



Removal of Phenolic Compounds from Water by Coagulation-Flocculation and Effect of Hardness Salts

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Abstract: The objective of this study is to evaluate the coagulation-flocculation efficiency of the aluminum sulfate on the removal of phenolic compounds (Catechol and Pyrogallol). Interest has focused on the impact of inorganic components of hardness which are often present in the inorganic matrix of Algerian waters "calcium and magnesium". Trials tests Jar-test has been conducted on the two phenolic compounds dissolved in distilled water only, then enriched with minerals". The tests were performed on synthetic solutions of distilled water enriched with Ca and Mg ions, introduced in various forms (CaCl₂, 2H₂O; CaSO₄, 2H₂O; CaCO₃; MgCl₂, 6H₂O; MgSO₄, 7H₂O). Several reaction parameters were varied, the effect of pH and the influence of the salt content and have a better understanding of the mechanisms of interaction phenolic compounds/calcium and magnesium salts. The obtained results indicate that the process efficiency depends on the number and position of phenolic groups on molecules. The main mechanisms would be either a physical adsorption, an exchange of ligand or complexation on the floc surface of aluminum hydroxide. And the addition of inorganic salts appears to improve removal efficiencies of tested phenolic compounds and have an effect on the optimal pH range for coagulation. The application of this process on mineralized waters (water drilling) leads to improve yields compared with those obtained in distilled water.

Keywords: Phenolic Compounds, Mineral Salts, Coagulation-flocculation, Aluminum Sulfate, Hardness Salt

1. Introduction

Groundwater and surface water contain both dissolved and suspended particles, comprising molecules with very complex structures of high molecular weight; but also, simple organic compounds (phenols, amino acids, sugars...) [1]. The entrance of phenolic compounds into the aquatic environment results from natural, industrial, domestic and agricultural activities. Their presence may be due to the degradation or decomposition of natural organic matter present in the water, through the disposal of industrial and domestic wastes into water bodies and through runoffs from agricultural lands [2, 3]. These chemicals, upon entry into the

water, have the tendency of undergoing transformations into other moieties that can even be more harmful than the original compounds. This transformation is normally due to their interaction with physical, chemical and biological or microbial factors in the water [4].

Phenolic compounds have been enlisted by the United States Environmental Protection Agency (USEPA) and the European Union (EU) as pollutants of priority concern. This enlistment is due to the fact that these chemicals are noted to be toxic and have severe short and long term effects on humans and animals [5]. The occurrence of phenolic compounds in the aquatic environment is therefore not only objectionable and undesirable but also poses a danger as far as human health and wildlife are concerned. 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 wastewaters prior to their disposal into water bodies so as to minimize the devastating effects of these chemicals on human and aquatic lives [6].

Many processes of treatment can be used for the elimination of the organic matter such as adsorption on activated carbon, filtration on sand, the exchange of ions and filtration on membrane [7,-10]. Currently, in the conventional stations of treatment, the process of coagulation flocculation is mainly used for the elimination of the organic matter [11]. A notable reduction in the humic substances was observed during various work of optimization of coagulation-flocculation [12-14]. The reagents used are generally coagulants containing salts of aluminum or iron [15]. In addition and to allow a better explanation of the mechanisms intervening between these substances and the coagulants, various research tasks related to simple organic molecules [16-19] of which structure chemical the most basic structure of the humic substances approaches.

However, most of this work has been conducted in mediums of dilution of very weak ionic force, even null and especially out of distilled water. However, certain work could show that mineral salt, by individual or synergistic effects, could influence the effectiveness of the flocculation of matter organics watery [12, 20-22].

Moreover, the influence of mineral salts on the flocculation efficiency of organic compounds has been little studied and involved only humic substances [23-26]. Then it is to highlight and clarify the impact of salts commonly found in the water to be treated, the observed effects whether are beneficials or inhibitors in relation to the process of removing phenolic compounds by the sulfate aluminum, as well as the mechanisms involved between these compounds and the coagulant.

The waters of the Northern Sahara in Algeria are highly mineralized and are characterized by excessive hardness with high levels of calcium, magnesium, chlorides, sulfates and sodium [27, 28].

We have undertaken to evaluate, in this study, 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 or magnesium salts. The application of such method was also performed on mineralized waters in the region of Biskra where located in the South East of Algeria (drilling water).

2. Materials and Methods

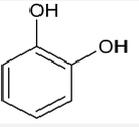
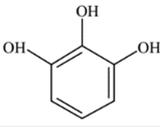
All experimental tests were carried out on underground and surface of hydraulic research laboratory (LARHYSS) of the University of Biskra (Algeria).

