TREATMENT OF TEXTILE INDUSTRY WASTEWATER USING ADSORPTION AND HETEROGENEOUS PHOTOCATALYTIC DEGRADATION PROCESSES

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MASTER OF ENGINEERING IN CHEMICAL ENGINEERING

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INTRODUCTION

Our biosphere is under continuous threat due to environmental pollution. Pollution is the process of introduction of contaminants into the environment. It is the process by which air, water and other parts of the earth become unhygienic, unsafe and unsuitable for use. It is created mostly by human actions, but can also be a result of natural disasters. Pollution has a negative effect on every living organism in an environment, making it virtually impossible to sustain life and hence harms the environment and its inhabitants in several ways. Pollution is the price we are paying towards social development through scientific advancement. Impact on its atmosphere, hydrosphere and lithosphere by anthropogenic activities cannot be ignored. Water pollution is an appalling problem, leading the world towards a path of destruction. We all know water is an easy universal solvent, enabling most pollutants to dissolve easily and contaminate it. Industrial waste, sewage and waste water, mining and marine activities, accidental oil leakage, chemical fertilizers and pesticides, burning of fossil fuels are causes of water pollution. The most primary effect of water pollution is suffered by organisms, vegetation that survives in water. It also includes amphibians. On human level, several people die each day due to consumption of infectious wastewater. Water covers over 70% of the earth surface. It is an important resource for people and environment. Three forms of water on earth are Surface water, ground water, & Rain water. Ground water and rain water although are available in plenty but their qualities are poor and cost are very high. Ground water is slowly getting contaminated due to percolation. Mercury, chromium, arsenic, copper, nickel salts & oils & dyes etc are contaminants of surface water. People are working on rainwater harvesting to collect and preserve rainwater in wells below ground level but they are insufficient in meeting the needs of the present generation.

Fresh water has been considered as one of the most important natural resources over the years. It is a body of water that which has less than 1% concentration of salt. 97% of the water found on Earth is saltwater. Thus only 3% of water is freshwater. 70%of this 3% freshwater is in the form of ice; glaciers, ice caps and permanent snow. Freshwater ecosystems include aquatic systems, drinkable water or water with almost no salt content. It used by people for various purposes like agriculture, industry, recreation tourism, sanitation, as well as food including fish and shellfish. There are different types of freshwater ecosystems; Lakes and ponds, rivers, groundwater, reservoirs, and wetlands, comes under fresh water resource. Human activities, modernizations are causing species to disappear at a very fast rate. Between 1975 to 2015, species extinction occurred at a rate of around 11%. Overfishing is one of the biggest threats to marine ecosystem. Organic matter, for example human waste, is one of the important causes of river pollution resulting in the generation of pathogenic microorganisms. Runoff generating from agricultural, industrial and urban areas containing contaminants such as sewage, heavy metals and fertilizer; the creation of dams and water diversion have caused damage to aquatic habitats and species and identified as challenges to fresh water environments[1]. Fertilizers containing Phosphates can change the biological balance of the freshwater region causing eutrophication. Hence water pollution results in huge growth of algal in freshwater ecosystem due to the nutrient contained in the fertilizers, animal manure, and wastewater-treatment plant effluents. When plants die and decompose, dissolved oxygen is depleted and gives rise to the death of living organisms in water. Textile industries are one of the prominent industries that have a huge contribution for generation of wastewater.

1.1. A BRIEF OVERVIEW OF WASTE WATER

Wastewater is water containing wastes from industrial processes including processes, products, cleaning, household uses such as showering, laundry and obviously flushing the toilets; agricultural activities, surface runoff or storm water; sewer inflow or infiltration and commercials.

Municipal wastewater contains sewage, gray water (e.g., water from sinks and showers).Large industries, such as refineries, also generate wastewater. So we need to remove the wastewater pollutants prior to discharge to protect the environment and public health. For example organic matter causes oxygen depletion in lakes, ponds, rivers, and streams. This biological decomposition of organics could kill fishes and create foul odors. Waterborne diseases are eliminated through appropriate wastewater treatment. Additionally, there are many pollutants that exhibit toxic effects on aquatic life and the public.

