SOLAR/UV PHOTOCATALYTIC DEGRADATION OF TWO COMMERCIAL TEXTILE DYES

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Abstract
Textile wastewater typically contains compounds such as dyes, which are biorecalcitrant, and as such need advance treatment methods such as advanced oxidation process (AOP). In this work, photocatalytic degradation of two commercial textile dyes with different structures has been investigated using TiO_2 immobilized on South African natural zeolite (clinoptilolite). Synthetic textile wastewater made from Mexican reactive red (MRD) and burgundy direct Red (BDD) was degraded under ultraviolet (UV) lamp and solar irradiation. Experiments were conducted to optimise various parameters such as the catalyst (TiO_2-zeolite) loading, initial concentration of the dye, pH and retention time. The results showed that the degradation efficiency of MRD was higher than that of BDD. Also, the degradation efficiency was higher under solar irradiation than that under UV. The optimum catalyst loading was found to be 15% (w/w), which gave up to 92% and 96% degradation of MRD with UV and solar irradiation, respectively after six hours of retention time. There was a decrease in degradation efficiency with increasing catalyst loading, which could be attributed to the attenuation of the irradiations by the catalyst particles.

Key words: Zeolite; TiO_2; Dye; photodegradation; clinoptilolite.

1. Introduction

Various methods have been developed for the treatment of textile wastewater. These methods include membrane technology, activated carbon adsorption, chemical precipitation and biological treatment. However, these methods have been ineffective because of the high salt contents resulting from reactive dying. (Barclay and Buckley, 2002).A method that is attracting the attention of many scholars is photocatalytic degradation. Photocatalytic degradation of textile water effluent is a purification process in which dye, mainly, is removed from the water by action of semiconductors under a source of light.

There are several designs of photocatalytic reactors that have been investigated for their efficiency in carrying out both UV and solar TiO_2 photocatalytic reactions. The different reactor configurations studied are parabolic trough, compound parabolic, inclined plate, double skin sheet, rotating disk, water bell, fibre optic, fixed bed and fluidized bed photocatalytic reactors (Braham and Harris, 2009). For photocatalytic degradation, two modes of application of TiO_2 have been studied: suspended TiO_2 and supported TiO_2 systems. The suspended TiO_2 systems have the advantage of high efficiency due to their high surface areas available for mass transfer but suffer the drawback of difficult separation of the TiO_2 particles from treated water after the photocatalysis (Qiu and Zheng, 2007). The problem of separation is as a result of the small TiO_2 particle size (<

0.5 μm) due to which the TiO_2 takes very long to settle in water. This necessitates the use of more costly membrane separation processes (Robert and Malato, 2002).

To address the problem of separation from solution, TiO_2 has been supported on various materials such as quartz sands, glass, ceramic particles, stainless steel, activated carbon, zeolite, nanofibres, photocatalytic membranes and mesoporousclays (Qiu and Zheng, 2007; Chong et al., 2010). Supporting the catalyst is considered more practical even though it reduces the photocatalysis reaction efficiency due to the reduced surface area available for mass transfer (Chong et al., 2010). The reduction in photocatalyst reaction efficiency can be minimized by applying the most efficient support and attachment method.

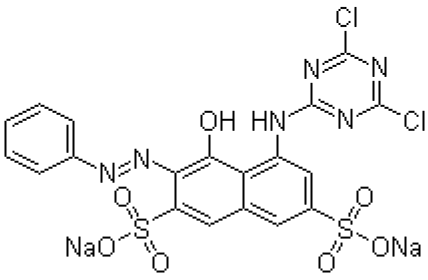
A suitable support should have a strong attachment to catalyst, maintain the reactivity of the catalyst, provide a high specific surface area and possess high adsorption capacity for the pollutants. Adsorbents such as activated carbon, silica and zeolites adsorb and concentrate the reactants near the TiO_2. Also, these adsorbents offer a large surface area for TiO_2 attachment thus improving the contact between pollutant and photocatalyst (Shan et al., 2010). The activity of the supported TiO_2 photocatalyst and the adherence stability of the TiO_2 on its support depend chiefly upon the method of attachment (Qiu and Zheng, 2007).

The aim of this study was to attach TiO_2 to clinoptilolite and apply it with solar and UV to photocatalytically degrade dyes and to investigate the effect of different parameters such as pH, dye concentration, catalyst loading, solar irradiation and reaction time.

