

New Approach to Remove Heavy Metals from Wastewater by the Coagulation of Alginate-Rhamnolipid Solution with Aluminum Sulfate

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Abstract: This study was conducted using alginate-rhamnolipid (Alg-Rh) solutions on copper ions (Cu^{2+}) as an application of coagulation with aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$). The results show that solid phases were rapidly formed as an output of the reaction between Alg-Rh and $\text{Al}_2(\text{SO}_4)_3$. It could be considered that the $\text{Al}_2(\text{SO}_4)_3$ concentration and the existence of Cu^{2+} have an impact on forming hard coagulation, in that the total volume has been increased with increasing $\text{Al}_2(\text{SO}_4)_3$ and the existence of Cu^{2+} . The number of ions of aluminum (Al^{3+}) and sulfate (SO_4^{2-}) were also increased with $\text{Al}_2(\text{SO}_4)_3$. The efficiency of Cu^{2+} removal was constant above 75.0%, hence the average value was 76.8%.

Keywords: heavy metals; remediation; rhamnolipid; alginate; coagulation

1. Introduction

Water is one of the most important resources in the world. It is already known that 71% of the Earth's surface is covered with water and only 2.5% of it is freshwater [1]. Nowadays, seawater has been found to be converted to freshwater, but freshwater is still an important resource for living organisms, including humans [2,3]. Despite such an important resource, water pollution has been induced by a variety of contaminants, such as heavy metals and organic pollutants [4–7]. In particular, the pollution by heavy metals has been increasing with the development of industry, and it has already been proved that a high concentration of heavy metals has a dangerous impact on living organisms and the environment as hazardous materials [8–10]. It can be accumulated in living organisms and inhibit their metabolism to the point of death [11,12]. Accordingly, water treatment has been essentially required, in that water quality should be improved for water resource recirculation in conditions of limited water resources. Moreover, the treatment of wastewater that contains solid material should include a separation process. Recently, various wastewater treatment technologies have been developed using biological, chemical, and physical methods but we have yet to develop high-efficiency remediation technology [13–15].

Alginate has been mainly used to form a capsulated medicine as a raw material to be connected with divalent ions for its special property [16]. This novel property makes it possible for various applications such as coagulation to remove heavy metals [17]. Rhamnolipids, a biosurfactant, also have proved their novel property to remediate heavy metals [18–21]. Both materials are bio-derived

and have relatively long chains [22,23]. Their combined properties and longer molecular chain would be expected to improve the efficiency of solid/liquid separation and heavy metal removal.

In view of the above, Alg-Rh complexes would form a longer chain than a simple alginate or rhamnolipid molecule. This molecular structure can coagulate with heavy metals as a long polymer by connecting together. Heavy metals are usually divalent ions or trivalent ions, and they are substituted with more than two sodium ions of sodium alginate to form a relatively round shape. Moreover, adding aluminum ions makes it more aggregated as supporting strong flocculation. The solid phase would form only one mass, and the mass does not tend to be fluid. Therefore, it would be much easier to separate the solid phase with a liquid phase.

Herein, we would like to suggest the possibility of using Alg-Rh complexes as a green coagulant for heavy metals and improve their efficiency for solid and liquid separation. Moreover, the water removing heavy metals would be investigated for characterization as a preliminary study.

2. Materials and Methods

2.1. Materials

Sodium alginate was supplied by Junsei Chemical Co., Ltd. (Tokyo, Japan), and the rhamnolipids (R90–100G) were purchased from AGAE Technologies (Corvallis, Oregon, USA). Additionally, copper standards (Kanto Chemical Co., Inc., Tokyo, Japan) were adjusted to make a 100 mg/L copper solution. A small amount of nitric acid (504–756 mg/L) is contained in the standard solution (980–1020 mg/L). Aluminum sulfate from Kanto Chemical Co., Inc., Tokyo, Japan, was also used as a coagulant.

2.2. Experimental Methods

Alginate solution (4% *w/v*) was mixed with a rhamnolipid solution (0.1% *w/v*) at 80 °C for 2 h, and then a copper standards solution was put into the mixture (Figure 1) [24–27]. A small amount of copper standard solution, 5 mL of 100 mg/L, was adopted for this preliminary study. To identify the effects of heavy metal in the mixture, samples have been also made without Cu^{2+} . Aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3$) solution at 0.1%, 0.3%, and 0.5% *w/v* of total volume was added as an additive to support coagulation. All the experiments for coagulation were conducted in 250 mL glass beakers. Then, a mass wrapped in a thin layer was formed and the liquid phase (water) was separated from the solid phase by gravity. The final step in this experiment is filtering the water using a 0.45 μm acrylic-based filter.

2.3. Analysis

After the reaction, the samples were analyzed using ion chromatography (Dionex™ Aquion™ Ion Chromatography (IC) System, Thermo Fisher scientific, Waltham, MA, USA) to investigate the sulfate ions. An inductively coupled plasma optical emission spectrometer (ICP/OES) (Optima 7300DV, Perkin Elmer, Waltham, MA, USA) was also used for Cu^{2+} and Al^{3+} . The total organic carbon (TOC) was determined using a UV-vis spectrophotometer (DR-5000, Hach, Loveland, CO, USA), followed by US EPA (United States Environmental Protection Agency) methods (method 10129).

