Fundamental Structure in Simultaneous Removal for Phytoplankton and Nutrient Salt in Lakes

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Abstract

The water quality in eutrophic lakes is affected by serious problems, such as abnormal increasing of *Cyanobacteria*. The purpose of this study was to investigate the possibility of a modified flotation system using a hybrid technique formed by chemical compounds and an electrostatic bridge. Therefore, experiments using the hybrid technique were performed to measure the zeta potential value on the phytoplankton surface and the removal efficiencies of phytoplankton, ammonia nitrogen, nitrate nitrogen and phosphoric acid.

The results were as follows: Firstly, the zeta potential of *M.aeruginosa* was observed to approach charge neutralization due to adhesion of magnesium hydroxide precipitate on the phytoplankton surface in the pH range 10.5 to 11. Secondly, the concentration of chlorophyll-a decreased from about 150 to 20μg/L, with a maximum removal efficiency of 84% due to coagulation with pH values higher than 10. Thirdly, the NH_4-N concentration was observed to decrease from 0.62 to 0.54mg-N/L (13%), and the PO_4-P concentration, which is a limiting factor to the formation of algae blooms, decreased from 0.27 to 0.02mg-P/L (92%). These findings suggest that the modified flotation system can be applied for the purification of the raw water of numerous lakes containing high phytoplankton populations and elevated pH.

Keywords : Flotation process, Magnesium compounds, Micro-bubble, *Microcystis aeruginosa*, Nutrient salt, Zeta potential

1. Introduction

The water quality in eutrophic lakes is affected by serious problems, such as explosive increases in *Cyanobacteria*. Some kinds of *Cyanobacteria* produce metabolites of musty substances and toxins in their cells. Damage to human health as a result of microcystin, one of the toxic, has been reported in many countries.[1)-3)] Therefore, it is necessary to remove the *Cyanobacteria* and nutrient salt from eutrophic lake water to improve the water quality. The pH of the water at the surface of many lakes is higher than pH 9 because of frequent algae blooms, which inhibits the coagulation of traditional coagulants.[4)]

The removal efficiencies of phytoplankton, ammonia nitrogen, nitrate nitrogen and phosphoric acid are discussed with respect to the hybrid technique: (a) chemical compounds, i.e. the formation of magnesium ammonium phosphate and magnesium hydroxide precipitation, and (b) the electrostatic bridging effect between micro-bubbles and phytoplankton.

1.1. Flotation Mechanisms
1.1.1. Electrostatic bridge effect

With the electrostatic bridging effect of a micro-bubble and phytoplankton, the Van der Waals and electrostatic forces between the substances are important factors. The electrostatic bridging effect of a micro-bubbles and phytoplankton is shown schematically in Fig.1. Micro-bubbles and phytoplankton are attached to magnesium hydroxide precipitates on their surfaces, which then approach the iso-electric point. Collisions between micro-bubbles and phytoplankton can be facilitated by charge neutralization. Consequently, electrostatic uniting constructs a bridge with the magnesium hydroxide precipitate, which allows micro-bubbles and phytoplankton to be adsorbed. Therefore, phytoplankton adsorbed onto the micro- bubbles are carried to the water surface with the micro-bubbles.
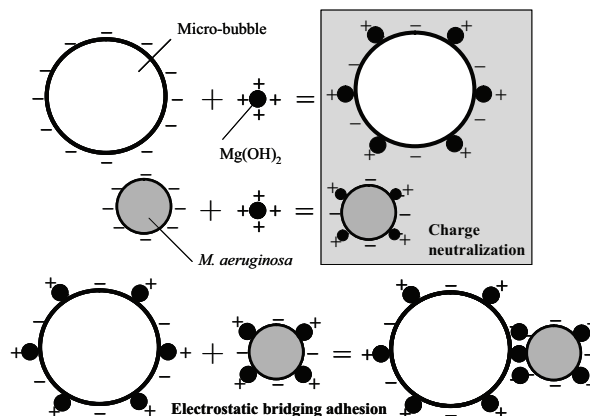

Fig. 1. Schematic diagram of the electrostatic bridging effect
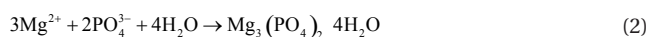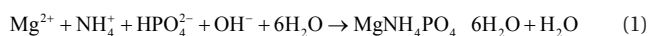
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1.1.2. Magnesium compounds

