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Article

Treatment of Dark Humic Water Using Photocatalytic Advanced Oxidation (PAO) Processes under Visible and UV Light

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Abstract: The aim of the study was to investigate the application of photocatalytic advanced oxidation (PAO) for the treatment of water contaminated with dark humic material from fynbos biome plants, which cannot be treated by conventional methods. The study used a fynbos species (*Aspalathus linearis*) to create a model wastewater that was compared with a brew made from black tea (*Camellia sinensis*). Two photocatalysts (TiO_2 and ZnO) and three light sources (natural, halogen light, and UV light) were tested, with and without hydrogen peroxide. The treatment of the two teas by only photolysis was observed to be minimal. The study found that natural sunlight was not effective, but a combination of ZnO and halogen lamp exhibited the best performance, with a 60% degradation in 20 min under solar irradiation. The optimum catalyst concentration was identified as 10 g/L for both photocatalysts. The influence of some process parameters showed that a combination of an optimum dose of 5 mM H_2O_2 and solar radiation improved the performance of TiO_2 from 16 to 47%. The photocatalytic reaction data were fitted to the pseudo first and second-order kinetic models in order to exploit the kinetic process of the photo-destruction reaction. The kinetic fits showed that the degradation reaction better adhered to the second-order kinetic model when only ZnO and solar radiation were applied, regardless of the tea type employed. The application of PAO in this novel and cost-effective way has potential for the abatement of contaminated water to potable water. The use of heterojunction photocatalysts could be explored in future research to further improve the process.

Keywords: photocatalytic advanced oxidation; humic water treatment; hydrogen peroxide; sustainable treatment; photocatalytic destruction

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1. Introduction

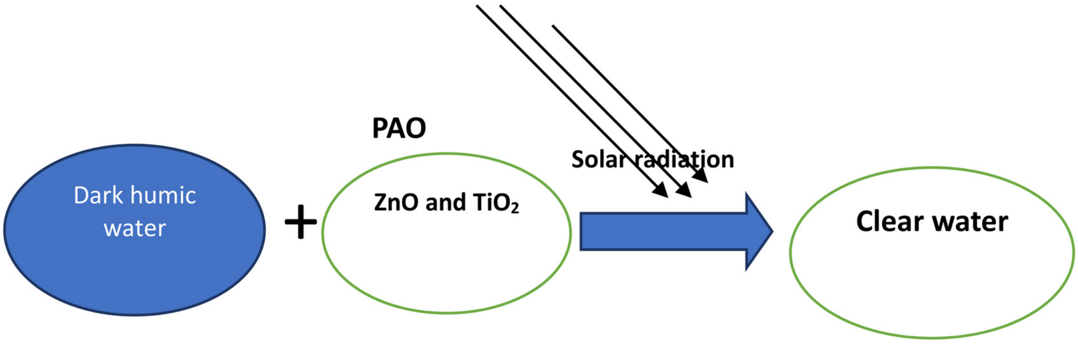
Raw water in the south-western Cape of South Africa is amongst some of the most darkly coloured humic water in the world. This is largely due to the character of the surrounding vegetation of the fynbos biome [1]. Organic matter in raw water is not toxic in itself, but it can have a serious impact on drinking water quality [2]. It can act as a carrier for toxic metals and can lead to unpleasant properties with regards to taste, colour, and odour [3]. Furthermore, it can lead to the formation of harmful disinfection by-products during chemical water treatment processes. It can also inhibit other treatment processes, as it contributes to membrane fouling and reduces the efficiency of adsorption processes [2,4–7]. Due to the low rainfall and lack of reservoirs in South Africa, there is the need to improve the quality of raw water supplies and, hence, increase the amount of potable water by developing sustainable advanced processing methods [8].

Advanced Oxidation Processes (AOPs) have been demonstrated to be highly effective for the removal of organic pollutants in water [3,9]. These work through the use of ozone (O_3), Fenton's reagent (H_2O_2 with ferrous ions), UV light, hydrogen peroxide, or a catalyst for in situ generation of strong chemical oxidants; the main oxidative species would be hydroxyl radicals [10–12]. Often, these AOPs are used in combination with biological treatment to provide a more effective and economical treatment of the contaminated water [13–15]. The main challenge this method faces is that, to reach full mineralisation of organics, large quantities of oxidants and/or long irradiation times are needed, which reduce economic feasibility [3].

In order to simulate the humic water, this study used brews produced from domesticated versions of the species responsible. Aspalathus linearis, cultivated to produce rooibos herbal tea, and Camellia sinensis, the Black tea plant, were used to reproduce the organic matter found in raw water supplies in these regions. In teas, phenolic substances make up a significant weight proportion, which contribute to a large amount of colour and character [16]. To date, fifteen main phenolic compounds have been identified in rooibos tea, most of which have molecular weights greater than 400 and can hence be considered relatively large [17,18]; it is anticipated that more will be identified as analytical techniques improve. It has been suggested that Photo-Fenton processes are most effective for the removal of lower molecular weight compounds, while UV/H_2O_2 or photocatalytic treatment is more effective for removal of higher molecular weight compounds [19,20]. This study will examine how photocatalysts and light sources affect the decomposition of brews made from the two teas.

Titanium dioxide (TiO_2) is the most commonly used photocatalyst, but it is restricted by its low quantum efficiency and large band gap (3.2 eV) [21–23]. Zinc oxide (ZnO) possesses the same band gap energy, but it exhibits a higher adsorption efficiency, and so it is a proposed alternative [9,15]. It is also significantly cheaper than other photocatalysts (including TiO_2) and is extensively found in nature [24]. The material is also considered to be environmentally friendly [25,26]. Recent studies have shown that both ZnO and TiO_2 at a concentration of 1 g/L are effective at degrading caffeine in wastewater [27].

