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Photocatalytic Decolourization of Wastewater from Black Tea (*camellia sinensis*) Processing Factories using Titanium Dioxide

Patrick K. Tum
Ph.D. Student, Department of Chemistry, University of Nairobi, Kenya
David K. Kariuki
Associate Professor, Department of Chemistry, University of Nairobi, Kenya
Fredrick D. O. Oduor
Senior Lecturer, Department of Chemistry, University of Nairobi, Kenya
John K. Wanyoko
Research Chemist, Tea Research Institute, Kericho, Kenya

Abstract:
Wastewater from black tea (camellia sinensis) processing factories is characterized by a persistent brick-red colour that conventional treatment works are unable to remove. Forty eight samples each of 500cm^3 were collected from three black tea processing factories from western highlands in Kenya and subjected to photocatalytic degradation on Titanium dioxide.
A layer of height of cca 2 cm on TiO_2 in a photocatalytic reactor was illuminated with artificial UV lamp producing radiation at wavelength 365 nm of intensity 3.0 mW/cm^2 for 3 hours. Another set of experiments was done using solar light of intensity 1.4 mW/cm^2. Samples of5 cm^3 were drawn every 15 minutes and analyzed using UV/Vis spectrophotometer at λ=410 nm. The results showed that decolourization of 70.4% - 78.5% of the wastewater was achieved in 3 hours. Solar illumination produced higher efficiency of 2.3% above artificial UV lamp irradiation. Decolourization of 59.7% solar and 54.4 % UV lamp was achieved in the first 60 minutes although the solar radiation intensity applied was less than half that of UV lamp.

Keywords: *Black tea, wastewater, decolourization, photocatalytic, titanium dioxide*

1. Introduction

Kenya is categorized as a water scarce country. Water pollution is very common. In addition, Kenya is a water scarce country with only 647 m^3/year of freshwater per capita. On average black tea processing requires 50m^3 i.e. (1/13 of available reserves) of freshwater. The Kenyan government predicts that by the year 2025, the per capita availability of fresh and safe water will drop from 647m^3 to about 235m^3, this is as a result of an expected significant rise in population. Since the 1970s, the world's population has more or less doubled raising the demand for clean and safe water for domestic consumption by almost six-fold (Tum *et al.,* 2016). Apart from the demand of water for domestic use, water required for industrial use has also rapidly increased putting a strain on the already scarce resource. The wastewater discharged from black tea processing factories in Kenya is characterized by a high load of various pollutants such as high organic matter, high suspended matter, heavy metals, odour, surfactants and high oxygen demanding parameters that make the water unpalatable.To treat the wastewater, Advanced Oxidation Processes (AOPs) using TiO_2 as a semi-conductor photocatalyst in the presence of UV light, has been suggested to treat wastewater loaded with pollutants (Onyatta *et al.,* 2016). Of great concern to the entire tea industry in Kenya, is the problem of persistent brick-red colour characteristic of wastewater discharged from the factories. The wastewater is discharged into the natural environment without effective treatment to acceptable standards. The persistent brick-red colour is as a result of polyphenols generated during tea processing. The polyphenols are characterized by a conjugated carbon-carbon double bonds that cause the colouring (Graham, 1992). Theaflavins, a class of polyphenols present in the wastewater is suspected to be the main culprit (Maghanga *et al.,* 2009).

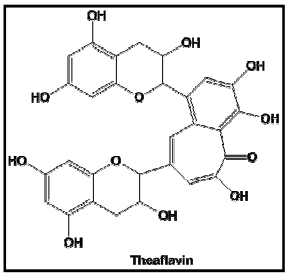

Figure 1: Theaflavins (source: India tea Institute)

Conventional methods of wastewater treatment such as flocculation and coagulation have proved ineffective in the treatment of wastewater loaded with high organic load (Habib *et al.,* 2013). Therefore, an effective method is required to deal with the problem. The use of semi-conductor photocatalysts such as TiO_2 has been examined in recent years to degrade organic and inorganic pollutants into water and carbon dioxide (Habib *et al.,* 2012; Mahmood *et al.,* 2003).The cleavage of the conjugated carbon–carbon double bonds of polyphenols by (·OH) radicals leads to the decolorization and subsequently the mineralization to CO_2 and H_2O.The important property of semiconductors is that the valence and conduction band are not on the same energy level (Hoffman *et al.,* 1995). Ultra violet light in the form of a photon with energy hv greater than band gap energy, E.g. promotes an electron from the valence band to the conduction band leaving a hole behind. The formation of holes allows adsorbed water to be oxidized to strong ·OH radicals OH radicals are very strong oxidative species (2.8 V vs. SHE) and are able to oxidize almost all organic molecules (Bizani *et al.,* 2006). The oxidation by (·OH) radicals is non-selective and organic molecules are mineralized to CO_2 and H_2O.
The equations below indicate the reactions that take place:

$$TiO_2 + hv \rightarrow e_{CB}^- + h_{VB}^+ \quad (1)$$

$$O_2 + e_{CB}^- \rightarrow O_2^{\cdot -} \quad (2)$$

$$H_2O + h_{VB}^+ \rightarrow OH^- + H^+ \quad (3)$$

TiO_2 exists in a number of crystalline forms of which the most important forms are anatase and Rutile.TiO_2 in the form of anatase is the most practical form that can be applied in photocatalytic environments such as in water purification, wastewater treatment and water disinfections. It is biologically inert and chemically stable with respect to photo-corrosion and chemical corrosion and is inexpensive (Sangari and Velusamy, 2016; Souther and Alspaugh, 1957). It been suggested that the hydroxyl radicals ·OH are the primary oxidizing species. As a semi-conductor photocatalyst, TiO_2 has been investigated due to its high photocatalytic activity, non-toxicity, high photochemical stability (Konstantinou and Albanis, 2004). However, a disadvantage of TiO_2 semi-conductor is its high band gap, (3.2 eV corresponding to 388 nm, which ensures that only the UV region (only about 4%) of the solar radiation is absorbed whereas the solar spectrum has about 40% visible region 400 nm to 700 nm (Aramendia *et al.,* 2008). Titanium dioxide as a semi-conductor has been successfully used as a photo catalyst for the oxidative degradation of organic compounds. Its anatase from is the most practical for photo catalytic environmental applications such as water purification, wastewater treatment and water disinfections (Fujishima and Rao, 2000; Pirkanniemi and Sillanpaa, 2002). In this study, as a source of UV irradiation, artificial UV lamps and solar light irradiation is used. The possibility of solar light supplying UV irradiation, is of great significance promising a sustainable process for environmental remediation (Ajmal *et al.,* 2014; Tachibana *et al.,* 2012).

2. Material and Methods

2.1. Materials

Wastewater samples were obtained from three processing factories in Nandi County, Kenya. The factories are Chebut (0°12´14´´N, 35°6´18´´E), Nandi Tea (0°5´32´´N, 35°11´20´´E) and Kibwari (0°3´0´´N, 35°7´60´´E). Sampling was done at the point of exit from the factories and the samples stored under refrigeration at 4°C for their preservation according to the procedure described in (APHA, 1992). The TiO_2 powder photocatalyst used in this study was supplied by Science Lab Chemicals, Nairobi, Kenya. All other chemicals and reagents used were of analytical grade and were used without further purification.

2.2. Preparation of TiO_2 Coated Layer

A particulate layer of dimensions (18 cm × 13 cm) containing immobilized TiO_2 powder photocatalyst was prepared by sedimentation from an aqueous suspensions c = (10 g/l) on a degreased and clean glass plate (borosilicate). The catalyst suspensions were pre-treated using an ultra-sound decibel (Model – UP 2005 ultrasonic homogenizer) to break down any agglomerates present and make the suspension uniform. The prepared layer is placed on a ceramic tile and allowed to dry at room temperature for about 45 mins and thereafter dried in an oven at 50°C for 2 hrs. The dried layer is further annealed at 200°C for 30 mins to fixate the powder photocatalyst on the glass. A volume of 28.8 cm^3 of the catalyst suspension was immobilized ensuring an optimum catalyst loading of 0.5 mg/cm^2.

