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Investigation on applying sapropel for removal of heavy metals (cadmium, chromium, copper, and zinc) from aqueous solutions

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Abstract: Sapropel is a layer of sediment composed of organic and inorganic substances that accumulates at the bottom of lakes. The water of such lakes often have elevated levels of heavy metals such as Cd, Cr, Cu, and Zn, which can pose risks to human health. Sapropel may be used as a biosorbent in removing these heavy metals from aqueous solutions. Various doses of sapropel ranging from 1 to 50 g/L and different mixing times from15 to150 minutes have been tested. The maximum removal efficiencies for Cd (93%), Cr (31%), Cu (84%), and Zn (84%) from aqueous solutions were achieved using the minimum doses of sapropel (50 g/L). The study has shown that mixing sapropel for 15 minutes is sufficient for the removal of Cr, 30 minutes for Cd and Cu, and 60 minutes for Zn.

Introduction

Drinking water quality is one of the key factors that affect human health. Due to inadequate water and wastewater treatment, coupled with increased industrial activity, water in developing countries is increasingly contaminated with heavy metals (HMs). According to the United Nations data, approximately 80 % of industrial and domestic wastewater enters the environment without prior treatment in developing countries (Joseph et al. 2019). In most countries in Asia and Africa, wastewater and drinking water have high concentrations of HM (Cd, As, Pb, Cr, Cu, etc.) (Rasool et al. 2016). The presence of HMs in water may result from natural processes and anthropogenic pollution. Environmental pollution with HMs occurs due to rapid economic growth, industrial development, and improper disposal of waste and wastewater (Tomno et al. 2020). HMs are biologically non-degradable, toxic, and easily accumulate even at low concentrations. Therefore, it is necessary to remove them from drinking water and wastewater. If drinking water and wastewater are not properly treated, HMs can enter the human body, causing various health problems and even death. Additionally, apart from affecting humans, HMs also harm plants and animals (Kumar et al. 2019, Falaciński and Wojtkowska 2021).

Cadmium (Cd) is a toxic metal that poses a threat to human and animal health. It is used in the production of Ni-Cd batteries, as a pigment in paint and galvanization, and in plastics manufacturing. Anthropogenic sources of Cd include smelting and refining of Cu and Ni, combustion of fossil fuels, and the use of phosphate fertilizers. Additionally, Cd is found in colored metal smelters and results from the recycling of electronic waste. Cd concentrations in the atmosphere, soil, and water can increase due to volcanic activity, soil and rock erosion, weathering processes, and forest fires. Tobacco is a significant source of Cd exposure for the general public (Jaishankar et al. 2014, Genchi et al. 2020). Cd negatively affects lung function by irritating breathing. When ingested, Cd can cause vomiting and diarrhea. Furthermore, it can impair kidney and liver function, induce lung edema, damage the adrenal gland, and lead to osteomalacia, Alzheimer's and Parkinson's diseases (Genchi et al. 2020). The permissible amount of Cd in drinking water is 3 μg/L according to the World Health Organization and 5 μg/L according to the Council Directive 98/83/EC (World …2011, Council…1998).

Zinc (Zn) is commonly used in industry for galvanization and the production of dry-cell batteries. A large part of Zn enters water through mining activities, Zn ore mining, steel production, coal combustion, and waste combustion (Noulas et al. 2018). Zn is an essential metal involved in various biological processes, including the regulation of carbohydrate and lipid metabolism, as well as the functioning of the heart, blood vessels, and nervous system. However, excessive intake of Zn can lead to stomach cramps, nausea, vomiting, and in extreme cases, anemia (Sanhkla et al. 2019). The permissible concentration of Zn in drinking water is 3 mg/L according to the World Health Organization.

Copper (Cu) typically enters the environment through anthropogenic activities, including fungicide spraying and mining, which can lead to soil or water contamination. Cu then enters the food chain primarily through food and water sources. Accumulation of Cu in the human body can cause brain and kidney damage, liver cirrhosis and chronic anemia (Cornu et al. 2017). The permissible concentration of Cu in drinking water is 2 mg/L according to both the World Health Organization and the Council Directive 98/83/EC (World…2011, Council…1998).

While chromium (Cr) is considered an essential micronutrient, it is associated with several pathologies in humans. Cr(VI) is prevalent in various industries such as galvanization, metal finishing, welding, wood, paint and pigment production, as well as in automobile emissions and cigarette smoke. It is also found in water contaminated with industrial wastewater, waste, and sewage (Pavesi and Moreira 2020). Notably, Cr(VI) is highly toxic and carcinogenic, posing serious health risks, sometimes leading to death. Additionally, Cr accumulation in the food chain disrupts human physiology, resulting in health issues like skin diseases, nasal irritation, hearing problems, and lung carcinoma (Manzoor 2020). The permissible concentration of Cr in drinking water is 50 μg/L, according to both the World Health Organization and the Council Directive 98/83/EC (World …2011, Council…1998).

Various methods are used for the removal of HMs from aqueous solutions, including precipitation, reverse osmosis, electrodialysis, ion exchange, and adsorption (Kumar et al. 2019). However, these HM removal technologies are expensive, time-consuming, and generate additional waste that pollutes the environment. To mitigate high costs and waste production, biosorbents can be used, such as agricultural waste, cement kiln dust, iron sand, magnetite, activated carbon, hematite, kaolinite, graphene, and sapropel (Birgelaite et al. 2016, Tahoon et al. 2020). An advantage of biosorption is its effectiveness even at very low concentrations of HM ions (Liu et al. 2021).

Sapropel is a layer of organic and inorganic sedimentary deposits that accumulate over thousands of years at the bottom of many lakes (Baksiene and Ciunys 2012). It is estimated that there are approximately 1 billion m^3 of pure sapropel and around 6 billion m^3 of sapropel with impurities (Filippidi 2016). Sapropel formation is most common in the middle-latitude climate zones of Asia and Europe (including Russia, the Scandinavian Peninsula, France, Germany, Poland, the Baltic States, Belarus, and Ukraine), as well as in the Great Lakes region of North America (Canada and the United States) (Stankevica 2013). Sapropel can be categorized into organic sapropel (containing 50-90 % organic matter), calcareous sapropel (containing 30-60 % calcium carbonate), siliceous sapropel (containing 25-45 % silicon dioxide), and various combinations thereof. Its chemical composition includes all macro- and micronutrients required by plants, as well as biologically active substances such as vitamins, enzymes, and antibiotics (Baksiene and Ciunys 2012).

