SYNERGISTIC INTERFACIAL CHEMISTRY OF HUMIC ACID AND ACTIVATED FLY ASH FOR HIGH-PERFORMANCE Mn^{2+} ADSORPTION

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Abstrak

This study developed a hybrid adsorbent derived from activated fly ash (FA) and humic acid (HA) for effective Mn^{2+} removal from aqueous solutions. Fly ash was activated using 1 M NaOH to increase its surface hydroxyl groups (≡Si–OH and ≡Al–OH) and enhance reactivity. The activated FA was then composited with HA, which contains abundant –COOH and –OH groups, forming an inorganic–organic hybrid with improved adsorption capability. The HA–FA composite with a 1:3 mass ratio exhibited the highest Mn^{2+} removal efficiency of 98.80% after 120 minutes, significantly outperforming both HA and FA individually. FTIR analysis confirmed the formation of Si–O–C and Al–O–C linkages, indicating strong chemical interactions between the mineral and organic phases. Statistical analysis (Shapiro–Wilk, Levene, and ANOVA; $p < 0.05$) demonstrated that both adsorbent composition and contact time significantly influenced the adsorption efficiency. Overall, the HA–FA hybrid represents a low-cost, sustainable, and high-performance adsorbent capable of efficiently removing heavy metals from wastewater, providing a promising approach for transforming industrial and natural wastes into functional environmental materials

***Kata kunci**: Adsorption, Activated Fly Ash, Humic Acid, Manganese, Heavy metal removal*

1. INTRODUCTION

Medium- to high-manganese steels have emerged as a major focus of development as next-generation candidates for Advanced High-Strength Steels (AHSS), particularly in automotive applications, due to their outstanding mechanical properties (Sedaghat-Nejad *et al.,* 2022). However, behind the promising innovation of these materials lies a paradoxical environmental challenge. The steel industry not only generates vast amounts of solid waste in the form of steel slag, amounting to nearly 50 million tons annually worldwide (Yusuf et al., 2014), but also produces liquid effluents containing hazardous levels of manganese (Mn).

Elevated Mn concentrations in industrial wastewater can lead to severe health effects, including respiratory disorders, methemoglobinemia, and pulmonary edema (Sunarsih *et al.,* 2018). Consequently, the direct discharge of untreated Mn-containing effluents poses a significant environmental threat. Thus, the development of sustainable wastewater treatment strategies to effectively reduce Mn levels prior to disposal is imperative to align industrial progress with the principles of environmental sustainability.

Various remediation strategies for manganese (Mn), including physical, chemical, and biological approaches, have been developed over the past decades to mitigate its toxic effects and maintain safe water quality. Among the different treatment methods employed, adsorption has emerged as a simpler, more efficient, cost-effective, and environmentally friendly alternative compared to conventional physical or chemical techniques (Duta *et al.,* 2021). This process operates through interactions between the adsorbent (the

solid phase) and the adsorbate (the dissolved species), with efficiency largely governed by the adsorbent's physicochemical properties. A wide range of materials, such as activated carbon, zeolite, chitosan, silica, bentonite, and alumina, have been utilized as adsorbents (Mthombeni *et al.,* 2016); however, many of these materials remain limited by high cost, limited availability, and insufficient selectivity toward specific metal ions. Therefore, the development of low-cost, effective, and sustainable adsorbent materials has become a crucial focus in addressing heavy metal pollution, including manganese contamination, from industrial wastewater (Zhang *et al.,* 2021).

Fly ash (FA) is a solid byproduct generated from coal combustion in coal-fired power plants that has attracted significant attention due to its abundant availability, favorable physical characteristics, and rich mineralogical composition. The combustion of coal produces approximately 85% fly ash and 10% bottom ash, and excessive FA generation can lead to environmental pollution if not properly managed, including respiratory disorders caused by fine particulate matter (Naldi et al., 2020). Chemically, FA is primarily composed of silica (SiO_2), alumina (Al_2O_3), and various metal oxides such as Fe_2O_3, CaO, MgO, K_2O, and Na_2O (Giyatmi & Fazliyana, 2018), which highlight its potential as an inorganic adsorbent material. Numerous studies have utilized FA as an adsorbent for the removal of heavy metals, inorganic anions, dyes, and organic pollutants from wastewater and flue gas, owing to its porous structure, low cost, and wide availability. For instance, Aigbe *et al.* (2021) reported the effectiveness of FA in adsorbing heavy metals and organic dyes, while other studies have demonstrated its capability in removing specific heavy metals such as Hg and As from flue gas and wastewater, as well as the synthesis of FA-based zeolites from municipal solid waste (Ajorloo *et al.*, 2022; Vogelsang *et al.,* 2023). Nevertheless, the adsorption capacity and selectivity of FA toward certain heavy metal ions remain limited, necessitating modification or the incorporation of supporting materials to enhance its adsorption performance and expand its applicability as an environmentally friendly adsorbent for industrial wastewater treatment.

