RESEARCH ARTICLE　　　　　　　　　　　　　　　　　　　　**Open Access**

Optimizing photo-mineralization of aqueous methyl orange by nano-ZnO catalyst under simulated natural conditions

Ahed Zyoud[1*], Amani Zu'bi[1], Muath H. S. Helal[2], DaeHoon Park[3], Guy Campet[4] and Hikmat S. Hilal[1]

Abstract

Background: Photo-degradation of organic contaminants into non-hazardous mineral compounds is emerging as a strategy to purify water and environment. Tremendous research is being done using direct solar light for these purposes. In this paper we report on optimum conditions for complete mineralization of aqueous methyl orange using lab-prepared ZnO nanopowder catalyst under simulated solar light.

Results: Nano-scale ZnO powder was prepared in the lab by standard methods, and then characterized using electronic absorption spectra, photolumenscence emission (PL) spectra, XRD, and SEM. The powder involved a wurtzite structure with ~19 nm particles living in agglomerates. Photo-degradation progressed faster under neutral or slightly acidic conditions which resemble natural waters. Increasing catalyst concentration increased photodegradation rate to a certain limit. Values of catalyst turn over number and degradation percentage increased under higher light intensity, whereas the quantum yield values decreased. The photocatalytic efficiency of nano-ZnO powders in methyl orange photodegradation in water with solar light has been affected by changing the working conditions. More importantly, the process may be used under natural water conditions with pH normally less than 7, with no need to use high concentrations of catalyst or contaminant. The results also highlight the negative impact of possible high concentrations of CO_2 on water purification processes. Effects of other added gaseous flows to the reaction mixture are also discussed.

Conclusion: ZnO nano-particles are useful catalyst for complete mineralization of organic contaminants in water. Photo-degradation of organic contaminants with ZnO nano-particles, methyl orange being an example, should be considered for future large scale water purification processes under natural conditions.

Keywords: Methyl orange, Contaminant mineralization, Solar simulated light, ZnO nanopowder

Introduction

Purification of water from hazardous chemicals is an important research area. Organic contaminants, such as industrial dyes, halocarbons and phenol derivatives, are among the main contaminants that demand complete safe removal [1]. Different strategies are being investigated for water remediation, including biological treatment [2, 3], ultra-filtration [4], adsorption methods [5] and others. Such methods may not be favored as they may not cause complete mineralization of the organic contaminant. They simply transfer the pollutant from one phase to another [6]. Advanced Oxidation Processes

(AOP) have been proposed as alternative routes for water purification. Among those, oxidation via ozone or hydrogen peroxide has been reported as an effective technique [7–11]. Unfortunately, such methods may be costly, as ozonation demands artificial UV radiations, and hydrogen peroxide is not available free of charge. Contaminant complete mineralization with natural solar light seems to be the most practical process for future water purification. A semiconductor photo-catalyst speeds up the action of light by first absorbing photon and producing electrons and holes [12]. With the abundance of cost-less solar radiations, a low cost catalyst may thus be useful. Different semiconducting materials, in the powder form, have been assessed as photo-catalysts [13, 14]. TiO_2 in its anataze form is the most widely used effective photo-catalyst for its high efficiency, photochemical

* Correspondence: ahedzyoud@najah.edu
[1]SSERL, Department of Chemistry, An-Najah National University, Nablus, Palestine
Full list of author information is available at the end of the article

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46

Page 2 of 10

stability, non-toxic nature and low cost. It has been described for degradation of a wide range of organic contaminants [15–22]. Zinc oxide ZnO is a semiconductor with a comparable band gap ~3.2 eV (with wavelength shorter than 400 nm), but has been investigated to a lesser extent in water purification. ZnO is evaluated in many advanced applications such as field-effect transistors, lasers, photodiodes, chemical and biological sensors and solar cells, but to a lesser extent in photo-degradation catalysis [23–26]. One main advantage for ZnO is that it absorbs a larger fraction of solar spectrum, than TiO_2 does [27]. The performance of ZnO in degrading a number of organic contaminants has been reported [28, 29]. The quantum efficiency of ZnO nano-particles in photo-degrading organic contaminants process is higher than that of TiO_2 [30, 31], due to its higher absorptivity in waves shorter than 400 nm, which accounts to about 5 % of the reaching solar light.

In this communication the photo-catalytic activity of ZnO powder in complete mineralization of organic contaminants is revisited, focusing on finding optimum conditions that yield highest contaminant removal, for the first time. For application purposes, it is necessary to emulate natural conditions of contaminated waters in terms of pH, low contaminant concentration, low allowable catalyst amount and moderate water temperatures. Influence of CO_2 and other gas flows on methyl orange photo-degradation process will also be assessed here for the first time. All such reaction parameters will be studied in order to assess feasibility of using ZnO activated photo-degradation of methyl orange in water under simulated natural conditions. To assess feasibility of ZnO catalyst to function on its own in simulated natural waters, multiple use of the added ZnO to photo-degrade fresh methyl orange samples will also be investigated. All such studies are being investigated for the first time.

Methyl orange, with molecular structure shown in Fig. 1, is a dye that is believed to be mutagenic [32]. It slightly dissolves in water. Its color changes with pH, from yellow (at pH higher than 4.4) to red (at lower pH

values), and therefore it is used as an indicator [33]. Methyl orange is also used as a dye in textile industry [34]. It is an example of the widely spread azo dies [35], which are resistant to complete biodegradation [36]. For these reasons, methyl orange is commonly used as a model dye to study in environmental cleanup, and this work is no exception.

In earlier study [37, 38], we reported on using commercial ZnO powders as catalysts in photo-degradation of methyl orange. As mentioned above, this work is intended to find optimum conditions for using ZnO nano-particles in methyl orange photo-degradation under natural water conditions, where ZnO is added to contaminated waters and allowed to function on its own under direct solar light.

Experimental
Chemicals
Hydrochloric acid, sodium hydroxide, and methyl orange were purchased from Merck. ZnO powder was prepared in the lab to obtain small particle sizes, as described earlier [39, 40]. A $ZnCl_2$ solution (250 mL, 0.25 M) was drop-wise added (within 40 min) to NaOH solution (200 mL, 0.90 M) with continuous stirring. The system was then left to settle, and the supernatant was decanted. The resulting precipitate was washed with water many times to remove any remaining ions. Enough amount of distilled water was added to convert the precipitate into slurry. The slurry was centrifuged at 6000 rpm for 10 min, and the supernatant was carefully decanted leaving the solid catalyst which was dried at 120 °C.

The CO_2 gas was prepared by adding concentrated HCl solution (5 M) drop-wise to Na_2CO_3 solid in a stoppered flask with only one outlet. The outlet was connected with a glass tube bubble the CO_2 through the reaction mixture at a flow rate 90 mL/L.