2.2.1. Photoreactor Prototype and Reaction set-up

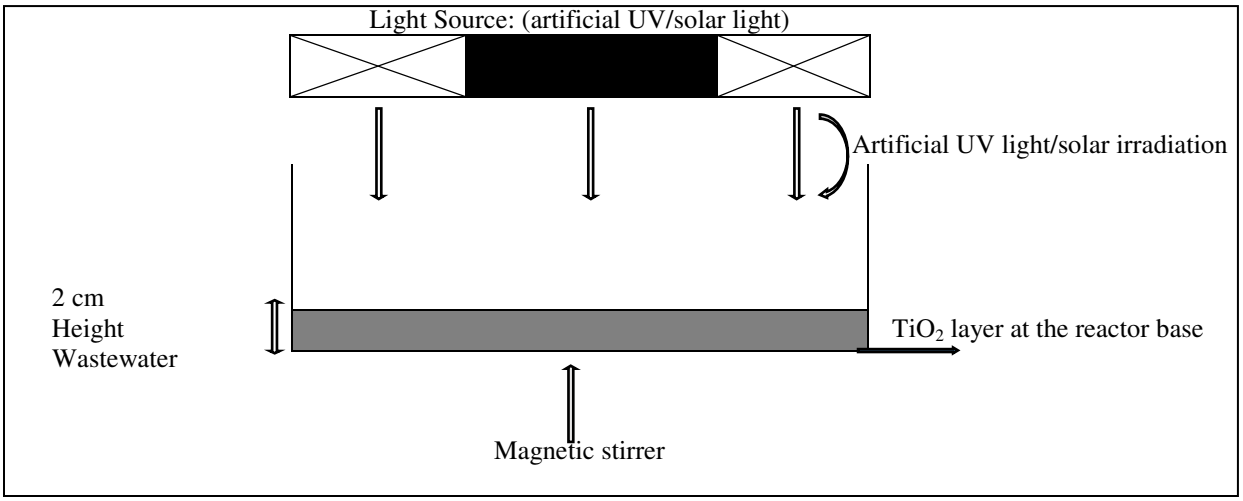

Figure 2: Batch photoreactor set-up

The decolourization experiments were done in a batch photoreactor (20 cm ✕ 15 cm ✕ 10 cm) as shown in fig.2 above. A filtered volume of 500 cm^3 of the wastewater was placed into the reactor. The reactor was placed on a magnetic stirrer to ensure perfect mixing. As a source of UV light, artificial UV lamps and solar energy were used. The coated layer was inserted to the base of the reactor. The dimensions of the reactor were (18 cm ✕ 13 cm) inserted to the bottom of the rectangular reactor. The distance between the surface of the solution and the UV lamps with a maximum irradiation wavelength at 365 nm from a distance of cca. 10 cm.

2.2.2. Artificial UV/TiO_2Coated Layer Photocatalytic Decolourization Experiments

Two 15 W near UV (black light) fluorescent lamps are used for irradiation with UV light. The fluorescent tubes emit light of wavelengths between 320-400 nm, maximum irradiation wavelength at 365 nm at a height of 10 cm. The average measured radiation flux density was 3.0mW/cm^2 to supply UV photons to the photoreaction. The reaction takes place at room temperature. The light intensity of the UV lamps was measured at 365 nm using a digital UVP.

2.2.3. Solar Light/TiO_2Coated Layer Photocatalytic Degradation Experiments

For this set of experiments sunlight was used to supply UV photons. The average measured solar irradiance flux density for Nandi County measured at 1.45 mW/cm^2 at wavelength 365 nm using a UVP digital radiometerover the duration of the photocatalytic degradation reactions. The decolourization reactions were done at room temperature.

2.3. Analyses

Changes in effluent colour with irradiation time was determined with a spectrophotometer (UV- Cecil 2020) for absorbance measurement and (UVP radiometer) for UV light irradiation flux density. The efficiency of the decolourization system was determined by calculating the percentage of colour removal with irradiation time.

3. Results and Discussions

3.1. UV/Vis Spectra for Raw Wastewater

From the graph, effluent from Chebut shows a lower absorbance. Effluent from Kibwari and Nandi tea are higher compared to Chebut and almost similar. Nandi Tea and Kibwari tea processing factories are located within the same geographical area i.e. near Nandi-Hills town. Chebut tea processing factory is located in Kapsabet town. Differences in soil and climatic conditions. Photocatalytic degradation experiments were measured at λ=410 nm.

