



Integrated system for recycling and treatment of hazardous pharmaceutical wastewater

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Received: 31 July 2021 / Revised: 4 November 2021 / Accepted: 1 May 2022 / Published online: 20 June 2022
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Abstract

This study aimed to investigate an integrated system that can deal with different pharmaceutical wastewaters. 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 were obtained by using calcium oxide and alum added 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, the 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 TiO₂ after 90-min irradiation and after 120 min in the case of TiO₂/P25 and TiO₂/UV 100 nanocomposites, while it is removed by 40% in case of using mesoporous TiO₂/Ta₂O₅. Effluent-treated water from previous routes was subjected to biological treatment and followed with disinfection by using UV as post-treatment. The final COD was 40, and it matches with the Egyptian practice code for water reuse in agriculture (ECP 501 in Egyptian code of practice for the use of treated municipal wastewater for agricultural purposes. The ministry of Housing Utilities and Urban Communities., n.d. No title, 2015). 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 (Jeong et al. in Water (Switzerland). <https://doi.org/10.3390/w8040169>, 2016).

Keywords Wastewater reuse · Chemical treatment · AOPs · Nanocomposites · Plant growth percentage

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, and the worldwide consumption of pharmaceuticals was found to be about 15 g per capita/year, while it goes as much as 50–150 g in the industrialized countries (Mylapilli and Reddy 2019; World Health Organization 2006).

To increase membrane hydrophilicity and decrease membrane fouling in pharmaceutical wastewater treatment, we construct polypropylene membrane by embedding carboxylated (–COOH) and polyethylene glycol-functionalized nanodiamond. The antifouling qualities of the membrane with –COOH and polyethylene glycol-functionalized nanodiamond were superior to that of the clean polypropylene membrane in the experimental procedures (Frag et al. 2016; Eessaa et al. 2018; Shahab et al. 2021). Nanoscale-sorbent materials offer distinct properties such as high absorption, large surface area, environmentally safe manufacture and a strong affinity for organic and

Editorial responsibility: Samareh Mirkia.

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inorganic compounds. This study lays the groundwork for future research into many of the present nanoscale materials for the remediation of pharma industrial wastewaters (Shehata et al. 2019; Aguilar-Perez et al. 2020).

The environmentally friendly manufacture of silver nanoparticles was from waste safflower (*Carthamus tinctorius* L.) aqueous extract and their antibacterial activity against *Staphylococcus aureus* (gram-positive) and *Pseudomonas fluorescens* (gram-negative). From the lowest dose tested (0.9 g/mL), nanoparticles suppressed the development of both species of bacteria. The as-synthesized silver nanoparticles were homogenous and spherical, with an average diameter of 8.67–4.7 nm, as determined by TEM and validated by SEM. The unique crystallinity of silver nanoparticles was revealed by electron diffraction and TEM investigations (Rodríguez-Felix et al. 2021).

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 is characterized by huge volume, complex and hazardous nature (Changotra et al. 2019). There are a lot of different technologies; both conventional and advanced technologies 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 for both aquatic life 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 that contains a high content of TSS (Changotra et al. 2019; Nasr et al. 2019). Consequently, in such cases advanced oxidation processes (AOPs) are most acceptable for pharmaceutical wastewater treatment, and they can enhance biodegradability as a pretreatment method (Klavarioti et al. 2009). One type of AOPs is Fenton oxidation; other types use nanocomposites. The potential use of nanomaterials for treating pharmaceutical wastewater has been explored and reviewed by many researchers (Meng-hui et al. 2019; 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 is no longer an option but has become inevitable, especially in countries that suffer from water shortage, and it can be reused in agriculture if it achieves limitation for irrigation reuse (Nasr et al. 2019).

This research aims to make an integrated system for the treatment of toxic non-biodegradable pharmaceutical wastewater, which has a high content of phenol. Additionally, we study the effect of using polluted and treated wastewater with a comparison of Nile water on germination ratio for bean and barely.