1.1.1. SOURCES OF WASTE WATER

Agriculture is one of the largest sources of water pollution. Water pollution source can be point source or non point source. Point source includes mines, oil wells, oil tank, sewage treatment plants etc. Non point source encompasses with seepage into groundwater, substances picked up in roof runoff, acid depositions etc. Apart from that there are several other sources such as

- Human waste
- Industrial toxic waste (metal plating, cyanide production, pesticide manufacturing, etc.)
- Cooling waters from industries (biocides, heat, slimes, silt)
- Black water
- Leakage of septic tank
- Highly acid or alkali wastewater from manufacturing, metal plating industries

1.1.2. CONSTITUENTS OF WASTEWATER

Constituent of varies widely depending on the source of origin. Some of its constituents are gives below.

- Total solids
- Colloidal matter and matter in solution
- Various pathogens
- Nutrients like nitrogen and phosphorus causes eutrophication;
- Pollutants, like oil; Heavy metals
- Industrial gases such as methane, hydrogen sulfide, carbon dioxide etc.
- Emulsions (i.e. paints, emulsified oils, adhesives, hair colorants, etc.)
- Dissolved inorganic such as sodium, calcium, potassium and sulphates.
- Refractory pollutants, like pesticides, phenols and surfactants
- Organic matter like paper fibers, plant material, urea, pharmaceutical wastes, sugars etc.

These components of waste water could be carcinogens, mutagens or highly toxic that can resist to conventional methods of treatment. Organic very harmful to humans, animals and the environment.

1.2.A BRIEF OVERVIEW OF INDUSTRIAL WASTEWATER

Industrial (including agro-industrial) wastewaters will have vivid compositions depending on the type of industry and materials processed. The wastewater from industries varies highly in both flow and pollution strength. Some of these wastewaters can be organically very strong, or largely inorganic, or potentially inhibitory. So, it is impossible to assign fixed values to their constituent. This means TSS, BOD_5 & COD values may be in the tens of thousands mg/l. They may be either excessively acid or alkaline resulting in the pH values well beyond the range of 6–9.High or low concentrations of colored matter are also observed. Because of very high concentration of organic or toxic materials and possibly pathogenic bacteria, industrial wastewaters may also be severely nutrients deficient. Wastewaters may also inherent with high concentrations of dissolved metal salts.

1.2.1. INDUSTRIAL WASTEWATER CHARACTERISTICS

Both municipal and industrial wastewater has physical and chemical characteristics. Physical Characteristics includes factors like solid content, colour, dour and temperature. The total solids in a wastewater comprises of the insoluble or soluble compounds. About 40 to 65 % of the solids in an average wastewater are suspended. Solids can be volatile or non volatile. Volatile solids are generally organic in nature. Colour shows qualitative characteristic that can be used to explain the general condition of industrial wastewater. Black wastewater is due to the formation of various sulphides, mainly ferrous sulphide or due to bacterial decomposition under anaerobic condition. Temperature is an important factor. Very high temperature industrial wastewater when discharged in water bodies its temperature also get increased and affect the aquatic ecosystem. Odour is also a crucial factor. It happens due to the presence of various compounds.

Source of unpleasant odours of some industries	
Industries	**Origin of odours**
lime kilns,Cement works,	Acrolein, mercaptans ,amines, , dibutyl sulphide, SO_2, etc
Pharmaceutical industries	Due to Fermentation
Food industries	Due to Fermentation
Food industries	Sulphides, H_2S,amines,mercaptans
Rubber industries	Sulphides, SO_2,amines,mercaptans
Textile industries	Phenolic compounds
Paper industries	H_2S, SO_2 etc
Organics compost	Ammonia, sulphur compounds

Chemical Characteristics includes extent of presence of organic and inorganic chemicals, volatile organic compounds, heavy metals (cyanides,mercury,lead etc)[2].