This study aims to compare the performance of zinc oxide and titanium oxide as photocatalysts for the decomposition of the tea brews' contaminated water over a range of concentrations under natural light, a halogen light, and a UV light, combined with hydrogen peroxide (Scheme 1). ZnO and TiO_2 are traditional photocatalysts, and their photocatalytic performances have been evaluated in this study. Previous studies, such as the work by Tum et al. [28] reported the destruction of black tea by ZnO application. Zhang et al. [29] degraded black tea by applying gut microbiota; Maghanga et al. [30] decolourized black tea by electrocoagulation, while Sabaikai et al. [31] reported the decolourization of oolong tea species by the photo-Fenton process. To the best of the knowledge of the authors, the comparative application of both ZnO and TiO_2 under varying light sources for the abatement of rooibos and black tea have not been previously reported. Successful destruction of the phenolic compounds, stemming from the teas used, can prove that this is a viable route to explore in the treatment of dark humic waters found in the Western Cape area of South Africa. This will provide the initial steps towards using water sources that are currently unusable because of the humic material content. It is intended that the method will be environmentally friendly and applicable on a realistic scale.



Scheme 1. Schematic diagram of the study [9].

2. Materials and Methods

2.1. Materials

Zinc oxide (ZnO, 99.9% purity) and anatase titanium dioxide (TiO_2, 99% purity) powders were purchased from Sigma Aldrich (Kempton Park, South Africa). The ZnO test powder was of particle size >5 µm and energy gap of 3.3 eV. The TiO_2 powder had a particle dimension of 21 nm, a BET surface of 35–65 m^2/g, and a 3.2 eV band gap. Hydrogen peroxide (H_2O_2) of minimum 30% assay was purchased from MERCK (Lethabong, South Africa). Black tea was of the brand JokoTM (Pietermaritzburg, South Africa), and Rooibos was the brand Laager® (Pinetown, South Africa). The tea solutions were prepared using water at 85 °C and one teabag (2 g of tea) per 500 mL of water, soaked for 5 min. These solutions were left to cool to room temperature overnight before use.

2.2. HPLC-MS Analysis of the Teas

HPLC analysis was performed using two mobile phases: (A) 0.1% formic acid in deionised water and (B) 0.1% formic acid in acetonitrile. Analysis was performed on a Thermo Scientific UltiMate 3000 UHPLC (Brucker, Johannesburg, South Africa) that used negative ionisation-mode ESI interface. This was performed using a C18 rapid resolution column. The chromatographic gradient was set at initial conditions of 98% eluent A followed by multiple subsequent gradients to 5% A at 24 min. A 0.3 mL/min flow rate was maintained throughout. Chromatographic separation was monitored using a Diode Array Detector (DAD) set to scan 200–500 nm coupled in Quadrupole time-of-flight mass spectrometry to an electrospray ionisation mass spectrometer (ESI-MS). Bruker Compass Data Analysis Software was used to identify key compounds, based on formulas, fragmentation profiles, retention times, area, tandem mass spectrometry data, and the literature values.

2.3. Photocatalytic Procedures

Experiments were conducted over the spring months, March to May, at the University of Witwatersrand in Johannesburg, South Africa. All experiments were performed in a glass batch beaker of 500 mL volume, using a magnetic stirrer. The light sources used were natural sunlight, an ASUMA (Pietermaritzburg, South Africa) 150 W Halogen Floodlight (solar radiation), and a UV strip light within an ESCO (Johannesburg, South Africa) laminar flow cabinet, wavelength 254 nm. The artificial light (UV and halogen light) sources were illuminated 20 cm above the free surface of the solution. Natural sunlight was provided in Johannesburg, South Africa, at approximately 2000 m above sea level during the autumn period from March to May. A catalyst concentration range of 1 to 10 g/L and H_2O_2 dose, was added to the tea solutions, with hydrogen peroxide when required, and allowed to equilibrate in the dark for 30 min prior to photodegradation experiments. After this, the solutions were exposed to the selected irradiation source to initiate the reaction. Constant agitation at 100 × G was maintained throughout in order to keep the suspension homogeneous. Catalyst concentrations of 1, 2, and 10 g/L and H_2O_2 doses of 5, 10, and

100 mM were tested. The pH was monitored and remained between 6.5 and 8.5 in all cases, ensuring that the photodecomposition of ZnO, which occurs around a pH of 4, did not happen. Samples were taken at 0, 30, 60, and 120 min and analysed using a SHIMADZU (Roodepoort, South Africa) UV-1800 UV-Vis Spectrophotometer and quartz cuvettes. The spectrum of tea within the range 190 to 400 nm exhibited a main band with a maximum at 200 nm for Rooibos tea and 204 nm for Black tea. Using the absorbance at this λmax indicates the degree of photodegradation X at a function of time, as shown in Equation (1):

