JCNaR
Journal of Chemical Natural Resources
Journal homepage: https://jcnar.usu.ac.id

Comparative Adsorption of Copper Ion (Cu^{2+}) onto Raw and NaOH-Modified Coal Fly Ash at Various Initial Concentrations

Ilham Aswi Syaputra, Farrah Fadhillah Hanum*, Aster Rahayu, and Rimadina Sukasuci Lestari

Magister of Chemical Engineering, Faculty of Industrial Technology, Ahmad Dahlan University, Yogyakarta, 55164, Indonesia

*Corresponding Author: farrah.hanum@che.uad.ac.id

ARTICLE INFO

Article history:
Received 10 June 2026
Revised 12 July 2026
Accepted 15 Juli 2026
Available online 16 July 2026

E-ISSN: 2656-1492

How to cite:
Ilham Aswi Syaputra, Farrah Fadhillah Hanum, Aster Rahayu, Rimadina Lestari. Comparative Adsorption of Copper Ion (Cu^{2+}) onto Raw and NaOH-Modified Coal Fly Ash at Various Initial Concentrations Journal of Chemical Natural Resources. 2025, 7(2):114-122.

This work is licensed under a Creative Commons Attribution-ShareAlike 4.0 International.
https://doi.org/10.32734/jcnar.v7i2.25935

ABSTRACT

Coal fly ash, a voluminous industrial solid by product generated during coal combustion in thermal power facilities, has garnered considerable scientific attention as a cost-efficient sorption material for eliminating heavy metal contaminants from industrial effluents. This study comparatively evaluates the adsorption performance of raw coal fly ash (FA) and NaOH-modified coal fly ash (FA-NaOH) at various initial concentrations for Cu^{2+} removal from synthetic wastewater using a batch system. Both adsorbents were characterized for moisture content and iodine adsorption capacity. Equilibrium sorption experiments were conducted across a Cu^{2+} initial concentration of 25-125 mg/L using 7.5 g of adsorbent in 200 mL solution at 500 rpm for 60 minutes at room temperature. Residual copper was analyzed by Atomic Absorption Spectrophotometry (AAS). FA-NaOH consistently outperformed FA, with removal efficiencies of 83.01-99.98% and a 22.3% increase in iodine adsorption capacity after alkali activation. This parallel improvement in surface reactivity and removal efficiency rather than the modest change in maximum adsorption capacity (qm = 2.4325 mg/g for FA-NaOH vs. 2.3250 mg/g for FA) suggests alkali activation enhances Cu^{2+} uptake mainly through improved surface accessibility. These findings support NaOH-modified coal fly ash as a mechanistically justified and promising adsorbent for Cu^{2+} removal from wastewater, pending further structural verification.

Keyword: Coal Fly Ash, NaOH Modification, Copper Ion Removal, Adsorption, Wastewater

ABSTRAK

Abu terbang batubara, produk samping padat industri yang bervolume besar yang dihasilkan selama pembakaran batubara di fasilitas pembangkit listrik termal, telah menarik perhatian ilmiah yang cukup besar sebagai bahan adsorpsi yang hemat biaya untuk menghilangkan kontaminan logam berat dari limbah industri. Studi ini secara komparatif mengevaluasi kinerja adsorpsi abu terbang batubara (FA) yang tidak dimodifikasi dan abu terbang batubara yang dimodifikasi NaOH (FA-NaOH) pada berbagai konsentrasi awal untuk penghilangan Cu^{2+} dari air limbah sintetis menggunakan sistem batch. Kedua adsorben dikarakterisasi untuk kadar air dan daya serap iodium. Eksperimen adsorpsi kesetimbangan dilakukan pada konsentrasi awal Cu^{2+} 25-125 mg/L menggunakan 7,5 g adsorben dalam larutan 200 mL pada 500 rpm selama 60 menit pada suhu kamar. Logam tembaga dianalisis dengan Spektrofotometri Serapan Atom (AAS). FA-NaOH secara konsisten mengungguli FA, dengan efisiensi penghilangan sebesar 83,01%-99,98%, dan peningkatan kapasitas adsorpsi iodium sebesar 22.3% setelah aktivasi alkali. Peningkatan paralel dalam reaktivitas permukaan dan efisiensi penghilangan dibandingkan perubahan pada kapasitas adsorpsi (qm =2.4325 mg/g untuk FA-NaOH vs. 2.3250 mg/g untuk FA) menunjukkan bahwa aktivasi alkali meningkatkan penyerapan Cu^{2+} terutama melalui peningkatan aksesibilitas permukaan. Temuan ini mendukung abu terbang batubara yang dimodifikasi NaOH sebagai adsorben yang secara mekanistik dapat dibenarkan untuk penghilangan Cu^{2+} dari air limbah, sambil menunggu verifikasi lebih lanjut.

