STUDY OF INFLUENCE OF pH VALUE ON REMOVING OF Cu^{2+} IONS FROM SOLUTION ONTO PERLITE

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Received: 06.06.2014
Accepted: 10.08.2014

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Abstract

The expanded perlite was studied as adsorbent for removing of Cu^{2+} ion from contaminated water. The test conditions were following: pH = 2 – 11; a perlite dosage 0,1 – 1 g; ratio solution: sorbent = 20 – 500 ml : 1 g; basic concentration of the Cu^{2+} ions 0,5 and 5 $mg.1^{-1}$, laboratory temperature. The results showed that the perlite shifts the pH value of solutions which have the pH in region of 4 – 9 to neutral region 6 – 7. The pH value of solution was adjusted by HCl/NaOH and McIlvaine (citric acid/Na_2HPO_4); and Sőrensen (Na_2HPO_4/KH_2PO_4) buffer. Top-tests were carried out with solution adjusted by HCl/NaOH. The removing of Cu^{2+} ions from water relates with the basicity of aqueous solutions. If the ratio of perlite to solution with Cu^{2+} concentration of 5 $mg.l^{-1}$ is 1 g : < 40 ml the removal of Cu^{2+} ions from solution rapidly increases in interval of pH from 4,5 to 5,5 and at pH ≥ 6 achieves a maximum. The removal of the Cu^{2+} ions from initial solution (5 $mg.1^{-1}$ of Cu^{2+}) is 90 – 95 % at an exposition time of 180 min. and pH > 6. The values from desorption test were about 25 – 30 % lower. The purpose of this paper was to show the influence of phosphate and citrate anions in aqueous solutions on removing of Cu^{2+} ions from diluted water solution, too. The results confirmed that the citrate anions in the McIlvaine buffer inhibit sorption of Cu^{2+} on perlite while phosphate anions in Sőrensen buffer generate conditions for formation of Cu^{2+} precipitates.

Keywords: perlite, heavy metal ion, copper, pH value

1 Introduction

Perlite is a hydrated glassy volcanic rock of the chemical composition: 71 – 75 % SiO_2, 12,5 – 18 % Al_2O_3, 4 – 5 % K_2O, 1 – 4 % Na_2O + CaO with 2 – 5 % water content. If crushed, raw perlite heats quickly to 780 – 1100 °C, forming a lightweight material. The escaped steam increases the perlite volume by 12 – 25 times. The expanded perlite is light, chemically and thermally stable material. The powdery density and the specific surface of expanded perlite is 80 – 250 $kg.m^{-3}$ and 1,7 – 2,1 $m^2.g^{-1}$. For these properties perlite is used as fireproof insulating material, sorbent of oil, filter material and vitrificator [1-7].

The more water contamination grows in nature, the more interest is focused at sorbents and immobilizers of surface–active substances. Different raw materials on carbonate and aluminosilicate base can be used to elimination of heavy metals from contaminated water [8-13]. Perlite is considered a suitable sorbent and immobilizer of metal cations, nanoparticles and microorganisms [10-19].

DOI 10.12776/ams.v20i3.327

As the works showed [11-20] removal of pollutants from water by perlite depends on the properties: pH value, kind of ions and their concentration in the solution, temperature surrounding. The sorption capacity of heavy metals on perlite is summarized in **Table 1**.

Table 1 Sorption capacity of expanded perlite (EP); (* raw perlite - RP)

ion	**efficiency of removal of ions from solution [%]**	**sorption capacity q_m [mg.g^{-1}]**	**lit**
Hg^{2+}	35-38	0,5	[14]
Cu^{2+}	90 - 95	1,95	
Ag^{+}	~ 100	8,46	
Pb^{2+}	~ 100	13,39	[17]
$*Pb^{2+}$	~ 100	8,906	
Pb^{2+}	~ 100	6,275	[15]
Co^{2+}	40-45	1,05	
Th^{4+}	85	-	[16]
Ni^{2+}	43 - 93	2,24	[18]
Cd^{2+}	33 - 87	1,79	
Cr^{3+}	40	-	[19]

Therefore, the surface properties of sorbent as isoelectric point and potential are very important at sorption Alkan et al. [20] investigated the electrokinetic behavior of perlite in electrolytes. The zeta potential measurings of raw and expanded perlite are compared and confirm that perlite surfaces have negative charge (-20 to -60 mV, -40 to -100 mV) in all regions of pH value form 2 – 11. The fact that perlite shows negative zeta potential is attributable to isomorphic transaction, defects in the crystal lattice and structural hydroxyl groups.

