



REVIEW ARTICLE

The utilization of alum sludge as constructed wetlands' media to reduce nutrient in communal wastewater treatment plant effluent

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Abstract

Communal wastewater treatment plants (WWTPs) typically used Anaerobic Baffled Reactors (ABRs) due to their low operational costs and ease of maintenance. However, studies indicated that nutrients such as ammonia and phosphate in ABR effluents often failed to meet quality standards. This issue became increasingly urgent as untreated nutrients significantly contributed to environmental degradation, including eutrophication in water bodies, which posed a severe threat to aquatic ecosystems and public health. The pressing need to explore efficient nutrient removal techniques highlighted the importance of investigating innovative approaches such as constructed wetlands using alum sludge. On the other hand, drinking water treatment processes usually required the addition of aluminum sulfate for coagulation, which generated sludge containing aluminum. This alum sludge was often disposed of without proper treatment, leading to environmental degradation. For the first time, this research connected two separate fields-wastewater treatment and alum sludge management-revealing an interdisciplinary approach that transformed alum sludge into a sustainable material for nutrient removal. This innovation addressed dual environmental challenges: mitigating nutrient pollution and repurposing waste materials. Research suggested that dried alum sludge from drinking water treatment plants had the potential to be used as media in constructed wetlands to reduce nutrient levels. A comprehensive literature review was conducted to explore methods of dewatering alum sludge before its use as constructed wetland media, various designs of constructed wetlands using alum sludge and the mechanisms of nutrient removal. This work unveiled promising business opportunities, particularly for industries focusing on sustainable waste reuse technologies and eco-friendly infrastructure development. Prospective directions for further research included optimizing the longevity and efficiency of alum sludge as constructed wetlands media under different wastewater conditions. Future challenges included addressing potential aluminum leaching, maintaining media performance over time and exploring scalability for industrial applications. The results indicated that alum sludge was typically air-dried and then oven-dried before being used as an alternative media in constructed wetlands. Key mechanisms for nutrient removal in constructed wetlands with alum sludge included adsorption through ligand exchange, nitrification-denitrification, microbial activity and plant uptake. Single-stage constructed wetland designs demonstrated higher removal efficiency compared to multi-stage designs, suggesting pathways for cost-effective implementation in decentralized wastewater treatment systems.

Keywords: alum sludge; constructed wetland media; nutrient removal mechanism; wastewater treatment design

Introduction

Water management was a global challenge, given the rising demands for clean water and the escalating impacts of water pollution. Domestic wastewater generation increased with population growth and urbanization, requiring sustainable and effective treatment technologies that aligned with global environmental and economic goals. The urgent need for comprehensive water management transcended regional boundaries, making this discussion equally relevant to diverse audiences worldwide. By focusing on solutions with global applicability, such as the utilization of alum sludge in constructed wetlands, this study contributed to the advancement of global water management strategies.

Technologies that were used in communal wastewater treatment plants (WWTPs) often aimed to balance

environmental sustainability and financial viability, two critical factors in sustainable implementation (1-3). For example, the implementation of Anaerobic Baffled Reactors (ABRs) was widely recognized for their reduced energy requirements and simpler maintenance. However, these advantages came with specific cost parameters. Operational costs for ABRs ranged from \$ 1.7 per m³ of wastewater treated, offering an accessible price point compared to advanced aerobic systems that could cost upwards of \$ 175 per m³ (4-6). It was essential to emphasize that for any wastewater treatment technology to be considered sustainable, it had to present a compelling business case for investors. Drawing from studies such as "The Analysis of Investment into Industries Based on Portfolio Managers" and "The Dynamic Effect of Micro-Structural Shocks on Private Investment Behavior," this research demonstrated how cost

efficiency and nutrient recovery significantly enhanced the attractiveness of alum sludge-based solutions.

Alum sludge, a by-product of drinking water treatment plants, was often disposed of with minimal or no processing, posing environmental risks. This material contained residual aluminum, which could negatively impact soil fertility and plant production if mismanaged. Research such as "Economic Impacts of Soil Fertility Degradation by Traces of Iron from Drinking Water Treatment" and "Ferrous Sludge from Water Clarification: Changes in Waste Management Practices Advisable" highlighted the critical need for improved alum sludge utilization strategies to mitigate these risks (7–9). Transforming alum sludge into a sustainable media for constructed wetlands not only addressed waste disposal challenges but also leveraged its properties for nutrient removal, creating a closed-loop system beneficial for both industries.

Current trends in wastewater management emphasized innovations in nutrient recovery and cost-effective sorbents. For instance, "Modified Biochars Present an Economic Challenge to Phosphate Management in Wastewater Treatment Plants" and "Novel Sorbent Shows Promising Financial Results on P Recovery from Sludge Water" demonstrated the growing interest in sustainable and economically viable recovery techniques. By aligning with these trends, the research outlined here contributed valuable insights to the evolving landscape of global wastewater treatment technologies.

The detrimental effects of improper alum sludge disposal and the inefficiencies in nutrient recovery often resulted in environmental and financial burdens. Nutrient recovery was not merely an environmental benefit but also a pathway to improved economic outcomes in water management systems, as discussed in "Economic Considerations on Nutrient Utilization in Wastewater Management" and "Economic Aspects of Carbon Management in Sewage Sludge Treatment." The integration of nutrient recovery into wastewater treatment could significantly offset operational costs while contributing to resource sustainability (10–14).

This review synthesized information on the potential for alum sludge to be used as media in constructed wetlands and evaluated its effectiveness in improving communal WWTP effluent quality. The central research hypothesis posited that alum sludge, when utilized in constructed wetlands, could serve as a cost-effective and environmentally beneficial medium for nutrient removal, addressing urgent global challenges in water management. The urgency and significance of this research lay at the environmental-economic nexus, aiming to mitigate pollution while creating scalable and financially viable water treatment solutions.

