Larhyss Journal, ISSN 1112-3680, n°53, Mars 2023, pp. 199-217
© 2023 All rights reserved, Legal Deposit 1266-2002

POLYMERIC HUMIC MATERIAL REMOVAL BY COAGULATION-FLOCCULATION STOICHIOMETRIC DOSAGE ALUMINUM SULPHATE/HUMIC ACID IN SALINE AQUEOUS MEDIA

***BACHA N.*[1, 2]*, ACHOUR S.*[2*]**

[1] Scientific and Technical Research Center on Arid Regions (CRSTRA), Campus of Mohamed Khider University, Biskra, Algeria
[2] Research Laboratory in Subterranean and Surface Hydraulics (LARHYSS)
Faculty of Science and Technology, Mohamed Khider University, Biskra, Algeria

(*) samia.achour@larhyss.net

Research Article – Available at http://larhyss.net/ojs/index.php/larhyss/index
Received February 8, 2023, Received in revised form March 5, 2023, Accepted March 7, 2023

ABSTRACT

The objective of this study is to examine the effectiveness of the removal of polymeric humic matter during coagulation-flocculation and to highlight stoichiometric relationships between the coagulant dosage and the organic substance content. It is therefore a question of assessing the influence of reaction parameters such as the dose of aluminum sulfate, the concentration of humic acid, the pH and the saline composition of the water during the coagulation-flocculation treatment.

To establish correlations between the initial organic compound content and the coagulant dosage, humic acid was dissolved at levels of 1 to 20 mg/l in distilled water and mineralized groundwater from the Biskra area at different pH values. Then, solutions were coagulated by increasing doses of aluminum sulfate. The organic compound final concentrations are deduced from the calibration curves, which were previously established for the tested compound in the various dilution media.

The results obtained indicate that the process efficiency as well as the coagulant dosage depend on the pH, the organic compound initial concentration and the characteristics of the dilution medium. The findings also showed that increasing water salinity had a promoting effect on humic acid removal. The predominant mechanisms of the tested organic acid removal process were complexation phenomena or ligand exchange with soluble or insoluble aluminum species. Demonstration of the stoichiometry of the reactions showed that the relationships linking the dosage of the coagulant to the initial concentration of humic acid essentially depended on the pH and the salinity of the different waters tested.

Keywords: Humic acid, Coagulation-flocculation, pH, Salinity, Mechanisms, Stoichiometry

INTRODUCTION

Natural waters, in particular surface waters, contain a multitude of organic compounds of various chemical structures. Diverse mixtures of aromatic and aliphatic carbon-rich compounds are found in these waters. The most important category corresponds to humic substances, whose contents can reach up to 90% of the total organic carbon (TOC) of natural water (Health Canada, 2019; Ma et al., 2001; Thurman, 1985). In Algeria, humic material may represent a significant part of the organic load of surface waters, approximately 60 to 90% of the TOC in several dams (Achour et al., 2009). Humic substances are extremely complex chemically, and their composition varies according to the origin and nature of the water in which they are found. Thus, those found in river and lake waters consist of mixtures of polyelectrolytic macromolecules such as humic and fulvic acids. Humic acid (HA) is a typical component of natural organic matter in water, accounting for approximately 50% to 90% of the total freshwater organic matter (Mahler and al., 2021).

Humic substances in a water supply are undesirable for several reasons. These substances must be eliminated because they generate both organoleptic problems (color, taste) and public health problems by retention or formation of toxic products (pesticides, metals, halogenated compounds) (Boggs et al., 1985 ; Garbin et al., 2007; Laglera et al., 2011; Rekhow et al., 1990). Humic substances found in natural waters have been shown to be particularly reactive with a variety of oxidants and disinfectants used for drinking water purification, particularly chlorine and ozone (Singer, 1999). Oxidation processes can change the chemical structure of humic substances that serve as precursors of low- and high-molecular-weight organic compounds that are formed during chlorination and ozonation processes. These disinfection byproducts, such as trihalomethane, haloacetic acids and aldehydes, are believed to be harmful to human health (Richardson et al, 2007; Yamamori et al., 1993; Wu et al, 2019).

Efficient removal of organics from water can be achieved through processes such as activated carbon adsorption, membrane filtration and advanced oxidation. However, these methods are often expensive and not always adopted in conventional treatment facilities. The coagulation-flocculation technique is one of the most effective and economically feasible processes used in water treatment (Zhu et al, 2021). It is now recognized that coagulation-flocculation optimization during clarification of surface water can significantly contribute to the removal of organic matter in both colloidal (turbidity) and dissolved forms. Because humic substances stabilize dispersed and colloidal particles, the removal of humic substances has been a focus of the coagulation process (Suffet et al., 1988).

Many studies are still devoted to finding the optimal conditions for the removal of organic matter from water by coagulation-flocculation. Overall, the appropriate choice of coagulant and optimization of parameters such as coagulant dose and pH of the organic compound dilution water can improve coagulation efficiency. Thus, interest has most often focused on the influence of pH, coagulant dosage and origin of humic substances (Lefebvre and Legube, 1990; Qin et al., 2006; Achour and Guesbaya, 2005). Moreover, several studies (Stumm and O'Melia, 1968; Edzwald and Van Benschoten, 1990; Jiang et Wang, 2009; Bacha and Achour, 2015) conclude that coagulation-flocculation is a stoichiometric reaction and that the stoichiometric coefficient (coagulant/organic matter) depends on these parameters.

To date, few studies have been devoted to the influence of inorganic salts on the coagulation-flocculation of humic substances (Jekel, 1986; Wang et al., 2010; Jeong et al., 2014; Afoufou et al., 2007). It should also be noted that Algerian waters are characterized by significant salinity. This is particularly the case for the waters in the south of the country, which often have excessive hardness and levels of chlorides and sulfates (Achour et al., 2008). Therefore, it would be wise to investigate the effect of water salinity on the removal of humic matter and the dosage of coagulant.

