GREY WATER DEGRADATION USING COUPLED PHOTOCATALYSIS AND PHOTOFENTON PROCESSES USING FIXED BED REACTOR

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of

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to

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May, 2019

STUDENT'S DECLARATION

I hereby declare that the work presented in the Project report entitled **“Grey Water Degradation Using Coupled Photocatalysis And PhotoFenton Processes Using Fixed Bed Reactor”** submitted for partial fulfilment of the requirements for the degree of Master of Technology in Civil Engineering with specialization in Environment Engineering at Jaypee University of Information Technology, Waknaghat is an authentic record of my work carried out under the supervision of **Dr. Saurabh Rawat**. This work has not been submitted elsewhere for the reward of any other degree/diploma. I am fully responsible for the contents of my project report.

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CERTIFICATE

This is to certify that the work which is being presented in the project report titled **“Grey Water Degradation Using Coupled Photocatalysis And PhotoFenton Processes Using Fixed Bed Reactor”** in partial fulfilment of the requirements for the award of the degree of Master of Technology in Civil Engineering with specialization in Environment Engineering submitted to the Department of Civil Engineering, Jaypee University of Information Technology, Waknaghat is an authentic record of work carried out by **Khushbu Raitka (172755)** during a period from August, 2018 to May, 2019 under the supervision of **Dr. Saurabh Rawat,** Department of Civil Engineering, Jaypee University of Information Technology, Waknaghat.

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ABSTRACT

Today world is facing a greater threat of water crisis, with not enough portable water available for present population. The need of freshwater can be reduced by using recycled wastewater. The present work is an experimental study performed in order to degrade greywater (type of wastewater) for non drinking purpose like kitchen gardening, toilet flushing and other. Reuse of greywater depends on the technology used in its purification. In this work, processes like fenton and photo-fenton were studied on laboratory scale for the degradation of greywater. The greywater was collected from different sources of such as Laundry, Hostel Mess and Girls Hostels. Greywater degradation was studied in two methods i.e. in control degradation process and Fixed bed reactor degradation process. A laboratory scale Fixed bed reactor was fabricated to achieve the greywater degradation. In control chamber, the greywater was degraded with and without addition of catalyst (TiO_2) and then impact of degradation was studied by testing its characteristics. Similarly in reactor the degradation was done in four different phases and then tested for its characteristics for each phase. It was found that highest value for BOD was recorded as 295. After few days and while first stage of treatment i.e control treatment, it was noticed that its BOD value was raised significantly with highest value recorded is 519. Further, there is not much effect is seen in alkanity and acidity character of greywater during degradation. Absorbance value for Fe recorded during control degradation was 0.554 which reduced in second stage of treatment to 0.551. Similar for Cr, in first stage of treatment, value of absorbance was 0.139, which was recorded as 0.004 in second stage. Approx 6% of reduction in pH has been noted. Fe and Zn percentage was found to be decrease by 2.5% and 0.5% respectively. Whereas Cr, Cu, Mn percentage shows huge decrease of 98%, 95.5% and 77.6% respectively.

Keyword: titanium dioxide; advanced oxidation process; photo catalysis; water treatment; degradation; Photocatalytic oxidation.

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LIST OF SYMBOLS

BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
LGW	Laundry Greywater
LR GW	Low Range Greywater
MR GW	Mid Range Greywater
HR GW	High Range Greywater
Cr	Chroumium
Cd	Cadmium
Fe	Iron
Cu	Copper
Pb	Lead
Ni	Nickel
Zn	Zinc
TiO_2	Titanium Dioxide
H_2O_2	Hydrogen Peroxide
TDS	Total Dissolved Solids
TSS	Total Suspended Solids
SGW	Shower Greywater
UV	Ultraviolet
AOP	Advanced Oxidation Process
NTO	Nano Crystalline Titanium Dioxide
LED	Light Emitting Diode
DCA	DiChloroacetic Acid
H_2SO_4	Suphuric Acid.

CHAPTER 1

INTRODUCTION

1.1 GENERAL

This chapter deals with the introduction to the problem statement. It highlights the need of degradation of grey-water as an alternative source to counter the problem of water scarcity. This chapter bring forth the concept of grey-water and subsequently various method used for its degradation. The basic mechanism of photocatalysis process and photofenton process is also described in this chapter. This chapter also outlines the organization of thesis.

1.2 NEED OF STUDY

The critical importance of sustainable development of water in the Millennium Development Goals has been clearly recognized. Freshwater is a fundamental requirement for human existence and socio-economic development and therefore it should be managed wisely. The need for fresh water can be reduced by using recycled waste water. There is considerable possibility of reuse of Greywater (laundry, shower, bathtub, sink and kitchen water discharge), due to its availability (approximately 70% of domestic wastewater) [1] and its low concentrations of pollutants compared to combined domestic wastewater.

It is a commonly observed that untreated sewage is directly disposed into the water bodies and surface land which poses threat to human life. The effects of insufficient treatment can be detrimental to a community at economic, cultural and health levels. In India, the cost of Un-managed household waste is of great vertical extent. Due to the plague epidemic of 1994 in India, $200 USD million was estimated as the loss due to decline in tourism [1]. A recent cholera-epidemic in Peru costed 3 times the amount of water and sanitation in the country.

Contaminated water by human activities can cause many kinds of diseases such as dengue, filariaria, malaria, trypanosomiasis, and yellow fever which can occur through direct or indirect intake or direct contact. Hereby, any other added type of involvement does not have any effect on the development and public health of any country compared to the state of clean distilled water and elimination of human waste.

The gain of reuse of treated waste should also be compared against the cost of not doing so at both environmental and economic levels. The cost associated with zero-discharge biological waste for agricultural recycling projectsmay not be too expensive. The full scale implementation of urban decorative waste for agricultural systems for city of 1 million people could cost around $5-6 USD.

The drawbacks of current-treatment technique are that they lack stability. The connective centralized system removes pathogenic bacteria from the residential area, uses large amount of water and often combines-domestic waste-water with rain-water, which leads to the flow of pathogenic waste-water in large quantities.

A leading contributor of highly utile water, especially for water-scarce countries, is mainly the urban waste water usually generated from household washing activities which is called "greywater". Greywater generally consists of less organic and pathogenic materials than wastewater from town or cities(which includes channel from toilets and kitchen sinks), making it ideal for retreatment of water.

Freshwater consumption for non-potable purposes focuses on recycling of grey water. Although there is no input of toilets or industrial wastewater, but for applications involving human exposure such as toilet-flushing and garden-irrigation, strong treatment of polluted greywater is required.

1.3 GREYWATER

Wastewater generated from any house - hold, institutional or residential building without any feed from the toilet, bidet, urinal or heavy polluted industrial process water is generally defined as Greywater.[4]. Greywatar is all waste-water which is dis-charged from a house, except black water (toilets water) comprising of shower, bathtub, sink, kitchen, dishwasher, laundry, bathtub and washing machine water. It usually includes, shampoo, soap, toothpaste, scraps, oil, detergent and hair. In terms of quantity waste water from households contribute to around 50-80% greywater. 100% of household wastewater can be regarded as greywater if toilet waste is included.

Percentage of grayness in greywater depends upon the type of waste it contains, thus all grey water are not equally grey. Waste water from kitchen and laundry are more contaminated compared to greywater from bathroom and shower sinks.Therefore, various treatment methods may be needed in different Greywater flows, which will provide the water suitable for reuse..

Even within a property quantity and quality of greywater varies to a great extent depending upon daily activities involved. Following are the characteristics of grey waterthat have been discussed by [3] Jefferson et al. (2000):

- Generates the need of storage because of large variable quantity.
- Needs vigorous treatment system because of large variation in quality.

Quality of greywater depends upon physical parameters such as pH, total suspended solids, BOD, COD, DOC, and volatile suspended solids. Heavy metals primarily (Cr) Chromium, (Ni) Nickel, (Pb) lead, Iron (Fe), Aluminum (Al) and Mercury (Hg) are also found in significant amount in greywater [4]. Various parameters such as Nitrogen and Phosporous along with hardness, color and turbidity are also considered necessary.

Considering the differences in approach and quality adopted to obtain the greywater yet it can be summarized under some general observations. Greywater stream usually has high temperatures, which favor favorable microbiological growth. Due to the precipitation of inorganic salts, bathroom greywater has comparatively little material for suspended solids, but possibly higher level of contamination. With highest alkalinity level obtained from clothes washing, greywater obtained from cooking area shows large BOD. High cod, nitrogen and phosphorus content are visible in both washing and kitchen greywater. In short, grey water from kitchen contains the top level of most chemically pollutants. Laundry water also contains such chemicals in abundance. On the contrary, bathroom grey water has low contaminants which are chemically toxic but forms the major source of faecal e – coli bacteria. Therefore, there exists high potential of pathogen level (Friedler-2004).

Bathroom grey water is classified as “light-grey” whereas grey water from cooking and washing is known as “dark grey” [32]. Though the terms ‘light grey’ and ‘dark grey’ reflects the amount of chemically active toxic material in greywater, they under estimate the quantity of microbial species in bathroom grey water.

1.4 WHY GREYWATER?

The foremost agenda of grey-water recycling is to replenish precious drinking-water in the applications which do not require drinking-water quality. Few applications of such re-use include the use of irrigation-water, industrial-water, laundry, and toilet-flushing depending on the technologies used in the purification process. Grey-water recycling makes it possible to reduce the fresh-water consumption along with waste-water production thus reducing the expenditure on water-bills. If greywater is considered as an add-on source of water, then increasing irrigation water supply can be ensured, thereby increasing agricultural produce.

Unlike rain-water harvesting, grey-water recycling does not dependent on season or variability of rain-fall and as such is a continuous, and a reliable water-resource. This results in smaller-storage facilities, than those needed for rain-water harvesting.

Treatment level and source of greywater determines its appropriate usage. Recycled water is mostly used for nondrinking purposes, such as agriculture, public parks, and land-scape. Some other nonpotable applications include industrial process water for facilities such as cooling water for electricity plants and oil refineries, carpet shoppers, dust-control, construction-activities, toilet-flushing and concrete-mixing.

Even though projects have been deployed to meet requirement of non-drinkable water demands, a number of projects uses treated water indirectly for drinking purposes. These projects include recharging the underground water aquifers and increasing the surface water reservoirs with recycled water. In order to prevent salt water intrusion in coastal areas and to replenish ground water, recycled water is injected .Such projects are named as ground water recharge projects. In conclusion, water recycling saves water, money and energy.

1.5DEGRADATION OF GREYWATER

With the main target of reduction of easily degradable organic compound, Greywater treatment has proven that conventional, primary and secondary treatment processes such as coarse filtration, biological and chemical processes to be less-effective and more costly. The major forerunner of disinfection in treated water when chlorine is used for disinfection is the organic matter by-products. Therefore removal of organic matter is basic requirement before chlorination. Some of the advanced wastewater treatment methods which include micro-filtration (MF) and ultra-filtration (UF) membrane systems are way too costly. Moreover, in case of grey water, despite several advantages, M-F and U-F systems offer poor removal of organic-pollutants during treatment process of grey-water. The grey water treatment technologies are complex and time consuming, hence their efficiency in degrading organic contaminants concentration falls below par as per required standards for greywater reuse acceptability. This shortcoming is easily overcome by numerous available advanced-oxidation-processes (AOPs) among which photo-catalytic processes has depicted significant efficiency.

Photo-catalysis is a advanced-oxidizing-process (AOP), which depends on the originality of highly reactive radical species using chemical, solar, or other forms energies, mainly hydroxyl radical (HO•) and superoxide's(O_2-•)ions.. This process has the ability to oxidize the organic material and even mineralize the intermediates into a non-hazardous form such as carbon dioxide Co_2, ammonia, nitrates, phosphates and H_2O. In addition, the process offers several advantages such as:

(i) It may leads to the formation of harmless end-product as compared to conventional treatment methods

(ii) It can be carried out in various media: gaseous phase, aqueous solutions as well as solid phase to some degree

(iii) Unlike energy intensive treatment processes, photocatalysis in the near future may be a candidate to use efficiently the renewable and pollution free solar energy

(iv) It has the potential to destroy toxic and recalcitrant organic compounds present in various wastewater streams

(v) The chemical reactions involved in the process are mild, require less chemical input and the reaction time may be modest, and finally.

(vi) Minimal secondary wastes are produced in the process due to efficient mineralization.

The commonly postulated chain reactions occurring in the photocatalytic process are given in eq^n 1.1 to 1.12 as:

Photocatalyst illumination (electron-hole pair generation)

$$\text{Hv} + \text{photo-catalyst} \rightarrow e^- + h^+ \quad (1.1)$$

Recombination of charge carriers

$$e^- + h^+ \rightarrow \text{Heat} \quad (1.2)$$

Super oxide radical formation

$e^{-} + O_2\,ads \rightarrow O_2^{-}\bullet$

(1.3)

Hydro-peroxyl radical and hydrogen peroxide formation

$O_2^{-}\bullet + H^{+} \rightarrow HOO\bullet$

(1.4)

$HOO\bullet + e^{-} \rightarrow HOO^{-}$

(1.5)

$HOO^{-} + H^{+} \rightarrow H_2O_2$

(1.6)

Hydroxyl radical formation / Decomposition of water

$e^{-} + H_2O_2 \rightarrow HO\bullet + OH^{-}$

(1.7)

$h^{+} + H_2O\,ads \rightarrow H^{+} + HO\,ads\bullet$

(1.8)

$h^{+} + OH\,ads- \rightarrow OH\,ads\bullet$

(1.9)

Mineralization of pollutant

h^{+} + Organics → CO_2+ H_2O

(1.10)

HO• + Organics → CO_2+ H_2O

(1.11)

HO• + Organics ads → CO_2+ H_2O

(1.12)

Electron and hole pairs generated by light illumination (Equation 1.1) are used in the redox reactions discussed below. If not, then the electrons and holes recombine and heat is evolved (Equation 1.2).

To minimize the recombination reaction, chemical species which consume the photo generated electrons are required. Hence oxygen (commonly used for electron scavenging) is fed to the reactor (Equations 1.3). The reactive form of oxygen produced may react with hydrogen ion to form hydro-peroxyl radicals (Equation 1.4). These radicals have oxygen like scavenging property prolonging the life span of photoelectrons and result in the formation of hydroperoxide ions (Equation 1.5), which further react with hydrogen ions to generate hydrogen peroxide (Equation 1.6). The hydrogen peroxide accepts conduction band electrons forming hydroxyl radicals and hydroxide ions (Equation 1.7). The positively charged holes (h^+) oxidize adsorbed water on the catalyst surface to produce hydrogen ions and hydroxyl radicals (Equations 1.8). Hydroxyl radicals can also be formed from the reaction between holes and adsorbed hydroxide ions (Equation 1.9). There is also the possibility of direct hole/organic species oxidation (Equation 1.10) resulting in the pollutant decomposition. For an aqueous photocatalytic system, water is used in excess compared to the degraded organic pollutant species. This helps for the formation of the hydroxyl radicals, which are used in the oxidation of organic compounds (Equation 1.11 - 1.12).

1.6 CATALYST: TITANIUM DIOXIDE (TiO_2)

Photo-catalytic oxidation is an innovative technique that is suitable for removing un-compromising organic compounds found in the grey-water. Titanium dioxide (TiO_2) gained undivided attention because of its biological and chemical inertness during the photo-catalitical oxidation of organic-matter present in waste-water. It does not require any additional chemicals to restrain itself from chemical-corrosion and to work at high temperature and pressure. Radiation produced from diffusion of titanium dioxide by UV (300-400) light creates highly reactive hydroxyl radicals. Thus attacking on pollutant molecules degrading them into CO_2, water and mineral-acids. This technique holds various advantages, such as integration at smaller locations, less maintenance costs and easy operation.

Titanium-dioxide (TiO_2) is described as a white colored inorganic solid substance (also known as Titania) that is highly thermally stable, insoluble in water, chemically inert, in-flammable and not categorized as a hazardous substance according Globally Harmonized System of Classification and labelling of Chemicals by United Nations. TiO_2 is widely used in industrial applications such as catalyst support (N-Type semi - conductor), dye-sensitized photo electrochemical solar cell, in consumer goods (paints, coatings, printing inks, cosmetics, ceramics, textiles etc.) and also in the pharmaceuticals sector. In addition to these TiO_2 continues to receive much attention from researchers for its application as a photo-catalyst.

As a family member of transition metal-oxides, it consists of 2p orbitals of O^{2-} in valency band along with the 3d orbitals of Ti in conduction-band. Titanium-dioxide, is the ninth most commonly available element present on earth, and is generally found in a variety of rocks and mineral-sands. TiO_2 exist in nature in any one of the four crystalline forms; anatase, brookite, rutile and the monoclinic TiO_2 (B). In addition to these common polymorphs, under high pressure two-forms have been made starting from rutile- TiO_2 (II), which has PbO_2structure and TiO_2 with hollandite structure. In TiO_2 (from now referring only to anatase, brookite and rutile), titanium (Ti^{+4}) ions are bonded to six oxygen (O^{2-}) ions forming a TiO_6 octahedron. Due to the difference in the arrangement of the octahedral units, and by the assembly patterns of the octahedral-chains the three crystalline forms differ in their crystal structure.

Anatase has a tetrahedral structure in which the octahedral units share their vertices (corners). Brookite belongs to orthorhombic crystal system in which both the vertices and edges are shared by the octahedral units while in rutile the octahedral share edges to give a tetrahedral structure. In the anatase phase the distortion of TiO_6 octahedron is slightly larger in comparison to rutile phase. Also, the Ti to Ti distances in anatase form for TiO_2 are larger compared to distance in rutile thermodynamically, rutile is the stable form of TiO_2 and under heat treatment (600-700°C) anatase and brookite phases can be transformed to rutile phase.

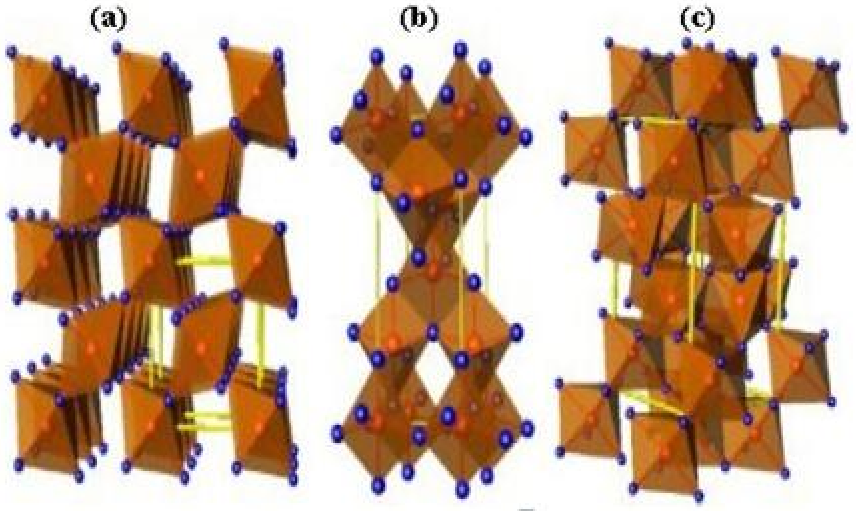


Fig : 1.1 Crystal structures of TiO_2 crystalline forms, (a) rutile, (b) anatase and (c) brookite; Ti_4+ (red spheres), O_2- (blue spheres) and yellow lines represent the unit [4].