Kata Kunci: Abu Terbang Batubara, Modifikasi NaOH, Penyisihan Ion Tembaga, Adsorpsi, Air Limbah

1. Introduction

Accelerated industrialization across sectors including electroplating, mineral extraction, and semiconductor fabrication has precipitated a substantial escalation in the discharge of heavy metal laden effluents into natural hydrological systems [1]. Copper (Cu^{2+}) represents one of the most significant heavy metal pollutants due to its inherent toxicity, resistance to biodegradation, and bioaccumulative behavior within ecological food chains [2]. Epidemiological data have established clear associations between chronic Cu^{2+} overexposure and a range of systemic health impairments, encompassing hepatotoxicity, nephrotoxicity, and neurological dysfunction [3]. Under the regulatory framework established by Indonesian Ministry of Environment and Forestry Regulation No. 5 of 2014, the ceiling concentration of Cu^{2+} permissible in industrial discharge is set at 0.5 mg/L.

Adsorption technology has established itself as a premier approach for heavy metal removal from industrial effluents, distinguished by its operational simplicity, high treatment efficacy, economic viability, and adaptability to diverse contaminant matrices [4]. Coal fly ash, generated in prodigious quantities as a combustion residue from coal-fired electricity generation, has emerged as an attractive low-cost sorbent candidate, principally due to its ubiquitous availability and the inherent reactivity of its aluminosilicate mineral phases [5-6]. The active sites of FA including silanol and aluminol groups can interact with heavy metal ions via surface complexation mechanisms [7]. However, the raw fly ash surface is often partially blocked such as CaO and organic contaminants, which limit its accessible active sites [8].

Alkaline activation of fly ash using NaOH represents an established and scalable surface engineering strategy. Treatment with NaOH selectively dissolves reactive silica and alumina phases through hydrolytic reactions, enlarging existing micropores, generating new porosity, and producing negatively charged surface groups ($\equiv Si–O^-$ and $\equiv Al–O^-$) with enhanced electrostatic affinity for cationic metal species such as Cu^{2+} [9-10]. Modified fly ash systems have demonstrated substantially improved heavy metal removal efficiencies, with several studies reporting Cu^{2+} removal exceeding 90% following alkaline activation [11-12]. Furthermore, the deployment of NaOH-modified FA within wastewater treatment systems contributes to the valorization of industrial solid waste streams, consistent with circular economy strategic frameworks [13].

Although NaOH-modified fly ash has been previously reported as an effective adsorbent for heavy metal removal, most existing studies emphasize either the modification chemistry or the isotherm fitting in isolation, without linking the extent of physicochemical change to the resulting adsorption performance across a systematically varied concentration range. This work therefore contributes a paired, identical condition comparison of raw and NaOH-modified fly ash using the same protocol and Cu^{2+} initial varying concentration for both materials. This research aims to characterize the physicochemical properties of raw fly ash (FA) and NaOH-modified fly ash (FA-NaOH), assess and compare their adsorption performance for Cu^{2+} removal across various initial concentrations under batch conditions, and investigate the adsorption equilibrium behavior using Langmuir and Freundlich isotherm models to provide a mechanistic understanding of the differences in adsorption performance. The findings are expected to offer valuable scientific insights for the advancement of sustainable adsorbent materials, supporting more effective wastewater treatment applications.

2. Materials and Methods

2.1. Materials

The coal fly ash in this research was obtained from a coal fired power plant located in Sulawesi, Indonesia. All chemical reagents employed were of analytical reagent grade: NaOH 1 M, $Cu(NO_3)_2$ solution (1000 mg/L), sodium thiosulfate ($Na_2S_2O_3$ 0.1 N), iodine solution 0.1 N, starch indicator (1% w/v), and deionised water. All experiment was conducted using laboratory equipment including glassware, oven, analytical balance, shaker, and Atomic Absorption Spectrophotometer (AAS).

2.2. Preparation and Activation of Coal Fly Ash

Raw coal fly ash was first homogenised by grinding, sieved through a 100-mesh screen, washed three times with deionised water to eliminate soluble impurities, and dried to constant mass at 105°C in oven to obtain FA. For alkaline modification, 7.5 g of FA was dispersed in 1 M NaOH solution at a solid to liquid ratio of 1:3 (w/v) in a beaker. The mixture was mechanically stirred at 500 rpm for 60 minutes, then soaked for 24 hours at room temperature. The activated sample was then retrieved through filtration, washed exhaustively with deionized water until the filtrate pH reached approximately neutral, and dried at 60°C for 12 hours. The resulting FA-NaOH was stored in an airtight container.

