Integrated System for Recycling and Treatment of Hazardous Pharmaceutical Wastewater

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Research Article

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Posted Date: June 14th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-489302/v1

Integrated System for Recycling and Treatment of Hazardous Pharmaceutical Wastewater

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Abstract

This study aimed to investigate an integrated system that can deal with different pharmaceutical wastewater. Pharmaceutical wastewater was subjected to biological, chemical, and advanced oxidation according to its pollutant's nature. Wastewater with high Total Suspended Solids (TSS 480 mg/l) was subjected to a conventional chemical treatment process utilizing different coagulants. The best results obtained by using Calcium Oxide and Alum aided with Calcium Oxide where, the removal efficiency of COD was 46.8% and 51 %. Highly loaded pharmaceutical wastewater (COD 9700 mg/l, BOD/COD 0.16) had been subjected to Fenton oxidation, removal of COD reached 80.4%, and the ratio of BOD/COD is enhanced to 0.6. Photocatalysis by using different nanomaterials was applied to pharmaceutical wastewater containing 10 mg/l of phenols. Phenol is completely removed by using Mesoporous TiO_2 after 90 min irradiation and after 120 min in the case of TiO_2/P25 and TiO_2/UV 100 nanocomposites while it is removed by 40% in case of using Mesoporous TiO_2/Ta_2O_5. Effluent treated water from previous routes was subjected to biological treatment and followed with disinfection by using UV as post-treatment. Final COD was 40 and it matches with Egyptian practice code for water reuse in agriculture. Results showed also using treated wastewater in irrigation of Barley and Bean seeds achieved germination ratio up to 71% in Barely and 70% in Bean compared

with that irrigated with Nile water which reached 70% and 75%, while it was about 16.6% and 30% in case of irrigation with untreated wastewater.

Keywords: Wastewater Reuse, Chemical Treatment, AOPs, Nanocomposites, Plant growth percentage.

1. Introduction

The treatment and reuse of industrial wastewater have been investigated to not only preserve the natural water resources from polluted effluents but also to face water scarcity in arid and remote areas. Due to rapid urbanization and sharp population growth, the development in the medical field had dramatically increased the consumption of pharmaceuticals, the worldwide consumption of pharmaceutics was found to be about 15 g per capita/year while it goes as much as 50 to 150 g in the industrialized countries (Mylapilli and Reddy, 2019). The pollution rate and amount of wastewater generated during pharmaceutical production are depending on the used raw materials, manufacturing operations, and the variety of process technologies being used in the production process. Considering the wastewater resulting from pharmaceutical manufacturing activity, it has been classified as a “red category” as this wastewater characterized by; huge volume, complex and hazardous nature (Changotra et al., 2019a). There are a lot of different technologies both conventional and advanced have been applied for pharmaceutical wastewater treatment each of them depends on the nature of the existing contaminants. Biological treatment can be used directly and efficiently in wastewater that has a high BOD/COD ratio. On the other hand, pharmaceutical wastewater is typically toxic in nature for both aquatic and biological life, with high COD and low biodegradability, which makes their biological treatment difficult and inefficient (Ferrari et al., 2003; Malik et al., 2019). In general, chemical treatment can be efficiently used as pretreatment in most industrial wastewater which contains a high content of TSS (Changotra et al., 2019b; Nasr et al., 2019). Consequently, in such cases advanced oxidation processes (AOPs) are most acceptable for pharmaceutical wastewater treatment and it can enhance biodegradability as a pre-treatment method (Klavarioti et al., 2009). One type of AOPs is Fenton oxidation, other types are using of nanocomposites. The potential use of nanomaterials for treating pharmaceutical wastewater has been explored and reviewed by many researchers (Bagheri et al., 2016; Cincinelli et al., 2015). The biodegradability of pharmaceutical wastewater can be enhanced by using nanocomposites (Ferrari et al., 2003). Reuse of treated wastewater no longer an option but has become inevitable especially in countries which suffer from water shortage and it can be reused in agriculture if it achieves limits for irrigation reuse. (Nasr et al., 2019; Pedrero et al., 2020). The aim of this research is to make an integrated system for the treatment of toxic non-biodegradable pharmaceutical wastewater which has a high content of phenol. Additionally, studying the effect of using polluted and treated wastewater with a comparison of Nile water on germination ratio for bean and barely.

2. Material and methods

2.1. Pharmaceutical wastewater

The examined wastewater was collected from a pharmaceutics company located at 6th of October industrial city, west of Cairo, Egypt. The main activity of the investigated company is producing different pharmaceutics such as antibiotics, multivitamins, urology, chest, and cold medicines.

2.2. Wastewater Characterization

The wastewater composite samples were collected during the operation period of the company throughout the day working shifts. The collected wastewater samples transported and stored at 4 ºC to be analyzed according to APHA, 2017.