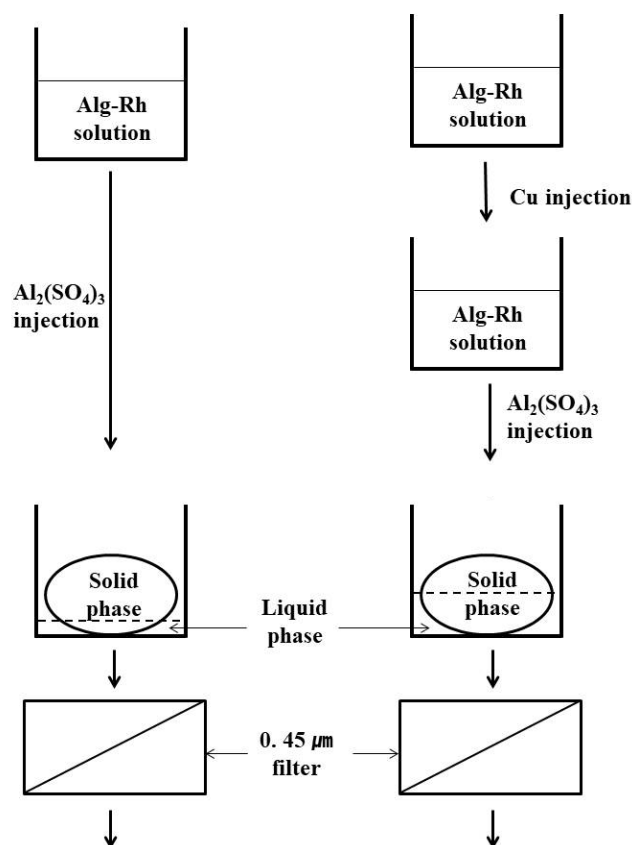


Figure 1. Schematic diagram of the experimental flow.

3. Results and Discussion

3.1. Characterization of the Purified Water

Several distinct characteristics of the purified water will be discussed in detail. As explained above, the water has been separated from the formed mass, the solid phase, by gravity. The mass shows a different degree of rigidity with different concentrations of the coagulant (Figure 2). The pressure generated in the separation process causes the formed mass to break and the liquid contents wrapped in a thin layer to flow out. Eventually, the separation process could no longer proceed. In the case of the busted sample, the obtained water contained lots of organic matter and heavy metals that flowed out from the mass. Therefore, the samples were excluded from the exact analysis. Figure 2a shows that the liquid in the mass spilled into the water because of the weak bond of the mass surface. The sample without Cu^{2+} was observed to be busted easily compared to the other samples. The sample with 0.1% $\text{Al}_2(\text{SO}_4)_3$ and Cu^{2+} made two separated phases which are not distinguishable in macroscopic view. However, the sticky liquid wrapped in the thin layer has been discovered to be separated (Figure 2b). In the case of Figure 2c, a remarkable change in the solid phase has been shown. The liquid in the mass has a sticky property because of the alginate and it makes lots of small bubbles inside the layer. The liquid has not been observed to be spilled to the water. The samples with 0.3% and 0.5% $\text{Al}_2(\text{SO}_4)_3$ solution are comparatively hard (Figure 2d). The image was taken in tilted form for a more distinctive change from the others. The separated water was observed to be very transparent.

