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Photocatalytic activity of green synthesized titanium dioxide nanoparticles and wastewater remediation

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Abstract
Titanium dioxide (TiO_2) nanoparticles are synthesized by a sol-gel combustion process using aloe-vera gel as precursor. Green synthesized TiO_2 nanoparticles are chemically stable, low toxic, low pollutant load, ecofriendly and cost effective. Due to high surface-to-volume ratio nano-sized TiO_2 is highly photocatalytic and hence with help of them, the wastewater remediation is well performed. The TiO_2 nanoparticles size has been reduced for increasing the reactive surface area to improve efficiency of the photocatalyst. TiO_2 photocatalyst degrade many organic and inorganic pollutants effectively and turn into CO_2 and other harmless inorganic anions. By adding TiO_2 nanoparticles in wastewater, the dissolved oxygen and p^H value of water both increase and further increase with time of fall of UV radiation. The kurtosis, skewness and correlation parameter of the given data are determined and discussed. The statistical results are strongly consistent with the spectral behaviour of the dissolved oxygen and p^H value of the water.

Keywords: Dissolved oxygen, green synthesis, photocatalysts, titanium dioxide nanoparticles, wastewater remediation

1. Introduction
Nanotechnology has a great importance and the researchers are focusing on the new applications of nanoparticles in the field of environment, industry, agriculture, pharmaceuticals, etc. Nanoparticles are interesting as they show unique and considerably different physical and chemical properties compared with their macro-scale counterparts [1]. A bulk material has constant physical properties regardless of its size, but at nano-scale, size dependent properties are often observed. Due to high surface to volume ratio, metal and metal oxide nanoparticles have fascinating properties like antimicrobial, magnetic, electronic, and photocatalytic activity. The green synthesis of TiO_2 nanoparticles is cost effective and ecofriendly [2]. The photocatalytic property of TiO_2 nanoparticles help in water remediation using hydrolysis technique. Its photocatalytic behaviour helps in degradation of impurities and increase the oxygen quantity. The objective of the research work is to focus on the aspects of green synthesis of TiO_2 nanoparticles and their utility in the field of wastewater remediation. Photocatalytic activities of TiO_2 nanoparticles are studied through photocatalytic water splitting, photocatalytic self-cleaning, wastewater remediation, photo-induced super hydrophilicity, photovoltaics, and antimicrobial activity [3-4]. TiO_2 photocatalysis performs the photo-degradation of various environmental contaminants like complex organic compounds and inorganic material which turn into CO_2 and harmless inorganic anions respectively. TiO_2 nanoparticles are freely suspended in wastewater or deposited on substrates during the decontamination process of waste water [5-6].
Photocatalytic activity of TiO_2 under the presence of ultraviolet (UV) light, is applied in the process of photocatalysis and photovoltaics. The TiO_2 nanoparticles are widely used in the area of sensors, lithium-ion batteries, super capacitors, catalyst support, microwave absorbent and biomedical applications [7-8]. These applications prove that the TiO_2 nanoparticles are helpful in serving human society and deserve much more applications. Various factors, like shapes, size, and special facets, are responsible for the photocatalytic properties of TiO_2 nanoparticles. TiO_2 nano-materials are n-type semiconductors and found in three polymorphs namely anatase, brookite and rutile structure. TiO_2 nanoparticles are frequently used as photocatalysts due to their optical properties, low cost, high photocatalytic activity, chemical stability, and non-toxicity [9-10].

In the photocatalytic process, light energy is converted into electrical or chemical energy. High surface to volume ratio of nano-materials plays an important role in their photocatalytic activity [11-12].

In the present work, an attempt is made to prepare green synthesized TiO_2 nanoparticles and further, waste water remediation through their photocatalytic activities is studied.

2. Green synthesis of titanium dioxide nanoparticles

All the ingredients and reagents needed to make TiO_2 nanoparticles were bought from Merck India Ltd. The leaves of Aloe Vera were collected at the Hindu College campus in Moradabad. Aloe Vera leaves were taken from the plant and properly cleaned before being chopped into little pieces. 100ml distilled water was boiled for 2 hours at 100 °C with 50 g of the leaves. Whatman filter paper was used to filter the extract. The filtrate was saved for nanoparticle synthesis.