Aside from its role in cleaning lakes, sapropel mining offers numerous benefits, as it can be used as a biosorbent, organic fertilizer, feed additive, building material, and in the cosmetics industry (Becic et al. 2014, Obuka et al. 2015). Wet sapropel is particularly noteworthy for its colloidal suspended phase structure, which enables its organic colloidal particles to absorb large amounts of water, making it a cost-effective biosorbent (Obuka et al 2015). Studies have shown that sapropel is capable of sorbing organic compounds and HMs (Birgelaite at al. 2016). The efficiency of sapropel in removing Pb from solutions has been reported to be 81.6 % and it is even more effective in sorbing Zn (97.57 %) (Birgelaite at al. 2016). This investigation aims to explore and compare the efficiencies of sapropel in removing other HMs such as Cd, Cr, Cu, and Zn from aqueous solutions.

Materials and Methods

Raw sapropel for research purposes was extracted from a depth of 2-3 meters in Apslavas Lake, located in Stabulankliai village, Leliunai local municipality, Utena district, Lithuania. The sapropel was washed twice with distilled water, followed by oven-drying at 110°C for 3 hours. Subsequently, the dried sapropel was ground using a porcelain grinder and sieved through a 0.2 mm mesh sieve. The dried sapropel is depicted in Fig. 1. The chemical composition of the dried sapropel was analyzed using an X-ray fluorescence spectrometer, while the carbon content was determined using the Carbon and Sulphur Analyzer CS-2000. The microstructure of sapropel was examined using the SEM JEOL JSM-7600F. For this study, four metals were selected as the most common water contaminants based on previous research literature: Cd, Zn, Cu and Cr. The concentrations of these metals in water solutions were determined based previous research by Rasool et al. (2016) and consisted of 1 mg/L Cd, 3 mg/L Zn, 2.5 mg/L Cu, and 0.7 mg/L Cr. Water samples were prepared using standard solutions of $Cd(NO_3)_2$; $Zn(NO_3)_2$; $Cu(NO_3)_2$; $Cr(NO_3)_2$, along with deionized water (pH ~ 5.5). For each trial, one-liter water samples were artificially contaminated with 1 mg/L Cd, 3 mg/L Zn, 2.5 mg/L Cu, and 0.7 mg/L Cr.

A total of 10 different doses of sapropel (1, 2, 3, 4, 5, 10, 20, 30, 40, 50 g/L) were used to remove Cd, Zn, Cu and Cr from water solutions. One-liter water samples contaminated with metal concentrations of 1 mg/L Cd, 3 mg/L Zn, 2,5 mg/L Cu, and 0.7 mg/L Cr were mixed for 15 and 150 minutes at 150 RPM. The most effective dose of sapropel was determined for each metal. The determined optimal dose was then used to mix 1 liter of water contaminated with 1 mg/L Cd, 3 mg/L Zn, 2.5 mg/L Cu, and 0.7 mg/L Cr concentrations for 15, 30, 60, 120 and 150 minutes at 150 RPM. After mixing for various durations with different doses of sapropel, 100 mL of water samples were collected from each container for HM determination. Each 100 mL of water was filtered through a 0.45 μm glass filter, and 20 mL of filtered water was tested for HMs. The concentration of Cd, Zn, Cu, and Cr in the aqueous solutions was determined according to LST EN ISO 15586:2004, titled "Water quality – Determination of trace elements using atomic absorption spectrometry with graphite furnace".

Statistical data analysis was conducted by calculating the arithmetic mean, sample standard deviation, relative standard deviation, and acceptable precision of the test results obtained. Quality assurance measures were implemented for each test method, establishing quality control conditions. Methods performance characteristics, including accuracy and precision, were assessed based on 10 repetitions of the same concentration sample. Standard solutions were utilized as control materials, and solutions of maximum permissible

Table 1. The chemical composition data of sapropel.

Element	w/w,%	Element	w/w,%
C	6.616	Cr	0.027
O	56.325	Fe	0.657
Si	30.383	Mn	0.010
Mg	0.279	Cu	0.001
Na	0.363	Ni	0.003
Al	2.602	Zn	0.003
S	0.165	Pb	0.007
P	0.040	Zr	0.024
Ca	0.890	Sr	0.005
K	1.422	Rb	0.005
Cl	0.011	Ba	0.013
Ti	0.147	Y	0.002

concentration were prepared from these standard solutions (0.005 mg/L Cd, 3 mg/L Zn, 2 mg/L Cu, 0.05 mg/L Cr). Upon measuring the control samples, no values exceeding the 10 % threshold of the standards set forth in the Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption (Council…1998) were observed. The analysis results were expressed as the average concentration of three samples where the distribution was less than 10 %. If the distribution percentage exceeded this threshold, the tests were repeated.

Results and Discussion

Composition of sapropel

The chemical composition of sapropel used in experiments is shown in Table 1.

The concentrations of other metals in sapropel are very low. The microstructure of sapropel is shown in Fig. 1.

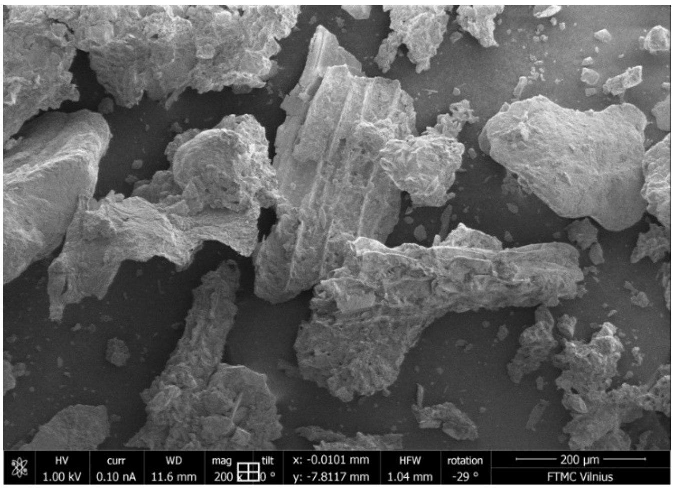

Figure 1. Microstructure of the sapropel

Based on the data presented in Table 1, it can be seen that sapropel is mainly composed of silicon (Si) at 30.383 % and oxygen (O) at 56.325 %. This indicates that silicon is the predominant element in sapropel, while oxygen is likely combined with other elements to form oxides. Carbon (C) accounts for 6.616 % of sapropel's composition, suggesting the presence of organic compounds. Aluminum (Al) is the dominant metal, constituting 2.602 % of sapropel, followed by potassium (K) at 1.422 %. Additionally, sapropel contains significant amounts of calcium (Ca) at 0.890 %, iron (Fe) at 0.657 %, sodium (Na) at 0.363 %, magnesium (Mg) at 0.279 %, and titanium (Ti) at 0.147 %. While significant amounts of K, Na, Ca, Mg and Fe are of mineral origin, originating from water or soil, the sources of substantial Al and Ti concentrations in sapropel warrant further investigation. Among the HMs present in sapropel, Cr is the most abundant at 0.027 %, followed by Zr at 0.024 %.

