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Original Research

Comparison of Copper and Zinc Sorption Depending on Temperature and Sorbents

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Abstract

In this paper, we compared the sorption of copper and zinc on three adsorbents - bentonite, zeolite, and dewatered digested sludge from a wastewater treatment plant. Sorption was carried out at 27ºC and subsequently at a reduced temperature of 10ºC and the results were compared. The reduced temperature positively affected the sorption efficiency and increased the adsorption capacity of the monolayer of each sorbent. Regardless of the temperature, the sorption progression was not linear. In the initial phase, the sorption proceeded rapidly, but after about 90 min the system reached equilibrium and the concentrations of metals in solution did not change significantly. The size of the specific surface area of the sorbents did not directly correlate with the removal efficiency of Cu^{2+} and Zn^{2+}. Copper sorption by bentonite reached a level of almost 100% at reduced temperature and 80% at room temperature. The efficiency of zinc removal by bentonite was found to be 40% at reduced temperature. The efficiency of copper removal using zeolite was approximately 90% at both laboratory and reduced temperature. For bentonite and zeolite, we confirmed their good sorption properties. The sludge showed low Cu^{2+} sorption efficiency, but Zn^{2+} removal efficiency was higher than bentonite and zeolite. In both cases, the reduced temperature had a positive effect on the sorption capacity of the sludge. Sludge as a waste material could be used for heavy metal removal by modifying the sorption conditions or its modifying, which should be further investigated.

Keywords: water contamination, water purification, physical-chemical water treatment, heavy metals, removal efficiency

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Introduction

Industrial processes generate a huge amount of wastewater that needs to be treated before being discharged into the environment [1]. Heavy metal pollution has emerged as one of the most serious current environmental challenges. Sources of heavy metals in the form of runoff can have a wide range of origins depending on the specific activity. Cu^{2+} ion is a heavy metal ion that is widely used in a variety of manufacturing industries [2], including fertilizers, paints, plating baths, and paper goods [3]. In addition to heavy metals, water contamination by dyes, pesticides [4,5], and drugs (e.g. atorvastatin) are currently the most discussed causes of pollution [6]. The agricultural and horticultural sector is also a major contributor to water pollution [5].

The removal of heavy metals from wastewater is of environmental importance due to their toxicity. Currently, the methods of contaminant removal discussed are sorption using waste materials after pretreatment [7]. Carbon nanotubes (CNTs) can also be used to reduce toxicity. Chemical interaction between CNTs and metal ions also occurs during the functionalization of the CNT surface, and subsequently, the ability of CNTs to remove metal ions increases due to the presence of a large number of active sites on the internal cavities, surface, and inter-nanotube space [8].

Unlike organic pollutants, heavy metals are not biodegradable and are persistent in the environment [9]. Examples of heavy metals include lead, copper, zinc, nickel, cadmium, and chromium [10].

At high concentrations, copper and zinc are toxic. Both elements are necessary for enzyme synthesis, bone, and tissue growth [11, 12]. Zinc helps in controlling chemical reactions in organisms and physiological processes. Zinc can cause health problems such as headaches, nausea, skin irritation, fever, and anemia at elevated concentrations. Copper at elevated concentrations causes hair loss, and anemia, and kidney damage [13].

Mine drainages are rich in heavy metals and sulfur, which are present in minerals [14, 15]. Heavy metals present in mine effluents include copper and zinc [16]. Copper can precipitate as CuS at extremely low pH ($pH \leq 1.0$) without precipitating other heavy metals, while Zn does not precipitate as ZnS until pH 1.3 [17]. In many cases, due to the neutralizing ability of waste minerals or human intervention such as the spreading of limestone to precipitate metals, the drainage may have higher pH values (4.5 to 8.5) and is then called neutral mine drainage (NMD) [18]. This can cause serious environmental problems in mining environments because heavy metals often present in high concentrations, can remain soluble at alkaline pH under suitable redox conditions [14, 19].

Currently, the main methods for the treatment of wastewater containing heavy metal ions include the ferrite method, chemical precipitation, electrochemical method, reverse osmosis, ion exchange, and adsorption [20]. Currently, the development of new adsorbents favors locally available and inexpensive natural materials, which are combined to obtain the desired adsorption properties [21]. Several cost-effective, natural, and renewable materials were confirmed as adsorbents e.g., chitosan, tea leaves, brown coal, waste sludge, agricultural waste, and biomass [22-24]. Organic waste materials can be used to remove metals from mine effluents by adsorption and precipitation, which serves as an effective low-cost substitute for activated carbon [25].

Among sludge treatment technologies, anaerobic digestion is the most used in large wastewater treatment plants (WWTPs) [26]. In addition to biogas, anaerobic digestion produces large quantities of anaerobically digested (AD) sludge [27]. Metal removal by adsorption onto suspended solids by municipal wastewater and subsequent removal in the waste sludge is an important mechanism for metal removal in wastewater [28]. Already in the past, activated sludge was used experimentally for the sorption of metals Hu et al. [29] or Chang et al. [30]. However, digested dewatered sludge was not used. This is also the novelty of our scientific paper.

Bentonite is a clay phyllosilicate consisting mainly of montmorillonite. The main characteristic of montmorillonite is its ability to absorb water molecules between its layers, leading to significant expansion [31]. The distance between the layers is not fixed because the layers can expand. Due to the layered structure, the mineral is characterized by an inner (i.e., interlayer) and an outer surface (i.e., rim). Various exchangeable cations can replace ions in the montmorillonite structure [32]. In the past, metal sorption using bentonite was addressed by Alexander et al. [33], Towyan et al. [34], Sathyanarayana, and Seshaiah [35].

Zeolites are natural, hydrated aluminosilicate minerals with a crystalline microporous structure and belong to the mineral type "tectosilicates". The structure of zeolite consists of three-dimensional SiO_4 and AlO_4 structures, which are connected by sharing oxygen atoms. The replacement of the tetravalent silicon by trivalent aluminum in the mineral structure produces a net negative charge, which is balanced by the presence of cations (usually Ca^{2+}, $Na^{+,}$ and K^{+}) found in the cavities [36, 37]. These cations are interchangeable with other cations including heavy metals. The framework structure of the zeolite encloses cavities occupied by large ions and water molecules that can move, allowing ion exchange [37]. They studied the sorption of metals using zeolite Ates and Akgül [38], Woolery et al. [47] and Ates [39, 40].

