BIO Web of Conferences **73**, 05003 (2023) https://doi.org/10.1051/bioconf/20237305003
CTReSS 5.0

Adsorption of Cu^{2+} Ions using Rubber-Based Hydrogel

Siti Salihah Jamaluddin[1], *Rozidaini* Mohd Ghazi[1*], *Nik Raihan* Nik Yusoff[1], and *Siti Fairus Mohd* Yusoff[2]

[1]Faculty of Earth Science, Universiti Malaysia Kelantan Jeli Campus, 17600 Jeli, Malaysia.
[2]Department of Chemical Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia.

Abstract. Hydrogels are one of the most powerful adsorbents for removing heavy metal ions among all adsorbents. However, most of today's hydrogels are synthetic polymers with high costs, non-environmentally friendly, and have low stability. Therefore, in this study, natural rubber (NR) was used as the basic material for hydrogels due to its high mechanical properties, plasticity or viscosity, elasticity, and tensile strength. This study is focusing on the Cu adsorption method using a rubber-based hydrogel that is prepared with a combination of acrylic acid (AA) and methylenebisacrylamide (MBA). The rubber-based hydrogel was immersed in the synthetic Cu wastewater, and the percentage removal was calculated. Cu initial concentration, contact time, and rotation speed were the three independent variables used for optimization using Response Surface Methodology (RSM). With an initial Cu concentration of 47.66 mg/L, a contact time of 10 hours, and a rotation speed of 91.32 rpm, RSM optimization shows that the best conditions for Cu removal are 72.19%. The SEM-EDX micrograph of the hydrogel before adsorption shows numerous pores, but after adsorption it is smoother and has fewer holes. This study will contribute to the development of a new method to remove Cu from wastewater.

1 Introduction

The percentage of water covered on earth surface is 70%. However, only 0.5% of water on earth accessible and available for human use. This water is come from aquifers, reservoirs, stream, lakes, rivers, and rainfall. The 97% of water is saltwater, which need to desalination before use, and 2.5% of water is frozen or stored as groundwater [1].

Metallic copper (Cu) is malleable, ductile, and a good conductor of heat and electricity. Because of its adaptability, it has a wide range of commercial applications. Pipes, cooking utensils, fittings, valves, coins, electrical wire, and building materials are all made of Cu. Munitions, alloys (brass, bronze), and coatings all contain it. Cu compounds are employed in lithography, engraving, azo dye manufacturing, petroleum refining, electroplating, and pyrotechnics, as well as in fungicides, insecticides, algicides, and wood preservatives. Cu

---

[*] Corresponding author: rozidaini@umk.edu.my

compounds can be used as a nutrient in fertilisers and animal feeds to help plants and animals flourish [2]. As stated by the USEPA [3], the Maximum Contaminant Level Goal (MCLG) established for Cu is 1.3 mg/L. The use of copper in the short term has the potential to cause gastrointestinal discomfort, however prolonged exposure to Cu can have detrimental effects on the liver or kidneys. The USEPA has classified Cu as Group D, not classifiable as to human carcinogenicity.

Rubber-based hydrogel is one of natural absorbent that can be used to remove heavy metal ion. Hydrogels are hydrophilic polymers that are cross-linked and have the ability to undergo significant water swelling when a crosslinking agent is added to the polymerization process. Since hydrogel was able to absorb and capture ionic dyes and metals, hydrogels of chains of hydrophilic polymer are also efficient adsorbents of dyes and heavy metals. Various forms of hydrogels, such as cellulose, polyvinyl alcohol, carboxymethyl cellulose, starch, and polyacrylamide, have been used as adsorbent in heavy metal removal. However, most of the hydrogels are synthetic polymers with high cost, non-environment friendly and low stability [4].

