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Solar photoradiation-induced oxidation of NOM from surface water using immobilized coated glass spirals of TiO_2

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ABSTRACT

The Advanced oxidation processes sunlight/photocatalyst is common for remediation treatments. During the oxidation processes, organic matter decomposed into smaller compounds, which affect the characteristics of the treated effluent. In the present work, two types of commercial TiO_2 (TiO_2 P-25 Degussa and commercial TiO_2 (A)) were supported on small glass spirals. The photooxidation of natural organic matters (NOMs) over immobilized TiO_2 using parabolic solar collector was investigated. The effects of addition of H_2O_2 as electron acceptor and pH values were also investigated. The degradation of NOMs was followed up by analysis of total organic carbon (TOC) and UV absorbance at 254 nm (A_{254}). It was found that NOMs were completely removed over immobilized TiO_2 on glass spirals under sunlight irradiation after 120 min. Also, approximately 77% of TOC was reduced from groundwater. Upon obtained results, solar energy could be used for photocatalytic degradation of NOMs in ground and surface waters and therewith lighten the process of preparing them to the potable water.

Keywords: NOM; Photocatalytic oxidation; Solar radiation; TiO_2; Surface water

1. Introduction

In remote and rural areas, accesses to potable water are often impossible. Consequently, local communities often rely on untreated rainwater, surface waters, and groundwater. The main causes of surface and groundwater contamination are industrial effluents, fertilizers (agrochemicals), and domestic waste landfills. Rural population is particularly affected by diseases related to consumption of contaminated water with bacteriological and organic pollutants.

Natural organic matters (NOMs) are defined as a complex matrix of organic materials present in all natural waters. They form as a result of the interactions between the hydrological cycle and the biosphere and geosphere. The surface and ground water used as drinking water resources generally contains NOMs. Thus, the amount, characteristics, and properties of NOMs differ considerably in waters of different origins, depending on the biogeochemical cycles of the

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surrounding environments [1]. Moreover, the range of organic constituent of NOMs may vary also on the same location seasonally [2–4], due to rainfall event, snowmelt runoff, floods, or droughts. Floods and droughts are the main impacts of climate change on water availability and quality. It has been suggested that these changes may be the reason for an increasing of the total amount of NOM [5,6]. NOMs have specific UV absorbance, have also increased. The changes in NOMs quantity and quality have a significant influence on selection, design, and operation of water treatment processes [7].

The relevance of NOMs to water treatment operators is highly significant. Some components can cause coloration of the water, it can include compounds that cause unpleasant taste and odor and it can act as a substrate for microbial growth. As well, NOMs may control coagulant and disinfectant demand; it may foul membranes, block activated carbon pores and compete with taste and odor compounds for available adsorption sites, reducing adsorption efficiency [8]. As a result, NOMs affect potable water quality by contributing to annoying color, taste, and odor problems, and as a carrier of metals and hydrophobic organic chemicals. In addition, NOMs are responsible for the majority of the coagulant and disinfectant use in water treatment [9]. Moreover, NOMs have contributed in the disinfection byproducts (DBPs) formation. DBPs have become a focus of attention in water treatment, since they have been reported to have adverse health effects [10]. More than 600 compounds of DBPs have been identified, where the most common among of them are trihalomethanes and haloacetic acids [11].