The mechanisms are as follows: Firstly, the positively charged magnesium hydroxide precipitate is formed at pH values higher than 9, which is then adsorbed onto the surfaces of the phytoplankton and micro-bubbles. Thus, phytoplankton attaches to the micro-bubble surface by uniting of an electrostatic bridging effect, and is then carried to the water surface. Secondly, magnesium ammonium phosphate (MAP, MgMH₄PO₄6H₂O) and magnesium phosphate precipitates (Mg₃(PO₄)₂4H₂O) are formed by the reaction of magnesium, phosphate and ammonium ions at high pH values. It is then anticipated that the phosphate and ammonium ions will be removed from eutrophic water. The positively charged magnesium hydroxide precipitate is firstly formed at pH values higher than 9,[5), 6)] and is adsorbed onto the surface of phytoplankton and micro-bubbles. Thus, phytoplankton is attached to the surface of a micro-bubble by an electrostatic bridging effect, and is then carried to the water surface. Secondly, magnesium ammonium phosphate (MAP), including phosphoric acid and ammonium ions, is formed at pH values higher than 5 to 7, as shown in Eq.1.[7), 8)] It has been reported that the formation of MAP crystals depends on the chemical species of phosphoric acid and ammonia present with variations in pH, and the generation of the magnesium phosphate progresses at pH values higher than 9, as shown in Eq.1 and 2. Therefore, it is suggested that phosphoric acid and ammonia can be removed by controlling the pH.

$$Mg^{2+} + NH_4^+ + HPO_4^{2-} + OH^- + 6H_2O \rightarrow MgNH_4PO_4 \ 6H_2O + H_2O \qquad (1)$$

$$3Mg^{2+} + 2PO_4^{3-} + 4H_2O \rightarrow Mg_3(PO_4)_2 \ 4H_2O \qquad (2)$$

In general, MAP crystals are formed under pH conditions >5-7. However, from our observations, these magnesium compounds that include phosphoric acid depend on the formation of phosphoric acid ions with variations in pH. On the other hand, the magnesium hydroxide precipitate is the main species under pH conditions >9-10, which will be formed by the hydrolysis reaction shown in Eqs 3 and 4 [5)]
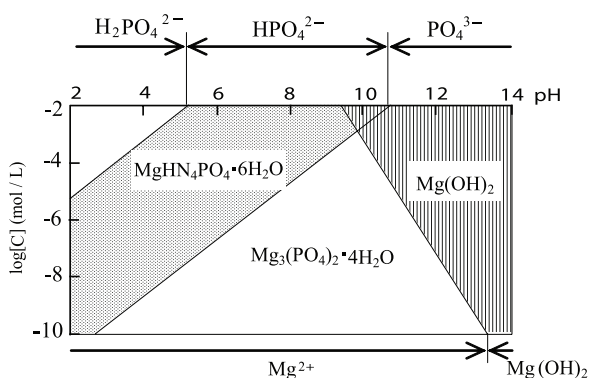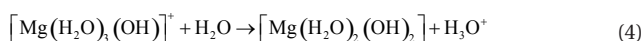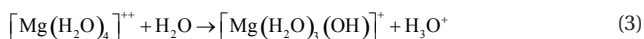
$$\left[Mg(H_2O)_4\right]^{++} + H_2O \rightarrow \left[Mg(H_2O)_3(OH)\right]^+ + H_3O^+ \qquad (3)$$

$$\left[Mg(H_2O)_3(OH)\right]^+ + H_2O \rightarrow \left[Mg(H_2O)_2(OH)_2\right] + H_3O^+ \qquad (4)$$

Fig. 2. Phosphate ion, magnesium ion species distribution as a function pH.

The variations in dissolved phosphate and magnesium ion species as a function of the pH are shown in Fig.2. Under neutral pH conditions, the hydrogen phosphate ion will be the main species, where MAP is formed. In the second region, i.e. under higher pH conditions, the concentration of dissolved magnesium ions will decrease with the formation of a magnesium hydroxide precipitate, and the phosphoric acid ion will be the main species, with the simultaneous formation of magnesium phosphate. Therefore, phosphate and ammonia are suggested to be removed in the under neutral pH conditions. On the contrary, it is expected that the removal efficiency of ammonia will decrease with the formation of a magnesium hydroxide precipitate.

