Encapsulation of halloysite with sodium alginate and application in the adsorption of copper from rainwater

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Abstract: As part of the work, experiments were carried out on a laboratory scale to assess the effectiveness of the use of composite capsules based on halloysite and sodium alginate for the adsorption of copper from rainwater. The halloysite was subjected to acid activation prior to the encapsulation process. The characteristics of the capsules obtained were determined by means of SEM surface imaging, nitrogen adsorption by the BET method and pH_{PZC} measurement by the suspension method. Adsorption was studied using various operational parameters such as adsorbent dose, contact time, pH and concentration of copper ions in the rainwater. A high percentage of copper ions removal was demonstrated, i.e. 72% for halloysite (H), and 83% for activated halloysite (HA) for a dose of 2.0 g/L. Adsorption of Cu (II) was consistent with pseudo-second order kinetics. The adsorbents showed a high adsorption capacity at the level of 11.03 mg/g, determined by the Langmuir isotherm model. This model fit well with the experimental data.

Introduction

Due to the fact that water resources become more and more limited, the concept of water reuse is becoming increasingly important. Recently, attention has been paid to the use of rainwater as an alternative water resource (Murat-Błażejewska and Błażejewski, 2020). Heavy metals, PAHs and microbiological contamination are among the most frequently indicated problems related to the quality of water flowing down from roofs (Richards et al. 2021). They pose a great threat to the natural environment. Water pollution with heavy metals, mainly lead, copper, chromium, nickel, iron, zinc and cadmium, is a serious environmental problem (Masindi and Muedi, 2018). According to the US Environmental Protection Agency (EPA), copper is on the list of hazardous priority pollutants. Based on the Regulation of the Minister of Health of 13 November 2015 on the quality of water intended for human consumption, the maximum permissible concentration of copper in drinking water is 2 mg/L (Dz.U. 2017 poz. 2294). Coloring of laundry and sanitary ware occurs at copper concentrations above 1 mg/L. At levels above 2.5 mg/L, copper gives the water an undesirable bitter taste, higher concentrations also affect the color of the water (blue-green). Copper can occur in two degrees of oxidation Cu^+ and Cu^{2+}, both forms differ diametrically in their properties. Copper Cu^{2+} is considered to be more toxic (Liao et al. 2021). The copper should be efficiently removed from the water, to not endanger aquatic organisms, plants and humans. There are many methods available to remove heavy metals from aqueous solutions including precipitation, coagulation/flocculation (Du et al. 2020), chemical oxidation processes (Peydayesh et al. 2020), nanofiltration (NF) (Patel et al. 2022), reverse osmosis (RO) (Mariana et al. 2021) and adsorption (He et al. 2019). Of the treatment options available, adsorption is generally considered to be a cost effective technique with high efficacy in combating a wide range of contaminants, simple design, easy handling and less formation of toxic by-products (Li et al. 2020). Currently, new sorption materials have been found for water purification that are readily available, economical and environmentally friendly. Clay materials are one of the cheap and natural adsorbents (Zhao et al. 2021). The use of natural clay minerals as adsorbents is widely used due to their high efficiency, relatively low operating costs and the possibility of recycling and regeneration (Derafa Garmia et al. 2018). Encapsulation has many advantages. One of them is the immobilization of the fine adsorbent powder. Adsorption with finely powdered material causes problems in recovering fine clay particles from the water, which additionally increases the turbidity of the water. Therefore, encapsulation of halloysite with sodium alginate polymer can be proposed as a solution to avoid these problems. Adsorbents should have good sorption capacity for heavy metals and appropriate porosity ensuring their removal (Pawar et al. 2020). As part of this study, laboratory-scale experiments were carried out to assess the effectiveness of the use of composite capsules based on halloysite and sodium alginate for the adsorption of copper

from rainwater. Sodium alginate is a natural polymer obtained mainly from brown seaweed, and has attracted great interest in water and wastewater treatment due to its strong affinity for toxic divalent cations and other hazardous contaminants. Moreover, sodium alginate is an attractive material for the immobilization of powder adsorbents. Polymer capsules prepared with the use of alginate have specific properties, such as high porosity, large surface area, and are easily biodegradable and non-toxic to the environment (Derafa Garmia et al. 2018). In order to improve the adsorption properties, halloysite was activated with sulfuric acid before the encapsulation process. It was found that acid activation of halloysite can significantly improve the adsorption efficiency of copper and other heavy metals due to better structural and textural properties (Pawar et al. 2020). Therefore, the aim of this study is to immobilize acid-activated halloysite for effective adsorption of copper from rainwater.

Materials and methods

Rainwater characterization

Rainwater was collected in October from Ruda Śląska, Poland. The rainwater harvesting system was equipped with rainwater concrete tank and Atlas Filtri FA BX filter that removes mechanical impurities, such as sand, rust, silt, corrosion particles, turbidity, sediments, some sparingly soluble iron compounds. A "25-micron cartridge" was used to remove contaminants not less than 25 microns. The basic physicochemical characteristics of raw rainwater are presented in Table 1.

Halloysite

Raw halloysite came from the Polish Dunino mine. The mineral was pulverized, sieved and washed with demineralized water. The chemical composition of halloysite was: 37% Al_2O_3, 39.6% SiO_2, 16.1% Fe_2O_3, 2.30% TiO2, 0.66% CaO, 0.13% MgO, 0.04% Na_2O, 0.05% K_2O , 0.52% P_2O_5, 0.01% SO_3 (Szczepanik et al. 2015). According to literature reports, raw halloysite from the Dunino mine has a specific surface area (S BET) of 45.64 m^2/g and a total pore volume (V pores) of 0.19 mL/g (Szczepanik et al. 2017).