One promising material for enhancing the adsorption capacity of fly ash is humic acid—a natural macromolecular polyelectrolyte containing functional groups such as –COOH, phenolic –OH, and alcoholic –OH. These functional moieties play a crucial role in complexation with heavy metal ions via deprotonation mechanisms, particularly at relatively high pH (Boguta *et al.,* 2019). Humic acid exhibits optimal adsorption performance in alkaline media, as its solubility increases significantly at pH ≥ 6, reaching≥ 95% (Xu *et al.,* 2021). This property enables humic acid to form stable complexes with heavy metal ions, making it a promising composite-forming agent to enhance the adsorption efficiency of adsorbent materials.

Previous studies on humic acid have predominantly focused on its application as a fertilizer or soil conditioner (Afrianti *et al.,* 2023; Shafi *et al.,* 2020; Shaila *et al.,* 2019), while research on enhancing its adsorption capacity has mainly involved physical or chemical activation processes (Harnowo *et al.,* 2019; Setyawan *et al.,* 2018; Nurhasni *et al.,* 2018). To date, no studies have reported the use of fly ash–humic acid composites as adsorbents for heavy metal removal. Therefore, the present study focuses on the synthesis and characterization of fly ash–humic acid composites as environmentally friendly adsorbents, to improve the stability and adsorption efficiency of manganese (Mn^{2+}) ions from steel industry wastewater.

2. EXPERIMENTAL

2.1. Tools and Material

The materials used in this research included fly ash obtained from a coal-fired power plant located in the Cilegon area, sodium hydroxide (NaOH), distilled water, Tri's buffer solution (pH 8.5), standard humic acid, and manganese ion (Mn^{2+}) solution. All reagents were of analytical purity.

The instruments used in this study included a pH meter, a centrifuge, and an oven, as well as analytical instruments: a Fourier Transform Infrared Spectrophotometer (FTIR, IRPrestige-21, Shimadzu, Japan) and an Atomic Absorption Spectrophotometer (AAS, AA-7000, Shimadzu, Japan). The glassware employed comprised a beaker, a magnetic stirrer, a separatory funnel, and an Erlenmeyer flask

2.2. Preparation of Fly Ash

Fly ash samples were first sieved using a 100-mesh sieve to obtain uniform particle sizes.

A total of 50 g of sieved fly ash was immersed in 100 mL of 1 M NaOH solution for 30 minutes. After soaking, the sample was filtered through Whatman No. 42 filter paper and dried in an oven at 105°C until a constant weight was achieved.

The activated fly ash was then neutralized with distilled water until the pH reached 7. The neutralized sample was dried again at 160°C to obtain activated fly ash. The activated fly ash was subsequently analyzed using an Atomic Absorption Spectrophotometer (AAS) to determine its metal content and characterized using a Fourier Transform Infrared Spectrophotometer (FTIR) to identify the functional groups formed.

2.3. Synthesis of Activated Fly Ash – Humic Acid Composites

One liter of distilled water was used as the solvent, into which activated fly ash and humic acid were added at mass ratios of 1.25:3.75, 2.50:2.50, and 3.75:1.25 (g/g). The mixture was adjusted to pH 8.5 using 0.1 M Tris buffer and stirred continuously with a magnetic stirrer for 12 hours at room temperature. The resulting suspension was filtered through Whatman No. 42 filter paper, and the obtained solid was dried at 160°C for 1 hour. The composite material was then characterized using FTIR to identify the functional groups and chemical interactions between fly ash and humic acid

2.4. Adsorption of Mn^{2+} Ions

2.4.1. *Adsorption Using Activated Fly Ash*

A Mn^{2+} ion solution was prepared by diluting a 1000 ppm Mn standard to 10 ppm in 100 mL of distilled water. A total of 5 g of activated fly ash was added to the solution, and the mixture was stirred at 200 rpm for 30 minutes. After adsorption, the suspension was filtered under vacuum, and AAS analyzed the filtrate.

