DEVELOPMENT OF A SUSTAINABLE TREATMENT PROCESS (MBR) FOR HIGH-STRENGTH INDUSTRIAL WASTEWATERS BY THE APPLICATION OF COMPOSITE COAGULANTS

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Abstract
High-strength industrial wastewater usually contains large concentration of recalcitrant compounds and their treatment by the application of simple biological processes is usually not sufficiently effective, resulting to a treated effluent of low quality. Therefore, the tertiary treatment of these wastewaters is often required and the coagulation/flocculation process may represent an appropriate technique that can be usually applied for the production of reclaimed water, having sufficient quality for reuse. However, the use of conventional chemicals, such as Al-or Fe-salts may not be sufficiently effective for the treatment of those wastewaters or may produce rather high sludge amounts, making the further management problematic. The aim of this study was the investigation of alternative coagulants for the treatment of representative industrial wastewaters such as those from tanneries, or from yeast-production (fermentation) plants, in order to be used latter, as the appropriate and effective coagulant, applied to a developed hybrid MBR system for the control of membrane fouling.
Composite coagulants (PSiFAC-polyaluminum ferric silicate chloride) were produced in this work under various conditions; the efficiency of coagulants was examined for the treatment of three industrial wastewater samples: (1) a tannery wastewater; (2) a yeast manufacturing wastewater, subjected to preliminary anaerobic treatment; (3) the latter sample was subsequently subjected to aerobic treatment. Coagulation experiments were carried out in a jar-test device;
Certain flocculant aids (polymers acting as polyelectrolytes) were added such as an anionic polyelectrolyte (Magnafloc-LT 25), or a combination of an inorganic coagulant and an anionic polyelectrolyte in one unique reagent PAPEFAC). Influent and effluent samples were then analyzed for the determination of major parameters. The optimum treatment of selected wastewaters by various coagulants was carried out, but without any further addition of polymeric flocculants; the addition of 100 mg/L PSiFAC in yeast wastewater resulted to a reduction of COD between 21-52%, of turbidity 35-40% and of phosphates 38-42%, respectively; in comparison with 8-20%, 40-46% and 27-41% respectively, with the use of polyelectrolyte. However, higher removal rates were obtained by the same PSiFAC dose in tannery wastewater, resulting to a reduction of COD 50%, 81% of turbidity and 62% of phosphates; compared to 51%, 81% and 52% respectively, with the use of polyelectrolyte;
Composite PSiFAC coagulants were manufactured and their efficiency was studied for treatment of high-strength industrial wastewater. The coagulants proved to be quite effective, depending upon the specific wastewater properties; therefore, their treatment process with this coagulant is recommended due to the use a composite Al-Fe coagulant, even without the requirement for the addition of flocculant aid (polyelectrolyte) as a result additional cost benefits may arise by the utilization of this material, including the avoidance of specific equipment for handling the polyelectrolyte (e.g. dissolution, pumping system);
Keywords: composite coagulants, high strength wastewaters, polyelectrolyte.

Aims

Domestic and industrial wastewaters can contain large concentration of recalcitrant compounds, rather high concentrations of phosphorous, nitrogen and other carbonaceous contaminants that are essential nutrients for the growth of organisms. However, many industrial and food process waste streams are inherently high in nutrients content, and their treatment by the application of simple biological processes is usually not sufficiently effective, resulting to a treated effluent of low quality causing severe eutrophication problems. Very important is considered the case of phosphorous (usually in the form of orthophosphates), which has to be removed efficiently from wastewaters [1].

The application of physicochemical pretreatments to industrial wastewater improves the water quality while enhancing the biodegradability. Chemical coagulation is employed to remove suspended colloidal particles within the 0.1-1-nm size range that do not settle out on standing and cannot be removed by conventional physical processes [2, 3]. Chemical coagulation/flocculation (C/F) is an effective and commonly used wastewater treatment option. It involves the addition of chemicals such as alum or ferric salts that coat the colloid with Al^{3+} or Fe^{3+} ions and form positively charged microflocs.

A Membrane Bioreactor (MBR) treatment system can be also effectively applied. The major problem during the operation of any MBR system is membrane fouling. Thus, the ultimate aim of this study is the development and application of efficient alternative composite coagulants to control fouling in membrane bioreactors.