Chemicals

All the chemical materials used in this study were purchased as analytical grade reagents. Sodium alginate, H_2SO_4 and NaOH were purchased from Sigma Aldrich (Poznań, Poland). The concentrations of cooper ions were monitored spectrophotometrically with Merck test kits. Copper standard solution ($CuCl_2$) was purchased from Merck (Merck sp. z o.o. Poland).

Preparation of samples

The acid activation of halloysite was performed with 1M H_2SO_4. The mineral was activated for 240 min at 65ºC. The mass ratio of halloysite to the acid solution was 1:1. The activated mineral was washed with distilled water to pH 7 and dried a temperature of 65ºC. Minerals (12 g) were dispersed in 50 mL of purified water with constant stirring. In a separate beaker, a 2% (w/v) suspension of alginate was prepared by thoroughly dissolving 4 g of sodium alginate in deionized water (200 mL). A homogenized suspension of halloysite and acid-activated halloysite (50 mL) was added to the alginate suspension (A), and then the mixture was stirred for 4 hours. When the mixture became homogeneous, the mixture was transferred to a separating funnel and slowly added dropwise to an aqueous coagulation bath containing 500 ml of a 2% $CaCl_2$ solution which was continuously stirred for 3h. After 3 hours, the beads were filtered and washed with distilled water (4×200 mL). Then they were dried at room temperature. Encapsulated halloysite raw was marked H, the encapsulated acid-activated halloysite was marked HA.

Characterization of adsorbents

The surface morphology of the studied minerals was investigated by scanning electron microscopy (SEM). There was used a scanning electron microscope, model JSM 6360LA 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 Brunauer-Emmett-Teller (BET) method.

Measurement of the zero point of charge (pH PZC) of H and HA capsules was performed as follows: pH was adjusted with 0.1 mol/L HNO_3/NaOH solutions, respectively, in the range 2–12 monitored by multifunctional analyzer CPC-505 (Elmetron, Zabrze, Poland). For this purpose, 50 mg of the adsorbent was added to 50 mL of distilled water with a different pH from 2 to 10 and stirred at room temperature for 24 h. Then

Table 1. Physicochemical characteristics of rainwater

Parameter	Unit	Rainwater (average value)
pH	–	6.28
Conductivity	µS/cm	28.20
Color	mgPt/L	12
Turbidity	FTU	6
COD	mg/L	63
Absorbance UV$_{254}$	1/cm	0.09
TOC	mg/L	5.10
N-NO$_3$	mg/L	1.1
P-PO$_4$	mg/L	1.4

the final pH of the solutions was measured. The difference between the initial and final pH values ($\Delta pH = pH_f - pH_i$) for each series was plotted as a function of pH_i. Then the pH of pzc was estimated at the point where it crossed ΔpH ($pH_i - pH_f$) = 0.0 (Sulyman, et al. 2021).

Adsorption experiments

The adsorption of Cu (II) was performed to evaluate the adsorption capacity of the encapsulation halloysite, by using batch experiment. The influence of the contact time and the adsorbent dose on the adsorption capacity was investigated. Adsorption was conducted in 100 mL glass flasks, in an incubator shaker at 300 rpm. The research of adsorption isotherms was carried out for copper concentrations in rainwater from 2 to 50 mg/L, for a fixed dose of 0.1 g of adsorbent and 50 mL solution volume, at a room temperature (20 ± 1°C) and dispersion pH (pH ≈ 6.4).

Two common adsorption isotherm models were used to fit the experimental data in this study: the Langmuir model and the Freundlich model. Each model is briefly described below. The Langmuir isotherm is represented by Eq. 1 (Vasanth Kumar and Sivanesan, 2007).

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{Q_m} \qquad (1)$$

Where: (mg/g) is the maximum adsorption capacity, and (L/mg) is the Langmuir fitting parameter.

The Freundlich model is shown in Eq. 2 (Vasanth Kumar and Sivanesan, 2007).

$$log\, q_e = log K_F + \frac{1}{n} log C_e \qquad (2)$$

Where: K_F ((mg/g)(L/mg)^n) is the Freundlich adsorption coefficient, and n is the number describing surface heterogeneity and sorption intensity.

The kinetic experiments were carried out as follows: 0.1 g of adsorbent was added to 100 mL of cooper solution (5 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, 240 min. The pH of the solution was kept constant. The concentration of copper was 5 mg/L. The adsorbent samples were separated from the liquid for analysis at predetermined time intervals.

In order to determine the adsorption kinetics, the experimental data were analyzed using pseudo-first-order and pseudo-second-order kinetic models, which are given in the equations (3) and (4) respectively (Kamińska and Bohdziewicz, 2016):

$$\ln \frac{qe - qt}{qe} = -K_1 * t \qquad (3)$$

$$\frac{t}{qt} = \frac{1}{K_2 * qe^2} + \frac{t}{qe} \qquad (4)$$

Where: qe and qt are the amount of Cu adsorbed at equilibrium and at time (t), K1 and K2 are the pseudo-first-order and pseudo-second-order constants, respectively.

Similarly, the effect of the adsorbent dose on the degree of the removal of copper ions from the rainwater solution was determined. The pH of the solution was kept constant at 6.4, the volume of the solution was 100 ml, the concentration of Cu (II) = 5mg/L. Mass of sorbents ranged from 0.25 g/L to 2 g/L. Batch experiments were also accomplished to study the effects of solution pH. The pH in the range from 2 to 10 was adjusted using 0.1 mol/L HNO_3/NaOH solution. The influence of a higher concentration of copper in rainwater on the adsorption of Cu (II) ions by means of composite beads was also investigated. In this study, an adsorbent dose of 1 g/L was used and the contact time was 2 h. The concentrations of Cu (II) remained at the levels of 20 mg/L, 30 mg/L, and 50 mg/L.