Performance of communal WWTPs and constructed wetlands

Effluent parameters of WWTPs

Several main parameters in WWTP's effluent that needed to be monitored for compliance with water quality standards were BOD, COD, TSS, pH and nutrients. These parameters not only reflected environmental performance but also played a role in evaluating economic feasibility. For example, ensuring compliance with effluent standards directly influenced operational costs by minimizing penalties and streamlining

maintenance protocols. Furthermore, technologies with higher nutrient recovery yielded economic benefits by facilitating resource utilization, such as phosphate extraction for fertilizer production, which improved the overall economy of water management. According to the Regulation of the Minister of Environment and Forestry No. 68/2016 concerning Domestic Wastewater Quality Standards, the maximum limit of BOD, COD and TSS that were allowed to be discharged into the environment were 30 mg/L, 100 mg/L and 30 mg/L, respectively. While the maximum range of pH was 6 – 9. Nutrients such as nitrogen and phosphorus were essential to all living organisms, but these 2 elements needed to be limited to a certain level so that they would not harm the environment (15).

Nitrogen entered the water in the form of organic and inorganic nitrogen. Inorganic nitrogen included ammonium (NH_4^+), nitrate (NO_3^-) and nitrite (NO_2^-) (16). According to the Regulation of the Minister of Environment and Forestry No. 68/2016 concerning Domestic Wastewater Quality Standards, the maximum limit of ammonia that was allowed to be discharged into the environment was 10 mg/L. Phosphorus in nature did not exist in isolation but always combined with other elements to form phosphate compounds (16). According to the Regulation of the Government of The Republic of Indonesia No. 22/2021 about National Water Quality Standards, Attachment VI, the total quality standard for total phosphate in river class I, II and III were 0.2 mg/L, 0.2 mg/L and 1 mg/L, respectively.

Anaerobic Baffle Reactor (ABR)

ABR was an upgraded version of a septic tank equipped with a series of baffles that forced the incoming to keep flowing through the baffles. Although ABR systems were cost-effective, the associated operational savings varied depending on wastewater conditions and design specifications. Precise cost data, where available, could have further elucidated these economic advantages—for instance, \$ 1.7 per cubic meter compared to \$175 for aerobic alternatives. After the Anaerobic Baffled Reactor (ABR) in a communal wastewater treatment plant (WWTP), the process often continued to a constructed wetland. Increasing the contact time, through the baffles, with active biomass (sludge) increased the efficiency of wastewater treatment (17). Several studies reported that most of the ABR WWTPs' effluent quality had not met the quality standards, especially for Total Nitrogen and Total Phosphorus (Table 1). Typically, after the Anaerobic Baffled Reactor (ABR) in a communal wastewater treatment plant (WWTP), the process continued to a constructed wetland. The pollutant removal efficiency of the constructed wetland utilizing sand and gravel media was be observed in Table 2.

Characteristics of Alum Sludge

The amount and characteristics of sludge collected in the sedimentation tank depended on several factors, including water quality, coagulant types and doses, operational efficiency, installation design and many other factors (18). Alum sludge had a bulk density of $1.18 \pm 0.11 \text{ g/cm}^3$ and a porosity of 45 %. With this character, alum sludge was considered prospective to be used as Constructed Wetlands material (19). The pH of the alum sludge ranged between 5.12 - 8 (20). Alum sludge generated from drinking water treatment plants possessed unique characteristics that were beneficial for wastewater treatment. In addition to its use in constructed

Table 1. Efficiency of pollutant removal in wastewater with ABR

Type and location of WWTP	Removal efficiency					Effluent (mg/L)	Ref.
	TSS	BOD	COD	NH ₄ ⁺	TP		
ABR in Malang City, Indonesia	66	74	-	43	21	TSS = 1506 BOD = 67 NH ₄ ⁺ = >10 TP = 3-5.5	(63)
"MCK Plus" in Tlogomas with anaerobic, aerobic and phyto-remediation treatment units	95	78	77	41	12	-	(59)
ABR for Livestock Waste in Denpasar City, Bali	-	-	51-60	50-58	-	COD = 4000 NH ₄ ⁺ = 15-17 TSS = 75-85	(60)
ABR in Bogor City	-	-	-	-	-	BOD = 38-47 COD = 80-90 NH ₄ ⁺ = 8-15 BOD = 38-47	(61)
ABR in Dar Es Salam, Tanzania	-	42.6	-	6	16.9	NH ₄ ⁺ = 8-15 TP = 12.34-16.1	(64)

^aTP = Total Phosphorus

Table 2. Efficiency of pollutant removal by constructed wetlands with sand and gravel as the media

Type of constructed wetlands	Removal efficiency	Ref.	
Sub-surface Vertical Flow Constructed Wetlands (SSFCW) with passive aeration planted with <i>Phragmites australis</i>	BOD = 80 - 95 % COD = 70 - 85 % NH ₄ -N = 75 - 90 %	(56)	
Sub-surface Vertical Flow Constructed Wetlands (SSFCW) planted with <i>Canna Indica</i>	BOD ₅ , COD, TKN, NH ₄ -N = >80 % PO ₄ ³⁻ -P = 15.63 %	(29)	
Constructed Wetlands (CWs) planted with <i>Phragmites australis</i> (Phr) or <i>Schoenoplectus Californicus</i> (Sch)	HSSF-Phr: COD = 55 - 63 % TSS= 88 - 92 % TN= 23 - 24 % TP= 1 - 4 %	HSSF-Sch: COD = 46 - 66 % TSS= 83 - 91 % TN= 18 - 23 % TP= 9 - 13 %	(27)
Horizontal sub-surface Flow Constructed Wetlands (HF CWs) planted with <i>Typha domingensis</i>	BOD = 35.2 - 80.6 % COD = 57.6 - 79.8 % TSS = 65 - 91.8 % NH ₄ -N (90 % TKN) = 28.4 % TP = 16.5 - 43.3 %	(37)	

wetlands, aluminum had promising applications in other industries, such as the production of aluminum nanoparticles. These nanoparticles significantly enhanced the competitiveness of (bio) diesel by improving combustion efficiency and reducing environmental impact, as discussed in "Aluminum Nanoparticles from Liquid Packaging Board Improve the Competitiveness of (Bio) Diesel" (20).

