Effects of riplox_based chemical complex on the control of urban lake water quality

Thi Thuy Bui[1*], Nguyet Anh Pham[1], Thuy Anh Tran[2], Duc Ha Tran[3]

Abstract: The objectives of this study were to prove the control of the lake water quality in terms of turbidity, total suspended solid (TSS), chemical oxygen demand (COD), and number of the algal cells by using the Riplox-based chemical complex (including ($Ca(NO_3)_2$) and ($FeCl_3$) at concentrations ranging from 5 mM to 50 mM, with the presence of $CuSO_4$ 4 mg/L), considering the effects of the chemical fraction, the chemical concentration, and the treatment time. Raw water was sampled from Trieu Khuc Lake and treatment process was carried out in the lab scale. Overall, the great treatment results were achieved from the application of $Ca(NO_3)_2/FeCl_3$ ratio of 1:1 (v/v) at a concentration of 0.5 M and the treatment time of 3 hours. The presence of $CuSO_4$ 4 mg/L in the Riplox-based chemical complex showed a good performance in reduction of number of the algal cells. The flocs formation when dissolving $Ca(NO_3)_2$ and $FeCl_3$ in the water and denitrification were found to be major mechanisms for enhancing treatment performance. The findings demonstrate that the application of Riplox-based chemical complex with the presence of $CuSO_4$ 4 mg/L would control the urban lake water quality and can be widely applied for the case of Vietnam

Keyword: Algal reduction, denitrification, flocculation, urban lake, water quality.

1. Introduction

Ponds and lakes are contributing their major roles in sewerage system as well as in landscape creation for urban area. As investigated, there are currently 125 lakes in 12 districts of Hanoi and most of them have been receiving run off and wastewater, existing with sediments, causing low water quality and harmful algal blooming (HSDC, 2019; Nguyen & Tran, 2004).

Recently, there have been several gains and attentions on improving the lake water quality for Hanoi city; including: separation of municipal wastewater and desludging highly polluted lakes, application of aquatic system as well as of chemical complex Redoxy-3C. Since 2016, Hanoi sewerage and drainage limited company has applied Redoxy-3C in 86 lakes to maintain water quality index less than those listed in National technical regulation on surface water QCVN 08-MT:2015/BTNMT, class B1 (MONRE, 2015). However, Redoxy-3C is used as its received from Germany, therefore its application is not addressed as a low cost solution. In addition, the use of Redoxy-3C has not been well-experimented that can give many challenges for the practical case of Hanoi.

Many researchers have been studied on the cheap and environmental-friendly chemical complexes, with the use of $FeCl_3$, $Ca(NO_3)_2$ and other chemicals into the lakes of Germany, Sweden, Brazil, *etc.*, resulting in improving water quality, especially inhibiting algal blooming, as known as Riplox process (Tran, 2018; Ripl, W. & Lindmark, G., 1978; Wauer, G. et al., 2005; Yamada, T. M. et al., 2012).

[1]Faculty of Chemistry and Environment, Thuyloi University, Vietnam
[2]Faculty of Environment Engineering, Hanoi University of Civil Engineering, Vietnam
[3]Institute for Water Supply, Sewerage and Environment, Vietnam
* Corresponding author
Received 27th Aug. 2022
Accepted 5th Oct. 2022
Available online 31st Dec. 2022

This process was then applied to control water quality in Huu Tiep Lake of Hanoi, with the addition of Riplox chemical and chemical preparations LOLO-pH104 (Tran et al., 2017). The findings of the aforementioned studies rely on the improvement of water quality; however, its operation and performance depend on the characteristic of the case study and require further studies. To demonstrate the efficiency of Riplox chemical complex, it is useful to study the impacts of the operational condition.

In the present study, we therefore provide the improvement of urban lake water quality for the application of canxi nitrate and ferric (III) chloride under the addition of copper sulfate 4 mg/L with respect to the effects of the $Ca(NO_3)_2$: $FeCl_3$, the chemical concentration, and the treatment time for a case study of Trieu Khuc Lake. The assessment of the treatment process was performed using turbidity, TSS, COD, and algal reduction. The results from this study prove the role of predominant species from the chemicals' dissolution on the water quality improvement under experimental conditions.