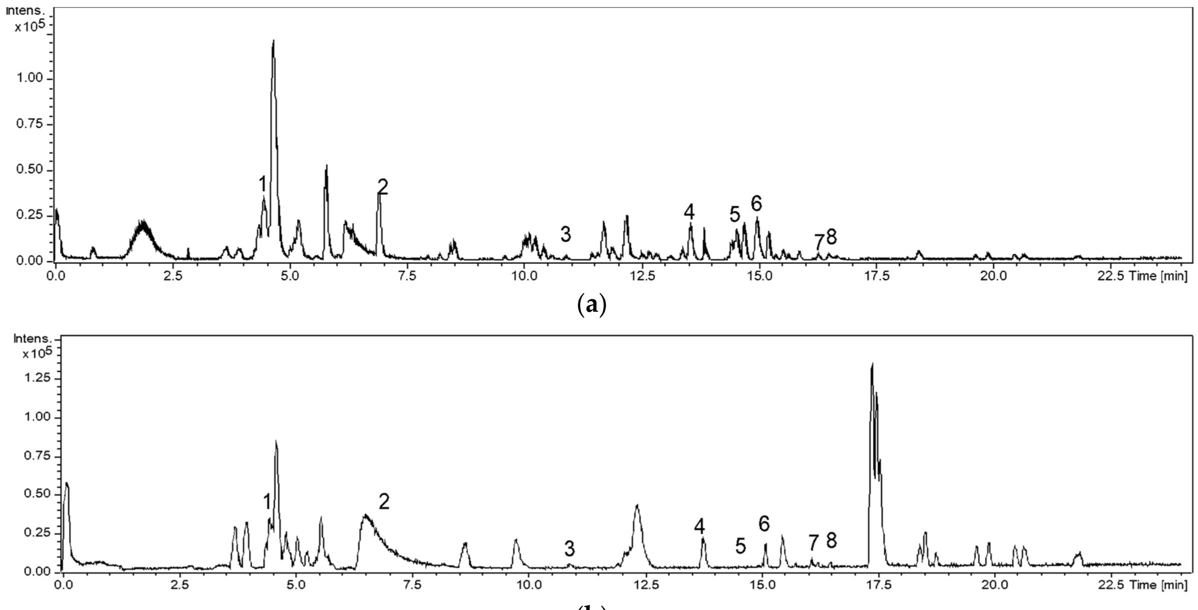
$$X = \left(1 - \frac{A_t}{A_0}\right) \tag{1}$$

where; A_0 is the initial absorbance of the sample, and A_t is the absorbance at time t [32].

3. Results and Discussion

3.1. Characterization of Rooibos and Black Tea

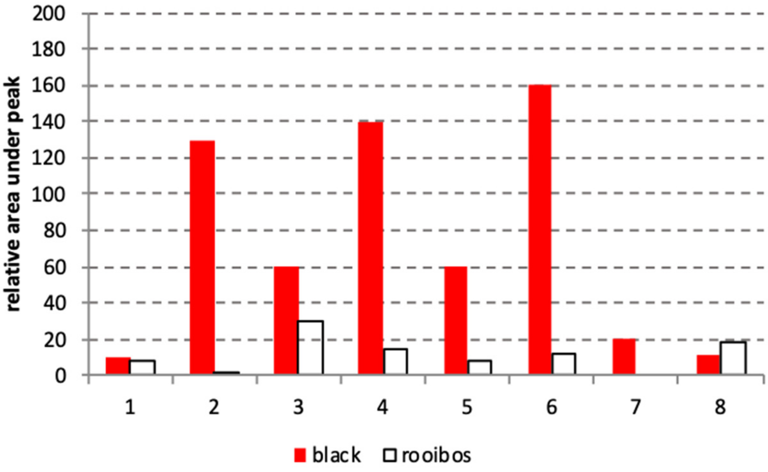
Figure 1a,b are HPLC-MS chromatograms of Black tea and Rooibos tea, respectively, showing a clear difference in the composition and explaining the different behaviours between them. Despite both teas being brewed using the same dry weight of tea, temperature, and brew time, a higher rate of extraction occurred in black tea, as shown by the much greater chromatographic intensity. The relative difference in concentration of the eight main components of tea is shown in Figure 1c, which is based on the area under the chromatographic peaks. The main differences are a greater level of theaflavin-3-gallate in Rooibos tea, but lower levels of all other compounds found. There is a significantly higher level of quercetin-rhamnosylgalactoside, gallic acid, quercetin-3-galactoside, and epicatechin-3-gallate in Black tea. It was also found that caffeine is present in Black tea, but not in Rooibos. These findings are consistent with the literature, as Rooibos is known to be caffeine free and have a lower polyphenolic content than black tea [18,33,34]. In addition to the verified compounds, the HPLC chromatograms in Figure 1a,b show further evidence of differences in composition between the brews. An example of this is that Rooibos tea contains compounds, which have a retention time of 17.5 min. These do not exist in black tea, and one of these is suggested to be vanillic acid [35].



(**a**)

(**b**)

Figure 1. *Cont.*



(**c**)

Figure 1. (**a**) HPLC-MS chromatogram of Black tea; (**b**) HPLC-MS chromatogram of Rooibos tea; (**c**) Comparison of area under peaks of chromatographically identified compounds. In all cases, the compounds are 1: epigallocatechin-3-gallate, 2: gallic acid, 3: Epicatechin, 4: quercetin-rhamnosylgalactoside, 5: quercetin-3-galactoside, 6: epicatechin-3-gallate, 7: theaflavin, and 8: theaflavin-3-gallate.

3.2. Photocatalytic Degradation with Sunlight

Clearly, a valid process using natural sunlight would significantly lower the costs of the process and would also provide extra flexibility for the location of any treatment system. However, poor degradation (<5%) was achieved in all cases in this study, even at a high catalyst concentration, showing the level of light intensity to be inadequate. It is also likely that the high catalyst concentrations provided a high optical thickness of the solution, further reducing the photocatalytic effect.

3.3. Photolysis with Halogen and UV Light without Catalysts

Figure 2 shows the degradation of Black and Rooibos teas when only the halogen (solar radiation) and UV light sources were used for photolysis, showing little difference. The difference in degradation, based on the tea type, was also demonstrated to be insignificant, and a maximum of 9% degradation was achieved in Black tea and 11% in Rooibos tea from UV photolysis.