Moreover, while the number of pages and references did not determine the quality of a review paper, focusing on identifying interdisciplinary connections and business opportunities was vital. Alum sludge's dual functionality in nutrient recovery and waste utilization offered opportunities for industries aiming to innovate sustainable practices and optimize economic returns.

Integration of advanced technologies such as AI further enhanced the analysis of multifactorial techno-economic problems (18). For instance, the utilization of generative AI and algorithmic big data simulation tools, as outlined in "Generative Artificial Intelligence of Things Systems, Multisensory Immersive Extended Reality Technologies and Algorithmic Big Data Simulation and Modelling Tools in Digital Twin Industrial Metaverse," enabled predictions the commercial success of alum sludge-based technologies.

Comparison with existing literature

Compared to existing approaches in wastewater management, the insights on alum sludge usage for constructed wetlands revealed deviations, particularly in phosphorus adsorption

efficiency and economic feasibility. These differences were attributed to the innovative ligand exchange mechanisms and the extended operational lifespan of alum sludge media.

Modern trends in wastewater management

Trends in developed countries, such as optimization of biosolids processing and changes in sewage sludge management, emphasized economically driven solutions. Papers such as "Appraisal of Changes in Sewage Sludge Management," "Advances in Economically Driven Optimization of Processing of Biosolids from Sewage Sludge," and "Residues from Water Precipitation via Ferric Hydroxide Threaten Soil Fertility" provided valuable insights into these advancements, demonstrating the balance between environmental protection and cost efficiency.

Proposals for future research

To improve alum sludge's application, future research could have focused on overcoming challenges related to aluminum leaching and media clogging. Exploring advanced drying techniques, such as microwave-assisted drying and optimizing operational parameters were expected to further enhance performance. Additionally, a deeper investigation into nutrient recovery strategies and the development of scalable technologies for industrial applications could have paved the way for broader implementation.

Driving mechanisms and original findings

This study uniquely integrated the economic and environmental dimensions of wastewater management, revealing driving mechanisms such as aluminum's chemical affinity for phosphorus and its potential for industrial reuse. These findings contributed significant value to the field by uncovering overlooked connections between wastewater treatment, alum sludge management and sustainable business opportunities.

Dewatering Alum sludge

The dewatering process of alum sludge aimed to reduce the volume of the water content in the alum sludge, lower transportation costs and simplify its transport. Drying was classified into 2 groups, namely natural and mechanical (21, 22). Two categories of natural drying based on depth existed: drying beds and lagoons. Meanwhile, mechanical drying utilized several types of equipment, such as filter presses, belt filter presses, or centrifuges (23). The thermal drying method with Microwave Drying (MWD) provided a fast and selective heating process. Hence, energy usage is efficient and increases product quality (22).

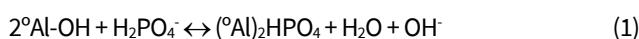
Alum sludge was bulky and gelatinous, especially before drying. The dried alum sludge had a rough surface and amorphous structure. The amorphous nature of the alum sludge increased its surface area and its chemical affinity for phosphorus (24). The rough surface of the dried alum sludge was ideal for biofilm growth (25).

Alum sludge's physical-chemical adsorption potential of phosphorus in communal WWTP effluent

Alum sludge was prospective for phosphate adsorption in the treated wastewater effluent. Some potential mechanisms included surface precipitation, electrostatic attraction, ligand exchange, outer-sphere complexation, inner-sphere bidentate surface complexation and ion exchange (14).

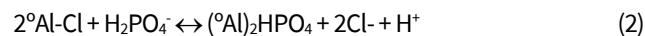
Ligand exchange

Studies reported that the phosphate adsorption by the alum sludge highly depended on 2 factors: the solution's pH and the surface characteristics of the alum sludge. Some processes occurred during the adsorption process, e.g., the rise of pH and sulphate ion (SO_4^{2-}), chloride ion (Cl^-) and total organic carbon (TOC) concentrations which followed the phosphate concentration drop in the solution. A slight decrease in total aluminium also occurred, indicating that phosphate replaced the functional groups from the surface of the alum sludge. This indicated that the ligand exchange was the predominant mechanism for removing phosphate. The ligand exchange process was represented as follows (26):

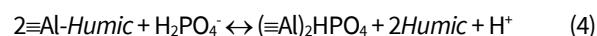


The presence of hydroxide ions, as shown in Equation 1, could have increased the pH of the solution. However, the pH increase was minimal due to the contribution of other phosphate adsorption mechanisms. The drop in phosphate concentration, followed by the rise of sulphate and chloride ions in the solution pointed that another mechanism of phosphate adsorption by alum sludge took place, i.e., the ligand exchange between phosphate and SO_4^{2-} and Cl^- ions in alum sludge. This mechanism resulted in the release of hydrogen ions into the solution, which later limited the pH

increase. The ligand exchange process was described as follows (27):



The increase of phosphate adsorption and the release of humic substances ($\text{C}=\text{C}$ and $\text{CO}=\text{}$) indicated that the desorption of organic matter had taken place. This occurred as a result of competition between phosphate and humic substances for surface sites (24).

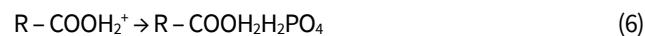


Surface complexation

Outer and inner-sphere complexation were similar mechanisms involving the adsorption of solutes onto solid surfaces. Inner-sphere complexation involved ligand exchange, while outer-sphere complexation depended on electrostatic attraction and was very sensitive to ionic strength. However, the latter resulted in weaker adsorption compared to inner-sphere complexation. This suggested slight sensitivity to ionic strength or, in other words, possessed greater adsorption capacity at higher ionic strength conditions (28).