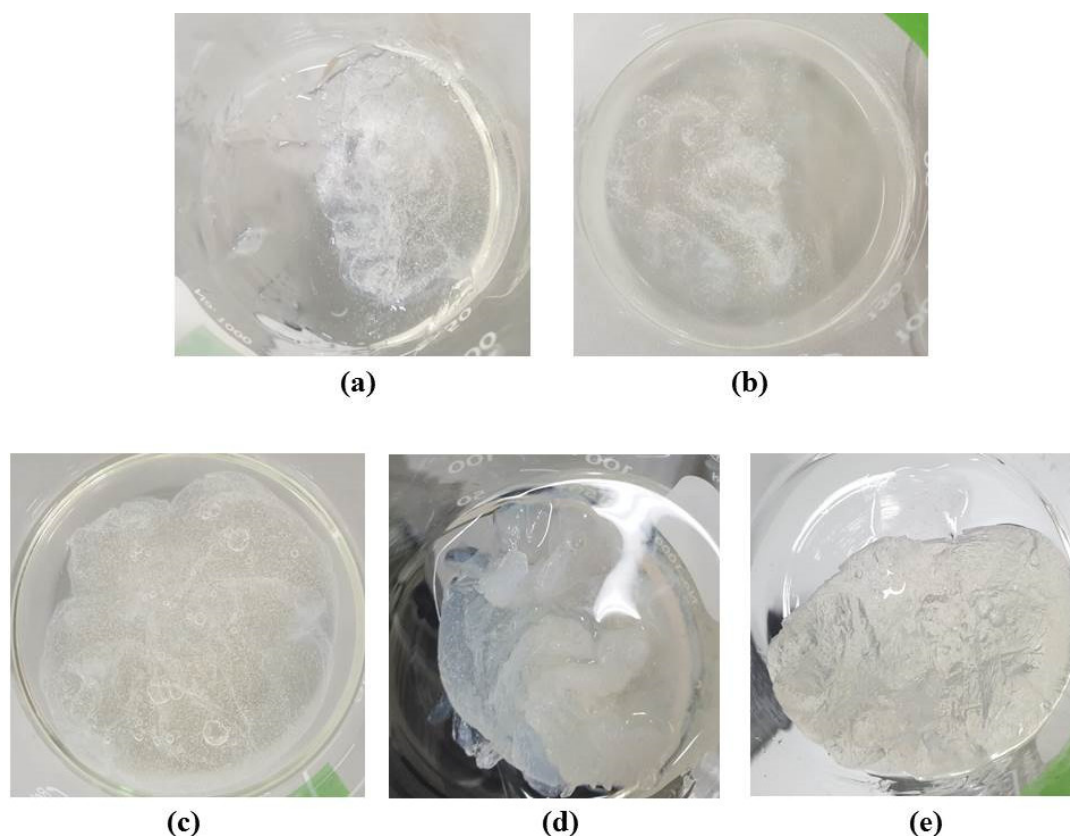


Figure 2. The difference depending on the Cu^{2+} and $\text{Al}_2(\text{SO}_4)_3$ concentrations ((a) 0.1% ($\text{Al}_2(\text{SO}_4)_3$) without Cu^{2+} , (b) 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , (c) 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , (d) 0.5% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , (e) the solid phase after separation).

Figure 3 shows the different volume of the liquid phase depending on samples which have different Cu^{2+} and $\text{Al}_2(\text{SO}_4)_3$ concentrations. The sample without Cu^{2+} shows the smallest total volume because it is difficult to separate the water without bursting the mass. The total volume of the samples with Cu^{2+} has been increased with increasing $\text{Al}_2(\text{SO}_4)_3$, and the obtained volume remained stable from 0.2% $\text{Al}_2(\text{SO}_4)_3$ sample. It would be considered that Cu^{2+} also has an impact on coagulation behavior. Divalent ions have already proved their property to substitute two sodium ions in alginate since they have been discovered [28].

TOC contents are also distinctive features in this experiment. Alginate and rhamnolipids have many carbons on their own, so it can be an important indicator of the remediation degree of the Alg-Rh complexes. As shown in Table 1, the highest TOC contents were observed in sample 1. The results indicate that Cu^{2+} works as another coagulant with $\text{Al}_2(\text{SO}_4)_3$. The bond of Al^{3+} or Cu^{2+} with alginate has been proved [29–31]. As Al^{3+} and Cu^{2+} ions gather the alginate and rhamnolipid more tightly, carbon would not be spilled out of the mass to liquid phase.

The concentration of sulfate ions (SO_4^{2-}) has been detected as a dominant material. The existence of Cu^{2+} played an important role, in that the SO_4^{2-} concentration in sample 1 was 1.43 times higher. This indicates that Cu^{2+} , the only controlled factor, is an important substance to support coagulation. The higher effects would be expected with higher contents of heavy metals inside the Alg-Rh solution. Not only Cu^{2+} but also other heavy metals with a strong ionic strength could be applied to this study. Except for sample 1, this is an increasing tendency among the samples. In comparison with sample 2, sample 3 and 4 have 3.39 and 5.71 times higher in SO_4^{2-} concentrations. Higher $\text{Al}_2(\text{SO}_4)_3$ shows higher sulfate ions. We can assume that Al^{3+} would react more extremely at higher $\text{Al}_2(\text{SO}_4)_3$ contents, suggesting a higher efficiency.

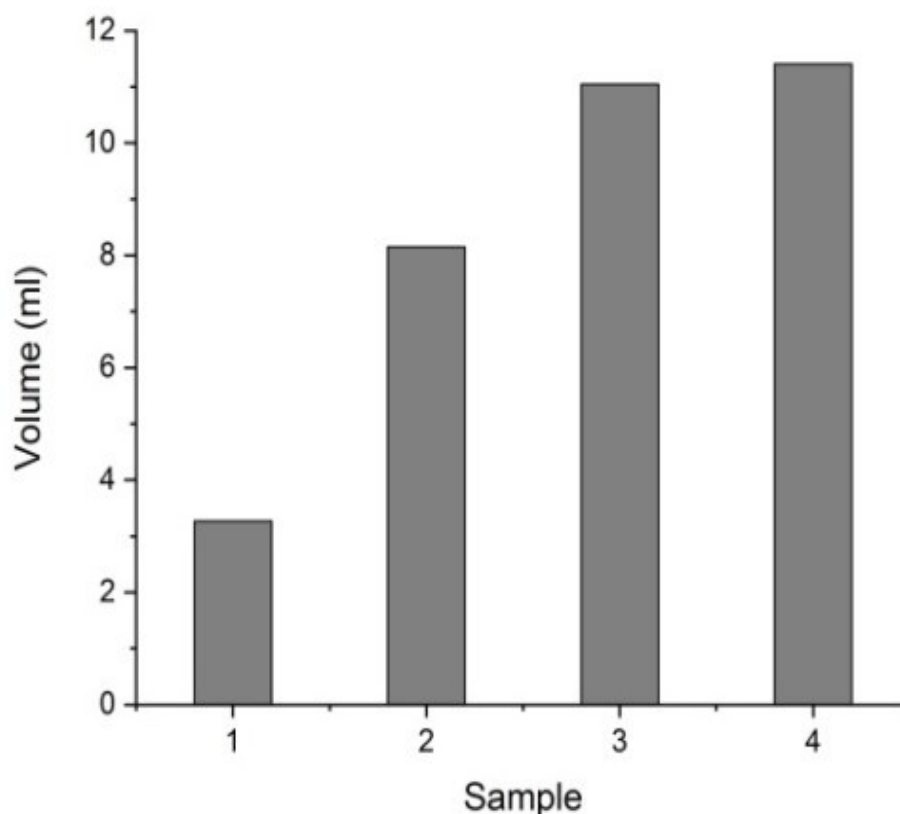


Figure 3. Total volume obtained from experiments in this research (1: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , 2: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , 3: 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , 4: the solid phase after separation).