2.3. Adsorbent Characterisation

According to SNI 06-3730-1995, moisture content and iodine adsorption number were determined as follows. For moisture content analysis, 1 g of each adsorbent was placed in a pre-weighed porcelain crucible, dried at 105°C for 2 h, cooled in a desiccator, and reweighed repeatedly until a constant mass was obtained. Moisture content was expressed as the mass fraction of water relative to the initial sample mass.

For iodine adsorption number determination, 0.5 g of the designated sorbent was brought into contact with 50 mL of 0.1 N iodine (I_2) solution within a stoppered Erlenmeyer under constant mechanical agitation for 15 minutes. Then it was filtered through Whatman filter paper, and a 10 mL aliquot of filtrate was subjected to titration against standardized 0.1 N $Na_2S_2O_3$ solution employing starch solution as the endpoint indicator.

2.4. Batch Adsorption Experimental

Synthetic Cu^{2+} working solutions at target concentrations spanning 25 to 125 mg/L were prepared by sequential dilution of a 1000 mg/L $Cu(NO_3)_2$ master stock solution in deionized water. For each adsorption experiment, 7.5 g of the adsorbent material (FA or FA-NaOH) was introduced into 200 mL of Cu^{2+} ion solution contained in a 250 mL Erlenmeyer flask. Agitation was maintained at 500 rpm using a magnetic stirrer for a fixed contact duration of 60 minutes at room temperature. The suspension was filtered through Whatman paper. Residual Cu^{2+} concentration was quantified by Atomic Absorption Spectrophotometer (AAS), using an air–acetylene flame at λ = 324.8 nm. Calibration standards were prepared from the certified Cu^{2+} stock solutions.

2.5. Adsorption and Isotherm Modelling

The equilibrium sorption capacity (qe, mg/g) and percentage removal efficiency (%R) were computed from experimental concentration measurements according to the following mathematical expressions (Equation 1 and 2):

$$q_e = \frac{Co-Ce}{m} \times V \qquad \text{(Equation 1)}$$

$$\%\ Removal = \frac{Co-Ce}{Co}\ \text{x}\ 100\% \qquad \text{(Equation 2)}$$

where, C_0 and Ce are the initial and equilibrium Cu^{2+} concentrations (mg/L), V represents solution volume (L), and m corresponds to the mass of the adsorbent (g).

2.5.1. Langmuir Isotherm

The Langmuir theoretical framework conceptualizes the adsorption process as a monolayer deposition phenomenon occurring upon a structurally homogeneous surface at which inter-adsorbate molecular interactions are assumed negligible. Its linearized mathematical expression is given by Equation 3:

$$\frac{Ce}{qe} = \frac{1}{qm\,KL} + \frac{Ce}{qm} \qquad \text{(Equation 3)}$$

In this formulation, Ce (mg/L) denotes the dissolved Cu^{2+} concentration at equilibrium; qe is the mass-specific quantity of Cu^{2+} adsorbed per unit sorbent mass at equilibrium (mg/g); qm represents the theoretical monolayer saturation capacity (mg/g); and kL is the Langmuir affinity coefficient (L/mg), reflecting the relative strength of the adsorbate-adsorbent binding interaction. Both qm and kL are derivable from the slope and intercept of the linear regression of Ce/qe against Ce.

2.5.2. Freundlich Isotherm

The Freundlich empirical model characterizes adsorption behavior on energetically heterogeneous surfaces exhibiting a non-uniform distribution of binding site affinities. Its linearized form is expressed as (Equation 4):

$$\log qe = \left(\frac{1}{n}\right) log\ Ce + \log Kf \qquad \text{(Equation 4)}$$

where $\log qe$ (mg/g) is the amount of adsorbate adsorbed at equilibrium, $\log Ce$ (mg/L) is the equilibrium concentration of adsorbate in solution, $\log Kf$ ((mg/g)(L/mg)$^{1/n}$ is the Freundlich constant related to adsorption

capacity, and n is the adsorption intensity constant indicating the favorability of the adsorption process. The values of $\log Kf$ and n can be determined from the intercept and slope of the linear plot of $\log qe$ versus $\log ce$.

