

Tropical Stormwater Chemical Oxygen Demand Degradation Using Nano TiO₂ in Photocatalytic Reactor Detention Pond

SAEED RAD^{1,*}, SUPIAH SHAMSUDIN², MOHD. RAIHAN TAHA² and SHAMSUDDIN SHAHID³

¹Hydraulic and Hydrology Department, Faculty of Civil Engineering, University Technology Malaysia, 81310 Johor, Malaysia

²Razak School of Engineering and Advanced Technology, University Technology Malaysia; Jln Semarak, 54100, Kuala Lumpur, Malaysia

³Department of Hydraulics and Hydrology, Faculty of Civil Engineering, University Technology Malaysia, 81310 Johor, Malaysia

*Corresponding author: Tel: +60 172 090290; E-mail: saeedrad1979@gmail.com

Received: 25 September 2014;

Accepted: 2 December 2014;

Published online: 17 March 2015;

AJC-17017

Photo-degradation of stormwater chemical oxygen demand in wet detention pond was monitored. A scale model pond was converted to photocatalytic reactor using immobilized nano titanium dioxide (TiO₂) as contamination remover under natural ultraviolet from tropical sunlight. Amount of chemical oxygen demand and dissolved oxygen within three weeks of experiment were measured with and without the catalyst for comparison and control. Mixture of nano TiO₂ in white and ordinary portland cement was applied as a thin layer to surround the body of the pond (reactor). Three different mixtures of 3, 10 and 30 % weight of anatase and rutile form of nano TiO₂ replaced with cement in concrete. Results shown that utilization of nano-TiO₂ can decrease the amount of chemical oxygen demand up to 43 % within two days and 68 % during three weeks. While in the regular pond were 16 and 19 %, respectively. Also, the amount of dissolved oxygen in the pond using TiO₂ was stable compared to 20 % oxygen depletion in normal pond after three weeks.

Keywords: Nano Titanium dioxide, dissolved oxygen, Detention pond, Stormwater, Photocatalytic reactor, Ultraviolet, Concrete.

INTRODUCTION

Detention ponds play an important role in terms of stormwater runoff quantity and quality control. Especially in tropical zone with regards to urbanization and high annual rainfall average. In developing areas like Malaysia economy and population growth rate, global warming and water resources limitation can cause water related disease and death¹. It can clearly show the necessity of research on stormwater quality enhancement methods as a source of usable water. Various methods, strategies and structures have been applied to achieve higher stormwater outflow quality in addition to quantity control. The best management practices (BMPs)², low-impact development (LIDs)³, filters, bio-retentions⁴, ponds and coagulation⁵⁻⁷ are some examples based on literatures.

Among these methods wet detention pond as a multi-objective structure can detain runoff during time to peak flow. It cause outflow quality improvement due to settlement, biological reactions and chemical reactions. But beside that as a drawback; ponds are not able to eliminate and decompose filtered pollutions. Re-suspension of settled contamination can transfer them to downstream and discharge to the rivers before any treatment; after the next precipitation. It is important especially in Malaysia which still 97 % of its usable water

source is from rivers⁸. Moreover during the time, accumulation of contamination in the pond will cause eutrophication.

Currently outflow quality enhancement in the ponds can be achieved *via* applying one of the following three methods. First method is to extend the detaining time to lighter size particles settlement⁹. But this option has the risk of downstream overflow following next rainfall event. Second method is pond size enlargement to increase storage volume; however it causes imposition of additional costs^{10,11}. Third treatment strategy is applying parallel techniques such as placing flow separator devices in the pond inlet^{12,13}; or in/off line sand filters¹⁴. This strategy in addition to costs needs ongoing maintenance¹⁵.

Importance of current research is to designing a more effective pond which nano-TiO₂ mixed concrete surrounds the body. Nano-TiO₂ can eliminate pollution sustainable due to photocatalytic phenomena. It will transform the detention pond to a photocatalytic reactor which has the function of which decompose stormwater contaminations and not just filtering. Nano titanium dioxide in the presence of ultra violet from sunlight is able to oxidize and reduce a wide range of pollution to H₂O, N and CO₂. High photo-degradation efficiency of nano-TiO₂ is depended to the intensity and the amount of ultra violet illumination¹⁶. This intensity in tropical zone is in between 5 to 6 KJ/m² which is remarkably high^{17,18}.

