

Removal of Carbonyl-Containing Effluents by Photodegradation Using β -Carotene Embedded onto Zinc Oxide Particles

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Abstract: Environmental pollution especially in the form of effluent wastewater from industries has been a major challenge. Carbonyl-containing organic standards and sewage sample were effectively photo degraded. ZnO nanoparticles were prepared by emulsification of zinc-carbamate solution using 1 N NaOH and grafted chemically by Molecular Layer Doping method at 180 °C with β -carotene extracted using methanol by refluxing at 50 °C at varying concentrations. Intrinsic and grafted β -carotene ZnO were characterized using FTIR (Fourier transform infrared spectroscopy) and their spectra differed in an additional peak at around 1,435 nm corresponding to the organ metallic bond Zn-C. UV-Vis spectra of the two composites indicated a blue shift in the grafted samples. This translated to a reduced band gap from 3.5 eV to 3.4 eV. Comparison in the rates of photodegradation of pure organic compounds, organic effluents and color change of dyes was in the order 1% grafted, 0.5% grafted, intrinsic ZnO and blank sample. When 10.0 mL of sewerage water was photo degraded using both sunlight and UV-Lamp for 40 minutes, the amount of carbonyls present decreased by 28.5% for β -carotene grafted ZnO, 24.5% for intrinsic ZnO and 0.6% for a blank sample.

Key words: Intrinsic ZnO, β -carotene, organic effluents, carbonyls, photo-degradation.

1. Introduction

Effluent organic pollution is a universal problem that affects aqua life. Most of these pollutants are long-chain natural products, acetogenic and alkaloidal in nature and their molecular structures are found coupled, with aromatics as well as coordination structures. For example, most textile dye effluents are released continuously, thus require a continuous controller [1]. Most are non-biodegradable thus have almost permanent effects that are encountered very slowly, mainly through bacteria action [2]. Dissolved oxygen in effluent waters is usually lower compared to clean water due to chemical and bio-chemical reactions that take place in the presence of these impurities [3]. Organisms in such water bodies are thus prone to

asphyxiation and reduced fitness which can lead to their death. On the other hand, increased particulates as a result of impurities increase the turbidity level of wastewater, hindering light penetration into the water [4]. Photosynthesis of planktons in these waters is thus reduced. Substratum composition at the bottom of water bodies is also altered by settling particulates and organic matter.

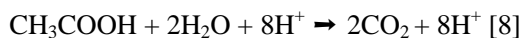
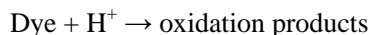
Most of these compounds are coordinate compounds and also incorporate heavy metals in them. When these compounds are up taken by planktons, they are then ingested by fish and later by humans or other higher animals [5]. Some leach into nearby plants and can either affect the plant itself or its feeders. Increased levels of heavy metals in the body cause neural and kidney disorders [3].

Over time, various methods have been employed to clean wastewater for domestic or industrial use. Unfortunately, most of the methods exploited have not

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yielded much. Actually, some traditional methods have been accused of transferring the pollutant matrix from one form to another, creating more harm than before. Some of the physical methods employed include carbon adsorption, reverse osmosis and ultrafiltration. While adsorption is quite effective, the method cannot work optimally for pollutants at very low concentration, not unless the active sites of the carbon are functionalized or expanded (which is expensive). Ultrafiltration and reverse osmosis are also quite expensive for most developing nations. Chemical methods used include coagulation, flocculation and ion exchange. Flocculation and coagulation by chemical agents are less effective for effluent removal while ion-exchange is quite expensive [6, 7].

With an ever-increasing human population, water treatment and recycling from effluents are very crucial [1]. Industrial effluent cleanup is therefore receiving more attention over time. Photochemical reactions using semiconductors like TiO_2 and ZnO are currently being used [8]. To enhance its effectiveness, chemists have tried to induce doping on its nanosurfaces, thus opening more channels for other studies, since the grafted surfaces are not only good photo catalysts but also anti-oxidants and promote electrical conductivity. Photocatalysis using zinc oxide particles in the presence of light has been proven to degrade wastewater to simpler and relatively friendlier compounds such as CO_2 , HCl and water [6, 9].