Photocatalytic activity of TiO_2 is a function of its physical properties, for example, the larger surface area of TiO_2 increases photo-catalytic reaction rates due to the greater-concentration of active sites in the periphery of the unit area; however, due to the presence of large amounts of crystalline defects, leading to poor performance in large surface area, usually in photoactivity, the surface of the electron hole is prone to recombination.

Amorphous TiO_2has negligible photocatalytic activity which indicates that crystallization is also an important requirement; Therefore, the balance between surface area and crystallinity is necessary for producing an effective photocatalyst. Particle size is also an important parameter that directly affects photochemical activity because recombination is dependent on the type (surface or volume recombination) and spectral shift (UV and visible) particle size. Similarly, photocatalytic activity of TiO_2 is also dependent on the surface hydroxyl groups because the hydroxyl group can cause the photo-generated holes to produce hydroxyl radicals, in which the strong oxidation power to degrade organic pollutant molecules is present.

The choice of crystal structure (anatase, rutile and brookite) and phase composition, as discussed earlier, also play an important role to predict TiO_2photocatalytic activity. In addition, catalyst surface adsorption desorption characteristics is also essential in defining the TiO_2 activity, because photocatalysis is mainly a surface phenomenon.

In conclusion, an optimized combination of the physicochemical properties of TiO_2 may be necessary to produce an efficient photocatalyst for the enhanced decomposition of organic compounds.

Photocatalytic reactions are initiated when a semiconductor catalyst is illuminated by light with energy equal to or larger than the semi-conductor band-gap energy ($h\nu \geq \Delta Eg$). The photons promote an electron from the filled valance band of the semiconductor photocatalyst to the conduction-band leaving behind a hole in the valance-band (Fig. 1.2).

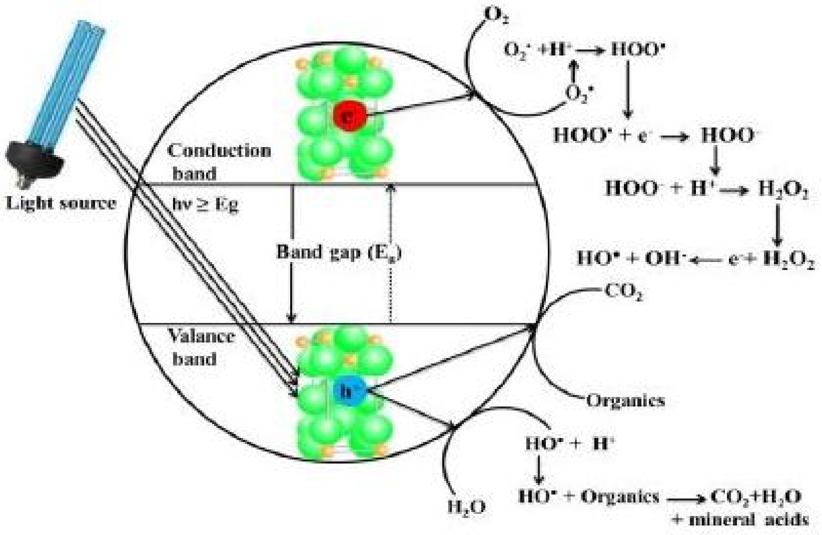


Fig 1.2: Photocatalysis mechanism [7].

Photocatalysis mechanism: On absorption of Ultraviolet-UV radiations from sun-light or illuminated light source (such as fluorescent-lamps), titanium-dioxide (TiO_2) produce conduction of electrons from conduction band to valency band. This produces extra electrons in valency band and holes in conduction band which occurs with an energy known as 'photoexcitation'. The transfer of electrons from conduction band of titanium-dioxide leads to the creation of a pair of negative-electron (e-) and positive-hole (h+). The "Band-Gap" in semi conductor such as TiO_2 requires a minimum wavelength of 388 nm of light from the band gap energy of 3.2 eV and using Plank's constant (h) as 1240.

Table 1.1: Band-gap energies of semi-conductor photo-catalytic materials [7].

Photo-catalyst	Band-gap (eV)	Photo-catalyst	Band-gap (eV)
TiO_2-(rutile)	3.02	V_2O_5	2.70
TiO_2-(anatase)	3.23	SiC	3.00
Fe_2O_3	3.10	α-Fe_2O_3	1.20
CdS	2.58	SnO_2	3.50
SnO_2	3.50	ZnS	3.70
WO_3	2.76	ZnO	3.20
CdSe	1.70	PbS	0.29
$SrTiO_3$	3.40	ZrO_2	3.87

Photocatalytic Oxidation

$$\text{Photocatalyst } (TiO_2) \xrightarrow{hv} e^- + p^+ \quad (1.13)$$

$$e^- + O_2 \longrightarrow O_2^- \quad (1.14)$$

$$p^+ + \text{Organic} \longrightarrow CO_2 \quad (1.15)$$

$$p+ + H_2O \longrightarrow HO^\cdot + H^+ \quad (1.16)$$

$$HO^\cdot + \text{Organic} \longrightarrow CO_2 \quad (1.17)$$

1.7 EFFECT OF H_2O_2 ADDITION

The addition of H_2O_2 in the photo-catalytic experiments to improve the degradation rate is now a well-known procedure. H_2O_2 plays a important role in the photo-catalytic oxidation as it results in the generation of OH· radical by accepting a photon-excited electron from semiconductor's conduction band.

1.8 FIXED-BED BIOREACTORS

The primary treatment involves removal of suspended particles from grey water by physical methods such as screening and sedimentation. Furthre more for better removal efficiency secondary greywater treatment is also employed. Dissolved carbon (C) and nitrogen (N) is removed by degradation by micro - organisms. In order to enhance the degradation of greywater, removal of phosphorus-containing components by micro-organisms is used as a tertiary treatment. Thereby enabling usage of biological treatment processes in secondary and tertiary phases of greywater treatment.

Two important types of bio-reactors used in organic waste-water treatment are active sludge process and fixed bed reactors. Micro-organisms are suspended in the liquid when conventional active sludge treatment is performed. Whenever fixation of microorganism is carried out on a stable support as in case of stable bed bioreactors, they are referred to as 'trickling filters'. Since many decades trickling filters have been the ancient form of fixed-bed bioreactors (Tchobanoglous and Schroeder-1985). But it has only been in the last few decades that fixedbed reactors have gained interest due to their small reactor size, high expulsion efficiency, less odor annoyance and strong hydraulic changes and inclined toxic shocks. Filtration of suspended-particles has been yet another distinct characteristic which makes the unit to operate without the down-stream cleaver, which constitutes the internal part of the active sludge process.

Fixed bed bio-reactors are usually operated with continuous flow available in feed concentration. Thus, biomass available in the reactor is not adjusted according to the different treatment capacity. Operating conditions are many times chosen very conservatively to not violate the quality demands on reactor outlets for the critical position. During this the inflow is tretaed to be dominant factor in optimizing the efficiency of a fixed bed bearing treatment.

It is practically impossible to operate this unit continuously, as bio-film development reduces the amount of reactor available for liquid and air flow thus, ultimately, stops the filter. Therefore, the operation has to be stopped, before clogging and the reactor is backwards. In practice, it is routinely backed up, i.e., every 24-or-48 hours based on setup. Therefore, due to the increasing bio film thickness of this process there is no stable condition which reduces the bed zero degree and thus, the flow of fluid and gas affects both the flow velocity.

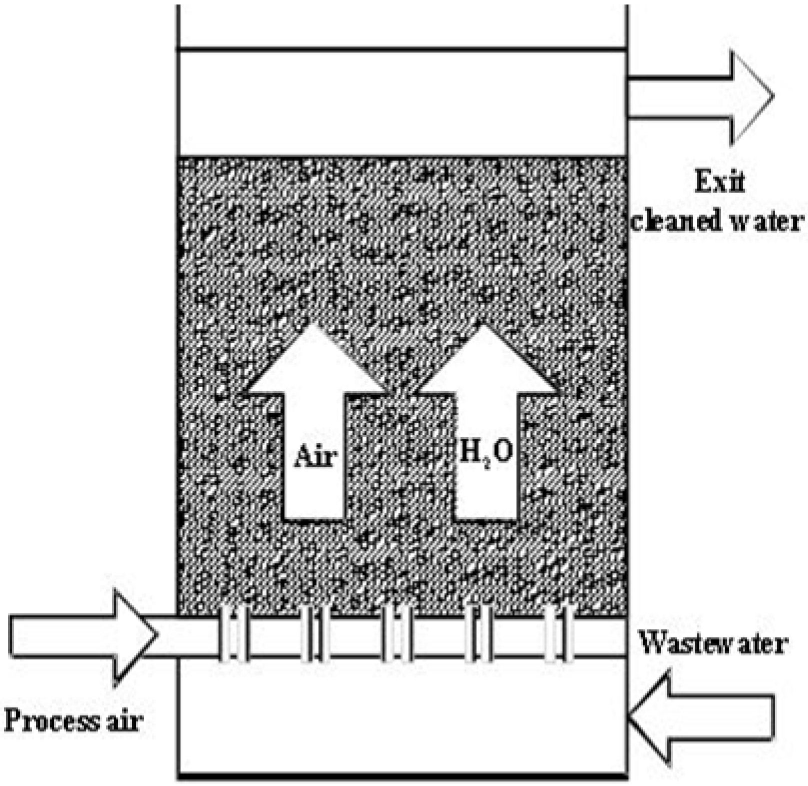


Fig: 1.3: Fixed – bed bioreactor [2].

Aerobic Fixed Bed is considered to be a very simple microscopic model of bioreactor, because in reference to marking the optimum strategy for bioreactors, such significant model is considered enough. The process-variables of interest are:

(i) The concentration of the substrate available in the waste-water

(ii) The immobilized bio-mass concentration.

Fixed-bed reactors better than Activated sludge because of its smaller reactor size, reduced odour annoyance, higher removal efficiency, and robustness towards toxic shocks in the inlet concentration and hydrodynamic variations.

1.9FENTON METHOD

The bio refractory nature of many never-ending organic pollutants has resulted in efforts to redesign chemical and physical methods of degrading organic pollutants found in waste water sources or in contaminated sites including soils, sediments, and groundwater.

Fenton reagents were first recognized in the year 1876 with Fenton-reagent (Fe^{3+} + H_2O_2) being reported by many researchers as an active reagent for degradation of organic dominant pollutants. The fenton-reagent primary transforms a huge variety of pollutants into stable bio-degradable products (Fig.1.4). Though it is inexpensive and readily accessible, generation of high amount of heat under aggressive conditions makes it difficulty in application for subsurface treatment.

Although Fenton did not explain the mechanism of the reaction named after him, its basic procedure was reported by various researchers as:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^{\cdot} + OH^{-}$$
(1.18)

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^{+} + HO_2^{\cdot}$$
(1.19)

$$Fe^{3+} + HO_2^{\cdot} \longrightarrow Fe^{2+} + H^{+} + O_2$$
(1.20)

$$Fe^{2+} + HO_2 \cong 6Fe^{3+} + HO_2^{-}$$
(1.21)

$$Fe^{2+} + \text{hydroxyl ion} \longrightarrow Fe^{3+} + HO^{-}$$

(1.22)

$$H_2O_2 + \text{hydroxyl ion} \longrightarrow H_2O + HO_2^{\cdot}$$

(1.23)

1.10 PHOTO–FENTON METHOD

An increase in the reaction rate of fenton process was observed under the effect of light which produced increased hydroxyl-radical. In the following reaction as shown between Eq. (1.24) to Eq. (1.26), it can be seen that pollutant-degradation under photo effect than dark Fenton-systems is more effective due to irradiation of iron-peroxide solutions.

$H2O2 + h\nu \longrightarrow 2HO^{\cdot}$

(1.24)

$Fe(OH)^{2+} + h\nu \longrightarrow Fe^{2+} + HO^{\cdot}$

(1.25)

$Fe^{3+}(C^{-}) + h\nu \longrightarrow Fe^{2+} + C^{\cdot}$

(1.26)

Where, C is an organic compound.

The concentration of Fe^{2+}marks as a key factor in determining the rate of hydroxyl-radical formation produced from hydrogen peroxide.

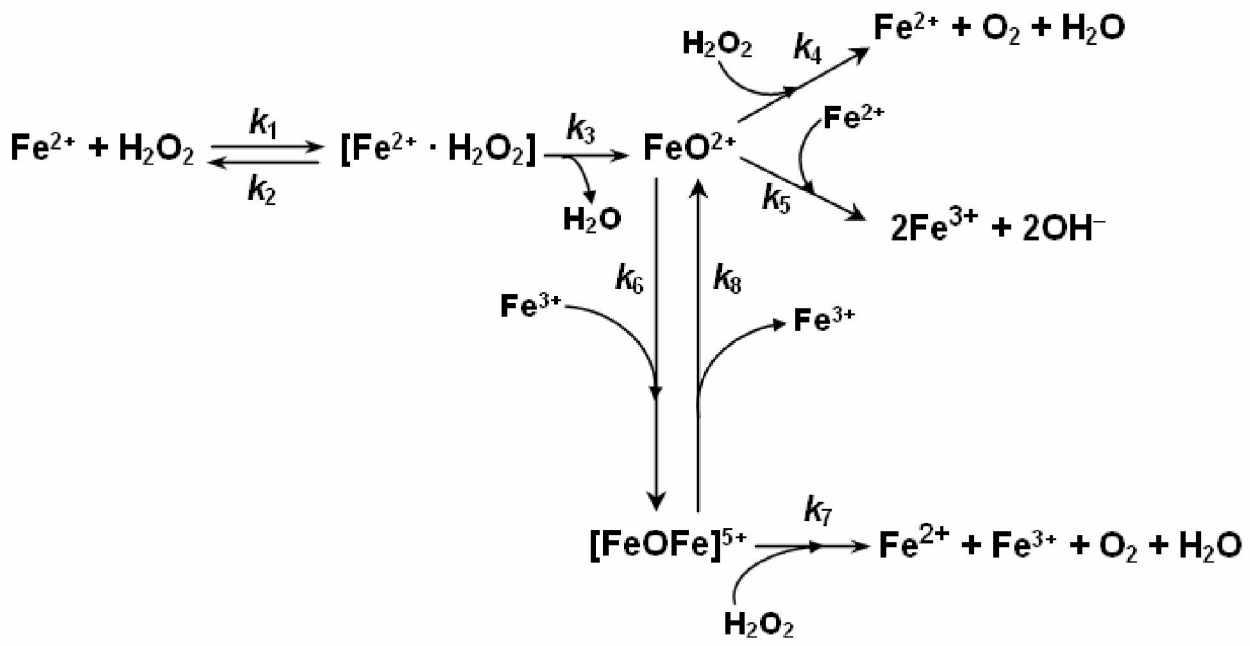


Fig. 1.4 Mechanism of Fenton process

Consequently, any process speeding up the reduction of Fe^{3+} to Fe^{2+}increases the formation rate of hydroxyl radical. However, additional mechanism is involved in the degradation of pollutant:

(i) Direct photolysis of H_2O_2 yields two hydroxyl-radicals

(ii) Fe $(OH)^{2+}$ is also photocatalyzed to form additional hydroxyl ions

(iii) Direct photolysis leads to absorption of a photon (γ) by the contaminant. This causes the excited contaminant molecule to degrade.

(iv) The process of Photo Fenton has been used for significant degradation of Chlorophenoxy herbicide, metolachlor and methyl parathion polychlorinated dibenzo-p-dioxins and dibenzofurans. The degradation process has shown substantial increase under the effect of UV radiations.

1.11 ORGANIZATION OF THESIS

Chapter 2 deals with the review of literature carried out for identifying the gaps prevailing in the present area of research. Reported literature from various source on experimental and analytical work based on grey-water degradation using UV. H_2O_2 photo catalysis and photo Fenton process.

Chapter 3 deals with the experimental methodology adopted for studying the grey water degradation. It comprise of elaborative description of material used phases of testing used along with the sampling testing details.

Chapter 4 highlights the testing results obtained for four different phases of reactor operation with discussion of significant results.

Chapter 5 brings forth the critical conclusions that are drawn from the reactor and sample testing result of grey water degradation.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

A comprehensive review of different literatures based on photocatalytic oxidation process, photofenton process and other degradation techniques using UV, H_2O_2 are included in this chapter. This chapter discuss the important outcomes of different studies made by various researchers for degradation of wastewater and greywater. The chapter also outlines the summary and gaps identified from published literature. The chapter ends with the objectives for the present study defined based on the gaps from literature.

2.2 ADVANCE OXIDATION PROCESSES

2.2.1 UV radiation and photocatalyst: Titanium dioxide (TiO_2)

Thiruvenkatachari, R[8] investigated the treatment of waste water using an advanced oxidation process which comprised of UV lights with Titanium Dioxide (TiO_2) as the photo-catalyst. UV-TiO_2 photo-catalytic study was conducted by the author with a view that degradation of organic compounds in waste water can be carried out because of complete mineralization of organic substances in presence of temperature and pressure. The authors made an attempt to comprehend into the mechanism oxidation process through studying the effectiveness of TiO_2 application in the form of catalyst, with a radiation source, with different types of reactors.

They also investigated the behaviour of catalyst as immobilized material on the photo-catalytic hybrid membrane system and surface. From their study, it was found that endocrine blockers (organic substances) can be effectively degraded using photo-catalysis along with TiO_2. The experimental results also reflected to the fact that Titanium Dioxide - suspended solution reactor provides a better efficiency in waste water treatment due to simplicity and increased aperture. However, suspended TiO_2 was required to be isolated with water even after photo-catalytic process. In order to remove the suspended TiO_2 in treated water, the authors studied the use of membrane hybrid system. The membrane hybrid system comprised of a two-stage process involving combination of coagulation and sedimentation processes. With this microfiltration hollow-fibre membrane process, it was observed that TiO_2 was completely removed from treated waste water (Fig. 2.1). The micro – filtration membrane set – up consisted of a feed vessel with a magnetic stirrer and pH electrode in an Acid (or base) solution. The solution was pumped using a peristaltic pump using a blocking valve. The instrumentation consisted of pH meter, pH controller, Frequency inverter, Flow meter, pressure gauge. A filter module was also placed between top water and permeates return line. It was also reported that retrieved TiO_2 from micro – filtration process can further be used for photo-catalytic process.

However, for using slurries in a photo-catalytic wastewater treatment system, it is essential to treat the wastewater even after removal of catalyst particles. In order to achieve this TiO_2 particles are separated from suspension through physical chemical processes such as filtration, coagulation and centrifugation. Since TiO_2 powders are fine material having an average approximate particle size of 21microns, but in the form of aqueous media, they tend to create aggregates within larger micron range. Hence, **Molinari et al. [45]** suggested the use of micro-filtration porous membrane for its dissociation.