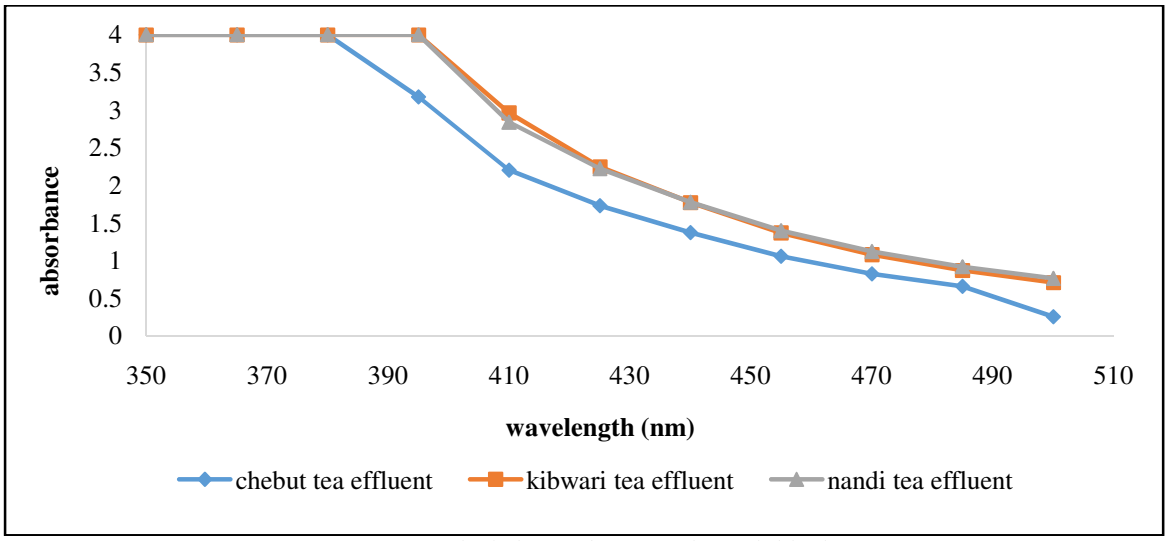

Figure 3: UV/Vis spectra for untreated Chebut, Kibwari and Nandi black tea processing wastewater

3.2. Photocatalytic decolourization of tea Wastewater using Artificial UV Light Source

Experiments to remove the colour from the wastewater from Chebut, Kibwari and Nandi tea factories. The efficiency of the photocatalytic degradation to remove colour was represented as a change in absorbance at λ=410 nm over a 3-hr. duration. The results obtained are shown in fig.4 below.

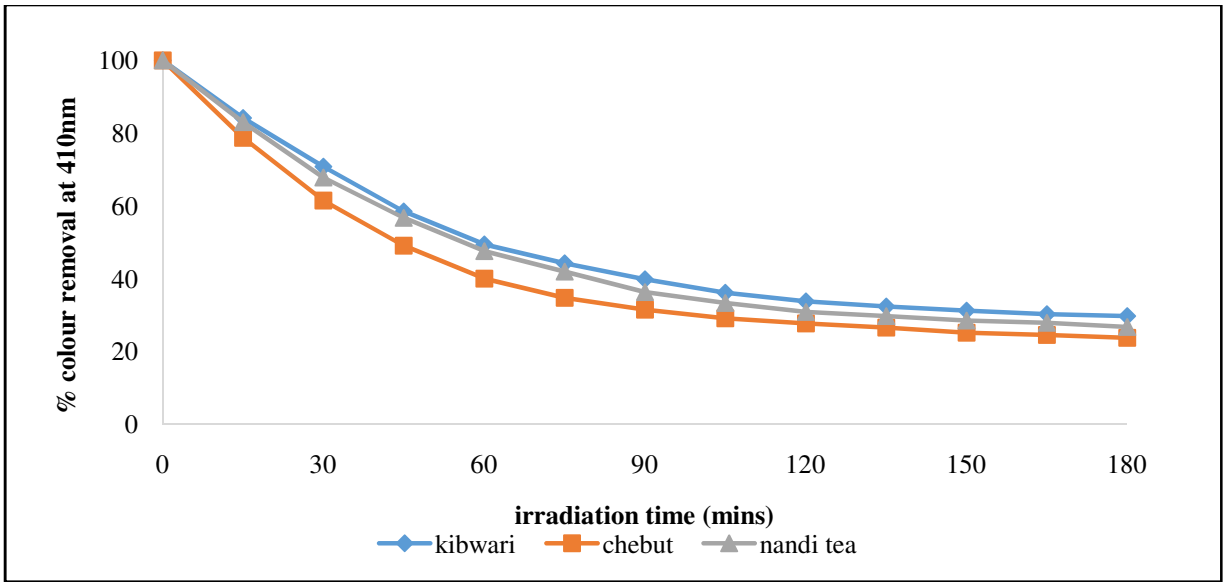

Figure 4: Photocatalytic colour removal of wastewater by TiO_2 and artificial UV light

The results show that after 1 hr. 60.03% of Chebut, 52.44% of Nandi and 50.6% of Kibwari colour had been removed. After 3 hrs., an average of 73.3 % of colour had been removed from the 3 samples. From fig.3 the concentration of Chebut wastewater is significantly lower compared to Nandi and Kibwari.

