

A REVIEW PAPER ON STUDY OF NANOMATERIALS TiO_2 & P25 DEGUSSA FOR PARAMETERS OF DAIRY WASTEWATER

¹MR. P. K. JADHAV, ²MR.S.S.JOSHI, ³DR.A. V. SHIVAPUR, ⁴ DR. V.V . KAJINNI, ⁵MR. S.P.KUDALE

^{1,2}Assistant Professor, ³Professor, ⁴Director, ⁵P.G. Student

³Department of Civil Engineering, VTU Belgavi

^{1,2,5}Department of Environmental Engineering,

KIT's College of Engineering (Autonomous), Kolhapur, Maharashtra, India

Abstract: The present studies provide the results of the comparison between the TiO_2 powder & P25 Degussa powder. The TiO_2 Photocatalyst & P25 Degussa Powder are used for the effluent treatment of Dairy wastewater. This review focuses on the mechanism of the UV- TiO_2 & P25 Degussa powder and application of doping and co-doping to improve the photocatalytic activity in the wastewater treatment. In this review, the application of nanotechnology is been done to treat the dairy industry wastewater with high efficiency and less time. The treatment is given for parameters such as pH, COD, BOD, TS, TDS, and compares them with the results of the conventional effluent treatment plant of the Dairy industry.

Keywords: Dairy Wastewater, Nanotechnology, TiO_2 Powder, P25 Degussa Powder, Mechanism, Photocatalytic activity

1.Introduction

The Dairy Industry is considered as the largest food processing industries in many countries. The water utility is higher in the dairy industry which results in higher wastewater generation. The population is increasing at a higher rate, so the wastewater from the dairy industry would also increase with increasing dairy production rate. With improving treatment standards the processes required should be considered stringently and thoroughly.

All steps in the dairy chain, including production, processing, packaging, transportation, storage, distribution, and marketing, impact the environment. Owing to the highly diversified nature of this industry, various product processing, handling, and packaging operations create wastes of different quality and quantity, which, if not treated, could lead to increased disposal and severe pollution problems. In general, wastes from the dairy processing industry contain high concentrations of organic material such as proteins, carbohydrates, and lipids, high concentrations of suspended solids, high biological oxygen demand (BOD) and chemical oxygen demand (COD), high nitrogen concentrations, high suspended oil and/or grease contents, and large variations in pH, which necessitates "specialty" treatment to prevent or minimize environmental problems. The dairy waste streams are also characterized by wide fluctuations in flow rates, which are related to discontinuity in the production cycles of the different products.

All these aspects work to increase the complexity of wastewater treatment. Because the dairy industry is a major user and generator of water, the wastewater of the Dairy industry should be treated properly before its disposal; the former prevailing technologies for treating Dairy wastewater are the conventional method with additional treatment, SBR method, MBBR method, and many more additional treatments. But these methods require Land requirements which is a near-future generation that would not be feasibly available for the development of future needs and the Economy costing increases with an increase in wastewater production. To overcome these problems for future new methods should be developed which requires less space for treatment and moderate capital cost.

1.1. Introduction to Nanotechnology

Nanotechnology is the term which says 'nano' means something which is in the range of 10^{-9} m i.e. very smaller in size, even smaller than micro-sized things and 'technology' means related to the technique of it, so nanotechnology means to be as the things which are in 10^{-9} m range scale and by using them at very minute scale the different work of techniques and things are carried out. In nanotechnology the work done can be with the same or higher effectiveness with the prevailing things and materials present, here only the size is changed and compacted to a 10^{-9} m size scale. In 1959 Mr. Richard Feynman described "There is a lot of space down there" in the session of American Physical Society.

The word nanotechnology was introduced firstly by N. Taniguchi in 1974 at International Conference on Industrial Production to work with nanoscale for industrial mechanism. In 1985 first nano molecule was discovered by five scientists Richard Smalley, Robert Curl, James Heath, Sean O. Brien and Harold Kroto at Rice University and named it as Buckminsterfullerene (C₆₀) now called as Carbon Ball or Fullerene Ball and by adjoining these ball in the chain they formed a carbon nanotube. In 1986, ideas of Feynman were developed by E. Drexler in his book 'Vehicles of Creation: The Arrival of the Nanotechnology Era'. Then with decade's no. of discoveries were made in nanotechnology. In today's world,

there are no. of discoveries made for nanotechnology-related with much modern technology for their compaction and is having a variety of applications in various fields.

1.2 Nano Materials :

TiO₂ powder- This material is a fine white powder composed of titanium oxide particles ranging from 10nm to 30nm in diameter.