The primary objectives of this study are to assess the performance and coagulation mechanisms of HA by aluminum sulfate and the effects of water salinity on both the HA removal efficiency and the relationship (coagulant dosage/humic acid concentration).

Throughout this study, we tested humic acid, which is a polyaromatic organic compound characterized by the presence of hydroxyl and carboxyl groups on the benzene ring (Suffet and Mac Carthy, 1988; Rajaei et al., 2021). The jar test experiments focused on solutions of this acid dissolved in distilled water and then in three mineralized borehole waters from the Biskra region. Several reaction parameters (initial humic acid concentration, coagulant dose, pH and salinity) are varied.

MATERIAL AND METHODS

Preparation of solutions

Solutions of humic acid

Solutions of ALDRICH humic acid (HA) with a carbon content of 51.5% were used in the coagulation-flocculation experiments. The molecular weight of HA was in the range from 2000 to 50,000 Da. The contents of the carboxylic and phenolic groups of HA are 3.8 meq/mg HA and 0.8 meq/mg HA, respectively (Achour, 2001). Table 1 specifies some characteristics of this humic acid.

The waters used as humic acid dilution media are, on the one hand, distilled water (pH = 6.07 to 6.79, conductivity = 2 to 5 µs/cm) and, on the other hand, groundwater (Drouh, Wadi Biskra, Ben Nacer Garden) taken from the Biskra region (South East of Algeria). The main water quality parameters are determined in the LARHYSS laboratory (Biskra) using standard methods of analysis (APHA, 2005; Rodier et al., 2016). They are shown in Table 2.

A stock solution of 100 mg HA/l was prepared by dissolving humic acid in distilled water, and the pH was adjusted to 4, 7 and 9 with HCl and NaOH 0.1 N. For further tests, Biskra groundwaters were spiked with HA at levels of 1 to 20 mg/l.

Table 1: Chemical characteristics of the studied HAs (Achour, 2001)

	C	H	N	O	Na
Elemental analysis (%)	51.5	4.6	0.7	29.3	0.7
Carboxyl function (meq.g^{-1} humic substance)			3.4		
Hydroxyl function (meq.g^{-1} humic substance)			0.8		

Table 2: Physicochemical characteristics of humic acid dilution water (borehole waters from the Biskra region)

	Groundwater samples		
Characteristics	**Drouh**	**Wadi Biskra**	**Ben Nacer Garden**
Temperature (°C)	16	19.5	18
pH	7.63	7.77	7.59
TH (°F)	70	85	95
TAC (°F)	10.7	20	30
Ca^{2+} (mg/l)	124	196	216
Mg^{2+}(mg/l)	93	86	96
Cl^- (mg/l)	444.68	678	720
SO_4^{2-}(mg/l)	33.5	720	610
NO_3^-(mg/l)	3.54	19.5	22.15
Na^+ (mg/l)	60.46	673.39	483.81
K^+ (mg/l)	2.33	8.7	8.7
PO_4^{3-}(mg/l)	2.75	0.078	0.13
Conductivity (ms/cm)	1.26	2.81	3.58

Coagulant solution

A stock solution of 10 g/l was prepared periodically by dissolving aluminum sulfate FLUKA reagent ($Al_2(SO_4)_3,18H_2O$) in distilled water.

Humic acid analysis

The residual concentrations of the organic compound tested (HA) were determined by measuring the UV absorption with a JENWAY 6305 UV/Vis spectrophotometer at 254 nm. A linear correlation is established between the UV reading and the humic acid concentration for each type of water. Table 3 shows the results of calibration curves for humic acid dissolved in different waters. It summarizes the equations of absorbance (Abs_{UV}) as a function of humic acid concentration (C_0) for each dilution water.

Table 3: Results of calibration curves of absorbance in UV (Abs_{UV}) versus initial concentrations (C_0) of humic acid solutions (λ = 254nm)

1	$Abs_{UV} = f(C_0)$	Determination coefficient R^2
Distilled water	$Abs_{UV} = 0.025\ C_0$	1
Drouh	$Abs_{UV} = 0.014\ C_0 + 0.005$	0.994
Wadi Biskra	$Abs_{UV} = 0.010\ C_0 + 0.001$	0.999
Ben Nacer Garden	$Abs_{UV} = 0.018C_0 + 0.002$	0.999

Description of the Jar test

All the coagulation-flocculation tests were carried out according to the "Jar-Test" protocol on a flocculator with six stirrers (Ficher 1198), which makes it possible to simultaneously stir the solutions of humic acid and coagulant. Each sample was stirred rapidly at 200 rpm for 2 minutes after the coagulant was added. Subsequently, the speed was reduced to 60 rpm for 30 minutes. Finally, the flocs were allowed to settle for 30 minutes before filtration through a 0.45 µm cellulose membrane (Bacha and Achour, 2015). The supernatant was sampled for analysis of the residual humic acid by spectrophotometry.

The humic acid removal efficiency is evaluated by the following relationship:

$$R\,(\%) = 100\frac{C_0 - C_f}{C_0} \quad (1)$$

where C_0 and C_f in mg/l represent the initial and final concentrations of humic acid, respectively.

RESULTS AND DISCUSSION

Effect of aluminum sulphate dosage and pH on removal of various humic acid concentrations in distilled water.

Our preliminary tests focused on the coagulation-flocculation of HA in distilled water. For increasing doses of coagulant, we observed the efficiency of the removal of HA (E%) during the variation of the initial concentration of HA (C_0) and that of the pH of the solutions (Fig. 1).

