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Olive Mill and Winery Wastewaters Pre-Treatment by Coagulation with Chitosan

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The pre-treatment of both winery wastewater (WW) and olive mill wastewater (OMW) by coagulation, using a natural organic coagulant, was investigated as a possible alternative to conventional metal based coagulants, in order to produce a potentially reusable organic sludge. Chitosan was chosen as a model natural organic coagulant and the coagulation process was optimized investigating different coagulant doses and pH values. In spite of the notably lower polluting load for the WW compared to the OMW, the efficiency of the chitosan coagulation was found to be high in terms of total suspended solids (81% and 80% for OMW and WW respectively) and turbidity (94% and 92% for OMW and WW respectively) removal for both wastewaters, but a notable difference was observed in terms of organic matter removal (32% and 73% in terms of COD for OMW and WW respectively). Taking into account that the best performances of the coagulation process by chitosan were achieved at the actual pH for OMW as well as no significant differences were observed for WW as the pH was changed, no chemicals addition is required to adjust pH.

Keywords agro-industrial wastewater; chemical oxygen demand; chitosan; natural organic coagulants; total suspended solids; turbidity

INTRODUCTION

The disposal of agro-industrial wastewaters such as olive mill wastewaters (OMWs) and winery wastewaters (WWs) is a serious environmental problem, in particular in the Mediterranean Sea region, the most important area in the world for olive oil and wine production. The concern for the environment is due to the characteristics of these effluents which are acidic (pH 4.0–6.0), with a high organic matter (5.0–200 $g\,L^{-1}$ and 3.0–30 $g\,L^{-1}$ of chemical oxygen demand (COD) for OMWs and WWs respectively), and suspended solids (1–100 $g\,L^{-1}$ and 2–18 $g\,L^{-1}$ of total suspended solids (TSS) for OMWs and WWs respectively) content (1–4). Amongst other organic compounds, OMWs and WWs contain high concentrations of phenols (2–10 $g\,L^{-1}$), which make them difficult to treat by biological processes because they result in phytotoxicity and toxicity to bacteria (4–6). Several technologies have been attempted for organic matter degradation by chemical and biological processes as well as their combinations (7–10). Taking into account that the high TSS content of OMWs and WWs can interfere in different ways with the processes used for organic matter removal, a separation process is necessary in order to improve the efficiency of subsequent treatment steps.

Coagulation is a chemical process typically used in wastewater treatment in order to remove suspended solids as well as to improve the removal of COD. By means of this process the tendency of small particles in an aqueous suspension to attach to one another can be significantly improved. The interaction among the particles results in the formation of larger aggregates that can be removed from the water by sedimentation and/or filtration. The process by which the particles in suspension are modified in order to increase their tendency to aggregation is known as destabilization. The destabilization mechanism by surface charge neutralization occurs as metal- (mainly aluminium and iron) based coagulants, the most widely used chemicals in the coagulation process (11–13), are added to the suspension. These compounds form hydrolysis products characterized by a charge opposite in sign to the net surface charge of the particles (typically, in water and wastewater treatment the average charge of the suspension is negative), therefore aggregation among the particles can occur. Another destabilization mechanism typically used to explain the removal of particles in water and wastewater coagulated suspensions is "interparticle bridging" (14). In this case, destabilization occurs when high molecular weight polymer entraps more particles forming an interparticle bridge. Two conditions are necessary in order for this mechanism to take place. The polymer must be long enough to extend beyond the electrical double layer as well as the particle to be entrapped must have sites available for adsorption. Taking into account the above-mentioned coagulation mechanisms, the contribution of the

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coagulation process to COD removal is related to the trapping of particulate COD and adsorption of soluble COD by means of particle aggregates/flocs.