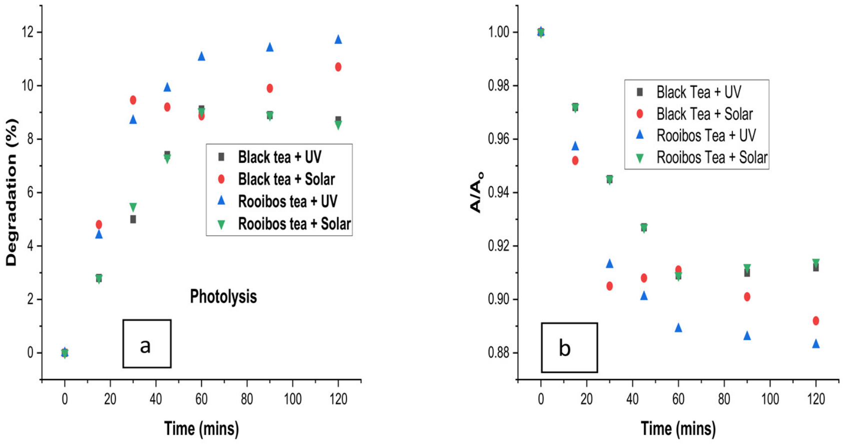


Figure 2. (**a**) Degradation of Rooibos and Black tea by solar and UV photolysis. (**b**) Normalized photolysis plots.

3.4. Impact of Catalyst Concentration under Artificial UV and Solar Irradiation

It has been reported that the amount of catalyst used directly influences the overall photocatalytic reaction rate up until the saturation stage. After this, the light photon adsorption coefficient decreases (the light cannot penetrate as far into the solution), and a light-screening effect can be created by any excess photocatalyst, reducing the surface exposed to irradiation and, hence, the efficiency [9]. Therefore, it is essential that the optimal catalyst dosage is determined for greatest efficiency. Figure 3 shows the maximum level of degradation achieved at three catalyst loads for the treatment of Rooibos and Black teas, using ZnO and TiO_2 under the halogen lamp (solar radiation), with 10 g/L giving the best results. Adsorption onto the photocatalyst probably plays a role here, as the concentration of TiO_2 is unrealistically high for photocatalysis, which takes place only on a thin layer near the interface. TiO_2 shows better performance for the degradation of Rooibos tea, while ZnO shows better performance for the degradation of Black tea, demonstrating how the composition of the wastewater is an important factor in catalyst selection. It is likely that the ability to degrade polyphenols is significant.

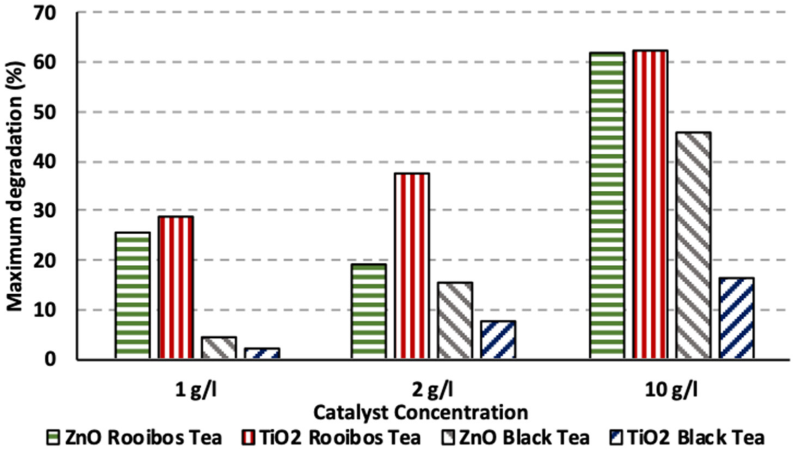


Figure 3. Impact of catalyst concentration on maximum degradation within 120 min under halogen light (solar radiation).

Figure 4 shows the level of degradation of the teas using the catalysts with a UV light source. As with halogen light (solar radiation), the optimal catalyst load in all cases is 10 g/L. However, the difference in degradation between the systems is less significant than with halogen light. TiO_2 under UV irradiation is the preferred choice for both teas.

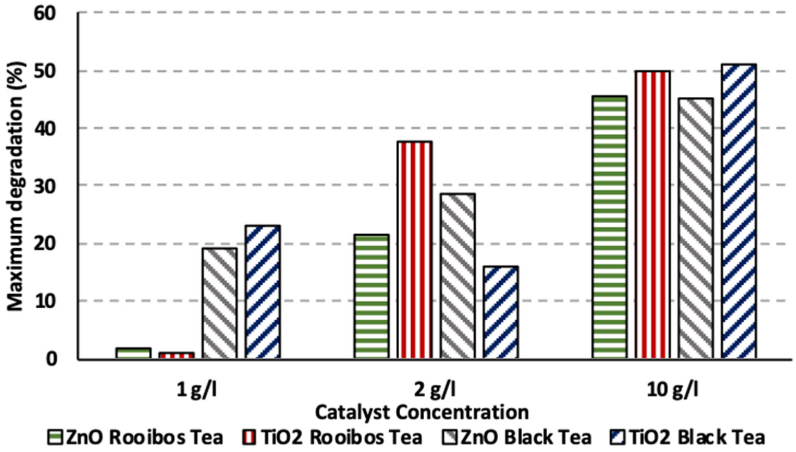


Figure 4. The impact of the catalyst concentration on the maximum degradations within 120 min under UV light.

When comparing the results from solar radiation (halogen) and UV photocatalytic degradation (Figures 3 and 4), the halogen light (solar radiation), using either catalyst, at the optimal loading of 10 g/L, is most effective for treatment of Rooibos tea. A 62% degradation using both TiO_2 and ZnO is achievable under solar irradiation compared with 45% and 50% with ZnO and TiO_2, respectively, for UV irradiation. When considering the treatment of Black tea, the use of UV light is preferable, whilst the use of halogen light from a halogen lamp is not appropriate if the photocatalyst TiO_2 is used, but ZnO achieves the same level of degradation (45%), regardless of the light source selected.

