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Removal of copper and lead ions from rainwater with an alginate-bentonite composite: batch and column studies

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ABSTRACT

The study was conducted on a laboratory scale and the main objective was to evaluate the feasibility of using bentonite and calcium alginate-based granules to adsorb pollutants from rainwater in a columnar system. Therefore, in this study, the fine powder of clay materials was mixed with calcium alginate to obtain capsules that can be easily separated and recovered. These granular sorbents were found to be a new and inexpensive solution for removing heavy metals from water. On the basis of the pollutant adsorption study, the sorption capacities of the adsorbent and bed, adsorption rates, and bed breakthrough time were determined. Characterisation of the structural features of the granules using modern observational and spectroscopic techniques, that is, scanning electron microscopy, Brunauer–Emmett–Teller, and Fourier-transform infrared spectroscopy, was also an important part of the study. The aim of the study was to conduct the adsorption process under dynamic conditions to determine the efficiency of removing copper and lead ions from rainwater. Static adsorption showed a high percentage of copper removal of 72.75% and lead removal of 84.5% for a dose of 2.0 g/L. The column adsorption system showed a high removal rate. Regeneration showed a high efficiency of copper and lead adsorption. In the fourth cycle in the case of Cu(II), 60%, column 2 - 52.5%, column 3 - 30%, for Pb(II) for column 1 - 73%, column 2 - 76%, column 3 - 50% were obtained.

Keywords: Adsorption; Bentonite; Calcium alginate; Heavy metals; Fixed-bed column

1. Introduction

The ecosystem is under increasing pressure due to anthropogenic activities such as urbanisation, agriculture, industry and infrastructure development [1]. Due to current global water scarcity, finding strategies that can effectively guarantee water security and sustainable use has become an urgent problem that needs to be solved [2,3]. Rainwater is a kind of clean energy, and the method of treating and reusing rainwater has become a key problem to consider [2]. Collecting rooftop rainwater with high water quality and large water volume can alleviate the water resource crisis [4,5]. More practical, easy to design, inexpensive, environmentally sustainable and environmentally friendly methods are needed to provide access to clean water [6–8]. Rainwater can be contaminated with both inorganic substances, such as toxic heavy metals, and organic substances, such as dyes and pesticides. Human exposure to heavy metal ions leads to various human diseases, such as respiratory problems, kidney disease, neurological disorders, and cancer. Although it is scientifically impossible to completely prevent heavy metal ions from leaching into the environment, the elimination of heavy metals from wastewater has been achieved through the use of polymeric materials and clay minerals. Among the processes used in water treatment, adsorption is an important method with high removal

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efficiency and no harmful by-products [9,10]. Adsorption is an attractive approach to water purification, especially if the adsorbent is inexpensive and does not require pretreatment before use [11].

However, presently, the use of inexpensive natural adsorbents dominates. The search for new sorption materials for water purification is on for materials that are readily available, economical, and environmentally friendly. Much research is being done on the use of bentonite or chitosan. One of them is the production of composite hydrogel beads based on magnetic bentonite/carboxymethyl chitosan/sodium alginate by Zhang et al. [12]. They used this adsorbent to remove Cu(II) from water. Another example is the removal of Cd(II) from water using alginate-based composite beads filled with phosphate and bentonite washing sludge [13]. Pawar et al. [14], on the other hand, used activated bentonite-alginate composite beads to effectively remove Cu(II) and Pb(II) from water.

As can be seen, a popular and inexpensive adsorbent is clay materials. It is known that sorbents should have a good sorption capacity for heavy metals and sufficient porosity to ensure their retention [9,15,16]. The role of clay minerals in the environment is due to their ability to exchange cations in the transport of toxic materials. The low cost, availability, and recovery of clay give it an additional advantage as an effective adsorbent. Adsorbents can also remove pollutants' cations or anions because their surface charge can be positive or negative, depending on their pH state [17,18]. In the present study, we used fine powder from clay materials with calcium alginate to obtain capsules that can be easily separated and recovered. These granular sorbents were found to be a new and inexpensive solution for removing heavy metals from water.

It should be emphasised that the innovation is the use of alginate-bentonite capsules for adsorption of pollutants from real solutions, which were contaminated with rainwater. The study considered the influence of colour and organic compounds on the adsorption capacity in relation to heavy metals. The study was carried out in a static and column system. The sorption capacities of the adsorbent and bed, adsorption rates, and bed breakthrough time were determined in contaminant adsorption studies. An important part of the study was also the characterisation of the structural features of the granules using modern observational and spectroscopic techniques, that is, scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), and Fourier-transform infrared spectroscopy (FTIR). The first stage of the research was to determine the efficiency of adsorption under static conditions, where the dose and time of adsorption, as well as the effect of pH, on the adsorption of metal ions were determined. The second stage of the research was to carry out adsorption in a column system with and without the addition of sand in the adsorption column. The last stage of the research was to consider the possibility of regenerating the adsorption columns.

2. Material and methods

2.1. Rainwater

Rainwater collected in May from Gliwice, Poland, was spiked with a sufficient volume of copper and lead solution to obtain a concentration equal to 3 and 0.1 mg/L. Rainwater came from the reservoir located in the gutter on the ground. The roof was made of heat-sealable roofing felt. The water was characterised by a high concentration of colour and a chemical oxygen demand (COD) index. The basic physicochemical characteristics of raw rainwater are presented in Table 1.

2.2. Materials

Egyptian bentonite (Ben) powder was obtained from the Al Barkan region on the northwest Egyptian coast and was supplied by the Egypt Bentonite and Derivatives Company, Alexandria, Egypt (Table 2). All the chemical materials used in this study were purchased as analytical grade reagents. Sodium alginate, HCl and $CaCl_2$ were purchased from Sigma-Aldrich (Poznań, Poland). Copper ion concentrations were monitored spectrophotometrically with Merck test kits. The standard copper and lead solution ($CuCl_2$ and $PbCl_2$) was purchased from Merck (Merck sp. z o.o., Poland).

