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# Comparison of Algal Removal by Coagulation with Clays and Al-based Coagulants

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**Abstract:** Coagulation with both metal coagulants and clays can effectively remove algal cells from water. Pre-polymerized inorganic coagulants (e.g., polyaluminium chloride, PACl) normally contain high positive charge and the charge neutralization is one of algal removal mechanisms by coagulation, then, a better performance of PACl in the removal of algae is expected. The excellent algal removal efficiency by bentonite (Bent) and montmorillonite KSF (Mont-KSF) was observed in this study but for the turbidity reduction, Bent did not perform as well as Mont-KSF and then the most suitable clay to be considered is Mont-KSF. It has been proposed that the maximum algal removal efficiency by clays would be achieved when the particle size of clays is close to that of algal cells. However, under this study conditions, the particle size alone does not correlate the good removal efficiency of Bent and Mont-KSF. It is thus proposed that the nature of microstructure of clay particles could contribute to good algal removal efficiency.

**Keywords:** Algal removal, clay coagulants, coagulation, particle size distribution, prepolymerised coagulants, water treatment

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## INTRODUCTION

Algae are most common aquatic species which grow and habitat in sea, lakes and rivers. Very rapid growth of algae can therefore cause problems in the water supply industry, such as water discolouration, taste, odour and blockage of filters. In particular, some types of algae (e.g., blue-green algae) can be toxic to humans and other organisms. If an excessive growth of algae occurs, endogeneous toxins (e.g., microcystin and nodularin) emitted act as hepatoxins, while anatoxin and saxitoxin act as neurotoxins; these may cause serious damage to both humans and animals alike (1, 2). Therefore, the blooming of algae not only worsens water treatment performance and then deteriorates water quality, but also results in the toxic effect on human beings and animals.

It has been found that effective removal of algae is required prior to filtration to reduce filter-clogging problems associated with the treatment of algae-laden waters. One technology could be considered is micro screening with a mesh of 20 to 50 μm which is effective for the algae removal from algae-laden water prior to filtration. On the other hand, both pre-oxidation and chemical coagulation could be used for this purpose. Pre-oxidation (e.g., with chlorine or ozone) can cause cell membrane damage that leads to the release of intracellular taste and odour causing compounds and toxins into the bulk water (3). In addition, prechlorination of algae-laden water will result in the formation of halogenated disinfection by-products (DBP) in the product water. In contrast, coagulant chemicals and water mixing conditions do not affect the integrity of algae cells and due to this, coagulation will not result in the release of intracellular toxins and taste/odour causing compounds. Instead, intracellular toxins and taste/odour causing compounds can be removed by coagulation, via either charge neutralization or co-precipitation, and subsequent sedimentation and filtration processes. However, it should be pointed out that continuous sludge removal should be carried out in sedimentation basins to minimise the release of taste and odour compounds and toxins from decaying algae cells in sludge (4).

Both aluminium sulphate (AS) and polyaluminium chloride (PACl) are established commercial coagulants and used widely in water industries. In practice, residual Al concentrations in the treated effluent could exceed to the up-limit of the drinking water standards which is 0.2 mg/L (5) if the operating conditions go wrong. Therefore, many water industries are looking for the alternatives to replace the Al based coagulants. One effort that has been made is to investigate the use of clays as water treatment chemicals. Natural mineral clays possess specific surface chemical properties, e.g., cation exchange capacity and adsorptive affinity for some organic and inorganic compounds, which have led to investigations on the potential use of clays either as adsorbents (6) or as coagulants (7) for treating heavy metals and organic pollutants, and results achieved are promising.

This study aims to compare the performance of Al-based coagulants and various types of clays in the removal of *Microcystis aeruginosa sp*., which is one of the dominant species in Korean lakes, particularly in the Daechung Lake (Daejon, Korea).

