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Original Research Article

Model-Based Assessment of Heavy Metals Leaching Behavior in Wasted Activated Sludge Utilization

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Abstract

Advanced sludge treatment remains a critical challenge as global wastewater production increases, with waste-activated sludge (WAS) posing ecological and health risks due to heavy metal accumulation. This study characterized WAS based on solid parameters and metal content, focusing on As, Cd, Cr, Cu, Fe, Pb, Ni, Mg, Mn, and Zn, which exceed organic fertilizer thresholds. Using Visual MINTEQ, heavy metal leaching behavior was modelled under pH-independent and pH-dependent conditions. The pH-independent simulation identified As as the least leachable metal (2.166×10^{-13} mgAs/L) and Cu as the most leachable (1.261×10^{-4} mgCu/L). The pH-dependent simulation (pH 1.5–13.5) revealed significant leaching for Fe (21.777 mgFe/L) and Cu (1.98×10^{-3} mgCu/L), with Ni (0.120 mgNi/L) and Pb (2.7×10^{-4} mgPb/L) posing chronic risks to aquatic ecosystems. Metals like Cr, Cd, and Ni exhibited distinct leaching patterns influenced by pH and WAS composition. The findings highlight the critical role of pH, along with WAS composition, in governing heavy metal leaching, providing insights to mitigate risks and support sustainable sludge management practices.

Keywords: Sewage sludge; leaching; heavy metals; Minteq; sludge utilization

1. Introduction

The global increase in domestic wastewater production, driven by population growth, has heightened the demand for effective wastewater treatment and sludge management strategies. Biological processes, widely used in domestic wastewater treatment, face a critical challenge: excessive sludge production (Wang et al., 2017; Wei et al., 2003). In conventional activated sludge systems, sludge yield is typically 0.5 kg per kg of treated wastewater (Metcalf & Eddy, 2014). For example, the annual excess sludge production averages 3 million wet tons in Australia and 240 million wet tons in Europe, the USA, and China combined (Pritchard et al., 2010; Wang et al., 2017).The treatment and disposal of sewage sludge from wastewater treatment plants (WWTPs) contribute to 50–60% of the total cost of wastewater treatment (Wei et al., 2003). Common disposal methods such as landfill, agricultural use, and incineration incur significant costs, ranging from $30–70 per wet ton in Australia to €30–100 per wet ton in Europe (Batstone et al., 2011). However, under the right conditions, waste-activated sludge (WAS) can serve as a valuable resource.

WAS, a byproduct of biological wastewater treatment, is rich in essential nutrients (nitrogen, phosphorus, potassium) and micronutrients (copper, molybdenum, zinc) (Barnett et al., 2012; Otieno et al., 2023; Su and Li, 2012). Potential applications include its use as fertilizer and soil conditioner in agriculture, co-substrate in anaerobic digestion (AD) for renewable energy, resource recovery (e.g., bioplastics and nutrients), additives in construction materials (e.g., concrete), and biochar production for water and wastewater treatment (Khan et al., 2023; Kim et al., 2021; Luo et al., 2024; Otieno et al., 2023; Raheem et al., 2018). Despite these promising applications, the presence of heavy metals, pathogens, and organic pollutants necessitates careful selection of utilization technologies. Economic feasibility must also be considered, based on the market demand for recovered products.

Among these concerns, heavy metal content in WAS is particularly pressing, as it poses significant environmental and health risks. Reported concentrations of heavy metals in WAS include Zn (793–1448 mg/kg), Cu (342–1196 mg/kg), Cr (129–151 mg/kg), Pb (60–487 mg/kg), Ni (27–129 mg/kg), Cd (2.3–34 mg/kg), Hg (18–34 mg/kg), and others (Garg et al., 2021; Meulepas et al., 2015). Heavy metals in WAS exist in various forms, such as acid/alkaline-soluble, reducible, oxidizable, and residual fractions, which influence their mobility and environmental impact (Garg et al., 2021; Gawdzik and Gawdzik, 2012). Improper handling of WAS can increase the bioavailability and bioaccumulation of these metals in aquatic ecosystems, leading to contamination.

The mobility of heavy metals in WAS is influenced by factors such as pH and treatment conditions during utilization (Garg et al., 2021; Gawdzik and Gawdzik, 2012; Zhang et al., 2022). Metal mobilization through leaching poses risks to soil health, crop safety, and human health (Sugurbekova et al., 2023; Villar and Garcia, 2003). Risk assessments based solely on total metal concentrations are insufficient, as the chemical form of the metals (e.g., bound to organic matter or as free ions) plays a critical role in determining their environmental impact.

Modelling heavy metal leaching behavior from WAS can provide a better understanding of potential ecological and health risks and help identify mitigation strategies. While previous studies have analyzed heavy metal leaching from municipal solid waste (MSW) fly ash, research on leaching behavior from activated sludge remains limited. Studies on MSW fly ash have shown that heavy metal leaching for Pb and Cd is primarily controlled by dissolution/precipitation mechanisms, while Zn and Ni leaching is influenced by surface adsorption reactions at certain pH ranges (Zhang et al., 2008). Similarly, leaching behavior is pH-dependent, with metals like Cr and Zn becoming insoluble at pH > 6.5, and amphoteric elements such as Pb showing increased solubility at pH > 7 (Chiang et al., 2009). However, there is a lack of studies specifically examining leaching behavior from WAS under varied conditions, despite its frequent use in soil applications.

