Identifying the linkage between particle characteristics and understanding coagulation performance

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Abstract The coagulation/flocculation process is important for particle separation in water treatment. However, difficulties arise when coagulation is not optimised for the dominant particle. This paper investigates the surface characteristics and floc properties of three common systems – natural organic matter (NOM), algae and clay – in order to aid understanding of the coagulation/flocculation process. It was demonstrated that charge density and specific surface area are important parameters with respect to coagulant demand for charge neutralisation for all systems. However, extracellular organic matter (EOM) affected the coagulant demand of algae to the extent that it appears that the presence of EOM could dominate the coagulation process. Controlling the zeta potential of the systems prompted improved particle aggregation and hence removal efficiency in all cases. Floc growth profiles revealed that algal flocs required five times the flocculation period to reach a steady-state floc size compared to NOM and clay and on exposure to increased shear were much weaker. Despite similarities between algae and NOM in terms of organic content and coagulant demand, the fact that algae is a dynamic, biological system as opposed to an inert system creates numerous problems for the coagulation/flocculation process.

Keywords Algae; clay; coagulant demand; floc strength; natural organic matter

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Introduction

Coagulation/flocculation is an important and established process in water treatment for removing suspended particles. The nature of the contaminant load varies from source to source. For example, source water originating from rivers can have a high proportion of suspended clay colloids, whereas upland, peaty areas are generally dominated by natural organic matter (NOM). In all source waters algae are ubiquitous, although abundance differs depending on the extent of eutrophication. Seasonal algal growth can interfere extensively with a process that has been optimised for either clay or NOM systems. This typically results in algal and coagulant carry over, increased coagulant demand and filter clogging (Mouchet and Bonnélye, 1998).

The coagulation process is generally optimised for a particular system in terms of coagulant dose and pH, achieved through a series of bench-scale jar tests. However, a limitation of such an approach is that particle characteristics are not linked to treatment optimisation. An understanding of the differences and similarities between systems could aid optimisation; for example, coagulation of NOM is thought to be principally driven by charge neutralisation mechanisms and as such, monitoring of the charge properties of the raw waters is extremely useful (Jefferson *et al.*, 2004).

The current paper presents a comparison of the surface characteristics and floc properties of three systems: kaolin, algae and NOM. The aim of this work is to determine similarities and differences between the fundamental characteristics of these systems in order to improve current understanding of the coagulation/flocculation process.

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Method

Materials

Preparation of kaolin suspension. 200 g of lab grade kaolin (acid rinsed) was blended at high speed with 500 ml of deionised water for 20 minutes at pH 7.5, adjusted using 0.1 M NaOH. The resultant suspension was made up to 1 litre in a measuring cylinder using deionised water and left overnight. Subsequently, 500 ml was decanted and the concentration was determined gravimetrically. A stock solution of 50 g l^{-1} was prepared from which further dilute suspensions were made as required using tap water (hardness – 104 mg l^{-1} as $CaCO_3$; alkalinity – 55 mg l^{-1} as $CaCO_3$).

Cultivation of Chlorella vulgaris. *C. vulgaris* (211/11B) culture was obtained from the Culture Collection of Algae and Protozoa (CCAP), Oban, Scotland. Cultures were grown using 50 ml of autoclaved Jaworski medium, prepared as advised by CCAP, in 250 ml conical flasks. Samples were grown on a Patterson Scientific Bibby Stuart SO1 shaker under 24 hour radiation using a Sun-glo 30 W aquatic light. Samples were taken at the end of the log growth phase and diluted with tap water to a population concentration of approximately 5×10^5 cells ml^{-1}.

Natural organic matter (NOM). NOM rich water was obtained from a reservoir fed by an upland peat catchment system, situated in Halifax, UK. It was stored at 4 °C until use.

The characteristics of each of the above systems are summarised in Table 1.

Experimental procedures

Isoelectric point. Varying doses of aluminium sulphate (alum), $Al_2(SO_4)_3.18\ H_20$, were added to 100 ml aliquots of kaolin, *C. vulgaris* or NOM suspensions and mixed thoroughly. The pH adjusted accordingly to give a range of pH 2–10 with 0.1 M HCl and 0.1 M NaOH. The zeta potential was subsequently measured using a Malvern ZetaSizer 2000HSA (Malvern Instruments, UK) and the isoelectric point (i.e.p.) was plotted.

