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CATECHOL ELIMINATION BY COAGULATION-FLOCCULATION PROCESS USING ALUMINUM SULFATES

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Received: 12/09/2021 Accepted: 23/02/2022 Published online: 15/03/2022

Abstract

The objective of this work is to observe the effectiveness of the coagulation flocculation by aluminium sulfate on the removal of organic compound based on phenolic (catechol). Jar-Test tests were performed on this compound dissolved in distilled water without pH adjustment and several reaction parameters were varied such as the coagulant dose, the pH effect and the initial concentration of catechol. The results obtained indicate that :

The percentage removal of 1 mg/l of catechol is appreciable and reaches a value of 86.67% for a dose of 5 mg/l of aluminum sulfate. The percentage of removal of the initial concentration of 2 mg/l is also important, the maximum yield obtained is about 56.25 % for a dose of 30 mg/l of aluminum sulfate. The percentage of removal of the initial concentration of 5 mg/l is medium; the optimum yield obtained is about 20 % for a dose of 20 mg/l of aluminum sulfate. Although the two remaining initial concentrations 10 and 20 mg/l are not well removed, the maximum yield obtained is of the order of 8.33% and 6.67% for a dose of 50 mg/l and 120 mg/l aluminum sulfate respectively. Then no stoichiometric law could clearly be demonstrated. In addition the process efficiency depends on the number and position of phenolic groups on molecules. Finaly, The main mechanisms would be either a physical adsorption, an exchange of ligand or complexation on the floc surface of aluminum hydroxide.

Keywords: *Aluminium sulfate, Coagulation-flocculation, Jar-Test, Catechol elimination.*

I. Introduction

Catechol (1,2-dihydroxybenzene) is a widespread phenolic pollutant in many industrial effluents and is used in various applications. It is used as a reagent in photography, fur dyeing, rubber and plastic production and in the pharmaceutical industry [1; 2]. Skin contact with catechol causes eczematous dermatitis in humans. In addition, high doses of catechol can cause central nervous system (CNS) depression and prolonged elevation of blood pressure in animals [3]. The United States Environmental Protection Agency [4] has ranked phenols 11th on a list of 126 toxic chemicals that have been designated as priority pollutants and strict restrictions have been imposed by local authorities on the levels of phenolic contaminants in water and wastewater. According to Egyptian regulations, the concentration of phenols in industrial effluents should not exceed 0.05 to 1 mg/l to be discharged into wastewater [5]. Therefore, the removal of catechol from water or wastewater is of great importance. A number of technologies have been used for catechol removal from water and aqueous solutions. These include oxidation processes, ultrafiltration, biological methods, adsorption and coagulation-flocculation. It is a classical process used in drinking water production plants and also in primary wastewater treatment. The efficiency of this process depends on the composition of the aqueous medium, the nature of the coagulant introduced as well as the structure of the organic compounds to be eliminated, in particular the functional groups, which they carry [6].

The objective of this work is to study the evolution of the elimination of catechol by coagulation-flocculation with aluminum sulfate, at different concentrations. Different reaction mechanisms are proposed to explain the interactions between the hydrolyzed forms of the coagulant reagent and the proposed compound.

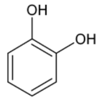
II. Material and methods

All the tests were carried out at the laboratory of the CRSTRA center (Center for Scientific and Technical Research on Arid Regions).

II.1. Preparation of solutions of organic compound

The organic compound tested is catechol has a hydroxylated (OH) ring in its structure. The product used in the laboratory is marketed by Aldrich of 99% purity. The determination of catechol was carried out on a spectrophotometer "UV/vis, Hack LANGE DR 6000" at a wavelength of 270 nm.