2.1. Preparation of Solutions of Phenolic Compounds

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/l of each of the phenolic compounds tested. Table 1 shows their characteristics.

Table 1. Characteristics and chemical structure of phenolic compounds.

Common name	Catechol	Pyrogallol
Chemical name	1,2-Dihydroxybenzene	1,2,3-trihydroxybenzene
Chemical Structure		
Molecular formula	C ₆ H ₆ O ₂	C ₆ H ₆ O ₃
Molar Mass (g/mole)	110.11	126.11
pK-OH at 20°C	pK ₁ =9.25 pK ₂ =13	pK ₁ =9.0 pK ₂ =11.2 pK ₃ =14
Purity (%)	99	98
Reference	[29]	[30]

2.2. Dilution Waters of Phenolic Compounds

The distilled water used throughout this study has a conductivity varying between 2 and 5 μs/cm and a pH varying between 6.18 and 6.73. Aqueous dilution media environments are groundwater initially free of organic matter from boreholes located in Biskra region (South-east of Algeria) using for drinking water (water of Ifri, Chetma and Biskra). The main physico-chemical characteristics of these waters have been determined in accordance with the standard methods of analysis [31] (Table 2).

2.3. Preparation of Coagulant Solution

The coagulating reagent used was aluminum sulfate [Al₂(SO₄)₃, 18H₂O], with a molar mass equal to 666.6 g/mol. A stock solution of 10 g/l was prepared periodically in distilled water.

Table 2. Physico-chemical characteristics of dilution water of phenolic compounds.

	Dilution water	Water of Ifri	Water of Chetma	Water of 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/l)		80	320	246.4
Mg ²⁺ (mg/l)		19.20	86.4	126.72
Cl (mg/l)		80	988	590
SO ₄ ²⁻ (mg/l)		45	485	690
Na ⁺ (mg/l)		21	450	255
K ⁺ (mg/l)		3	8	5
Conductivity (ms/cm)		0.439	1.99	2.95

2.4. 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 tower/min. The speed was subsequently reduced to 60 rpm for a period of half an hour [31]. After a decantation of 30 minutes, the supernatant was recovered and filtered under vacuum on an

OSMONICS INC membrane of 0.45 μm porosity. The filtrate then was assayed by spectrophotometric analysis.

2.5. 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 $\lambda=270$ nm for the Catechol [29] and the Pyrogallol [30]. The residual concentrations of the compounds are determined from the calibration curves (absorbance $A=f(C_0)$) for each dilution medium. The elimination yield of the compound is defined by:

$$Y\%=(1-C_f/C_0).100 \quad (1)$$

C_0 : initial concentration of the phenolic compound expressed in mg/l.

C_f : residual concentration at the end of the test expressed in mg/l.

3. Results and Discussions

3.1. Effect of the Coagulant Dose

The tests of coagulation-flocculation are carried on synthetic solutions containing a constant concentration of phenolic organic compounds (20 mg/l) out of distilled water (pH not adjusted). Increasing doses of aluminum sulfate are introduced in the various solutions. Figure 1 presents the final results obtained. They show that removal efficiencies of organic compounds evolve differently, depending on the chemical structure of these compounds. Moreover, the effect of the coagulant dose introduced varies from one compound to another.

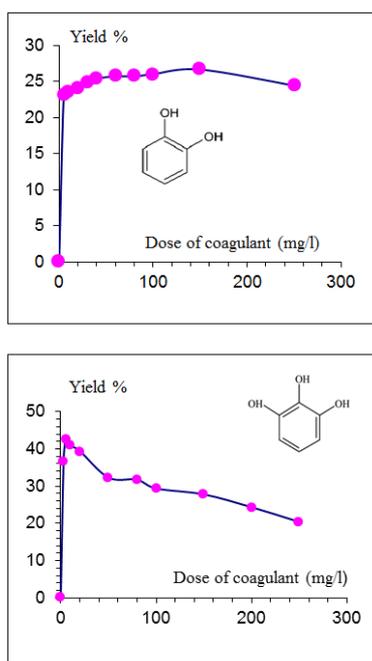


Figure 1. Effect of coagulant dosage on the removal of phenolic compounds (20mg/l), pH not adjusted.

In view of the results presented, It seems possible to distinguish that Pyrogallol and Catechol are partially eliminated under the conditions of our tests. At the optimum, the Pyrogallol removal reaches is 42.62% while that Catechol reaches is 26.70%. These yields are observed respectively for a dose of 150 mg/l and 05 mg/l of aluminum sulfate. Moreover, we can see that the evolution of the elimination efficiencies 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 sulfate dosage.