3. Results and Discussion

3.1. X-Ray Fluorescence (XRF)

The raw coal fly ash used in this study was obtained from the same batch and source as that previously characterized in our earlier work [7]. Therefore, the previously reported XRF composition is presented to describe the chemical characteristics of the adsorbent. The XRF composition of the raw coal fly ash (FA) used in this study is presented in Table 1.

Table 1. XRF composition of coal fly ash (FA)

Compound	Chemical composition (%)
Fe_2O_3	34.8
SiO_2	29.6
CaO	23
Al_2O_3	9.7
TiO_2	1.4
K_2O	1.2
MnO	0.3

The XRF analysis showed that Fe_2O_3 (34.8%), SiO_2 (29.6%), CaO (23%), and Al_2O_3 (9.7%) were the dominant oxides in the fly ash, indicating that the material is an aluminosilicate-based matrix with a comparatively high iron oxide content and a substantial calcium oxide fraction. The combined SiO_2 and Al_2O_3 content (39.3%) confirms that reactive silica and alumina phases capable of undergoing NaOH hydrolysis and forming the negatively charged ≡Si–O^- and ≡Al–O^- surface groups discussed above are indeed present in sufficient abundance to support the alkaline activation mechanism proposed for this fly ash.

3.2. Moisture Content and Iodine Adsorption Capacity

These activation parameters were selected based on prior reports that a NaOH concentration of approximately 1 M is sufficient to dissolve reactive silica and alumina phases and generate new porosity without excessive framework collapse, that a solid to liquid ratio in the 1:3-1:5 (w/v) range provides adequate alkali contact while remaining practical for bench scale handling, and that a 24 h soaking period allows the hydrolysis reaction to approach completion without requiring elevated temperature [9-10,16]. Moisture content and iodine adsorption number were selected as rapid, standardized bulk indices commonly used for a first pass screening of activated carbon type and ash-based adsorbents, and were sufficient to demonstrate that alkaline treatment altered the surface hydrophilicity and microporosity of the fly ash. NaOH modification produced notable changes in both moisture content and iodine adsorption capacity, reflecting measurable alterations in the surface chemistry and pore structure of the fly ash. The physicochemical characterization results for FA and FA-NaOH are summarized in Table 2.

Table 2. Characterization of coal fly ash (FA) and FA-NaOH

Parameter	FA	FA-NaOH
Moisture content (%)	0.37	0.43
Iodine adsorption capacity (mg/g)	126.18	154.35

The moisture content of FA (0.37%) slightly increased after NaOH modification to 0.43%. This is consistent with the alkaline activation mechanism, whereby NaOH reacts with silica and alumina components on the fly ash surface, producing negatively charged groups (≡Si–O^- and ≡Al–O^-) and new silanol (≡Si–OH) and aluminol (≡Al–OH) groups that are inherently hydrophilic [14]. These polar hydroxyl groups enhance the surface affinity for water molecules through hydrogen bonding, explaining the marginal increase in moisture content. Although the increase appears minor, its significance lies in the role of the surface water layer as a

facilitating medium for ionic diffusion the thin hydration layer on FA-NaOH promotes the transport of Cu^{2+} ions toward active adsorption sites [15].

The iodine adsorption capacity, an indirect proxy for micropore surface area and accessible active sites, increased markedly from 126.18 mg/g (FA) to 154.35 mg/g (FA-NaOH), representing a 22.3% improvement. Alkaline treatment with NaOH partially dissolves silica and alumina through hydrolytic reactions, enlarging existing pores and creating new micropores [16]. The formation of amorphous aluminosilicate structures further contributes to the expanded active surface area. The higher iodine number of FA-NaOH confirms superior micropore development and a greater density of accessible active sites compared to raw FA.

3.3. Adsorption Performance of Cu^{2+} by FA and FA-NaOH

This study focused specifically on the initial concentration dependence of Cu^{2+} removal. The solution pH, adsorbent dosage, and contact time optimization were not varied factorially in the present design and are identified as necessary follow up experiments to fully define the operating envelope and further elucidate the adsorption mechanism. Adsorption equilibration experiments were conducted over a 60-minutes contact period using Cu^{2+} solutions spanning initial concentrations of 25-125 mg/L, while sustaining constant orbital agitation at 500 rpm. Following sorption, the liquid phase was recovered by filtration and subjected to AAS analysis for residual Cu^{2+} quantification. The derived sorption efficiency data were subsequently utilized to assess adsorbent effectiveness and evaluate concentration-dependent performance across the studied range. The comparative sorption performance of FA and FA-NaOH as a function of initial Cu^{2+} concentration is graphically represented in Figure 1.