Table 1. Presents the main characteristics of catechol [7]

Common name	Catechol
Chemical name	1,2-Dihydroxybenzene
CAS	120-80-9
Chemical structure	
Molecular formula	$C_6H_6O_2$
Molecular weight (g/mol)	110.11
pK-OH	$pK_1 = 9.25$ $pK_2 = 13$
Purity %	99

We prepared a stock solution of 100 mg/l of this phenolic compound tested, this one was used on the one hand, in the preparation of the standard solutions during the determination of the calibration curve (figure 1), and on the other hand during the tests in synthetic solutions. During the period of our tests, we used distilled water which has a conductivity varying between 2 µs/cm and 5 µs/cm and a pH between 6.18 and 6.73.

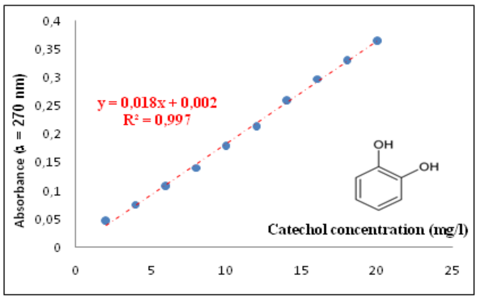


Figure 01 : Calibration curve of catechol in distilled water

II.2 Preparation of coagulant

As coagulant salt, aluminum sulfate powder $[Al_2(SO_4)_3\ ,18H_2O]$ was used. A stock solution of 10 g/l was prepared periodically by dissolving this powder in distilled water.

II.3 Description of the floculation tests

Jar-testing was performed on a six-stirrer flocculator (Fisher Flocculator 1198). This flocculator allows six tests to be performed simultaneously in 500 ml glass beakers. During the study, the solutions enriched with organic compounds and coagulant were subjected for 3 min to rapid stirring at 200 rpm. The speed was subsequently reduced to 60 rpm for half an hour. After settling for 30 min [8], the supernatant was collected for filtration through a syringe filter of pore size (0.2 µm) (figure 02).

Figure 02: Syringe filter (0.2 µm)

The filtrate was then assayed by spectrophotometer analysis. The percentage of organic compounds removal was evaluated by the yield which is expressed as:

$$R\% = \frac{Co - Cf}{Co} x100 \quad (1)$$

C_0 and C_f represent respectively the initial and final concentrations of organic compound expressed in mg/l.

III. Results

Different tests were carried out on synthetic solutions containing an increasing concentration of catechol dissolved in distilled water at unadjusted pH and coagulated by increasing doses of aluminum sulfate. These tests were conducted to better understand the mechanisms of their reaction with the coagulant. Figure 3 shows the final results at the tested concentrations of catechol (1, 2, 5, 10, and 20) mg/l, and Table 2 represents the values of the optimal percentage removal of each tested concentration of the previously mentioned catechol with their dose of the coagulant and corresponding final pH values.

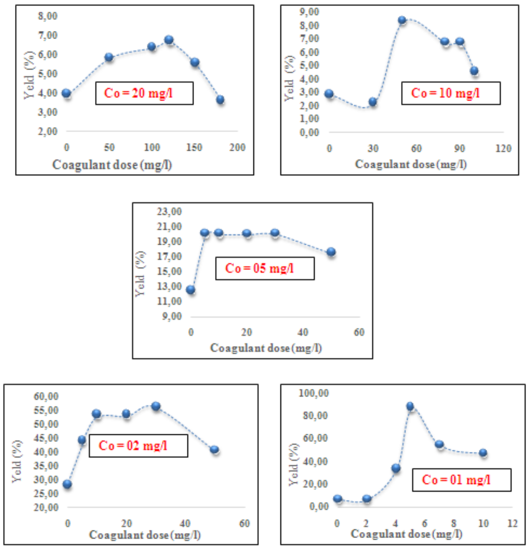


Figure 03: Influence of the coagulant dose on the elimination of catechol at different initial concentrations in distilled water (unadjusted pH, λ = 270 nm)

Table 2: Influence of the coagulant dose on the change in yield during the elimination of catechol in distilled water at different concentrations.