Unfortunately, the release of metal residuals in the effluent, when metal salts coagulants are used in wastewater treatment, may result in adverse effects for the receiving water body. Moreover, the sludge produced in the coagulation step may not be reused because of the presence of the metals, thus the necessity of a proper disposal will increase the management costs. On the opposite side, the use of natural organic coagulants (NOCs) could result in no toxic effect on the water bodies; moreover, the organic sludge produced from the coagulation process may be reused thus saving money for sludge disposal. NOCs have been successfully applied in the last several years in water and wastewater treatment (15–19). NOCs can be classified according to the natural source they are extracted from: plants seeds, plants, animals. Chitosan is a linear cationic polymer of high molecular weight obtained by deacetylation of chitin, a cellulose biopolymer widely distributed in nature, especially in marine invertebrates, insects, fungi, and yeasts. Chitosan was successfully investigated for the removal of particulate and dissolved contaminants from aqueous solutions (20) as well as it was applied in the treatment of drinking water (21), dairy (22), pulp and paper (23), dye (24), and coal mining (25) wastewaters. Meyssami and Kasaeian (26) investigated the coagulation of OMW model solutions by chitosan alone and as a “coagulant aid” in combination with alum; the combination chitosan-alum resulted in the best turbidity removal (90%) for the investigated emulsion. Moreover, chitosan was found to be effective in the removal of the main acid components of vinasse (27), liquid waste remaining after distillation during the production of wine brandies.

The aim of the present work was to investigate the coagulation of OMWs and WWs by NOC, as possible alternative to conventional metal based coagulants, in order to produce a potentially reusable organic sludge. Chitosan was chosen as model NOC and the coagulation process was optimized investigating different coagulant doses and pH values, according to turbidity and TSS removal. The removal of organic matter was also investigated in terms of COD and UV absorbance measurements.

EXPERIMENTAL

Materials

0.1 N sulphuric acid (H_2SO_4) and 0.2 N NaOH from Carlo Erba (Italy) were used to adjust pH. Commercial fine grade chitosan (ChitoIndustrial 40500: dry matter >90%, ash <1%, degree of deacetylation >95% (colloidal titration), solubility >99% (in 1% acetic acid solution)) from Primex (Iceland), made from fresh shrimps shells (*Pandalus borealis*), was used as coagulant. 2 M HCl (Carlo Erba) was used to prepare chitosan stock solution. All stock solutions were prepared using deionized water (Millipore).

Wastewaters Samples

OMWs sample used in this study was taken downstream of the extraction phase of a three-phase olive mill located in Salerno province (Campania, Italy). WWs come from a wine production firm located in Avellino province (Campania, Italy) during the nonvintage season; the samples were taken just downstream of the equalization tank of the wastewater treatment plant (upstream of biological process unit).

Samples were collected in 2 L PEHD bottles, stored at 4°C, and shaken each time before coagulation tests. At the beginning of each one experiment the untreated sample was monitored by measuring all parameters as control (COD, pH, TSS, turbidity, UV absorbance).

Preparation of Chitosan Solutions

5000 $mg\,L^{-1}$ chitosan stock solution was prepared as follows: 500 mg of ChitoIndustrial 40500 were dissolved in 2.5 mL of 2 M HCl solution and 47.5 mL of deionized water (Millipore); after 60 minutes, 50 mL of deionized water were added.

Coagulation/Flocculation Experiments

The efficiency of the coagulation process was investigated under actual pH conditions (4.4 and 6.8 for OMW and WW respectively), changed pH conditions (4, 5 and 6), and different coagulant dosages (in the range 20–600 $mg\,L^{-1}$). The coagulation/flocculation experiments were carried out by means of Jar-tests apparatus (Isco, USA) at room temperature (about 20°C). The pH value was adjusted by adding a strong base (0.1 M NaOH) or a strong acid (0.1 M H_2SO_4) to the suspension throughout the experiments. Following the addition of the coagulant, the samples were subjected to a rapid mixing step at 100 rpm for 2 min, a slow mixing step at 30 rpm for 30 min and a subsequent sedimentation step for 60 min. The samples were taken after the sedimentation step to be analyzed for UV absorbance, turbidity, COD, and TSS. Coagulation/flocculation experiments were duplicated for some of the investigated conditions (seasonality of olive oil and wine production, variability of wastewater characteristics, and operating problems limit the amount of wastewater samples available for the experiments). Although the results from jar tests were confirmed by the duplication of some experiments, they are not considered sufficient to perform any statistical processing.

Analysis

The measurements of absorbance spectra were carried out using a λ12 UV-Vis spectrophotometer from Perkin Elmer. TSS and COD were measured according to standard methods (28). Turbidity was detected by HACH turbidimeter (model 2100 N). Hanna Instruments probe (model HI 8314) was used for pH measurements.