Materials and methods

Pharmaceutical wastewater

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

Wastewater characterization

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

Wastewater treatment process

According to the nature of pollutants, the wastewater was passed through three scenarios as shown in Fig. 1. The first scenario is a direct biological treatment for 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, which is applied in case of the high content of phenol and other toxic pollutants and subsequent BOD/COD ≤ 0.40 .

Biological treatment

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

Chemical treatment

Treatments using coagulants include alum, ferric chloride, lime, and ferrous sulfate that are used separately and

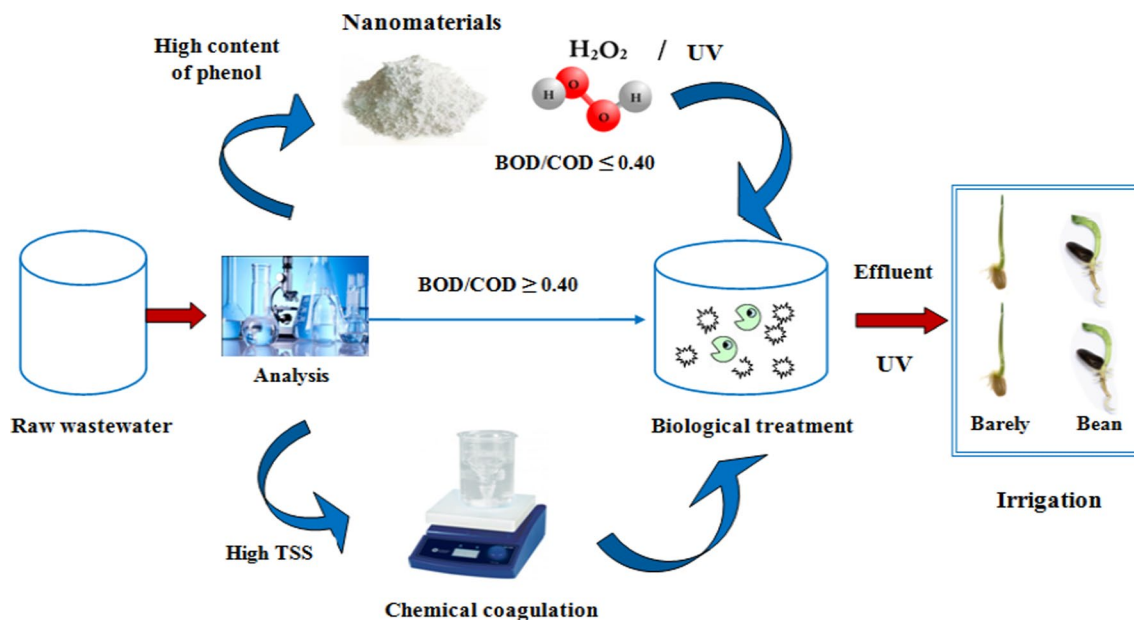


Fig. 1 Schematic diagram of the suggested system

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 were allowed to be settled. COD and TSS were measured to indicate the efficiencies and to get the optimal coagulant with its operating conditions (El-Shamy et al. 2017a, b, 2018).

AOPs treatment

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.

Preparation of mesoporous nano- TiO_2 Mesoporous TiO_2 is prepared via a sol–gel process in the presence of an F127 triblock copolymer as a structure-directing agent. Molar ratios $\text{Ti}(\text{O}i\text{Bu})_4/\text{F127}/\text{C}_2\text{H}_5\text{OH}/\text{HCl}/\text{CH}_3\text{COOH} = 1:0.02:50:2.25:3.75$, 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 the 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 (Japan) 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, it will be used to treat the collected wastewater and will be compared by utilizing the commercially TiO_2 -P25 and TiO_2 -UV100.

Effect of treated effluent on germination and plant growth

Barely and bean seeds bought from a market in Giza, Egypt, was 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 to growth state is recorded using Eq. (1) (Jacob et al. 2020). A similar experimental condition from light intensity, room temperature, and humidity was considered. The used light intensity was controlled to



be 12-h light/ 12-h dark throughout the experimental period of eight growing days.