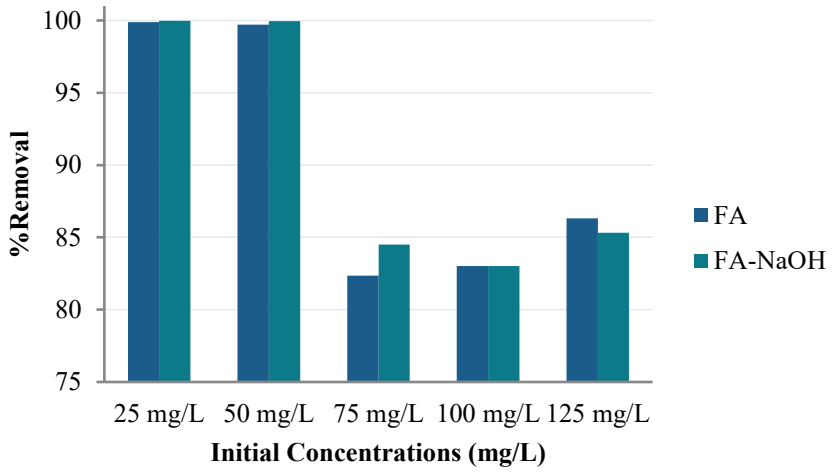


Figure 1. Percentage removal of Cu^{2+} between FA and FA-NaOH at varying initial concentrations.

At low initial concentrations (C_0 = 25 and 50 mg/L), both adsorbents achieved near complete Cu^{2+} removal (>99%), effectively reducing the final Cu^{2+} concentration. At these concentrations, the available active sites on both FA and FA-NaOH far exceed the quantity of Cu^{2+} ions present in solution, enabling virtually complete adsorption regardless of adsorbent quality. The superior surface chemistry of FA-NaOH is most clearly expressed at higher concentrations (75-125 mg/L), where competition for active sites becomes limiting.

At C_0 = 75 mg/L, the removal efficiency of FA-NaOH (84.51%) exceeded that of FA (82.36%). This difference, though modest in absolute value, reflects a meaningful enhancement in active site availability following NaOH activation. The newly formed negatively charged surface groups (≡Si–O^-, ≡Al–O^-) in FA-NaOH interact electrostatically and through surface complexation with Cu^{2+} cations, while the expanded micropore network provides additional accommodation sites [17][18]. The adsorption mechanism can be represented as Equation 5.

$$\equiv Si - OH + Cu^{2+} \rightarrow \equiv Si - O - Cu^{+} + H^{+} \qquad \text{(Equation 5)}$$

It should be noted that this surface complexation pathway is proposed by analogy with the XRF-confirmed SiO_2/Al_2O_3 composition (Table 1) and with established reaction mechanisms reported for alkali-activated aluminosilicates in the literature [9][17][18]. The mechanism should therefore be regarded as the most

chemically plausible interpretation of the observed trends, pending future spectroscopic FTIR confirmation. The equilibrium sorption loading (qe) displayed a monotonically increasing trend with rising initial concentration for both sorbents, progressing from approximately 0.666 mg/g at 25 mg/L to 2.84–2.88 mg/g at 125 mg/L. This behavior reflects the escalating concentration gradient driving force at elevated C_0 values, which promotes enhanced interfacial mass flux from the bulk solution toward the sorbent surface. The consistently qe values of FA-NaOH at elevated initial concentrations substantiate the functional contribution of alkaline surface activation to adsorption performance.

3.4. Equilibrium Isotherm Analysis

Equilibrium adsorption data were subjected to quantitative modeling through both Langmuir and Freundlich isotherm frameworks to elucidate the fundamental mechanistic characteristics of the sorption process and to interrogate the interactive behavior between dissolved Cu^{2+} species and the sorbent surface [7]. The derived isotherm parameters for both sorbent materials are compiled in Table 3.

Table 3. Langmuir and Freundlich isotherm parameters for FA and FA-NaOH

Adsorbent	Langmuir			Freundlich		
	qm (mg/g)	kL (L/mg)	R^2	kF	n	R^2
FA	2.3250	1.5646	0.8863	1.4240	6.0396	0.8162
FA-NaOH	2.4325	1.2042	0.9077	1.6073	8.2034	0.7880

For FA, both Langmuir (R^2 = 0.8863) and Freundlich (R^2 = 0.8162) models provided moderate fits, with the Langmuir model showing a marginally better correlation. The maximum adsorption capacity (qm) of FA based on the Langmuir model was obtained as 2.3250 mg/g, and the Langmuir constant kL = 1.5646 L/mg indicated a relatively high affinity of FA surface sites toward Cu^{2+} at lower concentrations. The Freundlich n value of 6.04 (n > 1) for FA also indicated favorable, cooperative adsorption characteristics.