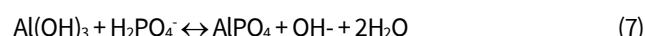
Electrostatic attraction

As the pH increased (e.g., more than 8.6), the surface of the adsorbent becomes negatively charged, which was not favourable for electrostatic attraction. The negative charge on the surface of the alum sludge repelled the phosphate ions in the solution so that the phosphate ions cannot be adsorbed to the surface of the alum sludge (29). The increasing zeta potential at lower pH enhanced the electrostatic interaction, which led to an upgrade in the phosphorus adsorption capacity due to the positive surface charge (30). However, although the zeta potential decreased as the pH rose, ligand exchange compensated for reduction in electrostatic attraction so P adsorption remained relatively stable (31). The electrostatic reaction was represented as follows (32):



Surface precipitation

In addition to surface adsorption, phosphate was also able to form surface precipitates on the surface of Al oxide (33). Adsorption was favoured when the ionic strength and the phosphate concentration were low, while surface precipitation was preferred under conditions of high phosphate concentration and high ionic strength. The mechanism of surface precipitation was considered a continuation of surface complexation processes. Hence, at the beginning of the process, adsorption predominate. As the phosphate concentration increased, surface precipitation indicated (34). The following equations illustrated the surface precipitation (32, 35):



The results of Bleam's study, indicated that the species:

$\text{^{\circ}\text{AlH}_2\text{PO}_4}^{0(s)}$, $\text{^{\circ}\text{AlPO}_4}^{2-}{}^{(s)}$, $\text{^{\circ}\text{AlHPO}_4}^{-(s)}$, depended on pH (36). The adsorption capacity by alum sludge for phosphorus was presented in Table 3.

Table 3. Research collection on phosphorus adsorption capacity by alum sludge

Max. P adsorption capacity	pH at max. P adsorption capacity	Initial P in accordance with max. adsorption capacity P	Alum sludge particle size (mm)	Adsorbent dosage	Experiment type	Temp.	Agitation (rpm)	Retention time	Explanation	Ref.
1125 mg P/g	4	10.5 (mg P/L)	< 2.36	5 g/L	Batch	-	250	6 hr (to reach equilibrium)	When pH = 3, the dominant phosphate species is H_3PO_4 When pH = 4-10, the dominant phosphate species are $H_2PO_4^-$ and HPO_4^{2-}	(52)
15.57 mg PO_4^{3-} /g (>13 % than at neutral pH)	4	150 mg PO_4^{3-} /L	< 0.3 - >1.18	2.5 ± 0.05 g/L	Batch	40 ± 2 °C; 30 ± 2 °C	-	24 hr (P removal close to 99 %) (if pH 7 - 8, needs > 48 hours)	When pH > 10, the dominant phosphate species is PO_4^{3-} There was an increase in the adsorption rate 21% at 40 ± 2 °C than 30 ± 2 °C With the same % removal, alum sludge with in fine particles took 7 hr, sizes 1.18 - 4 mm took 24 hr and sizes > 4 mm required > 24 hr	(35)
Removal P ± 96 % (47.62 mg P/g DAS) (Sludge B)	6	50 mg P/L	0.15 - 0.6	2.5 g/L	Batch	-	200	21 hr mixing	Experiments were carried out with 3 types of alum sludge with various aluminium content: Sludge B (144000 mg/kg Al), Sludge C (112000 mg/kg Al), Sludge D (105000 mg/kg Al)	(47)
20.1 - 22.4 mg P/g DAS	4.3	100 mg P/L	< 0.063	1 - 5 g/L	Batch	-	200	48 hr mixing (to reach equilibrium)	Experiments were carried out in various pH: 4.3, 6, 7, 8.5, 9	(57)
Orthophosphate: 10.2 mg PO_4^{3-} /g DAS Polyphosphate: 7.4 mg PO_4^{3-} /g DAS Organic Phosphate: 4.3 mg PO_4^{3-} /g DAS	4	14.7 mg/L Orthophosphate + 10.8 mg/L Polyphosphate + 3.3 mg/L Organic Phosphate	< 2.36	1 - 5 g/L	Batch	21 ± 2 °C (constant)	200	24 hr (to reach equilibrium)	Experiments were carried out in various pH: 4, 5.5, 7, 9 Agitation was carried out at various intervals, up to 24 hr. More P was mobilized when the adsorbent dose was 5 g/L than 1 g/L.	(67)
Removal P >80%	6.78 - 7.2	50.8 mg/L Orthophosphate + 18.1 mg/L Polyphosphate + 6.5 mg/L Organic	< 2.36	-	Continuous flow column	-	-	30 days	For this experiment, it was carried out for about 60 days, but due to the high P load, the P removal efficiency decreased rapidly especially after 30 days of operation.	(67)
4.52 mg P/g DAS	4	5.4 mg P/L	1.18	1 - 5 g/L	Batch	-	-	48 hr mixing (to reach equilibrium)	Experiments were carried out in various pH from 4-9 The percentage of P removal increased while increasing the adsorbent dose up to 5 g/L.	(67)
Removal P 90 % (2.66 mg P/g DAS) (Sludge A)	-	-	1.18	-	Continuous flow column	-	-	140 days	After 140 days, the adsorption capacity decreased from 90 % to 30 %.	(67)
Orthophosphate removal 99 % (4.86 mg P/g) (Sludge B)	4	55 mg/L	1.65 - 1.98	12 g/L	Batch	Not controlled	200	90 min (1.5 hr) mixing	Experiments were carried out with 2 types of alum sludge with different aluminium content: Sludge A (174.60 mg/g Al) & Sludge B (108.00 mg/g Al)	(58)
Orthophosphate removal 98 % (1.58 mg P/g)	5.5	55 mg/L	1.65 - 1.98	30 g/L	Batch	Not controlled	200	80 min (1.33 hr) mixing	Experiments were carried out at 10, 20, 30, 40, 50 g/L.	
85%	6	5 mg/L	0.5	50 g/L	Batch	25 ± 1 °C	0	6 days without mixing (to reach equilibrium)	Phosphorus removal percentage increased while increasing the weight of alum sludge (maximum at 50 g/L)	(59)
% Removal P with particle size 2.36 mm > % Removal P with particle size 4.75 mm	-	10 mg/L and 5 mg/L	2.36 and 4.75	-	Fixed Bed Column	25 ± 1 °C	0	-	Increasing the bed depth will increasing the breakthrough time and solute contact time in the column. % removal will be the same if: Q (water rate) = 6 L/day with H (bed depth) = 0.25 m; Q = 10 L/day with H = 0.415 m The percentage of phosphorus removal increased with the increasing contact time and adsorbent surface area	(59)

