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Original Research

A Field Experiment on Restoration of a Hyper-Eutrophic Urban Shallow Pool Using Polyaluminium Chloride in Thailand

Intira Tongman[1], Santi Poungcharean[2], Pailin Jitchum[2], Ratcha Chaichana[1]*

[1]Department of Environmental Technology and Management, Faculty of Environment, Kasetsart University, Bangkok, Thailand
[2]Department of Fisheries Biology, Faculty of Fisheries, Kasetsart University, Bangkok, Thailand

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Abstract

Water bodies in cities often suffer from intense eutrophication due to excessive nutrient addition. Hence, the restoration of a eutrophic water body to its original healthy state is crucial. Therefore, this research investigated the possible use of polyaluminium chloride (PAC) to restore a shallow pool in Thailand. A dosage of PAC at 30 g/m^2 was applied as slurry in a shallow pool in 2021. Water quality and sediment properties were monitored before, during, and after the application of PAC (four consecutive weeks). The results revealed that before the application of PAC, this shallow pool was hypereutrophic (mean total nitrogen of 0.74±0.32 and mean total phosphorus of 3.24±0.88 mg/l). Mean chlorophyll a was exceptionally high (887.45±48.33 μg/l). The predominant species were *Spirulina* sp. and *Microcystis* sp. After the application of PAC, the water quality parameters improved. The total phosphorus, chlorophyll a and turbidity were reduced significantly ($p<0.05$), and the transparency depth was enhanced. Furthermore, intact phytoplankton cells were shifted from cyanobacteria to green algae. Flocs were observed in the surface water and on the sediment. This method proved to be practical to use, low in operational cost, and did not affect freshwater fauna due to its low toxicity.

Keywords: eutrophication, plant nutrient, polyaluminium chloride, shallow pool, water quality

Introduction

Eutrophication and plankton blooms have long been the primary environmental concerns for freshwater ecosystems in Thailand and worldwide [1-3]. The main cause of the problem is the addition of excessive plant nutrients originating from various sources, such as agricultural areas, wastewater treatment plants, industrial sectors, and residential areas. These nutrients stimulate rapid growth of phytoplankton, especially cyanobacteria, which can lead to degradation of water quality. Eutrophication causes an unpleasant hue and odor of water bodies as well as the production of cyanotoxins by cyanobacteria, such as *Microcystis*, *Planktothrix* and *Anabaena* [4, 5]. These biotoxins can cause acute and chronic health problems for humans and other living organisms exposed to contaminated water. These health effects include allergies, skin and eye

*e-mail: fscircc@ku.ac.th

irritation, vomiting, diarrhea, weakness, and damage to internal organs (kidney and liver) [6-8]. A recent study in Thailand revealed that severe eutrophication has occurred in many urban shallow pools located in North, Northeast and Central Thailand, and led to a dominance of cyanobacteria, with high microcystin content up to 3.62±0.43 μg/l [2]. Blooms of phytoplankton in these eutrophic water bodies have prevented their use as water resources.

Intervention is essential to restore a eutrophic water body. There are several measures (physical, chemical, and biological) that can be used to mitigate eutrophic conditions. One of the widely used methods is the application of polyaluminum chloride ($Al_2Cl(OH)_5$), known as PAC. PAC is powdery and is commonly applied as a coagulant in wastewater treatment and in eutrophic pool restoration [9]. PAC contains up to 30% Al_2O_3 (an important coagulant component) and provides higher coagulation efficiency than other chemicals such as aluminum sulphate ($Al_2(SO_4)_3$) or alum. Phosphorus removal from the water column takes place when PAC is dissolved in water and then Al^{+3} ion reacts with PO_4^{-3} to form a precipitate of aluminum phosphate ($AlPO_4$) that subsequently sinks to the bottom [10]. In addition, PAC can reduce turbidity, organic suspended particles, and phytoplankton cells. Once dissolved in water, PAC hydrolyzes into positively charged aluminum which can neutralize the negative charge of colloids/algal cells (charge neutralization). This creates an opportunity for particles to form larger flocculate particles (flocculation) that can then be removed from the water column with high efficiency [11, 12]. Thus, application of PAC results in low turbidity and clear water. Studies in many countries in Europe, North and South America, and Asia have reported on the efficacy of PAC used as a pool restoration measure [10, 12-14].

