Aluminium sulfate as coagulant for highly polluted cork processing wastewater: Evaluation of settleability parameters and design of a clarifier-thickener unit

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Abstract

This is the second part of a master project on the chemistry of aluminium as coagulant in the treatment of highly polluted cork-process-wastewater. The main aim of this second part was to determine the influence of the operating conditions on the system's settleability parameters. It is well known that it is just as important to achieve good settleability parameters in the physico-chemical treatment of wastewaters as it is to attain a high level of decontamination. These parameters will determine the dimensions of the required equipment, and hence the costs of the installation. This part of the study therefore analyzes the influence of the different operating variables on the following settleability parameters: sediment volumetric percentage, settling velocity, sludge volume index and total suspended solids just after mixture with the coagulant. The ranges used for the experimental variables were: coagulant dose (83–166 mg L^{-1} of Al^{3+}), coagulation mixing time (5–30 min), stirring rate (60–300 rpm), contamination level of the wastewater (Wastewater II COD $\approx$ 2000 mg O$_2$ L^{-1}, Wastewater III COD $\approx$ 3000 mg O$_2$ L^{-1}), and pH (5–11). The optimal conditions found for the settling process were not the same as those that had been determined for the organic matter removal. In this case the optimal conditions were: coagulation mixing time (30 min), stirring rate (60 rpm), coagulant dose (83 mg L^{-1} of Al^{3+}) and pH (7–9). Finally, the Talmadge–Fitch method is used to apply the results to the design of a clarifier-thickener unit to treat 2 m^3 h^{-1} of wastewater. The required minimum area of the unit would be 4.11 m^2.

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1. Introduction

There are few investigations related to the depuration of cork processing wastewater. The complicated nature of this wastewater (BOD$_5$/COD = 0.19) makes biological treatment ineffective. Minhalma and de Pinho [1,2] found that polyphenolic compounds present in cork processing wastewater are responsible for membrane fouling and drastic flux decline in ultrafiltration process. Benitez et al. [3] studied the purification of cork processing wastewaters by ozone, aerobic biodegradation and by their two sequential processes. On the other hand, Beltrán-Heredia et al. [4] have evaluated Fenton oxidation for the removal of

organic matter. Moreover, Silva et al. [5] have carried out a comparative between different homogeneous (H$_2$O$_2$/UV–vis and H$_2$O$_2$/Fe^{2+}/UV–vis) and heterogeneous (TiO$_2$/UV–vis and TiO$_2$/H$_2$O$_2$/UV–vis) systems, with degradation performances being evaluated in terms of total organic carbon (TOC) removal. Results obtained in a batch photo-reactor show that photocatalysis with TiO$_2$ is not suitable for this kind of wastewater.

However, due to the large amount of total solids present in this wastewater (about 2000–3000 mg/L), we have considered that a single coagulation/flocculation treatment by Al^{3+} and Ca(OH)$_2$ should reduce these solids, so reducing COD, BOD, color and odor. In this sense, a bibliographic search on treatment of this wastewater using Al^{3+} as coagulant did not provide results. We found only one work using iron as coagulant [6].

Hydrolysing metal salts of aluminium are widely used as primary coagulants in wastewater treatment to promote the formation of floc, and hence reduce the concentration of particulate

Nomenclature

A_c	minimum clarification area (m^2)
A_e	minimum thickener area (m^2)
C_c	critical sludge concentration (g mL^{-1})
C_u	desired sludge underflow concentration (g mL^{-1})
C_0	initial sludge concentration (g mL^{-1})
D	aluminium coagulant dose (mg L^{-1})
h_0	initial height of the water in the graduated cylinder (cm)
H_c	interface height at the critical concentration C_c (cm)
H_u	interface height at the underflow sludge concentration C_u (cm)
H_0	initial interface height (cm)
m	slope obtained in the settling test (mL min^{-1})
P_1	mass of capsule plus filter before the filtration (g)
P_2	mass of capsule plus filter after filtering a volume
Q	flow rate of effluent through the tank (m^3 h^{-1})
Q_c	flow rate of clarified water (m^3 h^{-1})
SP	sediment volumetric percentage (%)
SVI	sludge volume index (mL g^{-1})
t_m	mixing time with the coagulant (min)
t_u	time required to reach the underflow sludge concentration C_u (min)
TSS	total suspended solids after adding the coagulant (g L^{-1})
V_s	settling velocity (cm min^{-1})
V_m	of water and drying at 105 °C (g)
V_m	stirring rate (rpm)
V_w	volume of water filtered in the determination of P_2 (mL)
V_0	initial water volume (mL)
V_{30}	volume beneath the supernatant–suspension interface after 30 min of sedimentation (mL)
V_{60}	volume beneath the supernatant–suspension interface after 60 min of sedimentation (mL)

matter and dissolved organic compounds. This type of treatment – using chemical means to transform non-sedimentable particles into coagulated sedimentable particles – yields a suspension with uniform flocs that, after settling and appropriate elimination of the sludge, leaves the clearest possible supernatant.

