The removal efficiency and reaction mechanism of the aluminum coagulant on phenolic compounds in the presence of hardness salts

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Abstract: This study is the evaluation of the coagulation efficiency of the aluminum sulfate on the removal of catechol and pyrogallol. The study has focused on the impact of inorganic components of hardness Algerian waters. Jar-test trials were conducted on the two phenolic compounds dissolved in distilled water only, which was later enriched with minerals. Several reaction parameters varied, including the effect of pH and the influence of the salt content, and this approach yielded a better understanding of interaction between phenolic compounds and calcium/magnesium salts. The results indicate that the process efficiency depends on the number and position of OH in molecules. The main mechanisms would be either a physical adsorption, an exchange of ligand, or complexation on the floc surface of aluminum hydroxide. Moreover, the addition of inorganic salts appears to improve removal efficiency of tested phenolic compounds and have an effect on the optimal pH range for coagulation.

Keywords: phenolic compounds, hardness salt, aluminum sulphate, coagulation-flocculation, mechanism

INTRODUCTION

Phenol is an important organic intermediate for products of industry and agriculture [BRUCE *et al.* 1987]. For example, hydroxy aromatic compounds, such as catechol, have been used widely as industrial solvents. Catechol (1,2-dihydroxybenzene) and pyrogallol (1,2,3-trihydroxybenzene) are also widely used to produce food additive agents, hair dyes, and antioxidants [CAMPANELLA *et al.* 1993]. Phenolic compounds can be found in effluents from such industries as textile, paper and pulp, steel, petrochemical, petroleum refinery, rubber, dye, plastic, pharmaceutical, cosmetic, etc. and in wastewater from synthetic coal fuel conversion processes [DIXON, PAIVA 1995; IGNAT *et al.* 2011]. Their presence may be due to the degradation or decomposition of natural organic matter present in water which originates from the disposal of industrial and domestic waste into water bodies and runoffs from agricultural land [KHERIFI *et al.* 2019; WALLACE 1996]. Upon entry into the water, these chemicals have the tendency to undergo transformation into other moieties that can even be more harmful than their original compounds. This transformation is normally due to their interaction with physical, chemical, biological or microbial factors in water [KULKARNI, KAWARE 2013].

Therefore, phenol and its derivatives form one of the largest groups of environmental pollutants owing to their presence in industrial effluents. Phenol is in the list of priority pollutants of the US Environmental Protection Agency (EPA) and it has toxic, carcinogenic, and mutagenic effects on humans, animals, and aquatic organisms [JIANG *et al.* 2016]. The fatal concentration of phenol in blood is around 1500 mg·dm^{-3} and its toxic concentration ranges are 10–24 and 9–25 mg·dm^{-3} for human and fish, respectively [ERYILMAZA, GENÇA 2021]. As a result, a number of wastewater treatment techniques have been developed and used for the removal of phenolic compounds from industrial, domestic, and municipal wastewater prior to its disposal into water bodies so as to minimise the devastating

effects of these chemicals on human and aquatic organisms [Anku et al. 2017].

Various treatment processes can be used to eliminate organic matter, such as adsorption on activated carbon, filtration on sand, exchange of ions, and the filtration on a membrane [Bacha, Achour 2017; Croue et al. 1999; Domany et al. 2002; Humbert et al. 2008]. Currently, in the conventional treatment stations, the process of coagulation flocculation is mainly used to eliminate organic matter [Wang et al. 2002]. A notable reduction in the humic substances was observed during various attempts to optimise coagulation-flocculation [Achour, Guesbaya 2006; Bacha, Achour 2013; Rezeg 2010]. The reagents used are generally coagulants containing salts of aluminum or iron [Degrémont 2005]. In addition, to allow a better explanation of mechanisms that intervene between these substances and coagulants, various research tasks have been performed related to simple organic molecules [Achour, Guesbaya 2005; Hecini, Achour 2017; Lefebvre, Legube 1993; Rahni 1994], which show the most basic structure of humic substances.

However, most of this work has been conducted in mediums that dilute to produce very weak ionic force, even null, especially based on distilled water. However, it can be shown that mineral salt, by individual or synergistic effects, could influence the effectiveness of the flocculation of organic matter [Achour, Guesbaya 2006; Bernhardt et al. 1986; Hecini, Achour 2014; 2018].