According to literatures nano-TiO₂ is non-toxic and stable with no chemical inertness. Sustainability, applicability under natural ultra violet, fast reaction time and environmentally friendly¹⁹ are some signs of safety of nano-TiO₂ to use as a stormwater purifier^{20,21}.

UV irradiation and photon absorbance on TiO₂ surface as a photocatalyst²² can provide enough energy for electrons movement. This movement is from valence band to conduction band and causes electron-holes pair creation. Reaction between positive holes and pollution or water adsorbed at the titanium dioxide surface can reduce or oxidize harmful contaminations to harmless species^{16,23}. Moreover it can form super-oxide anion and hydroxyl radicals, as two highly reactive substances.

Nowadays titanium dioxide has various applications such as a purifier for water^{20,21,24-35} and air^{23,35-37}; under artificial or natural UV source have increased intensively¹⁶. High removal efficiency with only few hours UV illumination in presence of nano titanium dioxide on algae³², chemical oxygen demand³⁸, total organic carbon^{23,39}; volatile organic compounds²¹, phenol¹⁸, chloroform⁴⁰, nitrogen compounds and oil spills²³, viruses and bacteria^{41,42}, have been reported. Applying this novel product in self-cleaning tiles, building's exterior and interior surfaces^{35,37} as cement mixture or in paint^{26,43}; has already been started in scale up.

American National Aeronautics and Space Administration's (NASA) earth science in 2007 has worked on applying floatable nano titanium dioxide coated balls in order to improve ponds outflow quality⁴⁴. Researches on application of photocatalyst by nano titanium dioxide immobilized in concrete; especially for stormwater quality enhancement are very less. Moreover, most of the researches have used nano-TiO₂ powder as suspended catalyst in polluted water due to the high contact and efficiency in suspension form^{15,45}. Practically applying nano-TiO₂ in cement initiated by Italcementi Corporation in 2000⁴³. Hüsken *et al.*³⁶ evaluated the air purification capability of nano titanium dioxide in concrete for NO with 40 % removal efficiency. Tarmizi *et al.*²⁷ utilized nano-TiO₂ as powdered scattering on concrete for degradation of phenol in stormwater and succeed phenol removal of 67 and 97 % using two different nano-TiO₂ particle size. Study on applying nano-TiO₂ for water purification is in laboratory scale yet.

In current study, utilization of nano titanium dioxide in a detention pond applying free daylight ultraviolet in tropical area initiated. TiO₂ is the most strong pollution remover an oxidizer among semiconductors. Experiment was to evaluate and monitor nano TiO₂ contribution capability to generate a new pond. This new detention pond is able to remove stormwater contamination sustainable and as an outcome pond eutrophication and oxygen depletion process postponement.

Photocatalytic reactors for water treatment have four main types. These four are consisting composite parabolic concentrator (CPC), photo-electrochemical cell (PEC), slurry batch and finally fixed bed reactor. Fixed bed is the last and most suitable type among photocatalytic reactors to convert a pond. Identical physical, technical and maintenance requirements lead to select the fixed bed model for this research. It was having regard to not compatibility of other three types with detention pond characteristics. For example maintenance requirements of other types such as recycling of suspended

TiO₂ particles or filtering¹⁶ which is almost impossible in detention pond. Therefore a photocatalytic reactor (fixed bed model) applying nano-TiO₂ on its body was designed for a low rate ongoing flow. Especially low outflow and slow mass movement which is a deficiency in photocatalytic reactors⁴⁵ is a privilege in detention ponds to provide desirable catalyst and contamination contact time. Moreover, since detention ponds needs to be built as flood control facility with an ordinary shotcrete of nano titanium dioxide concrete mixed on the body will be converted to a scale-up photocatalytic reactor as well cost effectively.

EXPERIMENTAL

The whole plan for experiment was the following four steps. First to design a detention pond for an assumed watershed; second to set up a 1:20 scale model of the designed pond; third to convert it to a photocatalytic reactor and forth to test and measure the stormwater quality parameters.

In first step a pond was designed for an assumed watershed of 10 acres as the minimum watershed area to construction a pond. Pond was in a tropical area including 55 % residential and 45 % green area. The detention pond must detain 95 % frequency occurrence precipitations⁴⁶ and also be able to hold 2 up to 10 years and pass a design storm with 100 years return period⁴⁷. As per United States Environment Protection Agency guidelines for a pond an optimum depth of 2 meters; a length to width ratio of 2:1 and surface area of 450 m² (30 × 15) which is almost 1 % of the assumed watershed filed were considered. With 3 % average slope, 25 min. concentration time and 63 % runoff coefficient, 0.077 m³/s maximum discharge obtained using rational method as shown in Table-1.