While referring to the bibliographical data [16, 17, 32], the aromatic compounds presenting two acid groupings into contiguous (COOH or OH) facilitates the elimination of the organic molecules by coagulation-flocculation. It is the case of Pyrogallol under our experimental conditions. This, contrary to aromatic compounds with only one function such as the phenol or 2 noncontiguous functions such resorcinol [18] because probably of the instability of the complex formed [24]. Former works [33, 34] had also been able to highlight which the phenol and phloroglucinol were very little eliminated whatever the amount from coagulant.

While always referring to the bibliography, two great types of mechanisms are distinguished [16, 24] to explain the interactions between the organic matter and the aluminum and ferriiron oxo-hydroxides. The first corresponds to the reactions of the organic matter on the surface of the oxo-hydroxy-metal solids. It acts for this last mechanism of the phenomenon of adsorption which will be able to be established by various types of reactions. The second mechanism considers reactions between the organic matter and the metal hydrolyzed soluble forms.

Using experiments of coagulation-flocculation by the iron salt addition with molecules like the Catechol, the salicylic acid or the tannic acid [35], it is noted the appearance of a coloring of the medium by formation of a complex absorbing in the visible one, coloring and complex who disappear for the optimum from coagulation-flocculation. The same one phenomenon is observed in the case of our tests on the Catechol and Pyrogallol. The introduction aluminum sulfate in the presence of this compound could lead to formation of a complex which would induce a bathochrome effect and thus one displacement of the absorbance of UV towards the visible one. This is explained primarily by the coloring of the formed product.

3.2. Influence pH of Coagulation-flocculation

The purpose of this phase of the study is to appreciate the influence of the pH on the elimination of the Catechol and Pyrogallol. Aluminum sulfate amounts introduced corresponding to the optimum of their elimination (150 mg/l for the Catechol and 5 mg/l for Pyrogallol). The adjustment of the pH (range of pH between 2 to 11) was carried out during the fast phase of agitation, and was carried out grace to solutions of HCl (1N) and NaOH (2N). We present, on figures 2 and 3, the evolution of the outputs of elimination of each organic compound according to the initial pH of the solutions.

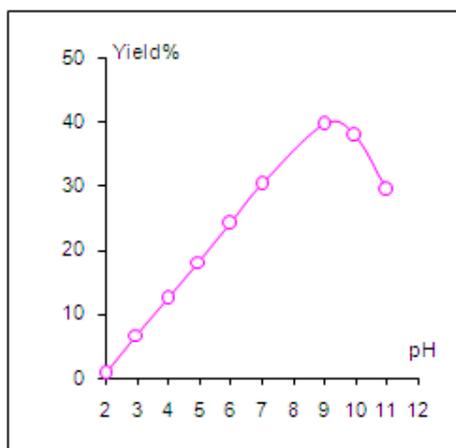


Figure 2. Effect of the pH on the coagulation of Pyrogallol (20mg/l), coagulant dose is 05 mg/l.

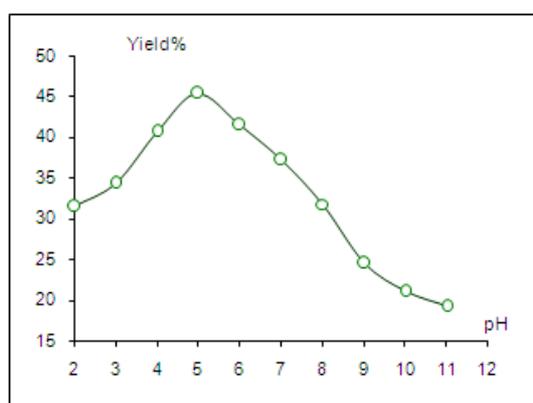


Figure 3. Effect of the pH on the coagulation of Catechol (20mg/l), coagulant dose is 150 mg/l.

We can observe that the optimum of the elimination of Pyrogallol corresponds to pH acids, and on the other hand the optimum of the elimination of the Catechol corresponds to a basic pH. A colouring was observed for Pyrogallol from pH=7 and for the Catechol from pH=9 (Figure 4). It should be noticed that with optimal pH, the improvement of the outputs appreciable for the two made up ones is tested. Thus, the values of the ideal efficiencies pass from 39.56% to pH not adjusted to 45.33% to pH=5 for Pyrogallol, and from 26.70% with pH not adjusted to 34.29% with pH=9 for the Catechol.

