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# A multifaceted aggregation and toxicity assessment study of sol–gel-based $TiO_2$ nanoparticles during textile wastewater treatment

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**ABSTRACT**

Innovative textiles have been concern of emerging risk of nanoparticles (NPs) to human and environment. This study aimed to investigate the aggregation, removal and biological, and ecotoxicological effects of sol–gel-based $TiO_2$ NPs while the treatment of textile wastewater. Fe(II) and alum coagulants were applied for the removal of spiked $TiO_2$ NPs from textile wastewater. Particle size distribution, absorbance values (UV–vis range), and residual $TiO_2$ NPs were followed to define aggregation mechanism, including pH variation during treatment of wastewater. The effect of $TiO_2$ on activated sludge treatment was followed by monitoring of oxygen uptake rate (OUR). Ecotoxicity of sol–gel and coagulated samples was observed by *Ceriodaphnia magna* immobilization test. Adjustment of pH to 8 enlarged mean particle size distribution of sol–gel-based $TiO_2$ NPs from 30 to 450 nm. After alum and Fe (II) coagulations, average particle size distributions were observed to be 650 and 960 nm, respectively. Coagulation with alum and Fe(II) resulted over >95% removal of $TiO_2$ from biologically treated textile wastewater (BTTWW). The value for residual $TiO_2$ concentration in BTTWW was reduced from 120 μg/L to around 8 μg/L $TiO_2$ NPs exhibited slight/no toxicity on the OUR while toxicity to *Ceriodaphnia dubia* increased in some coagulated samples, most probably due to higher residual coagulant concentrations.

*Keywords:* Aggregation; Ecotoxicity; Nanoparticles; Oxygen uptake rate; Sol–gel; Textile wastewater; Titanium dioxide; Treatment

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## 1. Introduction

The textile industry uses various toxic chemicals such as wettings, softening finishing agents, oils, wax, phenols, pesticides, surfactants, dyes, benzenes, and many other additives. As a result, textile processes produce highly toxic wastewater [1,2]. Many researchers found that textile wastewaters were toxic even after biological, chemical, and advanced treatment [1–3].

The application of nanotechnology to textile products is still in its infancy, but it is already proving to be a useful tool in improving the performance of textiles. The purpose of nanofinishing in the textile industry is to create new functions on textile surfaces without corrupting the basic performance properties required of textile structures. The use of nanotechnology allows new features of textiles, such as oil resistance, wrinkle resistance, water repellency, antibacteria, anti-allergic, anti-static, self-cleaning, flame retardation, energy storing, and so on [4,5]. On the other hand, development of nanotechnology in textile industry faces with environmental impact risk because the nanoparticles (NPs) are likely to release into the air or water [6]. There has been increasing number of scientific literature indicating negative effects of NPs on human health and the environment [7–15]. *Ceriodaphnia dubia* [13] for the case of their insufficient entrapment in the wastewater treatment plants [16,17].

$TiO_2$ is the superior photocatalyst used for the treatment of water and wastewater [18–21]. Nanosized $TiO_2$ particles in both crystalline and noncrystalline forms are the most common NPs used in textile processes as dyeing, bleaching, flame retarding, self-cleaning, and UV blocking agents [4,5,22–30]. Windler et al. [6] showed that $TiO_2$ in the range of 60–350 nm might be released from textile surfaces into washing waters, but the amounts are relatively low and mostly not in the nanosized range. To the best of our knowledge, there is a lack of information available on the aggregation, removal and effect of $TiO_2$ NPs to biological treatment, and to aquatic organisms in textile wastewater.

In this study, morphologically well-defined sol–gel-based $TiO_2$ NPs were introduced to textile wastewater. Then, coagulation and bench-scale biological treatment were carried out to remove the $TiO_2$ NPs as biological treatment and chemical coagulation are the most common processes for the treatment of textile wastewater, wastewater containing $TiO_2$ NPs were introduced to the lab-scale reactor activated sludge to evaluate the inhibitory effect on respiration rate. Furthermore, the ecotoxicity of $TiO_2$ NPs waste tested to *Ceriodaphnia magna* exposed to coagulated and biological treated samples.