RESULTS AND DISCUSSION

Samples Characteristics

The characteristics of OMW strongly depend on the type of olive and the process used for olive oil extraction (2,6). The OMW sample was characterized by high polluting loading in terms of COD (53.1 g L^{-1}), TSS (6.7 g L^{-1}) and turbidity (10000 NTU), and low pH (4.4). WW is extremely variable in quality and discharge volume through the year depending on the specific winery operation (6,29). In this study WWs were collected during the bottling phase, therefore, as expected, they showed a high pH value (around 6.8) because of alkaline products used in the cleaning operations (29) and the dilution effect due to the washing process. Moreover, dilution also decreased COD, TSS, and turbidity (1550 mg L^{-1}, 750 mg L^{-1} and 180 NTU respectively) compared to the vintage phase.

Effect of Coagulant Dosage

The removal of turbidity and TSS from OMW and WW samples by means of chitosan coagulation, without any pH adjustment, is shown in Fig. 1 and Fig. 2 respectively.

The coagulation efficiency by chitosan was investigated in the range of 100–600 mg L^{-1} for OMW according to the results achieved in our previous work (31), and in the range of 20–500 mg L^{-1} for WWs, taking into account the lower initial loading in terms of TSS and turbidity compared to OMW. The optimum chitosan dosage for OMW treatment was found to be 400 mg L^{-1} which allowed to reach a residual turbidity of 600 NTU (94% removal). As chitosan dosage was increased over 400 mg L^{-1}, residual turbidity stabilized at 600 NTU until the maximum chitosan dosage was investigated. A similar behavior was observed when the coagulation process was monitored in terms of TSS, with 81% removal at 400 mg L^{-1} coagulant dose (Fig. 2). In some way, this result finds confirmation in the work of Ahmad and co-workers (30), a study which compared chitosan, alum, and PACl in the coagulation of palm oil mill effluent. Although a similar behavior was observed between the turbidity and TSS removal by chitosan, some differences can be emphasized. TSS concentration drastically decreased as 200 mg L^{-1} of chitosan were added (62% removal) (Fig. 2); instead, when turbidity was monitored, 100 mg L^{-1} of chitosan were enough to decrease (68% removal) the initial turbidity (Fig. 1). Moreover, as chitosan dosage was increased over 400 mg L^{-1}, TSS concentration started to increase.

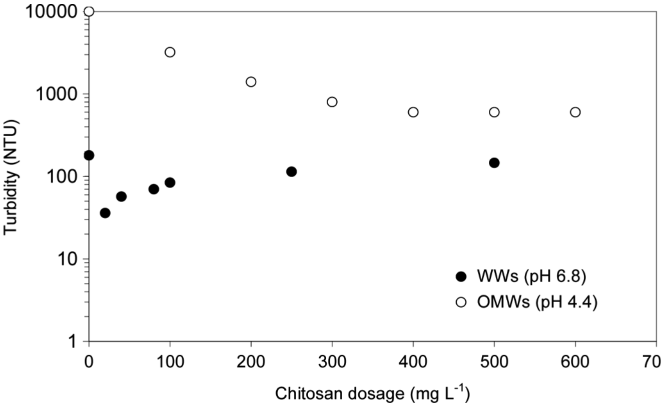


FIG. 1. Effect of different chitosan dosages on the turbidity removal.

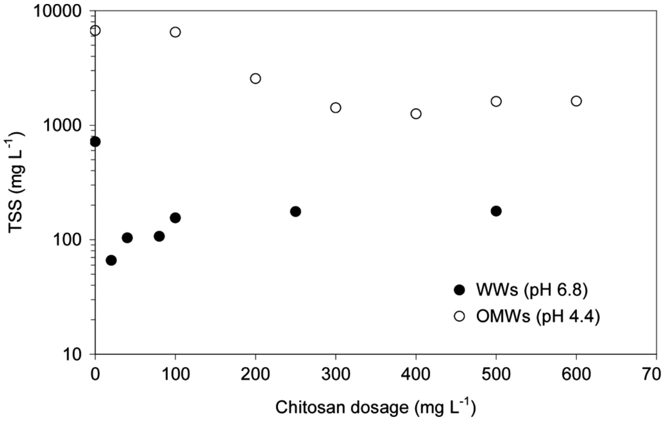


FIG. 2. Effect of different chitosan dosages on TSS removal.