2.3. Preparation of samples

Bentonite (12 g) was dispersed in 50 mL of deionized water with constant stirring. In a separate beaker, a 2% (w/v)

Table 1
Physico-chemical characteristics of rainwater

Parameter	Rainwater (average value)
pH	6.9
Conductivity, μS/cm	204.5
Color, mg·Pt/L	154
COD, mg/L	150
TOC, mg/L	15.6

Table 2
Chemical composition of raw bentonite

Main constituents	Weight (%)[a]
SiO_2	51.33
TiO_2	1.34
Al_2O_3	17.64
Fe_2O_3	4.19
MnO	0.02
MgO	2.67
CaO	6.19
Na_2O	2.96
K_2O	1.09
P_2O_5	0.13
SO_3	0.18
F	0.21
Cl	0.44
LOI	11.51
Total	99.9

[a] Data obtained by X-ray fluorescence using an Axios Panalytical 2005 apparatus.

suspension of alginate was prepared by thoroughly dissolving 4 g of sodium alginate in deionised water (200 mL). A homogenised suspension of diatomite (50 mL) was added to the alginate suspension and then the mixture was stirred for 4 h. When the mixture became homogeneous, the mixture was transferred to a separate funnel and slowly added dropwise to an aqueous coagulation bath containing 500 mL of a 2% $CaCl_2$ solution which was stirred continuously for 3 h. After 3 h, the beads were filtered and washed with deionised water (4 × 200 mL). The beads were dried for 24 h at room temperature and then in a laboratory drier at 60°C. The humidity of the adsorbents was not determined. Before starting each stage of the investigation, the beads were dried in an oven at 60°C.

2.4. Characterisation of adsorbents

The surface morphology of the studied minerals was investigated by SEM. Scanning electron microscope of the JSM 6360LA model manufactured by JEOL-Japan. The structural properties of the adsorbents were determined by measuring the surface area and pore size distribution using the low-temperature nitrogen adsorption and desorption technique according to the BET method. The functional groups on the adsorbent surface were determined using the FTIR technique. A series of measurements of infrared spectra was performed using the ATR technique on a Bruker FTIR TENSORII spectrometer. Measurement range: 400–4000 cm^{-1} with a resolution of 1 cm^{-1}.

2.5. Batch adsorption studies

The adsorption of Cu(II) and Pb(II) was performed to evaluate the adsorption capacity of the encapsulation diatomite by using a batch experiment. The effects of contact time and dose on the adsorption capacity of the compounds were investigated. The research was carried out in a multi-component solution. Adsorption was carried out in 100 mL glass flasks with 100 mL of solution at room temperature (20°C ± 2°C) in an incubator shaker at 300 rpm. The mass of the sorbents varied in the range of 0.25–2 g/L. Kinetic experiments were carried out as follows: 1 g/L of sorbent was added to 100 mL of feed water (C_0 = 4 mg/L) in a glass flask, the flask was shaken at 300 rpm/min for the following times: 15, 30, 45, 60, 90, 120, 180, and 240 min. In studies of the pH of the effect of solution on adsorption, the pH was adjusted with 0.1 M HNO_3/NaOH solutions. In these studies, an adsorbent dose of 1 g/L was used and the contact time was 2 h.

2.5.1. Adsorption isotherms

The experimental data were fitted by two common adsorption isotherm models. The Langmuir model and the Freundlich model. All calculations used in the article have been described in the previous paper by Marszałek et al. [19].

2.5.2. Kinetics of adsorption

To determine the adsorption kinetics of adsorbent, the experimental data were analysed using pseudo-first-order and pseudo-second-order kinetic models, which have been described in the article by Kamińska and Bohdziewicz [20].

Errors were estimated on the standard deviation of three replicates of each analysis. Error values for all tested samples did not exceed 5%.

2.6. Column adsorption studies

Dynamic adsorption experiments were performed at room temperature under laboratory conditions. Three adsorption columns were designed. The depth of the bed was column (1): 10 cm contained sand (15 g) + bentonite/alginate beads (10 g), column (2): 10 cm contained bentonite/alginate beads (10 g) + sand (15 g), column (3): 5 cm contained only bentonite/alginate beads (10 g) [21].

The rainwater flow rate was 1 mL/min. Additionally, copper and lead were added to the rainwater. with a fixed concentration (Cu(II) = 3 mg/L, Pb(II) = 0.2 mg/L). A photo of the test equipment is shown in Fig. 1.

2.7. Desorption

The study of the possibility of reusing adsorbents based on bentonite and calcium alginate was carried out in four cycles. Regeneration was carried out by passing 4% HCl through the columns for 2 h. The columns packed with the adsorbent were then washed several times with deionised water until the pH was neutral. The process of adsorption of pollutants from rainwater was carried out again.

3. Results

3.1. SEM analysis

The surface morphology of the composite pellets was examined by SEM analysis, as illustrated in Fig. 2. Images of wet and dry pellets are shown in Fig. 3A and B. The surface of the pellets is rough with irregular pores. Numerous bulges were observed on the composite beads. This is also confirmed by other studies [22].

3.2. FTIR study

Then, the chemical structure (functional groups) of the tested samples was determined. Changes in the chemical composition of the tested samples were investigated. The FTIR spectrum of bentonite is shown in Fig. 4B, calcium alginate is shown in Fig. 4A, and alginate-bentonite beads are shown in Fig. 4C. The FTIR spectrum of the calcium alginate balls shown in Fig. 3 is characterised by the presence of the following bands: band located at 3,320 cm^{-1}, derived from tensile vibrations of the OH group, two signals corresponding to tensile vibrations of groups CH, located at 2,910 and 3,050 cm^{-1}, bands derived from asymmetric vibrations at 1,590 cm^{-1} and symmetric at 1,420 cm^{-1} tensile vibrations of the COO^- group [23].

Intense bands of approx. 1,000 cm^{-1} indicate tensile vibrations Si, Al–O. In the range of about 1,050 cm^{-1} there are very clear tensile vibrations of Si–O silicon oxides; these are also bands characteristic of minerals containing montmorillonite [24]. In the lowest absorption ranges, approx. 670 cm^{-1}, vibrations of the Al–OH, Si–O, and Al–O groups

Fig. 1. Columns with fixed beds.

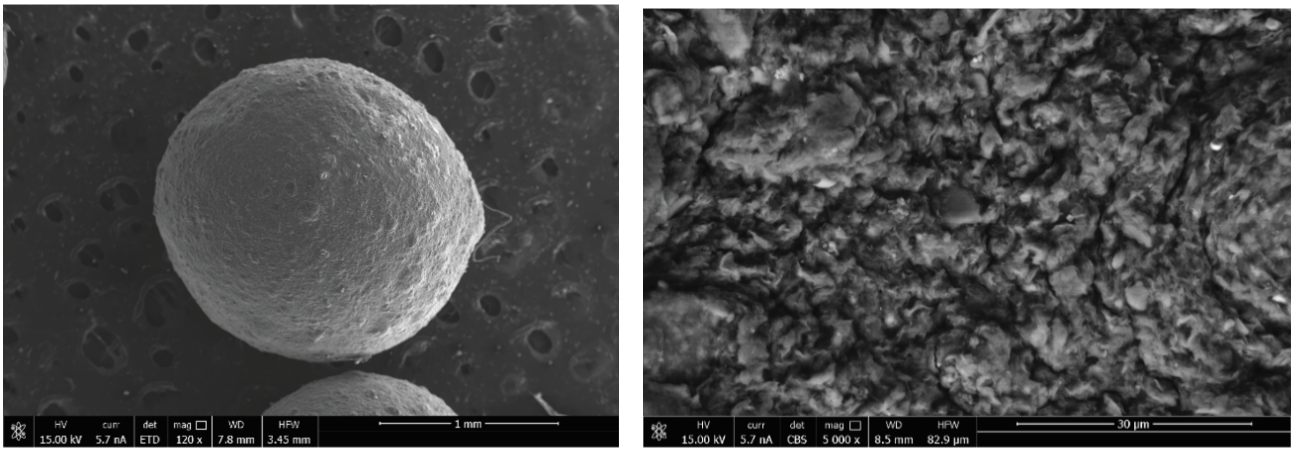

Fig. 2. SEM images of bentonite/alginate bead, 100×, 5,000×, respectively.