The adsorption isotherms provide information about the adsorption process. The analytical forms of the adsorption isotherm equations depend on the type of surface phase, which can be considered as monolayer or multilayer and as localized, or mobile. These models are complicated because of the structural and energetic heterogeneity of adsorbent surfaces, which is characteristic of many adsorbents used on an industrial or experimental scale [41].

In this work, we investigated the removal of Cu and Zn using stabilized digested dewatered sludge (SDDS), bentonite, and zeolite.

Material and Methods

In this experiment, we used three different sorbents – bentonite, zeolite, and digested dewatered sludge to remove Cu and Ni from neutral mine drainage.

Characterization of Sorbents and Neutral Mine Drainage

We used ground fine bentonite obtained from the Kopernica site, zeolite obtained from Nižný Hrabovec, and stabilized dewatered digested sludge (SDDS) obtained from the wastewater treatment plant in Vlkanová. Basic criteria were chosen for the sample collection - low humidity and fineness of the samples. The samples had to be odorless - the smell could indicate the presence of another material (bentonite, zeolite) or insufficient stabilization (sludge).

Stabilized sludge was used specifically to remove pathogenic microorganisms that could cause hygienic complications when this sorbent is applied to the aquatic ecosystem. The sludge was dried and sieved to a fraction below 2 mm. After stabilization, the excess sludge is dewatered on sludge presses after the anaerobic stage. After this filtration, all its storage and disposal.

Neutral mine drainage was taken from the Voznická dedičná štôlňa adit in Štiavnica-Hodruša mine district (Central Slovakia) - 48º27'N and 18º42'E. Generated neutral mine drainage represents a relict of mining processes in the area. The estimated total historical production of the mines in the mining district is estimated at 4 000 t of Ag and 80 t of Au. Base metal mining, which was active from the 19th century until 1992, yielded approximately 70 000 t of Zn, 55 000 t of Pb, and 8 000 t of Cu^{2+} [42]. The average pH over 2 years in neutral mine drainage was 7.24.

For sorption processes, we used solutions of mine water with modified concentrations of Cu^{2+} and Zn^{2+} for the needs of 5 input concentrations. Mine drainages are environmental pollutants that flow into the aquatic environment. Chemicals for adjusting the input concentration of the samples were obtained from the Technical University of Zvolen.

Characterizations of sorbents and neutral mine water are summarized in Table 1 and Table 2.

The crystal size microscopic images of the used sorbents 37 x 40 x 60 µm for zeolite, 500 x 200 x 80 µm for sludge, and 1100 x 1000 x 630 µm for bentonite, measured with a VHX-7000 digital microscope (Keyence).

Table 1. Chemical and mineral composition of bentonite and zeolite.

Sorbent	Chemical composition [%]											Source
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	Na_2O	K_2O	MnO	P_2O_5	SO_3	
Bentonite	59.02-74.6	12.07-26.67	2.01-3.29 bentonite bonded	0.99-1.74	1.03-3.47	0.13-0.24	0.16-0.88	0.68-1.28	–	–	–	Supplier
	66.09	23.96	2.69	1.9	2.93	0.15	0.43	1.68	0.05	0.01	0.11	[43]
Zeolite	70.37	11.98	1.76	3.57	0.31	–	–	–	–	–	–	Supplier
	64.18-75.5	10.93-14.80	0.12-2.45	1.43-11.68	0.29-1.43		0.10-2.97	1.24-4.24	–	–	–	[44]
	Mineral composition [%]											
Sorbent	Montmorillonite	Plagioclase	K-feldspar	Biotite	Quartz-cristobalite	Volcanic glass	Loss by annealing	Smektite	Feldspar	Kaolinite	Clinoptilolite	Source
Bentonite	50-98	2.53	1.89	5.33	13.44	5.13	0.48	–	–	–	–	Supplier
	–	–	2.5		1.5	–	–	80	8	2	–	[43]
Zeolite												Supplier
											82-84	[44]

Table 2. Metal content in sorbents and neutral mine drainage.

Sample	Copper	Manganese	Zinc	Iron	Lead	Cadmium	Aluminium
	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}	mg.kg^{-1}
Bentonite	2.70	106	13.8	4121	25.2	0.068	8929
Zeolite	3.32	115	39.6	5352	9.28	0.147	39375
SDDS	415	182	1348	19034	38.5	1.89	17335
Neutral mine drainage	0.117	3.09	6.13	8.81	0.094	0.024	3.06

Sorption of Heavy Metals

The adsorption was carried out at 27ºC and 10ºC in Erlenmeyer flasks. The sample volume was 100 ml in each flask. Before sorption, a 500 ml solution was made for each input concentration – a total of 5 input concentrations. We took 100 ml to determine the initial concentration. Then 100 ml of solution was added to each flask and mixed with 5 g.dm^{-3} of sorbent. After 30, 60, 90, and 120 minutes, the sorption was stopped by filtering out the sorbent in individual bottles and then the concentration of metals – copper or zinc was measured. Temperature reduction to 10ºC was carried out in an incubator. The sorption of each input concentration was repeated 5 times for the relevance of the evaluation – a total of 6 measurements were made for each input concentration for each sorbent at each temperature. The addition of $CuSO_4$ was used to vary the input concentrations for Cu sorption. For changes in input concentrations for Zn sorption the addition of $ZnCl_2$ was used. Sorption was carried out by continuous stirring to ensure better contact with the aqueous phase with the sorbent.

Determination of Heavy Metal Concentrations During the Sorption Process

The concentrations of metals were determined by atomic absorption spectrometry (AAS). An AAS AVANTA Σ flame atomization spectrometer (GBC Scientific) was used for the determination of metals. A hollow cathode lamp with a supply current of 3.00 mA was used as the radiation source. Air/acetylene was used as the flame type at flow rates of 11.50 dm^3.min^{-1} for air and 1.10 dm^3.min^{-1} for acetylene. The relative errors of the AAS measurements were less than 5 %. The instrument operation as well as the evaluation of the results was carried out with the GBC Avanta software ver. 2.0.

