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Chitosan flocculation of cardboard-mill secondary biological wastewater

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ABSTRACT

Flocculation is a common secondary treatment procedure for the removal of suspended solids, colloids and organic matter present in industrial wastewater. In the present study, the flocculation of cardboard industry wastewater, treated by a biological process in an aerated lagoon, was examined using commercial grade polyaluminium chloride (PAC) and chitosan (CHITO) dissolved in acetic acid as flocculating agents. A series of flocculation jar-tests was conducted under different conditions. The influence of the flocculant dosage and the temperature of the lagoon on the quality of the treated wastewater was investigated. Optimum temperature for PAC was in the range 13–21 °C for a dosage of 0.3–0.4 $mL\,L^{-1}$ but the results were highly temperature-dependent; PAC lowered chemical oxygen demand (COD) by 40–45% and turbidity by 55–60%. With CHITO, the process was more efficient than with PAC for an effective dosage of 7 $mL\,L^{-1}$ and no influence of temperature was observed. Chitosan lowered the COD by over 80% and turbidity by more than 85%. It generated bigger flocs making settling faster than with PAC. It also removed residual colour and led to a significant decrease in the amount of heavy metals present in the effluent.

1. Introduction

Among industrial wastewaters, wastewater from pulp and paper industries is one of the most difficult to treat [1,2]. This is because the problems encountered are generally complex as the effluents contain many pollutants of various types depending on their origin. Their major features include a high level of suspended solids (SS), turbidity, chemical oxygen demand (COD), biochemical oxygen demand (BOD), heat, acidity or alkalinity, organic and inorganic contaminants including heavy metals, phenolics and dyes. These effluents are a major source of aquatic pollution and will cause considerable damage to the receiving waters if discharged untreated [3–5]. For instance, Bilotta and Brazier [5] reported that suspended solids cause serious ecological degradation of aquatic environments, a decline in the fisheries resources, and unacceptable water quality deterioration leading to aesthetic issues. Most pollutants, except colour, can be significantly reduced by general physical, chemical and biological methods such as coagulation/flocculation, chemical or electrochemical oxidation, biological processes, adsorption and membrane separations [1].

Flocculation using flocculating agents is widely used in industrial processes including water and wastewater treatment [6,7]. The flocculation process consists of combining insoluble particles (suspended solids, colloids) and/or dissolved organic matter into large aggregates, thereby facilitating their removal in subsequent sedimentation, floatation and filtration stages. The flocculating agents used can be classified into three groups [6–8]: (i) mineral additives including metal salts such as polyaluminium chloride (PAC), (ii) synthetic organic polymer such as polyacrylamide- and polyacrylate-based materials and (iii) naturally occurring flocculants such as sodium alginate and starches. One of the most frequent flocculants used in industry and in particular in pulp and paper wastewater treatment is PAC.

The general scheme for pulp and paper wastewater treatment generally involves two main stages [1]: (i) a primary clarification (or primary treatment) using physico-chemical methods such as a coagulation/flocculation process with a flotation or decantation step to remove mainly the suspended solids (SS) and colloids, and (ii) a decontamination step (or secondary treatment) using biological methods (mainly aerated lagoon) assisted by a flocculation step to remove biodegradable organic matter. Aerated lagoons are commonly used for domestic and industrial wastewater treatment due not only to their efficiency, their low cost and minimal operational requirements, but also to their integration into the environment.

It is well-known that treatment of industrial wastewater by the two previous steps is efficient to remove pollutants, especially when the main objectives are to decrease turbidity and COD.

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Primary clarification removes most SS and biological treatment lowers both BOD and COD very efficiently. However, the results are temperature-dependent, with the season playing an important role in performance. PAC too is inefficient in cold water [6]. There is also another problem, involving the potential ecotoxicity of metallic flocculants such as PAC in the flocculation steps. Using these chemical substances has two important environmental consequences: production of large volumes of (toxic) sludge and an increase in metal concentration in the water finally released (which may have human health implications) [9–11]. For these reasons, alternative flocculants such as biopolymers have been considered for environmental applications.

Among the biopolymers, chitosan, a partially deacetylated polymer obtained from the alkaline deacetylation of chitin extracted from shellfish sources, may be considered as one of the most promising bioflocculants for environmental and purification purposes [12,13] although it is more expensive than PAC. Chitosan has the characteristics of both a coagulant and a flocculant, i.e., high cationic charge density, long polymer chains, bridging of aggregates and precipitation. As it is a biomacromolecule, chitosan has the advantage of being non-toxic and biodegradable, non-corrosive and safe to handle. It is not a pollutant itself whereas PAC can be. Compared with conventional chemical flocculants, chitosan avoids secondary contamination by metals. In addition, this biopolymer is efficient in cold water and possesses outstanding chelation behaviour which renders it very efficient in interactions with both particulate and dissolved substances [12]. Hence, it can potentially be applied in water and wastewater treatment [6,13].

In this work, the flocculation of cardboard industry wastewater from a biological treatment plant using an aerated lagoon was examined comparing commercial polyaluminium chloride (PAC) and chitosan (CHITO) dissolved in acetic acid as flocculant agents. A series of flocculation jar-tests was conducted under different conditions. The influence of the flocculant dosage and the temperature of the lagoon on the quality of treated wastewater was investigated. The main objective of this study was to show the feasibility of the use of chitosan flocculant as an alternative to conventional PAC.

2. Experimental

2.1. Materials

The sample of chitosan (commercial grade) was supplied by France Chitine (Orange, France) and used without further purification. The main characteristics of the biopolymer were: chitin origin = shrimp shells, form = powder, degree of deacetylation = 85% and molecular weight = 1.8×10^5 g mol^{-1}. The choice of this chitosan was dictated by its cost (chitosan price = 17 € kg^{-1} and final solution = 1 € L^{-1}). However, the effects of the degree of deacetylation and molecular weight of the chitosan used were studied but no significant results were obtained concerning flocculation performance.