The particles of sapropel have been observed to exhibit an irregular shape. They are dispersed unevenly and contain fragments (Fig. 2).

Removal of HM from aqueous solution by using sapropel

Fig. 2 shows the efficiency of Cd removal depending on the different doses of sapropel. The mixing time is 30 min.

The efficiency of Cd removal does not show significant improvement with smaller doses of sapropel (1, 2, 3, 4, and 5 g/L). Results show a slight increase in removal efficiency as the the doses of sapropel increase. With the largest dose of 5 g/L of sapropel, the efficiency of removal grows to 19 %. However,

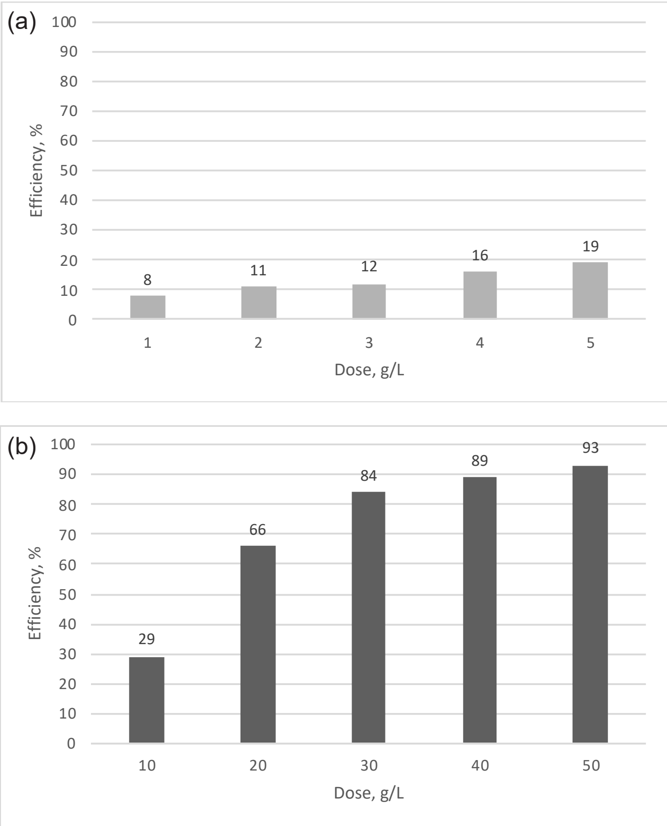

Figure 2. The efficiency of Cd removal from the aqueous solution by using different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

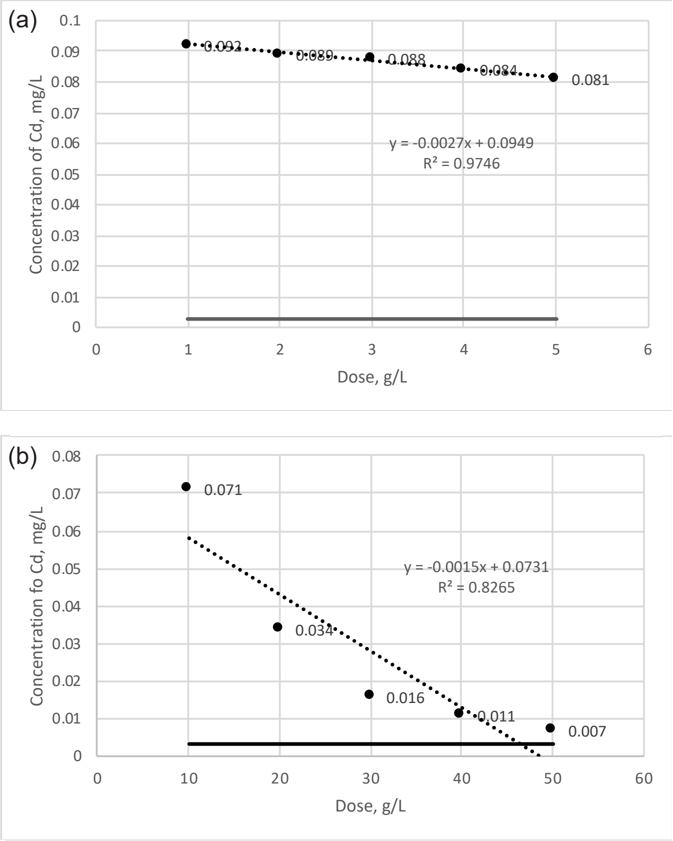

Figure 3. The dependency of Cd concentration on different amounts of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

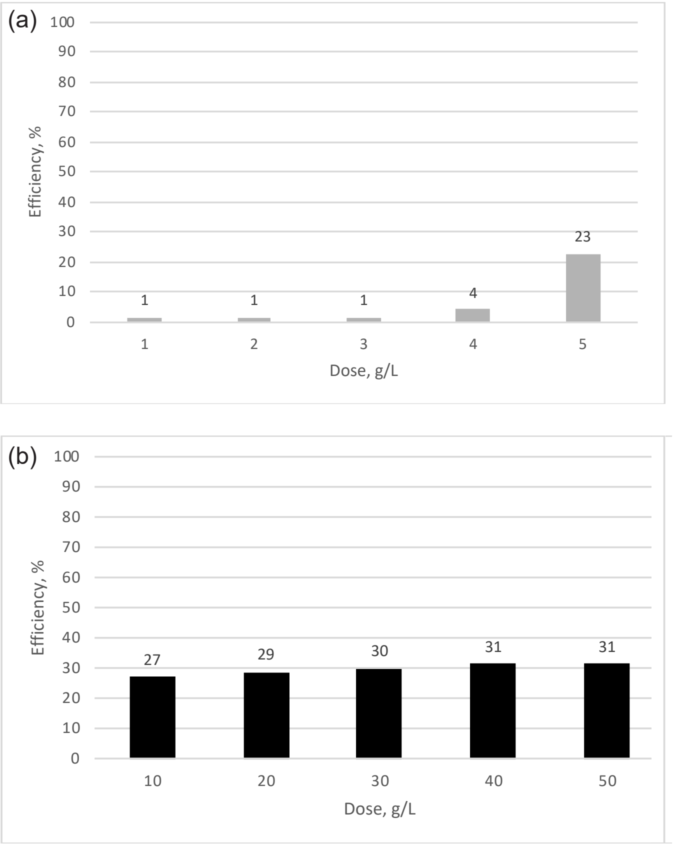

Figure 4. The efficiency of Cr removal from the aqueous solution by using different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

the most notable improvement in Cd removal efficiency is observed with larger doses of sapropel (10, 20, 30, 40, and 50 g/L). Fig. 2b shows that the efficiency of Cd removal markedly increases when the doses of sapropel increase.