Germination Percentage

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

Statistical analysis

The least significant difference (L.S.D) will be used to study the germination and growing of irrigated seeds. In 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 .

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

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

If $|\bar{Y}_i - \bar{Y}_j| \geq \text{LSD}$, H_0 is rejected and there is a significant difference

S_I^2 or MSE can be obtained also from the ANOVA table (3)

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

Results and discussion

Characterization of wastewater

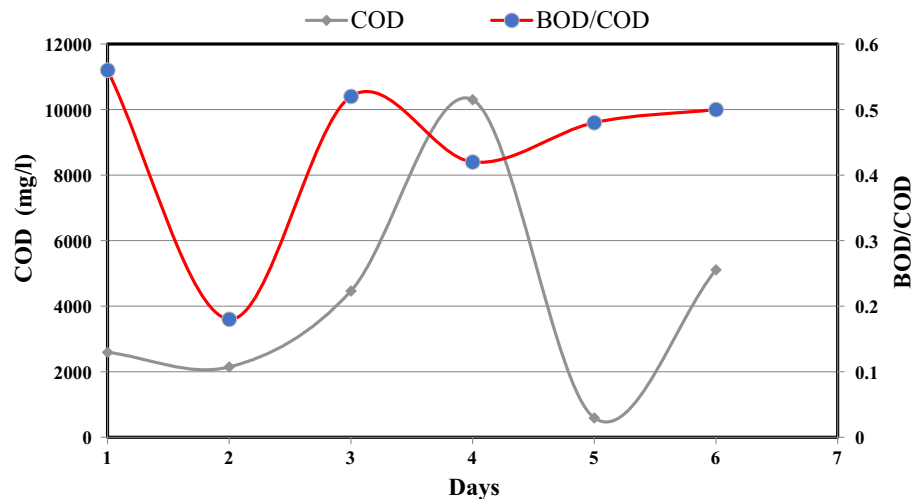
According to the obtained results of the analysis, pharmaceutical wastewater has a large variety of its organic load, where a large variation of COD and BOD was observed (Fig. 2). This variation returns to the batch system for pharmaceutical production. Each pharmaceutical product is produced under specific operating conditions, resulting in different organic pollutants, different amounts of washing water, and finally, different concentrations of organic loads, and this is 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.

Wastewater treatment

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_p , 4700 mg/L, and COD_s , 2900 mg/L. In this study, it was found in Table 1 that all used coagulants were efficient in COD_i 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 as a part of COD_s . However, reduced COD in the case of CaO with alum was slightly more than 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. Using alum, ferric chloride, and ferrous sulfate to treat pharmaceutical wastewater containing COD

Fig. 2 Variation of COD for raw wastewater



2800 mg/L, the percentage removal was 48.5%, 44.2%, and 32.1%, respectively (Saleem 2007).

Treatment by Fenton oxidation

The optimum dose of ferrous sulfate and H_2O_2 was 0.5 g/100 mL and 5 mL/100 mL, and the reaction time was 15 min, the removal of COD reached 79.7% (Fig. 3a, b) and

Table 1 COD removal with different coagulants

Coagulant	Dose (g/L)	pH	SV (ml/L)	COD removal (%)	Cost (\$/m ³)
CaO	0.6	11	75	42.5	0.27
	0.15	8.5	75	46.8	0.07
FeSO ₄	0.6	6	–	44.6	–
CaO/FeSO ₄	0.15/0.6	7	116	44.6	–
FeCl ₃	0.6	4.5	115	46.6	0.36
CaO/FeCl ₃	0.15/0.25	7.5	–	45.7	0.22
Alum 50%	0.60	5.5	135	48.3	0.16
CaO/Alum 50%	0.15/0.60	5	135	51.0	0.23

BOD/COD increased from 0.2 to 0.55. These results are compatible with Zhang et al. (2019).