The eutrophication crisis in Thailand should be addressed and managed. It is clear from the literature that the use of PAC to treat eutrophic water bodies is practical and that it performs well [9, 10, 15]. However, research on restoration of water bodies in Thailand is still scarce and should be further explored [16, 17]. Therefore, the main objective of the current research was to investigate the efficacy of PAC application in the restoration of a severely hypereutrophic water body in Bangkok, Thailand. This study measured the changes in water quality (physical, chemical, and biological parameters) before, during, and after the application of PAC. In addition, the study included determination of phytoplankton diversity and structure, and changes in the phytoplankton community and density after the application of PAC. Sediment properties and formation of flocs from suspended particles on the bottom were determined. The outcome of this research should be useful and can be applied in the restoration of eutrophic water bodies in Thailand. Water resources are valuable and important; therefore, they must be protected and restored to maintain their integrity and to enable their sustainable use.

Material and Methods

Research Area

The study site was located in Petch Siam village, Bangkok, Thailand (13°53′00′′N-100°38′02′′E). The shallow pool was small, and highly eutrophic with dense phytoplankton blooms. It had lost its recreational value and function. The shallow pool had a water surface area of approximately 472 m^2 and an average depth of 0.7 m. The influx of nutrients was primarily from the drainage system of a village and from duck feeding.

Application of Polyaluminum Chloride

Commercial-grade polyaluminum chloride (PAC) (Al_2O_3>30%) was purchased from Thai PAC Industry Company Limited, Bangkok. The experiment was conducted in situ during July-August 2021. We used a dosage of PAC at 30 g/m^2 and therefore, approximately 15 kg of PAC was applied to this water body in total. PAC powder was added to water at a ratio of 1:5 in a 200 l plastic container and mixed well to dissolve. Then the PAC in solution was sprayed on the shallow pool surface using a spray unit. Water samples were taken in four consecutive weeks: week one (before PAC application), week two (during PAC application), week three (one week after PAC application) and week four (two weeks after PAC application).

Water Quality Analysis

Water samples were collected from five sampling points at two depths (surface water and near-bottom water). We monitored the water depth (m) and environmental variables, consisting of temperature (ºC), transparency (cm), pH, dissolved oxygen (DO, mg/l), conductivity (μs/cm), and total dissolved solids (TDS, mg/l) using a multiparameter analyzer (Consort 633) and an EXO4-Port water quality sonde. In addition, water samples were collected in plastic bottles, kept in plastic containers at 4ºC, and then analyzed for chemical variables in the laboratory. Total nitrogen (mg/l), total phosphorus (mg/l), alkalinity (mg/l), biological oxygen demand (BOD_5, mg/l), and chlorophyll a (μg/l) were analyzed in triplicate (Table 1). The microcystin content (μg/l) in the water was determined using a Microcystins-Adda ELISA kit (Abraxis, USA) and the absorbance was read at a wavelength of 450 nm using a microplate spectrophotometer with two replicates. Before analysis, all water samples were filtered through glass microfiber filter grade GF/C diameter 47 mm. The TN-to-TP ratio was calculated to identify the nutrient limiting factor(s), with a ratio lower than 10 indicating that phosphorus is a limiting factor, and a ratio higher than 17 indicating that nitrogen is a limiting factor. A ratio between 10 and 17 indicates that either nitrogen or phosphorus could be a limiting factor [18].

Table 1. Water chemistry parameters and sediment properties, analytical methods and detection limits.

Type of sample	Parameter	Analytic method	Detection limit
Water	Total nitrogen (mg/l)	Alkaline persulfate oxidation method	0.01 mg/l
	Total phosphorus (mg/l)	Ascorbic acid method	0.05 mg/l
	Total aluminum (mg/l)	Atomic absorption spectrometry	25 µg/l
	Chlorophyll a (µg/l)	Acetone extraction method	1 µg/l
	Microcystin concentration (µg/l)	Microcystins-Adda ELISA kit	0.10 µg/l
Sediment	Total nitrogen (g/kg)	Alkaline persulfate oxidation method	0.01 g/kg
	Total phosphorus (g/kg)	Ascorbic acid method	0.05 g/kg
	Total aluminum (g/kg)	Atomic absorption spectrometry	25 µg/kg

Phytoplankton community and structure were determined using a 20 µm plankton net. A sample (1 L) of water was collected from the center of the shallow pool and then poured through a phytoplankton net. Samples were preserved using four percent formaldehyde and identified to the species level. Plankton was counted and calculated for density and composition in the laboratory using a Sedgwick-Rafter counting chamber under a compound light microscope.