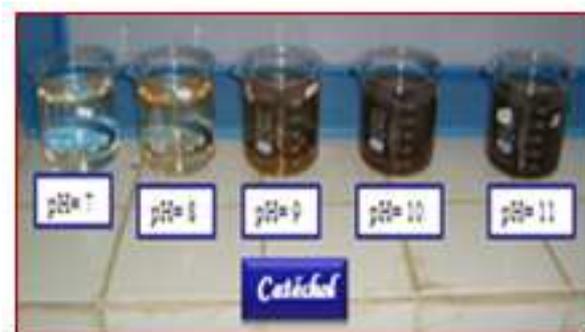


Figure 4. Appearance of a colouring for Pyrogallol starting from the neutral pH and of basic pH for the Catechol.

The results obtained confirm the bibliographical data [17, 18, 32, 33, 36] concerning the elimination of organic molecules for pH ranging overall between 5 and 7 according to the structure of made up as well as nature of the coagulant (ferric sulfate or of aluminum, ferric chloride). Also let us recall that with acid pH (5 to 6), the cation hydrolyzed species of aluminum are dominating. The possible reactions would be the formation of soluble or insoluble complexes according to the structure of made up and nature of the functional groupings present. During our tests, that could apply to the coagulation-flocculation of Pyrogallol.

We as could observe as with pH basic superiors with 7, the outputs of phenolic elimination of the compounds decrease for Pyrogallol and the Catechol. This can be explained by a competitive complexation of the OH⁻ of the medium with aluminum. The hydrolyzed shapes of aluminum can be consisted flocs comprising a mixture of Al(OH)₃ amorphous 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 mechanism of surface would consist of a complexation or an exchange of ligand with the groupings hydroxyls on the surface of the floc (specific adsorption).

In addition, the Catechol has a higher output of elimination with pH 9. With basic pH, it is possible that this compound is transformed into colored quinonic compound which can be then complexed with the anion species of aluminum. An electrostatic mechanism of neutralization of loads by the anion shapes of the 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 [37]. We can thus consider for these two made up a physical adsorption on the flocs of aluminum hydroxide bringing into play forces of Van Der Waals or hydrogen bonds, and a specific adsorption. The possibility of exchange of ligand on the Al(OH)₃ surface is thus probable but tiny in the only condition that there' is the presence of two groupings hydroxyls in position ortho in the case of the aromatic compounds. This assumption is formulated by [24] during its tests of coagulation by iron.

3.3. 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/l for Catechol and 05 mg/l for Pyrogallol. For pH values between 2 and 11, we produced the results summarized in figures 5 and 6. Note that adjusting the pH of solutions was carried out during the rapid phase of agitation, and carried out with solutions of HCl (1N) and NaOH (2 N).

On the tested phenolic compounds, the calcium and magnesium ions lead to improved efficiency of removal of Catechol and Pyrogallol. When adding calcium or magnesium salts, the percentage of removal of phenolic compounds tested increases gradually as the number of hydroxyl functional groups increases in the structure of these compounds in the order Pyrogallol > Catechol.

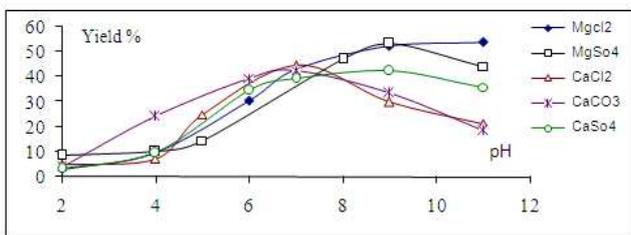


Figure 5. Effect of pH on the removal of Catechol (20 mg/l) in the presence of mineral salts [Ca²⁺]=[Mg²⁺]=100 mg/l, the coagulant dose=150 mg/l.

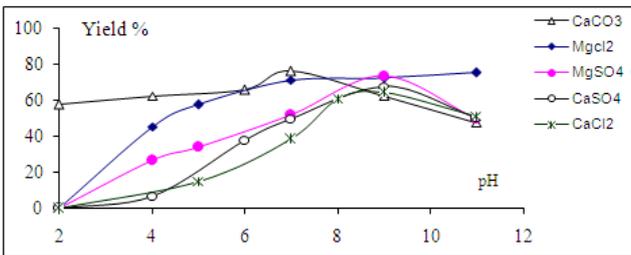


Figure 6. Effect of pH on the removal of Pyrogallol (20 mg/l) in the presence of mineral salts [Ca²⁺]=[Mg²⁺]=100 mg/l, the coagulant dose=05 mg/l.

