International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.4, No.3, pp 862-866, July-Sept 2012

Membrane Separation Processes and Advanced Oxidation Processes of Dyes in Bubble Column Reactor-A Keen and Far Reaching Overview

Sukanchan Palit[1,2]

[1]Consultant, 43, Judges Bagan, Post Office – Haridevpur, Kolkata-700082, India
[2]Lecturer-Chemical Engineering, Salalah College of Technology, Salalah, Oman.

Corres.author: sukanchan68@gmail.com, sukanchan07@yahoo.com

Abstract: The vision of environmental engineering is wide, varied and unparalled. The changing world has prompted scientists to target towards green chemistry and green engineering. Green engineering encompasses environmental engineering. The path of success is visionary. Environmental engineering along with dye degradation techniques is ushering in a new era and new vision environmental pollution control. Conventional and traditional textile wastewater and effluent treatment procedures are a challenge to environmental engineers and environmental scientists because of the restrictions on effluent quality by the environmental pollution control authorities. Dyes cannot be destroyed by primary and secondary treatments. Primary treatment encompasses coagulation and flocculation while secondary treatment involves activated sludge process. Both of these treatments do not successfully degrade textile dyes and the dyes are recalcitrant to these treatments. So the need for tertiary treatment process-advanced oxidation process such as ozonation. Bubble column reactor is an efficient and visionary alternative to the environmental pollution problem. The present aim and objective is to present and project effectively the importance of bubble column reactor and ozonation of dyes as the reaction medium in it. The vision of advanced oxidation process will move towards a newer direction if science and technology surges in this new visionary area.
Keywords: bubble, textiles, dyes, ozonation, Oxidation.

1.0 Introduction:

Environmental engineering is moving towards a new era because of the stringent regulations. It is an issue which cannot be neglected. A scientist's particularly an environmental scientist's vision is widened as newer wastewater treatments are devised. The effluent from textile industries is a serious concern and a burning issue to the human being particularly to the environmentalist and environmental practitioners. The effluent contains a large variety of dyes and chemicals which is non degradable , non-biodegradable and a challenge for the entire textile industry. The major pollution in textile wastewater comes from dyeing and finishing processes. These processes involve the input of complex organic compounds. So their degradation is very difficult and an inevitable concern. So the scientific endeavour, concern and surge towards advanced oxidation processes which includes ozonation, H_2O_2/UV, O_3/UV, O_3/ H_2O_2, O_3/ H_2O_2/UV. The major concern is that only 43% of 87 of dyestuff are biodegradable. From literature it has been effectively seen that the residual colour is usually due to insoluble dyes which have low biodegradability as reactive blue 21, direct blue 80 and vat violet with COD/ BOD ratio of 59.0,17.7 and 10.8 respectively. These are the difficulties in the conventional oxidation treatments of dyestuffs used in textile industry. In order to ease the concept, advanced oxidation processes(AOP's) have been developed to generate hydroxyl free radicals by different techniques. AOP's are combination of ozone(O_3), hydrogen peroxide(H_2O_2) and UV irradiation which showed the greatest potential to treat and degrade textile wastewaters.

The major concern is that BOD/COD ratio of the composite textile wastewater is around 0.25 which implies that the wastewater contains large amount of non-biodegradable organic matter.

2.0 Advanced oxidation process(AOP's) and its visionary importance :

The goal and objective of any AOP's design is to generate and apply hydroxyl free radical($HO^{'}$) as strong oxidant to destroy compound that cannot be oxidized by conventional oxidant. The goal and vision of advanced oxidation processes is the production of $OH^{'}$ radicals and the effectivity-selectivity of attack which is an useful positive side for an oxidant. AOP is very much versatile and intensive scientific endeavour since they provide possible and different ways for OH' radicals . Generation and production of HO' is commonly accelerated by combining O_3, H_2O_2, TiO_2, UV radiation, electron-beam irradiation and ultrasound. Of these avenues , O_3/ H_2O_2, O_3/UV and H_2O_2/UV hold the greatest potential to oxidize textile wastewater. The visionary importance suggests that advanced oxidation processes will move science and technology towards a newer and pathbreaking direction.

3.0 Bubble column reactors and its versatile importance:

The application area of bubble column reactors is immense and versatile. It is a great and of visionary potential. Multiphase reactions and multiphase analysis will usher in a new area.