This study aims to simulate the heavy metal leaching behavior of WAS over a wide pH range to evaluate its potential environmental impact under specific conditions of reuse. By identifying optimal pH conditions to minimize heavy metal risks while preserving valuable sludge properties, this research offers new insights into sustainable waste sludge management. Using Visual MINTEQ, the study modells metal dissociation and stabilization mechanisms in WAS, contributing to environmental protection and resource recovery in line with circular economy goals.

2. Methods

2.1. Research Design and Approach

This study adopts a quantitative experimental design to investigate the leaching behavior of heavy metals from waste-activated sludge (WAS). The research involves laboratory characterization, advanced chemical analysis, and predictive simulation modeling using Visual MINTEQ 4.0. This approach integrates empirical data collection and computational modeling to evaluate the environmental implications of heavy metal leaching under different conditions. The methodology is structured to systematically address the problem of heavy metal mobilization in WAS and its potential risks in various reuse applications. A detailed methodology flow diagram illustrating the step-by-step processes is provided in the **Error! Reference source not found.** Figure 1.s for further reference.

2.2. Sample collection

This study utilized waste-activated sludge (WAS) collected from a centralized domestic wastewater treatment plant in South Jakarta, which operates with a Moving Bed Biofilm Reactor (MBBR) system for organic and nitrogen removal. The treatment facility has a capacity of 950 m^3/h. Sludge samples were obtained from the sludge waste line prior to the addition of chemicals for further dewatering process.

2.3. Sludge Characterization

A comprehensive analysis was conducted to characterize the sludge, focusing on its solid content, nutrient composition (nitrogen and phosphorus) and the presence of various metals. The solid content such as total solid (TS), volatile solid (VS), mixed liquor suspended solid (MLSS), and mixed liquor volatile suspended solid (MLVSS), were determined following the guidelines outlined in the Standard Method (APHA/AWWA/WEF, 2017). Additionally, Total Kjedahl Nitrogen (TKN) was analyzed was analyzed using the same standard methodology.

Concurrently, concentrations of additional metals in the solid phase of sludge, including Phosphorus (P), Aluminum (Al), Arsenic (As), Barium (Ba), Cadmium (Cd), Calcium (Ca), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Mercury (Hg), Nickel (Ni), Potassium (K), Sodium (Na), Tin (Sn), and Uranium (U), were analyzed using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) in accordance with the USEPA 3050B/APHA 3125B standard method. Prior to ICP-MS analysis, the sludge underwent thermal combustion at 550°C for 2 hours, transforming it into ash.

2.4. Leaching modelling

The leaching estimation for each metal was systematically modeled using Visual MINTEQ 4.0, a software developed by KTH Sweden that has been widely recognized for its ability to accurately predict the behavior of metals under various environmental conditions. Visual MINTEQ is particularly advantageous in handling complex systems involving multiple chemical and physical processes, making it an ideal tool for wastewater treatment studies where diverse factors influence metal behavior.

This modelling involved predicting the concentration of metals leached, their saturation index (SI), and the stability of resulting precipitates, all based on the composition of the waste-activated sludge. Metal leaching potential was evaluated based on the SI values, where an SI value below 0 indicates potential leaching, while a positive SI value suggests a stable crystalline state for the metal. The SI was calculated using **Error! Reference source not found.**, where IAP represents ion activity, and Ksp is the e quilibrium constant for precipitate solubility following equation (1):

$$\boldsymbol{SI = log\frac{IAP}{Ksp}} \tag{1}$$

The SI calculation in Visual MINTEQ 4.0 was conducted at a liquid-to-solid (L/S) ratio of 20 (Lima et al., 2012). The simulation conditions included a temperature of 25°C, activity corrections based on the Davies equation (Dijkstra et al., 2008), concentrations expressed in mg/L, and ionic strength calculated automatically by the software. Modelling scenarios were divided into two conditions: one without pH adjustment and another with pH variation ranging from 1.5 to 13.5. This pH range serves as a crucial benchmark, simulating real-world conditions where waste-activated sludge is utilized either as a co-substrate of AD, fertilizer, or as ash in construction material mixtures (Raheem et al., 2018). It is important to note that this simulation focused solely on the inorganic composition of WAS and did not incorporate the influence of organic matter.

3. Result and Discussion

3.1 Characterization of waste activated sludge

3.1.1 Solid content

The solid content in the activated sludge in this experiment was characterized by TS, VS, MLSS, and MLVSS (**Figure 1**). The TS value, representing the total solids and moisture content in the waste activated sludge, was found to be 8.807 ± 0.17 g/L, corresponding to 0.76% ± 0.16% on a percentage basis, with a water content of 99.23%. Compared to typical TS values in domestic WWTP activated sludge (0.8–1.2%) (Bozkurt and Apul, 2020; Metcalf & Eddy, 2014), the TS in this experiment is slightly below the typical range but not significantly different. It is important to note that the WAS used in this study was collected from a Moving Bed Biofilm Reactor (MBBR)-activated sludge system, which generally produces lower WAS volumes compared to conventional suspended activated sludge systems. This is due to solids remaining attached to the media for a longer time rather than being wasted as sludge (Czarnota and Masłoń, 2019; Li et al., 2022; Metcalf & Eddy, 2014). Meanwhile, the VS content in this experiment was approximately 85.23% ± 1.86% of TS concentration, indicating a mixture of organic waste from the influent and microorganisms responsible for biological processes. Optimizing the solid content in the sludge could significantly enhance sludge recovery in the downstream process.