The elimination process of metallic ions by perlite from water is most commonly explained by adsorption mechanism with ion exchange [14-16]. The low adsorption at $pH < 4$ can be explained by increasing of the positive charge density on the surface. The electrostatic repulsion occurs between the metal ions and the groups with positive charge on the sorbent. At higher pH values the surface of perlite becomes negatively charged and thus electrostatic repulsion decreases with an increase in pH value. The negative charge on surface and metal adsorption grows with increase of pH value. An important fact is that more addition of perlite to water with $5 < pH < 6{,}5$ and to water with $7{,}5 < pH < 9$ shifts pH to 7.

The aim of this work is to point out to the effect of pH value, effect of citrate, phosphate and chloride anions on removal of the Cu^{2+} ions from contaminated aqueous solutions by perlite. The results of sorption are checking by desorption test. The Cu^{2+} concentration (5 and 0,5 mg.l^{-1}) in the simulated solutions moderately exceeds the permitted limit in contaminated mining waters and industrial wastewaters (1 – 0,5 mg.l^{-1}) [21].

2 Experimental material and methods

2.1 Characteristic of sorbent

The expanded perlite EP 100, product of Kerkotherm, a.s. Košice (Slovakia) made of raw perlite coming from the deposit Lehôtka pod Brehmi (Slovakia) was tested. The basic characteristics of the sample are listed in **Table 2**. The expanded perlite was characterized by thermal analysis (Derivatograph Netzsch STA 449 F3), by X-ray diffraction (Mikrometa II with Cu Kα radiation) and investigated by SEM-EDS analysis (JEOL JSM-7000 F). The surface area was measured by nitrogen gas sorption analyzer (Quantochrome-NOVA-1000).

The particle size of expended perlite is less than 6 mm. The vitreous character of fragile particles of expanded perlite (**Fig. 1**) was confirmed by X-ray diffraction analysis, too. The thermal analysis record confirms the structural bound water in expanded perlite.

Table 2 The characteristic of expanded perlite (EP)

chemical composition [wt. %]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O
	65 - 73	14 - 16	1,5 - 1,8	2 - 2,3	~ 0,2	2 - 2,8	2,6 - 3,0
loss by ignition [wt.%]			1,7- 2,1				
loss by drying [wt.%]			0,7				
powder density [$kg.m^{-3}$]			85 – 110				
specific surface area [$m^2.g^{-1}$]			1,1 – 1,5				
alkali ions washed from 1 g perlite by 20 ml of distilled water (pH -5,7) [$mg.l^{-1}$]			Na	K	Ca	pH	
			1,9 – 2,3	0,2 – 0,6	0,7 – 1,5	6,3 – 6,9	

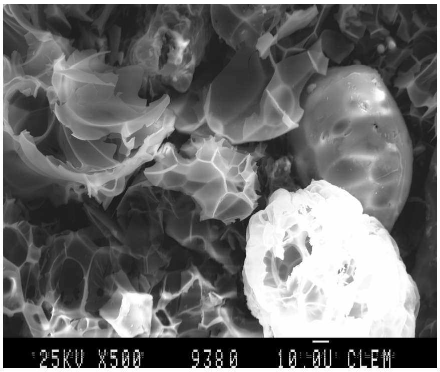

Fig. 1 Fine particles of expanded perlite (scale – 10 μm)

2.2 Preparation of solution

The basic solution of a concentration of 10 $mg.l^{-1}$ Cu^{2+} was prepared from $CuCl_2$ (p.a.). The pH value of the primary solution was 5,5. The pH value of distilled water was 5,6 – 5,8.