Zinc oxide used as a photocatalyst is gradually growing populace due to its multiple attributes. The compound is widely available making it cheap. Zinc oxide is also found in several forms, most of which have excellent physical and chemical characteristics. Zinc oxide reacts with most organic and inorganic chemicals at ambient conditions. Its band gap is wide enough and is naturally n-type semiconducting

material [10, 11]. The compound is environment friendly and non-toxic. Zinc oxide has been used in numerous photovoltaic applications due to its extensive light absorbance [12, 13]. Its photocatalytic activity at low cost and using natural sunlight makes it a favorite compound for photovoltaic works [7, 14]. The band gap of zinc oxide particles ranges at about 3.36 eV ($\lambda = 388 \text{ nm}$). β -carotene is a suitable dopant, as due to its conjugation system absorbs both UV and Vis-light just as ZnO [15].

With a rapidly increasing human population: natural resource index, there is more demand for cleaner water. Since the current water sources are slowly being depleted, it is pertinent for reclamation of the polluted water by cleaning it using cheap and efficient methods. Organic photocatalysis is one such method. This study purposed to minimize organic pollutants from wastewaters by use of photocatalysis using beta carotene powder embedded onto zinc oxide particles. Both beta carotene and zinc oxide can optimally absorb at normal sunlight wavelength. Beta carotene can easily be sourced from *Opuntia stricta* cacti, abundant in arid and semi-arid regions of southern part of Rift valley, Kenya.

2. Materials and Methods

2.1 Experimental Design

Beta carotene was prepared from cacti *Opuntia stricta* and carrot peels then characterized before grafting onto zinc oxide particles prepared by emulsification of zinc carbamate at alkaline conditions. The grafts were performed at high temperature of 150-180 °C. Thereafter, the intrinsic and grafted zinc oxide particles were coated onto aluminium foil reactor and test analytes degraded. Standards of carbonyl containing organic compounds (formaldehyde and acetone) were run before samples of dyes (methyl blue and 2,4-DNP hydrazine) and sewage water samples were run. Effective carbonyl removal was tested using titration method and a *t*-test run to compare the rates of removal between intrinsic

and grafted zinc oxide.

2.2 Materials

Chemicals: methanol, 98% ethanol, toluene, *n*-hexane, zinc nitrate, urea, sodium hydroxide, acetone, formaldehyde, sodium bisulfite, methyl blue indicator and 2,4-dinitrophenyl hydrazine. All chemicals were from Sigma-Aldrich products.

Apparatus: -10-360 °C Range Thermometer, 10 mL and 100 mL glass measuring cylinders, #41 Whatmans filter papers, stirring rods, stop watch, 30 test-tubes, 5 droppers, 5 filter funnels, round bottomed flask, liebig's condenser with adapter, about 1.5 m² 20 mm thick aluminium sheet, 12 100-mL glass beakers.

Access to: analytical balance, source of heat, magnetic stirrer, gas syringe or gas flow meter, UV-Vis (UV-550; Jasco, Japan) and FTIR (Fourier transform infrared spectrometer), Shimadzu.

2.3 Extraction of β -Carotene

Solid carrot and cacti *Opuntia stricta* fruits paste (50 g) are run through 30 minutes in 150 mL methanol. (ratio 3:1) with samples taken and evaluated every fifth minute between 40 and 65 °C. After 60 °C, the paste extracted was dark orange with the sample extracted at 70 °C very dark in color. The samples were refrigerated then filtered using normal filter paper (size 41). The samples were initially tested by solubility in which case they were found to be soluble in benzene and hexane but insoluble in water [15]. Samples were stored in dark. Thereafter, an FTIR spectra was run to confirm correspondence with library spectra.

2.4 Preparation of ZnO Particles

Zinc nitrate of mass 0.7 g and 0.2 g of urea was dissolved in 100 mL distilled water. Slowly the solution was stirred until the crystals fully dissolved. By now the solution is transparent. Three-five drops of 1 N NaOH solution (0.5 g in 20 mL water) are added to adjust the solution to pH 12.0. As NaOH is

added, the solution becomes turbid, producing a whitish cloudy precipitate. It was then heated for 15 minutes and a white dispersion that is slightly blue is seen. This slightly blue color indicates presence of nanoparticles. They were characterized using FTIR and UV-Vis.

2.5 Sol-Gel Dipping Process to Coat β -Carotene Grafted Zinc Oxide on Aluminium Sheets

An aluminium sheet of size 21 by 11 cm was cleaned by scrubbing the surface gently to remove any impurities or oxide layers on the surface. The cleaned sheet was then dipped in the grafted zinc oxide solution for about 10 minutes. The sheet was then gradually removed from the solution and air-dried for 2 hours [16]. This was repeated two more times for uniform coating thickness to be obtained.