Generally, high levels of solar energy are available at locations of problems occurrence, and the overcoming of water sanitation problems using solar light has many advantages. Saudi Arabian Kingdom is considered one of the regions of the world's Sunbelt. Therefore, water detoxification by solar energy would seem to be a promising method to solve water supply problems. Sunlight-based photocatalytic oxidation over TiO_2 has been demonstrated as a decontamination process for aqueous organic contaminants leading to total mineralization of organic compounds [12]. Moreover, advanced oxidation processes (AOPs) of H_2O_2/O_3 and H_2O_2/UV processes have less effect on total organic carbon (TOC) reduction. However, O_3 showed a significant decrease of UV_{254}. The O_3/UV process showed increased performance in reducing UV_{254} comparing with others AOPs. The H_2O_2/UV process has a lower power for UV_{254} reduction than the O_3/UV process [13]. Also, UV/TiO_2 slurry system was previously used for photocatalytic oxidation of all the NOMs surrogates (L-glutamic acid, L-aspartic acid, glycine, Leucine, L-serine, D-mannose, D-xylose, tannic acid, and resorcinol). This is particularly so for tannic acid, resorcinol, L-glutamic acid, glycine, and D-xylose where residual DOC levels were reduced lower 1 mg/L after 10 min of oxidation by UV/TiO_2 system. For the other compounds the removals were > 70% and greater than expected for conventional processes such as coagulation but no trend was identified between the chemical character and removal [14]. The UV/H_2O_2, the reactor (Philips TUV 8 W, G8T5) was used for effluent organic matter secondary effluents from a Conventional Activated Sludge and a Membrane Biological Reactor system. It was concluded that ozonation and UV/H_2O_2 processes efficiently eliminate the different NOMs fractions of the treated effluents via oxidation processes [15]. Hence, many studies investigated the feasibility of coating the photocatalyst on inert surfaces like glass, polythene fibers, and cement surface. Immobilization of the catalyst on a stationary support could simplify the separation of the catalyst from the reaction mixture without any leaching. Over recent years, much work has been done in this area and has led to the use of a variety of supports; silica gel, quartz optical fibers, glass fibers, glass beads, ceramics, cellulose membranes, polymer films, zeolites, etc. [16]. Furthermore, the interest of application of this method for water detoxification has been grown in the last decade. In this work, coupling of supported TiO_2 and solar energy will be used for photocatalytic destruction of NOMs from water resources. The objective of this study is to examine the practical usefulness of solar photocatalytic oxidation of NOMs content in water using solar parabolic collector, in the presence of immobilized TiO_2 on glass support. Also, TiO_2 catalyst is supported on glass spirals. The effect of solar UV light irradiation, addition of H_2O_2, and pH were examined.

2. Experimental

2.1. Well water characterization

These studies were carried out using ground water containing NOMs which may appear as possible. The groundwater was taken from an approx. 200-m-deep well located near an industrial region. Table 1 shows the general physicochemical well water parameters used in this study averaged over the period of the experimental series.

2.2. Types of photocatalysts

Two different crystalline forms of TiO_2 were provided from Merck, Germany and used without further

Table 1
Average physical and chemical properties of the well water used in this study

Parameter	Unit	Value
pH	–	7.9–8
Absorbance	A(254) nm, (cm^{-1})	2.4–2.8
TOC	mg/L	7.3–7.7
Turbidity	NTU	1.5–2.1
Iron	μg/L	80
$KMnO_4$ consuming capacity	mg/L	95
Aluminum	μg/L	63

purification. TiO_2 P-25 Degussa (anatase/rutile, 3.8:1.2, surface area 56 m^2 g^{-1}, nonporous) and a commercially available TiO_2 (A) (100% anatase) were used for all the heterogeneous photocatalytic experiments. TiO_2 (A) was chosen due to its relatively good photocatalytic properties and its lower price in relation to TiO_2 P-25.

2.3. Immobilization of TiO_2

TiO_2 (A) and TiO_2 P-25 Degussa powders were immobilized on small cylindrical glass spirals (4 mm diameter, weight 0.5 g) as follows. The glass spirals were etched with dilute hydrofluoric acid (2.5 mM) for 24 h in order to fabricate a rough surface for better contact of TiO_2 on glass surface. TiO_2 slurries were prepared with 2 g TiO_2 of each type in 100 mL distilled water and magnetically stirred overnight. The slurry and roughened glass spirals were added to a rotating flask immersed in water bath, which was connected to a vacuum pump. Then coated spirals were calcined in an oven for 24 h at 120˚C after which they were thoroughly washed with distilled water to remove weakly adhered TiO_2 particles. Finally, the spirals were calcined at 200˚C for 240 min. The TiO_2 content in glass spirals was nearly 60–70%.