Composed of high-surface-area nanocrystals or nanodots, these materials exhibit unique magnetic and antibacterial properties that make it ideal for usage across a broad range of domains. other names for this material include titanium dioxide, dioxo titanium, rutile, or flamenco nanoparticles.

P25 Degussa- Degussa (Evonik) P25, Peroxide TiO₂ P 25, is a Titania photocatalyst that is used widely because of its relatively high levels of activity in many photocatalytic reaction system. Anatase is one the mineral of Titanium Dioxide out of three minerals: Anatase, Rutile and Brookite. Anatase is in white powdered form in nanoscale. It is the rarely found mineral of TiO₂ as compared with Rutile mineral of it. Brookite is highly unstable form of mineral. All minerals of TiO₂ are insoluble in water. Anatase in nanoscale is in the range of approx. 20nm-25nm. It is mainly used in paints, ceramics, tile polishing, varnishes, etc.

2. Literature Review:

2.1 Mojtaba Afsharniaa, Mojtaba Kianmehr, Hamed Biglaria, Abdollah Dargahic, Abdolreza Karimid, 22 January 2018. Disinfection of dairy wastewater effluent through solar photocatalysis processes

In this paper, the treatment for dairy wastewater is given for the parameter of pH by using the photocatalysis process. In this experiment, the TiO₂ powder is used with different dosages, and by using a concave dish the wastewater is exposed to sunlight. In the pH-CS process, almost 95% of bacteria were killed after treatment. From this, the results indicate a definite effect of disinfection from the samples obtained from dairy effluent at almost neutral and alkaline pH.

2.2 Beata Zielińska, Joanna Grzechulska, Barbara Grzmil, Antoni W. Morawski*23 June 2001

Photocatalytic degradation of Reactive Black 5 A comparison between TiO₂-Tytanpol A11 and TiO₂-Degussa P25 photocatalysts

In this paper, the studies & comparison between the two photocatalysts TiO₂ & P25 Degussa powder has been done. In this experiment, the photoreactions of dye decompositions were carried out in the quartz bath photoreactor with the light source of a VT-400 mercury lamp with a power of 180w. The wastewater was treated with different dosages of TiO₂ & P25 Degussa powder. The results were obtained on pH by using both the nanomaterials.

2.3 M. R. Al-Mamun*1, 2, S. Kader2, M. S. Islam2, M.Z.H. Khan1 29 June 2019

Photocatalytic Activity Improvement and Application of UV-TiO₂ Photocatalysis in Textile Wastewater Treatment: A Review

In this paper, the treatment on the wastewater of the textile industry is been done using TiO₂ using the photocatalysis process. The removal of organic dyes and phenolic compounds of the textile wastewater is been done. The doping and non-metal are been done using the photocatalysis process. It can be concluded that metal and non-metal doping on TiO₂ can increase photocatalytic performance.

2.4 M.C. Bordes, M. Vicent, R. Moreno, J. GarcíaMontaño, A. Serra, Enrique Sánchez July 2015

Application of Plasma-Sprayed TiO₂ coatings for Industrial Tannery Wastewater Treatment

In this paper, the treatment is given on the tannery wastewater by using TiO₂ Powder. The Fine structured TiO₂ Deposits were sprayed on the austenitic stainless steel coupons. The wastewater is been kept in the UVB high-pressure mercury lamp. They concluded that there is clear organic matter mineralization and color removal was done by using photocatalysis.

3. Proposed Work :

3.1 Introduction to Dairy Industry :

The Dairy Industry is considered as the largest food processing industries in many countries. The water utility is higher in the dairy industry which results in higher wastewater generation. The population is increasing at a higher rate, so the

wastewater from the dairy industry would also increase with increasing dairy production rate. With improving treatment standards the processes required should be considered stringently and thoroughly.

In general, wastes from the dairy processing industry contain high concentrations of organic material such as proteins, carbohydrates, and lipids, high concentrations of suspended solids, high biological oxygen demand (BOD) and chemical oxygen demand (COD), high nitrogen concentrations, high suspended oil and/or grease contents, and large variations in pH, which necessitates "specialty" treatment to prevent or minimize environmental problems. The dairy waste streams are also characterized by wide fluctuations in flow rates, which are related to discontinuity in the production cycles of the different products.

All these aspects work to increase the complexity of wastewater treatment. Because the dairy industry is a major user and generator of water, the wastewater of the Dairy industry should be treated properly before its disposal; the former prevailing technologies for treating Dairy wastewater are the – Conventional method with additional treatment, SBR method, MBBR method and many more additional treatments. But these methods require Land requirements which in a near-future generation would not be feasibly available for the development of future needs and the Economy costing increases with increase in the wastewater production. To overcome these problems for future new methods should be developed which requires less space for treatment and moderate capital cost.