Shi and Geisen [46], further studied the use of membrane reactors for separating TiO_2 used in Suspension. During the reactor performance it was observed that placing the membrane inside the photoreceptor was leading to damage of membrane. This membrane damage was accounted for oxidation of the membrane. Moreover, it was also reported that oxidation of membrane also reduced the depth UV light entry, due to the strong absorption and dissolution of organic species by TiO_2 under UV radiation lamps kept outside the reactor. Thus, it was interpreted that photocatalyitc process can result in significant decline in permeate flux due to inefficient membrane activity during TiO_2 particle isolation.

Furthermore, formation of dense cake like layers over the membrane surface can also result in deterioration of membrane and flux arising from incomplete degradation of organic matter in a photoreactor. This can be accounted for interaction between residual organic matter and TiO_2 photocatalyst. It is discovered that TiO_2 particles covered with organic matter offer four times more cake resistance with compression than uncovered TiO_2 particles alone.

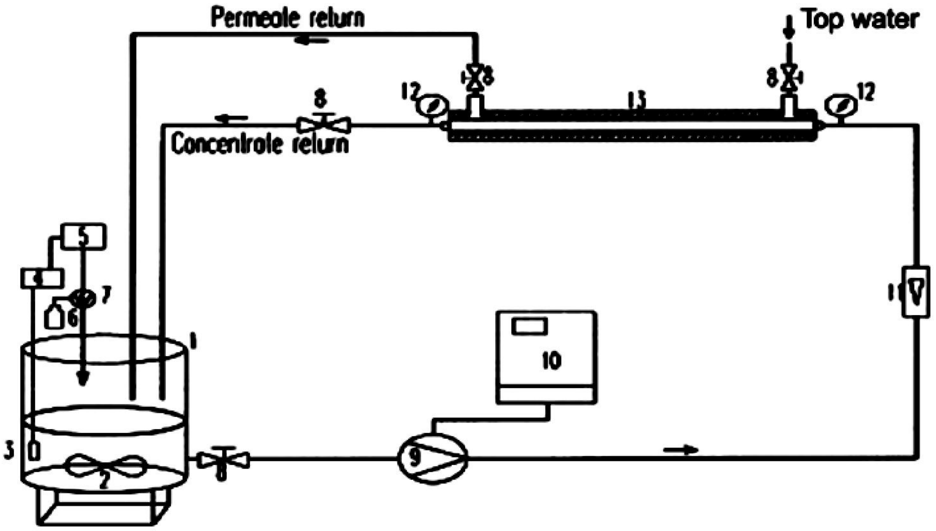


Fig: 2.1 TiO_2 separation using cross flow microfiltration membrane [8].

In order to minimize the fall of membrane, processes of coagulation and sedimentation are introduced between photochemical oxidation and membrane separation (Fig. 2.2). During the final stage submerged hollow fibre micro - filtration membrane (PVDF, 0.2 μm) was used to achieve reusable quality water.

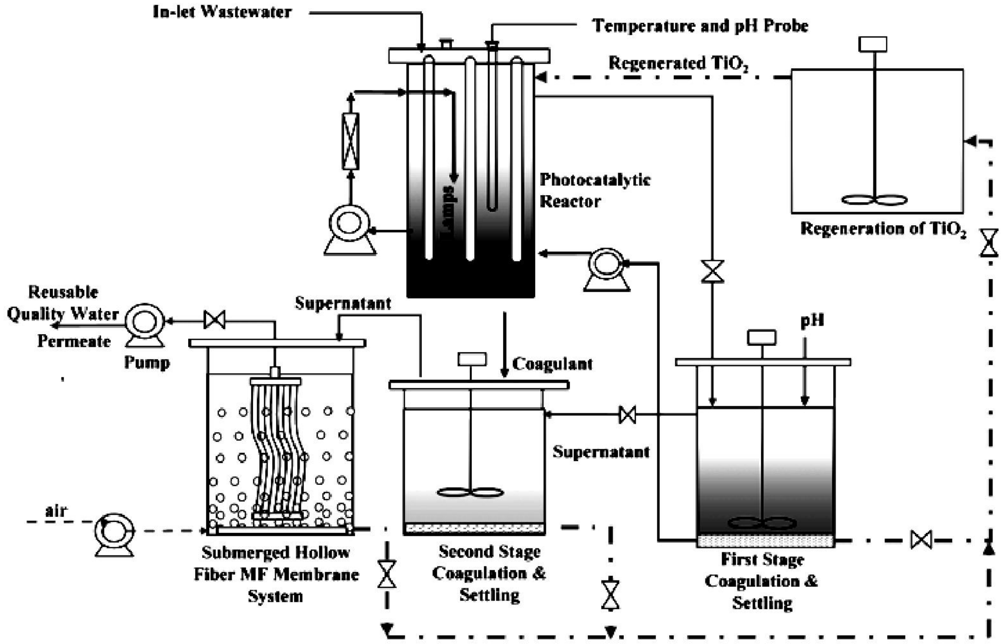


Fig: 2.2 Schematic of photo-catalytic membrane hybrid system [8].

2.2.2 Fenton, photo-fenton and UVC / H_2O_2

Chin, W. H. (2009) [12] studied the degradation of grey-water so as to seek a solution for water scarcity and provide freshwater for non-potable purposes. The author discovered that though grey-water do not includes wastewater from toilets or industrial wastewater, its reuse requires sufficient treatment prior to be used for garden irrigation and toilet flushing. It was observed that drinking water and waste water were being treated using advanced oxidation procedures (AOPs), however, in scenario of application for greywater treatment, only photocatalysis with UV / TiO_2 was utilized. Therefore, with the purpose of searching new advance oxidation processes, the authors investigated Fenton, Photo-Fenton and UVC / H_2O_2 processes for treatment of greywater. Raw Greywater was mixed with alum and ferrous sulphate coagulation and their supernatants were then treated with H_2O_2 under UV lights (Fig. 3).

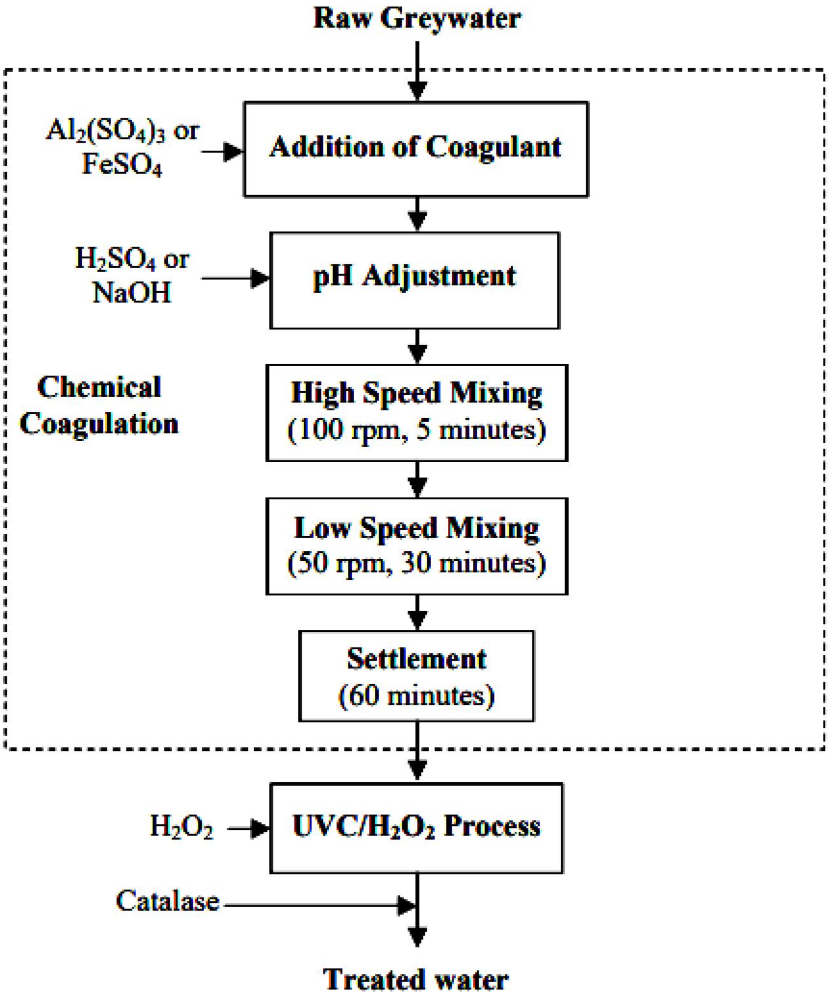


Fig. 2.3 Flowchart for sequential coagulation and UVC/H_2O_2 treatment [12].

The authors investigated the influence of pre-treatments with parameters such as pH, reagents dosage, reaction time, contaminant concentration and different type of greywater . The effect of the above listed parameters was studied with reference to the removal of chemical oxygen demand (COD). The variation of parameters with type of treatment such as physical separation and chemical oxidation was also reported. The authors found that with complexity in operation due to sludge formation, the required pH condition has to be maintained inorder to achieve a visual aesthetic of effluent. It was reported by the authors that alum coagulation removed about 73% COD in raw Greywater. With ferrous sulphate coagulation was achieved. Moreover, Fenton process removed 45% COD in comparison to Photo-Fenton process which yielded COD removal of 83%. Furthermore, with overnight disposal and later UVC with H_2O_2 treatment, COD removal efficiency was found to increase to 87%. A COD removal efficiency of 98% and 91% respectively, was also reported with alum and ferrous sulphate as sequential coagulation along with UVC / H_2O_2 treatment.

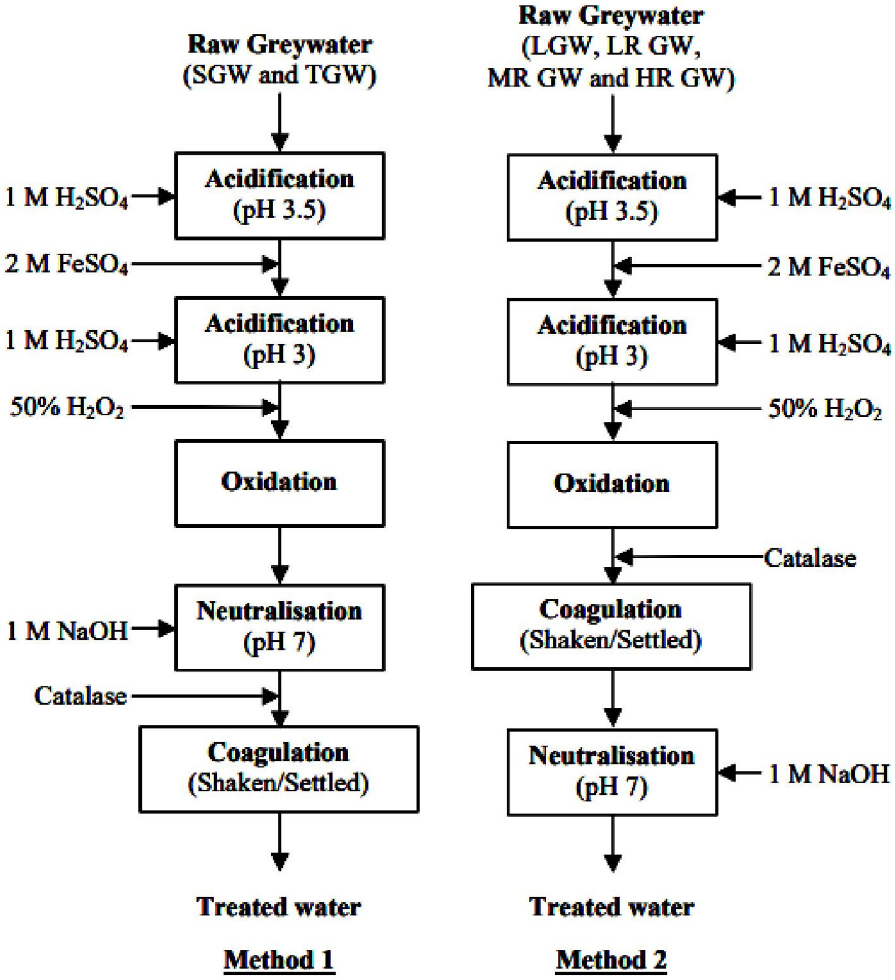


Fig: 2.4 Flowchart for Fenton and Photo-Fenton processes [12].

In order to study Fenton and Photo-Fenton processes two procedures were developed at different Fe^{2+}:H_2O_2 and H_2O_2: COD ratios. The first process included treatment of raw Greywater from bathroom in the form of 'Shower Greywater' and 'Teeth – brushing greywater' while the second process utilized raw greywater obtained from laundry in the form of Low-range Greywater (LR GW), Mid-range Greywater (MR GW) and High-range greywater (HR GW) (Fig. 2.4).

The UVC with H_2O_2 treatment phase for Greywater degradation involved investigation of pre-treatment parameters such as dosage of H_2O_2, pH, COD and overnight disposal of Greywater. For comprehending the effect of a overnight disposal, greywater was left in a tank for an entire night. It was observed that lint, hair and large particles settled out during this phase. The sample testing comprised of studying pH and COD material of greywater before and after the overnight disposal. Alternatively, pH of stored Greywater was adjusted with 1 Molarity of sulphuric acid or 1 Molarity of sodium hydroxide prior to its treatment under UVC / H_2O_2. A batch mode was employed for Greywater treatment under UVC / H_2O_2 with a quartz sleeve photo – reactor having capacity of 500 mL and 50% H_2O_2 solution. Moist CO_2 was fed with free air into the reactor under simultaneous irradiation from UVC lamps. Once the pre – determined radiation time and catalyst action over the 500 mL sample was completed, sampling was carried out and all sample were thoroughly shaken. As the residual H_2O_2 was found to fall below 2 mg/L, analysis was carried out.

2.2.3 Titanium dioxide (TiO_2) as a model photo-catalyst

With attributes of chemical stability combined with environmental friendly and cost effective behaviour, Titanium dioxide (TiO_2) serves as an ideal photo-catalyst. However, its high band gap of 3.2 eV limits its usage of sunlight radiation to only 4% of incident photons. Hence, its application is strictly limited to serve in Ultra violet (UV) environment. In order to increase its usage in conventional visible light spectrum, researcher have found analternative technique of coating/doping TiO_2 semiconductors with other lower band gap semiconductors, transition metals and non-metal ions. One such study was undertaken by **Schmidt, M (2007) [41]**, to investigate the synthesis of a photo-catalyst performing significantly under visible range with substantial photo-catalitical properties. To achieve this, the authors studied the effects of thermal and thermo - chemical ammonia treatment of nano-participatic TiO_2.

Pure commercial Nano-Participated TiO_2 Powder (Degussa P-25) with untreated TiO_2 as baseline was used to check the effects of thermal and thermo - chemical treatments. The performance of treated thermochemical TiO_2 was detected with temperature variations, time and gas flow rate. It was found that an easy and inexpensive method to alter the photocatalystic performance of Degussa P-25 TiO_2 can be achieved by modifying it with nitrogen, thus enabling TiO_2 the ability to create an efficient and better performing photocatalyst in view-light. The authors evaluated the temperature effects and variation of duration of treatment on thermally treated TiO_2 when subjected to cooling in dry root nitrogen (N_2) environment. It was observed that photocatalytic effects on untreated Degussa P-25 TiO_2 enhances with TiO_2 Simulated Solar Spectrum (SSS) at 375°C. TiO_2 (SSS) depicted a high photocatalytic efficiency which was almost twice that by Degussa P-25 TiO_2.

Titanium dioxide (TiO_2) has a high band gap with electrons in form of N-type semiconductors. Due to this high band gap, the absorbance of photons from solar radiation are limited to only 4%. The primary importance of TiO_2 to be utilized as photocatylst lies in its ability to oxidize large quantities of organic compounds. The oxidation of organic compounds primarily involves degradation into carbon dioxide (CO_2) and water (H_2O) molecule under ultraviolet light and possible solar light. The catalyst TiO_2 is photo-active within the band's interval. The transfer of electron between conduction band and valency band yields H^+/H_2 ions with reduction capacity and O_2 / H_2O with oxidation capacity. Thus, conductivity and validity band of TiO_2 always remains in an energetically favorable condition. This enables TiO_2 to reduce and oxidize any species of organic compounds, toxic materials or pollutants absorbed on its surface or in contact. This signifies that TiO_2 degrades the pollutant through oxidization and simultaneously disintegrates water molecules to make hydrogen gas by reduction potential. The reducing potential of TiO_2 for splitting H_2O into H_2 is significantly high and is equal to 21, which is of significant importance.

2.2.4 Photocatalytic degradation using nano – crystalline TiO_2

Mukhlish, M. Z. B (2012) [40] studied the photo-catalytic degradation of textile pigments; methylene blue (MB) and congo red (CR) using UV – V spectroscopy technique. To achieve this, the authors developed a synthetic TiO_2 using a one step sol-gel method. The method yielded a nano – crystalline TiO_2. The characterization of synthetic TiO_2 was carried out using SEM, XRD and EDS. Similarly, yield of synthetic TiO_2 was also detected by conducting a study on commercially available TiO_2. From the experimental results, it was revealed that synthetic TiO_2 demonstrated less photocatalytic activity as compared to commercial TiO_2. However, synthetic TiO_2 was reported to be more efficient in degradation of MB and CR. The experimental data was also found to fit for first order Frendlich Model. Based on the photocatalytic performance, it was confirmed that the sol-gel method is an efficient method for production of anatase TiO_2 nano-particle. The authors reported that catalyst's calculation also effect the decolourization and degradation efficiency.

Another study employing photocatalysis with nano-crystalline titanium dioxide (NTO) was conducted by **Lazar, M. A. (2012) [23]**. It has been observed that for an environmental friendly treatment process, the best known AOP has often resulted in Photocatalytic waste water treatment using nano-crystalline titanium dioxide (NTO). The mechanism of generation of electron-hole pairs with irradiation, pollutant degradation by the NTO is found to follow Langmuir-Hinselwood kinetics. Inorder to further strengthen the present knowledge in this field, the kinetics is required to be significantly accompanied by appropriate experimental evidences. Previous researchers are found to have reported an increase in photocatalytic efficiency with various NTO morphology or surface treatment. It has also been reported that reduction in energy consumption and minimization of post – separation steps can be done with improved designed photocatalytic reactors for water treatment processes. Moreover, combining NTO with other treatment processes on large scale is found to serve best. One such method is NTO doping with metals or non-metals. The doping reduces the band gap of the catalyst thereby enabling light absorption from visible area. Synthesis of various NTO morphologies has depicted effective improvement in photocatalytic erosion of different compounds. However, for further enhancing catalytic performance, NTOs can be superficially treated [23].