Determination of Specific Surface

The determined each sorbent̓s specific surface according to Blaine – ČSN EN 196-6. The fineness of materials is expressed as the specific surface calculated from the time required for a given amount of air to flow through a compacted bed of a measured material of a given size and porosity. The method̓s principle is based on comparing the time taken for a defined amount of air to pass through a barrier so prepared. This time is then compared with the time for a reference material having a known specific surface area. The specific surface is proportional to the square root of the time required for air to flow through the compacted material. At the same time, the bulk density was determined using a pycnometer, which is necessary to determine the specific surface of fine materials.

Determination of Heavy Metal Concentrations of Sorbents and Neutral Mine Drainage

The AES-ICP atomic emission spectrometry with inductively coupled plasma method was used to determine copper, manganese, iron, lead, cadmium, and aluminum. The EA-TCD - -elemental analysis with thermal conductivity detection method was used to determine zinc.

Calculations

Adsorption Capacity

From the measured concentrations, the adsorption capacity at equilibrium (qe) [45, 46], the amount of metal adsorbed per unit sorbent at time t (qt), and the percentage removal efficiency of Cu^{2+} and Zn^{2+} ions from the solution (Ads. %) were calculated.

The adsorption capacity at equilibrium and at time t, respectively, was calculated according to Equation (1):

$$q_e = \frac{(c_o - c_e)\,xV}{m} \tag{1}$$

Where: q_e is adsorption capacity at equilibrium and at time t (mg.g^{-1}), c_0 is the initial concentration of ions in solution (mg.dm^{-3}), c_e is the equilibrium concentration of ions in solution or the concentration of ions in solution at time t (mg.dm^{-3}), V is the volume of solution (dm^{-3}) and m is the mass of adsorbent added (g).

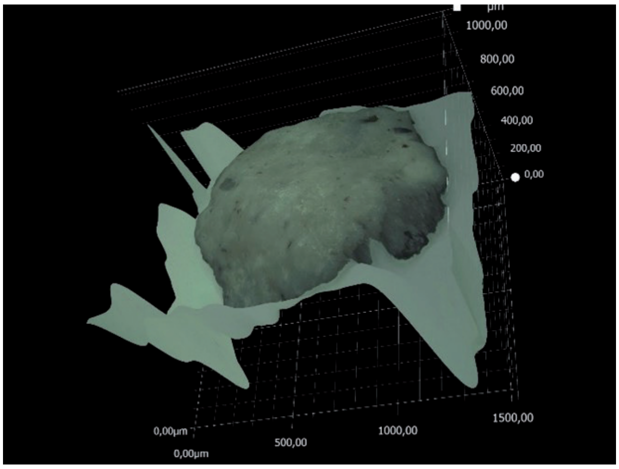

Fig. 1. Microscopic image - bentonite.

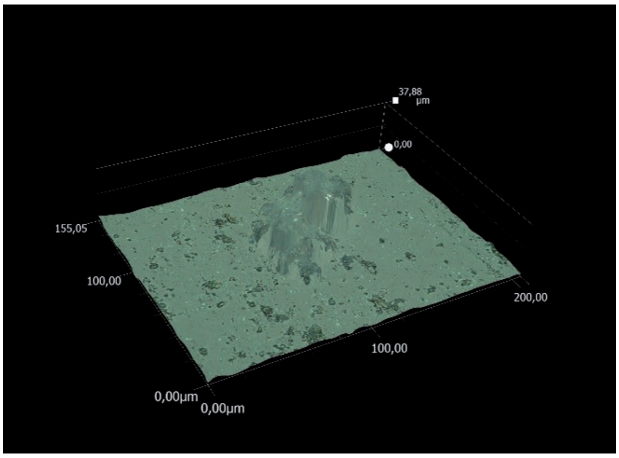

Fig. 2. Microscopic image - zeolite.

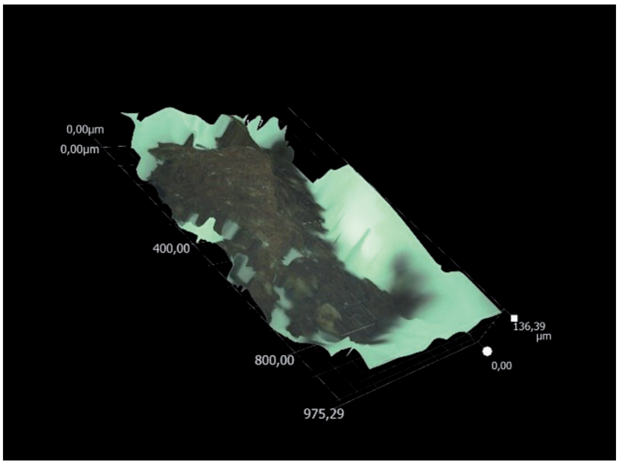

Fig. 3. Microscopic image - sludge.

Percentage of Metal Ion Removal Efficiency

The percentage removal efficiency of metal ions from the solution was calculated according to Equation (2):

$$\text{ds.\%} = \frac{(c_0 - c_e)}{c_o} \text{x} 100 \tag{2}$$

Experiments focused on the adsorption of copper and zinc were carried out with natural unmodified adsorbents in a closed system under constant stirring of the suspension at laboratory temperature. We monitored the progress of sorption depending on the sorbent used.

Freundlich and Langmuir Adsorption Isotherms

To express the dependence of the metal ion adsorbed amount on its equilibrium concentration in solution, Freundlich and Langmuir‘s isotherms were constructed for all adsorbents used. The isotherms were evaluated at 5 input concentrations.

Freundlich Adsorption Isotherm

The effect of initial metal concentration on adsorption is described by adsorption isotherms. Several empirical and semiempirical relationships have been proposed for the analytical expression of the isotherms, of which either the Freundlich or Langmuir isotherm is the most suitable for adsorption from solutions.