2.4.2. *Adsorption Using Humic Acid*

A 10 ppm Mn^{2+} solution in 100 mL was prepared from a 1000 ppm standard solution. A total of 5 g of humic acid was added to the solution, and the mixture was stirred at 200 rpm for 30 minutes. The suspension was filtered under vacuum, and AAS analyzed the filtrate to determine the residual Mn^{2+} concentration.

2.4.3. *Adsorption Using Fly Ash-Humic Acid Composites*

The fly ash–humic acid composites were prepared at three different mass ratios: 1.25 g humic acid : 3.75 g fly ash, 2.50 g humic acid : 2.50 g fly ash, and 3.75 g humic acid : 1.25 g fly ash. Each composite was used to adsorb 100 mL of a 10 ppm Mn^{2+} solution at 200 rpm for 30, 60, and 90 minutes. After adsorption, the suspension was filtered under vacuum, and AAS analyzed the filtrate to determine the adsorption efficiency of Mn^{2+} ions by the composite. The adsorption efficiency was calculated based on the difference between the initial concentration (C_0) and the equilibrium concentration (C_e) according to Equation (1):

$$\text{Adsorption Efficeincy (\%)} : \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where

C_0 = initial Mn^{2+} ion concentration (mg/L)

C_e = equilibrium Mn^{2+} ion concentration after adsorption (mg/L)

2.5. Experimental Design

The experimental design was arranged using a Completely Randomized Design (CRD) to determine the effect of contact time and composite composition on Mn^{2+} ion adsorption performance. The factors tested included composite composition (F) with three variations: F1 (1.25 g humic acid + 3.75 g fly ash), F2 (2.50 g humic acid + 2.50 g fly ash), and F3 (3.75 g humic acid + 1.25 g fly ash), as well as contact time (W) of 30, 60, and 90 minutes.

Each treatment combination was performed in duplicate, resulting in 18 experimental units, with a negative control used as a reference. All treatments were randomized to minimize bias, and the results were analyzed based on the decrease in Mn^{2+} ion concentration under each condition.

3. RESULT AND DISCUSSION

3.1. Activation of Fly Ash

Fly ash is a by-product of coal-fired power plants (CFPPs). It is classified as hazardous waste due to its fine particulate nature and the presence of various heavy metals at specific concentrations. The fly ash used in this study primarily consists of silica (SiO_2,

61.17%) and alumina (Al_2O_3, 7.50%), along with minor components such as Fe_2O_3, CaO, MgO, K_2O, and Na_2O. The high silica and alumina contents make fly ash a promising precursor for adsorbent materials to reduce heavy-metal concentrations in wastewater (Gupta *et al.,* 2021). However, raw fly ash exhibits limited surface activity due to its low specific surface area and impurities, necessitating activation to enhance its adsorption performance.

In this study, fly ash was activated with 1 M NaOH to improve its pore structure and increase its specific surface area. Alkaline activation partially dissolves the amorphous aluminosilicate phase and induces surface reorganization, thereby generating new, more reactive active sites. In addition, this treatment removes residual carbon and other contaminants that could hinder adsorption.

Chemically, NaOH activation involves reactions between metal oxides (mainly SiO_2 and Al_2O_3) and hydroxide ions (OH^-) from the alkaline solution. These reactions partially dissolve silica and alumina, forming water-soluble sodium silicate (Na_2SiO_3) and sodium aluminate ($NaAl(OH)_4$) (Li *et al.,* 2022). The partial dissolution reactions can be represented as follows:

$$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(l) \quad (2)$$

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2NaAl(OH)_4(aq) \quad (3)$$

This dissolution process enlarges the pore structure and increases the number of active sites on the fly ash surface. Following activation, the material was thoroughly washed with deionized water until reaching neutral pH (pH 7) to remove residual alkali and stabilize the surface. During this neutralization step, a fraction of the dissolved sodium silicate and sodium aluminate may undergo repolymerization, forming more open and porous Al–O–Si frameworks. The repolymerization reaction can be expressed as follows:

