Valorization of industrial by-products as coagulants in wastewater treatment

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Abstract
In the present research, industrial powdery by-products, specifically two different types of power station fly ash, calcareous and siliceous, as well as steelmaking dust were employed, as useful and cost-effective coagulants than as wastes, in wastewater treatment, in order to develop novel alternative applications of these secondary materials, which are annually produced in enormous quantities, towards sustainable use of resources. For that purpose, these industrial by-products were separately examined for their effectiveness in wastewater coagulation, in terms of turbidity removal capacity under various dosages, in comparison to conventional commercial coagulants. The industrial solid residues used contain iron and aluminum compounds, and therefore can act as coagulation-flocculation agents depending on the solubility rate of iron and aluminum in the aqueous medium. Beyond this possible contribution of the industrial powders to the coagulation-flocculation-sedimentation process of colloidal particles, the potential for concurrent beneficial adsorption of other substances present in the effluent wastewater to be treated should also be taken into account, thus enhancing the significance of this scientific endeavor. The wastewater coagulation experimental results obtained are encouraging, and principal factors affecting the coagulation-flocculation process, such as pH and electrical conductivity of the aqueous media, were also measured and are discussed as a function of the dosage of each coagulant used. Furthermore, the marble processing residues recovered were studied via SEM-EDAX.

Keywords
Coagulants; fly ash; calcareous; siliceous; steelmaking dust; wastewater treatment

INTRODUCTION

In the present study, calcareous and siliceous fly ashes, the by-products of lignite combustion in power generation units, as well as steelmaking dust, were investigated for their innovative use as possible beneficial and cost-effective coagulants in wastewater treatment.

Actually, industrial solid by-products, including power station and steel industry residues, are annually produced in enormous quantities worldwide. Limited amounts of these solid residues are currently recycled, mainly in cement industry and construction. Thus, alternative applications should be developed for their valorization as useful secondary materials rather than as wastes, towards sustainable use of resources and circular economy.

On the other side, wastewater treatment and water recovery/recycling/reuse is particularly important nowadays, and various technologies are employed for this purpose (Kalavrouziotis 2015; Moustakas and Malamis 2015; Matouq et al. 2014; Soutsas et al. 2010; Lyberatos and Nzihou 2009). Particularly, coagulation/flocculation appears to be a universal method extensively used, due to its simple operation, low cost, and the effectiveness in the elimination of a large number of substances with various particle sizes. An essential goal of coagulation/flocculation processes is to remove the colloidal material that causes coloration and turbidity, eliminating suspended solids and as much of the organic material as possible. This method can be applied by adding an appropriate compound as coagulant/flocculant in the aqueous medium, under vigorous stirring for a uniform dispersion of the reagent, inducing a suitable environment for the destabilization of the colloid micelles, leading to subsequent floc (aggregate) formation (Wang et al. 2015; Chowdhury et al. 2013; Sher et al. 2013; Syafalni et al. 2012). Various inorganic polymeric compounds, such as silica and other natural polymers, have been used as coagulation/flocculation reagents so far. Aluminium and iron salts are widely used today as coagulants/flocculants in water and wastewater treatment, as they are effective in removing a broad range of impurities from water, including colloidal particles and dissolved organic substances (Kishimoto and Kobayashi 2016; Domopoulou et al. 2015; Feng et al. 2015; Harif et al. 2012; Duan and Gregory 2003). Recently increasing attention is placed on the beneficial utilization of several industrial wastes, including red mud and other metallurgical slags, and even wastewater treatment sludge, for the development of waste-based coagulants (Ahmad et al. 2016; Tociu and Diacu 2015; Yildiz et al. 2015). The industrial solid residues under consideration in the present study contain useful iron and aluminum compounds, and therefore can actually act as coagulation-flocculation agents, depending on the solubility rate of iron and aluminum in the aqueous media. Factors affecting the coagulation/flocculation process, such as the type of by-product and dosage, pH, water properties etc. were examined.