Polyaluminium chloride (PAC), commercial grade, was obtained from the Novillars mill (Novillars, France) and used as received. The characteristics of the PAC are: appearance = pale yellow solution, Al_2O_3 = 18%, density = 1.3 (20 °C), pH 0.5–1.5, and solution price = 0.4 € L^{-1}. The popularity of aluminium-based materials arises not only from their effectiveness as flocculants/coagulants, but also from their ready availability and lower cost.

All other reagents used were of analytical grade and used as received.

2.2. Preparation of chitosan flocculant

To prepare 100 mL of solution, 3 g of chitosan powder was hydrated in 95 mL of distilled water and stirred for 24 h at room temperature (20 °C). Then 5 mL of acetic acid solution (99.7%, w/w, technical grade, Carlo Erba, France) was added. To dissolve chitosan completely this solution was further stirred for 3–4 h. The final working solution of chitosan flocculant was a yellowish transparent liquid with a pH close to 5.

2.3. Wastewater

Wastewater samples were taken from the mill of Papeterie Otor which is located in *Région of Franche-Comté* (Novillars, France). The process of the wastewater treatment plant is shown in Fig. 1. Table 1 indicates that the raw effluent can be potentially very polluting. The COD of raw effluent from the production process ranged between 5000 and 9000 mg L^{-1} with an annual average concentration of 6500 mg L^{-1}. The raw effluent also contained heavy metals (Table 1). The COD of the effluent in the discharge from the treatment plant had significantly lower levels, in the range of 200 and 1200 mg L^{-1}, depending on the season, with an annual average concentration of 600 mg L^{-1}. Local regulations governing the paper mill (for a flow of 35 m^3 h^{-1}) fixed the discharge standards to 1200 mg L^{-1} (1040 kg d^{-1}) for the COD and 300 mg L^{-1} (250 kg d^{-1}) for SS.

2.4. Experimental procedure

The conventional jar-test method was used for the study of flocculation using standard procedures [14,15]. Flocculation was carried out in a six-spindle multiple stirrer unit with stainless-steel paddles (FB15034 Flocculator, rectangular paddles, 75 mm × 20 mm, Fisher Bioblock Scientific, Illkirch, France). The solution was divided into several beakers each containing 400 mL of industrial biological suspension. A standard sample was always collected to measure the initial turbidity, COD, pH, conductivity, and heavy metal content. Different volumes of PAC and CHITO solutions were then added to the beakers maintained under stirring in the jar-test. Following the addition of flocculant, the beakers were stirred vigorously (300 rpm) for 2 min. The samples were then left to settle for 2 h. The behaviour of the flocculating agent was investigated in the range of 2–15 and 0.15–1.2 mL L^{-1} for chitosan and PAC, respectively. The industrial PAC flocculant dosage used in the plant was fixed at 0.4 mL L^{-1} in winter/spring and 0.3 mL L^{-1} in summer/autumn. The pH of the test solution was not adjusted prior to addition of flocculant. This protocol was chosen as a simulation of the industrial process, and with the objective of defining the influence of the temperature of the lagoon on optimum flocculation and to show the feasibility of the use of chitosan as an alternative to PAC. Samples were then collected in the upper part of the beaker to measure the various analytical parameters of the

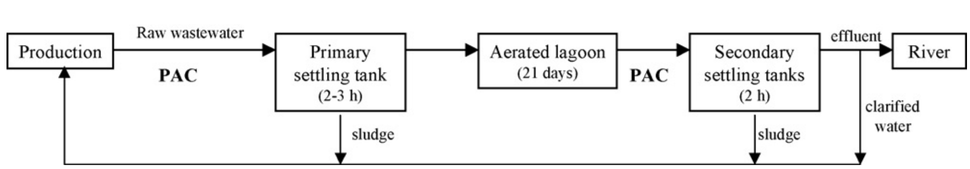

Fig. 1. The process in the wastewater treatment plant.

solution. All tests were carried out directly at the industrial site and at ambient temperatures of 3, 15, 25 and 17 °C in winter, spring, summer and autumn, respectively. A blank experiment was also systematically performed in the absence of flocculant to evaluate the natural decantation of the suspension under similar experimental conditions (temperature, pH, concentration of suspended solids). Five replicates were carried out for each test and for each analytical parameter (residual turbidity, COD, etc.). The mean value and standard deviation of the five replicates were computed.

2.5. Methods

In order to determine the physico-chemical characteristics of the effluent to be treated, the secondary wastewater was monitored through daily sampling and analysis. A large number of analyses were conducted on each sample and the following parameters were measured: turbidity, COD, SS, temperature, pH, conductivity and heavy metal content of the supernatant.

2.5.1. Estimation of chemical oxygen demand (COD), turbidity and suspended solids (SS) in raw and treated effluents

Samples for COD measurements were collected in 3 L plastic bottles and transported to the laboratory for analysis. COD was determined by the dichromate COD method based on the use of colorimetric measurement for high-range COD (0–1500 mg L^{-1} range) using potassium hydrogen phthalate solutions in the range 0–1500 mg COD L^{-1} as standards [14,15]. Samples and standards were placed on a preheated COD reactor (model FB15006, Fisher Bioblock Scientific, Illkirch, France) for 2 h at 150 °C. Following incubation, the absorbance was measured at 605 nm using a photometer (model COD Vaxio, Aqualytic PCCompact, Dortmund, Germany).

The turbidity was measured in triplicate using a turbidimeter (Aqualytic PCCompact, Dortmund, Germany); the value was measured at 875 nm in nephelometric turbidity units (NTU).

2.5.2. Temperature, pH and conductivity measurements of the effluent

Temperatures of all the samples and air were measured at the sampling site using a portable thermometer (EcoScan 4, Eutech Instruments, Singapore). The pH of each sample was measured using a portable pH meter (model 3110, WTW, Alès, France). Conductivity was measured with a low-frequency portable conductivity analyser (model C561, Turnhout, Belgium).

2.5.3. Determination of the Al, Pb, Ni and Zn concentrations

Al, Pb, Ni and Zn concentrations in the effluents were measured by furnace or flame atomic absorption spectrometry (Varian models 240Z and 240FS, France). Total metal concentrations were measured after mineralisation using acidic conditions with a Berghof microwave digestion system (model MWS-2, Germany). The accuracy of the analytical methods was checked by means of standard reference materials (Matrix reference ERM-CA011, LGC Promochem, Molsheim, France).