The Freundlich isotherm is usually valid for physical adsorption and for adsorption on heterogeneous surfaces with different active sites. It can be expressed by the relation:

$$q_e = K_f \text{x} c_e^{\frac{1}{n}} \tag{3}$$

To verify that the experimental data satisfies this isotherm, the relationship is linearized:

$$\log q_e = \log K_f + \frac{1}{n} \log c_e \tag{4}$$

Where: K_f (mg.g^{-1}) is a constant related to the adsorption capacity and *n* is an empirical parameter expressing the adsorption intensity, which varies with adsorbent heterogeneity.

Langmuir Adsorption Isotherm

The Langmuir isotherm is usually valid for chemisorption or electrostatic adsorption, where only a monomolecular layer is formed on the adsorbent surface and all active centers are equivalent. The Langmuir isotherm is expressed by the relation:

$$q_e = \frac{q_m \text{x}\, b\, \text{x} c_e}{1 + b\, \text{x} c_e} \tag{5}$$

respectively in linearized form:

$$\frac{c_e}{q_e} = \frac{1}{b\, \text{x} q_m} + \frac{1}{q_m} \text{x} c_e \tag{6}$$

Where: q_m (mg.g^{-1}) gives the maximum monolayer adsorption capacity and b is the equilibrium constant dependent on the sorption energy.

Determination of the Specific Surface of Fine Materials

The specific surface is calculated from the following equation at a given porosity of the material and a temperature of 20 ± 2ºC:

$$S = \mathrm{K}\frac{\sqrt{e^3}\sqrt{t}}{\rho\,(1-e)\sqrt{10\,\eta}} \tag{7}$$

Where:

- K is the instrument constant found from the measurement of the reference material,
- e porosity = 0,5,
- t is the time interval for the leveling of the gauge level of the two determined points,
- η is the dynamic viscosity of air at a given temperature,
- ρ is the bulk density (g . cm^{-3}) of the test material.

The result is in cm^2/g when the values are entered correctly.

Results and Discussion

Parameters of Adsorption Isotherms and Specific Surface Area

The parameters of adsorption isotherms present the ability and conditions for the sorption of individual sorbents. The overall picture of sorption is complemented by the specific surface area mechanism. Therefore, all sorbents at both temperatures with both Freundlich and Langmuir adsorption isotherm parameters were presented with the specific surface area mechanism in a summarized table. These findings can then be confronted with the adsorption capacity of the monolayer qm as seen in Table 3.

Metal Removal Depending on the Input Concentration

The temperature has a significant effect on the sorption process, there we decided to lead the experiment at two temperatures and compare the results Figs 4-9.

Metal Removal Depending on Time

Monitoring the kinetics of the sorption process is necessary from the point of view of the overall picture of the sorption progress. It is important to observe when sorption starts or at what time the process equilibrium of sorption occurs

Sorption of Copper and Zinc on Bentonite

When evaluating the linearity, we have to conclude that copper sorption on bentonite or zinc was not linear. Reduced temperature improved the sorption for both metals by more than 10 %. The decrease in temperature also led to an increase in the adsorption capacity of the monolayer qm. The progression of sorption was gradual for both zinc and copper at both laboratory and reduced temperature as a function of time to steady state. Liu and Zhou [47] sorbed copper and nickel using bentonite.

Table 3. Parameters of Freundlich and Langmuir adsorption isotherms pre bentonite, zeolite, and sludge.

Adsorbent	Specific surface area S (cm^2/g)	Density (kg/m^3)	Metal	Temperature (ºC)	Langmuir´s parameters			Freundlich´s parameters		
					q_m (mg.g^{-1})	B (dm^3.mg^{-1})	R^2	k_f	n	R^2
Bentonite	500.0	1944.2	Cu^{2+}	27	-0.2427	-0.8160	0.4363	0.9175	0.4163	0.7670
				10	2.0912	1.2190	0.1004	2.0338	0.9900	0.7194
			Zn^{2+}	27	0.0770	-0.7088	0.5228	0.4202	-1.1093	0.3281
				10	0.7019	0.2999	0.6125	0.1784	1.7712	0.6915
Zeolite	6673	1456.5	Cu^{2+}	27	3.0451	0.7668	0.0952	1.3280	1.8801	0.2264
				10	3.9246	0.4120	0.3039	1.1566	1.2713	0.8880
			Zn^{2+}	27	0.0650	-2.3492	0.5493	0.1002	-4.5830	0.0537
				10	0.1860	0.5811	0.6375	0.0885	3.6036	0.1982
SDDS	553	1194.1	Cu^{2+}	27	0.3937	1.2993	0.0463	0.1516	10.5686	0.0755
				10	1.1529	0.4776	0.8510	0.3673	1.6625	0.8351
			Zn^{2+}	27	0.1222	-0.7724	0.8363	1.6990	-1.1465	0.6554
				10	0.2272	-1.2022	0.9384	0.4929	-2.6082	0.4805

At pH 7, copper sorption of 70 % was achieved. Our results approximately correspond with this finding.

Melichová and Hromada [48] achieved Cu^{2+} sorption of approximately 90% using natural bentonite. Atkovska et al. [49] achieved the removal efficiency in respect of zinc cations above 98 %. On the other hand, Sen and Gomez [50] achieved a zinc removal rate of approximately 40 % on bentonite. Chang et al. sorbed Cu^{2+} and Ni^{2+} using bentonite and bentonite/GO composite [51]. In the study, approximately 70 % of Cu^{2+} was sorbed after 180 min of sorption at 25±1°C. The results show that the steady-state sorption occurred after 120 min. Comparable sorption was achieved in our study only at reduced temperature. Otherwise, the efficiency of copper sorption on bentonite was mostly at half level. Even Cheng et al. did not always observe a linear progression for copper sorption on bentonite (bentonite/GO). Cao et al. compared [52] the

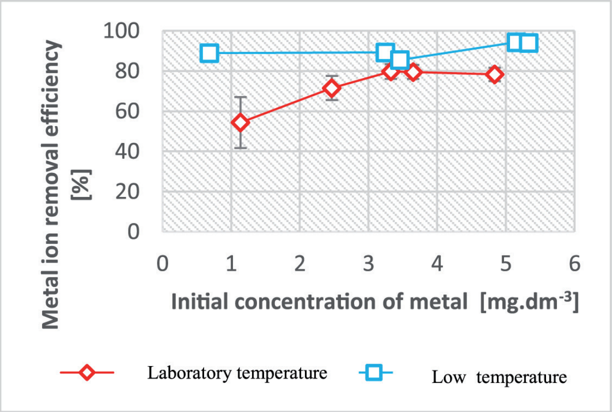

Fig. 4. Cu sorption on bentonite.

