

Aluminium sulfate as coagulant for highly polluted cork processing wastewaters: Removal of organic matter

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Abstract

This is the first part of a work on the chemistry of aluminium as coagulant in the treatment of highly polluted cork processing wastewater. The main aim of this first part was to determine the removal of organic matter – measured by reductions in chemical oxygen demand (COD), polyphenols (TP), and aromatic compounds (A) – that can be obtained using this physicochemical process. To this end, jar-test experiments were carried out to determine the optimal conditions for the process, in particular, the effective aluminium dosage, contamination level of wastewater, coagulant mixing time, stirring speed, and pH. The ranges of tested parameters for the coagulation process were: coagulant dose (33–166 mg L⁻¹ of Al³⁺), contamination of the wastewater (COD between 1060 and 3050 mg O₂ L⁻¹), mixing time (5–30 min), stirring speed (60–300 rpm) and pH (4–11). The resulting removal capacities were in the ranges of 20–55% for COD, 28–89% for polyphenols, and 29–90% for aromatic compounds. The best results were obtained with a coagulant mixing time of 5 min and a stirring speed of 300 rpm. The optimal choices of pH and coagulant dose fundamentally depended on the contamination level of wastewater.

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1. Introduction

In the industrial processing of cork, when the cork slabs arrive at the plant, those of best quality are parboiled in cookers for 1–1.5 h in near-boiling water (temperature around 99 °C). This process has two fold purposes of disinfecting the cork (elimination of fungi, insects, reptiles, and tannins and other detrimental substances) and improving its mechanical properties (elasticity, texture, consistency, etc.). These cookers are filled with clean water on the first day of the working week, and 8–10 batches of raw cork are treated per day. The water is changed twice weekly, so that it may be used to treat between 15 and 25 batches, depending on the requirements and the rate of work. This water also vary greatly over the course of the week, depending on the number of batches that it has been used to treat. Furthermore, it contains very high organic load, including chlorinated organic compounds, tannins, and other harmful substances.

Coagulation is a commonly used process in water/wastewater treatment in which compounds such as aluminium salts are added to effluents in order to destabilize the colloidal material and cause that small particles agglomerate into larger and settleable flocs. The effectiveness of this process will depend on the coagulating agent used, the dosage, the solution pH, the concentration and nature of the organic compounds present in the water [1]. In aqueous solution, when aluminium salts dissolve [2,3] the metallic ion (Al³⁺) hydrates and is hydrolysed to form monomeric – [Al(H₂O)₆]³⁺, [Al(H₂O)₅(OH)]²⁺ (pK₁ = 4.9), [Al(H₂O)₄(OH)₂]⁺ (pK₂ = 5.6), Al(OH)₃(s) (pK₃ = 6.7) and [Al(OH)₄]⁻ (pK₄ = 7.6) – and polymeric – [Al₂(OH)₂]⁴⁺, [Al₃(OH)₄]⁵⁺ or the known “Al₁₃” [Al₁₃O₄(OH)₂₄]⁷⁺ – species. Under very acidic conditions (pH < 3), [Al(H₂O)₆]³⁺ remains in solution, but as the pH or the coagulant concentration rises, hydrolysis occurs to form aluminium hydroxide, Al(OH)₃(s). The resulting metal hydroxide polymers have amorphous structures with very large surface areas and positive charges [1,2]. Aluminium has a strong tendency to form insoluble complexes with a number of ligands, especially with polar molecules and with oxygen-containing functional groups such as the hydroxyl

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or carboxyl groups [4]. These provide a local negative charge which reacts with the aluminium cation. Charge neutralization leads to colloid destabilization with the consequent precipitation of the aluminium cation and organic anions. This induces sweep-floc coagulation (also known as sweep flocculation or sweep coagulation)—the adsorption and bridging enmeshment of both particulate organic and inorganic solids to form large and amorphous flocs [5]. Dissolved organic compounds are removed primarily by adsorption onto the hydroxide surface.