1.2.2. SOURCES OF INDUSTRIAL WASTE WATER AND THE STRENGTH OF IT'S DIFFERENT PARAMETERS

There are various parameters (BOD, COD, pH etc) of industrial effluents that are at extreme ranges .Some of the industries several parameters are shown in the following table.

Apparel				
Type of industries	**pH**	**BOD_5(mg/l)**	**SS (mg/l)**	**COD (mg/l)**
Cotton	8 – 12	200 - 1000	200	400 - 1800
Wool scouring	9 – 11	2000 - 5000	3000 – 30000	2000 – 5000
Wool composite	9-10	1	100	-
Tannery	11 - 12	1000 - 2000	2000 – 3000	2000 - 4000

Laundry	8 – 9	1600	250 – 500	2700
Food				
Type of industries	**pH**	**BOD$_5$(mg/l)**	**SS (mg/l)**	**COD (mg/l)**
Brewery	4 – 8	850	90	1700
Distillery	-	7	Low	10
Dairy	Acid	600 - 1000	200 – 400	-
Cannery				
Type of industries	**pH**	**BOD$_5$(mg/l)**	**SS (mg/l)**	**COD (mg/l)**
Citrus	Acid	2000	7000	-
Pea	Acid	570	130	-
Farm	7.5 – 8.5	1000 - 2000	1500 – 3000	-
Slaughterhouse	7	1500 - 2500	800	-
Sugar beet	7 – 8	450 - 2000	800 – 1500	600 - 3000
Poultry	6.5 - 9	500 - 800	450 – 800	600 - 1050
Material				
Type of industries	**pH**	**BOD$_5$(mg/l)**	**SS (mg/l)**	**COD (mg/l)**
Pulp(sulfite)	-	1400 - 1700	Variable	-
Pulp(kraft)	7 – 9.5	100 - 350	75 – 300	170 - 600
Paperboard	-	100 - 450	40 – 100	300 - 1400
Coke oven	7 – 11	780	70	1650
Oil refinery	2 – 6	100 - 500	130 – 600	150 - 800

1.2.3.CONTAMINANTS OFVARIOUS INDUSTRIAL WASTE WATER

Origin of Wastewaters	Contaminants
Acetate rayon, beet root manufacturer	Acetic acid
Chemicals manufacturer, mines, textiles manufacturer	Acids
Gas and coke and chem. manufacture	Ammonia
Sheep dipping	Arsenic
Plating	Cadmium
Plating, chrome tanning, alum anodizing	Chromium
Soft drinks and citrus fruit processing	Citric acid
Copper plating, copper pickling	Copper
Wool scouring, laundries, textile industry	Fats, oils, grease
Laundries, paper mills, textile bleaching	Free chlorine
Oil refining, pulp	Mercaptans mills
Dyeing, wine, leather, chem. manufacture	Tartaric acid
Textile industry, tanneries, gas manufacture	Sulfides
Food processing, textile industries	Starch
Gas and coke manufacture., chem. plants	Phenols

1.2.4. CLASSIFICATION OF INDUSTRIAL WASTEWATER

The different types of wastewater are as follows[3]:

Thermal waste: Source of thermal wastes is cooling processes of thermal plants that generate electricity. Often, enforcing agencies tell to cool thermal waste before it is introduced into water bodies since thermal waste can kill aquatic life.

***__Inorganic waste__*:** Inorganic waste comes from many industries like from blast furnaces, cupola furnaces, coal industries, refuse and sludge incineration plants, steel industry, aluminum works, nonmetallic minerals industry, industries for the surface processing of metals and also from domestic and commercial facilities. It results in wastewater containing mineral and inorganic substances in dissolved and undisclosed form. Chemicals used in industries such as floor cleaners, acids, scrubbers etc. are sources of inorganic wastes that can enter water bodies. Soil, sand, and grit that are washed down into drain are another source of inorganic waste from industrial facilities. Salt, ice-melting agents etc are used on the roads during snow or ice storms are also source of inorganic waste that are entering receiving streams by means of runoff, or through drainage pipes. Suspended matters are present in these wastewaters in large amount. Sedimentation along with chemical flocculation (iron, aluminum salts) helps to reduce the waste. Inorganic wastes are toxic to aquatic life and are to be kept away from receiving streams.

