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Irrigation water quality assessment and a new approach to its treatment using photocatalytic technique: Case study Yaakob village, SW Sohag, Egypt

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Abstract

Agricultural and human effluents into water resources have an adverse effect on water quality. This work investigates the current status of irrigation water quality and presents new approaches for organic residuals and bacteria contaminants removal from water in Yaakob village SW Sohag Governorate, Egypt. The studied physico-chemical parameters of water samples indicate the suitability of water for irrigation, except its considerable high content of Chemical Oxygen Demand (COD) and bacteria. The GC-MS results indicate the presence of herbicide (Pyridine carboxylic acid) and fungicide (3,4-dihydrothienyl-[3,4,B]-5-carboxythiophene) residuals in the studied samples. The application of advanced photocatalytic technique using TiO_2 doped with nitrogen and fluorine in presence of UV-Visible light for the removal of organics and bacteria from water has been evaluated. It has shown good efficiency towards the removal of about 86.9% and 100% of the dissolved organics and bacteria, respectively. The mechanism of photocatalytic degradation of organics and bacteria has been illustrated

1. Introduction

The main challenge facing Egypt is the quantity and quality of water in the recent years. Since 2005, Egypt is classified as water scarce country as well as discharging domestic and industrial effluents and irrigation drainage water into the River Nile led to water quality degradation [1]. The pollution of water resources has reverse impact on their surroundings environment and to great extent on human health [2, 3]. The most popular pollutants of water are heavy metals [3] and biological pathogens [4]. In the period from 1952 to1989 the Egyptian farmers have been used about $65*10^7$ Kg of about 200 different types of pesticides [5]. The pollution of irrigation waters by organic compounds and bacteria and their potentially toxic effects on aquatic life did not have any considerable focus in Egypt. Toxic levels of Phthalate esters and PAHs in the soil of Sohag Governorate, Egypt are recorded [6]. The presence of bacterial indicators in water can cause many diseases [7] and also accelerate the transport of water pollutants [8].

The irrigation water must have appropriate salt concentrations and free of chemical and biological pollutants. High salts in irrigation water are reducing plant growth and affecting the structure, aeration, permeability and texture of soil [9, 10]. The aridity of the study area could raise the irrigation water impact on soil through the concentrate of minerals in soil by the evaporation process [11]. The salt water increases the osmotic pressure in soil solution and accordingly restriction of water uptake by plants [9, 12].

Heterogeneous photocatalytic oxidation is considered one of promising and green techniques for water treatment as well as it has been the subject of a wide range of researches [13 - 16]. Much attention has been paid to the photocatalytic oxidation of organics with titanium dioxide (TiO_2) particles due to its relatively low price, its chemical stability and non-toxicity [17, 18]. Photocatalytic degradation of methylene blue dye using TiO_2 has been studied. Treatment of TiO_2 with electron beam has improved the photocatalytic activity of titania and increased the rate of methylene blue degradation [19]. Solar light induced degradation of a dye as an organic pollutant has been investigated using TiO_2 as phocatalyst [20]. The photocatalytic degradation of Methyl orange has been studied using dynamic solar photoreactor in presence of TiO_2 photocatalyst [21]

The present work aims at the evaluation of the current status of the irrigation water in Yaakob village SW Sohag Governorate, Egypt as well as studying the efficiency and effectiveness of a photocatalytic technique using N, F doped TiO_2 as photocatalyst in presence of UV-visible irradiation in the removal of microbial and dissolved organics from irrigation water.

2. Materials and methods

2.1. *Study area*

Yaakoob is one of the SW villages of Sohag Governorate in Upper Egypt, between longitudes 31° 52` 30`` and 31° 53` 00`` E and latitudes 26° 15` 30`` and 26° 14` 30`` N (Figure. 1). It's mainly residential and agricultural area. The village doesn't contain sewer system and so the main way to get rid of sewage is pit latrine. The farmers apply different verities of chemical fertilizers and pesticides. Many people in this village suffer from renal failure, cancer and hepatitis.