Moreover, the influence of mineral salts on the organic compound flocculation efficiency has been little studied and involved only humic substances [Afoufou, Achour 2006; Guesbaya 1998; Lefebvre 1990; Wais Mossa, Mazet 1991]. Then, we need to highlight and clarify the impact of salts commonly found in water to be treated. It is necessary to determine whether aluminum sulphate stimulates or inhibits the process of removing phenolic compounds, as well as what mechanisms take place between these compounds and the coagulant.

The waters of the Northern Sahara in Algeria are highly mineralised and are characterised by excessive hardness with high levels of calcium, magnesium, chlorides, sulfates, and sodium [Bouchahm et al. 2016; Bouchemal et al. 2011].

In this study, we have undertaken to evaluate the efficiency of coagulation-flocculation with aluminum sulfate on simple organic molecules of aromatic hydroxyl (catechol and pyrogallol) in distilled water enriched with mineral salts. We studied the influence of pH in the presence of calcium and magnesium salts. The application of such method was also performed on mineralised water in the region of Biskra located in the South East of Algeria (drilling water).
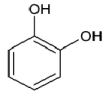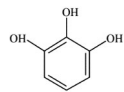
MATERIALS AND METHODS

PREPARATION OF SOLUTIONS OF PHENOLIC COMPOUNDS

All experimental tests were carried out in the Subterranean and Surface Hydraulics Research Laboratory (LARHYSS) of the University of Biskra, Algeria.

The organic compounds used for the purposes of our study are products marketed by Aldrich. For each dilution medium, we prepared a stock solution of 100 mg·dm^{-3} of each phenolic compound tested. Table 1 shows their characteristics.

Table 1. Characteristics and chemical structure of phenolic compounds

Item	Catechol acc. to Suresh et al. [2012]	Pyrogallol acc. to Upadhyay et al. [2010]
Chemical name	1,2-dihydroxybenzene	1,2,3-trihydroxybenzene
Chemical structure		
Molecular formula	$C_6H_6O_2$	$C_6H_6O_3$
Molar mass (g·mole^{-1})	110.11	126.11
pK-OH at 20°C	$pK_1 = 9.25$ $pK_2 = 13.0$	$pK_1 = 9.0$ $pK_2 = 11.2$ $pK_3 = 14.0$
Purity (%)	99	98

Source: own elaboration based on literature.

DILUTION WATERS OF PHENOLIC COMPOUNDS

The conductivity of distilled water used throughout this study varies between 2 and 5 µS·cm^{-1} and a pH between 6.18 and 6.73. The aqueous dilution media include groundwater initially free of organic matter from boreholes (Chetma and Biskra) of the terminal complex aquifer (Miopliocene), located in the Biskra region (south-eastern Algeria) that provides drinking water. The depth of this water varies from 100 to 900 m, with a flow varying between 20 and 60 dm^3·s^{-1} [Sedrati 2011], whereas the Ifri water is distributed in plastic bottles of 1.5 dm^3, and it is an Algerian brand of mineral water. It is abstracted in the village of Ifri in Kabylie, 150 km east of Algiers. The sampling was performed between October 2006 and June 2007. The main physicochemical characteristics have been determined in accordance with the standard analysis methods [Rodier et al. 2009] (Tab. 2).

Table 2. Physicochemical characteristics of dilution water

Characteristics	Water of		
	Ifri	Chetma	Biskra
T (°C)	18	18	18
pH	7.48	7.77	7.95
TAC (°F)	20	15	17
TH (°F)	28	116	114.4
Ca^{2+} (mg·dm^{-3})	80	320	246.4
Mg^{2+} (mg·dm^{-3})	19.20	86.4	126.72
Cl^- (mg·dm^{-3})	80	988	590
SO_4^{2-} (mg·dm^{-3})	45	485	690
Na^+ (mg·dm^{-3})	21	450	255
K^+ (mg·dm^{-3})	3	8	5
Conductivity (mS·cm^{-1})	0.439	1.99	2.95

Explanations: T = temperature (°C), TAC = full alkalimetric title (°F), TH = title hydrotimetric (°F).
Source: own elaboration.

PREPARATION OF COAGULANT SOLUTION

The coagulating reagent used was aluminum sulphate [$Al_2(SO_4)_3$, $18H_2O$], with a molar mass equal to 666.6 g·mol^{-1}. A stock solution of 10 g·dm^{-3} was prepared periodically in distilled water.