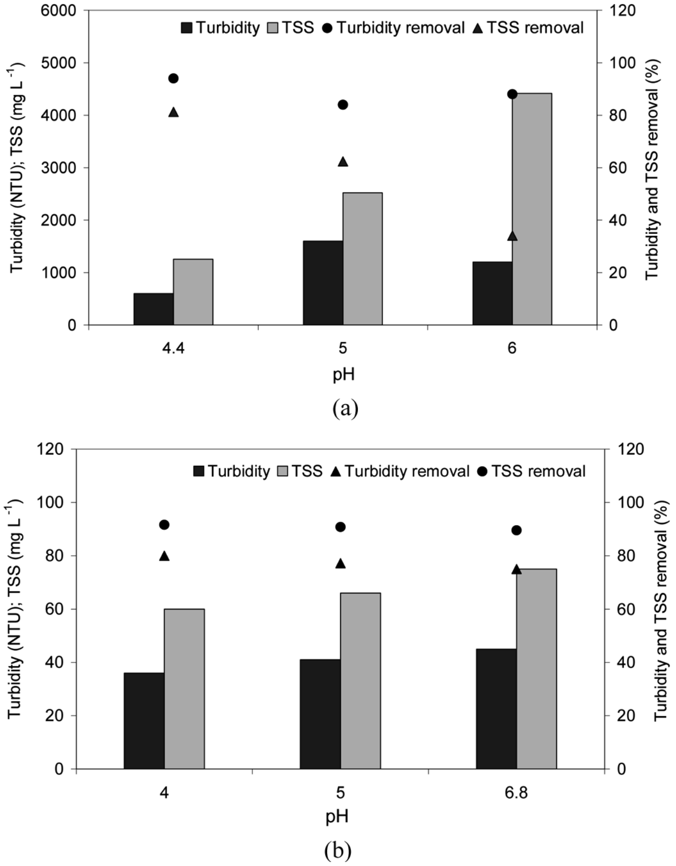
The optimum chitosan dosage in terms of turbidity removal from WWs was found to be 20 mg L^{-1} which allowed to reach a residual turbidity of 36 NTU (80% removal) (Fig. 1). Further increases in coagulant dosage resulted in a decreased efficiency of the process. A similar trend was observed for TSS removal (Fig. 2). TSS concentration drastically decreased as 20 mg L^{-1} of chitosan were added (92% removal), but when the coagulant dosage was increased over 20 mg L^{-1}, TSS concentration increased as well. Such a low optimum chitosan dosage compared to OMW coagulation tests can be explained by the differences in terms of initial TSS and turbidity; a higher initial concentration of TSS and turbidity resulted in an increased coagulant demand in the OMW sample to destabilize the suspension.

This result, observed in previous work too (30), can be explained by the flocculation mechanisms of particles by polymers as a result of "polymer bridging" and subsequent restabilization mechanism. Under batch experimental conditions, as chitosan was added to the suspension at dosages lower than the optimum one, particles bridging occurred and aggregates were effectively settled. On the other hand, as chitosan dosage exceeds the saturation, an inversion of the charge in the suspension might have occurred due to a higher formation rate of positive charged chitosan-solids aggregates, so an electrostatic repulsion among them resulted in a less effective settling.

Effect of Initial pH

In the present study the coagulation efficiency of OMW by chitosan was investigated at a maximum initial pH value of 6.0, because in our previous work (31), as pH was increased over 6.0, a dramatic change occurred in the wastewater suspension which resulted in an evident restabilization. The effect of initial pH was investigated at optimum coagulant dosage (400 mg L^{-1} for chitosan). The best removal (94%) in terms of turbidity (Fig. 3a) was detected at actual pH (4.4).

In spite of the wide pH range investigated at optimum coagulant dosage (20 mg L^{-1}), the residual turbidities of WWs samples only slightly decreased (turbidity removal changed from 75 to 80%) as the pH was decreased from 6.8 to 4 (Fig. 3b), suggesting that the efficiency of WWs coagulation by chitosan is only slightly influenced by the pH change. Moreover, a better behavior in terms of TSS removal compared to turbidity was observed for WWs. Therefore, taking into account the pH range investigated, the chitosan dosage can be assumed as the major parameter determining the coagulation efficiency for WWs.