2.4. Materials characterization

Characterization of prepared TiO_2/GS was investigated by X-ray diffraction (XRD), and scanning electron microscope (SEM). Powder XRD measurements were performed on Bruker D8 diffractometer employing Cu Kα radiation, Ni filters, and operated at 40 kV and 40 mA with angular scanning range $2\Theta = 4–90^\circ$. The morphology of TiO_2 particles was determined by SEM employing a JEOL microscope equipped with XL-30 ESEM NEW XL-30 135-10 microanalysis system. The specimens were mounted on 15 mm diameter stubs coated with a thin layer of carbon paste. The materials were also characterized by FT-IR spectroscopy using Varian 3100 FT-IR Excalibur Series instrument.

2.5. Configurations of the solar collector

Fig. 1 shows the parabolic concentrator and the photoreactor used to perform heterogeneous photocatalysis oxidation under solar irradiation. The solar reactor consists of a UV transparent glass tube (1.5 m long and 40 mm in diameter) connected with a feed tank in a recirculation loop with a constant flow maintained by a peristaltic pump. An irradiated surface of 2.1 m^2 made of borosilicate glass is placed on fixed support as a parabolic concentrating collector that is to be oriented about a horizontal east-west axis so as to constantly minimize the angle of incidence and thus maximum the incident beam radiation [10].

2.6. Solar irradiation experiments

All solar photocatalytic experiments were carried out under similar conditions during August and September under clear sky between 11 am and 3 pm The problem of varying intensity of the sunlight even under a clear sky was overcome by conducting several sets of consecutive experiments and comparing the results between these sets of experiments. Each experimental run was carried out using the following procedure: (1) the samples of lake water were carried in 25 L polycarbonate resin containers and kept in refrigerator (−4˚C) for maximum seven days, (2) the tube of the solar parabolic collector was filled with a fixed amount of TiO_2-coated glass spirals, (3) the wastewater was continuously circulated at a constant flow rate of 50 L/h, (4) the wastewater was irradiated by sunlight which was focused onto the photoreactor glass tube mounted in the focal point of the parabolic reflector, and (5) samples were taken at regular time intervals every 20 min from the solar reactor. Several series of experiments were conducted to study the effect of types of photocatalyts, pH values, and effect of the addition of H_2O_2 as electron acceptor. For each new series of experiments, the coated spirals were changed with new coated spirals. The initial pH value was adjusted with H_2SO_4 or NaOH. In the experiments with added hydrogen peroxide to the dye solution (H_2O_2 solution, 35% w/w provided by Merck), hydrogen peroxide was injected before the start of the solar catalytic oxidation.

2.7. Solar light intensity measurements

Solar light intensity was measured every 30 min with a LT Lutron LX-10/A Digital Lux meter (Electricals Electronics Enterprise, Chennai) and the intensity was 581 mW/m^2 incident onto the reactor; at the position where maximum intensity was measured. The

