

Article **Graphene Oxide**/**Fe-Based Composite Pre-Polymerized Coagulants: Synthesis, Characterization, and Potential Application in Water Treatment**

Athanasia K. Tolkou * and Anastasios I. Zouboulis [*](https://orcid.org/0000-0003-1120-3105)

Laboratory of Chemical and Environmental Technology, Department of Chemistry, Aristotle University of Thessaloniki, GR-54124 Thessaloniki, Greece

***** Correspondence: tolkatha@chem.auth.gr (A.K.T.); zoubouuli@chem.auth.gr (A.I.Z.); Tel.: +30-2310-997794 (A.I.Z.); Fax: +30-2310-997730 (A.I.Z.)

Received: 14 June 2020; Accepted: 28 June 2020; Published: 30 June 2020

Abstract: This study presents for the first time the synthesis and characterization of GO (graphene oxide), PFSiC (polyferric silicate chloride), and hybrid GO-PFSiC derivatives, aiming to enhance synergistically the performance of coagulation, when applied for the treatment of water. The structure and the morphology of composite GO-PFSiC coagulants were studied in detail by the application of FTIR, XRD, and SEM characterization techniques. Furthermore, the proposed coagulants were applied for the treatment of simulated turbid surface water. The effects of the reagent's dosage, pH value, and experimental/operational conditions on the coagulation efficiency, applied mainly for the removal of turbidity, were examined. The results, obtained from the FTIR and XRD measurements, showed the presence of a bond between the PFSiC and the GO surface, indicating that the PFSiC particles are distributed uniformly on the surface of graphene, which was also confirmed by the SEM images. Especially, the composite compound $GO-PFSiC_{1.5-15-0.5}$ presents the most uniform distribution of iron on the surface of graphene oxide and exhibits the optimum coagulation efficiency, while it significantly reduces the turbidity for doses above 3–5 mg/L, i.e., achieving the respective legislation limit as proposed by WHO. Specifically, at the alkaline pH values (>7.9), the removal of turbidity reaches 96%. Consequently, the results of this study render these materials as potential coagulant agents for further research and applications, aiming to also achieve the co-removal of other water components.

Keywords: graphene oxide; pre-polymerized coagulants; composites; Fe-based; water treatment; coagulation

1. Introduction

The rapid development of nanomaterials, which present the advantages of larger surface areas and more activated functionalized sites, brings an alternative way for the preparation of novel specific reagents, dedicated to enhanced water purification [\[1,](#page-10-0)[2\]](#page-10-1). Carbon-based nanomaterials are the most known representatives in this category, due to their numerous unique advantages, and considerable number of existing studies [\[3](#page-10-2)[–6\]](#page-10-3). The most promising materials for treating and delivering pure water are considered those that incorporate nanoscale features and tailorable chemical properties [\[7\]](#page-10-4).

Graphene [\[8,](#page-10-5)[9\]](#page-10-6), a two-dimensional (2-D) material, has attracted increasing interest in the field of composite materials, because of its excellent thermal [\[10\]](#page-10-7), electrical [\[11\]](#page-10-8), and mechanical [\[12\]](#page-10-9) properties. This unique 2-D plane structure, coupled with an extremely high surface area, makes graphene an ideal support material. Multifunctional hybrid materials that can take advantage of the extraordinary properties of both graphene and other participating functional materials have been already reported [\[13–](#page-10-10)[16\]](#page-10-11). In addition, graphene oxide (GO) can be readily obtained from cheap natural graphite in large quantities. Thus, hybrid multifunctional materials based on GO can be much more applicable, than those, e.g., based on other relatively more expensive nanomaterials, such as the functionalized one-dimensional carbon nano-tubes (CNTs). Recently, GO-based composite materials have been applied for the removal of certain inorganic pollutants from water sources [\[17\]](#page-10-12). Another challenge is the environmental concerns, regarding GO materials. Although previous reports [\[18](#page-10-13)[,19\]](#page-10-14) indicate that GO has better biocompatibility than CNTs, the exposure to residual GO in water may still pose possible risks to human health. Noting, however, that the relevant literature is rather limited [\[18](#page-10-13)[,19\]](#page-10-14) and inconsistent results have been reported, showing that GO can exhibit either nontoxicity or dose-dependent toxicity. Therefore, more detailed investigation concerning these issues is necessary.

Coagulation, which is a widely applied process, especially for water treatment, because of its high efficiency and facile operation, is considered among the most important industrial technologies for water/wastewater treatment, noting that the appropriate selection and application of coagulant reagents during this process is significant, thus affecting its final performance. In fact, previous studies [\[17\]](#page-10-12) have already shown that GO is an efficient absorbent to remove metal ions and various types of organic matter and pollutants from water sources. On the other hand, there are some reports in the literature about the incorporation of GO flakes within a membrane material with the aim of water desalination and/or purification, thus optimizing water transport through graphene-based membranes [\[20\]](#page-11-0). Membrane fouling is considered as the main process drawback. A graphene-based nanocomposite membrane dip-coated by polydopamine (PDA), which is known for its antifouling properties, was proposed [\[21\]](#page-11-1). The presence of GO also increased the mechanical stability of the membrane. However, a rather limited number of publications have addressed the subject of using GO as a coagulant reagent so far [\[22](#page-11-2)[–24\]](#page-11-3).

The pre-polymerized inorganic coagulants represent a relatively new category of coagulant agents, which was developed in order to increase the effectiveness of the convenient coagulation process. More recently, composite polymeric aluminum and/or iron products, such as PFSiS (polyferric silicate sulfate) [\[25\]](#page-11-4), PASiC (polyaluminium silicate chloride) [\[26\]](#page-11-5), PSiFAC (poly aluminum ferric silicate chloride) [\[27\]](#page-11-6), and PSiFAC-Mg (poly aluminum ferric silicate magnesium chloride) [\[28\]](#page-11-7), have been examined during mainly laboratory experiments, regarding, for example, the removal of turbidity [\[27\]](#page-11-6), arsenic [\[29\]](#page-11-8), and high-strength industrial wastewaters [\[30\]](#page-11-9), as well as for the reduction of membrane fouling in MBR (Membrane bioreactor) systems [\[31\]](#page-11-10).