3.2 Sources of Wastewater generation in Dairy Industry :

- i. Receiving station: Rejected milk, cleaning of cans.
- ii. Cheese making: Whey.
- iii. Milk tank: washing of cans (hot water, alkali & acids, detergents, steam & hot air).
- iv. Water softening plant: rejected water
- v. Butter making- butter milk
- vi. Washing of floors, equipments, tanks and pipes (at the end of every batch)- acids, detergents and hot water.
- vii. Steam condensate and cooling water
- viii. It is estimated that avg. 2% of milk processed reaches to drain as wastewater

3.3 Conventional Treatment in Dairy Industry :

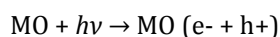
- 3.3.1 Screen Chamber:** The general purpose of screens is to remove large objects such as rags, paper, plastics, metals, etc. These objects, if not removed may damage the pumping and sludge- removal equipment, hangover wires, and block valves; thus creating serious plant operation and maintenance problems.
- 3.3.2 Grit chamber with Oil and Grease removal:** It is used to remove dust, bone chips, coffee grounds, seeds, eggshells, and other materials in wastewater that are non-putrescible and higher than organic matter. Oil and Grease chamber is to remove the Oil, Grease and Fat matter which comes to upper part in the tank due to lesser density than water after retentive time and also by providing aerators the oil particles flow to the surface and this oil and grease are then skimmed from the top through mechanical or labor means.
- 3.3.3 Equalisation Tank:** Here the wastewater effluent of Oil and Grease chamber comes and this tank is provided to equalize the flow and hold additional wastewater in peak hours. In this tank, aerators can be provided to thoroughly mix the wastewater, aerate, and to mix the acidic and basic wastewater from different processing units.
- 3.3.4 Aeration Tank:** Here the aeration is provided using surface aerators or dissolved aerators or both combined to convert the dissolved organics to soluble organics.
- 3.3.5 Secondary Clarifier:** The tank in which the dissolved organic matter after aeration which had been transferred to soluble organics gets settled at the bottom of the tank forming the sludge and the sludge is further sent for treatment.

4. One Solution for Conventional Treatment :

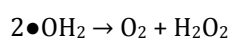
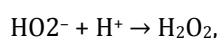
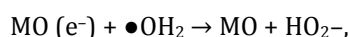
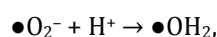
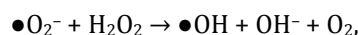
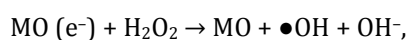
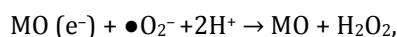
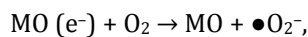
4.1 Photocatalysis: Heterogeneous photo-catalysis is a rapidly expanding technology for water and air treatment. It can be defined as the acceleration of a photoreaction in the presence of a catalyst. The initial interest in the heterogeneous photo-catalysis was started when Fujishima and Honda discovered in 1972 the photochemical splitting of water into hydrogen and oxygen with nanomaterials. From this date, extensive work has been carried out to produce hydrogen from water by this novel oxidation-reduction reaction using a variety of semiconductors.

In recent years interest has been focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase. This method has been suggested in environmental protection due to its ability to oxidize organic and inorganic substrates. In heterogeneous photo-catalysis, two or more phases are used in the photocatalytic reaction. A light source with semiconductor material is used to initiate the photoreaction.

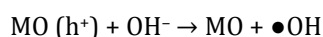
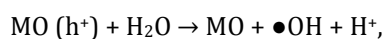
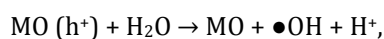
The fundamental process during photocatalysis is given as,



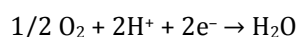
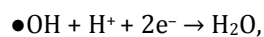
Where, MO represents a metal oxide photocatalyst like TiO₂, ZnO, etc. Photo-generated electrons lead to the formation of superoxide anions ($\bullet O_2^-$), hydrogen peroxide molecules (H₂O₂), hydroxyl radicals ($\bullet OH$), hydrogen dioxide anion (HO₂⁻) and the hydro peroxy radicals ($\bullet HO_2$)



While the oxidation reactions initiated by the photogenerated holes are:



The reactions are terminated as:



This is how the reaction occurs as per given in the found literature.