The “classical model” shows various mechanisms that can destabilize colloids: (a) an increase in the concentration of ionic species, thereby destabilizing the colloid particles by compression of the electric bi-layer, (b) a reduction of the zeta potential, due to adsorption of polynuclear anionic species – aluminium(III)–hydroxo complexes – onto the colloid surface and (c) sweep-floc coagulation, in which the colloidal particles are swept out of suspension by becoming enmeshed in the aluminium hydroxide precipitate. The single most determining factor in the coagulation process is undoubtedly the pH, since it affects all the hydrolysis equilibria resulting from the addition of the metal cation. At low pH and low coagulant dose the predominant mechanism is charge adsorption–neutralization, and at high pH and high coagulant dose it is sweep-floc coagulation [3,6,7].

On the other hand, Dentel [8] introduced a new model to explain coagulation in water treatment by the hydrolysis of metal salts, “precipitation charge neutralization model (PCN)”. Although this model was presented in a quantitative form [9], this aspect will not be covered here. According to the PCN model, coagulation with aluminium salts involves three steps: (a) destabilization begins after addition of a dose of coagulant that exceeds the operational solubility of aluminium, (b) aluminium hydroxide species are then deposited onto colloidal surfaces, and (c) under typical conditions, the metal hydroxide is positively charged, while the original colloidal particles are negatively charged. So the deposition process can result in charge neutralization or charge reversal of the colloidal particles. When the positively charged adsorbed species are in the form of isolated regions, then a form of “electrostatic patch” attraction may be important. It has to be noted that the PCN model does not cover bulk hydroxide precipitation sweep-floc coagulation. There is no doubt that, at the correct dosage, charge

neutralization by the adsorbed hydrolysis products and hydroxide precipitate can cause negatively charged particles to become destabilized and hence to coagulate. When charge-neutralization is the predominant destabilization mechanism, then there should be a stoichiometric relationship between the particle concentration and the optimal coagulant dosage [10]. At low particle concentrations, only low coagulant dosages should be required. Under such conditions coagulation rates can be very low, thereby causing problems in water treatment. Another practical difficulty is that the optimal coagulant dosage range can be quite narrow, which means that fairly precise dosing control is needed. These difficulties can be overcome by using higher coagulant dosages, for which extensive hydroxide precipitation occurs, giving rise to sweep-floc coagulation.

The particular objective of the present study was the optimization of the coagulation process for the treatment of wastewater from the cork processing industry.

2. Experimental/materials and methods

2.1. Wastewater

The wastewaters of the present study were provided by cork processing industry “Corchos de Mérida S.A.” (Extremadura Autonomous Community, Spain). The samples were taken at different times during the week, corresponding to different numbers of batches, and hence with different organic matter concentration. Table 1 lists the nomenclature that will be used for these waters, with their principal physicochemical characteristics.

2.2. Materials and methods

Coagulation studies were performed in a conventional model Velp Scientifica JLT4 jar-test apparatus, equipped with four 1-L beakers. The calculated quantity of coagulant $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was added to the wastewater, and the pH was adjusted to the required value using $\text{Ca}(\text{OH})_2$. Both products were provided by Merck. The mixture was stirred at the rate and during the time fixed for each experiment. It was then transferred to a 1-L graduated cylinder for the sedimentation test. After the settling period, the samples were taken for aromatics, polyphenols, and COD determination.

Table 1
Main physico-chemical characteristics of cork process wastewaters^a

Parameter	Water I	Water II	Water III	Unit
pH	5.2	4.92	4.65	
COD	1060	1855	3047	mg L ⁻¹
BOD ₅	356	630	1035	mg L ⁻¹
Aromatic compounds (A)	2560	4644	6055	mg L ⁻¹ of phenol
Total polyphenols (TP)	165	287	381	mg L ⁻¹ of caffeic acid
Conductivity	554	806	1184	μS cm ⁻¹
TSS	0.123	0.189	0.281	g L ⁻¹
TS	1.10	1.92	2.89	g L ⁻¹
Turbidity	115	180	278	NTU
Ca ²⁺	17.1	30.6	54.2	mg L ⁻¹
Cl ⁻	33.6	64.1	108.9	mg L ⁻¹

^a All the values are affected by an error of ±5%.