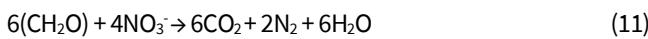
Biologically nutrient removal in communal WWTP effluents by constructed wetlands

Biologically, the transformation of nitrogen compounds occurred due to processes of mineralization, nitrification, denitrification, nitrogen fixation and plant uptake (37). Macrophytes (plants) and bacteria (microorganisms) were the key to the removal of nitrogen compounds (38). The ammonia removal by microbes in Constructed Wetlands usually involved nitrification, denitrification and annamox. Nitrification was a two-step aerobic process involving 2 groups of microorganisms, one group of microorganisms that oxidized ammonia-N to N-nitrite (partial nitrification or nitrite) (Equation 8) and another group oxidized nitrite-N to nitrate-N (Equation 9) (38). The stoichiometry of nitrification was represented as follows (39):



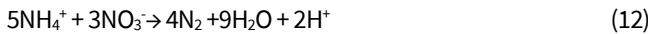
Nitrification was affected by temperature, pH, water alkalinity, inorganic C source, humidity, microbial population, ammonium-N concentration and dissolved oxygen. The optimum temperature for nitrification ranged from 25 °C - 35 °C for pure culture and 30 °C - 40 °C for soil. The optimum pH was between 6.6 and 8. However, acclimatization was relevant for nitrification at much lower pH values (40).

Denitrification was a multi-step process for transformed nitrate to nitrite and finally to nitrogen gas. The stoichiometry of denitrification was as follows (41):



Factors affected the rate of denitrification included the absence of O₂, redox potential, soil moisture, temperature, pH, presence of denitrifiers, soil type, organic matter, nitrate concentration and the presence of water on it. The optimum pH ranged between 6 and 8. When the pH was below 5, denitrification occurred more slowly but could still be significant. Denitrification by organotrophs was negligible or absent at pH value below 4. Denitrification was also highly dependent on temperature with the degree of denitrification increasing to a maximum at 60 °C - 75 °C (42).

Anammox bacteria (Anaerobic Ammonium Oxidation) were capable of using both nitrite and nitrate to oxidize ammonia to nitrogen gas. The stoichiometry of the anammox process was represented as follows (38):



Periphyton and microorganisms were also capable of taking up phosphorus (P), but most of it was released after cell death (43). Plants absorbed and metabolized organic xenobiotics and release root exudates, which enhanced the biotransformation of compounds (44). Plants in constructed wetlands performed 2 significant indirect functions: their roots increased the surface area available for microbial attachment and they transport atmospheric gases (including oxygen) into the roots zone, allowing the plant to survive in anaerobic environment. This formed a thin aerobic layer surrounding the root hairs, which provided an oxygenated zone where NH₄⁺ was nitrified to NO₃⁻. Consequently, an anaerobic region

surrounded the aerobic zone (45). Root biomass played a significant role in nitrogen removal in constructed wetlands in particular, because it supplied denitrifies with carbon through exudates enabling the removal nitrates. Nitrates diffused from out of the root zone into anaerobic sediments where denitrification occurred (46).

Although plants contributed to P removal, plant uptake represented less than 20 % of P removal (47). The uptake of nutrients (i.e., phosphorus and nitrogen) by plant was only effective in low-load systems. The absorption and storage of phosphorus in biomass had limited capacity and therefore did not support long-term sustainable removal. Phosphorus was released back from the biomass to the constructed wetlands ecosystem after plant decomposition. Each plant species followed a different growth sequence indicating that the uptake contribution of each plant species varied (48-51).

Removal mechanism in constructed wetland

In terms of reducing nutrients, especially phosphorus and ammonia, each part of the Constructed Wetlands-based alum sludge, namely plants, microorganisms and the alum sludge substrate, had a distinct role. Several mechanisms occurred in the constructed wetland resulted in nutrient removal. Biological removal using living organism as medium such as microorganism and plant to reduce nutrient in the wastewater. In addition to biological processes, chemical and physical removal mechanism were also observed. In this study, these two removals were obtained by using adsorption.

Chemical and physical removal

Several previous studies concluded that the most influential in the removal of phosphorus was the adsorption by the alum sludge as a substrate. Among various available phosphorus adsorption mechanisms, ligand exchange was the most dominant adsorption mechanism. Factors affecting the adsorption of phosphorus included pH, adsorbent particle size, retention time or contact time, competitive anion, adsorbent dose, temperature, initial phosphorus concentration and shaking or agitation.

pH

Almost all adsorption experiments stated that adsorption was highly dependent on pH. Optimum phosphorus adsorption generally occurred in the pH range of 4-6 (35, 52, 53), specifically for orthophosphate as it was the most powerful phosphorus species and the most easily adsorbed by alum sludge in solution. When the pH was low, H⁺ ions dominated the surface of the alum sludge. It triggered the release of OH ions into the solution, creating a free active site for phosphate adsorption. The presence of the active site of the hydroxyl group (-OH) created an opportunity for ligand exchange between phosphate ions and OH ions that occur on the surface of the adsorbent resulting in an increasing adsorption capacity of phosphorus. However, a lower pH, e.g., below 3, was also not great because at pH of 3 the dominant phosphate species was H₃PO₄, which was weak to be bound to the adsorption site (52).