Initially, the Addition of a 10 g/L dose of sapropel results in insignificant efficiency of Cd removal, standing at 29 %. However, upon introducing a second dose of 20 g/L to the aqueous solution, the efficiency of Cd removal doubles to 66 %. Subsequent increases in sapropel doses further enhance Cd removal. The highest dose of 50 g/L of sapropel achieves 93 % efficiency in Cd removal. These results show that bigger doses of sapropel effectively eliminate Cd from aqueous solutions. However, it is important to establish the relationship between Cd concentration and different amounts of sapropel, as well as to identify the optimal sapropel dose required to effectively reduce Cd levels in drinking water to permissible levels. The World Health Organization recommends a permissible Cd level of 3 µg/L in drinking water. The dependency of Cd concentration on different amounts of sapropel is depicted in Fig. 3, with an initial Cd concentration of 1 mg/L.

Fig. 3a shows that the addition of smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) results in a linear decrease in Cd concentrations, described by the equation C_{Cd} = 0.0949-0.0027Sp. The correlation coefficient for this equation is R=0.987, with a determination coefficient of R^2 = 0.975. The results presented in Fig. 3a demonstrate that all smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) used for treating Cd-polluted solutions failed to reduce Cd concentration to the permissible level of Cd in drinking water (3 µg/L). In Fig. 3b, the addition of larger doses of sapropel (10, 20, 30, 40, and 50 g/L) results in a more pronounced decrease in Cd concentration, as demonstrated by a linear regression described by the equation C_{Cd} = 0.0731-0.0015Sp. The correlation coefficient for this equation is R=0.909, with a determination coefficient of R^2 = 0.827. However, despite this stronger linear decrease, bigger doses of sapropel (10, 20, 30, 40, and 50 g/L) also fail to reduce Cd concentrations to the permissible level of Cd in drinking water (3 µg/L).

Fig. 4 shows the efficiency of Cr removal depending on the different doses of sapropel. The mixing time is 30 min.

For smaller doses of sapropel (1, 2, 3, 4, and 5 g/L), the efficiency of Cr removal is very poor. The first three doses (1, 2, and 3 g/L) of sapropel remove only 1% of Cr, while 4 g/L of sapropel removes only 4 % of Cr. Only the fifth dose (5 g/L) of sapropel removes 23 % of Cr. Adding bigger doses of sapropel (10, 20, 30, 40, and 50 g/L) to the solution results in a more significant efficiency of Cr removal, but the percentage is still not very high, ranging from 27 % to 31 %. Fig. 4b shows that the efficiency of Cr removal remains almost the same even though the doses of sapropel are increased. The difference in removal efficiency between the smallest dose (10 g/L) and the biggest dose (50 g/L) is only 4 %. The results demonstrate that larger doses of sapropel are not very effective in eliminating Cr from aqueous solutions. It is important to determine the exact dependency between the Cr concentration and the different amounts of sapropel used, as well as to determine the dose of sapropel needed to remove Cr from aqueous solutions to reach the permissible value of Cr in drinking water, which amounts

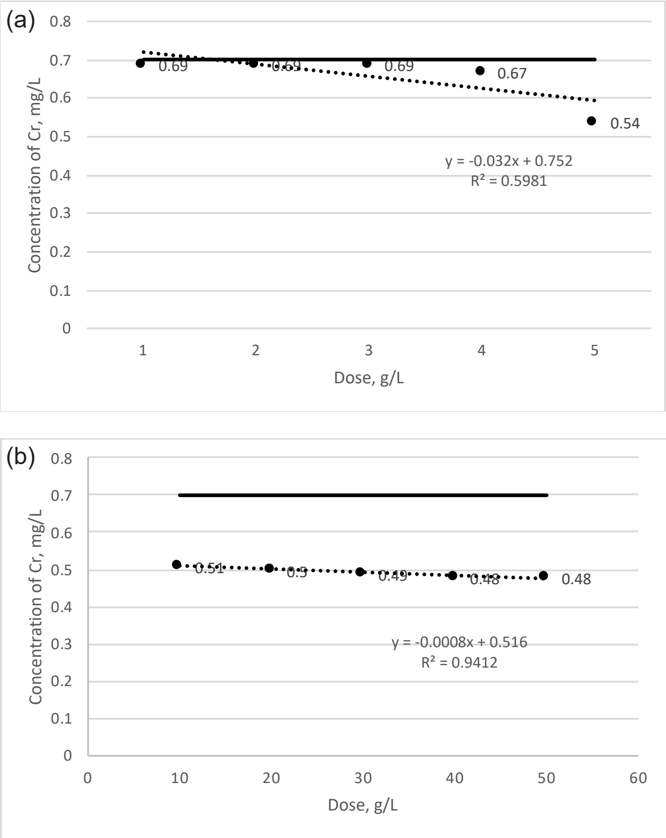

Figure 5. The dependency of Cr concentration on different amounts of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

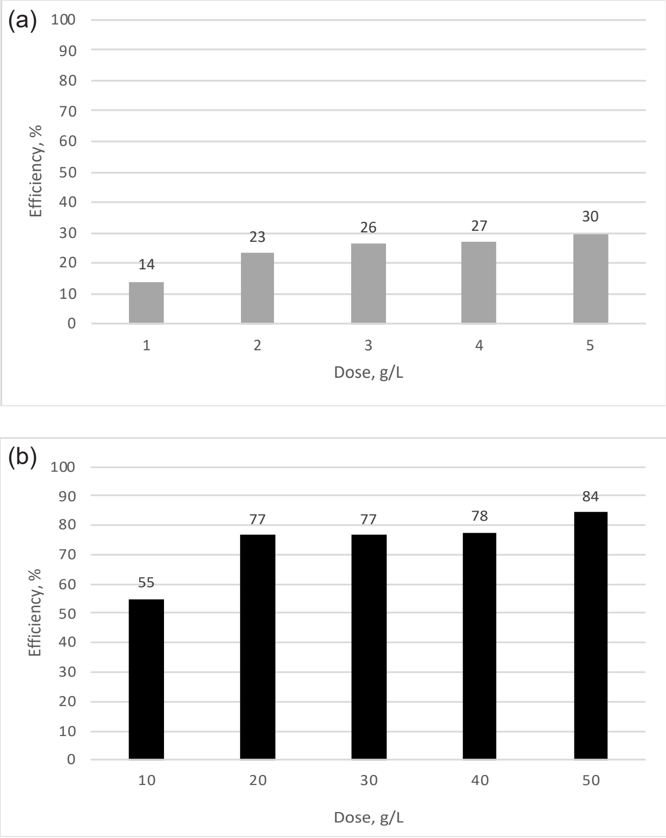

Figure 6. The efficiency of Cu removal from the aqueous solution by using different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

to 50 µg/L according to the World Health Organization. The results presented in Fig. 5 demonstrate the dependency between the Cr concentration and the different amounts of sapropel. The initial concentration of Cr is 0.7 mg/L.