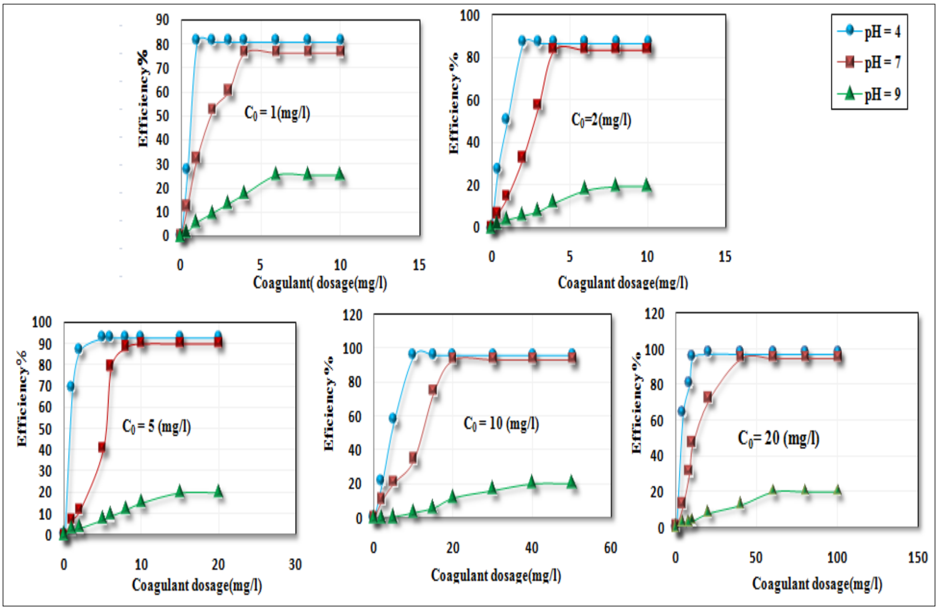


Figure 1: Aluminum sulphate dosage and pH effect on various humic acid concentrations C_0 removal in distilled water.

Based on the results of Fig. 1, we observe that the optimal coagulant doses increase with the initial concentration of HA, and the optimum efficiencies are variable according to not only the initial concentrations but also the pH of the solution.

The HA removal percentages are globally significant and sometimes exceed 80 to 90%. Beyond the optimal dose, elimination percentages stabilize. Nevertheless, the doses of coagulant required to obtain the best removal of HA are greater when going from pH= 4 to pH=9. HA removal efficiencies decrease from pH 4 to pH 9.

Coagulation mechanisms of humic acid at different pH values in distilled water

In the past, the interpretation of the action of aluminum salts was performed in a relatively simplistic way in terms of charge neutralization and precipitation of aluminum hydroxide (Tardat-Henry, 1989). It is now well established that the hydrolyzed aluminum species of coagulants play an essential role in the coagulation process.

When aluminum salts are introduced into water, various reactions can take place, several of which are simultaneous and/or reversible.

In solution, alum releases hydrated Al^{3+} ions, which play a negligible role in coagulation because they are present only below a pH of 4.5. Above this pH, the hydrolysis reaction is immediate, and hydrated Al^{3+} reacts to form monomeric, polymeric species and a solid precipitate. In general, it should be noted that the higher the pH is, the greater the degree of hydrolysis becomes (Fig. 2). This results in a series of hydroxy-aluminum complexes $Al(OH)^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$ $Al(OH)_4^-$,…) Benschoten & Edzwald, 1990; Dentel, 1991). The hydrolysis reaction can be generalized using the following equation (Berrak, 1997):

$$xAl^{3+} + yH_2O \leftrightarrow Al_x(OH)_y^{3-y} + y\ H^+$$

Aluminum can therefore be quickly transformed into a series of hydrolyzed species with different structures, charges and polymerization characteristics. The diversification of polymerized species is a function of pH and dosage and possibly of inorganic and organic coagulant-ligand interactions (Tardat-Henry, 1989; Kong et al., 2021).

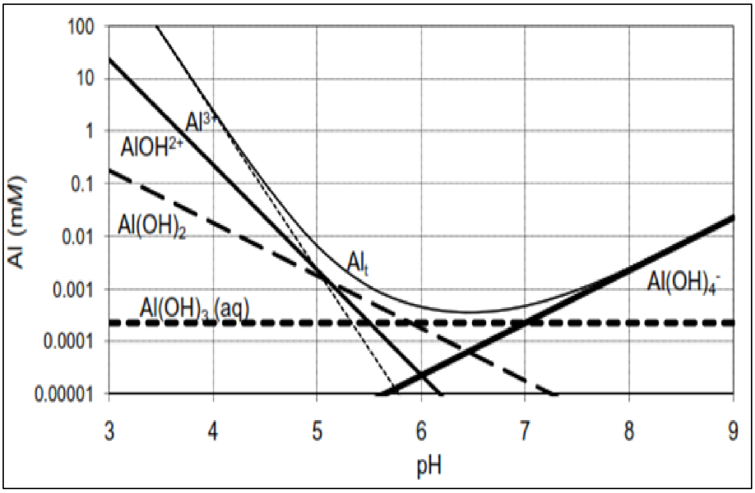


Figure 2: Solubility of hydrolyzed aluminum species as a function of pH (Driscoll and Schecher, 1990)

The results in Fig. 1 confirm those of numerous studies that have previously concluded that pH has a significant impact on the optimal removal of organic compounds during coagulation-flocculation. The study of this parameter is important because it conditions, on the one hand, the dissociation of functional groups existing in the structure of organic compounds according to their pKa and, on the other hand, the speciation of the coagulant (soluble or insoluble hydrolysis products, charged or neutral).

As early as 1961, the work of Black and Willems and then that of Semmens (1979) on very colored American waters, and therefore loaded with humic material, showed that the optimal pH for coagulation is generally acidic, slightly more acidic for iron (pH = 4 to 4.6) than for aluminum (pH = 5.2 to 5.7). It should also be noted that the optimum conditions for the elimination of organic matter do not always coincide with those for the best reduction of turbidity. Furthermore, in some highly buffered waters, adjusting the pH to an optimal value is not easily achievable. In this case, the coagulation pH is very close to neutrality, and there is a predominant formation of the hydroxide precipitate, which is supposed to produce a "sweep flocculation" due to the adsorption of pollutants on the voluminous hydroxide precipitate of aluminum or iron (Lefebvre and Legube, 1990; Wang et al., 2010; Harrat and Achour, 2016).