__Radioactive waste:__ Radioactive wastes are hazardous waste. It enter into water bodies and create problems to the surrounding areas. The sources of radioactive wastes are from power plants, research facilities etc. Radioactive waste possess a threat to human, aquatic, animals life.

__Organic waste__*: Organic waste comes from a variety of sources like chemical industries which are associated with organic substances generating from chemical reactions. Domestic wastewater is another source of organic waste. Other large contributors of these wastes are vegetable and fruit packaging, meat packaging, tanning, processing of poultry, dairy processing, oil, paper, and wood, pharmaceuticals, cosmetics, synthetic detergents, pesticides, herbicides etc. Organic wastes are the main causes depletion of oxygen and the horrid odors in receiving streams and in wastewater streams.

1.3. A BRIEF OVERVIEW TEXTILE EFFULENTS

The textile industry need huge volume of water for all its operations from the washing of fibers to washing of final products including other intermediate steps like dyeing, bleaching. Textile industry such as cotton industries produces almost 400 million meters of cloth and almost 1000 million Kg of yarn annually and so is one of the biggest industries in the country. Almost 200 liters of freshwater are required to manufacture around l kg of textiles thus generating the large amount of waste water. Textile industries manufacturing processes are known as intensive water users. A process flow diagram shows the steps of water consumption and generation of effluents of textile industries. A large volume of waste water thus originated from the different processes contain various inorganic substances like oxidizing and reducing agents, alkalis, salts, acids and organic substances such as surfactants, biocides, ionic metals complexes, organic acids, thickeners, finishing agents and dyes. If these are discharged prior to proper treatment it can cause damage to the environment. Many textile mills presently discharge their wastewater to local wastewater treatment plants after only pH neutralization. Large mills discharge effluents of about 2 million/day. Of all the steps involved wet processing creates the greatest volume of wastewater.

