.2 falls between 97.2% and 99.0%. The presence of competitive ions (Ca, Mg, Na, K) in the initial solution slightly inhibited the adsorption of Cu(II). The results show that powdered Devonian dolomite could be used as an effective reactive material for the removal of Cu(II) from groundwater.

Key words: powdered Devonian dolomite, groundwater contamination, copper, mineral sorbents, adsorption processes.

1. INTRODUCTION

Increased concentrations of heavy metals in the soil-water environment are connected with their release from anthropogenic sources, which include power stations, electroplating, combustion, mining, smelting activities and the road infrastructure (Akar et al., 2009). Such contamination, due to its cancer-causing properties and toxicity even in low concentrations poses a serious risk to living organisms, from microorganisms and plants to animals (Gupta & Ali, 2004; US EPA, 2007). Heavy metals, including copper, do not undergo biological decomposition and can accumulate in living organisms, interfering with the natural functioning of ecosystems (Wan Ngah & Hanafiah, 2008). Moreover, copper can occur in the environment in many forms such as free ionic copper, soluble and insoluble complexes formed by copper bound with inorganic and organic ligands. Free ionic copper and monohydroxo Cu(II) are the most easily accessible and, therefore, the most toxic to living organisms. The remaining complexes are not as toxic to aquatic life forms (Brooks et al., 2007; USEPA, 2007). Free water soluble ions are observed at a pH lower than 6, in an environment characterized by low anion ligand content. Copper is most often precipitated as $Cu(OH)_2$ hydroxides within a range of average pH values (6.5 - 12.0) and the process is strictly dependent on the concentration of the metal, presence of other ions (e.g., SO_4^{2-}, PO_4^{3-}, HCO_3^-, NO_3^-, CO_3^{2-}), temperature and time required to meet thermodynamic balance (Cuppett et al., 2006). The harmful effect of copper, especially in soils with a low pH, has been well documented in literature on the subject (Reddy et al., 1995; Andersen et al., 1994). Copper is a microelement absorbed by plants and used, i.a., for activating numerous enzymes (Buchanan et al., 2000). In the case of soil contamination, the risk of metal accumulation is significant due to the strength at which the majority of heavy metals are bound to the sorption complex. These elements usually become immobilized, which means that the metal continues to be a problem even when the source from which it comes has been eliminated (Abat et al., 2012).

In Poland, the amount of heavy metals released into the environment is equal to approximately 3,000 tons per year. We can find so called "hot spots", characterized by the highest levels of contamination by heavy metals in the country, which pose a severe risk to the environment. The permissible limits of heavy metal concentration in soil have been shown to be exceeded around mines and copper foundries in the Dolny Śląsk Voivodeship (Kowaliński & Weber, 1988). It is believed that their presence in soil contaminated by metallurgy will continue to have a negative impact on the environment for at least another 200 years (Degryse et al., 2006), posing a threat to the quality of drinking water, crops and human well-being. The maximum permissible level of copper discharge onto the land surface is 3.0 mg/L, in heavy soils - 100 mg/kg and in drinking water - 0.05 mg/L.

Currently, many methods are used to remove heavy metals from the environment, including chemical precipitation, ion-exchange, reverse osmosis, the process of electrolysis, etc. (Naddafi et al., 2007; Akar et al., 2009; Ismael & Kharbish, 2013). When compared to adsorption methods, reverse osmosis, ion-exchange and electrolysis are very costly, consuming a lot of energy or using high quantities of chemical reagents. Adsorption, on the other hand, is a fast, cheap and widely applied method of removing metals from liquids. What is more, the method is universal, because it can be used to remove dissolved and undissolved contaminants (Naddafi et al., 2007; Kalavathy et al., 2005).