Initial catechol concentration (mg/l)	Coagulant dose (mg/l)	Percentage of elimination (%)	pH (final)
1	5	86.67	5.69
2	30	56.25	5.24
5	20	20	5.21
10	50	8.33	5.17
20	120	6.67	4.96

We can globally observe that the percentage of catechol removal decreases beyond the optimum for each initial concentration tested. Moreover, the effect of the coagulant dose introduced is variable from one concentration to another. We could also observe that the percentage of catechol removal decreases as the initial tested catechol content increases, and the dose of aluminum sulfate introduced increases. The monitoring of the final pH of the flocculated solutions, shows a progressive decrease as the dose of coagulant increases. At the optimum, the pH is around 5 to 7.

IV. DISCUSSION

The results presented in figure 3 show that the removal efficiency of catechol evolves differently according to the initial concentration of this compound. We can distinguish that the percentage of removal decreases as the initial concentration is increased. The elimination of the two initial concentrations (10 and 20) mg/l are low, the maximum yields obtained are lower than 10 %. These yields are observed respectively for a dose of 50 mg/l and 120 mg/l in aluminum sulfate. Moreover, a slight elimination is observed for the initial concentration (5 mg/l) is reached 20 % for a dose of 20 mg/l of aluminum sulfate. At the optimum the two remaining concentrations (1 and 2) mg/l, the yields obtained are higher than 50%. The percentage of elimination of 1 mg/l of catechol is appreciable and reaches a value of 86.67 % for a dose of 5 mg/l of coagulant. The percentage of removal of the initial concentration of 2 mg/l is also important, the maximum yield obtained is about 56.25 % for a dose of 30 mg/l of coagulant. The tests carried out allowed us to conclude that no stoichiometry could be highlighted as shown in the following figure

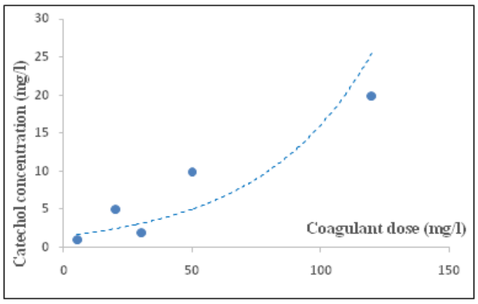


Figure 04: Relationship between initial catechol concentrations and optimal aluminum sulfate dose

The obtained results confirm the literature data [9, 10, 11, 12, 13], regardless of the tested concentration in the studied range, low concentrations are better removed than high concentrations.

Hecini and Achour [14], studied the effect of varying the initial concentration of hydroxylated compounds (phenol and catechol) in distilled water at unadjusted pH. Different thresholds of pollution were studied from 1 to 30 mg/l. The coagulation of these solutions by a dose of 40 mg/l for phenol and a dose of 150 mg/l of aluminum sulfate. The study showed that catechol appeared to be better eliminated than phenol for all concentrations tested and no stoichiometry could be demonstrated. The possible mechanism would be an adsorption process.

Lefebvre [6] indicates that aromatic compounds with at least two identical or different acid functions in ortho position are eliminated. This is the case for catechol in our experimental conditions. The presence of two contiguous acid groups (COOH or OH) on these compounds seems to give them a behavior similar to humic substances.

Hecini and Achour [13] ; Rezeg [15] also show that the elimination of compounds such as catechol, pyrogallol and pyromellitic acid is a function of the initial concentration of these compounds and the pH of the medium.

According to Hecini and Achour [14], simple compounds with phenolic groups such as pyrogallol or catechol are best removed by coagulation-flocculation. The elimination of an organic compound depends on the nature and the number of functional groups as well as their position.

It should be noted that this study was carried out on aqueous solutions at unadjusted pH. The evolution of the pH as a function of the increase in the dose of coagulant (figure 05) shows a progressive decrease of this pH.