3.3. Photocatalytic decolourization of Tea Factory Effluent with Solar Light

Experiments to remove the colour from the wastewater from Chebut, Kibwari and Nandi tea factories. The efficiency of the photocatalytic degradation to remove colour was represented as a change in absorbance at λ=410 nm over a 3-hr. duration. The results obtained are shown in fig.5 below.

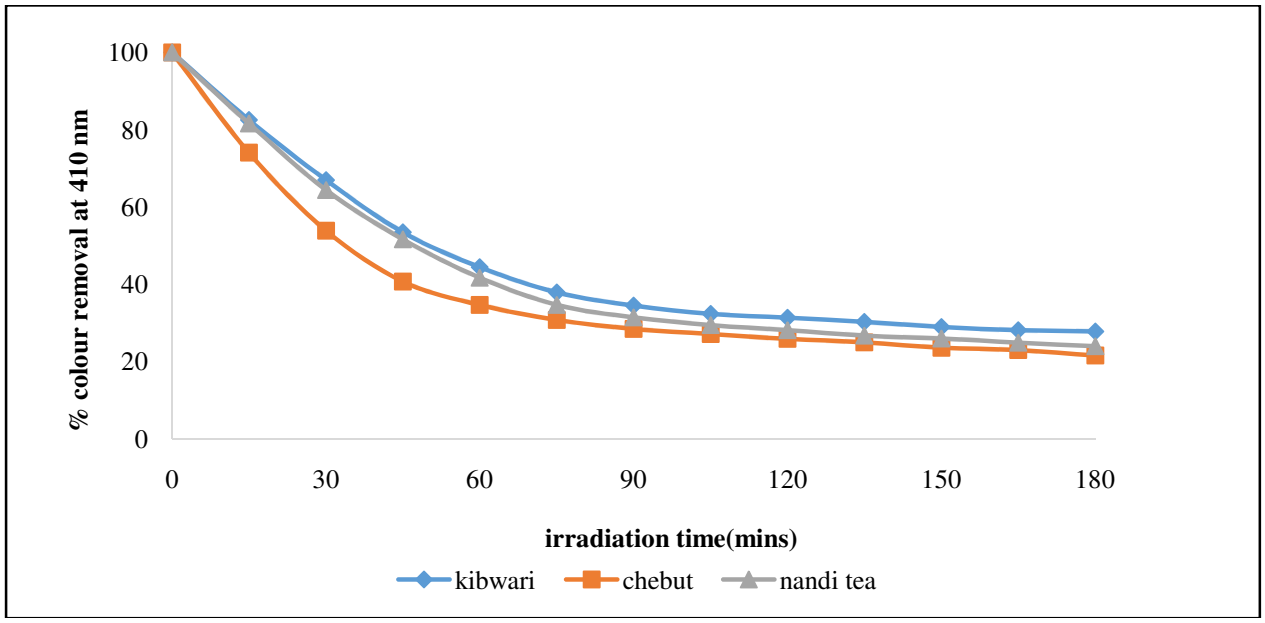

Figure 5: Photocatalytic colour removal of wastewater using TiO_2 and solar light

The results show that after 1 hr. 65.39% of Chebut, 58.3% of Nandi and 55.55% of Kibwari colour had been removed. After 3 hrs., an average of 75.6% of colour had been removed from the 3 samples. From fig.5 the efficiency of colour removal was higher in Chebut and least in Kibwari. The results are consistent with those in Figure 4 where UV photons were supplied by artificial light.

3.4.Comparison of Decolourization Efficiency between Artificial UV Light/Solar Light

The experiments in fig.6, 7 and 8 show results comparing the efficiency between the photocatalytic discolourization of wastewater by artificial UV and solar light source.

3.3.1. Kibwari Tea Wastewater Comparison of Artificial Solar UV Light Using Tio_2

Solar energy experiments were slightly more efficient to artificial light. The amount of UV light irradiation from solar energy was almost 50% lower than in artificial UV light. For Kibwari wastewater colour removal was 72.3 % for solar energy and 70.4% for artificial light.