Table 1. Characteristics of the liquid phase separated from the mixed phase with solid.

Sample Number	TOC (mg/L)	SO_4^{2-} (g/L)
Sample 1	116.3 (± 5.3)	2.244 (± 0.190)
Sample 2	32.00 (± 2.5)	1.573 (± 0.078)
Sample 3	15.50 (± 4.4)	5.340 (± 0.184)
Sample 4	14.17 (± 2.0)	8.976 (± 0.734)

Sample 1: 0.1% $\text{Al}_2(\text{SO}_4)_3$ without Cu^{2+} , Sample 2: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 3: 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 4: 0.5% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} .

3.2. Respective Correlation

As explained above, the Alg-Rh solution has high contents of carbon, and the contents are closely related to the reaction with $\text{Al}_2(\text{SO}_4)_3$. Therefore, the contents of Al^{3+} , SO_4^{2-} , and Cu^{2+} in the water are also expected to have a correlation with TOC as the result of the reaction. As shown in Figure 4, the sulfate ions have been increased with increasing $\text{Al}_2(\text{SO}_4)_3$. This does not seem to have a correlation with TOC without Cu^{2+} , in that there is not a dramatic change comparing the significant change in TOC between sample 1 and 2. With Cu^{2+} , the concentrations have been increased in multiples, as explained above, not showing a specific relation with TOC. Indeed, the TOC contents of sample 2 and 3 decreased 0.48 and 0.44 times compared to sample 1, contrary to the constantly increased SO_4^{2-} .

Al^{3+} concentrations also have been constantly increased similar to SO_4^{2-} (Figure 5). A difference is that Al^{3+} was used to form coagulation as an effective coagulant, so the contents are definitely lower than those of SO_4^{2-} . The concentrations are respectively remarked at 0.360, 0.236, 0.854, and 1.400 g/l. Compared to sample 1, more Al^{3+} in sample 2 is expected to react with the Alg-Rh solutions, detecting a lower Al^{3+} in sample 2.

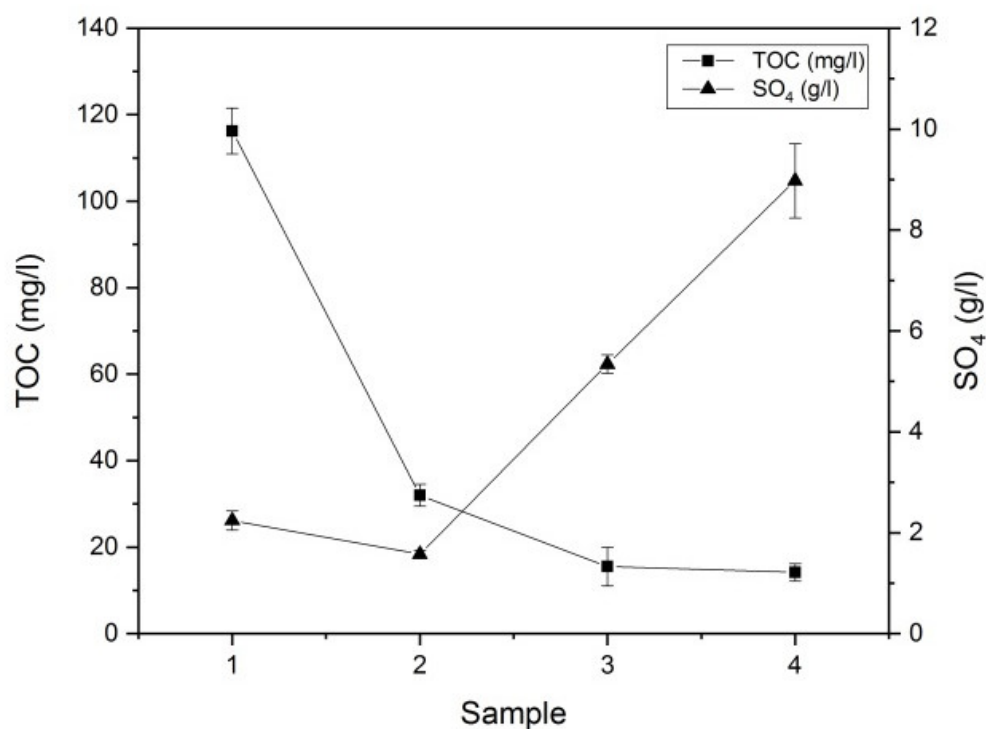


Figure 4. Variation in TOC and SO_4^{2-} depending on samples (Sample 1: 0.1% $\text{Al}_2(\text{SO}_4)_3$ without Cu^{2+} , Sample 2: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 3: 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 4: 0.5% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+}).