Fig. 5a shows that adding smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) decreases the concentration of Cr in a linear regression, described by the equation C_{Cr} = 0.752-0.032Sp. The correlation coefficient for this equation is R=0.773, with a determination coefficient of R^2 = 0.598. The results presented in Fig. 5a demonstrate that using smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) for Cr concentrations fails to decrease Cr concentration to the permissible level of 50 µg/ in drinking water. Fig. 5b demonstrates that higher doses of sapropel (10, 20, 30, 40, and 50 g/L) also fail to strongly decrease the Cr concentration in a linear regression compared to the linear regression in Fig. 5a. The regression equation is C_{Cr} = 0.516-0.0008Sp, with a correlation coefficient of R=0.970 and a determination coefficient of R^2 = 0.941. However, Fig. 5b shows that higher doses of sapropel (10, 20, 30, 40, and 50 g/L) start decreasing the Cr concentration to the permissible level of 50 µg/L in drinking water when the doses of sapropel are 30 g/L and higher, albeit the decrease is insignificantly low. Fig. 6 shows the efficiency of Cu removal depending on the different doses of sapropel, with a mixing time of 30 min.

Adding smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) does not lead to any significant efficiency of Cu removal. The results show that Cu removal efficiency slightly increases as the doses of sapropel increase: with the smallest dose of 1 g/L, the removal efficiency only reaches 14 %, while with the largest dose of 5 g/L of sapropel, it increases to 30 %. In contrast, adding larger doses of sapropel (10, 20, 30, 40, and 50 g/L) increases the efficiency of Cu removal much more significantly. Fig. 6b shows that Cu removal efficiency markedly increases with higher doses of sapropel. The addition of the first dose of 10 g/L of sapropel boosts the efficiency of Cu removal to as much as 55 %, and subsequent doses (20 and 30 g/L) of sapropel further increase the efficiency of Cu removal to 77 %. Moreover, increasing doses of sapropel continue to enhance Cu removal efficiency. The largest dose, 50 g/L of sapropel, achieves an efficiency of removal to 84 %. The results show that larger doses of sapropel effectively eliminate Cu from aqueous solutions. However, it is important to determine the dependency of Cu concentration on different amounts of sapropel and the optimal dose of sapropel required to reduce Cu concentration to the permissible level in drinking water, which stands at 2 mg/L according to the World Health Organization. Fig. 7 demonstrates the dependency of Cu concentration on different amounts of sapropel. The initial concentration of Cu is 2.5 mg/L.

Fig. 7a shows that the addition of smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) decreases Cu concentrations in a linear regression, described by the equation C_{Cu} = 2.161-0.086Sp. The correlation coefficient for this equation is R=0.912, with a determination coefficient of R^2 = 0.832. Fig. 7a shows the results for all the smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) and demonstrates that the concentration of Cu decreases to the permissible level of Cu in drinking water (2 mg/L) when 2 g/L of sapropel is used. In Fig. 7b, the addition of larger

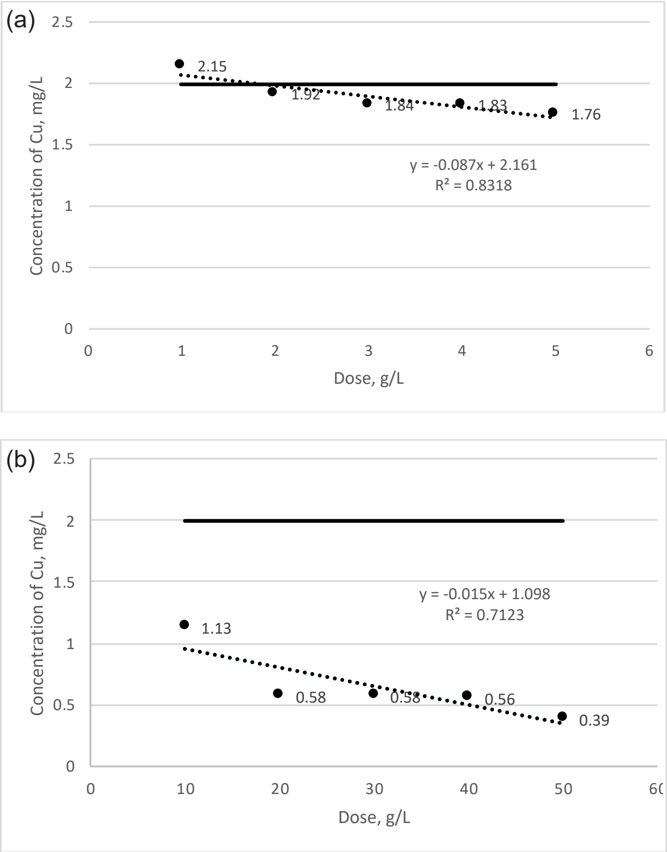

Figure 7. The dependency of Cu concentration on different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

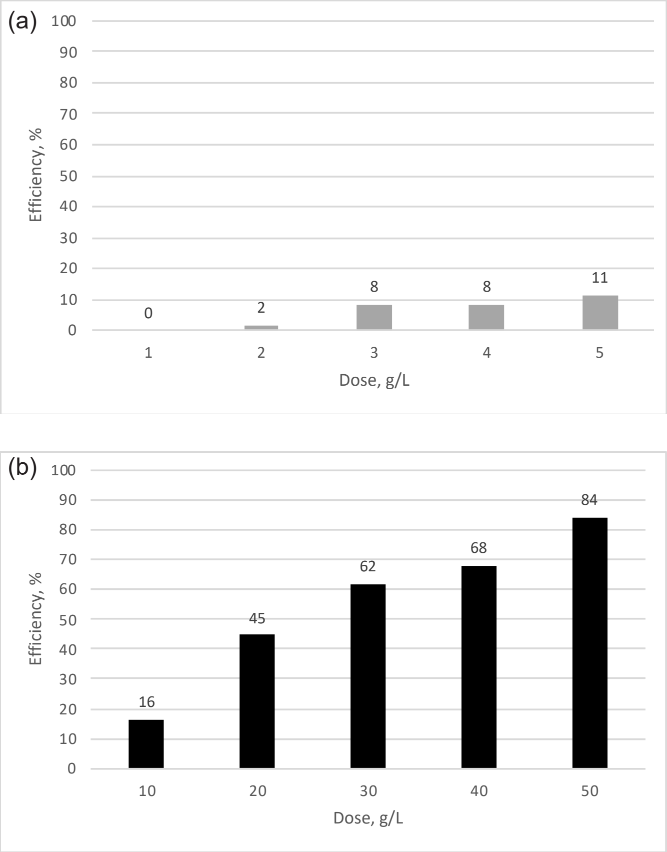

Figure 8. The efficiency of Zn removal from the aqueous solution by using different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

doses of sapropel (10, 20, 30, 40, and 50 g/L) also decreases Cu concentrations in a linear regression, described by the equation C_{Cu} = 1.098-0.015Sp. The correlation coefficient for this equation is R=0.844, with a determination coefficient of R^2 = 0.712. These results indicate that for larger doses of sapropel (10, 20, 30, 40, and 50 g/L), the concentration of Cu decreases to the permissible level of 2 mg/L in drinking water from the very first dose, which is 10 g/L. The concentration of Cu in the aqueous solutions decreases from 1.13 to 0.39 mg/L. Fig. 8 shows the efficiency of Zn removal depending on the different doses of sapropel, with a mixing time of 30 min.