When protecting the soil-water environment, the permeable reactive barrier (PRB) technology, which involves stimulating naturally occurring cleansing processes of the aquiferous layer, is finding wider and wider application. In this method, contaminated groundwater is forced through a decontamination zone, filled with an appropriate reactive material, e.g., zerovalent iron (ZVI), activated carbon, zeolite or saw dust (Gavaskar et al., 2000). PRB technology has gained wide interest due to its effective removal of contamination, relatively low costs and low impact on the conditions within the water-soil environment. Due to the fact that one of the most important stages of designing a PRB is choosing an appropriate filler for the barrier, many research centers are searching for new reactive materials (mineral and organic) in order to improve the effectiveness of decontamination. The application of ZVI in removing chlorinated hydrocarbon, sulphates, nitrates and heavy metals has been scientifically confirmed (e.g., Gavaskar et al., 2000; Bolwes et al., 2000; Roehl et al., 2005). Activeted carbon is also common applied as a PRB filler (e.g., Di Natale et al., 2008; Kalinovich et al., 2012) as well as zeolites (Jun et al., 2009; Erto et al., 2011) which sorb contaminants on their surface and limestone, which, as a result of changes in the pH, leads to the precipitation of heavy metals and traps them within the barrier (Komnitsas et al., 2004; Gibert et al., 2011).

The article presents the results of kinetic and equilibrium batch tests in an effort to determine the usefulness of powdered Devonian dolomite in the decontamination of groundwater polluted with copper(II) ions. Although dolomites have been applied in the stabilization/solidification method of contaminated soils along with carbonates and industrial by-products of an alkaline nature such as combustion ash (US EPA, 2004) their use as a filler material of PRBs has not yet been proposed.

2. MATERIALS AND METHODS

2.1. Sorbent characterization

Powdered Devonian dolomite, the deposits of which are found in south-eastern Poland (N 50º44' 3.407", E 21º21' 41.256"), was selected for the studies. Samples of raw dolomite were dried at a temperature of 105ºC for 24 hours. The rock was crushed and the powder was further sieved using standard mesh sieves. The grain size of the material used in experiments was 0.125 - 0.25 mm. In order to characterize the material, the following analyses were performed: mineralogical composition by X-ray diffraction (Philips X'Pert APD, Netherlands), specific surface area and volume of pores using the nitrogen adsorption method (ASAP 2020M Micromeritics, USA), and surface morphology by scanning electron microscopy (FEG Quanta 250, USA).

2.2. Chemical solutions

All reagents were of analytical grade chemicals. The copper solutions were prepared from $CuCl_2 \cdot 2H_2O$, calcium with $CaCl_2$, potassium with KCl, sodium with NaCl and magnesium with $MgCl_2 \cdot 6H_2O$ (Merck, Germany). Copper concentration in the solutions was measured by means of the atomic adsorption method, using an ICE-3000 spectrophotometer (Thermo Scientific, USA), while pH using the SCHOTT measure (Germany).

2.3. Adsorption studies

The mechanism of Cu(II) adsorption from aqueous solutions was investigated in batch mode. The experiment was conducted in acid-washed polyethylene flasks, 250 mL in volume, which were then placed in a rotary shaker set at 15 rpm. Studies on adsorption kinetics were conducted in order to determine the time necessary to reach chemical equilibrium between the solution and sorbent. The procedure of studies on the kinetics of adsorption processes was conducted as follows: two grams of sorbent was agitated in 100 mL of copper solution (with an initial copper concentration of 32 mg/L) for 10, 20, 30, and 40 minutes as well as 1, 3, 5, 7, 24, 30, 48 and 54 hours.

Studies on the influence of the dose (that is the ratio of the mass of the sorbent to the volume of the solution) were conducted shaking 100 mL of the copper solution with varied sorbent mass (0.050, 0.100, 0.200, 0.500, 1.000, 2.000 g). In order to determine the influence of the initial copper concentration on the adsorption processes, the study was conducted in three series, with an initial concentration of 12, 32, and 54 mg/L. At this stage of the studies, the pH values of the initial solutions were not adjusted. The samples were agitated for 54 hours.

In adsorption equilibrium studies, two grams of sorbent were mixed with 100 mL of an aqueous solution with varied initial copper ion contents (1, 6, 12, 20, 25, 32 mg/L) for a period of 54 hrs. The pH of the original solutions was not adjusted and fell into the range of 5.8 - 6.8.

Studies on the influence of pH on the intensity of sorption processes were carried out using copper solutions with a concentration of 32 mg/L and pH values ranging from 2.0 ± 0.2 to 8.0 ± 0.2 (every 1 unit). The pH of the solution was adjusted adding 0.1M NaOH and 0.1M HCl. The total volume of solutions added to adjust the pH did not exceed 1% of the volume of the copper solution. Two grams of the sorbent were shaken in 100 mL of the solution for a period of 54 hours.