2.3. Wastewater treatment process

According to the nature of pollutants, the wastewater passed through three scenarios as shown in (Fig. 1). The first scenario is a direct biological treatment for the pharmaceutical wastewater in the case of the ratio BOD/COD ≥ 0.40 (Fawzy et al., 2018). The second scenario is using chemical coagulation followed by biological treatment in case of high TSS. The third scenario is carried out by using AOPs and nanomaterials followed by biological treatment, applied in case of the high content of Phenol and other toxic pollutants and subsequent BOD/COD ≤ 0.40.

2.3.1. Biological treatment

Biological treatment was carried out by using Plexiglas column capacity 2.5 L. The column was filled with aerated sludge containing different flora of microorganisms. The initially mixed liquor suspended solids (MLSS) were ranged from 3 to 4 g/l, sludge volume index (SVI) 150, and volatile matters 75%. Dissolved oxygen in column maintained at 2 - 3 mg/l by using an air pump.

2.3.2. Chemical treatment

Treatments using coagulants including alum, ferric chloride, lime, and ferrous sulfate these coagulants used separately and in combinations in different concentrations. A Jar test unit was used to obtain the optimal doses of each coagulant; a series of coagulants at their optimal operating conditions were obtained. The coagulants were flash mixed with raw wastewater at 250 rpm for 1-2 min. followed by flocculation at 25-30 rpm then the formed flocks allowed to be settled. COD and TSS were measured to indicate the efficiencies and to get the optimal coagulant with its operating conditions.

2.3.3. AOPs treatment

2.3.3.1. Treatment by Fenton

It was carried out by using H_2O_2 (250 g/l) and ferrous sulfate as catalysts. Fenton is applied in high COD and non-biodegradability. Determination of the optimum dose of ferrous sulfate and the optimum dose of H_2O_2 will be performed.

2.3.3.2. Preparation of mesoporous nano-TiO_2

Mesoporous-TiO_2 is prepared via a sol-gel process in the presence of F127 triblock copolymer as structure-directing agent. Molar ratios $Ti(OBu)_4/F127/C_2H_5OH/HCl/CH_3COOH$ = 1: 0.02: 50: 2.25: 3.75 and it employed to synthesize the desired mesoporous nanomaterials. Typically, 1.6 g of F127 was dissolved in 30 ml of ethanol with stirring for 60 min, and then 2.3 ml of CH_3COOH, 0.74 ml of 30% HCl and 3.5 ml of Titanium butoxide (TBOT) were added to the F127 solution under magnetic stirring for 30 min (Ismail and Bahnemann, 2011). The prepared mesophase is transferred into a 40% humidity chamber at 40 °C for 12 h to evaporate ethanol and form gel. The produced gel is aged at 65 °C for 24 h. Then, it will be calcined at 450 °C in an air for 4 h at a heating rate of 1 °C/min and a cooling rate of 2 °C/min to take off the F127 surfactant and to get mesoporous TiO_2 (Ismail and Bahnemann, 2011). To give information on the atomic packing, a high-resolution transmission electron microscopy (HRTEM) including Selected Area Electron Diffraction (SAED) was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1 k-CCD camera to obtain EEL spectra. After preparation of the mesoporous TiO_2 as well as the TiO_2-TaO as doped nano-oxide using the sol-gel method and it will use to treat the collected wastewater and will be compared with utilizing the commercially TiO_2-P25 and TiO_2-UV100.

2.4. Effect of treated effluent on germination and plant growth

Barely and Bean seeds bought from a market in Giza, Egypt were used for germination experiments. The seeds were irrigated with raw wastewater, treated effluent and compared with irrigation by Nile water. For Barley, 180 seeds were put equally in 15 dishes divided into three groups and then distributed randomly. For beans, 90 seeds were put equally in 15 dishes divided into three groups and then distributed randomly. Dishes were daily irrigated to keep the moisture at the required level for germination and growth. Every day, the ratio of germination and growth state was recorded using eq. (1) (Jacob et al., 2020). A similar experimental condition from light intensity, room temperature, and humidity were considered. The used light intensity was controlled to be 12 h light/ 12 h dark throughout the experimental period of eight growing days.

$$\text{Germination Percentage} = \frac{\text{Number of germinationseeds}}{\text{Total number of seeds kept for germination}} \times 100 \qquad (1)$$

2.4.1. Statistical analysis

The Least Significant Difference (L.S.D) will be used to study the germination and growing of irrigated seeds. One-way analysis of variance, null hypothesis $H_0: \mu_1 = \mu_2 = \mu_3$, Since H_0 is rejected, we run the LSD test seeking to identify which means caused the rejection of H_0.

$$\mathrm{LSD} = t_{05}\sqrt{\frac{2S_I^2}{n}} \qquad (2)$$

$$S_I^2 = \frac{\sum_{i=1}^{k}\sum_{j=1}^{n}\left(Y - \bar{Y}\right)^2}{N - k} \qquad (3)$$

If $|\bar{Y}_I - \bar{Y}_J| \geq \mathrm{LSD}$, H_0 is regected and there are a significant difference

S_i^2 or MSE can be obtained also from ANOVA table

where, N is the total number of observations, k is the number of treatments and n number of replicates is the same for each group.