We can also mention the results of Achour and Guesbaya (2005) concerning the comparison of the coagulation of two simple aromatic compounds (phenol and resorcinol) with that of a sodium humate (SH) whose structure was close to acid fulvic. For a pH range between 4 and 10, the results obtained concerning the optimum removal efficiency of each of the organic compounds in distilled water correspond to acidic pH values between 5 and 7 for the pH phenolic compounds and 5 and 6 for the SH.

It is interesting to note that, for these pH values, phenol and resorcinol are present in a neutral, nondissociated form, given their respective pKa values (9.89 and 9.81). The removal efficiency of these compounds decreases for pH=10, so it is obvious that their dissociated form would be much less reduced by flocculation with aluminum sulfate.

According to Achour and Guesbaya (2005), simple compounds with phenolic groups are less affected by coagulation-flocculation. However, the nature and position of the substituents (OH and COOH) on the aromatic ring of organic compounds can lead to differences in removal efficiencies by the coagulant (Lefebvre and Legube, 1993; Rezeg and Achour, 2009). Among the organic acids tested, the compounds exhibiting the behavior closest to that of humic substances are especially pyromellitic and gallic acids (Bacha and Achour, 2017; Rezeg and Achour, 2009) as well as pyrogallol (Hecini and Achour, 2014), which result in high removal efficiencies at acidic pH, close to 5 to 6.

For the sodium humate (SH) studied by Achour and Guesbaya (2005), its elimination was significantly greater than that of phenol and resorcinol, especially at acidic pH.

Humic substances can be considered anionic polyelectrolytes of indeterminate structure but overall of high molecular weights, of which a small part is in colloidal form. The higher SH removal efficiencies may be attributable to the high size and molar weights of the different SH fractions. The chemical structure of humic material and, in particular, the presence of numerous reactive chemical groups, such as hydroxyl or carboxyl groups, could also condition the efficiency of the flocculation process of these substances.

Similarly, in the case of the humic acid that we tested (Fig. 1), the mechanisms involved during the coagulation of humic acid could be more complex because, at the optimum pH for elimination (pH = 4), it is possible that the COOH groups are dissociated. Note that the pKa of the COOH and OH functions carried by humic material are on the order of 4.2 and 8.7, respectively.

Given the simultaneous presence of several hydrolyzed species of aluminum (soluble or insoluble) and the partially dissociated form of this HA at these pH values, the reactions involved are probably numerous.

At pH = 4, the predominant hydrolyzed species of aluminum are soluble cationic complexes such as $Al(OH)^{2+}$ and $Al(OH)^{+}_{2,}$ which could condition the coagulation-flocculation mechanisms. A complexation mechanism would lead to the formation of insoluble complexes between humic acid and soluble hydroxo-aluminum compounds.

At neutral or basic pH, the elimination of HA in distilled water is much less efficient than at pH = 4 and could be explained by a competitive complexation of the OH^- in the medium with aluminum. This reduces the affinity of aluminum for organic ligands (Chow, 1992).

Hydrolysis reactions of aluminum to the $Al(OH)_3$ form could thus be favored at the expense of complexation reactions between soluble hydroxo-metallic compounds and organic matter; this leads to a reduction in the efficiency of elimination of HA. Note that Edzwald Van Benschoten and. (1990) reported that at pH = 7, good humic matter removal yields can be obtained provided that much higher coagulant dosages are used. According to Dentel (1991) and Zhu et al. (2021), at pH = 7, coagulation of humic substances by aluminum is a competition between surface complexation by humic substances and polymerization reactions of aluminum hydroxide. At this pH, the hydrolyzed species of aluminum would be flocs comprising a mixture of amorphous $Al(OH)_3$ and soluble cationic positively charged species such as $Al(OH)^{2+}$ and $Al(OH)_2^+$, which could condition the mechanisms of coagulation-flocculation.

Moreover, under our experimental conditions (pH = 7), the residual concentrations of aluminum that we measured are very low or even zero. Therefore, this is in favor of the predominant formation of insoluble organoaluminum products by surface reactions with amorphous aluminum hydroxide precipitates.

We also observed that at basic pH values above 7, the removal efficiencies of organic compounds decrease. This is verified both for natural organic matter and for simpler aromatic structures with acid functions (Jekel, 1986; Bacha and Achour, 2015; Rezeg and Achour, 2009). At pH = 9, the predominant hydrolyzed species of aluminum would be soluble anionic complexes such as $Al(OH)^-_4$ and $Al(OH)^{2-}_5$ (Fig. 2) with minimal formation of aluminum hydroxide. The molecules of humic acid will be largely dissociated and therefore negatively charged, and repulsion between the two species would occur.

Stoichiometric relationship between aluminum sulfate and HA at different pH values in distilled water.

In the coagulation of humic substances, a stoichiometric relationship has frequently been proposed between the concentration of these compounds to be removed and the required dose of hydrolyzed metal salts or polyelectrolytes. Narkis and Rebhun (1997) even suggested that this stoichiometry constituted one of the basic characteristics of HS coagulation. According to Edzwald and Tobiason (1999), the presence of organic matter in the water induces a coagulant demand for the different hydrolyzed species of aluminum, resulting in a stoichiometric relationship between the aluminum sulphate dosage and the DOC content that is pH dependent. In wastewater, Liang et al. (2010) showed the existence of a stoichiometric relationship between the concentration of melanoidin-dominated organics and the dosage of hydrolyzing metal salts (ferric chloride and aluminum sulfate). Van Breemen et al. (1979) also found a stoichiometric relationship between fulvic acid concentration, coagulant dose and carboxylic function content. This aspect was again confirmed by the work of Lefebvre and Legube (1990), who focused on several humic substances extracted from French waters and coagulated by ferric iron. By coagulating a sodium humate with properties close to the soluble fulvic acid fraction, Afoufou et al. (2007) as well as Achour and Guesbaya (2005) obtained, for an unadjusted pH, a mass ratio of 2 mg of sulfate of aluminum per mg of sodium humate.