Three types of solutions for adjusting pH were prepared:

i) non-buffer solutions: the pH value of distilled water was adjusted from 2,2 to 11 by HCl and/or NaOH;
ii) solutions with McIlvaine buffer; pH = 2,2 – 8 (citric acid/Na_2HPO_4) [22];
iii) solutions with Sőrensen buffer; pH = 6 – 8 (Na_2HPO_4/KH_2PO_4) [22].

2.3 Flow and batch test

The influence of perlite on pH of aqueous medium was proved by flow column and batch test.

Flow test: The glass column (length 700 mm x ϕ 1,3 mm) was filled with 7 g of expanded perlite. Distilled water was forced bottom up through the column by pump (PCD 21 M). The water flow and pH value (pH–meter MS11, Tesla) have been measured for one day. The results are shown in **Fig. 2**.

Batch test: The 20 ml of adjusted solution and 20 ml basic solution of Cu^{2+} concentration (10 $mg.l^{-1}$) was mixed in a PE-bottle and then the pH value of solution was measured. After adding of expanded perlite (1 g) to this mix the sample was shaken in rotator "Multi RS-60 biosan" for a period of 180 min. and then it was filtered. The pH value of filtrate was measured; the results are shown in **Fig. 3**.

2.4 Sorption and desorption tests

Filter test: The basic solution of Cu^{2+} and solutions with adjusted/buffered pH were mixed in ratio 1 : 1. The concentration of Cu^{2+} ions in solutions was 5 $mg.l^{-1}$. The solutions were filtered through filter paper "slow" and "very slow". The concentrations of ions in filtrate were analyzed by AAS (Elmer Perkin 3100). Verification of effect of filtration has explicitly shown that the content of Cu^{2+} ions in the filtrate of adjusted solutions by HCl/NaOH with pH above 3 slowly, gradually decreases. This was the reason why after sorption tests desorption tests were done.

Orientation tests of sorption capacity: The perlite and solution (Cu^{2+} concentration 10 $mg.l^{-1}$; pH = 5,5) in different ration (0,1 - 1 g : 50 ml) in PE-bottle were shaken in rotator "Multi RS-60 biosan" at laboratory temperature for 20 h.. The filtrate was analyzed. First the pH value was measured then the filtrate was acidified by one drop of concentrated HCl to pH ~ 1 and analyzed for Cu^{2+} ion by AAS. The amount of Cu^{2+} adsorbed on perlite was detected by desorption test in acid solution (pH ~ 1). The results are shown in **Table 3**.

Sorption test: 1 g of perlite was added to a mix of 10 ml solution with adjusted pH value and 10 ml solution with Cu^{2+} concentration of 10 $mg.l^{-1}$, eventually 19 ml : 1 ml. The ratio of perlite to solution was constant namely 1 g/ 20 ml. The mixtures were shaken in rotator for 3 h. After filtration the pH value of the filtrate was measured. The concentration of Cu^{2+} ion was determined after acidification of the filtrate by AAS.

Desorption test: The wet perlite from the filter paper was carried over to PE-bottle without using of solution and HCl solution (20 ml) with a pH ~1 was pipetted to the perlite. The perlite in the acid solution was shaken by rotator for 1 h.. After filtration the concentration of Cu^{2+} ions in filtrate was analyzed. The filter cake of perlite was dried and weighted. It is very difficult to determinate correctly how much wet perlite was in the desorption test. The results are shown in Fig. 4-5.

2.5 Evaluation of results

The adsorbed amount of Cu^{2+} ion on perlite was evaluated from concentration changes of Cu^{2+} in solution as follows:

- The adsorption efficiency (S) was calculated according to equation:

$$S = \frac{C_o - C_S}{C_o}.100\ \%, \tag{1.}$$

where C_o and C_S [$mg.l^{-1}$] - the initial and final Cu^{2+} ion concentration in solution, respectively.

- The amount of Cu^{2+} adsorbed per unit amount of perlite (q_s [$mg.g^{-1}$]) was calculated with the formula:

$$q_s = \frac{V}{m}(C_o - C_s) \tag{2.}$$

where V [l] - volume of the solution, m [g] - weight of perlite sample.