3. Results and discussion

3.1. Characterization of wastewater

According to the obtained results of the analysis, pharmaceutical wastewater has a large variety of its organic load. Where a large variation of COD and BOD was observed (Fig. 2). This variation returns to the batch system for pharmaceutical production. Each pharmaceutical product is produced under specific operation conditions resulting in different organic pollutants, different amount of washing water and finally different concentration of organic loads and this is totally agreed with previous studies (Azizan et al., 2020). The route of the selected treatment method is essentially depending on the nature and concentration of these pollutants.

3.2. Wastewater treatment

3.2.1. Chemical treatment

Jar test (coagulation, flocculation, and sedimentation) was performed to find the effectiveness of each used chemical coagulant in COD removal. Raw wastewater had pH 7.5, TSS 418 mg/l, COD_t, 4700 mg/l and COD_s 2900 mg/l. In this study, it was found as shown in Table 1 that all used coagulants were efficient in COD_t removal where removal efficiency was 46.8%, 48.3%, and 51% in the case of CaO, Alum and CaO combined with alum and it is also removed a part of COD_s. However, reduced COD in the case of CaO with Alum was slightly more than of those in separated CaO but economic cost recommends that CaO is preferable. The residual COD of about 2500 mg/l will be acceptable for the following biological processes. These results are in strong agreement with those results obtained by Saleem, 2009, who used Alum, Ferric Chloride, and Ferrous Sulfate for treatment of pharmaceutical wastewater, COD 2800 mg/l, percentage removal reached 48.5%, 44.2%, and 32.1% (Saleem, 2007).

3.2.2. Treatment by Fenton Oxidation

The optimum dose of ferrous sulfate and H_2O_2 were 0.5 gm/100ml and 5 ml/100ml, and the reaction time was 15 min, the removal of COD reached 79.7% (Fig. 3a & b) and BOD/COD increased from 0.2 to 0.55. this results compatible with Zhang et al., 2019.

3.2.3. Phenol removal by Nanomaterials and Nano

The HRTEM and SAED images for prepared mesoporous TiO_2 and other commercial nanocomposites materials are indicted in Fig. (3). All nanocomposites have cubic crystal structure, but TiO_2/UV 100 nanocomposites have smallest particles size and TiO_2/P_{25} nanocomposites were the largest crystal size. A SAED image of reveals ring structure which indicate a poly crystalline structure with some agglomeration. Arcs of the ring in Fig. (4a), shows some preferred orientation (low crystallinity). On the other hand, diffraction pattern in Fig. (4b & c) show very sharp rings which indicate a very fine nanoparticles with poly crystalline structure (high crystallinity). On the contrary SAED of TiO_2/UV 100 nanocomposites reveals weak crystallinity due to very small nanoparticles (Fig. 4d). Almost all used nanomaterials were sufficient in removal of phenol, where the removal rate reached to 100% by using mesoporous nanoparticles. On the other hand, the removal efficiency was limited in the case of (TiO_2/Ta_2O_5) it reached only 36% (Fig. 5). The removal rate by mesoporous TiO_2 is much higher than those obtained by Mangrulkar et al., (2008), they used mesoporous MCM-41, around 44% removal was achieved, after 24 h. of irradiation. On the other hand, these results were totally agree with results of Wang et al., 2012, where, the removal rate reached 99% after 3 h irradiation time in batch treatment.

3.3. Germination and plant growth

The seeds starting to grow sharply until it reaches to the maximum germination ratio then it remains constant. The maximum germination ratio for both irrigated groups with the treated wastewater and Nile water was about 71% while it was about 16.6% in seeds which directly irrigated with untreated raw wastewater (Fig. 6). While the germination percentage for beans indicated that using raw water with a high concentration of phenol made the maximum germination ratio is about 30% and no ability of plants to continue growing up. On the other hand, irrigation with treated wastewater achieved a germination ratio up 70%, that agree with Springer and Mornhinweg, (2019), they reported that, after 7 days, the germination ratio of barley ,Winter malt 50.1b, seeds were 70.6% with greenhouse environment condition of 15 and 25 ˚C and artificial light to provide for a 13 h/day length.

3.4. Growth of barley and bean

The results showed that, the average plant lengths of barley were (5.82 cm, 1.45 cm, and 8.96 cm) with dry weight (0.38 g, 0.12 g, and 0.45 g) and the average plant lengths of beans were (1.02 cm, 0.6 cm, and 0.92 cm) with dry weight (7.59 g, 4.97 g, and 9.95 g) in case of Nile water, raw wastewater, and treated water. It was noticed that the seeds irrigated with the treated water showed an improvement in growing up comparing with those irrigated with raw wastewater and the Nile water by virtue of the redundancy of nutrients, nitrogen and phosphorus in treated water. Moriyama et al. (2020) mentioned that the presence of nitrogen and phosphorus in irrigation water increases the Oven-dried plant weight by about 100%.