This study presents for the first time the combined application of GO (graphene oxide) and PFSiC (polyferric silicate chloride) materials, i.e., an Fe-based composite pre-polymerized coagulant reagent, as a promising approach to synergistically enhance the water treatment, taking into account the specific advantages of each material. To the best of our knowledge, this category of combined coagulants has never been previously applied for water treatment, while the use of hybrid GO-PFSiC reagent is firstly reported in the literature. The structure and the morphology of composite GO-coagulants were studied in detail by the application of FTIR, XRD, and SEM characterization techniques. Furthermore, the proposed coagulants were applied for the treatment of simulated surface water contaminated with clay. The World Health Organization (WHO) has established that the turbidity of drinking water should be not more than 5 NTU, and should be better below 1 NTU [\[32\]](#page-11-11).

2. Materials and Methods

All used chemical reagents were of analytical grade. De-ionized water (with low conductivity, <0.5 µS/cm) was used to prepare all solutions, while de-ionized carbonate-free water was used for the preparation of stock solutions, regarding the coagulants.

2.1. Preparation of Graphene Oxide (GO)

The graphite flakes, used for the preparation of graphene oxide, were purchased from Sigma Aldrich (USA). Graphite oxide (GrO) was prepared by using the modified Hummer's method [\[33\]](#page-11-12), as improved by Debnath et al. (2014) [\[34\]](#page-11-13). In brief, graphite flakes (5.0 g) and NaNO₃ (2.5 g) were mixed with 120 mL of H_2SO_4 (95%) in a 500-mL flask. The mixture was stirred for 30 min in an ice bath. Afterwards, 15.0 g KMnO₄ was added into the mixture under vigorous stirring, keeping the reaction temperature lower than 20 ◦C. The mixture was further stirred at room temperature overnight. Thereafter, another 15.0 g of $KMnO₄$ were added into the previous mixture and stirred at room temperature for another 2 h, aiming to oxidize totally any remaining graphite. On addition of the deionized water into this mixture, a yellowish paste was obtained, and the temperature was increased to about 98 ℃ with effervescence. This diluted suspension was then stirred for another 4 h and 50 mL of H_2O_2 (30%) were added afterwards to the mixture. As the reaction progressed, the color of the pasty mixture gradually turned into light brownish. The mixture was subsequently washed with 100 mL of 5% HCl and 30% H_2O_2 (five times) to purify it from any residuals of MnO_2 and sulfates. Finally, a solid was obtained after drying at 60 ◦C under vacuum.

Graphene oxide (GO) was prepared from the solid graphite oxide by sonicating the solid in double distilled water, aiming to convert it into a stable colloidal suspension. Then, the colloidal graphene oxide (GO) was precipitated by using 0.1 M NaOH solution and the solid precipitates were subsequently filtered through a 0.45-mm nylon membrane filter to separate the liquid phase and finally, they were subjected to drying at 60 ◦C under vacuum and the GO was obtained as grey powder.

2.2. Preparation of PFSiC

Composite poly-ferric-silicate chloride (PFSiC) coagulants were produced at room temperature $(22^{\circ}$ C), according to a modified procedure of Zouboulis and Moussas (2008) [\[25\]](#page-11-4) and Tolkou et al. (2015) [\[27\]](#page-11-6) under various experimental conditions. The initial solutions used for the preparation of pre-polymerized coagulants were 0.5 M FeCl₃·6H₂O (Merck) and 0.5 M NaOH (Merck, as the added alkaline agent). The 0.5 M polysilicic acid solution (pSi) was prepared according to the respective literature [\[26\]](#page-11-5): 1.74 mL of pSi solution were added to 20 mL of 0.5 M FeCl₃·6H₂O solution, under vigorous stirring (0.3 mL/min, 20 rpm), and subsequently, 30 mL of alkaline solution were added slowly under magnetic stirring (0.1 mL/min, 70 rpm) in the mixture at the temperature of 30 °C. The produced composite pre-polymerized material, termed as $PFSiC_{1.5-15}$ to indicate the proportions of the aforementioned components, was left under stirring to mature for about 1 h and then diluted with water to the final concentration of 0.1 M (relevant to Fe). The main physico-chemical properties of this coagulant agent (used in the subsequent experiments) were pH value 1.9, turbidity 65 NTU, and conductivity 29 ms/cm.

2.3. Preparation of Composite GO-PFSiC Material

The Fe-containing graphene oxide composite materials were prepared after the impregnation of prepared graphene oxide with the pre-polymerized Fe-based coagulant (PFSiC), followed by thermal treatment at 85 °C. For a typical impregnation procedure, taking, e.g., GO-PFSiC_{1.5-15-1} as a typical case with a molar ratio of $[GO]/[Fe] = 1100$ mg of GO were dispersed in 100 mL of water (1 g/L). The appropriate amount of aquatic solution of PFSiC_{1.5-15}, i.e., 100 mg Fe (as 17.3 mL of 0.1 M coagulant solution) were added. Because of the highly acidic pH value of $PFSiC_{1.5-15}$, the precipitation of ferric (hydro)oxide species [\[35\]](#page-11-14) was avoided. After 30 min of stirring, the dispersion was sonicated for 30 min. It was then filtrated, washed with deionized water, and finally, it was dried in the air. A weighed amount of dried impregnated graphene oxide composite was placed in a furnace and heated up overnight to 85 ◦C. Two more relevant materials, but with different molar ratios, were also synthesized by following the same procedure, i.e., 100 mg GO/200 mg Fe to obtain the ratio [GO]/[Fe] = 0.5 and 100 mg GO/333.3 mg Fe to obtain the ratio [GO]/[Fe] = 0.3, and the resulting impregnated GOs are

presented in Table [1,](#page-3-0) while the weight ratio of Fe to GO was increased stepwise in order to define the most efficient coagulant.