Each experiment was performed in duplicate and the mean value was computed to ensure quality assurance.

Results and discussion

Material structure

The surface morphologies of minerals were observed using SEM. The SEM images of H and HA are presented in Figure 1, and Figure 2 shows wet and dry beads photos. A photo of only active halloysite is shown. The photographs of raw and activated halloysite do not differ visually.

It was observed that the acid activation affected the halloysite topography. The ball made of raw halloysite was characterized by a more compact structure. The acid, on the contrary, caused a slight disruption. The surface of the HA beads was rougher. This fact is also confirmed by literature reports on acid activation of other clay materials, e.g. bentonite (Derafa Garmia et al. 2018, Pawar et al.2020).

It was found that the nitrogen adsorption capacity of halloysite increased significantly after the acid activation process. New pores are formed that increase the specific surface area, the cations Al^{3+}, Fe^{3+} and Ca^{2+} are replaced with H^+ and the amorphous silica phase is formed. When activating the clay with mineral acids, the acid dissolves some of the Al_2O_3 and also the MgO from the lattice, which leads to the opening of the crystal lattice and an increase in the internal surface. (Gao et al. 2020)

Specific Surface Area (SSA) and pore size distribution of H and HA are shown in Table 2. As can be seen, inactivated halloysite has a BET surface area of 2.1 m^2/g and a pore volume of 0.0056 mL/g. After acid treatment, a significant increase in BET surface area and pore volume was detected. In particular, the BET surface area increased to a value of 6.82 m^2/g and a pore volume of 0.018 mL/g. The increase in surface area and pore volume are directly related to the selective dissolution of octahedral AlO.

Sodium alginate has good gelling properties, however, hydrogels formed by sodium alginate are usually dense, low in porosity, and poor in stability. The pore size and surface area of the alginate-based adsorbent cannot be detected by BET due to the low resistance of these materials to low temperatures. It is recommended to find a cost effective matrix or synthesis method to improve the adsorbent structure (Cavallaro et al. 2013). The $CaCl_2$ cross-linked alginate (A) has a very low BET surface area. Therefore, the encapsulation of halloysite resulted in a significant reduction of the SSA surface area. However,

it was noticed that due to activation with sulfuric acid, the HA capsules had a 3 times larger surface area of the SSA. It was also found that the pore size of the capsules remained almost unchanged. It is also known that calcium cross-linked alginate has good selectivity towards divalent ions, however, the adsorption efficiency on monovalent ions is relatively low (Cavallaro et al. 2013). The activation of clay materials with acid causes an increase in the surface and volume of pores for halloysite. Increase in acid concentration or treatment time is also important. For these reasons, acid etching is of great interest for new applications such as composite adsorbents.

On the basis of the obtained results, it was found that the surface of the adsorbents based on sodium alginate and halloysite had a neutral charge because the pHpzc was 7 and 7.01. respectively for HA and H. When the pH of the solution < pH$_{PZC}$, the adsorbents react as a positive surface charge and react as a negative surface charge when the pH of the solution >pH$_{PZC}$ (Derafa Garmia et al. 2018).