The addition of mineral salts appears to have an effect on the optimal range of coagulation-flocculation pH of simple organic compounds. Furthermore, the addition of SO₄²⁻, Cl⁻ and CO₃²⁻ ions expands the range of optimum pH towards alkaline pH favoring the formation of anionic species of aluminum. These anions, such as SO₄²⁻, Cl⁻ and CO₃²⁻ can be considered as competing ligands of the hydroxyl ions. They can interfere with the precipitation of aluminum hydroxides by moving the OH⁻ ions [25, 38].

In the case of the Catechol, The optimum pH is lower than the pKa (pK₁=9.85 and pK₂=13) of this compound in the

presence of the calcium salts and the magnesium salts. On the other hand, in the case of Pyrogallol, it appears that the pKa (pK₁=9; pK₂=11.2 and pK₃=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 by extension, various hypotheses have been advanced [36, 39].

Calcium ions are thus likely to reverse the negative charge of the hydrolyzed species of aluminum even at basic 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 Ca²⁺ ions on the flocs of aluminum hydroxide may also play a role of bridge between the 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 Mg²⁺ and Ca²⁺ and inhibitor one of sulfates, chlorides and carbonates.

The effects of Ca²⁺ and HCO₃⁻/CO₃²⁻ could be antagonists with a promoting effect of calcium and an inhibitory effect of HCO₃⁻/CO₃²⁻.

3.4. Effect of Content in Mineral Salts

This phase of the study was undertaken to test the effect of increasing levels of Ca²⁺ or Mg²⁺ 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/l) of each compound tested. We added increasing amounts of Ca²⁺ or Mg²⁺ ranging from 10 to 400 mg/l and the solutions are coagulated by the same constant doses of aluminum sulfate. It is 150 mg/l for Catechol and 05 mg/l for Pyrogallol. Tables 3 and 4 summarizes the values of differences (Ec%) of removal percentages of phenolic compounds tested in distilled water, compared to removal percentages in the presence of increasing amounts of Ca²⁺ or Mg²⁺ at the optimum removal, expressed by:

$$Ec\% = \frac{X_0 - X_1}{X_0} \times 100 \quad (2)$$

X₀ and X₁ respectively represent the removal percentages of the tested compound only in distilled water and in the presence of mineral salts.

Table 3. Summary of changes in percentages of removal of Pyrogallol in the presence of mineral salts.

Pyrogallol	mineral Salts					
	Distilled wate without adding 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	7	9
% removal	37.11	24.6	90.83	75.04	90.02	38.95 71.24
Ca ²⁺ or Mg ²⁺ content (mg/l)	0	0	250	50	250	100 50
Ec%	-	-	72.92	67.22	72.67	4.72 65.47

Table 4. Summary of changes in percentages of removal of Catechol in the presence of mineral salts.

Catechol	mineral salts		Distilled water without adding salts	$MgSO_4 \cdot 7H_2O$	$MgCl_2 \cdot 6H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCl_2 \cdot 2H_2O$	$CaCO_3$		
adjusted pH	7	9	9	9	9	7	9	7	9	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/l)	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

The summarized 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 of salts of calcium sulfate results in a degradation of removal efficiencies.

In solutions with pH close to neutrality, the formation in significant amounts of aluminum hydroxide can take place. The latter then promotes the phenomenon of physical adsorption or ligand exchange with the OH^- ions to the surface of this hydroxide. Hydrolyzed 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 ion.

Moreover, the inhibitory effect of sulfates and bicarbonates could be explained by the adsorption of these anions on the metal hydroxides thus lowering the surface charge or even at the limit changing of sign. Under our experimental conditions, the following anions are ranked in ascending order of inhibitory power vis-à-vis the removal of phenolic compounds: $SO_4^{2-} > Cl^- > CO_3^{2-}$. When adding $CaCO_3$, a coloration of the medium is observed by 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 colored quinone compounds.

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

Thus, the more positive the potential (Ca^{2+} addition) and the more simple the removal of organic compounds. The same is true for the addition of 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.