In order to overcome these limitations, the raw material that was utilised was natural rubber (NR). The reason for this can be attributed to the high mechanical properties exhibited by natural rubber (NR). NR exhibit characteristics such as plasticity or viscosity, elasticity, and tensile strength. NR is derived from the rubber tree, scientifically known as *Hevea brasiliensis*, which possesses a cis 1,4-polyisoprene chain. The unsaturated C=C bond present in its chain create natural rubber with poor heat resistance to weather and reagents [4]. The hydrophilic polymer known as acrylic acid (AAc) is subjected to crosslink in order to enhance its adsorption flux and hydrogel selectivity. This is due to the fact that the functional group present in hydrophilic polymers, such as AAc, can directly interact with water molecules [5, 6].

Various types of pollutants such as nickel, methylene blue, and malachite green have been previously studied using rubber-based hydrogel [4, 7, 8]. Several low-cost agriculture wastes have adsorption capability for removing Cu from wastewater, such as rice husk [9], banana peel, fish scale [10], chitosan [11], sawdust [12], neem leaves [13], waste tea leaves [14], coconut shell, orange peel [15] and watermelon rind [16]. However, there is no report on the application of rubber-based hydrogel for Cu adsorption. Therefore, the aim of this study is to assess the adsorption capacity of a hydrogel composed of rubber-based materials derived from liquid natural rubber (LNR) and acrylic acid (AAc). This will be achieved through the utilisation of N,N-methylenebisacrylamide (MBA) as a crosslinking agent and potassium persulfate (KPS) as an initiator. Optimization using Response Surface Methodology (RSM) was also studied and discussed.

2 Methodology

2.1 Materials

The Rubber Research Institute of Malaysia (RRIM) provided the supply of natural rubber (NR). The AAc monomer, MBA, potassium persulfate (KPS), and copper sulphate pentahydrate ($CuSO_4 \cdot 5H_2O$) were purchased from Sigma Aldrich. Sodium dodecyl sulphate (SDS) was purchased from Systerm.

2.2 Synthesis of Rubber-based hydrogels

The procedure employed by Azhar et al. [17] was utilised to produce liquid natural rubber (LNR) without any modifications. For the synthesis of rubber-based hydrogels, 4 g of maleic anhydride (MaH) in 20 mL toluene and 0.3 g of free radical initiator benzoyl peroxide (BPO) in 20 mL toluene were added into 6 g of LNR solution to produce maleated LNR. The mixture was stirred for 2 hours at 80°C, followed by a further drying process in a vacuum oven at 40°C for 24 hours. Then, 8 mL of distilled water was added to the 0.3 g of the powder obtained and it was sonicated at 60°C. Following a duration of 30 minutes, a solution consisting of 88 mg of potassium persulfate (KPS) and 28 mg of sodium dodecyl sulphate (SDS) was prepared by dissolving these substances in 5.5 mL of distilled water. Subsequently, this solution was added into the mixture. The sonication process continued for another 30 minutes. Then, 0.08 g of crosslinking agent N,N-methylenebisacrylamide (MBA) was dissolved in 16 mL distilled water and added to the mixture. Lastly, 4 g of acrylic acid (AA) hydrophilic monomer was added into the mixture and sonicated for approximately 1.5 hours until the hydrogel was formed. The hydrogel underwent a drying process in a vacuum oven at 70°C for 24 hours.

2.3 Preparation of Cu synthetic wastewater

The present study utilised synthetic wastewater containing copper (Cu) for experimental purposes. In order to create a Cu stock solution with a concentration of 1000 mg/L, approximately 0.396 g of $CuSO_4 \cdot 5H_2O$ were dissolved in 100 mL of deionized water. The initial stock solution was diluted to achieve the desired concentrations of 20, 50, and 80 mg/L. The concentration of Cu was recorded by employing an Atomic Absorption Spectrophotometer (AAS).

2.4 Optimization of Cu Removal

The effect of reaction parameters on the percentage of Cu removal was investigated using RSM through the implementation of a Box-Behnken design. The data was analysed using Design Expert Software version 6.0.8. A rubber-based hydrogel, weighing 0.1 g, was submerged in roughly 10 mL of synthetic wastewater containing Cu. In the experimental procedure, the Cu initial concentration, the effect of contact time, and rotation speed were adjusted according to the conditions outlined in Table 1. A series of 17 experimental runs was done using the RSM approach. The residual content of Cu was analysed using AAS. The Cu removal percentage was determined using Eq. 1.

$$\text{Percentage removal (\%)} = \frac{(C_0 - C_e)}{C_e} \times 100 \qquad (1)$$

where C_0 and C_e was the initial and final Cu solution concentrations (mg/L), respectively.