Effect of adsorbent type and its dose on removal percentage

The influence of the dose of H and HA adsorbent on the concentration of copper in rainwater was investigated. Activation of halloysite with acid was found to have a good effect as the concentration of Cu (II) in rainwater in the case the HA adsorbent was 40% lower than that of the adsorbent H at the 2.0 g/L dose. As shown in Fig. 4, the removal efficiency clearly changed with increasing adsorbent dose. The observed increase can be explained by the available sorption sites on the surface of halloysite beads. In the case of the dose of 1 g/L, quite satisfactory effects were obtained for chemically activated halloysite. Copper concentration in rainwater was lower than
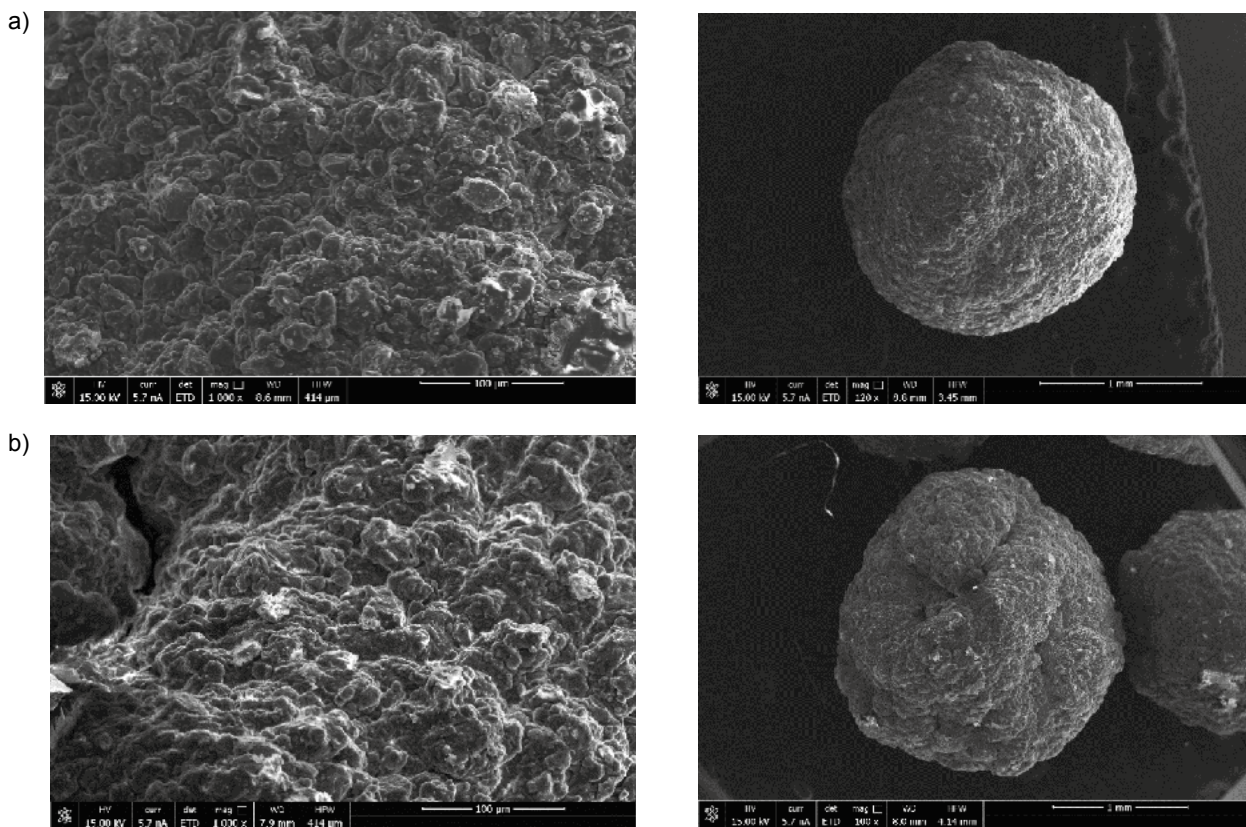
Fig. 1. SEM scanning images of (a) H bead and (b) HA bead, 1000×, 100×, respective
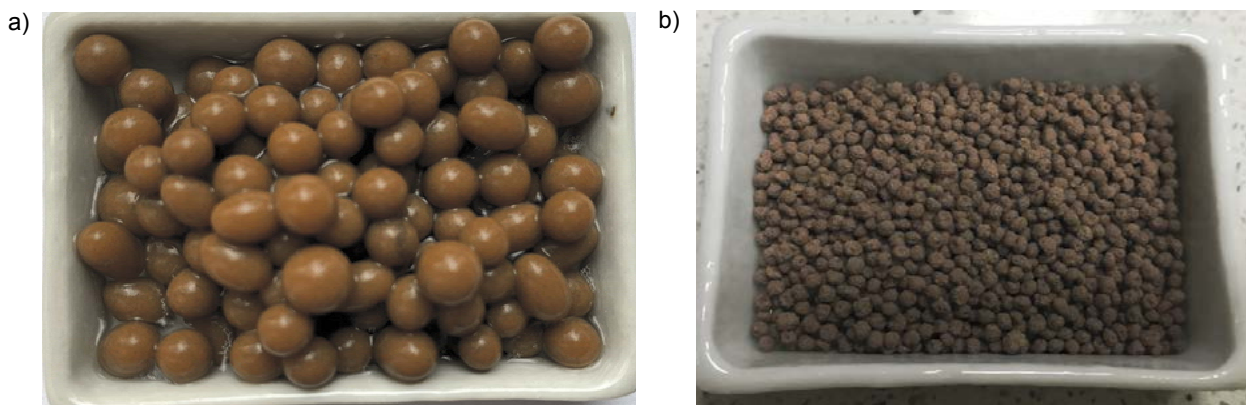
Fig. 2. Beads photos: (a) Wet HA beads, (b) Dry HA beads

its standard value (2 mg/L) according to the Regulation of the Minister of Health of December 7, 2017 on the quality of water intended for human consumption. Therefore, the optimal dose of 1 g/L was applied in the subsequent analyses.

Influence of the solution pH

Based on the literature, it was found that the pH of the solution is an important parameter having a significant impact on the effectiveness of Cu (II) adsorption (Pan et al. 2019). Fig. 5 shows the effectiveness of Cu (II) adsorption depending on pH, for a constant concentration of copper in the rainwater (5 mg/L), at a dose of halloysite 1 g/L, for an adsorption time of 120 min and a temperature of 25°C.

The change in the pH of the solution has the greatest influence on the adsorption efficiency of adsorbing materials. This is due to the protonation or deprotonation of the surface charge or functional group on the adsorbing materials as the pH changes (Pawar et al.). The influence of this parameter on the adsorption of Cu (II) on H and HA was investigated in the range of pH 2–10 at the initial concentration of copper in the solution at the level of 5 mg/L.

The figure showed that the adsorptive removal of Cu (II) was limited at the lower pH. This causes a strong interaction of the adsorbent with Cu (II) ions. This can be explained by the fact that in a strongly acidic environment, excess protons compete with cationic metal ions, which results in a very low uptake of Cu (II). As the pH increases, the H + concentration decreases, thus reducing the competition between metal ions and protons for adsorption sites on the particle surface (Oussalah et al. 2019). The highest efficiency was obtained for a solution with pH of 6–7, i.e. close to the pH of the real solution.