Equipment
A 400 W Osram Tungsten Halogen lamp was used as a source for solar simulator light. The lamp spectrum is a
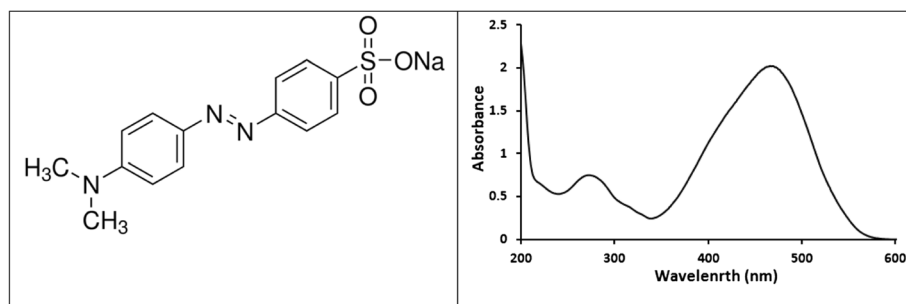

Fig. 1 Molecular structure and UV–vis absorption spectrum of methyl orange

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46

Page 3 of 10

bell curve typical with little (~5 %) in the UV region, just like natural solar light that reaches earth. A light meter (Model lx-102) from Lutron was used to measure the radiation intensity at the reaction mixture surface. A Shimadzu UV-1601 spectrophotometer was used to measure remaining methyl orange concentration using calibration curves, pre-prepared at different pH values, as methyl orange spectra may change with pH value.

The electronic absorption spectra were measured on a Shimadzu UV-1601 spectrophotometer for ZnO powders as suspensions in minimal water amounts. Photoluminescence (PL) Emission Spectra were measured for aqueous suspensions of ZnO powder on a Perkin-Elmer LS50 Luminescence Spectrometer. Excitation wavelength 325 nm was used. XRD patterns were measured on a Philips XRD XPERTPRO diffracto-meter with Cu K_α radiation (λ = 1.5418 Å) located in the labs of Dansuk Industrial Co., LTD., South Korea. Field Emission-Scanning Electron Micrographs (FE-SEM) were measured on a Jeol Model JSM-6700 F microscope, in the labs of Dansuk Industrial Co., LTD. South Korea. Atomic absorption spectra (AAS) were used to measure zinc ions resulting from possible degradation of ZnO. The AAS results were measured on an ICE3000 Thermoscientific Atomic Absorption Spectrophotometer equipped with a zinc lamp.

Catalytic experiment

Photo-catalytic experiments were conducted under direct irradiation from the solar simulator lamp. Water samples pre-contaminated with known concentrations of methyl orange were placed inside a 250 mL beaker. Known nominal amounts of the catalyst ZnO powder were added. The mixture was magnetically stirred with a magnetic bar for 15 min in the dark, to allow adsorption equilibrium and to assess amounts of adsorbed methyl orange on the solid catalyst. The pH of the reaction mixture was controlled by adding drops of dilute HCl or NaOH solutions. The solar simulator lamp, vertically clamped above the solution with an adjustable stand, was then switched on with continuous stirring. The desired irradiation intensity on the mixture surface was achieved by controlling the lamp distance. The reaction time was calculated the time the lamp was switched on. Certain experiments were conducted in duplicate to check the reproducibility of the process.

The reaction progress was followed by measuring the amount of remaining methyl orange with time. This was performed by syringing out small aliquots of reaction mixture at certain times. The aliquots were then centrifuged at high speed (5000 rpm) for 5 min. The liquid phase was then carefully syringed out and analyzed spectrophotometrically at 480 nm.

Results and discussion

Zinc oxide powder characterization

Solid state electronic absorption spectra were measured for the prepared ZnO nano-powder as aqueous suspension. ZnO showed absorption with a maximum at ~368 nm (equivalent to 3.37 eV), Fig. 2. The wide band gap is presumably due to small average particle size, since smaller particles exhibit wider band gap values [41].

The photoluminescence emission spectrum was measured for lab-prepared ZnO powder as dispersion in water, using excitation wavelength 325 nm. The ZnO suspension showed an emission peak at ~385 nm (~3.2 eV), Fig. 3. The other two emission peaks at ~445 nm and ~483 nm are attributed to the presence of oxygen vacancies which cause crystal imperfections, as reported earlier [42]. The value of the band gap is not far different from that measured by electronic absorption spectra discussed above.

Figure 4 shows the XRD patterns for ZnO nano-powder. The ZnO clearly involves a wurtzite form, based on comparison with earlier literature results [43]. Based on Scherrer equation approximations, the average particle size was calculated to be ~19 nm.

SEM was used to study the surface morphology and to further estimate the particle size of prepared ZnO powders, Fig. 5. The micrograph showed elongated nano-rods (with rice-shape) of ZnO agglomerates. The agglomerates involved nano-particles of less than 20 nm size.

Methyl orange photo-degradation

Exposure of aqueous solutions of methyl orange to solar simulator lamp, in the presence of ZnO nano-powder, caused appreciable de-colorization of methyl orange solution in soundly short times. Control experiments conducted in the dark, using catalyst while keeping other conditions the same, showed no detectable de-colorization. This means that no degradation occurred in the dark, and that the ZnO powder adsorbs only little fraction of the contaminant. Control experiments conducted with irradiation in the absence of ZnO did not show any noticeable de-colorization with prolonged exposure. This indicates the necessity of the ZnO particles to activate the methyl orange
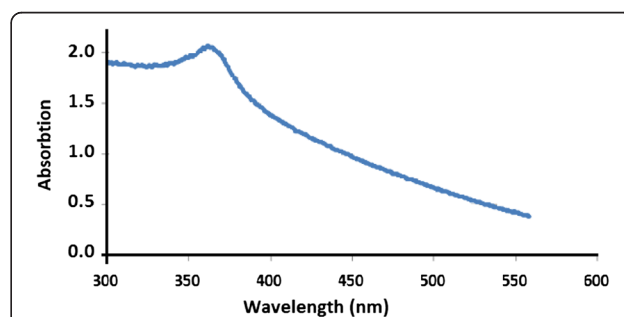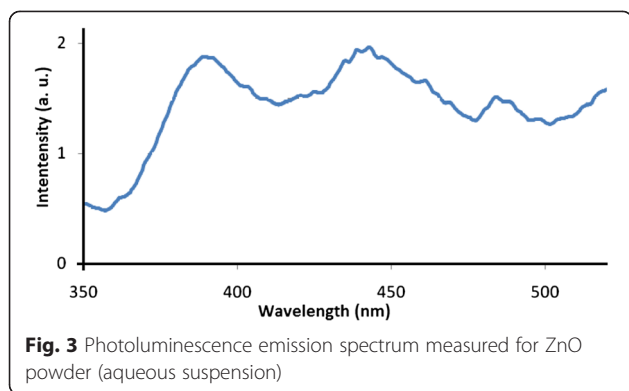
Fig. 2 Electronic absorption spectrum for lab-prepared ZnO powder (aqueous suspension)

Fig. 3 Photoluminescence emission spectrum measured for ZnO powder (aqueous suspension)

Fig. 5 SEM micrograph of lab-prepared ZnO powder

degradation. Using a cut-off filter (that blocks light 400 nm and shorter) caused severe lowering in methyl orange degradation. Collectively, these results indicate that light waves shorter than 400 nm are the driving force for the degradation of methyl orange, and that the ZnO particles are needed to observe the degradation process. Degradation is thus due to the shorter wave length tail available in the lamp light. With a band gap more than 3.2 eV, ZnO powder catalyst employs photons with wavelength shorter than 400 nm in the photo-degradation process.

Therefore, methyl orange de-colorization here, even in case of incomplete process, is due to complete mineralization of the degraded molecules. This was evident from the disappearance of absorbance bands in the range 200–300 nm (characteristic for the phenyl group) and the range 400–500 nm (characteristic for the azo group). When left for enough time, complete removal and complete mineralization were observed, as shown in Fig. 6 below. Therefore, the reacted phenyl group is believed to be completely degraded leaving no organic products. The reacted azo group is also believed to escape as N_2 gas [44, 45]. Complete photo-mineralization of methyl orange molecules lost under the working conditions is well documented [37, 46–54].