The MLSS and MLVSS concentrations in this experiment were 3.89 ± 1.18 g/L and 2.3 ± 0.03 g/L, respectively (**Figure 1**). These values indicate the total solids (inorganic and organic) and the volatile solids (organic content) in the activated sludge, indirectly reflecting microbial activity. The MLSS and MLVSS concentrations are within the range typically found in domestic WWTPs (900–10000 mg/L) (Jin et al., 2014; Metcalf & Eddy, 2014; Mohan and Nagalakshmi, 2020), depending on the biological processes applied. The WAS used in this study was collected from an MBBR-activated sludge system. Given the nature of MBBR, some microorganisms and solids remain attached to the media for longer time instead of being wasted as sludge (Metcalf & Eddy, 2014). Additionally, MLSS concentrations exceeding 4000 mg/L can cause sludge bulking during sedimentation, potentially obstructing tertiary treatment (BGMEDRI, 2007; J. Zhang et al., 2021). The near-upper-limit MLSS value in this study suggests that the activated sludge condition may hinder subsequent processes if not properly managed in the WWTP.

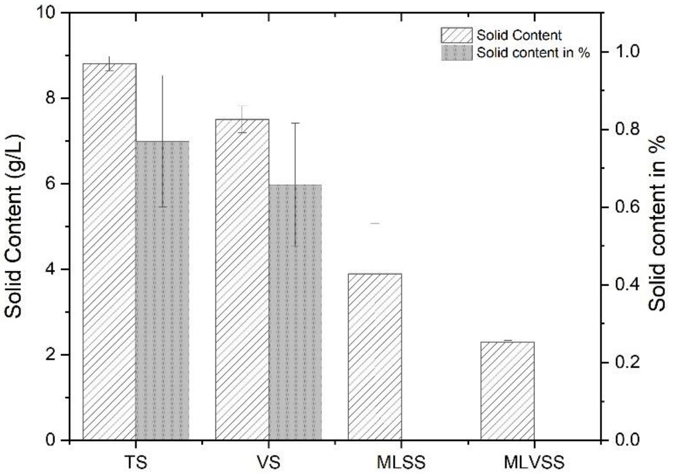


Figure 1. Solid content characterization data in Waste Activated Sludge

The MLVSS/MLSS ratio, a critical indicator of sludge activity, was 0.59 in this study, which is lower than the typical value of 0.75 (Wentzel et al., 2002). This low ratio indicates reduced sludge activity, likely due to the accumulation of inorganic solids in the biological reactor (Gagliano et al., 2020; Trego et al., 2020). While high MLSS with low MLVSS ratios can hinder biological performance, it may benefit solid-liquid separation during the sludge recovery process (Metcalf & Eddy, 2014). Thus, to optimize reactor performance, it is essential to manage sludge age by recycling, and wastage effectively. These measures ensure not only efficient wastewater treatment but also enhanced recovery of sludge in downstream processes.

3.1.2 Elemental composition

Table 1. shows the average elemental composition of waste-activated sludge (WAS) as determined by ICP-MS analysis. The concentrations of carbon, nutrients, metals, and salts are compared against the Regulation of the Minister of Agriculture of the Republic of Indonesia for both liquid and solid organic fertilizers. Notably, Indonesia currently lacks specific regulations for the recovery and reuse of WAS from domestic wastewater. The table indicates that several metals and salts in the WAS exceed the national thresholds for both liquid and solid organic fertilizers. Specifically, cadmium, iron, lead, and nickel levels surpass the upper limits for both fertilizer types, while arsenic, chromium, copper, magnesium, manganese, and zinc exceed the standards for liquid organic fertilizers. Direct application of WAS to land may pose risks of toxicity and bioaccumulation associated with these metals (Gu et al., 2020; Wen et al., 2014). Furthermore, environmental conditions may enhance the leaching of these compounds into the liquid phase, increasing the potential for environmental and human health hazards.

In terms of nutrient requirements for organic fertilizers, the regulation does not specify the minimum NPK concentration. However, when compared to phosphorus fertilizer industry standards and EU recommendations, the phosphorus content in this experiment's sludge is significantly lower. The recommended minimum phosphorus content is approximately 2% dry weight, whereas the WAS in this study contains only 0.04% phosphorus (see **Table 1**) (Johansson et al., 2017). Domestic WAS recovery for fertilizer often focuses on phosphorus due to its limited availability and high agricultural demand (Cieślik and Konieczka, 2017; Yu et al., 2021). For areas with high population densities generating large amounts of WAS, pre-treatment methods could be implemented to concentrate carbon, nitrogen, and phosphorus for reuse as fertilizer. However, modelling heavy metal leaching is essential to mitigate the risk of contamination to the environment.

