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Wastewater treatment for reuse employing industrial by-products as alternative coagulants

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ABSTRACT

In the current research, three industrial by-products containing useful iron and aluminum chemical components were introduced as potential alternative coagulants in marble processing wastewater treatment for possible water reuse. Specifically, the coagulation performance of lignite highly calcareous fly ash, siliceous fly ash (FAs) and electric arc furnace dust (EAFD) was compared with that of two commercial coagulants ($Al_2(SO_4)_3\cdot 18H_2O$ and $FeCl_3\cdot 6H_2O$). The kinetic studies were conducted at times up to 60 min by using coagulant dosages up to 4 mg/L. Turbidity (NTU), pH and conductivity were recorded during the kinetic studies. FAs and EAFD revealed enhanced coagulation performance, having similar turbidity removal efficiencies (%ΔNTU) to those of commercial coagulants, with short sedimentation times (~5 min). The pH values recorded for the three industrial by-products/coagulants were in the basic range of 7–9.7. Only the pH values for EAFD, at high dosages, were found to be close to neutral, while, for all commercial coagulants, neutral pH values were recorded at intermediate dosages. The experimental results presented may contribute to the formation of integrated and cost-effective strategies for marble wastewater management with low environmental footprint.

Keywords: Marble wastewater; Treatment; Coagulation; Lignite fly ash; Calcareous; Siliceous; Steelmaking dust

1. Introduction

Nowadays, marble is the foremost natural stone produced in the world. Marble production covers 50% of the natural stone production worldwide. Significant amounts of marble waste are generated by the marble industries, during marble processing. Moreover, in contemporary marble processing industries, decent water quality, which should not contain solids or salts, is required in order to safely perform the shaping and cutting procedures. From a financial perspective, the freshwater cost is rather high, due to the high demand of freshwater. Therefore, the development of low-cost and environmentally benign wastewater treatment and management procedures for possible water reuse, which may be applied to the marble processing industry, is quite important [1–4].

Coagulation/flocculation seems to be a generic procedure widely used nowadays in water recycling and wastewater treatment, due to the fact that it possesses many advantages:

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simple operation, low cost and increased precipitation and removal efficiency of substances with various particle sizes [5,6]. A wide range of impurities, either in the form of colloidal particles or dissolved organic substances can be removed from various types of wastewater via coagulation [7–9]. Coagulation is performed by adding an appropriate substance (coagulant/flocculant) in the aqueous medium under vigorous stirring in order to achieve a uniform dispersion of the coagulant. In this manner, suitable conditions for the destabilization of the colloidal micelles (or sols) are achieved. This destabilization induces finally the floc (aggregate) formation [10–13]. The efficiency of the coagulation/flocculation process is determined by the ability of the reagent to remove the inorganic and organic suspended matter, which render the colloidal solution turbid and colored. Even though the coagulation process has many advantages, especially from a practical standpoint, there is one major disadvantage: the production of large amounts of sludge that may contain various contaminants. In that sense, the resulting sludge needs to be further processed in order to reduce the environmental risks [14]. This increases the overall treatment cost. Nevertheless, the resulting sludge deriving from the coagulation process may be used as raw material for the production of ceramic products, toward circular economy [15–20].

Several substances, either organic or inorganic, have been used as coagulation agents up to now. Most common of them include natural polymers [21–23], inorganic polymers [24,25], aluminum and other metal salts [9,26–32] as well as a combination of polymer and metal salt [33,34]. A very recent trend is the usage of various types of industrial waste as coagulants in the coagulation/flocculation processes [35]. Some studies have reported that various types of sludge could be efficiently recovered, recycled and reused as coagulants [36–43]. Mahmoued [44] reported the utilization of cement kiln dust to primarily treat municipal wastewater. Furthermore, Gungor et al. [45] investigated the possibility of re-using aluminum etching wastewater in a coagulation procedure for tannery wastewater treatment. Other studies reported the usage of natural stone or marble processing residues in the coagulation/flocculation process [46–49]. Coal fly ash (FA) was used as coagulant in some wastewater treatment procedures [50–58]. Also, some coagulants based on metal slags have also been tested in various coagulation processes [35,59–61], while some other major steel industry by-products, such as electric arc furnace dust (EAFD), have not been thoroughly investigated [62,63]. EAFD and FA are both produced in large quantities nowadays [64] and they contain several iron and aluminum compounds. Depending on the solubility rate of iron and aluminum in the aqueous media, FA and EAFD can actually serve as coagulation–flocculation agents in industrial processes. However, there are several types of FA (calcareous or siliceous) and their coagulation ability should be reconsidered depending on the predominant compounds which are present in FA. At the same time comparative studies regarding the assessment of the coagulation ability of the different types of FA and steel slags (e.g., EAFD) are still missing.

