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MECHANISM OF COAGULATION OF COLOURED WATER WITH ALUMINIUM SULPHATE

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ABSTRACT : Flocs are produced by additions of aluminium sulphate as a coagulant in a coloured raw water. The water was typical of those derived from moorland catchments, Scotland being coloured due to the presence of humic substances and low turbidity. The pH appeared to be the critical parameter controlling the mechanism of coagulation. Around pH 4.5, the mechanism of coagulation appeared to be adsorption and change neutralization (ACN) where change of Al species is maximum. The mechanism is different from ACN at higher pH.

KEY WORDS : Flocculation, Mechanism of Coagulation, zeta potential

INTRODUCTION

Many surface waters are characterized by low turbidity and are highly coloured due to the presence of organic matter. These organic matter are often referred to collectively as humic substances (Hall and packham, 1965). Alum is generally used as coagulant to remove colour i.e. Humic substance (HS). The mechanisms that are responsible for the removal of humic substances (in association with alum) are often uncertain.

In this paper species of Al produced from alum and several works of alum-humic interactions were reviewed and attempt was made to identify the mechanism of coagulation of coloured water and alum on the basis of electrophoretic behavior of flocs.

DESTABILIZATION OF WATER BY AQUEOUS AL

Aluminium (III) salts are the most widely used coagulants in water treatment. The different aluminium species exhibited in water are directly associated with coagulation. Thus it is necessary to consider the aqueous chemistry of these coagulants.

There is a little doubt that the aqueous chemistry of aluminium is complex and diverse because of numerous hydrolysis intermediates formed prior to precipitation of aluminium hydroxide, $Al(OH)_3(s)$. Matijevic et.al (1964) provided a fairly clear description of the hydrolysis species of Al^{3+} and interactions with the colloids in the context of coagulation and restabilization. When aluminium salts are added to water, the metal ion Al^{3+} hydrates, coordinating six molecules of water and forming an aquometal ion, $Al(H_2O)_6^{3+}$. The aquometal ion can then react and form several hydrolysis species. Some of the simplest being

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monomeric and dimeric hydroxocomplexes where coordination occurs with OH^- ligands that replace the six coordinated water molecules.

Stumm and Morgan (1962), Packham and Sheiham (1977) and others have given the stepwise conversion of the tripositive aluminium ion to the negative aluminium ion as pH increases are as follows :

$[Al(H_2O)6]^{3+}$

↓

$[Al(H_2O)_5(OH)]^{2+}$ → $[AL(H_2O)_4 (OH)_2]^+$

↓

$Al_6(OH)_{15}]^{3+}$

↓

$[Al_8(OH)_{20}]^{4+}$

↓

$[Al(OH)_3(H_2O)_3](S)$

↓

$[Al(OH)_4]$-

Amirtharajah and Mills (1982), Vik et. al (1985) and others have reported a number of aluminium polymers that may possibly be involved in coagulation and flocculation processes. These are : $Al_{13}(OH)_{34}{}^{5+}$, $Al_7(OH)_{17}{}^{4+}$, $Al_8(OH)_{20}{}^{4+}$, $Al(OH)_{15}{}^{3+}$, $Al_2(OH)_2{}^{4}+$, $Al2(OH)^{5+}$, $Al_4(OH)_8{}^{4+}$, $Al_{13}O_4(OH)_{24}{}^{7+}$, $Al_3 (OH)_4{}^{5+}$, $Al_{13}(OH)_{32}{}^{7+}$ and $Al_{14}(OH)34^{8+}$, to name but a few.

Dempsey et al.(1984) contend that the evidence for the existence of such polymers in myrial and indirect. However, the degree of alkalinity in the solution is an important determinant in aluminium speciation. Other dominant factors include the concentration of reactants, contamination by other substances, pH, temperature and reaction time. Matijevic et. al.(1964) have found that the hydroxometal complexes readily adsorb on surfaces and the charges that they carry may cause charge reversals of the surfaces that they adsorb on, second, the sequential hydrolysis reactions release H+ ions, which lowers the pH of the solution in which they are formed; and the concentration of the various hydrolysis species will be controlled by the final concentration of H^+ ions, that is, by the pH. These findings are in keeping with the individual suggestions O'Melia and Stumm (1967) and O'Melia (1972).