Beyond fertilizer reuse, WAS is also utilized for energy recovery via AD or gasification, biorefinery for enzyme production, and as a component in construction materials like cement and concrete (Raheem et al., 2018; Smol et al., 2015). Several studies have highlighted that high concentrations of heavy metals can hinder anaerobic co-digestion of activated (Al, 2022; Nguyen et al., 2019; Zhang et al., 2024). For instance, concentrations of heavy metals such as Zn, Cr, and Cu above 10 ppm are detrimental to biogas production in AD, while Pb exhibits lower toxicity at concentrations up to 30 ppm (Al, 2022; Nguyen et al., 2019). **Table 1** indicates that the concentrations of Zn, Cr, Cu, and Pb in this study's WAS exceed 30 ppm, suggesting that direct utilization for co-digestion may hinder biogas production if metal content is not properly assessed. Furthermore, the fermentation process during AD can reduce pH levels, potentially increasing heavy metal leaching into the digestion process (Bułkowska, 2024; C. Zhang et al., 2021).

Table 1. Elemental concentration in waste activated sludge

Element	Concentration (mg/ dry Kg)	Liquid Fertilizer threshold concentration (mg/ dry kg)*	Solid Fertilizer threshold concentration (mg/ dry kg)*
Carbon	7517		150000
TKN	835		
C/N	9		≤ 25
Phosphate (P)	41.496		
Potassium (K)	3540		
N + P_2O_5 + K_2O			20000
Aluminium (Al)	81700		
Arsenic (As)	9.8	5	10
Barium (Ba)	560		

Element	Concentration (mg/ dry Kg)	Liquid Fertilizer threshold concentration (mg/ dry kg)*	Solid Fertilizer threshold concentration (mg/ dry kg)*
Cadmium (Cd)	4.13	1	2
Calcium (Ca)	52900		
Chromium (Cr)	81.6	40	180
Cobalt (Co)	34.3		
Copper (Cu)	507	25-500	
Iron (Fe)	65500	90-900	15000
Lead (Pb)	141	5	50
Magnesium (Mg)	7080	25-500	
Manganese (Mn)	7710	25-500	
Mercury (Hg)	0.031	0.2	1
Nickel (Ni)	71.3	10	50
Sodium (Na)	1810	2000	
Tin (Sn)	38.2		
Uranium (U)	12.4		
Zinc (Zn)	3740	25-500	5000

Regarding the use of WAS in construction materials, metal composition also plays a critical role in product quality. High metal content in WAS mixed with construction materials can lead to leaching, corrosion, and failure to meet existing construction material quality standards (Kasina et al., 2021; Lynn et al., 2015). Therefore, modelling the leaching behavior of heavy metals in WAS utilization is crucial to assess associated risks and inform sustainable practices.

Hence, the results suggest that the direct application of WAS poses significant environmental and human health risks due to its concentrated metal content. However, the utilization of WAS as fertilizer, an energy source in anaerobic digesters, or as a component in construction materials is feasible if appropriate pre-treatment processes are employed to stabilize the metal behavior in WAS and mitigate its leaching potential.

3.2 Simulation of leaching behaviour in waste activated aludge without pH modification

The modelling of leaching behavior in this study focused on compounds that exceed the quality standards for fertilizers, as listed in **Table 1**. These compounds include As, Cd, Cr, Cu, Fe, Pb, Ni, Mg, Mn, and Zn. The simulation of leaching behavior without pH modification was designed to determine the leachability of these compounds in WAS during its direct use or final treatment in WWTP. All modelling results are provided in the Error! Reference source not found.. The saturation index (SI) and phase of each c ompound were analyzed to determine its leaching potential. Compounds without an aqueous phase o were excluded from further modelling. Based on the data (Error! Reference source not found.), only As, C d, Cr, Cu, Fe, Ni, and Pb were identified as having the potential to form aqueous leachates under pH-independent conditions. Notably, Fe was found to have a stable solid phase under these conditions, indicated by its SI value exceeding 0, and therefore showed no measurable leaching.

The results of the pH-independent simulation are presented in Figure 2. Among the identified leaching metals, concentrations ranged from 2.166×10^{-13} to 1.261×10^{-4} mg/L. The lowest leached concentration was for As at 2.166×10^{-13} mg As/L, which is significantly lower than the critical toxicity threshold in aquatic systems of 3.4 nmol/L or 2.547×10^{-7} mg As/L (Li et al., 2014). On the other hand, the highest leached concentration was for Cu at 1.261×10^{-4} mg Cu/L, which remains below the aquatic toxicity threshold of 0.6–0.9 mg/L (Angel et al., 2021; Casares et al., 2012). These findings indicate that while some metals exhibit low leaching potential, others, like Cu, may still pose environmental concerns depending on the specific application or environmental context.

It is important to note that these leaching results were obtained under pH-independent conditions. In real-world scenarios, local geological or reactor conditions during WAS utilization may significantly influence leachability. Factors such as metal speciation, solubility, exposure to precipitates, interactions with organic ligands, and changes in mineral phases of precipitates must also be considered. These factors can impact the toxicity, mobility, and overall environmental risk posed by the metals in WAS.