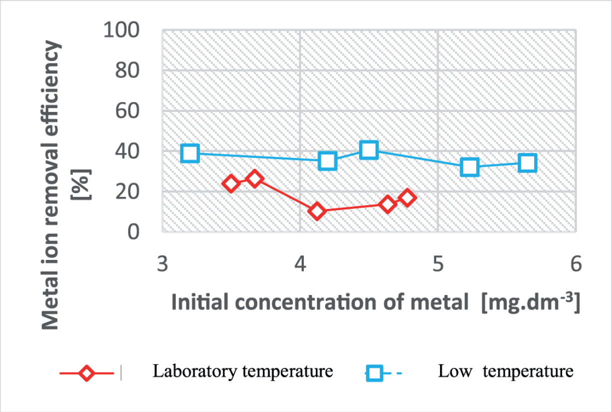

Fig. 5. Zn sorption on bentonite.

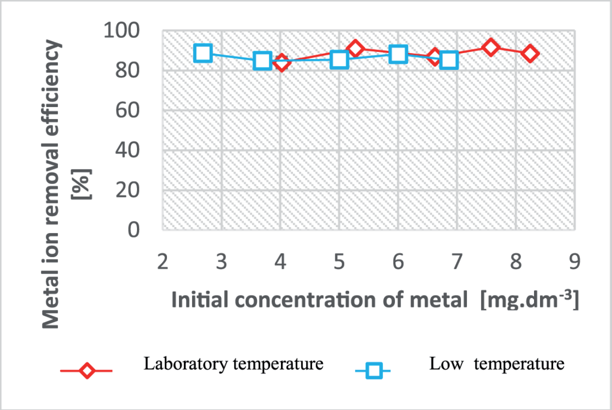

Fig. 6. Cu sorption on zeolite.

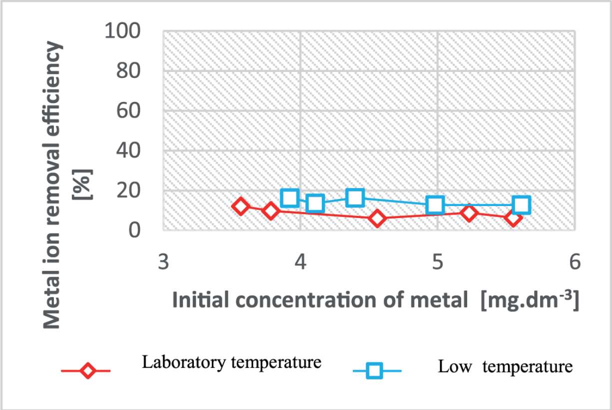

Fig. 7. Zn sorption on zeolite.

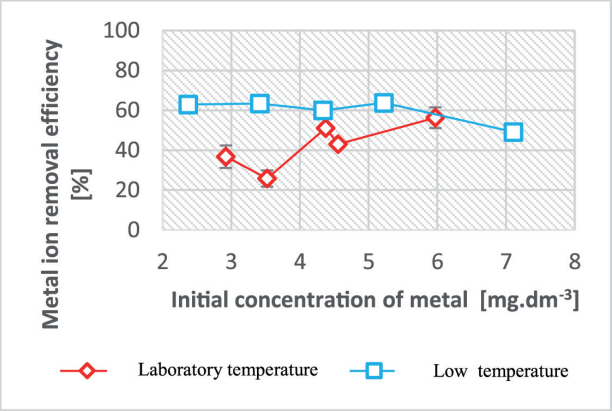

Fig. 8. Cu sorption on SDDS.

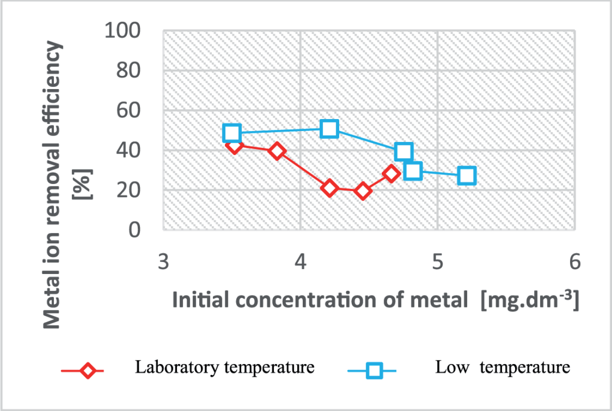

Fig. 9. Zn sorption on SDDS.

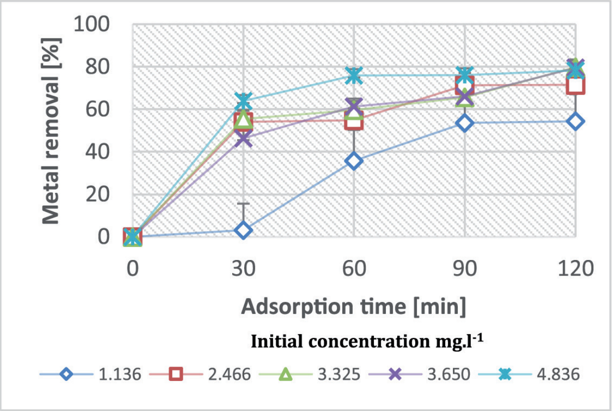

Fig. 10. Cu sorption on bentonite at laboratory temperature.

