UV/H$_2$O$_2$/TiO$_2$/Zeolite Hybrid System
for Treatment of Molasses Wastewater

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ABSTRACT: *Wastewater from molasses processing contains a large amount of coloured substances that give a recalcitrant dark brown colour and high organic load to the effluent. Photocatalytic decolourization of molasses wastewater was performed using titanium dioxide catalyst coated on the surface of South African natural zeolite using the solid-solid dispersion method. Addition of hydrogen peroxide as an oxidant was investigated and 30W UV-Clamp was used as source of irradiation. The Chemical Oxygen Demand (COD) of the wastewater treated was varied from 20 g/L to 1 g/L. Batch experiments were conducted in a thermostatic shaker fitted with the UV lamp. The effects of pH, catalyst loading, oxidant dosage and irradiation time on the COD reduction and decolourization of the Molasses Waste Water (MWW) were investigated in this study. The highest colour removal of more than 90% was achieved at pH = 4 and oxidant dosage of 1.47 mM, while low COD removal (< 20%) was observed during photodegradation. A H$_2$O$_2$/UV/TiO$_2$ system achieved higher colour removal of 97% compared to a UV/TiO$_2$ system which achieved 44% while H$_2$O$_2$/UV system achieved 34% colour removal. The rate of decolourization was found to fitpseudo - first order reaction kinetics with the highest rate constant value of 1.36 x 10^{-2} min^{-1}.*

KEY WORDS: *Zeolite, Molasses, Titanium dioxide, Photodegradation, Hydrogen peroxide.*

INTRODUCTION

The increasing demand for sugar as well as molasses fermentation products such as ethanol and baker's yeast has led to a rapid growth in the sugar cane processing industries. These industries are able to produce millions of tonnes of sugar for domestic and industrial uses while at the same time molasses is produced as a by-product.

Most of the molasses produced is used by distillery industries to manufacture ethanol while some leave the sugar industry as waste in the effluent. Still at the distillery industry, a large amount of the molasses remains in the fermentation residues after product recovery. Discharge of molasses wastewater to the receiving water causes environmental stress, largely to the aquatic organisms. This is due to the fact that the molasses wastewater has high Chemical Oxygen Demand (COD) in the range of (80,000–100,000 mg/L), Biological Oxygen Demand (BOD) in the range of (40,000–50,000 mg/L), strong odour and is acidic in nature [1]. Worsestill, the molasses wastewater contains a dark brown recalcitrant colour which impedes the penetration of sunlight to the aquatic photosynthetic plants and therefore reduces dissolved oxygen in river courses. The dark brown pigment is generally called melanoidin formed due to Maillard amino-carbonyl reaction. It is a product of non-enzymatic reaction between sugars and amino compounds [2].

To solve the environmental problems associated with the molasses wastewater, various treatment methods have been applied. Biological treatments with certain bacteria and fungi have been applied with achievement of high organic removal but notable low colour removal efficiencies [3,4]. In fact, [5,6] reported that the conventional anaerobic–aerobic treatment processes can accomplish the degradation of melanoidins only up to 6% or 7% while [7] reported that colour can even increase during the biological treatment due to repolymerization of compounds. For significant colour removal of molasses wastewater, studies have now focused on the use of Advanced Oxidation Processes (AOPs) since they have proved to be efficient [8]. The AOPs are defined as processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize organic pollutants present in the effluent water [9].

These processes include photocatalytic oxidation, which involves the use of ultraviolet radiation, visible light or Sun light in the presence of semiconductor catalyst [10-12] and oxidation using hydrogen peroxide or ozone. The generated hydroxyl radicals are powerful oxidizing reagents with an oxidation potential of 2.8 eV[13] and exhibit fast rates of oxidation reactions. The hydroxyl radicals react with organic solutes with high rate constants [9].

Titanium dioxideis the most preferred semiconductor photocatalyst employed in the photocatalytic treatment of wastewater due to its large photocatalytic activity, high stability, non-environmental impact and affordable cost [8]. Application of zeolite as support material for TiO_2 during the photodegradation process has been reported [14]. The TiO_2 is coated on zeolite surface to integrate its photocatalytic activity with the adsorption properties of the zeolite, which induces a synergistic effect, resulting in the enhancement of photodegradation efficiency. This also facilitates post treatment separation of the catalyst from the treated water, an activity which becomes very tedious and expensive if suspended catalyst is used [15].

Advanced oxidation processes can be combined in various ways to form hybrid systems that reduce degradation time and can treat a wide variety of recalcitrant organic pollutants in wastewater streams. Some of the hybrid systems which have been used for wastewater treatment include UV/H_2O_2, UV/ozone, UV/H_2O_2/ozone, UV/TiO_2 and $UV/H_2O_2/TiO_2$ [16-18]. In this study the efficiency of the hybrid system constituting AOP in which TiO_2 coated on South African natural zeolite (clinoptilolite) is used as catalyst, UV as radiation source and chemical oxidation where hydrogen peroxide is used as the oxidant was examined in the COD removal and decolourization of molasses wastewater.

EXPERIMENTAL SECTION
Materials and equipment

Molasses was purchased from a local commercial outlet at Vanderbjilpark, South Africa. The South African natural zeolite was purchased from Pratley mining company in South Africa and crushed to particle size of 2 mm diameter. Titanium dioxide powder (Technical grade, 99% purity) was purchased from Sigma Aldrich. The experiments were carried out in a thermostatic shaker fitted with a 30 W UV-C lamp. Nanocolor UV-Vis spectrophotometer was used to analyze the COD of the molasses solution.