Fig. 3. Photos of beads: (A) wet beads and (B) dry beads.

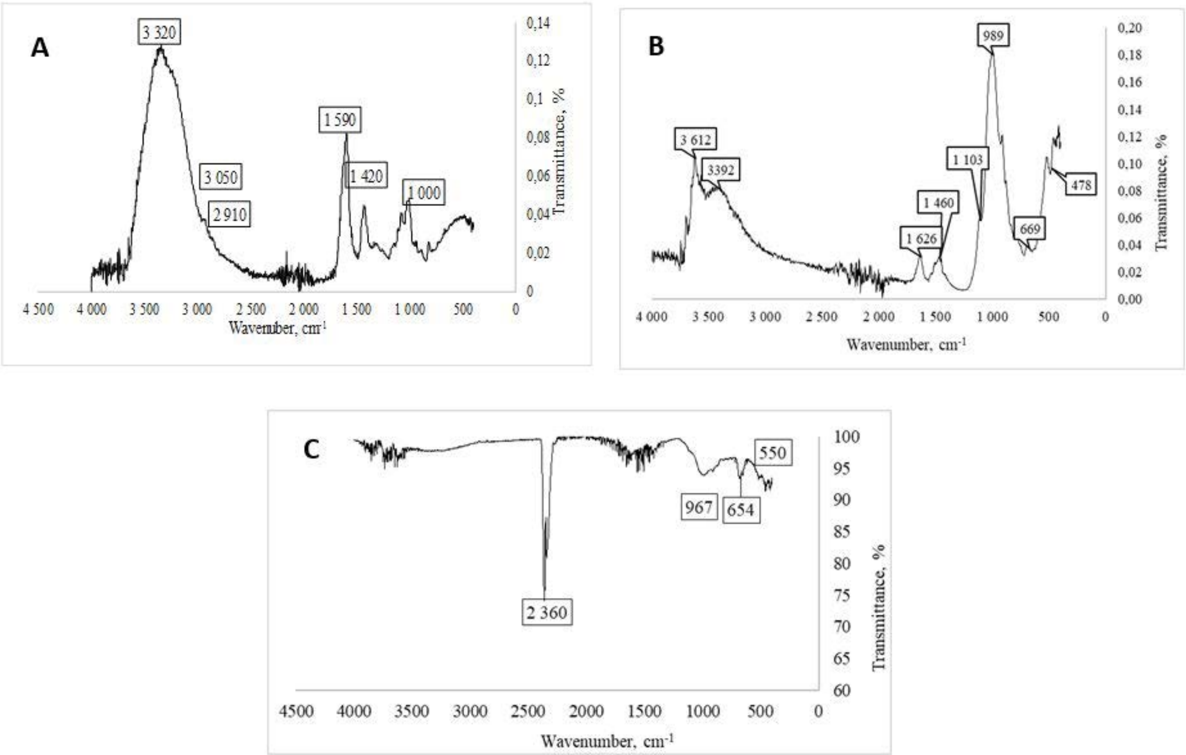

Fig. 4. (A) IR spectra of the calcium alginate sample, (B) IR spectra of the bentonite sample, and (C) IR spectra of the cross-linked calcium alginate bentonite sample.

appear which are difficult to clearly identify. The characteristic absorption band visible for 1,630 cm^{-1} is related to the occurrence of water in the structure of the material (tensile vibrations O–H–O). The most important bands in the absorption area between 3,700 and 3,400 cm^{-1} are caused by tensile vibrations of OH groups. The most common tensile vibrations in this range are symmetrical –OH (~3,600 and ~3,400 cm^{-1}) [24]. These are vibrations of water globules from the interpacket space of layered aluminosilicates and hydroxyl groups.

The strong band observed at 982 cm^{-1} is attributed to the Si–O stretching vibrations characteristic of layered silicates [22]. A characteristic band in the range of 2,360 cm^{-1} indicating the presence of atmospheric carbon dioxide that does not originate from the sample can also be observed in the FTIR spectrum shown. The presence of a broad band in the range resulting from the presence of molecular water, a band characteristic of the OH group [25] was observed. The presence of a band resulting from the stretching vibrations of the octahedral aluminosilicate layer at the 674 cm^{-1} position and the Si–O band at 550 cm^{-1} in the recorded FTIR spectra confirms the presence of bentonite in the spherical sample.

3.3. BET study

A nitrogen adsorption–desorption method was used to evaluate the pore structure of the granules to determine the specific surface area and pore structure of the samples and is shown in Table 3. The specific surface area and pore volume of natural bentonite were 30.35 m^2/g and 0.0712 cm^3/g, respectively; After encapsulation of bentonite, the specific surface area and pore volume values decreased to 10.945 m^2/g and 0.0225 mL/g, respectively. On the other hand, had a lower specific surface area because alginate blocks the porosity of clays. In contrast, the pore size was not significantly reduced. This means that the granule contained fewer of them, while encapsulation did not affect their size.

Table 3
Characteristics of and from nitrogen sorption–desorption measurements

Adsorbent	Specific surface area (SSA) (m^2/g)	Total volume in pores (mL/g)	Pore size (nm)
Bentonite	30.3524	0.0712	2.152
Bentonite beads	10.945	0.0225	2.095

3.4. Effect of the adsorbent dose and process time on the adsorption of copper and lead from rainwater

The influence of the adsorbent dose on the efficiency of removal of copper and lead ions from rainwater was investigated. As shown in Fig. 5A, the removal efficiency clearly changed with increasing adsorbent dose. This increase is explained by the sorption sites on the surface of the granules. The highest efficiency was obtained for two 2 mg/L for both metals.

Contact time is an important factor that influences the adsorption of heavy-metal ions by the adsorbent. The study investigated the effect of contact time on the interaction between bentonite/alginate granules and metal ions in a periodic experiment. The results obtained are shown in Fig. 5B. The obtained results indicate that lead adsorption was at a higher level than that of copper. You can see that the copper adsorption is stable after half an hour of the process. On the other hand, in the case of lead, the adsorption increased with time and was fixed only after 180 min.