- The results of desorption tests (SD) were calculated to equation:

$$SD = \frac{V_D.C_D}{V.C_o.m_D}.100\ \% \qquad (3.)$$

where C_D [mg.l^{-1}] - Cu^{2+} ion concentration in solution after desorption test with correction on perlite moisture, V_D - volume of the desorption solution, ($V = V_D$), m_D - weight of perlite at desorption test.

3 Results and discussion

3.1 Change of pH value of solution due to perlite

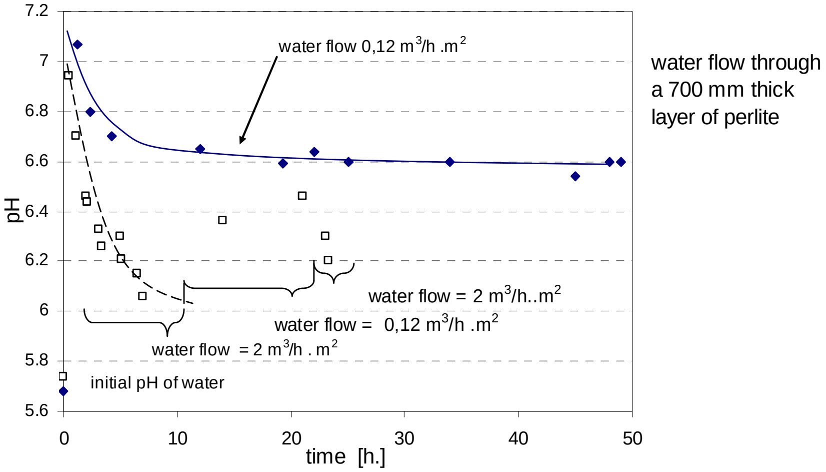

Fig. 2 Influence of perlite on the pH value water, water flow through a 700 mm thick layer of perlite

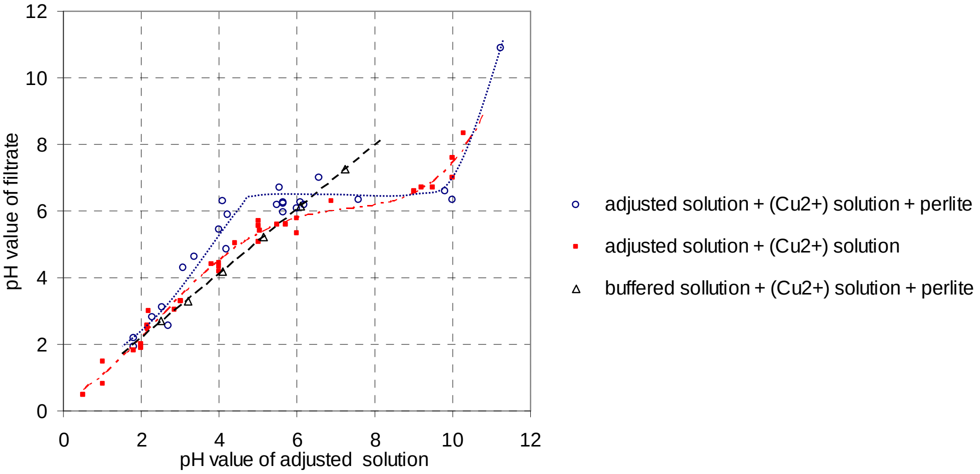

Fig. 3 Influence of perlite addition to solutions on the pH value: □ - solution adjusted by HCl/NaOH without perlite, ○ - solution adjusted by HCl/NaOH with perlite addition, Δ - solution adjusted by buffer ($C_6H_8O_7$, Na_2HPO_4) with perlite addition

The influence of perlite on pH value change of water is apparent from results of column tests in **Fig. 2**. The perlite moves the pH of distilled water to 7 at the beginning. This causes probably the release of more alkaline metal and alkaline earth ions from perlite into water (Table.1). The pH value of passing water depends on velocity of alkali leaching form perlite as well as on water flow. The perlite moves the pH to region of 6,2 – 6,7 at slow water flows. Acceleration of flow will reduce the pH to initial value of water.