Preparation of TiO₂/Zeolite catalyst

The Solid State Ddispersion (SSD) method was used for preparing the zeolite-based photocatalyst. In this method, TiO_2 was added to zeolite and mixed using agate pestle and mortar, ethanol was used as solvent. The solvent was then removed by evaporation at 105^oC. The samples
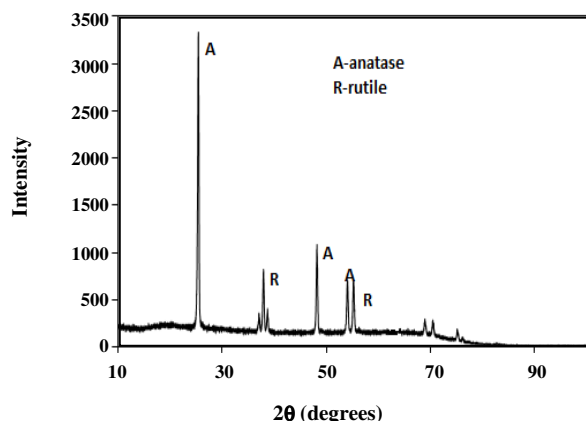
Fig. 1: XRD peaks for TiO₂ powder.

Fig. 2: EDX analysis of zeolite.

prepared by this method were dried and calcined at 450ºC for 4 hour to obtain TiO_2-supported zeolite catalyst. The catalyst (TiO_2) was attached to zeolite to obtain 5, 10, 15 and 20 wt% TiO_2 loading [14].

Catalyst characterization.

Scanning Electron Microscopy (SEM), model FEI NOVANANO SEM 230, fitted with Energy Dispersive X-ray spectrophotometry (EDX) was used to study the surface morphology of the TiO_2-zeolite catalyst and the elemental composition of zeolite. X-ray deffractiometer, model Bruker D8, was used to study the crystalline structure of the TiO_2 particles using nickel copper filtered Cu K (α) radiation (40 kV and 40 mA).

Photogradation experiments.

To synthesize wastewater, molasses was dissolved in distilled water while stirring to form COD concentration of 20 g/L, total nitrates of 0.57 g/L, total phosphates of 0.14 g/L and pH of 4.25. Serial dilutions were then done to obtain lower COD of 5 g/L and 1 g/L solutions. A sample of 3.0 g of the TiO_2-zeolite catalyst was weighed then transferred into 100 mL conical flask and 50 mL of the wastewater was then added. The composition of TiO_2 on the composite catalyst was varied between 5 wt% to 20 wt%. Effect of hydrogen peroxide addition in the range of 0.735 mM, 1.47 mM, 2.205 mM and 2.94 mM was investigated. The selected H_2O_2 range was adopted from that of Huang et al. [18] with modification to suit the degradation of the recalcitrant melanoidin in the molasses wastewater. The flasks were then put in the thermostatic shaker for a specified period. Adsorption experiments
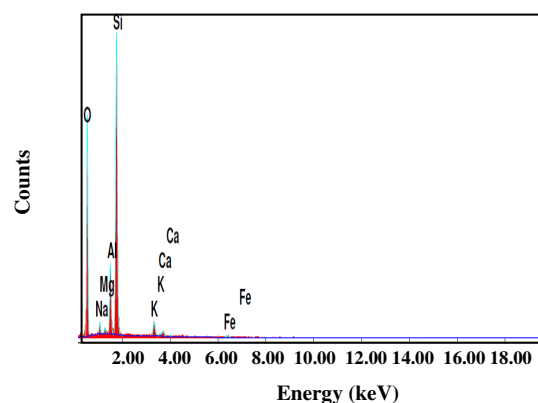
were also carried out whereby the samples were prepared in the same manner but wrapped with aluminium foil to block UV rays to prevent photodegradation. Degraded wastewater was left to settle then filtered before measuring absorbance using UV-Vis spectrophotometer model DR 2800 (HACH). Standard reflux method was employed in the determination of Chemical Oxygen Demand (COD) of the samples and colour measured using Nanocolor UV-Vis spectrophotometer.

RESULTS AND DISCUSSION
Catalyst characterization

X-ray power diffraction was used to analyse the crystalline structure of the catalyst (TiO_2 and zeolite) particles. In Fig. 1, the characteristic of XRD peaks of the anatase was observed at $2\theta = 25.4$, other peaks corresponding to anatase also appeared at $2\theta = 48.3$ and 54.9 as was earlier reported by [19]. The amount of rutile in the sample was calculated as[20]:

$$X_R = \frac{1}{\left(1 + \dfrac{0.8I_A}{I_R}\right)} \tag{1}$$

Where X_R is the mass fraction of rutile, I_A and I_R are the intensities of anatase and rutile respectively. It was found that the TiO_2 had 95.6% anatese phase.

To determine the elemental composition of the zeolite, EDX analysis was carried out, the results are shown in Fig. 2 and Table 1. The results indicated that South African clinoptilolite has higher silicates than aluminates within its structure. From this, it can be deduced that the zeolite has an overall negative charge

Table 1: EDX results for elemental composition of South African natural zeolite.