2.6 Preparation of β -Carotene Grafted Zinc Oxide Nanoparticles

ZnO particles were grafted chemically by Molecular Layer Doping. Varying concentrations of β -carotene powder were calcinated and blown onto Zinc Oxide-NP solution coated on aluminium sheet at around 150 °C (annealing). Surface characterization was done using FTIR and UV-Vis spectrophotometers.

2.7 Experimental Set-Up and Procedure

A ZnO coated aluminium sheet was folded to make a continuous reactor of length 40 cm with an external diameter of 10 cm then folded to make an open cylinder. The ends were not joined together. The setup was inclined at an angle of around 10° for slow movement of the test samples. The front side was connected to an overturned bottle from which the test samples will be flowing from. On the rear side a collecting glass was placed to collect the degraded samples.

2.8 Analysis of Test Samples

Ten (10) mL samples of 1 M and 14.5 M acetone, 1

M formaldehyde, 98% ethanol and sewerage water were tested for the percentage of carbonyl groups present determined by titration using sodium bisulfite and 1 N alkali solution (caustic soda) before and after degradation in the above reactors for 40 minutes. The following formula was used:

$$\%C = O = \{(V_S - V_B/W) \times N \times M/1,000\} \times 100$$

where V_S is volume of titre, V_B is volume of blank, W is weight of alkali solution, N is molar mass in g/mol of test sample (carbonyl) and M is concentration of titrating solution (NaHSO_3 + Test sample).

3. Data Results and Discussions

Beta carotene extracts were characterized for functional group as shown in Fig. 1 and below.

The major peaks in spectra (Fig. 1) are a trans-conjugated alkene at around 962 nm, asymmetric stretching vibration of CH_2 at 2,922 nm, in-plane CH at 1,033 nm and CH_2 scissoring at 1445 nm.

The major peaks in Fig. 2 are a Zn-O bond at 460-560 nm, O-H vibration at around 3,420 nm and specifically for nanoparticles due to absorption at

early UV region, a stretch at 2,370 nm. The UV-Vis spectra of ZnO nanoparticles indicate absorption at around 330 nm [11].

The major peaks (in Fig. 3) in FTIR of p-grafted ZnO are Zn-O at 460-560 nm, O-H vibration at around 3,420 nm, an absorption at around 2,370 nm and an additional organometallic bond, Zn-C at 1,435 nm [8, 11] UV-Vis spectrum of p-grafted ZnO showing a slight enhanced absorption (300-355 nm) from that of intrinsic ZnO.

From FTIR spectra in Fig. 3, the major peaks are a Zn-O band stretch at around 460-560 nm and an O-H band at around 3,420 nm. An extra band is inserted around 1,458 nm corresponding to addition of the organometallic bond, Zn-C. This illustrates the doping effect of the carotenoids.

From UV-Vis spectrum, the nanocomposites are seen to absorb radiations of this wavelength at the region between 300-360 nm. One can thus conclude that they can absorb early UV (A and B) which is abundantly available in the natural sunlight and is significant for photo degradation of industrial wastewaters. The UV-Vis spectrum of grafted ZnO is

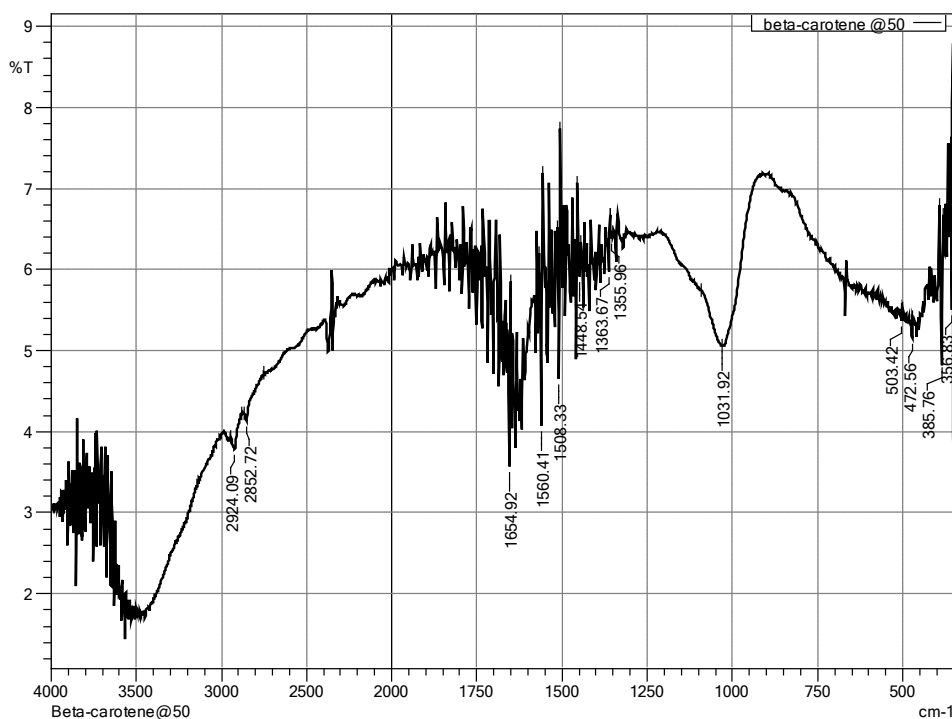


Fig. 1 FTIR spectra of β -carotene extracted at 50 °C.