Table 1. Preparation conditions for the laboratory-synthesized composite coagulant agents, examined in this study.

2.4. Characterization

2.4.1. Scanning Electron Microscopy (SEM)

Small portions of coagulant powders were obtained after drying the aquatic solution of PFSiC in the oven $(\sim40\degree C)$. GO and GO-PFSiC composites were already in powdered form and used to observe the morphology of respective products, by employing a ZEISS EVO 50 scanning microscope, at EHT = 10 kV. The SEM sample was prepared by placing a drop of dilute ethanol dispersion of the prepared composites onto a copper plate attached to an aluminum sample holder and the solvent was allowed to evaporate at room temperature.

2.4.2. FT-Infrared Spectroscopy (FTIR)

FTIR spectra of the prepared composite products were recorded in the range of 4000–400 cm⁻¹, by using a Nicolet 380 FTIR Spectrometer-Thermo Scientific spectrophotometer to allow the observation of surface species and the possible polymeric interactions between the components.

2.4.3. X-ray Diffraction Spectroscopy (XRD)

The X-ray diffraction spectroscopy (XRD) is an important tool for the identification of crystalline compounds and it was applied to identify the possibly formed crystalline phases. The Malvern Panalytical Xpert instrument (Cu-K radiation) was used and the solid samples were analyzed in the range of 20 $^{\circ}$ -80 $^{\circ}$ 2 θ with a scan rate of 1 $^{\circ}$ /min.

2.5. Batch Coagulation Experiments

2.5.1. Coagulation Experiments Performed by Jar-Tests

Convenient jar-test experiments were applied for the examination of coagulants' efficiency, by using a jar-test apparatus (Aqualytic), equipped with six paddles, employing 1-L glass beakers. The simulated contaminated surface water (1 L) was prepared by using tap water of Thessaloniki (N. Greece) and clay (kaolin) suspension of an initial concentration of clay suspended particles of 10 mg/L. The pH was properly adjusted by using HCl or NaOH solutions of appropriate concentrations (1–0.01 M) and measured by a Metrohm Herisau pH meter. The properties of water samples are presented in Table [2,](#page-3-1) while the conditions used in the jar-test experimental runs are shown in Table [3.](#page-4-0)

Table 2. Initial sample properties (simulated surface samples).

2.5.2. Turbidity Removal

After the coagulation treatment, samples were collected from the supernatant of each beaker and were analyzed for the determination of turbidity (NTU), by using a HACH RATIO/XR Turbidimeter. In order to evaluate the synergistic effect of GO and PFSiC in water treatment, residual turbidity values, obtained by the application of combined materials, were compared with those obtained with standalone GO and PFSiC reagents.

For clay suspension, the residual turbidity percentage (*RT*, %) was expressed as:

$$
RT(\%) = \left(\frac{T}{T_o}\right) \times 100\% \tag{1}
$$

where *T* and *T^o* are the turbidities of the treated and raw water, respectively.

3. Results and Discussion

3.1. Characterization

The characterization of the new composite materials by using FTIR measurements was carried out to confirm the bonding or types of functional groups of molecules that are being present in the GO and can be impregnated into the new GO-PFSiC materials. FTIR analysis was performed at wavenumbers 400–4000 cm⁻¹, where in this range the characteristic absorption of functional group vibrations, as presented by the GO and the composites, can be identified. In Figure [1,](#page-4-1) the FTIR spectra can be shown, comparing the different examined materials, i.e., GO, $PFSiC_{1.5-15}$, GO- $PFSiC_{1.5-15-1}$, GO-PFSiC_{1.5-15-0.5}, and GO-PFSiC_{1.5-15-0.3}. In the FTIR spectra, primary hydroxyl C–OH (1380 cm⁻¹) groups, epoxy C–O groups (1186 cm⁻¹), and carbonyl C=O (1820 cm⁻¹) groups can be detected in the GO spectrum, which reveals that large numbers of oxygen-containing groups have been introduced/interact into/with the GO structure [\[36](#page-11-15)[,37\]](#page-11-16); noting also that there is an absence of absorption at the wavenumber 1725 cm−¹ , which matches with the characteristics of C=C aromatic stretching vibration, indicating that GO is completely oxidized [\[38\]](#page-11-17).

Figure 1. FTIR spectra comparing the examined materials GO, PFSiC_{1.5-15}, GO-PFSiC_{1.5-15-1}, GO-PFSi $C_{1.5-15-0.5}$, and GO-PFSi $C_{1.5-15-0.3}$.

The band at 1038 cm−¹ , which was found only in the spectra of pre-polymerized coagulants, can be **GO** assigned to the asymmetric Si–O stretching vibrations of Si–O–Si bonds, which is indicative of the high polymerization degree of silica. In addition, two characteristic peaks exist at 1100 and 1080 cm−¹ that **GO-PFSiC1.5-15-0.5** could be attributed to the asymmetric stretching vibration of Fe–O–Fe [\[30\]](#page-11-9) and Si–O–Fe bonds [\[39\]](#page-11-18), respectively. Moreover, in the spectra of PFSiC_{1.5-15} and also of the composites GO-PFSiC, it can be observed that there is a peak at the wavenumber 3279.75 cm−¹ , which indicates the characteristic absorption of stretching vibrations from the –OH group. The wide peaks in these vibration ranges **1000** are characteristic of –OH groups that undergo hydrogen bond formation. The absorption at the wave number 1623.36 cm⁻¹ expresses the characteristic of vibration stretching from the C=C group. FTIR analysis can also provide a strong clue to the formation of the co-ordination bond C-O-Fe between the GO sheets and the iron particles. This can be noticed from the presence of the characteristic absorption bands of the stretching vibrations of Fe–O in the PFSiC material that were found at the **0** wavenumber 617.19 cm−¹ , which confirms the success of PFSiC loading/interactions with the GO **4000 3500 3000 2500 2000 1500 1000 500** sheets. The difference that can be observed between the FTIR spectrum of GO and the GO-PFSiC materials is that there is a weakening of the absorption intensity at the wave number around 1580 cm⁻¹, **Figure 1.** The settle in the composite GO-PFSiC, as compared to simple GO, which at the wave number 1580 cm⁻¹ is considered as an absorption characteristic of the carboxyl group. This shows that there has been a reduction in the quantity of carboxyl groups, because they are playing role as a ligand that can interacts with the Fe atoms of PFSiC $[38,40,41]$ $[38,40,41]$ $[38,40,41]$. to since. It addites
the asymmetric stription
of a peak at the way
ng vibrations from