Element	Wt%
OK	57.41
NaK	1.52
MgK	0.63
AlK	6.5
SiK	30.63
KK	1.99
CaK	0.73
FeK	0.57
Total	100%
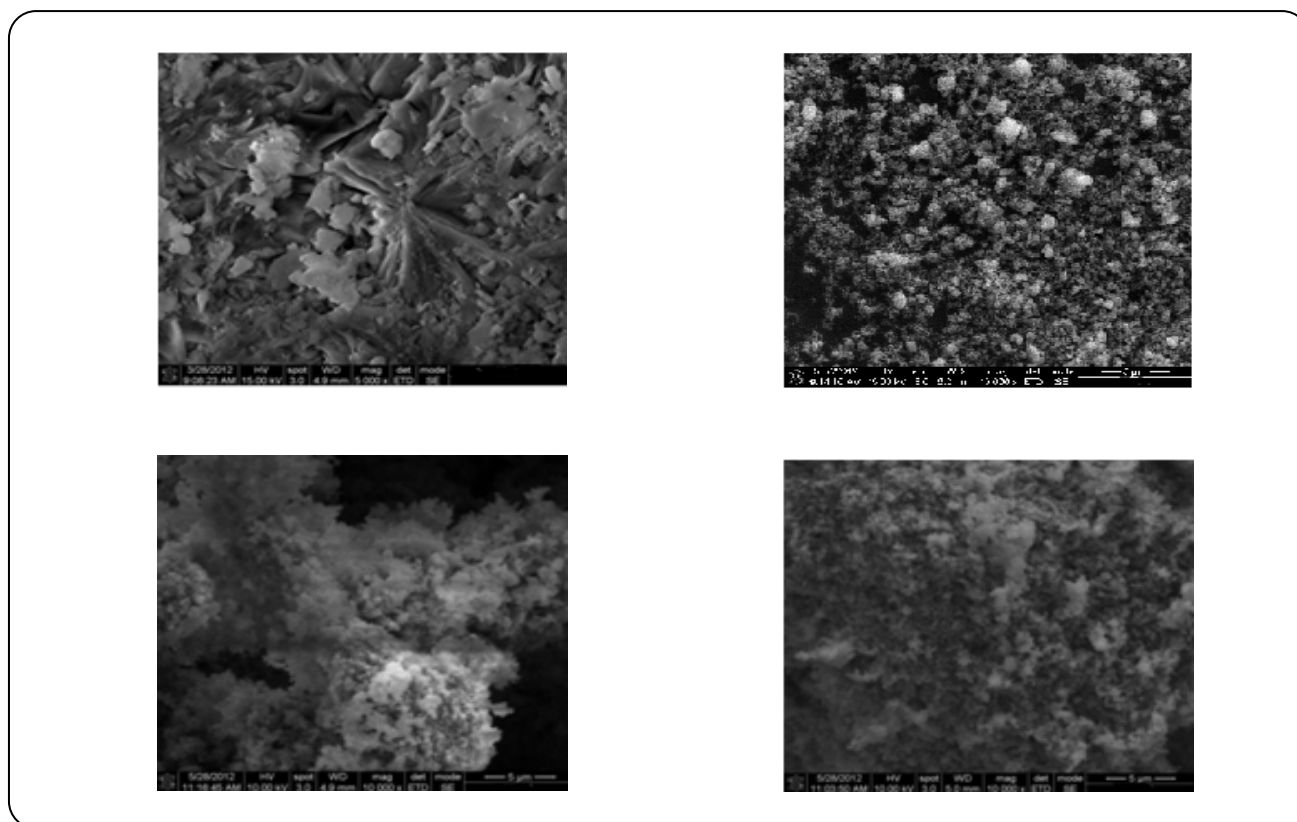
Fig 3: SEM analysis for (a) zeolite (b) TiO$_2$ and TiO$_2$-zeolite catalyst (c) before degradation and (d) after degradation.

on its surface since the Si/Al ratio determines the overall surface charge of zeolites, zeolites with higher Si/Al ratio are negatively charged[21].

Fig. 3 shows the results for SEM analysis for zolite, TiO$_2$ and the TiO$_2$/zeolite composite catalyst before and after degradation. Comparing Fig. 3a (zeolite only) and Fig. 3c (TiO$_2$ attached on zeolite), it can be seen that the TiO$_2$ attached well on the surface of zeolite. It can also be seen that even after degradation (Fig. 3d) TiO$_2$ was still attached on the zeolite though the density had reduced as some might have fallen off due to attrition of the particles caused by shaking/ agitation during the reaction.

Effect of molasses concentration.

It is reported that molasses wastewater and wastewater from distillery industries have COD concentration of about 100 g/L. In this work, concentrations of 20 g/L to 1 g/L were studied since concentrations above 20 g/L did not show
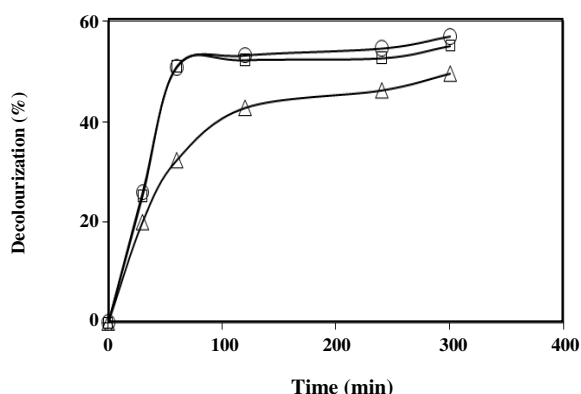
Fig 4: Effect of concentration on degradation at pH 4 and TiO₂ loading of 15%, (△) 20 g/l, (□) 5 g/l and (○) 1 g/l.

Fig 5: Effect of hydrogen peroxide dosage on photocatalytic degradation of molasses wastewater in acidic medium.

any appreciable degradation probably due to the fact that the colour was too intense for the UV rays to penetrate through. Fig. 4 shows that the degradation reduced when molasses concentration was increased. This observation may be due to the fact that at high substrate concentrations, the colour of the solution became more intense thus hindering penetration of the UV light rays. The faster degradation observed during the first hour in each case may have been due to the fact that during this time, the molecules could be fast adsorbed onto the catalyst surface as there were many adsorption sites available, this made the molecules to be in close contact with the catalyst therefore facilitating their photodegradation. However, the rate of degradation levelled off after sometimes, this observation could be attributed to the fact that during this time the catalyst adsorptive sites had become saturatedand therefore the mechanism of concentrating the pollutants on the catalyst surface was hindered. It was also observed that the overall degradation achieved when diluted solution of 1 g/L was used was not so much higher than that for 20 g/L, the degradation efficiencies were 57% and 49% respectively. The results show that it is therefore not economical to dilute the wastewater below 20 g/L before photodegradation. In order to improve the degradation efficiency of the 20 g/l, the effect of hydrogen peroxide dosage on the degradation was investigated.