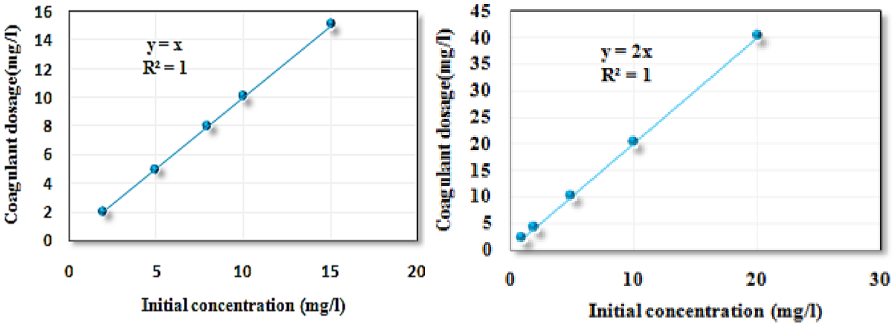
It is therefore necessary to establish this relationship between aluminum sulfate and humic acid HA tested in distilled water at several pH values. The adjustment of the pairs of values of the two parameters (optimal dose of aluminum sulfate and initial concentration of HA) by the method of linear least squares leads to a linear stoichiometric relationship. The relationship is obtained with excellent correlation coefficients but differs depending on the pH of the medium for diluting HA (Fig. 4).

Fig. 3 relates to the stoichiometric relationship (coagulant dosage/initial concentration of HA) established for pH=4, 7, and 9. Thus, for the removal of 1 mg of HA, these results highlight the stoichiometries of 1, 2 and 3 mg of aluminum sulfate for pH = 4, 7 and 9, respectively.

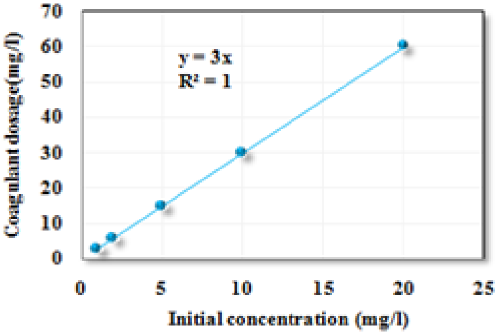
It should be emphasized that at acidic pH, the cationic species of aluminum are preponderant, and one of the possible reactions is the formation of insoluble complexes between the SH and the soluble hydroxo-aluminum compounds. Therefore, at pH =4, it seems that the mechanism of interaction between humic acid and dissolved aluminum polycations is indeed a stoichiometric reaction. The stoichiometric coefficient is then equal to 1 (Fig. 3a).

Fig. 3b relates to the stoichiometric relationship obtained at pH=7. It highlights a linear law as well, but with a mass ratio of aluminum sulfate dose/initial concentration of HA equal to 2, higher than the stoichiometric coefficient of that at pH =4. According to Jeckel (1986), the high demand for aluminum at pH = 7 can be explained by a competition between surface complexation by humic substances and polymerization reactions of aluminum hydroxide.

Fig. 3c shows the stoichiometric relationship obtained when HA solutions are adjusted to pH=9. The stoichiometric coefficient or coagulant/Ha mass ratio is 3. At pH=9, the coagulant demand is higher than at pH=4 and 7 if we refer to the results of the various stoichiometric coefficients. At basic pH, the coagulant demand can increase because of the competitive reactions between HA and OH^- in the medium with respect to their complexation with hydrolyzed aluminum.



(a) pH = 4 (b) pH= 7



(c) pH= 9

Figure 3: Stoichiometric relationship between coagulant demand and HA concentration in distilled water.

Effect of water salinity on humic acid coagulation-flocculation

In the second step of our study, we tested the behavior of HA during coagulation-flocculation when various concentrations of HA (1 to 20 mg HA/l) were added to saline groundwater from the Biskra region. The characteristics of these borehole waters (Drouh, Wadi Biskra, Ben Nacer Garden) were previously reported in Table 1.

Fig. 4 shows, as an example, the evolution of the efficiency of elimination of 5 mg HA/l as a function of the dose of coagulant.

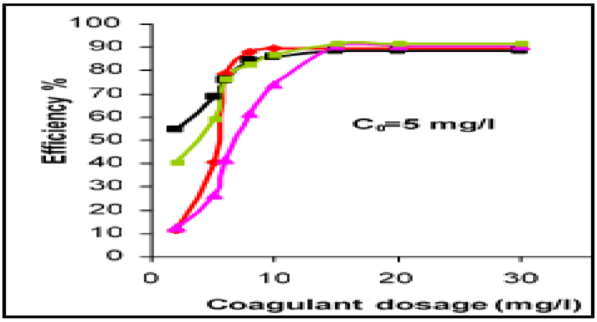


Figure 4: Influence of the aluminum sulfate dose on the removal of HA (5 mg/l) in waters of varying salinity. ♦Distilled water ■Drouh ▲Wadi Biskra ■BenNacerGarden

Whatever their dilution medium, and in fact also whatever the initial content of the HAs, the same shape of the curves is observed. We can thus observe that globally, two zones are to be distinguished:

- a first zone where the yield increases significantly up to a value corresponding to the optimum HA removal.
- a second zone where performance stabilizes even in the presence of excess coagulant.

Optimal coagulant dosage and HA removal effectiveness for varying water salinities.

Table 4 summarizes the HA removal yield values and optimum dosage of aluminum sulfate for each concentration of HA tested and for each type of dilution water.