In this study, two different types of industrial by-products that contain valuable iron and aluminum compounds were tested in order to identify their coagulation ability and performance. Specifically, the valorization of both calcareous fly ash (FAc) and siliceous fly ash (FAs) from lignite-fed power stations as well as EAFD, as alternative coagulants in marble processing wastewater treatment, was investigated. Moreover, various system parameters affecting the coagulation process were examined: the type of by-product and its dosage, the coagulation time, the pH and the conductivity of the wastewater colloidal solution. Furthermore, the coagulation performance of the aforementioned industrial by-products was compared with that of some commonly used commercial coagulants.

2. Experimental

2.1. Wastewater

The wastewater deriving from marble processing plants is an effluent containing marble residue (dust) particles. Synthetic wastewater was used in this study consisting of water and marble residue. The marble residue was acquired from marble processing units in the region of Western Macedonia, Greece, in the form of fine powder. The wastewater was produced by adding 4 g of solid marble residue into 1 L of pure water. Subsequently, this colloidal solution was vigorously stirred at 160 rpm. The physiochemical characteristics of the synthetic marble wastewater used in this study are summarized in Table 1.

2.2. Coagulants

Both types of FA used in this study were obtained from lignite-fed power stations situated in Greece. In particular, highly FAc was obtained from a power unit situated in the Region of Western Macedonia, Northern Greece. FAs was received from a plant situated in Megalopolis, Southern Greece. In Table 2, the chemical composition of the two different types (FAc and FAs) of FA is tabulated. FAc mainly

Table 1
The physiochemical characteristics of the marble wastewater used in this study: turbidity (NTU), electrical conductivity and pH

Turbidity (NTU)	Electrical conductivity (μS/cm)	pH
1,567	38.2	9.43

Table 2
Characterization of the calcareous (FAc) and the siliceous (FAs) fly ash used

(% wt)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LoI
FAc	30.16	14.93	5.10	34.99	2.69	6.28	1.01	0.40	3.95
FAs	49.54	19.25	8.44	11.82	2.27	3.91	0.53	1.81	2.10

Note: LOI – Loss on ignition.

consists of CaO (34.99%), while large quantities of SiO_2 (30.16%) are also present. On the other hand, FAs is composed mainly of SiO_2 (49.54%), whereas the CaO amount is significantly lower (11.82%) in this case. Several other oxides such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O and K_2O were found in both FAc and FAs, which is in good agreement with the findings reported in literature [65–67].

EAFD, in the form of red/brownish fine powder, was derived from a steel scrap melting plant. The main constituents of the EAFD are iron and zinc oxides (Fe_2O_3 and ZnO). The complete chemical analysis results of this by-product are given elsewhere [68].

Scanning electron microscope (SEM) micrographs of the industrial powdery by-products, used as alterative coagulants, are shown in Fig. 1. EAFD (Fig. 1(a)) consists of fine particles (with diameters in the sub-micrometer range) aggregated in larger complexes. Likewise, the two types of FA (FAc and FAs) also consist of sub-micrometer particles, concentrated in much larger aggregates. However, the particles of FAc and FAs (Figs. 1(b) and (c)) are much larger compared with those of EAFD.

The two commercial coagulants (analytical grade, in hydrated form) used in this study were aluminum sulfate 18-hydrate [$Al_2(SO_4)_3{\cdot}18H_2O$], with molecular weight 666.42 g/mol, purchased from Panreac Quimica S.A., Barcelona, Spain, and ferric chloride 6-hydrate [$FeCl_3{\cdot}6H_2O$], with molecular weight 270.29 g/mol, from Fisher Scientific UK, Loughborough, UK.

2.3. Jar test

The industrial by-products (FAc, FAs and EAFD) were separately examined for their effectiveness in wastewater coagulation, in terms of turbidity removal capacity of marble wastewater. The turbidity removal effectiveness of the industrial by-products was compared with that of the commonly used commercial coagulants already mentioned (i.e., aluminum sulfate 18-hydrate and ferric chloride·6-hydrate). For all coagulants, four different concentrations (dosages) were tested: 0.8, 1.0, 2.0 and 4.0 mg/L.