3.5. Statistical analysis

The data obtained from the statistical analysis by using ANOVA and LSD show that both for barley and bean there was no significant difference between germination in case of Nile and treated water. On contrary, the results indicated that there is a significant difference between the germination in the case of Nile water at raw wastewater and this return to the toxic effect of phenol in irrigation water which damages the seed cells (Table 3).

Conclusion

This study introduced an integrated system that had the ability to deal with all different pollutants in pharmaceutical wastewater either they were toxic or not. Treatment route of pharmaceutical wastewater depends mainly on the nature of its pollutants. Conventional chemical treatment can be used as a pretreatment to remove apart of organic load, economic route including calcium oxide (CaO), coagulant, can achieve removal of near 50% of total COD for wastewater with high content of TSS. AOPs including Fenton oxidation, nanomaterials and nanocomposites are recommended in case of highly toxic or non-biodegradable wastewater with lower values of BOD/COD ratio to avoid higher treatment costs. This research provided integrated system for treatment of different kinds of pharmaceutical wastewater, more than 99% removal of COD, 100% removal of phenols and disinfected effluents that examined as a safe source of irrigation water in comparison with Nile water.

Supplementary Information: The online version does not contain supplementary material.

Author Contribution: Ibrahim Abdelfattah, Mohamed Abuarab, and Ehab. Mostafa analyzed the data and wrote the manuscript; Hamdy El-Awady act as consultant for the scientific information; Karim Aboelghait designed and supported the experiment; and Ashraf El-Shamy helped perform the analysis with constructive discussions.

Funding: This work was supported by own

Data Availability: The datasets used or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval: Ethical approval was obtained from the Water Pollution Research, Agricultural Engineering and Physical Chemistry Cairo University and National Research Centre

Consent to participate: All authors are informed and agree to the study.

Consent to publish: All the authors agree to publication in the journal.

Conflict of interest: The authors declare no competing interests.

Acknowledgement

The authors greatly thank The National Research Center for supporting this work through internal project No. 11070107.