3.5. Flocculation of Organic Compounds in Mineralized Waters

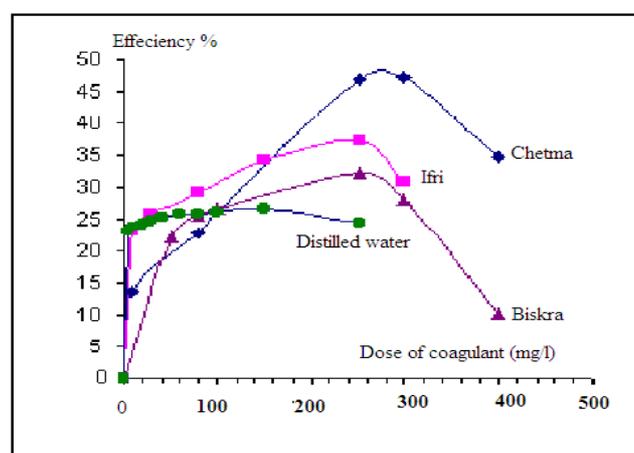
The results in figure 7 show that optimal removal efficiencies of these organic compounds vary from one water to another. Compared with results in distilled water, we can see that the mineralization of environments of dilution

appears to alter the elimination of organic compounds by coagulation-flocculation. It is necessary to note that the effect of total mineralization appears to be beneficial in the removal of Catechol and Pyrogallol.

The presence of appreciable amounts of calcium and magnesium, forming the hardness of water, may also contribute to improving the elimination of tested organic compounds. The pH of the water conditions the aluminum forms and thus the predominant mechanism of flocculation. In highly mineralized and buffered waters with pH close to neutrality, the formation in significant amounts of aluminum hydroxide can take place. Then it would promote of a physical adsorption phenomenon or a ligand exchange with the OH^- ions to the surface of this hydroxide.

Comparing the results of our tests with those obtained by other authors, [25, 39, 40] on simple organic compounds (phenol, resorcinol, pyrogallo, phloroglucinol, etc....), highlights some aspects of the possible mechanisms of coagulation-flocculation of organic matter in natural waters. Thus, the presence of mineral salts and their relative proportions, between promoter and inhibitory elements, influences directly on the removal efficiency of organic matter and coagulant dose required. The chemical structure of organic compounds, including aromatic type, will also be critical in optimizing its elimination.

The reactivity of the phenolic compounds vis-à-vis the coagulant may be dependent; 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 interactions of the mineral salts with the functional groups of these compounds.



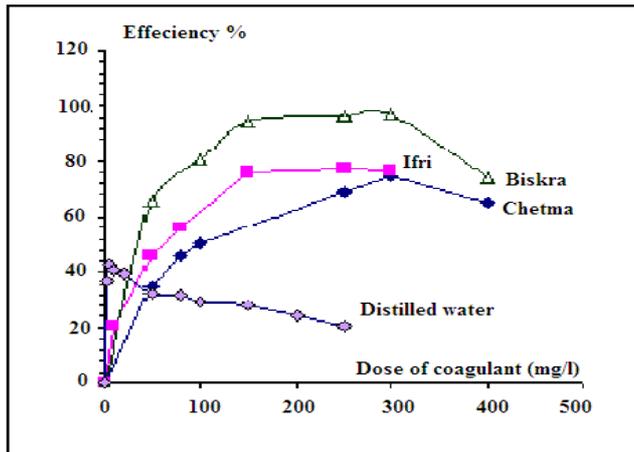


Figure 7. Evolution of the percentage of removal of phenolic compounds (20 mg/l): a) Catechol; b) Pyrogallol in waters of variable mineralization.

4. Conclusion

The experimental study we conducted was devoted to the elimination, by flocculation with aluminum sulfate, of Catechol and Pyrogallol in distilled water enriched with mineral salts and in mineral waters in the region of Biskra.

The results highlighted the complexity of the mechanisms involved and their close dependence of the nature and number of functional groups substituting the aromatic cycle. Thus, according to the bibliography, the Pyrogallol and the Catechol are partially eliminated. Indeed, aromatic compounds having two or three hydroxyl groups in ortho position are eliminated. Moreover, the reactivity of these compounds appeared to be influenced by the variation of the pH and a 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 would be a reaction of these compounds on the surface of solid metal hydroxides. The hydrolyzed species of aluminum can indeed be formed by flocs comprising an amorphous mixture of $\text{Al}(\text{OH})_3$ and cationic forms of $\text{Al}(\text{OH})_2^+$ and $\text{Al}(\text{OH})_2^+$. The adsorption can be of electrostatic 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 the hydroxyl groups on the surface of the floc (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 basic.

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 showed 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 observe by testing magnesium sulfate or calcium sulfate. Under our experimental conditions, the magnesium ion plays a preponderant role in relation to calcium ions.

Regardless of the pH treatment, the 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 of elimination of these compounds, in the presence of calcium or magnesium salts, are close to neutral or basic.