More energy – efficient rotating the disk-type reactor model, NTO-immobilized catalyst beds and Re-use of Post-Separation / NTO Powder Catalyst can be obtained by utilizing UV / visible light-emitting diode (LED) as light sources in lab reactors. It has been reported that LED-based photocatalytic reactors are found to be more energy-efficient systems. The coupled energy efficient reactors are found to have performed better in erosion of various colours (methyl orange, methylene blue, rhodiumine and malachain green) using combined UV-LEDs and NTO Powder or NTO nano - tube or fixed NTO. **Nickel et al. []** fabricated a UV-LED photoreactor with a micro circulating fluid pump for continuous mixing of reactive solution and in-stream sensor unit. For real time measurement of methyl orange dye concentration reduction, the authors used a sensor unit with an assembly of a fluid flow cell with transparent windows, an LED lamp and a photodiode monitor (Fig. 2.5). With wavelength varying between 450 to 600 mm, four strips of LEDs (i.e. white, green, blue and yellow) was used in the reactor. The visible light of Bisephanol was also found to be replaced by LEDs with carbon-nitrogen and co-doped NTOs. The authors also emphasized the feasibility of developed photoreactor based on its light weight, low production cost and flexibility in laboratory and field work applications.

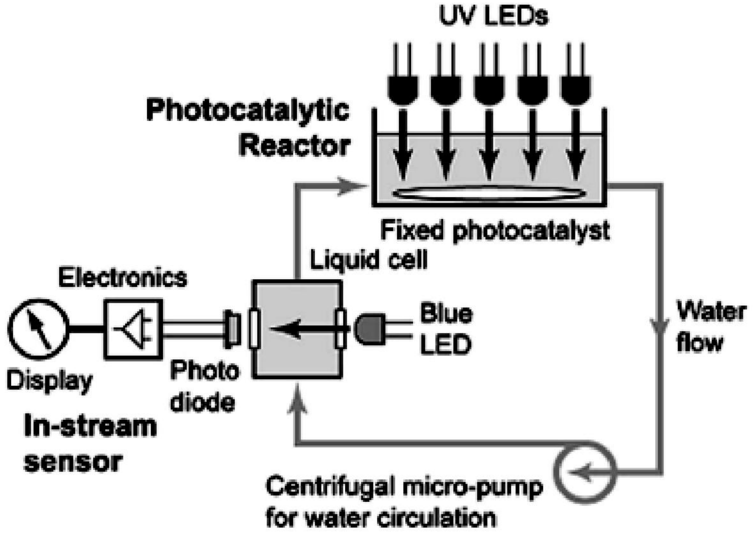


Fig: 2.5 Photocatalytic reactor with in – stream sensor [23].

2.2.5 Photocatalyst fluidized/fixed – bed reactors

Nogueira R. F. P. et al. [47] examined degradation of dichloroacetic acid (DCA) using a bench scale photocatalytic reactor with fixed (immobilized) catalyst as TiO_2 (Degussa P25). The catalyst was used on a glass plate and the various parameters such as flow rate, reactor geometry, plate slope and light intensity. The solar energy was used as the source of radiation (Fig. 2.6). It was found that degradation occurred linearly with solar light intensity. The degradation suggested that no mass transfer occurred in the system under one flow cycle and with recirculation. The degradation of DCA under 2 min of solar radiation was found to decrease from 5 mmol/L to 2 mmol/L and also led to production of chloride ions. With increase in flow rate the degradation was found to increase, achieving saturation at 1.5 mmol DCA/min.

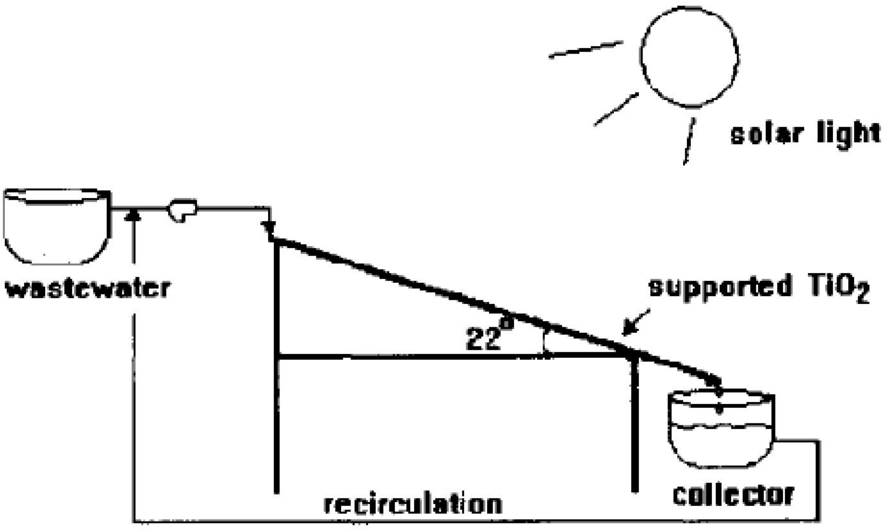


Fig: 2.6 Photocatalyst TiO_2 fixed – bed reactor **[47]**

The mineralization of Dichoroacetic acid showed enhanced degradation with solar light in clear sky condition varying from 20 to 30 W/m^2. However, it was found that degradation decreased under cloudy sky. With different flow rates and concentrations of DCA, it was found that no biomass transfer occur in the reactor. This is accounted to the thin fluid film over the catalyst. The degradation of DCA is found to bear an exponential decay but with limitation of low flow rate. The authors further suggested checking the feasibility of reactor performance with high flow rates of contaminated water and large working areas.

David, P. et al. [48] studied the optimization of treatment process using an aerobic fluidized bed reactor (AFBR) (Fig. 2.7). The treatment of Greywater obtained from washing machine was evaluated based on biodegradation kinetics emphasizing on residence time distribution (RTD) approach. The authors measured parameters such as dissolved organic carbon (DOC) and respirometry. No disfunction was reported by the authors based on RTD determination. It was observed that the performance of fluidized bed reactor was analogous to continuous stirred tank reactor. The authors also investigated a sensitivity study on operating conditions of DOC biodegradation and formulated a first order reaction [$C(t) = 0.593 \times C_0 \times e^{-kt}$] for degradation process occurring in the reactor.

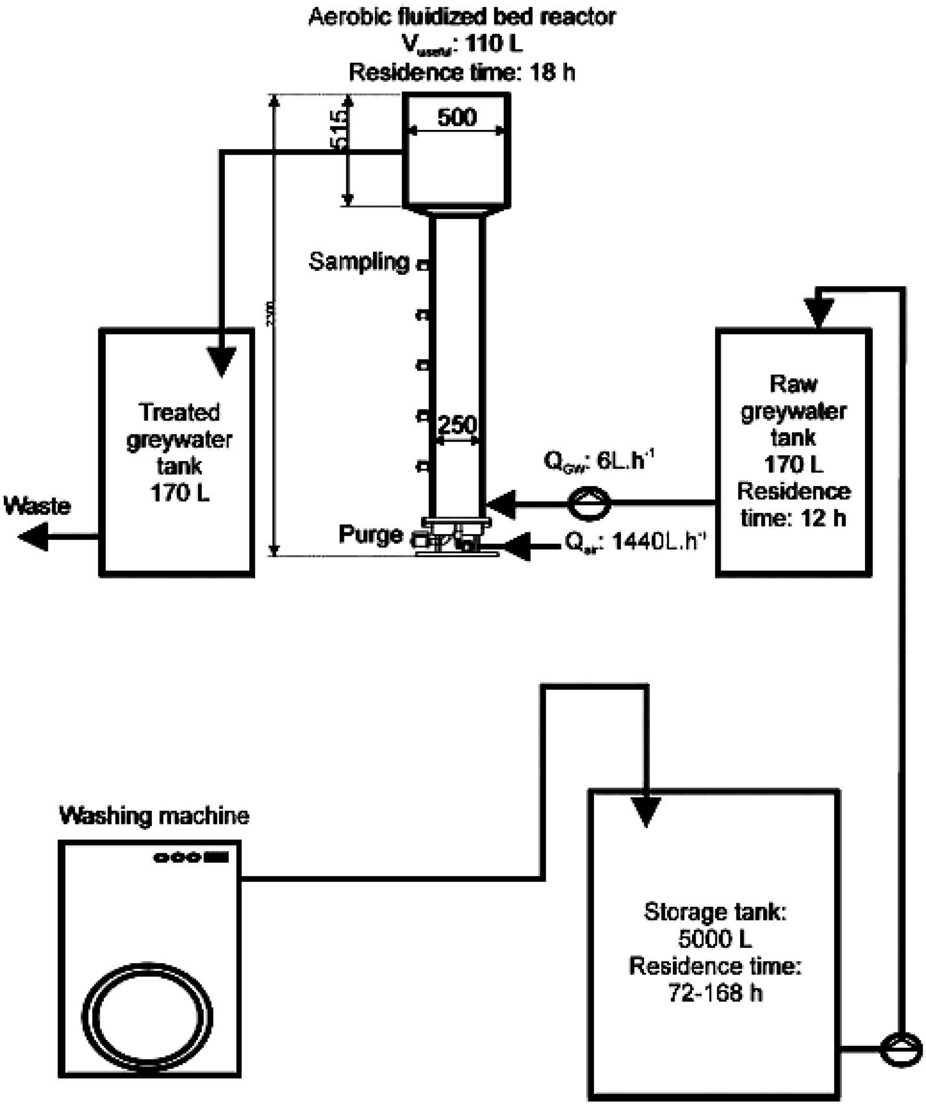


Fig: 2.7 Aerobic Fluidized Bed Reactor (AFBR) [48]

The study revealed that kinetic constant (*k*) is 0.011 per hour with biomass carrier (Fig. 2.8). The results also depicted a low carbon content of 15 mg/L. The study also suggested using analysing microbial parameters for ensuring safe reuse of green space irrigation.

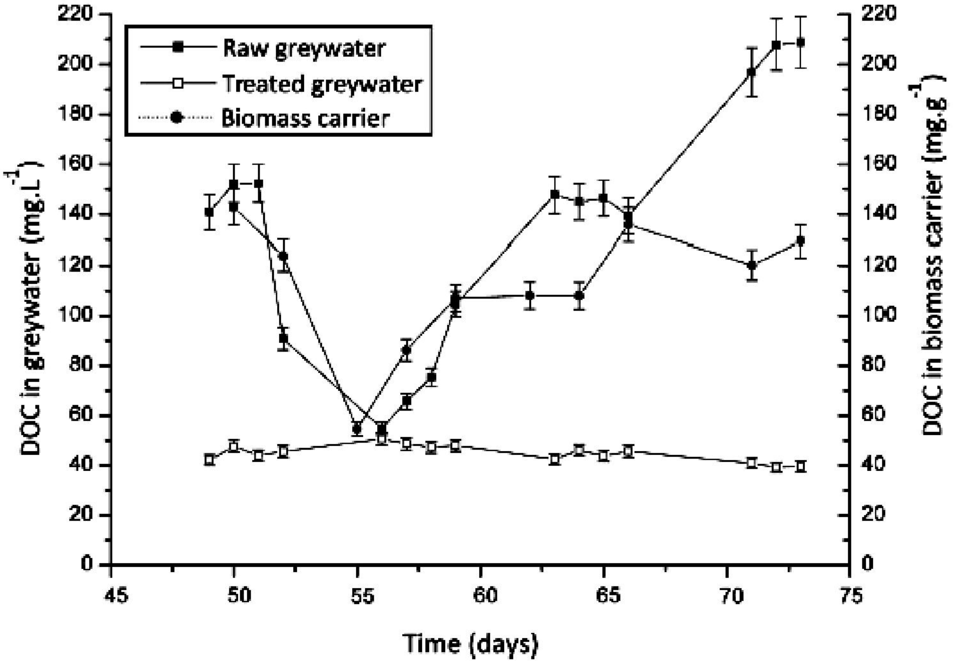


Fig: 2.8 Dissolved organic carbon variation with time for treated and untreated Greywater on biomass carrier.

Saran, S. et al. [49] achieved decentralized treatment of Greywater from girl's hostel of Pondicherry University using a slurry type tubular Ag- TiO_2 photocatalyst reactor. Using the local material, the fabrication of photoreactor was carried out as shown in Fig. 2.9. The coating of Ag over TiO_2 was done through photodeposition. The coating of Ag was found to act as an electron trap which enhanced the photocatalytic activity. With catalyst concentration of 200 ppm and optimum reactor concentration complete degradation of Greywater was achieved under 2 hours of reactor operation. The optimum condition included 5.0 mM of H_2O_2 and an initial pH of 2. The solar light intensity was maintained at 1.0 mW/cm^2 for a flow rate of 15L. The catalyst observed in effluent was filtered through filtration which could be reused for further catalytic activity.

It was reported that Greywater degradation increased twice with TiO_2 coated with Ag as compared to uncoated TiO_2. The COD of grewater was also found to subside with treatment. The addition of H_2O_2 further increased the abatement of COD. Under optimum condition. The slurry type reactor was found to deliver 99% decrease in COD within 2 hours of reactor operation. The reactor also performed satisfactorily for 5 cycles of greywater treatment depicted by absence of Ag in the effluent. However, the author recommended decentralized treatment of Greywater so as to make it portable water.

Fig: 2.9 Tubular Slurry type Ag – TiO_2 photoreactor [49]

Chong et al. [50] studied the removal of Reactive Black 5 (RB5) dye using a TiO_2 based photocatalytic treatment from synthetic greywater effluent as it caused serious aesthetic issues. It was observed that photoreactor (Fig. 2.10) with 0.1 g/L of TiO_2 and pH of 5 depicted 97% removal of RB5 dye. The removal effecieny was found to satisfactory even after 150 min, which however decreased to 76% after 330 min. The removal of oil and grease was found to be 60% with 54% removal of COD and 69% removal of BOD_5.

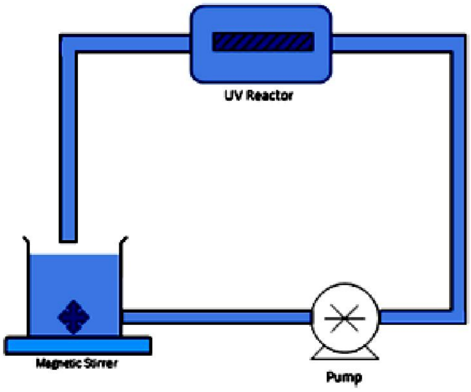


Fig: 2.10 UV reactors for removal of RB5 dye [50]

Tsoumachidou S. et al. [51] developed a Bench-scale slurry fountain photoreactor using a in a thermostated pyrex cell with a capacity of 0.5 L as shown in Fig. 2.11. The reaction vessel consisted of a centrally fitted blue UV-A lamp with specification of 9W/78, 350 e400 nm. The interaction with outside light was prohibited using a black cloth. The intensity of radiation from UV lamp was 1.232 x 10^{-4} E/min. Based on potassium ferrioxalate actinometry the radiation intensity of UV lamps was determined. Since limited mineralization was achieved using TiO_2, the reactor was fed with 0.5 g/L of H_2O_2. Within 210 min of treatment it was observed that 60% of synthetic Greywater was degraded.

Moreoever, 0.5 g/L addition of $S_2O_8^{-2}$ (salts of potassium or sodium) resulted in an increased removal of dissolved organic carbon. It was observed by the authors that as the catalyst concentration were increased to 1 g/L, mineralization was found to increase. However, beyond 1 g/L, the reaction rate was found to become independent of catalyst concentration. pH of 6.5 was reported to deliver the maximum mineralization of 65% which declined with increase in pH to 9. The degradation was found to drop to 32% removal of DOC. Moreover, with fenton based mineralization using 0.0035 g/L of Fe^{+3} in addition to 0..5 g/L of H_2O_2 and 0.5 g/L of TiO_2, higher degradation of DOC equal to 72% was achieved after 210 min. of treatment. The degradation was also found be effected by the illumination used. With UV based irradiation TiO_2 exhibited about 70% elimination of organic matter which was only 60% using solar light both under fenton environment.

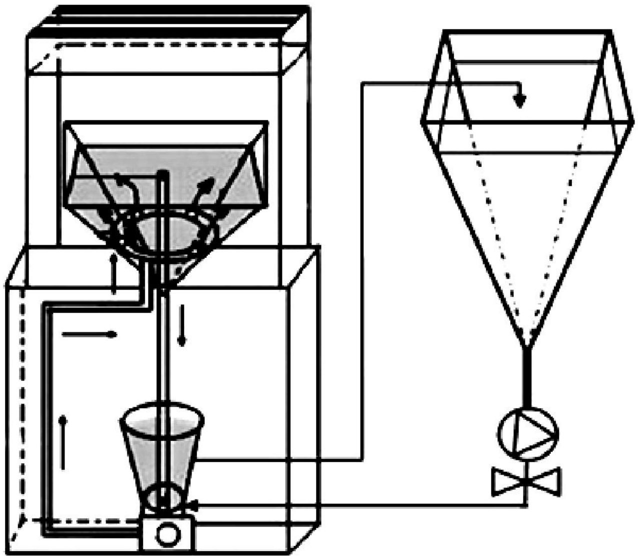


Fig. 2.11 Bench-scale slurry fountain photoreactor [51]

Evaluation of biodegradability of raw Greywater and synthetic Greywater was done using the following formula as given in Eq. (1):

$$\%\, BIODEGRADABILITY = \left[1 - \frac{(C_t - C_B)}{C_0 - C_{B0}}\right] \times 100 \tag{1}$$

Where: C_0 = DOC after 3h from start of test (mgC/L); C_t = DOC at time of sampling (mgC/L); C_B = DOC for blank sample (mgC/L); C_{B0} = DOC for blank sample after 3h from start of test (mgC/L). The raw Greywater and synthetic Greywater was found to be biodegraded to 70% after 10 days which reached its effective bio-degradability at around 7 days.

2.3 SUMMARY OF LITERATURE REVIEW

The review of literature clearly reflects the fact that Greywater can serve a best solution for prevailing water scarcity worldwide. The Greywater degradation is realized from the need of developing portable water which is free from contaminants primarily oil and grease and organic components. The use of Greywater for irrigation, gardening or washing is better off when carried out with treated Greywater as it will not only make environment friendly nut also pose less threat to human health.

From the literature review, it can be evaluated that past researchers have realized the degradation potential of TiO_2 as effective catalyst. It was further found that doped catalyst clearly enhances the mineralization of contaminants primarily organic matter in Greywater degradation. The solar intensity can further be increased by using UV irradiation. The photocatalytic reactor has shown sufficient efficiency in removal of DOC for mineralization of Greywater. The Greywater degradation has been studied using fluidized bed reactor. Hence a scope of studying using fixed bed reactor is realized. Moreover, this further enhances the possibility of utilizing an inert material for forming the fixed bed. The literature lacks in the usage of any waste material for forming the fixed bed. Thereby the present study suggests the use of copper slag as base material for forming the surface of catalyst. The optimization of TiO_2 and H_2O_2 reflected better mineralization efficiency and hence should be carefully maintained. The use of tubular geometry for photoreactor was also suggested for satisfactory performance of photoreactor.

Fenton process has been employed by past researchers for further increasing the greywater degradation. Researchers have employed individual process either photocatalysis or photofenton processes but no literature reveals the use of coupled photocatalysis and photo fenton process for Greywater degradation. Therefore, it forms another gap which should be investigated.