3. Results

3.1. The treatment of Novillars paper mill effluent

The mill uses recycled paper and cardboard as raw materials for the manufacture of corrugated cardboard (210 tonnes/day). This consumes substantial volumes of water, generating similar volumes of wastewater (~5 m^3 per tonne of paper produced). The wastewater treatment plant involved two main steps (Fig. 1): the first is primary treatment by flocculation and decantation (settling time = 2–3 h), and the second is biological treatment in an aerated lagoon (system residence time = 21 days) followed by a flocculation/decantation step (settling time = 2 h) before discharge into the aquatic environment. Flocculation accelerates floc formation, influences the physical characteristics of flocs formed (i.e., their strength, size and density), and governs the final number concentration of destabilized particles. The flocculating agent used is PAC. Part of the clarified water and all the sludge formed are reused in the pulp for corrugated cardboard production. PAC is also used in paper production as a mineral additive which explains the fact that aluminium can be found in the raw effluent.

Table 2 shows that the biologically treated effluent can be potentially highly polluted, the degree of pollution being dependent on the temperature of the lagoon and thus the season. The SS values were usually in the range of 50–500 mg L^{-1}. The turbidity of the biological effluent was 46, 229, 357 and 469 NTU for effluent Nos. 3, 2, 4 and 1, respectively. In summer and spring, turbidity was significantly lower due to the fact that higher temperatures favoured

Table 1
Characteristics of the raw industrial wastewater and biologically processed wastewater (water for discharge into the natural environment) using the process of wastewater treatment shown in Fig. 1.

Parameter	Winter effluent (effluent 1)		Spring effluent (effluent 2)		Summer effluent (effluent 3)		Autumn effluent (effluent 4)	
	Raw wastewater	Biologically processed wastewater[a]	Raw wastewater	Biologically processed Wastewater[a]	Raw wastewater	Biologically processed wastewater[a]	Raw wastewater	Biologically processed wastewater[a]
T_1[b]	3	3	15	15	25	25	17	17
T_2[c]	48	9	51	13	55	21	47	14
pH	6.4	7.7	6.3	7.2	6.6	7.3	6.4	7.3
Conductivity[d]	3670	2190	3540	2140	3580	2170	3010	2180
SS[e]	6000	240	7000	130	6200	180	6600	200
Turbidity[f]	1648	273	2739	124	1679	153	1704	173
COD[e]	6331	979	6736	457	6807	312	7308	740
Al (mg L^{-1})	74.4	14.7	66.1	11.3	61.2	2.4	56.2	4.7
Pb (μg L^{-1})	17.3	7.1	13.9	5.5	14.3	2.75	15.5	3.2
Ni (μg L^{-1})	11.3	4.1	18.3	5.7	12.4	0.7	22.3	7.6
Zn (μg L^{-1})	55.3	25.2	51.2	17.3	49.3	0.1	57.3	29.3
Colour	Greyish	Brownish	Greyish	Brownish	Greyish	Brownish	Greyish	Brownish

[a] Water discharges into the natural environment.
[b] Ambient temperature in °C.
[c] Wastewater temperature.
[d] In μS cm^{-1}.
[e] In mg L^{-1}.
[f] In NTU.

Table 2
Characteristics of settled effluent after biological treatment (effluent without post-treatment with PAC).

Parameter	Effluent 1	Effluent 2	Effluent 3	Effluent 4
Ambient temperature (°C)	3	15	25	17
Lagoon temperature (°C)	9	13	21	14
Season	Winter	Spring	Summer	Autumn
pH	7.7	7.7	8.1	7.8
Conductivity ($\mu S\,cm^{-1}$)	2478	2432	2584	2429
SS ($mg\,L^{-1}$)	440	280	60	380
Turbidity (NTU) before settling	753	652	457	629
Turbidity (NTU)	469	229	46	357
COD ($mg\,O_2\,L^{-1}$) before settling	2439	860	521	1199
COD ($mg\,O_2\,L^{-1}$)	1774	2127	934	1486
Al ($mg\,L^{-1}$)	21.7	10.6	9.5	10.3
Pb ($\mu g\,L^{-1}$)	11.2	7.3	1.90	7.9
Ni ($\mu g\,L^{-1}$)	5.3	13.5	1.4	10.2
Zn ($\mu g\,L^{-1}$)	31.2	21.2	0.17	44.3
Colour	Brownish	Brownish	Brownish	Brownish

settling. The seasonal effect of the wastewater temperature on the COD values can be also verified in Table 2. The COD of raw effluent from the lagoon was within the range of 1000–3000 $mg\,L^{-1}$ with an average concentration of 2000 $mg\,L^{-1}$. After settling, the COD values oscillated between 500 and 1800 $mg\,O_2\,L^{-1}$ depending on the temperature of the lagoon. During winter, COD reduction efficiency in the lagoon was lower due to lower bacterial activity. Higher temperatures are associated with higher microbial growth rates [18,19]. It is also possible that the microbial community changes under various environmental conditions; in particular the presence of heavy metals can have a toxic effect on the biomass. Metal cations influence microbial biomass growth, and thus also affect the depurative efficiency of the treatment. Bruins et al. [20], and Said and Lewis [21] reported that some heavy metals (Cu, Zn and Cd) exert toxicity and may also simultaneously affect organic biodegradation owing to heavy metal accumulation in the microbial cells. The pH of the lagoon effluent always remained between 7.5 and 8 ± 0.1 in more than 95% of the measurements. A detailed analysis of the ions present (Table 2) indicated that the major heavy metals in the biologically treated wastewater were aluminium (9.5–21.7 $mg\,L^{-1}$), nickel (1.4–13.5 $\mu g\,L^{-1}$), zinc (0.17–44.3 $\mu g\,L^{-1}$) and lead (1.9–11.2 $\mu g\,L^{-1}$).