The addition of smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) results in insignificant efficiency of Zn removal. Specifically, the first dose of sapropel (1 g/L) fails to remove Zn altogether, while the second dose removes only 2 % of Zn. Doses of 3 g/L and 4 g/L of sapropel remove 8 % of Zn, and only the fifth dose (5 g/L) removes 11 % of Zn. In contrast, the addition of bigger doses of sapropel (10, 20, 30, 40, and 50 g/L) results in a more significant efficiency of Zn removal. Fig. 8b shows that the efficiency of Zn removal markedly increases with higher doses of sapropel. The addition of the first dose of 10 g/L of sapropel fails to achieve significant efficiency of Zn removal, with the efficiency remaining as low as 16 %. However, the addition of the second dose (20 g/L) increases the efficiency of Zn removal to 45 %. Further addition of bigger doses of sapropel continues to increases the efficiency of Zn removal. The largest dose of 50 g/L of sapropel increases the efficiency of Zn removal to 84 %. These results show that bigger doses of sapropel effectively eliminate Zn from aqueous solutions. It is important to determine the dependency between Zn concentration and different amounts of sapropel, as well as to determine the right dose of sapropel to be used for removing Zn from aqueous solutions to the permissible level recommended by the World Health Organization, which stands

Table 2. Summary of the study into the removal of HM from aqueous solutions.

Metal	The initial concentration, mg/L	The permissible value mg/L	The most efficiency dose, g	Removal efficiency, %	The dose of sapropel where concentration of metal lower than permissible value, g/L
Cd	1.0	0.005	50	93	50
Cr	0.7	0.05	50	31	2
Cu	2.5	2.0	50	84	2
Zn	3.0	3.0	50	84	2

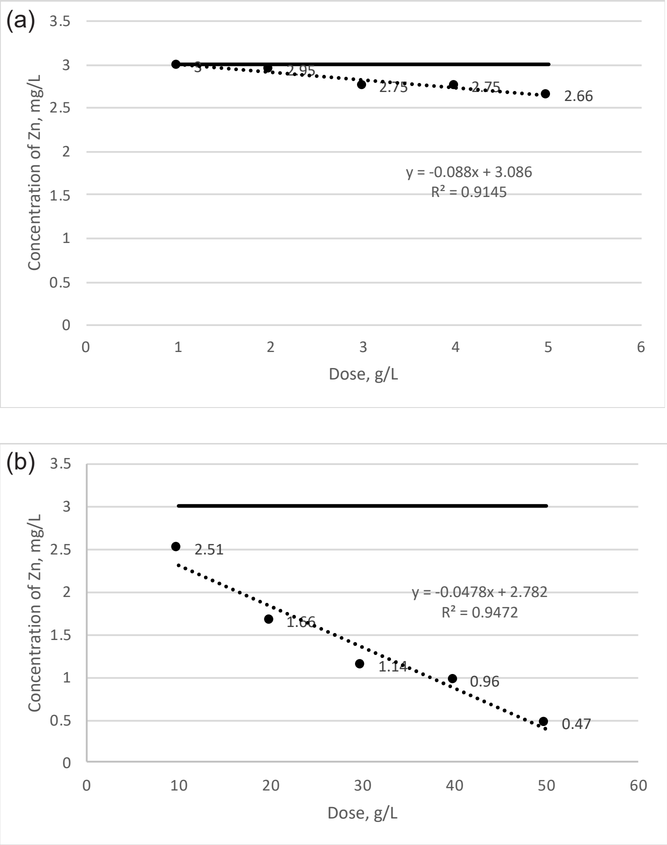

Figure 9. The dependency of Zn concentration on different doses of sapropel (a) 1, 2, 3, 4, and 5 g/L, (b) 10, 20, 30, 40, and 50 g/L.

at 3 mg/L. Fig. 9 presents the dependency of Zn concentration on different amounts of sapropel, with the initial concentration of Zn set at 3 mg/L.

Fig. 9a shows that the addition of smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) decreases Zn concentration in a linear regression, described by the equation C_{Zn} = 3.086-0.088Sp. The correlation coefficient for this equation is R=0.970, with a determination coefficient of R^2 = 0.915. These results indicate that using any of the smaller doses of sapropel (1, 2, 3, 4, and 5 g/L) decreases Zn concentration to the permissible level of 3 mg/L in drinking water, provided a dose of at least 2 g/L of sapropel is used. Fig. 9b demonstrates that the addition of bigger doses of sapropel (10, 20, 30, 40, and 50 g/L) decreases Zn concentration in a linear regression. This regression is described by the equation C_{Zn} = 2.782-0.0478Sp. The correlation coefficient for this equation is R=0.973, with a determination coefficient of R^2 = 0.947. Fig. 9b shows that starting from the very first dose of 10 g/L, bigger doses of sapropel effectively decrease the Zn concentration to the permissible level of 3 mg/L in drinking water. The Zn concentration in the aqueous solution decreases from 2.51 to 0.47 mg/L.