TABLE-1
WATERSHED ASSUMPTIONS AND POND DESIGNATION

Watershed area	10 acre
Return period	10 years
Watershed slope	3 %
Time of concentration (Tc)	25 (min)
Optimum pond depth	2 (m)
Pond surface area (length × width)	30 × 15 (m)
6 hours rainfall depth (P)	40 (mm)
Runoff coefficient	0.63
Q (Maximum discharge)	0.077 (m ³ /s)

The relation of catalyst surface area (m²) to reactor magnitude (m³)⁴⁵, source of ultraviolet illumination⁴⁸, rate of outflow, the contact time between pollution and nano-TiO₂, absorption of ultraviolet¹⁸, necessities for secondary treatment¹⁶ and feasibility were thought-about to line up the pond/reactor, as crucial criteria in each the pond and also the reactor designation.

A 1:20 scale model⁴⁹ of the mentioned designed detention pond was placed in an open area at the UTM environmental laboratory in Malaysian capital. The latitude was solely 3°:10' N and line of longitude of 101°:43' E in order to reap ultraviolet from daylight. The experiment was done throughout the month of August; but there is no variation in the average quantity of ultraviolet received throughout completely different months in this latitude⁵⁰. A rectangular shape fiberglass container with 1.5 m length, 0.75 m width and 0.12 m depth was applied at

1:20 designed pond as the scale model having relation to the assumptions, laboratory house and relevancy to be converted to a fixed bed photocatalytic reactor (Fig. 1)



Fig. 1. 1:20 Scale model of designed pond with nano-TiO₂ concrete sheets under the sunlight

The most capability that the basin may hold was 135 L (1/8000 of designed pond). 67 % of this amount might be discharged throughout 48 h and therefore, the remaining 33 % was held as the water quality volume throughout the inter-event time. The designed diameter for the outlet pipe was 1 mm to harness storm-water throughout the discharge time.

During the experiment, concrete sheets with a median thickness of 4 mm thickness were placed to surround the body of pond. To produce these panels, every 15 × 13 centimeter mesh panel (Fig. 2a) was stuffed with nano titanium dioxide blended cement concrete (Fig. 2b). The panel's thickness was 4 mm even supposing lower thickness sheets that were additional price effective might be applied. However an acceptable thickness can enable a maintainable photocatalytic reactor system throughout the lifetime of the structure having relation to the erosion phenomena. The cement content in the concrete was a typical standard⁵¹ of 350 kg/m³. Nano titanium dioxide in 3, 10 and 30 % weight of the cement substance was swapped with^{27,36,52}. Titanium dioxide powder source was held anatase and rutile form, commonly from Sigma-Aldrich, USA. It was a blend of 78 g titanium(IV) dioxide anatase 99.7 % metal bases with particle size of more modest than 25 nm and 22 g titanium(IV) dioxide rutile 99.5 % metal bases, particle size of littler than 100 nm. These extent were recommended as the best extent to accomplish higher effectiveness in decay of contamination⁵³.

The analytical supplies utilized for the measure of the chemical oxygen demand and dissolved oxygen in specimens was Spectrophotometer D/R2700 HACH which was aligned with HACC principles. Arachem Malaysia company gave the chemical oxygen demand and dissolved oxygen reagents to test. The concrete boards were made of two sorts of cement; white and standard portland cement (OPC) at diverse doses of nano powder. They were dry blended by hand before 1 h adding distilled water in. Later it mixed for another 0.5 h, after adding the water to accomplish greatest possible homogeneous nano-TiO₂ distribution. The panels were then submerged in water for two days following the drying section. The specific end



Fig. 2. (a) galvanized mesh before filling with concrete (b) nano-TiO₂ concrete mixed Panels

goals were to increase the panel's strength and to evacuate those particles that had not held fast to the surface. Finally, the sheets were installed on the body of the pond to cover its interior surface and convert it to a fixed bed photocatalytic reactor. In this experiment⁵⁴, a ratio of 7.7 (m²/m³) for catalyst surface area (m²) to the reactor volume (m³) was acquired (eqn. 1).