For FA-NaOH, the Langmuir model provided the best fit with a higher coefficient of determination (R^2 = 0.9077) compared to the Freundlich model (R^2 = 0.7880). The maximum Langmuir adsorption capacity (qm) of FA-NaOH was 2.4325 mg/g, representing a 4.6% improvement over FA (2.3250 mg/g). This enhancement is attributed to the increased density of negatively charged surface groups (≡Si–O^- and ≡Al–O^-) formed during NaOH activation, which expand the accessible active surface area and provide additional coordination sites for Cu^{2+} binding via inner-sphere complexation [17]. The Langmuir constant kL for FA-NaOH (1.2042 L/mg) was slightly lower than that of FA (1.5646 L/mg), indicating a moderate reduction in initial binding affinity at low concentrations. This observation is consistent with the alkaline dissolution of some high affinity surface mineral phases during NaOH treatment, which are partially replaced by newly formed amorphous aluminosilicate structures with more uniformly distributed, albeit slightly lower affinity, binding sites [16]. The favorable dimensionless separation factor (RL = 0.0064-0.0076), well below unity for all initial concentrations tested, confirms thermodynamically favorable and near irreversible Cu^{2+} uptake by FA-NaOH.

The Freundlich heterogeneity parameter n for FA-NaOH (n = 8.2034) was notably higher than that of unmodified FA (n = 6.0396), with both values exceeding unity (n > 1, i.e. 1/n < 1), confirming favorable adsorption at heterogeneous surface sites for both adsorbents [19]. The higher n value for FA-NaOH indicates a more homogeneous energy distribution of adsorption sites following alkali activation, consistent with the systematic restructuring of the fly ash surface during NaOH treatment. The Freundlich capacity constant Kf was also higher for FA-NaOH (1.6073) compared to FA (1.4240), further confirming the greater adsorption capacity of the modified adsorbent at equivalent equilibrium concentrations.

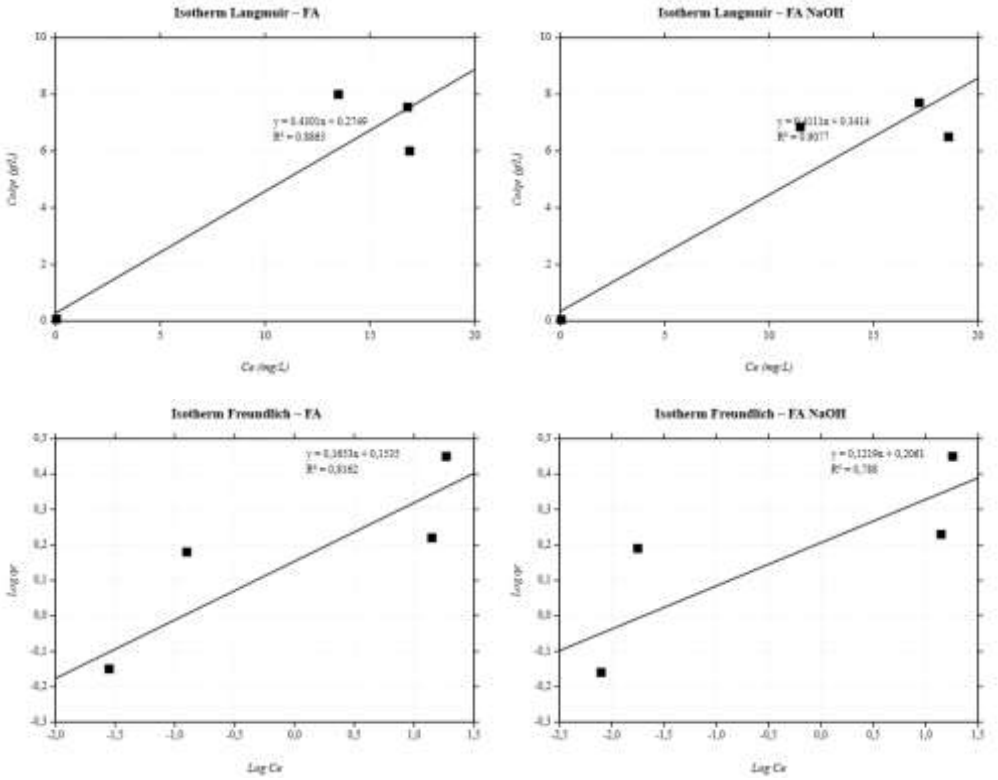


Figure 2. Adsorption isotherm curves for Cu^{2+} ions onto FA and FA-NaOH with the Langmuir and Freundlich models