MATERIALS AND METHODS

Highly-calcareous fly ash (YT) was obtained from the electrostatic precipitators of a lignite-fed power plant situated in Northern Greece (Region of Western Macedonia). Strongly-siliceous fly ash (FAm) was obtained from lignite power unit situated in Southern Greece (Megalopolis). Almost half of it consists of SiO_2, while lesser amounts of Ca-bearing species are also present. The chemical content of these ashes is given in Table 1. Steelmaking dust (EAFD), a red/brownish fine powder, is generated from the volatilization of metals when steel scrap is melted in the electric arc furnace. Iron and zinc are its main constituents.

Table 1. Chemical content (%) of calcareous (YT) and siliceous (FAm) lignite fly ashes used.

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LoI	
YT	30.16	14.93	5.10	34.99	2.69	6.28	1.01	0.40	3.95	*CaO_f: 10.87%
FAm	49.54	19.25	8.44	11.82	2.27	3.91	0.53	1.81	2.10	*CaO_f: 5.95 %

These as-received industrial powdery residues (YT, FAm and EAFD) were separately examined under various dosages in comparison to conventional commercial coagulants, for their effectiveness in wastewater coagulation, in terms of turbidity removal capacity of a marble processing plant wastewater.

Marble processing wastewater treatment is actually important, because a good water quality is required for safe cutting and shaping procedures in a modern marble processing industry. In fact, the water used should not contain any suspended solids or salts. Consequently, the operation of a marble processing plant arises significant water management issues, while also fresh water cost is usually high given the high volumes consumed. Hence, it is more advantageous to recycle the used water, thus contributing to the development of an environmentally-friendly process with a low water footprint. Thus, cost-effective techniques should be applied for the removal of solid particles incurred during cutting, and the recovery, recycling and reuse of the treated effluent in the marble processing devices (Domopoulou et al. 2016; Bayel et al. 2015; Capitano et al., 2014; Oates, 1998).

Wastewater samples were collected from marble processing plants in the Region of Western Macedonia, Greece. The chemical content of these marbles is shown in Table 2. The mineralogical composition of marbles from this area consists in 98% calcite, 1% dolomite, 0.5% quartz and 0.5% muscovite. The main physico-chemical properties of the wastewaters treated are given in Table 3.

Table 2. Chemical composition (%) of marbles from Western Macedonia, Greece.

CaO	MgO	SiO_2	Fe_2O_3	Al_2O_3	K_2O	Na_2O	MnO	CO_2
53.50	1.52	0.25	0.18	0.25	0.02	0.04	0.01	44.4

Table 3. Properties of wastewater samples from two marble processing plants.

Parameters	Sample 1	Sample 2
Temperature (^oC)	20	20
pH	5.4	8.17
Conductivity (μS/cm)	2.01	684
Turbidity (NTU)	396	6450

The industrial by-products under investigation (YT, FAm and EAFD), as well as two commercial hydrated coagulants/flocculants, namely aluminum sulfate·18-hydrate ($Al_2(SO_4)_3 \cdot 18H_2O$) and ferric chloride· 6-hydrate ($FeCl_3 \cdot 6H_2O$) for comparison reasons, were examined for their solids removal potential. The chemical reagents used were of analytical grade. Deionised water was used for the preparation of aqueous solutions. All coagulants were prepared in 0.1 M stock solution. Volumes of stock solutions were added to 500 mL sample volumes to obtain the desired final concentrations: 0.8, 1.0, 2.0 and 4.0 mg/L for the industrial by-products and aluminum sulphate and ferric chloride.

A jar-test apparatus (Figure 1) was used for the coagulation/flocculation experiments (22^oC), equipped with four 500mL beakers. 500 mL of wastewater sample was added into the beakers followed by the addition of the appropriate volume of coagulant solution. The mixture was rapidly mixed at 160 rpm for 2 min, followed by a slow stirring period at 60 rpm for 10 min. Finally, the mixture was allowed to settle for 20 min, and a sample was withdrawn from the supernatant for further analysis. Kinetic studies were carried out by the collection of 25 mL samples at various time intervals at the end of the slow stirring period, i.e. at 5, 10, 15, 20, 30 and 60 min. The water samples were analyzed for the determination of pH (Orion 710A pHmeter), electrical conductivity (Crison EC-meter GLP31+ conductivity meter) and turbidity (LaMotte 2020we turbidity meter).