$$K_1 = \frac{\text{Catalyst surface area (m}^2\text{)}}{\text{Reactor volume (m}^3\text{)}} = 7.7 \quad (1)$$

To observe the impacts of nano titanium dioxide on chemical oxygen demand and dissolved oxygen in stormwater, seven continues sets of tests were conducted. Each set was together with seven tests for total of 49 single tests. Experiment was during a complete of 21 days underneath ultraviolet ray from tropical sunlight. First set was throughout a short term of two days normal pond detaining time. The subsequent sets were at 19 day inter-event period to quantify the effects on the remained water quality volume in the pond. Before sunrise, real samples were collected and then transferred to the site using 20 L plastic containers. Samples were from the closest detention pond named Danau Kota detention pond in Kuala Lumpur. The containers and scale model pond were washed and cleaned *via* distilled water to avoid effects of any organic or inorganic substances. Within rained and during the night the scale model was lined with a glass sheet to manage the ambient conditions. It could protect the pond from insects, dust and any alternative external factors which might interfere to the outcomes.

The experiment conducted the two most vital quality parameters that cause algae bloom and eventually eutrophication within the ponds, specifically chemical oxygen demand (COD) and dissolved oxygen (DO). Prior to begin of the tests, eight standard stormwater quality criteria based on INWQS (national water quality standards for Malaysia) were measured and indicated (Table-2).

The technique applied for chemical oxygen demand was reactor digestion method. It is a measure of the amount of oxygen that consumed during the reactions to chemically oxidize organic pollution to inorganic form. In fact it can show the amount of organic compounds in the sample. For each test a 500 mL specimen were gathered in a blender and homogenized for 2 min. The 2 mL of homogenized specimen were

TABLE-2
STORMWATER SAMPLE QUALITY INDICATORS

Parameter	Values
Temperature	27.13 °C
TSS	0.02 mg/L
pH	7.6
COD	111 mg/L
DO	8.40 mg/L
BOD	72 g/L
Nitrate	9.17 mg/L
Phosphate	1.80 g/L

spilled in a chemical oxygen demand reagent vial and inverted several times to mix the contents. For this method digestion applying sulfuric acid for low range chemical oxygen demand estimation (3 to 150 mg/L) was utilized. In the meantime, a blank sample with 2 mL deionized water was prepared. After 2 h reaction period in reactor in 150 °C and another 20 min. to cool the vials to 120 °C, the samples were inverted several times while still warm. Then samples placed in a rack until vials cool to room temperature. Prepared and blank wiped and placed into the cell holder and finally amount of chemical oxygen demand were measured and results recorded.

Dissolved oxygen tests conduct using an indigo carmine method (AccuVac Ampules) in the high range of 0.3 to 15 mg/L. To measure the dissolved oxygen, the round sample cell was filled with 10 mL of sample and insert to the cell holder to zero the spectrophotometer. The sample cells were shaken vigorously for 60 s. Then sample left undisturbed for a 5 min. The amount of dissolved oxygen measure and recorded in mg/L was compared to the blank sample. The temperature and pH for two crucial requirements, were likewise measured all around the test for entire samples.

RESULTS AND DISCUSSION

Outcomes showed high chemical oxygen demand degradation of 68 % in stormwater in the presence of nano-TiO₂ compared to the normal condition which was only 19 % after three weeks. Normal chemical oxygen demand reduction in the typical detention ponds in two separate trials were 38 % removal⁵⁵ and moderate reduction⁵⁶. Fig. 3 shows the amount of chemical oxygen demand in stormwater in the vicinity of nano titanium dioxide for 21 days under natural ultraviolet from daylight. The results were acquired from 49 tests on submerged concrete panels. The panels were holding 3, 10 and 30 % weight of nano titanium dioxide white and Portland cement blended in seven basins. Three basins contained concrete panels with 3, 10 and 30 % weight nano titanium dioxide white cement blended and another three contained Portland cement. The last one (seventh basin) held stormwater in ordinary condition with no concrete or nano titanium dioxide as reference or control.