Background

The Inorganic Polymeric Flocculants (IPFs), or pre-polymerized coagulants, such as polyaluminum chloride (PACl) represent a relatively new category of coagulation reagents, which was developed in order to increase the efficiency of coagulation/flocculation (C/F) process, but there is still need for further improvement of their properties [4, 5].

More recently, composite polymeric aluminum products, such as PASiC (aluminum-silicate polymer composite) [6, 7] and Polyferric silicate sulphate (PFSiS) [8]**,** have been also tested in laboratory experiments, as well as in full-scale applications. Latterly, several investigators [9-12] have studied the simultaneous addition of Al (III), Fe (III) and polysilicic acid solution (pSi) and the coagulation efficiency of poly-aluminum-ferric-silicate-chloride is mainly affected by the Al/Fe/Si ratio and the respective preparation techniques.

Additionally, synthetic polyelectrolytes have been utilized in C/F process for water purification for more than four decades. Due to their wide usage, it is not surprisingly to consider them as alternative additives in the pre-polymerized coagulants composition for the production of new modified coagulation reagents [8].

The aim of this study was the examination of the effectiveness of C/F process using polyaluminum ferric-silicate-chloride coagulants and an anionic polyelectrolyte (Magnafloc-LT 25) as the flocculant aid for the treatment of wastewater samples. Furthermore, the combination of coagulant and polyelectrolyte in one unique reagent was examined in order to increase further their flocculation efficiency, by replacing the inorganic polysilicate additive with the organic polyelectrolyte in their structure. Hence, providing the respective comparison results for the coagulation performance of all the prepared coagulants, applied in wastewater treatment.

Experimental

All chemical reagents used were analytically pure chemicals. De-ionized water with conductivity lower than 0.5 mS/cm was used to prepare all the solutions, except of the solutions used for the preparation of coagulants. In this case, de-ionized water made carbonate free by boiling, was used.

Procedure for the preparation of composite coagulants

Composite polyaluminum ferric silicate chloride (PSiFAC) coagulants were produced in this work at room temperature, according to a procedure proposed by *Tolkou et al.*, 2013

[13], under various experimental conditions. The used initial solutions were 0.5 M $AlCl_3 \cdot 6H_2O$ (Merck), 0.5 M $FeCl_3.6H_2O$ (Merck), 0.5 M NaOH (Merck) - as the added base - and the prepared polysilicic acid solution (pSi), according to *Tzoupanos et al.*, 2009 [14]. The most effective coagulant obtained during preliminary experiments [13, 15], i.e. $PSiFAC_{1.5\text{-}10\text{-}15}$, was used in this study.

A poly-acrylamide co-polymer (Magnafloc LT-25, Ciba SC LTD, commercially available) as an anionic polyelectrolyte (APE) was obtained (0.01 % w/v) and used both as the flocculant aid (in [Al]/[APE] = 10 molar ratio) and the organic additive for the synthesis of composite coagulants (PAPEFAC). The specific polyelectrolyte is commonly used as a flocculant aid in water or wastewater treatment plants, especially in Greece [16, 17]. Table 1 presents the preparation conditions of all prepared coagulants.

Table 1. Preparation conditions of all laboratory prepared coagulants.

Coagulant type	Molar ratios	Procedure
$PSiFAC_{1.5\text{-}10\text{-}15}$	[OH]/[Al]: 1.5 [Al]/[Fe]: 10 [Al+Fe]/[Si]: 15	Co-polymerization technique: Appropriate amount of $FeCl_3$ solution was added in $AlCl_3$ solution, under vigorous stirring. Then, the resulted FpA solution was added to pSi solution at desired ratios of [Al+Fe]/[Si] and base solution was added slowly (under magnetic stirring) in the mixture at the desired [OH]/[Al] molar ratio.
$PAPEFAC_{1.5\text{-}10\text{-}15}$	[OH]/[Al]: 1.5 [Al]/[Fe]: 10 [Al+Fe]/[APE]: 15	Co-polymerization technique: Appropriate amount of $FeCl_3$ solution was added in $AlCl_3$ solution, under vigorous stirring. Then, the resulted FpA solution was added to APE solution at desired ratios of [Al+Fe]/[APE] and base solution was added slowly (under magnetic stirring) in the mixture at the desired [OH]/[Al] molar ratio.