Table 4: Summary of optimal aluminum sulfate (AS) dose values and HA removal efficiencies (E%)

C_0 (mgHA/l)	**Dilution water of HA**							
	Distilled Water (pH = 7)		Drouh pH=7.63 C=1.26mS/cm TH=70°F		Wadi Biskra pH=7.77 C=2.81mS/cm TH= 85°F		Ben Nacer Garden pH=7.59 C=3.58mS/cm TH= 95°F	
	AS dose (mg/l)	E %	AS dose (mg/l)	E %	AS dose (mg/l)	E %	AS dose (mg/l)	E %
1	2	76.09	4	76.68	3	78.81	2	81.75
2	4	83.74	6	84.30	6	84.93	6	86.57
5	10	90.64	15	88.71	15	90.53	15	91.86
10	20	93.65	60	91.97	50	92.47	30	94.50
20	40	94.08	90	93.22	70	94.63	60	95.09

From the results in Table 4, many key aspects can be deduced. Thus, as in distilled water, the higher the initial concentrations of HA, the greater the coagulant dosage and removal efficiency. The HA removal efficiencies remain high regardless of the salinity of the water. Among the groundwaters tested, and for close pH values, the hardest and most mineralized waters seem to promote better coagulation of HA. The presence of promoter salts based on calcium and magnesium could significantly improve the HA removal efficiencies. Various studies (Jekel, 1986; Wais Mossa and Mazet, 1991; Afoufou et al, 2007) have demonstrated the beneficial effect of calcium and magnesium salts on the elimination of humic substances of various origins during coagulation-flocculation. However, the presence and proportion of complexing and inhibiting anions will be decisive for the effectiveness of the flocculation of organic matter (Bernhardt et al., 1986; Hecini et Achour, 2014; Bacha and Achour, 2017).

Although the presence of calcium or magnesium salts can, through bridging or complexation effects with the organic compound, facilitate interactions with aluminum, the presence of large quantities of inorganic anions can significantly reduce the efficiency of coagulation-flocculation. Ions such as sulfate, phosphate or chloride can indeed compete with the COOHs of organic compounds and complex aluminum. They would therefore considerably interfere with the formation reaction of aluminum hydroxide, which should be the main product of the hydrolysis of the coagulant at the pH of the natural waters tested.

Moreover, the results of Fig. 4 indicate, just as in distilled water, that there is no restabilization of the particles formed even beyond the optimum and therefore for an excess of coagulant. This is explained by the presence of several competitive mechanisms between the hydrolyzed aluminum species (soluble or insoluble) and the humic material. However, the coagulation-flocculation mechanisms of humic acid in the presence of mineralized water may differ significantly from those observed in distilled water.

Our experiments highlighted a range of pH values for which the elimination of HA is optimal and which is acidic to neutral for distilled water and close to 7 for strongly buffered mineralized waters of the Biskra region. It can thus be assumed that the increase in mineralization and, in particular, that of promoter inorganic elements (calcium, magnesium) could widen the optimal pH range.

In the case of distilled water, whose pH is acidic and can be lower than 5, there was essentially complexation between the soluble cationic forms of aluminum and HA.

On the other hand, in mineralized waters whose pH is close to neutrality, the formation of a significant quantity of $Al(OH)_3$ can take place and promote a phenomenon of physical adsorption or an exchange of ligand with the OH- at the surface of this hydroxide. In addition, the mineral component of these waters and especially the cations such as calcium or magnesium can promote a bridging effect between the HA and the aluminum hydroxide sites or even with the soluble anionic forms of aluminum for basic pH.

Stoichiometric relationship between coagulant dosage and HA in saline water.

It is obvious that the mineral composition of the groundwater tested contributed to the variation in coagulant demands, probably involving different HA flocculation mechanisms depending on the nature and the relative proportions of characteristic elements of the mineral matrix of the waters.

For distilled water, we will try to establish a stoichiometric relationship between the optimal dose of coagulant and the initial concentration of HA for each of the mineralized waters. The adjustment of the pairs of values of the two aforementioned parameters by the method of linear least squares results in several relationships. These vary according to the mineral characteristics of each water and are valid for HA concentrations between 1 and 20 mg/l (Table 5).

By comparing the results in mineralized waters with those in distilled water, we can deduce that such a relationship still exists, despite the change in mineralization of the HA dilution medium .

Therefore, for water that is both loaded with humic substances and highly mineralized, it is reasonable to assume that the optimization of the coagulant dosage is closely linked to the concentration of humic material but also to the inorganic content and to the associated proportions of promoters or inhibitory compounds with respect to the coagulation mechanisms.

At neutral pH, speciation of positively charged Al species decreases with increasing temperature (Edzwald and Tobiason, 1999). This can lead to a higher dosage of alum for waters with higher temperatures, as is the case in Algeria and particularly in the south of the country.

Table 5: Stoichiometric relationship between coagulant and HA for various salinities of water. Y= coagulant dose; X= C_0 initial concentration of HA.

Water dilution of HA			
Distilled water (pH=7)	**Drouh**	**Wadi Biskra**	**Ben Nacer Garden**
Y=2X	Y=4X	Y=3X	Y=2X
R^2 =1	R^2 = 0.990	R^2 =0.972	R^2 = 0.995

CONCLUSION

Through this study, we pointed out that the tested humic acid (HA) has properties typical of weak anionic polyelectrolytes. It is characterized by a molecular weight of several thousand and contains weakly acidic functional groups such as carboxylic and phenolic groups. Our experiment aimed to study the behavior of this humic acid dissolved in waters of varying salinity during the process of coagulation-flocculation by aluminum sulfate.

In general, when aluminum sulfate is used as a coagulant, positively charged aluminum hydrolysis species will complex with negatively charged humic substances, followed by precipitation and/or adsorption onto aluminum hydroxide solids. However, the coagulation-flocculation process has revealed various mechanisms, often complex and highly dependent on the pH of the water to be treated.

By testing humic acid in distilled water at different pH values, we concluded that pH affects both humic acid and coagulant speciation. Consequently, the pH has a significant influence on the coagulant demand and the effectiveness of humic acid removal by the coagulant.