DESCRIPTION OF FLOCCULATION TESTS

The jar test was carried out on a 6-stirrer flocculator (Fisher 1198 flocculator). During our study, the solutions enriched with organic compounds and coagulants were subjected for 3 min to a rapid stirring of 200 rpm. The speed was subsequently reduced to 60 rpm for a period of half an hour [RODIER et al. 2009]. After a decantation of 30 min, the supernatant was recovered and filtered under vacuum on an OSMONICS INC membrane of 0.45 µm porosity. The filtrate then was assayed by a spectro-photometric analysis.

DOSAGE OF PHENOLIC COMPOUNDS

The phenolic compounds are assayed by spectrophotometry of the "Spectrophotometer Jenway 6405 UV/VIS" type by measuring the absorbance (A) at the wavelength λ = 270 nm for the catechol [SURESH et al. 2012] and the pyrogallol [UPADHYAY et al. 2010]. The residual concentration of these compounds is determined based on calibration curves (absorbance $A = f(C_0)$) for each dilution medium. The elimination yield (Y) of the compound is defined by:

$$Y = \left(1 - C_f/C_0\right) \cdot 100\% \qquad (1)$$

where: Y = elimination yield (%), C_f = residual concentration at the end of the test (mg·dm^{-3}) C_0 = initial concentration of the phenolic compound (mg·dm^{-3}).

RESULTS AND DISCUSSIONS

EFFECT OF THE COAGULANT DOSE

Coagulation-flocculation tests are carried on synthetic solutions containing a constant concentration of phenolic organic compounds (20 mg·dm^{-3}) out of distilled water (pH not adjusted). Increasing doses of aluminum sulphate are added to various solutions. Figure 1 presents final results obtained. They show that the organic compound removal efficiency varies depending on the chemical structure of these compounds. Moreover, the effect of the coagulant dose introduced varies from one compound to another.

In view of the results presented, it seems possible to distinguish that pyrogallol and catechol are partially eliminated under the test conditions. At the optimum, the pyrogallol removal reaches is 42.62% while that of catechol is 26.70%. These yields are observed respectively for a dose of 150 mg·dm^{-3} and 5 mg·dm^{-3} of aluminum sulphate. Moreover, we can see that changes of the elimination efficiency is more or less affected by the dosage of the coagulant. The catechol appears to be insensitive to the variation and increase in the aluminum sulphate dosage.

While referring to bibliographical data [LEFEBVRE, LEGUBE 1993; RAHNI 1994; SEMMENS, AYERS 1985], aromatic compounds containing two acid groupings into contiguous (COOH or OH) facilitate the elimination of organic molecules by coagulation-flocculation, e.g. pyrogallol under our experimental conditions. This, contrary to aromatic compounds with only one function, such as phenol, or two noncontiguous functions, such as resorcinol [ACHOUR, GUESBAYA 2006], probably because of the instability of the complex formed [LEFEBVRE [1990]. Former works [HECINI, ACHOUR 2013; REZEG, ACHOUR 2005] have also highlighted that phenol and phloroglucinol were very little eliminated regardless the amount of coagulant.

While referring to the bibliography, two great types of mechanisms can be distinguished to explain interactions between organic matter and aluminum and iron oxo-hydroxides [LEFEBVRE 1990; LEFEBVRE, LEGUBE 1993]. The first corresponds to reactions of the organic matter on the surface of oxo-hydroxy-metal solids. The mechanism of adsorption can be established by various types of reactions. The second mechanism involves reactions between organic matter and metal hydrolysed soluble forms.