The comparative isotherm analysis underscores the significant contribution of NaOH surface modification to the enhancement of coal fly ash adsorption performance. The superior fit of the Langmuir model for FA-NaOH indicates that alkaline activation transforms the heterogeneous raw fly ash surface into a more structurally ordered adsorption system, wherein active sites become energetically more uniform and accessible. The novelty of this study lies in its systematic and direct comparison of the physicochemical and adsorption equilibrium behavior of unmodified and NaOH-modified coal fly ash under identical batch conditions, providing a rigorous mechanistic foundation for the rational selection and optimization of alkali-activated fly ash as a sustainable, cost-effective adsorbent for Cu^{2+} removal. This contributes to the broader effort of valorizing coal combustion by-products in alignment with circular economy principles [5][20].

Two limitations of the present study should be acknowledged. First, the adsorption experiments were designed to evaluate the influence of initial Cu^{2+} concentration under fixed operating conditions, while other influential parameters such as solution pH, adsorbent dosage, and contact time were maintained constant. Future studies are therefore encouraged to investigate the combined effects of these operational variables on adsorption performance. Second, advanced characterization techniques, including SEM, FTIR, and BET analyses, were not incorporated into the present work. Although these techniques would provide more comprehensive evidence regarding the structural and surface modifications induced by NaOH activation, the adsorption performance evaluated through conventional physicochemical characterization and equilibrium adsorption analysis provides an appropriate preliminary assessment of the effectiveness of alkaline activation. Future work integrating advanced characterization with adsorption experiments is expected to further clarify the adsorption mechanism and strengthen the scientific interpretation of the results.

4. Conclusion

This study provides preliminary evidence that NaOH modification enhances the physicochemical properties and Cu^{2+} adsorption performance of coal fly ash. FA-NaOH showed a 22.3% increase in iodine adsorption capacity (154.35 vs. 126.18 mg/g) and a 4.6% improvement in maximum Langmuir adsorption capacity (q_m = 2.4325 vs. 2.3250 mg/g) relative to FA. While these results suggest that improved surface reactivity and porosity underlie the enhanced Cu^{2+} uptake, this interpretation remains tentative pending structural characterization (FTIR, SEM, BET) and statistical validation of the observed differences. Future work should therefore prioritize such characterization, along with adsorption kinetics, the effects of pH, adsorbent dosage, contact time, and competing ions, column system performance, and adsorbent regeneration, to build a more complete evidence base before scale up for industrial applications is pursued.

5. Acknowledgements
The authors gratefully acknowledge the Energy and Mineral Resources Laboratory of North Sumatera Province for their technical support of this research.