$$Na_2SiO_3(aq) + Al(OH)_4^-(aq) + H^+(aq) \rightarrow$$

$$Al\text{–}O\text{–}Si(s) + Na^+(aq) + H_2O(l) \quad (4)$$

These chemical transformations yield a new aluminosilicate structure enriched with surface hydroxyl groups (≡Si–OH and ≡Al–OH). Such hydroxyl groups act as active sites that play a key role in heavy-metal adsorption through electrostatic interactions, ion exchange, and surface complexation. Consequently, NaOH activation effectively enhances the chemical reactivity, porosity, and specific surface area of fly ash. The initially inert fly ash is thus transformed into an active adsorbent with superior affinity toward heavy-metal ions such as Pb^{2+}, Mn^{2+}, Cu^{2+}, and Cd^{2+} (Chen *et al.,* 2023). Alkaline activation not only increases the number of pores and functional groups but also improves surface morphology, thereby enabling more efficient adsorption.

3.2. Activation of Fly Ash – Humic Acid Composite

The preparation of the activated fly ash–humic acid composite aims to integrate the inorganic mineral surface characteristics of fly ash with the organic chelating capability of humic acid. This combination is expected to yield a hybrid material with enhanced adsorption capacity toward metal ions, particularly manganese (Mn^{2+}).

Activated fly ash primarily contains silica (SiO_2) and alumina (Al_2O_3) with an open pore structure and active hydroxyl groups (≡Si–OH and ≡Al–OH), which function as inorganic adsorption centers. In contrast, humic acid is a complex macromolecular organic substance derived from the decomposition of natural organic matter, rich in polar functional groups such as carboxyl (–COOH), phenolic hydroxyl ($–OH_{phenol}$), and alcoholic hydroxyl ($–OH_{al}c_{ohol}$). These groups possess strong metal-binding capabilities through ion exchange, surface coordination, and chelation mechanisms (Boguta *et al.*, 2019; Alhawas *et al.,* 2023).

In this study, the composite was synthesized via purely physical mixing without the use of any binders. The activated fly ash and humic acid were contacted for 12 hours under continuous stirring to promote stable interfacial interactions between the –OH and –COOH groups of humic acid and the silanol (Si–OH) and aluminol (Al–OH) groups of fly ash. These interactions form hydrogen bonds and weak coordination linkages that are sufficient to establish a homogeneous composite structure without altering the intrinsic chemical nature of each component.

An alkaline pH was maintained during the compositing process to promote deprotonation of the carboxylic and phenolic acid groups of humic acid, as described by the following equilibria:

$$R\text{–}COOH \rightleftharpoons R\text{–}COO^- + H^+$$

$$Ar\text{–}OH \rightleftharpoons Ar\text{–}O^- + H^+ \quad (5)$$

Under alkaline conditions, the formation of carboxylate ($–COO^-$) and phenolate ($–O^-$) ions increases the negative surface charge density of humic acid, thereby strengthening electrostatic interactions with positively charged metal ions such as Mn^{2+}. Consequently, maintaining an alkaline environment is essential for activating humic acid's functional sites and maximizing its heavy-metal adsorption capacity.

When humic acid interacts with activated fly ash, interfacial bonding occurs through hydrogen bridges and the formation of Al–O–C or Si–O–C linkages between the two materials. This mechanism enhances the structural stability of the composite while providing new active sites at the inorganic–organic interface, facilitating more efficient adsorption of metal ions (Xue *et al.*, 2024). The following reactions can express schematic representation of the composite formation and Mn^{2+} adsorption:

$$\equiv Si\text{–}OH + R\text{–}COOH \rightarrow \equiv Si\text{–}OOC\text{–}R + H_2O$$

$$R\text{–}COO^- + Mn^{2+} \rightarrow R\text{–}COO\text{–}Mn\text{–}OOC\text{–}R \quad (6)$$

The first reaction illustrates the formation of Si–O–C bridges between fly ash and humic acid. In contrast, the second represents chelate complexation between Mn^{2+} ions and the carboxylate groups of humic acid. Therefore, the incorporation of humic acid not only increases the number of active sites but also strengthens metal binding through the formation of stable multidentate complexes.