2.3. Analysis

The aromatic content was determined by measuring the absorbance in the ultraviolet region at 254 nm wavelength, at which aromatic and unsaturated compounds present the maxi-

um absorption [11,12]. The result is expressed in terms of a reference aromatic compound: mg L^{-1} of phenol [13].

The polyphenol content of a water can be determined colorimetrically using the Folin–Ciocalteu reagent (a mixture of molybdophosphoric and tungstophosphoric acids). The formed

Table 2
Influence of variables on COD, total polyphenol and aromatic removals (X_{COD} , X_{TP} and X_{A})

Experiment	Water	Agitation rate, V_m (rpm)	Mixing time, t_m (min)	Coagulant dose, D (mg L^{-1} of Al^{3+})	pH	X_{COD} (%)	X_{A} (%)	X_{TP} (%)
C-1	I	150	5	66	7	48	76	80
C-2		150	15	66	7	38	76	79
C-3		150	30	66	7	40	62	71
C-4	II	300	5	83	5	50	85	81
C-5		300	15	83	5	48	81	80
C-6		300	30	83	5	47	78	78
C-7	III	300	5	83	5	26	48	44
C-8		300	15	83	5	25	47	41
C-9		300	30	83	5	24	47	40
C-10	I	60	5	66	7	44	81	83
C-11		150	5	66	7	48	76	80
C-12		300	5	66	7	50	80	82
C-13	II	60	5	83	5	50	79	77
C-14		150	5	83	5	51	79	79
C-15		300	5	83	5	50	85	81
C-16	III	60	5	83	5	19	29	28
C-17		150	5	83	5	20	41	30
C-18		300	5	83	5	26	48	44
C-19	I	300	5	66	4	45	75	73
C-20		300	5	66	5	54	86	81
C-21		300	5	66	6	50	81	81
C-22		300	5	66	7	50	80	82
C-23		300	5	66	8	50	80	80
C-24		300	5	66	9	49	80	81
C-25	II	300	5	83	5	50	85	81
C-26		300	5	83	6	49	71	73
C-27		300	5	83	7	38	61	66
C-28		300	5	83	8	36	58	67
C-29		300	5	83	9	40	57	67
C-30	III	300	5	83	5	26	48	44
C-31		300	5	83	6	31	47	46
C-32		300	5	83	7	38	47	50
C-33		300	5	83	8	41	48	54
C-34		300	5	83	9	43	53	62
C-35		300	5	83	10	49	74	74
C-36		300	5	83	11	53	78	85
C-37	I	300	5	33	5	32	61	63
C-38		300	5	50	5	47	81	78
C-39		300	5	66	5	54	86	81
C-40		300	5	83	5	56	87	83
C-41		300	5	100	5	55	88	84
C-42		300	5	133	5	55	89	84
C-43	II	300	5	83	5	50	85	81
C-44		300	5	100	5	53	84	83
C-45		300	5	133	5	53	87	84
C-46		300	5	166	5	55	87	89
C-47	III	300	5	83	5	26	48	44
C-48		300	5	100	5	37	68	66
C-49		300	5	133	5	51	79	77
C-50		300	5	166	5	54	83	82

Table 3
Range of variables studied

Variable	Water	Range	Unit
Mixing time	I–III	5–30	min
Agitation rate	I–III	60–300	rpm
Coagulant dose	I	33–133	mg L ⁻¹ of Al ³⁺
	II	83–166	
	III	83–166	
pH	I	4–9	
	II	5–9	
	III	5–11	

blue complex is measured at a wavelength of 725 nm [14]. The results are expressed in mg L⁻¹ of caffeic acid, since this acid is a very common phenolic compound in a large variety of waters.

For the COD determination, it was used a Selecta mod. Tembloc oven, a PF-10 Macherey–Nagel photometer, and test cuvettes pre-prepared for the desired measurement range (the range of concentrations selected was 100–1500 mg O₂ L⁻¹).