Removal efficiency. Jar testing of all three systems was conducted using a PB-900 variable speed jar tester (Phipps and Bird, Camlab, UK) with flat paddle impellers (76 × 25 mm) with 800 ml suspensions in cylindrical jars. The procedure comprised a 3 minute rapid mix period at 200 rpm for addition of varying coagulant doses and subsequent pH adjustment using 0.1 M HCl to pH 5 for algae, pH 5.5 for NOM and pH 7 for kaolin. This was followed by a 15 minute flocculation period at 30 rpm and settling

Table 1 Characteristics of NOM, algal and kaolin systems

	NOM	Algae	Kaolin
Concentration	8.8–14 mg l^{-1}	5×10^5 cells ml^{-1}	50 mg l^{-1}
Turbidity (NTU)	5.9–7	3.2	50
Particle size (μm)[1]	0.15 ± 0.02	4.5	0.2
Density (g cm^{-3})	1.00 (dissolved)	1.07	2.67
Specific surface area ($m^2\ g^{-1}$)	40	1.09	9.09
Charge density (meq g^{-1})	10–15[2]	Variable[3]	0.1 – 1[2]
Zeta potential (mV)	−18 at > pH 3	−15 at > pH 3	−50 at > pH 6
i.e.p.	1.5	1.5	2

[1]NOM particle size was obtained using a Malvern Zetasizer 3000HSA (Malvern Instruments, UK) and that of algae and kaolin using a Malvern Mastersizer 2000 (Malvern Instruments, UK)
[2]Edzwald (1993)
[3]Gregor *et al.* (1996) determined that alginate, a typical cell component, consumes twice the coagulant as NOM on a weight basis

period of 20 minutes. The treated suspensions were analysed for zeta potential and turbidity (using a HACH 2100N Turbidimeter, Camlab, UK) for all systems in addition to DOC for NOM (using a Shimadzu TOC-5000A analyser).

Floc size and strength. Jar testing was conducted under optimum conditions of pH and coagulant dose, which were checked by measurement of the zeta potential. A feed pump connected the suspension from the jar tester to a dynamic laser diffraction instrument (Malvern Mastersizer 2000, Malvern, UK) to measure the average floc size every minute. Suspensions were flocculated at 30 rpm after rapid mix as for standard jar tests for 15 minutes (NOM and kaolin) and 25 minutes (algae) before the shear was adjusted by increasing the paddle speed. In all cases flocs were subjected to 30 rpm, 40 rpm, 50 rpm, 75 rpm, 100 rpm and 150 rpm paddle speeds for a further 15 minutes.

Results and discussion

Coagulant demand

The organic particles required a colloid to coagulant weight ratio of 1–10 mg mg^{-1} to reach the i.e.p. (Figure 1). By comparison, the colloid to coagulant ratio required for kaolin was 100 times greater. Theoretically, the difference between kaolin and NOM can be explained in terms of the specific surface area (SSA) and charge density as both parameters are far greater for NOM (Table 1). This observation is in accordance with conclusions drawn by a similar study as DOC was demonstrated to control coagulation as opposed to turbidity (Edzwald, 1993). However, with respect to algae, the relatively low SSA (1.09 m^2 g^{-1}) does not fit the observed data despite the high charge density. The observed difference is likely to be due to the excretion of extracellular organic matter (EOM). EOM comprises neutral and acidic components such as polysaccharides and uronic acids (Hoyer *et al.*, 1985) and is known to interfere significantly with the coagulation process (Bernhardt *et al.*, 1985). If it is assumed that the charge density of the cells and associated EOM is similar (Gregor *et al.*, 1996) and that stoichiometry exists between neutralisation and coagulant addition, the EOM must be significantly contributing to the coagulant demand, possessing a larger SSA. This has been similarly demonstrated in a study where EOM concentrations by mass were determined to be three times greater than that of the cells (Leppard, 1997). This was attributed to the increased surface area of the EOM, as it was assumed that the surface area per volume (SA/V) of 0.005 μm fibrils must be greater than the SA/V of the particles >0.45 μm. This infers that the presence of EOM in algae laden water could dominate water quality changes as opposed to the cells themselves. This suggests that algae laden water should be treated similarly to water with

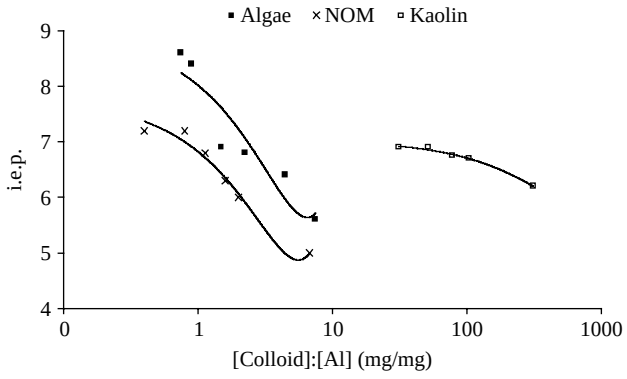

Figure 1 The colloid to coagulant weight ratio vs i.e.p. for kaolin, algae and NOM systems

high NOM concentrations rather than water with a high turbidity. The implications are that monitoring algal abundance would be insufficient as an indication of coagulant demand and DOC monitoring is equally, if not more, important.