Conditions under which studies on the influence of the presence of competing ions on the intensity of copper ions removal were conducted were similar to those analyzing the influence of pH. Calcium, magnesium, sodium and potassium were chosen as the competitive ions. Solutions containing two ingredients were used and, in addition to copper (32 mg/L), contained one of the above mentioned ions at an initial concentration of either 10, 20 or 30 mg/L.

After desired agitation time, the samples were centrifuged for 5 minutes at a speed of 3,000 rotations per minute and subjected to physicochemical analysis. All tests were conducted twice and mean values were calculated. The mass of absorbed copper q_e (mg/g) was calculated according to the following formula:

$$q_e=((C_0-C_e)\cdot V)/m \qquad (1)$$

and the Cu(II) removal ratio R(%) was calculated by:

$$R=((C_0-C_e)\cdot V\cdot 100)/C_0 \qquad (2)$$

where C_0 and C_e (mg/L) - initial and equilibrium concentrations of copper in a liquid phase, V (L) – volume of solution, m (g) – mass of adsorbent.

3. RESULTS AND DISCUSSION

3.1. Sorbent characterization

The mineral composition of a material can be determined by analyzing XRD spectra (Fig. 1) and EDX mapping (Fig. 2).

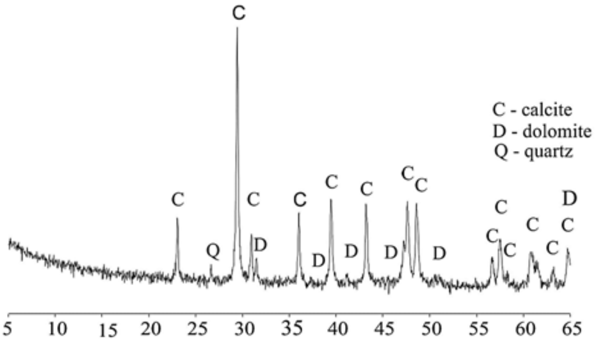

Figure 1. XRD spectra of powdered Devonian dolomite.

The composition of powdered Devonian dolomite is very close to the formula $CaMg(CO_3)_2$, with the chemical composition in oxide (wt.%) C_2O – 20.18%, N_2O_2 – 22.30%, Fe_2O_3 – 4.41%, CuO – 2.28%, MgO – 1.29%, Al_2O_5 – 4.51%, SiO_2 – 6.91%, and CaO – 38.12%. SEM photographs of dolomite (Fig. 2) show the irregular shape and rough surface of the agglomerates. Moreover, studies on the sorption of nitrogen revealed that dolomite has a specific surface area of 1.22 m^2/g, an average pore size of 133.4 Å, and is characterized by a non-porous structure. The specific surface area of the analyzed material is higher than specific surface area of natural Turkish dolomite – 0.84 m^2/g (Pehlivan et al., 2009), similar to the specific surface area of raw dolomite from western Algeria – 1.82 m^2/g (Boucif et al., 2010), but smaller than the specific surface area of Irish dolomite – 4.63 m^2/g (Albadarin et al., 2012), selected silt minerals, such as bentonite – 40.90 m^2/g (Ibrahim et al., 2013) as well as fly ashes (Franus, 2012).