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Figures

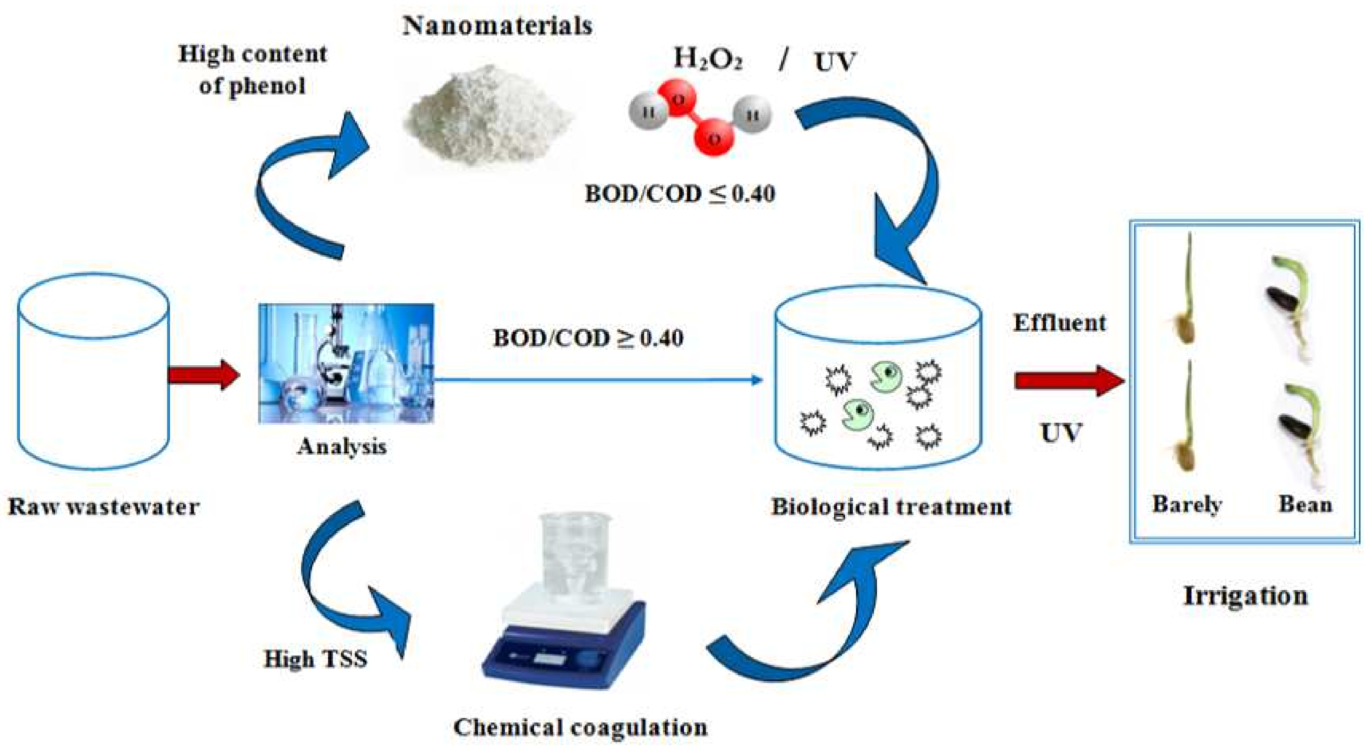

Figure 1

Schematic diagram of the suggested system

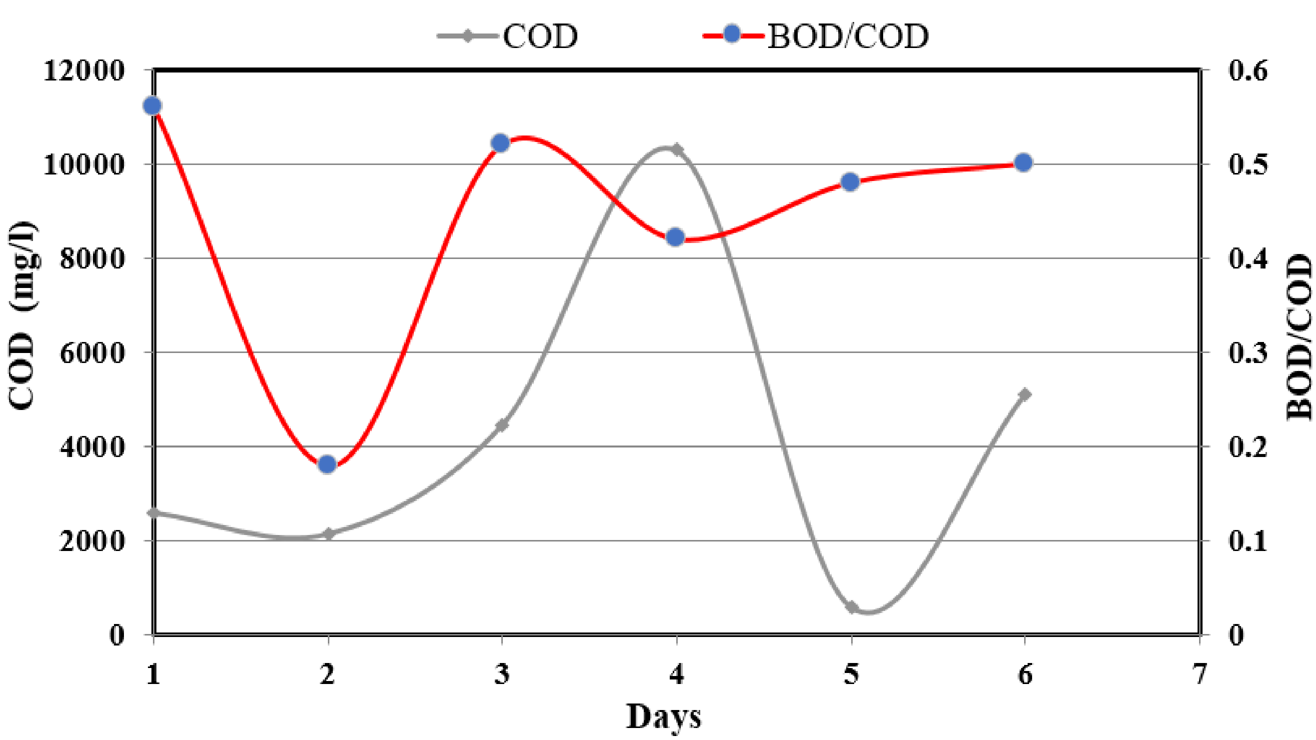

Figure 2

Variation of COD for raw wastewater.