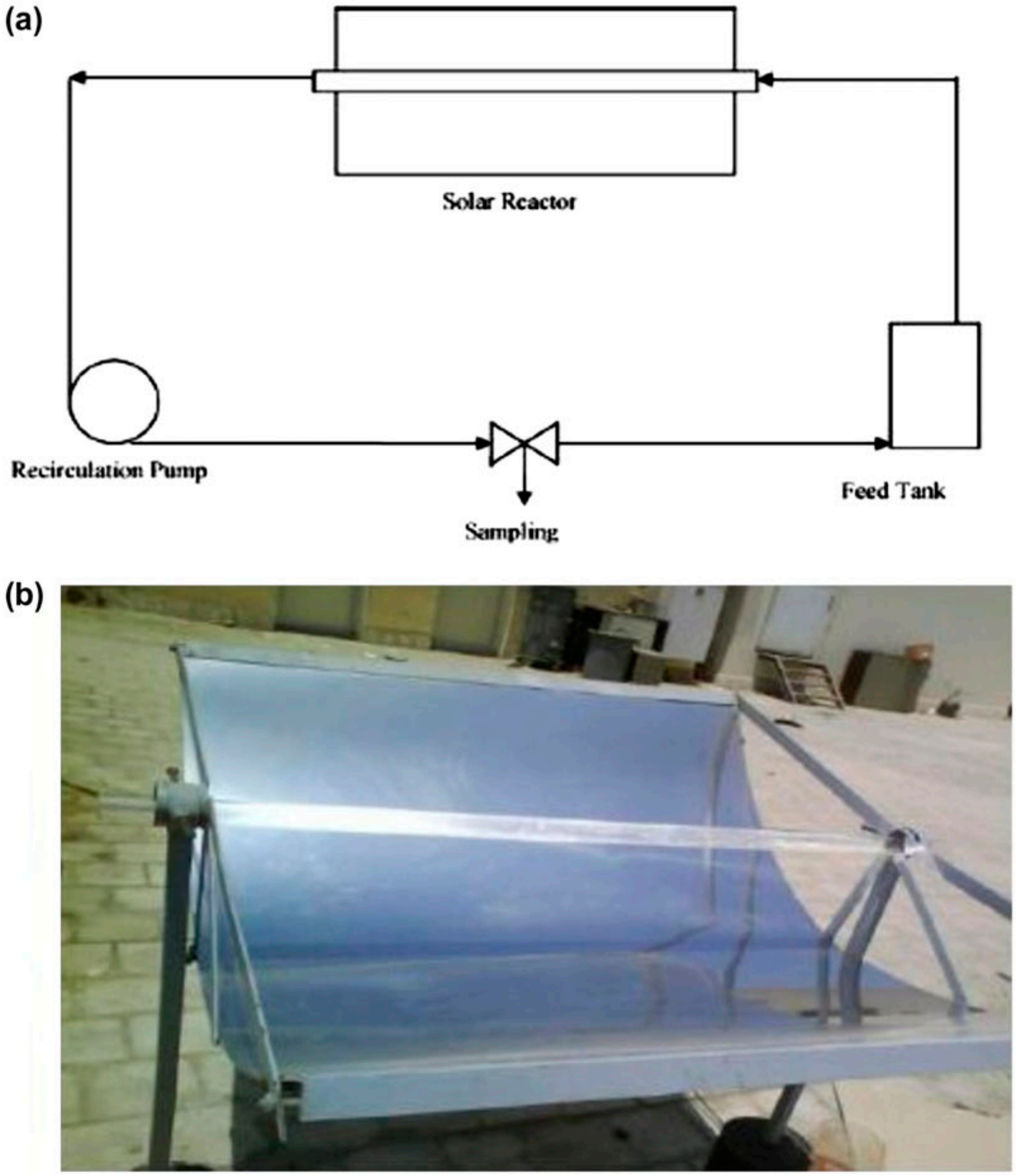

Fig. 1. (a) Schematic diagram of solar catalytic oxidation unit. (b) Solar parabolic collector used in the study.

intensity was found to be nearly constant during the experiments. Taking this value of the solar flux a lower bound of the photocatalytic efficiency is obtained.

2.8. Analysis

Analytical measurements of TOC and NOMs content in water were determined, after filtration through 0.45 mm membrane, with TOC analyzer type 5050, Shimadzu Co., Japan, and with spectrophotometer UV–vis, type (PD-303 UV spectrophotometer APEL Type) from Japan, for absorbance measurement. Turbidity was measured with a laboratory turbidimeter Model 2100 N (Hach, USA). Hydrogen peroxide was detected by a modified iodometric titration method. The pH of the solution was measured by using a HANNA pH (model H 198107) digital pH meter.

3. Results and discussion

3.1. Solar photodegradability

Figs. 2 and 3 shows the results of the removal rate of NOMs using spectrophotometric analysis from groundwater as a function of irradiation time in the

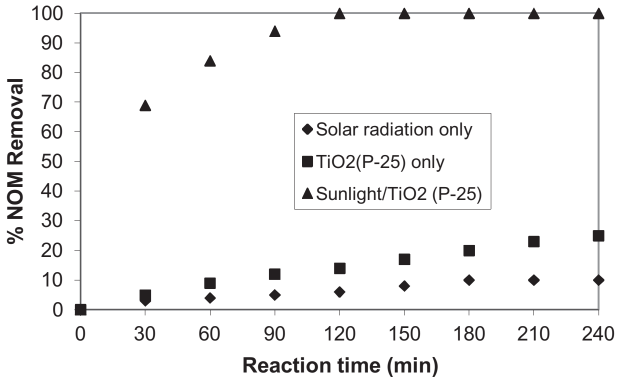

Fig. 2. Removal percentage of NOM of ground water under solar radiation only, TiO_2 Degussa and solar/TiO_2 Degussa.