For statistical calculations, the three independent variables were labelled A (Cu initial concentration), B (contact time) and C (rotation speed). The value for each parameter was used based on preliminary test. The statistical techniques employed in this study included analysis of variance (ANOVA), regression analysis, and the generation of response plots. These methods were utilised to examine the observed outcomes and identify the optimal conditions for the reaction.

Table 1. Parameter Affecting Cu Percentage Removal.

Parameter level	-1	0	+1
Initial Concentration of Cu, A (mg/L)	20	50	80
Contact time, B (h)	2	13	24
Rotation Speed, C (rpm)	0	50	100

2.5 Characterization of Rubber-Based Hydrogel

The study involved the examination of the morphology of the rubber-based hydrogel both before and after adsorption. This was accomplished through the utilisation of an Field Emission Scanning Electron Microscope (FESEM, FEI Verios 460L), equipped with Energy Dispersive X-ray Spectroscopy (EDX), at various levels of magnification.

3 Results and Discussion

3.1 Optimization of Cu Removal

The optimization of Cu removal by rubber-based hydrogel was conducted using RSM via Box-Behnken Design. The reaction design with three parameters i.e., contact time, initial concentration, and rotation speed, was employed for Cu adsorption. The Design Expert software version 6.0.8 was utilised to employ a model-fitting technique in order to determine the expected values for the parameters. Table 2 presents the percentage removals that were obtained from 17 experimental runs.

Table 2. Box-Behnken Design for all parameter and their percentage removal.

Standard Order	Contact Time (h)	Initial Concentration (mg/L)	Rotation speed (rpm)	Percentage Removal (%)	
				Actual	Predicted
1	2	20	50	10.43	12.55
2	24	20	50	49.01	48.43
3	2	80	50	32.73	33.31
4	24	80	50	13.02	10.90
5	2	50	0	18.63	15.70
6	24	50	0	56.79	56.57
7	2	50	100	58.69	58.91
8	24	50	100	28.57	31.50
9	13	20	0	34.74	35.55
10	13	80	0	31.4	33.75
11	13	20	100	53.55	51.20
12	13	80	100	37.05	36.24
13	13	50	50	66.81	64.72
14	13	50	50	53.36	64.72
15	13	50	50	72.03	64.72
16	13	50	50	68.07	64.72
17	13	50	50	63.33	64.72

The findings indicate that there was a strong correlation between the observed data and the expected values. A quadratic polynomial equation for the rubber-based hydrogel was the best fit for the data. Eq. 2 provides an empirical relationship between the response variable and the independent variables inside the coding unit, as inferred from the experimental data.

$$\begin{aligned} Percentage\ removal\ (\%) &= +64.72 + 3.36A - 4.19B + 4.54C - 18.74A^2 - 18.47B^2 - 5.58C^2 \\ &- 14.57AB - 17.07AC - 3.29BC \end{aligned} \tag{2}$$

where the coded variables A, B, and C represent the initial concentration of Cu solution, reaction time, and rotation speed, respectively.

The primary linear (A, B, C), quadratic (A^2, B^2, and C^2), and interaction (AC and BC) effects, characterised by positive and negative signs, demonstrate distinct impacts on the percentage of adsorption. Positive signals imply a synergistic effect, while negative values indicate an antagonistic effect. Table 3 shows the statistical findings related to the quadratic equation of removal percentage of rubber-based hydrogel, as analysed by ANOVA method. According to Bezerra et al. [18], a higher F value and a lower P value indicate a greater level of significance for the related coefficient term.

Table 3. ANOVA of the response from of Cu^{2+} removal using rubber-based hydrogel.