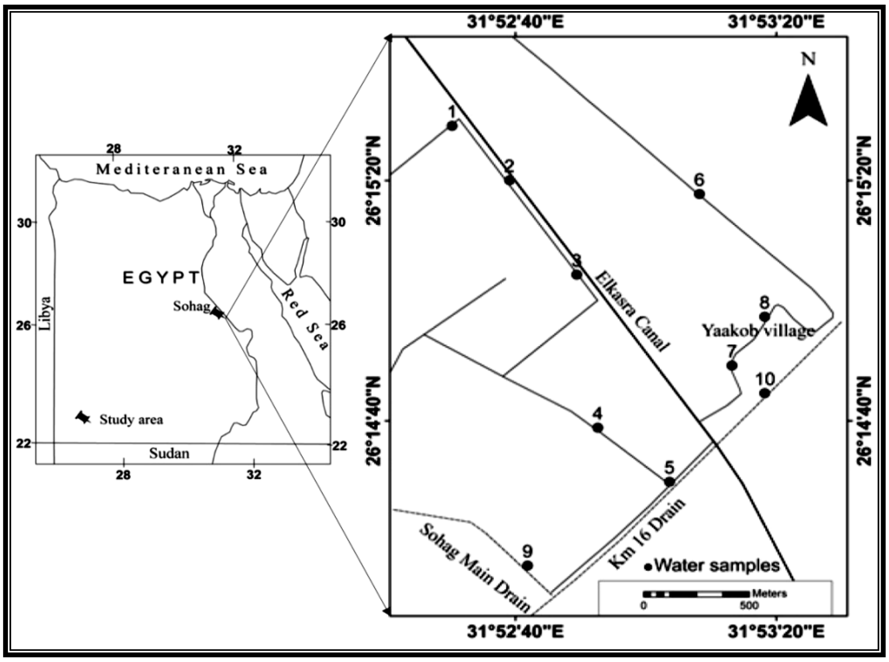

Figure 1: Location map of the study area and sampling sites.

2.2. *Sampling and analysis*

Expert sampling techniques, high purity chemicals and clean apparatuses and glassware were used during all stages of sample collection, handling and analysis to prevent contamination.

For assessment of irrigation water quality, eight samples from canals (1-8) and 2 samples from drains (9 and 10) were collected and analyzed for various chemical parameters according to APHA [22]. Temperature (T), pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured in situ by using portable HANNA combined electrode (HI 991301). In the laboratory the samples were filtered through 0.45 μm filter paper to remove suspended materials. Sodium (Na^+) and potassium (K^+) were determined by flame photometer. Total hardness (TH) as $CaCO_3$, calcium (Ca^{2+}), magnesium (Mg^{2+}), carbonate $(CO_3)^{2-}$, bicarbonate $(HCO_3)^-$ and chloride (Cl^-)were analyzed by volumetric methods. Sulfates $(SO_4)^{2-}$, nitrate $(NO_3)^-$ and ammonium $(NH_4)^+$ were estimated by using the calorimetric technique. The Chemical Oxygen Demand (COD) was determined by $K_2Cr_2O_7$ open reflux method. For GC-MS analysis 1L of sample was extracted with a mixture of dichloromethane, hexane and ether at pH 2 and 11. The extracts were diluted with dichloromethane and analyzed by gas chromatography using a Thermo scientific, Trace GC Ultra/ISQ single Quadrupole MS, TG-5MS fused silica capillary column (30 m×0.25 mm×0.25 µm). The GC oven was heated from 40 °C to 280 °C at a rate 5 °C/min. The analysis was carried out in the splitless mode. Helium was used as a carrier gas. Mass spectra were recorded at EI 70 eV and Helium was used as carrier gas. The identification of compounds was performed based on NIST and Willy library data of the GC-MS system Samples for microbiological analysis were collected in 1-liter sterile dark glass bottle and immediately transported to the laboratory in an ice bucket at 4^oC. Total bacterial counts (at 22 ºC and 37 ºC) and total coliform were counted using poured plate and MPN (Most Probable Number) methods, respectively according to APHA [23].