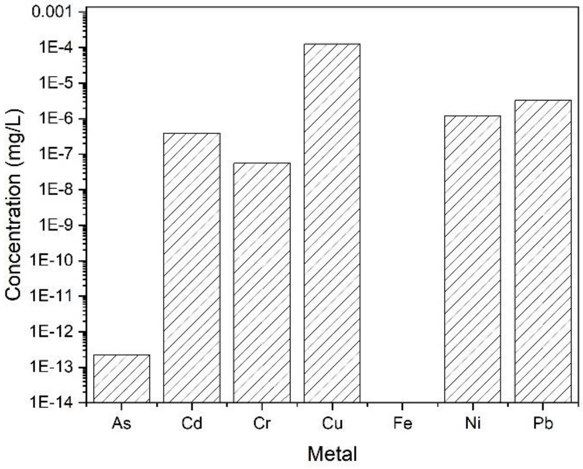


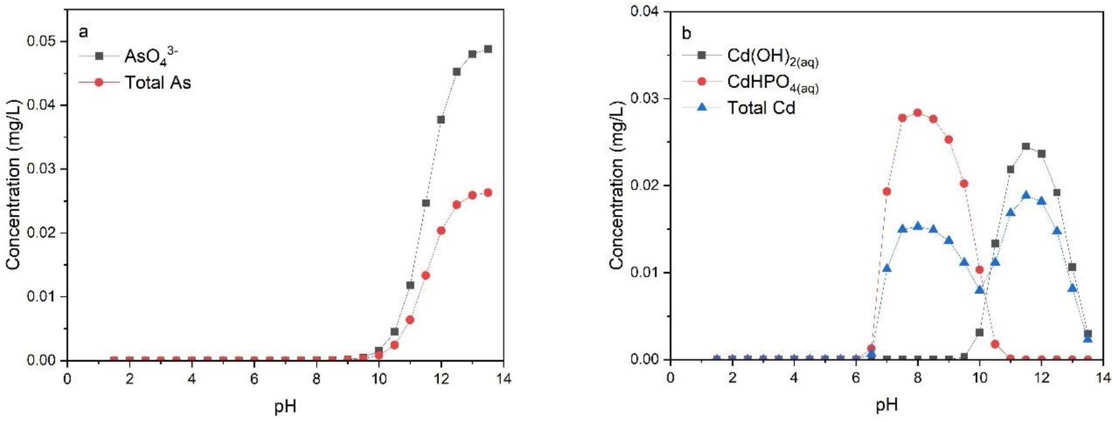
Figure 2. Concentration of leached compounds from WAS in pH-independent simulation using Visual Minteq.

3.3 Simulation of leaching behaviour in waste activated sludge with pH modification

The pH-dependent simulation presented in this section demonstrates the variation in metal solubility across different pH levels. The differences in solubility across pH ranges highlight the influence of metal speciation on phase differentiation. Contrary to several studies that hypothesize heavy metals are more easily leached at low pH (Liu et al., 2011; Van Herck et al., 2000; Wu et al., 2019; Zhang et al., 2009, 2008), the results from this WAS modelling indicate that each metal exhibits a unique leaching pattern. Interestingly, at higher pH levels, the WAS mixture leached more heavy metals compared to lower pH levels. This phenomenon is likely influenced by metal speciation, where pH plays a critical role in determining the interactions among metals (Yesil et al., 2021; Zhang et al., 2009). Furthermore, in the complex mixture of WAS, released metals may immediately precipitate with other metals, forming new insoluble compounds. Despite these variations, it can be concluded that pH is one of the critical factors governing the leaching behavior of metals from WAS.

Figure 3 (a). depicts the leaching behavior of arsenic (As) species under various pH conditions. The highest observed concentration of leached as occurred at pH 13.5, with 0.0263 mg as/L, corresponding to 53.69% leaching of the initial As concentration in the WAS. It was determined that the primary leached species was AsO_4^{3-}, representing arsenic in its as (V) oxidation state. AsO_4^{3-}, categorized as inorganic arsenic, is generally more toxic than organic arsenic forms (Montoro Leal et al., 2018)., although As (V) is less toxic than As (III) (Hare et al., 2020).

In terms of toxicity, the leached As concentration from the model exceeds the standard for drinking water (0.01 mg/L) but remains below the critical value for protecting aquatic life (0.077 mg/L) (Lee et al., 2020; Sharma, 2020). Regarding speciation, it was observed that AsO_4^{3-} was leached at low concentrations between pH 1.5–3 and at higher concentrations between pH 6.5–13.5, but fully precipitated between pH 3.5–6. This behavior aligns with previous studies that reported AsO_4^{3-} solubility increases above pH 8 (García-Carvajal et al., 2019; Sharma and Sohn, 2009). This can be attributed to the weaker dissociation force of as (V) at lower pH, resulting in reduced leaching, while higher pH conditions promote greater as solubility and leaching.



(a) (b)

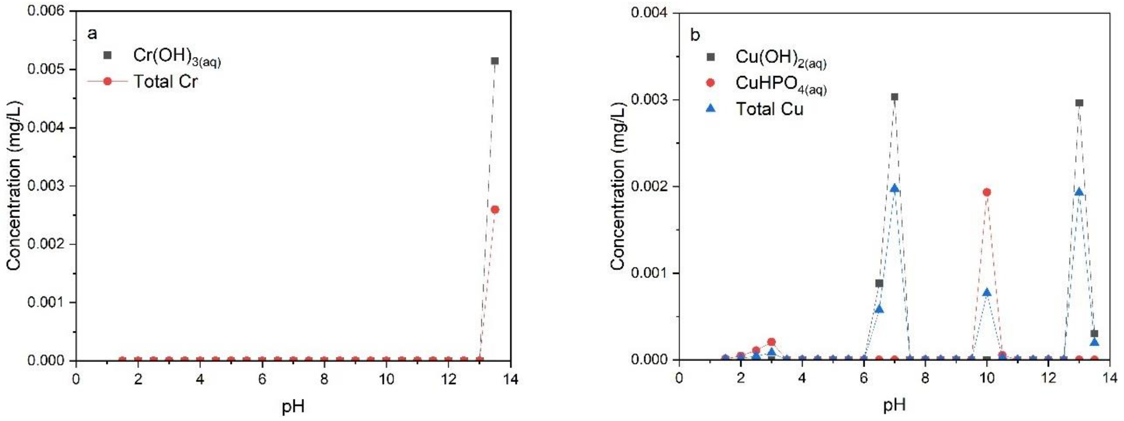
Figure 3 The effect of pH on the leaching concentration of (a) arsenic (As) and (b) Cadmium (Cd)