For the coagulation experiments, a standard jar test apparatus was used. This apparatus was equipped with four beaker positions. The beakers used in this study had a volume of 600 mL. Initially, marble wastewater sample was added into the beakers up to the operative volume, and stirred at 160 rpm. Following the addition of the coagulant the resulting colloidal solution continued to be vigorously stirred for 2 min, at 160 rpm. Afterward, a slow stirring phase for 10 min at 60 rpm was carried out. Finally, the colloidal solution was allowed to settle for 60 min. The variation of turbidity (NTU), pH and conductivity as a function of time (kinetic study) was measured. The recording was initiated at the end of the slow-stirring period and was continued during the 60 min settling period at distinct time intervals. All experiments were carried out at room temperature (22°C).

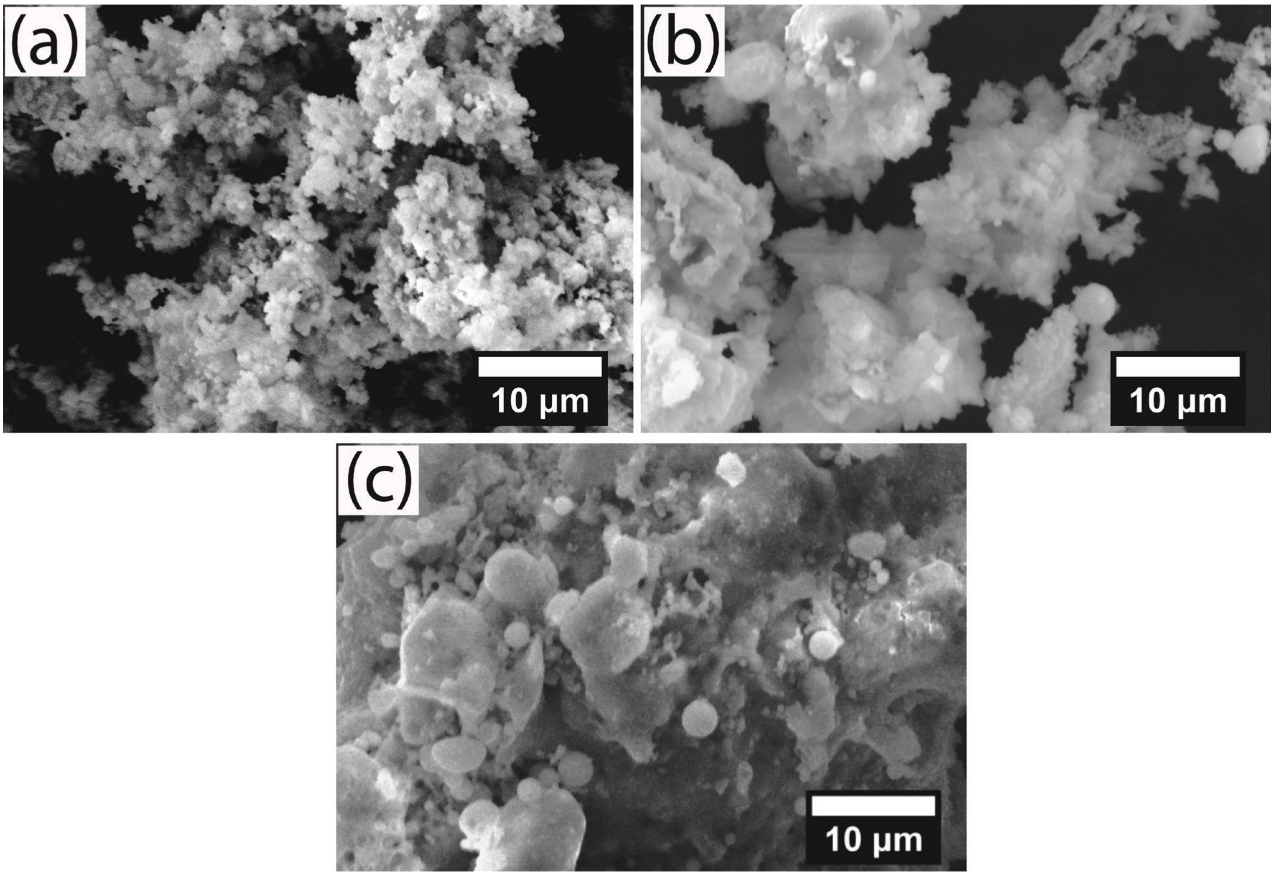

Fig. 1. SEM micrographs of the alternative coagulants used in this study: (a) EAFD, (b) FAc and (c) FAs.