In order to assess the ability of ZnO to photo-degrade aqueous methyl orange under simulated natural conditions
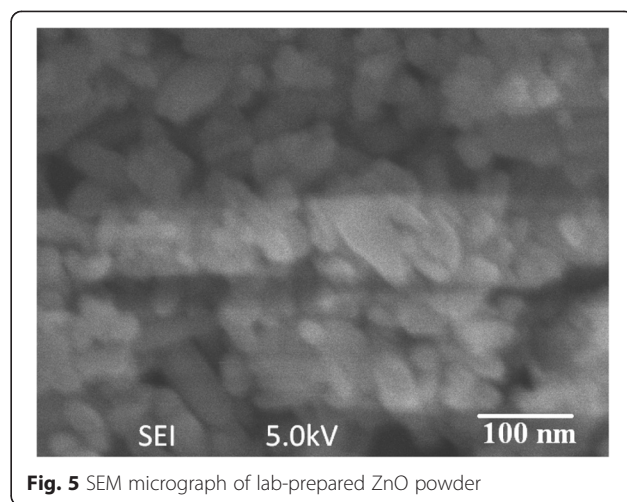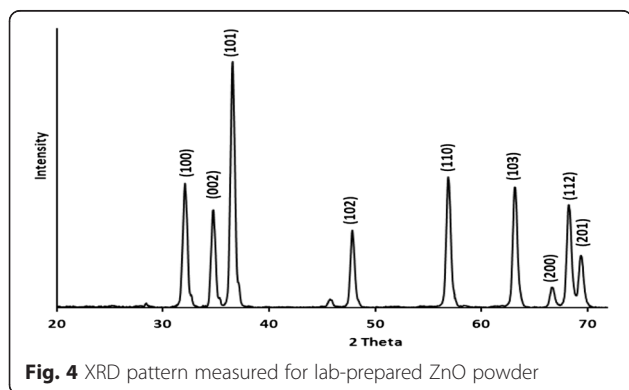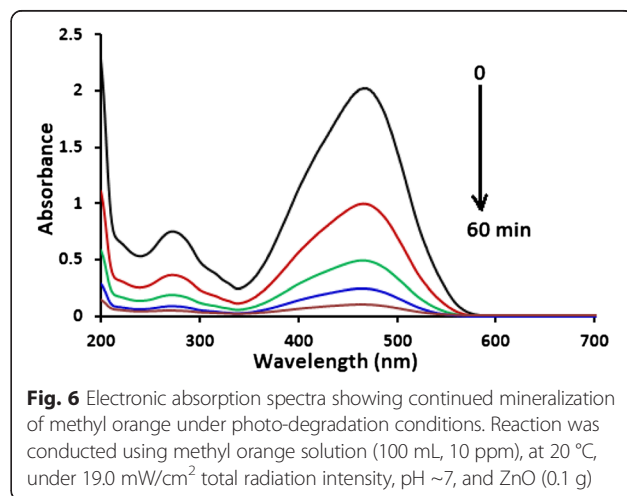
different parameters were investigated here. Effects of different reaction parameters, such as pH, catalyst concentration and contaminant concentration, on rate of photo-degradation were reported earlier [55]. The parameters (initial nominal pH, methyl orange concentration and ZnO amount) have been revisited here together with other new parameters (aqueous CO_2 concentration, temperature, light intensity and catalyst reuse).

The remaining methyl orange concentrations were plotted with exposure time. The catalytic efficiency is better understood in terms of turnover number, T.N. (degraded molecules/Zn atoms) and quantum yield, Q.Y., (degraded molecules/total incident photons) measured after 30 min exposure to radiation.

Effect of pH on photo-degradation process

Because the amphoteric nature of ZnO, it is necessary to study the effect of the pH value on the methyl orange photo-degradation process. This is also necessary as

Fig. 4 XRD pattern measured for lab-prepared ZnO powder

Fig. 6 Electronic absorption spectra showing continued mineralization of methyl orange under photo-degradation conditions. Reaction was conducted using methyl orange solution (100 mL, 10 ppm), at 20 °C, under 19.0 mW/cm² total radiation intensity, pH ~7, and ZnO (0.1 g)

Zyoud et al. Journal of Environmental Health Science & Engineering (2015) 13:46

Page 5 of 10

natural waters normally have pH values in the range 5–8 [56, 57].

The pH value affects the ZnO surface OH groups [58], the methylene orange and the aqueous solution species. The pH value affects the generation of the oxidizing species (•OH, $O_2\bullet^-$, H_2O_2 and $HO_2\bullet$) that result in the reaction system [59, 60]. The nature of methyl orange molecule varies with pH value, as stated above. ZnO has a point of zero charge at pH 9.0, above which the ZnO surface is predominantly negatively charged [13]. The electrical properties of the ZnO surface may thus vary with the pH.

Experiments were carried out at pH values of (2.5, 5, 7, 9 and 11), Fig. 7. The slightly acidic solution (pH ~5) showed highest T.N. and Q.Y. values, followed by neutral solution. Both solutions with pH 5 and 7 showed complete removal of methyl orange after 60 min of irradiation. As discussed above removal of methyl orange involves complete mineralization, which shows the practicality of using the photo-degradation in natural systems. More acidic or basic solutions (less 2.5 or higher than 9) showed T.N. and Q.Y. values nearly half of those under mild solutions. Table 1 summarizes these results.

In basic media, ZnO becomes $Zn(OH)_2$ form with lower semiconducting properties [61]. Under lower pH conditions the lowering in removal efficiency is possibly due to the dissolution of ZnO into Zn^{2+} ions [62], and in highly basic media the ZnO yields zincate ion ZnO_2^{-2} [63]. The results show that the optimum photo-degradation is close to natural water conditions (neutral to slightly acidic), which adds to the credibility of using ZnO catalyst system. Therefore, unless otherwise stated, all results described here-in-after were obtained under initial nominal pH 7.
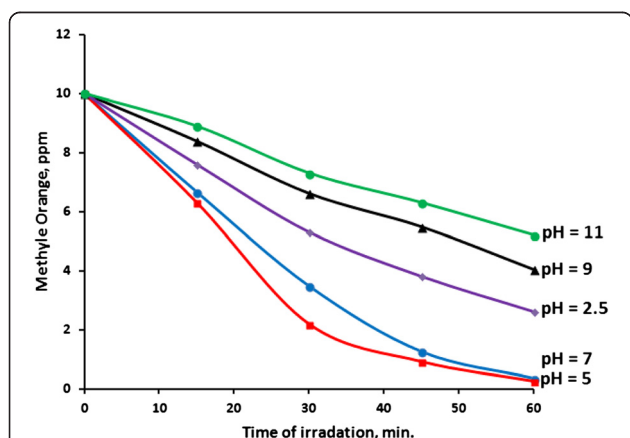
Table 1 Effect of pH on photo-degradation of aqueous methyl orange. Reactions were conducted using methyl orange solutions (100 mL, 10 ppm) and ZnO (0.1 g) at 20 °C under total radiation intensity 19.0 mW/cm^2

pH	~7	~5	~2.5	~9	~11
T.N.	1.62×10^{-3}	1.94×10^{-3}	1.17×10^{-3}	8.42×10^{-4}	6.71×10^{-4}
Q.Y.	4.36×10^{-4}	4.28×10^{-4}	2.92×10^{-4}	2.12×10^{-4}	1.74×10^{-4}
% Degradation	100 %	100 %	73 %	60 %	48 %

Effect of temperature

At temperatures in the range 20–40 °C, the ZnO catalyst showed sound activity, reaching up to 85 % methyl orange removal within 60 min. At lower temperatures, ~ 10 °C, the reaction went slower, reaching up to 65 % removal within 60 min. Figure 8 shows effect of working temperature on the methyl orange phtodegradation reaction profiles. If left for longer time, methyl orange is expected to continue even at lower temperatures. Table 2 summarizes values of TN, QY and degradation% measured at different temperatures. The results show the applicability of using the ZnO system in removing methyl orange with simulated solar light. In this work, unless otherwise stated, all study was performed at 20 °C.