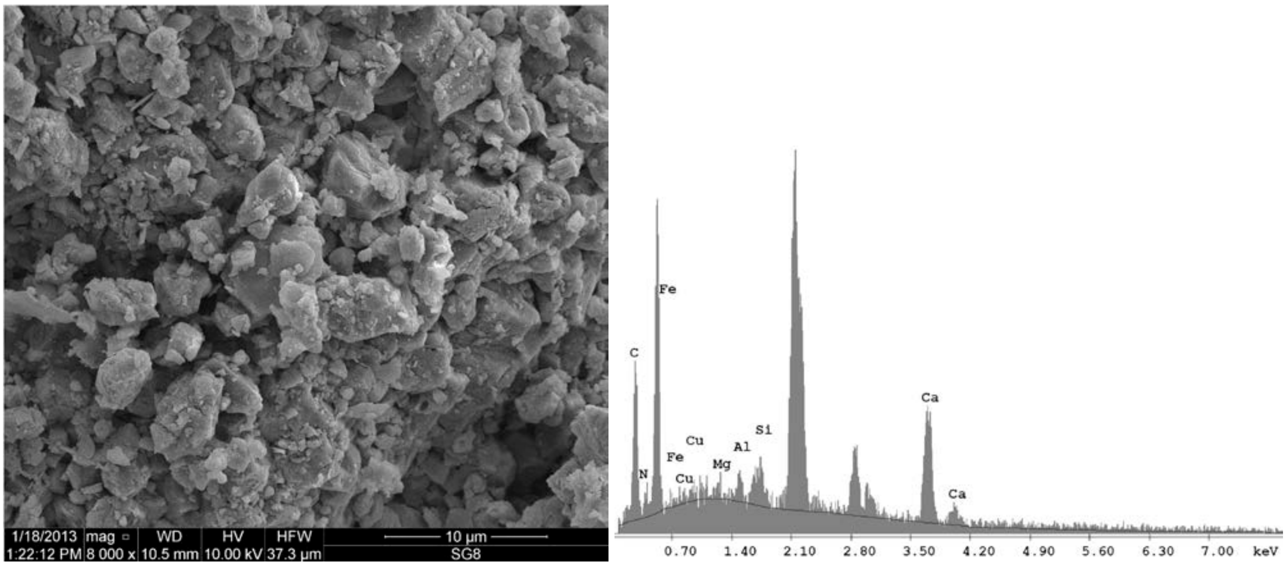

Figure 2. SEM image and energy dispersive X-ray mapping (EDX) of powdered Devonian dolomite.

3.2. Adsorption kinetic studies

Analyzing kinetic models is important, not only when determining the time after which equilibrium between the sorbent and the solution is reached, but also for the proper execution of the design stage of water-treatment systems treating groundwater. The effect of contact time on the removal of Cu(II) by adsorption onto dolomite at an initial concentration of 32 mg/L, 22ºC, pH of 5, and adsorbent dose of 20 g/L is shown in table 1. For contact times of up to 60 min the amounts of Cu(II) adsorbed increase by 44 - 62%. Moreover, the results show that adsorption increases most intensively in the first 24 hrs of the process. Further extension of the contact time does little to influence the effectiveness of adsorption. The research therefore indicates that the rate of adsorption is higher at the beginning of the studies, due to the availability of a uncovered specific surface area of the sorbent (Sölener et al., 2008).

The pseudo-first-order, pseudo-second-order, and Elovich kinetic models were used to describe the kinetic characteristics of copper ions adsorbed onto powdered Devonian dolomite. The calculated parameters of the above-mentioned models have been presented in table 2. Figure 3 shows the dependency of the adsorption capacity on the duration of the reaction. The graph illustrates that the adsorption capacity of Cu(II) takes on relatively high values after just 60 minutes. Similarly to studies presented by Walker et al., (2004), the data is in agreement with the pseudo-second-order kinetic model, showing good correlation over the entire range of data and a regression coefficient of R^2=0.99.

Table 1. Effect of contact time on removal of Cu(II) by adsorption onto powdered Devonian dolomite

Contact time (min)	Percentage of copper removal
10	44.28
20	46.29
30	53.60
40	59.31
60	62.48
180	64.84
300	71.88
420	73.92
1440	90.88
1800	98.52
2880	99.12
3240	99.33

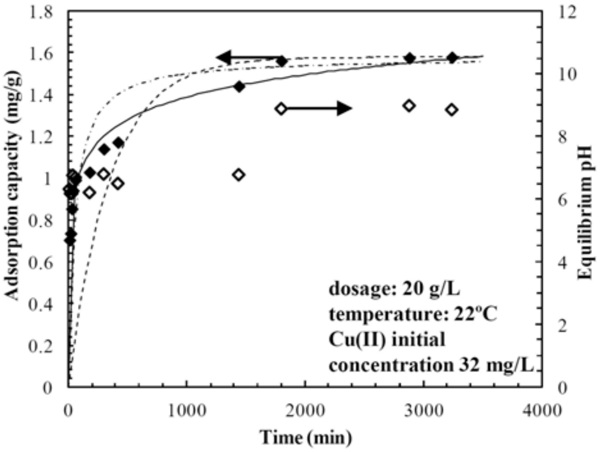

Figure 3. Effect of contact time on Cu(II) adsorption onto powdered Devonian dolomite; (- - -) fitting of pseudo-first order model, (– - –) fitting of pseudo-second order model, (—) fitting of Elovich kinetic model.