## 2. Material and methods

### 2.1. Samples collection and conservation

Wastewater samples were collected from a cotton textile finishing factory located in the Denizli Organized District, Turkey. The mixed wastewater originated from the sources of washing, scouring, peroxide bleaching, dyeing, and finishing processes is treated in biological treatment plant. Biologically treated textile wastewater (BTTWW) samples were transported to the laboratory and kept refrigerated (+4˚C) during experiments.

### 2.2. Preparation of NPs

Titanium (IV) isopropoxide (Aldrich CAS #: 546-68-9) was used as a precursor for preparing sol–gel derivative $TiO_2$ colloidal suspensions. Twenty milliliters of Titanium (IV) isopropoxide was added to a nitric acid solution to keep the ratio of $H_2O/H^+/Ti$ at 200/0.5/1. The solution was continuously stirred to form a stable colloidal suspension. This suspension was dialyzed against Milli-Q water to pH 2.8 by using a Micropore 3,500 MW cut-off membrane. The resulting sol–gel solution contained approximately 30 g/L $TiO_2$. An appropriate amount of sol–gel derivative $TiO_2$ was introduced to ultrasonication for 15 min and settling for 1 h to prepare nanosized particles. Finally, the supernatant, was removed to be used in further experiments.

### 2.3. Aggregation and removal of NPs

To investigate the effect of pH on the aggregation of $TiO_2$, 1 g of sol–gel derivative $TiO_2$ was added to distilled water and its pH was adjusted to 4, 6, 7, 8, and 10. After 1 h settling time, the supernatant was removed and the residual $TiO_2$ concentration was measured as titanium.

To find out the aggregation and removal of $TiO_2$ NPs from BTTWW, a nanoscale $TiO_2$ suspension was prepared by adding 1 gr of sol–gel derivative $TiO_2$ into 1 L BTTWW sample. After 15 min of ultrasonication and 1 h precipitation, the supernatant was taken from the sample to measure residual $TiO_2$.

### 2.4. Coagulation and flocculation

Further to BTTWW, the effect of coagulation–flocculation process on aggregation and removal of $TiO_2$ NP, alum and Fe(II) coagulations were applied at different concentrations after adjusting the pH value of the supernatant to 8.0. Fe(II) ($FeSO_4{\cdot}7H_2O$) and alum ($Al_2(SO_4)_3{\cdot}18H_2O$) of commercial grade (Merck) were utilized for the experiments. Jar test experiments were

carried out at the original pH values of BTTWW applying 2 min rapid mixing at 100 rpm, 20 min slow mixing at 30 rpm and 1 h for settling in accordance with the literature [1,2]. All experiments were performed at room temperature (20 ± 2˚C) using 500 mL sample.

### 2.5. Inhibition of activated sludge respiration

The adverse effect of $TiO_2$ NPs on activated sludge by means of oxygen uptake rate (OUR) inhibition was investigated according to standard ISO method [31]. Two 2-L lab-scale fill-and-draw reactors (F&DRs) were seeded with activated sludge obtained from an urban wastewater treatment plant in Denizli city of Turkey. The reactors were operated at a hydraulic retention time of 1 d by feeding with synthetic sewage (as described in ISO method [31]) at fixed F/M ratio of 0–3. The acclimation of biomass was observed up to a steady state removal of chemical oxygen demand (COD) parameter. Hach nitrification inhibitor (Formula 2533™) was added to the reactors at a concentration of 0.16 g for 300 mL volume according to the standard method. Initial dissolved oxygen concentration in 50 mL airtight vessels (DO), measured by oxygen meter (WTW OXI 740 model, Inolab), was kept about 7–8 mg/L and pH was adjusted to between 6.5 and 7.5. OUR and soluble COD concentration were calculated to determine the toxicity effects of $TiO_2$ NPs on the activated sludge system [31,32].