6. Conflict of Interest
The authors hereby declare that no conflicts of interest exist.

References
[1] J. Briffa, E. Sinagra, and R. Blundell, "Heliyon Heavy metal pollution in the environment and their toxicological effects on humans," *Heliyon*, vol. 6, no. 9, p. e04691, 2020, doi: 10.1016/j.heliyon.2020.e04691.
[2] I. Rahman, C. Shakhawat, M. Abu, J. Mazumder, and A. Al Ahmed, *Removal of lead ions - (Pb 2 +) from water and wastewater : a review on the low - cost adsorbents*, vol. 12, no. 8. Springer International Publishing, 2022. doi: 10.1007/s13201-022-01703-6.
[3] F. F. Hanum, S. Salamah, A. Rifai Sanuhung, and B. Setya Wardhana, "Study on The Potential Contamination of Heavy Metals: Analysis of Cr and Pb Contents From Power Plants in Indonesia Using the Batch Leaching Method," *Sains Nat. J. Biol. Chem.*, vol. 14, no. 1, pp. 53–61, 2024, doi: 10.31938/jsn.v14i1.689.
[4] A. M. Badran, U. Utra, N. S. Yussof, and M. J. K. Bashir, "Advancements in Adsorption Techniques for Sustainable Water Purification : A Focus on Lead Removal," pp. 1–26, 2023.
[5] N. B. S. Anupam, A. Anindita, and D. P. Singh, *Coal fly ash : an emerging material for water remediation*, vol. 1. Springer Nature Singapore, 2022. doi: 10.1007/s40789-022-00512-1.
[6] A. Kumar and R. Supriya, "State of the art review on physiochemical and engineering characteristics of fly ash and its applications," *Int. J. Coal Sci. Technol.*, vol. 6, 2022, doi: 10.1007/s40789-022-00472-6.
[7] B. S. Wardhana, F. F. Hanum, Z. Mufrodi, A. V. Febriani, and S. Salamah, "Jurnal Kimia Sains dan Aplikasi Comparison of Activation Methods for Coal Ash as an Adsorbent in the Removal of Lead (Pb 2 +) from Aqueous Solution," vol. 28, no. 8, pp. 452–462, 2025.
[8] W. Jadaa, "Wastewater Treatment Utilizing Industrial Waste Fly Ash as a Low-Cost Adsorbent for Heavy Metal Removal: Literature Review," *Clean Technol.*, vol. 6, no. 1, pp. 221–279, 2024, doi: 10.3390/cleantechnol6010013.
[9] Y. Chen, S. Wang, and Y. Zhou, "Structural alteration within fly ash-based geopolymers governing the adsorption of Cu^{2+} from aqueous environment: Effect of alkali activation," *J. Hazard. Mater.*, vol. 377, pp. 305–314, 2019, doi: 10.1016/j.jhazmat.2019.05.086.
[10] Y. Gong, J. Sun, S. Y. Sun, G. Lu, and T. A. Zhang, "Enhanced desilication of high alumina fly ash by combining physical and chemical activation," *Metals (Basel).*, vol. 9, no. 4, p. 411, 2019, doi: 10.3390/met9040411.
[11] G. Buema *et al.*, "Adsorption performance of modified fly ash for copper ion removal from aqueous solution," *Water*, vol. 13, no. 2, p. 207, 2021, doi: 10.3390/w13020207.
[12] G. Buema, L. M. Trifas, and M. Harja, "Removal of toxic copper ion from aqueous media by adsorption on fly ash-derived zeolites: kinetic and equilibrium studies," *Polymers (Basel).*, vol. 13, no. 20, p. 3468, 2021, doi: 10.3390/polym13203468.
[13] M. Ahmaruzzaman, "A review on the utilization of fly ash," *Prog. Energy Combust. Sci.*, vol. 36, no. 3, pp. 327–363, 2010, doi: 10.1016/j.pecs.2009.11.003.
[14] F. Ningsih, A. Pambudi, and E. Wahyudi, "Optimized NaOH and KOH treatments for interfacial and mechanical enhancement of agro-marine ash reinforced aluminum composites," *Sci. Rep.*, vol. 15, p. 10842, 2025, doi: 10.1038/s41598-025-21038-x.
[15] Y. Feng, J. Gong, and L. Zhang, "Removal of toxic copper ion from aqueous media by adsorption on fly ash-derived zeolites: Kinetic and equilibrium studies," *Materials (Basel).*, vol. 14, no. 20, p. 6106, 2021, doi: 10.3390/ma14206106.
[16] W. Franus, M. Wdowin, and M. Franus, "Synthesis and characterization of zeolites prepared from industrial fly ash," *Environ. Monit. Assess.*, vol. 186, no. 9, pp. 5721–5729, 2014, doi: 10.1007/s10661-014-3815-4.
[17] T. H. Pham, B. K. Lee, and J. Kim, "An effective way to utilize solid waste resources: The application of modified fly ash in removing Cu2+ and Pb2+ in wastewater," *J. Environ. Chem. Eng.*, vol. 4, no. 2, pp. 1738–1745, 2016, doi: 10.1016/j.jece.2016.02.033.
[18] L. Lăzăr, G. Ioniță, L. A. Colar, G. Lisă, A. Ioanid, and V. Harabagiu, "Hydrothermally modified fly ash for heavy metals and dyes removal in advanced wastewater treatment," *Appl. Surf. Sci.*, vol. 303, pp. 14–22, 2014, doi: 10.1016/j.apsusc.2014.02.025.

[19] P. Chen, J. Wu, L. Li, Y. Yang, and J. Cao, "Modified fly ash as an effective adsorbent for simultaneous removal of heavy metal cations and anions in wastewater," *Appl. Surf. Sci.*, vol. 624, p. 157165, 2023, doi: 10.1016/j.apsusc.2023.157165.
[20] A. Kumar and R. Supriya, "State of the art review on physiochemical and engineering characteristics of fly ash and its applications," *Int. J. Coal Sci. Technol.*, 2022, doi: 10.1007/s40789-022-00472-6.