Sullage Treatment by Photo-Catalysis

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ABSTRACT

Sullage, the wash water of bathrooms, is also known as grey wastewater1. Detergent is the main impurity in this. Considering the modern day problem of water scarcity, there is a great need to purify this water and reuse it. However conventional technologies are not successful in treatment of detergent containing wastewaters. Photo –catalysis is a promising technology for these wastewaters. In the present work, sullage of SSBT's College of Engineering and Technology Bambhori, Jalgaon has been treated by photo –catalysis. The process parameters are first optimized. The optimization is done using artificial samples (dissolving detergent is the distilled water). An indigenous rector using UV lamps has been designed for reactions. Raw sullage is characterized. Then it is treated under optimum conditions of process parameters using solar energy. It is found to be effective and viable.

***KEYWORDS** : Sullage, Photo catalysis, Detergents, Optimization.*

INTRODUCTION

Water is a precious resource in 21ST century. Water pollution is a great crisis. Earlier BOD had been a major concern in wastewaters. With the development in science and technology; its impact on our life style and industrialization, the wastewater characteristics have also changed 2. Now days, non-bio degradable organics are increasingly present in wastewaters. They have got persistent nature and they join food chain. They exhibit carcinogenity, mutagenity, genetic disorders, allergies and other disorders 3. Conventional water/ wastewater treatment techniques are unable to remove them. Adsorption, ultra filtration etc can remove them but it is simply phase change. Photo catalysis is the only technique to completely demineralize them. The present work is for the removal of detergent from sullage, the wastewater of bathrooms. Detergents not only cause health impacts by join food chains, they cover water surface and hinder aeration.

The synthetic detergents are made from petrochemicals 4. The first forerunner of today's synthetic detergent was made in 1834. Basically the petroleum industry had, as a waste product, the compound propylene, CH_3-CH=CH_2. By joining four of these propylene molecules together and if benzene is attached at the double bond, the resulting compound reacts with sulfuric acid. Then sodium hydroxide is added to neutralize and a sodium salt is obtained. The substance thus obtained is an excellent detergent.

The photo-catalysis process

Oxidation is a process in which a molecule emits out electron. There must be an electron acceptor available to receive the electron. Chemical bonding with oxygen is called as oxidation as oxygen is an electron acceptor. Oxidation of organic molecules is generally results into their breaking down to simpler compounds finally leading to mineralization as CO_2 and H_2O. Most of the organic wastewaters can be mineralized with help of biomass. Yet there are non-biodegradable organics. Photo-catalysis is very effective in their mineralization. It is described as:

Semiconductor + UV rays = semiconductor+ + electron

H_2O = H+ + OH-

OH- + semiconductor+ = OH* + semiconductor

OH* + organic matter = CO_2 + H_2O + minerals

The commonly used semiconductor is TiO_2. The reaction is driven by photonic energy in UV range. The same can be obtained from UV lamps or Sun.

Earlier it was thought that the non-biodegradable organics are essentially non-recyclable by nature. However nature had a mechanism that was recognized later 5. Naturally the phenomenon was going on since ever. Goodeve and J. A. Kitchener noticed it first in 1930s 6. The technology can be applied to wastewaters for cleaning up. The technology is now being used in slurry phase reactor as well as in fixed bed reactors 7. The present work has used the slurry phase reactors. The process variables this type of reactors are identified by Chong et al 8 e.g. intensity of radiation, starting concentration of organic pollutant, concentration of photocatalyst, particle size of photocatalyst etc.

Selection of photo-catalyst

METHODOLOGY

The methodology has two parts, characterization of materials, and reactor design.

Particle size and surface area determination of photo-catalyst

Photocatalysis is a phenomenon that takes place only with nano-size of the particle. The particle size is determined by Transmission Electron Microscopy (TEM) and by X-ray Difractometry (XRD). These values are adopted from Ph D thesis of Suhas 10. The specific surface area is taken as 50 m^2/g.