If higher temperatures (above 45 °C) are used, the reaction goes slower. This is due to possible escape of the oxygen molecules dissolved inside oxygen. The oxygen molecules are involved with the mechanism of photodegradation reaction. Similar results were observed in earlier reports [53].

Effect of CO_2 and other gas flows

The effect of CO_2 flow on methyl orange photo-degradation was investigated by measuring the reaction profiles for the process while passing a flow of CO_2 gas. The stream of CO_2 (90 mL/min), while keeping all other

Fig. 7 Effect of pH on photo-degradation of aqueous methyl orange. Reactions were conducted using methyl orange solutions (100 mL, 10 ppm) and ZnO (0.1 g) at 20 °C under total radiation intensity 19.0 mW/cm^2

Fig. 8 Effect of temperature on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 20 ppm) at different temperatures, using ZnO catalyst (0.1 g) under total irradiation intensity of 19.0 mW/cm^2 at pH ~7

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46
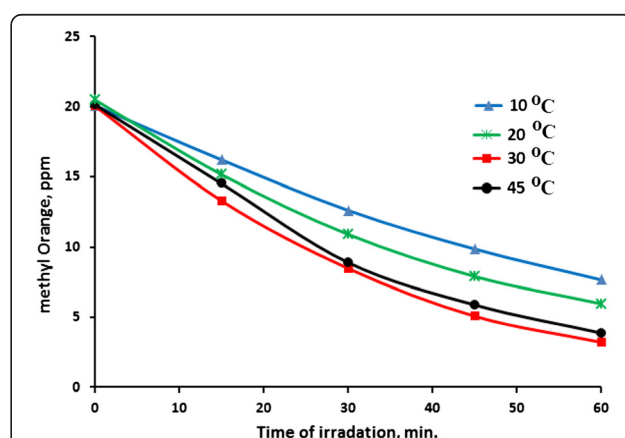
Page 6 of 10

Table 2 Effect of temperature on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 20 ppm) at different temperatures, using ZnO catalyst (0.1 g) under total irradiation intensity of 19.0 mW/cm^2 at pH ~7

Temp.	10 °C	20 °C	30 °C	45 °C
T.N.	1.86×10^{-3}	2.38×10^{-3}	2.87×10^{-3}	2.80×10^{-3}
Q.Y.	3.52×10^{-4}	4.28×10^{-4}	5.44×10^{-4}	5.29×10^{-4}
% Degradation	62 %	70 %	84 %	81 %

Table 3 Effect of gas streams on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 20 ppm) under 19.0 mW/cm^2 irradiation using ZnO (0.1 g) with continuous stirring at 20 °C

	Exposed to air only	Air flow	N_2 flow open system	CO_2 and air flows together	CO_2 flow
T.N.	2.87×10^{-3}	1.72×10^{-3}	1.44×10^{-3}	0.75×10^{-3}	1.03×10^{-3}
Q.Y.	5.44×10^{-4}	3.25×10^{-4}	2.72×10^{-4}	1.42×10^{-4}	1.95×10^{-4}
% Degradation	84 %	52 %	50 %	25 %	19 %

reaction parameters the same, significantly slowed down the removal of the methyl orange, as shown in Fig. 9. Table 3 summarizes values of TN, QY and degradation% while using CO_2 gas stream. The mode of action of CO_2 on lowering the reaction rate is not due to lowering the solution pH, as the pH was lowered only slightly, from 6.8 (the nominal used pH) to 6.4, after 60 min. As discussed above the pH in the range 5–8 does not inhibit methyl orange removal process. Alternatively, the mode of action of CO_2 is thus due to its ability to react with the radicals formed during the photo-degradation process. As reported earlier, *"CO_2 may interact with some free radical species and may either propagate or inhibit free radical chain reactions"* [64]. In this work the CO_2 clearly inhibits photo-degradation of methyl orange by interacting with the free radicals believed to be formed during the reaction process. The results reflect a warning signal about the negative impact of possible

CO_2 higher concentrations in natural waters, which would result from increased atmospheric CO_2 concentration. Having natural waters with higher CO_2 concentrations may negatively affect future water purification processes.

CO_2 gas stream may arguably affect photodegradation rate by removing oxygen dissolved in the reaction mixture. This was investigated using two continuous streams of CO_2 and air together. Figure 9 shows that using the air (1000 mL/min) stream with the CO_2 stream (90 mL/min) did not show significant enhancement in photo-degradation reaction rate. This result further confirms the discussion above, where CO_2 captures the free radicals necessary for the photodegradation to occur.

Adding a stream of air alone did not increase the reaction rate. Figure 9 shows that the air stream lowered the reaction rate by about 25 % compared to experiments conducted under normal air. In a well known mechanism [40], oxygen molecule is assumed to abstract one electron from the excited ZnO particle leading to $O_2\bullet^-$ radical anion species as explained in the equation [$e^- + O_2 \rightarrow O_2\bullet^-$]. The $O_2\bullet^-$ species is believed to react with the other H_2O_2 resulting species to yield the chemically active OH$^\cdot$ radical as in the equation [$H_2O_2 + O_2\bullet^- \rightarrow OH^\bullet + OH^- + O_2$]. This radical is assumed to react with an organic contaminant molecule and degrade it.

Therefore, the presence of O_2 in water is necessary. However, as the results here show, excess of O_2 in water inhibits the photodegradation reaction. This is due to the adverse effect of excess O_2 which blocks OH$^\bullet$ radical as shown in equation [$H_2O_2 + O_2\bullet^- \rightarrow OH^\bullet + OH^- + O_2$].