### 2.6. C. magna *immobilization test*

The potential toxicity of wastewaters was measured using 24 h *C. magna* without and with 50% dilution according to the standard method given for *Daphnia magna* [33]. Toxicity tests were performed in quadruplicate using five daphnids in each test beaker with 100 mL effective volume as the details are given elsewhere [1]. The total number of immobile organisms was divided by the total number of test organisms (20) to report percent immobilization after 24 and 48-h exposure times.

### 2.7. Analysis

$TiO_2$ has very low solubility. For the quantification of residual $TiO_2$ in supernatant aqueous solutions, $TiO_2$ was transformed into ionic forms by $HNO_3$/$H_2SO_4$ digestion, as described by Standard Methods [34]. The digested samples were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Perkin Elmer ICP-OES Optima 2100DV). Residual Aluminum and Fe(II) concentrations in jar test experiments were monitored using the same ICP-OES.

The zeta potential of $TiO_2$ NPs and their hydrodynamic size distributions were measured by dynamic light scattering (Nano/Zetasizer, ZS90, Malvern Instruments Ltd.). $TiO_2$ NPs were suspended in a 1 mM NaCl solution and the solution pH was adjusted by adding either NaOH (0.1–1 mol/L) or HCl (0.1–1 mol/L) solutions (Aldrich, USA). Before measurements, all $TiO_2$ samples were dispersed by ultrasonication for 15 min. Wastewater characterization of textile wastewater was conducted according to Standard Methods [34].

## 3. Results and discussion

### 3.1. Characterization of textile wastewaters

Table 1 shows the characterization of the inflow and BTTWW in the textile industry. According to Table 1, the raw wastewater displayed a typical character of cotton finishing textile wastewater [1–3].

### 3.2. Aggregation of $TiO_2$ NPs

The pH value of sol–gel-based $TiO_2$ solution was around 3.0. Above that pH, titanium particles turn into gel form and precipitate in the solution. pH is one of the most important parameters for the aggregation and precipitation of NPs in aqueous solution [35–37]. The average hydrodynamic diameter of $TiO_2$ NPs depends on its zeta potential, and thus on pH

Table 1
Physico-chemicals characteristics of textile wastewater treatment plant

| Parameter | Raw wastewater | BTTWW |
|---|---|---|
| pH | 8.5 | 8.5 |
| COD (mg/L) | 1,050 | – |
| SCOD (mg/L) | 550 | 170 |
| $BOD_5$ (mg/L) | 165 | – |
| TSS (mg/L) | 390 | 65 |
| VSS (mg/L) | 245 | 50 |
| TKN (mg/L) | 55 | 5 |
| $NH_3$–N (mg/L) | 40 | 2 |
| Total hardness ($mgCaCO_3$/L) | 280 | 275 |
| Conductivity (μS/cm) | 9,900 | 7,200 |
| Chloride (mg/L) | 1,710 | – |
| Sulphate (mg/L) | 600 | – |

Note: BTTWW: Biologically treated textile wastewater.

values and solution ionic strength. Instability of particles, and thus aggregation, are generally expected at the point of zero charge pH value. Due to the repellence between negatively- or positively-charged $TiO_2$ NPs, the mean particle size of $TiO_2$ in aqueous solution decreases sharply at the higher or lower pH values, respectively [35,36]. As it can be seen from Fig. 1, the minimum $TiO_2$ concentration (28 μg/L) was observed at pH 7.0. Thus, the highest $TiO_2$ removal at pH 7.0 was attributed to the point of zero charge of $TiO_2$, which was pH 6.3 in this study. When the initial $TiO_2$ load varied from 05 to 10 g/L, residual $TiO_2$ concentration fluctuated between 28 and 68 μg/L independently of initial $TiO_2$ dose at pH 8.0.