Adsorption isotherms of Cu²⁺ on H and HA

In this study, the equilibrium data obtained for the adsorption of copper by halloysite beads and activated halloysite beads were analyzed by Langmuir and Freundlich. The Langmuir model (Fig. 6) fit the experimental data better than the Freundlich model. It is found that the correlation coefficients R^2 obtained from the Langmuir model were closer to unity indicating that the adsorption equilibrium data is fit well with this model. From the calculated higher Qm values presented in Table 3 it was identified that the activated halloysite has more potential to remove copper from aqueous solution. G. Cavallaro et al. suggested that the presence of halloysite in the alginate beads improves the adsorption process (Cavallaro et al. 2013). It was observed that the percentage of Cu (II) removal gradually decreased with increasing initial concentration. It was found that the maximum Langmuir sorption capacity for Cu (II) was 11.03 m/g for HA and 8.54 mg/g for H. Pawar et al. obtained Cu (II) adsorption at the level of 17.3 mg/g when using bentonite--alginate beads. Gao et al. suggested that the main sorption process in the case of alginate beads is the exchange of toxic metals (Pb, Cr, Cd) with cations available on the surface of the beads (Gao et al. 2020).
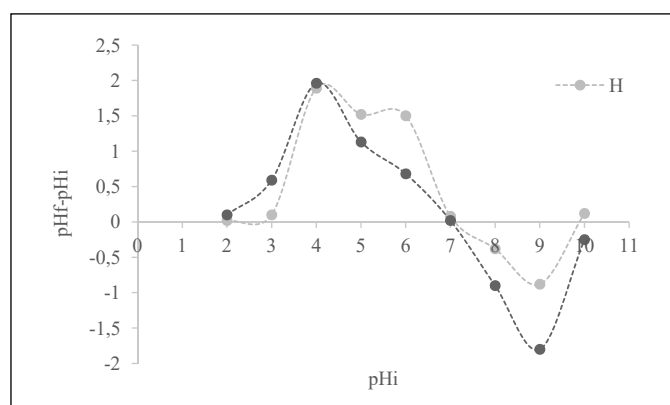
Adsorption kinetics of Cu2+ on H and HA

The kinetic adsorption curves for Cu (II) on H, and HA are shown in Figure 7. A pseudo-first and pseudo-second-order model was used to correlate the kinetic data. The calculated values (Q(t(cal)) corresponded well with the experimental data (Q(t(exp)). This suggests that their adsorption kinetics was consistent with the model, which can therefore be used to determine appropriate kinetic parameters. In each case the time needed to reach the equilibrium state was long (180 min), which indicates difficult availability of the adsorption sites.

The maximum adsorption capacities q_e, K_1, K_2 and the correlation coefficient R^2, calculated on the basis of the pseudo-first and pseudo-second models, are presented in Table 4. Considering R^2 values it was found the adsorption is in line with the pseudo-second order model.

Table 2. Characteristics of H and HA from nitrogen sorption-desorption measurements

Adsorbent	Specific Surface Area (SSA), (m²/g)	Total Volume in Pores, (cm³/g)	Total Area in Pores, (m²/g)	Pore size, (nm)
A	0.42	0.00043	1.11	1.8
H	2.1	0.0056	7.85	1.79
HA	6.82	0.018	20.9	1.81

Fig. 3. Points of zero charge (pHPZC) of H and HA
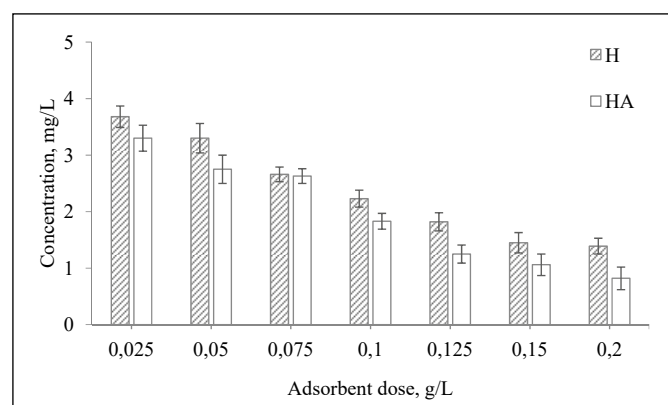


Fig. 4. Effect of sorbent dose (H and HA) on concentration Cu²⁺ in rainwater (C₀=5 mg/L). Error bars: standard deviation

The pseudo-first and pseudo-second order equations are the most commonly used functions to evaluate adsorption kinetics. The pseudo-first order equation is based on the diffusion process, while the pseudo-second order equation assumes that the adsorption rate is determined by the square of the available sorption sites. The result shows that the pseudo-second order model fits better with the kinetic data due to the higher R^2 values (Table 1), suggesting that chemisorption plays a major role during adsorption (Zaghouane-Boudiaf et al. 2014). In the use of many composite materials composed of sodium alginate, a second-order kinetic model was found

(Belhouchat et al. 2017, Gao et al. 2020, Pawar et al. 2020, Pan et al. 2019).