Hundt and O'Melia (1988) reported the work of Baes and Mesmer (1976). In this, they described the aqueous chemistry of Al using five monomers Al^{3+}, $Al(OH)^{2+}$, $Al(OH)^{2+}$, $Al(OH)_3$ and $Al(OH)^4$; three polymers $Al_2(OH)_4{}^{2+}$, $Al_3(OH)_4{}^{5+}$ and $Al_{13}O_4(OH)_{24}{}^{7+}$ and a solid precipitate $Al(OH_3(s)$. They also have discussed the influence of the chemical behaviour of anions of Al in solution. The presence of anions with a strong affinity for Al, such as sulphate, greatly affects the Al species in solution. Sulphate, a tetrahedral polyvalent anion, tends to link OH-Al polymers together, but in a distorted arrangement. Therefore, most basic salts containing sulphate are amorphous. In the presence of sulphate less alkali is necessary to produce a visible precipitate than when solutions containing chloride or nitrate salts are titrated. They also presumed a screening effect, that accelerates the formation of polymers and assists in the linking of planer complexes to form the solid lattice.

Sullivan and Singley (1968) have estimated the quantity of mononucleus aluminium species (monomers) at different pH. The estimates are given in Figure 1. The dominant species upto pH 4.5 is Al^{3+}, from 4.5 to 8.0 it is $Al(OH)_3$ and above pH 8 it is $Al(OH)_4$-.

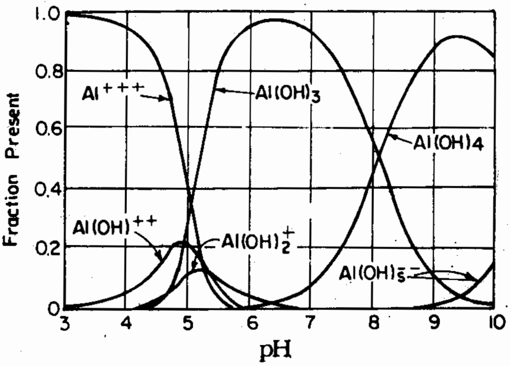


Fig 1. Species present as function of pH for $1x10^{-4}$ M Aluminium perhlorate (Sullivan & Singley, 1968)

HUMIC SUBSTANCE - ALUM INTERACTION

Humic substances (HS) are ubiquitous in surface water suppliers, are the major organic colour producing constituent and are present in soluble form the coagulation of HS has been the subject to numerous investigations. For example Miller (1925) stated that in the coagulation of HS with alum, the aluminium ion was the active coagulant and in fact, since that time, the water industry has tended to use alum as a means of removing colour. The mechanisims that are responsible for the removal of humic substances (in association with alum) are often uncertain but may include direct precipitation of HS by dissolved aluminium species; adsorption of humic substances on solid aluminium hydroxide $[Al(OH)_3(s)]$; or a combination of the two.

Humic substances are anionic polyelectrolytes and their degree of ionization is pH dependent. From a series of experiments, Edwards and Amirtharajah (1985) observed that at pH ranges of approximately 5.75 or more, the humic acid (HA) alum interaction appears to be related to the physical attachment of the colour particles to aluminium hydroxide precipitate. Hundt and O'Melia (1988) observed this mechanism to coagulate fulvic acid (FA) with aluminium salts at pH greater than 5.0.

Aluminium species present in water are pH dependent. Generally it is observed that at lower pH (<5.5) monomers and polymers are the principal coagulant products with less $Al(OH)_3(s)$. The interaction of HA with the monomers, polymers and $Al(OH)_3(s)$ is termed as "charge neutralizaiton-precipitation" (CNP) by Edwards and Amirtharajah (1985). They obtained this mechanism at pH ranges of less than 5.75, where as according to Edzwald (1979), the charge neutralization would occur as a removal mechanism of HA with aluminium salt over a pH range 4.0 - 6.0. Working with FA and aluminium salt, Hundt land O'Melia (1988) observed that the mechanism of FA removal is directly related to the form of coagulant product in solution; CNP occurs in the presence of Al monomers and polymers (generally less than pH 4.75). Moreover, at pH values at which both $Al(OH)_3(s)$ and Al monomers and polymers exist, concurrent reactions by both mechanisms appear to cause simultaneous ppt. Hall and Packham (1965) observed that the hydrolyzed aluminium ion which interacts with humid or fulvic acids is $Al(OH)_{2.5}$. Hall and Packham also observed that the coagulation of water with aluminium sulphate, organic colour (in the form humic and fulvic acids) is removed by the ppt of an insoluble basic humate or fulvate.