If the pH was high (7), then hydroxyl ions (OH⁻) will dominate the solution. There was competition between hydroxyl ions (OH⁻) and phosphate (PO₄³⁻) to fill the active site on the surface of the alum sludge. More OH⁻ ions occupied the

active sites, forming a counter ion layer, which reduces P adsorption. There was a change in the zeta potential, which was correlated with the surface charge of the alum sludge, from positive to negative when the pH of the solution changes from acidic to alkaline. The increasing pH reduced the phosphate adsorbed by the alum sludge. However, a very low pH was not favourable, as it increased the solubility, thereby causing aluminium leaching from the alum sludge (54–56). pH played a crucial role and significantly influenced the process. The differences in phosphorus adsorption at maximum capacity under neutral pH conditions were observed in Table 4.

Adsorbent particle size

The various particle sizes were used in some experiments and were difficult to compare. However, it was concluded that phosphorus adsorption was better and optimum when using small/fine particles compared to large particles because the surface area of small/fine particles was larger than the surface area of large particles.

Retention time / contact time

It was found that with an increase in retention time/contact time in the adsorption process, there was an increase in phosphorus removal or adsorption capacity. Retention time varied in each experiment because there were variations of parameters each experiment. As long as other factors (i.e., alum sludge particle size, temperature, pH, presence of competitive substances/anions and agitation) were optimal, contact time does not always play a significant determining factor.

Competitive anion

Alum sludge contained various substances. Due to the same charge, the phosphate and other anions competed to occupy the same site on the cation surface of the alum sludge. These competitive substances/anions interfered with the adsorption of phosphate. The surface of the alum sludge contained many reactive functional groups, such as -OH, -Cl, -SO₄ and humic substances. These groups acted as competitive anions to phosphorus in the ligand exchange mechanism for adsorption. At alkaline pH, hydroxyl ions attracted aluminium more than phosphate did. However, several studies also showed that the presence of competitive ions did not significantly affect the adsorption phosphate but indicated that phosphate had a lower competitive strength than some other anions present in wastewater.

Adsorbent dosage

In principle, increasing the dose of alum sludge increased the P removal capacity because the number of active sites or the total surface area for adsorption also increased. However, the increase of P removal capacity varied from among studies.

Temperature

The adsorption capacity increased with increasing temperature (35). However, the statement regarding temperature affecting the adsorption capacity still required further research as most research on this topic does not use temperature as a variable.

Initial concentration of phosphorus

The time required to reach saturation decreased as the concentration increased. Hence, there was an increase in the adsorption capacity of phosphorus by alum sludge once there is

an increase in the initial phosphorus concentration. This occurred due to a correlation between the increased driving force for mass transfer and increased solute concentration. Also, the concentration gradient controlled the diffusion rate (57).

Agitation

The absence of shaking/agitation prolonged the time to reach equilibrium (58). An increase in agitation also increased the adsorption capacity of phosphorus (52). With increasing agitation, the rate of diffusion of the adsorbate from the solution to the liquid boundary layer around the adsorbent particles increased due to the increase in turbulence and decrease in the thickness of the liquid boundary layer, which increased the adsorption rate (52).

Biological removal

The roles of plants and microorganisms in the removal of phosphorus were in a much smaller percentage. Phosphorus was removed biologically by plant uptake or microbial uptake but was only significant for low-load systems. The factor that affected the biological removal of phosphorus was the amount of phosphorus that entered the system.

Removal ammonia by microorganisms

Macrophytes (plants) and bacteria (microorganisms) were the keys to ammonia removal in wastewater effluent. Factors that affected bacterial performance in ammonia removal included temperature, pH, organic matter and dissolved oxygen. The mechanism of aerobic and anaerobic in constructed wetland was illustrated in Fig. 1. Nutrient removal efficiency at each stage was presented in Table 5.

pH

The optimum pH for nitrification and denitrification ranged between 6.6 - 8. For a much lower pH, acclimatization could occur (59, 60).

Organic compounds

Facultative chemolithotrophic bacteria that played a role in the second step of the nitrification process (i.e., oxidation of nitrite to nitrate) were able to use organic compounds (other than nitrite) to produce energy for growth. As for denitrification, organic compounds were needed as electron donors and cellular carbon sources (51). The calculation of CW using sand and gravel media was presented in Table 6, while using alum sludge as media was shown in Table 7.

Dissolved oxygen

Chemolithotrophic bacteria playing a role in the first step of the nitrification process (i.e., oxidation of ammonium to nitrite) fully depended on oxygen for oxidize ammonia and produce energy for growth (46). Several experiments used Constructed Wetlands with a tidal flow system to provide bed rest time to take oxygen from the atmosphere.

Removal ammonia by macrophytes

Factors that affected the performance of macrophytes (plants) in ammonia removal were plant species and seasons. Each species had a different ability to absorb nutrients, resulting in differences in the growth rate of these plants. Plant growth was linear with biomass production. In addition, in its application, it was necessary to adjust the types of plants that were tolerant of metal elements in the alum sludge.