The achievement of equilibrium of adsorption may result from a decrease in the time of the available adsorption sites on the adsorbent, which in turn leads to limited mass transfer of adsorbate molecules from the liquid to the outer surface of the adsorbent [26]. The difference in the adsorption capacity of bentonite granules for lead and copper may result from the different nature of the tested metals, which can be explained by their ionic radius. The effective ion radius Pb (1.19 Å) differs from the Cu radius (0.73 Å) in the ionic state [27]. This could possibly have played a role in the interaction of these metals with the surface of the granules used because the smaller the ionic radius, the closer the electrons are to the nucleus, and therefore these electrons are strongly attracted to the nucleus and less available for binding to the adsorbent surface. Therefore, a higher efficiency in the removal of lead was observed, which took over the adsorption sites for copper.

3.5. Influence of the pH of the solution

The pH of the solution plays an important role and has a significant impact on the adsorption efficiency of heavy metals. Fig. 6 shows the adsorption efficiency of copper and lead as a function of pH for their constant concentration in rainwater of 4 mg/L, at a dose of 1 g/L beads, for an adsorption time of 120 min at 25°C.

The pH value of an aqueous solution affects both the surface charges of the adsorbent and the degree of ionisation of heavy substances of the metal ion. Therefore, it is a variable that affects the adsorption effect. Heavy metal ions in aqueous solutions occur in various forms; therefore, they can adsorb on the surface of the adsorbent or precipitate on its surface to varying degrees. Therefore, the specification of the metal form directly affects the adsorption process. The adsorption process is more effective at alkaline pH (pH 8.0–10.0) than at acidic pH (pH 4.0–6.0) [28]. Such a tendency was shown by the adsorption of lead ions, where as the pH increased, its concentration in rainwater decreased.

However, in the case of the adsorption of copper ions, a different course was shown, in the pH range of 4.0–8.0 it increased, and after reaching the pH value of 8.0 it decreased rapidly. When considering the adsorption of Cu(II) and Pb(II), it should be noted that speciation forms of metals occur up to pH 6.0, above which the concentration of solid CuO and $Pb(OH)_2$ increases. The ions were best adsorbed in the pH range of 8.0–10.0. When the chemical characteristics of the studied metals are analysed, it can be assumed that their electronegativity and ionic radiation values are responsible for the adsorption of copper and lead. Therefore, the adsorption of Cu(II) was also influenced by the presence of Pb(II) ions in the rainwater solution, which were first adsorbed [29].

3.6. Adsorption isotherms and adsorption kinetics of lead and copper

The data obtained for copper and lead adsorption were analysed using Langmuir and Freundlich models. The parameters, equations, and correlation coefficients of Freundlich and Langmuir for the adsorption of Cu(II) and Pb(II) in capsules are shown in Table 4 and in Fig. 7A and B.

Comparison of the correlation coefficients of the Freundlich and Langmuir models on alginate-bentonite capsules shows that the best model describing the adsorption of copper and lead may be the Langmuir isotherm.

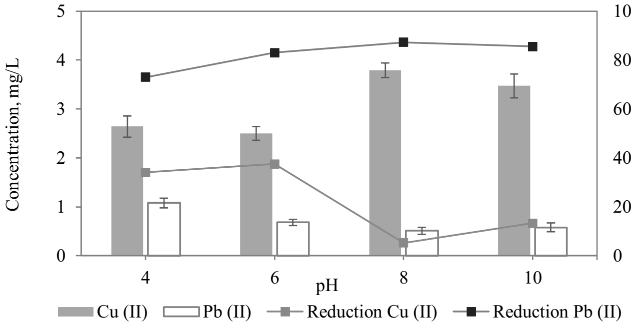

Fig. 6. Influence of rainwater pH on Cu(II) and Pb(II) adsorption.

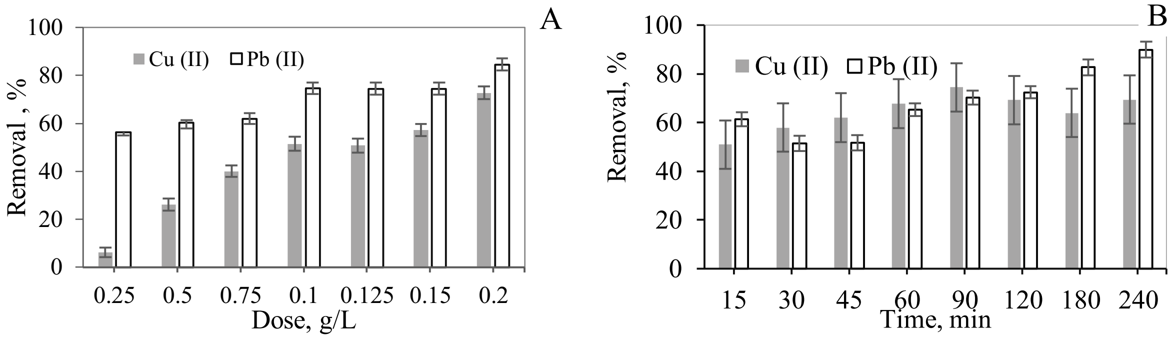

Fig. 5. Effect of the adsorbent dose (A) and the processing time (B) on the effectiveness of the removal of copper and lead from rainwater.

Table 4
Parameters of Freundlich, Langmuir and the equations, and the correlation coefficients for the adsorption of copper and lead on the studied sorbents

Adsorbent	Langmuir			Freundlich		
	Q_m (mg/g)	K_L (L/mg)	R^2 (–)	K_F ((mg/g)(L/mg)^n)	n (–)	R^2 (–)
Cu(II)	2.884	0.913	0.725	1.362	2.427	0.655
Pb(II)	41.152	0.061	0.880	2.240	0.578	0.761