3.5. Impact of Hydrogen Peroxide Addition on Photocatalytic Degradation

The addition of H_2O_2 in photocatalytic advanced oxidation processes has been shown to improve the degradation of organic pollutants due to the formation of OH. radicals [36,37]. The role of H_2O_2 in this study is to ascertain its effect on the efficiency of the applied semiconductor photocatalysts in addition to the photodecolourization process. However, at too high a dose, H_2O_2 becomes a powerful hydroxyl scavenger [38]. As a result, it is important to investigate the optimal dosing. Using the halogen light the optimal hydrogen peroxide dose was found to be 5 mM for both catalysts and teas tested (Figure 5).

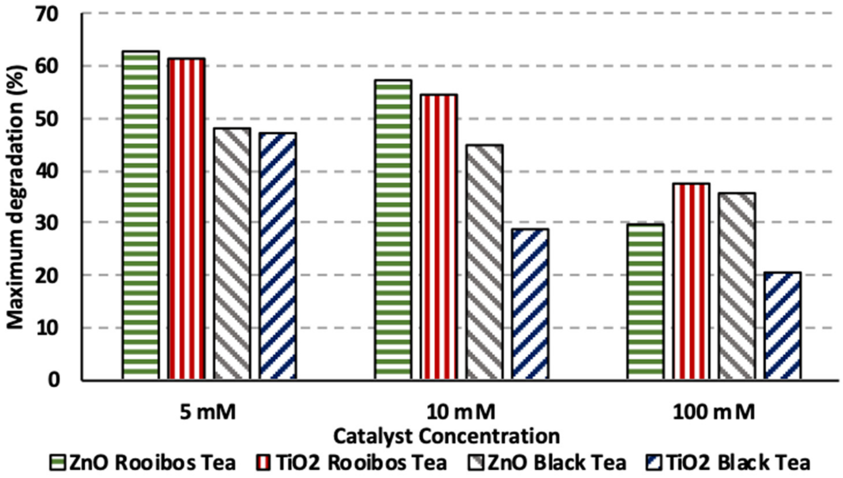


Figure 5. The impact of hydrogen peroxide addition on the maximum photocatalytic degradations at a 10 g/L catalyst concentration within 120 min under halogen light.

Degradation was achieved to a greater level in Rooibos tea compared with Black tea, which is consistent with Figure 2. The addition of hydrogen peroxide does not improve the level of degradation in Rooibos tea, and this is also the case when ZnO is used to treat Black tea. However, dosing with hydrogen peroxide is significant when a halogen lamp and titanium dioxide are used to degrade Black tea. The level of degradation was improved from 16% to 47%, making the TiO_2/halogen treatment method a viable option when hydrogen peroxide is added to the solution in small quantities. This suggests that the interaction between TiO_2 and H_2O_2 causes dissociation of hydrogen peroxide to form hydroxyl radicals or, alternatively, it could reduce the recombination of the valence band hole and conduction band electron. The work by Li et al. [39] is in agreement with this, and it was found that H_2O_2 extended the photo-response of TiO_2. It is unlikely that the visible light alone caused significant dissociation of H_2O_2 due to the negligible improvements seen in the other cases.

An amount of 5 mM of H_2O_2 is the preferred dose for Rooibos tea, but a higher dose of 10 mM is favoured for the treatment of black tea for both catalysts tested when UV irradiation is the light source, as shown in Figure 6. This is explained by the higher polyphenolic content of the black tea, which negates the hydroxyl scavenger nature of H_2O_2, as there is a significantly higher quantity of organic matter compared to the quantity of hydrogen peroxide. This increases the likelihood of the hydroxyl radicals' consumption by interaction with organic matter over interaction with H_2O_2 [40].

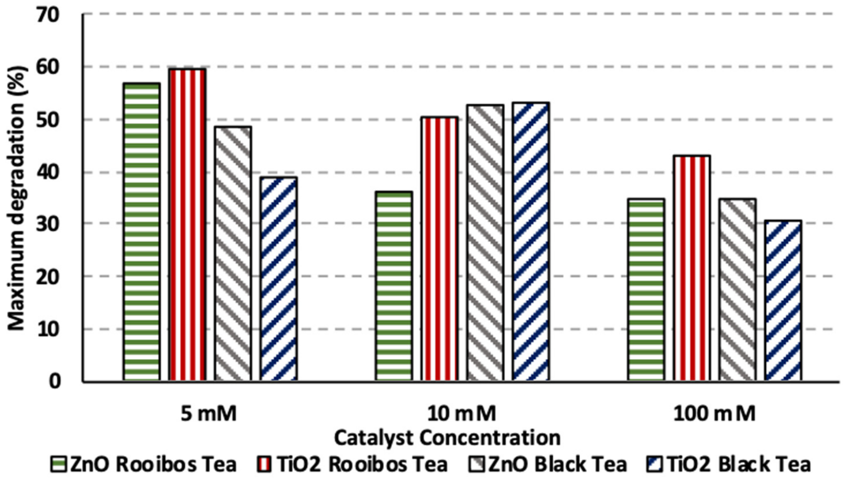


Figure 6. The impact of hydrogen peroxide addition on the maximum photocatalytic degradations at a 10 g/L catalyst concentration within 120 min under UV light.

Unlike the systems degraded by halogen light, the addition of hydrogen peroxide to systems under UV light leads to significant improvements in performance. $ZnO/UV/H_2O_{260}$ treatment of rooibos tea improved degradation by 12% from 45 to 57% compared with ZnO/UV, while the addition of 5 mM H_2O_2 to 10 g/L TiO_2 increased Rooibos tea degradation from 50% to 59%. Black tea degradation by ZnO under UV light was improved from 45% to 52% when 10 mM H_2O_2 was added. Degradation with TiO_2 and H_2O_2 improves from 48% to 53%. This result is in agreement with Li et al. [39], who found that H_2O_2 directly dissociates under UV light, but not to a significant degree under visible light.