Physico-chemical processes are commonly used in water treatment [7–9]. Compounds such as aluminium salts are added to the effluent to destabilize the colloidal material present, and cause small particles to agglomerate into larger, settleable flocs. The effectiveness of the process is influenced by the choice of coagulant, the dosage, the pH and ionic strength of the solution, and the concentration and nature of the organic compounds present [8]. The coagulation/flocculation treatment of a water generally consists of two stages:

(a) *Mixing*. The addition of coagulants and flocculants to achieve the formation of floc suitable for elimination in the subsequent sedimentation stage.

(b) *Sedimentation*. The floc from the previous stage is left to settle out under gravity to consolidate into a sludge that will be appropriately removed, leaving as clear a liquid as possible.

1.1. Nature of the process

The process of sedimentation of particles that have formed is different from that of discrete particles. As they descend, flocs merge with each other by adsorption or coalescence. As they increase in size, their settling velocity increases. In a suspension, the manner in which the particles settle depends on the concentration of the suspension and the characteristics of the particles. Fitch [10] describes the following types of sedimentation:

(1) *Type 1—clarification*. The particles descend as individual entities, without any interaction with neighbouring particles. In the case of flocculent suspensions, the flocs are separate, and settle independently.
(2) *Type 2—flocculent sedimentation*. The particles interfere with each other, agglomerating as they descend, forming flocs. As the flocs increase in mass, their settling velocity also increases.
(3) *Type 3—zonal settling*. The particles agglomerate into a compact mass which settles as a blanket, with a distinctive interface between the settled sludge and the clarified effluent.
(4) *Type 4—compression or compaction*. The particles are concentrated forming a structure, and sedimentation is only possible as the result of compression of this structure. The compression is produced by the weight of the particles which are constantly being added to the structure by sedimentation from the supernatant.

1.2. Sedimentation zones

In the sedimentation of a concentrated suspension of solids, the particles are so close to one another that there is interference between their respective velocity fields. Furthermore, as the liquid is displaced upwards, it acts to brake the descent of the particles [11].

Fig. 1 is a schematic representation of the settling zone phenomenon during the sedimentation of the flocculent suspension formed during the process of coagulation. At the initial time, t_0, the suspension is theoretically homogeneous, so that there is a single *zone U* of uniform concentration, C_0, and the height of the interface is H_0. The settling velocity in zone U is characteristic of the concentration. Some time later, there appears a column of clear liquid, *zone L*, and two new zones—a transition zone, *zone T*, located immediately beneath the uniform suspension, in which the settling velocity is reduced by the increasing concentration of the suspension, and a compression zone, *zone D*, located below the transition zone, in which the particles are in physical contact with those below them.
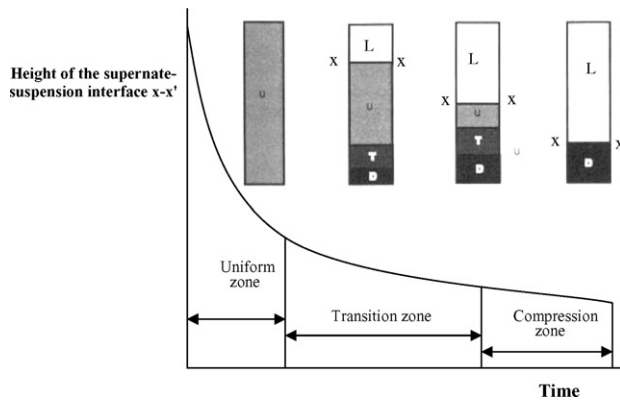
Fig. 1. Zones formed during the sedimentation phenomenon. Height of the supernate–suspension interface x–x' *vs.* time.

2. Experimental/materials and methods

2.1. Materials

The wastewaters of the present study were provided by cork processing industry, Corchos de Merida S.A; Extremadura Autonomous Community, Spain. The samples were taken at different times during the week, corresponding to different numbers of batches (Water II and Water III), and hence with different organic matter concentrations. Table 1 lists the nomenclature that will be used for these waters, with their principal physico-chemical characteristics.

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 $Al_2(SO_4)_3 \cdot 18H_2O$ was added to the wastewater, and the pH was adjusted to the required value with $Ca(OH)_2$. Both products were provided by Merck. The mixture was stirred at the rate and for the time fixed for each experiment. It was then transferred to a 1-L graduated cylinder for the sedimentation test.

2.2. Determination of the settleability parameters

2.2.1. Sediment percentage (SP)

The sediment percentage is the ratio between the volume beneath the supernatant–suspension interface after 60 min of

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

Parameter	Water II	Water III	Unit
pH	4.92	4.65	
COD	1855	3047	$mg\,L^{-1}$
BOD$_5$	630	1035	$mg\,L^{-1}$
Aromatic compounds (A)	4644	6055	$mg\,phenol\,L^{-1}$
Total polyphenols (TP)	287	381	$mg\,caffeic\,acid\,L^{-1}$
Conductivity	806	1184	$\mu S\,cm^{-1}$
TSS	0.189	0.281	$g\,L^{-1}$
TS	1.92	2.89	$g\,L^{-1}$
Turbidity	180	278	NTU
Ca^{2+}	30.6	54.2	$mg\,L^{-1}$
Cl$^-$	64.1	108.9	$mg\,L^{-1}$

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

sedimentation, V_{60}, and the initial wastewater volume, V_0, expressed as a percentage. It is a measure of the sludge volume and it is given by the following expression [12]:

$$SP\,(\%) = \left[1 - \left(\frac{V_0 - V_{60}}{V_0}\right)\right] \times 100 \tag{1}$$

2.2.2. Settling velocity (V_s)

The mean settling velocity corresponds to the first 15 min of the settling process, and is expressed in $cm\,min^{-1}$. It is given by the following expression [12]:

$$V_s = \frac{mh_0}{V_0} \tag{2}$$

where h_0 is the height (cm) of the initial column of wastewater, V_0 the initial wastewater volume (mL), and m is the slope obtained from a plot of the data—volume beneath the interface (mL) *versus* time (min).