How the perlite added to different solutions changes their final pH value at batch test is shown in **Fig.3**. The addition of solution (10 mg.l^{-1} Cu^{2+}; pH ~ 5,5) to solutions adjusted by HCl to an extent of pH (2 – 4) shifts pH to a bit higher values but in case of solutions adjusted by NaOH to an extent of pH 6 – 10 the shift to pH 6,5 is more remarkable. Perlite addition to mixture with pH 4 – 9 stabilizes the pH to ~ 6,5. Heterogeneity of expanded perlite can be the reason of dispersion of data. As Fig. 3 can show, the McIlvaine buffer keeps the pH on constant value even if the perlite is added to mix solution. The observed results correlated with the results of works [16, 20].

3.2 Orientation tests of sorption of Cu^{2+} on perlite in distilled water

Variations of ratio V : S influence the pH solution as well as the equilibrium. The perlite has lower affect on pH change of solution if the ratio solution to solid increases. This is obvious from **Table 3**. The data in table 3 show that the ratio solution to perlite is very important, not only the pH of solution. Simultaneously the pH value gently increases and the Cu^{2+} ions remove as the perlite content increases, nevertheless the content of Cu^{2+} adsorbed on 1 g perlite decreases. The sorption capacity of perlite is very low, lower than presented by the work [14] (1,95 mg.g^{-1}). The desorption test, leaching of used perlite in acid solution (pH ~ 1, HCl), confirmed the removed Cu^{2+} amount by perlite.

Table 3 Sorption on raw and expanded perlite (RP and EP) at condition: 20 °C/ 20 h., different ratio solution : sorbent (V: S); initial solution - 10 mg.1^{-1} of Cu^{2+} with pH = 5,5

ratio V : S x ml : 1 g	**sorbent**	**pH after test**	S adsorption efficiency [%]	extracted **Cu^{2+} [mg.g^{-1}]**	**sorbent**	**pH** after test	S adsorption efficiency [%]	extracted **Cu^{2+} [mg.g^{-1}]**
500	**EP-expanded perlite**	5,6	7	0,350	**RP – row perlite**	5,55	20	0,992
200		5,9	11	0,213		5,7	31	0,611
100		6,15	23	0,224		6,0	48	0,476
50		6,3	46	0,227		6,1	62	0,304

3.3 Sorption of Cu^{2+} on perlite in solution adjusted by HCl/NaOH

The sorption of Cu^{2+} ions from solution on perlite were carried out in interval of pH from 2 to 10. The exposure time of 180 min. is adequately long to approached equilibrium as the mentioned work [14] declares. The dependence of removal of Cu^{2+} ions by perlite on pH value of adjusted solution by HCl/NaOH is shown in **Fig. 4**.

The Cu^{2+} ions begin to be extracted from solution by perlite above pH > 4,5. The content of Cu^{2+} ions in solutions go down sharp in case of pH > 4,5 and at 6 is removed more than 85 % (determined by sorption). This is in correlation with study [14]. The results of tests with Cu^{2+}

concentration of 5 and 0,5 mg.l^{-1} at a ratio of $V_{solution}$/ $m_{perlite}$ (20 ml /l g) are in accordance. The Cu^{2+} ions from solutions are removing well at pH ≥ 6. The results from sorption (S) are higher than from desorption (SD), but are in correlations.