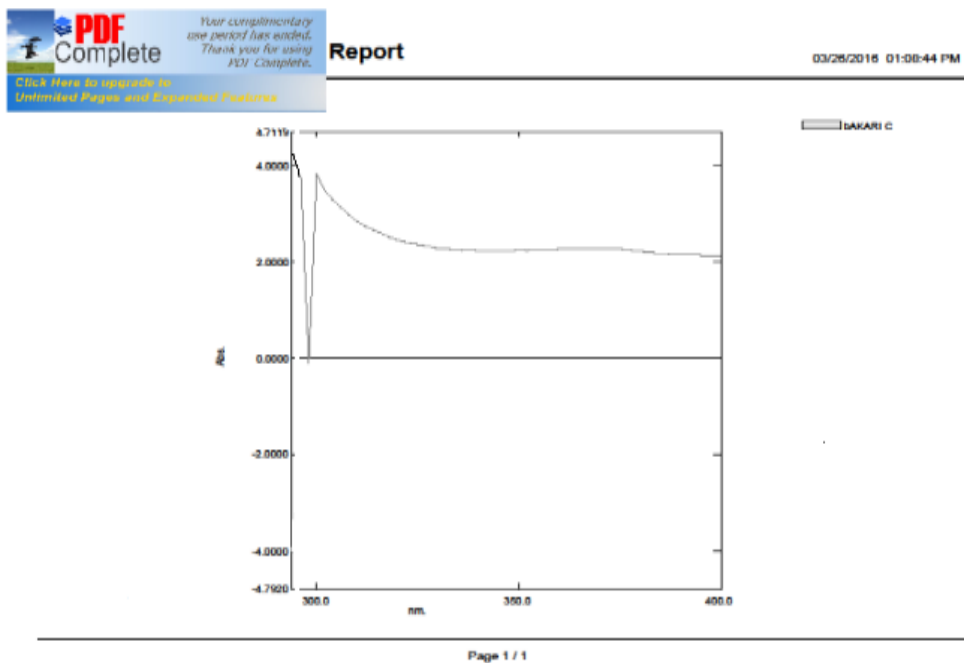
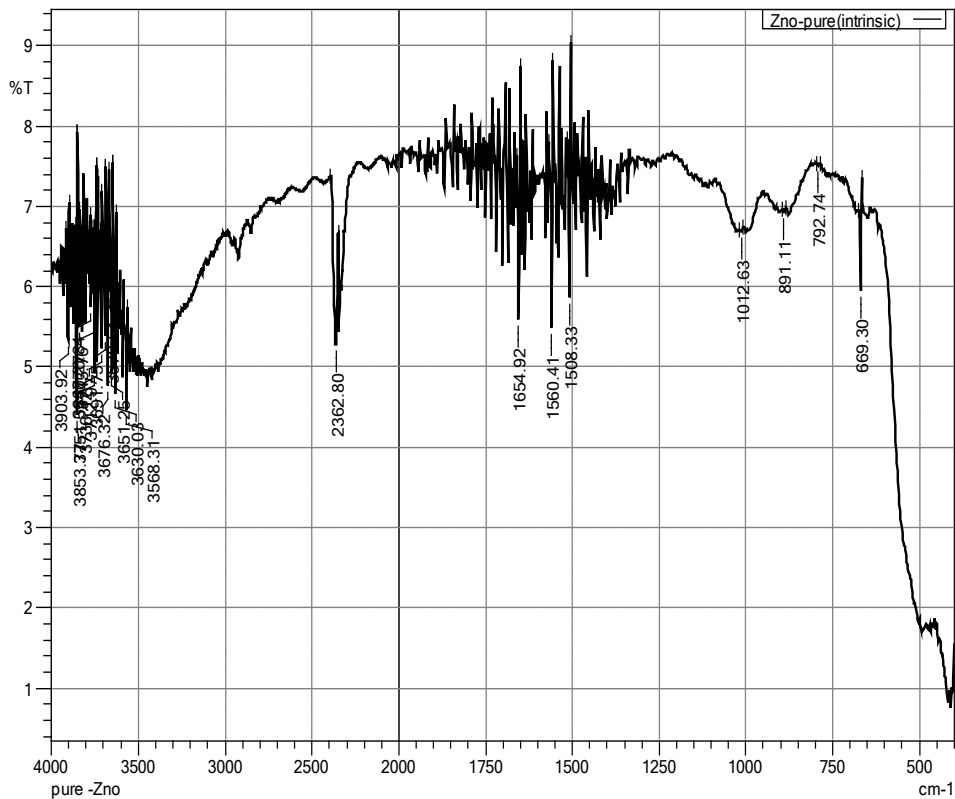