As regards the dissolution of cadmium (Cd), Figure 3 (b). shows that the primary soluble Cd species are $Cd(OH)_2$ and $CdPO_4$. The highest concentration of leached $Cd(OH)_2$ occurred at pH 11.5, with a concentration of 1.8×10^{-2} mgCd/L, whereas the highest concentration of leached $CdPO_4$ was observed at pH 8, with a concentration of 0.015 mgCd/L. The total soluble Cd reached its peak concentration at pH 11.5, with 0.188 mg Cd/L, corresponding to 91.1% leachability, predominantly contributed by $Cd(OH)_2$, with negligible contributions from $CdPO_4$. Both Cd species are in the +2 oxidation state, which is the dominant state of dissolved Cd in aquatic environments (Dong et al., 2015).

In terms of crystal stability, $CdPO_4$ is more stable than $Cd(OH)_2$, and leaching is more pronounced at lower pH levels (Oyetade et al., 2018). Conversely, $Cd(OH)_2$ dissociates more readily at higher pH (Oyetade et al., 2018), explaining the distinct peaks of soluble Cd in Figure 2.b. The potential release of soluble Cd into the environment poses significant ecological risks. The criterion maximum concentration (CMC) for Cd in water bodies, based on its toxicity, is 6.46×10^{-3} mg/L (Ding et al., 2020). The total simulated leached Cd from WAS was approximately 29 times higher than the CMC, highlighting the substantial ecological risk posed from WAS utilisation.

Figure 4 (a). depicts the dissolution behavior of chromium (Cr). The aqueous phase of Cr is primarily contributed by $Cr(OH)_3$, with the highest concentration observed at pH 13.5, reaching 2.6×10^{-3} mgCr/L, which corresponds to 0.636% leachability from the WAS. Although Cr solubilization occurs at acidic pH, the soluble Cr at pH 13.5 is approximately 10^5 times higher, resulting in negligible soluble Cr values at acidic pH in the graph. Similar Cr leaching behavior based on pH was also reported in other studies, where favorable solubilization of $Cr(OH)_3$ occurs under neutral to alkaline conditions (Ali Redha, 2020; Yuan et al., 2023).

In terms of toxicity, the potential leached Cr from WAS based on the simulation shows a relatively low concentration, remaining below the drinking water standard (0.05 mg/L) (Amanatidou, 2023). Significant accumulation in aquatic plants occurs only above 10 mg/L, and toxicity to aquatic organisms is observed above 2.613 mg/L (Garza-León et al., 2023; Gemeda et al., 2019),. These thresholds are much higher than the simulated leached Cr values from WAS. The low concentration of dissociated Cr can be attributed to the complex metal composition in WAS. The Visual MINTEQ model also suggests the possibility of Cr precipitating with Mg to form $MgCrO_4(s)$, indicating that leached Cr may re-precipitate with Mg, forming a stable solid phase.



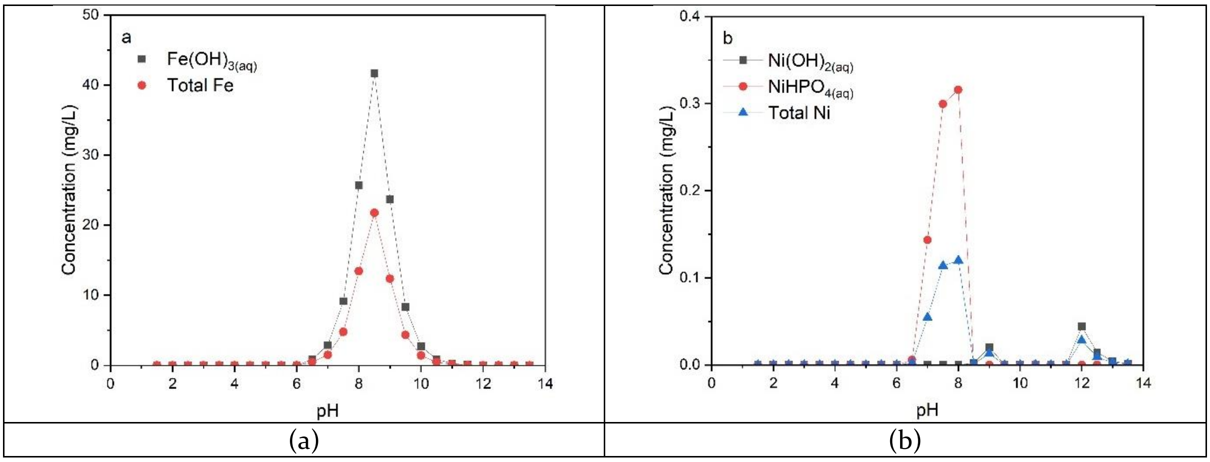
(a) (b)