2. Experimental Procedure

Microcystis was used as the *Cyanobacteria* in this study, and were bred in artificial raw water, with the chlorophyll-a concentration maintained at approximately 120µg/L in each experiments. The NH₄-N and PO₄-P concentrations were adjusted to 0.8 or 6 mg-N/L and 0.2 or 1 mg-P/L respectively; similar quality conditions as those found in eutrophic water. The pH conditions of the raw water was maintained within the range 8~12 as shown in Table 1. The flotation experiment procedure was as follows: First, a *M. aeruginosa* suspension was introduced into the flotation tank (40L) and the regulation tank (60L). After the addition of magnesium chloride (0, 30, 60 and 600mg-Mg/L) and NaOH (0, 1, 4 and 8 mg-Na/L) to the regulation tank, the contents were circulated between the flotation tank and regulation tank for five minutes. Micro-bubbles were then continuously injected into the *M. aeruginosa* suspension within the flotation tank until 100L of the raw water had been introduced into the flotation tank. The initiation time for monitoring of the time taken for separation was decided at this time, i.e. 0 minute. After 90 minutes, the treated water was sampled from the sampling valve on the lower part of the flotation tank, as shown in Fig.3. The flotation efficiency of phytoplankton and removal rate of nutrient salt were then calculated from the concentrations of chlorophyll-a, ammonia-nitrogen and phosphoric acid. Here, micro-bubbles were produced from the dissolved air system, at a rate of 0.8L/min; the mean diameter of the bubbles was about 60µm.

The removal efficiency of *M.* aeruginosa was calculated from the chlorophyll-a concentration using Eq.5. To evaluate froth separation, the removal rate due to flotation was calculated from the thicknesses of the froth and sedimentation layers using Eqs 6 and 7.

$$R = \left(1 - \frac{A}{B}\right) \times 100 \qquad (5)$$

$$M_{(F)} = W \cdot (B - A) \cdot \frac{C}{(C+D)} \qquad (6)$$

$$R_{(F)} = \frac{M_{(F)}}{B \cdot W} \times 100 \qquad (7)$$

Where R is the removal efficiency of chlorophyll-a (%), $M_{(F)}$ the weight of froth (mg), $R_{(F)}$ the flotation efficiency (%), A the final concentration of chlorophyll-a at t = 90min (mg/L), B the initial concentration of chlorophyll-a at t=0min (mg/L), C the thickness of the froth layer (mm), D the thickness of the sedimentation layer (mm) and W the volume of *M. aeruginosa* suspension (= 60L).
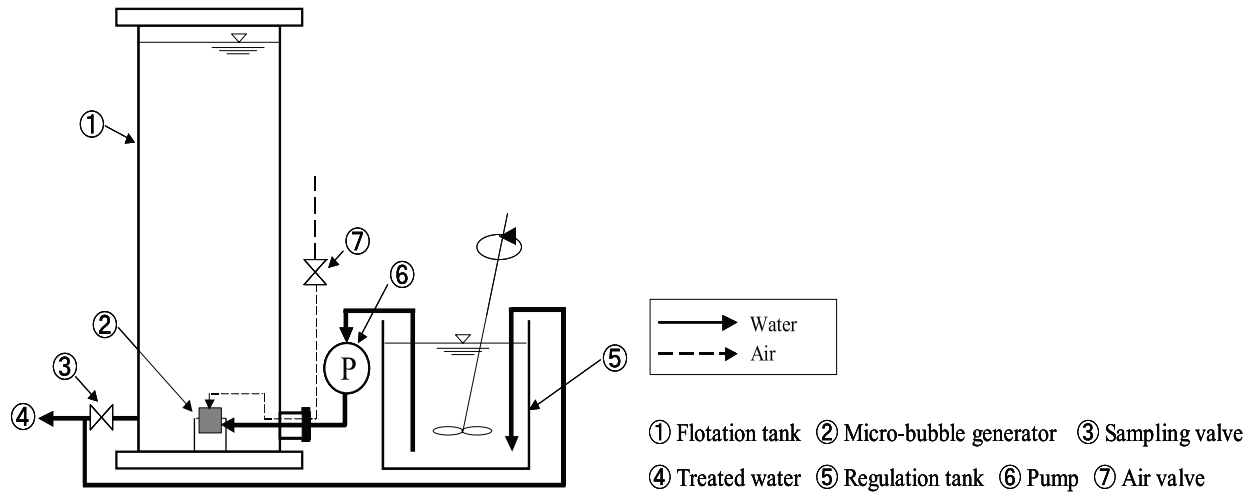
Water
- - - → Air