Table 2. Kinetic parameters of Cu(II) by adsorption on powdered Devonian dolomite

Pseudo-first-order		Pseudo-second-order		Elovich kinetic model		
k_1 (1/min)	R^2	k_2 (mg/(g min))	k_1 (1/min)	R^2	k_2 (mg/(g min))	R2
0.0028	0.88	0.0117	0.0028	0.88	0.0117	0.97
$\ln(q_t\text{-}q_{max})=\ln q_{max} - k_1 t$		$t/q_t=1/k_2 q_{max}^2 + 1/q_{max}$		$q_t = b+k_E \ln t$		

k_1 (min^{-1}), k_2 (mg/(g min)), k_E (mg/(g min)) denote the adsorption rate constants, b – Elovich kinetic model constant, q_{max} (mg/g) – maximum adsorption capacity of metal ions, q_t (mg/g) – adsorption capacity of metal ions at time t (min).

The results indicated that the rate-limiting step in the adsorption of Cu(II) onto powdered Devonian dolomite was chemisorption, the adsorption follows the Langmuir equation and that the adsorption rate was proportional to the number of unoccupied sites (Ho & McKay, 1999). Moreover, good correlation between the test data and the pseudo-second-order model suggest that pore diffusion is an important element of the adsorption processes (Wang & Wu, 2012).

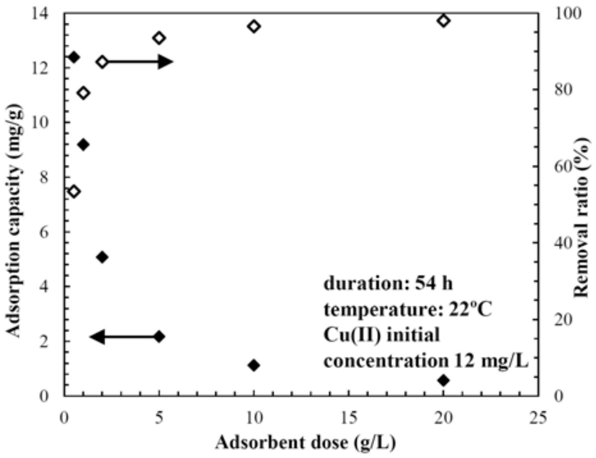

Figure 4. Effect of dolomite dose on Cu(II) ion adsorption (initial Cu concentration - 12 mg/L).

3.3. Effect of adsorbent dosage and initial Cu concentration

The influence of the adsorbent dosage on the intensity of the adsorption of copper ions has been presented in figures 4 - 6. The removal ratio of copper ions under conditions of equilibrium increases along with an increase in the dose of the adsorbent, which is caused by the increasing specific surface area and thus, the higher availability of adsorption sites. For all of the initially applied Cu(II) concentrations (12 mg/L , 32 mg/L, and 55 mg/L), the highest changes in the adsorption capacity were observed when the dosage was increased to 5 g/L. A further increase in the dosage did not lead to a significant decrease of the adsorption capacity. At the initial concentration of copper ions of 12 mg Cu/L, the adsorption capacity decreases from 12.39 mg/g to 0.57 mg/g; for 32 mg Cu/L – from 58.63 mg/g to 1.85 mg/g; for 55 mg Cu/L – from 58.02 mg/g to 2.72 mg/g. This may be caused by the decreasing gradient of ion concentrations between the solution and surface area of the adsorbent (Albadarin et al., 2012).