The separation of commercial $TiO_2$ NPs from aqueous solution is difficult [21]. $TiO_2$ photocatalysts NPs are in crystalline form and super hydrophilic [38], whereas $TiO_2$ NPs prepared by sol–gel method are in amorphous phase and exhibit no hydrophilic effect [39]. Thus, it seems that sol–gel derivative $TiO_2$ NPs can be efficiently removed from textile wastewater simply by self-precipitation. Therefore, simple pH adjustment and subsequent precipitation may be an effective means of transferring 98% of sol–gel-originated $TiO_2$ NPs from sol–gel solution to sludge.

### 3.3. *$TiO_2$ NPs in textile wastewater and application of coagulation treatment*

One can figure out to deposit sol–gel $TiO_2$ NPs onto textiles before the washing–scouring steps. Hence, the concentration of $TiO_2$ NPs in segregated or mixed wastewater in textile industry can vary according to the sequence of applied processes. The sample was taken from the mixed water treating BTTWW effluent. After adding $TiO_2$ to BTTWW, its absorbance value increased in the range of 310–600 nm (Fig. 2).

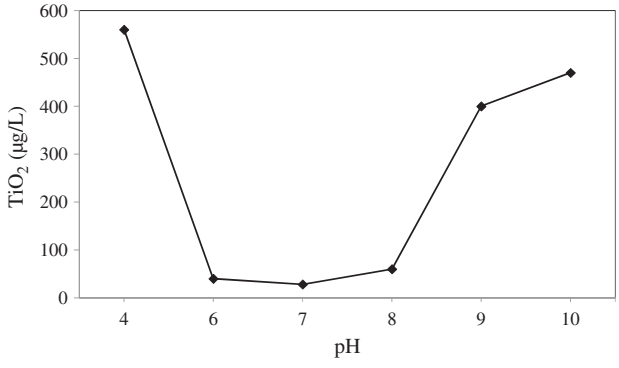


Fig. 1. Effect of pH on the precipitation of sol–gel based $TiO_2$ NPs in distilled water.

This was attributed to the light scattering and absorbance properties of $TiO_2$ NPs at 300–380 nm wavelengths [21,35,36]. Conversely, the absorbance value in the 310–230 nm range decreased in the coagulated wastewater, probably due to the adsorption of organics on the precipitated $TiO_2$ NPs too. The concentration of $TiO_2$ NPs in the BTTWW was found to be twice of distilled water (Fig. 3).

$TiO_2$ NPs were removed efficiently from the samples after both alum and Fe(II) coagulations (Table 2). The effect of coagulants doses on the removal of $TiO_2$ from distilled water was investigated at pH 8 using 0–300 mg/L coagulants. More than 98% of $TiO_2$ was removed from distilled water by the addition of 50 mg/L of alum and Fe(II). The optimum doses for

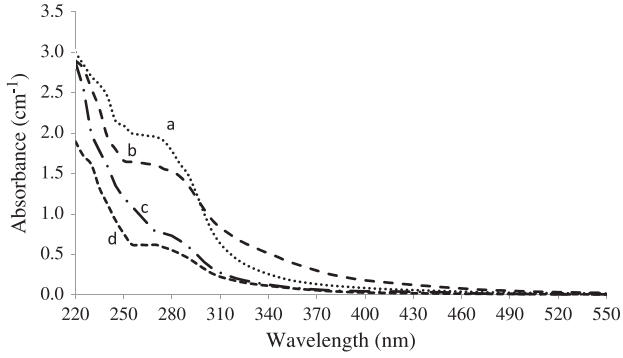


Fig. 2. UV–vis spectra of $TiO_2$ containing wastewaters before and after coagulation–flocculation treatment; (a), biologically treated textile wastewater (BTTWW), (b) BTTWW after mixing $TiO_2$ sol–gel, (c) 100 mg/L alum added treatment, (d) 100 mg/L Fe(II) added treatment.