To synthesize the TiO_2 nanoparticles, dissolve 1.0 M of Titanium Tetraisopropoxide in 100 ml of Millipore water. Drop by drop, leaves extract was added with constant stirring until the pH of the solution reached 7. The mixture was continuously stirred for 5 hours at 50 degrees Celsius. This process resulted in the formation of nanoparticles, which were then separated using what man filter paper and washed with water repeatedly to remove by-products. The nanoparticles were dried on a hot plate at 100 °C for 2 hours before being calcined at 500 °C for 5 hours [13-14].

3. Photocatalytic Activity of Nano-sized TiO_2

Nano-sized titanium dioxide is an environmentally friendly photo semiconducting material. In the ground state of TiO_2 both the electrons and holes lie in the valence band. The TiO2 nanoparticles are n-type semiconductors. When light is made incident over a semiconducting surface, electrons are transferred from the Valence Band to the Conduction Band by absorbing light of the particular wavelength and causes creation of holes (h^+) in the valence band. In this way the electron–hole pairs are formed. Electrons reduce and holes oxidize the reactants absorbed by the semiconductor. The photo induced electrons and holes exhibit high reduction and oxidation potential in comparison of the hydrogen and ozone. That is why, the photo induced electron-hole pairs work as a strong redox device. The holes in the valence band generate hydroxyl radicals by the oxidation of H_2O molecules adsorbed on the TiO_2 semiconductor surface and the electrons in the conduction band perform reduction of O_2 molecules present in the absorbed air and form peroxyl radicals. The hydroxyl and peroxyl radicals can oxidize and degrade organic and inorganic materials [15]. The photocatalytic hydrogen production and wastewater remediation take place form reduction and oxidation process respectively. The photo-generated electrons and holes can re-join in bulk or on the surface of the semiconductor within a very short time and release energy in the form of heat or photons.

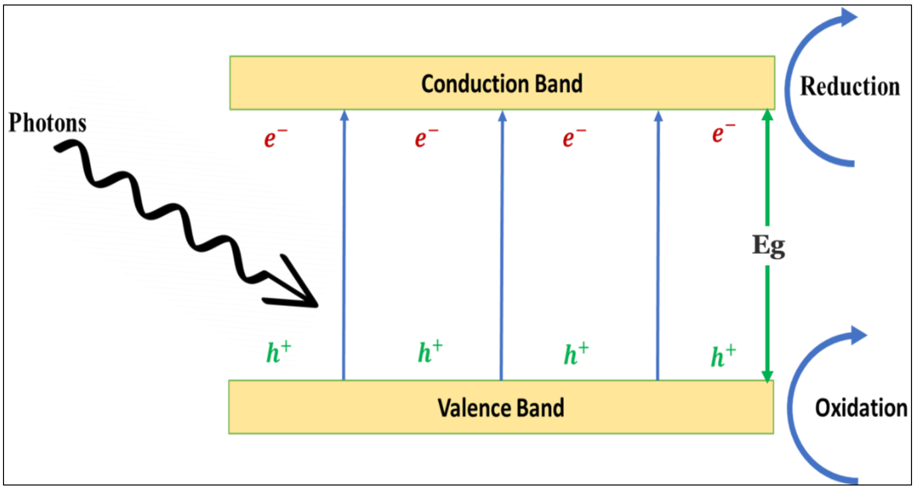

Fig 1: Photocatalytic Action

When photon of energy greater than energy gap Eg (3.23 eV for anatase, and 3.02 eV for rutile), is made incident on the TiO_2 nanoparticles, the energy of a photon is absorbed and an electron makes transition from the valence band to the conduction band. This transition of electrons creates a hole in the valence band.

$$TiO_2 + h\nu \rightarrow e^-_{cb} + h^+_{vb}$$

Under aerobic conditions, the adsorbed oxygen molecule captures the conduction band electron producing O_2^-* ion which is readily protonated in acidic media [9].