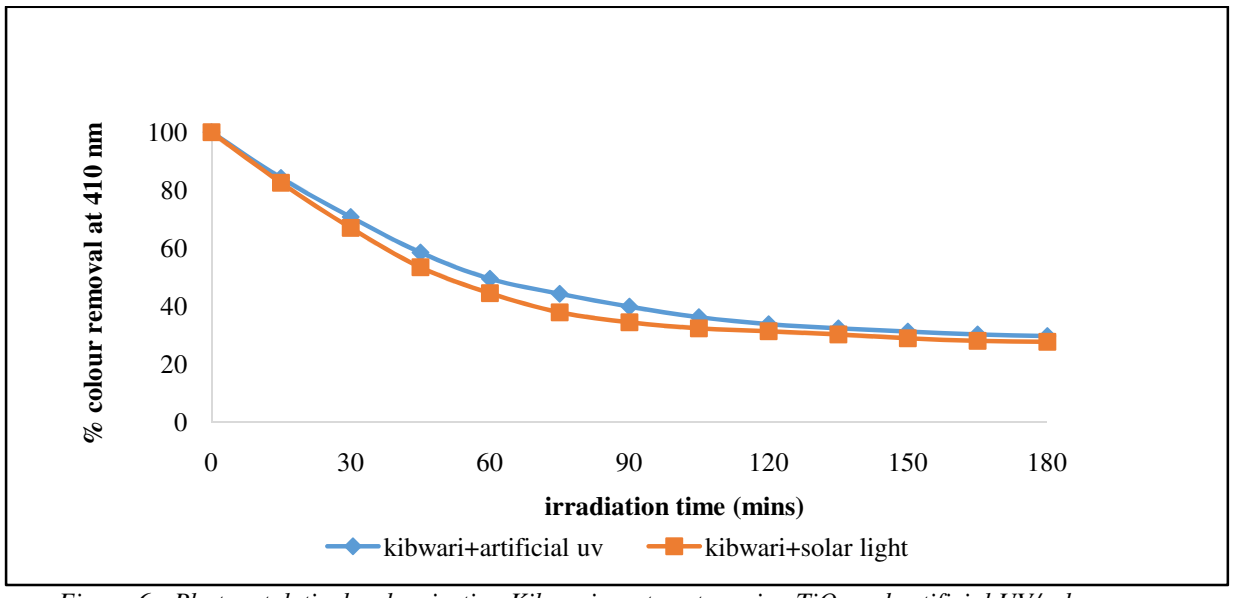

Figure 6: Photocatalytic decolourization Kibwari wastewater using TiO_2 and artificial UV/solar energy

3.4.2. Chebut Tea Wastewater: Solar/Artificial UV Sources

Solar energy experiments were slightly more efficient to artificial light. The amount of UV light irradiation from solar energy was almost 50% lower than in artificial UV light. For Chebut wastewater colour removal was 78.5% for solar energy and 76.3% for artificial UV light.