The morphology and structure of GO and of the relevant composites were further examined by obtaining representative SEM images of these materials. As typical examples, the SEM images of GO, PFSiC, and GO–PFSiC materials are shown in Figure 2. Both the pristine GO and the prepared impregnated GO–PFSiC materials were found to exhibit a typically wrinkled sheet-like structure, as it can be observed, indicating that iron was homogeneously distributed onto the GO sheets. Especially, the composite GO-PFSiC_{1.5-15-0.5}, as illustrated in Figure [2d](#page-6-0), presents the most uniform distribution of iron on the surface of graphene oxide.

Figure 2. *Cont.*

Figure 2. SEM images of hybrid_{/composite materials, obtained after convenient drying in an} μ (d) Ω PFSiC₁.5-15; α (e) Ω PFSiC₁.5-15; (**b**) α) μ Figure 2. SEM images of hybrid/composite materials, obtained after convenient drying in an oven under constant rather low temperature $(\sim 40 \degree \text{C})$; (a) GO; (b) PFSiC_{1.5-15}; (c) GO-PFSiC_{1.5-15-1};
(d) CO-PFSiC_{1.5-15-1}; and (a) CO-PFSiC_{1.5-15-1}; $G = \frac{1}{2}$ (d) GO-PFSiC_{1.5-15-0.5}; and (e) GO-PFSiC_{1.5-15-0.3}. $H = 0.5 \pm 0.07$ is observed that with the increase of the Figure 3e, $F = 0.5 \pm 0.07$ to Figure 3.

 $\text{PFSIC}_{1.5\text{-}15}$ (Figure 3b), and GO-PFSiC hybrids (Figure 3c–e). From the XRD patterns, similar diffraction peaks at 35.6°, 43.3°, 53.6°, 57.3°, and 62.8° in Figure 3b–e can be detected, which are the characteristic peaks of cubic Fe $[42]$, indicating that the respective peaks of $PFSIC_{1.5-15}$ are formed in the composites and that the PFSiC particles are distributed uniformly on the surface of graphene, which was also confirmed by the SEM images (Figure [2\)](#page-6-0) [\[43\]](#page-12-2). The results obtained from the XRD analysis are presented in Figure 3 for the cases of GO (Figure [3a](#page-6-1)), μ ration, and anong [th](#page-6-1)e material material materials are presented in Figure 5 for the cases of GO she $\frac{38.8}{\pi}$. The partially oxidized part that shows few layers of graphene, and to naturally obtained part that shows few layers of graphene, and to naturally denote an unit of graphene, and to naturally denote a set o

(d) GO-PFSiC_{1.5-15-0.5}, (e) GO-PFSiC_{1.5-15-0.3}, and (f) comparison between them. **Figure 3.** XRD diagrams of the examined materials; (a) GO, (b) $\text{PFSiC}_{1.5\text{-}15.4}$ (c) GO- $\text{PFSiC}_{1.5\text{-}15\text{-}1}$

It should be noted, however, that the intense and characteristic peak at 45° belongs to the sample carrier during the analysis by the XRD instrument and not to another compound contained in the sample [\[24\]](#page-11-3). In addition, the sharp peak at 32° is observed only in Figure [3b](#page-6-1), which corresponds to $PFSiC_{1.5-15}$, and belongs to NaCl that is produced during the preparation of $PFSiC_{1.5-15}$ solution and it disappeared in Figure [3c](#page-6-1)–e, which present the XRD patterns of solid composite GO-PFSiC hybrids. However, it is observed that with the increase of the Fe/GO ratio (see Figure [3b](#page-6-1)–e, respectively), the intensity of the peak at 32◦ gradually decreases, indicating that at a higher [Fe]/[GO] ratio, amorphous ferric hydroxide materials are intercalated between the GO sheets and a homogeneous amorphous composite is formed [\[13\]](#page-10-10).

In addition, as shown in Figure [3a](#page-6-1), GO material presents two characteristic peaks at 25.58◦ and 38.8◦ , corresponding to the partially oxidized part that shows few layers of graphene, and to natural graphite, which undergoes imperfect oxidation, respectively. The presence of a bond between the PFSiC and the GO surface can be seen from the shift of the GO peak to 30.58°, which is caused by the reduction of some graphene oxides to graphene, due to the precipitation reaction of Fe ion [\[38,](#page-11-17)[44\]](#page-12-3).

3.2. Coagulation Performance

3.2.1. Determination of Optimum Coagulation Experimental Conditions

In Figure [4,](#page-7-0) the results of the experiments, as applied for the determination of optimum coagulation conditions during jar-test experimental runs, are presented. For this reason, GO and $PFSiC_{1.5-15}$ were compared, regarding the removal of turbidity and expressed as the residual turbidity (NTU), (a) in different sedimentation times, and (b) in different rapid mixing period times (Table [3\)](#page-4-0), based on previous research tests [\[27\]](#page-11-6), by using 10 mg/L as an indicative dosage.