Effect of H₂O₂ dosage on photodegradation.

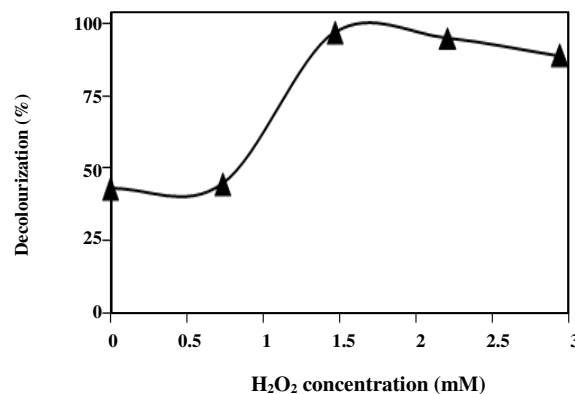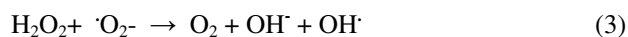The effect of H₂O₂ dosage on the UV degradation of 20 g/l molasses wastewater was investigated at a concentration range of 0,0.735 mM, 1.47 mM, 2.205 mM and 2.94 mM H₂O₂ (Fig 5). It was observed that the decolourisation rate increased with an increase in H₂O₂ concentration from 0 to 1.47 mM then there was a decrease. In the photocatalytic degradation process, addition of adequate H₂O₂ is beneficial to the formation of hydroxyl radicals as explained by the following chemical reaction [22].

$$H_2O_2 + e^- \rightarrow OH^- + OH^{\cdot} \tag{2}$$

$$H_2O_2 + {}^{\cdot}O_2{-} \rightarrow O_2 + OH^- + OH^{\cdot} \tag{3}$$

$$H_2O_2 + h\nu \rightarrow 2\,(OH^{\cdot}) \tag{4}$$

In equation (2), hydrogen peroxide can react directly with the photogenerated electrons in the conduction band to form the hydroxyl radicals, It can also produce more hydroxyl radicals by reacting with the reduced oxygen on the surface of TiO₂ (Eq. (3)). The peroxide can also be directly photolysed by the UV light to produce the hydroxyl radicals (Eq. (4)).

The hydroxyl radical (OH⁻) is a strong oxidant and a dominant species in photocatalytic process. This enables it to completely oxidize a variety of organic substances on the surface of TiO₂ irradiated by UV light. Therefore, H₂O₂ will facilitate the generation of OH radicals and promote the photodegradation efficiency (Fig 5). However, when H₂O₂ is added in excess amounts, it scavenges the hydroxyl radicals produced and the decolourization reaction becomes retarded as shown in Fig. 5, where the decolourization efficiency reduced when the peroxide dosage was above 1.47 mM. Scavenging of the radicals by excess peroxide takes place
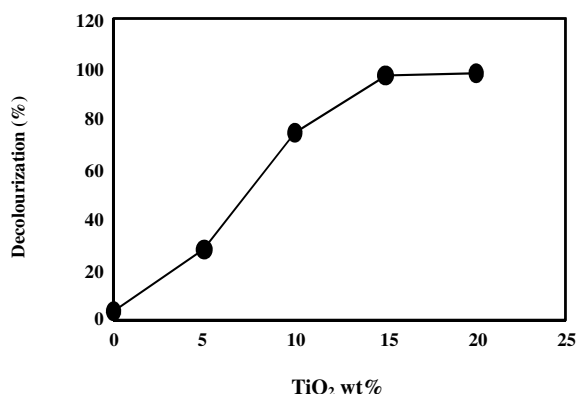
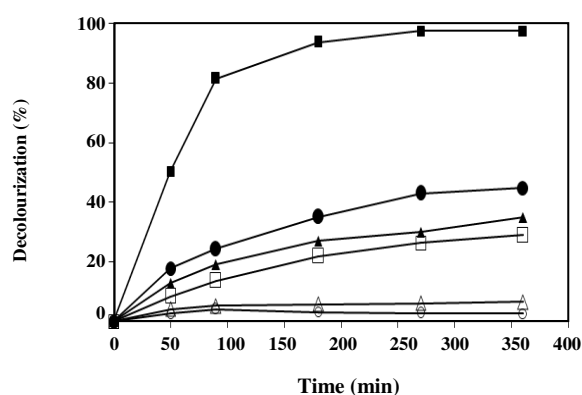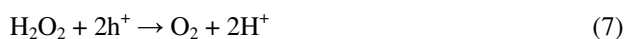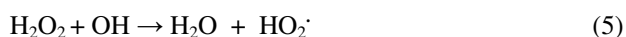**Fig. 6: Effect of catalyst loading on colour removal.**

Fig 7: Adsorption and effect of addition of H_2O_2 onthephotodegradationprocess, (■)H_2O_2 /TiO_2 /UV/ zeolite, (●)TiO_2 /UV/zeolite, (▲)H_2O_2 /UV, (□)H_2O_2, (Δ)UV photolysis and (○)adsorption

as shown in equations (5), (6) and (7). Similar observations were reported by [18] in the hydrogen peroxide assisted photodegradation of methylene orange using TiO_2 coated on zeolite

$$H_2O_2 + OH \rightarrow H_2O + HO_2^{\cdot} \tag{5}$$

$$HO_2^{\cdot} + OH \rightarrow H_2O + O_2 \tag{6}$$

$$H_2O_2 + 2h^+ \rightarrow O_2 + 2H^+ \tag{7}$$

Effect of catalyst loading.