Figure 4 The effect of pH on the leaching concentration of (a) Chromium (Cr) and (b) Copper (Cu)

Figure 4 (b). illustrates the leaching behavior of copper (Cu) at various pH levels. Two forms of Cu were identified in the aqueous phase: $Cu(OH)_2$ and $CuHPO_4$. $Cu(OH)_2$ was soluble under acidic conditions (below pH 3), neutral conditions, and alkaline conditions (above pH 13). Neutral and alkaline pH levels resulted in higher solubilization of $Cu(OH)_2$ compared to lower pH, where solubility was relatively insignificant. This behavior is attributed to the nature of $Cu(OH)_2$ speciation, which remains insoluble at lower pH (Cuppett et al., 2006; Tegenaw et al., 2020). In contrast, $CuHPO_4$ was only soluble at pH below 3 and above 10, precipitating at intermediate pH ranges (3–10). These results align with previous studies, which found that cupric phosphate predominantly forms a solid under neutral conditions (Grunder et al., 2019; Liu and Zhao, 2007).

Figure 4 (b). also shows that the highest concentration of Cu released into the liquid phase occurred at pH 7, with 1.98×10^{-3} mgCu/L, contributed solely by $Cu(OH)_2$, corresponding to 0.078% solubilization. Meanwhile, the highest concentration of $CuHPO_4$ was observed at pH 10, with 7.7×10^{-4} mgCu/L. In general, at lower pH, free Cu(II) ions are more bioavailable and toxic, increasing their mobility and ecological risk. The potential leached Cu concentration from WAS slightly exceeded the typical criterion maximum concentration (CMC) for freshwater (1.39×10^{-3} mg/L) (Zhang et al., 2017) but remained below the concentration known to cause physiological stress in aquatic animals, such as red sea bream (0.003 mg/L) (Kim et al., 2018).

Figure 5 (a). shows the Fe solubilization behavior modelled by Visual MINTEQ from WAS at various pH levels. The solubilized Fe compound is predominantly $Fe(OH)_3$, with the highest concentration observed at pH 8.5, reaching 21.777 mg Fe/L. The WAS leaching model shows that Fe potentially leaches at pH < 3 and pH > 6.5, which is consistent with findings from other studies on highly concentrated salt metal solutions. $Fe(OH)_3$ has been observed to solubilize within a neutral to alkaline pH range (6–10.5) (Li et al., 2019; Millero, 2001). Based on Indonesian river water quality standards, the limit for iron content in river water is 0.3 mg/L, indicating that Fe leaching from WAS far exceeds the acceptable standard if such leaching into water bodies occurs. Previous research found that the chronic value of Fe(III) for general aquatic life is 0.251 mg/L (Cadmus et al., 2018). Another study proposed bioassessment-based benchmarks, stating that Fe concentrations of 0.21–1.74 mg/L are acceptable for protecting aquatic community structure and function (Linton et al., 2007). It should be noted that the Fe content in WAS is very high, necessitating effective management to minimize Fe leaching and prevent environmental pollution and harm. One potential alternative for managing high Fe concentrations is incorporating this iron-rich sludge into construction materials, where Fe can be utilized effectively, such as in cement or concrete production.



(a) (b)

Figure 5 The effect of pH on the leaching concentration of (a) Iron (Fe) and (b) Nickel (Ni) .

Figure 5 (b). illustrates the Ni leaching behavior modelled at various pH levels. The simulation identified two soluble Ni species, $Ni(OH)_2$ and $NiHPO_4$, with similar speciation patterns across pH variations. $Ni(OH)_2$ was predicted to leach at pH < 3, between pH 6.5–9, and above pH 12, while $NiHPO_4$ was approximated to leach at pH < 3, between pH 6.5–8, and above pH 10.5. The highest dissociation of $Ni(OH)_2$ occurred at pH 12, with 2.79×10^{-2} mg Ni/L, whereas the highest concentration of soluble $NiHPO_4$ occurred at pH 8, with 0.1198 mg Ni/L. At lower pH, $NiHPO_4$ leaching was more pronounced than $Ni(OH)_2$, while the reverse was observed at higher pH levels. This atypical behavior may be attributed to the high Mn content in the sludge (Table 1), suggesting that dissolved PO_4^{3-} preferentially bonds with Mn rather than Ni (Hu et al., 2024). Furthermore, the Visual MINTEQ model predicted a high likelihood of $MnHPO_4(s)$ precipitation at pH < 3, making $NiHPO_4$ dissociation more favorable in such acidic conditions.

Figure 5 (b). further demonstrates that the highest total concentration of leached Ni occurred at pH 8, reaching 0.12 mg Ni/L, corresponding to 91.14% leachability from WAS, predominantly contributed by $NiHPO_4$. This potential leached concentration exceeds the lowest class of Indonesian river water quality standards, which limits soluble Ni to below 0.1 mg/L. However, the acute toxicity threshold for Ni in freshwater fish species ranges from 19.3–61.2 mg/L (Svecevičius, 2010), which is significantly higher than the maximum simulated Ni concentration. Nevertheless, chronic exposure guidelines suggest protective concentrations as low as 0.08 mg/L (Klemish et al., 2018), indicating that prolonged exposure to soluble Ni from WAS could negatively impact the surrounding ecosystem.

