# On the importance of pH value in coagulation

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## ABSTRACT

Many studies have overlooked the role of pH in optimizing coagulation. Herein, the authors emphasize the importance of pH value in coagulation during the production of drinking water. We investigate the influence of pH value on the surface charges and forms of coagulants and impurities intended for removal. A methodology is suggested for optimizing key parameters for efficient coagulation – coagulant dosage and pH value. The study points out that various optimal pH ranges are required for coagulation of specific impurities and their mixtures. For natural organic matter of both humic and algogenic origin, acidic pH values are favourable for their removal through charge neutralization mechanism. Algal cells are effectively coagulated at slightly acidic to neutral pH values due to interactions with coagulant hydroxide precipitates. Inorganic particles are eliminated preferably at around neutral pH values. When mixtures of impurities are coagulated, mutual interaction between the impurities may impact dose of coagulant and also optimal pH ranges.

**Key words** | coagulant dosage, coagulation, jar test, pH optimization

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## INTRODUCTION

In the treatment of drinking water, a key factor in coagulation is pH value. (In the literature, 'coagulation' usually denotes the destabilization of particles while 'flocculation' refers to aggregate (floc) formation. However, such terminology is not employed consistently in studies, and the terms are often applied interchangeably. Thus, the terms 'coagulation' and 'flocculation' are considered to be the same for the purposes of this paper and the term 'coagulation' is utilized herein.) Not only does it impact the form and surface charge of coagulants utilized, but also the self-same parameters for the impurities that are to be removed. Within the coagulation process, the charges of the participating particles/molecules govern interactions that occur with other particles/molecules present in the water, thereby crucially affecting charge neutralization and adsorption mechanisms during coagulation.

In relation to the most frequently utilized coagulants, e.g., iron or aluminium-based salts, pH values influence hydrolysis, polymerization and the resultant species. In brief, at low pH values (<2.2 for ferric coagulants and <4.5 for aluminium ones), $Fe^{3+}$ and $Al^{3+}$ ions occur as hexaaqua complexes $[Fe(H_2O)_6]^{3+}$ and $[Al(H_2O)_6]^{3+}$ in an aqueous medium. Hydrolysis takes place alongside the increase in pH, forming species with ever greater reduction in charge. Besides hydrolysis, formation occurs of polynuclear species (hydroxopolymers), the best known of these being $Al_{13}O_4(OH)_{24}^{7+}$ ($Al_{13}$), and consequently, amorphous precipitates of $Fe(OH)_3$ and $Al(OH)_3$ (Stumm & Morgan 1996; Duan & Gregory 2003). The hydrolysis of Al is linked with a much narrower pH range than Fe, which is ascribed to a reduced coordination number for Al (from 6 to 4), while the number for Fe remains at 6 for all hydrolysed species. Pre-hydrolysed Fe or Al coagulants (e.g., polyferric sulphate (PFS), polyaluminiumchloride (PACl)) contain a significant portion of polymeric species (such as $Al_{13}$) that carry a high cationic charge. Even though these pre-formed polymers remain stable across a wide spectrum of pH values, do not consume alkalinity and reduce pH value due to hydrolysis as markedly as

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non-pre-hydrolysed coagulants, they still undergo hydrolysis and precipitation in parallel with rise in pH value. Effect of pH on the speciation transformation of alum and PACl of different basicities is well described by Wang *et al.* (2004).

It should be noted that the charge and the structure of polymeric coagulants, such as organic coagulants (e.g., chitosan, starch, alginate, microbial extracellular polymeric substances, *Moringa oleifera* seeds) or polyacrylamide-based synthetic coagulants, also undergo alteration upon change in pH as their functional groups accept protons or dissociate, depending on the given pH value.

Similarly to coagulants, dependence on pH value is seen for the surface charges of both organic and inorganic impurities. Most inorganic particles, such as those of kaolin or quartz (frequently applied as model particles in research on water treatment), possess a point of zero charge at low pH values and carry a negative charge across a wide pH range (Bernhardt *et al.* 1985; Stumm & Morgan 1996; Safarikova *et al.* 2013). The most common organic impurities – natural organic matter (NOM), which comprise humic substances (HS), algal cells and products of said cells (algal organic matter (AOM)), contain various functional groups (–OH, –COOH, –SH, $-NH_3^+, =NH_2^+$) capable of releasing or accepting a proton depending on the pH conditions. Overall, algal cell suspensions, HS and most AOM show a negative charge across a spectrum of pH values (Bernhardt *et al.* 1985; Paralkar & Edzwald 1996; Stumm & Morgan 1996; Newcombe *et al.* 1997; Henderson *et al.* 2008a, 2008b; Liu *et al.* 2009; Pivokonsky *et al.* 2015). It should be noted that certain organic substances, e.g., proteins, may carry an overall positive charge. By way of illustration, Pivokonsky *et al.* (2012) showed that the isoelectric points of peptides and proteins isolated from the cosmopolitan cyanobacterium *Microcystis aeruginosa* ranged between 4.8 and 8.1. In addition, it is evident that pH value impacts the structure of organic matter in aqueous solutions. For instance, changing the level of pH causes variation in the structures and sizes of proteins as a consequence of protein folding and unfolding. Many proteins unfold at a pH of less than 6 or greater than 9, accompanied by increase in their size and access to their functional groups (Creighton 1993).