Bubble column reactors belong to the general class of multiphase reactors which consist of three main categories namely, the trickle bed reactor(fixed or packed bed), fluidized bed reactor and the bubble column reactor[1]. A bubble column reactor is basically and primarily a cylindrical vessel with a gas distributor at the bottom. The gas is sparged in the form of bubbles into either a liquid phase or a liquid-solid suspension. When a solid phase exists, these reactors are generally referred to as slurry bubble column reactors. Bubble column reactors are primarily used in chemical processes involving reactions such as oxidation, chlorination, alkylation, polymerization and hydrogenation, in the manufacture of synthetic fuels by gas conversion processes and in biochemical processes such as fermentation and biological effluent treatment. Bubble column reactors have excellent heat and mass transfer characteristics , meaning high heat and mass transfer coefficients. Other characteristics are little maintenance and low operating costs due to lack of moving parts and compactness.[1]

4.0 Bubble columns and its importance in dye degradation:

Bubble column reactors are found to be the most effective tool in dye degradation.[1] It will open up new vistas in the arena of environmental engineering. From mass transfer and heat transfer point of view it is found to be very effective. Conversion levels in dye degradation are also very high. Bubble column's hydrodynamic characteristics is a marvel in the domain of environmental engineering science.[1]

5.0 Experimentation done in the field of ozonation of dyes:

Detailed experiments are done in the field of dye ozonation in a simple bubble column reactor and a fixed bed bubble column reactor. Fixed bed showed increased conversion of dyes. The conversion of dyes also shows dependence on pH and oxidation-reduction potential of the dyes. It has also been found that reaction rate constant as well as order of reaction depends strongly on pH and oxidation reduction potential .

6.0 Research potential in the field of advanced oxidation processes:

Research potential in this domain is wide and versatile. It opens up a new age of wastewater treatment. A small attempt is made in bringing to the forefront the magnificence of the advanced oxidation processes. The research potential will be exhaustive and far- reaching.

Rashed et al(2005)[2] gave an overview on chemical oxidation technology in wastewater treatment. They gave a detailed discussion on different chemical oxidation processes. Processes such as chlorination, ozonation, irradiation, electrochemical treatments and processes based in $OH^{'}$ radical attack have been investigated looking for the best effectiveness to eliminate these toxic soluble substances. This review focuses on different oxidation technologies which can be used for destruction of organic pollutants. This article is concerned especially with advanced chemical oxidation technologies and the application of "Fenton Oxidation" as a practical example for this technology(AOT)'S for removal of organic pollutants from wastewater. Kamenav et al (2003)[3] dealt with wastewater treatment in oil shale chemical industry. Process water and phenol balances for the two processes of oil shale thermal treatment, Kiviter(in vertical retort) and Galoter(with solid heat carrier) were compiled in details. Options of wastewater treatment in Kiviter process were analyzed in more detail. Laboratory experiments of biological oxidation of the process water after the dephenolation stage without other effluents and municipal wastewater were carried out. Wu et al(2004)[4] described in a short communication the treatment of landfill leachate by ozone based advanced oxidation processes. In this study , laboratory experiments are conducted to compare the efficacy using several ozone-based advanced oxidation processes . In this study, laboratory experiments are conducted to compare the efficacy using several ozone-based advanced oxidation processes (AOP's) such as O_3, O_3/H_2O_2 and O_3/UV to treat landfill leachate. Kos et al(2003)[5] gave a detailed overview of decolouration of real textile wastewater with advanced oxidation processes. The efficiency rates of advanced oxidation processes for the decolourisation of different types of textile wastewater taken from textile plants in Lodz, Poland were compared on the basis of the results obtained. Rubalcaba et al (2007)[6] gave a detailed research of advanced oxidation processes coupled to a biological treatment in phenol wastewater remediation. Different advanced oxidation processes were investigated as suitable precursors for the biological treatment of industrial effluents containing phenol . Rekabi et al(2007)[7] dealt with improvements in Wastewater Treatment technology. This is an extensive review process. This research work covers all advanced methods of wastewater treatments and reuse. Stasinakis(2008)[8] gave a detailed review on use of selected advanced oxidation processes (AOP s) for wastewater treatment. The advantages and drawbacks of these methods are highlighted , while some of the future challenges(decrease of operational cost, adoption of strategies for process integration) are discussed.