Similar findings were reported by Boguta *et al.* (2019), who demonstrated that humic acid enhances the adsorption capacity of silica- and clay-based materials by forming stable metal–organic complexes under alkaline conditions. Furthermore, Alhawas *et al.* (2021) reported that humic acid–inorganic porous composites exhibit significantly improved adsorption efficiency for transition metal ions such as Mn^{2+} and Pb^{2+} due to synergistic interactions between organic and inorganic sites.

In summary, the physical compositing of activated fly ash and humic acid under alkaline conditions proved to be an effective approach for producing a hybrid material with superior adsorption capacity. The synergistic interplay between the functional groups of humic acid and the porous structure of fly ash results in an increased number of active sites and enhanced metal ion binding through electrostatic and surface complexation mechanisms

3.3. Adsorption of Manganese Ions (Mn^{2+})

3.3.1. Adsorption of Mn^{2+} Ions by Activated Fly Ash

Fly ash activated with NaOH solution exhibited exceptionally high adsorption performance toward Mn^{2+} ions. In this experiment, 5 g of activated fly ash was contacted with 100 mL of a 10 ppm Mn standard solution under stirring at 200 rpm for 30 minutes. Atomic Absorption Spectrophotometry (AAS) analysis revealed a significant decrease in Mn concentration from 8.2731 ppm to 0.0309 ppm, corresponding to an adsorption efficiency of 99.63% (Table 1).

The remarkable removal efficiency indicates that alkaline activation with NaOH effectively enhanced the number of active sites and the specific surface area of the fly ash. Alkaline treatment is known to partially transform amorphous silica structures into hydrated silicate species, generate new pores, and introduce reactive hydroxyl groups on the adsorbent surface (Li *et al.,* 2022). The possible surface reaction during activation can be represented as follows:

$$Si\text{–}O\text{–}Si + NaOH \rightarrow Si\text{–}O\text{–}Na + Si\text{–}OH \quad (7)$$

The surface hydroxyl groups (–Si–OH and –Al–OH) formed during activation play a crucial role in the coordination of Mn^{2+} ions through surface complexation mechanisms:

$$\equiv Si\text{–}OH + Mn^{2+} \leftrightarrow \equiv Si\text{–}O\text{–}Mn^+ + H^+ \quad (8)$$

In addition to complexation, electrostatic interactions likely occur between the positively charged metal ions and the negatively charged surface of activated fly ash, particularly under neutral to slightly

alkaline conditions. These combined mechanisms contribute to the high adsorption efficiency observed in this study.

3.3.2. Adsorption of Mn^{2+} Ions by Humic Acid

In contrast to fly ash, humic acid naturally contains abundant active functional groups such as carboxyl (–COOH), phenolic hydroxyl (–OH), and alcoholic hydroxyl (–OH) groups capable of interacting with metal ions through coordination complex formation (Boguta *et al.,* 2019). However, the experimental results indicated that the adsorption performance of humic acid toward Mn^{2+} ions was lower than that of activated fly ash.

From an initial Mn concentration of 8.2731 ppm, the residual Mn concentration after adsorption was 6.8973 ppm, corresponding to an adsorption efficiency of only 16.63% (Table 1). This limited performance may be attributed to the solubility and structural flexibility of humic acid in aqueous media, which can lead to partial protonation of its functional groups or steric hindrance that restricts access to active binding sites.

Table 1. Adsorption Data of Mn^{2+} Ions by Activated Fly Ash and Humic Acid

Mn concentration before adsorption (ppm)	Contact Time (Minutes)	Adsorbent Composition	Mn Concentration After Adsorption (ppm)	Efficiency (%)
8,273	30	Activated Fly Ash	0,031	99,6
8,273	30	Humic Acid	6,897	16,6

The primary adsorption mechanism in humic acid involves the formation of weak chelate complexes, as represented by the following equilibrium:

$$R\text{–}COO^- + Mn^{2+} \leftrightarrow R\text{–}COO\text{–}Mn^+ \quad (9)$$

However, because most carboxylate groups remain protonated (–COOH) at near-neutral pH, the extent of complexation is limited, resulting in lower adsorption efficiency.