## MOTIVATION

Although pH value is obviously a key parameter in coagulation, it has largely been neglected by studies on the topic. Numerous examples simply optimized dosage of the coagulant at a fixed pH; hence, did not focus on pH as a separate variable. However, without optimizing the value for pH, it remains unclear whether the greatest coagulation efficiencies are actually achieved. Indeed, in some studies, only the resultant pH was measured; therefore, it is uncertain if the coagulation efficiency ascertained was a consequence of the dosage applied or the resultant pH value or both. Moreover, several manuscripts merely report the initial pH value prior to adding the coagulant, so no information is forthcoming on the given pH conditions during coagulation and thus coagulation pathways; since coagulants, especially traditional ones, may consume alkalinity and change pH value very quickly.

Herein, the authors devise a methodology for optimizing the two basic parameters of coagulation – the dosage of the coagulant and pH value – in natural and model waters. Furthermore, we present examples highlighting the influence of pH on coagulation performance.

## OPTIMIZING COAGULANT DOSAGE AND PH VALUE

Referring to relevant findings of studies in the literature, wherein corresponding impurities or natural raw water of similar composition have been utilized, provides researchers with suitable data for subsequent testing of coagulant dosages and pH values to aid them in optimizing coagulation. It should be noted that even if a study states an optimal pH value and coagulant dosage for a particular substance (e.g., humic acid, certain inorganic particles or the AOM of specific algal species), it is advisable to verify the results reported therein across a determined range. A recommendation is to investigate a pH range for model/natural raw water that has not been tested before, i.e., pH 4 to 10, after which, focus can be narrowed in later experiments. Similarly, testing for coagulant dosage could encompass a narrow range after preliminary testing is conducted over a wider range.

In water treatment plants, it is best to optimize coagulation upon every change that occurs in the parameters of

the raw water, such as pH, alkalinity, turbidity, manganese content, TOC (total organic carbon) concentration, $UV_{254}$, COD (chemical oxygen demand), optical density and the number of cells. When research involves coagulating model waters, it is necessary to optimize coagulation for each impurity or mixture of impurities being investigated.

We suggest that optimizing coagulant dosage and pH value is best achievable in two steps described in the two following sections. First, alkalinity and pH adjustment need to be specified to reach the target pH values. This step is crucial for pH optimization. Second, procedure of jar testing is suggested below.

## TESTING THE RESULTANT PH

In the case of coagulants that consume alkalinity, and thus might initiate reduction in alkalinity and pH value (e.g., coagulants based on iron and aluminium, including pre-hydrolysed coagulants), the resultant pH is dependent on the dosage of the coagulant applied. Therefore, this pH value needs to be tested for every coagulant dosage chosen. Note that it is not necessary to test the resultant pH if coagulants which do not consume alkalinity are applied, such as organic coagulants or polyacrylamide-based coagulants, although optimization of pH is still required.

For low pH and alkalinity (mostly coloured) surface waters' pre-treatment with lime, soda ash or caustic soda is normally required to ensure that the optimum coagulation pH is achieved. On the other hand, for high alkalinity or pH waters acid is dosed to decrease the pH/alkalinity to a lower value before dosing the coagulant. When model water (usually based on deionized or distilled water) is employed in research on optimizing coagulation, its alkalinity should be adjusted to correspond with that of natural waters. The alkalinity (or acid neutralizing capacity ($ACN_{4.5}$)) of natural waters usually ranges between 0 and 10 millimoles per litre ($mmol \cdot l^{-1}$), which is equal to the oft-used unit of milliequivalent per litre ($meq \cdot l^{-1}$). Alkalinity ($ACN_{4.5}$) is defined as the measure of the molar quantity of strong monobasic acid consumed by 1 litre of water to attain a pH of 4.5 (Stumm & Morgan 1996) at the point which $HCO_3^-$ and $CO_3^{2-}$ are transformed to $H_2CO_3$. Alkalimetric titration (Method 2320) is a suitable means of alkalinity measurement. To express alkalinity ($ACN_{4.5}$), units such as $mmol \cdot l^{-1}$ as $CaCO_3$ or $mg \cdot l^{-1}$ as $CaCO_3$ are also utilized. However, these units are misleading since they link the consumption of acid only with transformation of $CaCO_3$, but there are more acid consuming compounds/processes in natural waters. Millimoles per litre can be converted into these units as follows (Polasek & Mutl 1995):

$$1\ \text{mmol} \cdot \text{l}^{-1} = 0.5\ \text{mmol} \cdot \text{l}^{-1}\ \text{CaCO}_3 = 50\,\text{mg} \cdot \text{l}^{-1}\ \text{CaCO}_3$$