The tests carried out lead to the conclusion that the percentages of elimination of HA are very high and improve when the initial concentration of these humic substances increases, regardless of the dilution water (distilled water or mineralized water). Furthermore, the exploitation of the results of the jar test has shown that a stoichiometric relationship is always verifiable regardless of the medium of dilution of the HA and, in particular, the salinity of water. However, the stoichiometric coefficient of each relationship established seems to vary according to the constituents of the mineral matrix of water. This relationship depends on the type of organic substances to be treated, the type of coagulant and the conditions of the solution (such as pH, hardness, sulfate, alkalinity and temperature). The mineral composition of the waters we tested contributed to the variation in coagulant demands, probably involving different coagulation mechanisms of HA, depending on the nature and relative proportions of promoter mineral ions such as calcium and magnesium or possibly inhibitors such as bicarbonates or sulfates.

The existence of stoichiometric relationships between the concentrations of humic material and the optimal dose of coagulant is of real interest from a practical point of view. The extrapolation of these laws to the coagulation-flocculation of surface waters will, however, require the determination of more general relations taking into account not only the content and the nature of the organic matter of these waters but also of its mineral component and its effects on the speciation of coagulant and organic matter.

REFERENCES

ACHOUR S. (2001). Impact of chlorination, flocculation and adsorption on the evolution of organic and mineral compounds in natural waters. Doctoral Thesis in Hydraulic Sciences, University of Tizi-Ouzou, Algeria. (In French).

ACHOUR S., GUERGAZI S. and HARRAT N. (2009). Organic pollution of dam waters in eastern Algeria and effect of chlorination. "The state of water resources in the Maghreb in 2009", Part IV, Chapter 14, Ed. UNESCO and GEB-Environment, Rabat, Morocco. (In French)

ACHOUR S., GUESBAYA N. (2005). Coagulation-flocculation by aluminum sulphate of organic phenolic compounds and humic substances, Larhyss Journal, No 4, pp.153-168. (In French).

ACHOUR S., YOUCEF L., GUERGAZI S. (2008). Physico-chemical quality of groundwater and surface waters of the northern eastern Sahara of Algeria, L'Eau, l'Industrie, les Nuisances, No 311, pp.79-84. (InFrench)

AFOUFOU F., GUESBAYA N., ACHOUR S., (2007). Effect of the mineralization of natural waters on the elimination of aromatic organic compounds by coagulation – flocculation, Courrier du Savoir Scientifique et Technique,University of Biskra, No 8, pp.75-81. (In French).

APHA (2005). Standard methods for the examination of water and wastewater, 21st Edition, American Public Health Association Edition/American Water Works Association/Water Environment Federation, Washington DC.

BACHA N., ACHOUR S. (2015). Influence of reaction parameters on the stoichiometry of aluminum sulphate/natural organic matter in distilled water, Larhyss Journal, No 21, pp. 141-148. (In French)

BACHA N., ACHOUR S. (2017). Trials of pyromellitic acid coagulation in media with various degree of mineralization, Journal of Water and Environmental Sciences, Vol. 1, special number ICWR, pp. 235-242. (In French).

BENSCHOTEN J.E., EDZWALD, J.K. (1990). Chemical aspects of coagulation using aluminum salts—I. Hydrolytic reactions of alum and polyaluminum chloride, Water Research, Vol. 24, No 12, pp.1519-1526.

BERNHARDT H., LÜSSE B., HOYER O. (1986). the addition of calcium to reduce the impairment of flocculation by algogenic organic matter, Zeitschrift fur Wasser und Abwasser Forschung, Journal for Water and Wastewater Research, Vol. 19, No 1, pp. 219-228.

BERRAK A. (1997). Influence of some contaminants on the kinetic behavior of new aluminum-based coagulants, phD Department of Chemistry, University of Sherbrook, Quebec.

BLACK A.P., WILLEMS D.G. (1961). Electrophoretic studies of coagulation for removal of organic color, Journal American Water Works Association, Vol. 53, No 4, pp.438-443.

BOGGS J.R.S., LIVERMORE D.G., SEITZ M.G. (1985). Humic macromolecules in natural waters, Journal of Macromolecular Science, Part C, Vol. 25, No 4, pp.599-657.

CHOW W.M. (1992). behaviour of aluminum and its ecological significance in natural waters, Water Supply, Vol. 10, No 4, pp.1-10

DENTEL S.K. (1991). Coagulant control in water treatment, Critical Reviews in Environmental Control, Vol. 21, No 1, pp. 41-135.

DRISCOLL C.T., SCHECHER W.D. (1990). The chemistry of aluminum in the environment. Environmental Geochemistry Health, Vol.12, Issue 1-2, pp.28–49.

EDZWALD J.K. & TOBIASON J.E. (1999). Enhanced coagulation: US requirements and a broader view, Water Science and Technology, Vol. 40, Issue 9, pp.63-70.

EDZWALD, J. K., VAN BENSCHOTEN, J. B. (1990). Aluminum coagulation of natural organic matter. In Chemical Water and Wastewater Treatment; Hahn H., Klute R., Eds.Springer, New York.

GARBIN J.R., MILORI D.M.B., SIMOES M.L., DA SILVA W.T.L., NETO L.M. (2007). Influence of humic substances on the photolysis of aqueous pesticide residues, Chemosphere, Vol. 66, Issue 9, pp. 1692-1698.

HARRAT N., ACHOUR S. (2016). Behavior of humic substances from Zit El Amba dam during coagulation-flocculation in the presence of aluminum sulphate and activated carbon, Larhyss Journal, No 26, pp. 149-165. (In French)

HEALTH CANADA (2019). Guidance on Natural Organic Matter in Drinking Water-Document for Public Consultation, Government of Canada. https://www.canada.ca/en/health-canada/

HECINI L., ACHOUR S. (2014). Coagulation-flocculation by aluminum sulfate of organic phenolic compounds and effect of calcium and magnesium salts, Revue des Sciences de l'Eau, Vol. 27, No 3, pp. 189-280. (In French).

JECKEL M.R. (1986). Interactions of humic acids and aluminum salts in flocculation process, Water Research, No 20, pp.1535-1542.

JEONG S., SATHASIVAN A., KASTL G., SHIM W.G., VIGNESWARAN S. (2014). Experimental investigation and modeling of dissolved organic carbon removal by coagulation from seawater, Chemosphere, Vol. 95, pp.310-316.