During the first 6 h result indicated a high decrement of 33 % in the amount of chemical oxygen demand. It reduced continuously in lower rate of another 10 % throughout the following 42 h. After 2 days, which is regular stormwater detaining time in the ponds; while chemical oxygen demand in control sample reduced slightly (only 16 % reduction), in the samples contained nano titanium dioxide dropped to 43 % in outlet. During long term *i.e.*, after first, second and third

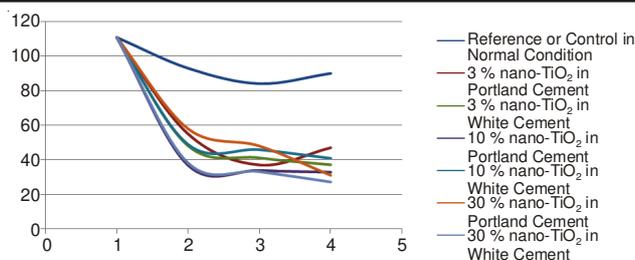


Fig. 3. Chemical oxygen demand in stormwater in mg/l during three weeks in the presence of various dosages of nano-TiO₂ white and Portland cement blended under natural ultraviolet

weeks, 57, 64 and 68 % chemical oxygen demand reduction achieved, respectively but in reference was just 19 %.

This remarkable drop in the outcomes is potentially because of the two ways which nano titanium dioxide diminished chemical oxygen demand, one way is immediately and another indirectly.

Direct way: Firstly nano TiO₂ can restrict organic substances such as microorganisms, viruses and microbes and limit total organic mass reproduction⁴⁰. It is due to the cell membrane of a microorganism can be deteriorated and decimated by titanium dioxide as a result of its oxidizing capacity^{16,21}. Secondly nano titanium dioxide can oxidize and convert ammonia (NH₃) as organic form of nitrogen to nitrogen and hydrogen. This conversion occurs following reduction of nitrate (NO₃⁻) (eqn. 2) and then nitrite (NO₂⁻) to ammonia (NH₃) (eqn. 3). Finally oxidation of ammonia (NH₃) as an organic pollution will evolve harmless nitrogen and hydrogen (eqn. 4) as follows⁵⁷:



In fact nano-TiO₂ will reverse nitrification process that cause nitrate (NO₃⁻) production as the most stable form of nitrogen compounds.

Indirect way: Phosphates (PO₄³⁻) as one of the main nutrients which is the regular form of phosphorus can be organic or inorganic (soluble orthophosphates). A great proportion of the organic part because of mineralization could be disintegrated by microorganisms and changed over to the inorganic orthophosphates. It is the stable form of phosphate and might be consumed straightforwardly by algae or other green growth and prompt eutrophication²⁵. Microorganism limitation by nano-TiO₂ will slow this mineralization process and consequently limit algae and other aquatic plants which are important sources of organic pollution after they die.

Moreover nano TiO₂ reduction ability can reduce the processed orthophosphate to phosphate which cannot be taken up by plants (unlike orthophosphate). It is due to instable electrons (ecb⁻) in conduction band of TiO₂ and produced hydroxyl radicals (*OH)⁵⁸ as exhibited in eqn. 5:



Particularly UV light in Malaysia quickens this procedure. It causes algae accessible phosphate confinement⁵⁹ and subsequently, eutrophication delay in the long term. Test results for dissolved oxygen in the first 48 h shows a slight increment of

2 % for all samples, while in reference it decreased for 12 %. During longer time (three weeks) again a gradual decline of 6 % in reference in normal condition observed but graphs plateau for all the samples which were in presence of nano-TiO₂ (Fig. 4). That means released dissolved oxygen was replacing in those samples contain TiO₂. Overall after third week there was 20 % difference in the amount of dissolved oxygen in the outlet between samples with and without nano TiO₂. It shows that applying nano TiO₂ as an oxygen generator is an effective method for oxygen depletion postponement in the ponds and eutrophication prevention consequently.

Fig. 4 shows the difference between amounts of dissolved oxygen in reference sample with the rest of the samples contains nano TiO₂.

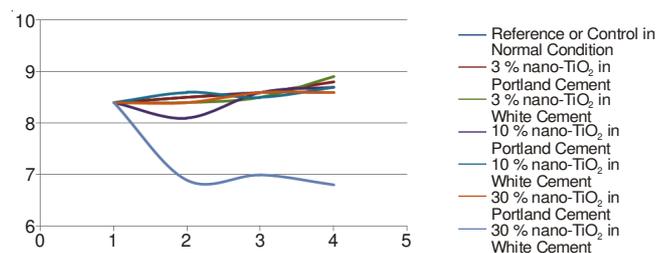


Fig. 4. Dissolved oxygen amount in stormwater measured in mg/L during three weeks in the presence of various dosages of nano-TiO₂ white and Portland cement blended under natural ultraviolet

Throughout the tests, pH and temperature were additionally measured. The pH was 6.4 to 7.9 and the temperature on normal was 25.5 °C.