Adding nitrogen to the reaction mixture together with CO_2 practically stopped the reaction progress (Fig. 9). The effect is perhaps dual in nature, where the CO_2 behaves as scavenger, as discussed above, while the nitrogen lowers concentration of oxygen that is necessary for the reaction to proceed. Adding a nitrogen flow (240 mL/min) to the reaction mixture, while exposed to atmospheric air, slowed down the process, but did not stop it completely. Nitrogen lowers concentrations of oxygen in the reaction but traces are left therein which are enough for the reaction to occur. All reactions above
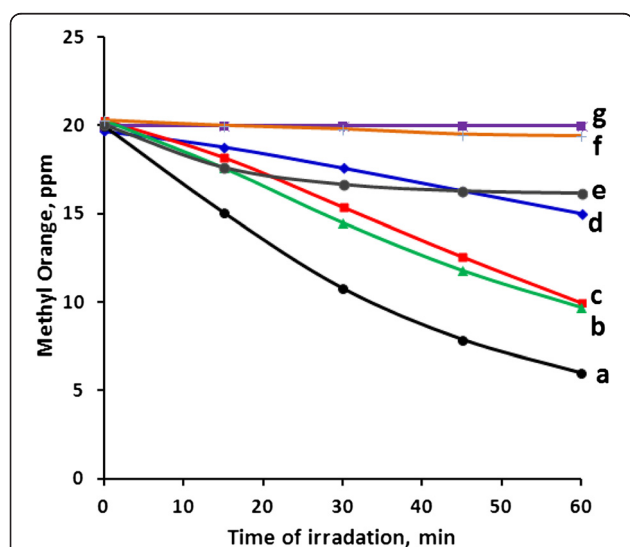

Fig. 9 Effect of gas streams on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 20 ppm) under 19.0 mW/cm^2 irradiation using ZnO (0.1 g) with continuous stirring at 20 °C with different gas flows: (**a**) exposed to air only, (**b**) air flow, (**c**) N_2 flow open system, (**d**) CO_2 and air flows together, (**e**) CO_2 flow, (**f**) closed system with nitrogen flow, (**g**) N_2 and CO_2 flows together

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46

Page 7 of 10

were conducted under exposure to atmospheric air. This is evident because complete coverage from air while under nitrogen stream caused complete reaction inhibition.

Effect of contaminant concentration

The effect of methyl orange concentration (10, 20, 30 and 40 ppm) on its photodegradation process was studied, Fig. 10. Values of percent methyl orange removal, after 60 min, were 100 % for 10 ppm, 70 % for 20 ppm, 66 % for 30 ppm, 45 % for 40 ppm, as summarized in Table 4. Despite the lowering in removal percentage with higher contaminant concentration, the average reaction rate increased. Values of T.N. and Q.Y. show comparable values for the 20, 30, and 40 ppm concentrations. Lower values were observed for the 10 ppm concentration, which is due to the fact that all added methyl orange molecules were mineralized with no more left. This naturally yields lower TN and QY values at lower contaminant concentrations. The results indicate the suitability of ZnO catalyst to function over a relatively wide range of contaminant concentrations. More importantly, the catalyst completely activates mineralization of low contaminant concentrations, which are more likely to occur in nature [37, 53].

Effect of catalyst nominal amount on photo-degradation process

Catalyst amount may affect photo-degradation processes. The effect of catalyst nominal amount on the photodegradation of methyl orange was investigated using different amounts of ZnO (0.05, 0.10, 0.20 or 0.30 g) in 100 mL solution of 10 ppm methyl orange, under 19.0 mW/cm^2 irradiation intensity. Figure 11 shows that the average reaction rate was unchanged with

Table 4 Effect of contaminant concentration on its photo-degradation. Reactions were conducted using different contaminant concentrations in aqueous solution (100 mL), pH ~7, at 20 °C with ZnO (0.1 g) under 19.0 mW/cm^2 irradiation intensity

	10 ppm	20 ppm	30 ppm	40 ppm
T.N.	1.73×10^{-3}	2.38×10^{-3}	2.37×10^{-3}	2.29×10^{-3}
Q.Y.	4.36×10^{-4}	4.28×10^{-4}	4.48×10^{-4}	4.17×10^{-4}
% Degradation	100 %	70 %	66 %	45 %

catalyst nominal amount. The T.N. value decreased with increasing ZnO amount, as shown in Table 5. This means that the relative efficiency of the catalyst is lowered by increasing catalyst loading. Similar results were observed in other photo-degradation processes [37, 53, 54, 65, 66]. This is attributed to the increased blocking of light with higher catalyst loading. With more catalyst particles, the short wave tail photons are not able to enter the reaction mixture, and the ZnO particles in the reaction mixture do not receive photons. Similar behaviors have been observed in earlier studies [14, 64, 65].

The QY value showed an increase with increasing nominal catalyst amount at the beginning, but then slightly decreased. Again the lowering in QY is due to the blocking of light by the abundant ZnO particles at the mixture surface which prevent photons from reaching other catalyst sites [14, 37, 53, 54, 65–67]. Agglomeration of smaller ZnO particles into larger ones, in case of higher concentrations, may also play a role, as the total number of surface active sites may decrease [67]. The results indicate that using smaller amounts of catalyst enhanced catalyst efficiency without lowering the average reaction rate or the removal percentage. This is
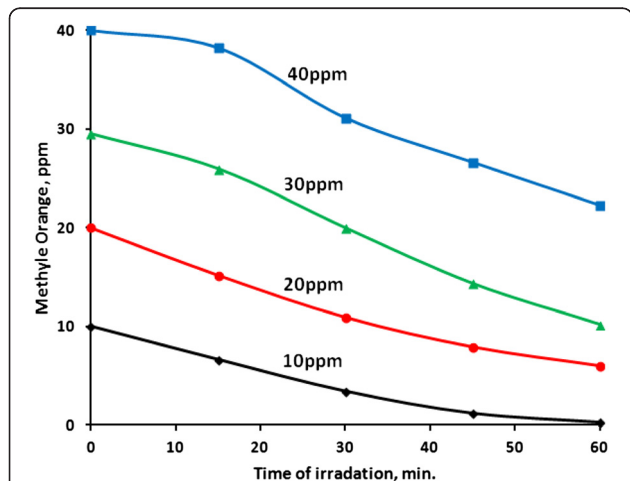

Fig. 10 Effect of contaminant concentration on its photo-degradation. Reactions were conducted using different contaminant concentrations in aqueous solution (100 mL), pH ~7, at 20 °C with ZnO (0.1 g) under 19.0 mW/cm^2 irradiation intensity
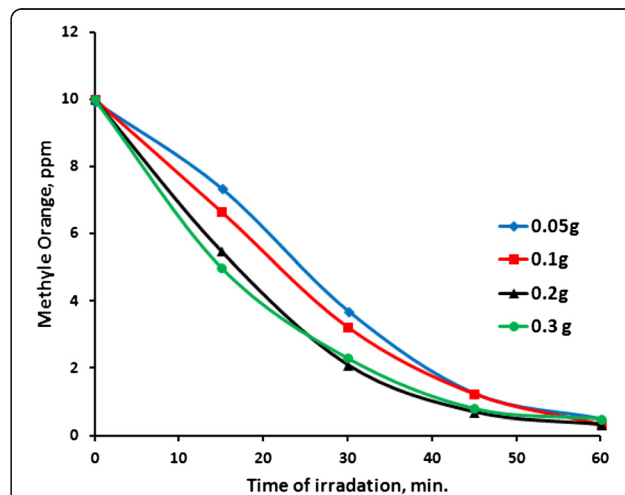

Fig. 11 Effect of catalyst amount on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 10 ppm) at 20 °C pH ~7, under 19.0 mW/cm^2

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46

Page 8 of 10

Table 5 Effect of catalyst amount on methyl orange photo-degradation. Reactions were conducted using methyl orange solution (100 mL, 10 ppm) at 20 °C pH ~7, under 19.0 mW/cm^2

	0.05 g	0.10 g	0.20 g	0.3 g
T.N.	3.10×10^{-3}	1.68×10^{-3}	9.82×10^{-4}	9.57×10^{-4}
Q.Y.	2.93×10^{-4}	3.19×10^{-4}	3.72×10^{-4}	3.62×19^{-4}
% Degradation	95 %	100 %	100 %	100 %

a positive feature of the ZnO catalyst described here, as in case of treating natural waters, smaller amounts of catalyst will be highly favored.