Control using zeta potential

The zeta potential of each of the systems was monitored and correlated with removal efficiency. In each instance the removal efficiency was greater as the magnitude of the zeta potential was reduced; resulting in optimum operational zeta potential ranges (Figure 2). These operational ranges were different depending on the system; for example, NOM was successfully removed between -10 mV and $+5$ mV, whereas the zeta potential band for kaolin was much wider at -20 mV to $+5$ mV. The algae had a symmetrical optimal removal band of -12 mV to $+12$ mV, which was more like the removal band for NOM than for kaolin. This implies that the organic particles are much more reliant on charge neutralisation for removal than inorganic particles. This observation could be related to differing coagulation mechanisms. Optimum conditions for organic particles required a low pH ($\sim$ pH 5–6) where the dominant removal mechanism is charge neutralisation by complexation reactions between the cationic coagulant and anionic organic ligands (Stumm and Morgan, 1962). However, for inorganic particles coagulation was conducted at pH 7. At this pH, not only would charge neutralisation occur to a degree, considered to be a result of physical adsorption of the cationic amorphous hydroxide onto the surface of the inorganic particle (Duan and Gregory, 2003), but sweep flocculation would also occur increasing the density of the flocs. Hence, organic particles are much more dependent on the decrease in the magnitude of the zeta potential and subsequent reduction in the electrostatic barrier to contact.

Despite the differing coagulation mechanisms dominating, so long as the appropriate coagulation pH is maintained, measuring zeta potential can be used to determine appropriate coagulant dose without having to complete numerous jar tests. In this way the fundamental surface characteristics of the particles, in terms of the negative zeta potential, could be linked to treatment optimisation.

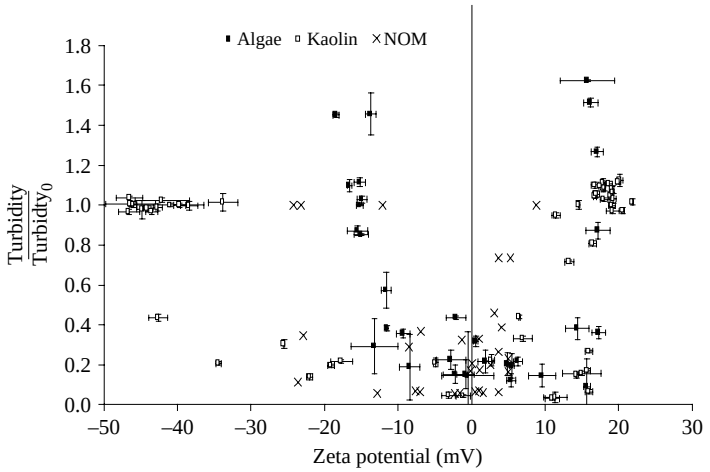

Figure 2 The correlation between zeta potential and removal efficiency for impurity particulates kaolin, algae and NOM systems

Floc growth profiles

Despite the similarities observed between organic particles with respect to their coagulant demand and removal mechanisms, the respective floc growth profiles were very different (Figure 3). Steady-state floc size was achieved after 4 minutes for NOM and 6 minutes for kaolin. The growth rate observed for NOM was double that for kaolin (565 μm min^{-1}