3. Results and discussion

Hydrolysing metal salts of aluminium are widely used as primary coagulants to promote the formation of flocs in water treatment. The present work studies the use of aluminium salts to purify highly polluted wastewaters (in this case cork processing wastewaters). The monitored parameters are: chemical oxygen demand (COD), total polyphenols (TP), and aromatic compounds (A). As can be seen in Table 1, Waters I–III had different organic loads. In all experiments, the volume of treated water was 1 L, and the reaction temperature was 20 °C. Tables 2 and 3 summarize all the experiments carried out and the modified variables.

3.1. Influence of stirring speed

Adequate mixing is necessary both when the coagulant is added and during the formation and growth of flocs. As particle sizes increase, stirring may break up existing flocs as a result of disruptive forces, and the collision efficiency of the particles in a shear field decreases [15,16]. A dynamic balance between floc

growth and breakage often leads to a steady-state floc-size distribution, where the limiting size depends on the applied shear rate [17]. If the effective shear rate is increased, pre-formed flocs can be broken in a manner that depends on the floc size relative to the turbulence microscale [17]. Flocs formed by hydrolysing coagulants tend to be rather weak, so that breakage occurs readily. In the case of sweep-floc coagulation, this breakage is not fully reversible, and flocs do not completely re-form when the original shear conditions are restored. The stirring speed in the present experiments had a moderate positive influence (see experiments C-10–C-18). Fig. 1a–c shows the effect on COD, aromatics and polyphenol removals, respectively (for Waters I–III). As can be seen, this influence is more pronounced for more contaminated waters (Water III). In general, the optimal speed was 300 rpm. The removals of COD, aromatics, and polyphenols for Water I (COD ≈ 1000 mg L⁻¹) and Water II (COD ≈ 2000 mg L⁻¹) were more greater than for Water III (COD ≈ 3000 mg L⁻¹), indicating that the coagulation was more effective in reducing these three parameters in waters with lower organic matter content.

3.2. Influence of coagulant mixing time

To study the influence of the coagulant mixing time, some experiments were carried out on Waters I–III (see experiments C-1–C-9 of Table 2). Fig. 2a–c shows that the shortest time (5 min) was the best for all the three parameters—COD, polyphenol (TP), and aromatic compound (A) removals. Therefore, this indicates that prolonged stirring leads to lower efficacy of the process [17]. One also observes from the figures that, for this 5 min mixing time, the COD, aromatic, and polyphenol removals in Waters I and II were greater than in Water III, confirming the greater efficacy of the process for waters with lower organic matter content.

3.3. Influence of coagulation pH

Within all the factors involved, those that most affect the process efficiency are pH and coagulant dose, since influence in the hydrolysis equilibria of coagulant species. Another reason for the importance of pH is that the addition of the metallic cation automatically decreases pH, being greater

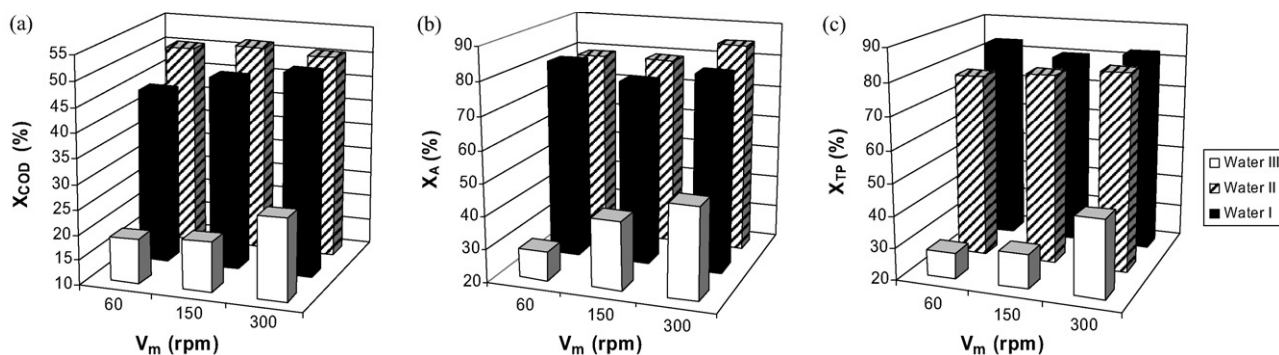


Fig. 1. Influence of stirring speed on (a) COD removal, X_{COD} ; (b) aromatics removal, X_{A} ; and (c) polyphenols removal, X_{TP} . Experimental conditions: pH 5, mixing time 5 min, coagulant dose 83 mg L⁻¹ of Al³⁺, $T = 20$ °C.