Effect of light intensity on the photodegraation process

The effect of incident light intensity on photodegradation rate of methyl orange was investigated, using solutions (100 mL each) with two different concentrations (10 and 20 ppm). Experiments were conducted under different light intensities using 0.10 g of ZnO lab prepared powder. In each contaminant concentration, four different light intensities (1.90, 5.12, 8.78 and 19.0 mW/cm^2) were used. This range includes the average reported daylight intensity of 120 W/m^2 (12 mW/cm^2) [68]. Figure 12 shows how methyl orange removal percentage changed with illumination intensity in a period of 30 min for each contaminant concentration. For the 10 ppm concentration case, up to 100 % removal was observed for the higher radiation intensities (5.12, 8.78, and 19 mW/cm^2), and up to 50 % removal for the lower intensity (1.9 mW/cm^2), in 30 min. For the 20 ppm concentration case, up to 70 % contaminant removal was observed in 30 min (at the higher radiation intensities, and up to 35 % at the lower irradiation intensity). The results indicate the applicability of using ZnO in

Table 6 Effect of light intensity on methyl orange photo-degradation. Reactions were conducted using two different methyl orange concentrations in 100 mL solution at pH ~7 with ZnO (0.1 g) at 20 °C

10 ppm	1.90 mW/cm^2	5.12 mW/cm^2	8.78 mW/cm^2	19.0 mW/cm^2
T.N.	6.96×10^{-4}	1.5×10^{-3}	1.58×10^{-3}	1.73×10^{-3}
Q.Y.	1.42×10^{-3}	1.35×10^{-3}	6.57×10^{-4}	4.36×10^{-4}
% Degradation	54 %	95 %	96 %	100 %
20 ppm	1.90 mW/cm^2	5.12 mW/cm^2	8.78 mW/cm^2	19.0 mW/cm^2
T.N.	7.96×10^{-4}	1.86×10^{-3}	1.99×10^{-3}	2.38×10^{-3}
Q.Y.	1.62×10^{-3}	1.41×10^{-3}	8.76×10^{-4}	4.28×10^{-4}
% Degradation	34 %	58 %	65 %	70 %

removing methyl orange from contaminated water even under radiation intensities lower than normal day light.

Values of TN and QY calculated after 30 min for each case are shown in Table 6. In case of 10 ppm, the lower irradiation intensity (1.9 mW/cm^2) showed lower TN value (about 50 %) than its higher intensity counterparts (5.12, 8.78, and 19 mW/cm^2). From the Table and the Figure, it can be seen that under 5.12 mW/cm^2 or higher, the removal percentage reaches approximately constant value. With lower intensity, lower TN value should be expected, as less photons are available for the catalyst sites. However, as radiation intensity is increased above 5.12 mW/cm^2, efficiency of light harvesting becomes less. This is evident from values of QY, which decreased when using higher irradiation intensities.

For the 20 ppm methyl orange concentration, similar behavior occurred, but the irradiation intensity 5.12 mW/cm^2 showed highest QY. Collectively the results suggest
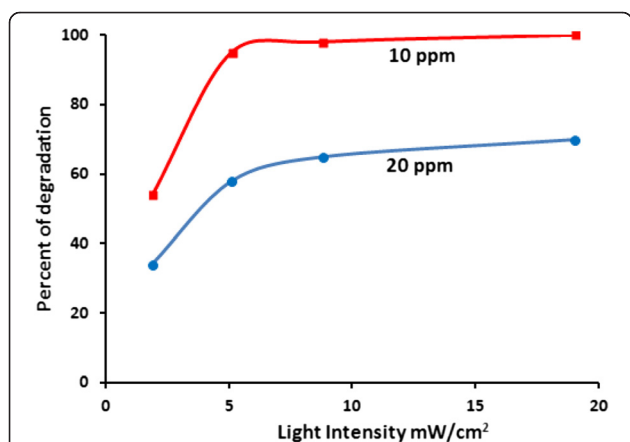

Fig. 12 Effect of light intensity on methyl orange photo-degradation. Reactions were conducted using two different methyl orange concentrations in 100 mL solution at pH ~7 with ZnO (0.1 g) at 20 °C
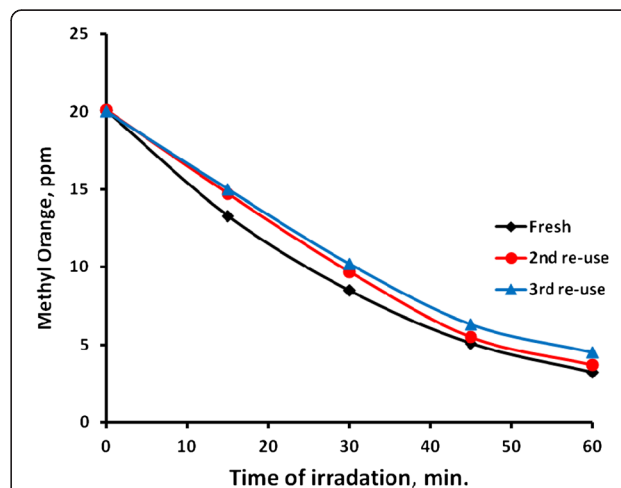

Fig. 13 Effect of catalyst reuse on methyl orange photo-degradation. Reactions were conducted using fresh methyl orange solutions (100 mL, 20 ppm) in multiple use of the ZnO catalyst (0.1 g) at 20 °C, pH 7 under 19.0 mW/cm^2 irradiation intensity

Zyoud et al. Journal of Environmental Health Science & Engineering (2015) 13:46

Page 9 of 10

that it is not necessary to use high irradiation intensities to remove methyl orange from water. This adds to the applicability of using ZnO in natural water purification processes in different environments with different light intensities.

Catalyst re-use experiments

Reusability of the ZnO catalyst for methyl orange photo-degradation in water was studied, by adding fresh amount of methyl orange to the stirred solution after earlier reaction cessation. Figure 13 shows reaction profiles for three time reuse experiments. The Figure shows that at the beginning of each reuse experiment, the measured amount of the methyl orange was 20 ppm. This is due to complete removal of the earlier methyl orange contaminant in the preceding study, as the reaction was left for enough time. In each experiment, after 60 min time of exposure, more than 80 % removal was achieved, showing only low loss of efficiency with reuse.

The amount of Zn^{2+} ions resulting from dissolution of the used ZnO catalyst (with different amounts 0.05–0.3 g per 100 mL solution) during photo-degradation experiments in neutral media was measured by AAS, and was found to be 6 ppm, when the mixture was left overnight. In case of more acidic media the amount was higher, up to 8 ppm. This indicates that only a small fraction of ZnO dissolved under the working conditions. Based on literature [69] the value for solubility of Zn ions resulting from nano-scale ZnO is about 7 ppm. The WHO recommended upper limit for Zn ions is ~5 ppm [70]. The Zn^{2+} ions dissolved in this work is not far from the recommended WHO threshold limits. The results add to the credibility of using ZnO in purification of natural waters.

Conclusion

Nano-scale ZnO particles can be effectively used as catalysts for complete mineralization of methyl orange in water with solar simulated light. The catalyst can be effectively used under different working conditions (including temperature and pH) that resemble natural waters, and can thus be investigated at larger scale in natural water purification. Adding streams of air, CO_2 gas, and/or N_2 gases may affect the reaction progress and may inhibit the reaction.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
AZ participated in supervising research, catalytic experimental design, experimental work, data analysis and writing up. AZ performed catalytic experiments. DP and GC conducted advanced characterization. MH participated with writing up, library search and research ideas. The preparations and catalytic study were performed in H. S. H. laboratory. He participated in writing up, provided technical solutions and new ideas. All authors read and approved the final manuscript.