The amount of alkalinity consumed by different hydrolysing coagulants is given by their stoichiometric reactions. For example, reaction of alum to form aluminium hydroxide precipitate indicates that $1\ mg \cdot l^{-1}$ of alum requires 0.009 $mmol \cdot l^{-1}$ of alkalinity ($0.45\ mg \cdot l^{-1}$ as $CaCO_3$):

$$\begin{aligned} &Al_2(SO_4)_3.18H_2O \rightarrow 2Al^{3+} + 3SO_4^{2-} + 18H_2O \\ &\quad \rightarrow 2Al(OH)_3 + 6H^+ + 3SO_4^{2-} + 12H_2O \end{aligned} \quad (1)$$

Similarly, $1\ mg \cdot l^{-1}$ of aluminium chloride ($AlCl_3.6H_2O$) requires $0.012\ mmol \cdot l^{-1}$ of alkalinity ($0.6\ mg \cdot l^{-1}$ as $CaCO_3$), $1\ mg \cdot l^{-1}$ of ferric sulphate ($Fe_2(SO_4)_3.9H_2O$) requires $0.0107\ mmol \cdot l^{-1}$ of alkalinity ($0.535\ mg \cdot l^{-1}$ as $CaCO_3$), $1\ mg \cdot l^{-1}$ of ferric chloride ($FeCl_3.6H_2O$) requires 0.011 $mmol \cdot l^{-1}$ of alkalinity ($0.55\ mg \cdot l^{-1}$ as $CaCO_3$). It is of note that these numbers go for coagulation, in which Al/Fe hydroxide precipitates are the main coagulant species. When coagulation is provided by hydrolysis species with lower degree of hydrolysis and polymerization (e.g., hydroxopolymers), the amount of consumed alkalinity is lower. The amount of alkalinity consumed by pre-hydrolysed coagulants depends on their basicity, i.e., [OH]/[coagulant] molar ratio, which governs the portion of monomeric, polymeric and high polymerized or colloidal species in coagulant. The effect of different basicities of PACl on alkalinity and pH can be seen, for example, in Figure 1(c) of Ye *et al.* (2007).

Alkalinity varies with the concentration of total carbon dioxide species in water (including carbons and hydrocarbons), acids or bases contained in water (humic acids, fulvic acids, proteins, acidic polysaccharides, phosphates, ammonium cation) and processes that impact pH and alkalinity (e.g., sorption of ions on mineral particles). Therefore,

the final pH value after the addition of coagulant is difficult to estimate and we recommend testing it before coagulation tests as follows. After adjusting the degree of alkalinity (for low/high alkalinity natural waters and model waters), the specific dosage of coagulant is added into samples of the model/natural raw water; the samples are then mixed, and the level of pH is measured. Under continuous mixing and measurement of pH, the sample is titrated by an acid (HCl) or a base (NaOH, KOH), and pH values are noted at chosen intervals. This procedure is repeated for all the coagulant dosages under investigation. Target pH values are reached after conducting coagulation tests (detailed below) by alkalinity adjusting and adding predetermined amounts of the acid or base prior to supplementation with the coagulant.

## COAGULATION TESTS

These are extremely useful for determining operational parameters, such as the following: coagulant selection and dosage; optimal pH; alkalinity addition and control; and optimization of energy and duration for mixing. In coagulation tests, the coagulant is dosed into water samples, and the resulting solutions are mixed in order to destabilize impurities and incorporate them into aggregates (flocs) that are removed via subsequent separation. After the dosage of coagulant has been applied, two agitation sequences are recommended. The first is rapid agitation, which favours mixing the reagents and destabilizing the particles/molecules. This is followed by a slow agitation phase to promote collisions between the destabilized particles, thus causing their aggregation (Bache & Gregory 2010). Rapid agitation utilizes velocity gradients (shear rates, G) $>100$–$300\ s^{-1}$ for dozens of seconds to minutes, while slow agitation utilizes $G < 100\ s^{-1}$ usually for 10–30 minutes. It is worthy of note that certain aggregate properties are suitable for a certain step of separation, e.g., by direct filtration, sedimentation filtration, flotation filtration or floc separation in a clarifier (Gregory 1998; Bache & Gregory 2010; Edzwald 2010; Bubakova & Pivokonsky 2012). We recommend performing coagulation experiments with paddle, turbine or anchor stirrers and jars with circular cross-sections. This equipment provides more uniform distribution of the velocity gradient, which impacts the properties of the aggregates formed, than the oft-used magnetic stirrers and jars with square cross-sections. Rapid and uniform dispersion of the coagulant aids the destabilization of particles and improves the efficiency of particle removal after coagulation (Polasek & Mutl 1995; Bache & Gregory 2007).