2.3. *Preparation of doped TiO_2Photocatalyst*

The nitrogen - fluorine doped TiO_2photocatalyst used in the present investigation prepared by sol-gel hydrothermal technique. Tetraethyl orthotitanate "TEOT" $Ti(C_2H_5O)_4$ was used as titanium source. Urea $CO(NH_2)_2$ and ammonium fluoride (NH_4F) in atomic ratios (N/Ti , N,F/Ti = 10/90) were used as (nitrogen and nitrogen & fluorine) sources respectively. The calculated amounts of urea and ammonium fluoride were dissolved in deionized water under stirring at room temperature and TEOT (TEOT/H_2O = 1/18) was added dropwise under the effect of magnetic stirring. The resultant mixture was stirred at room temperature for 2 hours and then transferred into a Teflon-lined stainless steel autoclave of 100 ml capacity. The autoclave was kept for 16 hours at 150 ˚C for crystallization. The precipitate gained was washed with deionized water, dried at 100 ˚C for 24 h and finally calcined at 400 ˚C in a muffle furnace for 2 h. The prepared doped TiO_2 were characterized using Diffuse Reflectance Spectra (DRS) that were recorded on a UV-Visible-NIR spectrophotometer, Jasco V-570 in the range 800-190 nm equipped with an integrating sphere and using powdered $BaSO_4$ as a reference. The specific surface area of the prepared photocatalysts were calculated using BET equation and the data were collected by a Quantachrome NOVA automated Gas sorption system.

2.4.*Photocatalytic treatment reactions*

The photocatalytic reactions were carried out using a PHOCAT 120 W solar photoreactor with 15 fluorescent bulbs generating approximately 120 W m^{-2} from 400-700 nm. Prior to irradiation, all of the samples were sonicated for 5 minutes. For all runs, the amount of photocatalyst suspended in the water solution was kept constant at 1 g/l. The constant photocatalyst content among the various runs guaranteed that the irradiation conditions of suspension do not change. During the photocatalytic reactions, the suspension was stirred and the temperature held constant at 25-30 ˚C. The products analysis was performed by COD and bacteria count analyses. A magnetic stirrer guaranteed satisfactory powder suspension and the uniformity of the reacting mixture. Photocatalytic runs were operated according to the following procedure: the photocatalyst (1g/l) was added in the dark to water and allowed to equilibrate for about 30 min. For recovery of the catalyst, the residual was filtered through 0.45µm membrane (HA, Millipore) for separation and regeneration. The removal efficiency of COD and bacteria was estimated by applying the following equation.

$$\text{Removal Efficiency (\%)} = (C_0 - C) / C_0 \times 100$$

Where C_0 *is the original content and* C *is the residual content in solution*

3. Results and discussion

3.1. *Quality of irrigation water*

The characteristics of irrigation water in the study area are presented in table (1). The water temperature, pH and electric conductivity measured during field collection of samples flocculated around 20.8° C, 7.7 and 452.3 µS/cm, respectively. Generally, there are no abnormal values were recorded as well as the EC and pH values are within the permissible limit for irrigation according to FAO standards [24]. However, samples 9 and 10 which represent the irrigation drainage in the study area have slightly high EC (>750 µS/cm) than the preferred standard for irrigation water. This slightly alkaline pH is preferable in waters, as heavy metals are removed by carbonate or bicarbonate precipitates [25]. The average concentration of Ca, Mg, Na and K were 40.6, 17.5, 48.3 and 4.2 mg/l, respectively (Table 1). The mean concentration of HCO_3, Cl, SO_4, NO_3 and PO_4 were 156.7, 72.8, 31.5, 14.4 and 0.8 mg/l, respectively. The ionic chemistry of the studied water samples is dominated by Na and HCO_3 with the highest concentration was recorded in the irrigation drains (samples 9 and 10) as a result of agricultural output. Accordingly, the studied samples are considered suitable for irrigation according to FAO standards. Nitrate in the studied water samples may come from biological fixation, atmospheric precipitation of burned materials, fertilizers and human sewage. This spatial variation in chemical composition of water samples may be attributed to variations in human activity, hydrological processes, and prevailing topography.

To determine the suitability of water for irrigation Sodium Absorption ratio (SAR) was used because it is responsible for the sodium hazard [26, 27]. The elevated Na reduces soil permeability and leads to the formation of alkaline soil [9]. SAR is determined by the following equation [28]:

$$SAR = Na / [(Ca + Mg)/2]^{½}$$

Where the concentration of all ions are in meq/l.