2. Experimental

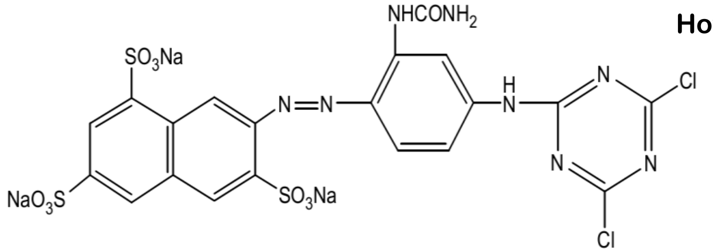
2.1. *Materials and Chemicals*

To prepare the photocatalyst, TiO_2 was supported on zeolite using the solid state dispersion (SSD) of TiO_2 procedure (Durgakumari et al., 2002). In this method, an appropriate amount of TiO_2/zeolite blend (2 – 20%) measured in crucibles was thoroughly mixed with ethanol using a pestle. The mixing was done over a heating plate to remove the solvent by evaporation. These samples were then dried at 110°C and calcined in air at 450°C for 6 h. The product was TiO_2 supported on zeolite catalyst denoted by TiO_2/zeolite-thermal (TZT) which was then used as the catalyst for the photodegradation of the Mexican red reactive dye (MRD) and burgundy direct dye (BDD). The dye solutions were prepared by dissolving the MRD and BDD powder in distilled water. Solution of 661, 1070, 722 and 361 mg/l were prepared. MRD was prepared with cold water at 13°C and BDD was prepared using hot water a 68°C and allowed to cool to room temperature. The MRD is often made of two different dyes namely; C.I. Reactive red 2 (50-70%) and C.I reactive orange 86 (15-30%). It is a cold water dye often used for cotton and wool .Molecular structure of reactive red 2, with a molecular weight of 615.33 g/mole. It is also known as disodium 5-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]-4-hydroxy-3-(phenylazo)naphthalene-2,7-disulphonate has a molecular formula of $C_{19}H_{10}Cl_2N_6O_7S_2 \cdot Na_2$ and structure of (Neppolian et al., 2002):



Scheme 1, Molecular tructure of reactive red 2.

The reactive orange 86 has a molecular weight 759.41g/mole and is also known as trisodium7-[2-[(aminocarbonyl)amino]-4-[(4,6-dichloro-1,3,5-triazin-2-yl)amino]phenyl]azo]-naphthalene-1,3,6-trisulphonate. Its molecular formula is $C_{20}H_{11}C_{l2}N_{8}O_{10}S_{3}.Na_{3}$ and the structure is (Akhtar et al., 2005):



Scheme 2. Molecular structure of reactive orange 86.

The structure of burgundy direct dye is not readily available in the open literature. However it was used in this study for comparison purposes since it is a popular dyes with wide application, in textile and cosmetics industries.

2.2. *Solar/UV photocatalytic reactors*

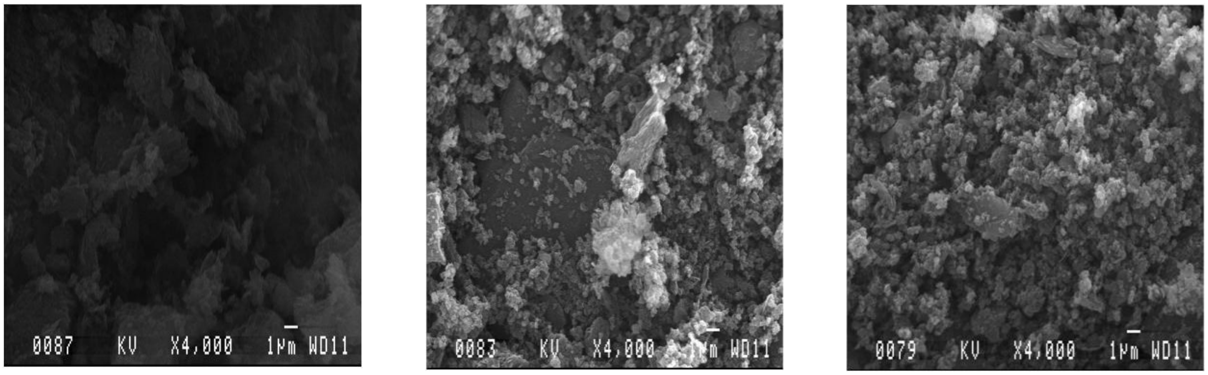
For the solar irradiation experiments, each parameter was investigated on the same day under the same atmospheric conditions to avoid the effect of weather variations on the reaction process. Before the reaction commenced the samples pH values were measured using the HANNA HI 4222 pH-meter while the sample was being agitated using the LabCon MSH10 magnetic stirrer both for solar and UV. The reactors were 100 ml glass conical flasks. In the case of solar photocatysis, aluminum foils were used to increase the illumination. UV photocatalysis was performed by putting the samples inside the thermostatic shaker equipped with a UV class C lamp (30W).