① Flotation tank ② Micro-bubble generator ③ Sampling valve
④ Treated water ⑤ Regulation tank ⑥ Pump ⑦ Air valve

Fig. 3. Flotation experimental apparatus

Table 1. Experimental conditions

	Phytoplankton	Water	Volume	pH	Magnesium chloride	Chlorophyll-a	NH$_4$-N	PO$_4$-P
			L		mg-Mg/L	μg/L	mg-N/L	mg-P/L
Run 1	M. aeruginosa	Tap water	15	8-12	0	120	0.8-6.0	0.2-1.0
Run 2	M. aeruginosa	Tap water	15	8-12	30	120	0.8-6.0	0.2-1.0
Run 3	M. aeruginosa	Tap water	15	8-12	60	120	0.8-6.0	0.2-1.0
Run 4	M. aeruginosa	Tap water	15	8-12	360	120	0.8-6.0	0.2-1.0

3. Experimental Results and Discussion

3.1. Adhesion of M.aeruginosa and Coagulant Materials

Generally, it is known that particles; *M.aeruginosa* and micro-bubbles, do not adhere to each other in water, as their surfaces are both covered by negative charges. Photo. 1., taken by SEM, shows the surface of *M.aeruginosa* at two different magnesium concentrations, 3 and 67 mg/L. Crystal magnesium hydroxide can be observed on the surface of the *M.aeruginosa* particle in Photo. 1. (B).
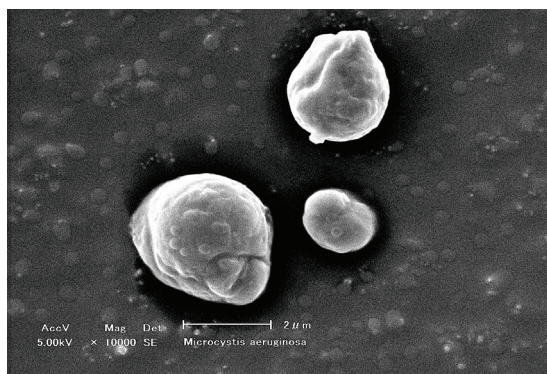
（A）*M.aeruginosa*（3 mg-Mg/L）
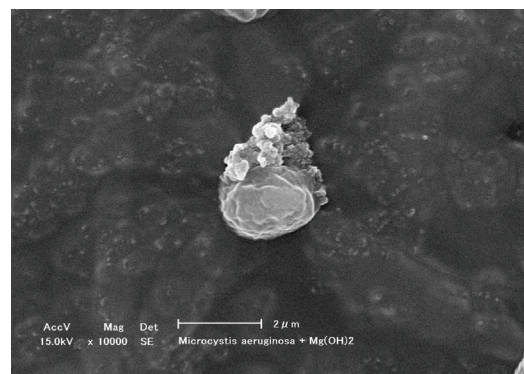
（B）*M.aeruginosa*（67 mg- Mg/L）

Photo. 1. Surface conditions of *M. aeruginosa* particles adhering crystal magnesium hydroxide.

3.2. Removal efficiency of Microcystis particles

The change in the removal rate of chlorophyll-a with respect to the magnesium chloride dosages and pH values is shown in Fig.4. Here, the shaded area is designated as the region of magnesium hydroxide settling. On the addition of magnesium chloride, removal efficiency of chlorophyll-a tended to increase with increasing pH in accordance with the formation of the magnesium hydroxide precipitate. A rapid increase in the removal rate of chlorophyll-a was observed within the pH range 10-11, with the maximum removal rates of 91-99% observed at pH 10.5 and 10.8 with 30 and 60mg-Mg/L, respectively. Here, the chlorophyll-a concentration decreased from 120 to 20-1μg/L and the rate of chlorophyll-a collection was also very high.[9]

When magnesium chloride was used as a coagulant, a high removal efficiency of chlorophyll-a was obtained in accordance with the formation of a magnesium hydroxide precipitate. Therefore, it is possible to use magnesium chloride as a coagulant for the solid-liquid separation under high pH conditions.
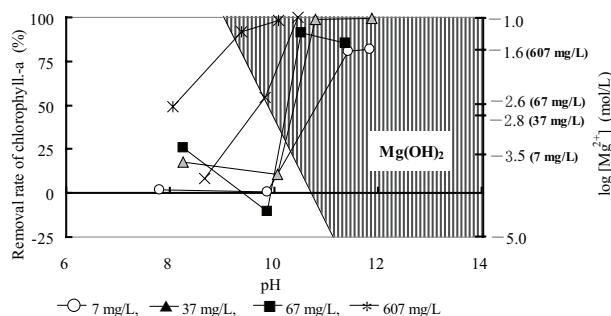