Fig. 2 FTIR spectra and UV-Vis spectra (R) of ZnO nanoparticles from emulsification of zinc carbamate.

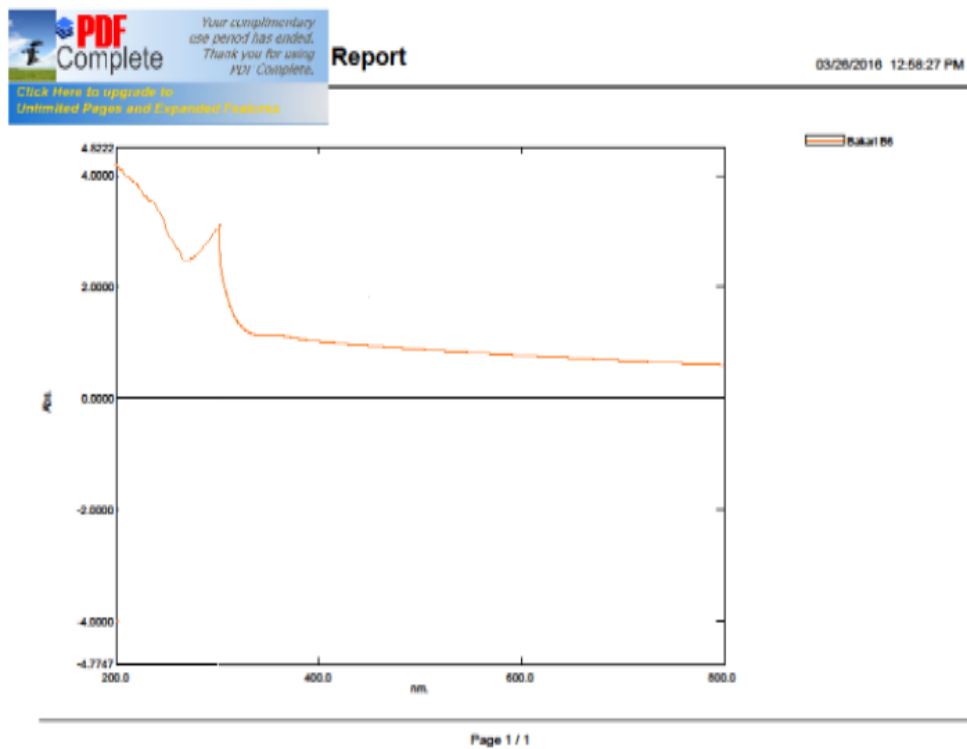
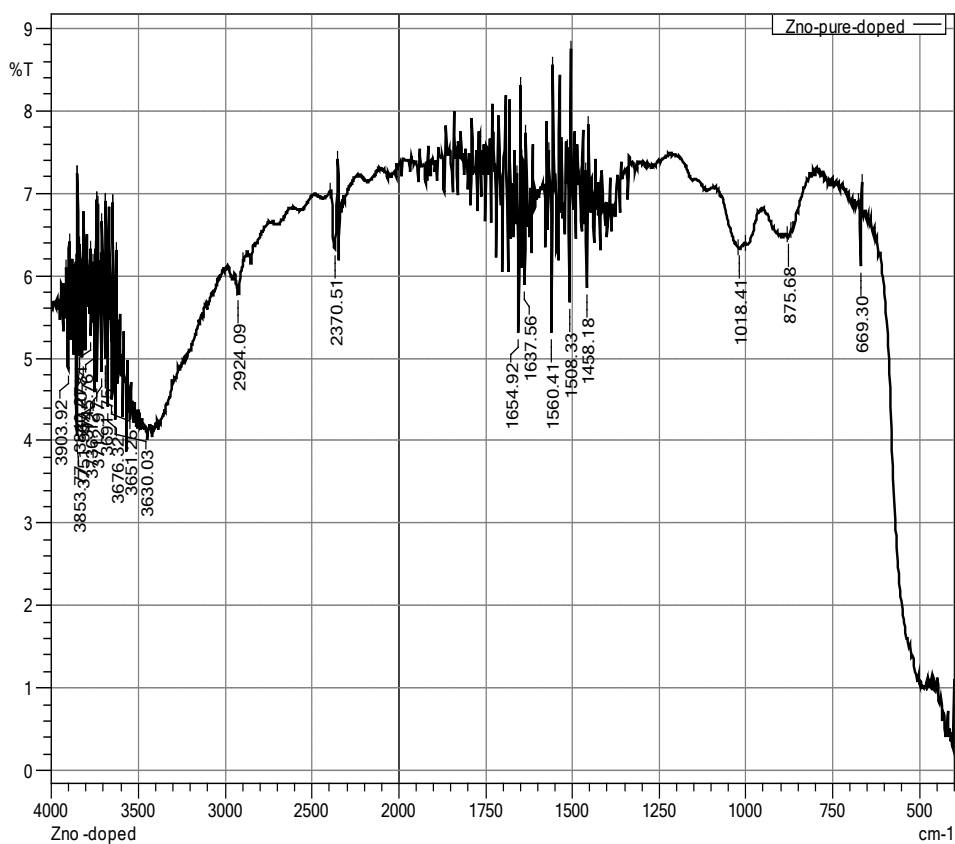