3.3.3. Adsorption of Mn^{2+} Ions by Activated Fly Ash – Humic Acid Composite

To enhance adsorption efficiency, a binder-free composite system was developed by combining activated fly ash and humic acid. This hybrid system was designed to integrate the advantages of fly ash —namely, high surface area and structural stability—with the chemical reactivity of humic acid, which is rich in electron-donating functional groups such as carboxyl (–COOH) and phenolic hydroxyl ($–OH_{phenol}$).

Composites with varying ratios of humic acid to fly ash (1:3, 1:1, and 3:1) were evaluated at contact times of 30, 60, and 120 minutes. Atomic Absorption Spectrophotometry (AAS) results revealed that the highest adsorption efficiency was achieved at a 1:3 ratio after 120 minutes, reaching 98.80%—reducing Mn concentration from 9.927 ppm to 0.119 ppm (Table 2). In contrast, the lowest efficiency (16.45%) was obtained at a 3:1 ratio after 30 minutes of contact.

The enhanced adsorption performance at higher fly ash content suggests that fly ash acts as the dominant provider of active sites and as a porous structural support. Meanwhile, humic acid reinforces chemical interactions through the formation of coordination complexes with Mn^{2+} ions, as represented by the following reactions:

$$\equiv Si\text{–}O^-Na + R\text{–}COOH \rightarrow \equiv Si\text{–}OOC\text{–}R + NaOH$$

$$\equiv Si\text{–}OOC\text{–}R + Mn^{2+} \leftrightarrow \equiv Si\text{–}OOC\text{–}R\text{–}Mn^+ \quad (10)$$

These reactions illustrate the formation of coordination bridges between the silica surface (derived from fly ash) and the carboxylate groups of humic acid, resulting in a structurally stable composite with enhanced metal-binding capacity. The alkaline conditions maintained during the mixing process are also crucial for deprotonating the –COOH and phenolic –OH groups, thereby increasing the negative surface charge density and strengthening electrostatic attraction toward Mn^{2+} ions.

These findings are consistent with the reports of Boguta *et al.* (2019) and Shao *et al.* (2022), which demonstrated that synergistic interactions between silica-based materials and humic substances markedly improve the efficiency of transition metal ion adsorption. This improvement arises from the combination of physical mechanisms

(porosity and high surface area) and chemical mechanisms (complexation and ion exchange), both of which contribute to enhanced adsorption performance in hybrid inorganic–organic materials.

Table 2. Adsorption Data of Mn^{2+} Ions by Activated Fly Ash -Humic Acid Composite

Mn concentration before adsorption (ppm)	Contact Time (Minutes)	Adsorbent Composition (Humic Acid : Fly Ash)	Mn Concentration After Adsorption (ppm)	Efficiency (%)
9,927	30	1 : 3	0,526	94,70
		1 : 1	0,449	95,48
		3 : 1	8,285	16,55
	60	1 : 3	0,360	96,37
		1 : 1	0,301	96,97
		3 : 1	7,595	23,50
	120	1 : 3	0,119	98,80
		1 : 1	0,155	98,44
		3 : 1	6,612	33,39

3.4. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was performed to identify the functional groups present in the adsorbent materials. As shown in Figure 1, the FTIR spectrum of the activated fly ash exhibited several characteristic absorption bands. A distinct stretching vibration band of the Si–OH group was observed at 3448.72 cm^{-1}, while a band at 1002.98 cm^{-1} corresponded to the Si–O stretching vibration. Additionally, absorption peaks at 771.53 cm^{-1}, 725.23 cm^{-1}, and 694.37 cm^{-1} were attributed to the asymmetric stretching vibrations of Si–O–Si and Al–O–Si linkages, whereas the band at 455.2 cm^{-1} indicated the bending vibration of Al–O bonds (Nasra, 2024).