Table 4. Comparison of phosphorus adsorption capacity at maximum and neutral pH

Max. P adsorption capacity	pH at max. P adsorption capacity	Neutral pH	Adsorption capacity at neutral pH	Agitation (rpm)	Retention time	Ref.
1125 mg P/g	4	7	1,067 mg P/g (94.8 % from Adsorption Capacity at pH 4)	250	6 hr (to reach equilibrium)	(52)
15.57 mg PO ₄ ³⁻ /g (± 99 %)	4	7 - 8	13.37 mg PO ₄ ³⁻ /g (87 % from Adsorption Capacity at pH 4)	-	24 hr	(35)
		7 - 8	± 99 %	-	> 48 hr	
		6	17 - 18.3 mg P/g			
20.1 - 224 mg P/g DAS	4.3	7	13.1 - 14.3 mg P/g	200	48 hr mixing (to reach equilibrium)	(57)
		8.5	1.1 - 2.8 mg P/g			
Orthophosphate: 10.2 mg PO ₄ ³⁻ /g DAS	4	7	Orthophosphate: 7.2 mg PO ₄ ³⁻ /g DAS (71 % from Adsorption Capacity at pH 4)			
Polyphosphate: 7.4 mg PO ₄ ³⁻ /g DAS			Polyphosphate: 3.7 mg PO ₄ ³⁻ /g DAS (50 % from Adsorption Capacity at pH 4)	200	24 hr (to reach equilibrium)	(67)
Organic Phosphate: 4.3 mg PO ₄ ³⁻ /g DAS			Organic Phosphate: 3.5 mg PO ₄ ³⁻ /g DAS (81% from Adsorption Capacity at pH 4)			
4.52 mg P /g DAS	4	6	4.05 mg P /g DAS (89.6 % from Adsorption Capacity at pH 4)	-	48 hr mixing (to reach equilibrium)	(65)
		7	3.12 mg P /g DAS (69 % from Adsorption Capacity at pH 4)			
		8	1.96 mg P /g DAS (43 % from Adsorption Capacity at pH 4)			
(Sludge A) Removal of orthophosphate 99 % (4.86 mg P /g)	4	6	± 98 %			
		7	± 95 %	200	90 min (1.5 hr) mixing	(29)
		8	± 75 %			
(Sludge B) Removal of orthophosphate 98 % (1.58 mg P /g)	5.5	6	± 97.5 %			
		7	± 96 %	200	80 min (1.33 hr) mixing	(29)
		8	± 95 %			
85 %	6	7	± 82 %	0	6 days without mixing (to reach equilibrium)	(57)

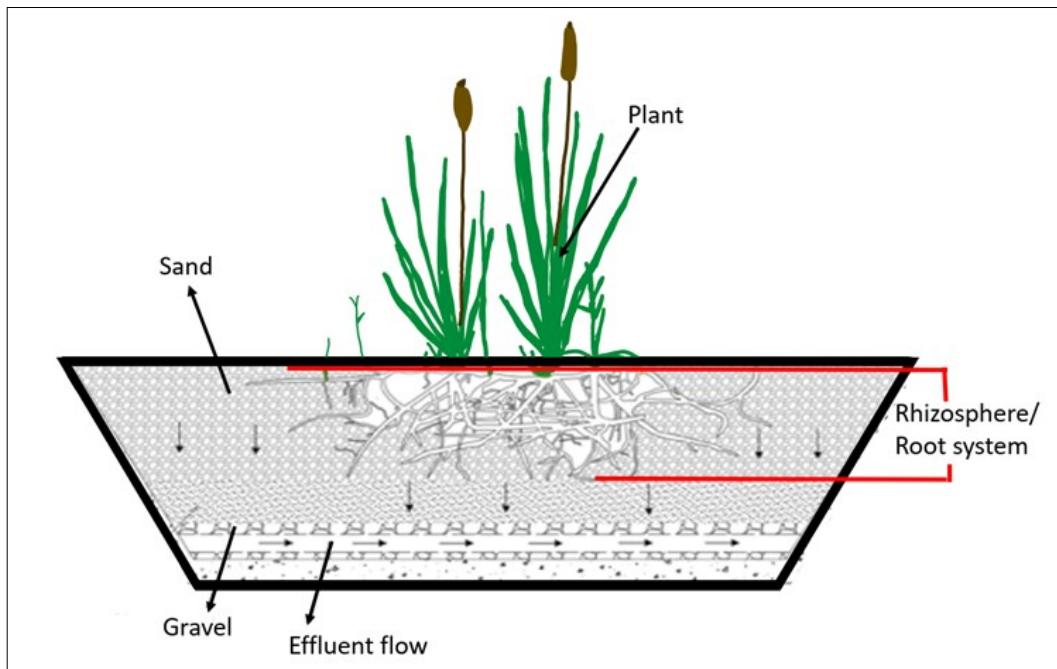
**Fig. 1.** Aerobic and anaerobic mechanisms in the root zone of sub-surface vertical flow constructed wetlands.

Table 5. Nutrient Removal Efficiency at Each Stage (80).

Parameters	Stage 1 (%)	Stage 2 (%)	Stage 3 (%)	Stage 4 (%)
% Removal of TP	80	55	22	10
% Removal of NH_4^+ -N	15	18	28	16
% Removal of COD	33	17	30	17
% Removal of BOD	40	25	29	33
% Removal of TSS*	55	55	55	55

*this is assumed, as TSS is not the focus in this simulation

Feeding operational: 80 % of the wastewater is pumped into the first stage, while the rest is pumped into the third stage.

Table 6. Calculation of constructed wetlands with commonly used media (sand and gravel)

Parameters	Effluent conc. of ABR (mg/L)	Wastewater quality standard (mg/L)	Influent Conc. (mg/L)	Percentage removal (%)	Effluent conc. (mg/L)
TSS	1506	30	1506	92	120.48*
BOD	67	30	67	90	6.70
COD	67	100	67	80	13.40
$\text{NH}_4\text{-N}$	50	10	50	85	7.50
TP	5.5	1	5.5	4	5.28*

*does not meet quality standards

Table 7. Calculation of constructed wetlands single stage-tidal flow with alum sludge as media

Parameters	Effluent conc. of ABR (mg/L)	Wastewater quality standard (mg/L)	Influent conc. (mg/L)	Percentage removal (%)	Effluent conc. (mg/L)
TSS	1506	30	1506	92	120,48*
BOD	67	30	67	94	4,02
COD	67	100	67	83	11,39
$\text{NH}_4\text{-N}$	50	10	50	96	5,37
TP	5,5	1	5,5	85%	0,83

*does not meet quality standards

In temperate climates, macrophyte uptake was most optimum in spring–summer because plants will grow optimally during this period. For example, new shoots appeared (biomass was still 0) in early spring and grew maximally in spring and early summer. In late summer, the growth reduced and shoots died completely in autumn (61, 62). But this factor was not relevant in Indonesia as the country only had 2 seasons.