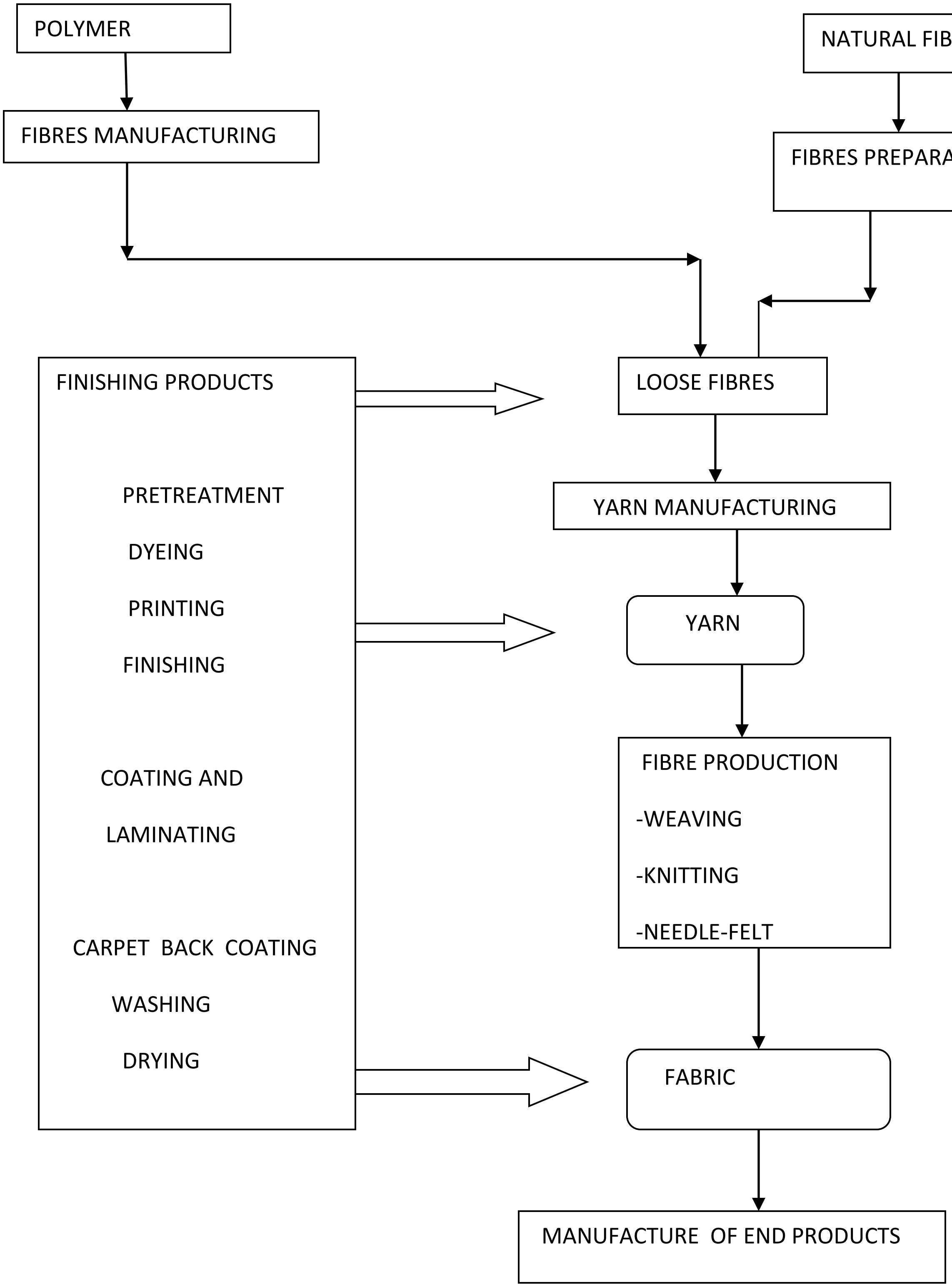


Fig I: Process flow diagram of a textile industry

Surfactants, salt, biocides, ionic metal complexes are the components that creates toxicity in water. Many textile dyes posses high toxicity in aqueous medium. Moreover, surfactants like emulsifiers, detergents and dispersants which are used in several textile processes also contributes in increasing effluent toxicity, foaming and COD, BOD. So heavy metals, nitrogen and dyestuffs are the substances which need to be removed. This effluent generated from the industries in several steps is far beyond the standard values and thus it is highly polluted and dangerous[4].

Characteristics of processed textile wastewater	
Parameter	*Range*
COD	300-1100
BOD_5	120-440
pH	8-11
TDS	200-5000

[5]

1.4.DYES IN TEXTILE INDUSTRIES

Substances that help to color textile fibres are called dyes. They are incorporated into the fiber by dispersion, chemical reaction or absorption. They are used because of their better dyeing conditions and bright colour. Dyes differ in their resistance to gas, alkalies sunlight, perspiration, washing, and other agents; their affinity for different fibers; their reaction with cleaning methods and agents; and their solubility and method of application. Dyeing can be performed at any stage of the manufacturing of yarn,,textile- fiber, fabric or a finished product including garments and apparels. The number of dyes presently in market used by textile industry is about 100000[6]. Among these dyes, the azo dyes constitute largest and the most popular class of commercial dyes. The N=N group of the dye molecules forms the chromophoric group and results in the production of (60–70) % of all textile dyestuffs[7]. There are two factors on which color fastness depends, They are selection of appropriate dye depending on the textile material that need to be dyed and selection of the method for dyeing the fiber, yarn or fabric. Azo dyes have two types of groups: chromophores and auxochrome. Chromophores, an electron withdrawing group add color to fibres. The another group, auxochrome being an electron donating substituent helps to intensify the colour. But 15% of the textile dyes are lost in water stream during dyeing operation[8]. Azo dyes are non-biodegradable under aerobic conditions. Their stability is proportional to the complexity of the molecule's structures. In anaerobic condition these dyes can degrade, but results in producing hazardous and carcinogenic aromatic amines. It is well known that azo dye structure when enter into our body, it get splitted by liver enzymes and intestinal flora and forms aromatic amines. These aromatic amines are responsible for causing cancer in humans [7]. Depending on the type of chromophores dyes can be classified into 20-30 groups. Dyes are classified based on different parameters.