APPROACH

Jar tests were performed in accordance with procedure set out in the water research association (1973). Tests were conducted on coloured water with aluminium sulphate as coagulant. Flocs were produced at range of pH 3.75 to 6.0 with varried alum dose [Al = 0.0 to 8.0 mg/1]. Flocs were examined in terms of their electrophoretic mobility.

DETERMINATION OF ELECTROPHORETIC MOBILITY (EM)

The determination of electrophoretic mobility of flocculated particles was carried out using the particle electrophoresis apparatus model Mark II of the Rank brothers on the basis of the following relationship :

$$EM = \frac{X/t}{V_e/L} \qquad (1)$$

where EM = electrophoretic Mobility in m V^{-1} S^{-1}

X = distance over which the particles were timed in m

t = time for covering distance X in S

Ve = applied voltage in V

L = inter electrode distance in m.

A flat cell was used during the measurements with the two stationary levels by use of the komagata formula (ref. Shaw, 1969). The interelectrode distance (L) was determined using conductivity method (ref. Shaw, 1969). A constant voltage (60V) was used and the mean velocity of the particles was determined for a distance of 0.05 mm (corresponding to one grid on the graduated eye piece). the temperature of the cell was kept constant at temperature (20.0 + 0.20°C) by cirulating water from a water bath. The particle mobility of the suspension was computed from the mean of 20 determinations.

RESULTS AND DISCUSSIONS

Mobility tests were performed on flocs (from coloured water) for [Al] range 0.0 to 8.0 mg/1 at different pH. The results are shown in Figure 2 and 3. Inspection of Figure 2 shows that the colloids have the greatest mobility (with negative charge) when Al = 0.0mg/1, mobility is reduced progressively with increasing [Al] dose until isoelectric point do not attain, presumably reflecting increasing proportion of aluminium hydroxide in floc. The isoelectric point is not attained unit [Al] = 5.0 mg/1.

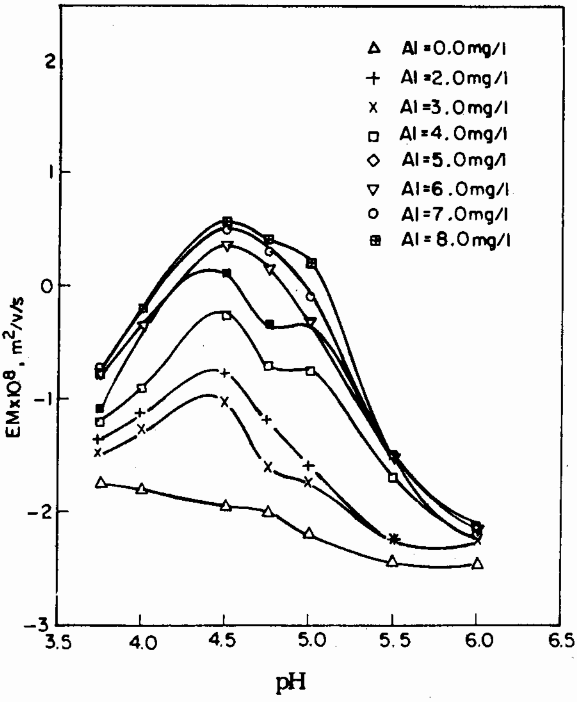
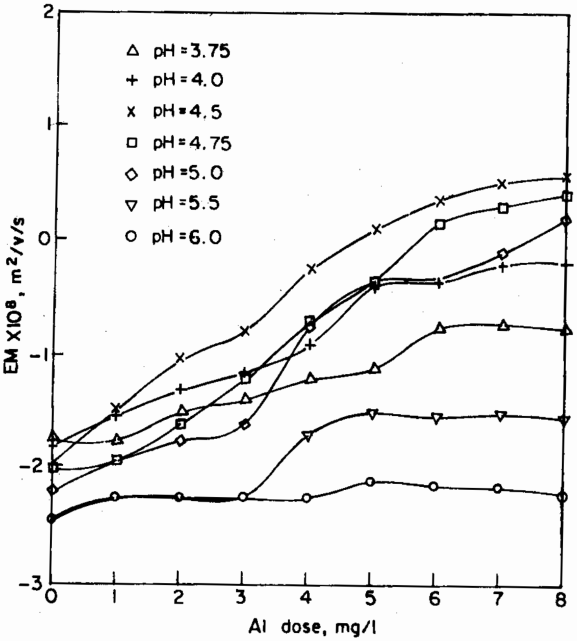


Fig 2. Electrophoretic mobility of Floc at constant dose

From Figure 3, it is evident that at pH 4.5 the rate of increase of the charge per unit increase of [Al] does is at a maximum (i.e. maximum slope), where as at pH 6.0 the EM is insensitive to the [Al] dose. These features are probably tied up with the characteristics of dfferent aluminium species present in the water such as indicated in Figure 1 having different charges.