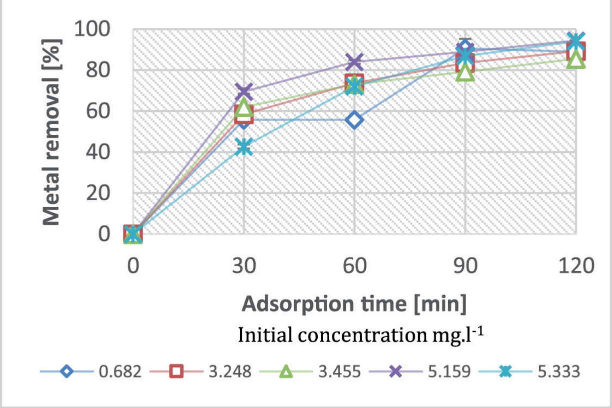

Fig. 11. Cu sorption on bentonite at 10ºC.

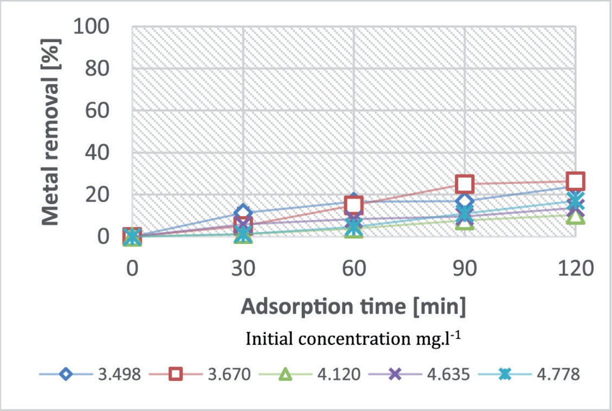

Fig. 12. Zn sorption on bentonite at laboratory temperature..

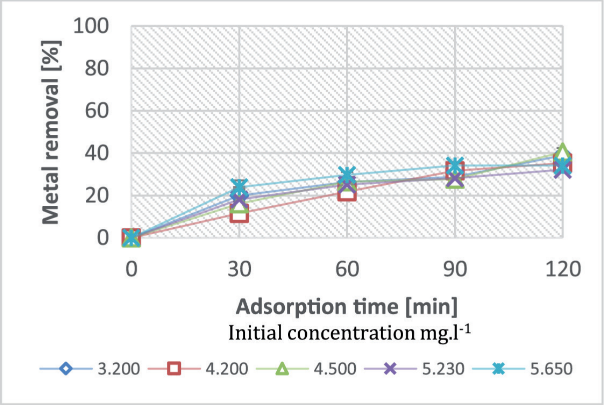

Fig. 13. Zn sorption on bentonite at 10ºC..

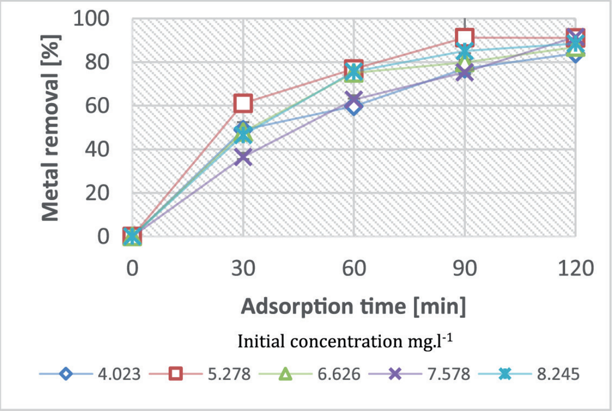

Fig. 14. Cu sorption on zeolite at laboratory temperature.

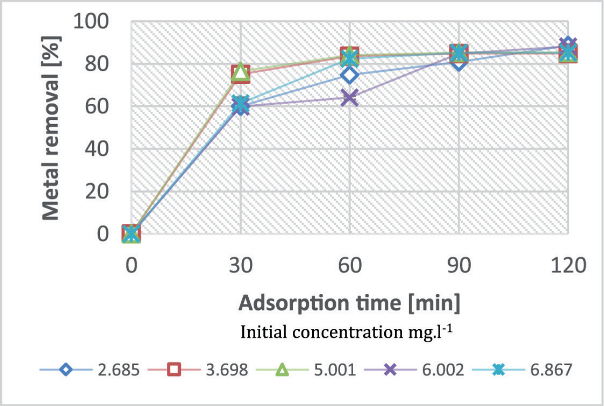

Fig. 15. Cu sorption on zeolite at 10ºC.

use of bentonite, bento-zeolite, and artificial zeolite for the sorption of Cu^{2+} and Zn^{2+} from wastewater. They achieved Cu^{2+} and Zn^{2+} removal efficiencies of 73.63%±2.58 and 54.46%±1.34, respectively. The better sorption of Cu^{2+} over Zn^{2+} was also confirmed by our research. The sorption of Cu^{2+} was also in agreement with our results, while the sorption of Zn^{2+} was higher compared to our results. Certain variations in the efficiency may, of course, be due to different sorbent compositions, and different conditions - temperature, and pH. Kakaei et al. discussed the sorption of heavy metals using bentonite and modified bentonites [53]. Their adsorption capacity of monolayer q_m was more than one order of magnitude higher compared to our values. This may be due to the different process conditions compared to our experiment.

Nowadays, some studies consider the modification of bentonite in combination with different materials. For

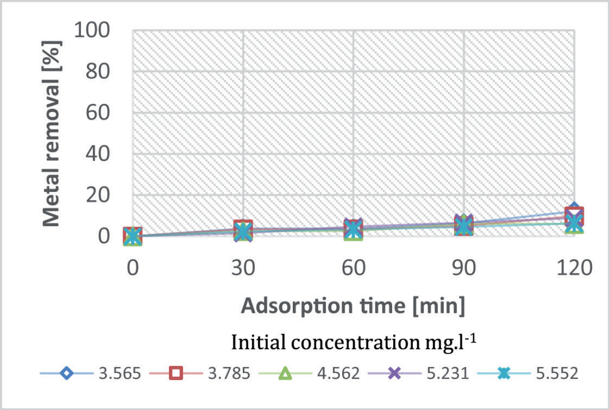

Fig. 16. Zn sorption on zeolite at laboratory temperature.