After the mixing period, the next step is to separate the formed flocs either by sedimentation (for 15–60 minutes, depending on the settling velocity) or centrifugation, which simulates rapid sand filtration (Bubáková *et al.* 2011). Afterwards, supernatants are withdrawn to measure the following: pH; alkalinity; the residual impurity or a variable representing the concentration of the residual impurity (dissolved organic carbon (DOC), turbidity, UV254, protein, saccharide or humic acid content, cell count, optical density, etc.); and the residual coagulant (e.g., Al, Fe, polyacrylamide). The lowest residual impurity and concentration of coagulant correspond to the optimal coagulant dosage and pH value. Notably, in the case of organic coagulants it may be difficult to distinguish between the residual content of organic coagulants and organic impurities in the treated water. For example, determining the extent of residual coagulant is important for polyacrylamide-based coagulants, as the derivatives of polyacrylamide and acrylamide monomer are neurotoxic, carcinogenic and non-biodegradable in the natural environment (Rudén 2004).

Figure 1 summarizes the recommended procedure of dosage and pH optimization. Testing a range of coagulant doses and pH values results in a matrix/graph of optimal coagulant and pH ranges. An example of such a matrix is given by Naceradska *et al.* (2019) in Figures 3 and 4 of that work.

Individual impurities, such as kaolin suspension or a single protein, pertain to a very narrow optimal pH range, while a wider optimal pH range is denoted for a mixture of impurities (Polasek & Mutl 1995; Safarikova *et al.* 2013; Pivokonsky *et al.* 2015). Note that – in a mixture of impurities – the means of optimal pH values and a sum of coagulant dosages for the individual impurities do not necessarily constitute the optimal values for the mixture itself (see Significance of pH value in coagulation, below). Therefore, separate optimization is needed for a mixture of impurities.

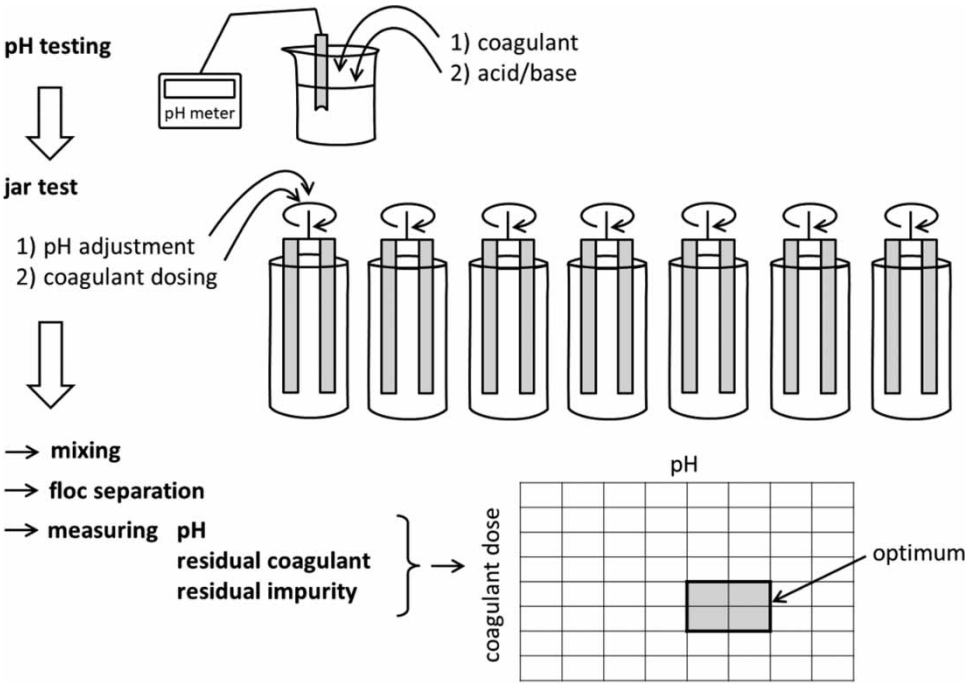



**Figure 1** | Recommended procedure of coagulant dosage and pH optimization.

## SIGNIFICANCE OF PH VALUE IN COAGULATION

An important role is played by pH value in the coagulation of both organic and inorganic particles/molecules. Turbidity caused by inorganic colloid particles is removed effectively by organic and Al/Fe-based coagulants. Natural organic coagulants are widely employed for removing turbidity due to their qualities of biodegradability, safety, affordability and general availability (Bolto & Gregory 2007). They eliminate turbidity effectually at approximately pH 7, but other pH values have not been widely tested (Ajao *et al.* 2018). Similarly, coagulants based on Al or Fe remove turbidity at around neutral pH values (Faust & Aly 1998). For instance, optimal pH values for kaolin removal lie between 6 and 8 for ferric coagulants, and between 7 and 8.5 for aluminium ones (Ching *et al.* 1994; Kim & Kang 1998; Safarikova *et al.* 2013). Kaolin is best removed through adsorption onto Fe/Al hydroxide precipitates facilitated by electrostatic interactions, exchanging reactions and hydrogen bonding (Shin *et al.* 2008).