3.2. Preliminary tests

Fig. 2 shows a comparison between biologically treated settled effluent without post-treatment and effluent treated with polyaluminium chloride (PAC) and chitosan (CHITO) as floc-

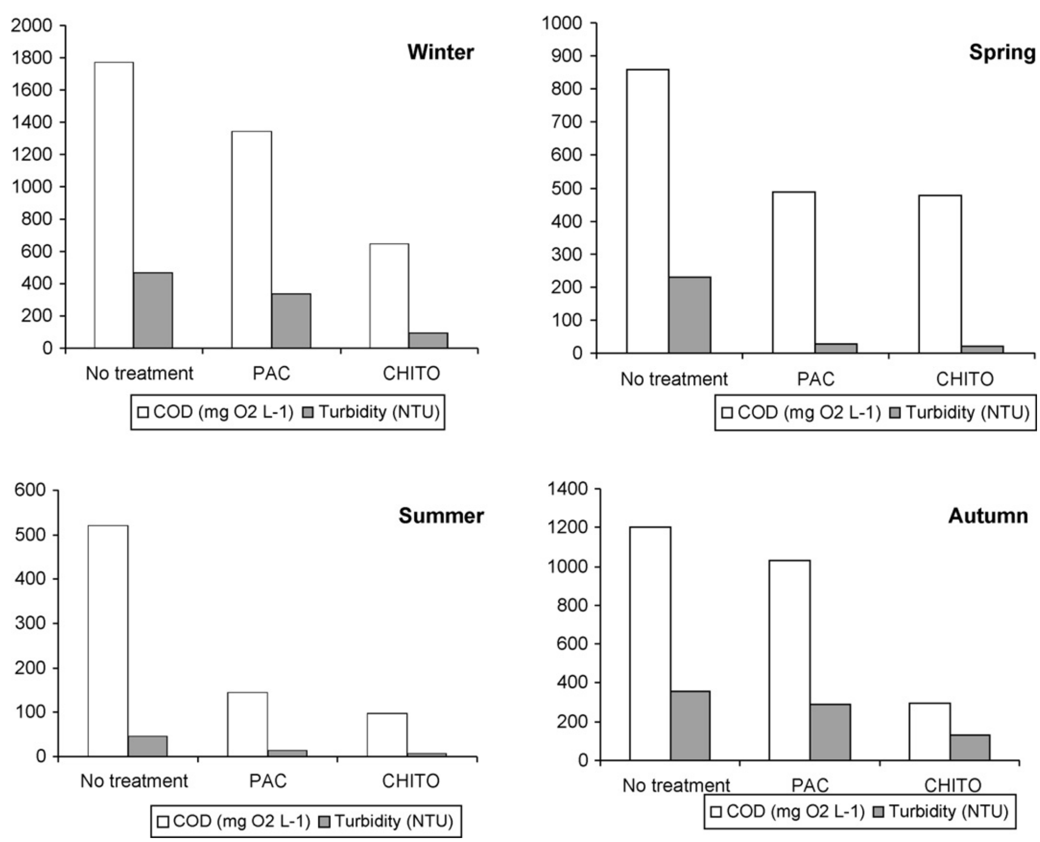

Fig. 2. Comparison between settled biologically treated effluent with or without post-treatment with polyaluminium chloride (PAC) or chitosan (CHITO) as flocculating agents on COD and turbidity reduction performance (PAC and CHITO dosage 1 and 7 $mL\,L^{-1}$, respectively; lagoon temperature 9 °C in winter, 13 °C in spring, 21 °C in summer and 14 °C in autumn).

culating agents on COD and turbidity reduction performance. The flocculant dosage was kept constant while the influence of lagoon temperature was studied. The optimum dosage determined in the laboratory and used for these experiments was 1 and 7 mL L^{-1} for PAC and CHITO, respectively. Lagoon temperature was 9 °C in winter, 13 °C in spring, 21 °C in summer and 14 °C in autumn (Table 2). The results showed that PAC lowered COD by 38% and turbidity by 55%. However, the results were highly temperature-dependent. As we can see in Fig. 2, PAC was efficient above all in summer and spring and optimum temperature for PAC was in the range 13–21 °C for a flocculant dosage of 1 mL L^{-1}.

With CHITO, process efficiency was greater than with PAC for an optimum and effective dose of 7 mL L^{-1} and no influence of temperature was observed. It lowered COD by more than 80% and turbidity by more than 85%. Irrespective of the season, chitosan formed bigger flocs with quicker solid settling than PAC. Chitosan as cationic bioflocculant had a higher potential than cationic PAC when acting as secondary flocculant in the treatment of industrial wastewater. Similar conclusions have been published in the literature [6,7,13]. The mechanism proposed is the following [6,7]: bioflocculation results from charge neutralization, patch flocculation, and/or polymer bridging. Patch flocculation occurs when dense macromolecules adsorb to particles and locally form positively and negatively charged areas on the particle surface. This results in strong electrical attraction between particles. Polymer bridging occurs when long-chain macromolecules adsorb onto the surface of more than one particle, thereby forming strong aggregates of large flocs.

Figs. 3 and 4 show the reproducibility of the measurements over five days for settled biologically treated effluent without post-treatment, and with PAC and CHITO treatment on COD and turbidity reduction performance, respectively. In Fig. 3, it should be pointed out that COD values in the settled effluent without post-treatment varied with time. Average COD values were 550 and 850 mg L^{-1} in summer and spring, respectively. For these effluents, PAC treatment is not necessary because the COD values are lower than the stipulated 1200 mg L^{-1}. This is due to the better ability of the effluent to settle when the temperature is high. The average COD values were 1800 and 1250 mg L^{-1} in winter and autumn, respectively. In this case, PAC treatment was necessary to reach acceptable standards.

After treatment with PAC, the average values were 200 and 450 mg L^{-1} in summer and spring (Fig. 3), respectively, showing that the PAC was efficient when the temperature was higher than 13 °C [16,17]. However, at lower temperatures, the results were dependent on the season. In particular in winter, for a lagoon temperature of 9 ± 1 °C, PAC was ineffective: the average COD values obtained being 1300 mg L^{-1}. It is well-known that, in winter, the biological activity in the lagoon is low [18,19]. This induces a lower biodegradation of the effluent and thus higher values of SS and turbidity, as reported in Fig. 4 and Table 2.