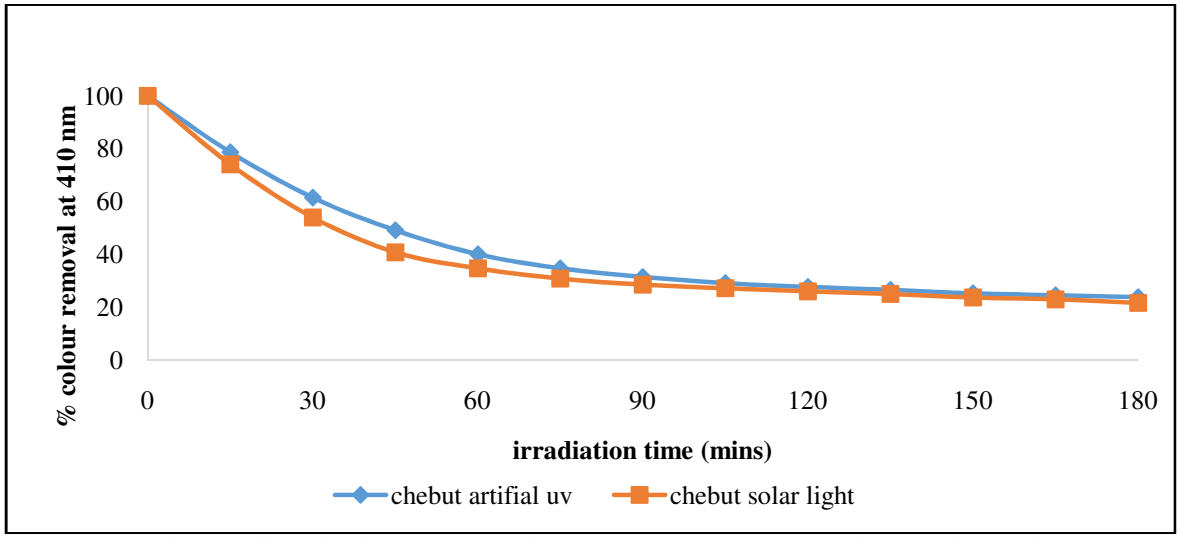

Figure 7: Photocatalytic decolourization Chebut wastewater using TiO_2 and artificial UV/solar energy

3.4.3. Comparison of Degradation of Nandi Tea Effluent Solar/Artificial

Solar energy experiments were slightly more efficient to artificial light. The amount of UV light irradiation from solar energy was almost 50% lower than in artificial UV light. Nandi tea wastewater colour removal was 76.1% for solar energy and 73.3% for artificial UV light.

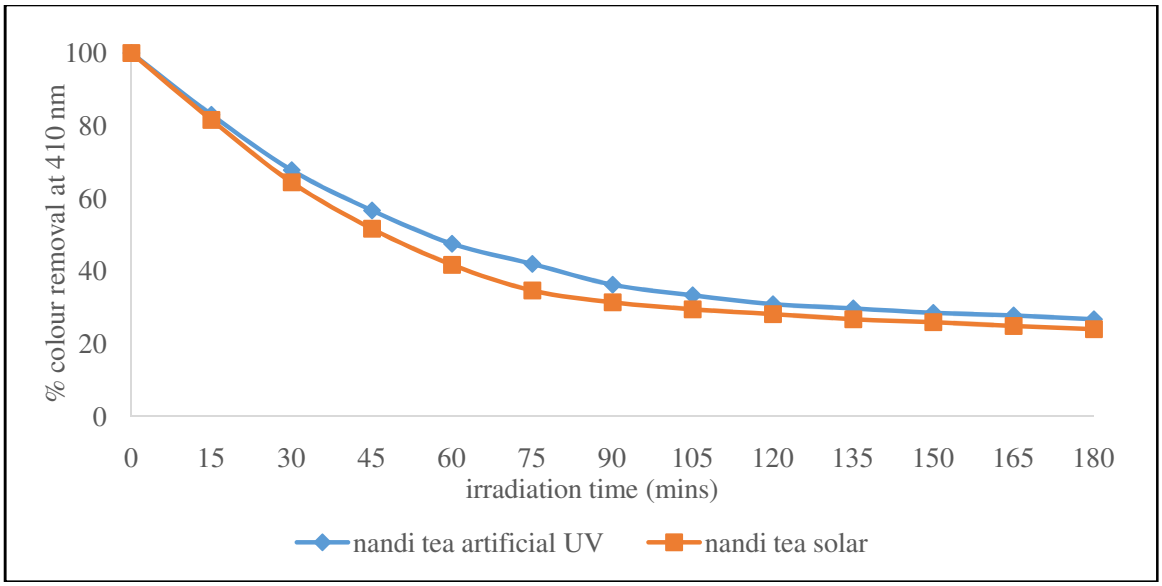

Figure 8: Photocatalytic degradation Nandi tea wastewater using TiO_2 and artificial UV/solar energy

4. Conclusions

The present findings indicate that suggest that the TiO_2/UV/sola light system is effective to decolourize wastewater discharged from tea processing factories. In addition, TiO_2 proved to be an effective semi-conductor photocatalyst under artificial UV light and solar light irradiation. The photocatalytic decolouring efficiency was higher with solar irradiation than with artificial UV light irradiation. Solar light irradiation proved efficient compared to artificial light since almost similar rates of decolourization efficiencies were achieved although the irradiation flux density was 1.4 mW/cm^2 for solar light and 3.0 mW/cm^2 for artificial UV light. We conclude that the TiO_2/solar light decolourization system proved more viable compared to UV/TiO_2. This maybe as a result of the role of photosensitized oxidation in decolourization where visible light in addition to UV light initiates decolourization. These systems can be scaled up to a large-scale wastewater decolourization to remedy the removal of persistent brick-red colour from tea wastewater in tea processing factories in Kenya.

5. Acknowledgements
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