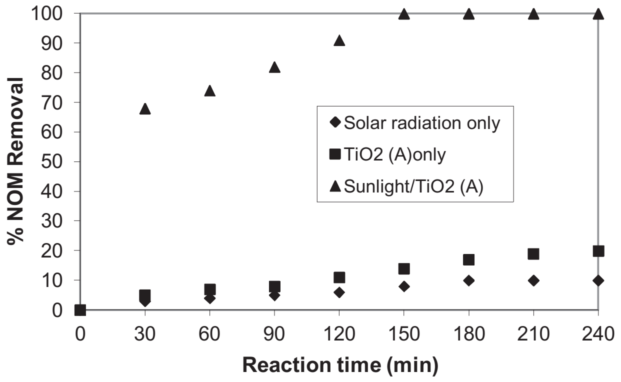

Fig. 3. Removal percentage of NOM of ground water under solar radiation only, TiO_2 A and solar/TiO_2 A.

solar photoreactor. In the absence of photocatalysts, it was found that removal rate of NOMs was very low upon solar irradiation. Hence, it is concluded that the wastewater is resistant to self-photolysis during solar light irradiation. In the presence of both photocatalysts in dark, the removal rate of NOMs is amounted 25 and 20% after 120 min of stirring. No further decrease was observed after longer time. This is thus attributed to adsorption of NOMs on the surface of coated TiO_2 glass spirals. Simultaneous irradiation and aeration in presence of coated TiO_2 spirals, 100% removal of NOMs is reached after 120 and 150 min irradiation time using supported TiO_2 Degussa and TiO_2 A on glass spirals (TiO_2-A/GS), respectively. This is attributed to the removal of NOMs under the effect of free hydroxyl radicals. According to the principle of photocatalysis, electron (e^-) and hole (h^+) pair are generated when TiO_2 is irradiated with sunlight. Separated electrons (e^-) and holes (h^+) diffuse to the surface of semiconductor and react with adsorbed water, hydroxyl group, and molecular oxygen on TiO_2 surface producing reactive radicals, such as $O_2^{-\bullet}$, $^{\bullet}OH$, H_2O_2, etc. These reactive radicals react with dye absorbed on TiO_2/GS and degrade it. Furthermore, the photocatalytic activity of TiO_2/GS mainly depends on two factors: (1) the electron–hole generation capacity i.e. high utilization of incident light (visible); (2) the separation efficiency of the photogenerated charge pair. TiO_2/GS could form defects which could provide a shallow trap for photogenerated hole to inhibit the recombination of electron–hole pair and extend the lifetime of charge separation. Therefore, the photogeneration rate of hydroxyl radicals could be enhanced and dye photodegradation was enhanced. It was found that decolorization of the dye is faster than the degradation. The obtained results are comparable to previous recorded results, where photocatalytic UV/TiO_2 slurry was used for removal of NOMs [14].

3.2. TOC degradation

Fig. 4 illustrates the effect of solar photocatalytic oxidation on TOC removal rate using TiO_2 Degussa/GS and TiO_2 A/GS, respectively. The main experiments were performed with the solar light (TOC) removal rate in all the experiments were between 70 and 77% of the saturation value. With further exposure to the solar light; no further TOC degradation was observed even after 180 min irradiation time. In comparing obtained results with previous photocatalytic oxidation of NOMs in slurry system, it was previously reported that DOC reduced by 90% after 10 min of UV irradiation [14]. In comparison, Duczmal and Sobczyński [17] reported a 80–85% DOC removal after 3 h irradiation with a 180 W medium pressure UV lamp and a TiO_2 dose of 0.3 g/L indicating that complete mineralization was not achieved. This is attributed to formation of intermediate