With CHITO, process efficiency was greater than with PAC for an effective dosage of 7 mL L^{-1}. Fig. 3 shows that, in summer and spring, CHITO and PAC had the same performance: the average COD

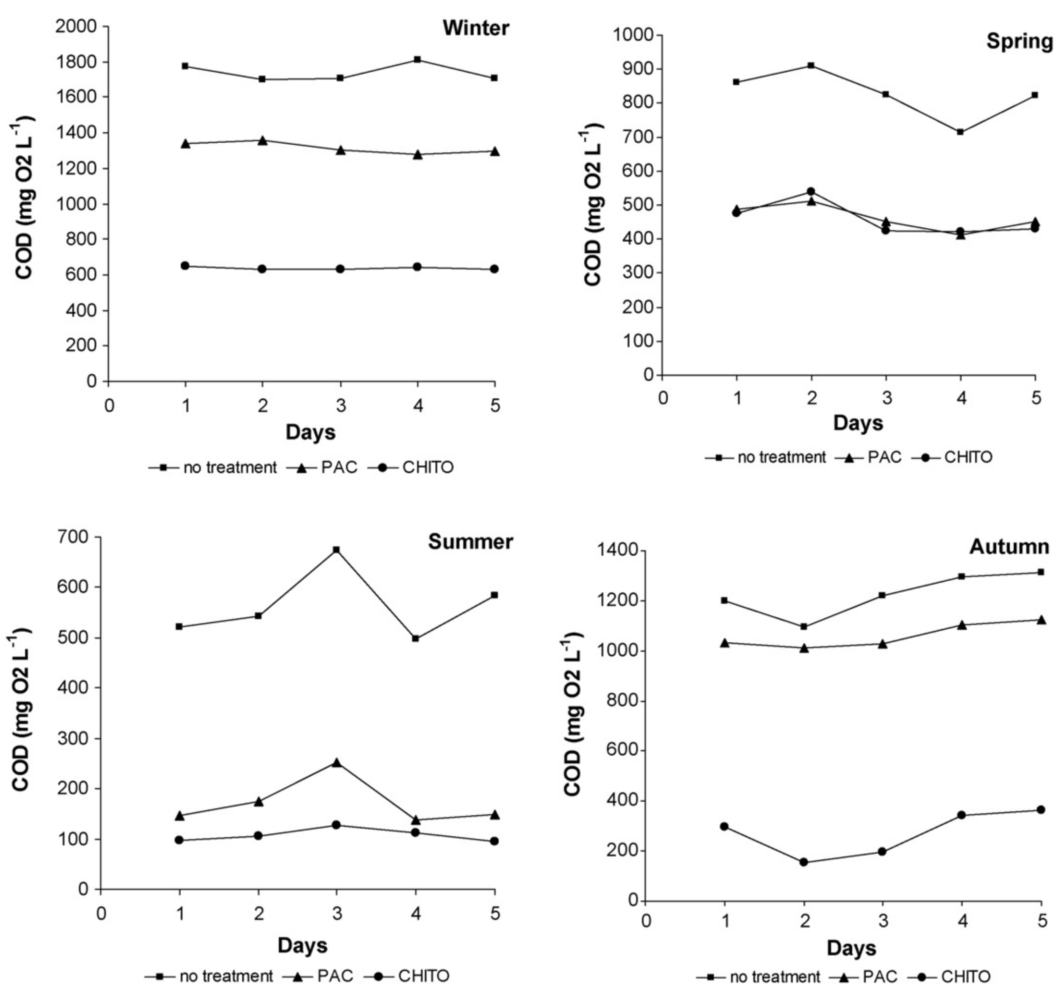

Fig. 3. COD measurements over five days for biologically processed settled effluent without post-treatment, and with polyaluminium chloride (PAC) and chitosan (CHITO) treatment (PAC and CHITO dosage 1 and 7 mL L^{-1}, respectively; lagoon temperature 9 ± 1 °C in winter, 13 ± 1 °C in spring, 21 ± 1 °C in summer and 14 ± 1 °C in autumn).

values were respectively 150 mg L^{-1} (200 for PAC) and 450 mg L^{-1}. A similar trend was observed for turbidity reduction (Fig. 4). However, with CHITO, no influence of temperature was observed for either COD or turbidity reduction (Figs. 3 and 4). Chitosan is efficient at lower temperatures [13]: the average turbidity values were 100 and 300 NTU for CHITO and PAC in winter, respectively, and 120 and 270 for CHITO and PAC in autumn, respectively.

In general, our results showed that chitosan reduced the COD by more than 80% and turbidity by over 85%, while PAC only lowered COD by 40–45% and turbidity by 55–60%.

3.3. Influence of the settling time

The influence of the settling time was also studied, the duration of the contact time of the experiments being fixed at 2 min in all cases. Fig. 5 shows the influence of the settling time on COD reduction performance. In winter, COD values were constant after 40 min while in other seasons, the plateau was reached in less than 20 min. Again, this is in relation with the issue of the settleability varying with temperature [16,17]. Similar conclusion can be drawn after PAC and CHITO treatment. The plateau was reached more rapidly in summer, spring and autumn with settling times in the range of 15–20 min, independent of the lagoon temperature, while in winter, settling time increased (40 min). The settling time used at the treatment plant was fixed at 2 h for technological reasons. This time was used in further studies.

3.4. Influence of the flocculant dosage

The influence of the flocculant dosage on COD and turbidity reduction performance is reported in Fig. 6. For these experiments, the settling time was 2 h as in the industrial conditions. Lagoon temperatures were 10, 14, 23 and 13 °C in winter, spring, summer and autumn, respectively. The COD and turbidity values decreased with the increase of the flocculant dosage. Similar results were obtained for PAC and CHITO. However, the optimum dosage for PAC was 1 mL L^{-1} while for CHITO the value was higher (7 mL L^{-1}).