2. Methodology

2.1. Study site

Figure 1. Location of Trieu Khuc lake (adapted from google map)

The study site was Trieu Khuc Lake, Van Trieu, Hanoi – (located at 20°58'47"N 105°48'00"E – Figure 1). It receives domestic wastewater via 03 discharge drains, causing pollution with algal blooming, sedimentary layer, and low water quality. In addition, there is a plenty of solid waste on the surface of the lake due to the low awareness from local residents. Water samples were daily taken from April 20th to June 30th 2022at the depth of 10 – 15 cm from water surface with a total volume of 10 L/day and stored at room temperature (~ 25^{o}C) until the experiments were conducted.

2.2. Experimental design

The improvement of water quality for Trieu Khuc Lake were observed after applying a combination of $Ca(NO_3)_2$ and $FeCl_3$ under the addition of copper sulfate $CuSO_4$ 4 mg/L. All chemicals were purchased from Vietchem Company and used after diluted in 1 L of filtered water in the volumetric flask. All experiments were undertaken at room temperature. The prepared chemicals were injected into a cylindrical reactor containing 1 L of the lake water. The treatment process was performed under conditions: the $Ca(NO_3)_2/FeCl_3$ ratio = 1/1; 1/2; 1/3; and 1/4; the chemical concentration = 0.1 M; 0.2 M; 0.5 M, and 1 M; and the treatment time = 1h, 2h, 3h, and 4h; as summarized in Table 1. Treated water samples with a volume of 100 mL was collected at the depth of 10 – 15 cm from the water surface of the reactor. During the experiments, dissolved oxygen, pH were observed using DO meter (Prosolo, model: YSI – 603069) and pH meter. The assessment of the treatment process was performed using turbidity, TSS, COD, and algal reduction. Turbidity was obtained from portable turbidity meter HACH 2100Q; TSS was measured with spectrophotometer HACH DR3900; COD was determined based on standard method TCVN 6491:1999; and algal cell number was counted by using hemocytometer.

Table 1. Summary of experimental using chemical complexes of $Ca(NO_3)_2$, $FeCl_3$ under addition of $CuSO_4$ 4 mg/L

Experimental condition	Description
Effect of chemical ratio	Chemical ratio $Ca(NO_3)_2$: $FeCl_3$ = 1:1; 1:2; 1:3; 1:4; Concentration of $CuSO_4$ C = 4 mg/L; Concentration of $Ca(NO_3)_2$ and $FeCl_3$ C = 5 mM; Treatment time t = 1 h; Mixing regime: Static Observation: Turbidity, TSS, COD
Effect of chemical concentration	Chemical ratio $Ca(NO_3)_2$: $FeCl_3$ = 1:1; Concentration of $CuSO_4$ C = 4 mg/L; Concentration of $Ca(NO_3)_2$ and $FeCl_3$ C = 5, 10, 25, 50 mM; Treatment time t = 1 h; Mixing regime: Static Observation: Turbidity, TSS, COD
Effect of treatment time	Chemical ratio $Ca(NO_3)_2$: $FeCl_3$ = 1:1; Concentration of $CuSO_4$ C = 4 mg/L; Concentration of $Ca(NO_3)_2$ and $FeCl_3$ C = 5 mM; Treatment time t = 1 h, 2h, 3h, 4h; Mixing regime: Static Observation: Turbidity, TSS, COD

2.3. Determination of possible aqueous speciation using Visual MINTEQ 3.1 software

In this study, Visual MINTEQ 3.1 software was used to determine the degree of dissociation of chemicals when added to water, aiming at treatment mechanism of chemical complexes in the lake water treatment process. Visual MINTEQ is a freeware chemical equilibrium model for the calculation of metal speciation, solubility equilibria, sorption etc. for natural waters. It combines state-of-the-art descriptions of sorption and complexation reactions with easy-to-use menus and options for importing and exporting data to/from Excel. The Visual MINTEQ application can simulate the chemical composition of solutions in contact with gases, solid compounds and particle surfaces. In this study, possible aqueous speciation was obtained from the calculation of charge and mass balance at 25 °C in Visual MINTEQ 3.1.