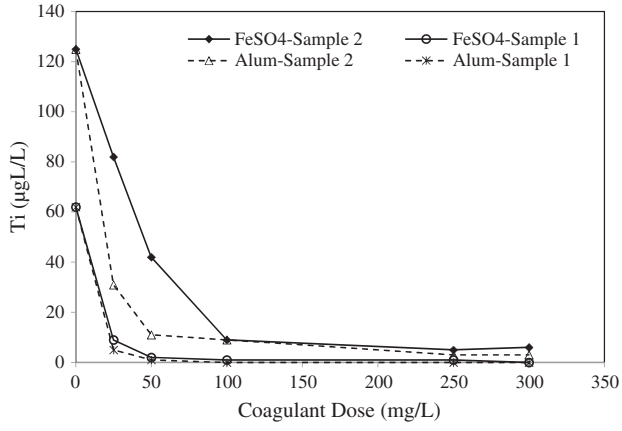


Fig. 3. Removal of residual $TiO_2$ after alum and $FeSO_4$ coagulation (Sample 1: $TiO_2$ containing distilled water; Sample 2: $TiO_2$ containing textile wastewater).

Table 2
Toxicity evolution of raw and coagulated textile wastewaters to *C. dubia (error bars are not displayed since standard deviations were found to be less than 5%)*

| Samples | Concentration (mg/L) | Wastewater concentration (%) | Immobilization (%) | | Residual coagulant (mg/L) |
|---|---|---|---|---|---|
| | | | 24 (h) | 48 (h) | |
| Raw textile wastewater | – | 100 | 100 | 100 | |
| | | 50 | 10 | 70 | – |
| $TiO_2$ sol–gel | – | 100 | 100 | 100 | |
| | | 50 | 100 | 100 | – |
| Raw textile wastewater spiked with $TiO_2$ sol–gel | – | 100 | 100 | 100 | |
| | | 50 | 10 | 70 | – |
| BTTWW | – | 100 | 80 | 100 | |
| | | 50 | 20 | 40 | – |
| BTTWW* | – | 100 | 60 | 90 | |
| | | 50 | 20 | 30 | – |
| Alum | 50 | 100 | 100 | 100 | 1.900 |
| | | 50 | 60 | 100 | 0.850 |
| | 100 | 100% | 100 | 100 | 0.261 |
| | | 50% | 0 | 0 | 0.130 |
| $FeSO_4$ | 50 | 100% | 100 | 100 | 0.24 |
| | | 50% | 10 | 50 | 0.012 |
| | 100 | 100% | 100 | 100 | 0.022 |
| | | 50% | 10 | 90 | 0.011 |

*Supernatant of biologically treated textile wastewater (BTWW) spiked with $TiO_2$ sol–gel, ultrasonicated for 20 min, precipitated for 60 min.

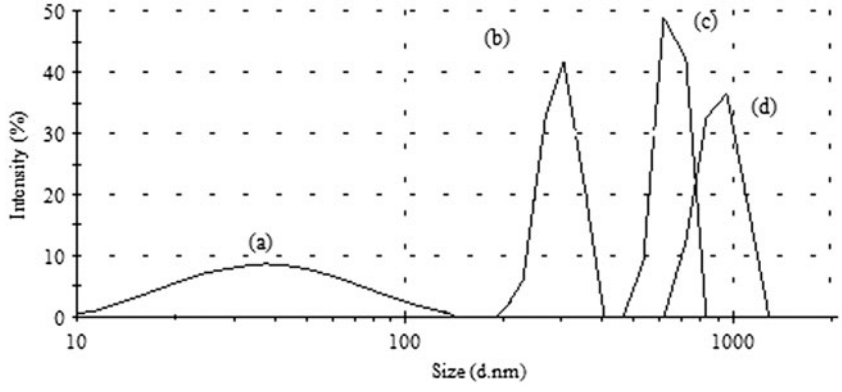


Fig. 4. Particle size distribution of $TiO_2$ containing solutions; (a) $TiO_2$ sol–gel, (b) after pH adjustment of BTTWW spiked with $TiO_2$ NPs to 8.0, (c) after alum treatment of BTTWW spiked with $TiO_2$ NPs, (d) after Fe(II) coagulation of BTTWW spiked with $TiO_2$ NPs.

the removal of $TiO_2$ from BTTWW were found to be 50 mg/L for alum and 100 mg/L for Fe(II).