Sediment Quality Analysis

In this study, sediment samples were collected from five sampling points and were analyzed for various properties: soil texture using a hydrometer, total nitrogen and total phosphorus contents (g/kg) using digestion, organic matter content (%) using the Walkley and Black titration method, and total aluminum content (g/kg) using atomic absorption spectrophotometry (Table 1). To study floc formation and accumulation on the bottom sediment, a gravity corer was used to take surface sediment samples from five sampling points before, during, and after PAC application. The surface sediment layer was studied by direct observation and photographs.

Statistical Analysis

Differences in water quality and environmental factors during the experiment were analyzed based on one-way ANOVA using the homogeneity of variance test. If the value was greater than 0.05, then the data were equally distributed, whereas if the value was 0.05 or less, the distribution was unequal. Differences were determined through the robust test of the equality of means (Welch). For the ANOVA analysis and the Welch test, a p value less than 0.05 determined a significant difference between variables. Then, further analysis of the different trial sets was performed with post hoc multiple comparisons. For case of equal distribution (equal variances assumed), Tukey's test was applied. If the distribution of the data was not equal (equal variances not assumed), Dunnett's T3 test was applied. Statistical analysis was performed using the IBM SPSS Statistics software, authorized user version 22 (USA). Results were presented as mean±standard deviation.

Results and Discussion

Water Quality

The current study highlighted the use of PAC and compared the water quality before, during, and after its application to restore a hypereutrophic urban shallow pool in Thailand. Before PAC application, this shallow pool was hypereutrophic with exceptionally high concentrations of nitrogen and phosphorus (Table 2) and this resulted in a high concentration of chlorophyll a, indicated by severe phytoplankton blooms. Transparency depth was low due to high turbidity and chlorophyll a values. The water quality had also deteriorated due to high BOD_5 values. The TN:TP value showed that the pool was nitrogen limited. In this shallow pool, phosphorus was more abundant than nitrogen and this may result from urban runoff and discharges from surrounding areas. During and after PAC application, the overall water quality improved markedly (Fig. 1). The water pH in this study decreased from 8.9±0.1 to 7.3±0.1 similar to [19] showing that the PAC themselves reduced the water's pH from approximately 8.15 to 7.6-7.8 due to the coagulant addition; however, it was still in the neutral and natural range. The phosphorus concentrations were markedly reduced and significantly different from those before the application of PAC and this could be explained by chemical precipitation between Al^{+3} and PO_4^{-3} which can remove phosphorus from the water column [10, 15]. A reduction of BOD_5 was observed since PAC hydrolyzes into positively charged aluminum which neutralizes the negative charges of colloids/organic contaminants/algal cells causing particles to form larger flocculate particles that sink to the pool bottom [11,12]. The total aluminum concentrations were not significantly different before and after PAC application. This study also detected microcystin (average concentration 0.19±0.07 µg/l). During application of PAC, the microcystin content

Table 2. Comparison of surface water quality before, during, and after restoration with polyaluminum chloride (PAC) (n=5).

Parameter	One week before PAC application	During PAC application	One week after PAC application	Two weeks after PAC application
Water temperature (^oC)	29±0^a	31±0^b	30±0^c	30±0^c
Dissolved oxygen (mg/l)	4.2±2.0^a	3.4±1.0^a	4.3±1.1^a	2.1±0.7^a
pH	8.9±0.1^a	7.3±0.1^b	7.4±0.0^b	7.3±0.0^b
Conductivity (µs/cm)	1,130±2^a	1,111±10^b	1,060±4^c	1,058±3^c
TDS (mg/l)	681±0^a	642±7^b	628±3^c	623±1^c
Alkalinity (mg/l)	199.20±20.06^a	184.67±11.39^a	186.40±4.77^a	194.00±4.00^a
BOD_5 (mg/l)	37.00±3.87^a	59.40±4.34^b	37.40±5.46^a	34.00±5.43^a
Total nitrogen (mg/l)	0.74±0.32^a	0.92±0.44^a	1.09±0.16^a	1.04±0.24^a
Total phosphorus (mg/l)	3.24±0.88^a	1.84±0.44^b	2.51±0.66^{ab}	2.29±0.40^c
Total aluminum (mg/l)	0.97±0.08^a	1.12±0.22^a	ND	ND
Microcystin concentration (µg/l)	0.11±0.01^a	0.27±0.02^b	0.22±0.05^{bc}	0.17±0.06^{ac}