3.6. Comparison of Degradation with Time for Optimised Treatment of Rooibos Tea

The degradation with time of the optimised ZnO photocatalysis processes is shown in Figure 7. Solar-based photocatalysis of Rooibos tea, using ZnO, is clearly preferential. UV-based photocatalysis, without any hydrogen peroxide added, is the least effective. Lee and An [41] found similar results, but with less significant differences seen. There is little variation between the other optimised methods. Therefore, from an environmental and economic perspective, Solar/ZnO photocatalysis would be the best option in this case.

The optimised processes of TiO_2 photocatalytic degradation of rooibos tea are shown in Figure 8. It is clear that UV/TiO_2 photolysis is the least effective method, with little difference seen between the other combinations examined. Regardless of the light source, the majority of degradation occurs within the first 30 min of treatment. This is beneficial as short treatment times could prove sufficient for less heavily polluted waters. The short degradation times can possibly be attributed to the short lifetime of the generated radicals destroying the organic material, which implies a limited destruction capability in the presence of an excess of natural organic matter and colour.

Using TiO_2 and ZnO without hydrogen peroxide with the halogen lamp, both achieved the same level of degradation (62%), and, so, either photocatalyst can be selected. Using ZnO would be preferable, as it is comparatively inexpensive and is widely available, as well as being easier to handle in bulk and having a high particle surface area. For this specific application, the pH remained neutral, and, so, there is no concern about ZnO's relatively high solubility in acidic conditions.

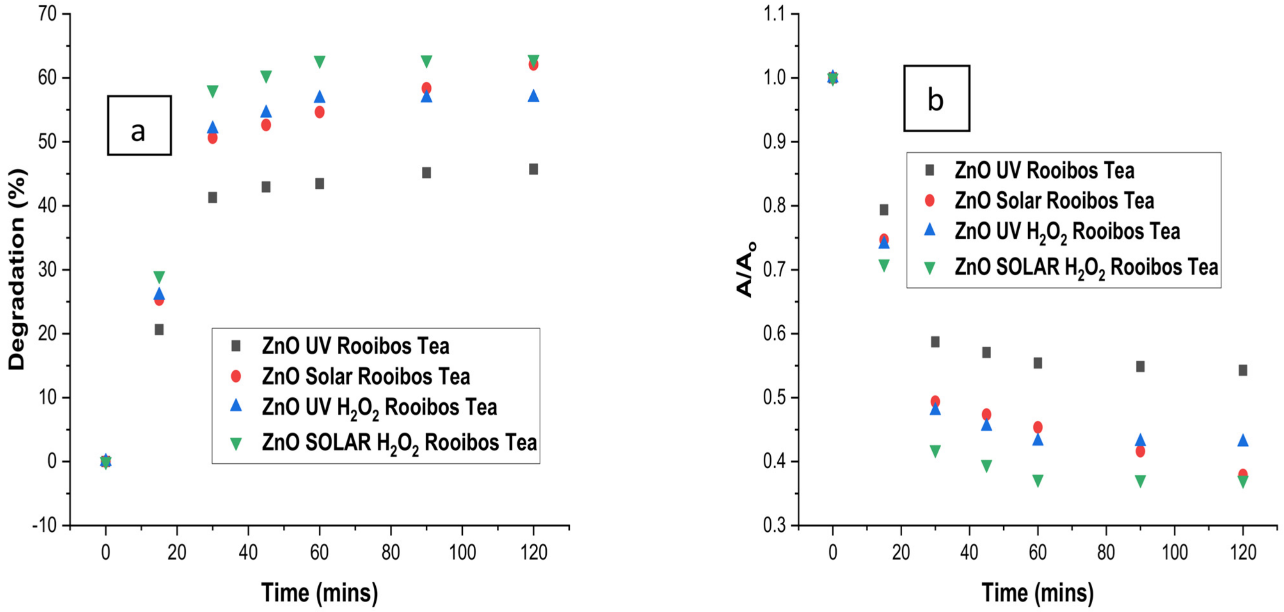


Figure 7. (**a**) ZnO photocatalytic degradation of Rooibos tea with time under halogen light at a catalyst concentration of 10 g/L and 5 mM H_2O_2 dose where applicable. (**b**) Normalized plot of ZnO photodegradation of Rooibos tea.