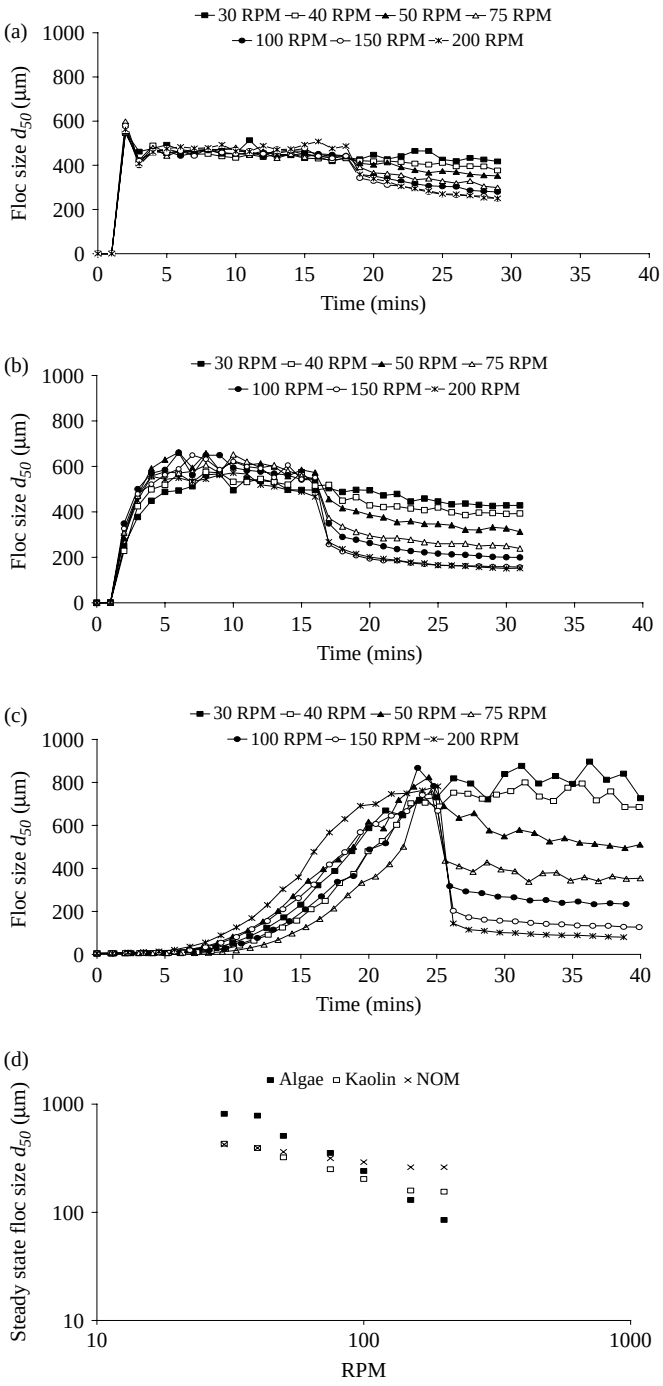

Figure 3 Floc growth profiles under optimum conditions for: (a) NOM + alum, (b) kaolin + alum, (c) *C. vulgaris* + alum, and (d) log log plot of steady-state floc size vs increasing levels of shear

and 290 μm min^{-1} for NOM and kaolin respectively), perhaps due to the requirement of a lag time for kaolin in order to allow larger hydroxide precipitates to form (Duan and Gregory, 2003). By comparison, algal flocs required 25 minutes to achieve steady-state floc size and during the first 6–7 minutes no agglomeration was observable. The algal floc growth rate was also extremely variable, ranging from 30 μm min^{-1} to 290 μm min^{-1} (taken between 10–20 minutes), and far slower than initial growth rate for the inert particles, especially that of NOM. These observations indicate the dynamic nature of the algal population in that population abundance and EOM concentrations can change in relatively short time spans affecting the growth rate of the flocs. The varying growth rate can be attributed to steric interactions by loosely bound EOM which has been demonstrated to interfere with coagulation (Bernhardt *et al.*, 1985). The time-lag observed prior to floc growth was attributed to the biological system's ability to react to changes in the immediate environment. Such an observation is supported by the work of Clasen *et al.* (2000) who reported that a 7 minute stabilisation time was required prior to measuring post-coagulation algae zeta potential. It was postulated that algae exude stored negative molecules to maintain negative charge when cationic hydrolysis products interact with the cell surface, thus remaining stable in suspension.

Initial floc strength was in the following order: algae > kaolin > NOM, as the steady-state floc size indicates the ability to withstand shear in the flocculator (Figure 3). Exposure to increased shear, which in this work was simply inferred using increasing rpm values (Jarvis *et al.*, 2004), altered the floc size of the algae by the largest proportion as flocs were reduced to 11% of their original size compared to the NOM and kaolin flocs which were reduced to 50% and 27% of their original size respectively on an increase to 200 rpm. Interestingly, the strength of the algal flocs resembled similar profiles obtained for polymer and NOM flocs, in terms of the initial size and floc breakage on exposure to increase shear, as they too reached approximately 800 μm and decreased to 23% of their original size (Parsons *et al.*, 2004). This infers that polysaccharide exudates from the algae play an important role in their flocculation. As such, it is likely that algal cells and any hydroxide precipitate are bridged together by polymeric substances forming large flocs at low shear, similar to that experienced while using a polymer.