3.0 Results and discussion

3.1 SEM analysis

The SEM pictures in Fig. 1 (a) show the typical morphology of zeolite surface where different pore sizes and distribution can be seen. Upon the introduction of the TiO_2 onto the zeolite surface (Fig. 1 (a) & (b)), the size of the pores appeared to decrease but the

number of pores increased. The surface became more homogeneous as compared to the unmodified surface. Further, it can be seen that surface covered by 10% TiO_2 is more homogeneous than that covered by 5% TiO_2.

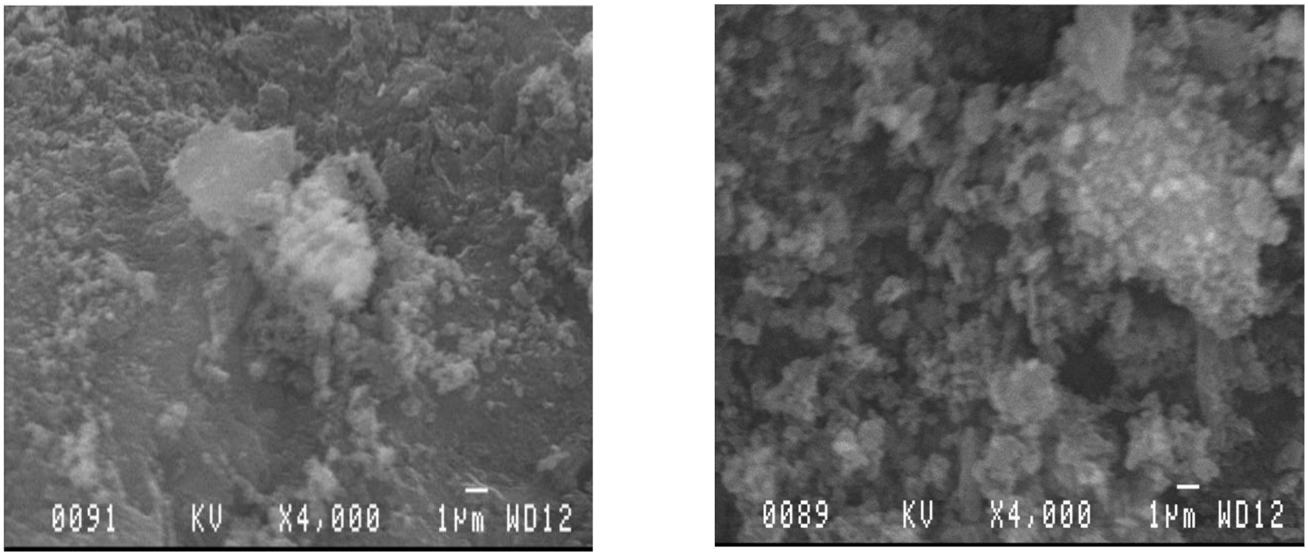


(a) **(b)** **(c)**

Fig. 1 SEM pictures of the clinoptilolite with: (a) 0% TiO_2, (b) 5% TiO_2, 15% TiO_2

There seems to be an agglomeration of the particles on the surface after calcination as shown in Fig. 2, and after the reaction the surface appeared to have more openings. This can be attributed to a possible loss of the TiO_2 particles collisions resulting from fluid flow and particle attrition during mixing. Calcination or thermal attachment of the catalyst on the surface may seem to cause a decrease in the pores sizes (Fig. 1a and Fig. 2a), however, without firm attachment, the catalysts would fall off the surface and this would result in problems with separation. It has been reported that photocatalystic activity increases with calcination temperature, however an increase in calcination temperature results in agglomeration of the catalyst particles (Song et al., 2008).