2.4 OBJECTIVES

Based on the literature review, following objectives for the present study are determined:

[1] To set-up of a lab – scale fixed – bed photoreactor.

[2] To assess the performance of photoreactor in Greywater degradation under coupled photocatalysis and photo - fenton process.

CHAPTER 3

METHODOLOGY

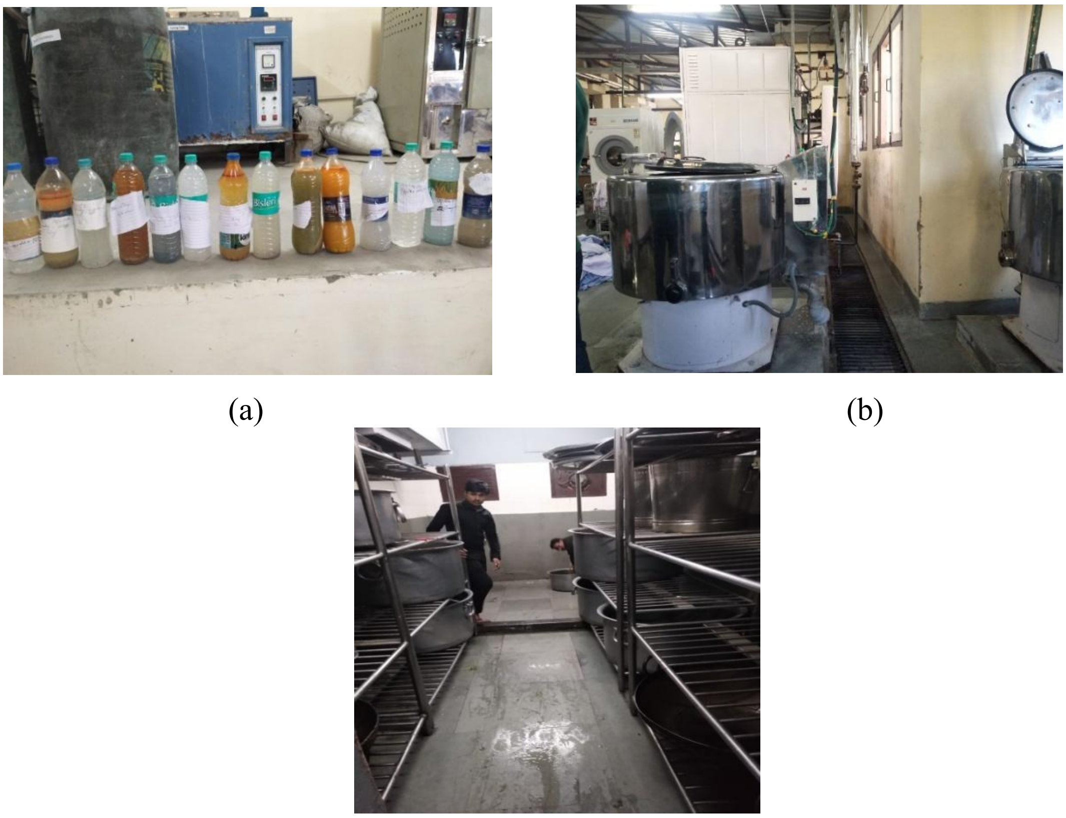
3.1 GENERAL

This Chapter discusses the material procurement process, which are used in making this experimental study. Sampling of greywater, fabrication of degradation reactor using various components, and formation of pellets etc is included in it. This chapter also discusses the experimental methodology/procedure performed for each experiment.

3.2 MATERIALS AND APPARATUS

3.2.1 Greywater

The sampling of greywater fro the present study is carried out from Laundry, Kitchen (Mess) and Hostel of Jaypee University of Information Technology, Waknaghat, Solan Himachal Pradesh, India (Fig. 3.1). The samples were collected weekly so as to form a sample of 30 L as given in Table 3.1.



(a) (b)

(c)

Fig: 3.1 Greywater collections: (a) Greywater collected from various source at Jaypee University (b) Greywater Source (Laundry Room) (c) Greywater Source (Kitchen Room).

3.2.2 Titanium dioxide (TiO_2)

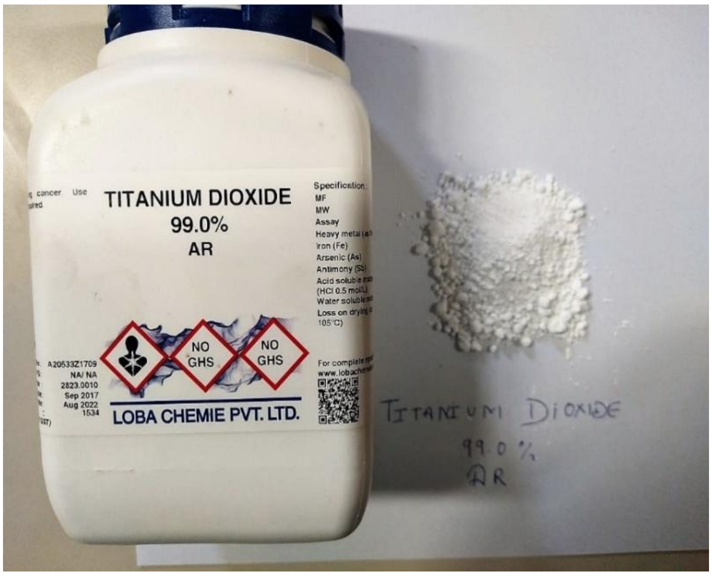


Fig: 3.2 Titanium dioxide (TiO_2)99.0% AR

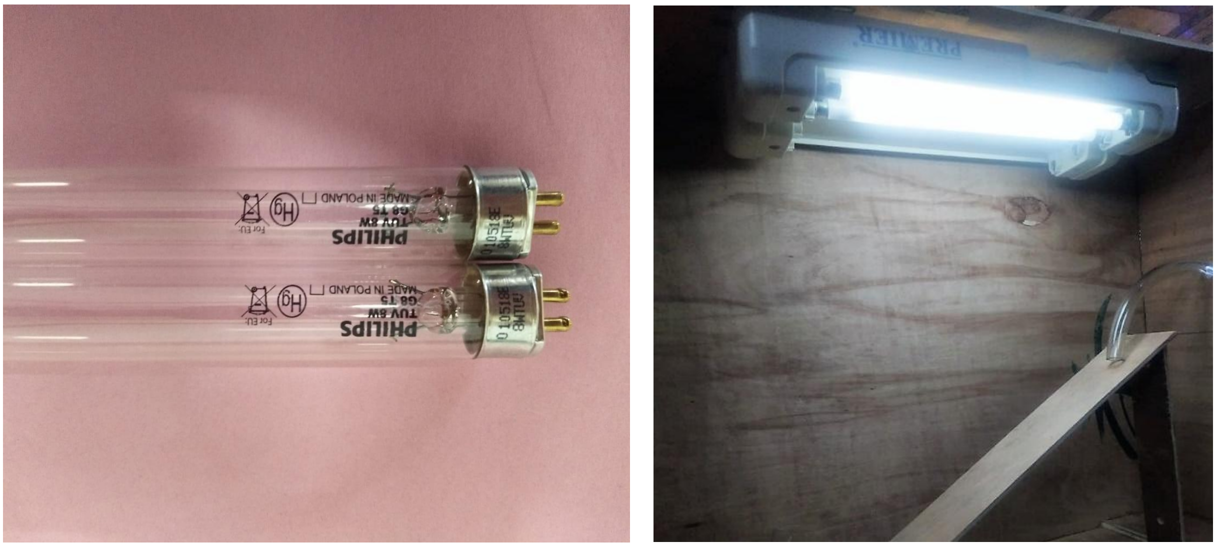
Catalytic agent Titanium dioxide (TiO_2) was purchased from international scientific and surgical (solan). It comprise of specification as 99% analytical reagents (AR), Assay of lower limit as 99.0% and 100.5% as upper limit. Concentration of heavy metals such as lead (Pb) with maximum limit 0.002%, Iron (Fe) having maximum limit of 0.02%, Arsenic (As) with maximum limit of 0.0003% and Antimony (Sb) of maximum limit as 0.005%.

3.2.3 Copper Slag

Fig: 3.3 Copper Slag.

In the metallurgical industries, wastes are generated from ore pre-treatment and refinement. Among these waste products, slag is produced in large quantities. Among nonferrous slag, Copper slag is particularly more important because of the worldwide production and use of copper slag.Extraction of copper by smelting produces copper-slag as by-product. During smelting, impurities become slag which floats on the molten metal. It was purchased online through a e-commerce website. It is physically in slag form and black in color as shown in image above.

3.2.4 UV Lamp



(a) (b)

Fig: 3.4 UV Lamp: (a) UV Lamp rods (b) UV Lamp fixed into reactor.

Oxidation of organic matterby catalytic chemical reaction from titanium dioxide and UVC exposure, converts pathogens, pollens, and mold spores into harmless inert by-products.Photochemical process is thecleansing mechanism of UV. Indoor environment consists of contaminants that are almost entirely organic carbon-based compounds and breaks down when exposed to high-intensity UV at 240 to 280 nm.

UV lamps were purchased online through E-commerce website with specification as given below

Specification:

- Length of tube: 11.9 Inch / 1 Feet,
- Diameter of tube, 16mm,
- Wattage : 8W

Purchased: Online (through E-commerce website)
https://www.amazon.in/dp/B07BP8VCVT/ref=cm_sw_r_apa_i_w6pPBb9GHQBNA

3.3 SAMPLING OF WASTEWATER

Table: 3.1 sampling of wastewater from three different source.

Source	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday
Laundry	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**
Mess	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**
Girls Hostel	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**	**2L**

- Total sample collected = 42 ltrs
- 30 ltrs of sample is used for testing

3.4 FABRICATION OF DEGRADATION REACTOR

3.4.1 Degradation Chamber

Degradation chamber was purchased online from Sun Acrylam Private limited. It is made up of transparent Acrylic material with Diameter 150mm and length 400mm. Both end were cover with cap called as inlet cap and outlet cap.

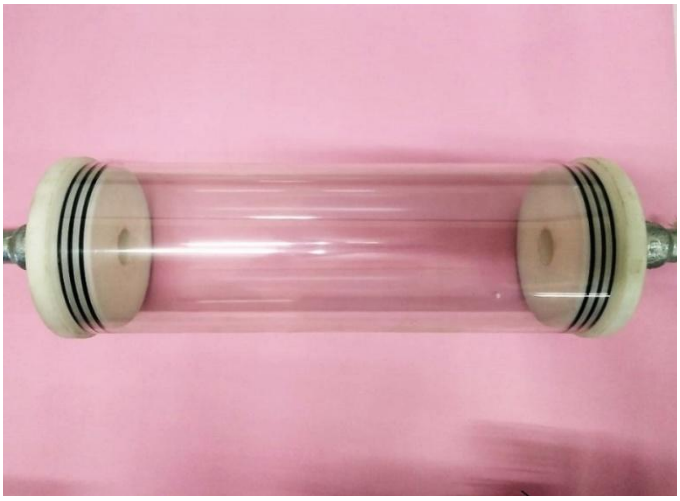


Fig: 3.5 Degradation Chamber.

A reactor consist of various component such as wooden support frame chamber, perspex degradation chamber, input tank, flow control valve, inflow and outflow pipe, UV lamp and a collection tank. Inside the wooden support frame, perspex degradation chamber is setup at an angle of 30 degrees with its upper end connected to inflow pipe and lower end connected to outflow pipe. UV lamp is fixed on the frame in such a way that it projects its light over the degradation chamber.

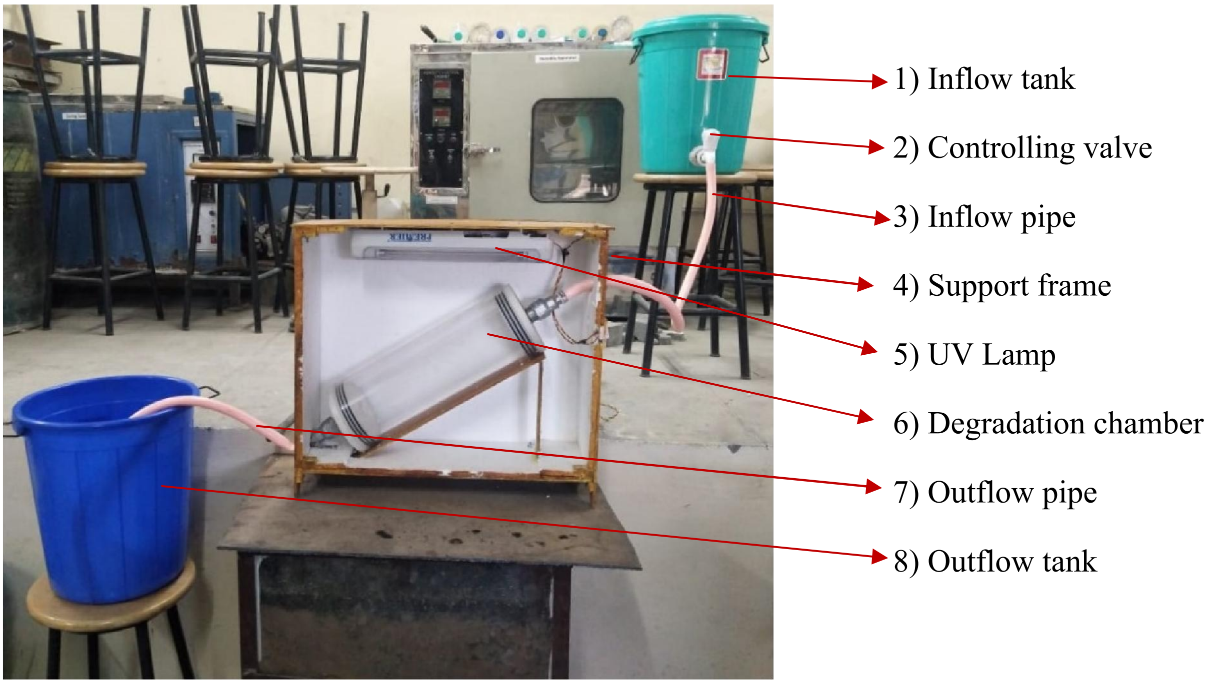


Fig: 3.6 Reactor set-up.

3.4.2 Collection Tanks

Two collection tanks of capacity 40 L was used for influent and treated greywater collection. The tanks were purchased locally so as to serve the input and output source to the photoreactor. The amount of greywater used in the study is 30L.

(a) **(b)**

Fig: 3.7 Sample Collecting Tank: (a) Inflow Tank (Contains Greywater) (30 LTRS)

(b) Outflow collecting Tank (Contains Degraded water) (30 LTRS)

3.5 CONTROL CHAMBER TESTING

3.5.1 Dark Chamber for Control testing

Fig: 3.8 Control dark chamber for testing of sample in controlled condition.

A dark chamber was fabricated using thermocol as insulator for assessing the control sample testing of greywater. The chamber was covered with black paper so as to avoid any interaction with the ambient light source.

3.5.2 Greywater only

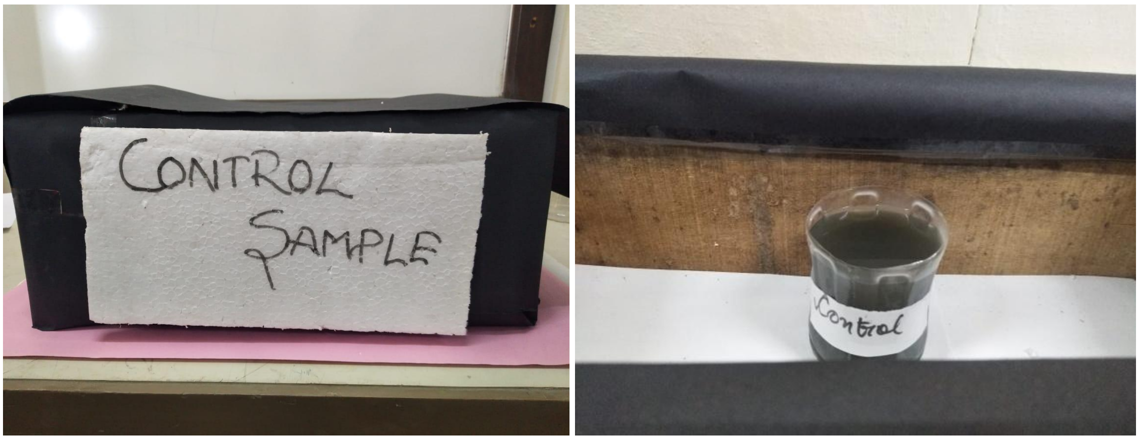


Fig: 3.9 Control test of Greywater only.

Procedure:

- Take 1 ltr. of greywater sample in a container.
- Note down its initial readings for p^H, BOD, COD, alkanity, acidity, and turbidity.
- Place the sample inside a control chamber box and leave it undisturbed, isolated from UV light for 7 days.
- Take out the sample and again test it to note the readings for various test as mentioned above.

3.5.3 Greywater + H_2O_2

For the removal of organic impurities , Hydrogen peroxide (H_2O_2) is used in certain waste-water treatment processes. In advanced oxidation processing, the Fenton reaction gives the highly reactive hydroxyl radical (·OH) which degrades organic compounds, including ordinarily robust, such as halogenated or aromatic compounds.

Calculation for Volume of H_2O_2 to be added:

H_2O_2> 30% w/v

30 gm in 100 ml

300 gm in 1000 ml

300000 ppm.

Addition of 0.2 ml of H_2O_2 in greywater sample.

300000 x 0.2ml= X x 250

X=240 mg/l

Fig: 3.10 Control test of Greywater + H_2O_2.

Procedure:

- Take 1 ltr. of greywater sample + H_2O_2 (240mg/l) in a container.

- Note down its initial readings for p^H, BOD, COD, alkanity, acidity, and turbidity.
- Place the sample inside a control chamber box and leave it undisturbed, isolated from UV light for 7 days.
- Take out the sample and again test it to note the readings for various test as mentioned above.

3.6 CONTROL CHAMBER TESTING USING PELLETS

3.6.1 Formation of pellets (Beads)

- Copper slag is first grinded into fine powder using a grinding machine.
- The fine copper powder is then sieved through a 0.075mm sieve.

Fig: 3.11 Copper slag for grinding.

- The powder which passed through 0.075mm sieve is then mixed with water making pellets. The diameter of pellets is kept 1 cm, measured manually through scale.

(a) (b)

Fig: 3.12 (a) Mixing of copper powder (b) Fabricated pellets

- After formation of pellets small holes were made using a needle, so that it absorbs greywater properly.
- These pellets were then placed in muffle furnace in 1000°C for 24 hrs.

Fig: 3.13 Formation of holes in pellet.