Fig. 4. Removal rate of chlorophyll-a

3.3 Removal efficiency of ammonia nitrogen and phosphoric acid

The removal efficiencies of NH_4-N and PO_4-P with magnesium chloride dosages are shown in Fig. 5. Here, the shaded part is designated as the region of MAP and magnesium phosphate formation. Firstly, in accordance with the formation of magnesium phosphate, the removal efficiency of phosphoric acid increased with increasing pH. Here, the phosphoric acid ion concentration decreased from 0.47 to 0.02 mg-P/L (pH>10.5). Secondly, the removal efficiency of ammonia was found to be a constant 5-7% in the pH range 8~12. Therefore, with respect to a magnesium chloride dose of 600mg-Mg/L, with high phosphoric acid and ammonia concentrations, the observed removal efficiency of ammonia was 13.7% in accordance with the formation of MAP.

Therefore, the results indicate that it is possible to remove phosphoric acid and ammonia from water; the removal of phosphoric acid from water, especially, was expected under high pH conditions.
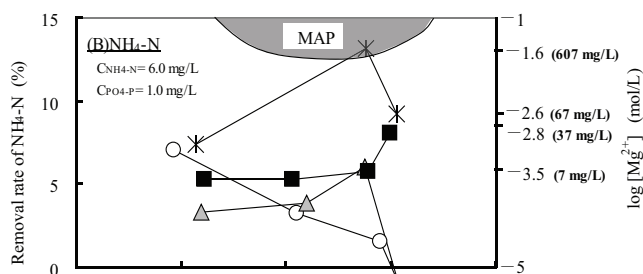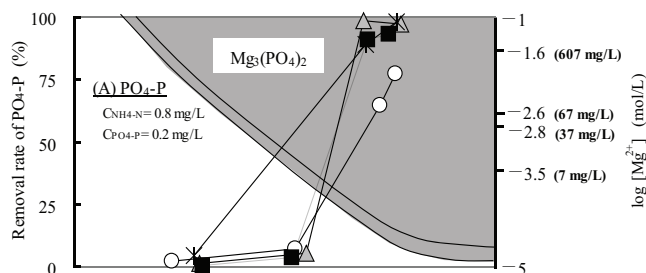

Fig. 5. Removal efficiency of PO_4-P and NH_4-N

3.4. Removal characteristic caused by magnesiumhydroxide

The changes in dissolved magnesium ions and removal efficiency of chlorophyll-a with respect to magnesium chloride dosages and pH are shown in Fig. 6; the percentages shown in this figure refer to the flotation efficiency, and was calculated from Eqs 6 and 7. The dotted line shows the dissolved magnesium ions calculated from Eq.8.

$$\log\left[Mg^{2+}\right] = \log K - 2\log K_w - 2\,pH \qquad (8)$$

Where K is the solubility product on $Mg(OH)_2$ (K=5.61×10^{-12}) and K_w the solubility product of water (K_w=10^{-14}).
Decreases in the dissolved magnesium ion concentration resulted from the generation of a magnesium hydroxide precipitate, which increased with increasing pH.

On the addition of magnesium chloride, the removal efficiency of chlorophyll-a tended to increase with increasing pH. The removal efficiency of chlorophyll-a was observed to rapidly increase within the pH range 10~11. The pH values changed with coagulant dosages. The chlorophyll-a concentration decreased from about 150 to 20μg/L. The maximum removal efficiency of chlorophyll-a was observed to be 84% at pH 10.6. Therefore, the results indicate it is possible to use magnesium chloride as a coagulant for the solid-liquid separation without regulating the pH and to obtain a natural high removal efficiency under high pH conditions.
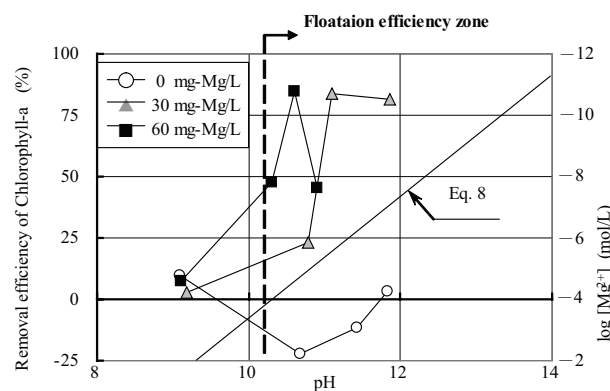

Fig. 6. Removal efficiencies of chlorophyll-a and Mg^{2+} ions concentration.