A comparison of the strength between the three systems (Figure 3d) shows that two distinct zones exist for the algal flocs as at 40 rpm and below the steady-state floc size does not change greatly, implying resistance to these shear levels and thus a high floc strength. At shear levels greater than 40 rpm, however, the degradation rate increased at a constant rate with increasing rpm. However, for NOM and kaolin flocs there was constant degradation until reaching 150 rpm upon which no further degradation occurred. This demonstrates that although the algae formed much stronger flocs initially at low shear, on exposure to higher shear levels they were more prone to breakage compared with NOM and kaolin flocs. These observations can be quantified in terms of the floc strength coefficient, log C (the y-axis intercept) and floc strength constant, γ (the gradient of the slope) (Jarvis *et al.*, 2005a). The larger the value of log C at a fixed shear the stronger the floc, while the response to increasing shear is quantified by the magnitude of γ. The floc strength constant can also be used as an indicator of the dominant floc breakage mechanism, where γ values of 0.5 are indicative of floc fragmentation while γ values of 1 suggest erosion mechanisms dominate. Comparisons of log C and γ values, extrapolated from Figure 3d, indicate conclusively that while algae flocs are initially much stronger than NOM and kaolin flocs, NOM flocs are far more resistant on exposure to increased shear (Table 2). The values obtained for NOM compare favourably with those obtained by other studies (Bache and Rasool, 2001; Bache *et al.*, 1999).

Table 2 The value of floc strength constants and floc strength coefficients for the three systems and literature values of other aluminium-based flocs for comparison

Type of floc	Log C	γ	Reference
C. vulgaris	9.3	4.3	Current study
NOM	4.0	0.96	Current study
Kaolin	5.0	1.6	Current study
High alkalinity and NOM	4.1	0.81	Bache and Rasool (2001)
Commercial humic acid	3.1	0.44	Bache *et al.* (1999)

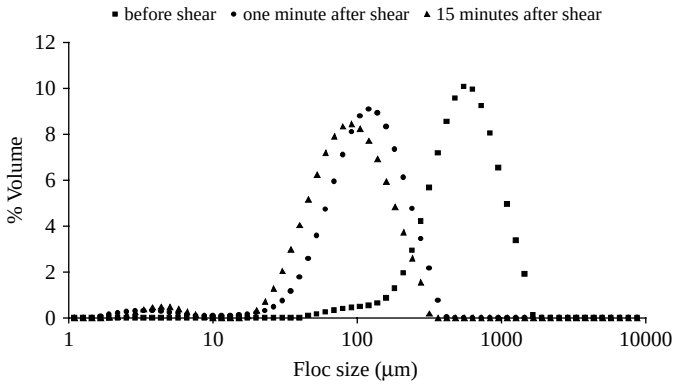

Figure 4 Floc breakage profile for algae + alum flocs before and after exposure to a shear of 200 rpm

The floc strength values are also indicative of surface erosion ($\gamma \geq 1$), particularly in the case of algae. However, examination of the breakage profile of algae suggests that large-scale fragmentation was dominant as the floc size was reduced to ~100 μm with almost no remnants of the 800 μm peak remaining after the initial exposure to increased shear of 200 rpm. The only evidence of surface erosion was a small increase in the volume of 5 μm, the size of the algal cell, after exposure to 15 minutes of increased shear (Figure 4). This contradicts the theory that γ values of 0.5 only are indicative of large-scale fragmentation. A floc breakage pattern indicative of surface erosion has been observed for NOM and alum flocs, while algal floc breakage profiles are more similar to NOM + polymer flocs (Jarvis *et al.*, 2005b). Hence, the suggestion that polymeric algal EOM has a significant influence on algal flocculation is reinforced.

Conclusions

The overall picture indicates that organic surface layers dominate coagulation processes such that NOM and algae systems have similar responses and will thus control coagulation if present in a turbidity based system. Similarly, EOM in an algal based system may control coagulation as opposed to the algal cells themselves. Zeta potential monitoring will provide useful insights in the optimisation and control of all of these systems. The results indicate that the relatively high levels of EOM (carbohydrates) on the surface of the algae produce floc networks of a very different nature to NOM and kaolin. As such algal flocs are initially much stronger compared to kaolin and NOM flocs but on exposure to increased shear are much weaker. In short, knowledge transfer between different coagulating systems is difficult and optimisation should be considered in terms of both removal and physical properties.

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