## METHODS

### Culture and Characterisation of Algae

*Microcystis aeruginosa sp.* was cultured in 1 litre erlenmeyer flask with a standard culture media and under the culture conditions of a constant temperature of 25°C, light exposing (2000 Lux) for 16 hours and dark intervals for 8 hours with shakings at a speed of 50 rpm. It took 12 days from lag phase to stationary phase and about 1 month to death phase (Fig. 1). Figure 2 shows a microscopic view of *Microcystis aeruginosa sp.* which was in a status of 10 days after being cultured. *Chlorophyll-a* concentration was analysed, using an estabilished method (8), to measure the density of the algae. Size distributions of algae were measured using IMAGE/Particle Analyser CIS-1 (GALAI).

### Particle Size Distributions of Clay Samples

Clay samples were prepared by mixing clays with methylene chloride to make a clay suspension with concentration of 300 mg/L, which were then

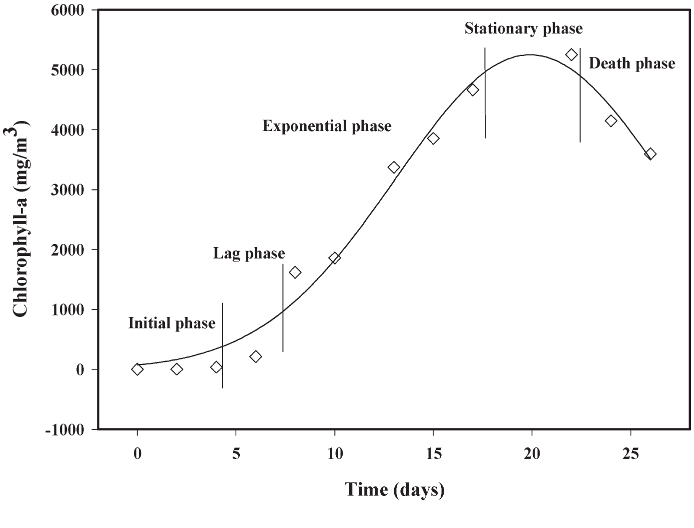


***Figure 1.*** Variation of *chlorophyll-a* concentration during the culture period.

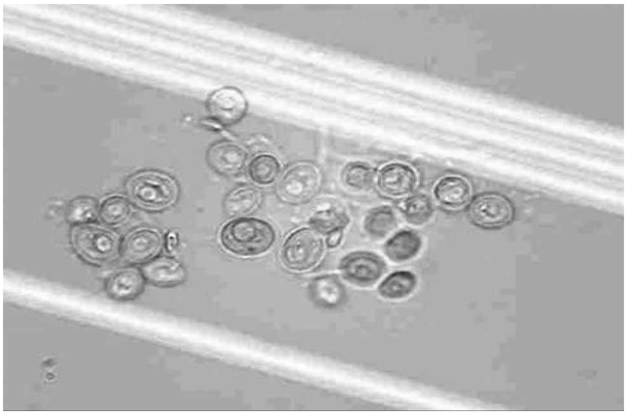

*Figure 2.* Photograph of *Microcystis aeruginosa sp.* for 10 days culturing (×400).



immediately shaken for minutes, withdrawn, and put into a cuvette for the measurement of particle size distribution using IMAGE/Particle Analyser CIS-1 (GALAI).

## Test Waters

Tests were carried out using synthetic model water which was made by mixing given amount of *Microcystis aeruginosa sp.* (taken from the exponential phase) plus kaolin particles (30 mg/L) with deionised water. The model water had following characteristics: pH, 7.0–7.5, alkalinity, 30–45 mg/L as $CaCO_3$, turbidity, 32–53 NTU and *chlorophyll-a* concentration, 57.9 μg/L.