Effect of catalyst loading on the degradation efficiency of MWW was investigated with TiO_2 loaded on zeolite to form compositions of 0,5, 10, 15 and 20 wt%. Due to the high recalcitrant nature of molasses wastewater 1.47 mM H_2O_2 solution was added

to the solution since decolourization without addition of the hydrogen peroxide were very low and a good trend could not be observed. In this experiment, 3 g of the composite catalyst, 50ml molasses solution was used and irradiation time of6 hours.

From the results shown in Fig. 6, it was observed that there was a general increase in the degradation with an increase in TiO_2 loading from 0% to 20%. A rapid increase in degradation when catalyst loading was increased from 0% to 15% was observed. On the other hand, a negligible increase in degradation when loading was increased from 15% to 20% was observed. These observations can be explained in terms of availability of active sites on the catalyst surface and the penetration of UV light into the solution [23]. The total catalyst active sites increase with increasing catalyst loading. At the same time, as the catalyst loading is increased above 15%, there is an increase in turbidity of the solution because the loading above 15% may be excessive and the catalyst particles begun to fall off into the solution. The same observation was made by [24] during photocatalytic degradation of azo dye acid red 14.

Colour removal by adsorption and effect of H_2O_2 addition on photodegradation.

In Fig. 7, the result for adsorption conducted in the absence of UV light is shown alongside the results for effect of H_2O_2 addition, UV photolysis and non-irradiated H_2O_2 on the degradation of molasses wastewater at pH 4. The adsorption on TiO_2/zeolite surface had the least colour removal of 4% compared to the systems comprising H_2O_2/UV/TiO_2/zeolite, oxidation by hydrogen peroxide alone and UV photolysis.It can be deduced that there is a role played by adsorption on concentrating the organic pollutants on the surface of the catalyst which enhances photodegradation. H_2O_2/UV/TiO_2/zeolite performed best since there was multiple sources of the reactive hydroxyl radicals viz; from the peroxide, UV, UV/TiO_2 and UV/H_2O_2. The performance of each source of hydroxyl radical on degradation was also investigated. Fig. 7 shows that there was very little colour removal by UV photolysis alone as compared to H_2O_2 and UV/H_2O_2 systems. It means that UV photolysis produced less hydroxyl radicals compared to those of H_2O_2 and UV/H_2O_2 systems during the photodegradation process. However these methods
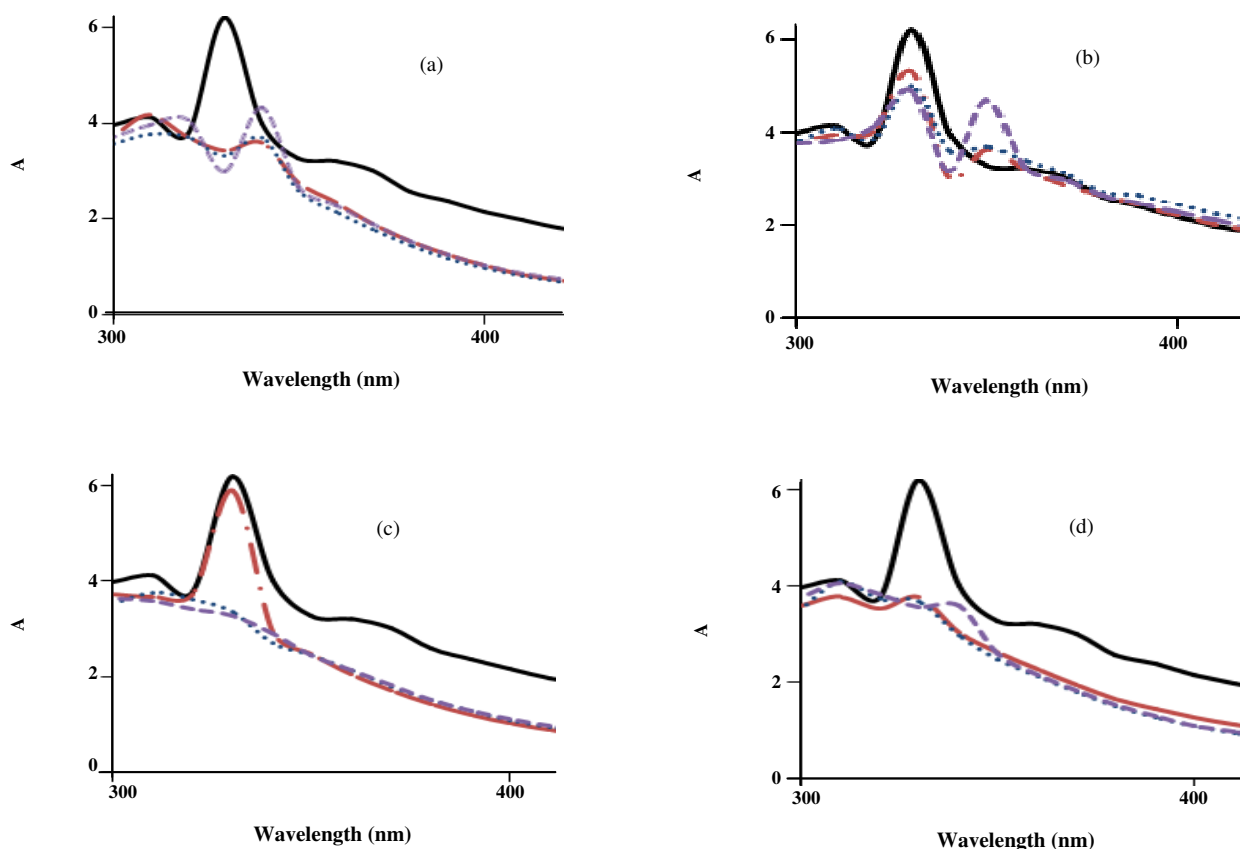
Fig 8: UV-Vis spectralchanges (a) H$_2$O$_2$/UV/TiO$_2$/zeolite, (b) UV photolysis, (c) UV/H$_2$O$_2$ and (d) H$_2$O$_2$, 0 hr(————), 1 hr (— · · —), 2 hrs (·········) and 3 hrs (— — —)