Fig 3 FTIR and UV-Vis spectra of 1% β -carotene grafted ZnO nanoparticles.

slightly blue ended as compared to that of the intrinsic ZnO. The valence bands can be calculated from the heights of the spectra as follows:

$$E = hc/\lambda$$

$$E = 1,240/360$$

$$E = 3.351 \text{ MeV}$$

3.1 Photodegradation of Organic Solutions

Fig. 4 indicates the rate at which 1 M acetone is photo degraded to CO_2 and H_2O for samples placed on a background of aluminium coated with ZnO and grafted ZnO. These samples quickly diminished as they were converted to the more labile CO_2 which is gaseous at the conditions of the reaction (1 atm pressure and around 33°C). The samples placed on background of β -carotene only evaporated with time and this can be proved from the time and volume of acetone left after 80 minutes. The sample evaporated is more than that on the blank aluminium foil because of β -carotene in the aluminium foil which is a conjugated molecule and shows enhanced light absorption [15]. The sample on the blank aluminium foil only slightly decreased under the same conditions as the other samples. Volume decrease on this sample can be wholly attributed to evaporation of volatile acetone and to a less extent blowing off by wind. The rates of photo degradation of acetone by intrinsic and grafted ZnO can be compared as below:

Average rate of photo degradation by intrinsic ZnO = $0.1667 \pm 0.00112 \text{ mL/min}$

Average rate of photo degradation of grafted ZnO = $0.200 \pm 0.00131 \text{ mL/min}$

From Fig. 5, it is clear that the rate of photo degradation of 1 M acetone with grafted ZnO is higher than that of intrinsic ZnO. i.e., $0.140 \text{ mL/min} < 2.00 \text{ mL/min}$.

This rate appeared similar to that of 1% grafted ZnO.

Five percent (5%) grafted ZnO appears to be slower than intrinsic ZnO with their rates being 0.1667 mL/min and 0.143 mL/min respectively (as seen in Fig. 6). It can thus be concluded that at this rate of

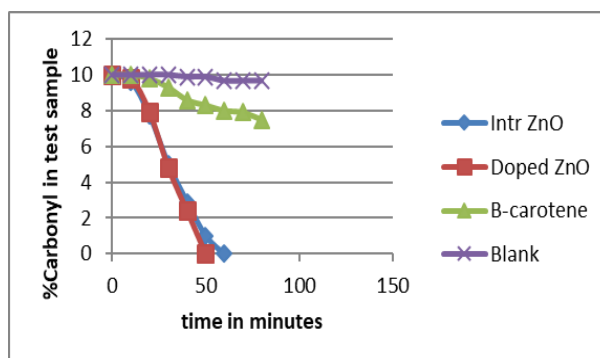


Fig. 4 1 M acetone when 1% β -carotene ZnO is used.