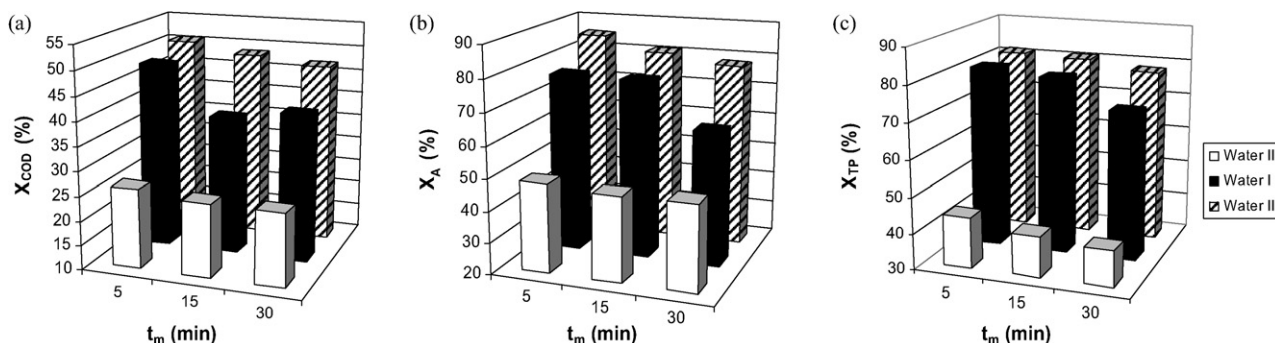


Fig. 2. Influence of coagulant mixing time on (a) COD removal, X_{COD} ; (b) aromatics removal, X_{A} ; and (c) polyphenols removal, X_{TP} . Experimental conditions: pH 5, 300 rpm, coagulant dose 83 mg L^{-1} of Al^{3+} , $T = 20^\circ\text{C}$.

with higher dose of coagulant and lower alkalinity of the water.

Some experiments on Waters I–III (experiments C-19–C-36 of Table 2) were carried out in order to study the effect of pH. Fig. 3a–c shows the results for final removals of COD, aromatics and polyphenols, respectively. With regards to Water I (COD $\approx 1000 \text{ mg L}^{-1}$), one observes that, in the range of pH studied, appears a maximum reduction at pH 5. At this low pH, below the isoelectric point (which in the case of aluminium hydroxide is pH 7.4) the charge adsorption–neutralization mechanism is the predominant. For all parameters, there is a maximum reduction at pH 5 with the Water II and the removal decreases between pH 5–8. At pH 9 these removals increase for COD and polyphenols. This second maximum can be justified by the “sweep-floc” coagulation mechanism [6,7]. Whichever the case, the net result is that the removals of COD, polyphenols and aromatics can occur by a combination of the two mechanisms over a wide range of pH. In the case of Water III (with more organic load, COD $\approx 3000 \text{ mg L}^{-1}$) the sweep-floc coagulation mechanism predominates [6,7] and the maximum removals of COD, aromatics and polyphenols shift rightwards to pH 11. Again the confirmation that the removals of COD, aromatics and polyphenols were always greater in the less contaminated waters is established.

3.4. Effect of coagulant dose

The aluminium dose to apply to a wastewater fundamentally depends on pH and organic matter concentration. The most appropriate interval of pH is closely related to the coagulant