Coagulation performance

The pH was measured by using a Metrohm Herisau pH-Metre, the conductivity by using a Crison CM 35 Conductivity Metre and the turbidity measurements were performed by a HACH RATIO/XR Turbidimeter. The UV absorbance at 254 nm, as a convenient indicator of natural organic matter presence, was measured with a Shimadzu UV/Vis spectrophotometer, by using a 1 cm path length quartz cuvette.

Jar-tests

Jar tests were used for the examination of coagulants' efficiency [18]. A jar-test apparatus (Aqualytic) equipped with six paddles was used, employing 1 L glass beakers. Three types of samples were used: (1) a tannery wastewater; (2) a yeast manufacturing wastewater, subjected to preliminary anaerobic treatment; (3) the latter sample was subsequently subjected to preliminary aerobic treatment. The properties of all samples are given in the following Table 2.

Table 2. Major physico-chemical properties of initial wastewater samples.

Type of wastewater to be treated	Turbidity (NTU)	Absorbance $UV_{254\ nm}$	COD (mg/L)	Phosphates (mg/L)
Tannery Wastewater	668	2.981	6800	1.76
Yeast wastewater (after anaerobic treatment)	418	3.748	11455	3.49
Yeast wastewater (the previous, but after post-aerobic treatment, as well)	143	3.307	4590	2.40

Water samples were collected from the supernatant of each beaker and were analyzed for the determination of: turbidity, absorption at UV_{254nm} that provides an indication of the amount of natural organic matter (NOM, COD (mg/L), and phosphates (mg/L).

Residual contaminant measurements

The residual percentage (RX, %) was expressed as:

$$RX(\%) = (X/X_0) \times 100\% \quad (1)$$

where X and X_0 are the parameters (turbidity, absorption at UV254nm, COD, and phosphates) of the treated and raw wastewater, respectively.

Result and Discussion

Table 3 displays the major physicochemical properties of laboratory prepared composite coagulants. It can be observed that the addition of pSi in an Al-Fe solution (FpA) to induce the formation of composite coagulants, results in the increase of turbidity, in comparison with the addition of APE in the same FpA solution.

Table 3. Properties of laboratory prepared coagulant.

Coagulant type	pH	Turbidity (NTU)	Conductivity (mS/cm)
$PSiFAC_{1.5-10-15}$	3.7	218.0	26.0
$PAPEFAC_{1.5-10-15}$	3.6	137.0	27.0

The most effective coagulant dosage obtained during preliminary experiments [19], i.e. 100 mg/L, was applied for the treatment of the aforementioned wastewater samples to evaluate its coagulation efficiency against these (considered as) relatively high-strength industrial wastewaters.