2.2.3. Sludge volume index (SVI)

The sludge volume index ($mL\,g^{-1}$) is the ratio between the volume and the weight of sludge formed after 30 min of settling. It is given by the following expression [12]:

$$SVI = \frac{V_{30}}{V_0\,TSS} \tag{3}$$

where V_{30} is the volume below the supernatant–suspension interface after 30 min of sedimentation (mL), V_0 the initial wastewater volume expressed in L, and TSS is the total suspended solids content of the wastewater in $g\,L^{-1}$.

2.2.4. Total suspended solids (TSS)

This parameter is the concentration of total suspended solids of the wastewater after the addition and mixing with the coagulant. It is determined gravimetrically from the solid fraction retained on a 0.45 μm pore-size glass-fibre filter [13]:

$$TSS = \left[\frac{P_2 - P_1}{V_m}\right] \times 1000 \tag{4}$$

where TSS is the total suspended solids ($g\,L^{-1}$), P_1 the mass of the capsule plus filter before the filtration (g), and P_2 is the mass of the capsule plus filter (g) after filtering a volume V_m (mL) of wastewater and drying at 105 °C for 12 h.

3. Results and discussion

This second part of the project looked at how the different operating variables – coagulant dose (83–166 $mg\,L^{-1}$ of Al^{3+}), coagulation mixing time (5–30 min), stirring rate (60–300 rpm) and pH (5–11) – influence the sedimentation process. As was noted above, it is just as important to obtain good settleability parameters as to achieve a high level of decontamination. In the first part of the project [14] was determined the removal of organic matter that can be obtained using this physico-chemical process. The resulting removal capacities were in the ranges 20–55% for COD, 28–89% for polyphenols, and 29–90% for aromatics. The best results were obtained with the shortest

coagulant mixing time, 5 min and a stirring speed of 300 rpm. The optimal choices of pH and coagulant dose fundamentally depended on the contamination level of the wastewater. It will be seen below that the optimal conditions for the sedimentation process were not found to coincide with the optimal conditions for the elimination of organic matter.

Due to the great complexity of the system, it is difficult to establish a theoretical or empirical formula that is applicable to the settling process in wastewaters; nonetheless, one can state the following:

(a) The larger the particles, the greater their settling velocity. There also seems to be a relationship between the size and the number of particles, since the process is itself the result of two phenomena—nucleation and floc growth [6]. A greater number of small particles would normally imply the predominance of nucleation over growth. Such a situation is more likely to enhance supersaturation of the solution.
(b) The sludge volume index, SVI, measures the compaction of the sediment. As will be seen below, there is a close relationship between the value attained by this parameter and particle size.
(c) The sediment percentage, SP, may also be related to the particle size and to all the other parameters (100-SP) measures the volume percentage of clarified liquid, and should therefore be as large as possible.
(d) With respect to the total suspended solids (TSS), the greater the concentration, the more effective is the elimination of suspended organic matter.
(e) The longer the retention time in the settling tank, the greater the efficiency attained in the clarification.

In the present study, series of experiments were carried out using aluminium sulfate as coagulant to determine the optimal conditions of stirring rate, mixing time, pH and coagulant dose for good sedimentation (in speed and in percentage of clarified liquid) that will produce lowest volume of sludge possible.

The operating variables used in the trials were: stirring rate (60, 150, 300 rpm), mixing time (5, 15, 30 min), pH (5–11) and coagulant dose (83, 100, 133, 166 mg L^{-1} of Al^{3+}). The study was performed using two wastewater types (Waters II and III). Table 2 shows a resume of the sedimentation tests carried out.