3. Results and discussion

3.1. Raw water quality

Raw water quality was analyzed and compared with the National technical regulation on surface water quality QCVN 08-MT:2015/BTNMT, class B1. As seen in the Table 2, the test results for turbidity, TSS, and COD were found to be exceeded to those mentioned in QCVN 08-MT:2015/BTNMT, class B1; with the average concentration of ~150

NTU, ~80 mg·L^{-1}, and ~133 mg·L^{-1}, respectively. The results show that Trieu Khuc Lake has been contaminated with organic matter, confirming a need of the control for water quality.

Table 2. Quality of raw water sample and National technical regulation on surface water quality QCVN 08-MT:2015/BTNMT, class B1

Parameter	Unit	Value		Comparison
		Trieu Khuc Lake Average (min – max)	QCVN 08-MT:2015/ BTNMT (MONRE, 2015)	
pH	-	7.0 (5.5-7.8)	5.5-9	
TSS	mg·L^{-1}	85 (70 – 98)	50	High
COD	mg·L^{-1}	128 (104 – 152)	30	High
DO	mg·L^{-1}	6.0 (5.5-7.0)	≥ 4	
Turbidity	mg·L^{-1}	147 (133 – 173)	-	-

3.2. Improvement efficiency

Figure 2, Figure 3, and Figure 4 summarize the turbidity, TSS, and COD removal efficiency for application of chemical complex with respect to the $Ca(NO_3)_2$: $FeCl_3$ ratio, chemical concentration, and treatment time.

As seen in Figure 2, higher performance was obtained with $Ca(NO_3)_2$: $FeCl_3$ of 1:1 under conditions: chemical concentration of 5 mM, and treatment time of 1h; with removal of turbidity ~28%, TSS ~ 42%, and COD ~ 60%.

As seen in Figure 3, higher performance was obtained with chemical concentration of ≥ 25 mM under conditions: $Ca(NO_3)_2$: $FeCl_3$ of 1:1 and treatment time of 1h; with removal of turbidity ~ 74 mg/L, TSS ~ 68%, and COD ~ 77%.

As seen in Figure 4, stable removals of turbidity, TSS, and COD was resulted at treatment time of 3h, $Ca(NO_3)_2$: $FeCl_3$ of 1:1, and chemical concentration of ≥ 25 mM.

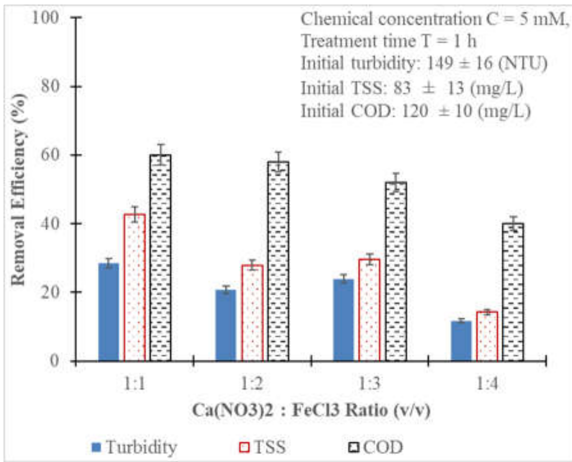

Figure 2. Effect of $Ca(NO_3)_2$:$FeCl_3$ ratio (v/v) on removal rate of turbidity, TSS, and COD