Furthermore, a study on the removal of HMs from aqueous solutions using different doses of sapropel has been conducted. The research has determined the most effective doses of sapropel for HM removal, as well as the doses required to keep HM concentration in drinking water within permissible limits in aqueous solutions. The research data are presented in Table 2. According to the data, the most effective dose for removing HMs from aqueous solutions is 50 g/L, while as little as 2 g/L

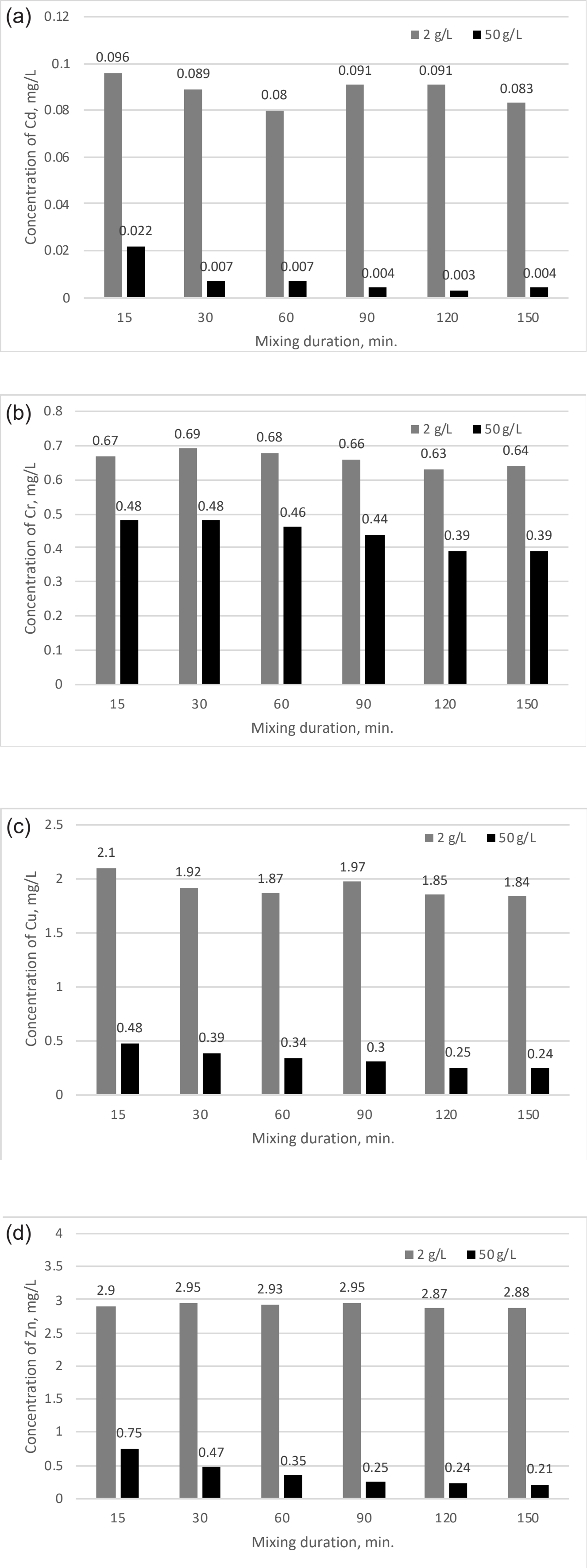

Figure 10. The efficiency of removal of HM from the aqueous solution by using different mixing durations (15, 30, 60, 90, 120, 150 min.) (a) – Cd, (b) – Cr, (c) – Cu, (d) – Zn

of sapropel is sufficient to keep HM concentrations within permissible limits in aqueous solutions, except for Cd.

A study was conducted to investigate how concentrations of heavy metals change over time when contaminated aqueous solutions are in contact with different doses of sapropel. In the first stage of the experiment, sapropel doses were mixed with the contaminated aqueous solution for 30 minutes. In the second stage, sapropel was mixed with contaminated aqueous solution for durations of 15, 30, 60, 90, 120, and 150 minutes. The sapropel doses used in the experiment were selected based on the most relevant data from Table 3, specifically doses of 2 g/L and 50 g/L.

Fig. 10 presents the results, demonstrating the efficiency of HM removal from the aqueous solution with different mixing durations.

The data presented in Fig. 10a show that when mixing the Cd-contaminated water solutions with a lower dose of sapropel (2 g/L) for various durations, there is a slight decrease in Cd concentration with increasing contact time, but the adsorption efficiency remains consistent. However, with the highest dose of sapropel (50 g/L), the efficiency of Cd removal increases, leading to a decrease in Cd concentration in aqueous solution. Despite the decrease in Cd concentration from 0.022 mg/L after 15 minutes of mixing to 0.004 mg/L after 150 minutes, extending the mixing time to 150 minutes appears unnecessary, as the same concentration is achieved after 90 minutes of mixing. Moreover, Cd concentrations after 30 and 60 minutes of mixing are very similar to those obtained with longer mixing times. Therefore, it can be concluded that a mixing time of 30 minutes is sufficient for effective removal of Cd from water solutions when using a sapropel dose of 50 g/L.

When a Cr-contaminated aqueous solution is mixed for different mixing durations with a smaller dose of sapropel (2 g/L), there is a slight decrease in Cr concentration as the contact time increases. However, extending the mixing duration has no significant impact on adsorption effectiveness. Similarly, as shown in Fig. 10b, with the highest sapropel dose (50 g/L) and extended contact duration, the efficiency of Cr removal from the aqueous solution remains largely unaffected. The Cr concentration changes only slightly as the mixing duration increases, decreasing from 0.048 mg/L after 15 minutes of mixing to 0.039 mg/L after 150 minutes. Therefore, it can be concluded that mixing duration has no significant effect on the removal of Cr from aqueous solutions, and the shortest mixing time of 15 minutes can be effectively used.

When mixing a Cu-contaminated aqueous solution for different durations with a smaller dose of sapropel (2 g/L), there is a slight decrease in Cu concentration as contact time increases (Fig. 10c). For instance, the Cu concentration in the aqueous solution is 2.1 mg/L after15 minutes of mixing, decreasing to 1.84 mg/L after 150 minutes. However, with the highest sapropel dose (50 g/L) and extended contact time, the efficiency of Cu removal from the aqueous solution increases. For example, the Cu concentration decreases from 0.48 mg/L after 15 minutes of mixing to 0.24 mg/L after 150 minutes. Nevertheless, extending the mixing duration to 150 minutes is unnecessary, as similar concentrations are achieved after 120 minutes of mixing, and only a minimal increase in concentrations is observed after 30, 60, and 90 minutes of mixing. Therefore, it can be concluded that a mixing time of 30 minutes is sufficient for effective removal of Cu from aqueous solutions when using a sapropel dose of 50 g/L.

The data presented in Fig. 10d shows that when mixing a Zn-contaminated aqueous solution for different durations with a smaller sapropel dose (2 g/L), the decrease in Zn concentration is negligible as contact time increases. Extending the mixing time has no significant impact on adsorption effectiveness. However, with the highest sapropel dose (50 g/L), extending the contact time increases the efficiency of Zn removal from the aqueous solution. For instance, the Zn concentration in the aqueous solution decreases from 1.24 mg/L after 15 minutes of mixing to 0.72 mg/L after 150 minutes. Nevertheless, extending the mixing duration to 150 minutes is unnecessary, as similar concentrations are achieved after 60 minutes of mixing, with only a minimal increase in concentrations observed after 30 and 90 minutes of mixing. Therefore, it can be concluded that a mixing time of 60 minutes is sufficient for effective Zn removal from aqueous solutions with a sapropel dose of 50 g/L.