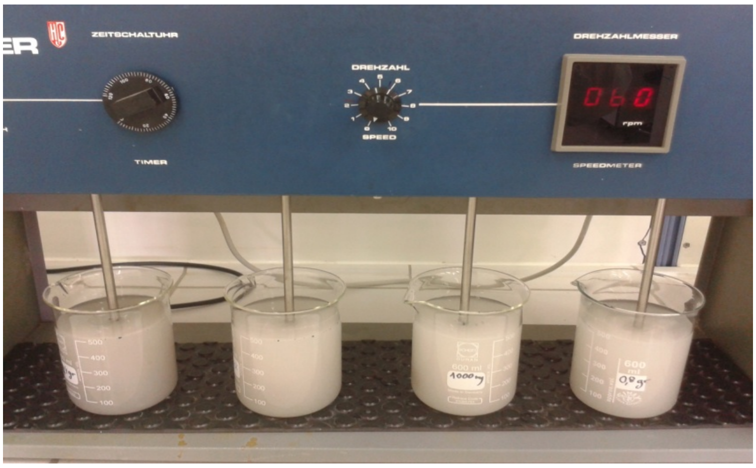

Figure 1. Jar test apparatus.

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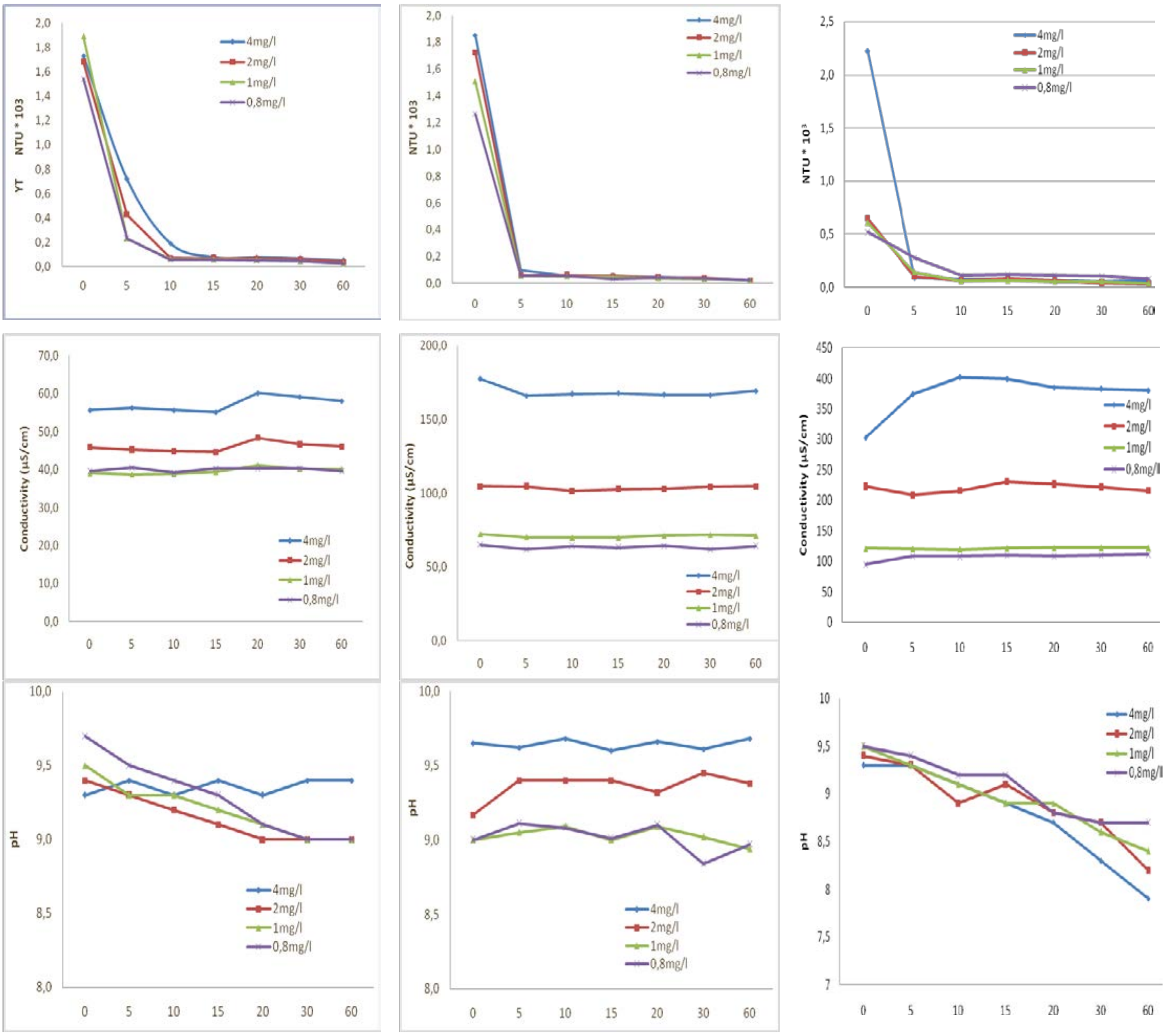
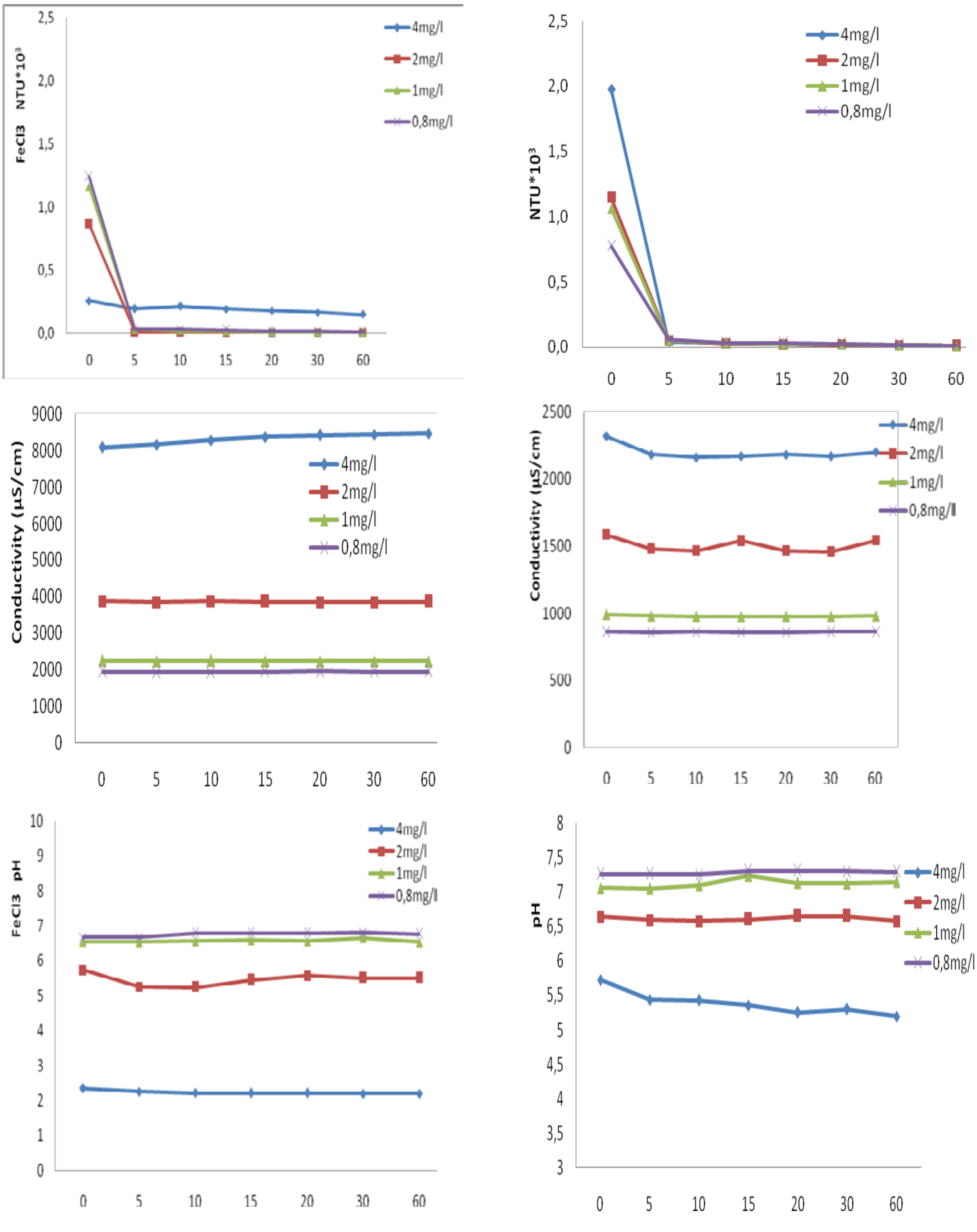
RESULTS