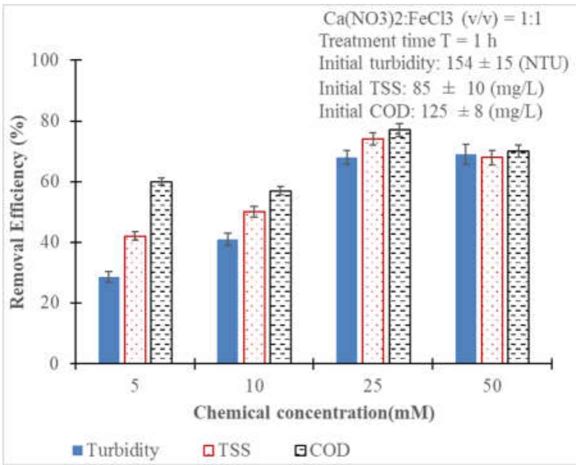

Figure 3. Effect of chemical concentration on removal rate of turbidity, TSS, and COD

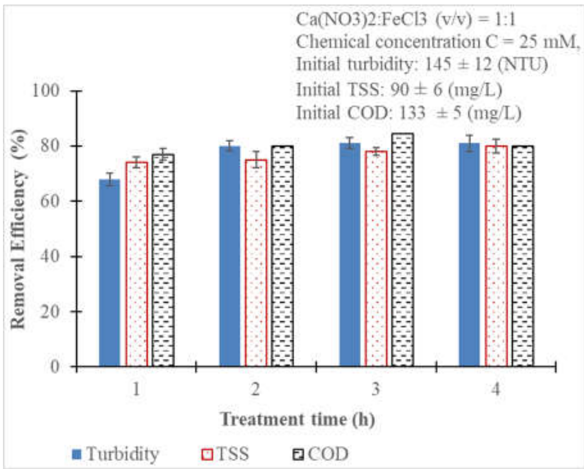

Figure 4. Effect of the treatment time on removal rate of turbidity, TSS, and COD

Experimental results show that the application of chemical complex with $Ca(NO_3)_2$: $FeCl_3$ ratio of 1:1, chemical concentration of 25 mM, and the treatment time of three hours provided the greatest removal efficiencies in terms of turbidity, TSS, and COD. Table 3 presents treated water quality for Trieu Khuc Lake at the optimal operations. It is seen that treated water quality of Trieu Khuc Lake is less than the limits as reported in the National technical regulation QCVN 08 MT:2015/BTNMT, class B1. In comparison with raw water quality, removal rates were obtained for turbidity of ~ 81%, TSS of ~ 68.31%, and COD of ~ 84.96%. At these optimal condition, algal reduction experiment was conducted by using hemocytometer and the result indicates that number of algal cells was reduced up to ~ 56% (seen in table 4).

Table 3. Quality of the treated water sample and National technical regulation on surface water quality QCVN 08-MT:2015/BTNMT, class B1

Parameter	Unit	Value	
		Water sample of Trieu Khuc Lake	QCVN 08-MT:2015/BTNMT
pH		7.66	5.5-9
TSS	$mg \cdot L^{-1}$	28	50
COD	$mg \cdot L^{-1}$	19.33	30
DO	$mg \cdot L^{-1}$	7.23	≥ 4
Turbidity	$mg \cdot L^{-1}$	18	-

Table 4. Control of algal cell under optimal operation ($Ca(NO_3)_2$: $FeCl_3$ = 1:1, C_m = 25 mM, treatment time t = 3h)

Parameter	In raw sample	In treated sample	Algal reduction
Number of algal cell ($cells \cdot L^{-1}$)	2.65×10^6	1.15×10^6	~ 56%

As mentioned, the Visual MINTEQ application was used to determine the dominant species presented in water when $FeCl_3$ and $Ca(NO_3)_2$ compound were added at a certain concentration, ca. C = 5 mM over pH. After entering data and calculating with Visual MINTEQ application, we export the data table excel file as shown in Table 5 and Figure 6.