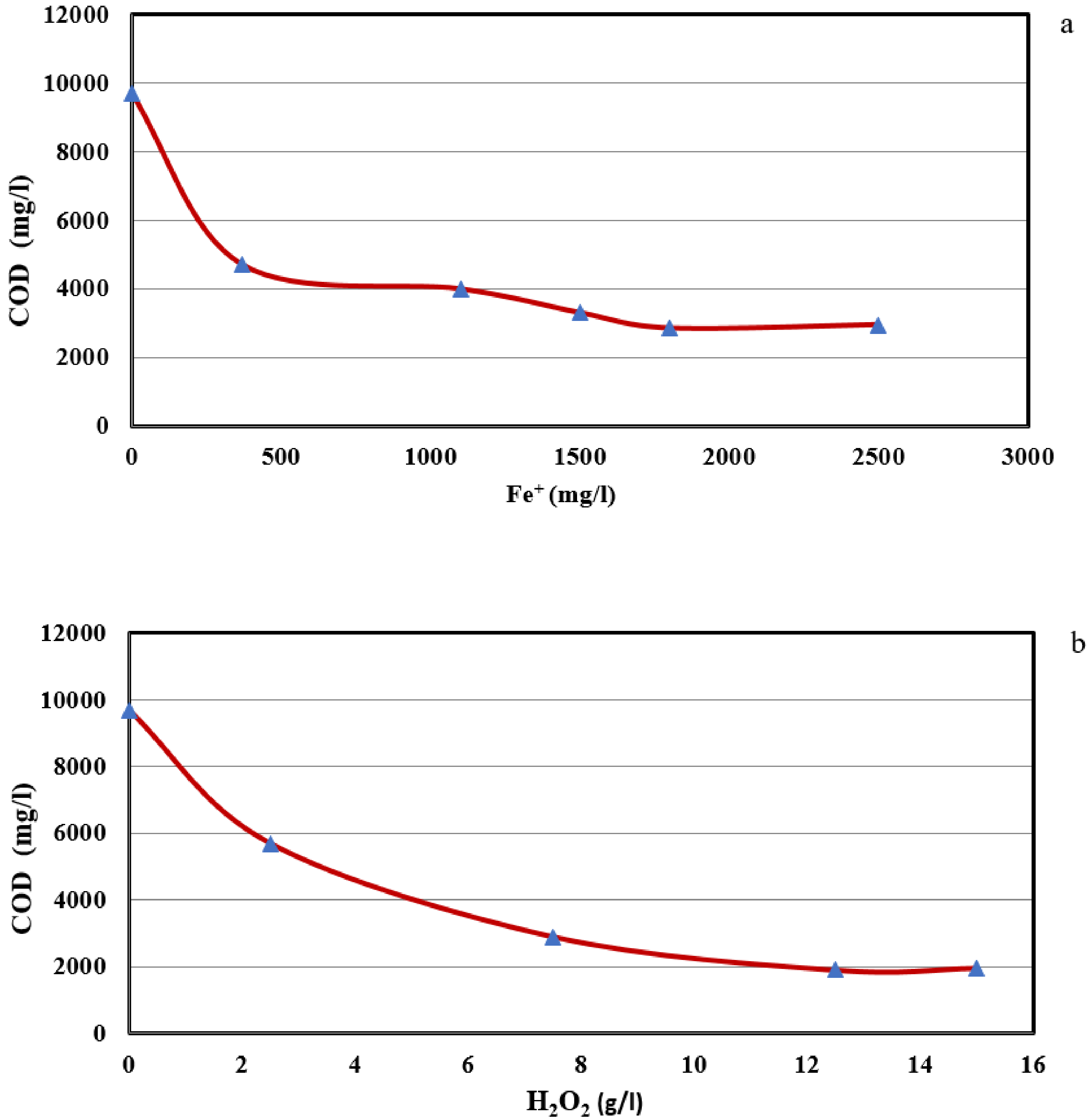

Figure 3

Variation of COD for raw wastewater.