3.1. Influence of the stirring rate on the settleability parameters

The stirring rate was found to have only a mild influence (compared with other variables) on the coagulation process (experiments S-7 to S-12 of Table 2). All these experiments were carried out at pH 5, mixing time 5 min and aluminium dose 83 mg L^{-1} of Al^{3+}. Figs. 2 and 3 show the influence of this factor on the sludge volume index (SVI) and on the settling velocity (V_s), respectively. The results obtained for Water II (COD $\approx$ 2000 mg L^{-1}) and Water III (COD $\approx$ 3000 mg L^{-1}) were similar. The lowest sludge volume index was obtained at 60 rpm for the two cases (SVI = 465 and 150 mL g^{-1} for
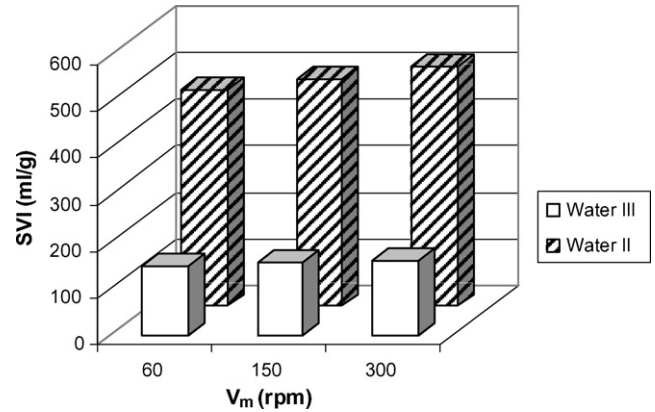

Fig. 2. Effect of stirring speed on the sludge volume index (SVI). Waters II–III, pH 5, mixing time 5 min, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20\,°C$.

Waters II–III, respectively). One observes that the lowest stirring rate, 60 rpm, gave the greatest settling velocity ($V_s = 0.8$ and 1.9 cm min^{-1} for Waters II–III, respectively). On the other hand, as can be seen in Table 2, the lowest stirring rate gave the greatest volume of clarified liquid (100-SP), and the lowest sediment percentage (SP = 32% and 13%, for Waters II and III). The total suspended solids (TSS) after mixing time remained practically constant with this variable for Water II (TSS = 0.9 g L^{-1}) whereas for Water III this parameter rises mildly (TSS = 1.1 g L^{-1} for 60 rpm and 1.3 g L^{-1} for 300 rpm). As can be observed, the best settleability parameters were obtained for the most polluted wastewater.

It therefore seems that, although the effect is only moderate, high stirring rate lead the floc to break up [15], with a consequent reduction in settling velocity, and a rise in sediment percentage. Bearing all the factors in mind, including the elimination of organic matter, the optimal mixing would be 300 rpm taking into account the removal of COD [14] and 60 rpm for obtaining the better settleability parameters. The conclusion is that the different parameters are interrelated. When the sediment percentage (SP) and sludge volume index (SVI) increase the settling velocity (V_s) decreases, i.e., more numerous and smaller flocs are produced, which undergo less compression and hence
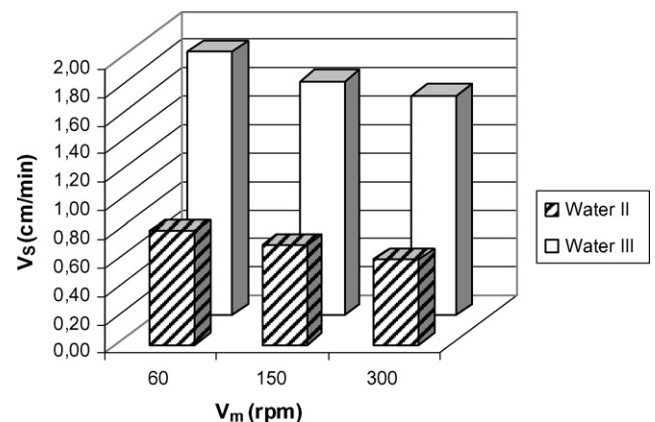

Fig. 3. Effect of stirring speed on the settling velocity (V_s). Waters II–III, pH 5, mixing time 5 min, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20\,°C$.

Table 2
Summary-table-of modified variables in the sedimentation tests

Experiment	Water	Agitation rate, V_m (rpm)	Mixing time, t_m (min)	Coagulant dose, D (mg L^{-1} Al^{3+})	pH	TSS (g L^{-1})	SP (%)	SVI (mL g^{-1})	V_s (cm min^{-1})
S-1	II	300	5	83	5	0.94	32	465	0.80
S-2		300	15	83	5	0.87	33	487	0.75
S-3		300	30	83	5	0.84	28	400	0.80
S-4	III	300	5	83	5	1.30	20	162	1.55
S-5		300	15	83	5	1.33	18	145	1.64
S-6		300	30	83	5	1.36	14	126	1.74
S-7		60	5	83	5	0.96	32	465	0.80
S-8	II	150	5	83	5	0.96	33	487	0.70
S-9		300	5	83	5	0.94	35	514	0.60
S-10		60	5	83	5	1.07	13	150	1.86
S-11	III	150	5	83	5	1.12	16	157	1.65
S-12		300	5	83	5	1.30	20	162	1.55
S-13		300	5	83	5	0.94	35	514	0.60
S-14	II	300	5	83	6	0.93	26	282	0.95
S-15		300	5	83	7	1.16	22	252	1.27
S-16		300	5	83	8	1.20	21	227	1.33
S-17		300	5	83	9	1.23	19	197	1.38
S-18		300	5	83	5	1.30	20	162	1.55
S-19		300	5	83	6	1.36	17	115	1.75
S-20		300	5	83	7	1.40	10	84	1.90
S-21	III	300	5	83	8	1.44	11	91	1.85
S-22		300	5	83	9	1.55	13	97	1.79
S-23		300	5	83	10	1.45	23	150	0.97
S-24		300	5	83	11	1.44	32	329	0.71
S-25		300	5	83	5	0.94	35	513	0.60
S-26	II	300	5	100	5	1.20	49	600	0.29
S-27		300	5	133	5	1.40	51	825	0.28
S-28		300	5	166	5	1.55	62	880	0.11
S-29		300	5	83	5	1.30	20	162	1.55
S-30	III	300	5	100	5	1.64	28	230	0.98
S-31		300	5	133	5	1.68	39	349	0.53
S-32		300	5	166	5	1.78	48	391	0.33

occupy a greater volume; therefore, because of the greater specific area of the solid adsorbent the removal of organic matter increases.