Table 5. Log concentration of possible aqueous speciation in the addition of $Ca(NO_3)_2$ and $FeCl_3$ at C = 5 mM over pH

pH	Log concentration of dominant species						
	Fe^{+3}	NO_3^{-1}	$Fe(OH)^{2+}$	$Fe(OH)_2^+$	$Fe(OH)_3$	$CaOH^+$	$CaNO_3^+$
6.4	-7,053	-1,327	-1,107	-1,107	-4,146	-7,978	-2,637
6.6	-7,403	-1,324	-1,058	-1,058	-3,894	-7,79	-2,647
6.8	-7,773	-1,323	-1,029	-1,029	-3,661	-7,598	-2,654
7.0	-8,16	-1,322	-1,014	-1,014	-3,445	-7,403	-2,658
7.2	-8,555	-1,321	-1,009	-1,009	-3,238	-7,206	-2,66
7.4	-8,956	-1,321	-1,009	-1,009	-3,038	-7,007	-2,662
7.6	-9,362	-1,321	-1,015	-1,015	-2,843	-6,808	-2,662

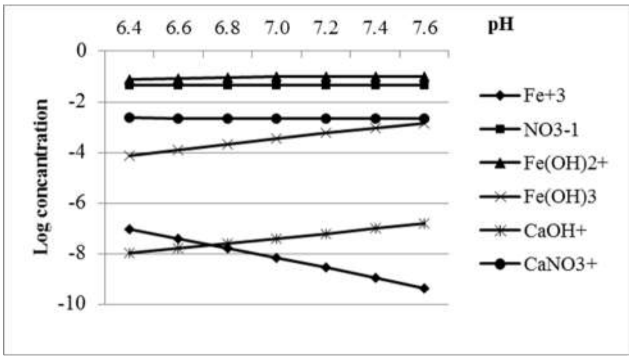

Figure 6. Log concentration of dominant species in water in the addition of $Ca(NO_3)_2$ and $FeCl_3$ at C_M = 5 mM

It is seen that in the range of pH from 6,4 to 7,6, dominant species presented in water were $Fe(OH)_2^+$; $Fe(OH)^{2+}$, $Fe(OH)_3$ and $CaNO_3^+$. These species are attributed to the major factors affecting treatment mechanisms/processes. Significant removals of turbidity and TSS were due to the presence of $FeCl_3$ in the treatment reagent. These chemicals when dissolving into water would result in positively charged species that played the major role in suspended solid-positive specie aggregates creation throughout electro-statistic attraction to increase the density and size, resulting in greater settling. In addition, the precipitation specie as $Fe(OH)_3$, that is demonstrated with positive surface charge, would become a bridge to combine with contaminants in water. During the $Fe(OH)_3$ settling process, the contaminants in water was also be settled down. This process would clarify water and a significant portion of ferric ions simultaneously adsorbs single phosphate to form the complex bond in the sediment, as given below:

$$FeCl_3 + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + 3Cl^-$$

$$Fe(OH)_3 \rightarrow FeO(OH) + H_2O$$

$$FeO(OH) + PO_4^{3-} \rightarrow FeO(OH) \sim PO_4^{3-}$$

$$2FeO(OH) + 3H_2S \rightarrow 2FeS + S^0 + 4H_20$$

As a major part in the chemical complex added into water, $Ca(NO_3)_2$ was dissolved and stay in the water until it is used by microorganism. Analysis results from Visual MINTEQ application illustrate that species as NO_3^- and $CaNO_3^+$ seemed to be predominant. NO_3^- was priority to electron acceptor when staying at liquid phase: the solution rapidly intruded into the sediment, playing its role in introducing oxygen into hypolimnion. This is a great oxygen source for anaerobic *denitrificans* and therefore denitrification process was occurred to oxidize organic matter. Also, $Ca(NO_3)_2$ prevented the creation of (H_2S), avoiding the odor release during the treatment process.