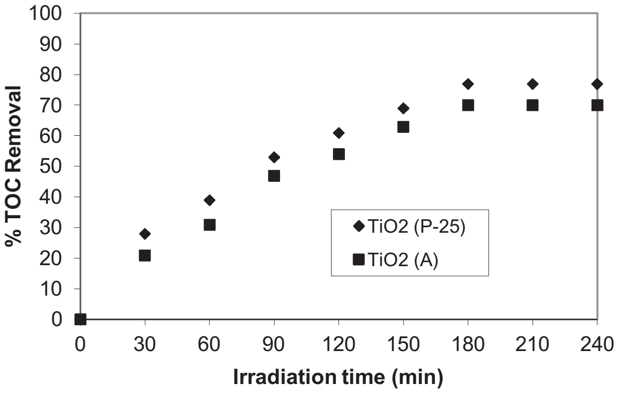

Fig. 4. Reduction of TOC during solar photocatalytic oxidation of raw well water using TiO_2 Degussa or TiO_2 A (pH 7).

compounds which absorb in the same wavelength region and which are resistant to photocatalytic oxidation. Those observations of present system (TiO_2/GS/sunlight) are consistent with system of slurry TiO_2/UV and suggest a real attention for groundwater treatment contaminated with NOMs where organic matter degradation has to deal with the control of toxic byproducts generation.

3.3. Effect of pH

An important parameter that influences the photocatalytic degradation is solution pH. Fig. 5 shows the NOM degradation efficiency as a function of pH. The effect of pH was examined in the range pH 3–11 in the presence of coated glass spirals coated with TiO_2 Degussa or TiO_2 A, respectively, analogous to the experiments described above. The results show a direct influence of pH of the well water on the heterogeneous photocatalysis process. The increase of pH of the well water from 3 to 9 results in an increase of the NOM removal from 75 to 100% using TiO_2 Degussa and from 70 to 93% after 120 min reaction. The photocatalytic reactions are evidently faster in alkaline pH rather than in the acidic pH range. Similar observations have been reported earlier [18]. This further supports that the photocatalytic degradation of NOM is due to hydroxyl radical attack, and not due to adsorption properties. The production of hydroxyl radicals in acidic medium is different from that in a basic medium. In acidic medium photogenerated holes react with water molecules thus producing hydroxyl radicals. At alkaline pH the negative charged OH^- covered TiO_2 surface acts as an efficient trap for the photogenerated holes and readily produce hydroxyl radicals [19].

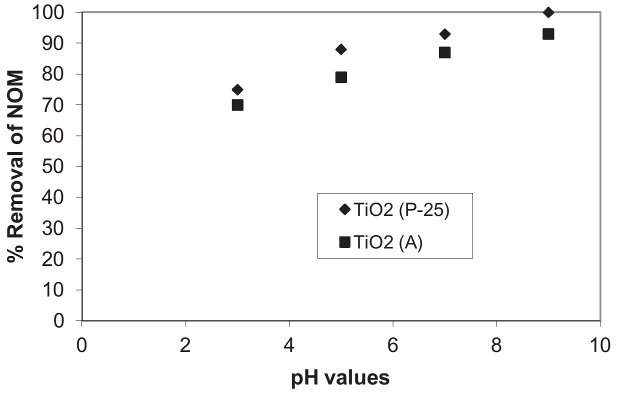

Fig. 5. Effect of pH values on removal percentage of NOM during solar photocatalytic oxidation (irradiation time 90 min).

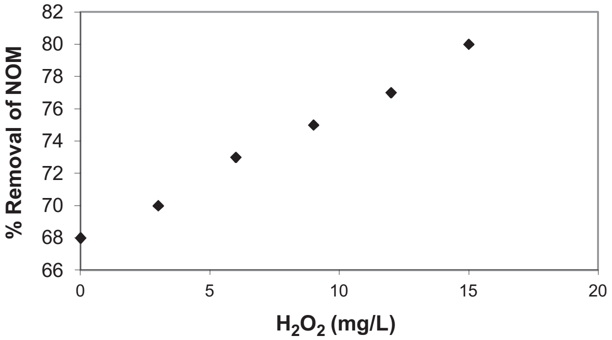

Fig. 6. Effect of H_2O_2 addition on removal percentage of NOM during solar oxidation in absence of photocatalyst (pH 7, irradiation time 90 min).