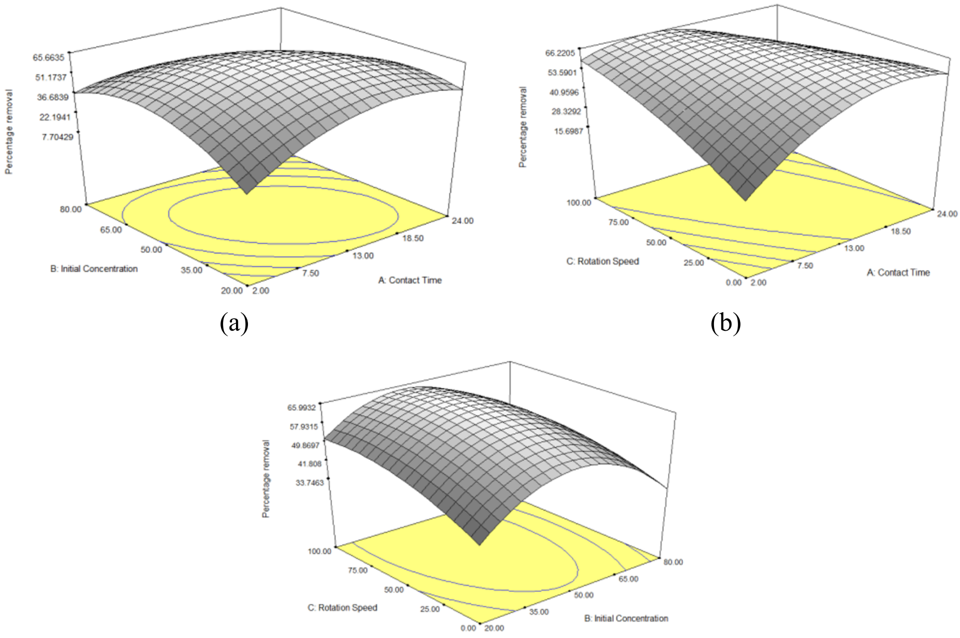
Sources	Sum of Squares	Degree of Freedom	Square	F Value	Prob > F	
Model	5991.23	9	665.69	19.47	0.0004	significant
A	90.52	1	90.52	2.65	0.1477	
B	140.53	1	140.53	4.11	0.0822	
C	164.71	1	164.71	4.82	0.0642	
A^2	1436.19	1	1436.19	42.01	0.0003	
B^2	1676.43	1	1676.43	49.04	0.0002	
C^2	131.16	1	131.16	3.84	0.091	
AB	849.43	1	849.43	24.85	0.0016	
AC	1165.54	1	1165.54	34.09	0.0006	
BC	43.3	1	43.3	1.27	0.2975	
Residual	239.31	7	34.19			
Lack of Fit	39.3	3	13.1	0.26	0.85	not significant
Pure Error	200.01	4	50			
Cor Total	6230.53	16				

Table 3 displays the F value and P value of lack-of-fit for the reaction involving the elimination of Cu^{2+} using a rubber-based hydrogel, which were determined to be 0.26 and 0.85, respectively. This implies that the F value for lack-of-fit is statistically significant, as the P value is lower than the predetermined significance level. Consequently, there is a high probability, approximately 85%, of observing lack-of-fit in the model. According to Shojaeimehr et al. [19], the hydrogel Box Behnken models are deemed appropriate for the experiment. The authors state that a model is considered well-fitted to an experiment when it exhibits regression and a lack-of-fit that is not statistically significant [19]. The coefficient of determination (R^2) for the quadratic model was determined to be 0.9616, suggesting a strong connection between the model and the observed data, as R^2 values above 0.9 are considered high. The R^2 values indicate that the independent variable accounted for 96.16% of the total variation in the observed outcomes. Meanwhile, the adjusted R-squared value (R^2 adj) was determined to be 0.9122. The adjusted R-squared value closely approximated the R-squared value, suggesting that the statistical model is robust in explaining the variation in the responses [19]. The response model exhibited a quadratic polynomial form in the rubber-based hydrogel, which proved to be highly sufficient in accurately representing the relationship between the response and the parameter.

3.2 Effect of Reaction Parameters

The utilisation of 3D response surface plots enhances understanding of the interaction influence between the initial concentration of Cu solution, reaction time, and rotation speed.