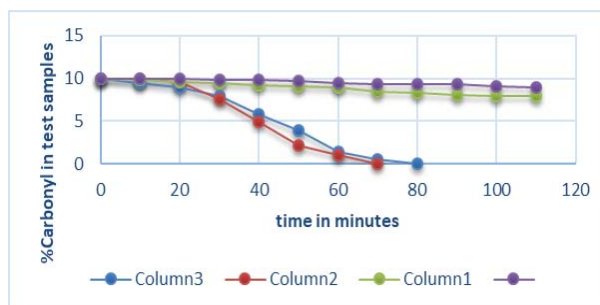


Fig. 5 1 M acetone when 0.5% grafted ZnO is used.

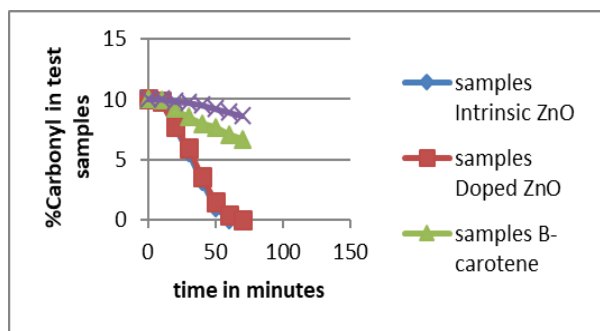


Fig. 6 1 M acetone when 5% grafted ZnO is used.

doping, the carotenoids agglomerate on surface of ZnO inhibiting its efficiency.

Conc. acetone was quickly degraded as compared to 1 M acetone. This can be attributed to the fact that in concentrated acetone, most of the moles are those of acetone. Therefore, any reaction will directly affect the acetones. The acetone molecules were thus quickly degraded. In dilute acetone, most of the moles are of water thus degradation of acetone only partially accounts for the rate of overall degradation. Thereafter, the water molecules left are more easily evaporated due to the latent heat of photo degradation left behind [2]. The rate of photo degradation using intrinsic and

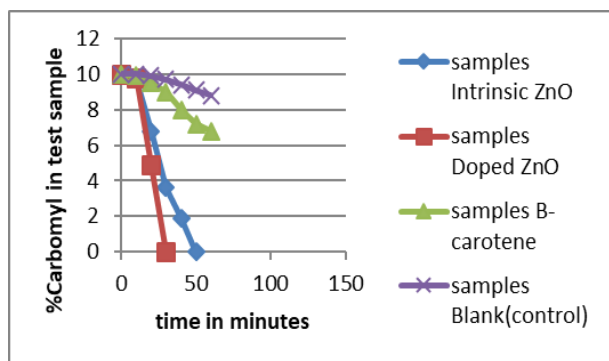


Fig. 7 14.5 M acetone with 1% grafted ZnO.

grafted ZnO at this concentration is 0.250 and 0.333 mL/min respectively. Fig. 7 shows that the order of rate of photodegradation is not affected by increasing the concentration of acetone and maintaining grafting level at 1%.

3.2 Photodegradation (Decolorization) of Colored Dyes

2,4-DNP-Hydrazine decolorization is one of the best indicators for a good photocatalyst. In following,

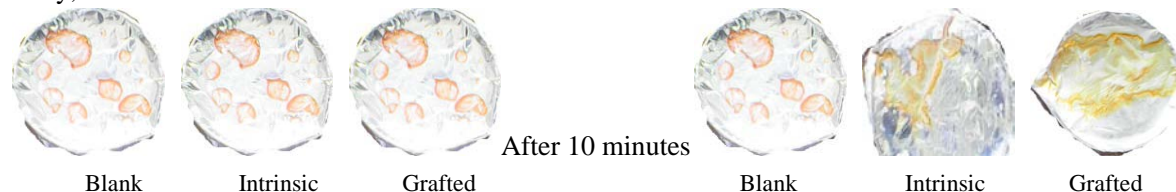
3.2.1 Using 100% v/v Methyl Blue Indicator

Initially,



3.2.2 Decolorization of 1% w/v 2,4-DNP Hydrazine

Initially,



3.3 Photodegradation of Organic Wastewater (Sewerage Water)

Table 1 below shows the percentage of carbonyl removal from waste water when natural light is used:

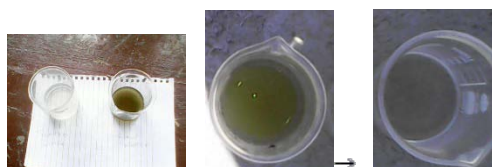
Table 1 Photodegradation of sewerage water carbonyls using sunlight.