Using experiments based on coagulation-flocculation and the iron salt addition with molecules like catechol, salicylic acid or tannic acid [RAKOTONAVIRO et al. 1989], the appearance of a colouring of the medium can be noted due to the formation of an absorbing complex, a complex which disappears at the optimum level of coagulation-flocculation. The same phenomenon is observed in the case of our tests on catechol and pyrogallol. The introduction aluminum sulphate in the presence of this compound could lead to the formation of a complex which would induce a batochrome effect and thus one displacement of the absorbance of UV towards the visible part of the spectrum. This is explained primarily by the colouring of the product formed.
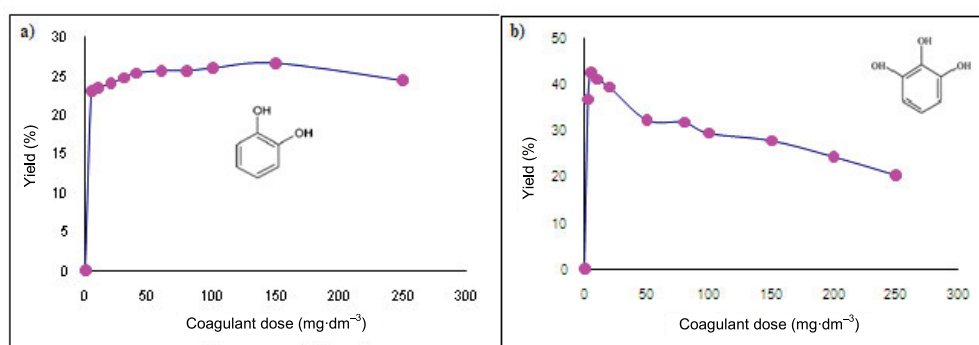

Fig. 1. Effect of coagulant dosage on the removal of phenolic compounds (20 mg·dm^{-3}): a) catechol, b) pyrogallol, pH not adjusted; source: own study

pH AND COAGULATION-FLOCCULATION

The purpose of this phase of the study is to determine the influence of pH on the elimination of catechol and pyrogallol. Aluminum sulphate is introduced corresponding to reach the elimination optimum (150 mg·dm^{-3} for catechol and 5 mg·dm^{-3} for pyrogallol). The adjustment of pH (range of pH between 2 to 11) was carried out during the fast phase of agitation, and it was carried out with the use of HCl (1N) and NaOH (2N) solutions. Figure 2 shows the evolution of outputs for each organic compound according to the initial pH of the solution.

We can observe that the optimum elimination of pyrogallol corresponds to acid pH, and the optimum elimination of catechol corresponds to base pH. A colouring was observed for pyrogallol from pH = 7 and for catechol from pH = 9 (Fig. 3). It should be noted that with an optimal pH, the improvement of outputs for the two substances is tested. Thus, the values of ideal efficiencies vary from 39.56% (pH not adjusted) to 45.33% (pH = 5) for pyrogallol, and from 26.70% (pH not adjusted) to 34.29% (pH = 9) for catechol.

The results obtained confirm literature data [ACHOUR, GUESBAYA 2005; JECKEL 1986; RAHNI 1994; REZEG, ACHOUR 2005; SEMMENS, AYERS 1985] concerning the elimination of organic molecules for pH ranging between 5 and 7 according to the structure of made up and natural coagulant (ferric sulfate or aluminum, ferric chloride). Moreover, with acid pH (5 to 6), the cation hydrolysed species of aluminum are dominating. A possible reaction would be the formation of soluble or insoluble complexes according to the structure of made up and natural functional groupings present. During our tests, that could apply to the coagulation-flocculation of pyrogallol.

The phenolic elimination of compounds decrease for pyrogallol and catechol. This can be explained by a competitive complexation of OH$^-$ for the medium with aluminum. The hydrolysed shapes of aluminum may consist of flocs comprising a mixture of amorphous Al(OH)$_3$ and species positively charged, such as Al(OH)$_2{}^+$ and Al(OH)$^{2+}$. Adsorption can be thus of electrostatic nature but also purely physical if the acid functional groupings are not dissociated. Another surface mechanism is complexation or an exchange of a ligand with hydroxyl groupings on the surface of the floc (specific adsorption).

In addition, the catechol has a higher output of elimination at pH 9. With base pH, it is possible that the compound is transformed into coloured quinoic compound which can be then combined with aluminum anions. An electrostatic load neutralisation mechanism by the anion shapes of partially dissociated organic compounds can then take place. It generally leads to significant variations of the Zêta potential measured on the flocs of aluminum hydroxide [JULIEN et al. 1994]. We can thus consider that a physical adsorption on the flocs of aluminum hydroxide bring into play Van Der Waals forces, hydrogen bonds, and a specific adsorption. The exchange of ligand on the Al(OH)$_3$ surface is thus probable but tiny, subject to the presence of two hydroxyl groupings in the ortho position of the aromatic compounds. This assumption has been formulated by LEFEBVRE [1990] during its tests of coagulation by iron.