The water can be classified based on SAR into excellent (SAR<10), good (10-18), doubtful (18-26) and unsuitable (>26) water for irrigation. The studied samples SAR are ranged from 0.9 to 2.7 (Table 4) with all values <10 indicating the excellence of water for irrigation. The plot of data (Fig. 2) on the US salinity diagram [28], shows that the samples fall in the field of good water quality (C2 – S1) except samples 9 and 10 which fall in the medium quality field (C3 – S1). These two samples represent the agricultural drainage which is reused for irrigation in the study area. Therefore, these waters can be used safely for irrigation purpose with little danger of developing harmful levels of exchangeable Na.

Table 1: Physical and chemical characteristics of water samples.

SN	pH	T	TDS	EC	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	PO_4	SAR
unit	-	^oC	mg/l	µS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	-
1	7.45	21.5	170.2	350.4	26	15	28.9	4.5	112.6	25	46.2	16	2.4	1.1
2	7.84	21.3	170.2	346.3	20	10	24.5	4.3	117.3	30	23.1	1.9	0.9	1.1
3	7.63	20.4	170.2	339.6	30	10	24.5	4.4	117.3	15	43.3	4.4	0.6	1.0
4	7.75	20.1	180.2	357.2	40	10	26.6	4.9	117.3	10	57.8	6.6	0	1.0
5	7.63	21.7	190.2	400.7	40	15	26.6	4.4	122.0	15	57.8	9	0.6	0.9
6	7.82	20.5	170.2	340.3	30	10	23.2	4.4	117.3	15	52.0	0.9	0.3	0.9
7	7.67	20.3	220.2	414.9	60	30	101.3	2.0	268.1	35	135.6	17.2	0.8	2.7
8	7.4	20.9	190.2	382.7	50	10	26.6	5.6	122.0	15	69.3	20.5	0.6	0.9
9	7.74	20.7	400.4	794.3	60	30	99.9	3.5	225.2	75	144.5	38.2	1	2.6
10	7.64	21	380.4	797.0	50	35	101.2	4.2	248.0	80	98.7	29.4	0.8	2.7
Average	7.7	20.8	224.2	452.3	40.6	17.5	48.3	4.2	156.7	31.5	72.8	14.4	0.8	1.5

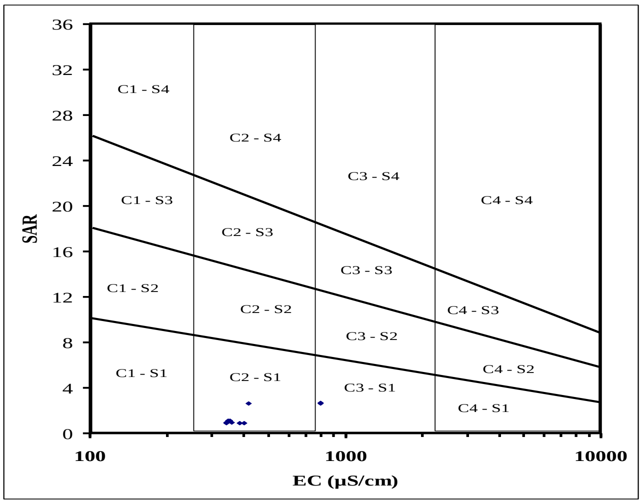

Figure 2: US salinity classification diagram for water suitability for irrigation.

On the other hand, the chemical oxygen demand (COD) analysis has been used to measure the organic pollution level in the studied water samples. Table (2) shows high concentration of COD, from 70 to 256 mg/l. Nearly all the samples have COD levels more than the permissible limit of COD in irrigation water is 75 mg/l [29] except sample (2) which represent the main canal in the study area. The presence of more than 20 mg/l COD in the studied samples indicates introduce of effluents to this water [30]. These high levels of COD may result from the small width of canals, low movement of water, human sewage, agricultural runoff and rubbish. The physical, chemical and biological characteristics of water body can be altered as a result of human activities [31]. The irrigation canals and drains were represented by samples 8 and 10, respectively for Gas Chromatographic mass (GC-MS) analysis. The compound 3,3-dimethyl-1,2-diphenylcyclopropene is a major in the two samples. In addition, canal sample (No.8) contains traces of 3-Pyridine carboxylic acid and 3,4-dihydrothienyl-[3,4,B]-5-carboxythiophene. While, in drainage sample (No. 10) the 3-Pyridine carboxylic acid is another major compound with traces of 4-Methyl-2-phenyl-1,3-dioxalane. These compounds have been indicted as causative agent in the production of abnormalities among animals ingesting crude cottonseed oil [32 - 34]. Pyridine carboxylic acid herbicides were developed to control a wide variety of broadleaf weeds and to remain effective for several months to years [35]. It is known that 3, 4 3,4- dihydrothienyl-[3,4,B]-5-carboxythiophene is used as fungicides [36] and 4-Methyl-2-phenyl-1,3-dioxalane is used as flavoring agents [37].