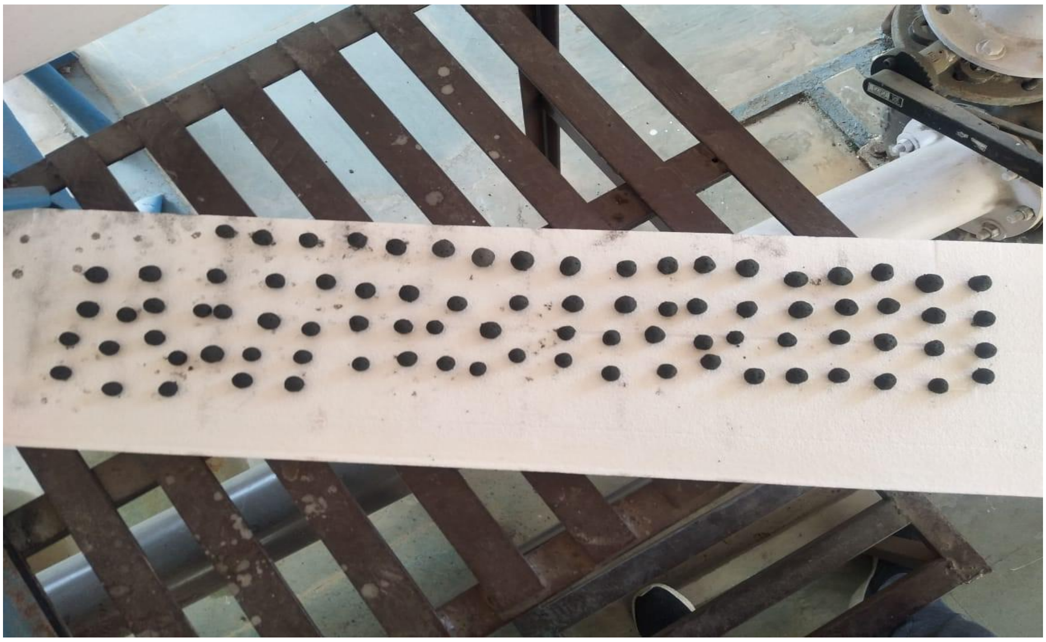


Fig: 3.14 Pellets after mufflefurnace treatment.

3.6.2 Control test of greywater with copper pellets

Procedure

- After formation of pellets, the grey water is then tested with the addition of pellets.
- The greywater sample is taken in a container and pellets were added into it.
- The sample is then placed inside the control chamber for treatment; testing and readings were taken after.

(a) **(b)**

Fig: 3.15 (a) Copper pellets dipped in greywater (b) Stirring of TiO2 in distilled water

3.6.3 Control test of greywater with copper pellets having TIO$_2$ coating.

Pellets coating procedure

- Take 1 gm of TiO$_2$ and mix it in distilled water 100ml.
- Place it in the stirrer in environment lab and keep it mixing for 2 hrs.
- Place all pellets in a tray and pour the mixture over it.
- Keep the pellets dipped in the mixture and regularly turn in the mixture. This has to be done till all the mixture is soaked by the pellets.
- Place it in muffle furnace at 300 ^{0}C for 2 hours.
- After coating of pellets with TiO$_2$ the pellet were dipped inside the greywater sample and is place inside the control chamber for testing.

Fig: 3.16 Copper pellets coated with TiO_2 dipped in greywater.

3.7 DEGARDATION OF GREYWATERUSING REACTOR

After control chamber treatment of greywater, the new sample from collected greywater is taken and is treated using degradation reactor. The treatment is done in four phases. In phase I, the greywater is treated under the influence of UV light. In phase II, H_2O_2 is added to the sample and then passed under the UV light. In phase III, H_2O_2 added grey water sample passed through degradation tube containing copper pellets, under the influence of UV light. In Phase IV, TiO_2 dipped copper pellets were used instead of copper pellets in similar set-up as in phase III to treat greywater.

3.7.1 Phase 1 :only uv degradation

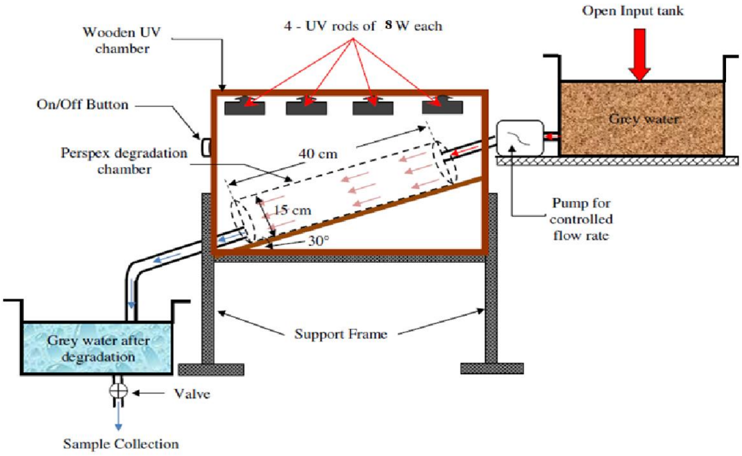


Fig: 3.17 Only UV Degradation

Procedure:

- 30 Ltrs of greywater sample is first collected in inflow tank.
- The sample (greywater) is then allowed to pass through reactor tube by opening the control valve. UV lamps were remained ON during the process.
- Degraded greywater is then collect at outflow collecting tank.
- The samples of degraded water were collect after intervals of 5, 10, 20, 30, 60, 90 and 120 minutes each.
- These collected samples were then tested for p^H, BOD, COD, Alkanity, Acidity, Turbidity, T.S.S, T.D.S, Dissoved Oxygen (D.O), Spectrometer test, Heavy Metals (Fe, Cr, Zn, pb, Cu, Ni, Mn) in laboratory.

Fig: 3.18 Laboratory Image for Only UV Degradation

3.7.2 Phase 2: UV+H_2O_2 Degradation

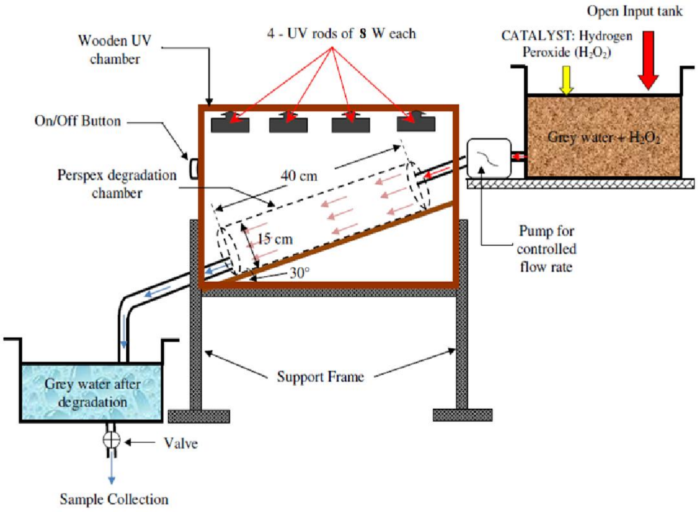


Fig: 3.19 UV+H_2O_2 Degradation

Procedure:

- Firstly H_2O_2, is added (240mg/l) to the greywater and 30 Ltrs of mix is made.
- This 30 Ltrs of greywater + H_2O_2 mix sample is then filled in inflow container tank.
- The sample is then allowed to pass through reactor tube by opening the control valve. UV lamps were remained ON during the process.
- Degraded greywater is then collect at outflow collecting tank.
- The samples of degraded water were collect after intervals of 5minutes, 10minutes, 20minutes, 30minutes, 60minutes, 90minutes and 120 minutes.
- These collected samples were then tested for p^H, BOD, COD, Alkanity, Acidity, Turbidity, T.S.S, T.D.S, Dissoved Oxygen (D.O), Spectrometer test, Heavy Metals (Fe, Cr, Zn, pb, Cu, Ni, Mn) in laboratory.

Fig: 3.20 Laboratory image for UV+H_2O_2 Degradation

3.7.3 Phase 3 : UV+H_2O_2+TiO_2 Degradation

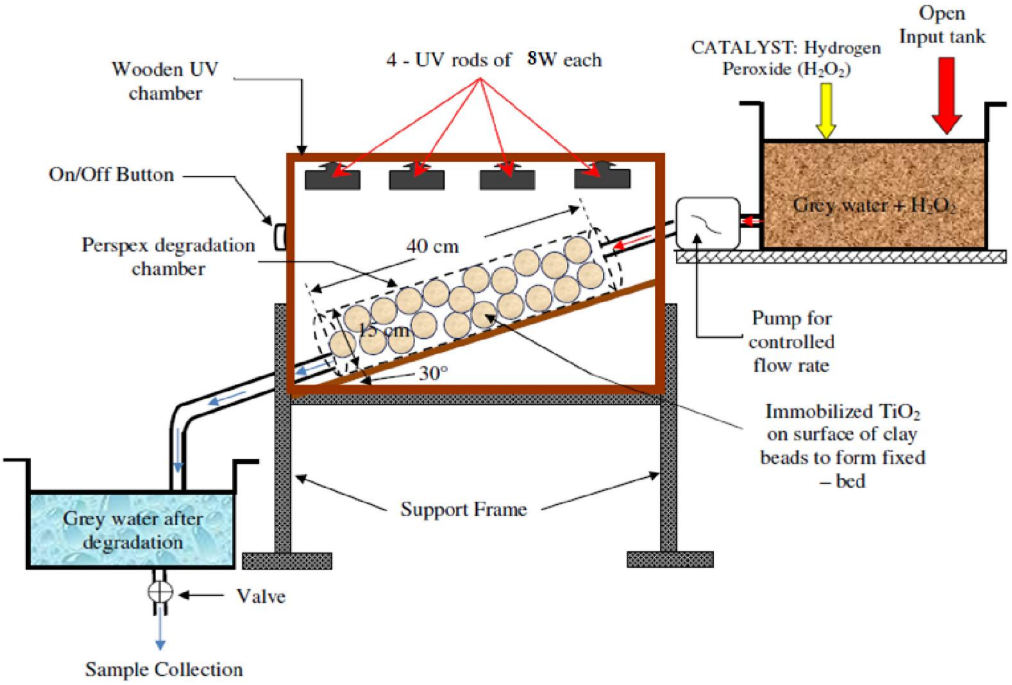
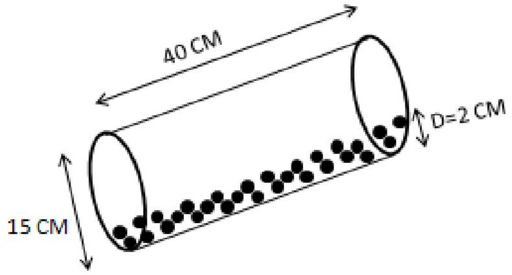


Fig: 3.21 UV+H_2O_2+TiO_2 Degradation.

Procedure:

- Before permorming actual experiment the first step is to prepare bed for reactor. The bed is made from copper pellets. The process for formation of pellets is explained vide 3.5.1. The number of pellets required for preparing of bed is calculated as below:-



Calculation for nos. of pellets:

Dia of 1 bead= 1cm

$V=L \quad R^2 \cos^{-1} \quad R-D \; - \; R-D \quad 2RD-D^2$

R= radius of cylinder

D= depth

dia=0.15m

L= length of cylinder

length=0.40m

Porosity req= 90%

depth=0.02m

n=90%

$V=0.56031 m^3$

$n=V_v/V \; =0.9= V_v/560 \; => V_v = 504 \text{ cm}^3$

Remaining vol containing pellets=> $V_s = V- V_v =56 \text{ cm}^3$

Vol of 1 pellet=$4/3\pi r^3$=$0.52m^3$ =>no of pellets=56/0.52=110 nos.

- After formation of bed for reactor, second step is to add H_2O_2, (240mg/l) to the greywater and 30 Ltrs of mix is made.
- This 30 Ltrs of greywater + H_2O_2 mix sample is then filled in inflow container tank.
- H_2O_2 added grey water sample is then passed through degradation tube containing copper pellets, under the influence of UV light.
- Degraded greywater is then collect at outflow collecting tank.
- The samples of degraded water were collect after intervals of 5, 10, 20, 30, 60, 90, and 120 minutes.
- These collected samples were then tested for p^H, BOD, COD, Alkanity, Acidity, Turbidity, T.S.S, T.D.S, Dissolved Oxygen (D.O), Spectrometer test, Heavy Metals (Fe, Cr, Zn, pb, Cu, Ni, Mn) in laboratory.

Fig: 3.22 Laboratory image for UV+H_2O_2+TiO_2 Degradation.

3.7.4 Phase 4 : UV+H_2O_2+TiO_2+Fe Degradation

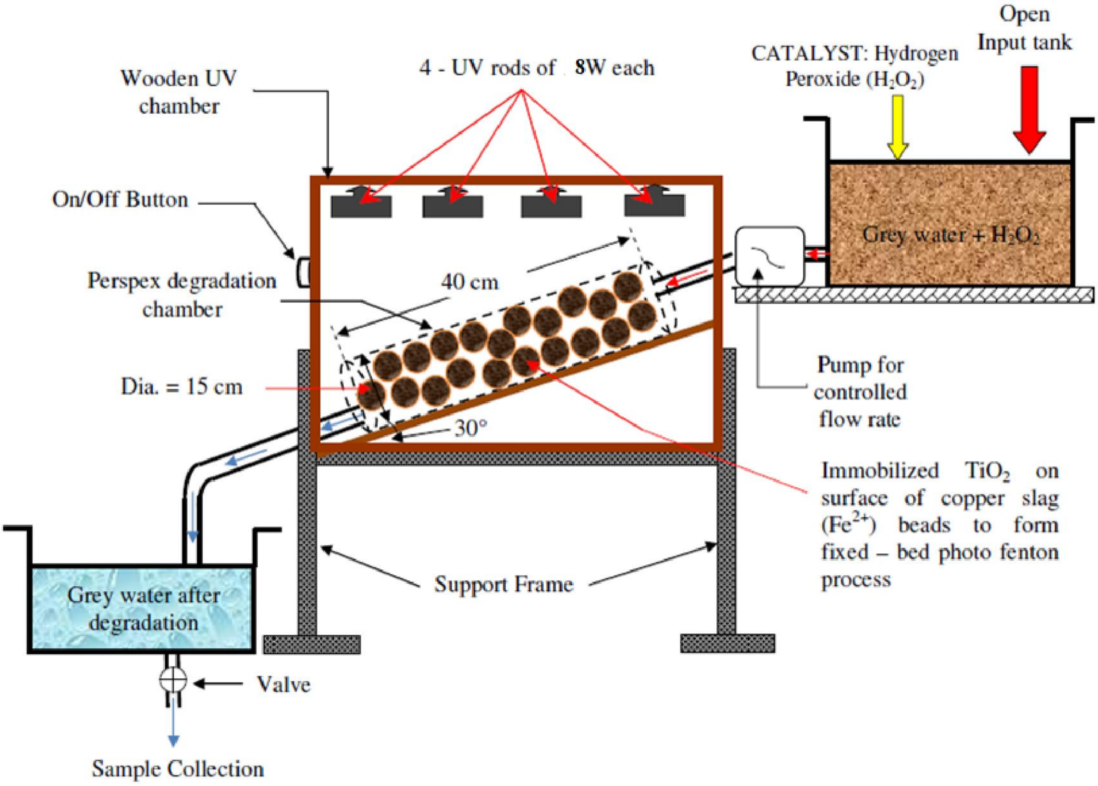


Fig: 3.23 UV+H_2O_2+TiO_2+Fe Degradation.

Procedure:

- In phase IV the bed of reactor is made up TiO_2 coated copper pellets. The procedure for coating of TiO_2 over copper pellet is explained earlier in 3.5.3.
- After coating, pellets are spread in layers to form bed.
- H_2O_2, is then added (240mg/l) to the greywater and 30 Ltrs of mix is made.
- This 30 Ltrs of greywater + H_2O_2 mix sample is then filled in inflow container tank.
- The sample is then allowed to pass through reactor tube by opening the control valve. UV lamps were remained ON during the process.
- Degraded greywater is then collect at outflow collecting tank.
- The samples of degraded water were collect after intervals of 5, 10, 20, 30, 60, 90, and 120 minutes.
- These collected samples were then tested for p^H, BOD, COD, Alkanity, Acidity, Turbidity, T.S.S, T.D.S, Dissoved Oxygen (D.O), Spectrometer test, Heavy Metals (Fe, Cr, Zn, pb, Cu, Ni, Mn) in laboratory.

Fig: 3.24 Laboratory image for UV+H_2O_2+TiO_2+Fe Degradation.

3.8 DETERMINATION OF CHARACTERISTICS OF GREY WATER

3.8.1 Determination of pH (IS 3025 PART 11 2002)

On a large scale, pH depends upon pH and alkalinity in the supply of water and usually occurs within the range of 5-9. pH plays a vital role in control and removal of metals when its value kept in between 7.5-8.

The pH value is found out through measurement of the electromotive forces of the cell, with the test solution and an indicator electrode immersed in an indicating electrode. The connection between the solution that has to be tested and the indicating electrode is generally obtained through a liquid juncture, which is configure as part of the indicating electrode. Electromotive force is examined with a pH apparatus, which has a high resistance voltmeter adjusted in the context of pH.

Procedure:

- Appratus required for measuring pH is a electronic pH meter, volumetric flask, wash bottle filled with distilled water, buffer solution of pH 4, 7, 9.
- Take 30 mL of each buffer solution and also put 50 mL of sample in a separate beakers.
- Put the electrodes(s) of pH meter into each buffer solution one by one. Adjust the pH apparatus if any adjustment is required.
- Now put the electrode(s) inside the sample to record its pH value.

Fig: 3.25 pH meter.

3.8.2 Determination of BOD (IS 3025 PART 44 1993)

BOD testing is primarily based on the bio-assay process, which calculate the oxygen used by microbs while decomposition and oxidation organic matter under aerobic conditions.

The most commonly used test of organic pollutants for both waste water, and surface water is a BOD_5. This finding requires the calculation of dissolved oxygen consumed by microbs in decomposition of organic content. BOD_5 is the total oxygen required by microbs in 5 days of breakdown of organic content. The following equations explain the process involved in biodegradation:

Organic content + O_2 + micro-organisms => CO_2 + H_2O + new microbs cells

Ammonia + O_2 + microorganisms => NO_3 + H_2O + new microbs cells

Procedure:

- Apparatus required are incubation bottle 300 milliliter vol., Air pump, 20°C incubator and Reagents for Dissolved Oxygen calculation.
- Add 2mL per liter of below mentioned reagents in distilled water to make their dilute solutions. a. Calcium chloride sol_n b. Sodium Sulfite sol_n c. Magnesium sulfate sol_n d. Phosphate buffer sol_n e. Ferric chloride sol_n.
- Add 1mL of alkali azide and after that 1mL of manganous sulfate sol_n to a given sample bottle. Thoroughly shake the bottle to make sure proper mixing and then keep it undisturbed for 5 min so precipitate get settle down. Add 2 ml of Con_c. sulphuric acid to it and place the cap on bottle. Mix it well so that precipitate gets dissolved.
- • Take a sample of 203 mL in the conical flask and give the titration with standard sodium thiosulfate solution($Na_2S_2O_3$) (0.025N) until it is converted from to light yellowish color. Then add some drops of starch indicator and continue until it turns either transparent or to its original color. Take into account the quantity of 0.025N sodium thiosulfate consumed.
- Calculate DO.

$$\text{DO in mg/L} = \text{mL of } Na_2S_2O_3 \text{ (0.025N) used.}$$

BOD:

- Preparation of BOD dilutions.
- Prepare 2 sets of sample by taking 300 mL of sample in BOD bottle. One set will be used for DO analysis for 0 day and another set of sample kept in a BOD incubator for testing BOD_5 at 20^o Celsius.
- Note down Dissolved Oxygen of various sample at t=0.
- Note down the reading for DO after incubating samples for 5 days in 20^oC.