2.4. Analytical methods

The micrographs of the industrial powdery by-products were recorded using a JEOL 6610 LV SEM. The chemical analysis of the raw materials was performed using a Spectro X-Lab 2000 ED-XRF device. Turbidity was determined via nephelometry using a LaMotte 2020we turbidity meter. The samples' pH was measured using an Orion 710A pH-meter, while the electrical conductivity of the samples was recorded by a Crison EC-meter GLP31 conductivity meter. All measurements were conducted in ambient conditions according to standard methods [69].

3. Results and discussion

In order to develop novel methodologies for marble wastewater treatment and water recycling/reuse, the turbidity removal efficiency of the coagulants and also the quality of the processed wastewater were investigated. In Fig. 2, the experimental results deriving from the jar tests are shown. Specifically, wastewater turbidity (NTU), electrical conductivity and pH as a function of time (min), using three different industrial by-products, namely EAFD (Figs. 2(a), (d) and (g)), FAc (Figs. 2(b), (e) and (h)) and FAs (Figs. 2(c), (f) and (i)) as coagulants at different dosages (mg/L), are presented. The blank sample measurements were conducted using

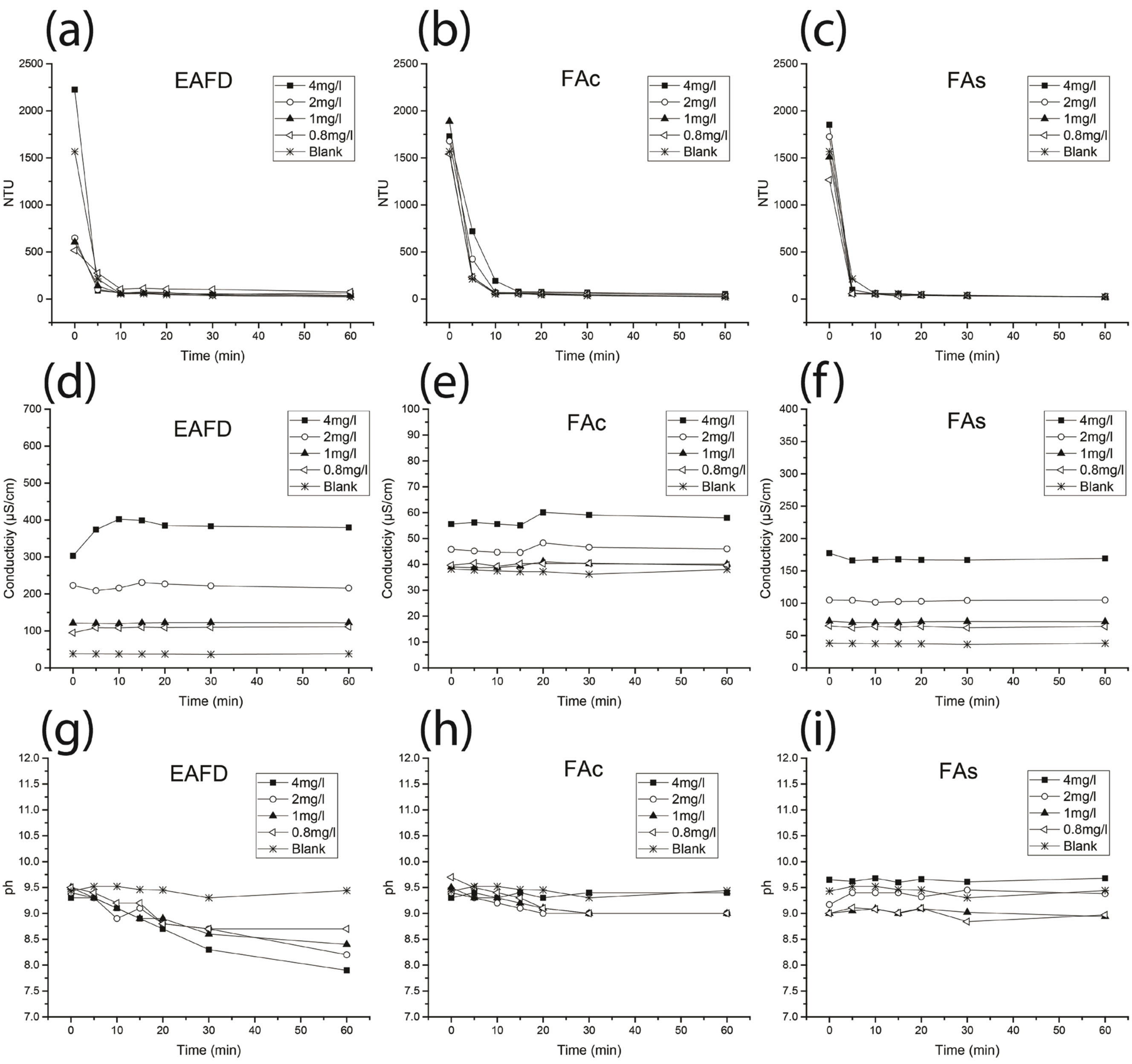

Fig. 2. Wastewater turbidity, NTU (a)–(c); electrical conductivity (d)–(f); and pH (g)–(i) as a function of time (min), using EAFD, FAc and FAs as coagulants, respectively (from left to right) at different dosages (mg/L). The blank sample measurements were conducted using only marble wastewater.

only marble wastewater, without adding any coagulant. An evident NTU decrease is observed after ~5 min for all three industrial by-product coagulants, while for longer times, the NTU values are not significantly affected (Figs. 2(a)–(c)). A slightly enhanced turbidity removal is observed for EAFD and FAs compared with FAc, since lower NTU values in shorter time are recorded. The coagulant dosage increase appears to have expectedly positive effect on the turbidity removal. Hence, lower NTU values are achieved at higher coagulant dosages.

The conductivity values (Figs. 2(d)–(f)) also depend on the type of the coagulant and the dosage being used. Higher conductivity values were recorded for EAFD, while much lower conductivity values were recorded for the two types of FA. A conductivity increase is recorded by increasing the coagulants' dosage. This may be ascribed to the fact that higher surface area for the accumulation of charges, exists in the colloidal solution by adding more particles.

pH is an important qualitative parameter of wastewater. It is worth noting that certain industrial processes may require the pH values to be adjusted in rather narrow ranges. However, in the case of the marble wastewater its pH values may vary significantly, even when the wastewater is taken from the same marble processing plant [35]. Therefore, no pH adjustment was carried out here. The pH of the three industrial by-products/coagulants (EAFD, FAc and FAs) was recorded, for every dosage, as a function of time (Figs. 2(g)–(i)). The pH values for all three coagulants are lower than 9.5. The pH values for the two types of FA remain largely unaffected as a function of time (min). The ash/coagulant dosage does not systematically influence the pH values.