Author details
[1]SSERL, Department of Chemistry, An-Najah National University, Nablus, Palestine. [2]College of Pharmacy and Nutrition, University of Saskatchewan, 116 Thorvaldson Building, Saskatoon S7N 5C9, Canada. [3]Dansuk Industrial Co, LTD. #1239-5, Jeongwang-Dong, Shiheung-Si, Kyonggi-Do 429-913, South Korea. [4]Institut de Chimie de la Matie're Condense'ie de Bordeaux (ICMCB), 87 Avenue du Dr. A Schweitzer, Pessac 33608, France.

References
1. Bianco Prevot A, Baiocchi C, Brussino MC, Pramauro E, Savarino P, Augugliaro V, et al. Photocatalytic degradation of acid blue 80 in aqueous solutions containing TiO_2 suspensions. Environ Sci Technol. 2001;35:971–6.
2. McMullan G, Meehan C, Conneely A, Kirby N, Robinson T, Nigam P, et al. Microbial decolourisation and degradation of textile dyes. Appl Microbiol Biotechnol. 2001;56:81–7.
3. Pearce C, Lloyd J, Guthrie J. The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes and Pigments. 2003;58:179–96.
4. Marcucci M, Nosenzo G, Capannelli G, Ciabatti I, Corrieri D, Ciardelli G. Treatment and reuse of textile effluents based on new ultrafiltration and other membrane technologies. Desalination. 2001;138:75–82.
5. Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol. 2001;77:247–55.
6. Tahir S, Rauf N. Removal of a cationic dye from aqueous solutions by adsorption onto bentonite clay. Chemosphere. 2006;63:1842–8.
7. Arslan I, Akmehmet Balcioğlu I, Tuhkanen T. Oxidative treatment of simulated dyehouse effluent by UV and near-UV light assisted Fenton's reagent. Chemosphere. 1999;39:2767–83.
8. Kuo W. Decolorizing dye wastewater with Fenton's reagent. Water Res. 1992;26:881–6.
9. Rice RG. Applications of ozone for industrial wastewater treatment—a review. Ozone Sci Eng. 1996;18:477–515.
10. Dodd MC, Buffle M-O, Von Gunten U. Oxidation of antibacterial molecules by aqueous ozone: moiety-specific reaction kinetics and application to ozone-based wastewater treatment. Environ Sci Technol. 2006;40:1969–77.
11. Glaze WH, Kang J-W, Chapin DH. The chemistry of water treatment processes involving ozone, hydrogen peroxide and ultraviolet radiation. Environ Sci Technol. 1987;39(10):3409–20.
12. Herrmann J-M. Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. Catal Today. 1999;53:115–29.
13. Daneshvar N, Salari D, Khataee A. Photocatalytic degradation of azo dye acid red 14 in water on ZnO as an alternative catalyst to TiO_2. J Photochem Photobiol A Chem. 2004;162:317–22.
14. Mai F, Chen C, Chen J, Liu S. Photodegradation of methyl green using visible irradiation in ZnO suspensions: determination of the reaction pathway and identification of intermediates by a high-performance liquid chromatography–photodiode array-electrospray ionization-mass spectrometry method. J Chromatogr A. 2008;1189:355–65.
15. Turchi CS, Ollis DF. Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J Catal. 1990;122:178–92.
16. Umebayashi T, Yamaki T, Tanaka S, Asai K. Visible light-induced degradation of methylene blue on S-doped TiO2. Chem Lett. 2003;32:330–1.
17. Tayade RJ, Surolia PK, Kulkarni RG, Jasra RV. Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO_2. Sci Technol Adv Mater. 2007;8:455–62.
18. Ding Z, Zhu H, Lu G, Greenfield P. Photocatalytic properties of Titania pillared clays by different drying methods. J Colloid Interface Sci. 1999;209:193–9.
19. Fox MA, Dulay MT. Heterogeneous photocatalysis. Chem Rev. 1993;93:341–57.

Zyoud *et al. Journal of Environmental Health Science & Engineering* (2015) 13:46

