Enhancing Water Quality: Application of Coconut Shell Activated Charcoal for Sulfide and Ammonia Removal from Tofu Industry Wastewater

Asnawati^[a], Novita Andarini^[a], Tri Mulyono*^[a], Maimunah Noer Aini^[a], Nur Fitriyah^[a], Siswoyo^[a], Zulfikar^[a], Yeni Maulidah Muflihah^[a]

Abstract: This study investigates the optimization of an adsorption process using activated coconut shell charcoal to reduce sulfide and ammonia levels in tofu industry wastewater. These pollutants pose significant environmental risks due to their biodegradable nature. Experimental parameters, including adsorbent particle size (50, 60, and 70 mesh), heating temperature (40, 80, 120 $^{\circ}$ C, and ambient), and contact time (15-60 minutes for sulfide, 20-100 minutes for ammonia), were

systematically varied to determine optimal conditions. The initial sulfide and ammonia concentrations in the wastewater exceeded regulatory limits at 0.169 mg/L and 8.177 ppm, respectively. The results indicate that 70-mesh activated charcoal at ambient temperature achieved maximum pollutant removal: 93.46% for sulfide with a 30-minute contact time and 93.693% for ammonia with a 40-minute contact time. These findings offer a promising approach to mitigating the environmental impact of tofu industry wastewater.

Keywords: adsorption, activated coconut shell charcoal, ammonia, sulfide, tofu industry wastewater.

INTRODUCTION

The tofu industry, while providing a valuable source of protein, generates significant amounts of liquid waste. This wastewater, laden with organic compounds, particularly proteins and sulfur-containing compounds, undergoes microbial decomposition [1], [2]. This process results in the formation of harmful pollutants such as ammonia and sulfide. These pollutants not only contribute to foul odors but also pose serious environmental risks, exceeding permissible limits set by environmental regulations [3], [4]. To address this issue, effective treatment methods are crucial to mitigate the negative impacts of tofu industry wastewater on the environment.

One common method for treating tofu industry wastewater involves adsorption using activated charcoal [5],[6] . This porous material effectively adsorbs impurities, preventing environmental pollution [7, 8, 9]. Activated charcoal offers several advantages, including low cost, simple production, and diverse raw material sources, such as coconut shells, wood, husks, bagasse, corn cobs, coconut fiber, bones, coal, and papermaking waste [10,11, 12].

Previous research has demonstrated the efficacy of activated charcoal for reducing pollutants in wastewater. Suryono et al. (2018) successfully reduced hydrogen sulfide and ammonia levels in pond water using coconut shell-based activated charcoal, achieving average reductions of 71.43% and 80%, respectively [13]. Amin et al. (2016) employed corn cob-derived activated charcoal to reduce ammonia levels by an average of 51.29% [14]. Additionally, Irmanto and Suyata (2009) utilized coffee ground-based adsorbents to reduce ammonia levels in tofu industry wastewater by 64.69% [15].

The aforementioned studies collectively indicate that coconut shell-based activated charcoal is a highly effective adsorbent for reducing sulfide and ammonia levels in wastewater. This study aims to further explore the potential of coconut shell-activated charcoal to adsorb sulfide and ammonia from tofu industry wastewater, thereby mitigating the associated foul odor and discoloration.

METHODS

Chemicals and Materials

The study utilized various chemicals and materials, including Sodium hydroxide (NaOH) and Hydrochloric acid (HCl) from Merck, p-Aminodimethylaniline dihydrochloride, Iron(III) chloride hexahydrate (FeCl₃ $\n 6H_2O$), Sodium sulfide nonahydrate ($Na₂S₉H₂O$), and Potassium iodide (KI) from Merck, and Mercury(II) iodide $(HgI₂)$ from RdH. Ammonium chloride (NH₄Cl) from Merck was also used. Additionally, commercial coconut shell activated charcoal, distilled water, and aquabides were employed for various experimental purposes. These materials were critical in achieving accurate and reliable results, ensuring the integrity of the study's findings.