Characterization of Detergent

The commercial detergents are complex mixer of basic detergents, boosters, binders, flavoring agents including the enzymes too. The work has been focused on the commercial detergents surf Excel. Detergent solution is prepared dissolving 1 g detergent in 1 L distilled water. The properties are given in Table 1.

Parameter	Value
pH	8.0
Phosphorous	5 mg/L
Kjeldahl Nitrogen	50 mg/L
Chloride	300 mg/L
Sulfates	250 mg/L

UV Radiation Flux Source

In the present study two types of sources are used. Sunlight, the natural source for outdoor experiments and UV lamp for indoor experiments. Characterization of the both sources of UV radiation is done by monochromater (Jobin Yvon Spex, HR-640, France) having photo multiplier tube (Hamamatsu, Photonics K. K., Type-R446HA, No.VU9293, spectral range 0 -1300nm)

UV Radiation Measurement Technique

Accurate measurement of radiation is essential as it is the driving force for the phenomenon of photocatalysis. Hence during experimentation, in case of solar radiation driven photocatalysis as well as artificial source of radiation. Radiation is measured by Radiometer

Radiometer:

The radiometer used in the present work is International Light, USA, Research radiometer, named IL-1700. It is having dynamic range 1 x 10^{-9} to 2.0 W/m^2 with a spectral range of 200 - 400.

Characteristics of Sunlight:

Fig 1 shows the characterization of solar radiation. Peak of UV spectrum band is found to be at 381 nm.

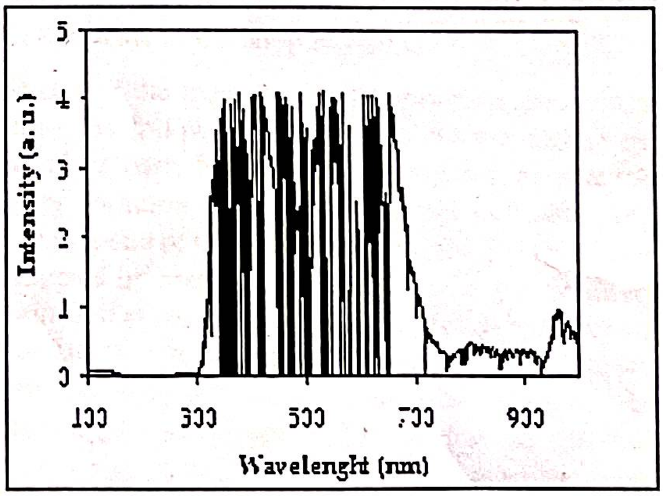
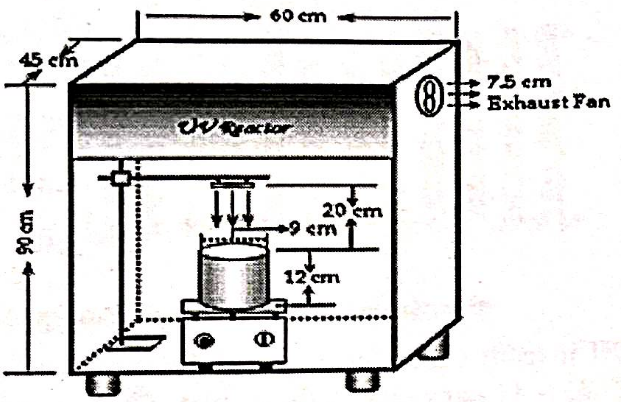


Fig 1: Spectrum of solar radiation

For indoor medium pressure mercury vapor lamps - Narva UVK-125 W (Germany) are used. Characterization of the same is shown in figure 3. Peak of UV radiaon is at 334 nm.



Indigenously designed reactor

Fig 2 COD as a probe parameter

The detergent is a complex mixture of boosters, binders, basic detergent etc. They all will get oxidized due to photocatalysis. The specific degradation of detergent can be monitored by spectrometric analysis. But in a complex system, it is better to observe the overall picture. Hence COD has been taken as a probe parameter to observe the overall mineralization. It serves the objective of study better. Moreover COD is a parameter that can be observed accurately and easily.