(a)

(b)

FIG. 3. Effect of initial pH chitosan dosages on the turbidity and TSS removal from OMWs (a) and WWs (b).

In terms of TSS removal the results from chitosan coagulation tests of OMWs and WWs showed an increasing trend in residual TSS concentration as the pH was increased, with the best TSS removal (81% and 92% for OMWs and WWs respectively) at low pH values (4.4 and 4 respectively). However, a negligible decreasing was observed in TSS removal from WWs at actual pH 6.8; whereas at pH 6.0 only 34% of TSS removal from OMWs could be achieved (Fig. 3a). Taking into account that the isolectric point of chitosan suspension can be around 9 (32), when the pH was increased from 4 to 7, the positive charge of chitosan is expected to significantly decrease. Accordingly, we could expect a different behavior of the coagulation process under different pH conditions for WWs. However, when the chitosan coagulation reached the optimum condition (20 mg L^{-1}) in which the residual turbidity, COD (the related data are discussed in the subsequent paragraph 3.4) and TSS values were lowest, no further improvements could be achieved varying the pH. This result may suggest that the aggregation of particles was mostly caused by interparticle bridging rather than the neutralization charge and/or adsorption mechanism.

Our results are in agreement with the work of Ahmad et al. (30). Although they investigated the coagulation of palm oil mill effluent by chitosan, alum, and PACl, they found chitosan to be the best coagulant in the removal of TSS under all pH conditions (3.0–6.0).

Organic Matter Removal

Although the coagulation process is mainly aimed at removing the turbidity and suspended solids in order to improve the efficiency of the subsequent treatment steps, usually a moderate effect on the removal of organic matter can be observed too. Changes in organic matter concentration (measured as COD) in OMW and WW after coagulation tests with different chitosan dosages (20–500 mg L^{-1}) are shown in Fig. 4. Under optimum conditions for chitosan (pH 4.4 and 400 mg L^{-1} dosage), 32% of COD was removed from OMWs.

Instead, the best results for WWs were obtained at 20 mg L^{-1} of chitosan dosage and pH 4, corresponding to 73% of COD removal. However, increasing the coagulant dose, no further COD removal was observed; on the other hand, higher chitosan concentrations resulted in a progressive COD removal decrease. A re-suspension might have occurred because of the cationic nature of chitosan. At lower coagulant dosages the polymer neutralized the average negative charge of the suspension but, as the coagulant dosage was increased over the point of zero charge, the average electric charge moved to a positive

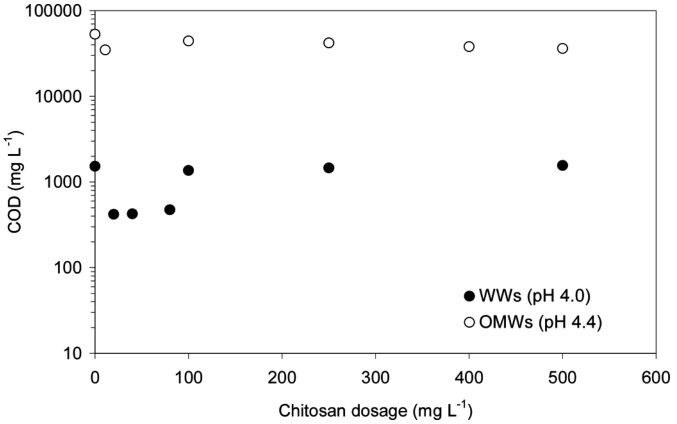
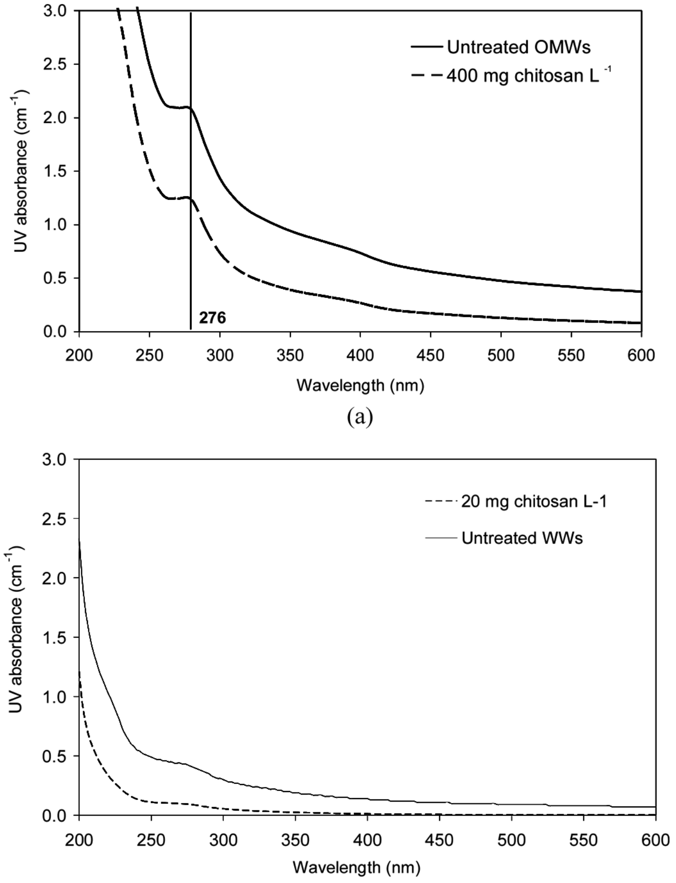