Equipment and Instruments

The equipment utilized in this study includes standard laboratory glassware, an analytical balance for precise mass measurements, GENESYS V-Vis spectrophotometer for absorbance and transmittance analysis, and edge® HI2002 digital pH meter for accurate pH measurement. These instruments were essential for conducting the experiments and obtaining reliable data.

Sampling Methodology

Liquid waste samples were collected from the final storage tank of a tofu factory situated in Gebang Subdistrict, Jember. Samples were obtained using the grab sampling method during peak production hours (06:00 WIB) and post-production (11:00 WIB)

[[]a] Asnawati, N. Andarini, T. Mulyono, M. N. Aini, N. Fitriyah, Siswoyo, Zulfikar, Y. M. Muflihah

Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Jember

^{*}e-mail: trimulyono.fmipa@unej.ac.id

Determination of Maximum Wavelength

Spectrophotometric analysis was employed to identify the optimal wavelength for quantifying sulfide and ammonia. A standard sulfide solution (0.02 mg/L) was reacted with paminodimethylaniline and FeCl3, while a standard ammonia solution (10 ppm) was treated with Nessler's reagent. Absorbance spectra were recorded for both solutions across the 400-700 nm and 300-600 nm ranges, respectively, at 10 nm intervals. The wavelength corresponding to maximum absorbance for each analyte was determined to establish optimal conditions for sensitive and accurate measurement.

Determination of Sulfide and Ammonia Content in Sample

Spectrophotometry was utilized to quantify sulfide and ammonia in liquid waste samples. A 10 mL aliquot of each sample was reacted with p-aminodimethylaniline and FeCl3 for sulfide analysis, while a 50 mL portion was filtered and treated with Nessler's reagent for ammonia analysis. The absorbance of the resulting solutions was measured at their respective maximum wavelengths using a UV-Vis spectrophotometer. Subsequently, the concentrations of sulfide and ammonia were calculated using pre-established calibration curves.

Preparation of Coconut Shell Activated Charcoal Adsorbent

a. *Determination of optimum particle size of activated charcoal*

Activated charcoal samples were sieved to 50, 60, and 70 mesh sizes to evaluate their adsorption capacity for sulfide and ammonia. For sulfide, 1 g of each size was contacted with 20 mL of liquid waste for 30 minutes, filtered, and analyzed using the paminodimethylaniline-FeCl³ method. For ammonia, 5 g of each size was contacted with 50 mL of liquid waste for 40 minutes, filtered, and analyzed using the Nessler's reagent method. The residual sulfide and ammonia concentrations in the treated samples were determined spectrophotometrically.

b. *Determination of optimum temperature of activated carbon* Activated charcoal samples of optimal particle size were

thermally treated at 40°C, 80°C, and 120°C for 2 hours to assess the effect of temperature on their adsorption capacity for sulfide and ammonia. A non-heated control sample was also prepared. For sulfide adsorption, 1 g of each sample was contacted with 20 mL of liquid waste for 30 minutes, filtered, and analyzed using the p-aminodimethylaniline-FeCl³ method. For ammonia adsorption, 5 g of each sample was contacted with 50 mL of liquid waste for 40 minutes, filtered, and analyzed using the Nessler's reagent method. The residual sulfide and ammonia concentrations in the treated samples were determined spectrophotometrically.

c. *Determination of optimum contact time of activated carbon*

To optimize the adsorption process, the contact time between the activated charcoal (optimally sized and thermally treated) and the liquid waste was varied. For sulfide adsorption, 1 g of activated charcoal was contacted with 20 mL of liquid waste for 15 minutes. For ammonia adsorption, 5 g of activated charcoal was contacted with 50 mL of liquid waste for 20, 40, 60, 80, and 100 minutes [16]. After filtration, the resulting filtrates were analyzed for residual sulfide and ammonia concentrations using UV-Vis spectrophotometry with the p-aminodimethylaniline-FeCl₃ and Nessler's reagent methods, respectively.