Phenol removal by nanomaterials and nano

The HRTEM and SAED images for prepared mesoporous TiO₂ and other commercial nanocomposites materials are indicated in Fig. 3. All nanocomposites have a cubic crystal structure, but TiO₂/UV 100 nanocomposites have the smallest particles size and TiO₂/P₂₅ nanocomposites were the largest crystal size. A SAED image reveals a ring structure that indicates a polycrystalline structure with some agglomeration. The arcs of the ring in Fig. 4a show some preferred orientation (low crystallinity). On the other hand, the diffraction pattern in Fig. 4b and c shows very sharp rings, which indicate very fine nanoparticles with polycrystalline structure (high crystallinity). On the contrary, SAED of TiO₂/UV 100 nanocomposites reveals weak crystallinity due to very small nanoparticles (Fig. 4d). Almost all used nanomaterials were sufficient in the removal of phenol, where the removal rate reached 100% by using mesoporous nanoparticles. On the other hand, the removal efficiency was limited in the case of (TiO₂/Ta₂O₅); it reached only 36% (Fig. 5). The removal rate by mesoporous TiO₂ is much higher than those obtained

Fig. 3 **a** Detection of optimum dose of ferrous sulfate, **b** detection of optimum dose H_2O_2

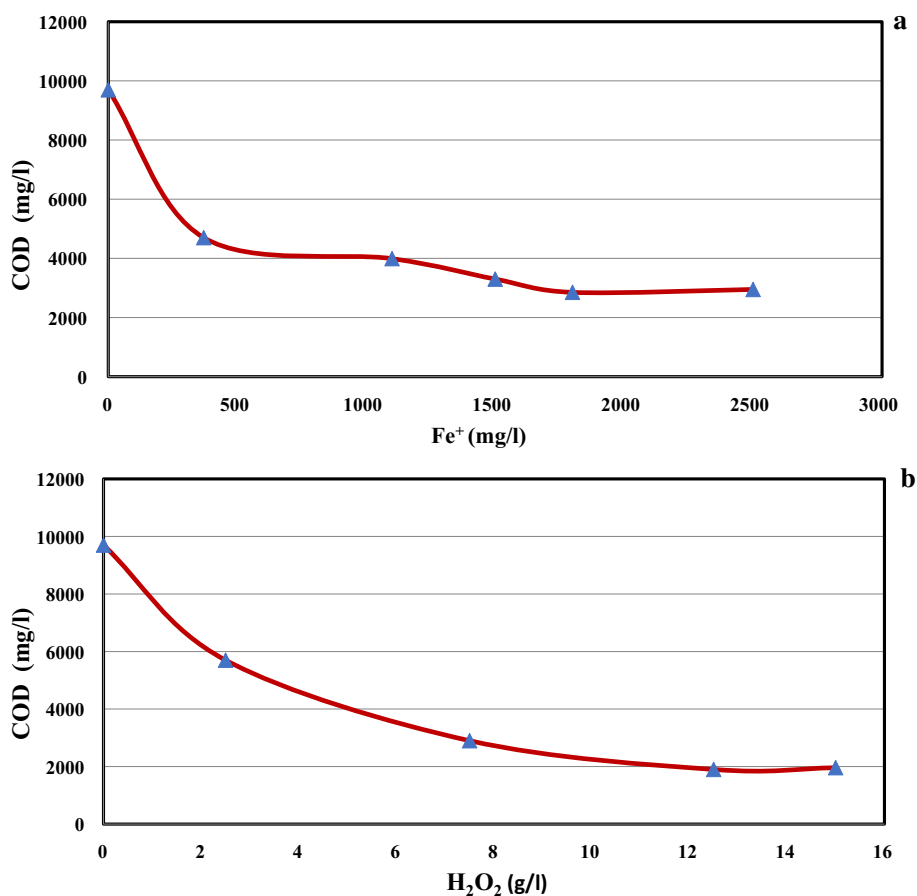
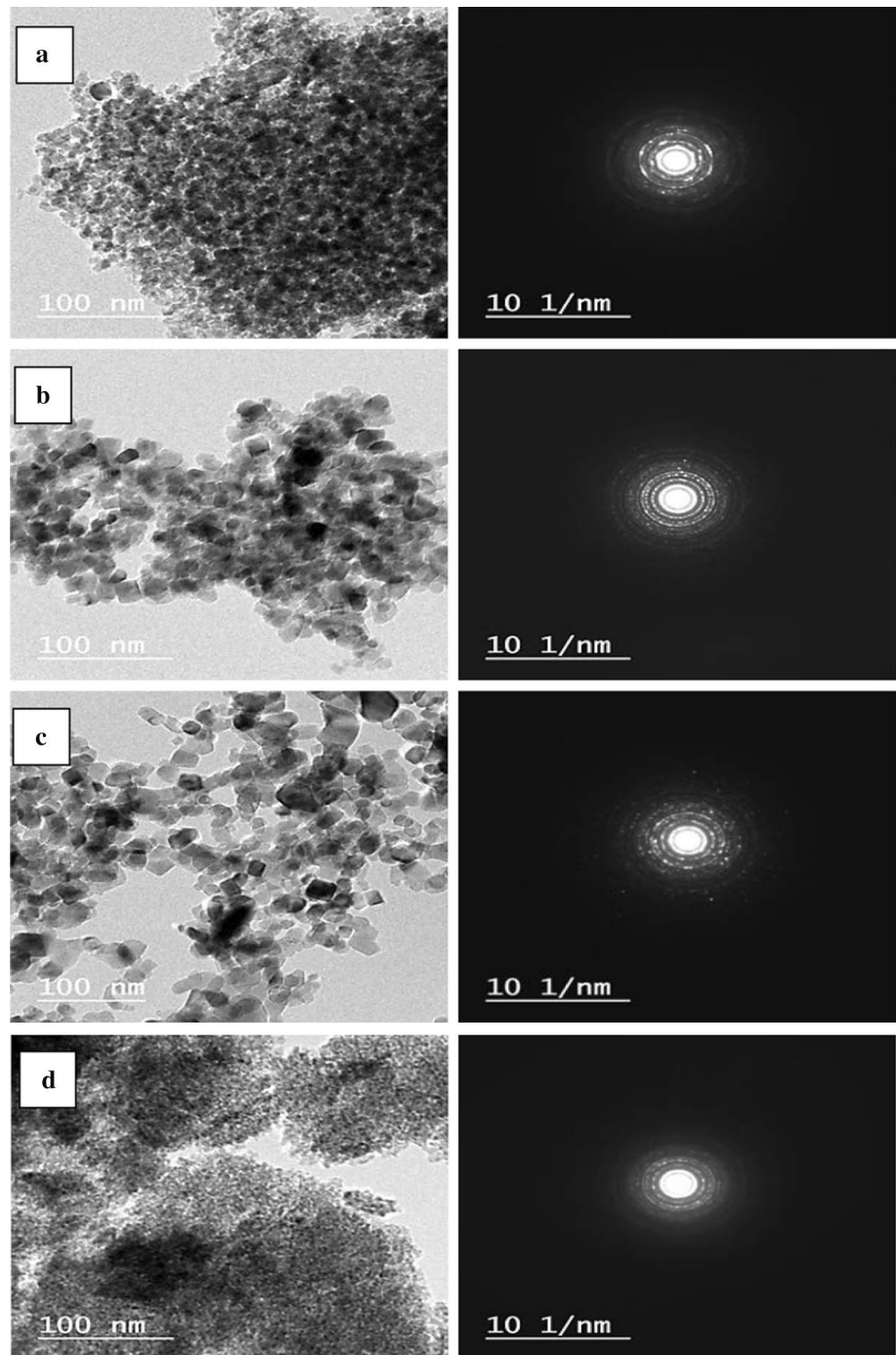


Fig. 4 HRTEM and SAED images of **a** mesoporous $\text{TiO}_2/\text{Ta}_2\text{O}_5$ nanocomposites, **b** mesoporous TiO_2 , **c** $\text{TiO}_2/\text{P}_{25}$ nanocomposites, and **d** $\text{TiO}_2/\text{UV 100}$ nanocomposites



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 agreed with the results of Wang et al. (2012), where the removal rate reached 99% after 3-h irradiation time in batch treatment.