were not sufficient to bring about high photodegradation efficiencies. Also, UV/TiO$_2$/zeolite achieved slightly higher degradation as compared to these other methods. From this observation, it can be deduced that holes generated by UV/TiO$_2$ are more effective in the generation of hydroxyl radicals than in cases where only hydrogen peroxide was the major source of the hydroxyl radicals. The H$_2$O$_2$/UV/TiO$_2$/zeolite combination doubled the colour removal due to the synergy in the hydroxyl generation process. In this system, in the first 100 minutes, thee was recorded very high reaction rate, this may be due to the fact that sufficient hydroxyl radicals were generated during this time period and also the substrate was available, time could have been the limiting factor in the reaction. The reaction profile then levels off after about 180 minutes suggesting that may be either the hydroxyl radicals or the substrate started to be depleted. In fact from the high colour removal of 97% attained

it can be deduced that it was substrate that got depleted. However, in the other systems, lower reaction rates were observed. This may be due to low generation of hydroxyl radicals, therefore it can be deduced that generation of the radicals was the limiting factor.

UV-Vis spectoral changes during photodegradation.

UV-vis scan was conducted to give some insight into the degradation profile of the molasses wastewater under various conditions. This study was conducted with 2 g of composite catalyst (15 wt% TiO$_2$) for 180 minutes with samples analysed after every hour. The untreated wastewater was found to have maximum absorbance at 330 nm as indicated on the graphs (t=0) in Fig. 8. Fig. 8a presents the profile for H$_2$O$_2$/UV/TiO$_2$/zeolite system where it was observed that after every hour there was reduction in absorbance at 330 nm but there was a peak which started to develop at around 340 nm.
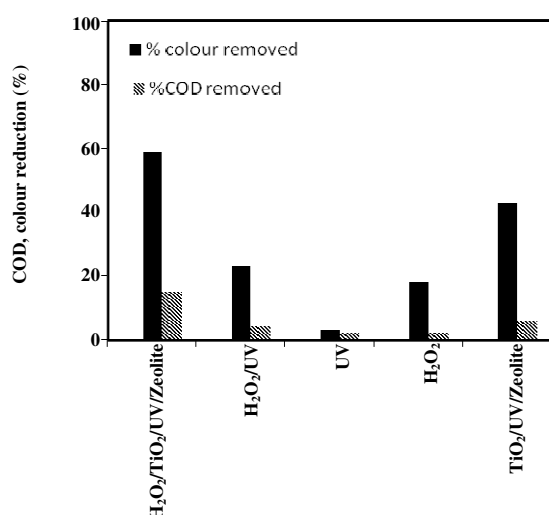
Fig 9: Effect of photodegradation on COD and colour removal.

As degradation progressed with time, the second peak became progressively eminent while the peak at 330 nm continued to diminish. This was also observed in Fig. 8b (UV only) where the second peak started to appear at 350 nm as degradation progressed. This is an indication that under these two conditions there were some intermediates which were formed as the reaction proceeded. These intermediates had lambda max at 340 nm and 350 nm respectively as compared to that of the untreated wastewater which was at 330nm. However, for UV/H_2O_2 (Fig. 8c) and H_2O_2 only (Fig. 8d) there were no intermediates observed since the peak at 330 nm progressively reduced with degradation time without emergence of other peaks elsewhere.This may be an indication that degradation path of molasses during advanced oxidation process varies depending on the source of the reactive hydroxyl radicals.

Effect of photodegradation on COD removal.

A study on the effect of photodegradation on COD removal in molasses wastewater was carried out and it was found that UV photolysis performed the poorest with only 2% COD removal after 3 hours of radiation and 2 g(15 wt% TiO_2) catalyst (Fig. 9). The H_2O_2 /TiO_2 /UV/ zeolite hybrid system attained the highest COD removal of about 15%. It was also observed that in all cases colour removal was always higher than COD removal and the order of colour removal and COD removal across all the systems was the same. Similar results were obtained

by [25], where COD removal of between 15% and 25% ware obtained in chemical oxidation treatment of wastewater from molasses fermentation with ozone. The low COD removal may be attributed to the fact that the brown compounds (melanoidin) present in the wastewater react with the generated hydroxyl radical, leading to organic compounds which still demand oxygen until their final degradation. It can therefore be concluded that there is some correlation between the colour of the wastewater and its COD. Carboxylic acids have been identified as products of melanoidin oxidation [26,27]. Photodegradation therefore is not an appropriate technology for COD removal in molasses wastewater because it attains very low COD removal. However, it is an efficient technology for colour removal since high efficiencies of colour removal can be obtained. From the low COD removal values obtained, it can also be deduced that the process hardly attained total mineralization of the organic substances present in the wastewater.

Effect of pH on the H_2O_2/TiO_2/UV/zeolite hybrid process.