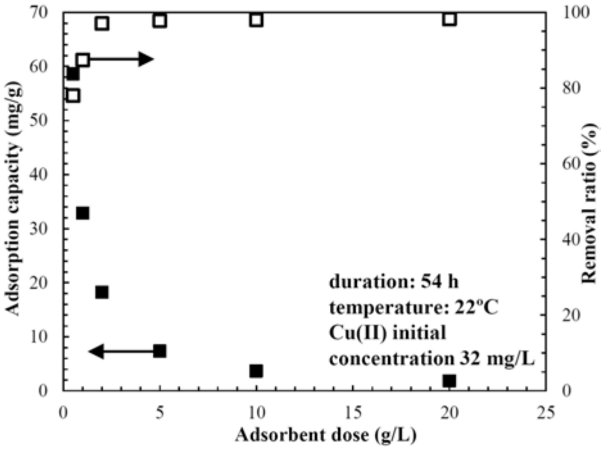

Figure 5. Effect of dolomite dose on Cu(II) ions adsorption (initial Cu concentration - 32 mg/L).

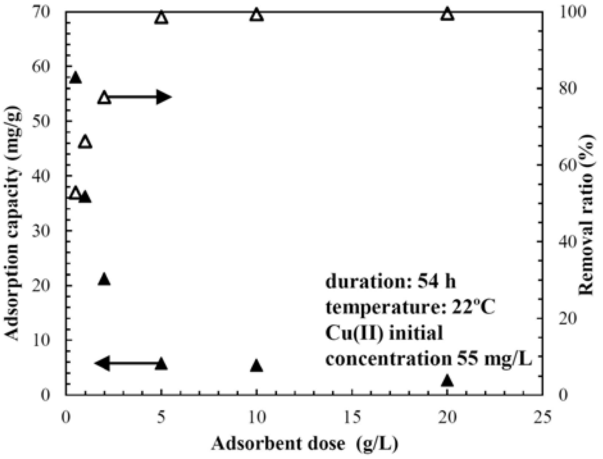

Figure 6. Effect of dolomite dose on Cu(II) ions adsorption (initial Cu concentration - 55 mg/L).

3.4. Adsorption equilibrium studies

An isotherm of copper ions adsorption on the analyzed material has been presented in figure 7. The adsorption isotherm illustrates the dependencies between the adsorption capacity and concentration of ions in the solution at a given temperature and under the conditions of equilibrium. During the study, an increase in the unit adsorption amount along with an increase in equilibrium concentration was observed, which suggests the possibility of determining the maximum adsorption capacity of the analyzed material. Langmuir, Freundlich and Redlich-Peterson equations, which have been presented in table 3 along with the indicated parameters, were used to describe the results of the study. The three isotherm equations fit the sorption isotherms of Cu(II) on powdered Devonian dolomite well, which is supported by good correlation coefficients (for all equations $R^2>0.90$). Based on the value of the correlation coefficient, it can be stated that the Redlich-Peterson isotherm was best suited for the data, followed by the Langmuir and then, the Freundlich isotherm. The maximum adsorption capacity of powdered Devonian dolomite in relation to Cu(II) ions is 3.025 mg/g, which is lower than values characteristic of commercially applied mineral products, such as Slovakian zeolite (q_{max} = 8.394 mg/g) (Fronczyk & Garbulewski, 2013, Fronczyk et al., 2010) and natural Turkish dolomite (q_{max} = 8.26 mg/g) (Pehlivan et al., 2009), but similar to the maximum adsorption capacity of activated carbon which is equal to 3.56 mg/g (Machida et al., 2005). The K_L parameter in the Langmuir equation is connected with sorption energy; the higher the value of this parameter, the higher the affinity between the heavy metal and the sorbent (Sparks, 2002). The binding energy on the surface of dolomite is uniform and adsorbed Cu(II) ions form a monolayer coverage of the material. In the Freundlich equation, K_F reveals relative adsorption capacity of the analyzed material in relation to metal ions, whereas N_F indicates that the adsorption processes taking place are endothermic processes that occur non-linearly, since N_F takes on values lower than one (Wu et al., 2011).

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms into a single equation. At low ion concentrations in the solution, the Redlich-Peterson isotherm approximates to linear Henry's isotherm (β=0), while at high concentrations, its behavior approaches that of the Langmuir isotherm (β=1) (Ho et al., 2002). The obtained value of β (between 0 and 1) indicates favorable adsorption.