% Carbonyl removal after 40 minutes	Blank	Intrinsic ZnO	1% grafted ZnO
Sample A ₁	0.3	18.0	27.0
Sample A ₂	0.0	22.0	25.0
Sample A ₃	1.7	26.0	32.0
Sample A ₄	1.0	28.0	28.0
Sample A ₅	3.0	29.0	31.0
Sample B ₁	1.0	12.0	15.0
Sample B ₂	0.0	33.0	42.0
Sample B ₃	1.0	15.0	21.0
Sample C ₁	0.0	45.0	47.0
Sample C ₂	1.0	14.0	17.0
Average	0.9	24.2	28.5
Median	1.0	24.0	27.5
Variance	0.876	103.511	104.528
Standard deviation	0.936	10.174	10.224

Table 2 Photodegradation of sewerage water carbonyls using UV-lamp.

Sample	Average % carbonyl removal by 1% β -carotene ZnO after 30 minutes in UV lamp
Blank	$0.00 \pm 0.00\%$
Sample A	$24.12 \pm 0.342\%$
Sample B	$24.12 \pm 0.333\%$
Sample C	$18.06 \pm 0.671\%$

Initially,

**Fig. 8** Sewerage water samples (C_1) which were barge in color but the samples in intrinsic and grafted ZnO decolorized after sunlight exposure.**Fig. 9** A photograph to illustrate raw (left) and photo degraded (right) sewerage water.

there is a clear resolution between the samples on intrinsic and grafted ZnO with the grafted sample showing more color change from red to yellow. The sample on blank remained red all through.

Table 2 above shows that sewage samples can also be degraded using light from UV-lamp source. The students t -test was calculated as $t = \frac{[x_1 - x_2]}{[A*B]}$ where x_1 and x_2 are the sample means for intrinsic ZnO and 1% β -carotene grafted ZnO data sets, $A = n_1 + n_2/n_1n_2$, $B = [(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2]/(n_1 + n_2 - 1)$.

$n_1 + n_2 - 2$ gives the degree of freedom for the two data sets. In this test, $t = 1.3333$ and the tabulated value for 18 degrees of freedom at $p = 0.10$ is 1.330. Fig. 8 above shows the color changes that take place when sewage effluent is photodegraded. Use of grafted zinc oxide was found to effectively purify the water; in the process its color changing from green to clear solution as shown in Fig. 9 above.

4. Conclusion

β -carotene was extracted from cacti *Opuntia stricta* seeds and carrot peels using methanol and grafted

chemically by Molecular Layer Doping method at 180°C onto zinc oxide particles prepared by emulsification of zinc carbamate solution to pH 12. The resulting grafts turned from white to slightly orange. FTIR spectra resulted in an additional peak at around 1,435 nm, assumed to correspond to Zn-C organometallic bond. The conjugation system of β -carotene introduces positive holes in the conduction band allowing electrons in valence band to skip to higher energy states thus lowering the band gap of ZnO. UV-Vis spectra indicate a slight blue shift and thus a corresponding decrease in band gap from 3.5 eV to 3.4 eV.

Zinc oxide grafted at between 0.5% and 1% using β -carotene was more reactive as compared to intrinsic zinc oxide nanoparticles while grafting ZnO at 5% level was slower due to agglomeration of carotenoids on ZnO surface. Blank aluminium surface was least photoreactive. Carbonyl containing compounds (acetone, formaldehyde and 98% ethanol) were successfully degraded against control experiments containing blank aluminium foils and a clear disparity in photo degradation was observed. An average

degradation rate of 0.2 ± 0.015 mL/min for 0.5-1% grafted ZnO and 0.16 mL/minute for intrinsic ZnO was recorded against that of 0.01 mL/min for blank samples, clearly indicating disparity in photo degradation when a 10.00 mL volume placed in a 10 cm diameter reactor. Samples degraded with 5% grafted ZnO had degradation rates of as low as 0.11 ± 0.005 mL/min.

Photodegradation of colored methyl blue, orange food color and 2,4-DNP hydrazine clearly indicated alterations of conjugation. Decolorization of 2,4-DNP-Hydrazine from red to orange after 15 minutes exposure to sunlight on a grafted ZnO background indicated photo catalytic activity of this compound. Colored wastewater was also decolorized after 45 minutes exposure on the same reactor.

Sewage water was tested for carbonyl concentration before and after degradation and a mean 28.5% removal rate was recorded in a 45 minutes exposure time. Samples degraded by intrinsic ZnO registered a removal rate of 24.5% while those on blank had a mean removal of 0.6%, attributed to loss of biomolecules such as bacteria due to exposure to UV light. The enhanced efficiency of β -carotene grafted ZnO as compared to that of intrinsic ZnO by 4.0% is due to decreased band gap as a result of p-doping.

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