d. *Adsorption of sulfide and ammonia*

Research Article INDONESIAN CHIMICA LETTERS

To mitigate sulfide and ammonia concentrations in liquid waste, an activated charcoal adsorption technique was implemented. A 20 mL aliquot of the sample was buffered and contacted with 1 g of activated charcoal under optimized conditions. Subsequently, the mixture was filtered, and 10 mL of the filtrate was reacted with p-aminodimethylaniline and ferric chloride.

For ammonia analysis, a 50 mL aliquot of the sample was buffered with universal buffer and contacted with 5 g of activated charcoal under optimized conditions. The mixture was filtered, and Nessler's reagent was added to the filtrate.

Both treated samples were analyzed using UV-Vis spectrophotometry to quantify the concentrations of sulfide and ammonia.

e. *Calculation of reduction in sulfide and ammonia content* Determination of the reduction in sulfide and ammonia content was performed using Equation:

% reduction
$$
=\frac{C_i - C_f}{C_i} \times 100\%
$$
 (1)

 C_i = Initial Concentration (before adsorption) C_f = Final Concentration (after adsorption).

RESULT AND DISCUSSION

This study aims to quantify sulfide and ammonia concentrations in tofu industry liquid waste and evaluate the efficacy of activated charcoal adsorption for their reduction. Sulfide levels were determined colorimetrically by forming a bluish-green complex upon the addition of paminodimethylaniline and ferric chloride (FeCl₃ \cdot 6H₂O) to the sample [17], [18]. The relevant chemical reactions are as follows:

$$
2 + s^{2} + 6 Fe^{3} + \cdots + s^{2} + 6 Fe^{3} + \cdots + s^{2} + 6 Fe^{2} + NH_{4}
$$

Ammonia concentrations in the samples were determined using the Nessler method, a colorimetric technique known for its accuracy and reliability [19]. This method involves the reaction of ammonia with Nessler's reagent, resulting in a color change that is proportional to the concentration of ammonia present in the sample. The intensity of the color, which varies from pale yellow to deep brown, is measured using a spectrophotometer, allowing for the precise quantification of ammonia levels [20], [21]. This approach ensures that even low concentrations of ammonia can be accurately detected and measured, providing essential data for the analysis. The underlying chemical reactions are as follows:

$$
NH_4^+ + 2[HgI_4]^{2-} + 4OH^- \longrightarrow Hg_2O(NH_2)I + 7I^- + 3H_2O
$$

yellow brown

Table 1. reveals that the sulfide concentration in the tofu industry liquid waste from the Gebang area, Jember, was measured at 0.169 mg/L. This value surpasses the maximum permissible limit of 0.1 mg/L for sulfide in Group B water quality standards. Similarly, the ammonia concentration of 8.177 ppm exceeds the allowable range of 0.02-0.1 mg/L for ammonia in

water quality standards.

	Sulfide		Ammonia					
Repetition	Absorbance	Concentration (mg/L)	Absorbance				Concentration (ppm)	
	0.205	0,168	3,004	3.001	3.000	8.184	8.177	8,172
2	0,207	0,169	3,002	3,000	3,001	8,178	8,172	8,175
3	0.207	0,169	3,000	3,003	3.003	8.172	8.179	8.179
Average Concentration		0,169				8,177		

Table 1. Sulfide and Ammonia Content in Tofu Industry Liquid Waste

Determination of Optimum Activated Carbon Particle Size

The particle size of activated carbon significantly influences the adsorption process, with smaller particle sizes generally enhancing adsorption efficiency. In this study, coconut shell activated carbon was utilized, with particle size variations of 50, 60, and 70 mesh. This variation in particle size was systematically examined to determine its impact on the adsorption capacity.