Figure 4. Determination of the optimum coagulation experimental conditions, comparing GO and **Figure 4.** Determination of the optimum coagulation experimental conditions, comparing GO and $\text{PFSiC}_{1.5-15}$ materials, regarding the removal of turbidity (expressed as the residual turbidity, NTU); $\text{PFSiC}_{1.5-15}$ (a) by using different sedimentation times, and (b) by applying different rapid mixing period times.

were stirred rapidly at 160 rpm for 2 min, followed by slow stirring at 40 rpm for 10 min, and then, the suspension was rested for 30–60 min without any stirring to allow the separation by sedimentation of the produced flocs. As noticed in Fi[gu](#page-7-0)re 4a, the optimum sedimentation time was found to be 50 min, where the system reaches a dynamic equilibrium, indicated by the relatively constant value of turbidity after 50 min of sedimentation. Particularly, when studying the different applied sedimentation times (Figure [4a](#page-7-0)), the solutions

Then, maintaining the optimal settling time at 50 min, the different durations of the initial rapid mixing period (Figure 4b) were tested [a](#page-7-0)t 160 rpm for 1, 1.5, 2, and 2.5 min, followed by the slow stirring at 40 rpm for 10 and 50 min of sedimentation. According to Figure 4b, the optimum time in this case was 2 min of rapid mixing. After that, the residual turbidity (NTU) remains rather constant. Therefore, the jar-test protocol selected for the optimization of coagulation performance was rapidly mixed at

160 rpm for 2 min, slowly stirred at 40 rpm for 10 min, and finally, sedimentation was performed for 50 min. materials shows a better coagulation efficiency than the pure graphene oxide (GO) or the simple P_{P} is the component of \sim 15 cm \sim 15 km \sim 15 km \sim 16 km \sim maily, scannenation was performed for found to significantly reduce the turbidity for dosages above $\frac{1}{\sqrt{2}}$, much lower than the than the than the than the than the turbidity for dosages above 3–5 mg/L, i.e., much lower than the turbidity for down the tu

3.2.2. Determination of the Optimum Dosage and Type of Material was increased, as the dosage of \mathcal{L}_1 .

The coagulant dosage is considered to be among the most critical parameters that present a significant effect on the efficiency of the coagulation process. All prepared coagulants in this study were compared in terms of turbidity removal (Figure 5) (expressed as NTU units), in order to obtain the optimum type of coagulant and subsequently, to determine the optimal dosage of the examined materials by treating simulated surface water samples, noting that the respective initial values of this water were 17.2 NTU and pH 7.6 \pm 0.2 (Table [2\)](#page-3-1).

Figure 5. Determination of the optimum dosage and best material type, by comparing GO, PFSiC_{1.5-15}, GO- $\text{PFSiC}_{1.5\text{-}15\text{-}1}$, GO- $\text{PFSiC}_{1.5\text{-}15\text{-}0.5}$, and GO- $\text{PFSiC}_{1.5\text{-}15\text{-}0.3}$ materials, regarding the removal of turbidity, treating simulated surface water samples, expressed (**a**) as % removal, and (**b**) as residual turbidity (NTU).

According to the obtained results, it can be observed that the application of composite/hybrid materials shows a better coagulation efficiency than the pure graphene oxide (GO) or the simple PFSiC_{1.5-15} coagulant. Particularly, the composite GO-PFSiC_{1.5-15-0.5} with the ratio [GO]/[Fe] = 0.5 was found to significantly reduce the turbidity for dosages above 3–5 mg/L, i.e., much lower than the relevant data found in the respective literature, e.g., >24 mg/L [\[23\]](#page-11-20). In addition, the turbidity removal was increased, as the dosage of $GO-PSiC_{1.5-15-0.5}$ was increased, reaching 93% (~1 NTU) for a dosage of 30 mg/L. According to the recommendations from the World Health Organization [\[32\]](#page-11-11), turbidity must be lower than 5 NTU before the water can be adequately sanitized for human consumption and should be ideally below than 1 NTU. It is worth noting that the optimum $GO-PFSiC_{1.5-15-0.5}$ material, as illustrated in Figure [2d](#page-6-0), presents the most uniform distribution of iron on the surface of graphene oxide.

3.2.3. Determination of Optimum pH

The effect of pH on the coagulation ability of optimal GO-PFSi $C_{1.5-15-0.5}$ material, as obtained from the previous experiments, was examined in the pH range 4–9, by using 10 mg/L of GO-PFSiC_{1.5-15-0.5}. The removal of turbidity, expressed as percentage (Figure [6a](#page-9-0)) and as residual values (NTU) (Figure [6b](#page-9-0)), is presented in Figure [6.](#page-9-0) According to the results, it is found that the treated water by the composite material GO-PFSiC_{1.5-15-0.5} can follow the respective legislation (by WHO) limits with an increase of pH values over 8. In particular, at more alkaline pH values (>7.9), the removal of turbidity reaches 96%, by applying only the 10 mg/L dosage, while in pH 6, where very small flocks rather slowly formed and barely settled, the relative percentage decreases significantly (68%). However, at pH 4–5, the turbidity removal efficiency was highly improved (up to 75–85%), in accordance with the relevant literature [\[23\]](#page-11-20). The original pH value of the examined simulated surface water (at pH 7.6 \pm 0.2) was

in the optimum pH range for the treatment of turbid water samples, in agreement with Figure 6 . In strong alkaline media, the formation of flocks was very quick and began even from the first minute of high-speed agitation.

Figure 6. Effect of pH values on (a) % turbidity removal, (b) residual turbidity, when treating simulated surface water samples, for an initial turbidity of 17.2 NTU and coagulant dosage of 10 mg/L, regarding in the contract of the the application of the optimal GO-PFSiC $_{\rm 1.5\text{-}15\text{-}0.5}$ material.

4. Conclusions

between GO (graphene oxide) and PFSiC (polyferric silicate chloride), i.e., an Fe-based pre-polymerized coagulant agent, as a promising hybrid material to synergistically enhance water treatment. The hybrid GO-PFSiC derivatives are firstly reported in the literature. This study presented the application of new composite materials obtained with the interaction

The structure and morphology of composite GO-PFSiC coagulants were studied in detail by the application of FTIR, XRD, and SEM techniques. According to the presented results, the success of PFSiC loading on GO sheets was confirmed by the FTIR spectra at a wavenumber of 617.19 cm⁻¹, corresponding to the Fe–O bond in the GO-PFSiC material. The XRD analysis confirmed the characteristic peaks of $PFSIC_{1.5-15}$ in the composites with GO, indicating that the PFSiC particles were distributed uniformly on the surface of graphene, especially in the composite GO-PFSiC_{1.5-15-0.5}, which was also confirmed by the SEM images.