dose—the greater coagulant dose, the wider effective pH interval for coagulation. Experiments were carried out on Waters I–III (experiments C-37–C-50 of Table 2) and dose of Al^{3+} was varied between 33 and 166 mg L^{-1} of Al^{3+} , maintaining the following variables constant: pH 5, stirring speed 300 rpm, and mixing time 5 min. Fig. 4a–c shows the results of the analysis of the supernatant. One observes that increasing the coagulant dose favoured the removals of COD, aromatics, and polyphenols for all types of wastewater. There are two mechanisms by which high coagulant dosages can increase the coagulation rate: (a) by increasing the concentration of metal hydroxide precipitate and thus the aggregation rate, and (b) by enmeshing particulates into ever larger aggregates by sweep-floc coagulation [2]. Furthermore, in this wastewater, the addition of a high coagulant dose favours the formation of a greater number of flocs, since increasing the supersaturation of aluminium hydroxide increases considerably the nucleation rate compared with the flocs growth rate. The result is a suspension with flocs that are smaller in size and greater in number, and that will hence remove a larger amount of organic matter because of the larger surface area available for adsorption. On the contrary, low coagulant doses favour the formation of larger, but fewer flocs because of the faster growth rate relative to nucleation rate, resulting in a smaller surface area available for the adsorption of organic matter. Doses of Al^{3+} of 66 mg L^{-1} for Water I, 100 mg L^{-1} for Water II and 166 mg L^{-1} for Water III yielded similar values of the removal of COD (approximately 55%), aromatics (approximately 85%), and polyphenols (approximately 80%) in the three types of water (see Fig. 4a–c). In Fig. 4, one observes a relative shift between the three bar-diagrams of about 60 mg L^{-1} of coagulant over

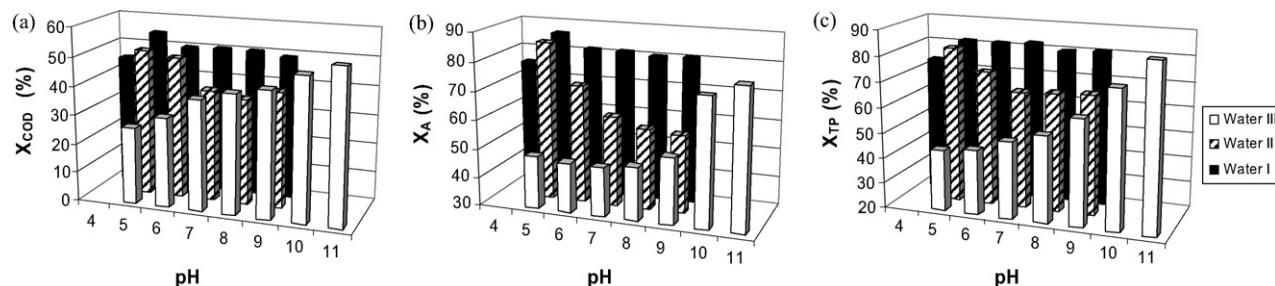


Fig. 3. Effect of coagulation pH on (a) COD removal, X_{COD} ; (b) aromatics removal, X_{A} ; and (c) polyphenols removal, X_{TP} . Experimental conditions: 300 rpm, mixing time 5 min, coagulant dose 83 mg L^{-1} of Al^{3+} , $T = 20^\circ\text{C}$.

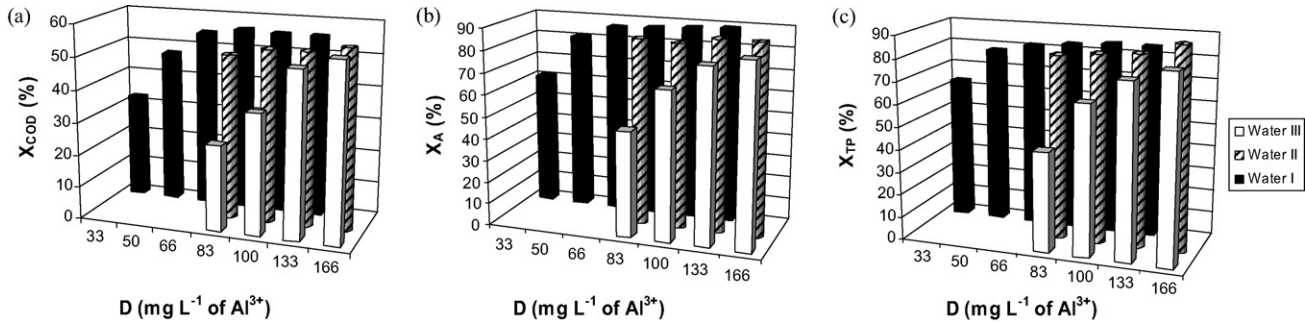


Fig. 4. Effect of the coagulation dose on (a) COD removal, X_{COD} ; (b) aromatics removal, X_A ; and (c) polyphenols removal, X_{TP} . Experimental conditions: pH 5, mixing time 5 min, 300 rpm, $T=20^\circ\text{C}$.