7.0 Progress in membrane separation processes in advanced waste water treatment:

In recent age and times, , it has become more and more relevant that conventional wastewater treatment processes such as biological conversion, sedimentation, flocculation etc. are often unsatisfactory when large quantities of industrial effluents, which contain large amounts of highly toxic, biologically nondegradable , or high oxygen demanding constituents , have to be treated[9] . Mainly in heavy industrialized areas which are in general also densely populated and where surface water is used for domestic water supply, the traditional wastewater treatment methods have to be substituted by more efficient or chemical procedures.

For many industrial wastewater effluents, however, there are procedures available which are not only efficient but also economical. There are membrane separation processes, especially reverse osmosis , ultrafiltration and to a lesser extent electrodialysis.[9]

During the last decade and last ten years, membrane separation processes have gained enhanced publicity and today they are well entrenched and used as standard procedures for many industrial and environmental engineering mass separation problems.[9]

8.0 Methodology:

In our research pursuit, we have done ozonation of dye (Direct Red 23 dye) in a 500ml Perspex cylindrical flask. Our future target and aim is to design a bubble column reactor for this particular type of ozonation reaction. The ozone output in the ENALY –CHINESE made ozonator is 200-300mg/hr. Our vision and scheme of research is as follows:[10],[11]

a) Dye ozonation kinetics studied at different initial ozone concentrations in a single media bubble column reactor.[10],[11]

b) Dye ozonation was studied in a fixed bed bubble column reactor.

c) Dye ozonation was studied in a single media bubble column reactor at pH's of near 4,7 and 10. The pH taken are acidic, neutral and alkaline.

d)Ph and Oxidation – reduction potential are monitored at various time intervals[11,12,13]

e) Nano-filtration of dye will be our future objective.

f) Ozonation and nanofiltration of different dyes-azo as well as anthraquinone dyes.

The dye taken was Direct Red 23 dye, a diazo dye which is soluble in water. Later in our ongoing research, dye ozonation kinetics of five different dyes will be attempted and pursued .

In the beginning of our research, dye ozonation kinetics of initial dye concentrations of 100mg/l, 110mg/l, 121mg/l and 134.5mg/l was pursued. Then a particular initial concentration of 100mg/l was taken and the kinetics at pH 4,7 and 10 are minutely investigated. Samples were collected from the cylindrical flask at times of 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50 minutes, then the samples were tested for their absorbances with the help of UV spectrophotometer (UNICAM made).

Before measurement of concentration, a calibration chart was made between absorbance and concentration .

The rate of dye degradation with time is evaluated with the help of Newton's Forward Interpolation Formula. Then we follow the following rate equation:

$$-\frac{d[D]}{dt} = k[D]^n \text{ ------------------------(4)}$$

Taking logarithm on both sides of the equation we get

$$\log(-\frac{d[D]}{dt}) = \log(k) + n\log(D) \text{ ----------(5)}$$

The rate constant (k) and order of reaction (n) are analysed by EXCEL LINEST function (least squares regression analysis function).

9.0 Results and discussion:

a) Our main positive conclusion is that there is a variation in order of reaction and rate constant with different pH of solution and different oxidation-reduction potential of solution.

b) Conversion of dye degradation is higher in fixed bed bubble column reactor in the presence of media such as gravels than simple dye solution degradation.

c) Rate constant is highly pH dependent.

d) Over 90% dye degradation is obtained in fixed bed bubble column reactor[10],[11],[12].

e) Rate constant and order of reaction is also dependent on oxidation-reduction potential(Table 1, Table 2).

Table1-Variation of conversion with different pH

Oxidation Reduction Potential(mV)	Conversion(%)
145-160	75
400-450	80
120-130	90

Table-2- Variation of conversion with different oxidation reduction potential

pH	Conversion (%)
2.3	78
3.9	75
6.7	80
7.8	69
9.6	89
9.9	91

10.0- Vision behind ozonation and advanced oxidation process:

A scientist's vision is wide and unparalled. Potential of both ozonation or advanced oxidation processes are remarkable and innovative. The conversion levels of dye degradation are very high in the ozonation process or other advanced oxidation processes. The world of chemical engineering and environmental engineering will cross one frontier over another. The vision of ozonation procedure will open up new avenues in the field of environmental science and technology.