3.2. Influence of mixing time on the settleability parameters

The mixing time of the coagulant with the wastewater was also a factor with only a moderate influence on the process (experiments S-1 to S-6 of Table 2). Figs. 4 and 5 show the results of the trials performed with Waters II–III aimed at determining the optimal mixing time. One observes that the largest time, 30 min, corresponded to the formation of the largest flocs (maximum $V_s = 0.8$ and 1.7 cm min^{-1} for Waters II–III, respectively) and the smallest volume of sludge (SP = 28 and 14% for Waters II and III). In these conditions, the sludge volume index is minimum (SVI = 400 and 125 mL g^{-1} for Waters II–III). The total suspended solids (TSS) after mixing time remained practically constant with this variable (TSS = 0.9 and 1.3 g L^{-1}, for Waters II–III). Taking into account the removal of organic matter, the best results were obtained using a mixing time of 5 min.

3.3. Influence of pH on the settleability parameters

The pH is the most influential factor because it affects all the hydrolysis equilibria that the coagulation produces, the for-
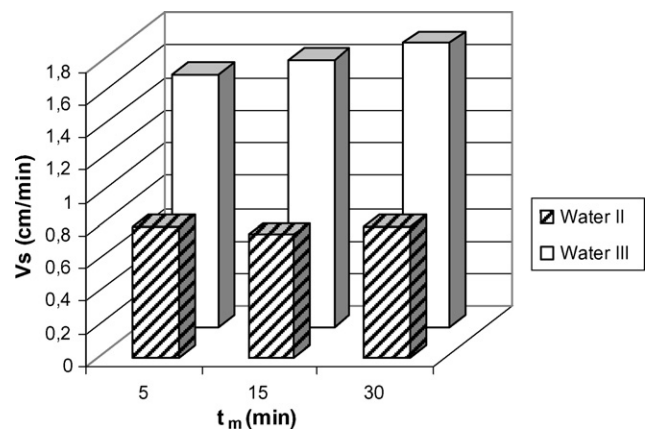

Fig. 4. Effect of mixing time on the settling velocity (V_s). Waters II–III, pH 5, stirring speed 300 rpm, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20$ °C.

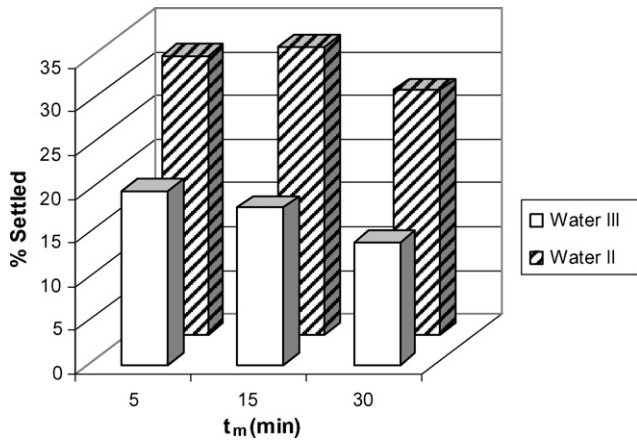Fig. 5. Effect of mixing time on % settled (SP). Waters II–III, pH 5, stirring speed 300 rpm, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20\,^{\circ}$C.

mation of mono- and polynuclear hydroxo complexes, and the concentrations of the different aluminium species in solution. All these factors will determine which type of sedimentation takes place (sweep-floc coagulation, adsorption, a combination of the two, etc.), and therefore the effectiveness of the treatment. It must also be taken into account that the wastewater will ultimately be discharged or re-used, so that the choice of an extreme pH would require a subsequent neutralization treatment.