RESULTS AND DISCUSSION

In the present work process design/process parameters are optimized. In photo-catalysis technology, researchers have given optimized values of the parameters. Yet mostly they have selected the range of variables in arbitrarily. The complex process of photo-catalysis process has interwoven parameters. Researchers have described that individual parameters cannot be optimized owing to their interwoven complex10. The present work has used the same approach. In this approach a set of operating and design conditions are optimized rather than an individual parameter. The practical range of catalyst concentration and effective depth of reactor for the light intensity are taken as <200 mg/L and <15 cm respectively. The detergent concentration is taken as 1000 mg/L as this is the most common value of detergent in domestic wastewater. With reference to these the other parameters are optimized.

There are several semiconductors which exhibit photo-catalytic activity like Fe_2O_3, ZnO, ZnS, WO_3, V_2O_5, SiO2, SnO2, Al2O3, CdS and TiO2. However, TiO2 is the first choice of the researchers owing to its economical availability and higher reactivity. Its anatase form is more reactive. Commercially available Degusa P- 25 form has been recommended by Pierre Pichat9. The same has been used here.There are several semiconductors which exhibit photo-catalytic activity like Fe_2O_3, ZnO, ZnS, WO_3, V_2O_5, SiO_2, SnO_2, Al_2O_3, CdS and TiO_2. However, TiO2 is the first choice of the researchers owing to its economical availability and higher reactivity. Its anatase form is more reactive. Commercially available Degusa P- 25 form has been recommended by Pierre Pichat9. The same has been

Optimization of pH:

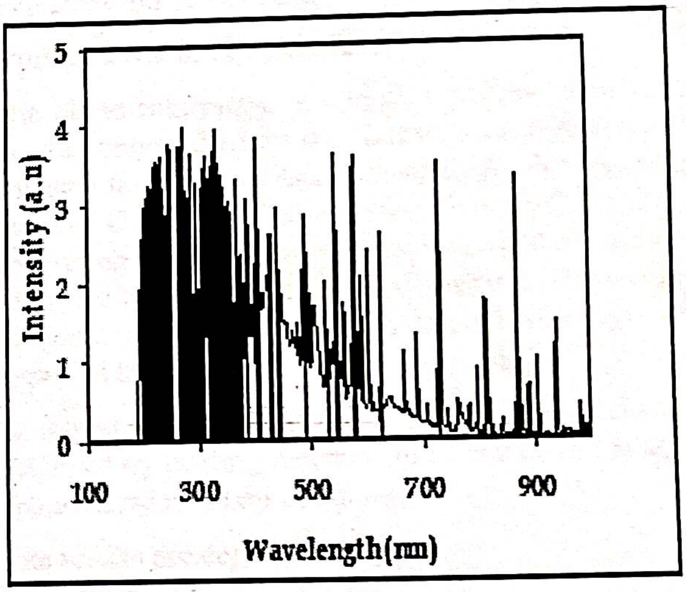


Fig 3: Spectrum of UV lamp radiation

pH is one of the most important operating parameters affecting the following parameters: electric charge on the catalyst particles, size of aggregates of catalyst etc. Any variation in the operating pH will affect the isoelectric point of the photocatalyst used. This has been investigated by many researchers11 – 13. pH needs to be optimized at the initial stage. The pH has been varied from 5.0 to 10.5 by HCL for lowering and by NaOH for elevating. Too high too low pH may be impracticable for field applications too. While varying the pH, the catalyst concentration, detergent concentration and liquid depth in reactor are kept as constant, respectively

200 mg/L, 1000 mg/L and 15 cm. COD of the slurry has been monitored at an interval of 30 minutes. The results are shown in fig 3.