As seen from the data presented in Table 1, sapropel has been found to consist of 30.383 % Si, and 56.325 % O. As sapropel is mostly made up of Si and O, it can be assumed to contain a significant percentage of silica. Scientists have found that silica and mixed oxides based on silica are efficient adsorbents for HM ions such as Pb, Sr, Ni, Cd, and Cs (Gunko et al. 2004). Inorganic materials, especially silica, offer a large surface area for enhanced adsorption capacity and exhibit great physical and chemical robustness, enabling them to withstand harsh environments. Highly structured mesoporous silica with incorporated bridging/complex-forming functional groups, such as mercapto or amino, serve as excellent adsorbents for the adsorption of Cu and Pb ions (Blitz et al. 2006). According to the research literature, the primary mechanism of cation adsorption on silica gel is the exchange of ions with the silano surface hydrogen ions, especially at low pH values. Adsorption of heavy and transition metal ions on functionalized silica gel surfaces occurs due to various interactions, including electrostatic forces, complex-formation, and hydrogen bonds, etc.) (Barany and Stelko 2013).

Studies have demonstrated that heavy metals (Cd, Cr, Cu, and Zn) can be removed from aqueous solutions using sapropel, albeit with varying degrees of efficiently for different metals. When small doses of sapropel (1, 2, 3, 4, and 5 g/L) were employed, Cr and Zn exhibited the least efficient removal, Cd showed moderate efficiency, and Cu was removed most efficiently. The sequence of removal efficiency can be described as Zn=Cr<Cd<Cu. This distribution of metals is similar to their distribution on the activity series of metals chart: Zn and Cr are the most active metals, with similar activity levels, while Cd is less active, and Cu is the least active. It is reasonable to assume that their activity levels affect the efficiency of their removal from aqueous solutions. However, when larger doses of sapropel (10, 20, 30, 40, and 50 g/L) were utilized, nearly all the metals were removed significantly more efficiently, with removal efficiency ranging from 84 to 93 %, except for Cr, which exhibited an efficiency of only 31 %. Furthermore, it has been established that the adsorption rate increases with reaction time until a balance is achieved between the absorbents, the metal ions adsorbed onto the sorbents, and the remaining metal ions in the solution.

In the initial stages, adsorption occurs rapidly, gradually slowing down as equilibrium is established between the metal in the liquid and solid phases. Different concentrations of metal ions reach equilibrium at different times, depending on factors such as the concentration of metal ions, absorbents, initial concentration, and solution temperature (Gupta et al. 2021). During the removal of heavy metals from aqueous solutions and with varying contact times, it has been observed that a smaller dose of sapropel (2 g/L), coupled with an increase in contact time, has a negligible effect on HM concentration. Extending the mixing time has had no significant impact on adsorption efficiency. However, when the largest sapropel dose (50 g/L) has been used, the efficiency of HM removal from the aqueous solution increases with an extension of the contact time, although not significantly. Nevertheless, the concentration of metal in the aqueous solution decreases with an extension of the mixing time. Studies investigating the mixing of sapropel for different durations have failed to identify a single effective duration for both the adsorbent and the contaminated solution. The duration required for removing all metals varies and ranges from 15 minutes for Cr removal, to 30 minutes for Cd and Cu removal, and to 60 minutes for removing Zn.

Conclusions

The study on the use of sapropel as a cost-effective bioadsorbent for the removal of Cd, Cr, Cu, and Zn from aqueous solutions has revealed variations in the removal efficiency for each metal. The use of different doses of sapropel and mixing durations for the removal of Cd (with an initial concentration of 1 mg/L) from aqueous solutions has demonstrated that Cd concentration decreases to levels permissible for drinking water when a sapropel dose of 50 g/L is used. The highest Cd removal efficiency of 93 % is attained with a sapropel dose of 50 g/L, and 30 minutes of contact proves sufficient for effective removal.

For Cr removal from aqueous solutions (with an initial concentration of 0.7 mg/L), various doses of sapropel and mixing durations were tested. The Cr concentration decreased to the permissible drinking water level at a dose of 2g/L of sapropel, with and effective removal time of 15 minutes. However, sapropel is not particularly effective in removing Cr from aqueous solutions. The most effective Cr removal rate of 31 % is achieved when a sapropel dose of 50 g/L is used.

When considering the removal of Cu from aqueous solutions (with an initial concentration of 2 mg/L) using different doses of sapropel and mixing durations, the Cu concentration decreases to the levels permitted for drinking water with a sapropel dose of 2 g/L. The most efficient Cu removal rate of 84 % is achieved with a sapropel dose of 50 g/L, and 30 minutes of contact is sufficient for effective removal.

In the context of removing Zn from aqueous solutions (with an initial concentration of 3 mg/L) using different doses of sapropel and mixing durations, the Zn concentration decreases to levels acceptable for drinking water with a sapropel dose of 2 g/L. The most effective Zn removal rate of 84 % is achieved with a sapropel dose of 50 g/L and 60 minutes of contact is sufficient for effective removal.

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Badania nad zastosowaniem sapropelu do usuwania metali ciężkich (kadmu, chromu, miedzi i cynku) z roztworów wodnych

Streszczenie. Celem tego artykułu jest zbadanie i porównanie skuteczności usuwania metali ciężkich (Cd, Cr, Cu i Zn) z roztworów wodnych przy użyciu sapropelu jako sorbentu. Surowy sapropel do celów badawczych wydobyto z głębokości 2-3 metrów jeziora Apslavas we wsi Stabulankliai, gmina Leliunai, rejon Utena, Litwa. Został umyty, wysuszony w piecu, zmielony i przesiany. Analizę przeprowadzono przy użyciu spektrometru fluorescencji rentgenowskiej, analizatora węgla i siarki CS-2000, SEM JEOL JSM-7600F. Stężenia Cd, Cr, Cu i Zn mierzono za pomocą spektrofotometru absorpcji atomowej Buck Scientific 210 VGP. Obliczono dane statystyczne. Maksymalna skuteczność usuwania Cd (93%), Cr (31%), Cu (84%) i Zn (84%) z roztworu wodnego przez sapropel została osiągnięta przy zastosowaniu minimalnych dawek sapropelu (50 g/L). Badanie wykazało, że mieszanie sapropelu przez 15 minut jest wystarczające do usunięcia Cr, 30 minut dla Cd i Cu oraz 60 minut dla Zn. Najwyższa skuteczność usuwania metali ciężkich z roztworu wodnego przez sapropel osiągnęła 93% dla Cd, 31% dla Cr, 84% dla Cu i 84% dla Zn, gdy zastosowano minimalne dawki sapropelu (50 g/L). Badanie wykazało, że mieszanie sapropelu przez 15 minut jest wystarczające do usunięcia Cr, 30 minut dla Cd i Cu oraz 60 minut dla Zn.