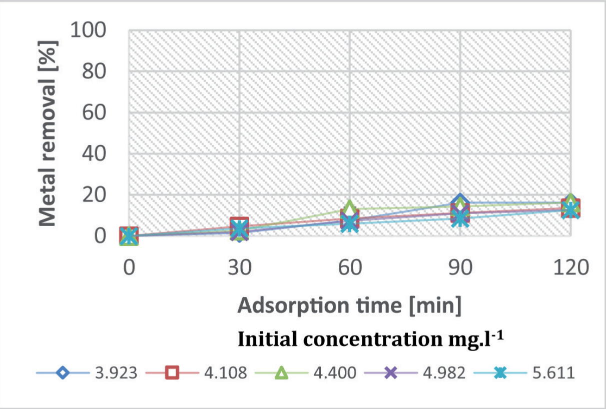

Fig. 17. Zn sorption on zeolite at 10ºC.

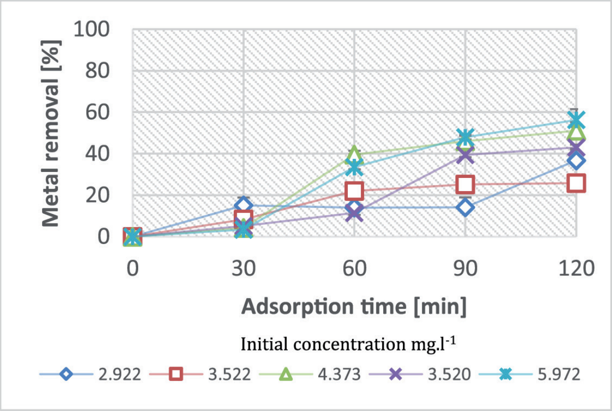

Fig. 18. Cu sorption on SDDS at laboratory temperature.

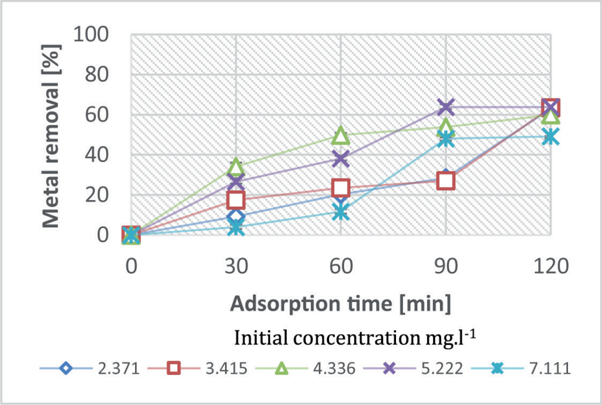

Fig. 19. Cu sorption on SDDS at 10ºC .

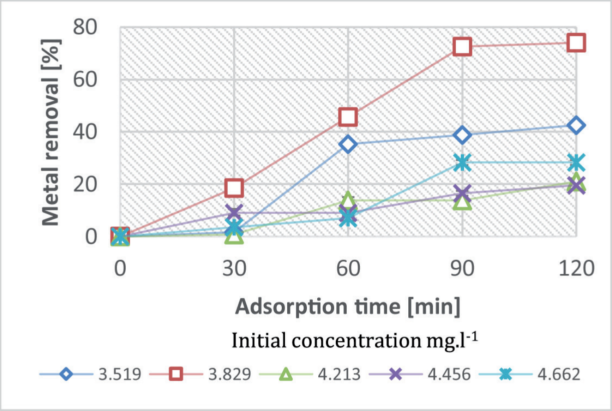

Fig. 20. Zn sorption on SDDS at laboratory temperature.

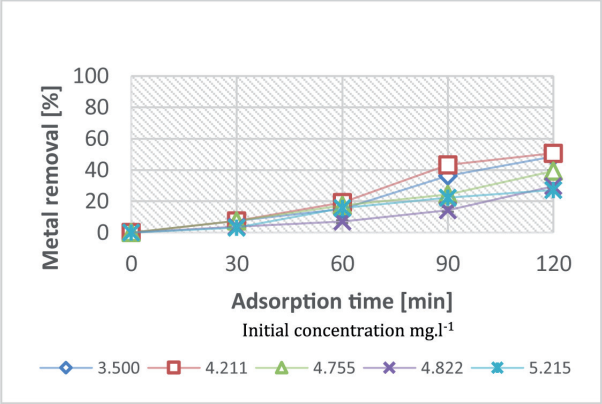

Fig. 21. Zn sorption on SDDS at 10ºC.

example Rashid et al. [54] used a composite of bentonite and dead fungal biomass. The adsorption of Zn(II) was recorded to be 56, 48.23, 32.27, 24.64, 19.77, and 16.45 using 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3 (g) adsorbent dose. Tahervand and Jalali [55] tested metal sorption on soil amended with bentonite, zeolite, and calcite. Zinc sorption on bentonite-amended soil, zeolite-amended soil, and calcite-amended soil at pH 2 were 3.5, 3.7, and 5.0 times that sorbed on control soil, respectively. Zinc sorption on calcite-amended soil ranged from 38.5 to 99.6% at pH 2 and 9, respectively with a mean of 64.7%. Modification of natural bentonite is required to improve its adsorption capacity and surfactants are widely used for such modification. Surface modification by the cationic surfactant (Bencylhexadecyldimethyl ammonium chloride, BCDMACl) improved adsorption capacities (q_{max} 50.76 and 35.21 mg.g^{-1} for Cu^{2+} and Zn^{2+}, respectively); about 2.5 and 2.0 fold improvements over natural bentonite. Kumararaja et al. [57] used chitosan-g-poly(acrylic acid)-bentonite composite for immobilization of heavy metals from contaminated soils. The adsorption pattern followed the Langmuir isotherm model, and the maximum monolayer capacity was 88.5, 72.9, 51.5, and 48.5 mg.g^{-1} for Cu^{2+}, Zn^{2+}, $Cd^{2,+,}$ and Ni^{2+}, respectively.