Removal comparison

Below was the comparison of the effectiveness of Constructed Wetlands with commonly used media (sand and gravel) with two designs of Constructed Wetlands with alum sludge as a media in treating communal WWTP effluent, i.e., Constructed Wetlands single-stage-tidal flow and Constructed Wetlands multistage-step feed-tidal flow. Secondary data for communal WWTP effluent used were TSS of 1506 mg/L, COD of 67 mg/L, NH_4^+ of 50 mg/L, TP of 5.5 mg/L (63), BOD of 67 mg/L (equal to the COD value). The calculation of Constructed Wetland using alum sludge as media could be seen in Table 8.

The pollutant removal efficiency for each Constructed Wetlands design was as follows:

- Pollutant removal efficiency in Constructed Wetlands with commonly used media (sand and gravel):

TSS = 92 %; TP = 4 % (57); COD = 80 %; NH_4^+ = 85 %; BOD = 90 % (64)

- Pollutant removal efficiency in Constructed Wetlands with a single stage system with single bed-tidal flow (65):

TSS = 92 %; COD = 83 %; NH_4^+ = 96 %; TP = 85 %; BOD = 94 %

- Pollutant removal efficiency in Constructed Wetlands with a multi-bed-steep feed-tidal flow in Table 5.

Advantages and Disadvantages of using alum sludge as constructed wetlands' media

The following were the advantages:

- The use of alum sludge from the drinking water treatment as an adsorbent for Constructed Wetlands can benefited both parties, WWTP and the drinking water treatment company.
- In long-term trials of the multi-stage Constructed Wetlands system, alum sludge was usable as the Constructed Wetlands medium for 4-17 years, depending on the P concentration of the wastewater (19).
- Aluminium leaching potential did not pose a risk if the pH of the alum sludge during operation remained neutral.
- The following were the disadvantages:

- Constructed Wetlands that use alum sludge as an adsorbent produced new sludge that required to be disposed of (24).
- The clogging of the adsorbent from a long-term operation reduced the effectiveness of phosphorus adsorption by alum sludge (66, 67)

Table 8. Calculation of constructed wetlands multi bed-step feed-tidal flow with alum sludge as media

Parameters	Effluent conc. of ABR (mg/L)	WW quality standard (mg/L)	Pumped 80% effluent conc. of ABR	Feed 1				Feed 2			
				Stage 1		Stage 2		Stage 3		Stage 4	
TSS	1506	30	1204,8	1204,80	55	542,16	55%	243,97	545,17	55%	245,33
BOD	67	30	53,6	53,60	40	32,16	25%	24,12	37,52	29%	26,64
COD	67	100	53,6	53,60	33	35,91	17%	29,81	43,21	30%	30,24
NH ₄ -N	50	10	40	40,00	15	34,00	18%	27,88	37,88	28%	27,27
TP	5,5	1	4,4	4,40	80	0,88	55%	0,40	1,50	22%	1,17
											1,06*

*does not meet quality standards

- Constructed Wetlands required regular aluminium monitoring to keep the level within the recommended safe limits, thus, requiring additional operational costs (19).
- When plants in Constructed Wetlands died or decomposed, phosphorus was released back from the biomass into the Constructed Wetlands ecosystem (both into the water and the soil).

Conclusion

The research confirmed the hypothesis that alum sludge could be effectively utilized as media in constructed wetlands for nutrient removal. Its chemical and physical properties, particularly the high affinity for phosphorus adsorption through ligand exchange mechanisms, demonstrated significant environmental and economic advantages. The concept proved industrially promising, offering a sustainable pathway for alum sludge reuse that aligned with circular economy principles and mitigated waste disposal issues.

This study revealed critical interdisciplinary connections for the first time, particularly between wastewater treatment and alum sludge management. Integrating these fields uncovered opportunities for transforming waste into valuable resources while addressing nutrient pollution in communal WWTP effluents. The breakthrough lay in demonstrating that alum sludge, typically considered waste, could provide dual benefits by functioning as an effective adsorbent in wastewater treatment and reducing environmental risks associated with sludge disposal.

Business opportunities highlighted by this research included the development of eco-friendly technologies for nutrient recovery, commercialization of alum sludge-based constructed wetlands and innovations in sustainable waste management practices. These applications not only created financial incentives for industries but also supported global sustainability goals. Further exploration into scalable systems and advanced drying techniques, such as microwave-assisted drying, would enhance industrial feasibility and long-term implementation.

Future research should have focused on optimizing operational parameters to improve media longevity and adsorption efficiency, addressing challenges such as aluminum leaching and media clogging. Investigating the integration of AI-driven predictive models could have supported economic and environmental assessments, enabling smarter investment decisions. Additionally, understanding nutrient recovery impacts on global water management trends and adapting systems to varied wastewater compositions would have provided robust solutions for industrial applications.

The primary challenges ahead included refining technologies to prevent aluminum leaching, maintaining constructed wetland media performance over extended operational periods and scaling systems for industrial applications. Tackling these challenges required multidisciplinary collaboration and innovative strategies to ensure sustainable development and global applicability.

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Authors' contributions

BDM provided the overall guidance, designed the study, conducted data analysis and interpretation and contributed to manuscript preparation. IA participated in the study design, provided support and throughout the process and read and approved the final manuscript.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interests.

Ethical issues: None

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