Influence of concertation Cu (II) in rainwater

Tests were also carried out to demonstrate the effectiveness of composite beads for adsorption at a higher concentration of copper from rainwater. The adsorption experiments were carried out by maintaining different concentrations of Cu (II) ions in the rainwater at pH 6. The concentrations of Cu (II) were maintained at 10 mg/L, 20 mg/L and 50 mg/L. The percentage removal of Cu (II) is shown in Fig. 8.
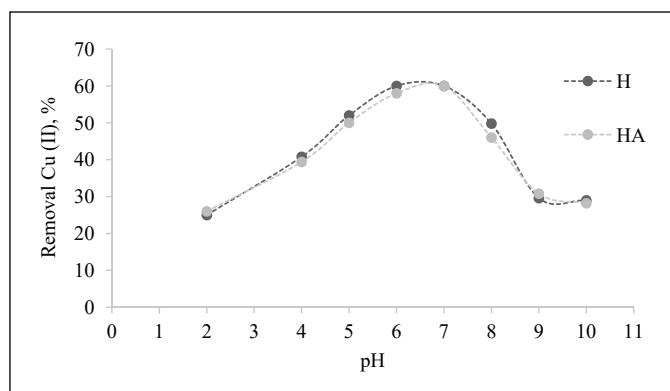
Fig. 5. Influence of rainwater pH on copper adsorption (C_0=5 mg/L.) Error bars: standard deviation
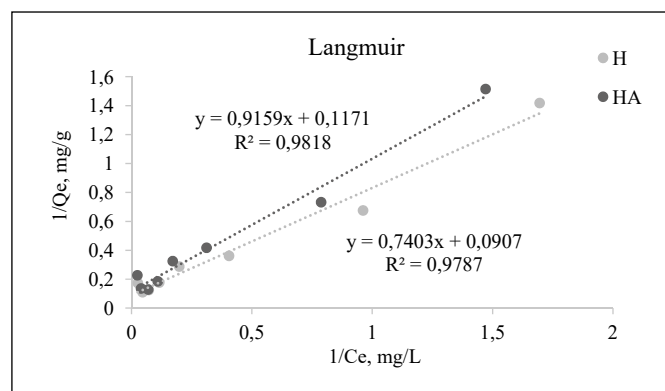
Fig. 6. Langmuir isotherm of Cu (II) on H and HA

Table 3. Parameters of Freundlich, Langmuir, equations, and the correlation coefficients for the adsorption of Cu (II) 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 (-)
H	8.54	0.128	0.982	1.15	1.84	0.8203
HA	11.03	0.123	0.979	1.37	1.79	0.8708

Table 4. Parameters for the pseudo-first and pseudo-second order kinetic model for the adsorption of copper on H and HA

Adsorbate	Pseudo-First-Order Equation Parameters			Pseudo-Second-Order Equation Parameters		
	K_1 (1/min)	Qe (mg/g)	R^2	K_2 (g/(mg·min))	Qe (mg/g)	R^2
H	0.0126	15.88	0.56	0.0037	4.5045	0.86
HA	0.02	27.83	0.79	0.003	5.05	0.9
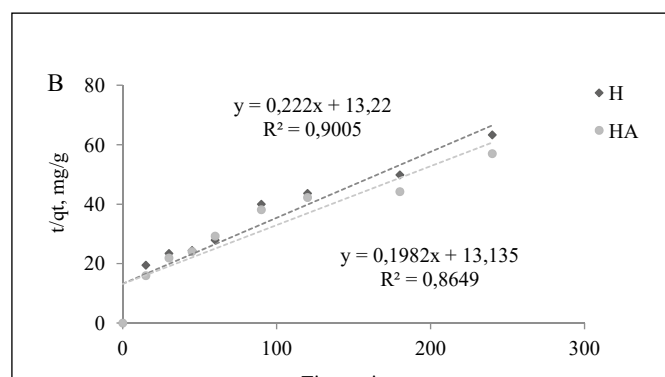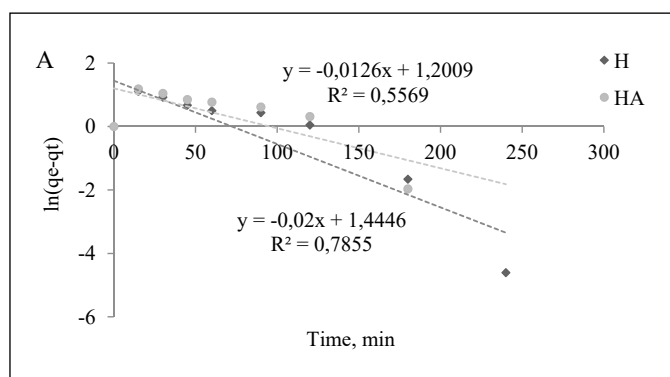
Fig. 7. Adsorption kinetic curves of Cu²⁺ on H and H by means of pseudo-first-order kinetics (A) and pseudo-second-order kinetics (B)
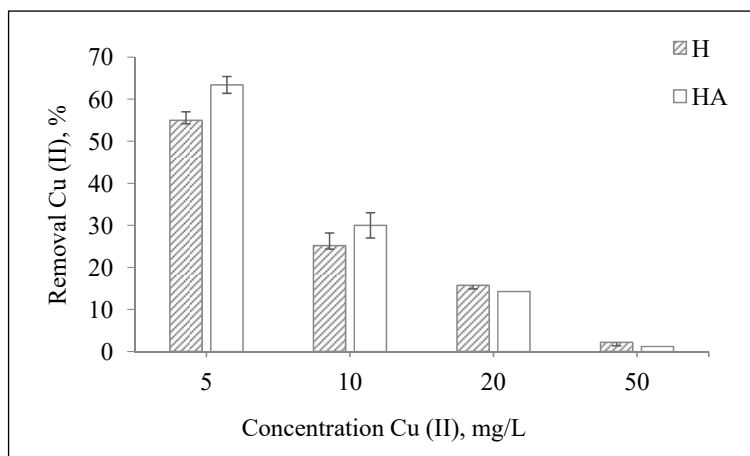
Fig. 8. Degree of Cu (II) removal at different concentrations in rainwater using H and HA adsorbents.
Error bars: standard deviation

A significant decrease in the efficiency of copper removal was observed with the increase in concentration. Studies have shown that at a copper concentration of 5 mg/L, most of the available adsorption sites were exhausted. For the concentration of 10 mg/L, only 30% Cu removal was obtained for chemically activated halloysite, with the assumed dose of adsorbent.