Germination and plant growth

The seeds start to grow sharply until it reaches 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



Fig. 5 Phenol removal by different nanomaterials

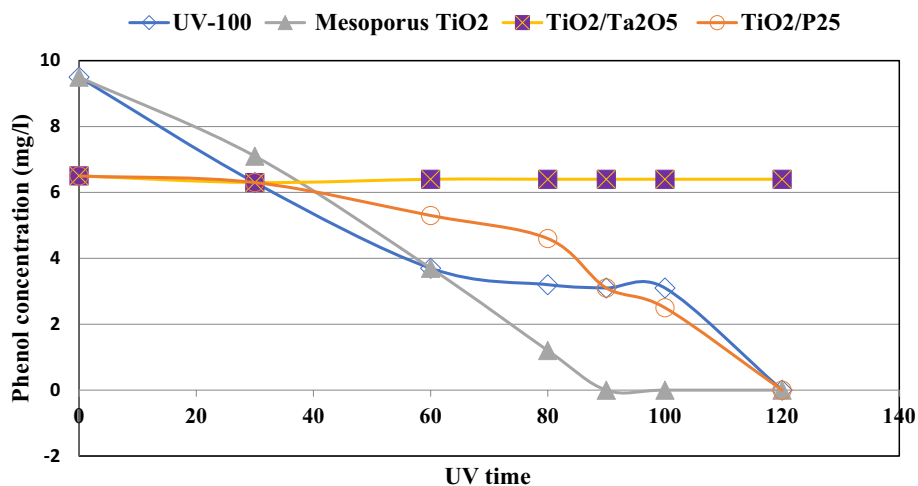
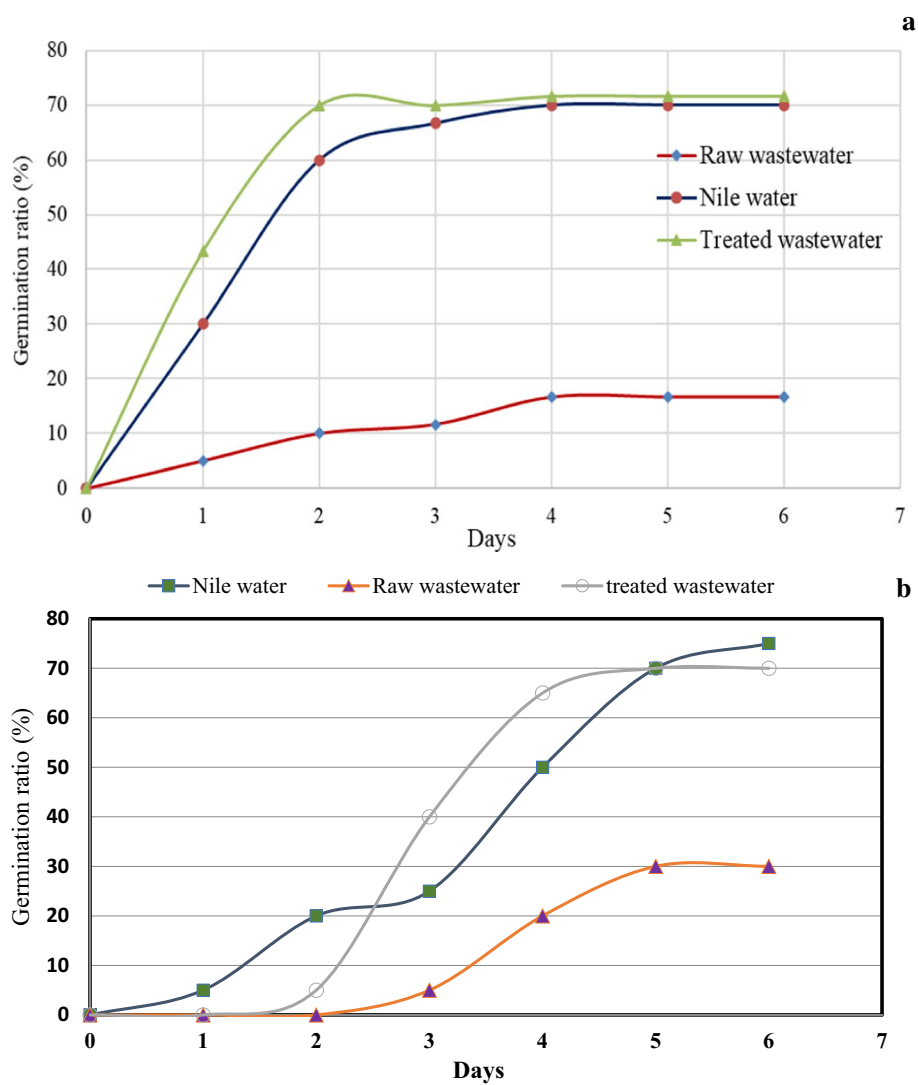