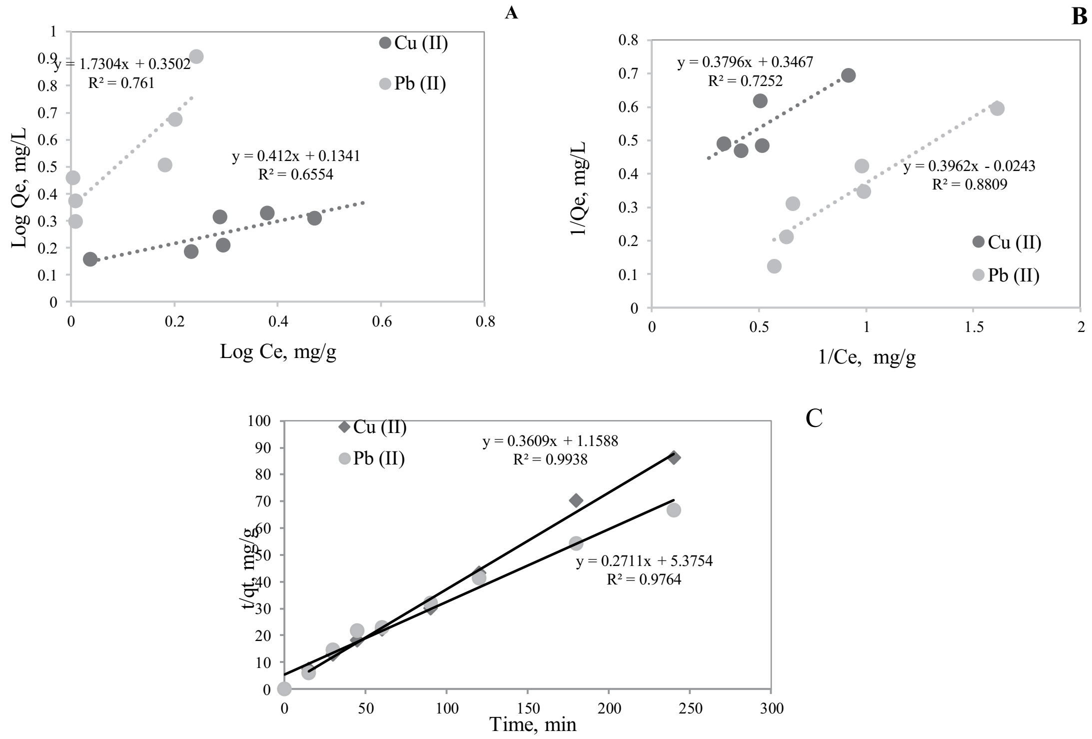

Fig. 7. Freundlich (A), Langmuir (B), and pseudo-second-order kinetic model (C) isotherms of Cu(II) and Pb(II).

Table 5
Parameters for the pseudo-first and pseudo-second-order kinetic models for the adsorption of copper and lead

Adsorbate	Pseudo-first-order equation parameters			Pseudo-second-order equation parameters		
	K_1 (1/min)	Q_e (mg/g)	R^2	K_2 (g/(mg·min))	Q_e (mg/g)	R^2
Cu(II)	0.0053	2,452	0.480	0.112	2.77	0.994
Pb(II)	0.0017	6.945	0.936	0.009	3.86	0.982

The Langmuir model is the most widely used isothermal model. It assumes that adsorption is limited to one molecular layer, all adsorption sites on the surface are energetically identical, and there is no interaction between adsorbate molecules [30]. The pseudo-second-order model described the adsorption of heavy metals into alginate-bentonite capsules very well, and the calculated parameters are presented in Table 5.

The calculated values corresponded well to the experimental data. This suggests that the adsorption of Cu(II) and Pb(II) follows second-order kinetics, and the model used can be used to determine the corresponding kinetic parameters.

3.7. Fixed-bed column investigations

The next stage of the research was an attempt to use capsules in a beads system. Many studies present results that determine that the metal absorption capacity of a fixed bed column reactor can be increased by increasing the height of the bed and decreasing the discharge rate [31,32]. Therefore, in this investigation, it was decided to keep the flow rate and the height of the bed constant, while changing the configuration of the bed fill. The study was carried out in three systems with sand at the column input (1), at the column outlet (2), and without sand (3). In column tests, the concentrations of heavy metals that were dosed into the rainwater were changed. The concentrations were selected according to the literature and DIN [33–35], suggesting possible amounts of these elements in water. The effect of column fill material on rainwater treatment and reduction of COD, colour, Pb, and Cu concentrations is shown in Figs. 8 and 9, respectively.

In the dynamic adsorption, the bed used, and the flow rate, there was no significant reduction in the COD value. The degree of this parameter was at the level for column 1 - 3%, column 2 - 20%, and column 3 - 23%. It was observed that, contrary to the adsorption of pollutants determined by the COD index, a reduction in the colour of the rainwater was observed. Rainwater taken from the roof with the roof had a high colour concentration at 154 mg·Pt/L. The best removal after 8 d of the process was recorded for column 1, that is, 43.5%, in which the sand was placed in the upper part of the bed. This was followed by column 2 = 40.3% and column 3 = 33.8%, which contained no sand. The degree of colour removal in the three columns is shown in Table 6.

It should be emphasised that the presence of organic compounds or other coexisting ions in solution affects the binding strength of the adsorbate and the adsorbent during the adsorption process [29]. Organic and inorganic compounds compete for adsorption sites on the adsorbent. In various studies carried out on single-component model solutions, alginate beads have been shown to be a good adsorbent of water dyes [36,37]. In the case of rainwater, which is polluted and has high COD and colour values, heavy metal adsorption will occur in the real multicomponent solution. On the other hand, it was observed that the adsorption column took quite a long time to run, as only in column 1, for example, lead appeared in the water after 36 h and at a low level of 0.02 mg/L. On the copper contrary, the concentration in the water was determined after the first hour of operation of the three columns. However, it was a low concentration at a maximum of 0.5 mg/L. It should be noted that the concentration allowed in drinking water according to the Ministry of Health Regulation [38] may be 2 mg/L. Other studies report that the effect of coexisting ions in solution such as

Table 6
Degree of colour removal depends on the time and the adsorption column used

Time, h	Column 1	Column 2	Column 3
	Removal degree, %		
1	43.5	45.5	31.8
2	43.5	47.4	28.6
3	40.9	47.4	33.8
4	47.4	47.4	33.8
8	46.8	46.1	37.0
12	47.4	46.8	37.7
36	44.8	39.0	27.3
60	53.2	50.6	35.7
84	47.4	44.2	27.9
108	49.4	41.6	32.5
132	48.1	44.2	34.4
156	46.1	42.9	30.5
180	44.8	41.6	31.8
204	43.5	40.3	33.8

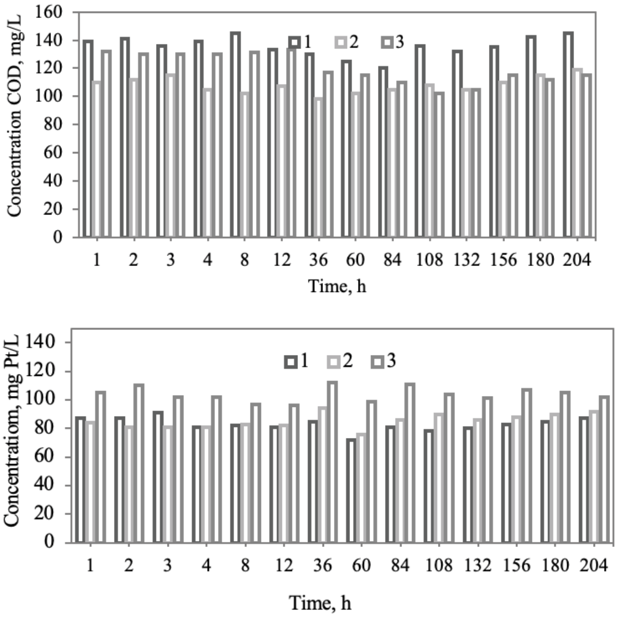

Fig. 8. Effect of time and type of bed on the effectiveness of COD and colour reduction in rainwater, C_{COD} = 150 mg/L, C_{colour} = 154 mg/L (1; 2; 3 means consecutive columns).