the entire range of doses. For example, to achieve the same COD removal in Waters I–II–III, it is necessary to increase the concentration of the coagulant by 60 mg L^{-1} (this supposes $\approx 5\text{--}6 \times 10^{-2}\text{ mg Al}^{3+}(\text{mg COD})^{-1}$). One deduces that there is a stoichiometric or quasi-stoichiometric relationship between the COD, polyphenol, or aromatic content of the wastewater and the dose of coagulant required to attain a given level of elimination. Other workers [18,19] report a stoichiometric ratio of $2\text{ mg Al}^{3+}(\text{mg TOC})^{-1}$ in the process of coagulation of various humic substances. In these conditions, it is not easy to determine the principal destabilization mechanism. Although the values of coagulant dose are high, which leads to think of a sweep-floc coagulation mechanism, the observed stoichiometric or quasi-stoichiometric dependence also makes to think that the charge adsorption–neutralization mechanism is acting with importance.

3.5. Effect of the organic load of the wastewater

For this purpose, Fig. 5 compares the experiments carried out on Waters I–III in the same experimental conditions: mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 83 mg L^{-1} of Al^{3+} (experiments C-4, C-7 and C-40). As can be deduced, the values of the removals of COD, polyphenols, and

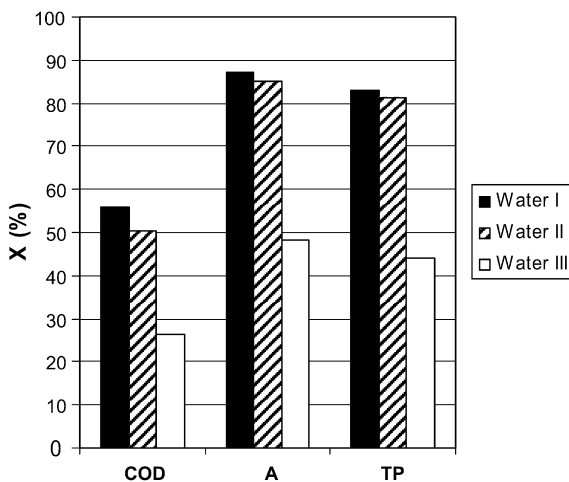


Fig. 5. Effect of the organic load of the wastewater. Comparison of the experiments carried out on Waters I–III in the same experimental conditions: mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 83 mg L^{-1} of Al^{3+} .

aromatics were always greater in the less contaminated waters (Water I > Water II > Water III). This observed stoichiometric or quasi-stoichiometric dependence also makes one think that the charge adsorption–neutralization mechanism is acting with relevance.

3.6. Optimization of the coagulation process

This section exposes the optimal conditions chosen for each type of water and the results obtained in these conditions. For Waters I and II the chosen conditions were: mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 83 mg L^{-1} of Al^{3+} (experiments C-4 and C-40). In the case of Water III, the optimal pH was pH 11 (experiment C-36), therefore in view of the possible discharge/reuse it is not recommended. The chosen conditions for Water III were: mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 133 mg L^{-1} of Al^{3+} (experiment C-49). Fig. 6 shows the removals obtained for COD, polyphenols and aromatics in the chosen optimal conditions for