High-Ca fly ash (YT) | Siliceous fly ash (FAm) | Steelmaking dust (EAFD)

Figure 2. Wastewater turbidity (NTU), electrical conductivity and pH as a function of time, at different dosages of an industrial by-product as coagulation agent (YT, FAm, EAFD, from left to right column).



$FeCl_3 \cdot 6H_2O$ $Al_2(SO_4)_3.18H_2O$

Figure 3. Wastewater turbidity (NTU), electrical conductivity and pH as a function of time, at different dosages of a commercial coagulant ($FeCl_3 \cdot 6H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, from left to right column).

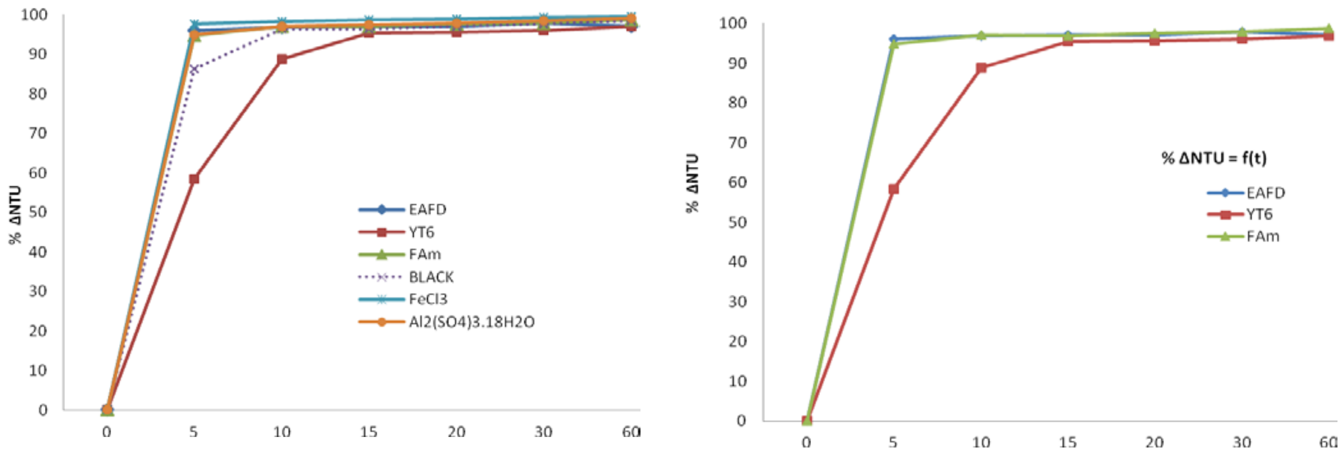


Figure 4. Kinetics of turbidity variation (ΔNTU) using an industrial by-product (YT, FAm, EAFD) in comparison to commercial coagulants ($FeCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$), at the optimal dosage.