3.4. Effect of hydrogen peroxide

Fig. 6 illustrates the removal percentage of NOM measured as change observed in absorbance at 254 (A_{254}) for groundwater treated with solar irradiation under different amounts of H_2O_2. A dose of 15 mg/L was the optimum H_2O_2 concentration. These results agree with results obtained from other previous studies on the impact of UV/H_2O_2 [20] demonstrating that the observed phenomena (i.e. degradation of aromatic species by reaction with OH$^{\bullet}$) were consistent over numerous experimental treatments. Fig. 7 illustrates the removal percentage of NOM for the solar photocatalytic oxidation of NOM using TiO_2 Degussa and TiO_2 A, respectively, at different concentrations of H_2O_2. The NOM degradation rate is observed to increase with increasing H_2O_2 concentration up to 3

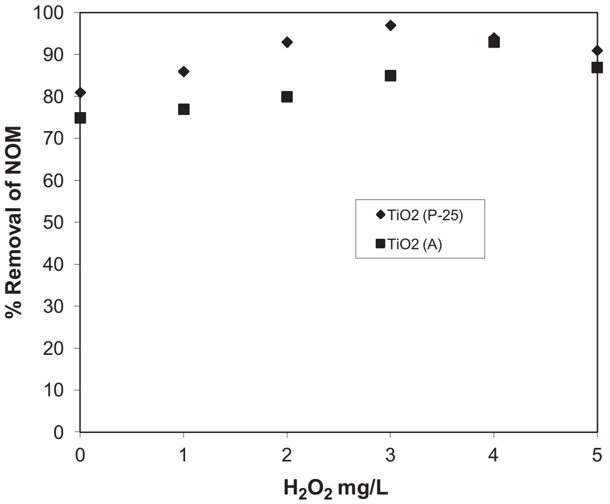

Fig. 7. Effect of H_2O_2 addition on removal percentage of NOM during solar photocatalytic oxidation (pH 7, irradiation time 90 min).

and 4 mg/L, while it decreases at higher concentrations. Since, hydrogen peroxide is a better electron acceptor than molecular oxygen it could act as an alternative electron acceptor to oxygen [21]. Thus, may inhibit the electron–hole recombination. Hydrogen peroxide may also be split photochemically to produce hydroxyl radical directly, as described in the studies of homogeneous photooxidation using UV/H_2O_2 [22]. At high concentrations H_2O_2 is a powerful $OH^{\cdot}$ scavenger [23]. We conclude that proper addition of hydrogen peroxide can accelerate the photocatalytic degradation rate of NOM. However, in order to keep the efficiency of the added hydrogen peroxide it is necessary to adjust the hydrogen peroxide concentration to the pollutant concentration, irradiation power, and amount (and type) of photocatalyst.

4. Conclusions

Under solar photocatalytic oxidation using two types of immobilized TiO_2 in coated glass spirals, the NOMs of raw well water were partially oxidized, but not mineralized, indicated by a significant reduction in NOMs absorbance and no simultaneous reduction in TOC. This attributed to the formation of intermediate compounds which hinders the progress of reaction of free hydroxyl radicals. Under basic pH values, the % removal of NOM is increased and the turbidity was reduced. Addition of hydrogen peroxide as an electron acceptor increased the NOM removal but behind different amounts. The system (TiO_2/GS/sunlight) is promising for groundwater treatment contaminated with NOMs where organic matter degradation has to deal with the control of toxic byproducts generation.

References

[1] R. Fabris, C.W.K. Chow, M. Drikas, B. Eikebrokk, Comparison of NOM character in selected Australian and Norwegian drinking waters, Water Res. 42 (2008) 4188–4196.

[2] E.L. Sharp, S.A. Parsons, B. Jefferson, Seasonal variations in natural organic matter and its impact on coagulation in water treatment, Sci. Total Environ. 363 (2006) 183–194.

[3] E.L. Sharp, S.A. Parsons, B. Jefferson, The impact of seasonal variations in DOC arising from a moorland peat catchment on coagulation with iron and aluminium salts, Environ. Pollut. 140 (2006) 436–443.