Likewise, algal and cyanobacterial cells easily combine with Al- and Fe-based coagulants at pH values between 6 and 8 (Henderson *et al.* 2008a, 2010; Gonzalez-Torres *et al.* 2014; Baresova *et al.* 2017), wherein coagulant hydrolysis species (mostly Al- or Fe-hydroxide precipitates) bear positive charges and are capable of neutralizing the slightly negatively charged surfaces of the cells. By way of illustration, Baresova *et al.* (2017) achieved maximum removal rates of 99% for cells of cyanobacterium *Merismopedia tenuissima* within the pH range of 6.0–7.7 using $Fe_2(SO_4)_3 \cdot 9H_2O$. Moreover, Gonzalez-Torres *et al.* (2014) reached 99.7% elimination of cyanobacterium *Microcystis aeruginosa* at pH 6 and 7 by applying $FeCl_3$. When natural polymers are employed as coagulants, different coagulation mechanisms may be expected, as shown by Cheng *et al.* (2011) for the coagulation of cells of *Chlorella variabilis* by chitosan. Therein, such coagulation of the cells was superior at pH 8.5 compared to pH 5.5 and 7. This indicates that the hydrogen bonds between the chitosan (a poly-glucosamine polymer with an isoelectric point of around 6.5) and cell wall polysaccharides are more important than electrostatic interactions.

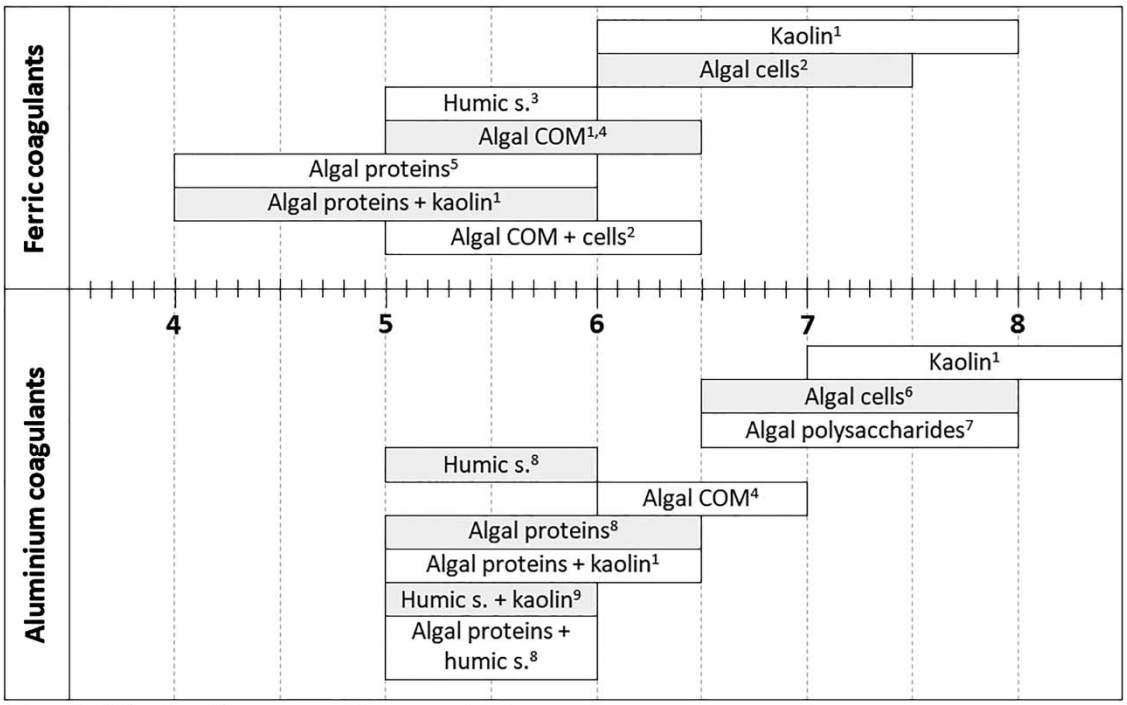
Unlike inorganic particles and cells, it is usually better to remove natural organic substances at acidic pH values. The