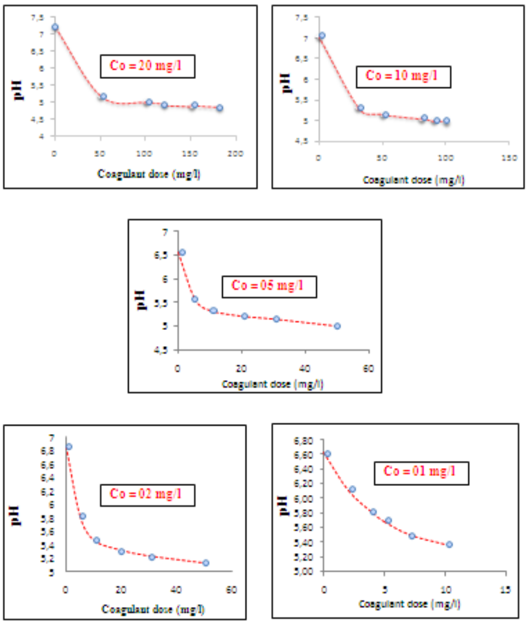


Figure 05: Influence of coagulant dose on pH evolution during catechol removal in distilled water at different concentration.

This was to be expected given the hydrolysis reactions of aluminium sulphate which allow the release of H^+ ions into the medium.

$$Al^{3+} + 1H_2O \Longleftrightarrow Al(OH)^{2+} + 1H^+$$

$$Al^{3+} + 2H_2O \Longleftrightarrow Al(OH)_2{}^{+} + 2H^+$$

$$Al^{3+} + 3H_2O \Longleftrightarrow Al(OH)_{3(s)} + 3H^+$$

$$Al^{3+} + 4H_2O \Longleftrightarrow Al(OH)_4{}^{-} + 4H^+$$

The study of the pH parameter is important because it conditions the dissociation of the functional groups existing in the structure of the organic compounds according to their pKa and the speciation of the coagulant (soluble or insoluble, charged or neutral forms). During our tests, the monitoring of the final pH shows that it is of the order of 5 to 7 according to the concentration and the coagulant. The acid dissociation constants (pKa) for catechol are both above pH 7: "pKa1=9.25"; "pKa2, 13.0" [16]. The dissociation of the constant acidity for the catechol radical can however be much lower, which explains the low abatement of this compound. As a result, the cationic species of aluminum are preponderant. The possible reactions would be the formation of soluble or insoluble complexes which could condition the mechanisms of coagulation-flocculation. We could thus observe that the elimination yields of catechol decrease. This can be explained by a competitive complexation of the OH- of the medium with aluminium.

The obtained results confirm the bibliographic data [10, 13, 17, 18, 19] concerning the elimination of organic molecules for pH ranging globally between 5 and 7 depending on the structure of the compound as well as the nature of the coagulant. On the other hand, hydrolyzed forms of aluminum can be constituted by flocs comprising a mixture of amorphous Al(OH)3 and positively charged species such as $Al(OH)_2{}^{+}$ and $Al(OH)^{2+}$. An electrostatic mechanism of charge neutralization by the partially dissociated anionic forms of catechol can then take place. It generally leads to significant variations of the Zeta potential measured on the aluminum hydroxide flocs [11]. At these pH a second mechanism already mentioned by Wais Mossa and Mazet [12] or Rahni [18] would correspond to an exchange reaction of hydroxide ions on the flocs (specific adsorption). Thus, depending on the degree of ionization of functional groups and therefore the pH of the medium, the addition of iron or aluminum salts to organic molecules can lead to the formation of a complex organic / hydrolyzed metal species (Figure 06).

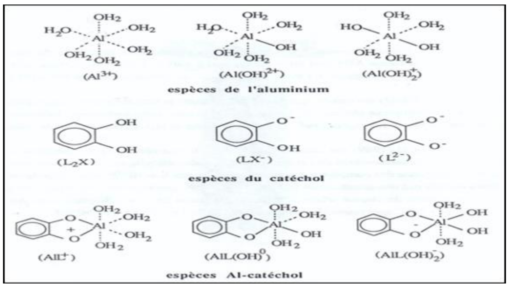
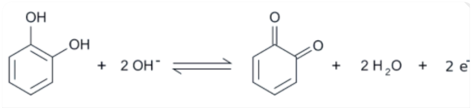


Figure 06 : Reaction scheme for the complexation of aluminum by catechol [22]

During coagulation-flocculation experiments by adding iron salts to molecules such as catechol, salicylic acid or tannic acid [12, 23], they noted the appearance of a coloration of the medium by the formation of an absorbing complex in the visible, coloration and complex which disappeared for the optimum of coagulation-flocculation. The same phenomenon is observed in the case of our tests on catechol.