Various dosages of nano titanium dioxide in concrete sheets were studied so as to advance the applicable quantity with efficient chemical oxygen demand decrement rate. Examination over the chemical oxygen demand reduction rates of utilizing different weight of nano titanium dioxide in cement indicated unimportant vacillation applying 3, 10 and 30 % weight (6 % different which 30 % were higher). This infers that even using 3 % weight nano titanium dioxide replacement in cement can eliminate up to 60 % of stormwater chemical oxygen demand which is a more practical choice (Fig. 5). It appears that the principle explanation behind this equality of results was the low concentration of contamination in the stormwater sample in the pond.

Future experiments with diverse specimens and more polluted samples must give various levels of chemical oxygen

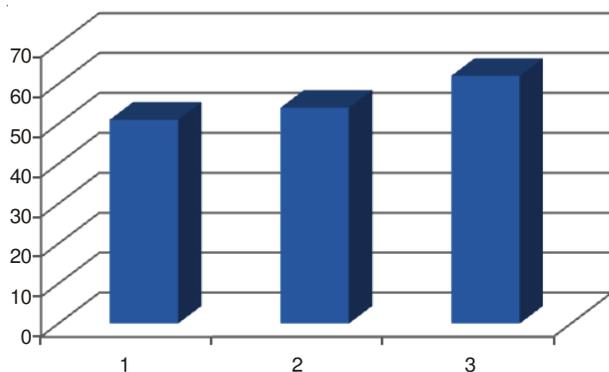


Fig. 5. Chemical oxygen demand decrement efficiency for applying 3, 10 and 30 % of nano-TiO₂ in cement

demand evacuation effectiveness in utilizing different weight of nano titanium dioxide to enhance the fitting mixture. Other paramount stormwater quality criteria must be measured to acquire a complete and clear picture of nano-titanium dioxide affects in wet detention pond contaminations elimination.

Additionally comparison between white and Portland cement does not show any difference in the reduction rate in applying different type of cement.

Conclusion

The test shows the ability of nano TiO₂ to be applied as a novel stormwater treatment procedure for chemical oxygen demand photo-degradation in wet detention pond. Consequently, indication shows that applying nano titanium dioxide concrete mixed to cover the pond body can remove a broad measure of contaminations under strong ultraviolet illumination. Particularly, in tropical zones (like Malaysia) that gain an extensive amount of annual natural ultraviolet from daylight throughout the entire year. As showed in this work 68 % chemical oxygen demand degradation in photocatalytic reactor-pond is high contrasted to 19 % decreased efficiency of reference samples. It is remarkably high even compared to 38 % decreased efficiency of traditional ponds in other researches⁵⁵. Additionally dissolved oxygen results shown that TiO₂ samples have 20 % higher dissolved oxygen than normal samples. Results demonstrate that nano titanium dioxide is capable of being used in wet detention ponds to generate a photocatalytic reactor and provide efficient photo-degradation of chemical oxygen demand. It also could replace a part of depleted oxygen in the pond compared to normal detention ponds. Covering the detention pond using meager layer of nano titanium dioxide blended concrete can create a new pond planned as a photocatalytic reactor. It can figure out to enhance stormwater outflow quality before releasing to the water resources. Especially in Malaysia where 97 % of water supply is from rivers and can be easily polluted with stormwater contamination. The general chemical oxygen demand elimination effectiveness rates were 27 and 49 % higher than typical pond two days later and after 21 days, respectively. Oxidation and reduction ability of this novel product and its application as a stormwater treatment technique can help to achieve a great improvement in nutrients, microorganisms and chemical oxygen demand degradation. It will cause stormwater quality enhancement and finally detention ponds eutrophication postponement in tropical zone. It will also help to improve water supply quality and sustainable development.