maximum removal of HS is found to occur at acidic pH values in the range of 4–7.5, depending on coagulant/HS ratio. Most studies set effectual pH to 5–6 for both ferric and aluminium coagulants (Jacangelo *et al.* 1995; Faust & Aly 1998; Lu *et al.* 1999; Cheng 2002; Liu *et al.* 2009; Pivokonsky *et al.* 2015). In this range, the main coagulation mechanism comprises charge neutralization between the positively charged Fe or Al hydroxopolymers and the ionized carboxylic and phenolic groups in HS. HS removal beyond pH 6–7 is dominated by adsorption of HS onto Fe/Al precipitates, but this does not engender satisfactory DOC removal (Cheng 2002; Duan *et al.* 2003; Liu *et al.* 2009). The pre-hydrolysed coagulant PACl also performs well at HS removal at slightly acidic pH values, although it may also be efficient at an alkaline pH level owing to the stability of $Al_{13}$ species across a wide pH range. For example, in the study by Gao *et al.* (2006), PACl was efficient in removing DOC from natural humic water (with efficiency of 80%) in the pH range 5–9. However, residual soluble aluminium concentration below 0.2 $mg \cdot l^{-1}$ was achieved only at pH 5. This does not apply to pre-hydrolysed coagulant PFS, which achieves HS removal in similar pH ranges as ferric chloride (Cheng 2002).

Only a handful of studies have investigated the impact of pH on the coagulation of AOM. These report that AOM is removed by Al- and Fe-based coagulants at acidic pH values, at which point the AOM negatively charged functional groups interact with positively charged coagulant hydroxopolymers (Widrig *et al.* 1996; Pivokonsky *et al.* 2009; Baresova *et al.* 2017). For example, Pivokonsky *et al.* (2009) observed the highest removals (about 40%) for cellular organic matter (COM) of *Microcystis aeruginosa* by ferric sulphate in the pH range of 5.5–6.5 and by aluminium sulphate in the pH range of 6–7. Likewise, Baresova *et al.* (2017) stated that the highest coagulation efficiencies (50%) for *Merismopedia tenuissima* COM by ferric sulphate are at pH 5.0–6.5. Several research papers have investigated the coagulation of algal peptides/proteins and non-proteinaceous compounds separately (Pivokonsky *et al.* 2012, 2015; Naceradska *et al.* 2019). Interestingly, while peptides/proteins are removed at acidic pH values (4–6 for ferric sulphate and 5.0–6.7 for aluminium sulphate), non-proteinaceous COM only undergoes coagulation to a limited extent (just 25% is removed under optimized conditions) at neutral to alkaline pH levels, i.e., 6.6–8.0 for aluminium sulphate and 7.5–9.0 for PACl (Naceradska *et al.* 2019). A detailed description of AOM coagulation and interactions between the AOM and coagulants is given by Pivokonský *et al.* (2018).

When a mixture of impurities is coagulated, the optimal pH and dosage of the coagulant may significantly differ from the values for single compound coagulation. As an illustration, adding COM peptides/proteins of *M. aeruginosa* into a suspension of kaolin particles shifts the pH of coagulation from neutral/alkaline to acidic pH values due to the adsorption of peptides/proteins onto the kaolin surfaces (Safarikova *et al.* 2013). Li *et al.* (2014) stated that, for a humic acid–kaolin mixture, the highest removal of DOC removal (60%) by PACl is achieved at a pH of around 6, while turbidity removal is high (>90%) throughout the entire pH range under test (4–9), slightly increasing in parallel with rise in pH. Similarly, Baresova *et al.* (2017) ascertain that mutual coagulation of COM of *M. tenuissima* together with its cells by ferric sulphate occurs at acidic pH values (5.0–6.5), while cells without COM are removed at an approximately neutral pH (6.0–7.7). Furthermore, ferric sulphate dosages for COM + cell mixtures fail to correspond with the sum of dosages for a single COM and cells, but are even slightly lower than those for single COM coagulation, owing to interactions between the COM and cell surfaces. Pivokonsky *et al.* (2015) described that interactions between HS and COM peptides/proteins of *M. aeruginosa* during coagulation bring about significant reduction in coagulant (aluminium sulphate) dosage. However, in this case, the optimal pH for a mixture of HS + COM (pH 5.0–6.2) related to optimal pH ranges for the coagulation of HS (5.0–6.0) and COM peptides/proteins (5.0–6.7). The impact on coagulation of interactions between AOM and other impurities present in raw water are detailed by Pivokonský *et al.* (2018).

Figure 2 depicts the optimum pH ranges for removing various impurities and their mixtures by hydrolysing coagulants. The differences in pH ranges effective for coagulation using ferric and aluminium salts is attributed to a difference in the hydrolysis product distributions of $Fe^{3+}$ and $Al^{3+}$ (Stumm & Morgan 1996). It should be noted that




COM = Cellular Organic Matter; Humic s. = humic substances
[1] Safarikova et al. 2013; [2] Baresova et al. 2017; [3] Duan et al. 2003; [4] Pivokonsky et al. 2009; [5] Pivokonsky et al. 2012; [6] Henderson et al. 2008a; [7] Naceradska et al. 2019; [8] Pivokonsky et al. 2015; [9] Li et al. 2014

**Figure 2** | The pH values of efficient removal of specific impurities and their mixtures by hydrolysing coagulants.

pre-hydrolysed coagulants may provide different optimum pH ranges (Gao *et al.* 2006; Naceradska *et al.* 2019).