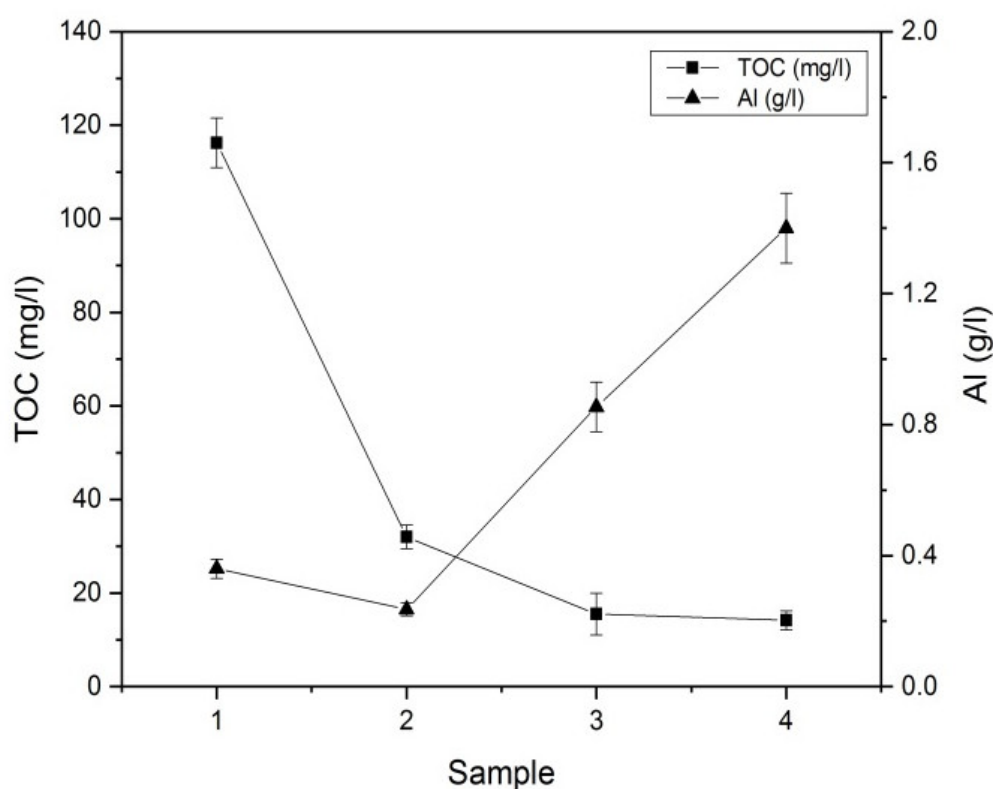


Figure 5. Change in the TOC and Al^{3+} depending on sample (Sample 1: 0.1% ($\text{Al}_2(\text{SO}_4)_3$) without Cu^{2+} , Sample 2: 0.1% ($\text{Al}_2(\text{SO}_4)_3$) with Cu^{2+} , Sample 3: 0.3% ($\text{Al}_2(\text{SO}_4)_3$) with Cu^{2+} , Sample 4: 0.5% ($\text{Al}_2(\text{SO}_4)_3$) with Cu^{2+}).

Figure 6 shows the Cu^{2+} concentrations with a change in $\text{Al}_2(\text{SO}_4)_3$. This is not remarked at sample 1 because Cu^{2+} was not put into sample 1. They are remarked at 23.150 (± 1.485), 26.850 (± 2.616), and

23.500 (± 0.281) with sample 2, 3, and 4. Cu^{2+} in samples 2 and 4 are quite similar, but sample 2 has more or less high value compared to them. The standard deviation of sample 2 is high. This indicates that there is a possibility to get a similar value with sample 2 and 4 during repeated experiments. However, the values show quite constant values, even though the TOC contents were decreased. Therefore, it is considered that Cu^{2+} has an effect on improving the efficiency to coagulate the solution with Al^{3+} , but the $\text{Al}_2(\text{SO}_4)_3$ and TOC contents do not affect the Cu^{2+} removal. There would be high potential to remove not only copper but also other di- and trivalent ions. This indicates that a bridging effect would be expected using heavy metals as a bridge and then it results in heavy metal removal. Moreover, as shown, Al^{3+} has a large effect on the Cu^{2+} removal. With these results, other heavy metals in wastewater may successfully replace the role of Al^{3+} . Therefore, it could be suggested that a variety of heavy metals in wastewater can be also removed at the same time.