Furthermore, the proposed coagulants were applied for the treatment of simulated surface water contaminated with clay. The effects of the dosage, pH, and experimental/operating conditions on the coagulation efficiency, regarding the removal of turbidity, were examined, aiming to determine the optimal turbidity removal conditions. The jar-test protocol selected for the best coagulation performance was rapid mixing at 160 rpm for 2 min, slow stirring at 40 rpm for 10 min, and finally, sedimentation for 50 min. According to the obtained results, the composite material GO-PFSiC_{1.5-15-0.5} with the ratio $[GO]/[Fe] = 0.5$ can significantly reduce the turbidity for dosages above 3–5 mg/L, i.e., much lower than the respective presented values in the relevant literature. The effect of pH on the coagulation ability of GO-PFSiC_{1.5-15-0.5} was tested in the pH range 4-9 by using a 10 mg/L dosage. It was found that the GO-PFSiC_{1.5-15-0.5}-treated water can follow the stringent legislation (by WHO) limits with an increase of the application pH values. In particular, at more alkaline pH values (>7.9), the removal of turbidity can reach 96%, by applying only a 10 mg/L as dosage.

Consequently, the results of this study render these materials as potential coagulants for further research and potential applications regarding the co-removal of other water components.

Author Contributions: Data curation, A.K.T.; Investigation, A.K.T.; Methodology, A.K.T.; Writing—Original draft, A.K.T.; Validation, A.I.Z.; Visualization, A.K.T. and A.I.Z.; Writing—Review and editing, A.K.T. and A.I.Z.; Supervision, A.I.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the European Union and the Greek State Program EPAN-II (OPC-II)/ESPA (NSRF): SYNERGASIA II, Project (FOUL-MEM), grant number 11SYN-8-1084, entitled "New processes for fouling control in membrane bioreactors".

Acknowledgments: The Onassis Foundation for receiving A. Tolkou a scholarship to participate in a summer school at the Foundation of Research and Technology (FORTH), Crete, Greece, for Nanoscience and Nanotechnology, emphasizing on Graphene and other 2D materials, in which the winner of the Nobel Prize in Chemistry for the discovery of graphene, Konstantin Novoselov, taught.

Conflicts of Interest: The authors declare that they have no conflict of interest.