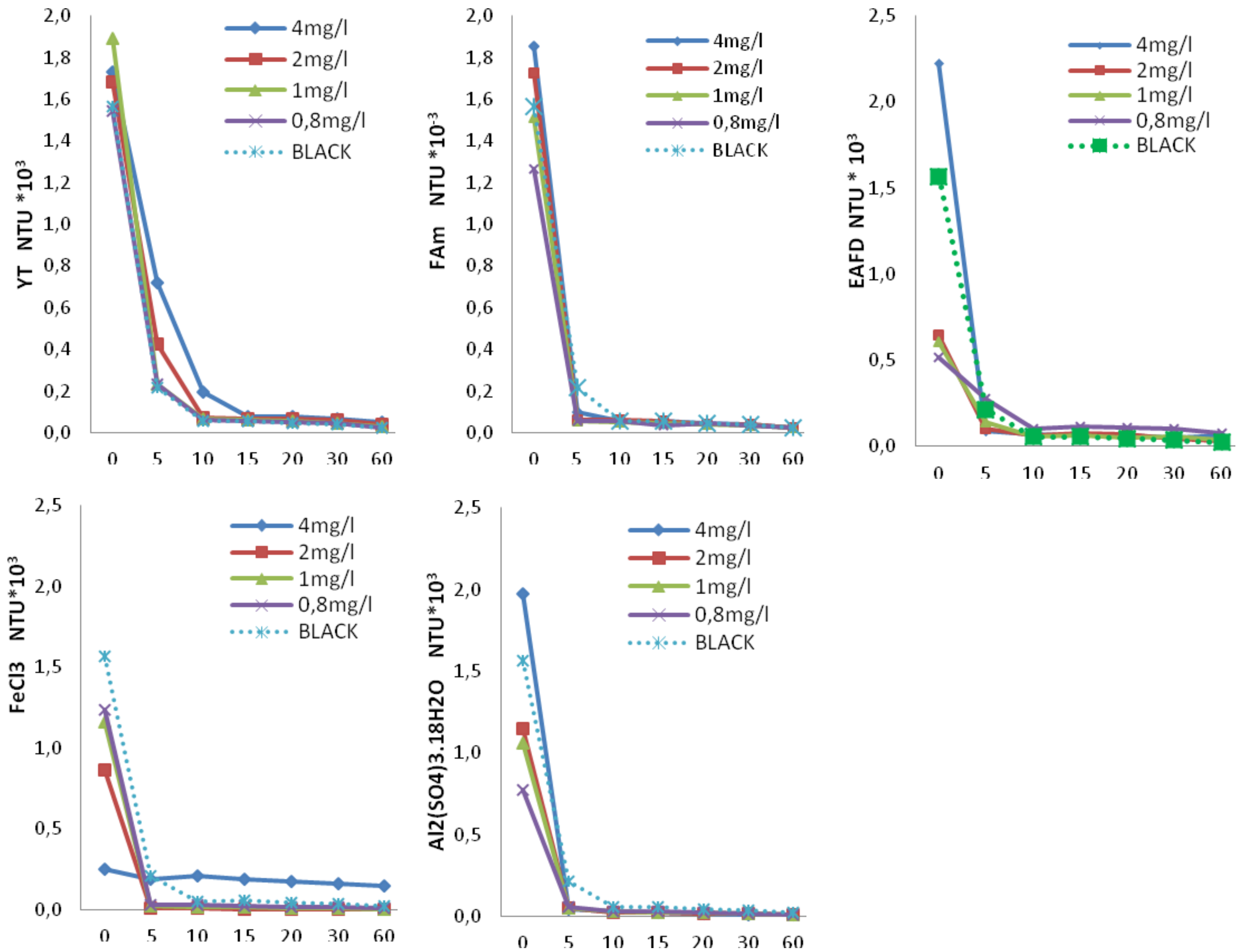


Figure 5. Wastewater turbidity (NTU) using industrial by-product (YT, FAm, EAFD) and commercial coagulant ($FeCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3{\cdot}18H_2O$) as a function of time at different dosages and Black (clean water) sample.

CONCLUSIONS

- Comparing the alternative coagulation/flocculation agents (industrial by-products) to the conventional (commercial) ones, by varying the dosage and pH, they are proved to be efficient coagulants, resulting in an effluent with negligible turbidity.
- pH values do not change for alternative and conventional coagulants, resulting in samples with a pH ranging between 6.5 and 9.5.
- Turbidity removal rates appear to be very high as deduced by kinetic studies, revealing a high removal capacity in short sedimentation times of about 5 min.
- Beyond this possible contribution of the industrial powders to the coagulation-flocculation-sedimentation process of colloidal particles, their potential for concurrent beneficial adsorption of other substances present in the effluent wastewater to be treated should also be taken into consideration, which enhances the significance of the current scientific endeavor.

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