The apparent falling off of the TiO_2 particles and attrition of the modified zeolite complicates the analysis of the reaction mixture using equipment such UV VIS and photospectrometer. Care needs to be exercised to choose the analytical methods that may not solely depend on colour change.



(a). (b)

Fig. 2 SEM pictures of calcined zeolite with 5% TiO_2: (a) Before use, (b) After use

2.3. *Effect of pH*

Photodegradation process was examined at pH values ranging from 4 to 13 which are strong acid and base for all the two dyes. In all the experiments pH was adjusted by adding appropriate drop of H_2SO_4 or NaOH solution. The impact of pH was investigated under a time period of six hours for a constant dye concentration (0.361 g/l). The catalyst loading, as well as the dye solution volume, were kept constant (1 g of 15% catalyst in 100 ml dye solution). The natural pH of MRD and BDD were 5.44 and 8.87 respectively. The results in Table 1, indicate that there was a mild increase in degradation with an increase in pH. The results in Table 1 show that adjusting the pH does not have a significant impact on the degradation efficiency compared to the solutions natural pH values. It can also be observed that the percentage degradation is higher at pH values greater than 4 and less than 11. The solution pH affect the surface charge of TiO_2 and the availability of the hydroxyl radicals. At high pH values (>7), the surface of TiO_2 which has a pH_{pzc} of 6.25 (Hoffmann et al., 1995) is negatively charged.

Table 1. Effect of the pH on degradation

pH	Degradation, %			
	MRD		BDD	
	UV	Solar	UV	Solar
4.	20.60	16.74	15.63	12.63
5.4	35.50	39.20	29.40	13.42
7.0	33.48	35.80	32.99	40.60
8.9	34.90	35.20	48.80	37.12
11.0	27.50	36.10	32.20	21.35
13.0	21.90	27.32	20.99	16.70

According to Neppolian *et al.* (2002) at high pH values the hydroxyl radicals are so rapidly scavenged that they do not have the opportunity to react with dyes. The pH affects not only the surface properties of TiO_2, but also the dissociation of dyes and formation of hydroxyl radicals. The interpretation of pH effects on the efficiency of the photodegradation process is a very difficult task, because three possible reaction mechanisms can contribute to dye degradation, namely, hydroxyl radical attack, direct oxidation by the positive hole, and direct reduction by the electron in the conducting band Neppolian *et al.* (2002).

In their experiment, Siew-Teng Ong *et al.* (2010) reported that the degradation of the reactive dyes in their study was more efficient under acidic conditions than under basic conditions. The explanation given by the authors, was that under acidic conditions, the surface of the TiO_2 will be positively charged and absorb the dye molecules more readily. Under basic conditions, the numbers of negatively charged surface sites on the TiO_2 increase and this causes lower photodegradation efficiency due to the electrostatic repulsion. This could be a possible explanation for the behaviour of MRD.

Song *et al.* (2008) reported that the photocatalytic removal of colour for direct red 23 was faster at alkaline pH than at acidic pH and gave three possible reasons for that behaviour: First, it was stated that in alkaline solution (pH > 10.0), since OH radicals are generated more easily by oxidizing more hydroxide ions available on the catalyst surface, the efficiency of the process is enhanced. Secondly, it was mentioned in the work thereof that at low pH, reduction by electrons in the conducting band may play a very important role in the degradation of dyes due to the reductive cleavage of azo bonds. Thirdly, the catalyst particles tend to agglomerate under acidic conditions, and the surface area available for adsorption of dye and photon adsorption would be reduced. The results above can also apply for the behaviour of BDD. The different interpretation given by different authors with regards to the effect of pH on photodegradation of dyes is clearly point to the fact that the mechanisms for these reactions are still not well understood. The problem is compounded by the fact that the molecular structure of some of the dyes such as BDD is still not precisely known.

2.4. *Effect of initial concentration*

In order to find the optimum initial concentration, various amounts of dye were diluted in distilled water and kept at their natural pH values. The catalyst loading, as well as the dye solution volume, were kept constant (2 g of 15% catalyst in 100 ml dye solution), for a time period of 6 h. Table 2 shows that no colour removal was noticed for concentration greater than 0.361 g/l.