$$e^-_{cb} + O_2 \rightarrow O_2^- *$$

This photon generated hole converts the surface adsorbed water or hydroxide ion into a hydroxyl radical in the absence of reducing species [16]. This hydroxyl radical (HO*) can decompose the organic polymer into water and carbon dioxide.

$$h^+_{vb} + H_2O \rightarrow H^+ + HO*$$

Under alkaline conditions, the hydroxyl radical can be produced directly from the (OH^-) ion which interacts with the hole as follows:

$$OH^- + h^+_{vb} \rightarrow HO*$$

This hydroxyl radicals (HO*) are greater in numbers so that the photocatalytic ability becomes better.

In acidic conditions the excess H^+ interact with the free electrons (e-) and radicals H* are formed. The formation of this radical (H*) will cause a backlash with HO* and H* return to H_2O.

$H^+ + e^- \rightarrow H^*$

$H^* + HO^* \rightarrow H_2O$

The amount of the resulting hydroxyl radical in a photocatalytic activity is deduced under acidic conditions and the photocatalytic activity is decreased. Therefore, in the alkaline conditions, the photocatalytic activity is better than in neutral conditions.

4. Results and Discussion

Firstly, the dissolved oxygen and p^H value of the wastewater without sample is observed 1.9 mg/cc and is 7.26 respectively. Thereafter 100 mg of TiO_2 sample is added to the 100 ml. of the wastewater and again the dissolved oxygen and p^H value is observed. Now the water with TiO_2 sample is illuminated by the UV lamp of 11 watt for the duration of 30 minutes and this process is repeated several times and the readings are enlisted in table 1.

Table 1: Data of Dissolved Oxygen and p^H *Value*

S. No.	Time of fall of UV radiation (In hours)	Dissolved Oxygen (In mg/cc)	p^HValue
1.	0	1.9	7.26
2.	0.5	2.2	7.36
3.	1.0	2.4	7.46
4.	1.5	2.5	7.56
5.	2.0	2.6	7.66
6.	2.5	2.7	7.76
7.	3.0	2.75	7.86
8	3.5	2.8	7.96
9	4.0	2.85	8.06

The statical analysis of above data is performed and some statistical parameter are enlisted in table 2.

Table 2: Statistical Parameters of data

S. No.	Parameter	Dissolved Oxygen	p^HValue
1	Kurtosis	4.149099	-1.2
2	Skewness	-1.93401	-2.85486×10^{-16}
3	Correlation	0.860828462	

The spectral behaviour of the dissolved oxygen and p^H value are shown in figure 2 and 3 respectively.