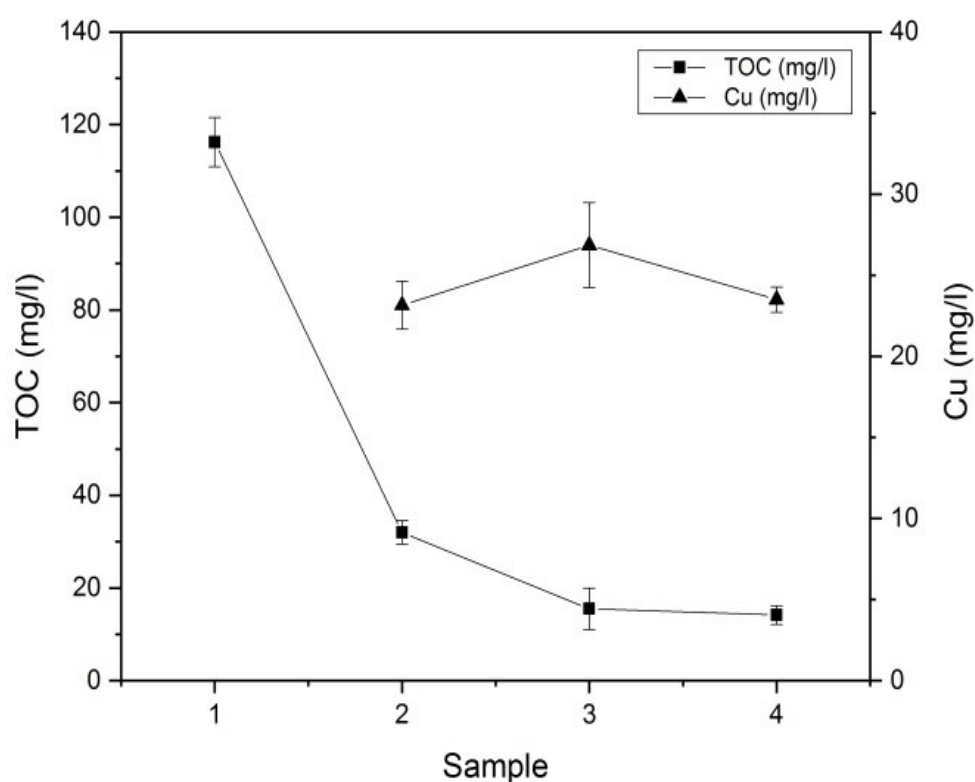


Figure 6. Change in TOC and Cu^{2+} depending on the sample (Sample 1: 0.1% $\text{Al}_2(\text{SO}_4)_3$ without Cu^{2+} , Sample 2: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 3: 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 4: 0.5% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+}).

Each effect of the factors is explained using regression analysis and expressed in Table 2. As discussed above, decreasing TOC indicates that Alg-Rh complexes are combined with heavy metals, resulting in carbon being decreased in the samples. However, aluminum and sulfate ions are evaluated to have relatively little influence. This is considered because the Alg-Rh complexes are also combined with copper ions.

Table 2. Regression analysis.

Specification	TOC	SO_4^{2-}	Al^{3+}
R^2	0.948	0.840	0.859
p value	0.004	0.094	0.089
F value	0.026	0.262	0.245

Note: R^2 coefficient of determination; $p < 0.05$, indicating significant difference; F value, indicating the degree of statistical confidence.

3.3. Efficiency of Heavy Metal Removal

Herein, the efficiency of Cu removal would be discussed as one of the important objectives to obtain clean water (Figure 7). As explained above, the Cu^{2+} contents were not extremely changed with the change in $\text{Al}_2(\text{SO}_4)_3$ concentrations. The efficiency of Cu removal is also depicted similarly, respectively at 78.7, 75.3 and 76.5%. Most of the removed Cu^{2+} concentrations would be considered to react with Alg-Rh solutions and $\text{Al}_2(\text{SO}_4)_3$. They are considered to be quite high amounts and deserve to be researched more in detail. Furthermore, a higher concentration of Cu^{2+} might have an impact on coagulation, and it also improves the efficiency to increase the Cu removal. As discussed above, other heavy metals with similar ionic states might be expected to have a similar role to that of Cu^{2+} . There were not observed to be a dramatic effect depending on the concentration of aluminum sulfate. However, both the concentration and kind of heavy metals would affect the degree of heavy metal removal. Further studies about these factors would be needed.

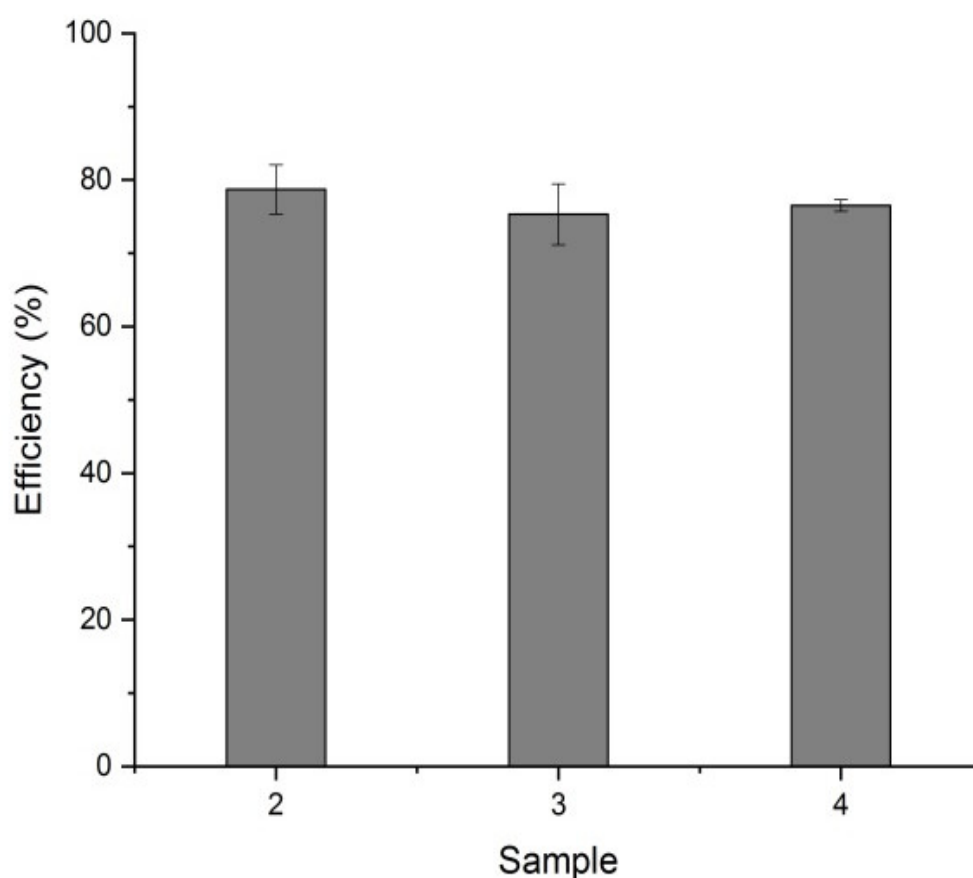


Figure 7. Removal efficiency change of Cu^{2+} in the liquid phase depending on the sample's conditions (Sample 2: 0.1% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 3: 0.3% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+} , Sample 4: 0.5% $\text{Al}_2(\text{SO}_4)_3$ with Cu^{2+}).