Figure 07: Phenomenon observed in the case of our tests on catechol (Appearance of coloration)

Hecini and Achour [12] studied the effect of the coagulant dose on the formation of the complex derived from catechol at pH = 5.5 in the visible at a wavelength of 500 nm. A complex could be formed after the introduction of aluminum sulfate in catechol situations at basic pH. Furthermore, the explanation for the coloration of catechol according to Lee et al [24], is that it occurs as white crystals sensitive to oxygen in the air and moisture, so it oxidizes rapidly upon exposure to 1,2-benzoquinone by an auto-oxidation process:



V. Conclusions

The objective of this study was to evaluate the elimination of catechol, a simple aromatic organic compound, comprising a benzene ring bearing two hydroxy substituents ortho to each other during the process of coagulation-flocculation by aluminum sulfate.

The tests were performed on synthetic solutions of the catechol dissolved at different initial concentrations in distilled water without adjustment of pH. The influence of the coagulant dose and the monitoring of the final pH of the coagulated solutions were studied.

The results and discussions brought during this study point to the following conclusions:

- The percentage removal of 1 mg/l of catechol is appreciable and reaches a value of 86.67% for a dose of 5 mg/l of aluminum sulfate. The percentage of removal of the initial concentration of 2 mg/l is also important, the maximum yield obtained is about 56.25 % for a dose of 30 mg/l of aluminum sulfate. The percentage of removal of the initial concentration of 5 mg/l is medium; the optimum yield obtained is about 20 % for a dose of 20 mg/l of aluminum sulfate. Although the two remaining initial concentrations 10 and 20 mg/l are not well removed, the maximum yield obtained is of the order of 8.33% and 6.67% for a dose of 50 mg/l and 120 mg/l aluminum sulfate respectively.
- Two categories of catechol concentration behavior can be distinguished. The first category includes concentrations of 20 mg/l and 10 mg/l which are weakly removed by coagulation-flocculation. The maximum yields obtained are less than 10%. The second category refers to the concentrations of 2 mg/l and 1 mg/l which are well eliminated under the conditions of our tests. At the optimum, the obtained yields are higher than 50%.
- The initial concentration of catechol and in particular the number and position of hydroxyl functions could condition the efficiency of the flocculation process of this compound.

Whatever the concentration tested, low concentrations are better eliminated than high concentrations.

- For catechol, no stoichiometry could be demonstrated between the initial concentration of this compound tested and the coagulant dose. The exploitation of our experimental results indicated that the adsorption could be specific adsorption. Moreover, the latter would react better with soluble and insoluble hydrolyzed species of aluminum.
- At the pH of our tests, the predominant mechanism would be a reaction of this compound on the surface of solid metal hydroxides. The hydrolyzed species of aluminum can indeed be constituted by flocs comprising a mixture of amorphous Al(OH)3 and cationic forms Al(OH)2+ and Al(OH)2+. These mechanisms would be essentially surface mechanisms, represented by a complexation with the hydrolysed cationic species of aluminium leading to soluble or insoluble organo-aluminium forms and an exchange of ligand with the hydroxyl groups on the surface of the flocs (specific adsorption).
- Appearance of a coloration of the medium in the case of our tests on catechol before the introduction of aluminum sulfate because this compound is sensitive to air oxygen and humidity, and it oxidizes rapidly upon exposure to 1,2-benzoquinone by an auto-oxidation process, and perhaps a complex could be formed after the introduction of aluminum sulfate.

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