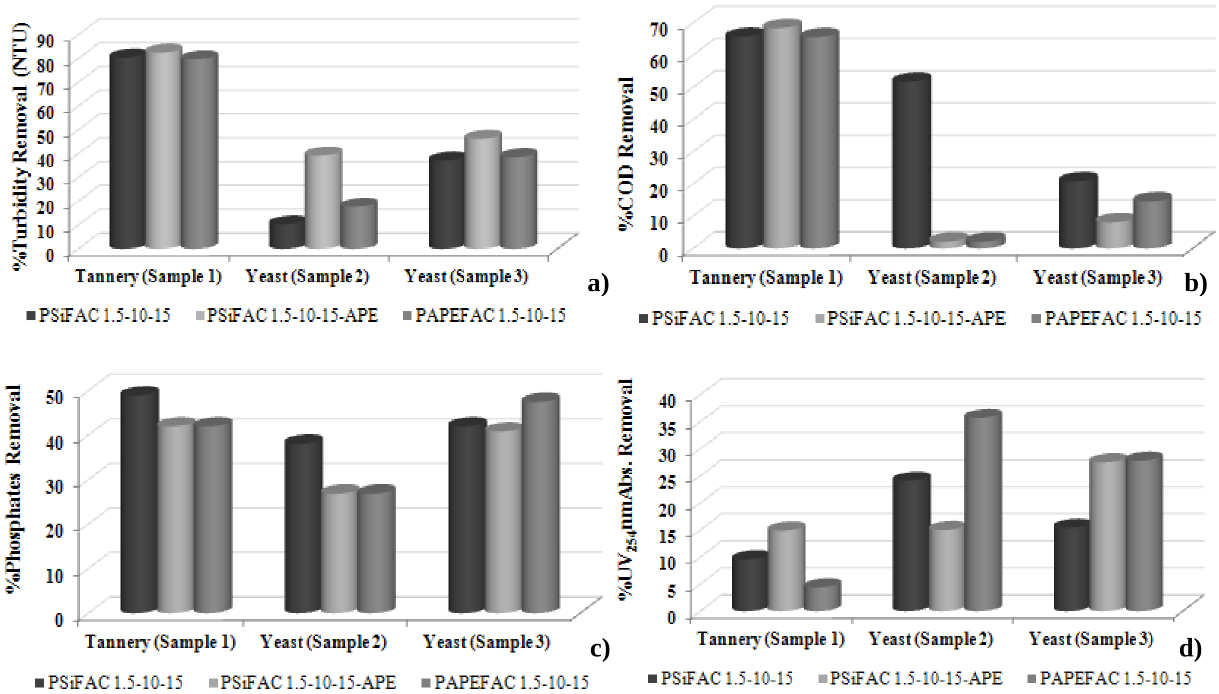

Figure 1. Residual contaminants percentage of the laboratory prepared coagulants (100 mg/L) for (1) tannery wastewater; (2) yeast manufacturing wastewater, subjected to

preliminary anaerobic treatment; and (3) yeast latter sample additionally subjected (subsequently) to aerobic treatment wastewater samples.

The results of coagulation experiments for (%) turbidity, absorption at UV_{254nm}, COD and phosphates removals of wastewater samples are given in Figure 1; the experimental results indicated that, the addition of 100 mg/L of $PSiFAC_{1.5-10-15}$, either with or without the addition of the flocculant aid (polyelectrolyte), in tannery wastewater, resulted to a reduction of COD 67%, and 96% for turbidity and 62% for phosphates. Although regarding the UV absorbance at 254 nm, the rates were found to be rather small (10%), as the wastewater sample was not subjected to any pre-treatment stage this is a highly contaminated sample, but coagulation was beneficial to the improvement of its quality.

Additionally, in yeast wastewater the addition of the same $PSiFAC_{1.5-10-15}$ dose resulted to a reduction of COD 56%, of turbidity 40%, of UV_{254nm} absorbance 25% and of phosphates 43%; and to a reduction of COD 22%, of turbidity 14%, of UV_{254nm} absorbance 15% and of phosphates 38% respectively to samples 2 and 3. However, from the Figure 1, it is obvious that higher removal rates were obtained when the coagulant and polyelectrolyte were combined in one unique reagent ($PAPEFAC_{1.5-10-15}$), but regarding COD removal, the use of $PSiFAC_{1.5-10-15}$ without the addition of the flocculant aid (polyelectrolyte), exhibits better and incomparable results.

Conclusions

In this study, composite polyaluminum ferric silicate chloride (PSiFAC) coagulants were manufactured and their efficiency was studied for treatment of high-strength industrial wastewaters, such as those from tanneries, or from yeast-production (fermentation) plants, as the appropriate and effective coagulant, applied to a developed hybrid MBR system for the control of membrane fouling. At the same time was studied the contribution of polyelectrolyte during the C/F process by two different types of process application; in the first type the polyelectrolyte was added in the sample as flocculation aid and in the second one the coagulant and polyelectrolyte were combined in one unique reagent (PAPEFAC) in order to increase further their flocculation efficiency. The coagulants proved to be quite effective, depending upon the specific wastewater properties; therefore, the addition of 100 mg/L of $PSiFAC_{1.5:10:15}$ in yeast wastewater resulted to a reduction of COD between 22-56%, of turbidity 14-40%, of UV_{254nm} absorbance 15-25% and of phosphates 38-43%, respectively, but higher removal rates were obtained in tannery wastewater (COD 67%, turbidity 96%, phosphates 62%, UV_{254nm} 10%). Conclusively, it was found that the $PSiFAC_{1.5:10:15}$, either with or without the addition of the flocculant aid (polyelectrolyte), provided a better effectiveness of the C/F process, especially regarding COD removal. As a result additional cost benefits may arise by the utilization of this material (i.e. $PSiFAC_{1.5-10-15}$), including the avoidance of specific equipment for handling the polyelectrolyte (e.g. dissolution, pumping system). In this way, the overall treatment procedure is simplified and the overall cost-effectiveness is also improved.

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