## Study Procedures

The coagulants used in this study included aluminium sulphate (AS) and polyaluminium chloride (PACl), which were provided by Kemira Chemical; AS has the Al content of 8% w/w as $Al_2O_3$ and PACl (PAX – XL9) has the Al content of 8.5% w/w as $Al_2O_3$ with the basicity of 53.8, and four clays, bentonite (Bent), sodium modified bentonite (Na-Bent), montmorillonite KSF (Mont-KSF), and montmorillonite K10 (Mont-K10), which were provided by Sigma-Aldrich. A standard jar test procedure was applied to assess the coagulation performance, which comprised of a 1-min fast mixing at 400 rpm, a 20-min slow mixing at 35 rpm and a 60 min sedimentation period. The coagulation pH was maintained at pH 7 by adding predetermined amount of either 1 M HCl or 1 M NaOH when dosing coagulants. The base of the selection of coagulation pH at 7 is to simulate the coagulation of natural algae-laden water. The supernatant was withdrawn for the measurement of water quality parameters (e.g., *chlorophyll-a* and turbidity) following the Standard Methods (9). The shape of algae-clay flocs was examined by a scanning electron microscope (SEM) (HITACHI S-3200).

## RESULTS AND DISCUSSION

### Particle Size Distributions of Algae and Clays

Typically, *Microcystis aeruginosa sp*. forms spherical colonies. When observed by a microscope, its border is irregular, extending lengthily in lobed or reticulate mass forms. Suspended colonies often appear as small blue-green "clots" to the naked eye. Individual cells are very small with conspicuous, highly refractive pseudovacuoles that cause the colonies to be buoyant and float to the surface. Cells of colonies were held together by a transparent and gelatinous matrix, which may be difficult to discern under microscopic examination. Therefore, the IMAGE/Particle Analyser was used to examine the algae size. Table 1 shows that Microcystis aeruginosa taken from the exponential phase had the mean size of 7.76 to 8.73 μm depending on the mixing duration, the standard deviation was in the range of 2 μm.

The measurement of clay size was conducted by suspending clays into either methylen chloride in order to prevent swelling of clays or into water in order to get information of clays' swollen size. Table 2 shows the clays' original size (in methylen chloride) ranges from 9.32 to 10.48 μm in average and the clays' swollen size (in water) does not increase significantly (increasing less than 1 μm for all clays) and ranges from 9.50 to 11.33 μm in average. It appears that the size of clays is 1–2.5 μm greater than that of algae.

### Algae Removal

The comparative algal removal performance can be seen in Figs. 3 and 4. Figure 3 shows that at low doses, PACl performed better than AS, 90%

***Table 1.*** Particle size of the algae

| Algae | In water | Median (μm) | Mean (μm) | S.D. (μm) | Remark |
|---|---|---|---|---|---|
| *Microcystis aeruginosa sp.* | 0 min | 8.52 | 8.73 | 2.25 | PND[a] |
| | 30 min | 7.63 | 7.83 | 2.14 | |
| | 60 min | 7.60 | 7.76 | 2.09 | |

*Table 2.* Particle size of clays

| | Median (μm) | Mean (μm) | S.D. (μm) | Remark |
|---|---|---|---|---|
| Bentonite | | | | |
| In methylen chloride | 8.67 | 9.95 | 5.48 | PND[a] |
| Swollen size (in water) | 8.81 | 10.44 | 4.84 | |
| Na-Bentonite | | | | |
| In methylen chloride | 9.95 | 9.32 | 3.19 | |
| Swollen size (in water) | 10.19 | 9.50 | 4.05 | |
| KSF | | | | |
| In methylen chloride | 9.07 | 10.48 | 5.66 | |
| Swollen size (in water) | 9.43 | 11.33 | 7.48 | |
| K10 | | | | |
| In methylen chloride | 9.37 | 10.42 | 5.08 | |
| Swollen size (in water) | 9.61 | 10.97 | 5.80 | |

[a]PND: Probability number distribution.



chlorophyll-a can be removed with PACl at a dose of 0.04 mM whilst at the same dose, AS can only achieve 75% removal. This is consistent with the previous work (10, 11), where polyferric sulphate (PFS), one of the pre-polymerized coagulants, was demonstrated to be superior to ferric sulphate in the respect of algal removal. Pre-polymerised inorganic coagulants (e.g., PACl) contain high positive charge than conventional one (e.g., AS), and charge neutralization is one of algal removal mechanisms by coagulation, then, this explains the better performance of PACl achieved.