4. Conclusions

In this research, we studied Alg-Rh solutions reacting with $\text{Al}_2(\text{SO}_4)_3$ to remove Cu^{2+} by coagulation. The total volume of the liquid phase separated from the solid phase has been increased with the existence of Cu^{2+} and the concentration of $\text{Al}_2(\text{SO}_4)_3$. Al^{3+} and SO_4^{2-} have been also increased with the concentration of $\text{Al}_2(\text{SO}_4)_3$. Furthermore, the efficiency of the Cu^{2+} removal constantly stayed above 75.0%. Therefore, this indicates that the existence of Cu^{2+} has an impact on tighter coagulation with $\text{Al}_2(\text{SO}_4)_3$ but $\text{Al}_2(\text{SO}_4)_3$ does not extremely affect removing Cu^{2+} . This knowledge is worth applying to other heavy metals. More detailed studies should be researched about the effect of Cu^{2+} and Alg-Rh concentration changes.

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References

1. Sivakami, M.S.; Gomathi, T.; Venkatesan, J.; Jeong, H.; Kim, S.; Sudha, P.N. Preparation and characterization of nano chitosan for treatment wastewaters. *Int. J. Biol. Macromol.* **2013**, *57*, 204–212, doi:10.1016/j.ijbiomac.2013.03.005.
2. Qasim, M.; Badrelzaman, M.; Darwish, N.N.; Darwish, N.A.; Hidal, N. Reverse osmosis desalination: A state-of-the-art review. *Desalination* **2019**, *459*, 59–104, doi:10.1016/j.desal.2019.02.008.
3. Yoon, J.; Do, V.; Pham, V.; Han, J. Return flow ion concentration polarization desalination: A new way to enhance electromembrane desalination. *Water Res.* **2019**, *159*, 501–510, doi:10.1016/j.watres.2019.05.042.
4. Yan, Z.; Pan, J.; Gao, F.; An, Z.; Liu, H.; Huang, Y.; Wang, X. Seawater quality criteria derivation and ecological risk assessment for oil pollution in China. *Mar. Pollut. Bull.* **2019**, *142*, 25–30, doi:10.1016/j.marpolbul.2019.02.033.
5. Quesada, H.; Baptista, A.; Cusioli, L.; Seibert, D.; Bezerra, C.; Bergamasco, R. Surface water pollution by pharmaceuticals and an alternative of removal by low-cost adsorbents: A review. *Chemosphere* **2019**, *222*, 766–780, doi:10.1016/j.chemosphere.2019.02.009.
6. Chu, Z.; Fan, X.; Wang, W.; Huang, W. Quantitative evaluation of heavy metals' pollution hazards and estimation of heavy metals' environmental costs in leachate during food waste composting. *Waste Manag.* **2019**, *84*, 119–128, doi:10.1016/j.wasman.2018.11.031.
7. Zhang, L.; Zhu, G.; Ge, X.; Xu, G.; Guan, Y. Novel insights into heavy metal pollution of farmland based on reactive heavy metals (RHMs): Pollution characteristics, predictive models, and quantitative source apportionment. *J. Hazard. Mater.* **2018**, *360*, 32–42, doi:10.1016/j.jhazmat.2018.07.075.
8. Zhang, Y.; Li, S.; Lai, Y.; Wang, L.; Wang, F.; Chen, Z. Predicting future contents of soil heavy metals and related health risks by combining the models of source apportionment, soil metal accumulation and industrial economic theory. *Ecotoxicol. Environ. Saf.* **2019**, *171*, 211–221, doi:10.1016/j.ecoenv.2018.12.023.
9. Rai, P.; Lee, S.; Zhang, M.; Tsang, Y.; Kim, K. Heavy metals in food crops: Health risks, fate, mechanisms, and management. *Environ. Int.* **2019**, *125*, 365–385, doi:10.1016/j.envint.2019.01.067.
10. Carolin, C.F.; Kumar, P.S.; Saravanan, A.; Joshiba, G.; Naushad, M. Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. *J. Environ. Chem. Eng.* **2017**, *5*, 2782–2799, doi:10.1016/j.jece.2017.05.029.
11. Peterson, B.; Tietböhl, T.; Marqueze, A. Interference of heavy metals present in the water of the Lagoa Tramandaí/RS on the carbohydrate metabolism of the GURI Sea Catfish (*G. genidens*) and Bay whiff (*C. spilopterus*). *Comp. Biochem. Physiol. Part C* **2019**, *219*, 42–49, doi:10.1016/j.cbpc.2019.01.007.
12. Houri, T.; Khairallah, Y.; Zahab, A.; Osta, B.; Romanos, D.; Haddad, G. Heavy Metals Accumulation Effects on the Photosynthetic Performance of Geophytes in Mediterranean Reserve. *J. King Saud Univ.* **2019**, doi:10.1016/j.jksus.2019.04.005.
13. Meena, R.; Kannah, Y.; Sindhu, J.; Ragavi, J.; Kumar, G.; Gunasekaran, M.; Rajesh, J. Trends and resource recovery in biological wastewater treatment system. *Bioresour. Technol. Rep.* **2019**, *7*, 100235, doi:10.1016/j.biteb.2019.100235.
14. Bora, A.; Dutta, R. Removal of metals (Pb, Cd, Cu, Cr, Ni, and Co) from drinking water by oxidation-coagulation-absorption at optimized pH. *J. Water Process Eng.* **2019**, *31*, 100839, doi:10.1016/j.jwpe.2019.100839.
15. Yun, Y.; Lee, E.; Kim, K.; Han, J. Sulfate reducing bacteria-based wastewater treatment system integrated with sulfide fuel cell for simultaneous wastewater treatment and electricity generation. *Chemosphere* **2019**, doi:10.1016/j.chemosphere.2019.05.206.
16. Kazi, C.; Yamamoto, O. Effectiveness of the sodium alginate as surgical sealant materials. *Wound Med.* **2019**, *24*, 18–23, doi:10.1016/j.wndm.2019.02.001.