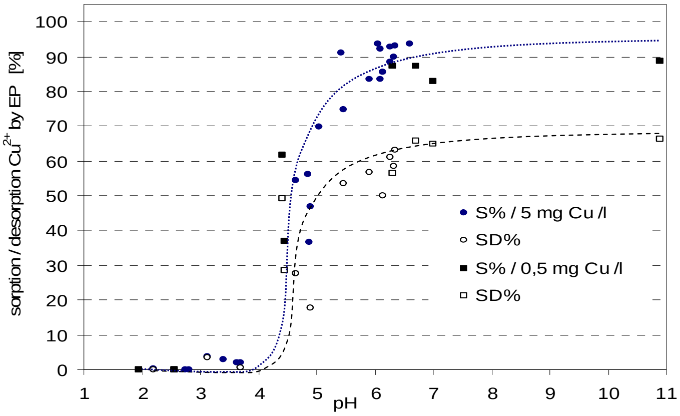

Fig. 4 Effect of Cu^{2+} extraction from adjusted water by HCl/NaOH at different pH value by expanded perlite (EP)

3.4 Sorption of Cu^{2+} on perlite in buffered solution

How important the anions in water medium are can be seen comparing Fig. 4 and Fig. 5. In case of citrate buffer results are different than in phosphate buffer and water. The citrate buffer (McIlvaine/ MB) inhibits the sorption of Cu^{2+} on perlite in all region of its buffer activity. The buffer activity decreases over pH value 7,4 therefore the citric acid concentration is too small in the solution. The phosphate concentration in buffer increases along the pH value. The increase of Cu^{2+} extraction from solution was detected in solution with pH above 7,5.

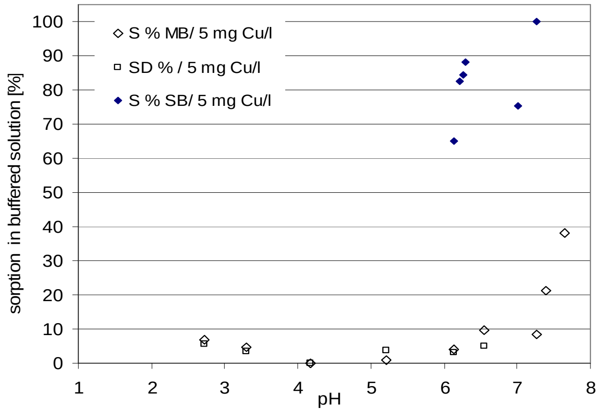

Fig. 5 Effect of Cu^{2+}extract by perlite from water buffered by McIlvaine buffer – MB (◇- sorption on perlite, ☐ - desorption form perlite) and Sőrensen buffer - SB (◆- sorption on perlite).

On the other hand the surroundings of phosphate buffer (Sőrensen / SB) carried out extraction of Cu^{2+} from solution in all region of its buffer activity (pH = 6 – 8). These results correspond with

DOI 10.12776/ams.v20i3.327

results of Cu^{2+} extraction from solutions adjusted by NaOH and basic solution with pH = 5,5, but in case the phosphate buffer creates the conditions for precipitation of $Cu_3(PO_4)_2$.
The solubility of $Cu_3(PO_4)_2$ is very low at temperature of 25 °C, lower than of $Cu(OH)_2$. The coefficient of $Cu_3(PO_4)_2$ solubility is pK = 36,9 and $Cu(OH)_2$ pK = 18,8. Therefore, the precipitation is probably responsible for decreasing of Cu^{2+} concentration in the solution. The concentration of all ions in solution but also basicity of solution and temperature are determining factors for precipitation.

4 Conclusions

The sorption capacity of perlite is low in order to allow it to be used to elimination of heavy metals from contaminated flowing waters. Furthermore, the sorption capacity of perlite is very much influenced by conditions of sorption: mainly pH, ratio V : S (solution : sorbent) and kind of ions in aqueous surroundings. In case of water (distilled and adjusted by HCl/NaOH) with pH value 4 – 9 the more perlite can shift the pH to region 6 – 6,5. The removal of Cu^{2+} ions from water by perlite rapidly increases in region of pH value at 4,5 – 6. Low concentrations of Cu^{2+} ion in water can be removed effectively by perlite at pH ≥ 6. The sorption efficiency was 85 - 95 % but desorption test confirmed 25 – 30 % lower effectiveness. The dependencies of Cu^{2+} removing vs pH value are comparable.
The citrate ions inhibit the adsorption of Cu^{2+} ion. On the other hand the phosphate anions are expected to precipitate.

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Acknowledgements

Authors are grateful for the support of experimental works by project VEGA No. 1/0596/12.