Page 10 of 10

20. Hagfeldt A, Graetzel M. Light-induced redox reactions in nanocrystalline systems. Chem Rev. 1995;95:49–68.
21. Hoffmann MR, Martin ST, Choi W, Bahnemann DW. Environmental applications of semiconductor photocatalysis. Chem Rev. 1995;95:69–96.
22. Panayotov DA, Yates JT. Spectroscopic detection of hydrogen atom spillover from Au nanoparticles supported on TiO_2: use of conduction band electrons. J Phys Chem C. 2007;111:2959–64.
23. Hong W-K, Sohn Jl, Hwang D-K, Kwon S-S, Jo G, Song S, et al. Tunable electronic transport characteristics of surface-architecture-controlled ZnO nanowire field effect transistors. Nano Lett. 2008;8:950–6.
24. Dorfman A, Kumar N, Hahm J-i. Nanoscale ZnO-enhanced fluorescence detection of protein interactions. Adv Mater. 2006;18:2685–90.
25. Bao J, Zimmler MA, Capasso F, Wang X, Ren Z. Broadband ZnO single-nanowire light-emitting diode. Nano Lett. 2006;6:1719–22.
26. Law M, Greene LE, Johnson JC, Saykally R, Yang P. Nanowire dye-sensitized solar cells. Nat Mater. 2005;4:455–9.
27. Sakthivel S, Neppolian B, Shankar M, Arabindoo B, Palanichamy M, Murugesan V. Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2. Sol Energy Mater Sol Cells. 2003;77:65–82.
28. Gouvea CA, Wypych F, Moraes SG, Duran N, Nagata N, Peralta-Zamora P. Semiconductor-assisted photocatalytic degradation of reactive dyes in aqueous solution. Chemosphere. 2000;40:433–40.
29. Lizama C, Freer J, Baeza J, Mansilla HD. Optimized photodegradation of reactive blue 19 on TiO2 and ZnO suspensions. Catal Today. 2002;76:235–46.
30. Lachheb H, Puzenat E, Houas A, Ksibi M, Elaloui E, Guillard C, et al. Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. Appl Catal Environ. 2002;39:75–90.
31. Kandavelu V, Kastien H, Thampi KR. Photocatalytic degradation of isothiazolin-3-ones in water and emulsion paints containing nanocrystalline TiO_2 and ZnO catalysts. Appl Catal Environ. 2004;48:101–11.
32. MSDS. Material Safety Data Sheet,Methyl orange MSDS, Fisher Scientific, 1 Reagent Lane, Fair Lawn, NJ 07410. 2000.
33. Sandberg RG, Henderson GH, White RD, Eyring EM. Kinetics of acid dissociation-ion recombination of aqueous methyl orange. J Phys Chem. 1972;76:4023–5.
34. Windholz M, Budavari S. The merck index. Merck and Co. Rahway; 1983.
35. Maynard C. Riegel's Handbook of Industrial Chemistry. In Book Riegel's Handbook of Industrial Chemistry (Editor ed.^eds.). City: JA Kent, ed; 1983.
36. Shih Y-H, Tso C-P, Tung L-Y. Rapid degradation of methyl orange with nanoscale zerovalent iron particles. Nanotechnology. 2010;7:16–7.
37. Hilal HS, Al-Nour GY, Zyoud A, Helal MH, Saadeddin I. Pristine and supported ZnO-based catalysts for phenazopyridine degradation with direct solar light. Solid State Sci. 2010;12:578–86.
38. Hilal SH, Nour G, Zyoud A. Photo-degradation of Methyl Orange with Direct Solar Light Using ZnO and Activated Carbon-supported ZnO. In: Water purification. New York: Nova Science Publishers, Inc; 2009. p. 227–46.
39. Hejjawi S. TiO_2 and ZnO photocatalysts for degradation of widespread pharmaceutical wastes: Effect of particle size and support. MSc Thesis, An-Najah N. University. 2013.
40. Amer H. ZnO nano-particle catalysts in contaminant degradation processes with solar light naked and supported systems. MSc Thesis, An-Najah N. University. 2012.
41. Gupta A, Bhatti H, Kumar D, Verma N, Tandon R. Nano and bulk crystals of ZnO: synthesis and characterization. Digest Int J Nanomat Biostruct. 2006;1:1–9.
42. Lopez-Romero S. Growth and characterization of ZnO cross-like structures by hydrothermal method. Matéria (Rio de Janeiro). 2009;14:977–82.
43. Akhtar MJ, Ahamed M, Kumar S, Khan MM, Ahmad J, Alrokayan SA. Zinc oxide nanoparticles selectively induce apoptosis in human cancer cells through reactive oxygen species. Int J Nanomedicine. 2012;7:845.
44. Dai K, Chen H, Peng T, Ke D, Yi H. Photocatalytic degradation of methyl orange in aqueous suspension of mesoporous Titania nanoparticles. Chemosphere. 2007;69:1361–7.
45. Attia AJ, Kadhim SH, Hussein FH. Photocatalytic degradation of textile dyeing wastewater using titanium dioxide and zinc oxide. J Chem. 2008;5:219–23.
46. Chen C, Wang Z, Ruan S, Zou B, Zhao M, Wu F. Photocatalytic degradation of Cl Acid Orange 52 in the presence of Zn-doped TiO_2 prepared by a stearic acid gel method. Dyes Pigments. 2008;77:204–9.
47. Zhou G, Deng J. Preparation and photocatalytic performance of Ag/ZnO nano-composites. Mater Sci Semicond Process. 2007;10:90–6.
48. Wang H, Xie C, Zhang W, Cai S, Yang Z, Gui Y. Comparison of dye degradation efficiency using ZnO powders with various size scales. J Hazard Mater. 2007;141:645–52.
49. Yu D, Cai R, Liu Z. Studies on the photodegradation of rhodamine dyes on nanometer-sized zinc oxide. Spectrochim Acta A Mol Biomol Spectrosc. 2004;60:1617–24.
50. Daneshvar N, Aber S, Dorraji MS, Khataee A, Rasoulifard M. Preparation and investigation of photocatalytic properties of ZnO nanocrystals: effect of operational parameters and kinetic study. Evaluation. 2008;900:6.
51. Shvalagin V, Stroyuk A, Kotenko I, Kuchmii SY. Photocatalytic formation of porous CdS/ZnO nanospheres and CdS nanotubes. Theor Exp Chem. 2007;43:229–34.
52. Byrappa K, Subramani A, Ananda S, Rai KL, Sunitha M, Basavalingu B, et al. Impregnation of ZnO onto activated carbon under hydrothermal conditions and its photocatalytic properties. J Mater Sci. 2006;41:1355–62.
53. Zyoud AH, Zaatar N, Saadeddin I, Ali C, Park D, Campet G, et al. CdS-sensitized TiO_2 in phenazopyridine photo-degradation: Catalyst efficiency, stability and feasibility assessment. J Hazard Mater. 2010;173:318–25.
54. Zyoud A, Zaatar N, Saadeddin I, Helal MH, Campet G, Hakim M, et al. Alternative natural dyes in water purification: anthocyanin as TiO_2-sensitizer in methyl orange photo-degradation. Solid State Sci. 2011;13:1268–75.
55. Hilal SH, Nour G, Zyoud A. Photo-degradation of methyl orange with direct solar light using ZnO and activated carbon-supported ZnO. Chapter Book Water Purif. 2009;Chapter 6:227–46.
56. Neal C, Hill T, Alexander S, Reynolds B, Hill S, Dixon AJ, et al. Stream water quality in acid sensitive UK upland areas; an example of potential water quality remediation based on groundwater manipulation. Hydrol Earth Syst Sci Discuss. 1997;1:185–96.
57. Hem JD. Study and interpretation of the chemical characteristics of natural water. Water Supply Paper 2254, Department of the Interior, US Geological Survey; Alexandria, 1985.
58. Zhang F, Zhao J, Shen T, Hidaka H, Pelizzetti E, Serpone N. TiO_2-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO_2 dispersions under visible light irradiation. Appl Catal Environ. 1998;15:147–56.
59. Chang C, Hsieh Y, Cheng K, Hsieh L, Cheng T, Yao K. Effect of pH on Fenton process using estimation of hydroxyl radical with salicylic acid as trapping reagent. 2008.
60. Zepp RG, Faust BC, Hoigne J. Hydroxyl radical formation in aqueous reactions (pH 3–8) of iron (II) with hydrogen peroxide: the photo-Fenton reaction. Environ Sci Technol. 1992;26:313–9.
61. Velmurugan R, Swaminathan M. An efficient nanostructured ZnO for dye sensitized degradation of reactive red 120 dye under solar light. Sol Energy Mater Sol Cells. 2011;95:942–50.
62. Marci G, Augugliaro V, Lopez-Munoz MJ, Martin C, Palmisano L, Rives V, et al. Preparation characterization and photocatalytic activity of polycrystalline ZnO/TiO2 systems. 2. Surface, bulk characterization, and 4-nitrophenol photodegradation in liquid–solid regime. J Phys Chem B. 2001;105:1033–40.
63. Laudise ER, Kolb E, Laboralories BT, Hiti IM, Jeriey N. The solubility of zincite in basic hydrothermal solvents. Amer Mineral. 1963;48:642.
64. Vesela A, Wilhelm J. The role of carbon dioxide in free radical reactions in organism. Physiol Res. 2002;51:335–40.
65. Zyoud AH, Hilal HS. Silica-supported CdS-sensitized TiO_2 particles in photo-driven water purification: Assessment of efficiency, stability and recovery future perspectives. Chapter in a book, Water Purification, Novascience Pub, NY (in Press, 2008) 2009.
66. Hilal HS, Nour GY, Zyoud A. Photodegradation of Methyl orange and phenazopyridine HCl with direct solar light using ZnO and activated carbonsupported ZnO, Water Purification Novascience Publ, NY. 2009. p. 227e246.
67. Chen C–C. Degradation pathways of ethyl violet by photocatalytic reaction with ZnO dispersions. J Mol Catal A Chem. 2007;264:82–92.
68. Guide W. Guide to Meteorological Instruments and Methods of Observation. In: Book Guide to Meteorological Instruments and Methods of Observation. Genf, Schweiz: Secretariat of the WMO; 2006.
69. Reed RB, Ladner DA, Higgins CP, Westerhoff P, Ranville JF. Solubility of nano-zinc oxide in environmentally and biologically important matrices. Environ Toxicol Chem. 2012;31:93–9.
70. Krenkel P. Water quality management. Elsevier; Burlington, e-Book 2012.