Table 2 Effect of catalyst loading on degradation

	Degradation, %			
	MRD		BDD	
Concentration (mg/l)	UV	Solar	UV	Solar
650	NCO	NCO	NCO	NCO
361	35.73	40.15	35.38	36.27
107	40	53.81	41.82	44.39
722	85.97	88.2	85.59	85.88
036	91.84	95.7	90.44	94.5

NCO: No change observed.

It can be seen in Table 2above that the percentage degradation increases with a decrease in dye concentration. The same observation was made by Neppolian *et al.* (2002) in their study of Solar/UV-induced photocatalytic degradation of three commercial textile dyes, as well as by Kavitha and Palanisamy (2011) during photocatalytic and sonophotocatalytic degradation of Reactive Red120 using dye sensitized TiO_2 under visible light.

The possible explanation for this behaviour is that as the initial concentration of the dye increases, the path length of photons entering the solution decreases and in low concentration the reverse effect is observed, thereby increasing the number of photon absorption by the catalyst in lower concentration. This suggests that as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the OH radical (primary oxidant) formed on the surface of TiO_2 is also constant. Consequently, the relative number of free radicals attacking the dye molecules decreases with increasing amount of the catalyst. (Neppolian *et al.*, 2002).

2.5. *Effect of catalyst loading*

The catalyst loading was evaluated in two different ways. Firstly, the various percentages of TiO_2 in the TiO_2-zeolite composite of1g were used with a constant volume (100 ml) and concentration of dye (0.0361g/l). The mixtures were placed on the sun for a constant period of six hours. Table 3 shows that higher percentage of TiO_2 in zeolite results in higher percentage of dye degradation.

Table 3. Effect of catalyst (TiO_2) loading 1 g of TiO_2-zeolite

Loading % w/w	**Degradation, %**			
	MRD		BDD	
	UV	Solar	UV	Solar
1.0	79.39	66.9	29.27	40.37
2.0	81.93	83.55	58.7	64.76
10.0	87.92	89.13	89.77	90.31
15.0	91.84	95.7	90.44	94.5

Secondly, for the best percentage of TiO_2, different masses (TiO_2-zeolite) were used with a constant volume (100 ml) and concentration of dye (361 mg/l) (Fig. 3). The mixtures were placed in the sun for a constant period of 3 h. This was only performed for solar degradation. Results in Figure 3 show that for the percentage degradation increases with an increase in catalyst loading.

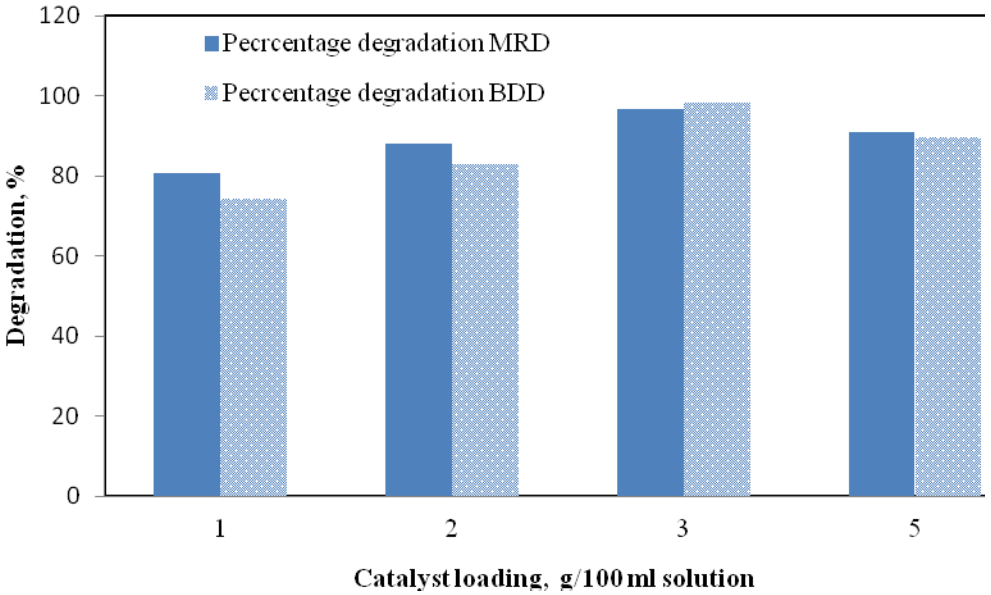
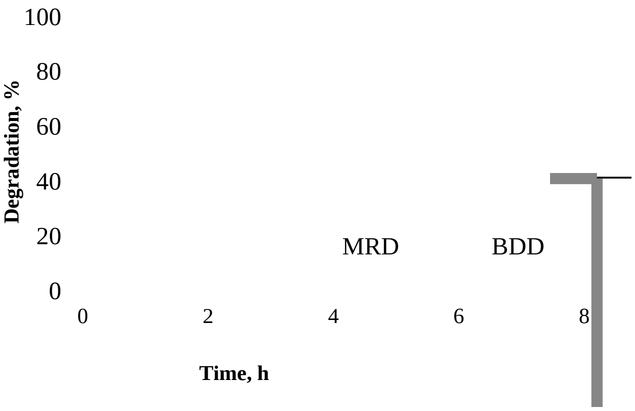