Al dose, mg/l
Fig 3. Electrophoretic Mobility of Floc at Constant pH

The zeta potential of flocs have been estimated form mobility (as 10°-8 $m^2v^{-1}s^{-1}$) after multiplication by 13 (basis; Hossain, 1990). The results are shown in Figure 4. Both from Figure 2 and 4, it is clear that the charge reversal takes place within the pH range 4.0 to 5.0 and zeta potential passes through a maximum (with respect to changing pH) at pH = 4.5. Tambo (1990) and Hossain (1990) observed that the maximum zeta potential of aluminium hydroxide complexes are at pH = 4.5. Highly charged hydroxides make maximum zeta potential of floc at pH 4.5 which is clearly adsorption and charge neutralization mechanism. And other than $Al(OH)_3$ species are involved in coagulation at pH 4.5.

Zeta potential is insensitive at pH around 6.0 with dose of coagulant. Observing Figure 1, the dominating species at pH 6.0 is Al(OH)3. Which is theoretically zero charged and makes the zeta potential insensitive. The mechanism of coagulation at pH 6.0 is other than charge neutralizing and probably accomplished by enmeshment within the hydroxides of the coagulant. The mechanisms are agreeable with the observations of Edwards and Amirtharajah (1985) and Hundt and O'melia (1988).

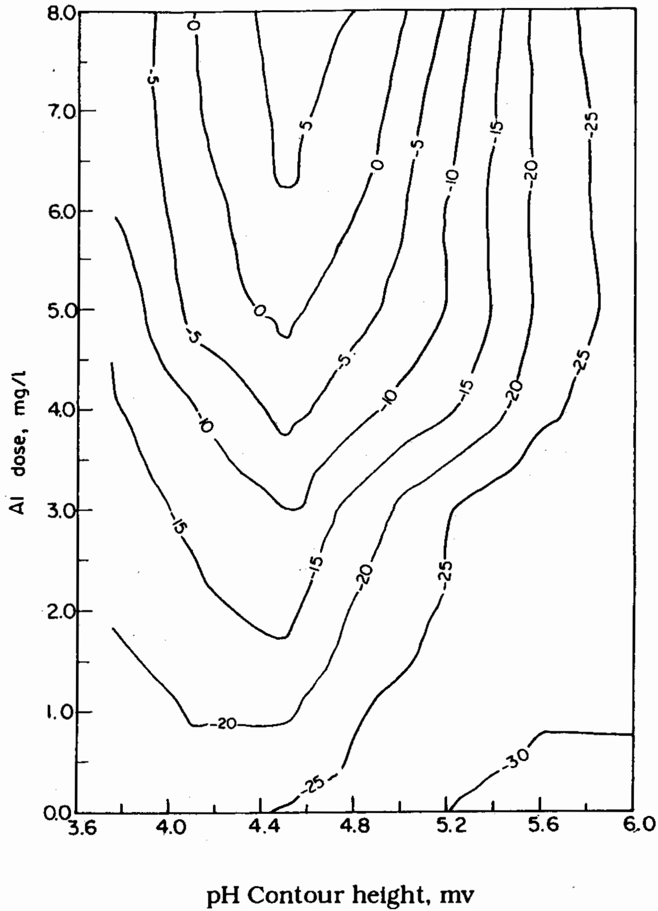


Fig 4. Contour map of zeta potential of floc

CONCLUSIONS

The mechanism of coagulation of this coloured water depends on pH. At pH 4.5, the mechanism of coagulation is adsorption and charge neutralization (ACN); where as at higher pH the mechanism is different from ACN probably Adsorption and enmeshment in $Al(OH)_3$.

Maximum positive charge of floc was found at pH 4.5. The rate of increase of the charge with increase of [Al] dose was also observed at pH 4.5. With increasing dose, the pH range was observed to broaden for a given state of charge on the floc charge.

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