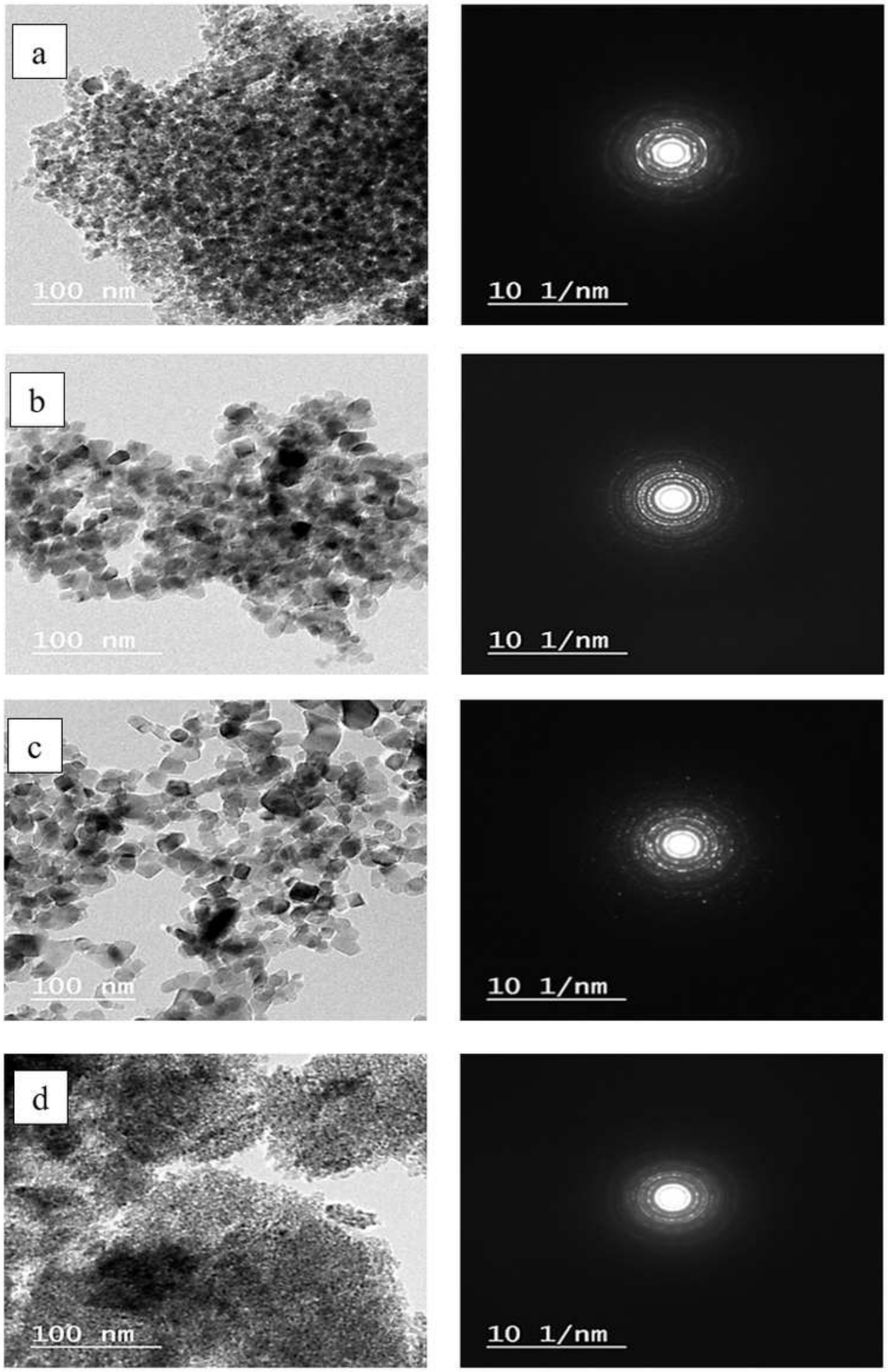

Figure 4

HRTEM and SAED images of a) Mesoporous TiO2/Ta2O5 nanocomposites, b) Mesoporous TiO2, c) TiO2/P25 nanocomposites, and d) TiO2/UV 100 nanocomposites.