## CONCLUSION

Since pH values affect the surface charges and forms of the coagulants and impurities to be removed, controlling the level of pH would significantly improve the coagulation process. Therefore, not only coagulant dosage, but also pH value should be optimized to maximize the removal of impurities present in raw water. Our investigation of studies on coagulation has revealed that turbidity caused by inorganic particles is removed at around neutral pH values. Algal and cyanobacterial cells are eliminated at a slightly acidic to neutral pH, while their products (AOM) correspond with acidic pH values. These values are also favourable for removing HS. For mixtures of impurities, mutual interactions between the constituent parts influence both the pH of coagulation and coagulant dosage, suggesting that an instance of separate optimization should be performed when a new impurity arises in raw water.

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## REFERENCES

Ajao, V., Bruning, H., Rijnaarts, H. & Temmink, H. 2018 Natural flocculants from fresh and saline wastewater: comparative properties and flocculation performances. *Chemical Engineering Journal* **349**, 622–632.

Bache, D. H. & Gregory, R. 2007 *Flocs in Water Treatment*. IWA Publishing, London, UK.

Bache, D. H. & Gregory, R. 2010 Flocs and separation processes in drinking water treatment: a review. *Journal of Water Supply: Research and Technology–AQUA* **59** (1), 16–30.

Baresova, M., Pivokonsky, M., Novotna, K., Naceradska, J. & Branyik, T. 2017 An application of cellular organic matter to coagulation of cyanobacterial cells (*Merismopedia tenuissima*). *Water Research* **122**, 70–77.

Bernhardt, H., Hoyer, O., Schell, H. & Lusse, B. 1985 Reaction mechanisms involved in the influence of algogenic matter on flocculation. *Zeitschrift für Wasser- und Abwasser Forschung* **18** (1), 18–30.

Bolto, B. & Gregory, J. 2007 Organic polyelectrolytes in water treatment. *Water Research* **41** (11), 2301–2324.

Bubakova, P. & Pivokonsky, M. 2012 The influence of velocity gradient on properties and filterability of suspension formed during water treatment. *Separation and Purification Technology* **92**, 161–167.

Bubáková, P., Pivokonský, M. & Pivokonská, L. 2011 A method for evaluation of suspension quality easy applicable to practice: the effect of mixing on floc properties. *Journal of Hydrology and Hydromechanics* **59** (3), 184–195.

Cheng, W. P. 2002 Comparison of hydrolysis/coagulation behavior of polymeric and monomeric iron coagulants in humic acid solution. *Chemosphere* **47** (9), 963–969.

Cheng, Y.-S., Zheng, Y., Labavitch, J. M. & VanderGheynst, J. S. 2011 The impact of cell wall carbohydrate composition on the chitosan flocculation of *Chlorella*. *Process Biochemistry* **46** (10), 1927–1933.

Ching, H. W., Tanaka, T. S. & Elimelech, M. 1994 Dynamics of coagulation of kaolin particles with ferric chloride. *Water Research* **28** (3), 559–569.

Creighton, T. E. 1993 *Proteins: Structures and Molecular Properties*, 2nd edn. W.H. Freeman and Company, New York, USA.

Duan, J. & Gregory, J. 2003 Coagulation by hydrolysing metal salts. *Advances in Colloid & Interface Science* **100–102**, 475–502.

Duan, J., Graham, N. J. D. & Wilson, F. 2003 Coagulation of humic acid by ferric chloride in saline (marine) water conditions. *Water Science and Technology* **47** (1), 41–48.

Edzwald, J. K. 2010 Dissolved air flotation and me. *Water Research* **44** (7), 2077–2106.

Faust, S. D. & Aly, O. M. 1998 *Chemistry of Water Treatment*, 2nd edn. CRC Press, Boca Raton, FL, USA.

Gao, B. Y., Abbt-Braun, G. & Frimmel, F. H. 2006 Preparation and evaluation of polyaluminum chloride sulfate (PACS) as a coagulant to remove natural organic matter from water. *Acta Hydrochimica et Hydrobiologica* **34**, 491–497.

Gonzalez-Torres, A., Putnam, J., Jefferson, B., Stuetz, R. M. & Henderson, R. K. 2014 Examination of the physical properties of *Microcystis aeruginosa* flocs produced on coagulation with metal salts. *Water Research* **60** (1), 197–209.

Gregory, J. 1998 The role of floc density in solid-liquid separation. *Filtration & Separation* **35** (4), 367–371.

Henderson, R., Parsons, S. A. & Jefferson, B. 2008a The impact of algal properties and preoxidation on solid-liquid separation of algae. *Water Research* **42** (8–9), 1827–1845.

Henderson, R. K., Baker, A., Parsons, S. A. & Jefferson, B. 2008b Characterisation of algogenic organic matter extracted from cyanobacteria, green algae and diatoms. *Water Research* **42** (13), 3435–3445.