The addition of EAFD in the marble wastewater colloidal solution renders the pH of the basic solution, due to the presence of some basic oxide phases (K_2O, CaO) in EAFD [68]. Nevertheless, in the case of EAFD an evident decrease of pH to lower pH values, closer to 7, is recorded as a function of time (min). Moreover, the EAFD dosage appears to have a significant effect on the pH values: lower pH values are recorded for higher EAFD dosages. The reason for the pH decrease in the case of EAFD, as a function of time and by increasing its dosage, is twofold. First, the observed pH decrease may be ascribed to the acidic products that occur due to the enhanced solubilization/dissolution of the aluminum species [70], found in EAFD [68]. Second, the SO_3, which was identified in EAFD [68], easily hydrolyzes in water to form sulfuric acid (H_2SO_4) [71]. On the other hand, pH values close to neutral are highly desirable, since liquid effluents with neutral pH values are less aggressive for the metal parts in wastewater treatment infrastructures.

Two commercial coagulants were also tested, for comparison reasons. In Fig. 3, the experimental results from the jar tests of the two coagulants are shown. Particularly, wastewater turbidity (NTU), electrical conductivity and pH as a function of time (min), using ferric chloride 6-hydrate (Figs. 3(a), (c) and (e), respectively) and aluminum sulfate 18-hydrate (Figs. 3(b), (d) and (f), respectively) as coagulation agents at different dosages (mg/L), are presented. The two specific coagulants were selected as they exhibited the best turbidity removal performance in industrial marble processing wastewater among other commercial coagulants, as shown in our previous work [72]. A conspicuous NTU decrease is observed after ~5 min for the two commercial coagulants, whereas, for longer times, NTU does not change significantly (Figs. 3(a) and (b)). The commercial coagulant dosage increase appears to have a generally positive impact on the turbidity removal, as also observed for the industrial by-products/coagulants. On the other side, the electrical conductivity (Figs. 2(c) and (d)) of the colloidal wastewater solutions using ferric chloride 6-hydrate and aluminum sulfate 18-hydrate increases with an increase in the coagulant dosage. As aforementioned, this may be ascribed to the higher surface area for the accumulation of charges. Nevertheless, the pH of the wastewater colloidal solutions decreases with an increase in the commercial coagulant dosage. It is worth noting that the addition of high dosages of aluminum sulfate 18-hydrate in the colloidal wastewater solution leads to pH values close to neutral, while the addition of high ferric chloride 6-hydrate dosages leads to acidic pH values (in the range of 7–2).