Figure 4 displays the overall performance of four types of clays in the removal of algae. Bent and Mont-KSF outperformed Na-bent and Mont-K10 in the removal of algal cells. For a dose of 200 mg/L as clays, both

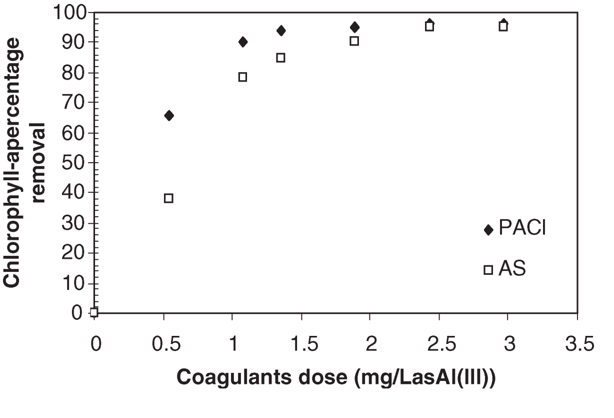


*Figure 3.* Comparative algal removal with PACl and AS.

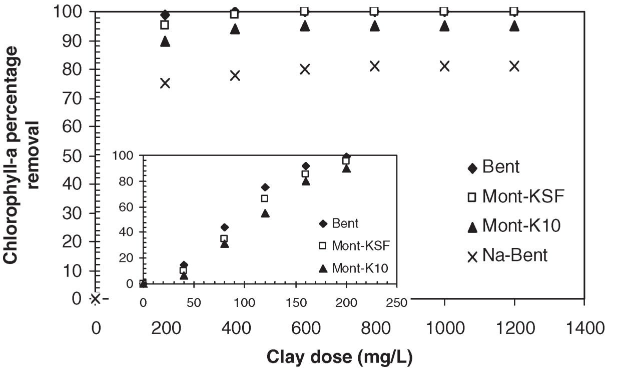


***Figure 4.*** Comparative algal removal with various clays.



Bent and Mont-KSF can remove 100% of the chlorophyll-a, which is superior to the performance achieved by the polymeric metal coagulant, PACl.

As stated previously that the test water posseses relative high turbidity (32–53 NTU), the evaluation of the turbidity reduction is thus important when selecting coagulants. The results demonstrated that both AS and PACl can achieve about 95% turbidity reduction for the doses above 2 mg/L. For the clay based coagulants, greater turbidity reduction was achieved by Mont-KSF; more than 99% turbidity can be removed at a Monf-KSF dose of 200 mg/L (see Fig. 5), i.e., the residual turbidity was below 5 NTU. This is even better than the performance achieved by Al-based coagulants. However, for all other three clays, the turbidity removal performance is not satisfied although Bent performed better than Mont-K10 and Na-Bent. Further treatment should be considered then for the clerification of clay treated water.