The influence of pH on the sedimentation was studied with Waters II–III (see Figs. 6 and 7, experiments S-13 to S-24 of Table 2). From pH 5 to 7, the sediment percentage (SP) and sludge volume index (SVI) decrease for both types of wastewater, while the settling velocity (V_s) increases, i.e., less numerous and greater flocs are produced, which undergo more compression and hence occupy a smaller volume (at pH 7, SP = 22 and 10% for Waters II–III, respectively). In the following interval,
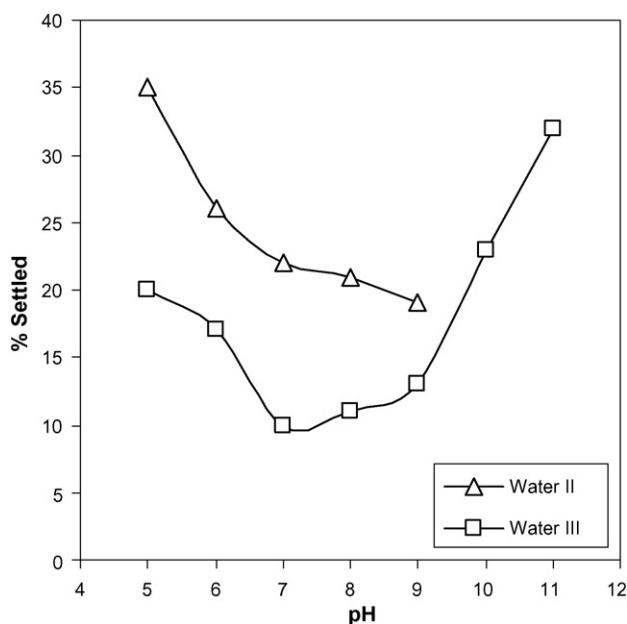
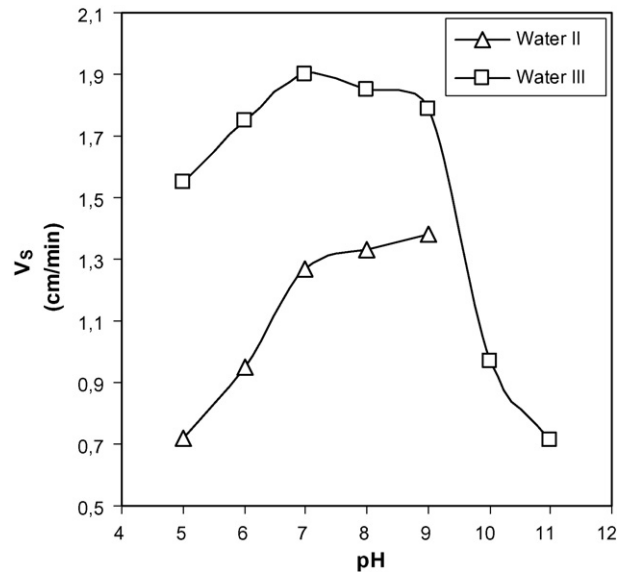

Fig. 7. Effect of pH on the settling velocity (V_s). Waters II–III, mixing time 5 min, stirring speed 300 rpm, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20\,^{\circ}$C.

pH 7–9, the values of V_s and SP almost changed. In this interval, probably the sweep-floc mechanism increases regarding to the mechanism of adsorption-neutralization that decreases in importance. As the pH rises from 9 to 11 (for Water III), the mechanism must be exclusively sweep-floc coagulation, since at these values of the pH the supersaturation would be very high, and consequently the floc nucleation rate would be far greater than the floc growth rate. One observes that the values of SP and SVI increase (for example SP for Water III increases from 10 to 33%) while V_s decreases (from 1.8 to 0.7 cm min^{-1}), a worse situation for the settleability parameters. As can be expected, the values of COD removal increases from 43% (pH 9) to 54% (pH 11), i.e., more numerous and smaller flocs are produced, which undergo less compression and hence occupy a greater volume; therefore, because of the greater specific area of the solid adsorbent the removal of organic matter increases. Taking into account both factors (organic matter removal and settleability parameters) the interval of pH 7–9 can be the most interesting.

3.4. Influence of coagulant dose on the settleability parameters

The influence of coagulant dose was studied in experiments S-25 to S-32, varying the dose from 83 to 166 mg L^{-1} of Al^{3+}. The coagulation dose affects the floc nucleation and growth rates, and the relative importance of the different mechanisms of organic matter removal (adsorption/neutralization or sweep-floc coagulation). The predominant removal mechanism at low doses is adsorption and charge neutralization, however at high doses is sweep-floc coagulation [6,11] by enmeshment in the aluminium hydroxide precipitate.

Fig. 8 shows the influence of the coagulant dose on the TSS just after mixing time. As could be expected, this parameter increases when the coagulant dose increases. This effect is more important up to a coagulant dose of 100 mg L^{-1} of Al^{3+}. On
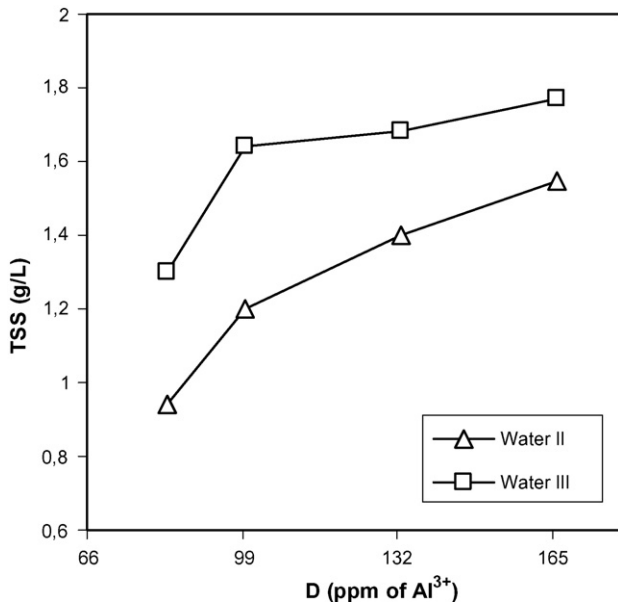

Fig. 6. Effect of pH on % settled (SP). Waters II–III, mixing time 5 min, stirring speed 300 rpm, aluminium dose 83 mg L^{-1} of Al^{3+} and $T = 20\,^{\circ}$C.