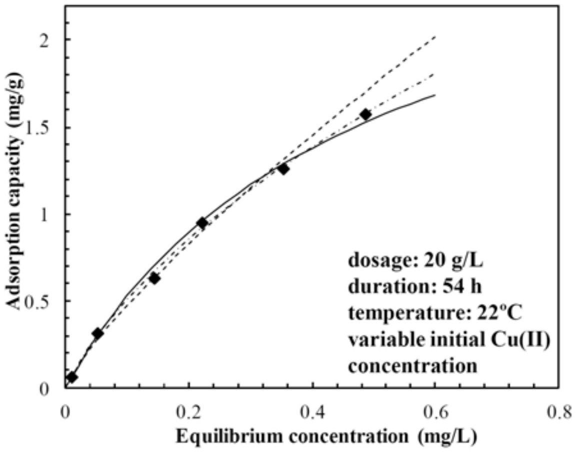

Figure 7. Adsorption isotherm of copper ions on powdered Devonian dolomite; (—) fitting of Langmuir isotherm, (- - -) fitting of Freundlich isotherm, (– – –) fitting of Redlich-Peterson isotherm.

3.5. Effect of initial pH

The pH value of the solution is one of the most important factors that can influence the removal of heavy metals from road runoff and contaminated groundwater. This stems from the fact that pH influences the solubility of metals and ionization states of the functional groups. The influence of pH on the intensity of Cu(II) adsorption has been presented in Fig. 8. Under the conditions assumed in the experiment, the pH of an initial solution has little effect on the amount of Cu(II) adsorbed by dolomite.

The Cu(II) removal percentage in pH ranging from 2.0 ± 0.2 to 8.0 ± 0.2 falls between 97.2% and 99.0%. Higher concentrations of copper in solutions characterized by low pH values may be caused by Cu^{2+} and H^+ competing for free sites on the surface of the analyzed material. Along with an increase in the pH of the solution, the amount of Cu(II) ions removed systematically increases, reaching its maximum value at an initial pH value of 6.

Table 3 Parameters of Langmuir, Freundlich and Redlich-Peterson isotherms

Langmuir isotherm		Freundlich isotherm		Redlich-Peterson isotherm	
q_{max} (mg/g)	3.025	K_F (L/g)	3.068	K_R (L/g)	8.237
K_L (L/g)	2.098	N_F	0.816	a_R (L/mg)	2.333
R^2 (%)	95.73	R^2	99.44	β	0.572
				R^2 (%)	99.82
$q_e=q_{max}K_LC_e/(1+K_LC_e)$		$q_e=K_FC_e^{NF}$		$q_e=K_RC_e/(1+a_RC_e^{\beta})$	

q_e (mg/g) – adsorption capacity, q_{max} (mg/g) – maximum adsorption capacity, K_L (L/g) – Langmuir adsorption equilibrium constant, C_e (mg/L) – equilibrium metal concentration in solution, K_F (L/g) and N_F – Freundlich constants related to the adsorption capacity and adsorption intensity of the sorbent, respectively, K_R (L/g), a_R (L/mg) and β (0 < β < 1) – Redlich-Peterson constants.

A further increase in pH resulted in a decrease in the amount of the adsorbed ions, though these changes were found to be insignificant. At higher values of pH, the precipitation of ions takes place, thus decreasing the amount of copper ions adsorbed on the surface of dolomite. The precipitation of $Cu(OH)_2$ begins in conditions when the value of pH exceeds 7. It should be noted that during the course of the experiment, the pH was not maintained at a constant level and thus, the pH of the equilibrium solutions was subject to change and fell into the range of 8.1 to 9.7 (Fig. 8). Therefore, it is probable that bulk precipitation of typically $Cu(OH)_2$ can occur within the pH range of these experiments. This is supported by the fact that copper ions can be completely removed from aqueous solutions in a strongly basic environment.