EFFECT OF pH IN THE PRESENCE OF MINERAL SALTS

This phase of the study aims to assess the influence of pH on the removal of catechol and pyrogallol in the presence of calcium or magnesium salts. The introduced dose of aluminum sulfate is 150 mg·dm^{-3} for catechol and 5 mg·dm^{-3} for pyrogallol. For pH values between 2 and 11, results are summarised in Figure 4. Note that the adjusting of pH in solutions was carried out during the
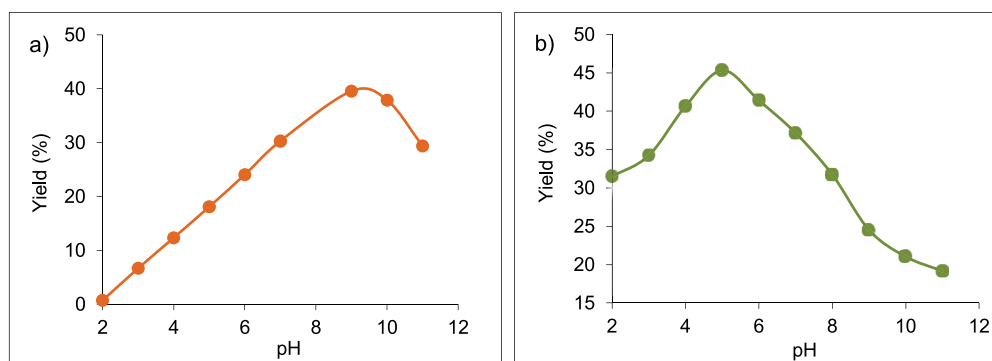

Fig. 2. Effect of pH on coagulation: a) pyrogallol (20 mg·dm^{-3}), coagulant dose is 5 mg·dm^{-3}, b) catechol (20 mg·dm^{-3}), coagulant dose is 150 mg·dm^{-3}; source: own study
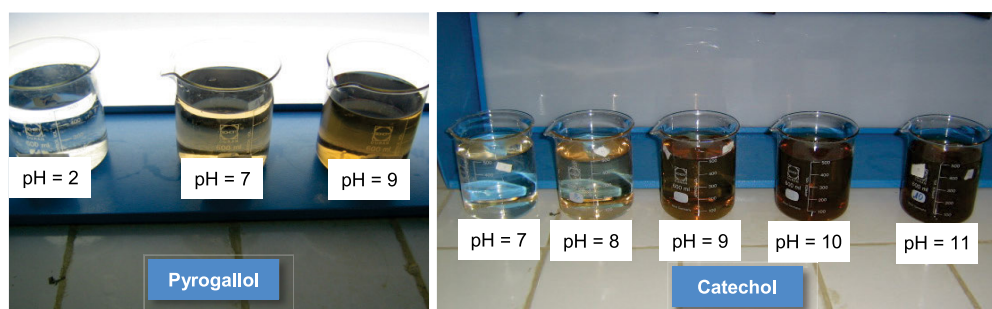

Fig. 3. Colouring for pyrogallol from neutral pH to base pH for catechol; source: own elaboration
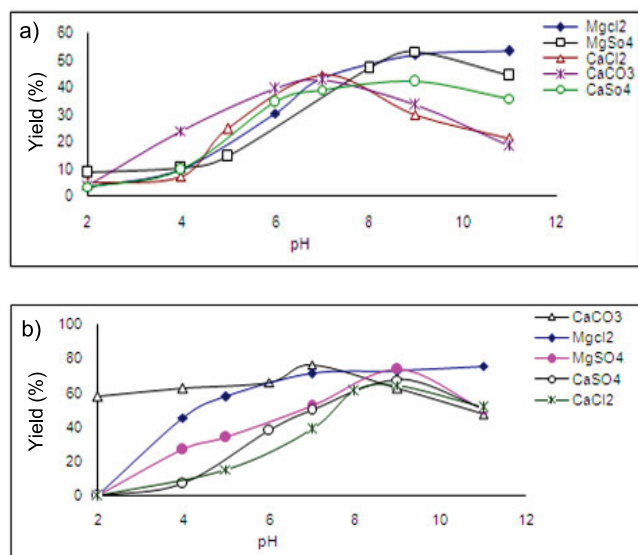
Fig. 4. Effect of pH during removal: a) catechol (20 mg·dm^{-3}) in the presence of mineral salts $[Ca^{2+}] = [Mg^{2+}] = 100$ mg·dm^{-3}, coagulant dose = 150 mg·dm^{-3}, b) pyrogallol (20 mg·dm^{-3}) in the presence of mineral salts $[Ca^{2+}] = [Mg^{2+}] = 100$ mg·dm^{-3}, coagulant dose = 5 mg·dm^{-3}; source: own study

phase of rapid agitation and carried out with solutions of HCl (1N) and NaOH (2N).