Henderson, R. K., Parsons, S. A. & Jefferson, B. 2010 The impact of differing cell and algogenic organic matter (AOM) characteristics on the coagulation and flotation of algae. *Water Research* **44** (12), 3617–3624.

Jacangelo, J. G., DeMarco, J., Owen, D. M. & Randtke, S. J. 1995 Selected processes for removing NOM: an overview. *Journal of the American Water Works Association* **87** (1), 64–77.

Kim, J. S. & Kang, L. S. 1998 Investigation of coagulation mechanisms with Fe(III) salt using jar tests and flocculation dynamics. *Environmental Engineering Research* **3** (1), 11–19.

Li, R., Gao, B., Huang, X., Dong, H., Li, X., Yue, Q., Wang, Y. & Li, Q. 2014 Compound bioflocculant and polyaluminum chloride in kaolin-humic acid coagulation: factors influencing coagulation performance and floc characteristics. *Bioresource Technology* **172**, 8–15.

Liu, H., Hu, C., Zhao, H. & Qu, J. 2009 Coagulation of humic acid by PACl with high content of al13: the role of aluminum speciation. *Separation and Purification Technology* **70** (2), 225–230.

Lu, X. Q., Chen, Z. & Yang, X. 1999 Spectroscopic study of aluminium speciation in removing humic substances by Al coagulation. *Water Research* **33** (15), 3271–3280.

Method 2320 2012 *Standard Methods for the Examination of Water and Wastewater*, 22nd edn. American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC, USA.

Naceradska, J., Novotna, K., Cermakova, L., Cajthaml, T. & Pivokonsky, M. 2019 Investigating the coagulation of non-proteinaceous algal organic matter: optimization of coagulation performance and identification of removal mechanisms. *Journal of Environmental Sciences* **79**, 25–34.

Newcombe, G., Drikas, M., Assemi, S. & Beckett, R. 1997 Influence of characterised natural organic material on activated carbon adsorption: I. Characterisation of concentrated reservoir water. *Water Research* **31** (5), 965–972.

Paralkar, A. & Edzwald, J. K. 1996 Effect of ozone on EOM and coagulation. *Journal of the American Water Works Association* **88** (4), 143–154.

Pivokonsky, M., Pivokonska, L., Baumeltova, J. & Bubakova, P. 2009 The effect of cellular organic matter produced by cyanobacteria *Microcystis aeruginosa* on water purification. *Journal of Hydrology and Hydromechanics* **57** (2), 121–129.

Pivokonsky, M., Safarikova, J., Bubakova, P. & Pivokonska, L. 2012 Coagulation of peptides and proteins produced by *Microcystis aeruginosa*: interaction mechanisms and the effect of Fe-peptide/protein complexes formation. *Water Research* **46** (17), 5583–5590.

Pivokonsky, M., Naceradska, J., Brabenec, T., Novotna, K., Baresova, M. & Janda, V. 2015 The impact of interactions between algal organic matter and humic substances on coagulation. *Water Research* **84**, 278–285.

Pivokonský, M., Načeradská, J., Novotná, K., Čermáková, L. & Vašatová, P. 2018 Flocculation of AOM in water treatment.

In: *Flocculation: Processes and Applications* (E. Vollan, ed.). Nova Science Publishers, New York, USA, 107–142.

Polasek, P. & Mutl, S. 1995 *Guidelines to Coagulation and Flocculation for Surface Waters. Volume I.: Design Principles for Coagulation and Flocculation Systems*. PPA, Johannesburg, South Africa, pp. 34–52.

Rudén, C. 2004 Acrylamide and cancer risk – expert risk assessments and the public debate. *Food and Chemical Toxicology* **42**, 335–349.

Safarikova, J., Baresova, M., Pivokonsky, M. & Kopecka, I. 2013 Influence of peptides and proteins produced by cyanobacterium *Microcystis aeruginosa* on the coagulation of turbid waters. *Separation and Purification Technology* **118**, 49–57.

Shin, J. Y., Spinette, R. F. & O'Melia, C. R. 2008 Stoichiometry of coagulation revisited. *Environmental Science and Technology* **42** (7), 2582–2589.

Stumm, W. & Morgan, J. J. 1996 *Aquatic Chemistry*, 3rd edn. John Wiley and Sons, New York, USA.

Wang, D., Sun, W., Xu, Y., Tang, H. & Gregory, J. 2004 Speciation stability of inorganic polymer flocculant–PACl. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **243**, 1–10.

Widrig, D. L., Gray, K. A. & McAuliffe, K. S. 1996 Removal of algal-derived organic material by preozonation and coagulation: monitoring changes in organic quality by pyrolysis-GC-MS. *Water Research* **30** (11), 2621–2632.

Ye, C., Wang, D., Shi, B., Yu, J., Qu, J., Edwards, M. & Tang, H. 2007 Alkalinity effect of coagulation with polyaluminum chlorides: role of electrostatic patch. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **294**, 163–173.

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