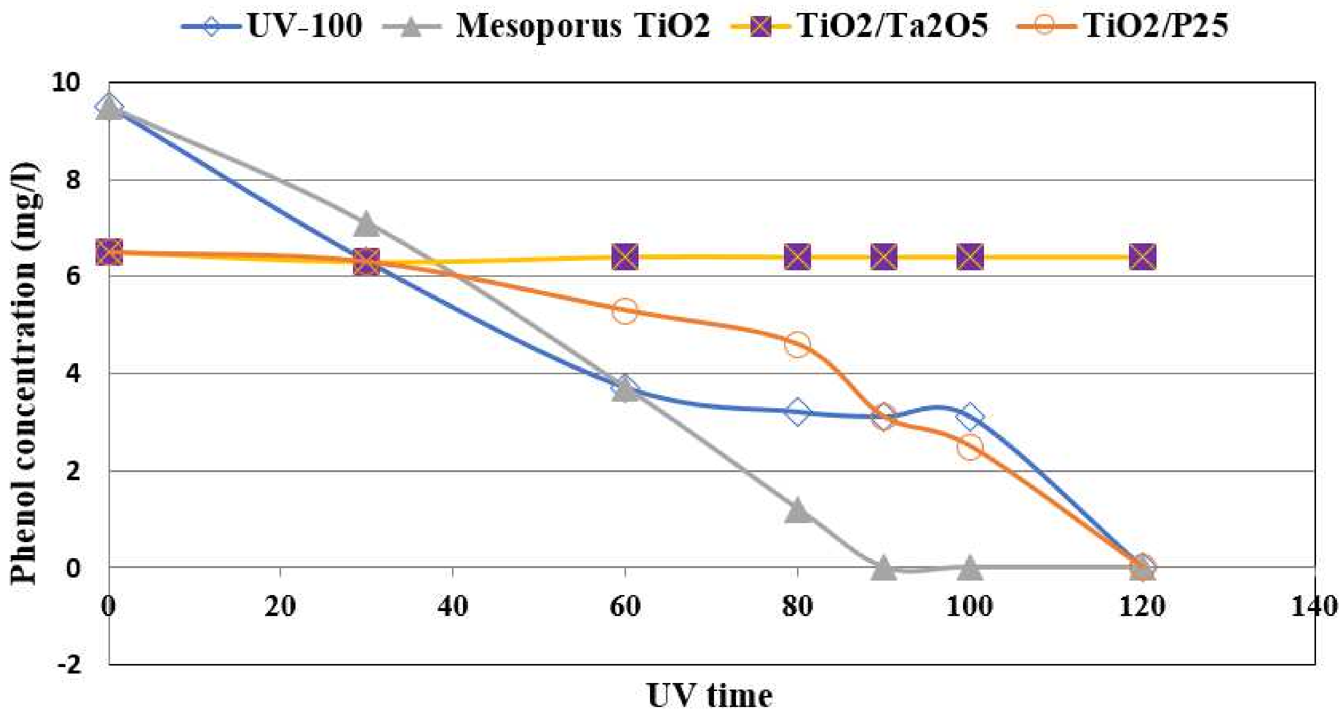

Figure 5

Phenol removal by different nanomaterials

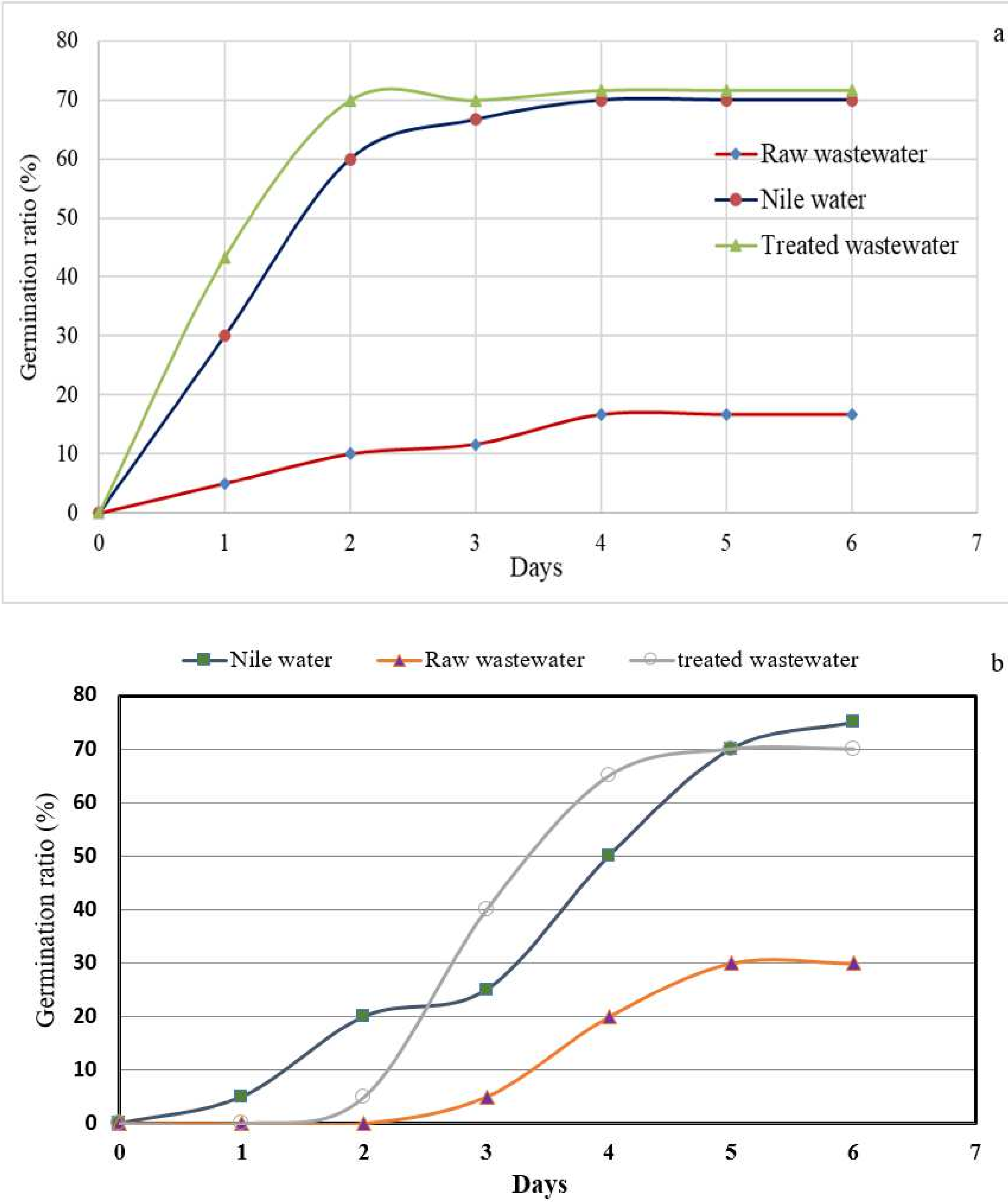

Figure 6

Daily germination percentage for a) barely and b) bean.