REFERENCES

1. M.D. Sobsey, *Managing water in the Home: Accelerated Health Gains from Improved Water Supply*, World Health Organization Geneva (2002).
2. M.L. Clar, B.J. Barfield and T.P. Connor, Document No. EPA/600/R-04 A, 121 (2004).
3. D.E. Line, R.A. Brown, W.F. Hunt and W.G. Lord, *J. Environ. Eng.*, **138**, 680 (2012).
4. M. Rodgers, G. Walsh and M. Healy, *J. Environ. Sci. Health, Part A*, **46**, 80 (2011).
5. E. Cical, G. Burtica and L. Lupa, *Trans. Chem.*, **50**, 64 (2005).
6. J.D.P. Theodoro, G.F. Lenz, R.F. Zara and R. Bergamasco, *Plast. Polym. Technol.*, **2**, 55 (2013).

7. Z. Othman, S. Bhatia and A.L. Ahmad, International Conference on Environment (ICENV) (2008).
8. A.B.M. Yassin, C. Eves and J. McDonagh, in Proceedings from 15th annual conference of the Pacific Rim Real Estate Society, Sydney, Australia (2009).
9. T.H.Y. Tebbutt, Principles of Water Quality Control, Butterworth-Heinemann, Boston, edn 5 (1997).
10. F. Papa, B.J. Adams and Y. Guo, *Can. J. Civ. Eng.*, **26**, 72 (1999).
11. B. Davis and G. Birch, *Environ. Sci. Policy*, **12**, 84 (2009).
12. S.P. Echols, Split-flow Stormwater Management Strategy: Development, Design Feasibility and Cost Comparison, Virginia Polytechnic Institute & State University, USA (2002).
13. T. Schwarz and S. Wells, Advances in Filtration and Separation Technology Volumes 13A and B, p. 219 (1999).
14. USEPA, United States Environmental Protection Agency, Office of Water (1999).
15. S. Ahmed, M.G. Rasul, R. Brown and M.A. Hashib, *J. Environ. Manage.*, **92**, 311 (2011).
16. T.C. Zhang, R.Y. Surampalli, C.K.Lai Keith, Z.Q. Hu, R.D. Tyagi and I.M.C. Lo, Nanotechnologies for Water Environment Applications, American Society of Civil Engineers (2009).
17. W.B. Lyons and I. Hawes, Ecosystems Processes in Antarctic Ice-Free Landscapes, Taylor & Francis Group (1997).
18. S.S. Priya, M. Premalatha and N. Anantharaman, *J. Eng. Appl. Sci.*, **3**, 36 (2008).
19. A. Fujishima and K. Honda, *Nature*, **283**, 37 (1972).
20. A. Fujishima, X. Zhang and D.A. Tryk, *Int. J. Hydrogen Energy*, **32**, 2664 (2007).
21. K. Hashimoto, H. Irie and A. Fujishima, *Jpn. J. Appl. Phys.*, **44**, 8269 (2005).
22. S.E. Braslavsky, A.M. Braun, A.E. Cassano, A.V. Emeline, M.I. Litter, L. Palmisano, V.N. Parmon and N. Serpone, *Pure Appl. Chem.*, **83**, 931 (2011).
23. S. Kwon, M. Fan, A.T. Cooper and H. Yang, *Crit. Rev. Environ. Sci. Technol.*, **38**, 197 (2008).
24. A.J. Attia, S.H. Kadhim and F.H. Hussein, *E-J. Chem.*, **5**, 219 (2008).
25. A.N. Sharpley, T. Daniel, G. Gibson, L. Bundy, M. Cabrera, T. Sims, R. Stevens, J. Lemunyon, P. Kleinman and R. Parry, Best Management Practices To Minimize Agricultural Phosphorus Impacts on Water Quality, U.S. Department of Agriculture, Agricultural Research Service, ARS-163, pp. 50 (2006).
26. A. Folli and D.E. Macphee, 8th Fib Phd Symposium in Kgs. Lyngby, Denmark, June 20-23 (2010).
27. A. Tarmizi, N.H. Jamal, P.M. Ismail, A. Karim and I. Sopyan, *J. Instit. Eng., Malaysia*, **70**, 49 (2009).
28. M. Heredia and J. Duffy, in Proceedings of The Solar Conference American Solar Energy Society; American Institute of Architects (2007).
29. J.-M. Herrmann, *Catal. Today*, **53**, 115 (1999).