17. Bang, S.; Choi, J.; Cho, K.; Chung, C.; Kang, H.; Hong, S. Simultaneous reduction of copper and toxicity in semiconductor wastewater using protonated alginate beads. *Chem. Eng. J.* **2016**, *288*, 525–531, doi:10.1016/j.cej.2015.12.025.
18. Wang, S.; Mulligan, C.N. Rhamnolipid biosurfactant-enhanced soil flushing for the removal of arsenic and heavy metals from mine tailings. *Process Biochem.* **2009**, *44*, 296–301, doi:10.1016/j.procbio.2008.11.006.
19. Di Palma, L.; Petrucci, E.; Pietrangeli, B. Environmental effects of using chelating agents in polluted sediment remediation. *Bull. Environ. Contam. Toxicol.* **2015**, *94*, 340–344, doi:10.1007/s00128-014-1437-9.
20. Mao, X.; Jiang, R.; Xiao, W.; Yu, J. Use of surfactants for the remediation of contaminated soils: A review. *J. Hazard. Mater.* **2015**, *285*, 419–435, doi:10.1016/j.jhazmat.2014.12.009.
21. Chen, W.; Qu, Y.; Xu, Z.; He, F.; Chen, Z.; Huang, S.; Li, Y. Heavy metal (Cu, Cd, Pb, Cr) washing from river sediment using biosurfactant rhamnolipid. *Environ. Sci. Pollut. Res.* **2017**, *24*, 16344–16350, doi:10.1007/s11356-017-9272-2.
22. Kim, G.; Seo, Y.; Kim, I.; Han, J. Co-production of biodiesel and alginate from *Laminaria japonica*. *Sci. Total Environ.* **2019**, *673*, 750–755, doi:10.1016/j.scitotenv.2019.04.049.
23. Zeftawy, M.A.; Mulligan, C. Use of rhamnolipid to remove heavy metals from wastewater by micellar-enhanced ultrafiltration (MEUF). *Sep. Purif. Technol.* **2011**, *77*, 120–127, doi:10.1016/j.seppur.2010.11.030.
24. Kaygusuz, H.; Uzaşçı, S.; Erim, F.B. Removal of Fluoride from Aqueous Solution Using Aluminum Alginate Beads. *Clean-Soil Air Water* **2014**, *43*, 724–730, doi:10.1002/clen.201300632.
25. Wang, M.; Yang, Q.; Zhao, X.; Wang, Z. Highly efficient removal of copper ions from water by using a novel alginate-polyethyleneimine hybrid aerogel. *Int. J. Biol. Macromol.* **2019**, *138*, 1079–1086, doi:10.1016/j.ijbiomac.2019.07.160.
26. Li, Y.; Xia, B.; Zhao, Q.; Liu, F.; Zhang, P.; Du, Q.; Wang, D.; Li, D.; Wang, Z.; Zia, Y. Removal of copper ions from aqueous solution by calcium alginate immobilized kaolin. *J. Environ. Sci.* **2011**, *23*, 404–411, doi:10.1016/S1001-0742(10)60442-1.
27. Papageorgiou, S.; Katsaros, F.; Kouvelos, E.; Nolan, J.; Deit, H.; Kanellopoulos, N. Heavy metal sorption by calcium alginate beads from *Laminaria digitate*. *J. Hazard. Mater. B* **2006**, *137*, 1765–1772, doi:10.1016/j.jhazmat.2006.05.017.
28. Blando, A.; Macias, M.; Cantero, D. Formation of calcium alginate gel capsules: Influence of sodium alginate and CaCl₂ concentration on gelation kinetics. *J. Biosci. Bioeng.* **1999**, *88*, 686–689, doi:10.1016/S1389-1723(00)87103-0.
29. He, X.; Abdoli, L.; Li, H. Participation of copper ions in formation of alginate conditioning layer: Evolved structure and regulated microbial adhesion. *Colloids Surf. B Biointerfaces* **2018**, *162*, 220–227, doi:10.1016/j.colsurfb.2017.11.062.
30. Liu, Y.; Li, Z.; Wang, J.; Zhu, P.; Zhao, J.; Zhang, C.; Guo, Y.; Jin, X. Thermal degradation and pyrolysis behavior of aluminum alginate investigated by TG-FTIR-MS and Py-GC-MS. *Polym. Degrad. Stab.* **2015**, *118*, 59–68, doi:10.1016/j.polymdegradstab.2015.04.010.
31. Zhou, Q.; Xiaoyan, L.; Bin, L.; Xuegang, L. Fluoride adsorption from aqueous solution by aluminum alginate particles prepared via electrostatic spinning device. *Chem. Eng. J.* **2014**, *256*, 306–315, doi:10.1016/j.cej.2014.06.101.

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