In order to gain better understanding regarding the performance of the industrial by-product and commercial coagulants in the coagulation process, two additional comparative diagrams were produced. In Fig. 4, the percentage turbidity removal efficiency (%ΔNTU) as a function of time (min), for all coagulants (at their optimal dosage – 4 mg/L) tested in this study, is shown. The %ΔNTU values increase rapidly only after 5 min, while the %ΔNTU values slightly increase till 60 min. The highest %ΔNTU values were recorded after 60 min. As it can be seen from Fig. 4, the %ΔNTU values achieved for the industrial by-products/coagulants after 60 min are higher than 96%, while the highest %ΔNTU value was achieved for FAs (98.77%). However, the highest %ΔNTU, only after 5 min, was recorded for EAFD. Furthermore, the %ΔNTU recorded for the commercial coagulants is more than 99%, after 60 min. Therefore, the industrial by-product coagulants (EAFD, FAc and FAs) examined in this study can be efficiently used as coagulants in marble processing wastewater treatment.

The mechanisms which are responsible for the turbidity removal from wastewater are based on charge neutralization of a negatively charged colloidal solution. It should be noted that the physical phenomena related to the coagulation mechanisms may occur concurrently, partly affecting the overall turbidity removal efficiency. Generally, the coagulation process is realized via the colloidal particles' destabilization, which implicates charge neutralization in the colloidal solution, due to the addition of substances with cationic chemical species. Moreover, coagulation occurs via the formation of sizable iron and aluminum hydroxide flocs, due to the aggregation of the hydrolysis products of the Fe^{3+} and Al^{3+} ions [14,73]. The coagulation mechanisms mainly depend on the pH and the coagulant dosage [74]. Since marble wastewater deriving from industry may have quite different pH values, it is not possible to have a universal methodology for the manipulation of the pH values of marble wastewater. Subsequently, the coagulant dosage should be considered the most important parameter in order to improve the turbidity removal efficiency, in the case of marble wastewater.

For the commercial (hydrolyzing) coagulants used (i.e., ferric chloride 6-hydrate and aluminum sulfate 18-hydrate), the turbidity removal efficiency is related to the destabilization and coagulation of the negatively charged colloidal marble wastewater solution. This destabilization