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

Mineralized water, the removal efficiency of the tested phenolic compounds are closely related to the mineralization parameters; more particularly the proportion of hardness compared to the total mineralization. The reactivity of the phenolic compounds opposit the coagulant may be dependent, not only on the chemical structure of these compounds, 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.

References

- [1] E. Lefebvre, J. P. Croue. Modification of the organic matter in conventional purification treatment of water, *Rev. Sci. Water*, 8, pp 463-479. (1995).
- [2] J. Wallace, "Phenol" In: Kirk-Othmer encyclopedia of chemical technology. 4th Ed.: John Wiley and Sons, New York, pp. 592-602. (1996).
- [3] W. Kherifi, L. Hecini, F. Bekiri, H. Kherici-Bousnoubra «Faecal contamination of water in the Lake Mellah and its catchment area, north-eastern Algeria». *Journal of Water and Landdevelopment*. No. 42 (VII-IX) p. 110-116. (2019). DOI: 10.2478/jwld-2019-0051.
- [4] S. J. Kulkarni and D. J. P. Kaware. Review on research for removal of phenol from waste water. *International Journal of Scientific and Research Publications*, 3, pp. 1-4, (2013).
- [5] Mahugo-Santana, Z. Sosa Ferrera., M. E. Torres-Padrón and J. Santana-Rodríguez. Analytical methodologies for the determination of nitroimidazole residues in biological and environmental liquid samples: a review. *Analytica Chimica Acta* 665, pp. 113-122, (2010).
- [6] William W. Anku, Messai A. Mamo and Penny P. Govender.; Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods; Chapter 17; pp 24. (2017). <http://dx.doi.org/10.5772/66927>.
- [7] J. P. Croue, Violleau D., Bodaire C. & Legube B; Elimination of hydrophobic and hydrophilic constituents by anion exchange resin. *Water Science and Technology*, 40, 207-214. (1999).