The utilisation of a 3D response surface plot enables the determination of the ideal level for each parameter of interest in determining the response. Figure 1 displays the response surface plots illustrating the effect of the factors on the percentage of Cu removal.



(a) (b)

(c)

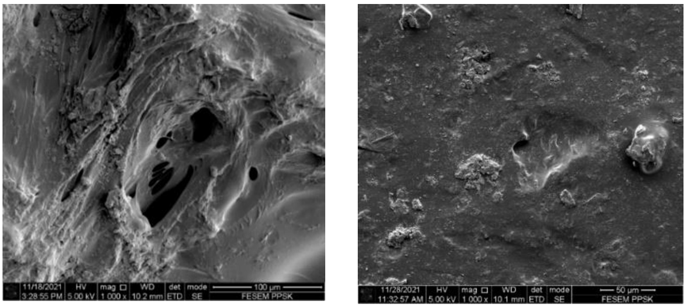
Fig. 1. Response surface plots for the effects of the parameters on the percentage Cu removal (a) initial concentration of Cu solution and the reaction time contact time (b) rotation speed and the reaction time (c) rotation speed and the initial concentration of Cu solution.

The response surface plot presented in Figure 1(c) indicates that the maximum percentage removal of Cu observed was 64.72%. This occurred under the following conditions: an initial concentration of 50 mg/L, a reaction period of 13 hours, and a rotation speed of 50 rpm. As the concentration of Cu solution increases, there is an observed rise in the adsorption of Cu molecules on the surface of the rubber-based hydrogel. This leads to a corresponding decrease in the availability of active sites [8].

The validation of experimental results indicate that the optimal rotation speed achieved was 91.32 revolutions per minute (rpm) when the contact duration was set at 10 hours. At this configuration, the percentage removal of the Cu reached 72.19%. The adsorption capacity and efficiency of heavy metal removal were enhanced with an increase in the shaking speed. The enhancement of shaking speed resulted in an improvement in the efficacy of heavy metal removal and adsorption. The dispersion of heavy metal ions from the hydrogel surface and pores can be achieved in a rapid and efficient manner [20].

3.3 Characterization of Rubber-Based Hydrogel

As shown in Figure 2, the morphology of rubber-based hydrogel before and after analysis have been examined using FESEM.

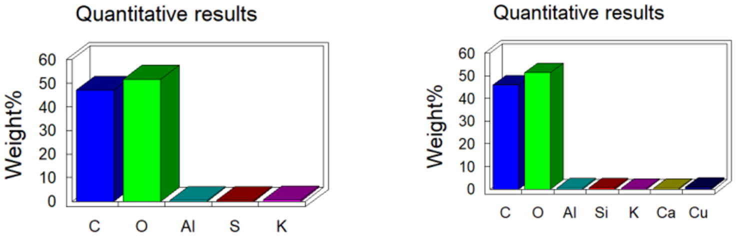


(a) (b)

Fig. 2. FESEM micrograph of hydrogel (a) before adsorption (b) after adsorption.

The porosity and mean pore size of a hydrogel determine its water absorbency and retention rate. In Figure 2(a), the holes on the polymer's surface, which are visible and dispersed over the surface. The existence of holes in hydrogel networks aided the transit and retention of water molecules. As the concentration of Cu rises, the hydrogel morphology becomes smoother and less holes are visible, as illustrated in Figure 2(b). This finding illustrates that an increase in the Cu concentration within the hydrogel leads to an increase in the network density of the hydrogel, thereby leading in a reduction in the number and size of pores [4].

Figure 3(a) and Figure 3(b) show the morphology of a rubber-based hydrogel before and after adsorption, as determined by EDX. The magnification of EDX is 500x.



(a) (b)

Fig. 3. EDX analysis of rubber-based hydrogel (a) before and (b) after adsorption.

Figure 3(a) shows that there were no Cu elements found before adsorption process, but Figure 3(b) shows that 0.2 % atomic Cu was found on the surface of the rubber-based hydrogel after adsorption. Heavy metal ions on the polymer have been found using EDX analysis. The Cu element is scattered across the hydrogels' surface.