Fig. 3 Effect TiO_2-Zeolite mass.

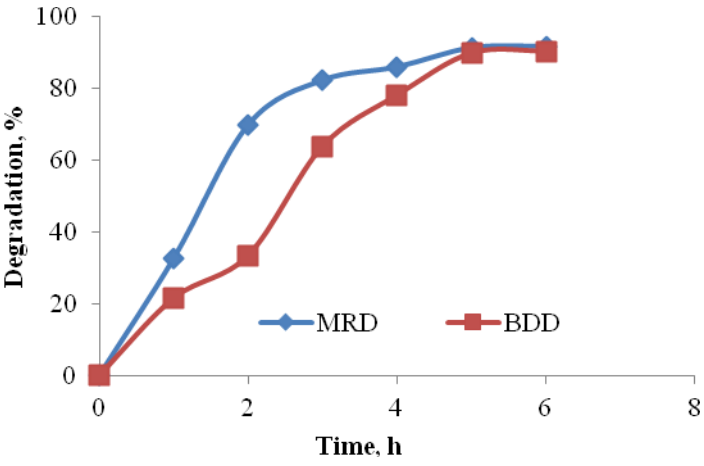
However, with 5 g of catalyst, the degradation efficiency decreased for both dyes. Results indicate that in this case, the large amount of catalyst had an inhibitory effect, reducing the amount of light needed for the reaction. Neppolian *et al.* (2002)suggested that the decreased percentage degradation at higher catalyst loading may be due to deactivation of activated molecules by collision with ground state molecules. Molato *et al.* (2009) reported that the rate of photomineralization is generally found to increase with catalyst concentration towards a limiting value at high TiO_2 concentration. This limit depends on the geometry and working conditions of the photoreactor and is for a definite amount of TiO_2 in which all the particles, i.e., the entire surface exposed, are totally illuminated. When catalyst concentration is very high, after travelling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst mass has to be found in order to avoid excess catalyst and ensure total absorption of efficient photons.

2.6. *Effect of reaction time*

As expected, it is shown in Fig. 4 that the photocatalytic degradation reaction is time dependent. The longer the time, the higher the percentage of dye removed. However, from process economics point of view, the optimum time is that duration beyond which there is very little improvement in the degradation.



(a) Effect of time on solar degradation



(b) Effect of time on UV degradation

Figure 4. Effect of time on degradation (a) Solar degradation. (b) UV degradation

The maximum percentage degradation for UV/solar photoreaction is achieved after a period of 5 h, beyond which no further dye mineralisation was observed. The rate of degradation of BDD was observed to be less than that of MRD. Figure 6 shows that the percentage degradation of BDD increases considerably only after a period of 3 h. Both dyes reach maximum degradation after a period of 5 h.

2.7. *Effect of illumination on degradation efficiency*

Table 4 shows that placing the samples on an aluminium foil improves the degradation of dyes considerably. In case of MRD for example, adding the aluminium foil improved the dye removal by 50.5%, and for BDD the increase was 41.4%.