- [8] Z. Domany, I. Galambos, G. Vatai & E. Molnar, Humic substances elimination from drinking water by membrane filtration. *Desalination*, 145, 333-337. (2002).
- [9] Humbert H., H. Gallard, H. Suty & J. P. Croue, Natural Organic Matter (NOM) and pesticides elimination using a combination of ion exchange resin and powdered activated carbon (PAC). *Water Research*, 42, 1635-1643. (2008).
- [10] Bacha N., Achour S. Essais de coagulation de l'acide pyromellitique en milieux aqueux minéralisés, *Journal of Water and Environmental Sciences*, Vol. 1, Numéro spécial ICWR 2, pp. 235-242. (2017).
- [11] Wang G. S., S. F. Kang, H. J. Yang, S. Y. Pai, H. W. Chen, Elimination of dissolved natural organic matter from source water with alum coagulation. *Environmental Technology*, 23, 1415-1423. (2002).
- [12] S. Achour, N. Guesbaya; Tests for flocculation of humic substances in aqueous mineralized media, *Larhyss Journal*, 5, Juin, 171-178. University of Biskra, Algeria. (2006).
- [13] A. Rezeg. Study of the mechanisms of elimination of organic matter by a combined flocculation-adsorption process in the presence of metal oxides and salts, These of Doctorate in hydraulic sciences, University of Biskra. Algeria. (2010).
- [14] N. Bacha, S. Achour, Influence of reaction parameters on the stoichiometry of aluminum sulfate/pyromellitic acid in distilled water, *LARHYSS Journal*, n°13, pp. 109-123. (2013a).
- [15] Degremont, *Memento technique of water*, 10th Edition. Paris. France. (2005).
- [16] E. Lefebvre, B. Legube, Coagulation-flocculation by ferric chloride of some acids and phenols in aqueous solution, *Wat. Res.*, Vo. 27, N°3, 433-447. (1993).
- [17] Rahni M., Coagulation-flocculation of some organic compounds by ferrous iron in aqueous medium: Study of mechanism and comparison with adsorption, Thesis of Doctorate, University of Poitiers, France. (1994).
- [18] Achour S., N Guesbaya, Coagulation-flocculation by aluminum sulfate of phenolic organic compounds and humic substances. *Larhyss Journal*, 04, 153-168, University of Biskra, Algeria. (2005).
- [19] HECINI. L and Samia ACHOUR Tests and mechanisms for flocculation of phenylalanine and catechol in the presence of «aluminum sulfate». *LARHYSS journal* N° 29 pp 341-354. (2017).
- [20] H. Bernhardt, O. Hoyer, B. Lusse. The addition of calcium to reduce the impairment of flocculation by allogenetic organic matter, *Z. Wasser. Abwasser. Forsch*, 19, 219-228. (1986).
- [21] L. Hecini, S. Achour., Study of the interactions of aluminum sulphate with phenolic compounds and effect calcic and magnesichardness water hardness. *Courrier du savoir journal* n° 18, pp. 83-88. University of Biskra. Algeria. (2014).
- [22] L. Hecini, S. Achour; Incidence of calcic, sulfates and phosphates salts on the coagulation-flocculation of organic compounds by aluminium sulfate. *International Journal of «Engineering Research in Africa»*. ISSN: 1663-4144, Vol. 34, pp 59-69. (2018). Doi: 10.4028/www.scientific.net/JERA.34.59.
- [23] M. Mazet, T. Mossa Wais, Influence of mineral salts on the adsorption of humic acids on iron hydroxide preformed flocs, *Envir. Techno*, 12, 725-730. (1991).
- [24] Lefebvre, Coagulation of aquatic humic substances by ferric iron in aqueous environment. Effect of preoxidation, Doctorate Thesis, Poitiers University. (1990).
- [25] N Guesbaya, Elimination of organic compounds by the coagulation-flocculation process, Magister's thesis in hydraulic sciences, University of Biskra. Algeria. (1998).
- [26] F. Afoufou, S. Achour, Effect of potassium permanganate preoxidation on the elimination of humic substances by flocculation, *Courrier du Savoir*, N°2, 41-46 (2002).
- [27] N. Bouchahm; L. Hecin, W. Kherifi,; Softening of groundwater in the eastern region of the Northern Algeria Sahara: Case of the Biskra region. ISSN: 1718-8598 *Revue des Sciences de l'Eau* 29 (1), 37-48 (2016).
- [28] F. Bouchemal., N. Bouchahm et S. Achour, Quality of Waters of Aquifer Webs of Biskra Region. *J. Fundament. Appl. Sci.*, 3 (1), 35-46. (2011).
- [29] Suresh S., V. C. Srivastava and I. M. Mishra.: Adsorption of catechol, resorcinol, hydroquinone, and their derivatives: a review. *International Journal of Energy and Environmental Engineering*. Springer 3: 32. 19 p. (2012).
- [30] G. Upadhyay, P. G. Satya, Om Prakash, P. S. Mahendra; Pyrogallol-mediated toxicity and natural antioxidants: Triumphs and pitfalls of preclinical findings and their translational limitations. 183, 333-340, (2010).
- [31] J. Rodier, B. Legube, N. Merlet, R. Brunet, *Water analysis - 9th edition, - Natural waters, wastewater, seawater: Water analysis*, 9th edition, Paris, Dunod. (2009).
- [32] M. J. Semmens, K. Ayers, Removal by coagulation of trace organics from Mississippi River, *Journal AWWA*, 77, 5, 79-84. (1985).
- [33] A. Rezeg, S. Achour. Elimination of aromatic organic acids by coagulation-flocculation with aluminum sulfate, *LARHYSS Journal*, N°4, 141-152. (2005).
- [34] L. Hecini, S. Achour, Elimination of phenol and pyrogallol by coagulation-flocculation, journal "Sciences, Technologies and Developpement. N° 8- VOL. II- ANDRU, 2011, El Harrach, Algeria, (2011).
- [35] E. Rakotonaviro, C. Tondre., J. Y. Bottero, J. Mallevalle. Complexation of aluminium (III) polymerise et hydrolyse with ions salicylates, *Wat. Res.*, 23, 9, 1137-1145. (1989).
- [36] M. Jeckel. Interactions of humic acids and aluminum salts in flocculation process, *Wat. Res.*, 20, 1535-1542. (1986).
- [37] F. Julien, B. Gueroux, M. Mazet, Comparison of the elimination of organic molecules by coagulation-flocculation and by adsorption on preformed metal hydroxide flocs, *Water. Res.* 28, 12, 2567-2574. (1994).
- [38] M. Clement, R. Seux, B. Moussa, Studies of the factors determining the leak aluminum in drinking waters prepared from clarified water with salts of this metal, *Trib. Cebedeau*, 480, 336, 469-481. (1983).
- [39] S. Achour, Effect of chlorination processes, flocculation and adsorption on the evolution of organic and inorganic compounds in natural waters, Doctorate thesis -Tizi-Ouzou University, (2001).

- [40] A. Rezeg. Elimination of hydroxylated and carboxylated organic acids by coagulation-flocculation with aluminum sulfate, Magister Thesis in hydraulic science, Biskra University. (2004).