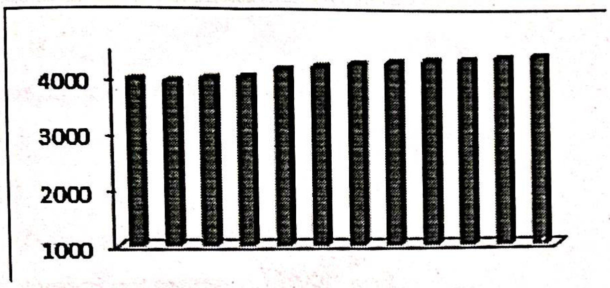


Fig 4 Optimization of catalyst concentration

Number of researchers have reported the effect of TiO_2 loadings on the photo-catalysis efficiency14 – 16. Yet they have worked independently and results are not comparable. Patil10 has proposed the range of catalyst to be <200 mg/L with reactor depth to be 15 cm. In order to optimize the catalyst concentration, it is varied from 50 mg/L to 200 mg/L, at an interval of 25 mg/L. pH is kept as 5.5. The results are shown in fig 5.

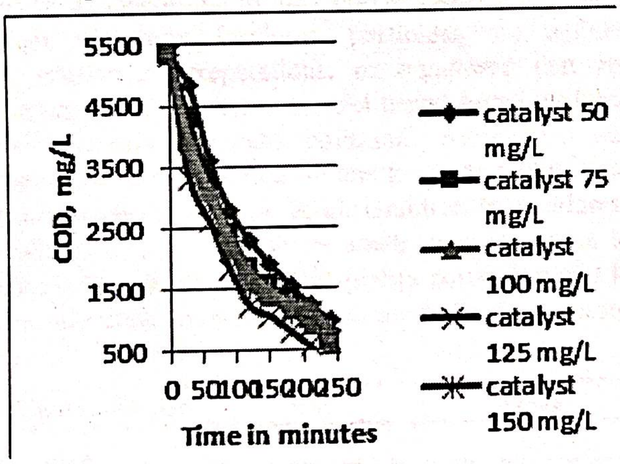


Fig 5: Effect of catalyst concentration on COD removal rate. Detergent concentration = 1000 mg/L, pH = 5.5

It is clear that maximum reaction rate is observed with catalyst concentration 125 mg/L.

Optimization of detergent concentration

Researchers 11 – 13 have investigated the effect of pollutant concentration on kinetics using synthetic wastewaters. Researchers 17 – 21 have done studies using real wastewaters. However, the photo-killing mechanism is as yet unclear as it involves a variety

Detergent concentration is varied from 500 to 2000 mg/L at a step of 250 mg/L. The results are presented in fig 6.

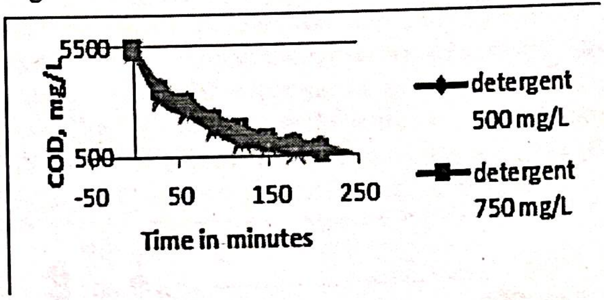


Fig 6: Effect of detergent concentration on COD removal rate. Catalyst concentration 125 mg/L, pH = 5.5

The highest removal rate is observed at detergent concentration of 1250 mg/L.

Optimization of temperature

The photo-catalysis is a complex process. According to Arrhenius theory the higher temperature will enhance the reaction rate. Temperature also promotes the recombination of charge carriers and disfavour the adsorption of organic compounds onto the TiO_2 surface. Thus, the temperature needs optimization. Dependency of photocatalytic reaction on temperature has been explored by 21 – 23.

In this study the temperature higher than ambient is achieved by heating mechanism of stirrer and lower is achieved by room air conditioner.

The results are depicted in fig 7.