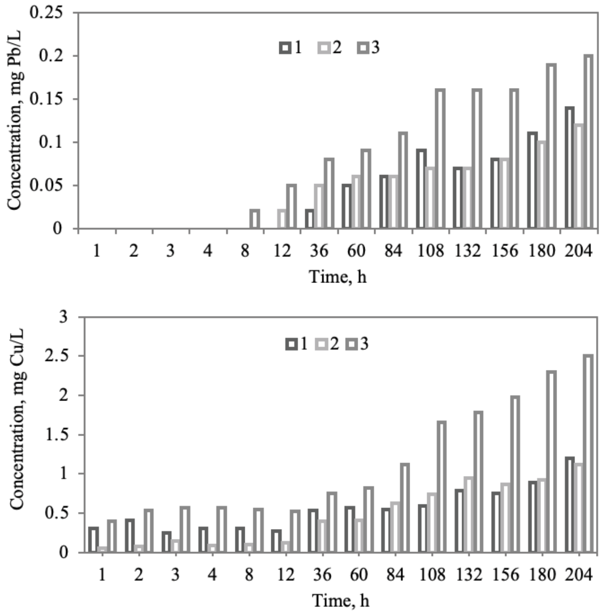

Fig. 9. Effect of time and bed type on the efficiency of lead and copper adsorption from rainwater (1; 2; 3 means consecutive columns).

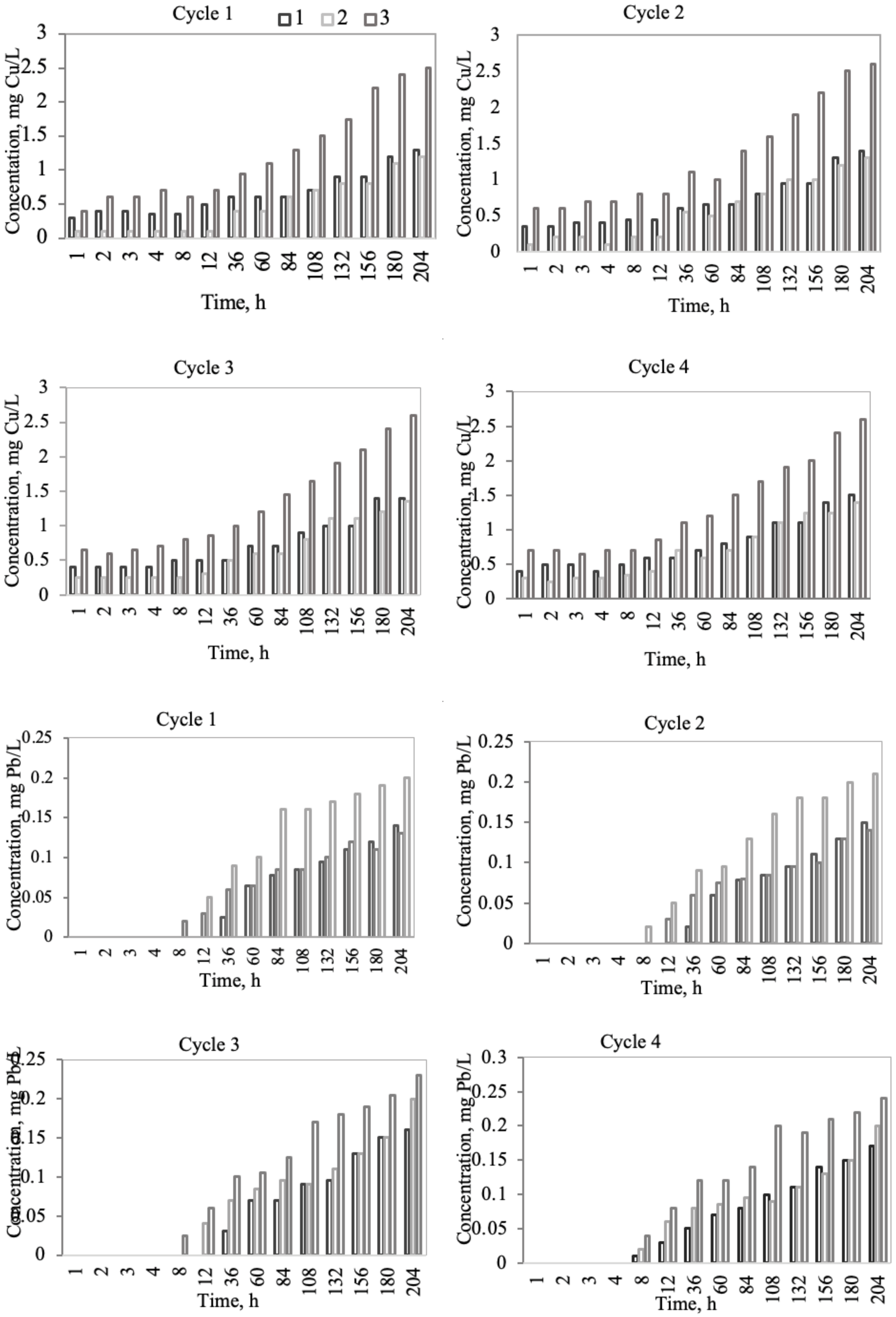

Fig. 10. Pb(II) and Cu(II) concentration depending on the adsorption time and the column used after four regeneration cycles (1; 2; 3 means consecutive columns).

NaCl and KCl has no significant effect on the removal of copper and lead using alginate/bentonite composite beads. This study was conducted by Pawar et al. [39] and established the suitability of ABn composite beads for the effective and selective removal of toxic copper and lead from a natural water matrix or wastewater.

The study also concluded that sand in column systems increased the efficiency of removal. Higher removal rates of concentration of colour and removal heavy metal ions were shown on the column with a sand charge at both the bottom and top of the column. The efficiency of the column filled with bentonite/alginate beads alone was found to be lower than that with sand charge. The effluent of column 3 exceeded the normalised value with respect to lead in 84 h of process execution, while columns 1 and 2 exceeded it in 180 h of adsorption. In the case of copper ions, the concentration value in columns 1 and 2 was not exceeded during the study and a three-column breakthrough occurred at 180 h.