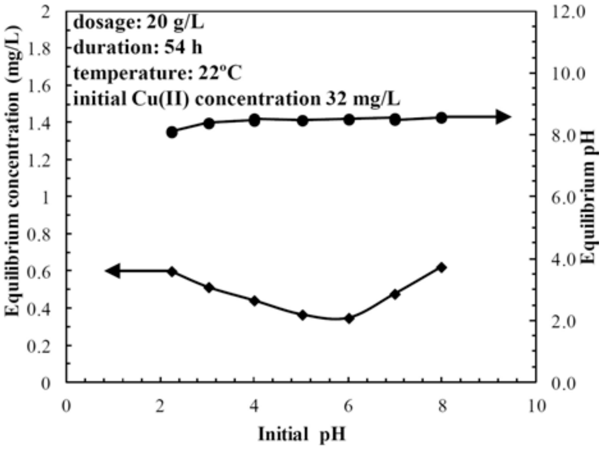

Figure 8. Variation in Cu(II) concentration in equilibrium solution with varying initial solution pH.

3.6. Effect of competitive cations

The presence of salts in runoff water from roads as well as groundwater may be an important factor influencing the intensity of heavy metal ion removal by means of adsorption. Figure 9 reveals a reduction in the concentration of copper ions in the presence of ions which may compete with one another for sorption sites on the surface of dolomite. Ca, K, Mg and Na ions were not shown to significantly influence the removal of copper (decreasing reduction by 0.18% to 6.70%). The obtained results are in accordance with the thesis that the influence of alkaline earth cations on the sorption of a transitional group divalent cation (Cu(II)) should be weak (Wu et al., 2011). This may suggest that dolomite is highly selective for Cu(II). In the case of the presence of competitive ions in the initial solution at a concentration of 10 mg/L, the decrease in copper concentration reduction is insignificant (Ca - 0.18%, Mg - 0.31%, K - 0.35, Na - 1.04%). At a 20 mg/L concentration of competitive ions, the decrease in copper concentration reduction was as follows: Ca - 0.20%, Mg - 0.41%, K - 0.82%, Na - 1.46%. Finally, an initial competitive ion concentration of 30 mg/L resulted in decreases of copper concentration reduction of: Ca - 0.95%, K - 1.39%, Mg - 3.05%, Na - 6.70%. The highest initial cation concentration of Ca(II), K(I), Mg(II), and Na(I) can be characterized by the following decreasing order of influence on the reduction of copper concentration: Na > Mg > K > Ca. Calcium ions also exhibited the least influence in the case of lower initial concentrations, with sodium ions exhibiting the strongest effect; however, the influence of Mg and K ions was, in this case, reversed - higher for potassium.

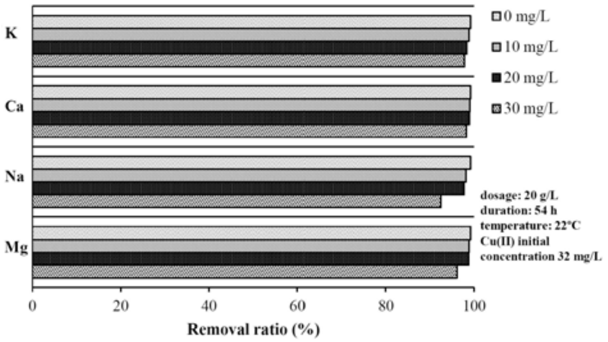

Figure 9. Removal ratio (%) of Cu(II) in respect to competitive ions.

4. CONCLUSIONS

The presented research results indicate that powdered Devonian dolomite can be applied as a reactive filler material of PBRs for the removal of copper ions from water. The Redlich-Peterson isotherm was found to be the most suitable for the equilibrium data, followed by the Langmuir and then, the Freundlich isotherm. The maximum adsorption capacity of powdered Devonian dolomite in relation to copper Cu(II) ions is 3.025 mg/g. Moreover, the results of kinetic tests showed that maximum adsorption capacity was achieved in 24 hrs. More than 90% of copper ions were removed by studied material from aqueous solution. A pseudo-second-order kinetic model could be adapted to describe the adsorption process of copper (II) ions onto powdered Devonian dolomite. Furthermore, the results indicated that the rate-limiting step in the adsorption of Cu(II) onto powdered Devonian dolomite was chemisorption, and that the adsorption rate was proportional to the number of unoccupied sites. The initial pH value did not significantly influence the effectiveness of removing copper ions from the solution. The maximum percentage of removal was observed at a pH of 6. What is more, the presence of salts ($CaCl_2$, KCl, $MgSO_4$ and NaCl) slightly inhibited the adsorption of Cu(II).

Acknowledgments

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