But, the concentration of PAC was fixed by the mill at 0.3 and 0.4 mL L^{-1} in summer/autumn and winter/spring, respectively. In general, using these concentrations, average industrial process efficiency varied between 40% and 50% for COD and 50% and 60% for turbidity, depending of the season. The optimum concentration of PAC (i.e., 1 mL L^{-1}) was not used at the treatment plant because it leads to problems such a drop in the pH, the development of lighter flocs that do not settle as well and also an increase in cost of the treatment process.

3.5. Effect of flocculation on the amount of heavy metals present in the biologically treated wastewater

The results demonstrated chitosan was effective as a flocculating agent for the two main industrial objectives which are the

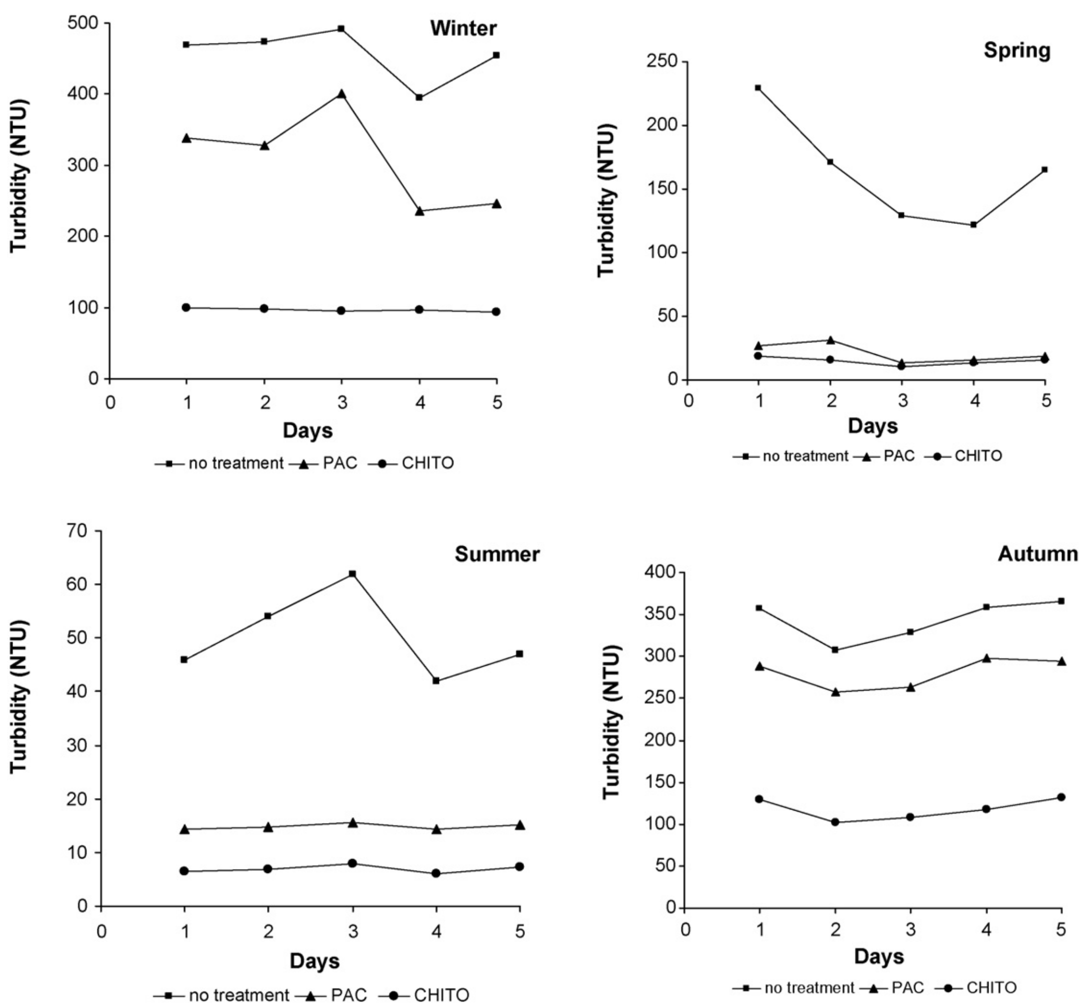

Fig. 4. Turbidity measurements over five days for biologically processed settled effluent without post-treatment, and with polyaluminium chloride (PAC) and chitosan (CHITO) treatment (PAC and CHITO dosage 1 and 7 mL L^{-1}, respectively; lagoon temperature 9 ± 1 °C in winter, 13 ± 1 °C in spring, 21 ± 1 °C in summer and 14 ± 1 °C in autumn).