In the high pH zone, the experimental results for the removal efficiencies for NH4-N and PO_4-P with magnesium chloride dosage are shown in Table 2. The removal efficiencies and the differences in the NH_4-N and PO_4-P concentrations with respect to pH from the start to finish of the experimental period are shown in parentheses. The removal efficiency of PO_4-P increased with increasing pH. With a magnesium chloride dose of 60mg-Mg/L, the NH_4-N concentration decreased from 0.62 to 0.54mg-N/L (13%), and that of PO_4-P decreased from 0.27 to 0.02mg-P/L (92%). The maximum removal efficiencies and decreases in the

NH_4-N and PO_4-P concentrations before and after the change in pH were observed to be 6.7% (0.04mg-P/L) and 63.6% (0.07mg-N/L), respectively. This also infers that the decreases in the NH4-N and PO_4-P molarities were 6×10^{-6} and 8×10^{-6} mol, respectively, and implied the formation of MAP. On the other hand, without the addition of magnesium chloride, the magnesium ions included in the *M. aeruginosa* suspension were thought to affect the increasing removal efficiencies of NH_4-N and PO_4-P. Therefore, it is possible that a drop in the magnesium chloride dose decreased the NH_4-N and PO_4-P concentrations.

Table 2. Removal efficiencies of ammonia nitrogen and phosphoric acid

	pH	9.1		10.7		11.4		11.8
0mg-Mg/L	PO_4-P (mg/L)	0.21	(0.02)	0.19	(0.03)	0.16	(0.05)	0.11
	Removal efficiency (%)	0.0	(9.5)	9.5	(15.8)	23.8	(31.3)	47.6
	NH_4-N (mg/L)	0.65	(0.05)	0.6	(0.07)	0.53	(0.05)	0.48
	Removal efficiency (%)	0.0	(7.7)	7.7	(11.7)	18.5	(9.4)	26.2
	pH	9.1		10.3		10.6		10.9
60mg-Mg/L	PO_4-P (mg/L)	0.27	(0.16)	0.11	(0.07)	0.04	(0.02)	0.02
	Removal efficiency (%)	0.0	(59.3)	59.3	(63.6)	85.2	(50.0)	92.6
	NH_4-N (mg/L)	0.62	(0.02)	0.6	(0.04)	0.56	(0.02)	0.54
	Removal efficiency (%)	0.0	(3.2)	3.2	(6.7)	9.7	(3.6)	12.9

4. Conclusion

This study examined the possibility of using a flotation system combining a hybrid technique (chemical compounds and electrostatic bridge) for application to raw water with a high pH containing phytoplankton, as well as the zeta potential value of the phytoplankton surface and the removal efficiency of phytoplankton, ammonia, nitrogen, and phosphoric acid. The results obtained from various experiments were as follows:

1. The flotation system using a hybrid technique (chemical compounds and electrostatic bridge) can be applied to raw water with a high pH containing phytoplankton. The maximum removal efficiencies of phytoplankton, ammonia, nitrogen and phosphoric acid were also estimated

2. The chlorophyll-a concentration decreased from about 150 to 20μg/L, with a maximum removal efficiency of 84% at pH 10.5.

3. It is possible to remove NH_4-N and PO_4-P from eutrophic water. The concentrations of NH_4-N and PO_4-P decreased from 0.62 to 0.54mg-N/L (13%) and from 0.27 to 0.02mg-P/L (92%), respectively. the optimal pH conditions for the maximum removal of chlorophyll-a were also obtained; the removal efficiencies and amounts of NH4-N and PO4-P removed before and after the change in pH were observed to be 6.7% (0.04mg-P/L) and 63.6% (0.07mg-N/L), respectively.

4. The zeta potential on the surfaces of *M.aeruginosa* particles were observed to be charge neutral on the adhesion of magnesium hydroxide precipitate in the pH range 10.5 to 11.

In the field of water basin management, this hybrid system combining magnesium compounds and an air flotation technique will be an efficient system as a water quality purification technology.

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