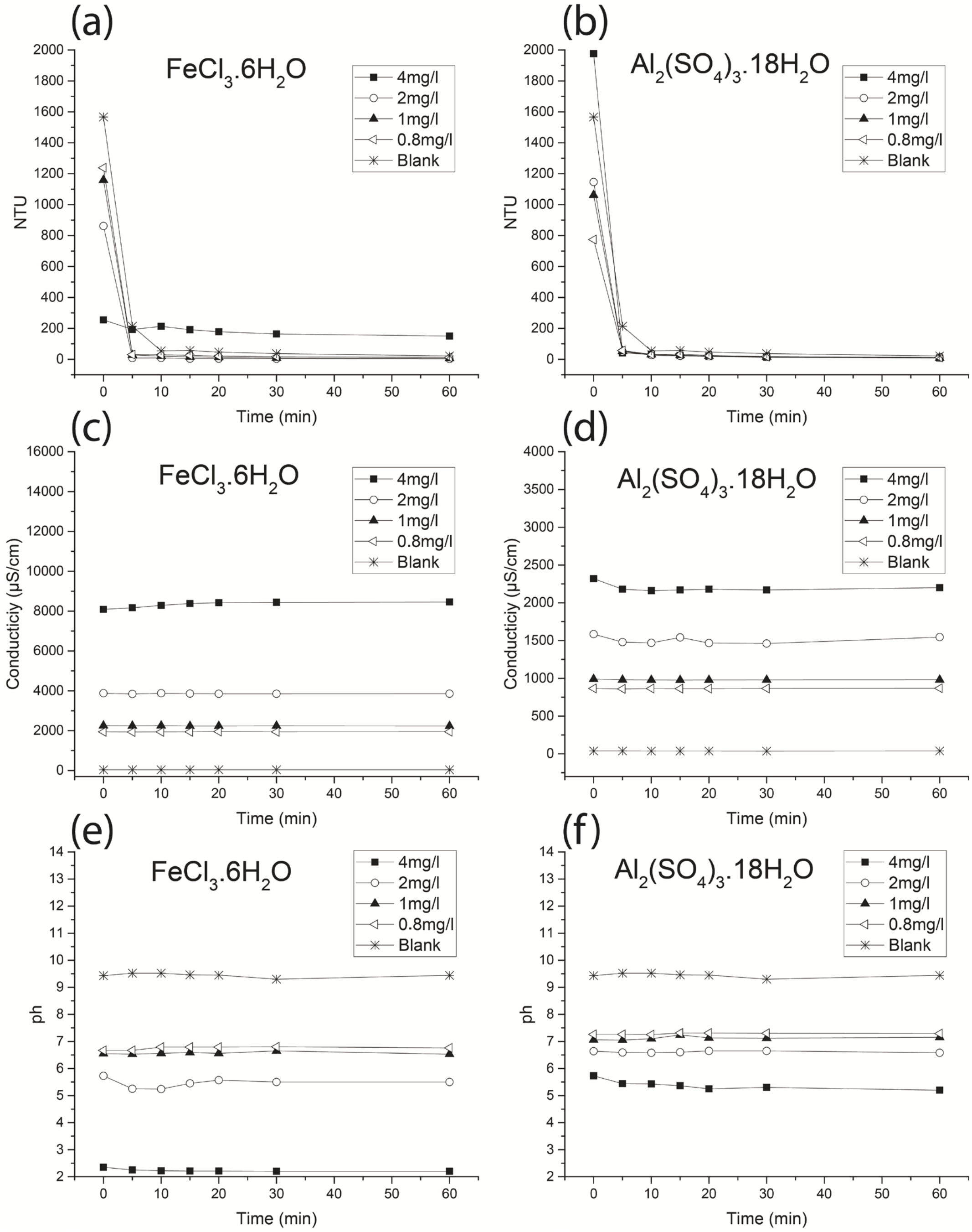

Fig. 3. Wastewater turbidity, NTU (a) and (b); electrical conductivity (c) and (d); and pH (e) and (f) as a function of time (min), using two different commercial coagulants ($FeCl_3{\cdot}6H_2O$ and $Al_2(SO_4)_3{\cdot}18H_2O$, respectively) at different dosages (mg/L). The blank sample measurements were conducted using only marble wastewater.

and coagulation may occur in two ways, depending on the dosage of the coagulant. At lower coagulant dosages, the products of cationic hydrolysis may adsorb charges, which render the particles in the colloidal solution charge-neutral. This results to destabilization and coagulation. At higher coagulant dosages, extensive precipitation of hydroxides takes place, due to the fact that concentration of metal ions is much higher than the one of the amorphous hydroxide. The hydroxide precipitation is possibly assisted by the inclusion of the impurities in the growing amorphous hydroxide precipitate. This leads to sweep coagulation [74].

Except from the aforementioned destabilization and coagulation mechanisms, another mechanism may occur in the case of using industrial by-products (i.e., EAFD, FAc and FAs) as coagulants. Charge neutralization may occur from the adsorbed species on the surface of the industrial by-product. However, this mechanism is possible to occur mostly in the case of EAFD, since charge neutralization from the adsorbed