FIG. 4. Degradation of organic matter for OMWs and WWs.



(a)

(b)

FIG. 5. Behavior of UV absorbance spectra before and after coagulation by chitosan for OMWs at pH 4.4 (a) and WWs at pH 4.0 (b).

value and suspension was stabilized. Similar results were obtained by Lalov et al. (27) treating wastewater from distilleries (COD 28200 mg L^{-1} and pH 2.9), although they used chitosan as ion exchanger. In their study, five chitosan concentrations were investigated (2, 3, 5, 10, 15 g L^{-1}). However, increasing chitosan loading over 10 g L^{-1} only negligible changes in the process efficiency were observed. In spite of the fact that the polluting load was significantly higher, the optimized conditions allowed to achieve a COD removal >90%.

Due to high phenols content of OMWs and WWs, and the aromatic nature of phenols, the organic matter removal can be also characterized by means of UV absorbance measurements. Figure 5 shows the behavior of UV absorbance spectra before and after coagulation by chitosan under optimum conditions for OMWs (Fig. 5a) and WWs (Fig. 5b). A characteristic peak can be observed at 276 nm wavelength (UV_{276}) in the absorbance spectra of OMWs; 40% removal of aromatic fraction of organic matter (possibly phenols) was observed at UV_{276} for OMWs, according to our previous results (31). This result may be explained by the electrostatic interaction between negatively charged phenols and protonated amino groups of chitosan in the solution (33).

For WWs the peak is not so evident, although a small bump can be observed in the wavelength range typical for aromatic structure substances, therefore assuming UV absorbance at 280 nm as a reference to investigate the removal of aromatic compounds, 78% removal of aromatic fraction was observed.

CONCLUSIONS

In the present work the coagulation of real OMWs and WWs by chitosan was investigated as a possible alternative to conventional metal based coagulants, to produce a potentially reusable organic sludge. The main results can be summarized as follows:

- OMWs: chitosan provided high performances in terms of turbidity (94%) and TSS (81%) removals under optimized conditions (pH 4.4., 400 mg chitosan L^{-1} as coagulant dosage), as well as under all the initial pH values investigated (4.4–6.0).
- WWs: chitosan was very efficient for the coagulation of WWs from the bottling phase. A chitosan dosage of 20 mg L^{-1} allowed to achieve 94% TSS removal, 80% turbidity removal, and 73% COD removal at pH 4. Moreover, pH only slightly affected the TSS and turbidity removals, suggesting that interparticle bridging may be the main coagulation mechanism.

Taking into account that the best performances of the coagulation process by chitosan were achieved at actual pH for OMWs, and no significant differences were observed for WWs as pH was changed, no chemicals addition is required to adjust the pH. Besides, although the use of NOC such as chitosan can allow to achieve a potentially reusable organic sludge, thus saving money on sludge disposal, chitosan is still quite expensive compared to conventional metal-based coagulants. Therefore, the successfully investigation of cheaper NOC, such as those extracted from plant seeds (e.g., *Moringa oleifera*), may constitute the coagulation pre-treatment of agro-industrial wastewater by NOC a cheap and environmentally-friendly process.

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