Figure 1. Relationship Curve between Coconut Shell Activated Charcoal Particle Size and Absorbance of Tofu Industry Liquid Waste Samples

Figure 1 illustrates that the optimal particle size for activated charcoal is 70 mesh, corresponding to the lowest absorbance values of 0.121 for sulfide and 1.201 for ammonia. This reduction in absorbance can be attributed to the increased surface area of the smaller particle size, enhancing the adsorption capacity for sulfide and ammonia in the sample.

Determination of the Optimal Temperature for Activated Carbon

The optimal temperature for activated carbon is the temperature at which it exhibits maximum adsorption capacity. Temperature significantly influences the adsorption process. Elevating the temperature can improve the pore structure of activated carbon, thereby enhancing its adsorption capacity.

Figure 2 indicates that the lowest absorbance values were achieved using unheated coconut shell activated charcoal (27℃), with absorbance values of 0.013 for sulfide and 0.346 for ammonia. The unheated activated charcoal demonstrated superior adsorption capacity for sulfide and ammonia compounds in tofu industry liquid waste compared to the heated activated charcoal. This enhanced performance can be attributed to the fact that heating the activated charcoal reduces its surface area, thereby diminishing its adsorption efficiency.

Determination of Optimal Contact Time for Activated Carbon

The optimal contact time for activated carbon is the duration required for the activated carbon to achieve maximum adsorption efficiency on the sample. Adequate contact time is essential for coconut shell activated carbon to effectively adsorb sulfide and ammonia compounds present in tofu industry liquid waste samples.

Figure 3 demonstrates that the optimal contact time for activated charcoal to reduce sulfide levels in tofu industry liquid waste samples is 30 minutes, resulting in a minimum absorbance value of 0.020. For ammonia reduction, the optimal contact time is 40 minutes, corresponding to an absorbance value of 0.287. Beyond these optimal contact times, a decrease in adsorption efficiency is observed, as indicated by an increase in absorbance

values. This trend suggests that the coconut shell activated charcoal reaches saturation, limiting further adsorption capacity.

The stable absorbance values observed for Sulfide over time suggest that its adsorption is either unaffected by the treatment or reaches equilibrium rapidly. Conversely, Ammonia displays a more complex adsorption profile, characterized by an initial decrease followed by a steady increase in absorbance. This contrasting behavior indicates that the treatment process exerts a distinct influence on Ammonia adsorption compared to Sulfida.

The rise in Ammonia absorbance after 40 minutes may be attributed to desorption, reduced adsorption efficiency due to saturation, or other dynamic interactions. This graphical analysis offers valuable insights into the adsorption behaviors of Sulfide and Ammonia, highlighting the efficacy and limitations of the employed treatment process. Further research is warranted to elucidate the underlying mechanisms driving these variations, potentially leading to optimized treatment conditions for enhanced waste management

Reduction of Sulfide and Ammonia Levels in Liquid Waste

Treatm	Repetit	Absorb	Absorb	Concentr	Concentr		
ent	ion	ance	ance	ation	ation		
			average	(mg/L)	average		
Before	1	0,205		0.168			
immers	2	0,207	0,206	0,169	0,169		
ion	3	0,207		0,169			
		0,021		0,017			
	1	0,023		0,019			
		0,024		0,020			
After		0,005		0,004			
immers	2	0,008	0,013	0,006	0,011		
ion		0,010		0,008			
		0,008		0,007			
	3	0,009		0,007			
		0,013		0,011			
Differe			0,193		0,158		
nce							
Table 2. Decrease in Ammania Contant in Samples							

Table 2. Decrease in Sulfide Content in Samples

Research Article INDONESIAN CHIMICA LETTERS

The reduction in levels refers to the decrease in concentration of a substance within a sample after treatment. In the specific context of sulfide and ammonia, this reduction is achieved through adsorption onto coconut shell activated charcoal. This process effectively lowers the concentrations of these pollutants in the liquid waste, thereby improving the overall quality of the treated effluent, as evidenced by Tables 2 and 3.