Table 2: COD values of irrigation water before and after treatment process.

SN	COD Before treatment (mg O_2/l)	COD after treatment (mgO_2/l)	Removal %
1	192	5.6	97.1
2	70	24	65.7
3	200	19	90.5
4	144	45	86.8
5	152	19	70.4
6	192	18	90.6
7	96	16	83.3
8	216	5	97.7
9	232	21	90.9
10	256	10	96.1

Table (3) illustrates the total bacterial count (TBC) and total coliforms (TC) levels in the studied water samples. The average TBC at 22°C and 37°C were 8.63x103 and 22.5x103 cfu/ml, respectively while the TC was 3.76x103 MPN-index/100ml. The high TBC indicates the biological pollution of water while TC indicates of the sanitary role in pollution [38]. Both of TBC and TC are above the recommended level for irrigation which was 100cfu/ml [39] and 1000 cfu/100ml [40], respectively. The presence of bacteria in irrigation water can pose deadly health impact to farmers [41]. The vegetables irrigated with polluted water were found to be contaminated by bacterial [42]. The current results are higher than those recorded by [43] at Sohag Governorate who reported 1996 cfu/ml, 3981 cfu/ml and 126 MPN-index/100ml for TBC at 22^{o}C, TBC at 37^{o}C and TC, respectively. The presence of bacteria in water increases the rate of transportation of heavy metals [8] due to the binding of these metals into the negatively charged surface of bacteria [44, 45].

Table 3: The total bacterial count total coliform in the water samples

SN	TBC 22^{o}C cfu/ml	TBC 37 ^{o}C cfu/ml	Total coliform MPN-index/100ml
1	$8.7x10^2$	$1.1x10^3$	$2.6x10^2$
2	$4.2x10^3$	$8.4x10^3$	$1.5x10^3$
3	$2.1x10^3$	$7.1x10^3$	$2.0x10^2$
4	$7.9x10^3$	$1.5x10^4$	$1.5x10^3$
5	$9.1x10^3$	$2.2x10^4$	$1.1x10^4$
6	$2.2x10^4$	$4.6x10^4$	$1.1x10^4$
7	$1.1x10^4$	$2.3x10^4$	$4.3x10^2$
8	$9.3x10^3$	$1.2x10^4$	$3.9x10^2$
9	$1.1x10^4$	$7.6x10^4$	$1.1x10^4$
10	$8.8x10^3$	$1.4x10^4$	$3.0x10^2$
average	$8.63x10^3$	$22.5x10^3$	$3.76x10^3$

3.2. Photocatalytic treatment of irrigation water

The prepared N, F doped TiO_2 shows better absorption of light than commercial P25 TiO_2 especially in visible light as shown in DRS spectra (Figure 3). The measured surface area using BET measurements was 135m^2g^{-1} that is better than that of P25 TiO_2 (50 m^2g^{-1}).

The incorporation of nitrogen or nitrogen and fluorine stabilizes the nanotitania in the anatase phase and enhances the absorption in the visible region and as a result a remarkably higher photocatalytic activity is observed. The band gap becomes narrow in N, F, -TiO_2 and BET surface area increases. The lowering of band gap energy value may be attributed to the promotion of electrons from nitrogen centers (which are located just above the valence band) directly to the conduction band by visible light [46].