References

- 1. Simate, G.S.; Iyuke, S.E.; Ndlovu, S.; Heydenrych, M. The heterogeneous coagulation and flocculation of brewery wastewater using carbon nanotubes. *Water Res.* **2012**, *46*, 1185–1197. [\[CrossRef\]](http://dx.doi.org/10.1016/j.watres.2011.12.023) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/22212884)
- 2. Zhao, G.; Jiang, L.; He, Y.; Li, J.; Dong, H.; Wang, X.; Hu, W. Sulfonated graphene for persistent aromatic pollutant management. *Adv. Mater.* **2011**, *23*, 3959–3963. [\[CrossRef\]](http://dx.doi.org/10.1002/adma.201101007) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/21800380)
- 3. Gallios, G.; Tolkou, A.; Katsoyiannis, I.; Stefusova, K.; Vaclavikova, M.; Deliyanni, E. Adsorption of arsenate by nano scaled activated carbon modified by iron and manganese oxides. *Sustainability* **2017**, *9*, 1684. [\[CrossRef\]](http://dx.doi.org/10.3390/su9101684)
- 4. Danô, M.; Viglašová, E.; Galamboŝ, M.; Rajec, P.; Novák, I. Sorption behaviour of pertechnetate on oxidized and reduced surface of activated carbon. *J. Radioanal. Nucl. Chem.* **2017**, *314*, 2219–2227. [\[CrossRef\]](http://dx.doi.org/10.1007/s10967-017-5532-3)
- 5. Deliyanni, E.A.; Kyzas, G.Z.; Triantafyllidis, K.S.; Matis, K.A. Activated carbons for the removal of heavy metal ions: A systematic review of recent literature focused on lead and arsenic ions. *Open Chem.* **2015**, *13*, 699–708. [\[CrossRef\]](http://dx.doi.org/10.1515/chem-2015-0087)
- 6. Giannakoudakis, D.A.; Kyzas, G.Z.; Avranas, A.; Lazaridis, N.K. Multi-parametric adsorption effects of the reactive dye removal with commercial activated carbons. *J. Mol. Liq.* **2016**, *213*, 381–389. [\[CrossRef\]](http://dx.doi.org/10.1016/j.molliq.2015.07.010)
- 7. Sweetman, M.J.; May, S.; Mebberson, N.; Pendleton, P.; Vasilev, K.; Plush, S.E.; Hayball, J.D. Activated carbon, carbon nanotubes and graphene: Materials and composites for advanced water purification. *C J. Carbon Res.* **2017**, *3*, 18. [\[CrossRef\]](http://dx.doi.org/10.3390/c3020018)
- 8. Novoselov, K.S.; Geim, A.K.; Morozov, S.V.; Jiang, D.; Zhang, Y.; Dubonos, S.V.; Grigorieva, I.V.; Firsov, A.A. Electric field effect in atomically thin carbon films. *Science* **2004**, *306*, 666–669. [\[CrossRef\]](http://dx.doi.org/10.1126/science.1102896)
- 9. Geim, A.K.; Novoselov, K.S. The rise of graphene. *Nat. Mater.* **2007**, *6*, 183–191. [\[CrossRef\]](http://dx.doi.org/10.1038/nmat1849)
- 10. Ghosh, S.; Calizo, I.; Teweldebrhan, D.; Pokatilov, E.P.; Nika, D.L.; Balandin, A.A.; Bao, W.; Miao, F.; Lau, C.N. Extremely high thermal conductivity of graphene: Prospects for thermal management applications in nanoelectronic circuits. *Appl. Phys. Lett.* **2008**, *92*, 151911–151913. [\[CrossRef\]](http://dx.doi.org/10.1063/1.2907977)
- 11. Lu, Y.H.; Chen, W.; Feng, Y.P.; He, P.M. Tuning the electronic structure of graphene by an organic molecule. *J. Phys. Chem. B* **2009**, *113*, 2–5. [\[CrossRef\]](http://dx.doi.org/10.1021/jp806905e) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/19072320)
- 12. Lee, C.G.; Wei, X.D.; Kysar, J.W.; Hone, J. Measurement of the elastic properties and intrinsic strength of monolayer graphene. *Science* **2008**, *321*, 385–388. [\[CrossRef\]](http://dx.doi.org/10.1126/science.1157996) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/18635798)
- 13. Zhang, K.; Dwivedi, V.; Chi, C.; Wu, J. Graphene oxide/ferric hydroxide composites for efficient arsenate removal from drinking water. *J. Hazard. Mater.* **2010**, *182*, 162–168. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jhazmat.2010.06.010) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/20580161)
- 14. Setshedi, K.Z.; Bhaumik, M.; Onyango, M.S.; Maity, A. High-performance towards Cr (VI) removal using multi-active sites of polypyrrole–graphene oxide nanocomposites: Batch and column studies. *Chem. Eng. J.* **2015**, *262*, 921–931. [\[CrossRef\]](http://dx.doi.org/10.1016/j.cej.2014.10.034)
- 15. Mohamud, H.; Ivanov, P.; Russell, B.C.; Regan, P.H.; Ward, N.I. Selective sorption of uranium from aqueous solution by graphene oxide-modified materials. *J. Radioanal. Nucl. Chem.* **2018**, *316*, 839–848. [\[CrossRef\]](http://dx.doi.org/10.1007/s10967-018-5741-4)
- 16. Yang, A.; Zhu, Y.; Li, P.; Huang, C.P. Preparation of a magnetic reduced-graphene oxide/tea waste composite for high-efficiency sorption of uranium. *Sci. Rep.* **2019**, *9*, 6471. [\[CrossRef\]](http://dx.doi.org/10.1038/s41598-019-42697-7)
- 17. Tolkou, A.K.; Katsoyiannis, I.A.; Zouboulis, A.I. Removal of arsenic, chromium and uranium from water sources by novel nanostructured materials including graphene-based modified adsorbents: A mini review of recent developments. *Appl. Sci.* **2020**, *10*, 3241. [\[CrossRef\]](http://dx.doi.org/10.3390/app10093241)
- 18. Jastrzebska, A.M.; Kurtycz, P.; Olszyna, A.R. Recent advances in graphene family materials toxicity investigations. *J. Nanopart. Res.* **2012**, *14*, 1320–1340. [\[CrossRef\]](http://dx.doi.org/10.1007/s11051-012-1320-8)
- 19. Sanchez, V.C.; Jachak, A.; Hurt, R.H.; Kane, A.B. Biological interactions of graphene-family nanomaterials: An interdisciplinary review. *Chem. Res. Toxicol.* **2012**, *25*, 15–34. [\[CrossRef\]](http://dx.doi.org/10.1021/tx200339h)
- 20. Muscatello, J.; Jaeger, F.; Matar, O.K.; Müller, E.A. optimizing water transport through graphene-based membranes: Insights from nonequilibrium molecular dynamics. *ACS Appl. Mater. Interfaces* **2016**, *8*, 12330–12336. [\[CrossRef\]](http://dx.doi.org/10.1021/acsami.5b12112)
- 21. Alammar, A.; Park, S.-H.; Williams, C.J.; Derby, B.; Szekely, G. Oil-in-water separation with graphene-based nanocomposite membranes for produced water treatment. *J. Membr. Sci.* **2020**, *603*, 118007. [\[CrossRef\]](http://dx.doi.org/10.1016/j.memsci.2020.118007)
- 22. Yang, Z.; Yan, H.; Yang, H.; Li, H.; Li, A.; Cheng, R. Flocculation performance and mechanism of graphene oxide for removal of various contaminants from water. *Water Res.* **2013**, *47*, 3037–3046. [\[CrossRef\]](http://dx.doi.org/10.1016/j.watres.2013.03.027)