Sorption of Copper and Zinc on Zeolite

In the case of copper sorption on zeolite, the reduced temperature did not contribute to better sorption. For neither metal was the sorption pattern at both temperatures linear, depending on the input metal concentration? For zinc sorption on zeolite, the reduced temperature promoted sorption. The improvement in zinc sorption was confirmed by an increase in the adsorption capacity of the monolayer q_m. For copper sorption, the most efficient sorption occurred during the first 30 min of sorption. Zn^{2+} sorption on the zeolite gradually increased throughout the sorption. Svilovic et al. [58] carried out copper sorption at different temperatures using zeolite. An increase in Cu sorption was found as a function of increasing temperature. Our experiment proved the opposite effect of temperature on the progress of sorption. Shaheen et al. achieved in their work [59] using zeolite, the sorption of Cu^{2+} and Zn^{2+} at rates of 80% and 60 %, respectively. The lower sorption of Zn^{2+} compared to Cu^{2+} was confirmed by our research. Elboughdiri and Garcia in their study [60] used natural zeolite to remove various heavy metals from industrial wastewater. At a sorbent concentration of 50 g.l^{-1}, they achieved Cu^{2+} removal rates of approximately 80%. Interestingly, the same Cu^{2+} removal was achieved in our study with ten times less amount of sorbent for the same volume of wastewater. The Cu^{2+} removal efficiency might have fluctuated due to the zeolite composition or other properties of the zeolite. Wang et al compared in their work [61] metal sorption on natural zeolite and SiO_2 encapsulated natural zeolite (SiEZ). With the addition of 3 g.l zeolite^{-1} (close to the addition of sorbent in our study), Cu^{2+} sorption and Zn sorption were obtained at 81% and 86%, respectively. Better sorption of Zn over Cu was demonstrated, which is the portion of our finding. The level of Cu^{2+} removal was very close to our value. Rocha et al. demonstrated in their work a progression of sorption with increasing temperature, which contradicts our findings [62]. Sorption according to our hypothesis can be improved by decreasing the temperature, since in that case the desorption effect is reduced. Moreover, Rocha et al. showed an increase in q_m with increasing temperature (their q_m values were several times higher compared to our study), which also contradicts our study. Also, other studies reported natural zeolite as a sorbent for the removal of heavy metals and other compounds [63-66].

Sorption of Copper and Zinc on SDDS

For both Cu^{2+} and Zn^{2+} sorption on SDDS, the sorption efficiency increased with decreased temperature. The reduced temperature also promoted an increase in the adsorption capacity of the monolayer. The only linear progression was observed for zinc sorption on SDDS at 10ºC. Both Cu^{2+} and Zn^{2+} sorption proceeded gradually throughout the experiment. In our study, better sorption of Cu^{2+} compared to Zn^{2+} was also found, but the sorption levels were lower at about 60% and 40%, respectively. The drying of the sludge reduced the sorption of both metals in the study by Ong et al. This sorption level of Cu^{2+} (45%) and Zn^{2+} (30%) is more consistent with our results. Dewatered sludge was used in our study. The sorption of Zn and Cu^{2+} by the sludge was approximately 30% lower compared to the work of Kurniawan et al. [67]. According to other studies, activated sludge can also be used for the removal also elements like U^{6+} [68] or other chemical compounds like tetracycline [69], silver nanoparticles [70], or dyes (aniline blue, Nile blue, Bismarck brown Y and safranin O) [71]. Xu et al. [72] investigated sludge-based adsorbents for heavy metal removal, which can be prepared by carbonization, physical activation, and chemical activation.

Some studies investigated the adsorption of heavy metals on biochar derived from anaerobically digested sludge mainly for Pd removal [73-75]. However, this could be the aim of the next research.

Comparison of Metal Sorption on Different Sorbents

In the past, positive sorption on sludge has been demonstrated [76], however, the highest sorption of copper was observed when bentonite and zeolite were used. The highest sorption of zinc was obtained by sorbing on zeolite. The highest adsorption capacity of the monolayer was found with zeolite both at the laboratory and at reduced temperature. In general, copper was sorbed better than zinc. The hydration radius, among other factors, may influence this phenomenon. When we compare the hydration radius of Cu and Zn according to Calvo [77] the hydration radius of Cu^{2+} and Zn^{2+} reaches 4.19 and 4.30, respectively.

Different sorbents have quite variable removal efficiency. Ahmed et al. [78] reported the removal efficiency of activated dolomite at 80 % and bone char at 76%. Aden et al. [79] stated removal efficiency for bark and fly ash at 54%. Other studies declared the removal efficiency of sludges at level 46% [80], nano bentonite 74% [81], hydroxyapatite 62% [82], minerals such as goethite 46% [83], and modified asphaltite ashes 48% [84].

Sorption in most cases, in contrast to other studies [51-53, 58, 85] was not linear. This phenomenon may have been due to the continuous mixing of the sorbent with the neutral effluent solution. The intense contact of the phases may have promoted metal desorption, thus decreasing the removal intensity of both metals from the solution.

Conclusions

The reduced temperature contributed to metal sorption on bentonite and sludge. The effect of temperature on copper sorption on zeolite was not as pronounced. The sorption was not linear in most cases. This may have been due to continuous mixing to ensure intense contact between the phases, which may have promoted desorption processes. The sorption of copper was better than that of zinc. The sorption was mostly smooth for the sorbents. Only copper sorption on zeolite at both reduced and laboratory temperature had a rapid progression during the first 30 min of sorption. The progress of sorption of both metals at both temperatures was not linear. The only exceptions were the Cu sorption on sludge at reduced temperature and Zn - both temperatures.

The improvement in the sorption of metals at reduced temperature was confirmed by the increase in the adsorption capacity of the monolayer q_m. The specific surface area size of the sorbents did not directly correlate with the sorption efficiency. Therefore, other factors with a significant influence on sorption should also be taken into account. In the future, it will be interesting to investigate the sorption capacity of sludge or other waste materials at a larger range of temperatures.

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Conflict of Interest

The authors declare no conflict of interest.

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