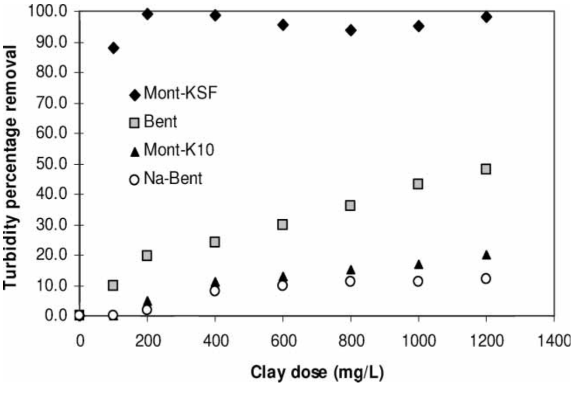


***Figure 5.*** Turbidity removal with various clays.

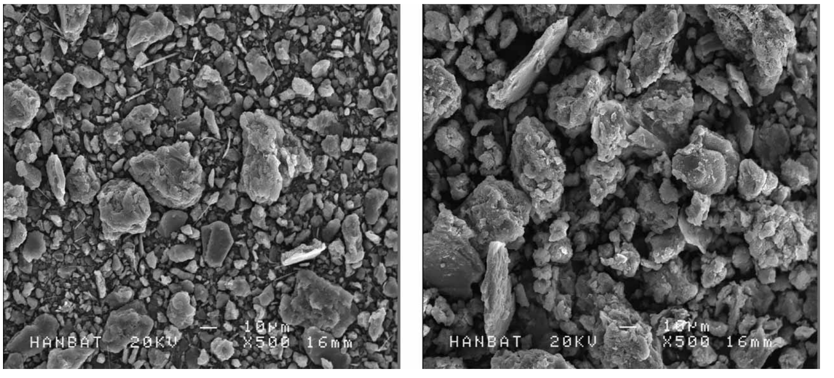


***Figure 6.*** SEM images of *Microcystis a.*-clay flocs, Left) *Microcystis a.*-Mont-K10 and Right) *Microcystis a.*-Mont-KSF.



In order to explore the mechanism of algae removal by clays, the relationships between the removal efficiency and the size of algal cells and clays were studied previously (12). Results from trajectory analysis (12) disclose that the collision efficiency, and therefore the removal efficiency, is very sensitive to the size of clay particles. Consequently, the selection of the proper clay particle size in accord with the size of algal cells encountered is considered very important. It has been proposed that the maximum algal removal efficiency by clays would be achieved when the clay particle size is close to that of the algal cells.

In this study, the mean size of all clays studied is slightly different from that of *Microcystis aeruginosa sp. (Microcystis a.)*; the swollen size of all clays is 1–2.5 μm greater than that of *Microcystis a.* (Tables 1 and 2). Obviously, this partly explains the good performance of Bent and Mont-KSF. However, the particle size effect alone does not explain the relative weak performance achieved by another two clays, Na-bent and Mont-K10.

It is thus proposed that there should be some other mechanisms contributing to algae removal by clays; and the microstructure of clay-algae flocs was studied by examining images of the flocs using scanning electron-microscopy (SEM). The images show that flocs obtained by Na-Bent or Mont-K10 connected with *Microcystis a.* cells had loose strucutre, whilst the flocs resulting from the Bent or Mont-KSF with *Microcystis a.* flocculation had more networking structure which are large in size, hold the algal cells tightly and then catch the cells effectively. Figure 6 shows an example of such images.

## OVERALL DISCUSSION AND CONCLUDING REMARKS

Coagulation with both metal coagulants and clays can effectively remove algal cells. Pre-polymerized inorganic coagulants normally contain high positive charge and charge neutralisation is one of algal removal mechanisms by coagulation. Then, in comparison with aluminium sulphate (AS), poly-aluminium chloride (PACl) achieved a better performance in respect of algal removal, it is evident of the above-mentioned assumption.

The excellent algal removal efficiency of the clays Bent and Mont-KSF was observed. For a dose of 200 mg/L, the percentage removal of *chlorophyll-a* achieved by both clays was 100% which is greater than that the PACl could achieve, over whole dose ranges studied. However, for the turbidity reduction, Bent did not perform as well as Mont-KSF and then the most suitable clay to be considered is Mont-KSF. Although the dose of clay (200 mg/L) is relatively high in comparison with the doses of PACl (1.5 mg/L as Al(III)), the abundant availability, low cost, together with non-harmful chemical residuals in the treated water by clays have demonstrated advantages, and this could provide water industries with an alternative treatment reagent in coping with the problems of algae.

This study demonstrates that particle size effect alone can not explain a better performance of algae removal with clays. Four clays studied have a similar particle size to the algae, Microcystis a., but Bent and Mont-KSF out-performed the other two clays. It is then proposed that the microstructure of clay-algae flocs play important roles to contribute to a good performance in the respect of algae removal.



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