- 23. Abdelmeguid, E.; Aboubaraka, A.E.; Aboelfetoh, E.F.; Ebeid, E.-Z.M. Coagulation effectiveness of graphene oxide for the removal of turbidity from raw surface water. *Chemosphere* **2017**, *181*, 738–746.
- 24. Wen, X.; Jin, X.; Wang, F.; You, Y.; Chu, D.; Zetterlund, P.B.; Joshi, R.K. Cation-induced coagulation in graphene oxide suspensions. *Mater. Today Chem.* **2019**, *13*, 139–146. [\[CrossRef\]](http://dx.doi.org/10.1016/j.mtchem.2019.06.003)
- 25. Zouboulis, A.I.; Moussas, P.A. Polyferric silicate sulphate (PFSiS): Preparation, characterization and coagulation behavior. *Desalination* **2008**, *224*, 307–316. [\[CrossRef\]](http://dx.doi.org/10.1016/j.desal.2007.06.012)
- 26. Tzoupanos, N.D.; Zouboulis, A.I.; Tsoleridis, C.A. A systematic study for the characterization of a novel coagulant (polyaluminium silicate chloride). *Colloids Surf. A Physicochem. Eng. Asp.* **2009**, *342*, 30–39. [\[CrossRef\]](http://dx.doi.org/10.1016/j.colsurfa.2009.03.054)
- 27. Tolkou, A.K.; Zouboulis, A.I. Synthesis and coagulation performance of composite poly-aluminum-ferric-silicate-chloride coagulants in water and wastewater. *Desalin. Water Treat.* **2015**, *53*, 3309–3318. [\[CrossRef\]](http://dx.doi.org/10.1080/19443994.2014.933614)
- 28. Tolkou, A.; Mitrakas, M.; Katsoyiannis, I.; Ernst, E.; Zouboulis, A. Fluoride removal from water by composite Al/Fe/Si/Mg pre-polymerized coagulants: Characterization and application. *Chemosphere* **2019**, *231*, 528–537. [\[CrossRef\]](http://dx.doi.org/10.1016/j.chemosphere.2019.05.183)
- 29. Katsoyiannis, I.; Tzollas, N.; Tolkou, A.; Mitrakas, M.; Ernst, M.; Zouboulis, A. Use of novel composite coagulants for arsenic removal from waters—Experimental insight for the application of polyferric sulfate (PFS). *Sustainability* **2017**, *9*, 590. [\[CrossRef\]](http://dx.doi.org/10.3390/su9040590)
- 30. Tolkou, A.; Zouboulis, A. Application of composite pre-polymerized coagulants for the treatment of high-strength industrial wastewaters. *Water* **2020**, *12*, 1258. [\[CrossRef\]](http://dx.doi.org/10.3390/w12051258)
- 31. Gkotsis, P.K.; Mitrakas, M.; Tolkou, A.K.; Zouboulis, A.I. Batch and continuous dosing of conventional and composite coagulation agents for fouling control in a pilot-scale MBR. *Chem. Eng. J.* **2017**, *311*, 255–264. [\[CrossRef\]](http://dx.doi.org/10.1016/j.cej.2016.11.099)
- 32. World Health Organization. *Water Quality and Health—Review of Turbidity: Information for Regulators and Water Suppliers*; WHO: Geneva, Switzerland, 2017.
- 33. Hummers, W.S.; Offeman, R.E., Jr. Preparation of graphitic oxide. *J. Am. Chem. Soc.* **1958**, *80*, 1339. [\[CrossRef\]](http://dx.doi.org/10.1021/ja01539a017)
- 34. Debnath, S.; Maity, A.; Pillay, K. Impact of process parameters on removal of Congo red by graphene oxide from aqueous solution. *J. Env. Chem. Eng.* **2014**, *2*, 260–272. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jece.2013.12.018)
- 35. Katsoyiannis, I.A.; Gkotsis, P.K.; Castellana, M.; Cartechini, F.; Zouboulis, A.I. Production of demineralized water for use in thermal power stations by advanced treatment of secondary wastewater effluent. *J. Environ. Manag.* **2017**, *190*, 132–139. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jenvman.2016.12.040)
- 36. Ramesha, G.K.; Kumara, A.V.; Muralidhara, H.B.; Sampath, S. Graphene and graphene oxide as effective adsorbents toward anionic and cationic dyes. *J. Colloid Interface Sci.* **2011**, *361*, 270–277. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jcis.2011.05.050)
- 37. El-shafai, N.M.; El-khouly, M.E.; El-kemary, M. Fabrication andcharacterization of graphene oxide—titanium dioxidenanocomposite for degradation of some toxic insecticides. *J. Ind. Eng. Chem.* **2019**, *69*, 315–323. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jiec.2018.09.045)
- 38. Neolaka, Y.A.B.; Lawa, Y.; Naat, J.N.; Riwu, A.A.P.; Iqbal, M.; Darmokoesoemo, H.; Kusuma, H.S. The adsorption of Cr(VI) from water samples using graphene oxide-magnetic (GO-Fe $_3$ O $_4$) synthesized from natural cellulose-based graphite (kusambi wood or Schleichera oleosa): Study of kinetics, isotherms and thermodynamics. *J. Mater. Res. Technol.* **2020**, *9*, 6544–6556. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jmrt.2020.04.040)
- 39. Moussas, P.A.; Zouboulis, A.I. Synthesis, Characterization and coagulation behavior of a composite coagulation reagent by the combination of Polyferric Sulphate (PFS) and cationic polyelectrolyte. *Sep. Purif. Technol.* **2012**, *96*, 263–273. [\[CrossRef\]](http://dx.doi.org/10.1016/j.seppur.2012.06.024)
- 40. Sammaiah, A.; Huang, W.; Wang, X. Synthesis of magnetic Fe3O4/graphene oxide nanocomposites and their tribological properties under magnetic field. *Mater. Res. Express* **2018**, *5*, 105006. [\[CrossRef\]](http://dx.doi.org/10.1088/2053-1591/aadaab)
- 41. Danesh, N.; Hosseini, M. Magnetite graphene oxide/Lauric acid nanoparticles modified by ethylenediaminetetra acetic acid and its applications as an adsorbent for the removal of Pb(II) ions. *Synth. Met.* **2016**, *220*, 508–523. [\[CrossRef\]](http://dx.doi.org/10.1016/j.synthmet.2016.07.025)
- 42. Guo, J.; Wang, R.; Tjiu, W.W.; Pan, J.; Liu, T. Synthesis of Fe nanoparticles@graphene composites for environmental applications. *J. Hazard. Mater.* **2012**, *225*, 63–73. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jhazmat.2012.04.065) [\[PubMed\]](http://www.ncbi.nlm.nih.gov/pubmed/22609395)
- 43. Liu, P.; Zhong, W.; Wu, X.; Qiu, J. Facile synergetic dispersion approach for magnetic Fe₃O₄@graphene oxide/polystyrene tri-component nanocomposite via radical bulk polymerization. *Chem. Eng. J.* **2013**, *219*, 10–18. [\[CrossRef\]](http://dx.doi.org/10.1016/j.cej.2012.12.062)
- 44. Raghu, M.S.; Kumar, K.Y.; Prashanth, M.K.; Prasanna, B.P.; Vinuth, R. Adsorption and antimicrobial studies of chemically bonded magnetic graphene oxide-Fe3O4 nanocomposite for water purification. *J. Water Process. Eng.* **2017**, *17*, 22–31. [\[CrossRef\]](http://dx.doi.org/10.1016/j.jwpe.2017.03.001)

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://[creativecommons.org](http://creativecommons.org/licenses/by/4.0/.)/licenses/by/4.0/).