Remark: Values are mean±SD, different lowercase superscripts (^{a,b,c}) in same row indicate values are significantly different at $p<0.05$, ND is non detectable.

tended to increase. However, two weeks after application, the microcystin content had decreased, possibly because of the reduction in the levels of cyanobacteria. Microcystin content in the current study was comparable to other studies both in Thailand and other countries. For example, in Lake Oubeira, Algeria, where a predominant bloom of cyanobacteria occurred, the amount of microcystin toxin was in the range 0.028-13.4 µg/l, with the highest values in September [20].

From Fig. 1, the chlorophyll a concentration before PAC application was 887±48.33 µg/l. During the application of PAC, the chlorophyll a concentration was reduced by more than one-half (377.52±15.64 µg/l). After one and two weeks of PAC application, the chlorophyll a concentration remained lower than the initial concentration (327.80±29.32 and 392.92±45.39 µg/l, respectively). The trend for turbidity was similar to the chlorophyll a concentration, with a reduction after application of PAC. Reductions in the levels of chlorophyll a and turbidity after application of PAC, are possible through the mechanism of flocculation [15, 18] (Fig. 2). The reductions in chlorophyll a and turbidity resulted in increased transparency depth [21].

The water quality results for the near-bottom samples are presented in Table 3. Overall, the water quality changes were similar to those for the surface water. Before PAC application, the BOD_5 value was higher than after PAC application. DO concentrations increased after PAC application. The total nitrogen, total phosphorus, and total aluminum contents tended to increase during PAC application, but the differences due to the PAC application were not significant. In this study, the reduction of phosphorus was around 32% after one week of treatment, which was similar to a study in Poland that observed a reduction of TP content (28%) at the bottom of Lake Klasztorne Małe [22].

During and after PAC application, we observed no dead fish or dead organisms. Therefore, it can be stated that PAC application at the level used had no or low toxicity effects on the freshwater fauna. Acute toxicity of PAC was studied with juvenile zebrafish (*Danio rerio*) at approximately 2–3 months of age; the results showed that the mean±standard deviation of the LC50 at 96 hours was 749.7±30.6 mg/l [23]. The actual content of PAC used in the current study was much lower than that of LC50. However, polyaluminium chloride should be used with caution since some studies showed that PAC has a negative impact on charophytes, invertebrate and microbial community [24-26]. Aluminium in water of pH lower than six and higher than eight can occur in the soluble form (e.g., Al^{3+} ions) and can be harmful to freshwater fauna [24, 27].

Phytoplankton Assemblages

The number species of phytoplankton varied between 11 and 19 in this shallow pool. Before PAC application, the total density of phytoplankton was 843,400 units/l (Table 4), and the predominant species were *Spirulina* sp. and *Microcystis* sp. During PAC application, the total density of phytoplankton was reduced to 217,825 units/l and remained low toward the end of experiment. This could be explained that intact phytoplankton cells were removed by the formation of flocculation and sedimentation of algal cells [28, 29]. The dominant phytoplankton species shifted to *Spirulina* sp., *Oscillatoria* sp., *Navicula*