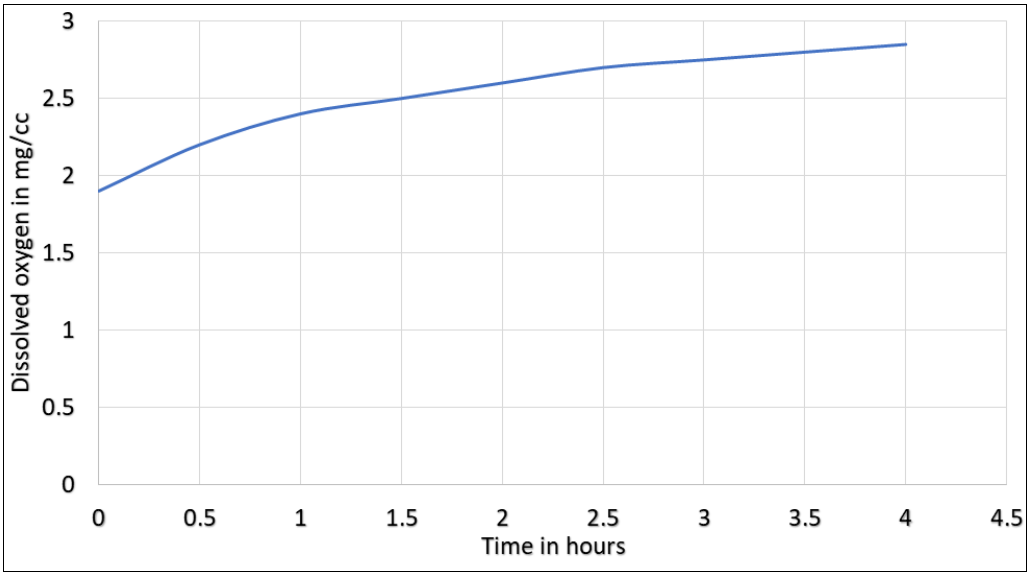

Fig 2: Dissolved oxygen with time of fall of UV radiation

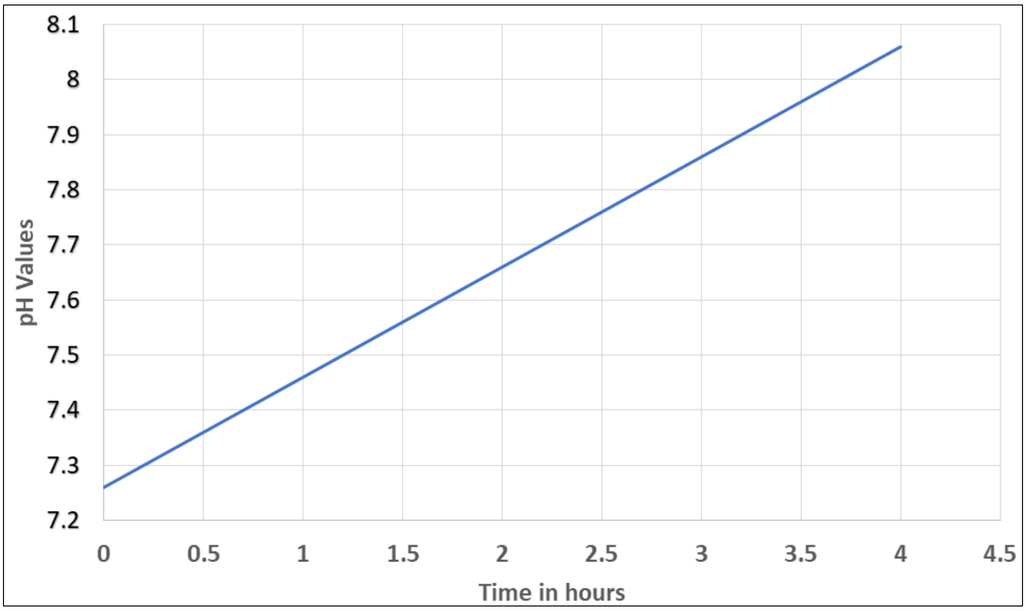

Fig 3: p^H *Value* with time of fall of UV radiation

Kurtosis parameter measures the flatness of the probability distribution of any signal. Positive value of kurtosis of the dissolved oxygen indicates the strong intermittency while negative value indicates weak intermittency in the data. Skewness is a measure that studies the degree and direction of departure from symmetry. Negative value of skewness indicates that the data is skewed to the left. Skewed left means that left tail is long relative to the right tail. Correlation describes the degree of linear relationship between two functions (or signals) [17]. The positive value of correlation means they are linearly related with same slope and high value means that dissolved oxygen and p^H Value are highly dependent.

5. Conclusion

Green synthesized titanium dioxide nanoparticles are eco-friendly photo semiconductors and their photocatalytic activity has attracted great attention from the researchers in the field of environmental remediation. The dissolved oxygen and p^H value of waste water increases when green synthesized nanosized TiO_2 sample is added to it and further increase when the waste water is illuminated by UV light. On the other hand, the impurities of waste water get reduced when green synthesized nanosized TiO_2 sample is added and further reduced when this is illuminated by UV light.

From the present analysis, we found that the dissolved oxygen and p^H values of the wastewater are strongly and weakly intermittent respectively. Skewness parameters are low and negative, and correlation is positive and high in that time period. With the statical analysis, we can say that there will be little flatness or broadness in probability distribution of dissolved oxygen in comparison of p^H values with slight decrement in degree and direction of departure from symmetry. By virtue of these results, we can say that the results of spectral analysis and the statistical analysis both are strongly consistent.

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