Conclusion

In conclusion, encapsulation of halloysite with sodium alginate was used to immobilize the fine clay material due to the problem of recovering clay particles from aqueous solutions. It is assumed that mixing sodium alginate with other materials can further increase the adsorption capacity and physical properties of the composite materials. It was found that acid activation of halloysite can improve the adsorption efficiency of copper and other heavy metals due to better structural and textural properties. Static adsorption showed that a high percentage removal of copper was obtained for the halloisyte namely, it was 72% and he activated halloysite was 83% for the 2.0 g/L dose. The best results were obtained for a rainwater solution with pH of 6–7. The equilibrium of Cu (II) adsorption on the composite H and HA was consistent with the Langmuir isotherm model. This means that Cu (II) adsorption was only a homogeneous process. It was found that for more concentrated solutions, more adsorbent dose is required. Adsorption of Cu (II) was consistent with pseudo-second order kinetics. The adsorbents showed an adsorption capacity at the level of 11.03 mg/g, determined by the Langmuir isotherm model. This model fit well with the experimental data. The H and HA composite beads can be used as a solid adsorbent for the removal of Cu (II) in rainwater.

Acknowledgments

References

Belhouchat, N., Zaghouane-Boudiaf, N. & Viseras, C. (2017). Removal of anionic and cationic dyes from aqueous solution with activated organo-bentonite/sodium alginate encapsulated beads, *Applied Clay Science*, 135, pp. 9–15. DOI: 10.1016/j.clay.2016.08.031

Cavallaro, G., Gianguzza, A., Lazzara, G., Milioto, S. & Piazzese, D. (2013). Alginate gel beads filled with halloysite nanotubes, *Applied Clay Science*, 72, pp. 132–137. DOI: 10.1016/j.clay.2012.12.001

Derafa, G., Zaghouane-Boudiaf, H. & Ibbora, C.V. (2018). 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, *International Journal of Biological Macromolecules,* 115, pp. 257–265. DOI: 10.1016/j.ijbiomac.2018.04.064

Du, J., Zhang, B., Li, J. & Lai, B. (2020), Decontamination of heavy metal complexes by advanced oxidation processes: A review, *Chinese Chemical Letters*, 31, 10, pp. 2575–2582. DOI: 10.1016/j.cclet.2020.07.050

Gao, X., Guo, Ch., Hao, J., Zhao, Z., Long, H. & Li, M. (2020). Adsorption of heavy metal ions by sodium alginate based adsorbent – a review and new perspectives, *International Journal of Biological Macromolecules*, 164, pp. 4423–4434. DOI: 10.1016/j.ijbiomac.2020.09.046

He, Y., Chen, Y., Zhang, K., Ye, W. & Wu, D. (2019), Removal of chromium and strontium from aqueous solutions by adsorption on laterite, *Archives of Environmental Protection,* 45, 3, pp. 11–20. DOI: 10.24425/aep.2019.128636

Kamińska G. & Bohdziewicz, J. (2016), Potential of various materials for adsorption of micropollutants from wastewater, Environ. Prot. Eng. 42, pp. 161–178. DOI: 10.5277/epe160413

Li, X., Liu, N., Tang, L. & Zhang, J. (2020). Specific elevated adsorption and stability of cations in the interlayer compared with at the external surface of clay minerals, *Applied Clay Science*, 198, 105814. DOI: 10.1016/j.clay.2020.105814

Liao, Z. Zhao, Z. Zhu, J. Chen, H. & Meng, D. (2021). Complexing characteristics between Cu(□) ions and dissolved organic matter in combined sewer overflows: Implications for the removal of heavy metals by enhanced coagulation, *Chemosphere*, 265, 129023. DOI: 10.1016/j.chemosphere.2020.129023

Oussalah, A., Boukerroui, A., Aichour, A. & Djellouli, B. (2019). Cationic and anionic dyes removal by low-cost hybrid alginate/ natural bentonite composite beads: Adsorption and reusability studies, *International Journal of Biological Macromolecules*, 124, pp. 854–862. DOI: 10.1016/j.ijbiomac.2018.11.197

Mariana, M., Khalil, A., Mistar, E.M., Yahya, E.B., Alfatah, T., Danish, M. & Amayreh, M. (2021). Recent advances in activated carbon modification techniques for enhanced heavy metal

adsorption, *Journal of Water Process Engineering*, 43, 102221. DOI: 10.1016/j.jwpe.2021.102221

Masindi, V. & Muedi K.L. (2018) Environmental Contamination by Heavy, *Heavy Metals,* 10, pp. 115–132. DOI: 10.5772/intechopen.76082

Mellouk, S., Belhakem, A., Marouf-Khelifa, K., Schott, J. & Khelifa, A. (2011). Cu(II) adsorption by halloysites intercalated with sodium acetate, *Journal of Colloid and Interface Science*, 360, 2, pp. 716–724. DOI: 10.1016/j.jcis.2011.05.001

Murat-Błażejewska, S. & Błażejewski, R. (2020). Converting sewage holding tanks to rainwater harvesting tanks in Poland, *Archives of Environmental Protection,* 46, 4, pp. 121–131. DOI: 10.24425/aep.2020.135770

Pan, L., Wang, Z., Zhao, X. & He, H. (2019). Efficient removal of lead and copper ions from water by enhanced strength-toughness alginate composite fibers, International *Journal of Biological Macromolecules,* 134, pp. 223 – 229. DOI: 10.1016/j.ijbiomac.2019.05.022