4 Conclusion

The technology of removing heavy metals in industrial effluent were very crucial in order to prevent heavy metal from entering our water body. This study focused on the technology in removing Cu from synthetic wastewater by using rubber-based hydrogel. 17 tests have been run and analysed their percentage removal using RSM. The characterization of the rubber-based hydrogel before and after adsorption have been done using FESEM-EDX. The findings of this study indicate that when the concentration of Cu solution increases, there is a corresponding increase in the adsorption of Cu molecules on the surface of the rubber-based hydrogel. Consequently, this leads to a decrease in the availability of active sites. The optimized percentage removal of Cu was 72.19% with 10 h contact time, 47.66 mg/L initial concentration of Cu solution and 91 rpm rotation speed. The pore on the rubber-based hydrogel before adsorption were bigger than the pore after adsorption. The Cu that is absorbed by the rubber-based hydrogel is observable on its surface.

Acknowledgement

The authors would like to express their gratitude to the Ministry of Higher Education Malaysia (MOHE), Universiti Malaysia Kelantan (UMK), and Universiti Kebangsaan Malaysia (UKM) for their valuable technical support and provision of facilities.

References

1. H. B. Beth, O. Austin, A. A. Caleb, Water Availability and Use, 163–174. (2016)
2. World Health Organization Cu in Drinking-water. WHO Guidelines for Drinking-Water Quality (2004).
3. US EPA. National Primary Drinking Water. RegulationsRetrieved from https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations. (2021)
4. F. Firdaus, M.S.F. Idris, S.F.M. Yusoff, J. Polym. Environ **27**(8), 1770–1780 (2019).
5. N.H. Ahmad, M.A. Mohamed, S.F.M. Yusoff. J. Solgel. Sci. Technol **94**(2), 322–334 (2020).
6. E. M. Ginting, N.M. Bukit, E. Frida, IOP Conf. Ser. Mater. Sci. Eng **223**(1), 012003 (2017).
7. N. F. Mohd Noor, S.F.M. Yusoff, Polym. Test **81**, 106200 (2020).
8. M. Krishnamoorthy, N.H. Ahmad, H.N. Amran, M.A. Mohamed, N.H.M. Kaus, S.F.M. Yusoff, Int. J. Biol. Macromol **182,** 1495–1506 (2021).
9. A.F. Malik, N. Hamidon, J. Adv. Ind. Technol. Appl **2**(01), 36–42 (2021).
10. A. Darge, S. J. Mane, Int. J. Sci. Res **4**(7), 2319–7064 (2013).
11. S. Yasmeen, M. Kabiraz, B. Saha, M. Qadir, M. Gafur, S. Masum, Int. Res. J. Pure Appl. Chem **10**(4), 1–14 (2016).
12. Z. Kovacova, S. Demcak, M. Balintova, Proc **16**(1), 52 (2019).
13. S.S. Al Moharbi, M.G. Devi, B.M. Sangeetha, S. Jahan, Appl. Water Sci **10**(1). 1–10. (2020).
14. H. Naihi. Mater. Sci. Forum. **997**, 113–120 (2020).
15. S. Tadepalli, K.S.R. Murthy, N.N. Rakesh, Int. J. Pharmtech Res **9**(5), 197–210 (2016).
16. W.J. Mwegoha, W. Lema, Int. J. Environ. Monit. Protec **5**(3), 40–51 (2018).
17. N.H.A. Azhar, H. Md Rasid, S.F.M. Yusoff, AIP Conf. Proc **1784**(1), 030024 (2016).
18. M.A. Bezerra, R.E. Santelli, E.P. Oliveira, L.S. Villar, L.A. Escaleira, Talanta **76**(5), 965–977 (2008)
19. T. Shojaeimehr, F. Rahimpour, M.A. Khadivi, M. Sadeghi, J. Ind. Eng. Chem **20**(3), 870–880 (2014).
20. N. Sezgin, N. Balkaya, Desalin. Water Treat **57**(6), 2466–2480 (2016).