- Nuclear structure – Dyes are classified depending on their structures. It is of two types – cationic (Basic Red 2) and anionic (Reactive green 19).
- Industrial use- Industries use different types of dyes depending on the category of substance i.e. acid, basic, azo, reactive, mordant, vat etc.
- Origin – Dyes are differentiated into different categories depending on source of origin. It can be synthetic or natural.

There are various types of dyes. Depending on their structures they are applied on different substrates. Some of them are as follows:

- **Direct dyes:** They are flat in shape. Their length helps them to increase vander wals force, hydrogen and dipole bonds. The basic structure is sulphonated azo dye. It is applied mainly on cellulose fibers, leather, paper, cotton, nylon etc.
- **Basic dyes:** There is an ionic interaction among copolymer's negative charges and dye's cationic groups and the. It's common structures are azo, diarylmethane, anthraquinone, triarylmethane. It is applied on paper ,synthetic fibers, ink.
- **Reactive dyes:** It forms covalent bonds with -OH, -NH or –SH groups. Complex azo, anthraquinone, phthalocyanine are its common structure. cotton, wool, silk, nylon, azo, metals are the materials on which it is used.
- **Acid dyes:**It is highly soluble in water. It also forms ionic interactions among the $-NH_3^+$ groups of fibers and the negative charge of the dyes and applied on wool, polyamide, silk, nylon, leather.azo, anthraquinone, triarylmethane are its common structure.
- **Disperse dyes:**These dyes are non-ionic in structure.It's functionality improves water solubility, van-der- Waals and dipole forces and the color. Polyamide, acrylic, acetate,

plastics, polyester are the adsorbates.Its common structures are mainly azo, anthraquinone, metal complex azo.

- **Pigment dyes:**They are insoluble in nature.The non-ionic compounds or saltshelps to retain their crystalline particulate. Paints, inks, plastics are the substrate on which it is applied.They are present in the form of metal complex and azo compounds.
- **Mordant dyes**: Their main characteristics is its metal salts that act as “fixing agent” to increase the color fastness .It is applied on wool, leather, silk,modified cellulose, fibers. Azo, oxazine, triarylmethane are its common structure.
- **Vat dyes:**Non soluble coloured dyes is its charecteristics.Substrate on which they are applied are cellulose,fibers, cotton, viscose, wool. Comon structure is Anthraquinone.
- **Solvent dyes:**These dyes are non ionic in nature that dissolve the substrate to which they bind.Its common structures are Di azo, , anthraquinone, triarylmethane phthalocyanine Substrate on which they are applied are plastics, varnish, ink, waxes, fats.
- **Sulphur dyes:**Dyeing with these dyes involves oxidation and reduction processes.They are in the form of complex polymeric aromatics. Cellulose fibers, cotton, viscose are the substrates.

To perform our experiments we have used a solution containing dye ***Reactive Green 19*** and here it is considered textile industrial wastewater.

Commercial Name:	C.I. Reactive Green19
Molecular Formula:	$C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$.
Molecular Structure:	Azo in nature
Colour:	Blue-green powder
Molecular Weight:	1418.94.
Solubility:	120 g/L at 20^{o}C, 150 g/L in 50^{0}C

Manufacturing Method: 3-Aminobenzene sulfonic acid and 2,4,6-Trichloro-1,3,5-triazine and 2,5-Diaminobenzenesulfonic acid condensation. In acidic and alkaline medium coupling its product (2moles) and 4-Amino-5 hydroxynaphthalene-2,7-disulfonic acid.

Applications: It is used for dyeing fabrics blended with polyester/stick or polyester/cotton . It is also applied on cotton with high economic value.