BOD_5 value of the sample at 20°C:

$$BOD_t = [DO_t - DO_0]/(P)$$

$$\text{Dilution factor, } P = 300 \text{ milliliter/(sample vol. in mL)}$$

3.8.3 Determination of COD (IS 3025 PART 58 2006)

The demand for COD is defined as quantity of a certain oxidizing envoy that responds with the sample, supervised under certain conditions and is indicated as oxygen equivalent. This specification specifies contamination of the organic content of water and is always higher BOD. It is uses as and helps to express the organic substance pollution that the body obtains the overall organic weight.

The COD test is carried out using the following reagents and determined using Eq. (3.1):

- Potassium dichromate + pinch of sulphonic acid

- Mercuic sulfate which helps in removal of interference of chlorides by forming complex with chloride ions.
- Ferrous ammonium sulfate was used as titrant.

Procedure:

- In reflux tube place about 0.4 g of $HgSO_4$. Add 20-milliliter of distilled water and blend it well, that Cl- are turned into deficiently ionized $HgCl_2$.
- Add 10-milliliter standard Potassium dichromate sol$_n$ and then add slowly 30 ml of H_2SO_4 which formally contained Ag_2SO_4. Shake or stir it well, if the color turned to greenish, take new sample with smaller quantity. Final con$_{c.}$ of sulphuric acid should be always 18 N.
- Connect the tubes to condensers and reflux for 2 h at 150+2°C. Cool and wash down the condensers with 60 ml distilled water.
- Cool-down and titrate against standard iron ammonium sulfate using ferroine as an indicator. The color near the end of the titration varies rapidly from green to green to red wine.

  • In a similar situation, reflux the spaces together with the sample.

$$COD, mg/l = \frac{(V_1 - V_2)N \times 8000}{V_0} \tag{3.1}$$

V_1 = vol. of Ammonium iron(II) sulfate required for titration against the blank, in ml

V_2= vol. of Ammonium iron(II) sulfate required for titration against the sample, in ml

N= Normality of Ammonium iron(II) sulfate

V_o= vol. of sample used in testing, in ml

3.8.4 Determination of alkalinity as $CaCO_3$ (IS 3025 PART 23 2003)

The alkanity of the water is a standard of its capability to neutralize acids. The alkanity of natural waters is mainly due to the salts of week acids. Bi-carbonates amounts to the major form of alkanity. Alkanity can be defined as follows:

Alkanity (mol/L) = [HCO3 -] + 2 [CO3 2-] + [OH^-] – [H^+]

Alkanity is important in various treatments of natural water and wastewater. Carbonates, bicarbonate and hydroxide materials are formed in the form of alkanity of much surface water, these components are also considered as indicators. Alkaline earth is important in defining the suitability of water for irrigation more than metal concentrations. Alkanity calculation is used in clarification of water and waste water treating operations. An alkanity is less or slightly higher than raw domestic waste water supply.

$$Total\ Alkalinity\ (as\ CaCO_3) = \frac{A \times N \times 50{,}000}{V} \tag{3.2}$$

3.8.5 Determination of acidity

Acid imparts to corrosion and affect chemical reaction rates, chemical speculation and biological processes. To react with a strong base for a specified pH, the acidity of water has its quantitative capacity. The last point used in measured pricing can be quite different with the pH. When studying the chemical composition of the sample is known as mineral acid, we can contribute to the measured acidity according to the method of determining weak acid such as carbonic and acetic and hydrolyzing salts such as iron or aluminum sulphate.

$$Total\ Acidity = \frac{V_2 \times N \times 50{,}000}{V} \tag{3.3}$$

3.8.6 Determination of sulphate (IS 3025 PART 24 2003) (Spectrophotometer Test)

Sulfate is found in all natural water in commendable quantities, especially in dry and semi-arid areas where the amount of salt in natural water is generally high. Sulfate salts are mostly soluble in water and provide hardness. Water containing high concentrations of it is a bitter in taste. Sulfate can be the cause of intestinal disorders.

Procedure:

Apparatus required: UV-visible spectrometer, sample tubes, standard flask, beaker, spatula, measuring cylinder, wash bottle etc.

Fig: 3.26 Spectrophotometer appratus.

Chemical required: Isopropyl alcohol, glycerol, Conc. H_2So_4, NaCl, Barium chloride, sodium-sulphate, distilled water

- Step 1 is preparation of standards i.e. 10, 20, 30, 40, 50, a blank (distilled water) and known volume of sample
- 5ml of conditioning reagent is then added to all the flasks

- Distilled water is added to make volume to 100 ml.
- Pinch of $BaCl_2$ is added to all the flasks.
- Turbidity is measured immediately using UV- visible spectrometer.
- Calculate the concentration of sulphate from graph obtained.

Fig: 3.27 conditioning reagent sulphate.

Fig: 3.28 Turbidity measuring using Spectrometer.

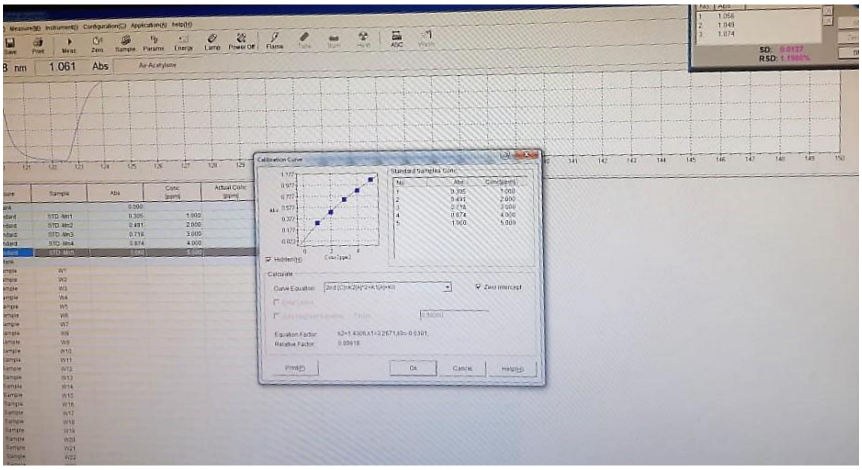


Fig: 3.29 Concentration curve for sulphate.

3.8.7 Determination of total phosphate (IS 3025 PART 31 1998)

Phosphorus is extensively found in various products such as fertilizer-compost, agricultural pest control, prepackaged food and detergents, which has augmented our life. However, it also pollutes environmental water by flowing into the rivers and lakes containing discharge from residential and industrial wastewater, or agricultural runoff. Phosphorus and nitrogen, causes increase in growth of plankton in the lakes, is used as an indicator of eutrophication. As a result, the measurement of phosphorus concentration is crucial for water quality management.

In determining the total phosphorus (TP) in an aquatic sample, phosphorus is based on the digestion of the sample to convert the compounds into orthophosphate, which can then be determined on the basis of spectrophotometer.

Procedure:

Apparatus required: UV-visible spectrometer, sample tubes, standard flask, beaker, spatula, measuring cylinder, wash bottle etc.

Reagent: Conc. H_2SO_4, Ammonium molybdate (VI) tetrahydrate, L-Ascorbic acid, Phosphorus standard solution, Hydrogen peroxide.

- Prepare the Solutions**:** H_2SO_4 solution, 10% Ascorbic acid solution, 2.5% Ammonium molybdate(VI) tetrahydrate solution.
- Phosphorus analysis involves the conversion of the phosphorus present in water in different forms to dissolved orthophosphate which is then estimated calorimetrically.

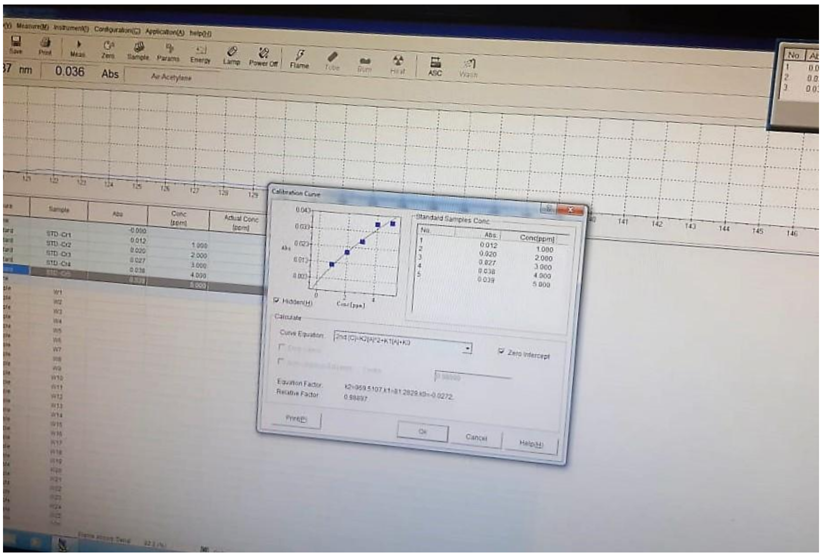
Fig: 3.30 Digestion of phosphorus.

- If the sample is more than pH 10, then dilute the red color with 1: 1 hydrochloric acid before diluting to 0.0.0.05 ml of phenolphthalin indicator and 100 ml for 50 ml of sample.
- Excessive color in the sample is removed by filtering approximately 50 ml of 200 mg of activated carbon in an Erierimeyer flask for 5 minutes and filter to remove the carbon.

- In a 50 ml volumetric flask, place 35 ml or less of sample, containing 0.05 to 1.0 mg of phosphorus (P).
- Put 10 ml vanadatemolybdate reagent, and dilute to the mark using distilled water.
- Prepare a blank in which 35 ml of distilled water is replaced for sample.
- Measure absorbance of sample vs blank at a wavelength of 470 nm after 10 min or more.
- The color is stable for days, and is not changed by variation in room temperature.
- Prepare a calibrating curve by using suitable vol. of standard phosphate solution and proceeding as given above. Read the concentration of the sample from the calibration curve for the given absorbance.

Phosphorus (P), mg/l = m/v 1 000

m = mg of phosphorus (in 50 ml of final volume), and v = vol. in ml of sample.



Standard Samples Conc

No.	Abs.	Conc[ppm]
1	0.012	1.000
2	0.020	2.000
3	0.027	3.000
4	0.038	4.000
5	0.039	5.000

☑ Hidden(H)

Calculate

Curve Equation: 2nd (C)=K2[A]^2+K1[A]+K0

☑ Zero Intercept

Equation Factor: k2=959.5107,k1=81.2829,k0=-0.0272

Relative Factor: 0.99897

Fig: 3.31 Concentration curve for total phosphate.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GENERAL

As per the Methodology the experiments were performed to understand the various characteristics of grey water such as COD, TOC, and BOD etc. This chapter includes the results of experiments which are done to study the effect of various degradation techniques on Grey water.

4.2 EXPERIMENTAL TESTING

4.2.1 Initial test results prior to degradation process

Table: 4.1 Initial test readings for greywater sample.

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.65	7.65	7.65	7.65	7.65	7.65	7.65
BOD	270	270	275	282	286	290	295
COD	500	480	480	470	455	447	430
Alkanity mg/L	290	290	290	290	290	290	290
Acidity mg/L	200	200	200	200	200	200	200
Turbidity (NTU)	53	51	50	44	44	44	44
DO	129	128	124	122	122	119	119
TDS	520	520	520	520	520	520	520
	5 minute		**Heavy Metals**			120 minute	
Fe	*__A.-__ 0.505 #__C.-__ 4.603					__A.-__ 0.505 __C.-__ 4.603	
Cr	__A.-__ 0.002 __C.-__ 0.139					__A.-__ 0.002 __C.-__ 0.139	
Zn	__A.-__ 0.556 __C.-__ 1.213					__A.-__ 0.556 __C.-__ 1.213	
Pb	__A.-__ 0.001 __C.-__ N/D					__A.-__ 0.001 __C.-__ N/D	
Cu	__A.-__ 0.014 __C.-__ 0.044					__A.-__ 0.014 __C.-__ 0.044	

Ni	**A.-** 0.006 **C.-** 0.569		**A.-** 0.006 **C.-** 0.569
Mn	**A.-** 0.033 **C.-** 0.79		**A.-** 0.033 **C.-** 0.79
	5 minute	**Spectro-photometer**	120 minute
Total-PO_{43}-	**A.-** 0.622 **C.-** 0.785		**A.-** 0.622 **C.-** 0.785
So_4	**A.-** 0.359 **C.-** 16.250		**A.-** 0.359 **C.-** 16.250

*A = Aorbance
$^\#$C = Centration

Greywater is generally found to have pH between 7.5 and 8. The inital value of pH for sample of collected greywater, prior to any treatment was measured as 7.65. With the passage of time and during the first stage of treatment i.e. control chamber treatment, its pH value raised to 7.89, which Clude that greywater is aging. It was noticed that initial pH value was less compared to latter stage. It was also observed that there is no significant change in pH after treating greywater, both in control and fixed bed degradation phases.

4.2.2 Test results from control chamber degradation

Table: 4.2 Test results for greywater only (control)

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.89	7.89	7.89	7.89	7.89	7.89	7.89
BOD	285	289	294	302	312	320	332
COD	560	558	550	534	522	509	496
Alkanity mg/L	300	300	300	300	300	300	300
Acidity mg/L	200	200	200	200	200	200	200
Turbidity (NTU)	53	51	50	44	44	44	44
DO	131	129	129	124	122	122	118
TDS	564	564	564	564	564	564	564
	5 minute		**Heavy Metals**			120 minute	

Fe	**A.-** 0.323 **C.-** 2.491		**A.-** 0.233 **C.-** 1.941
Cr	**A.-** 0.001 **C.-** 0.053		**A.-** 0.0009 **C.-** 0.048
Zn	**A.-** 0.549 **C.-** 1.1		**A.-** 0.469 **C.-** 1.032
pb	**A.-** 0.001 **C.-** N/D		**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.010 **C.-** 0.027		**A.-** 0.014 **C.-** 0.021
Ni	**A.-** 0.002 **C.-** 0.563		**A.-** 0.0016 **C.-** 0.560
Mn	**A.-** 0.032 **C.-** 0.71		**A.-** 0.029 **C.-** 0.62
	5 minute	**Spectro-photometer**	120 minute
Total-PO_{43}-	**A.-** 0.601 **C.-** 0.742		**A.-** 0.676 **C.-** 0.852
So_4	**A.-** 0.359 **C.-** 16.250		**A.-** 0.354 **C.-** 16.011

Initially when the greywater was fresh (young), its highest value for BOD was recorded as 295. After few days and while first stage of treatment i.e control treatment, it was noticed that its BOD value was raised significantly with highest value recorded is 519. This Cluded the presence of great amount of micro-organism i.e. aerobic bacterial in the grey water sample. But after treating in second stage i.e. fixed bed degradation, it was noticed that its BOD value lowers down to 320. Similar goes with COD, with its prior treatment value recoded as 500, and during first stage treatment it went high up-to 804 and after second stage of treatment it lowers down to 705. It can be Cluded from here, that photo degradation is a effective procedure to kill micro-organism present in the greywater.

Table: 4.3 Test results for greywater + H_2O_2 (control)

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.82	7.82	7.82	7.82	7.82	7.82	7.82
BOD	371	379	388	396	414	428	445
COD	804	792	785	771	759	742	730

Alkanity mg/L	240	240	240	240	240	240	240
Acidity mg/L	280	280	280	280	280	280	280
Turbidity (NTU)	45	45	45	45	45	45	45
DO	124	122	121	116	114	111	110
TDS	518	518	518	518	518	518	518
	5 minute		**Heavy Metals**			120 minute	
Fe	**A.-** 0.377 **C.-** 3.066					**A.-** 0.368 **C.-** 2.957	
Cr	**A.-** 0.002 **C.-** 0.139					**A.-** 0.0018 **C.-** 0.131	
Zn	**A.-** 0.584 **C.-** 1.291					**A.-** 0.574 **C.-** 1.268	
pb	**A.-** 0.001 **C.-** N/D					**A.-** 0.001 **C.-** N/D	
Cu	**A.-** 0.010 **C.-** 0.008					**A.-** 0.028 **C.-** 0.0189	
Ni	**A.-** 0.0034 **C.-** 0.767					**A.-** 0.0030 **C.-** 0.649	
Mn	**A.-** 0.034 **C.-** 0.83					**A.-** 0.029 **C.-** 0.74	
	5 minute		**Spectro-photometer**			120 minute	
Total- PO_{43-}	**A.-** 0.601 **C.-** 0.742					**A.-** 0.599 **C.-** 0.731	
So_4	**A.-** 0.355 **C.-** 15.355					**A.-** 0.349 **C.-** 14.899	

Further, there is not much effect is seen in alkanity and acidity character of greywater during degradation. Initially its alkanity was measured as 290 mg/l and acidity recorded as 200 mg/l, which increased to 300 mg/l with the time. After fixed bed degradation its alkanity was measured as 305 mg/l (slight increase) and its acidity was measured as 270 mg/l (noticeable decrease)

Table: 4.4 Test results for greywater + copper pellets (control)

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	6.71	6.71	6.71	6.71	6.71	6.71	6.71
BOD	395	402	419	429	442	456	469
COD	733	725	712	698	684	671	658
Alkanity mg/L	275	275	275	275	275	275	275
Acidity mg/L	300	300	300	300	300	300	300
Turbidity (NTU)	102	90.5	88.8	74	74	74	74
DO	129	129	129	124	118	116	116
TDS	532	532	532	532	532	532	532
	5 minute		**Heavy Metals**			120 minute	
Fe	**A.-** 0.529 **C.-** 4.918					**A.-** 0.570 **C.-** 5.023	
Cr	**A.-** 0.001 **C.-** 0.055					**A.-** 0.004 **C.-** 0.0125	
Zn	**A.-** 0.631 **C.-** 1.428					**A.-** 0.679 **C.-** 1.593	
pb	**A.-** 0.001 **C.-** N/D					**A.-** 0.001 **C.-** N/D	
Cu	**A.-** 0.017 **C.-** 0.057					**A.-** 0.028 **C.-** 0.0189	
Ni	**A.-** 0.044 **C.-** 0.838					**A.-** 0.052 **C.-** 0.873	
Mn	**A.-** 0.089 **C.-** 0.272					**A.-** 0.097 **C.-** 0.385	
	5 minute		**Spectro-photometer**			120 minute	
Total-PO_{43}-	**A.-** 0.632 **C.-** 0.805					**A.-** 0.677 **C.-** 0.893	
So_4	**A.-** 0.220 **C.-** 16.259					**A.-** 0.266 **C.-** 17.855	

Dissolved oxygen (D.O) and turbidity character of greywater remain almost same throughout the experiment. Dissolved oxygen usually get decrease with the passage of time, as it is used by micro-organism i.e. bacteria for decomposing organic matter present in water. According to this D.O in our experimental study should have been reduced, but as the greywater get treated, the bacteria present in it gets killed and D.O of greywater is recovered to the value same as recorded initially.