In the case of phenolic compounds tested, the calcium and magnesium ions lead to improved efficiency and the removal of catechol and pyrogallol. When adding calcium or magnesium salts, the removal of phenolic compounds increases gradually as the number of hydroxyl functional groups grow in the structure of these compounds in the pyrogallol > catechol order.

The addition, mineral salts appear to have an effect on the optimal range of coagulation-flocculation pH of simple organic compounds. Furthermore, the addition of SO_4^{2-}, Cl^- and CO_3^{2-} ions expands the range of optimum pH towards alkaline pH promoting the formation of anionic species of aluminum. These anions, such as SO_4^{2-}, Cl^- and CO_3^{2-}, can be considered as competing ligands of the hydroxyl ions. They can interfere with the precipitation of aluminum hydroxides by moving OH^- ions [CLEMENT et al. 1983; GUESBAYA 1998].

In the case of catechol, the optimum pH is lower than the pKa (pK$_1$ = 9.85 and pK$_2$ = 13) of this compound in the presence of calcium and magnesium salts. On the other hand, in the case of pyrogallol, it appears that the pKa (pK$_1$ = 9; pK$_2$ = 11.2 and pK$_3$ = 13) of the first and second function plays a role in the elimination of these compounds, especially in the presence of magnesium salt.

To explain the beneficial effect of calcium and magnesium, various hypotheses have been proposed [ACHOUR 2001; JECKEL 1986].

Calcium ions are thus likely to reverse the negative charge of hydrolysed species of aluminum even at base pH when the ionic strength is kept constant. Furthermore, the formation of Ca-organic compound complexes can directly lead to the formation of an insoluble form that can precipitate. The prior adsorption of Ca^{2+} ions on the flocs of aluminum hydroxide may also play a role of a bridge between separated organic compounds and aluminum hydroxide flocs. However, the results corresponding to the addition of divalent or monovalent cations and anions show that the presence of these ions leads to a competition between the promoter effect of Mg^{2+} and Ca^{2+} and the inhibitor one of sulfates, chlorides, and carbonates.

The effects of Ca^{2+} and HCO_3^-/CO_3^{2-} could be antagonistic, with a promotion effect of calcium and an inhibition effect of HCO_3^-/CO_3^{2-}.

EFFECT OF MINERAL SALTS CONTENT

This phase of the study was undertaken to test the effect of increasing levels of Ca^{2+} or Mg^{2+} on the removal of catechol and pyrogallol in distilled water. Flocculation tests were conducted on synthetic solutions of distilled water containing a fixed concentration (20 mg·dm^{-3}) of each compound tested. We added increasing amounts of Ca^{2+} or Mg^{2+} ranging from 10 to 400 mg·dm^{-3} and the solutions were coagulated by the same constant doses of aluminum sulfate, specifically 150 mg·dm^{-3} for catechol and 05 mg·dm^{-3} for pyrogallol. Tables 3 and 4 summarise different (Ec%) removal percentages of phenolic compounds tested in distilled water as compared to removal percentages in the presence of increasing amounts of Ca^{2+} or Mg^{2+} at the optimum removal, expressed by:

$$Ec\% = \frac{X_0 - X_1}{X_0} \, 100 \qquad (2)$$

where: X_0 and X_1 respectively represent removal percentages of the tested compound only in distilled water and in the presence of mineral salts.

The summarised results in this table show that the presence of calcium and magnesium ions leads to improved removal efficiencies compared to those observed in distilled water. However, in the case of catechol adjusted to pH = 9, the presence

Table 3. Changes (in %) of removal of pyrogallol in the presence of mineral salts

Specification	Distilled water without adding salts		Mineral salts				
			MgSO$_4$, 7H$_2$O	MgCl$_2$, 6H$_2$O	CaSO$_4$, 2H$_2$O	CaCl$_2$, 2H$_2$O	
Adjusted pH	7	9	9	9	9	7	9
% removal	37.11	24.6	90.83	75.04	90.02	38.95	71.24
Ca^{2+} or Mg^{2+} content (mg·dm^{-3})	0	0	250	50	250	100	50
Ec%	–	–	72.92	67.22	72.67	4.72	65.47

Source: own study.