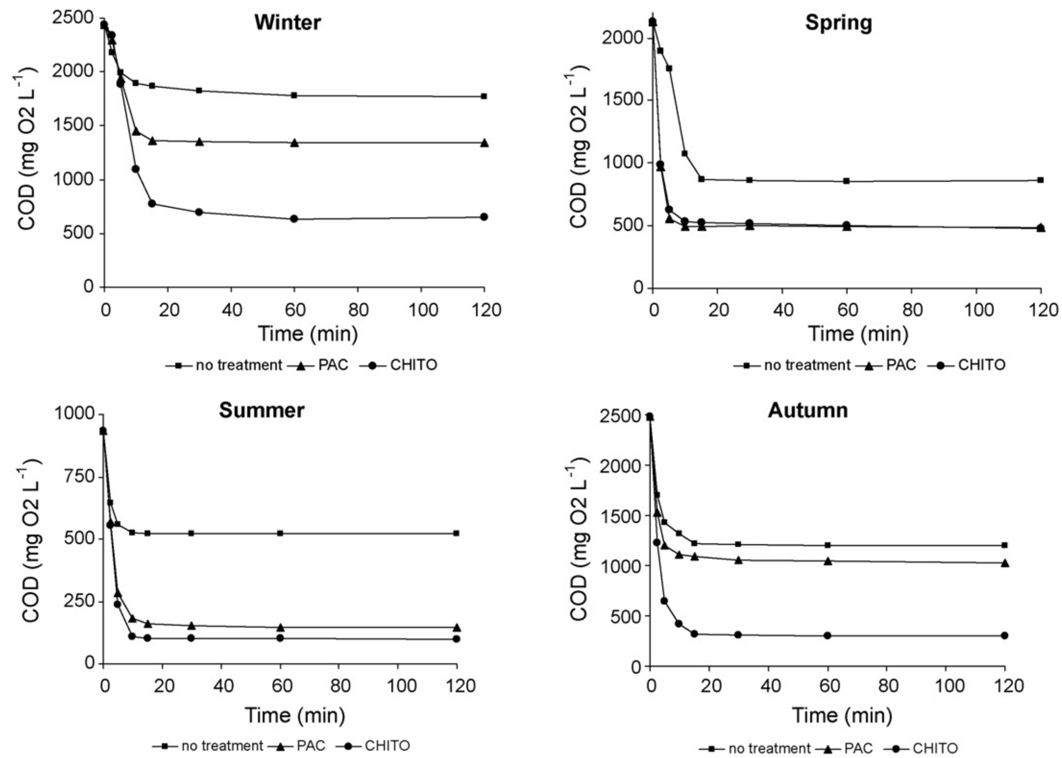

Fig. 5. Influence of the settling time on COD reduction performance (PAC and CHITO dosages 1 and 7 mL L^{-1}, respectively; lagoon temperature 9 ± 1 °C in winter, 13 ± 1 °C in spring, 21 ± 1 °C in summer and 14 ± 1 °C in autumn).

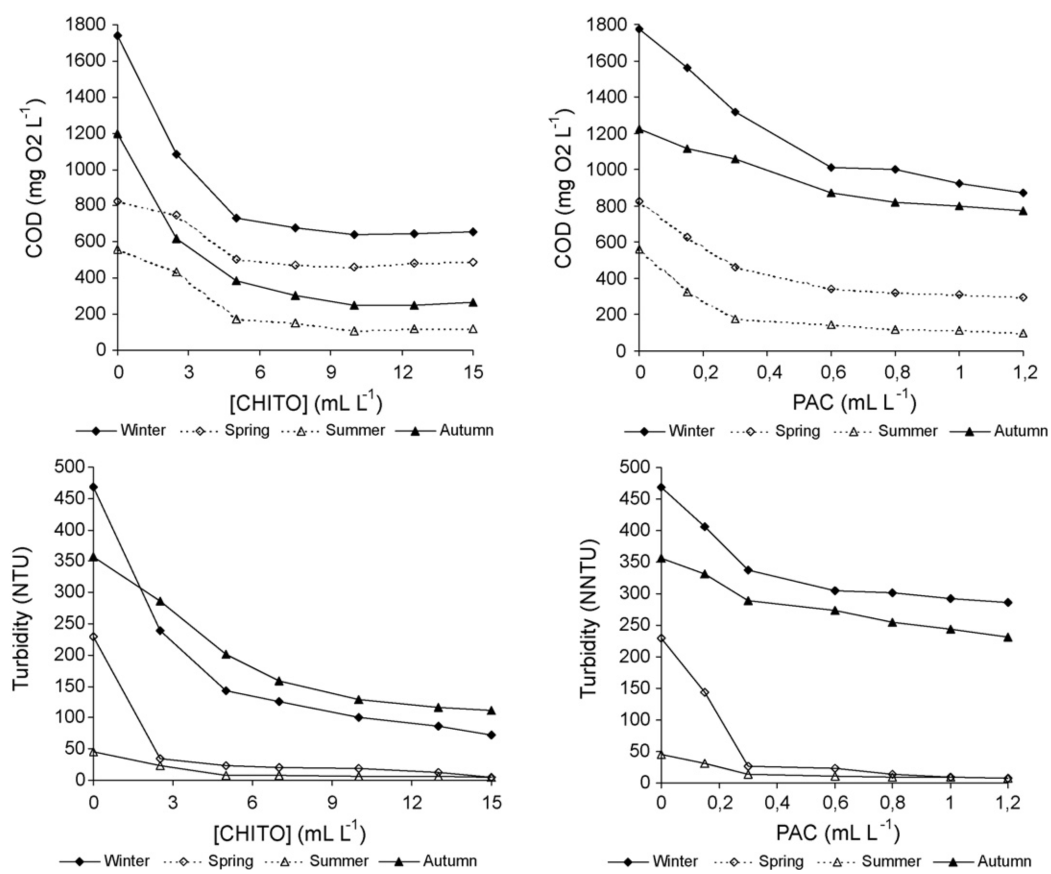

Fig. 6. Influence of the flocculant dosage on COD and turbidity reduction performance (settling time = 2 h; lagoon temperature 10 °C in winter, 14 °C in spring, 23 °C in summer and 13 °C in autumn).

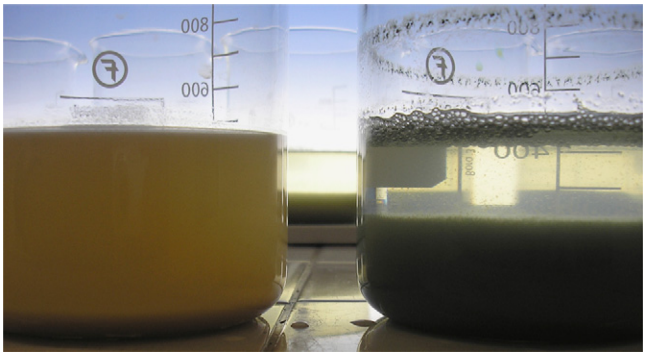

Fig. 7. Photograph of samples: biologically processed effluent without post-treatment (on the left) and treated with chitosan (on the right) (settling time = 2 h; CHITO dosage = 7 mL L^{-1}; lagoon temperature 9 °C in winter.

decrease of both turbidity and COD. Moreover, the results were temperature-independent. In this study, other interesting results were obtained: the chitosan removed both the residual colour (Fig. 7) and the heavy metals (Fig. 8).

The brownish colour of the biological effluent is mainly attributable to lignin and its derivatives, which are difficult to degrade by microorganisms. It is well-known that conventional biological treatment processes have little or no effect on wastewater decolourisation [1,22]. Fig. 7 shows the use of chitosan is also effective to remove the colour from the biologically treated effluent.