Table: 4.5 Test results for greywater + TiO_2 coated copper pellets (control).

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.1	7.1	7.1	7.1	7.1	7.1	7.1
BOD	451	459	468	470	487	501	519
COD	690	687	678	669	656	641	629
Alkanity mg/L	226	226	226	226	226	226	226
Acidity mg/L	274	274	274	274	274	274	274
Turbidity (NTU)	84.3	82	81	78	78	78	77
DO	131	130	130	128	126	122	119
TDS	535	535	535	535	535	535	535
	5 minute		**Heavy Metals**			120 minute	
Fe	**A.-** 0.534 **C.-** 5.213					**A.-** 0.554 **C.-** 5.811	
Cr	**A.-** 0.001 **C.-** 0.055					**A.-** 0.004 **C.-** 0.125	
Zn	**A.-** 0.587 **C.-** 1.328					**A.-** 0.603 **C.-** 1.422	
pb	**A.-** 0.001 **C.-** N/D					**A.-** 0.001 **C.-** N/D	
Cu	**A.-** 0.018 **C.-** 0.061					**A.-** 0.022 **C.-** 0.079	
Ni	**A.-** 0.042 **C.-** 0.836					**A.-** 0.057 **C.-** 0.886	
Mn	**A.-** 0.069 **C.-** 0.202					**A.-** 0.083 **C.-** 0.432	

	5 minute	**Spectro-photometer**	120 minute
Total-PO$_{43}$-	**A.-** 0.629 **C.-** 0.794		**A.-** 0.675 **C.-** 0.831
So$_4$	**A.-** 0.187 **C.-** 2.943		**A.-** 0.195 **C.-** 3.486

A. of heavy metals also noticed to reduced, but in very slight number. A. value for Fe recoded during control degradation was 0.554 which reduced in second stage of treatment to 0.551. Similar for Cr, in first stage of treatment, value of A. was 0.139, which was recorded as 0.004 in second stage. For Zn, in first stage treatment its value was 0.679, which didn't change in second stage. Minuteor increase in A. of Cu was noticed in second stage. Its value was 0.0189 in first stage of treatment, which goes up to 0.022 in later stage. A. value for Ni remains same i.e. 0.057, while C. of sulphate was reduced in second stage to treatment.

4.2.3 Test results from fixed bed reactor degradation

PHASE I : ONLY UV DEGRADATION

Table: 4.6 Test results for only UV degradation (Fixed bed reactor).

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.42	7.42	7.42	7.51	7.73	7.91	8.10
BOD	245	245	255	255	263	271	290
COD	705	705	705	705	670	650	610
Alkanity mg/L	180	180	180	165	165	165	165
Acidity mg/L	235	235	235	235	235	235	235
Turbidity (NTU)	135	135	137	135	143	145	145
DO	129	129	124	122	118	115	111
TDS	526	526	526	526	526	526	526
	5 minute		**Heavy Metals**			120 minute	

Fe	**A.-** 0.322 **C.-** 2.110		**A.-** 0.0298 **C.-** 2.004
Cr	**A.-** 0.002 **C.-** 0.39		**A.-** 0.0015 **C.-** 0.29
Zn	**A.-** 0.544 **C.-** 1.133		**A.-** 0.514 **C.-** 1.031
pb	**A.-** 0.001 **C.-** N/D		**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.014 **C.-** 0.044		**A.-** 0.026 **C.-** 0.096
Ni	**A.-** 0.002 **C.-** 0.866		**A.-** 0.040 **C.-** 0.838
Mn	**A.-** 0.023 **C.-** 0.46		**A.-** 0.08 **C.-** 0.59
	5 minute	**Spectro-photometer**	120 minute
Total-PO$_{43}$-	**A.-** 0.623 **C.-** 0.779		**A.-** 0.596 **C.-** 0.716
So$_4$	**A.-** 0.225 **C.-** 5.818		**A.-** 0.22 **C.-** 5.436

PHASE II : UV+H_2O_2 DEGRADATION

Table: 4.7 Test results for UV+H_2O_2 degradation (Fixed bed reactor).

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.14	7.14	7.14	7.10	7.10	7.10	7.10
BOD	240	240	236	234	225	225	225
COD	525	523	520	512	505	504	504
Alkanity mg/L	270	270	270	270	270	270	270
Acidity mg/L	180	180	180	180	180	180	180
Turbidity (NTU)	53	51	50	44	44	44	44
DO	125	125	117	116	110	107	108
TDS	516	516	516	516	516	516	516
	5 minute		**Heavy Metals**			120 minute	

Fe	**A.-** 0.333 **C.-** 2.508		**A.-** 0.309 **C.-** 2.198
Cr	**A.-** 0.002 **C.-** 0.136		**A.-** 0.0017 **C.-** 0.125
Zn	**A.-** 0.640 **C.-** 1.455		**A.-** 0.61 **C.-** 1.322
pb	**A.-** 0.001 **C.-** N/D		**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.014 **C.-** 0.444		**A.-** 0.022 **C.-** 0.689
Ni	**A.-** 0.043 **C.-** 0.873		**A.-** 0.057 **C.-** 0.906
Mn	**A.-** 0.059 **C.-** 0.168		**A.-** 0.049 **C.-** 0.155
	5 minute	**Spectro-photometer**	120 minute
Total- **PO_{43}-**	**A.-** 0.622 **C.-** 0.875		**A.-** 0.610 **C.-** 0.835
So_4	**A.-** 0.359 **C.-** 16.250		**A.-** 0.0296 **C.-** 13.665

PHASE III : UV+H_2O_2+TIO_2 DEGRADATION

Table: 4.8 Test results for UV+H_2O_2 + TiO_2 degradation (Fixed bed reactor).

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.30	7.30	7.30	7.30	7.25	7.25	7.25
BOD	280	280	280	276	276	254	254
COD	503	500	500	490	490	485	485
Alkanity mg/L	305	305	305	305	305	305	305
Acidity mg/L	160	160	160	160	160	160	160
Turbidity (NTU)	65	65	65	65	72	72	72
DO	125	125	116	112	112	110	107
TDS	516	516	516	516	516	516	516
	5 minute		**Heavy Metals**			120 minute	

Fe	**A.-** 0.498 **C.-** 4.413		**A.-** 0.55 **C.-** 5.26
Cr	**A.-** 0.002 **C.-** 0.053		**A.-** 0.0026 **C.-** 0.094
Zn	**A.-** 0.557 **C.-** 1.291		**A.-** 0.604 **C.-** 1.402
pb	**A.-** 0.001 **C.-** N/D		**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.023 **C.-** 0.018		**A.-** 0.036 **C.-** 0.067
Ni	**A.-** 0.043 **C.-** 0.767		**A.-** 0.054 **C.-** 0.806
Mn	**A.-** 0.099 **C.-** 0.302		**A.-** 0.103 **C.-** 0.433
	5 minute	**Spectro-photometer**	120 minute
Total-PO_{43}-	**A.-** 0.676 **C.-** 0.681		**A.-** 0.689 **C.-** 0.706
So_4	**A.-** 0.185 **C.-** 2.943		**A.-** 0.199 **C.-** 3.586

PHASE IV : UV+H_2O_2+TIO_2 + Fe DEGRADATION

Table: 4.9 Test results for UV+H_2O_2 + TiO_2 + Fe degradation (Fixed bed reactor).

Time	5 minute	10 minute	20 minute	30 minute	60 minute	90 minute	120 minute
pH	7.30	7.30	7.30	7.30	7.30	7.30	7.30
BOD	310	310	315	315	315	315	320
COD	450	450	430	430	420	418	418
Alkanity mg/L	270	270	270	260	260	260	250
Acidity mg/L	140	140	140	135	135	135	132
Turbidity (NTU)	65	65	65	65	72	72	72
DO	123	123	115	110	110	108	105
TDS	505	505	505	505	505	505	505
	5 minute		**Heavy Metals**			120 minute	

Fe	**A.-** 0.498 **C.-** 4.513		**A.-** 0.551 **C.-** 5.96
Cr	**A.-** 0.002 **C.-** 0.199		**A.-** 0.004 **C.-** 0.207
Zn	**A.-** 0.640 **C.-** 1.455		**A.-** 0.679 **C.-** 1.601
pb	**A.-** 0.001 **C.-** N/D		**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.016 **C.-** 0.052		**A.-** 0.029 **C.-** 0.088
Ni	**A.-** 0.040 **C.-** 0.838		**A.-** 0.054 **C.-** 0.899
Mn	**A.-** 0.054 **C.-** 0.150		**A.-** 0.067 **C.-** 0.222
	5 minute	**Spectro-photometer**	120 minute
Total-PO_{43}-	**A.-** 0.633 **C.-** 0.744		**A.-** 0.641 **C.-** 0.756
So_4	**A.-** 0.221 **C.-** 5.15		**A.-** 0.256 **C.-** 5.672

It can be Cluded that photo-degradation of the grey water (collected from various sources such as laundry, kitchen, hostels) by photo-Fenton like and photo-Fenton operations can notably reduce the surfactant quantity. The efficacy of the surfactant photo-degradation was observed to be superintend by TiO_2 dose, pH, H_2O_2 percentage, and the operational time for UV/TiO_2/H_2O_2system, and that of by Fe^{2+} and H_2O_2 quantity, pH and the UV exposure time for UV/Fe(II)/H_2O_2 (photo-Fenton) process. The ideal surroundings for both operations could be also prepared. It is also clearly established that UV/TiO_2/H_2O_2 process proven stronger activity in the reducing surfactant percentage than Fe^{2+}/H_2O_2 (photo-Fenton) did. Apart from this, it was also found that reduction in surfactant C. in wastewater, which meet standard quality (0.5 mg / L), using two (2) steps of both the processes of UV / TiO_2 / H_2O_2 and / Fe^{2+} / H_2O_2 Can be obtained.

4.3 VALIDATION OF RESULT

Table 4.10 Comparison of experimental results from control and photoreactor

	Critical values from all Phases	
Parameter	**Control**	**Reactor**
pH	7.89	7.42

BOD	519	320
COD	804	705
Alkanity mg/L	300	305
Acidity mg/L	300	270
Turbidity (NTU)	102	145
DO	131	129
TDS	564	526
Heavy Metals		
Fe	**A.-** 0.554 **C.-** 5.811	**A.-** 0.551 **C.-** 5.96
Cr	**A.-** 0.139 **C.-** 0.004	**A.-** 0.004 **C.-** 0.207
Zn	**A.-** 0.679 **C.-** 1.593	**A.-** 0.679 **C.-** 1.601
pb	**A.-** 0.001 **C.-** N/D	**A.-** 0.001 **C.-** N/D
Cu	**A.-** 0.0189 **C.-** 0.028	**A.-** 0.022 **C.-** 0.689
Ni	**A.-** 0.057 **C.-** 0.886	**A.-** 0.057 **C.-** 0.906
Mn	**A.-** 0.74 **C.-** 0.097	**A.-** 0.103 **C.-** 0.433
Spectro-photometer		
Total-PO_{43}-	**A.-** 0.0676 **C.-** 0.893	**A.-** 0.689 **C.-** 0.875
So_4	**A.-** 0.359 **C.-** 17.855	**A.-** 0.359 **C.-** 16.250

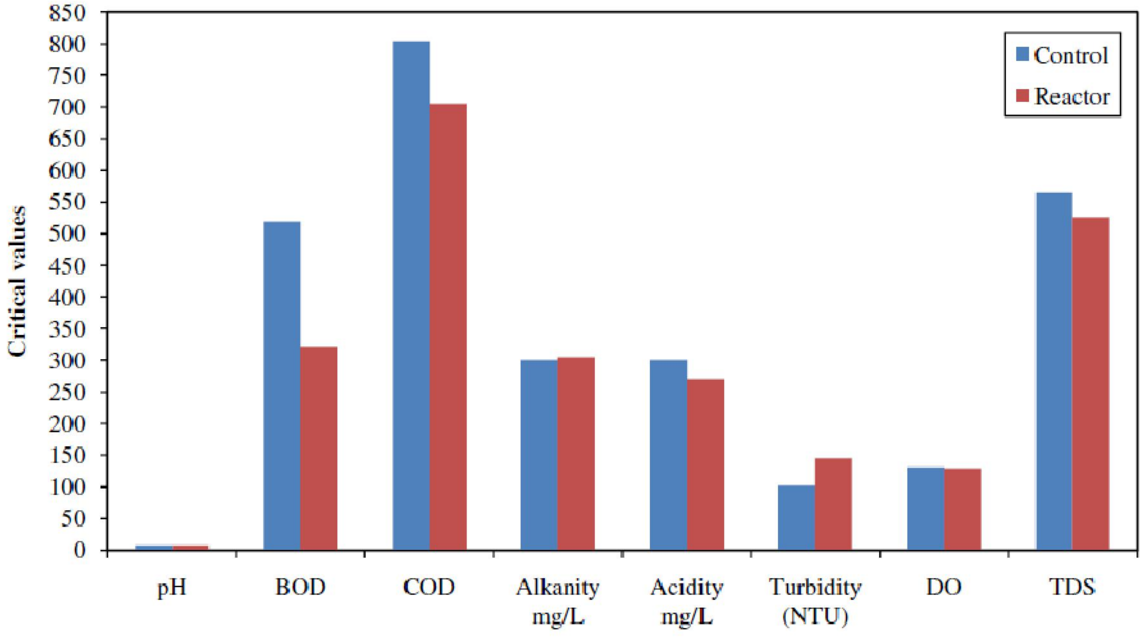


Fig: 4.1 Graph showing comparison of characteristics of greywater measured in control and reactor degradation.

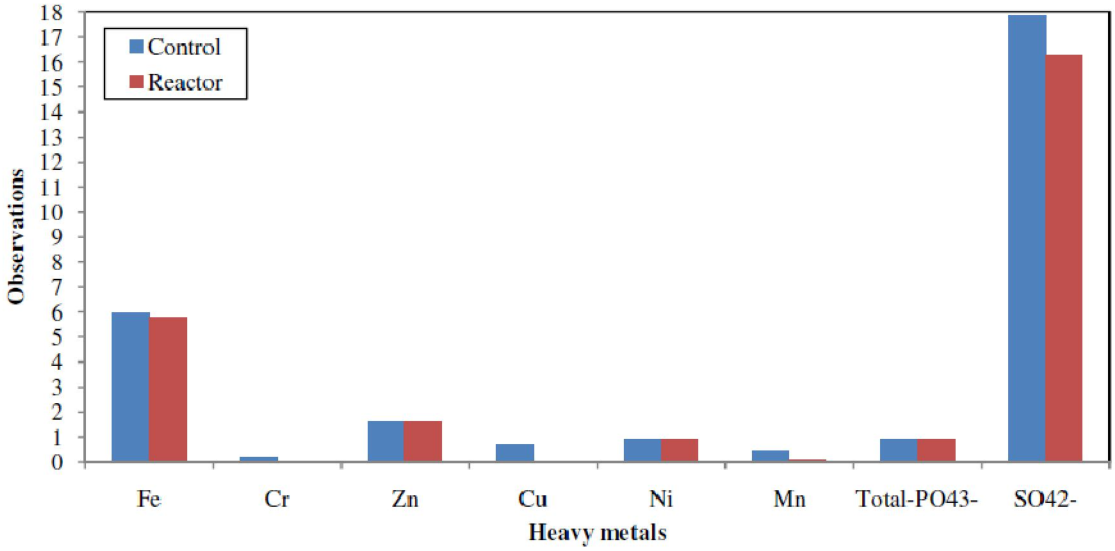


Fig: 4.2 Graph showing comparison of heavy metals measured in control and reactor degradation.

CHAPTER 5

CONCLUSIONS

5.1 GENERAL

The study demonstrates applicability of novel inert clay beads for catalyst stabilization for inclusion of in-situ double-effect, for the photo degradation of gray water. The results of these experiments can help in reducing the use of surface and ground water in all areas of consumption, with optional water resources to optimize the water usage efficiency through alternative options for fresh water and reuse. . These alternate resources include rain water and gray water.

5.2 CONCLUSIONS

Based on the experimental results from testing of treated greywater through photoreactor, following conclusions can be drawn:

[1] When tested after control degradation treatment, pH value was measure 7.89 and after fixed bed reactor treatment, it was recorded as 7.42. Approx 6% of reduction in pH has been noted. The BOD value recorded for control treatment was 519 and after Fixed bed treatment it was found to be 320. Approx 38.5% of reduction in BOD has been measured comparatively to Control treatment, which is very high and signifies the effectiveness of the treatment procedure. About 12.5% of reduction was measured in COD with its control reading recorded as 804 and reactor reading recorded as 705.

[2] About 10% of acidity of greywater was reduced after treating in Fixed bed reactor. There is not much of significant change was observed in DO of the greywater after treating both in control and Fixed bed reactor. However, a slight increase of 1.67% has been measured in case of alkanity. The total dissolved solid was reduced to 7% after treating in fixed bed reactor, comparing to control treatment.

[3] Upon comparative analysis of heavy metals under control and reactor degradation environment, following results are found: There is a slight decrease in Fe and Zn percentage i.e 2.5% and 0.5% respectively. Whereas Cr, Cu, Mn percentage shows huge decrease of 98%, 95.5% and 77.6% respectively. Percentage of Pb remains undermined. There is slight negative variation of 2.20% in Ni level.

[4] Percentage of Total PO_4^{-3} remains nearly the same with little decrease of 2.02%. The sulphate (SO_4^{-2}) ions shows considerable decrease of 8.99%.

5.3 SCOPE FOR FUTURE WORK

The future scope for the present study includes the assessment of feasibility of greywater for drinking purpose which can be achieved by disinfection. In order to achieve this E-coli killing should be studied. Another scope can be large scale implication of photo-catalysis and photo-fenton process should also be evaluated.

Another possible scope to use the UVC / H_2O_2 treatment method is in the form of prior treatment of biological treatment. Therefore, for treating the greywater with the low biodegradability, it is particularly useful to partially oxidize contaminants before the biological treatment by the UVC / H_2O_2 process as it is necessary to obtain the COD removal. It is not always possible to rely completely on AOP.

The capability of UVC / H_2O_2 has been depicted for the treatment of greywater, however the need for high energy should be recognized for the functioning of Ultra-Violet-C lamps. Therefore, further investigation is recommended in optimizing the reactor design. These include various types of lamp and photoreceptor research (including coaxial reactor with external lamp, reflector or vertical lamp positions, reflector, contact-free photo-reactor, etc.).

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