JIANG J.Q. & WANG H.Y. (2009). Comparative Coagulant Demand of Polyferric Chloride and Ferric Chloride for the Removal of Humic Acid, Separation Science and Technology, Vol. 44, No 2, pp.386-397.

KONG Y., MA Y., DING L., MA J., ZHANG H., CHEN Z., JIMIN SHEN. (2021). Coagulation behaviors of aluminum salts towards humic acid: Detailed analysis of aluminum speciation and transformation, Separation and Purification Technology, Vol. 259, pp.118-137.

LAGLERA L.M., BATTAGLIA G., VAN DEN BERG C.M.G. (2011). Effect of humic substances on the iron speciation in natural waters by CLE/CSV, Marine Chemistry, No 127, pp.134-143.

LEFEBVRE E., LEGUBE B. (1993). Coagulation-flocculation by ferric chloride of some organic acids and phenols in aqueous solution, Water Research, Vol.27, No 3, pp.433-447. (In French)

LEFEBVRE E., LEGUBE B. (1990). Iron (III) coagulation of humic substances extracted from surface waters: effect of pH and humic substances concentration, Water Research, Vol.24, No 5, pp.591-606. (In French).

LIANG Z., WANG Y., ZHOU Y., LIU H., WU Z. (2010). Stoichiometric relationship in the coagulation of melanoidins-dominated molasses wastewater, Desalination, Vol. 250, No1, pp. 42-48.

MAHLER C.M., DAL SANTO SVIERZOSKI N., BERNARDINO C.A.R. (2021). Chemical Characteristics of Humic Substances in Nature, Chap.8, In: Humic substances, Ed. A. Maken, IntechOpen Publications, Rijeka.

NARKIS N., REBHUN M. (1997). Flocculation in presence of organic macromolecules of natural water and secondary effluents, Water Science Technology, Vol. 36, No 4, pp.85–91.

QIN J.J., MAUNG HTUN OO, KEKRE K.A., KNOPS F., MILLER P. (2006). Impact of coagulation pH on enhanced removal of natural organic matter in treatment of reservoir water, Separation and Purification Technology, Vol. 49, Issue 3, pp.295-298.

RAJAEI F., TAHERI E., HADI S., FATEHIZADEH A., AMIN M. M., RAFEI N., AMINABHAVI T. M. (2021). Enhanced removal of humic acid from aqueous solution by combined alternating current electrocoagulation and sulfate radical. Environmental Pollution, Vol. 277, May 15, pp. 116632.

REKHOW D.A., SINGER P.C., MALCOLM R.L. (1990). Chlorination of Humic Materials: Byproduct Formation and Chemical Interpretations, Environmental Science Technology, Vol. 24, No 11, pp.1655-1664.

REZEG A. & ACHOUR S. (2009). Removal mechanisms of acid aromatic organics by aluminum sulphate and mineralization effect, Courrier du Savoir, University of Biskra, No 9, pp.25-31. (In French)

RICHARDSON S.D., PLEWA M.J., WAGNER E.D., SCHOENY R., DEMARINI D.D. (2007). Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection byproducts in drinking water: A review and roadmap for research, Mutation Research, Vol. 636, Issue1-3, pp.178–242.

RODIER J., LEGUBE B., MERLET N. (2016). Water analysis: control and interpretation, 10th Ed. Dunod, Paris.

SEMMENS M.J. (1979). organics removal by coagulation: A review and Research needs, Journal American Water Works Association, Vol. 71, N°10, pp. 588-603.

SINGER P.C. (1999). Humic substances as precursors for potentially harmful disinfection byproducts, Water Science Technology, Vol.40, N°9, pp.25-30.

STUMM W., O'MELIA C. R. (1968). Stoichiometry of coagulation. Journal American Water Works Association, Vol. 60, No 5, pp. 514–539.

SUFFET I.H., MAC CARTHY P. (1988). Aquatic Humic Substances: Influence on Fate and Treatment of Pollutants, 1st Ed., Eds. American chemical Society, Washington DC.

TARDAT-HENRY M. (1989). Evolution of aluminum derivatives used as coagulating agents. Revue sciences et techniques de l'eau, Vol. 22, No 4, pp.297-303. (In French).

THURMAN E. M. (1985). Developments in biogeochemistry: Organic geochemistry of natural waters, Ed. Nijhoff M./Dr W. Junk Publishers, Dordrecht, The Netherlands.

VAN BREEMEN A.N., NIEUWSTAD T.J., VAN DER MEENT-OLIEMAN (1979). The fate of fulvic acids during water treatment, Water Research, Vol. 13, No 8, pp.771-780.

WAIS-MOSSA M.T., MAZET M. (1991). Influence of mineral salts on the adsorption of humic acids on flocs of preformed iron hydroxides, Environmental Technology, Vol. 12, No 8, pp. 725-730. (In French).

WANG Y., GAO B. Y., XU X. M., XU W. Y. (2010). The effect of total hardness and ionic strength on the coagulation performance and kinetics of aluminum salts to remove humic acid, Chemical Engineering Journal, Vol. 160, No1, pp. 150-156.

WU B., ZHANG Y., HONG H., HU M., LIU H., CHEN X. (2019). Hydrophobic organic compounds in drinking water reservoirs: Toxic effects of chlorination and protective effects of dietary antioxidants against disinfection byproducts. Water Research, Vol. 166, No 12, pp.115-141.

YAMAMORI H., MATSUDA H., SATO T., OSE Y., NAGASE H., KITO H. (1993). Evaluation of mutagenic activity of ozonated and ozonated-chlorinated humic substances by sos chromotest, Journal of Environmental Science and Heath, Part A, Environmental Science and Engineering and Toxicology, Vol. 28, No 4, pp. 871-887.

ZHU G., XIONG N., WANG C., LI Z., HURSTHOUSE A. S. (2021). Application of a new HMW framework derived ANN model for optimization of aquatic dissolved organic matter removal by coagulation, Chemosphere, Vol. 262, Paper 127723.