Fig. 8 shows the influence of the flocculation process on the removal of the heavy metals present in the raw biologically treated effluent (the characteristics of the effluent are reported in Table 2). The heavy metals occurring were aluminium, lead, nickel and zinc. The concentrations obtained in winter (effluent 1) were 11.2, 5.3 and 31.2 μg L^{-1} for Pb, Ni and Zn, respectively, and 21.7 mg L^{-1} for Al. The results reported in Fig. 8a show a strong increase in Al content (in the range 24–33 mg L^{-1}, depending on the temperature) when the effluent was treated by PAC while with CHITO treatment, we observed a significant decrease for all the effluents. In winter we found 9.8 mg L^{-1} for Al following CHITO treatment instead of 21.7 mg L^{-1} in the control. The same reduction was observed for Pb, Ni and Zn for CHITO and PAC, but CHITO always gave the lowest levels.

4. Conclusions

In the present study, we compared the performance of polyaluminium chloride (PAC) and chitosan (CHITO) as agents for the flocculation of cardboard industry wastewater biologically processed in an aerated lagoon. A series of flocculation jar-tests was conducted under different conditions showing the influence of the flocculant dosage and the temperature of the lagoon on the quality of treated wastewater. PAC allowed a reduction of 40–45% in chemical oxygen demand (COD) and 55–60% in turbidity. The results were highly temperature-dependent. Process efficiency with CHITO was much higher than with PAC and with CHITO no influence of temperature was observed. Chitosan allowed the reduction of more than 80% of the COD and more than 85% of the turbidity. It also removed residual colour and led to a significant decrease in the amount of heavy metals present in the effluent. Although its price is higher than that of PAC, all the results showed that chitosan was more environmentally beneficial than conventional flocculant in wastewater treatment. Nevertheless, a cost–benefit analysis of using chitosan for this purpose needs to be conducted to judge the economic feasibility of its practical use. Undoubtedly, with the new legislation, it is expected that the price of chitosan will fall which will favour its use in wastewater treatment.

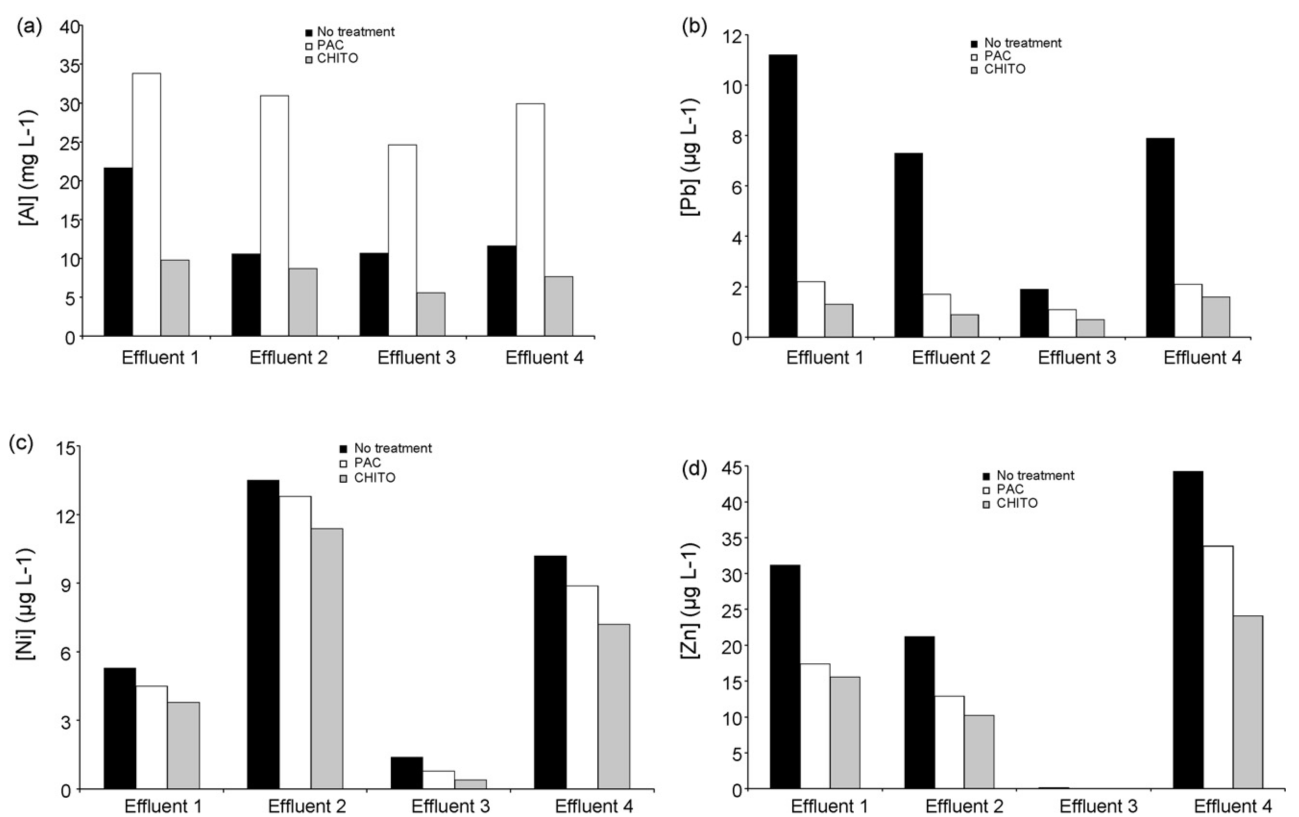

Fig. 8. Influence of the flocculation process on the removal of heavy metals: (a) aluminium (mg L^{-1}), (b) lead (μg L^{-1}), (c) nickel (μg L^{-1}) and (d) zinc (μg L^{-1}). Settling time = 2 h; PAC and CHITO dosage 1 and 7 mL L^{-1}, respectively; lagoon temperature 9 °C in winter, 13 °C in spring, 21 °C in summer and 14 °C in autumn.

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