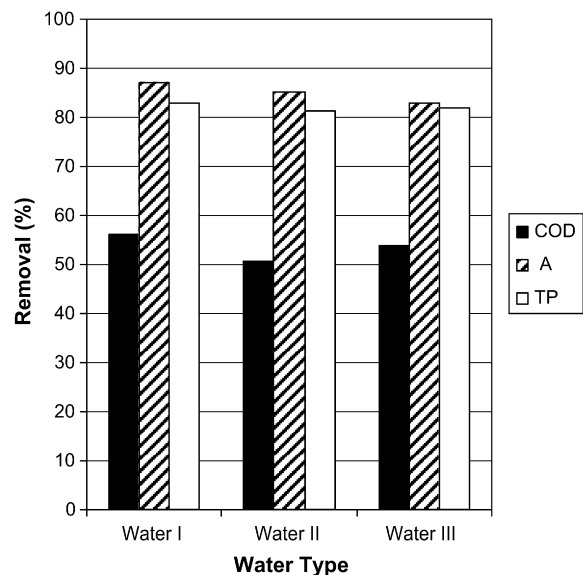


Fig. 6. COD, aromatic and polyphenol removals obtained for each type of water using different optimal conditions. For Waters I and II the chosen conditions were: mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 83 mg L^{-1} of Al^{3+} . In the case of Water III, mixing time 5 min, stirring speed 300 rpm, pH 5 and coagulant dose 166 mg L^{-1} of Al^{3+} .

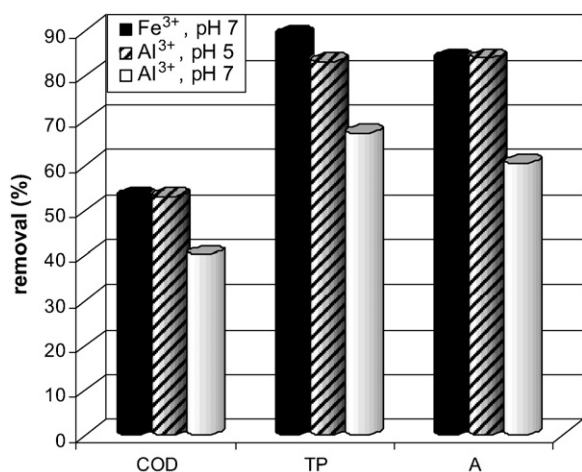


Fig. 7. COD, aromatic and polyphenol removals obtained in the same experimental conditions with iron (III) and with aluminium (III) at pH 7, and by aluminium (III) at pH 5. Experimental conditions: Water II (COD \approx 2000 mg L⁻¹), metal concentration [M³⁺] = 3.70 mmol L⁻¹, mixing time 5 min, stirring speed 300 rpm.

each water type. As can be seen for all cases the organic removal is similar.

3.7. Comparison with ferric chloride

Although nowadays, aluminium sulfate is preferred to ferric chloride as coagulant due to the color that ferric ion transfers to water. This section makes a comparison of both coagulants for organic matter removal from wastewater type II (COD \approx 2000 mg L⁻¹) using a metal concentration [M³⁺] = 3.70 mmol L⁻¹ in both cases. Fig. 7 shows the results obtained (COD, polyphenol and aromatic removals) at the optimal experimental conditions: mixing time 5 min, stirring speed 300 rpm, pH 5 (for Al³⁺) and pH 7 (for Fe³⁺). The optimal conditions for ferric chloride coagulation were determined by the authors in other work [20]. Fig. 7 also includes results obtained with aluminium sulfate at pH 7. As can be seen the use of aluminium sulfate at pH 5 and ferric chloride at pH 7 obtained similar results with regards to organic matter removal.

4. Summary and conclusions

The principal conclusions of this work are:

- (1) In general, the coagulation process gave greater percentage organic matter removal for the least contaminated water. The shortest coagulant mixing time, 5 min, was best suited for the process. Longer times led to reduction in the process's effectiveness. Vigorous stirring at the rate of 300 rpm favoured the coagulation process. In view of the possible discharge/reuse of the water, a treatment at pH 5 seemed to be the most favourable for Waters I and II; and pH 7–9 for Water III.
- (2) The optimal coagulant dose depends on the contamination level of wastewater, i.e., to attain the same COD removal in Waters I–II–III was necessary to increase the coagulant concentration 83–100–166 mg L⁻¹ of Al³⁺, respectively. This

influence was similar for the polyphenols and aromatic compounds.

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