3.8. Regeneration and reuse of the adsorbent

One of the most important factors in adsorption studies is the reusability of the adsorbent. For this purpose, four adsorption–desorption cycles were used for the tested capsules. The results showed that the possibility of using a given adsorbent is very high. The percentage of adsorption capacity after 4 d of column operation, after four cycles of use, was calculated for Cu(II) column 1 - 73%, column 2 - 52.5%, column 3 - 30%, for Pb(II) column 1 - 73%, column 2 - 76%, column 3 - 50%. The high efficiency of adsorption after regeneration of all columns used may be related to poor surface adsorption. It should be emphasised that the concentration of pollutants in the outflow of the columns was in accordance with the Polish regulation [38]. This decrease is often observed in similar studies and with similar alginate adsorbents [40–42]. These results demonstrate the excellent reusability of the beads to remove Cu(II) and Pb(II) ions from aqueous solution. Fig. 10 shows the concentration of lead and copper after four cycles of operation of each adsorption column.

4. Conclusions

In the studies carried out, alginate-bentonite capsules were used for real samples of contaminated rainwater. On the basis of the conducted research, the following conclusions were drawn:

- It was found that mixing sodium alginate with other materials can further increase the adsorption capacity and physical properties of composite materials.
- The best results were obtained with a rainwater solution with pH 6 for the Cu(II) and pH 8 for adsorption of Pb(II). The removal rate was 37% and 87%.
- The adsorption equilibrium of Cu(II) and Pb(II) on the composite was consistent with the Langmuir isotherm model.
- The pseudo-second-order model described the adsorption of heavy metals in alginate-bentonite capsules very well.
- Rainwater contamination (high COD and colour values) was found to affect the adsorption of heavy metal adsorption.
- Column studies also show that the sand in columnar systems increases the efficiency of removal. The higher efficiency of both colour and heavy metals was demonstrated in the sand column at both the bottom (column 1) and the top of the column (column 2).
- Regeneration showed a high efficiency of copper and lead adsorption. In the fourth cycle in the case of Cu(II), 60%, column 2 - 52.5%, column 3 - 30%, for Pb(II) for column 1 - 73%, column 2 - 76%, column 3 - 50% were obtained.

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References

[1] R. Shaheed, W.H.M.W. Mohtar, A. El-Shafie, Ensuring water security by using roof-harvested rainwater and lake water treated with a low-cost integrated adsorption-filtration system, Water Sci. Eng., 10 (2017) 115–124.

[2] X. Liu, Z. Ren, H.H. Ngo, X. He, P. Desmond, A. Ding, Membrane technology for rainwater treatment and reuse: a mini review, Water Cycle, 2 (2021) 51–63.

[3] V.K. Gupta, I. Ali, Environmental Water: Advances in Treatment, Remediation and Recycling, Elsevier, UK, 2012.

[4] X. Du, R. Ma, M. Xiao, W. Song, Y. Tan, Z. Wang, A. Hay-Man Ng, W. Zhang, Integrated electro-coagulation and gravity driven ceramic membrane bioreactor for roofing rainwater purification: flux improvement and extreme operating case, Sci. Total Environ., 851 (2022) 158197, doi: 10.1016/j.scitotenv.2022.158197.

[5] G. Lofrano, M. Carotenuto, G. Libralato, R.F. Domingos, A. Markus, L. Dini, R.K. Gautam, D. Baldantoni, M. Rossi, S.K. Sharma, M.C. Chattopadhyaya, M. Giugni, S. Meric, Polymer functionalized nanocomposites for metals removal from water and wastewater: an overview, Water Res., 92 (2016) 22–37.

[6] H.G. Zaman, L. Baloo, R. Pendyala, P.K. Singa, S.U. Ilyas, S.R.M. Kutty, Produced water treatment with conventional adsorbents and MOF as an alternative: a review, Materials, 14 (2021) 7607, doi: 10.3390/ma14247607.

[7] D.S. Dlamini, J.M. Tesha, G.D. Vilakati, B.B. Mamba, A.K. Mishra, J.M. Thwala, J. Li, A critical review of selected membrane- and powder-based adsorbents for water treatment: sustainability and effectiveness, J. Cleaner Prod., 277 (2020) 123497, doi: 10.1016/j.jclepro.2020.123497.

[8] İ. Sevgili, Ö.F. Dilmaç, B. Şimşek, An environmentally sustainable way for effective water purification by adsorptive red mud cementitious composite cubes modified with bentonite and activated carbon, Sep. Purif. Technol., 274 (2021) 119115, doi: 10.1016/j.seppur.2021.119115.

[9] D. Doulia, Ch. Leodopoulos, K. Gimouhopoulos, F. Rigas, Adsorption of humic acid on acid-activated Greek bentonite, J. Colloid Interface Sci., 340 (2009) 131–141.

[10] P.N. Diagboya, B.I. Olu-Owolabi, F.M. Mtunzi, K.O. Adebowale, Clay-carbonaceous material composites: towards a new class of functional adsorbents for water treatment, Surf. Interfaces, 19 (2020) 100506, doi: 10.1016/j.surfin.2020.100506.

[11] M. Nel, F.B. Waanders, E. Fosso-Kankeu, Adsorption Potential of Bentonite Clay and Attapulgite Applied for the Desalination of Seawater, 6th Int'l Conf. on Green Technology, Renewable Energy & Environmental Eng. (ICGTREEE'2014) Nov. 27–28, Cape Town (SA), 2014.

[12] H. Zhang, A.M. Omer, Z. Hu, L. Yang, Ch. Ji, X. Ouyang, Fabrication of magnetic bentonite/carboxymethyl chitosan/sodium alginate hydrogel beads for Cu(II) adsorption, Int. J. Biol. Macromol., 135 (2019) 490–500.

[13] I. Ayouch, I. Barrak, Z. Kassab, M. El Achaby, A. Barhoun, K. Draoui, Improved recovery of cadmium from aqueous medium by alginate composite beads filled by bentonite and phosphate washing sludge, Colloids Surf., A, 604 (2020) 125305, doi: 10.1016/j.colsurfa.2020.125305.

[14] R.R. Pawar, Lalhmunsiama, P.G. Ingole, S.M. Lee, Use of activated bentonite-alginate composite beads for efficient removal of toxic Cu^{2+} and Pb^{2+} ions from aquatic environment, Int. J. Biol. Macromol., 164 (2020) 3145–3154.

[15] E.L.M. Amutenya, F. Zhou, J. Liu, W. Long, L. Ma, M. Liu, G. Lv, Preparation of humic acid-bentonite polymer composite: a heavy metal ion adsorbent, Heliyon, 8 (2022) e09720, doi: 10.1016/j.heliyon.2022.e09720.