Performance of UV/H_2O_2/TiO_2/zeolite system was investigated under different pH conditions and with 1.47 mM hydrogen peroxide. The colour removal was investigated as a function of irradiation time and data were fitted to a pseudo first-order reaction model (Eq. (9)) as reported by various authors who have worked on photodegradation of various organic contaminants [13,28].

$$\ln\left(\frac{A_o}{A}\right) = kt \tag{9}$$

where A_0 and A_t are the respective absorbances of solution at irradiation times 0 and t, k is the rate constant (min^{-1}) and t is the irradiation time (min). Fig. 10 and Table 2 show that the discolouration reaction was faster at pH 4 and slowest at pH 10. This can be attributed to the fact that under alkaline condition some of the H_2O_2 undergo photodecomposition to water and oxygen rather than to hydroxyl radical as shown by Eq. (10) [29].

$$2\,H_2O_2 \rightarrow 2\,H_2O + O_2 \tag{10}$$

Moreover, in an alkaline medium the oxidising species hydroperoxy anion (HO$_2^-$) is formed (HO$_2^-$ anion is the conjugated base of H_2O_2). This HO$_2^-$ anion reacts with ·OH radical and residual H_2O_2 according to equations (11) and (12) consequently lowering the removal rate. The same observation was reported by [13]

Table 2: Rate constants (K) and R^2 values at various pH conditions

pH	R^2	K (min^{-1})
4	0.9794	0.0136
7	0.9671	0.0112
10	0.9701	0.0086
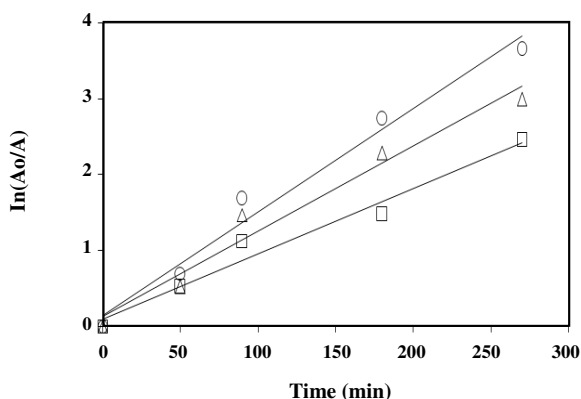
Fig 10: Effect of pH on H_2O_2/TiO₂/UV/zeolite hybrid system pH 4 (○), pH 7 (Δ) and pH 10 (□).

in a study of photodegradation of reactive azo dye with UV/H_2O_2 process.

$$H_2O_2 + HO^-_2 \rightarrow H_2O + O_2 + \cdot OH \tag{11}$$

$$OH + HO^-_2 \rightarrow H_2O + O^-_2 \tag{12}$$
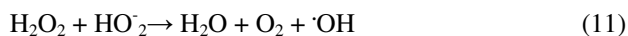
The difference in degradation rate under different pH medium may also be explained by the change in surface property of the composite catalyst under different pH conditions. Melanoidin, the main constituent of molasses wastewater, is negatively charged, zeolite and TiO₂ also have negatively charged surfaces.It has been reported that TiO₂ has zero point charge of 6.25 [30]. At low pH values the surface of TiO₂-zeolite acquires positive charges and thus has the ability to attract the negatively charged melanoidin molecules on its surface thereby increasing degradation rate.However, in the basic medium the surface of the catalyst acquires negative charges and therefore does not attract the negatively charged melanoidin molecules therefore lower degradation is obtained.

CONCLUSIONS

UV photodegradation treatment of wastewater containing molasses was studied.It was found that a UV/TiO₂ system alone could not effectively treat the wastewater as low degradation was achieved. However, a H_2O_2/UV/TiO₂/zeolite hybrid system was found to be a viable technology for the decolourization of the molasses wastewater, even though this technology does not perform well on COD removal. From this observation, it can be proposed that the photodegradation can be integrated with anaerobic degradation to achieve both colour and COD removal for the MWW treatment. It was also observed that under various conditions of photodegradation, there were some intermediates which were formed. Finally, the rate of reaction under the hybrid system was found to be highest under acidic medium and lowest under basic medium.

REFERENCES

[1] Satyawali Y., Balakrishnan M., Wastewater Treatment in Molasses-Based Alcohol Distilleries for COD and Color Removal: A Review, *Journal of Environmental Management,* **86**: 481-497 (2008).

[2] Martins S.I.F.S., van Boekel M.A.J.S., A Kinetic Model for the Glucose/GlycinMaillard Reaction Pathways, *Food Chemistry*, **90** (1-2): 257-269 (2004).

[3] Gonzalez G., Pena M.M., Cristobal N., Heras C., Color Elimination from Molasses Wastewater by Aspergillus Niger, *Bioresource Technology*, **57** (3): 229-235 (1996).

[4] Miyata N., Mori T., Iwahor iK., Fujita M., Microbial Decolorization of Melanoidin-Containing Wastewaters: Combined use of Activated Sludge and the Fungus Coriolushirsutus, *Journal Bioscience and Bioengergy*, **89** (2): 145-150 (2000).

[5] Gonzalez G., Pena M.M., Garcıa M.T., Urue~na M.A., Decolorization of Molasses Effluents by Coagulation-Flocculation Process, *Zuckerindustrie*, **124** (5): 406-410 (1999).

[6] Guimaraes C., Bento L., Mota M., Biodegradation of Colorants in Refinery Effluents Potential Use of the Fungus Phanerochaetechrysosporium, *International Sugar Journal,* **101** (1205): 246-251 (1999).

[7]   Pefia M., Gonzfilez B.G., Cristoba N., Heras N.C., Color Elimination from Molasses Wastewater by Aspergillusniger, *Bioresource Technology*, **57**: 229-235 (1996).