Fig. 4 presents particle size distributions of $TiO_2$ NPs. Mean particle size distribution of sol–gel-based $TiO_2$ NPs was 30 nm. After adjusting pH 8.0, it increased from 30 to 450 nm. After coagulation, using alum and Fe(II), average particle size distributions were measured as 650 and 960 nm, respectively, due to the promoting effects of divalent ions on the aggregation of $TiO_2$ NPs [37].

### 3.4. Effect of $TiO_2$ NPs on activated sludge respiration rate

Raw wastewater taken from the influent of biological treatment plant in textile industry was spiked with appropriate amount of sol–gel $TiO_2$ and

then ultrasonicated for 20 min, later settled for 1 h. Residual $TiO_2$ in the raw textile wastewater was found to be 180 μg/L.

After introducing 1 g/L sol–gel $TiO_2$ spiked raw wastewater to 2 L lab-scale (F&DR) in parallel to $TiO_2$ non added blank reactor [32], the changes in soluble COD in both reactors were observed over 240 min reaction period. As shown in Fig. 6, insignificant fluctuations were observed in biological reactors. Levels of SCOD degradation in both blank and $TiO_2$ NPs reactors were almost same over 60 min, but over prolonged periods, remaining SCOD was approximately 5% less in the reactors containing $TiO_2$ NPs (Fig. 5). The results indicated that $TiO_2$ NPs has no inhibitory effect on SCOD removal. The OUR profiles of the activated sludge reactors are plotted in Fig. 6. The OUR concentrations in both reactors fluctuated, but the trend in OUR concentrations at 240 min was similar in both reactors. The concentration of residual $TiO_2$ was almost stable (20 μg/L) over prolonged time periods. Thus, residual $TiO_2$ decreased from 180 to 20 μg/L after biological treatment. As reported by Kiser et al. [16], the results of the present study showed that activated sludge flocs in the biological treatment system enhanced coagulation and adsorption of sol–gel-based $TiO_2$ NPs.

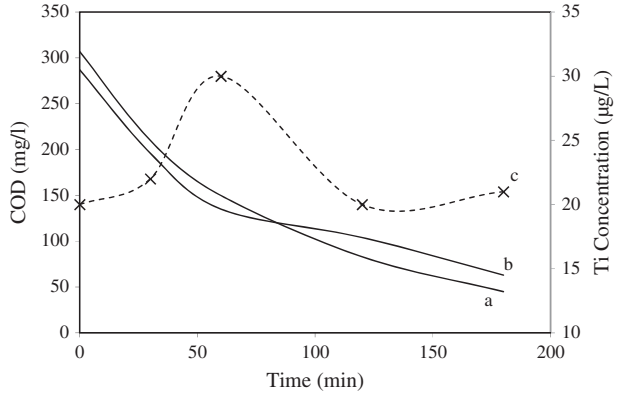


Fig. 5. Changes in the residual $TiO_2$ and soluble COD in the activated sludge batch reactors (a) SCOD degradation in the $TiO_2$ containing wastewater, (b) SCOD degradation in blank solution, (c) changes in residual $TiO_2$ in the $TiO_2$ spiked wastewater.

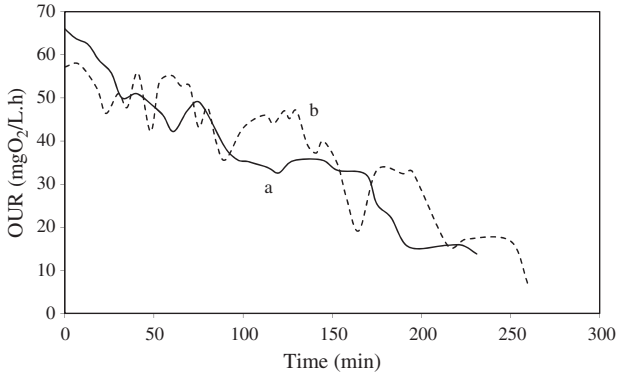


Fig. 6. The OUR profiles obtained for blank (a) and for 1 g/L $TiO_2$ NPs added activated sludge biological reactors.