Fig. 8. Effect of coagulant dose on TSS after mixing. Waters II–III, mixing time 5 min, stirring speed 300 rpm, pH 5 and $T = 20\,°C$.

Fig. 10. Settleability parameters; SP, SVI and V_s, obtained in the same experimental conditions by iron(III) and aluminium(III) at pH 7, and by aluminium(III) at pH 5. Experimental conditions: Water II, metal concentration $[M^{3+}] = 3.70\,mM$, mixing time 5 min, stirring speed 300 rpm.

the other hand, Fig. 9 shows, for Water III, the influence of the coagulant dose on the different settleability parameters. Similar results were obtained for Water II. One observes that there is a practically linear increase in SVI and SP over the entire range of doses, the settling velocity, however, shows a practically exponential decline over the entire range. The results are coherent with the interpretation being put forward in this work. A greater coagulation dose increases the nucleation rate and reduces the floc growth rate. With more numerous, but smaller flocs, the settling velocity (V_s) decreases, while SP and SVI increase.

It may therefore be concluded that, while a high coagulant dose is beneficial for the removal of organic matter, it is detrimental for the settling process since it reduces the settling velocity, generating a larger volume of less consolidated sludge.

3.5. Comparison with iron

This section makes a comparison of both coagulants with regard to settleability parameters (SP, SVI and V_s) in Water II. Fig. 10 shows the results obtained for both coagulants using a metal concentration $[M^{3+}] = 3.70\,mM$, a mixing time 5 min, stirring rate 300 rpm, pHs 5, 7 (for Al^{3+}) and pH 7 (for Fe^{3+}). As can be seen, iron at pH 7 obtains the best settleability parameters. Moreover, aluminium at pH 7 improves settleability parameters with regard to pH 5, however worsens the organic matter removal.

3.6. Design of a clarifier-thickener unit

On the basis of the data from the settling trials and other relevant factors, we calculated the design of a clarifier-thickener unit according to the Talmadge and Fitch method [11,16]. The operating conditions chosen were: mixing time 5 min, Water II, $T = 20\,°C$, stirring rate 300 rpm, pH 7 and coagulant dose 100 mg L^{-1} of Al^{3+}. The choice was made taking into account economic factors (coagulant dose), possible discharge of the water (pH), and optimal reaction conditions.

The design area required for a clarifier-thickener that must handle concentrated suspensions under a continuous flow regime is determined by the settling and thickening characteristics of the suspension. Talmadge and Fitch indicate that the information from batch settling trials, such as is illustrated in the settling curve of Fig. 11, can be used to estimate the required clarification and thickening areas. The clarification area depends on the initial
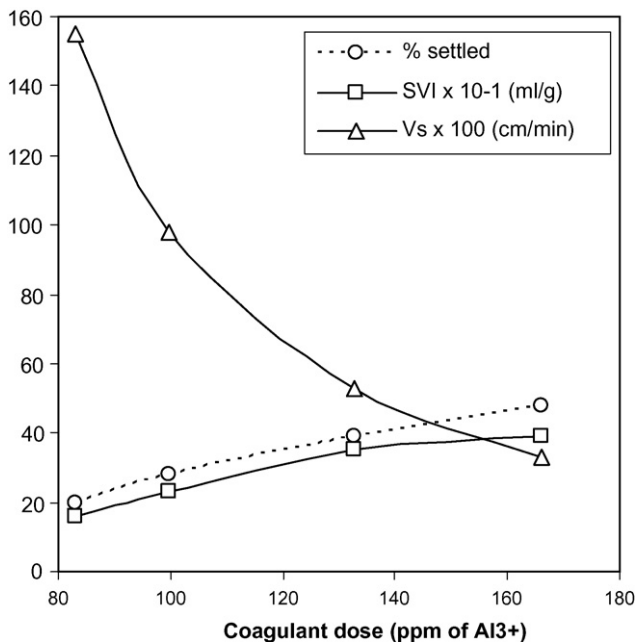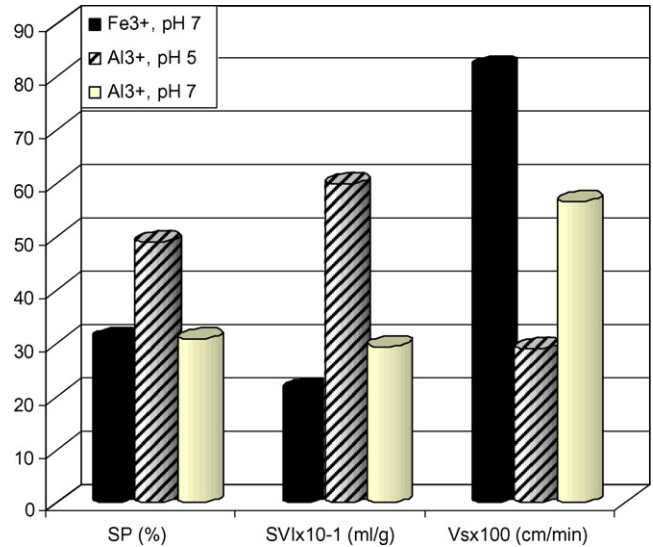