4.2 Principle Mechanism :

Photo-catalysis over a semiconductor oxide such as TiO₂ is initiated by the absorption of a photon with energy equal to, or greater than the bandgap of the semiconductor (ca.3.2 eV for anatase), producing electron-hole (e^-/h^+) pairs, as written in the equation (1-1):



Where **CB** is conduction band and **vb** is the valence band

Consequently, following irradiation, the TiO₂ particle can act as either an electron donor or acceptor for molecules in the surrounding medium. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical effect. Otherwise, the charges can move to "trap" sites at slightly lower energies. The charges can still recombine, or they participate in redox reactions with adsorbed species. The valence band hole is strongly oxidizing, and the conduction band electron is strongly reducing. At the external surface, the excited electron and the hole can take part in redox reactions with adsorbed species such as water, hydroxide ion (OH⁻), organic compounds, or oxygen. The charges can react directly with adsorbed pollutants, but reactions with water are far more likely since the water molecules are far more populous than contaminant molecules. Oxidation of water or OH⁻ by the hole produces the hydroxyl radical ($\bullet OH$), an extremely powerful and indiscriminate oxidant. OH, radicals rapidly attack pollutants at the surface, and possibly in solution as well, and are usually the most important radicals formed in TiO₂ photo-catalysis. An important reaction of the conduction band electron is the reduction of adsorbed O₂ to O₂⁻. This both prevents the electron from recombining with the hole and results in an accumulation of oxygen radical species that can also participate in attacking contaminants.

4.2.3 Advantages of Nanotechnology for wastewater Treatment :

- i. The cost of treatment can be reduced by using nanotechnology for wastewater treatment.
- ii. The space requirement is less as compared to the conventional treatment plant.
- iii. The efficiency of treatment by using nanomaterials is high as compared to conventional treatment units.
- iv. The time required for treatment using nanomaterials is less as compared to conventional treatment units.
- v. The labor requirement is also less for treatment using the photocatalysis process.

5. Conclusion :

The treatment using nanomaterials using the photocatalysis process is efficient in removing different parameters such as pH, COD, BOD₃, TS & TDS. The efficiency is more as compared to conventional treatment for the Dairy industry wastewater. Also, the treatment is cost-effective with fewer space requirements. The treatment using nanomaterials TiO₂ & P25 Degussa can be the best one for the effluent of Dairy wastewater.

6. References :

- [1] J.J. Murcia, M. Hern and EZ-Laverde, et al.j 2018, "Study of the effectiveness of the flocculation-photocatalysis in the treatment of wastewater coming from dairy industries", Journal of Photochemistry and Photobiology A: Chemistry
- [2] Priscilla de Abreu¹, Erlon Lopes Pereira 2013, "Photocatalytic Oxidation Process (UV/H₂O₂/ZnO) in the treatment and sterilization of dairy wastewater", Acta Scientiarum. Technology
- [3] Mojtaba Afsharnia, Hamed Biglaria 2018, "Disinfection of dairy wastewater effluent through solar photocatalysis processes", Faculty of Health, Gonabad University of Medical Sciences, Gonabad
- [4] Ashish Tikariha, Omprakash Sahu 2014, "Study of Characteristics and Treatments of Dairy Industry Waste Water", Journal of Applied & Environmental Microbiology
- [5] Nicholas T. Nola, Michael K. Seery 2009, "Spectroscopic Investigation of the Anatase-to-Rutile Transformation of Sol-Gel-Synthesized TiO₂ Photocatalysts", J. Phys. Chem. C, Vol. 113, No. 36
- [6] B. Ohtani, O. O. Prieto-Mahaney, D. Li and R. Abe, 2010 What is Degussa (Evonik) P25? Crystalline Composition Analysis, Reconstruction From Isolate Pure Particles and Photocatalytic Activity Test, J. of Photochemistry and Photobiology A Chemistry 2010 Volume 216, pp 179-182
- [7] Chitpisud Supha, Yuphada Boonto, Manee Jindakaraked, JirapatAnanpattarachai & Puangrat Kajitvichyanukul, 2015 Long-term exposure of bacterial and protozoan communities to TiO₂ nanoparticles in anaerobic sequencing batch reactor, Int. J. Science and Technology of Advanced Materials 16 pp 12
- [8] Deanna C. Hurum, Alexander G. Agrios and Kimberly A. Gray, 2003 Explaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO₂ Using EPR, J. Phys. Chem. B 2003 Volume 107, pp 4545-4549
- [9] Dharmendra K. Tiwari, J. Behari and Prasenjit Sen, 2008 Application of Nanoparticles in Wastewater Treatment, World Applied Sciences Journal 2008, pp 417-433
- [10] Haithem Bel Hadjltaief, Abdessalem Omri, Mourad Ben Zina, Patrick Da Costa and Maria Elena Galvez, 2015 Titanium Dioxide Supported on Different Porous Materials as Photo-catalyst for the Degradation of Methyl Green in Wastewaters, Int. J. Advances in Material Sci. and Eng. Volume 2015 pp 10