Table 4 Effect of illumination on dye removal

Dye	Dye colour intensity, Pt-Co Initial	Final, AF-On	Final, AF-Off	Increase in colour removal (%)
MRD	197	50	99	50.51
BDD	166	55	133	41.35

AF: Aluminium foil; Pt-Co: Platinum-cobalt colour scale

A possible reason for this increased photodegradation efficiency is the reflection of the sunlight on the aluminium foil, which causes a “double-illumination” effect; this means that the reactor receives light from the sun above and from the surface of the aluminium foil below, thus increasing the efficiency. Neppolian *et al.* (2002) observed that under higher intensity of light irradiation, the enhancement was considerably higher due to the fact that the electron–hole formation is predominant and, hence, electron–hole recombination is negligible. However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby, causing less effect on the percentage degradation of the dyes.

Ollis *et al.* (1991) reviewed the studies reported for the effect of light intensity on the kinetics of the photocatalysis process of dye and stated that:

- At low light intensities (0–20 mW/cm2), the rate would increase linearly with increasing light intensity (first order).
- At intermediate light intensities beyond a certain value (approximately 25 mW/cm2), the rate would depend on the square root of the light intensity (half order).
- At high light intensities the rate is independent of light intensity.

This is likely; because at low light intensity reactions involving the electron–hole formation are predominant and the electron–hole recombination is negligible. However, at increased light intensity electron–hole pair separation competes with recombination, thereby causing lower effect on the reaction rate. In our study, the enhancement of the rate of decolorization as the light intensity increased was also observed and agreed with the other studies (Konstantinou and Albanis, 2004). It is evident that the percentage of decolorization and photodegradation increase with the increase in irradiation time. The reaction rate decreases with irradiation time and this is typical of apparent first-order reaction kinetics.

Comparing to two methods (Fig. 5) it can be noted that photodegradation efficiency is greater under solar irradiation than that under UV (MRD: 91.84% under UV and 95.7% under solar light). This is in agreement with the results of Kansal et al. (2006) who found that the decolorization of MeO occurred at a faster rate with solar light in comparison to UV light. It is difficult to specify the exact reasons, considering that other factors such as the outdoor temperature changes, the variations in sunlight intensity throughout the day might have affected the reaction; whereas UV photoreaction occurred under steady conditions with constant irradiation rate and intensity.

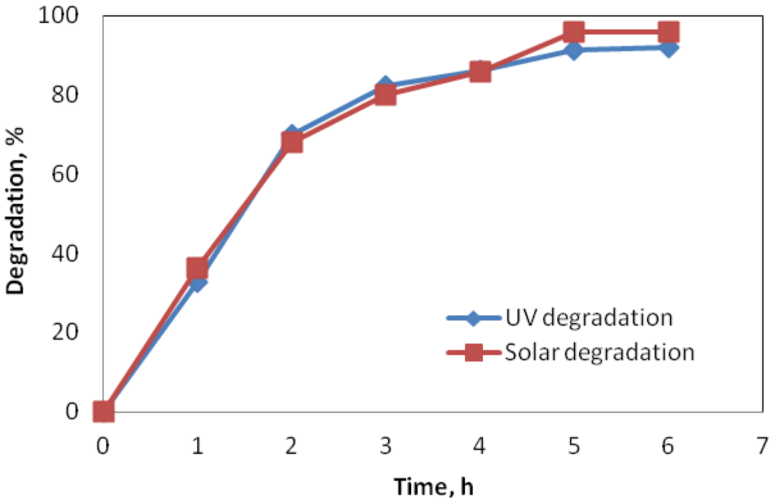


Fig. 5: Variation of photodegradation with light intensity

It can also be noted that the percentage degradation of MRD is greater than that of BDD. Both dyes were degraded under different pH values to find the optimum range for efficient degradation. It was observed that MRD degraded more efficiently at pH values between 5.44 and 8.87 whereas BDD degraded better at pH values between 7 and 11. A similar result on direct dye was reported by Song *et al.* (2008).