The dissolution pattern of Pb at various pH levels is illustrated in Figure **6**. The modelling results show two species contributing to Pb leaching: $Pb(OH)_2$ and $PbHPO_4$, both of which contain lead in the +2 oxidation state (Pb^{2+}). The dissolution of $Pb(OH)_2$ occurs at pH < 3 and neutral pH, while the leaching process of $PbHPO_4$ occurs at pH < 3 and above pH 10. The highest concentration of dissociated Pb was contributed solely by $Pb(OH)_2$ at pH 7, with a concentration of 2.07×10^{-4} mg Pb/L, accounting for 0.029% leachability. Meanwhile, the highest concentration of $PbHPO_4$ was observed at pH 10, with a concentration of 1.74×10^{-4} mg Pb/L. These results are relatively contrary to several studies, which presume that both $Pb(OH)_2$ and $PbHPO_4$ are naturally soluble under acidic conditions (Ioannidis et al., 2007; McBride et al., 2019). However, other studies performing Pb adsorption experiments using Visual MINTEQ show that $Pb(OH)_2(aq)$ predominates at neutral to alkaline pH (Niu et al., 2019). This variation may be due to multiple factors affecting Pb leaching, including the composition of the material and the presence of other metals, which can significantly influence the leaching behavior of Pb.

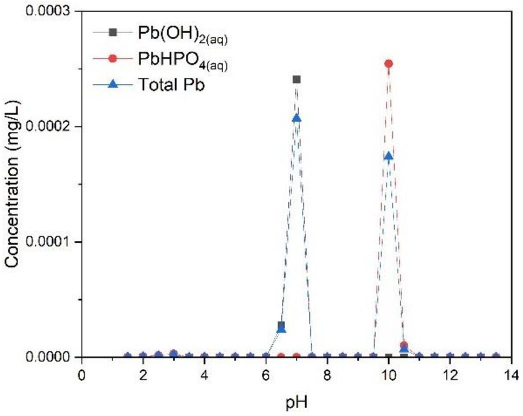


Figure 6. The effect of pH on the leaching concentration of Lead (Pb)

In terms of toxicity, the potential leached Pb from WAS is lower than the Indonesian river water quality standards (0.03 mg/L). Comparing chronic and acute toxicity levels, Pb exposure to aquatic organisms could lead to bioaccumulation at concentrations of 3.5×10^{-3} mg/L and 0.001 mg/L (Besser et al., 2005; Mouchet et al., 2007), respectively. The maximum potential Pb leaching from WAS is relatively lower than these hazardous limits. However, it is important to note that the critical concentration of Pb^{2+} in water that leads to toxicity in aquatic environments depends on factors such as water hardness and the specific aquatic organisms involved.

From the results of leaching modelling under various pH conditions, it was observed that both pH and the complex composition of WAS significantly affect the leaching behaviour of the heavy metals. This model provides an overview of how the heavy metal content in WAS may leach into the environment under varying pH conditions. For any utilisation of WAS, particularly in agriculture, it is essential to consider the composition of WAS, including heavy metals and organic content, and assess the site's pH conditions where WAS will be applied. The use of WAS as a co-substrate in anaerobic digestion should also account for its heavy metal content, as these metals can impact methane yield during digestion. WAS utilisation for construction materials is a safer alternative for WAS utilisation than direct soil application, as the solidification process would immobilise the heavy metals. However, it is important to consider potential leaching due to acid rain, which may release heavy metals, albeit in lower concentrations.

4 Conclusions

This study successfully simulated the heavy metal leaching behavior of waste-activated sludge (WAS) over a wide pH range, providing critical insights into its potential environmental impact under reuse scenarios. Elemental characterization revealed that metals such as As, Cd, Cr, Cu, Fe, Pb, and Ni exceeded thresholds for organic fertilizers, highlighting the risks associated with the direct application of WAS to land. Simulations using Visual MINTEQ showed that under pH-independent conditions, As had the lowest leaching potential, while Cu exhibited the highest. In the pH-dependent simulations, Cr, Cd, and Ni displayed unique leaching patterns, demonstrating that pH plays a critical role in governing metal leaching behavior. Neutral to alkaline pH levels did not necessarily inhibit leaching, challenging typical assumptions due to metal interactions and species transformations influenced by pH.

The high leaching potential of Fe and Cu, which exceeded water quality standards, presents a clear risk of groundwater contamination and ecosystem disruption if WAS is not properly managed. Fe leaching can lead to sediment discoloration, while excessive Cu leaching may harm microbial populations that are critical for soil fertility. Additionally, the risks posed by Ni and Pb, primarily through chronic exposure, raise concerns about bioaccumulation and toxicity in aquatic organisms, potentially affecting food chains and biodiversity. These findings highlight the critical need for monitoring and controlling pH conditions during WAS utilization to effectively mitigate these risks.

To address these challenges, targeted pre-treatment strategies, such as chemical stabilization or pH adjustments, should be implemented to reduce heavy metal mobility. Furthermore, site-specific assessments considering local pH conditions and sludge composition should guide WAS reuse applications in agriculture, construction materials, or energy recovery processes. Future research should include the role of organic matter interactions and field conditions to refine risk assessments and improve the predictive accuracy of metal leaching simulations.

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