[16] J. Starý, J. Jirásek, F. Pticen, J. Zahradník, M. Sivek, Review of production, reserves, and processing of clays (including bentonite) in the Czech Republic, Appl. Clay Sci., 205 (2021) 106049, doi: 10.1016/j.clay.2021.106049.

[17] J. Wilson, D. Savage, A. Bond, S. Watson, R. Pusch, D. Bennett, Bentonite: A Review of Key Properties, Processes and Issues for Consideration in the UK Context, QRS-1378ZG-1, February 2011.

[18] F.O. Nwosu, O.J. Ajala, R.M. Owoyemi, B.G. Raheem, Preparation and characterization of adsorbents derived from bentonite and kaolin clays, Appl. Water Sci., 8 (2018) 195, doi: 10.1007/s13201-018-0827-2.

[19] A. Marszałek, G. Kamińska, N.F.A. Salam, Simultaneous adsorption of organic and inorganic micropollutants from rainwater by bentonite and bentonite-carbon nanotubes composites, J. Water Process Eng., 46 (2022) 102550, doi: 10.1016/j.jwpe.2021.102550.

[20] G. Kamińska, J. Bohdziewicz, Potential of various materials for adsorption of micropollutants from wastewater, Environ. Prot. Eng., 42 (2016) 161–178.

[21] G. Kamińska, Removal of organic micropollutants by grainy bentonite-activated carbon adsorbent in a fixed bed column, Water, 10 (2018) 1791, doi: 10.3390/w10121791.

[22] D. Garmia, H. Zaghouane-Boudiaf, C.V. Ibbora, Preparation and characterization of new low-cost adsorbent beads based on activated bentonite encapsulated with calcium alginate for removal of 2,4-dichlorophenol from aqueous medium, Int. J. Biol. Macromol., 115 (2018) 257–265.

[23] E.W. Maina, H.J. Wanyika, A.N. Gacanja, Instrumental characterization of montmorillonite clay by FT-IR and XRD from J.K.U.A.T Farm, in the Republic of Kenya, Chem. Mater. Res., 7 (2015) 43–49.

[24] J. Yu, J. Wang, Y. Jiang, Removal of uranium from aqueous solution by alginate beads, Nucl. Eng. Technol., 49 (2017) 534–540.

[25] A. Oussalah, A. Boukerroui, A. Aichour, B. Djellouli, Cationic and anionic dyes removal by low-cost hybrid alginate/natural bentonite composite beads: adsorption and reusability studies, Int. J. Biol. Macromol., 124 (2019) 854–862.

[26] D. Humelnicu, M. Ignat, M. Suchea, Evaluation of adsorption capacity of montmorillonite and aluminium-pillared clay for Pb^{2+}, Cu^{2+} and Zn^{2+}, Acta Chim. Slov., 62 (2015) 947–957.

[27] A. Adewuyi, F.V. Pereira, Nitrilotriacetic acid functionalized *Adansonia digitata* biosorbent: preparation, characterization and sorption of Pb(II) and Cu(II) pollutants from aqueous solution, J. Adv. Res., 7 (2016) 947–959.

[28] Y. Deng, X. Li, F. Ni, Q. Liu, Y. Yang, M. Wang, T. Ao, W. Chen, Synthesis of magnesium modified biochar for removing copper, lead and cadmium in single and binary systems from aqueous solutions: adsorption mechanism, Water, 13 (2021) 599, doi: 10.3390/w13050599.

[29] U.O. Aigbe, K.E. Ukhurebor, R.B. Onyancha, O.A. Osibote, H. Darmokoesoemo, H.S. Kusuma, Fly ash-based adsorbent for adsorption of heavy metals and dyes from aqueous solution: a review, J. Mater. Res. Technol., 14 (2021) 2751–2774.

[30] M. Bilgin, Ş. Tulun Use of diatomite for the removal of lead ions from water: thermodynamics and kinetics, Biotechnol. Biotechnol. Equip., 29 (2015) 696–704.

[31] M. Yusuf, K. Song, L. Li, Fixed bed column and artificial neural network model to predict heavy metals adsorption dynamic on surfactant decorated graphene, Colloids Surf., A, 585 (2020) 124076, doi: 10.1016/j.colsurfa.2019.124076.

[32] G. Kamińska, Removal of organic micropollutants by grainy bentonite-activated carbon adsorbent in a fixed bed column, Water, 10 (2018) 1791, doi: 10.3390/w10121791.

[33] J. Górski, Ł. Bąk, A. Sałata, K. Górska, A. Rabajczyk, Changes of heavy metal concentration in rainfall wastewater in urban catchment, Desal. Water Treat., 117 (2018) 257–266.

[34] DIN EN 17093 - Domestic Appliances Used for Drinking Water Treatment Not Connected to Water Supply - Jug Water Filter Systems - Safety and Performance Requirements, Labeling and Information to be Supplied.

[35] K. Górska, M. Sikorski, J. Górski, Occurrence of heavy metals in rain wastewater on example of urban catchment in Kielce, Ecol. Chem. Eng. A, 20 (2013) 961–974.

[36] S. Kondaveeti, D.F.S. Petri, H.E. Jeong, Efficiency of air-dried and freeze-dried alginate/xanthan beads in batch, recirculating and column adsorption processes, Int. J. Biol. Macromol., 204 (2022) 345–355.

[37] V. Rocher, J.M. Siaugue, V. Cabuil, A. Bee, Removal of organic dyes by magnetic alginate beads, Water Res., 42 (2008) 1290–1298.

[38] Regulation of the Minister of Health of 7 December 2017 on the Quality of Water Intended for Human Consumption (in Polish).

[39] R.R. Pawar, P.G. Ingole, S.M. Lee, Use of activated bentonite-alginate composite beads for efficient removal of toxic Cu^{2+} and Pb^{2+} ions from aquatic environment, Int. J. Biol. Macromol., 164 (2020) 3145–3154.

[40] A.B. Amor, M. Arenas, J. Martín, A. Ouakouak, J.L. Santos, I. Aparicio, N. Hamdi, Alginate/geopolymer hybrid beads as an innovative adsorbent applied to the removal of 5-fluorouracil from contaminated environmental water, Chemosphere, 335 (2023) 139092, doi: 10.1016/j.chemosphere.2023.139092.

[41] I.A. Kumar, N. Viswanathan, Fabrication of zirconium(IV) cross-linked alginate/kaolin hybrid beads for nitrate and phosphate retention, Arabian J. Chem., 13 (2020) 4111–4125.

[42] L. Zhang, Q. Li, J. Zhu, H. Liu, X. Liu, Y. Wang, L. Li, H_2O_2 modified peanut shell-derived biochar/alginate composite beads as a green adsorbent for removal of Cu(II) from aqueous solution, Int. J. Biol. Macromol., 240 (2023) 124466, doi: 10.1016/j.ijbiomac.2023.124466.