Meanwhile, the FTIR spectrum of humic acid, as illustrated in Figure 13, displayed a broad and intense absorption band at 3425.58 cm^{-1}, assigned to the stretching vibrations of hydroxyl (–OH) groups. This broad band is characteristic of humic substances, arising from the presence of phenolic (–OH) and alcoholic (–OH) functional groups. The absorption at 2924.09 cm^{-1} was associated with aliphatic C–H stretching, while the band at 1573.91 cm^{-1} corresponded to carboxylate (C=O) stretching vibrations. Furthermore, the band at 1381.03 cm^{-1} was assigned to acetylene (CH_2) groups, followed by a peak at 1033.85 cm^{-1} indicating C–O stretching, and an absorption at 910.4 cm^{-1} corresponding to aromatic C–H vibrations.

After the fly ash-humic acid compositing, the FTIR spectrum showed notable spectral shifts, indicating chemical interactions between the two materials. The broad O–H stretching bands at 3448.72 cm^{-1} (fly ash) and 3425.58 cm^{-1} (humic acid) shifted to 3410.15 cm^{-1}, accompanied by a decrease in intensity, suggesting the formation of hydrogen bonds between hydroxyl groups. Additional shifts were observed at 1419.61 cm^{-1} and 1573.91 cm^{-1}, which merged into a new band at 1558.48 cm^{-1}. The corresponding increase in intensity for fly ash and decrease for humic acid indicate the involvement of carboxylate (C=O) groups in the composite formation. Moreover, the band at 1033.85 cm^{-1} was attributed to overlapping C–O or Si–O stretching vibrations, while the peak at 694.37 cm^{-1} represented the asymmetric stretching of Si–O–Si and Al–O–Si linkages. An additional shift appearing at 478.35 cm^{-1} corresponded to the bending vibration of Si–O–Si, further confirming the establishment of chemical interactions between the activated fly ash and humic acid within the composite structure.

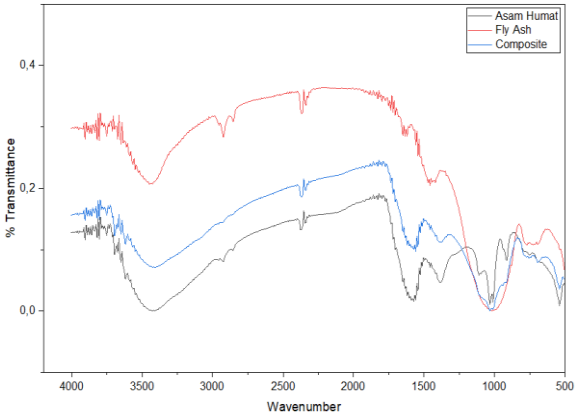

Figure 1. FTIR Analysis of Activated Fly Ash, Humic Acid and Activated Fly Ash – Humic Acid Composite

3.5. Statistical Analysis

To ensure the validity and reliability of the adsorption data, comprehensive statistical analyses were conducted, including prerequisite and inferential testing. Prior to parametric testing, the data were examined for normality and homogeneity. The Shapiro–Wilk test confirmed a normal distribution ($p > 0.05$), while the Levene's test indicated data homogeneity ($p > 0.05$). With these assumptions satisfied, a parametric Analysis of Variance (ANOVA) was performed to evaluate the effects of adsorbent composition and contact time on the adsorption efficiency of Mn^{2+} ions.

The ANOVA results revealed that both independent variables—adsorbent composition and contact time—had a statistically significant influence on adsorption efficiency ($p < 0.05$). This finding indicates that these operational parameters strongly govern adsorption performance, consistent with previous reports emphasizing the importance of physicochemical optimization to enhance metal–adsorbent interactions.

3.5.1. Efect of Adsorben Composition

The adsorbent composition, expressed as the mass ratio of humic acid to fly ash, significantly affected the Mn^{2+} adsorption efficiency. Among the tested ratios (1:3, 1:1, and 3:1), the 1:3 composition (humic acid:fly ash) exhibited the highest adsorption efficiency across all contact times, reaching a maximum of 98.80% at 120 minutes. This composition provided an optimal balance between the abundance of active functional groups (–COOH, phenolic –OH, and alcoholic –OH) from humic acid and the high surface area and porosity contributed by fly ash.

Humic acid served as the organic component, providing chemical binding sites via metal complexation and electrostatic interactions. At the same time, fly ash acted as an inorganic scaffold rich in SiO_2, Al_2O_3, and Fe_2O_3 minerals, reinforcing structural integrity and enhancing ion diffusion. The synergy between these two components led to a dual adsorption mechanism—surface complexation and electrostatic interactions—that collectively enhanced the metal-binding capacity.