The calculated percentage reductions in sulfide and ammonia levels in tofu industry liquid waste, achieved through the application of coconut shell activated charcoal as an adsorbent, were notably significant. Specifically, the reduction in sulfide levels was measured at 93.46%, while the reduction in ammonia levels reached 93.693%. These results underscore the high efficacy of coconut shell activated charcoal in adsorbing both sulfide and ammonia contaminants from the liquid waste. Such substantial reductions not only highlight the potential of this adsorbent material in improving waste treatment processes but also demonstrate its capability to contribute to environmental protection and regulatory compliance by effectively lowering pollutant concentrations in industrial effluents.

CONCLUSION

The use of coconut shell activated charcoal as an adsorbent resulted in a significant reduction of 93.46% in sulfide levels and 93.693% in ammonia levels in tofu industry liquid waste. These substantial reductions demonstrate the effectiveness of coconut shell activated charcoal in adsorbing both sulfide and ammonia from the liquid waste. These high percentage reductions suggest that this adsorbent material offers a highly efficient and sustainable solution for treating industrial liquid waste, ensuring environmental safety and compliance with regulatory standards.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the Department of Chemistry, University of Jember, for providing the necessary research facilities.

REFERENCES

- [1] S. A. Avia, B. Kamulyan, and A. T. Yuliansyah, "Bioremediation of tofu industry liquid waste using Effective Microorganism-4 (Em4) solution (Case study of Tofu Sentosa Industry, Yogyakarta)," *ASEAN J. Syst. Eng.*, vol. 6, no. 1, pp. 21-26, 2022, doi: 10.22146/ajse.v6i1.75615.
- [2] W. Widayat, J. Plilia, and J. Wibisono, "Liquid waste processing of tofu industry for biomass production as raw material biodiesel production," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 248, p. 12064, Apr. 2019, doi: 10.1088/1755-1315/248/1/012064.
- [3] M. T. Piccardo, M. Geretto, A. Pulliero, and A. Izzotti, "Odor emissions: A public health concern for health risk perception," *Environ. Res.*, vol. 204, p. 112121, 2022, doi: https://doi.org/10.1016/j.envres.2021.112121.
- [4] S. S. Shetty *et al.*, "Environmental pollutants and their effects on human health," *Heliyon*, vol. 9, no. 9, p. e19496, 2023, doi: https://doi.org/10.1016/j.heliyon.2023.e19496.