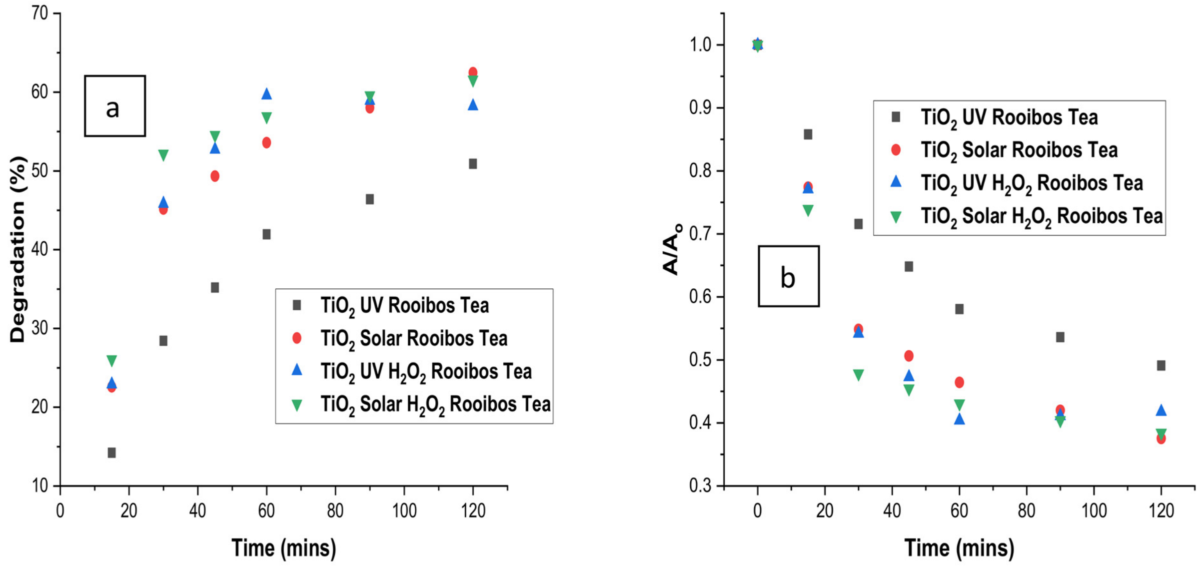


Figure 8. (**a**) TiO_2 photocatalytic degradation efficiency of Rooibos tea with time under halogen light (solar radiation) at a catalyst concentration of 10 g/L and 5 mM H_2O_2 dose where applicable. (**b**) Normalized plot of the TiO_2 photodegradation of Rooibos.

3.7. Comparison of Degradation with Time for Optimised Treatment of Black Tea

Figure 9 shows that ZnO was a suitable catalyst in all systems for the degradation of Black tea, but Figure 10 shows that hydrogen peroxide is required if using a halogen lamp with TiO_2. Degradation is improved further by using UV light. These results clearly show that ZnO is more suitable for degrading Black tea.

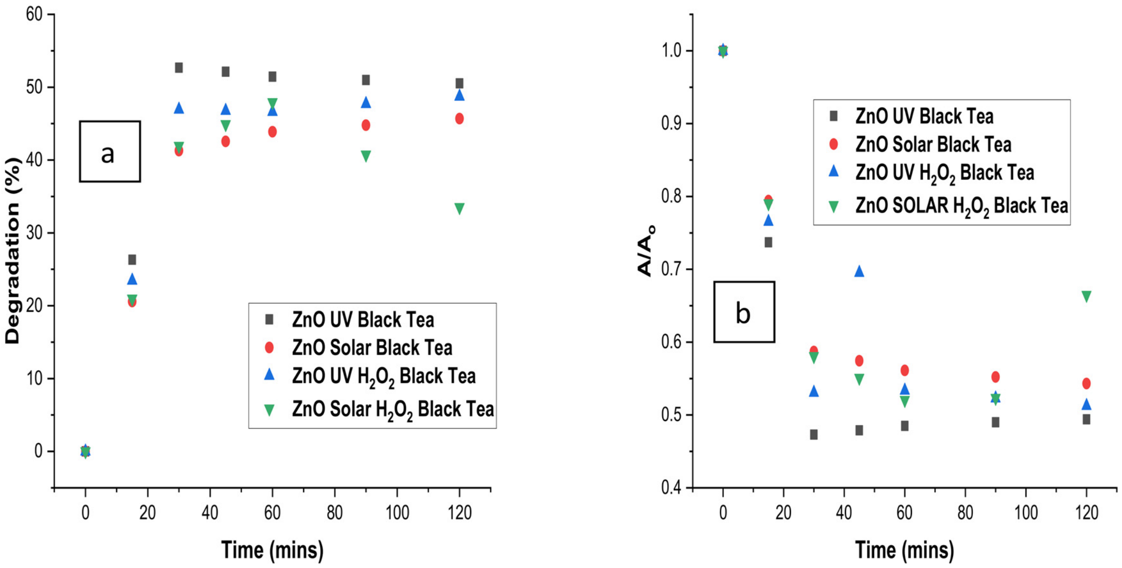


Figure 9. (**a**) The ZnO photocatalytic degradation efficiency of Black tea with time under halogen light (solar radiation) at a catalyst concentration of 10 g/L and 5 mM H_2O_2 when in the solar process and 10 mM H_2O_2 when with UV. (**b**) A normalized plot of the ZnO photodegradation of Black tea.

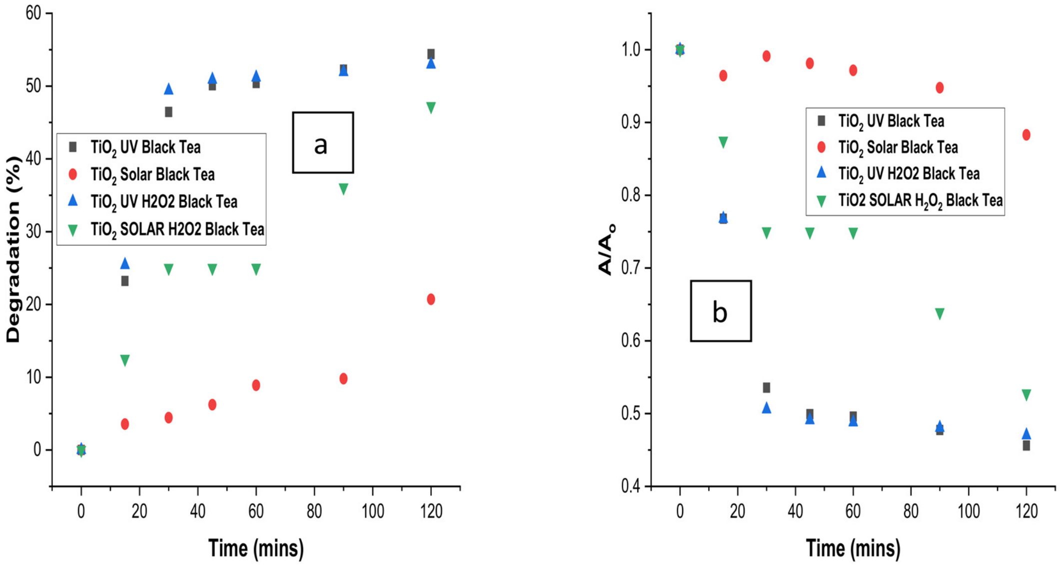


Figure 10. (**a**) The TiO_2 photocatalytic degradation efficiency of black tea with time under halogen light at a catalyst concentration of 10 g/L and 5 mM H_2O_2 when in the solar process and 10 mM H_2O_2 when with UV. (**b**) Normalized plot of the TiO_2 photodegradation of Black tea.