Table 4. Changes (in %) of removal of catechol in the presence of mineral salts

Specification	Distilled water without adding salts		MgSO$_4$, 7H$_2$O	MgCl$_2$, 6H$_2$O	CaSO$_4$, 2H$_2$O		CaCl$_2$, 2H$_2$O		CaCO$_3$	
Adjusted pH	7	9	9	9	7	9	7	9	7	9
% removal	30.3	39.5	52.3	51.8	53.3	37.3	64.7	57.5	57.2	44.8
Ca^{2+}or Mg^{2+} content (mg·dm^{-3})	0	0	100	150	5	50	150	50	150	80
Ec%	–	–	24.5	23.7	43	−5.81	53	31.3	46.9	11.89

Source: own study.

of salts of calcium sulfate results in a reduction of removal efficiency.

In solutions with pH close to neutral, the formation of significant amounts of aluminum hydroxide can take place. The latter then promotes physical adsorption or ligand exchange with the OH⁻ ions to the surface of the hydroxide. Hydrolysed cationic forms are negligible due to the high pH of these solutions. In addition, inorganic anions can strongly compete with hydroxides vis-à-vis the complexation of aluminum ions.

Moreover, the inhibitory effect of sulphates and bicarbonates could be explained by the adsorption of these anions on metal hydroxides, thus lowering the surface charge or even at the verge of changing the sign. Under our experimental conditions, the following anions are ranked in an ascending order of their inhibitory power vis-à-vis the removal of phenolic compounds: $SO_4^{2-} > Cl^- > CO_3^{2-}$. When adding CaCO$_3$, a colouration of the medium is observed due to the formation of a complex for pyrogallol and catechol.

This coloration or complex does not disappear for optimum coagulation-flocculation; it's possible that these compounds are converted into coloured quinone compounds.

The possible explanation of this effect is that pH evolves towards clearly base values, favoring the formation of anionic species of aluminum, which results in the complexation of these species with transformed quinone compounds. However, this evolution is somewhat less pronounced when carbonates are introduced in their calcium form, which highlights the beneficial effect of calcium ions.

Thus, the more positive the potential (Ca^{2+} addition), the more simple the removal of organic compounds. The same is true when we add Mg^{2+}. On the other hand, the addition of the

anions, such as sulfates or bicarbonates, results in a significant decrease in the zeta potential. A competition between these negative ions and the dissociated forms of the simple organic compounds occurs during agitation.

FLOCCULATION OF ORGANIC COMPOUNDS IN MINERALISED WATER

The results in Figure 5 show that optimal removal efficiencies of these organic compounds vary from one water to another. Compared with results in distilled water, we can see that the mineralisation of diluted environments alters the elimination of organic compounds by coagulation-flocculation. It should be noted that the effect of total mineralisation appears to be beneficial for the removal of catechol and pyrogallol.

The presence of appreciable amounts of calcium and magnesium, contributing to the hardness of water, may also contribute to an improved elimination of tested organic compounds. The pH of water influences aluminum forms, and thus the predominant mechanism of flocculation. In highly mineralised and buffered waters with pH close to neutral promote the formation of significant amounts of aluminum hydroxide. Then, it would promote of a physical adsorption or a ligand exchange with OH⁻ ions to the surface of this hydroxide.