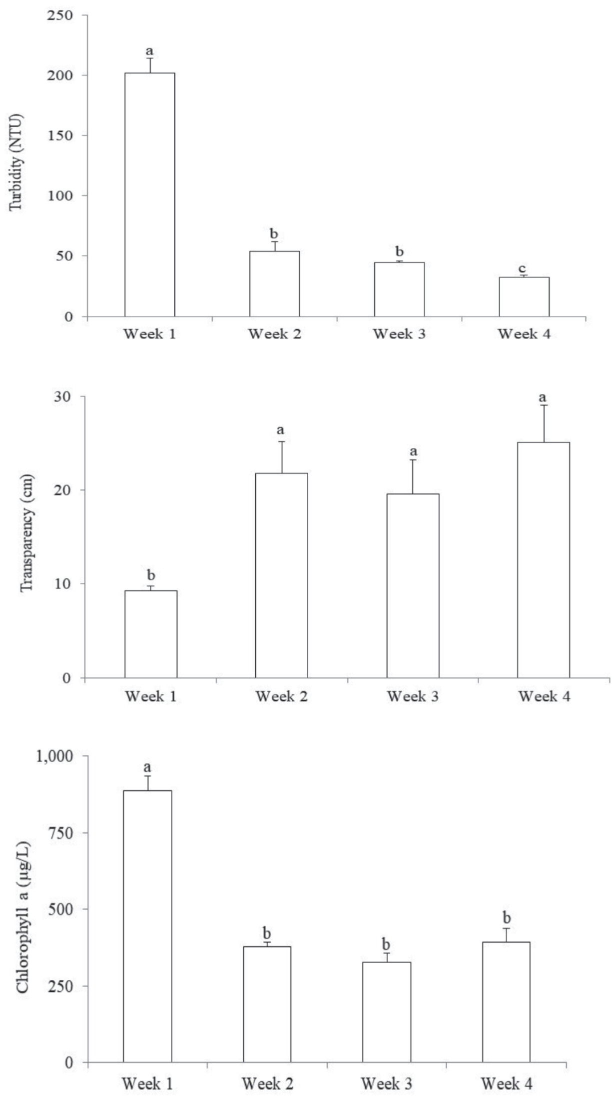

Fig. 1. Marked improvement in water quality parameters (chlorophyll a, turbidity, and transparency) before and after application of PAC in a hypereutrophic pool. Bar charts present mean values with standard error bars; different letters (a,b,c) above bars indicate means that are significantly different at $p<0.05$.

sp., and *Anabaena* sp. PAC may have a particularly adverse effect on cyanobacterial cells, and were able to remove them from the water column [30]. Overall, the phytoplankton reduction was more than 70% after application of PAC. A study in Feldberger Haussee, Germany also revealed a similar result in that following the treatment of PAC, the cyanobacteria disappeared and resulted in alteration of the phytoplankton community structure [31]. We also observed that flocs developed and were suspended in the surface water for a few hours during application of PAC. This is consistent with a laboratory experiment showing that high doses (≥16 mg Al/l) of PAC resulted in large flocks of cyanobacteria aggregating in the top of test tubes [32].

Sediment Properties

The sediment characteristics are presented in Table 5. The texture of the sediment was clay. The sediment particles were fine and loosely amorphous. Most sediment parameters (organic matter and total nitrogen) remained constant throughout the experiment. It was observed that during the application of PAC, flocs formed and sank to the bottom of the shallow pool. The approximate height of the flocs was 10-15 cm (Fig. 3). One week after PAC application, the formed flocs had disappeared from the sediment surface. The organic matter content was in the range 7.86-11.06%, which was quite high and this may have been due to the high accumulation of organic materials such as phytoplankton cells in the water body, which can become a crucial internal nutrient source. Therefore, it is suggested that the increase in the total organic carbon of the sediments can be minimized by planting submerged macrophytes [33]. The total phosphorus content tended to decrease after application of PAC. In contrast, the total aluminum content significantly increased after the addition of the PAC and this may help reduce the PO_4^{3-}-P release by P-binding [34] with aluminium from internal sediment under anoxic conditions [35-37]. The increased aluminum content was directly caused by application