3. Conclusion

Solar and UV photocatalytic degradation of textile dyes (MRD and BDD) has been investigated using TiO_2 immobilized on zeolite. The results show that the photocatalytic degradation for both RMR and DBR depends on the pH, dye concentration and catalyst loading. The degradation was more effective at 1:9 TiO_2 to zeolite ratio and with 361 g/l of the initial concentration of the dyes. Solar irradiation provided better results than UV, and since sunlight is abundantly available, it is economically preferable to UV light. The reaction time can be minimize by increasing the mass of catalyst loaded into the reactor; however, it is important to load the correct amount of catalyst to avoid wastages and keep the mineralisation at it optimum since an excessive load will decrease the percentage degradation. Supplying irradiation from all angles to the reactor was found to be more efficient than that from only one direction. In the case of solar degradation, the addition of an aluminium foil provided irradiation from many different angles, thus increasing the percentage degradation.

Acknowledgement

The support by the Water Research Commission (WRC) of South Africa, through research grant no. K5/2105, is gratefully acknowledged.

References

Akhtar, S., Khan, A. A., Husain, Q.,(2005), Potential of immobilized bitter gourd (Momordica charantia) peroxidases in the decolorization and removal of textile dyes from polluted wastewater and dyeing effluent, *Chemosphere*, 60: 291–301.

Barclay, S and Buckley, CA (2002) Waste minimisation guide for the textile industry. *Water Research Commission Report NoTT139/00.*

Braham, R. J. and Harris, A. T. 2009. Review of Major Design and Scale-up Considerations for Solar Photocatalytic reactors*. Ind.l Eng. Chem.Res.*, 48(19), pp. 8890-8905.

Chong, M.N., Jin, B., Chow, C.W.K. And Saint, C., 2010. Recent developments in photocatalytic water treatment technology: A review. *Water Res.,* 44(10), 2997-3027.

Durgakumari, V., Subrahmanyama, M., Rao, S.K.V., Ratnamala, A., Noorjahan, M., Tanaka, K. (2002). An easy and efficient use of TiO2 supported HZSM-5 and TiO2 + HZSM-5 zeolite combinate in the photodegradation of aqueous phenol and p-chlorophenol, *Applied Catal. A: General,* 234 155–165.

Hoffmann, M.R. Scot T. M., Choi, W. and Detlef W.B. (1995). Environmental Applications of Semiconductor Photocatalysis, *Chem. Rev.* 1995, 95, 69-96 69

Kavitha, S.K and Palanisamy, P.D. (2011). Photocatalytic and Sonophotocatalytic degradation of reactive Red 120 using dye sensitized TiO_2 under visible light*. Inter. J. of Civil and Environ. Eng*. 3:1

Molato, S., Fernandez-Ibanez,P., Maldonado, MI., Blanco, J., Gernjak, W. (2009).Decontamination and disinfection of water by solar photocatalysis. *Catal. Today* 147 1-59

Nappolian, B., Choi, HC, Sakthivel, S, BanumathiArabindoo, Murugesan, V. (2002) Solar/UV induced photocatalytic degradation of three commercial textile dyes. *J.of Hazard. Mater* B89 303-317.

Ollis DF, Pelizzetti E, Serpone N (1991). Destruction of Water Contaminants. *Environ. Sci. Technol*. 25: 1523.

Qiu, W. and Zheng, Y., 2007. A comprehensive assessment of supported titaniaphotocatalysts in a fluidized bed photocatalytic reactor: Photocatalytic activity and adherence stability. *Applied Catal.s B: Environ.,* 71(3-4), 151-162.

Robert, D. and Malato, S., 2002. Solar photocatalysis: a clean process for water detoxification. *Science of The Total Environment,* 291(1-3), pp. 85-97.

Shan, A.Y., Ghazi, T.I.M. And Rashid, S.A., 2010.Immobilisation of titanium dioxide onto supporting materials in heterogeneous photocatalysis: A review. *Applied Catalysis A: General,* 389(1-2), pp. 1-8.

Siew-TengOng, Pei-Sin Keng, Wan-Tung Liw, Sheer- Leen Wan, Yung-Tse Hung (2010). Photodegradation of Congo Red and Reactive Yellow 2 Using Immobilized TiO_2 under sunlight Irradiation. *World Appl .Sci. J.* 9(3):303-307

Song, S. Xu, L. He, Z. Ying, H. Chen, J. Xiao, X. Yan B. (2008). Photocatalytic degradation of C.I. Direct Red 23 in aqueous solutions under UV irradiation using $SrTiO_3/CeO_2$ composite as the catalyst, *J. of Haz. Mater.* 152(3), 1301-1308.