30. S.U. Khan, M. Al-Shahry and W.B. Ingler, *Science*, **297**, 2243 (2002).
31. W.L. Kostedt IV and D.W. Mazyck, *Fl. Water Resour. J.*, **58**, 44 (2006).
32. T. Ochiai, T. Fukuda, K. Nakata, T. Murakami, D.A. Tryk, Y. Koide and A. Fujishima, *J. Appl. Electrochem.*, **40**, 1737 (2010).
33. K. Wada, M. Nishikawa, and N. Kishimoto, *Water Practice Technol.*, **6**(1), (2011).
34. K. Hashimoto, H. Irie and A. Fujishima, *Japan. J. Appl. Phys.*, **44**, 8269 (2005).
35. X.T. Zhang, O. Sato, M. Taguchi, Y. Einaga, T. Murakami and A. Fujishima, *Chem. Mater.*, **17**, 696 (2005).
36. G. Hüskén, M. Hunger, H.J.H. Brouwers, *Build. Environ.*, **44**, 2463 (2009).
37. F.-L. Toma, G. Bertrand, D. Klein, C. Coddet and C. Meunier, *J. Thermal Spray Technol.*, **15**, 587 (2006).
38. T. Ochiai, K. Nakata, T. Murakami, A. Fujishima, Y. Yao, D.A. Tryk and Y. Kubota, *Water Res.*, **44**, 904 (2010).
39. M. Fujihira, Y. Satoh and T. Osa, *Nature*, **293**, 206 (1981).
40. H.-y. Song, H. Jiang, X. Liu and G. Meng, *Am. J. Environ. Sci.*, **2**, 60 (2006).
41. L. Brunet, D.Y. Lyon, E.M. Hotze, P.J.J. Alvarez and M.R. Wiesner, *Environ. Sci. Technol.*, **43**, 4355 (2009).
42. Z. Huang, P.-C. Maness, D.M. Blake, E.J. Wolfrum, S.L. Smolinski and W.A. Jacoby, *J. Photochem. Photobiol. Chem.*, **130**, 163 (2000).
43. L. Cassar, C. Pepe, G. Tognon, G.L. Guerrini and R. Amadelli, 11th International Congress on the Chemistry of Cement, Durban (2003).
44. K. Varne, State of the Science Literature Review: Nano Titanium Dioxide Environmental Matters, Contract No. EP-C-05-059, Task Order No. 94 (2010).
45. A.K. Ray and A.A. Beenackers, *Catal. Today*, **40**, 73 (1998).
46. USEPA, Technical Bulletin, Nitrogen dioxide (NO_x), Why and How They are Controlled, EPA-456/F-99-006R), Research Triangle Park, NC (1999).
47. R. Pitt, S. Chaturvedula, V. Karri and Y. Nara, Source Verification of Inappropriate Discharges to Storm Drainage Systems, WEFTEC, New Orleans, September (2004).
48. R.E. Huffman, Atmospheric Ultraviolet Remote Sensing, Vol. 52, Academic Press (1992).
49. F.A. Price and D.R. Yonge, *Transp. Res. Rec.*, **1483**, 105 (1995).
50. W.B. Lyons, C. Howard-Williams and I. Hawes, Ecosystems Processes in Antarctic Ice-Free Landscapes, Proceedings of an International Workshop, On Polar Desert Ecosystems, Christchurch, New Zealand July 1-4 (1996).
51. J. Newman and B.S. Choo, Advanced Concrete Technology: Testing and Quality, Butterworth-Heinemann, Oxford, UK (2003).
52. A. Nazari, S. Riahi, S. Riahi, S.F. Shamekhi and A. Khademno, *J. Am. Sci.*, **6**, 98 (2010).
53. B. Ohtani, O.O. Prieto-Mahaney, D. Li and R. Abe, *J. Photochem. Photobiol. Chem.*, **216**, 179 (2010).
54. P.S. Mukherjee and A.K. Ray, *Chem. Eng. Technol.*, **22**, 253 (1999).
55. M. Buren, W. Watt and J. Marsalek, *Water Sci. Technol.*, **33**, 325 (1996).
56. J. Arnold, Storm Water Management Guidance Manual (1993).
57. S. Rengaraj and X. Li, *Chemosphere*, **66**, 930 (2007).
58. G.N. Zaimes and R.C. Schultz, Phosphorus in Agricultural Watersheds, Department of Forestry, Iowa State University, Ames, Iowa, USA (2002).
59. P.M. Haygarth and A. Sharpley, *J. Environ. Qual.*, **29**, 10 (2000).