3.8. Kinetic Study

The photodecolourization data were fitted into pseudo-first order and second-order reaction kinetic models in order to exploit the kinetic study of the photodestruction process. The pseudo-first-order equation is given in Equation (2):

$$ln\left(\frac{A}{A_0}\right) = -kt \tag{2}$$

where A_o is the initial concentration of the reference contaminated water, A is the final concentration of the contaminated water at different treatment time, t is the time in minutes, and k is the apparent kinetic rate constant for different photocatalysts. Plotting a graph of *ln* (A/A_0) against *t* yields a slope equivalent to the apparent kinetic rate constants. The integrated rate law for the second-order reaction is shown below:

$$\mathrm{A} \rightarrow \mathrm{P} \text{ is } 1/[\mathrm{A}]\_\mathrm{t} = \mathrm{kt} + 1/[\mathrm{A}]\_0 \tag{3}$$

Because this equation has the form $y = mx + b$, a plot of the inverse of [A] as a function of time yields a straight line.

Kinetic fits of the photocatalytic degradation of the two tea solutions with ZnO and TiO_2 photocatalysts under various conditions indicate that, when only light radiation is employed in conjunction with ZnO, the degradation reaction follows second order kinetics, regardless of the tea type employed. In the case of using light radiation (UV and sunlight) together with the TiO_2 photocatalyst, there is no clear indication whether first- or second-order kinetics prevail during the degradation reaction of both tea types. When the oxidant hydrogen peroxide is utilised together with light radiation, and ZnO is the photocatalyst employed, the degradation reaction of both teas tend towards obeying first-order kinetics. Under similar conditions, but employing TiO_2 as the photocatalyst, one could once again not discern any definite tendency towards either first or second order kinetics in the degradation of both black and Rooibos teas. Therefore, while clear kinetic patterns could be discerned in the degradation reactions of the two teas with ZnO as the photocatalyst, this was not the case when TiO_2 was employed as the photocatalyst. The corresponding 1st and 2nd order values are presented in Table 1.

Table 1. Table showing the tea type, treatment type, 1st-order kinetics, and 2nd-order kinetic fits.

Tea Type	**Treatment Type**	R^2 **(*ln*(A/A_o))**	***K*** **(min^{-1})**	R^2 **($1/A$-$1/A_o$)**	K_2 **($\mathrm{L\ mg^{-1}\ min^{-1}}$)**
Black	ZnO + UV	0.349	0.107	0.931	0.0009
Black	ZnO + Solar	0.934	0.008	0.939	0.0016
Black	ZnO + UV + H_2O_2	0.859	0.0017	0.235	0.0028
Black	ZnO + SOLAR + H_2O_2	0.723	0.0018	0.499	0.0030
Rooibos	ZnO + UV	0.853	0.0070	0.841	0.0014
Rooibos	ZnO + Solar	0.899	0.0102	0.997	0.0068
Rooibos	ZnO + UV + H_2O_2	0.849	0.0098	0.651	0.0024
Rooibos	ZnO + SOLAR + H_2O_2	0.849	0.0116	0.659	0.0031
Black	TiO_2 + UV	0.918	0.0016	0.929	0.0032
Black	TiO_2 + Solar	0.915	0.0012	0.907	0.0013
Black	TiO_2 + UV + H_2O_2	0.929	0.0007	0.934	0.0015
Black	TiO_2 + SOLAR + H_2O_2	0.897	0.0041	0.885	0.0064
Rooibos	TiO_2 + UV	0.948	0.0040	0.968	0.0069
Rooibos	TiO_2 + Solar	0.988	0.0041	0.996	0.0092
Rooibos	TiO_2 + UV + H_2O_2	0.534	0.0025	0.629	0.0054
Rooibos	TiO_2 + SOLAR + H_2O_2	0.975	0.0024	0.984	0.0068

4. Conclusions

The study investigated the effectiveness of the application of photocatalytic advanced oxidation (PAO) for the treatment of raw water contaminated with humic material from fynbos biome plants, using Black and Rooibos teas as the model solutions. The study tested ZnO and TiO_2 and three light sources (natural sunlight, halogen light, and UV light). The treatment of the two teas by only photolysis was observed to be minimal. Results obtained from the study showed that over 50% degradation was achieved when a dose of 10 mM H_2O_2 was used in the degradation of black tea. However, a combination of solar and H_2O_2 showed a 47% efficiency for both photocatalysts. When only solar radiation (halogen light) was applied, TiO_2 showed a poor performance in the decolourization of black tea. The study suggests that TiO_2 is efficient under specific solar radiation conditions. The kinetic study found that, when ZnO was used with solar radiation alone, the degradation reaction followed second-order kinetics for both tea types. However, there was no clear indication of whether the pseudo first- or second-order kinetics prevail during the degradation reaction of both types under UV and sunlight when TiO_2 was applied. The photodegradation reaction of both teas were observed to conform to the pseudo first-order kinetics when ZnO was applied in combination with H_2O_2 and solar radiation.

The results obtained from the study suggest that ZnO is a more effective photocatalyst than TiO_2 in the treatment of dark humic matter under solar radiation, without the need for H_2O_2 to enhance its performance. Despite being more extensively used because of a greater knowledge of its photocatalytic properties, TiO_2 was shown in this study to be a less suitable catalyst choice.

The stability and reusability of the photocatalysts in the tea solutions are recommended for future studies. Heterojunction photocatalysts should be explored in the future to improve the process further.

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