- Organic matter oxidizing: $5CH_2O + 4NO_3^- + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$

- Inorganic mater oxidizing: $5S^{2-} + 8NO_3^- + 3H^+ + H_2O \rightarrow 5SO_4^{2-} + 4N_2 + 5OH^-$

Eutrophication with the harmful algal blooming is addressed as the most common issue for the urban lakes, especially in tropical countries. As reported in many researches, $CuSO_4$ should be added in order to prohibit the excessive growth of algae for water basin. When dissolving $CuSO_4$ into water, it will produce Cu^{2+} to prohibit algae' photosynthesis, resulting in algal reduction. Previous researchers highlighted the optimal concentration of $CuSO_4$ in the range of 0,001 ~ 0,4 $mg \cdot L^{-1}$ for the best performance in algal reduction (Ripl, W., & Lindmark, G., 1978). It is noted that free Cu^{2+} is a toxic agent to algae and others aquatic animals, so that it can cause secondary pollution when excessively applied. When $CuSO_4$ is added, its dissociation will rapidly decrease and its sedimentation is occurred through several mechanisms, i.e. settling in the insoluble oxides or hydroxides formation, adsorption layer on clay surface, microorganism biomass synthesis and plant (algae) uptake, adsorption into sludge (sediment).

4. Conclusion

Experimental results have demonstrated the effectiveness of treating lake water pollution by a combination of chemicals including calcium nitrate, ferric chloride and copper sulfate 4 mg/L. At optimal conditions, the chemical ratio $Ca(NO_3)_2 : FeCl_3 = 1:1$ at a concentration of 25 mM after the treatment time t = 3h, the treatment efficiency for water quality indicators such as turbidity of ~82%, TSS of ~77%, COD of ~85% and the number of algae cells was reduced from 2.65×10^6 ($cells \cdot L^{-1}$) to 1.15×10^6 ($cells \cdot L^{-1}$). The addition of 4 mg/L $CuSO_4$ played an important role in inhibiting algal growth. Formation of colloidal flocs from pollutants and positively charged ions or chemical components upon dissolution of $Ca(NO_3)_2$ and $FeCl_3$ in water and the penetration of NO_3^- ions into the water enhanced the activity of *denitrificans* to oxidize organic substances are the main mechanisms. The results from this study confirm that the use of $Ca(NO_3)_2$ and $FeCl_3$ under the addition of $CuSO_4$ 4 mg/L would be a reliable tool for pollutants reduction, looking forward to control of the urban lake water quality.

References

HSDC (Hanoi Sewerage and Drainage Company) (2016), *Report on assessment of water quality control by using Redoxy-3C in the lakes of Hanoi* (in Vietnamese)

MONRE (2015), "QCVN08-MT :2015/BTNMT – *National technical regulation on surface water quality"*

Nguyen Xuan Nguyen, Tran Duc Ha (2004), *"Water quality of river and lake and protection of aquatic environment",* Publishing House of Science and Technology, Hanoi.

Tran Duc Ha, John Xing, Nguyen Van Minh, Vu Tien Anh, Phan Tuan.(2017), "*Improve aquatic environment of urban lake by using Riplox process in addition with chemical preparations Lolo-pH 104".* Journal of Environment, ISN: 1859-042X, No. 1/2017, pg. 6-10.

Tran Duc Ha (2018), *"Eutrophication and sedimentation in drinking water reservoirs",* Water Supply and Sanitation, 3(119), pg. 43-47.

Ripl, W. (1976), *"Biochemical oxidation of polluted lake sediment with nitrate: a new lake restoration method"*, Ambio, 132-135.

Ripl, W., & Lindmark, G. (1978), *"Ecosystem control by nitrogen metabolism in sediment"*. Vatten.

Willenbring, P. R., Miller, M. S., & Weidenbacher, W. D. (1984), *"Reducing sediment phosphorus release rates in Long Lake through the use of calcium nitrate"*, Lake and Reservoir Management, 1(1), 118-121.

Wauer, G., Gonsiorczyk, T., Casper, P., & Koschel, R. (2005), *"P-immobilisation and phosphatase activities in lake sediment following treatment with nitrate and iron"*. Limnologica, 35(1-2), 102-108.

Yamada, T. M., Sueitt, A. P. E., Beraldo, D. A. S., Botta, C. M. R., Fadini, P. S., Nascimento, M. R. L., ... & Mozeto, A. A. (2012), *"Calcium nitrate addition to control the internal load of phosphorus from sediments of a tropical eutrophic reservoir: microcosm experiments",* Water research, 46(19), 6463-6475.