### 3.5. *Ecotoxicity of $TiO_2$ NPs to* C. magna

Many researchers have reported that textile wastewaters were toxic even after biological and chemical treatments [1–3]. Similarly, in this study, raw and BTTWW samples were found to be 100% toxic to *C. dubia* (Table 2). Higher immobilization percentage indicates greater toxicity of a sample. High toxicity of raw wastewater tested at 50% dilution ratio, to *C. magna* was attributed to high ammonia and organic contents [1]. Low biodegradability (low BOD/COD ratio) is also an indicator to assess toxic this sample [1–3]. The lower toxicity of BTTWW sample is in a way of conformity of above-mentioned issues.

When the supernatant of $TiO_2$ sol–gel sample was tested and added to distilled water, it resulted in 100% toxic event at 50% dilution of testing volume. Low concentration (180 μg/L) of NPs did not exhibit additive toxicity to raw wastewater sample. While addition of $TiO_2$ NPs to BTTWW resulted in lesser toxicity with respect to no NPs added BTTWW sample in parallel to the decrease in residual $TiO_2$ NPs (20–30 μg/L). This may be due to: (i) $TiO_2$ may alter (coagulate organics and other NPs) the sample content [39] including removing ammonia content [40]; (ii) increased particle size while absorbance was influenced by the presence of NPs [13,35,36]; or (iii) simply ultrasonication perhaps altered the toxicity of NPs [13,35,36].

The toxicity effect of coagulation on the textile wastewater was studied in a previous studies [1,2], which reported that coagulated wastewaters may be more toxic, probably due to the residual coagulant concentration and its interaction with organic compounds in the textile wastewater. To evaluate the ecotoxicological effect of $TiO_2$ during chemical treatment, alum and Fe(II) coagulation experiments were carried out for the treatment of $TiO_2$ containing BTTWW. Higher Fe(II) dose increased toxicity from 50 to 90% in the BTTWW sample spiked with $TiO_2$ (50% diluted). Unlike Fe(II), increasing alum dose (from 50 to 100 mg/L) posed no toxicity in parallel to lower residual aluminum concentration in accordance with the literature [2].

## 4. Conclusions

In this study, $TiO_2$ NPs prepared by the sol–gel method was used to investigate the fate and transport pathways of $TiO_2$ NPs in the textile industry wastewater cycle. The main results of the study can be outlined as follows:

- The pH of the solution (or point of zero charge) was found to be important for the separation of sol–gel derivative $TiO_2$ NPs from aqueous solution.
- At pH 8, the 30 nm mean particle size distribution of sol–gel-based $TiO_2$ NPs enlarged after neutralization and coagulation. Any increase or decrease in the pH level caused the remaining $TiO_2$ concentration to increase in the supernatant.
- After 1 h self-precipitation of distilled water containing 1 g/L $TiO_2$, the residual $TiO_2$ concentration in the descended distilled water was 28 μg/L at pH 7.
- More than 98% of $TiO_2$ or similar NPs in textile wastewater may be removed in the activated sludge biological treatment process.
- $TiO_2$ NPs exhibited no toxicity or inhibitory effects on the activated sludge biological treatment process.
- Alum or Fe(II) coagulation (with or without biological pre-treatment) enables residual $TiO_2$ NPs to be entirely removed from textile wastewater containing $TiO_2$.
- The toxicity following coagulation experiments using Alum and Fe(II) fluctuated and coagulant dose–detoxification response was not observed. Furthermore, residual $TiO_2$ concentration was insignificant (8 μg/L) in the coagulated samples.
- Addition of 1 g/L $TiO_2$ did not change the toxicity level of biologically treated textile wastewater.
- Further studies should be undertaken, not only to identify toxic interactions of $TiO_2$ NPs in textile wastewater, but also to address aggregation and removal of NPs in the effluent and sludge of both biological and chemical treatments.

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