11.0-Vision of membrane separation processes and advanced oxidation processes from environmental engineering point of view:

Membrane separation process and advanced oxidation processes are unraveling the secrets of hidden depths of science. Membrane separation can give a breakthrough in desalination technology. A scientist's vision will be widely acceptable to nature's vulnerabilities. Intense research work is undertaken in these two widely accepted marvels of science and technology. The advancements of these two domains will reach the citizens of earth in the grassroots level with application areas of drinking water treatment and wastewater treatment. Knowledge will unfold the intricacies and difficulties of these two domains and it will surge towards a new vision.[11],[12],[13]

12.0 Future vision of ozonation and future flow of thoughts:

Both ozonation and advanced oxidation processes are crossing one frontier over another. They are pathbreaking domains of environmental engineering science. In the future world , environmental engineering will dominate every sphere of science and technology . Man's vision is to overcome one difficulty over another. In that context , environmental engineering science is crossing one boundary over another. Research pursuit and research hardship is continuing in every nook and corner of the world and thus showing its tremendous potential.[11],[12],[13]

13.0 Acknowledgement:

The author is grateful to Dr. Bhaskar Sengupta, Dr. Des Robinson, Dr John Mckinley , Faculty, Queen's University, Belfast, United Kingdom under whose guidance the author did research work in the field of ozonation of dye[11],[12],[13].

14.0 References:

1. Kantarci, N., Borak.F., Ulgen.K.O., (2005), Bubble Column Reactors, Process Biochemistry, 40(2005)2263-2283
2. Rashed. I.G., Hanna.M.A., El-Gamal. H.F., Al-Sarawy.A.A., Wali. F.K.M., (2005), Overview on chemical oxidation technology in wastewater treatment, Ninth International Water technology Conference,IWTC9 2005, Sharm. Al-Sheikh, Egypt.,
3 Kamenav. I., Munter. R., Pikkov.L., Kekisheva.L.,(2003) Wastewater treatment in oil shale chemical industry, Oil Shale , 2003, Vol. 20, No.4. , Estonian Academy of Publishers.
4. Wu.J.J., Wu.C.C., Ma.H.M.,Chang.C.C.,(2004) Treatment of landfill leachate by ozone based advanced oxidation processes, Chemosphere, 54(2004), 997-1003
5. Kos.L., Perkowski . J., Decolouration of real textile wastewater with advanced oxidation processes, Fibres and Textiles in Eastern Europe, October/ December,2003, Vol.11, No.4(43)
6. Rubalcaba.A., Suarez-Ojeda. M.E., Stuber.F., Fortuny.A., Bengoa.C., Metcalfe.I., Font.J., Carrera.J., Fabregat.A.,(2007), Phenol waste water remediation: advanced oxidation processes coupled to a biological treatment, Water Science & Technology, Vol.55, No.12,pp 221-227
7. Al-Rekabi, Oiang.He, Qiang Wei Wu,(2007) Improvements in wastewater technology, Pakistan Journal of Nutritution, 6(2): 104-110, 2007
8. Stasinakis.A.S.(2008) Use of selected advanced oxidation processes (AOP's) for wastewater treatment-a mini review, Global NEST Journal, Vol.10, No.3, pp 376-385(2008)
9. Strathmann.H., Membrane separation processes in advanced wastewater treatment, Pure & Applied Chemistry, Vol.46, pp213-220, Pergamon Press , 1976
10. Palit Sukanchan,(2010) Studies on Ozone-oxidation of Dye in a bubble column reactor at different pH and different oxidation-reduction potential, International Journal of Environmental Science and Development, Vol. 1, No.4, October,2010
11. Palit Sukanchan(2009) Ozonation of Direct Red – 23 dye in a fixed bed batch bubble column reactor, Indian Journal of Science and Technology, Vol.2 , No.10,Oct,2009.
12..Palit Sukanchan(2011)Ozonation associated with nanofiltration as an effective procedure in treating dye effluents from textile industries with the help of a bubble column:A review, International Journal of Chemistry and Chemical Engineering, Vol 1, Number 1(2011) pp 53-60.
13..Palit Sukanchan,An overview of ozonation associated with nanofiltration as an effective procedure in treating dye effluents from textile industries with the help of a bubble column reactor, International Journal of Chemical Sciences, 10(1),2012, 27-35.

*****