Heterogeneous photocatalytic system consists of semiconductor nano-particles (photocatalysts) that are in close contact with a liquid reaction medium. Exposing the photocatalyst to solar irradiation, excited states may be generated that are able to initiate subsequent processes like “redox reactions” and molecular transformations. The photocatalyst could react with water to produce the highly reactive hydroxyl radicals (OH•) that are very powerful oxidants, which could oxidize most organic contaminants as well as bacteria.

$$H_2O + h^+ \rightarrow OH^{\cdot} + H^+$$

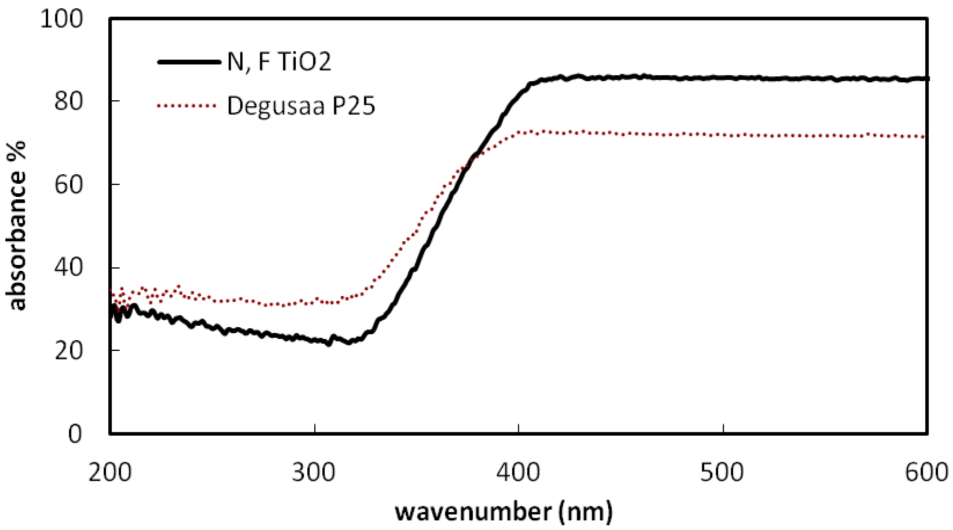

Figure 3: Diffuse reflectance spectra of Degussa and N.F doped TiO_2

In general, air oxygen acts as electron acceptor by forming the super-oxide ion $O_2^{\cdot}$

$$O_2 + e^- \rightarrow O_2^{\cdot -}$$

Super-oxide ions are also highly reactive particles, which are able to oxidize organic materials and bacteria [47, 48]. The overall process is the semiconductor mediated photocatalyzed oxidative mineralization of the organic pollutants [13, 14, 15, and 16] and can be represented by the following equation:

$$\text{Pollutant (organics and bacteria)} + O_2 \xrightarrow{(h\nu \geq Ebg\text{ , semiconductor})} CO_2 + \text{Water}$$

The COD removal % using photocatalytic treatment is within the range 65.7 - 97.7 % (Table 2). Unfortunately, the treatment process has negligible effect on the studied heavy metals. Table (4) shows that the bacteria were totally removed from all samples using the photocatalytic degradation process.

Table 4: Bacteria content of water after treatment and removal %.

SN	TBC 22°C cfu/ml	TBC 22°C Removal %	TBC 37 °C cfu/ml	TBC 37 °C Removal %	TC MPN-index/100ml	Removal %
1	31	97.18	18	97.9	ND	100
2	2	99.98	ND	100	ND	100
3	1	99.99	ND	100	ND	100
4	22	99.85	4	99.9	ND	100
5	33	99.85	15	99.8	ND	100
6	233	99.49	186	99.2	ND	100
7	ND	100	ND	100	ND	100
8	ND	100	ND	100	ND	100
9	32	99.96	11	99.9	ND	100
10	72	99.49	53	99.4	ND	100

ND: not detected

Conclusions

The studied water samples are suitable for irrigation according to its physicochemical characterisitics. As well as these water samples fallen in the good irrigation water classes (class C2-S1 and C3-S1) of the US salinity diagram. On the other hand, this water was polluted with organic residuals and bacteria from waste effluents. The application of photocatalytic treatment technique using TiO_2 doped with nitrogen and fluorine as photocatalyst has shown good activity toward the removal of pollutants in presence of UV-visible light irradiation. The removal efficiencies were found to be 86.9% and 100% for the removal of dissolved organics and bacteria, respectively. Accordingly, it is considered environmentally safe, cheap and effective technique for water treatment.

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