[8]   Mounir B., Pons M.N., Zahraa C., Yaacoubi A., Benhammou, Discolouration of Red Cationic Dye by Supported TiO$_2$ Photocatlysis, *Hazardious Materials*, **148**: 513-520 (2007).

[9]   Parag R.G., Aniruddha B.P., Imperative Technologies for Wastewater Treatment I: Oxidation Technologies at Ambient Conditions: A Review, *Journal of Advances in Environmental Research,* **8**: 501-551 (2004).

[10] Bhatkhande D.S, Pangarkar V.G., Beenackers A.A.C.M., Photocatalytic Degradation for Environmental Applications: a Review, *Journal of Chemical Technology and Biotechnology*, **77** (1): 102-116 (2002).

[11] Blake D.M., in "Bibliography of Work on Photocatalytic Removal of Hazardous Compounds from Water and Air" .NRELyTP-430-22197, National Renewable Energy Laboratory, Golden (1997).

[12] Herrmann J.M., Heterogeneous Photocatalysis: Fundamentals and Applications to Removal of Various Types of Aqueous Pollutants, *Catalysis Today*, **53**: 115-129 (1999).

[13] Muruganandham M., Swaminathan M., Photochemical Oxidation of Reactive Azo Dye with UV–H$_2$O$_2$ Process, *Journal of Dyes and Pigments*, **62**: 269-275 (2004).

[14] Durgakumari V., Subrahmanyama M., Subbra., Rao K.V., Ratnamala A., Noorjahan M, Keiichi T., An Easy and Efficient use of TiO$_2$ Supported HZSM-5 and TiO$_2$ + HZSM-5 Zeolite Combinate in the Photodegradation of Aqueous Phenol and p-Chlorophenol, *Applied Catalysis A: General*, **234**: 155-165 (2002).

[15] Zhang X., Lei L., Effect of Preparation Methods on the Structure and Catalytic Performance of TiO$_2$/AC Photocatalyst, *Hazardous Materials*, **153**: 827-833 (2008).

[16] Rezaee A., Ghaneian M.T., Hashemian S.J., Moussav i.G., Khavanin A., Ghanizadeh G., Decolorization of Reactive Blue 19 Dye from Textile wastewater by the UV/H$_2$O$_2$ Process, *Jornal of Applied Science*, **8**: 1108-1122 (2008).

[17] Crittenden J.C., Trussel, R.R., Hand D.W., Howe K.J., Tchobanoglous G., In "Water Treatment: Principles and Design", Second Edition. John Wiley & Sons, New Jersey (2012).

[18] Huang M., Xu C., Wu Z., Huang Y., Lin J., Jihuai W., Photocatalyticdiscolorization of Methyl Orange Solution by Pt Modified TiO$_2$ Loaded on Natural Zeolite, *Dyes and Pigments*, **77**: 327-334 (2008).

[19] Wang C.C., Lee C.K., Lyu M.D., Juang L.C., Photocatalytic Degradation of C.I. Basic Violet 10 Using TiO$_2$ Catalysts Supported by Y Zeolite: An Investigation of the Effects of Operational Parameters, *Dyes and Pigments*, **76**: 817-824 (2008).

[20] Xiao Q., Jiang Z., Chong X., Zhichun S., Xiaoke T., Solar Photocatalytic Degradation of Methylene Blue in Carbon-Doped TiO$_2$ Nanoparticles Suspension. *Solar Energy*, **82**: 706-713 (2008).

[21] Montalvo, S., Guerrero, L., Borja, R. , Enrique, S., Milán, Z.,Isel, C. and Rubia M., Application of Natural Zeolites in Anaerobic Digestion Processes: A Review, *Applied Clay Science*, **58**: 125-133 (2012).

[22] Konstantinou, I. andAlbanis, T. A., TiO$_2$-Assisted photocatalyticdegradationofazo Dyes in Aqueous Solution: Kinetic and Mechanistic Investigations. *Applied Catalysis B: Environmental*, **49**: 1-14 (2004).

[23] Goncalves M.S.T., Oliviera A.M.F., Pinto E.M.S., Placensia P.M., Queiroz M.J.R., Photochemical Treatment of Solutions of Azo Dyes Containing TiO$_2$, *Chemosphere*, **39**: 781-786 (1999).

[24] Daneshvar N., Salari D., Khataee A.R., Photocatalytic Degradation of Azo Dye Acid Red 14 in Water on ZnOas an Alternative Catalyst to TiO$_2$, *Journal of Photochemistry and Photobiology A*, **162**: 317-322 (2004).

[25] Pena M., Coca G., Gonzalez R., Rioja M., Garcıa, T., Chemical Oxidation of Wastewater from Molassesfermentation with Ozone, *Chemosphere*, **51**: 893-900 (2003).

[26] Kim S.B., Hayase F., Kato H., Decolorization and Degradation Products of Melanoidins on Ozonolysis, *Agricultural and Biological Chemistry*, **49**(3):785-792 (1985).

[27] Hoigne J., Bader H., Rate Constants of Reactions of Ozone with Organic and Inorganic Compounds in Water. I.Non-Dissociating Organic Compounds. *Water Research*, **17**:173-183 (1983).

[28] Wong C., Chu W., The Direct Photolysis and Photocatalytic Degradation of Alachlor at Different TiO_2 and UV Sources, *Chemosphere*, **50**: 981-987 (2003).

[29] Galindo C., Kalt A., UV-H_2O_2 Oxidation of Mono Azo Dyes in Aqueous Media: a Kinetic Study, *Dyes and Pigments*, **40**: 27-35 (1998).

[30] Kaur S., Vasundhara S., TiO_2 Mediated Photocatalytic Degradation Studies of Reactive Red 198 by UV Irradiation, *Journal of Hazardous Materials*, **141**: 230-236 (2007).