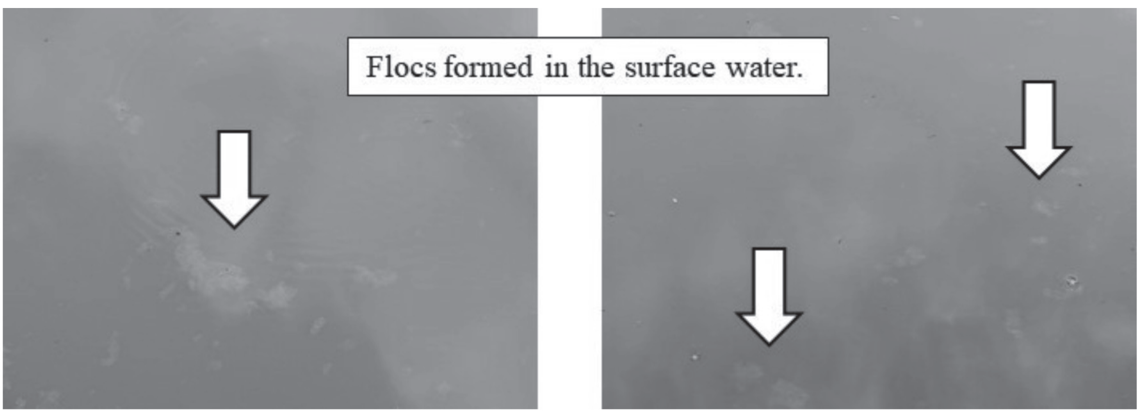

Fig. 2. Flocculation of phytoplankton and suspended particles in the surface water in the pool during application of PAC.

Table 3. Comparison of near-bottom water quality before, during, and after restoration with polyaluminum chloride (PAC) (n = 5).

Parameter	One week before PAC application	During PAC application	One week after PAC application	Two weeks after PAC application
Water temperature (^{o}C)	29±0^{a}	31±0^{b}	30±0^{b}	30±0^{b}
Dissolved oxygen (mg/l)	2.3±0.7^{a}	2.9±0.8^{ab}	5.0±0.3^{b}	3.9±1.5^{ab}
pH	8.4±0.1^{a}	7.2±0.0^{b}	7.6±0.2^{c}	7.4±0.0^{bc}
Conductivity (µs/cm)	1,118±6^{a}	1,107±20^{a}	1,070±3^{b}	1,050±8^{b}
TDS (mg/l)	672±5^{a}	645±9^{b}	629±1^{c}	618±4^{c}
BOD_5 (mg/l)	42.33±3.79^{a}	32.67±2.08^{b}	39±2.65^{ab}	23.33±2.31^{c}
Total nitrogen (mg/l)	0.31±0.03^{a}	0.97±0.52^{b}	0.64±0.52^{a}	0.75±0.24^{a}
Total phosphorus (mg/l)	2.22±0.10^{a}	2.24±0.47^{a}	1.51±0.13^{a}	2.03±0.41^{a}
Total aluminium (mg/l)	0.83±0.07^{a}	0.92±0.27^{a}	ND	ND

Remark: Values are mean±SD, different lowercase superscripts (^{a,b,c}) in same row indicate values are significantly different at $p<0.05$, ND is non detectable.

Table 4. Species and densities of phytoplankton (units/l) before, during, and after application of PAC.

Phytoplankton	One week before PAC application	During PAC application	One week after PAC application	Two weeks after PAC application
Chroococcus sp.	0	0	100	13
Microcystis sp.	321,875	250	100	250
Merismopedia sp.	575	2300	1,487	100
Oscillatoria sp.	4,838	11,038	14,087	125
Spirulina sp.	514,438	190,225	207,950	650
Anabaena sp.	0	0	0	12
Eudorina elegans (Ehrenberg)	0	12	12	0
Pediastrum duplex (Meyen)	0	0	25	0
Pediastrum simplex (Meyen) Lemmermann	12	0	25	0
Tetraedron gracile (Reinsch) Hansgirg	0	0	337	12
Tetraedron minimum (A.Braun) Hansgirg	0	0	25	0
Tetraedron trigonum (Naegeli) Hansgirg	50	87	437	150
Coelastrum asteroideum (De Notaris)	25	0	500	0
Scenedesmus acuminatus (Lagerheim) Chodat	687	125	9,000	0
Scenedesmus bernardii GMSmith	0	100	50	0
Scenedesmus quadricauda (Turpin) Brébisson	112	37	1,812	0
Actinastrum hantzschii (Lagerheim)	0	25	0	0
Strombomonas sp.	12	475	687	250
Lepocinclis ovum (Ehrenberg) Lemmermann	0	0	50	25
Lepocinclis pseudo-ovum (Conrad)	0	50	0	50
Navicula sp.	775	6,025	9,262	462
Nitzschia sp.	0	7,075	5,462	25
Species total	11	14	19	13
Total (units/l)	843,400	217,825	251,413	2,125