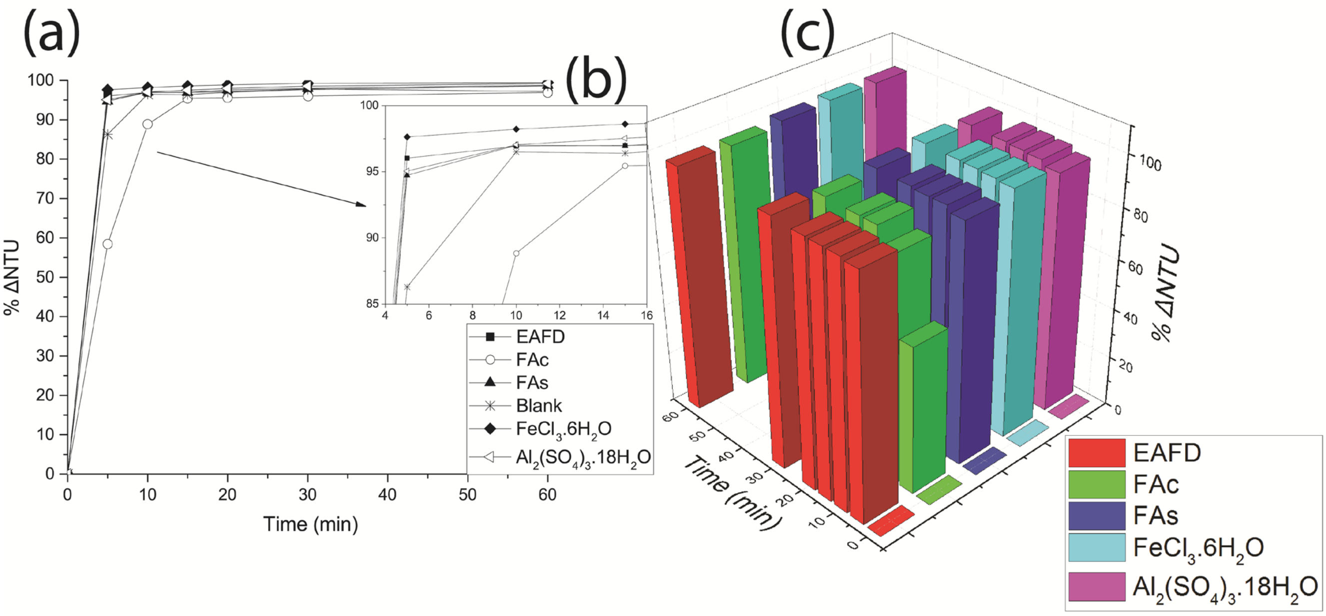

Fig. 4. The turbidity removal efficiency (%ΔNTU) as a function of time (min) for all coagulants tested in this study, at the optimal coagulant dosage (4 mg/L). Three different graphical representations are presented: (a) normal line and dot chart, (b) magnified inset of the upper-left (line overlapping) region as observed in the normal line and dot chart and (c) bar chart.

species on the surface is promoted in neutral pH values. Furthermore, charge neutralization from the adsorbed species on the surface of the coagulant may be also possible to occur in the case of the commercial coagulants at medium dosages, since the pH values recorded are close to neutral (Fig. 3).

As aforementioned, the turbidity removal efficiency of EAFD was higher than the one recorded for the two types of FA (especially for FAc), after 5 min. The reduced coagulation performance of FAc in short times, may be attributed to possible organometallic complexes formation between metal species (i.e., Al^{3+} and Fe^{3+}) present in FA and organic substances potentially remaining inside the pores of ash (FAc exhibits higher loss on ignition than FAs). Such organometallic complexes are reported to exhibit reduced ability for floc formation [75]. Furthermore, the lower turbidity removal efficiency observed for FAc compared with FAs may be attributed to calcium species (i.e., Ca^{2+}) that are mostly present in FAc. Actually, Ca^{2+} ions are less efficient at charge neutralization due to their divalent charge, compared with Al^{3+} and Fe^{3+} which have trivalent charge [14].

4. Conclusions

Coagulation was successfully applied to marble wastewater treatment, by adding three industrial by-products as secondary coagulants (EAFD, FAc and FAs), in relatively low dosages (up to 4 mg/L). The kinetic studies carried out (for times up to 60 min) revealed enhanced coagulation performance for EAFD and FAs, having similar turbidity removal efficiencies to those of commercial coagulants ($Al_2(SO_4)_3 \cdot 18H_2O$ and $FeCl_3 \cdot 6H_2O$), with short sedimentation times (~5 min). In that sense, marble wastewater with negligible turbidity is obtained via a brief coagulation procedure using alternative low cost coagulants. The pH values recorded for the three industrial by-products/coagulants were in the basic range (higher than 7). Only, the pH values recorded for EAFD at high dosages were found to be close to neutral, while for the commercial coagulants neutral pH values were recorded at intermediate dosages. The pH values were also found to be dose-dependent in many cases. The preliminary experimental results presented may contribute to the formation of integrated and cost-effective strategies for marble wastewater management with low environmental footprint. However, future research work aiming at the investigation of the turbidity removal efficiency of these industrial by-products in other more challenging wastewater treatments should be considered, since the marble wastewater, tested in this work, is a rather simple colloidal solution. Finally, future work related to the coagulation process should be destined toward the investigation of the industrial by-products/coagulants capability to adsorb any hazardous substances potentially present in marble processing wastewater.

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