[4] E. Smith, Y. Kamal, Presence and formation of disinfection by-product in Cairo residential water supply, Water Sci. Technol: Water Supply 9 (2009) 113–120.

[5] I. Delpla, A.-V. Jung, E. Baures, M. Clement, O. Thomas, Impacts of climate change on surface water quality in relation to drinking water production, Environ. Int. 35 (2009) 1225–1233.

[6] C.D. Evans, D.T. Monteith, D.M. Cooper, Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts, Environ. Pollut. 137 (2005) 55–71.

[7] B. Eikebrokk, R.D. Vogt, H. Liltved, NOM increase in Northern European source waters: Discussion of possible causes and impacts on coagulation/contact filtration process, Water Sci. Technol. 4 (2004) 47–54.

[8] M.C. Kavanaugh, Modified coagulation for improved removal of trihalomethane precursors, J. Am. Water Works Assn. 70 (1978) 613–620.

[9] J.G. Jacangelo, J. DeMarco, D.M. Owen, S.J. Randtke, Selected processes for removing NOM: An overview, J. Am. Water Works Assn. 87 (1995) 64.

[10] USEPA, Guidance Manual for Conducting Sanitary Surveys of Public Water Systems; Surface Water and Ground Water Under the Direct Influence (GWUDI), Texas, 1999.

[11] S.W. Krasner, H.S. Weinberg, S.D. Richardson, S.J. Pastor, R. Chin, M.J. Sclimenti, G.D. Onstad, A.D. Thruston Jr., Occurrence of a new generation of disinfection byproducts. Environ. Sci. Technol. 40 (2006) 7175–7185.

[12] O.M. Alfano, D. Bahnemann, A.E. Cassano, R. Dillert, R. Goslich, Photocatalysis in water environments using artificial and solar light, Catal. Today 58 (2000) 199–230.

[13] N.J. Peill, M.R. Hoffmann, Development and optimization of a TiO_2 coated fiber optic cable reactor photocatalytic degradation of 4 chlorophenol, Environ. Sci. Technol. 29 (1995) 2974–2981.

[14] L. Rupa, M.E. Walsh, A.G. Gagnon, Comparison of advanced oxidation processes for the removal of natural organic matter, Water Res. 45 (2011) 3263–3269.

[15] K.K. Philippe, C. Hans, J. MacAdam, B. Jefferson, J. Hart, S.A. Parsons, Photocatalytic oxidation of natural organic matter surrogates and the impact on trihalomethane formation potential, Chemosphere 81 (2010) 1509–1516.

[16] O. González, A. Justo, J. Bacardit, E. Ferrero, J.J. Malfeito, C. Sans, Characterization and fate of effluent organic matter treated with UV/H_2O_2 and ozonation, Chem. Eng. J. 226 (2013) 402–408.

[17] Ł. Duczmal, A. Sobczyński, Photocatalytic water purification: Destruction of resorcinol by irradiated titania, React. Kinet. Catal. Lett. 66 (1999) 289–295.

[18] B. Neppolian, H.C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO_2 assisted degradation of textile dye reactive blue 4, Chemosphere 46 (2002) 1173–1181.

[19] P.C. Heimenz, Principle of Colloid and Surface Photochemistry, Marcel Dekker, New York, NY, 1986.

[20] S.R. Sarathy, M. Mohseni, The fate of natural organic matter during UV/H_2O_2 advanced oxidation of drinking water, Can. J. Civ. Eng. 36 (2009) 160–169.

[21] A.A. Khodja, T. Sehili, J.-F. Pilichowski, P. Boule, Photocatalytic degradation of 2-phenylphenol on TiO_2 and ZnO in aqueous suspensions, J. Photochem. Photobiol. A 141 (2001) 231–239.

[22] M.I. Stefan, J.R. Bolton, Reinvestigation of the acetone degradation mechanism in dilute aqueous solution by the UV/H2O2 process, Environ. Sci. Technol. 33 (1999) 870–873.

[23] S.R. Cater, M.I. Stefan, J.R. Bolton, A. Safarzadeh-Amiri, UV/H_2O_2 treatment of methyl tert-butyl ether in contaminated waters, Environ. Sci. Technol. 34 (2000) 650–658.