Fig. 9. Effect of coagulant dose on settleability parameters; % settled, SVI and V_s. Water III, mixing time 5 min, stirring speed 300 rpm, pH 5 and $T = 20\,°C$.
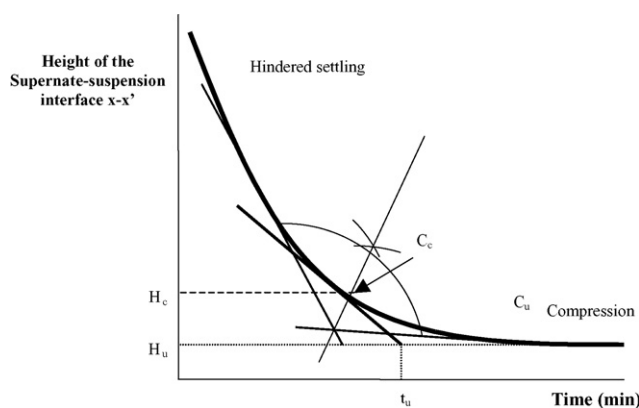
Fig. 11. Graphical analysis of the settling curve of the supernate–suspension interface.

settling velocity of the supernatant–suspension interface. The rate of loading the clarification surface must be less than the settling rate of the suspension, so that the minimum area required for clarification (A_c) is given by:

$$A_c = \frac{Q_c}{V_s} \tag{5}$$

where V_s is the settling velocity for hindered settling, determined from the first 15 min of settling, and given by Eq. (2), and Q_c is the flow rate of clarified water that can be estimated by the expression:

$$Q_c = Q \left[\frac{H_0 - H_c}{H_0} \right] \tag{6}$$

where Q is the flow rate of effluent through the tank, H_0 the initial interface height, and H_c is the interface height corresponding to the critical concentration, C_c, that will be estimated as described below. We shall assume for the present case that there are two deposits of cork-wastewater that supply an inflow to the tank of $2\,\mathrm{m}^3\,\mathrm{h}^{-1}$.

To calculate the thickener area, A_e, according to Talmadge–Fitch method [11,16], the thickening capacity can be determined from the data of a batch settling experiment corresponding to thickened (concentrated) suspensions, with adequate thickening being attained when A_e is given by the expression:

$$A_e = \frac{Q t_u}{H_0} \tag{7}$$

where t_u is the time required to reach the desired underflow sludge concentration, C_u, determined from the batch settling trials. There exist a critical concentration that gives a maximum required area. This critical concentration is to be the basis for the design.

Eckenfelder and Milbinger [17] estimated this critical concentration by taking the bisectrix of the angle formed by the tangents to the hindered settling zone and to the compression zone in the settling curve (the height of the supernatant–suspension interface *versus* time, see Fig. 11). The intersection of the bisectrix with the curve gives the point at which the concentration is critical (C_c).

The value of t_u is obtained from the intersection of the horizontal line traced from the height H_u with the tangent to the curve at the critical point. H_u is the height of the interface that corresponds to the desired sludge underflow concentration C_u, and can be obtained from the mass balance equation:

$$C_0 H_0 = C_c H_c = C_u H_u \tag{8}$$

The areas required for clarification (A_c) and for thickening (A_e) were, respectively, $A_c = 1.74\,\mathrm{m}^2$ and $A_e = 4.11\,\mathrm{m}^2$. The thickening area was therefore that used for the design. These values can be compared with those obtained for iron(III) [6], $A_c = 2.36\,\mathrm{m}^2$ and $A_e = 4.01\,\mathrm{m}^2$, in the same experimental conditions (Wastewater II $[M^{3+}] = 3.70\,\mathrm{mM}$, mixing time 5 min, stirring rate 300 rpm and pH 7). Some workers [18] apply a scale factor in calculating these two areas. The factor recommended by Eckenfelder is 1.5 for A_c and 2 for A_e.

4. Summary and conclusions

The principal findings of this work are:

(1) The optimal conditions for the removal of organic matter do not coincide with the optimal conditions for sedimentation. The stirring rate and mixing time have only a moderate influence. At 60 rpm, a lower sediment percentage and greater settling velocity were achieved. A mixing time of 30 min leads to the formation of the largest flocs and the lowest sediment volume.
(2) The pH is one of the most influential factors. In the range 7–9, SP, SVI and V_s attain their best values.
(3) Increases in the dose of coagulant, in the range 83–166 mg L^{-1} Al^{3+}, worsen the settleability parameters (increase in SVI and SP). However, the removal of organic matter increases with increasing coagulant dose.
(4) According to the method of Talmadge–Fitch, a clarifier-thickener unit to treat a wastewater flow of $2\,\mathrm{m}^3\,\mathrm{h}^{-1}$ would require a minimum area of $4.11\,\mathrm{m}^2$.

Acknowledgements

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