Patel, H.K., Kalaria, R.K., Jokhakar, P.H., Patel, Ch.P. & Patel, B.Y. (2022) Chapter 17 – Removal of emerging contaminants in water treatment by an application of nanofiltration and reverse osmosis, Editor(s): Maulin Shah, Susana Rodriguez-Couto, Jayanta Biswas, *Development in Wastewater Treatment Research and Processes*, pp. 385–400. DOI: 10.1016/B978-0-323-85583-9.00005-3

Pawar R.R., Ingole, L.P.G. & Lee, S. (2020). Use of activated bentonite-alginate composite beads for efficient removal of toxic Cu^{2+} and Pb^{2+} ions from aquatic environment, *International Journal of Biological Macromolecules*, 164, pp. 3145–3154. DOI: 10.1016/j.ijbiomac.2020.08.130

Peydayesh, M., Mohammadi, T. & Nikouzad, S.K. (2020). A positively charged composite loose nanofiltration membrane for water purification from heavy metals, *Journal of Membrane Science*, 611, 118205. DOI: 10.1016/j.memsci.2020.118205

Regulation of the Minister of Health on 7 December 2017, On the Quality of Water Intended for Human Consumption (In Polish). Dz.U. 2017 poz. 2294

Richards, S., Rao, L., Connelly, S., Raj A., Raveendran, L., Shirin, S., Jamwal, P. & Helliwell, R. (2021). Sustainable water resources through harvesting rainwater and the effectiveness of a low-cost water treatment, *Journal of Environmental Management*, 286, 112223. DOI: 10.1016/j.jenvman.2021.112223

Sulyman, M., Kucinska-Lipka, J., Sienkiewicz, M. & Gierak, A. (2021) Development, characterization and evaluation of composite adsorbent for the adsorption of crystal violet from aqueous solution: Isotherm, kinetics, and thermodynamic studies, Arabian Journal of Chemistry, 14 (5), 103115. DOI: 10.1016/j.arabjc.2021.103115

Sutirman, Z.A., Sanagi, M.M. & Wan Aini, W.I. (2021). Alginate-based adsorbents for removal of metal ions and radionuclides from aqueous solutions: A review, *International Journal of Biological Macromolecules,* 174, pp. 216–228. DOI: 10.1016/j.ijbiomac.2021.01.150

Szczepanik, B., Słomkiewicz, P., Garnuszek, M., Czech, K., Banaś, D., Kubala-Kukuś, A. & Stabrawa, I. (2015). The effect of chemical modification on the physico-chemical characteristics of halloysite: FTIR, XRF, and XRD studies, *Journal of Molecular Structure*, 1084, pp. 16–22. DOI: 10.1016/j.molstruc.2014.12.008

Szczepanik, B., Rogala, P., Słomkiewicz, P.M., Banaś, D., Kubala-Kukuś, A. & Stabrawa, I. (2017) Synthesis, characterization and photocatalytic activity of TiO_2-halloysite and Fe2O3-halloysite nanocomposites for photodegradation of chloroanilines in water, *Applied Clay Science*, 149, pp. 118–126. DOI: 10.1016/j.glina.2017.08.016

Vasanth Kumar, K. & Sivanesan S. (2007), Sorption isotherm for safranin onto rice husk: Comparison of linear and non-linear methods, Dyes and Pigments, 72, pp. 130–133. DOI: 10.1016/j.dyepig.2005.07.020 .

Zhao H., Ouyang, X. & Yang, L. (2021) Adsorption of lead ions from aqueous solutions by porous cellulose nanofiber-sodium alginate hydrogel beads, *Journal of Molecular Liquids*, 324, 2021, 115122. DOI: 10.1016/j.molliq.2020.115122.

Zaghouane-Boudiaf, H., Boutahala, M., Sahnoun, S., Tiar, Ch. & Gomri, F. (2014). Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing the 2,4,5-trichlorophenol, *Applied Clay Science*, 90, pp. 81–87. DOI: 10.1016/j.clay.2013.12.030

Kapsułkowanie haloizytu alginianem sodu i zastosowanie w adsorpcji miedzi z wody opadowej

Streszczenie: W ramach pracy przeprowadzono eksperymenty w skali laboratoryjnej mające na celu ocenę efektywności wykorzystania kapsuł kompozytowych na bazie haloizytu i alginianu sodu do adsorpcji miedzi z wód opadowych. Haloizyt został poddany aktywacji kwasem przed procesem enkapsulacji. Charakterystykę otrzymanych kapsułek określono za pomocą obrazowania powierzchni SEM, adsorpcji azotu metodą BET oraz pomiaru pH_{PZC}. Adsorpcję badano za pomocą różnych parametrów operacyjnych, takich jak dawka adsorbentu, czas kontaktu, pH i stężenie jonów miedzi w wodzie deszczowej. Wykazano wysoki procent usuwania jonów miedzi, tj. 72% dla haloizytu (H) i 83% dla haloizytu aktywowanego (HA) dla dawki 2,0 g/L. Adsorpcja Cu (II) była zgodna z kinetyką pseudo drugiego rzędu. Adsorbenty wykazywały wysoką zdolność adsorpcji na poziomie 11,03 mg/g, wyznaczoną za pomocą modelu izoterm Langmuira. Model ten dobrze pasował do danych eksperymentalnych. Stwierdzono, że kapsułki kompozytowe haloizytu i aktywowanego haloizytu mogą być stosowane jako wydajny i tani adsorbent do usuwania miedzi z wody.