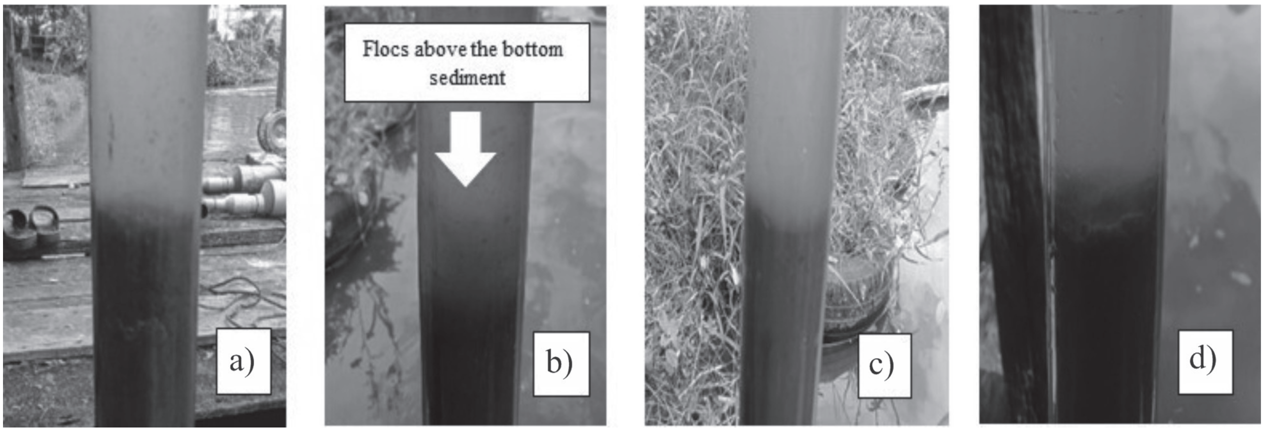

Fig. 3. Water-sediment interface in corer: a) one week before application of PAC, b) during application of PAC with presence of flocs, c) one week after application of PAC and d) two weeks after application of PAC.

Table 5. Sediment characteristics before, during, and after application of PAC (n = 5).

Parameter	One week before PAC application	During PAC application	One week after PAC application	Two weeks after PAC application
Organic matter (%)	11.06±3.02 [a]	7.86±1.27 [a]	10.51±2.08 [a]	9.48±0.85 [a]
Total nitrogen (g/kg)	4.58±1.30 [a]	3.41±0.53 [a]	4.62±0.91 [a]	3.57±0.35 [a]
Total phosphorus (g/kg)	0.84±0.17 [a]	0.69±0.11 [ab]	0.65±0.08 [ab]	0.54±0.07 [b]
Total aluminum (g/kg)	21.31±3.73 [a]	22.84±0.59 [ab]	26.47±2.11 [ab]	27.36±0.97 [b]

Remark: Values are mean±SD, and different lowercase superscripts ([a,b]) in same row indicate values are significantly different at $p<0.05$

of PAC in the shallow pool. This was consistent with a previous study showing the presence of flocs in the surface sediment at a depth of 0-10 cm during application of PAC [38, 39]. Binding efficiencies of aluminum can be enhanced when aluminum was applied directly into the sediment [40]. Lastly, it is suggested that long term monitoring of water quality should be conducted after the end of restoration to investigate the duration of PAC's effects since the longevity of the clear water state after chemical treatment varies from one year to several decades [41] depending on the input of exogenous nutrient loading.

Conclusions

This research described the application of PAC in a hypereutrophic shallow pool, which produced a noticed improvement in water quality parameters. After application of PAC, the water had higher transparency due to the reduced turbidity and chlorophyll a levels. Flocs were observed both in the surface water and on the bottom sediment, confirming the effect of PAC on the removal of suspended particles and phytoplankton cells in the water column. In addition, PAC appeared to have an adverse effect on the cyanobacterial group, with the phytoplankton shifting to green algal groups. It can be concluded that PAC can be an effective method to restore eutrophic/hyper-eutrophic water bodies due to its low cost, practical use, and low negative impacts on the environment.

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Conflict of Interest

The authors declare no conflict of interest.

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