Fig. 6 Daily germination percentage for **a** barely and **b** bean



high concentration of phenol made the maximum germination ratio which is about 30%, no ability of plants continues to grow up. On the other hand, irrigation with treated wastewater achieved a germination ratio up 70%, which agree with Springer and Mornhinweg (2019); they reported that, after 7 days, the germination ratio of barley, winter malt 50.1b, and seeds was 70.6% with greenhouse environment condition of 15 and 25°C and artificial light to provide for a 13-h/day length (Table 2).

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 of 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 of 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 compared with those irrigated with raw wastewater and the Nile water under 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%.

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 the case of Nile and treated water. On the contrary, the results indicated that there is a significant difference between the germination in the case of Nile water at raw wastewater and

this returns to the toxic effect of phenol in irrigation water, which damages the seed cells (Table 3).

Conclusion

This study introduced an integrated system that could deal with all different pollutants in pharmaceutical wastewater either they were toxic or not. The 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 includes calcium oxide (CaO), coagulant, that can achieve the 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 an integrated system for the treatment of different kinds of pharmaceutical wastewater, more than 99% removal of COD, 100% removal of phenols,

Table 3 Statistical analysis by using ANOVA and LSD

Plant type	Source of variation	S.S.	D.F.	Mean square	F
Bean	Treatments	0.48	2	0.24	4.8
	Error	0.61	12	0.05	
	Total	1.097	14		
	L.S.D.	0.30			
Barley	Treatments	155.06	2	77.35	47.85
	Error	19.45	12	1.62	
	Total	174.51	14		
	L.S.D.	1.72			

Table 2 Water quality of Nile, raw and after biological treatment and limitations for wastewater reuse in agriculture

Parameter	Nile water	Raw water*	Treated water**	ECP 501/2015***	WHO/USA****
pH	6.8	6.6	7.6	–	6–9
TSS	6	133–480	5	Food crops ≤ 15 Processed food ≤ 30	5
COD	10	670–9700	40	–	–
BOD	<5	280–1090	16	Food crops ≤ 15 Processed food ≤ 30	Food crops ≤ 10 Processed food ≤ 30
TKN	4	25–75	13	–	–
Phenol	ND	0.05–9.5	ND	≤ 0.05	–
Lead	≤ 0.001	≤ 0.001	≤ 0.001	1***	–
Copper	≤ 0.01	≤ 0.01	≤ 0.01	1.5 (soil content)	–
<i>Escherichia coli</i>	–	–	10–38	Food crops ≤ 20 Processed food ≤ 100	Food crops ND Processed food ≤ 200

*Rang values of five samples

**Final effluent after biological treatment

***ECP 501 (2015) and for lead and copper it depends on the content in soil

****Jeong et al. (2016), World Health Organization (2006)



and disinfected effluents that were examined as a safe source of irrigation water in comparison with Nile water.

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

Author contributions IA, MA and EM analyzed the data and wrote the manuscript; HE-A acts as a consultant for the scientific information; KA designed and supported the experiment, and AE-S helped perform the analysis with constructive discussions.

Funding Open access funding provided by The Science, Technology & Innovation Funding Authority (STDF) in cooperation with The Egyptian Knowledge Bank (EKB). 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

Conflict of interest The authors declare no competing interests.

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.

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