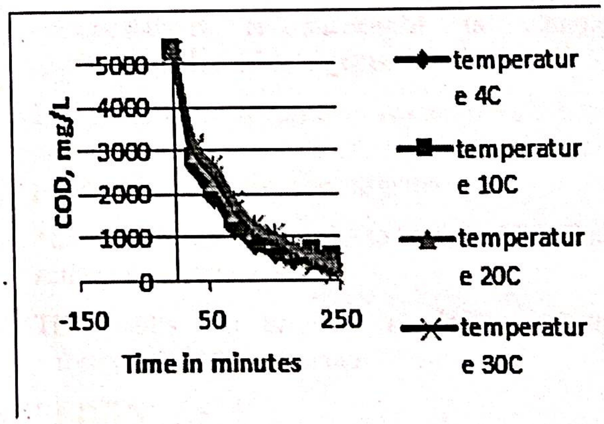


Fig 7: Effect of temperature on COD removal rate of detergent. pH = 5.5, catalyst concentration 125 mg/L, detergent concentration 1250 mg/L

Final set of optimal parameters:

The experimentation has resulted into set of optimum parameters. As summarized in table 2.

Table 2

Summary of optimal parameters

Parameter	Optimal value
pH	5.5
Catalyst concentration	125 mg/L
Detergent concentration	1250 mg/L
Temperature	100C

Characteristics of sullage:

The wash water coming from bathrooms in COET Campus has been characterized as shown in table 3.

Table 3

Tapi river coordinate in chopada & shirpur region Latitude: 21° 20' 53.56" N and Longitude: 74° 52' 49.26" E. According to the Code of Practice for Using Plant Protection Products, pesticides are defined as substances, preparations, or organisms that are formulated or applied to control pests. A major global issue is environmental pollution. Agriculture has become a prominent contributor to water pollution in enumerations of sources. While countries try to address maltreatments of their water assets, it is important to decide the reasons for water quality corruption and to measure contamination commitments from numerous sources. Table .2

Characteristics	Unit	Value
pH	-	7.6
COD	mg/L	210
BOD5 @ 200C	mg/L	55
Alkalinity	mg/L as CaCO3	22
Phosphorous	mg/L as P	3.2
Kjeldahal nitrogen	mg/L	12
Chloride content	mg/L	113
Sulfate content	mg/L	14
Detergent content	mg/L	87
Electrical conductance	130	micro-Siemens per cm

The sullage is treated under the optimum conditions, given in table 3. The experiment is performed by keeping the glass beakers under open sky. The solar radiation varies during the experimentation. It is recorded every 30 minute interval and its average value is used. The solar radiation is measured by solari-meter. The experiments are done around the solar noon duration, 12 O' Clock in day. The results are presented in fig 8, three set of experiments are performed.

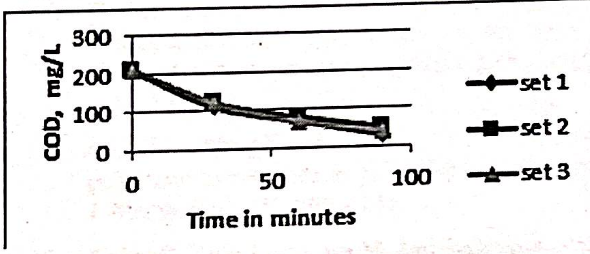


Fig 8: Degradation of sullage under solar radiation. pH = 5.5, temperature = ~30°C, solar radiation ~ 250 W/m², catalyst concentration 125 mg/L, depth of reactor = 15 cm.

Total solar radiation is measured by solari-mete. The UV radiation may be taken as 5% of the total (250*5/100 = 12.5 W/m²).

CONCLUSIONS

1. Researchers have established that presence of detergents in irrigation water has drastic impact on the soil productivity. Yet the authorities like Indian Standard Institutions and Central Board of Pollution Control have not established the permissible limits.
2. Photo-catalysis is successful in complete demineralization of detergents.
3. The photo-catalysis process is complex. It has so many variables interrelated. Here an approach is presented to optimize the variables.
4. The results can be applied to design a full fledge sullage treatment plant.
5. The results can be used to design industrial wastewater treatment plants.

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VOLUME 47 • SPECIAL ISSUE • NO. 2 • APRIL 2024 ISSN 0971-3034

THE INDIAN JOURNAL OF TECHNICAL EDUCATION

Published by
INDIAN SOCIETY FOR TECHNICAL EDUCATION
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