- [5] O. A. Odubiyi, A. A. Awoyale, and A. Eloka-Eboka, "Wastewater treatment with activated charcoal produced from cocoa pod husk," *Int. J. Environ. Bioenergy*, vol. 4, pp. 162-175, Dec. 2012.
- [6] K. Budhiary and I. Sumantri, "Langmuir and Freundlich isotherm adsorption using activated charcoal from banana peel to reduce Total Suspended Solid (TSS) levels in tofu industry liquid waste," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 1053, p. 12113, Feb. 2021, doi: 10.1088/1757- 899X/1053/1/012113.
- [7] X. Liu *et al.*, "Advanced porous nanomaterials as superior adsorbents for environmental pollutants removal from aqueous solutions," *Crit. Rev. Environ. Sci. Technol.*, vol.
53, no. 13, pp. 1289-1309, Jul. 2023, doi: 1289-1309, Jul. 2023, doi: 10.1080/10643389.2023.2168473.
- [8] A. Palliyarayil *et al.*, "Advances in porous material research towards the management of air pollution," *Emergent Mater.*, vol. 4, no. 3, pp. 607-643, 2021, doi: 10.1007/s42247-020-00151-9.
- [9] P. Franco, S. Cardea, A. Tabernero, and I. De Marco, "Porous aerogels and adsorption of pollutants from water and air: A review," *Molecules*, vol. 26, no. 15, Jul. 2021, doi: 10.3390/molecules26154440.
- [10] M. A. Tadda *et al.*, "A review on activated carbon: process, application and prospects," vol. 2, pp. 7-13, Jun. 2016.
- [11] Y. A. B. Neolaka *et al.*, "Potential of activated carbon from various sources as a low-cost adsorbent to remove heavy metals and synthetic dyes," *Results Chem.*, vol. 5, p. 100711, 2023, 100711, 2023, doi: https://doi.org/10.1016/j.rechem.2022.100711.
- [12] R. Kumar Mishra, B. Singh, and B. Acharya, "A comprehensive review on activated carbon from pyrolysis of lignocellulosic biomass: An application for energy and the environment," *Carbon Resour. Convers.*, vol. 7, no. 4, p. 100228, 2024, doi: https://doi.org/10.1016/j.crcon.2024.100228.
- [13] C. Suryono, I. Irwani, S. Suryono, E. Susilo, S. Subagiyo, and S. Widada, "Karbon aktif tempurung kelapa untuk peningkatan kualitas air tambak," *J. Kelaut. Trop.*, vol. 21, p. 71, Apr. 2018, doi: 10.14710/jkt.v21i1.2375.
- [14] A. Amin, S. Sitorus, and B. Yusuf, "Pemanfaatan limbah tongkol jagung (*Zea mays* L.) sebagai arang aktif dalam menurunkan kadar amonia, nitrit dan nitrat pada limbah cair industri tahu menggunakan teknik celup," *J. Kim. MULAWARMAN,* vol. 13, no. 2, Jun. 2016, [Online]. Available: https://jurnal.kimia.fmipa.unmul.ac.id/index.php/JKM/arti

cle/view/203

- [15] I. Irmanto and S. Suyata, "Penurunan kadar amonia, nitrit, dan nitrat limbah cair industri tahu menggunakan arang aktif dari ampas kopi," *Molekul*, vol. 4, p. 105, Nov. 2009, doi: 10.20884/1.jm.2009.4.2.68.
- [16] Setiyoningsih, D. Indarti, and T. Mulyono, "Pembuatan dan karakterisasi arang aktif kulit singkong menggunakan aktivator ZnCl2," *J. Kim. Ris.*, vol. 3, no. 1, pp. 13-19, 2018.
- [17] S. Sugahara *et al.*, "Colorimetric determination of sulfide in microsamples," *Anal. Sci.*, vol. 32, pp. 1129-1131, Oct. 2016, doi: 10.2116/analsci.32.1129.
- [18] B. K. Reese, D. W. Finneran, H. J. Mills, M.-X. Zhu, and J. W. Morse, "Examination and refinement of the

Research Article INDONESIAN CHIMICA LETTERS

determination of aqueous hydrogen sulfide by the methylene blue method," Aquat. Geochemistry, vol. 17,no. 4, pp. 567-582, 2011, doi: 10.1007/s10498-011-9128-1.

- [19] H. Jeong, J. Park, and H. Kim, "Determination of NH4+ in environmental water with interfering substances using the modified nessler method," *J. Chem.*, vol. 2013, Feb. 2013, doi: 10.1155/2013/359217.
- [20] H. Wu and A. Cao, "Preparation and adding methods of nessler's reagent having effects on determination of water quality ammonia nitrogen," *Adv. Mater. Res.*, vol. 726-731, pp. 1362-1366, Aug. 2013, doi: 10.4028/www.scientific.net/AMR.726-731.1362.
- [21] K. Lin, Y. Zhu, Y. Zhang, and H. Lin, "Determination of ammonia nitrogen in natural waters: Recent advances and applications," *Trends Environ. Anal. Chem.*, vol. 24, p. e00073, 2019, doi: https://doi.org/10.1016/j.teac.2019.e00073.