Comparison of the results of our tests with those obtained by other authors [ACHOUR 2001; GUESBAYA 1998; REZEG 2004] on simple organic compounds (phenol, resorcinol, pyrogallo, phloroglucinol, etc.), highlights some aspects of possible coagulation-flocculation mechanisms involving organic matter in natural water.
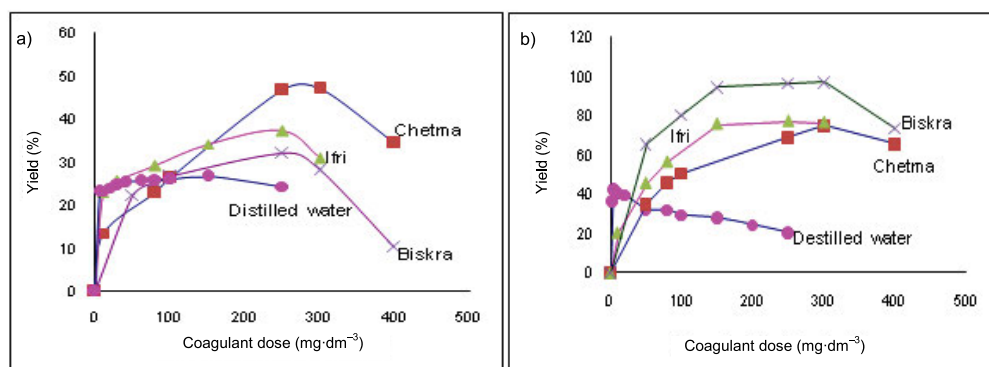
Fig. 5. Evolution of the percentage of removal of phenolic compounds (20 mg·dm^{-3}) in waters of variable mineralisation: a) catechol, b) pyrogallol; source: own study

Thus, the presence of mineral salts and their relative proportions, between promoter and inhibitory elements, influences directly the removal efficiency of organic matter and coagulant dose required. The chemical structure of organic compounds, including aromatic type, will also be critical to optimise its elimination.

The reactivity of phenolic compounds vis-à-vis the coagulant may depend not only on the chemical structure of these compounds and the importance of functional groups in the structure, but also on the mineral composition of water, and therefore on interactions of the mineral salts with functional groups of these compounds.

CONCLUSIONS

The experimental study we conducted has shown the elimination of catechol and pyrogallol from distilled water enriched with mineral salts and from mineral water in the region of Biskra.

The results highlighted the complexity of mechanisms involved and their close dependence of the nature and number of functional groups substituting the aromatic cycle. Thus, according to the bibliography, pyrogallol and catechol are partially eliminated. Indeed, aromatic compounds having two or three hydroxyl groups in ortho position can be eliminated. Moreover, the reactivity of these compounds appeared to be influenced by changes of pH and presure complex could be formed after the introduction of the aluminum sulfate in the catechol situations at basic pH and from the neutral pH for the pyrogallol.

The predominant mechanism is the reaction of these compounds on the surface of solid metal hydroxides. The hydrolysed species of aluminum can indeed be formed by flocs comprising an amorphous mixture of $Al(OH)_3$ and cationic forms of $Al(OH)^{2+}$ and $Al(OH)_2^+$. The adsorption can be electrostatic in its nature; but also merely physical, if the acid groups are not dissociated. Another surface mechanism can be represented by a complexing or ligand exchange with hydroxyl groups on the surface of flocs (case of pyrogallol). A mechanism for complexation with cationic or anionic soluble forms of aluminum may also occur depending on the pH either acidic or base.

To study the individual impact of each ion, we preferred to work in synthetic solution of distilled water enriched by Ca^{2+} and Mg^{2+} introduced in different forms. We were interested to determine the effect of the pH parameters and concentrations of mineral salts. The results and discussions made during this stage show the following conclusions.

The addition of mineral salts has shown a significant influence on the removal of phenolic compounds. The nature of inorganic ions presents in synthetic solutions, is an important factor in the reactivity of aluminum opposit organic molecules.

The presence of cations of Ca^{2+} and Mg^{2+} would be beneficial while the presence of anions of SO_4^{2-}, Cl^-, CO_3^{2-} is harmful. However, their inhibitory effect depends on the nature of the associated cation, as we could have observed by testing magnesium sulfate or calcium sulfate. Under our experimental conditions, magnesium ions play a preponderant role in relation to a calcium ions.

Regardless of the pH treatment, Ca^{2+} and Mg^{2+} lead to an improved removal efficiency of tested phenolic compounds; compared to those in distilled water only. However, the optimum pH for the elimination of these compounds, in the presence of calcium or magnesium salts, are close to neutral or base pH.

Anions, such as sulfates, chlorides or carbonates, can compete with the phenolic compounds OH^- and complexing aluminum.

In mineralised water, the removal efficiency of the tested phenolic compounds are closely related to mineralisation parameters, in particular the proportion of hardness compared to the total mineralisation. The reactivity of phenolic compounds opposite the coagulant may depend not only on the chemical structure of these compounds and the importance of functional groups in the structure but also on the mineral composition of water, and therefore mineral salts interactions with the functional groups of these compounds.

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