Conversely, at the 3:1 composition (fly ash-dominant), adsorption efficiency markedly decreased (16.45–33.39%), attributed to the reduced density of active organic groups and the predominance of the less reactive inorganic phase. These results reaffirm that an adequate organic fraction is essential to maintain a high density of effective binding sites for metal complexation (Murphy e*t al.,* 2023).

3.5.2. Effect of Contact Time

Contact time also exhibited a significant effect on adsorption efficiency ($p < 0.05$). The data showed that adsorption efficiency increased with increasing contact time. For the 1:3 composition, efficiency improved from 94.70–95.48% (30 min) to 96.97–98.80% (120 min). This trend reflects that extended contact durations allow more Mn^{2+} ions to interact with available adsorption sites until equilibrium is reached.

The initial adsorption phase is characterized by a rapid uptake rate due to the abundance of vacant active sites and strong diffusion driving forces from the bulk solution to the adsorbent surface. As sites become occupied, the rate slows due to limited ion diffusion into the internal pores. This behavior aligns with the pseudo-second-order kinetic model, indicating that the adsorption mechanism is dominated by chemisorption, where electron sharing or exchange between Mn^{2+} ions and active functional groups plays a crucial role (Murphy *et al.,* 2023).

3.5.3. Interaction Between Composition and Contact Time

Interaction analysis showed that the combined effect of adsorbent composition and contact time was synergistic in enhancing adsorption efficiency. The optimal condition—1:3 composition with 120 minutes of contact—demonstrated that both the physicochemical structure of the adsorbent and the duration of interaction jointly determine the total adsorption capacity. At shorter contact times (30–60 minutes), adsorption primarily occurred on the external surface, whereas at longer durations, intraparticle diffusion within the porous matrix became dominant (Murphy et al., 2023).

This behavior suggests that the humic acid–fly ash composite operates through two

complementary mechanisms: chemical interaction (chemisorption) via organic functional groups and intraparticle diffusion within the porous inorganic framework (Khairul *et al.,* 2021). The synergistic effect of these mechanisms enhances adsorption efficiency and reinforces adsorbent stability during multi-cycle use.

3.5.4. Optimum Condition and Implication

Under the optimal conditions—adsorbent composition of 1:3 (humic acid:fly ash) and contact time of 120 minutes—a maximum adsorption efficiency of 98.80% was achieved, reducing the residual Mn^{2+} concentration to approximately 0.12 mg L^{-1} from an initial 9.93 mg L^{-1}. The statistical significance ($p < 0.05$) and low inter-replicate variation confirm the high reproducibility and stability of the system. From a materials perspective, these findings demonstrate that integrating natural organic matter (humic acid) with inorganic industrial waste (fly ash) can yield a cost-effective, eco-friendly, and high-performance hybrid adsorbent, offering a promising route for sustainable wastewater treatment technologies.

4. CONCLUSION

This work demonstrates the successful synthesis of a humic acid–activated fly ash composite as an efficient and sustainable adsorbent for Mn^{2+} removal from aqueous systems. Alkaline activation of fly ash using NaOH effectively enhanced its surface area and porosity, generating abundant ≡Si–OH and ≡Al–OH groups that serve as active adsorption sites. The integration of humic acid introduced additional –COOH and –OH functional groups, facilitating strong metal binding through surface complexation and electrostatic interactions.

The composite with a humic acid-to-fly ash ratio of 1:3 exhibited the highest adsorption efficiency (98.80%) at 120 minutes of contact, representing the optimal balance between structural stability and chemical functionality. FTIR spectra confirmed the formation of Si–O–C and Al–O–C linkages, evidencing chemical interaction between the organic and inorganic phases. Statistical analysis (ANOVA, $p < 0.05$) verified that both adsorbent composition and contact time significantly influence Mn^{2+} uptake efficiency.

Overall, the synergistic combination of humic acid and activated fly ash provides a cost-effective and environmentally benign approach for removing heavy metals. This composite system exemplifies the value of natural and industrial by-products in the development of advanced functional materials for sustainable wastewater treatment.

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