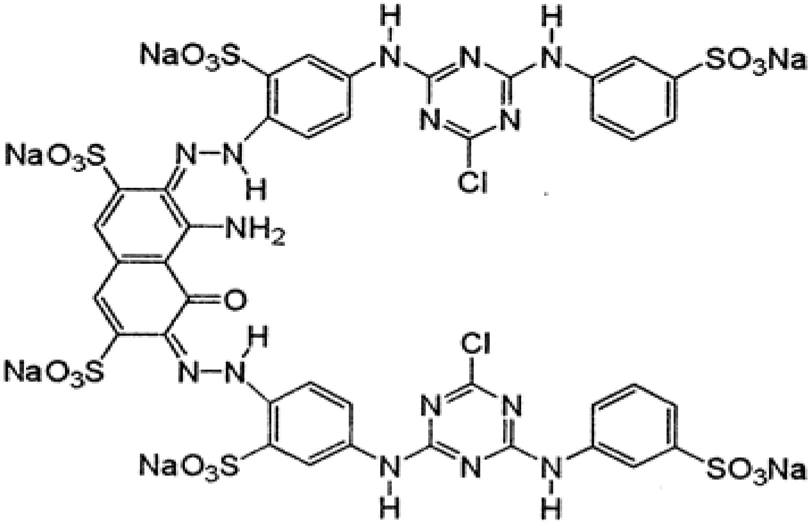


Fig II: Molecular Structure of RG19

1.4.1. DRAWBACKS OF DYES USED IN TEXTILE INDUSTRIES

Dyes of textile industries cause a large number of problems on the environment. The adverse effects faced by us due to dyes are as follows:

- The main problem regarding textile dyes is their reflection and absorption of sunlight that enters into water. Light absorption reduces photosynthetic activity done by the algae and has serious and adverse influence on the overall food chain.
- Sometimes many dyes and also their breakdown intermediate products are toxic to life and also have carcinogenic, mutagenic effects on organisms. Dyes are discharged into water bodies through effluents.
- Very small amount of dyes in water (< 1 mg/L) is also highly visible because of their brilliance nature.[8].

- Prolonged exposure and high concentration dyes of textile industries causes acute, chronic effects on organisms.
- For a very long period of time dyes remain in the environment because of its high thermal and photo stability properties. Hydrolyzed Reactive Blue 19 stay in the environment for nearly 46 years at neutral pH and 25°C because that is it's half-life
- It causes respiratory diseases, skin irritation, allergies in eyes etc.

1.5. TRADITIONAL METHODS OF WASTEWATER TREATMENT

Several physical and biological methods have been developed for decontamination of municipal, industrial waters and wastewaters. They are as follows.

Chemical Precipitation: Chemical precipitation is used to eliminate ionic constituents from water by adding coagulants such as iron salts, lime ,alum, and other organic polymers to reduce the solubility. It is used basically for the removal of metallic cations and anions (fluoride, cyanide, and phosphate). Organic molecules such as aromatic amines and phenols are removed by this method. Production of large amount of sludge containing toxic compounds throughout the process is the main drawback.

Microfiltration: It is a pressure driven membrane process. For removing heavy metals this process use porous membranes .In this process filtration of a colloidal suspension or other fine particles of dimension roughly 0.02 µm to 10 µm is done. In ultra filtration the only difference is in particle size which lies in the range of 0.15 µm to $5x10^{-2}$ µm .The main drawback of both the processes are generation of sludge.

Reverse Osmosis: It helps in separating only dissolved solids from wastewater through a semi-permeable membrane when the pressure is larger than the osmotic pressure. The drawback of this method is it's cost.

Electro dialysis: It is a membrane process where separation of ions is done through the membrane through the application of electrical potential. Membranes allow selective transfer of cations or anions.The drawback of the process is the production of hydroxides of metals which will clog the membrane.

Ion-exchange: Here metal ions of dilute solutions get exchanged with ions held through electrostatic forces on exchange resin. The drawbacks include partial removal of certain ions and high cost.

Photo-remediation: Here we use certain plants to clean up sediment, soil, and water contaminated with metals. The drawbacks include: long time to metal removal, the difficulty in regenerating plant for further bio-sorption .

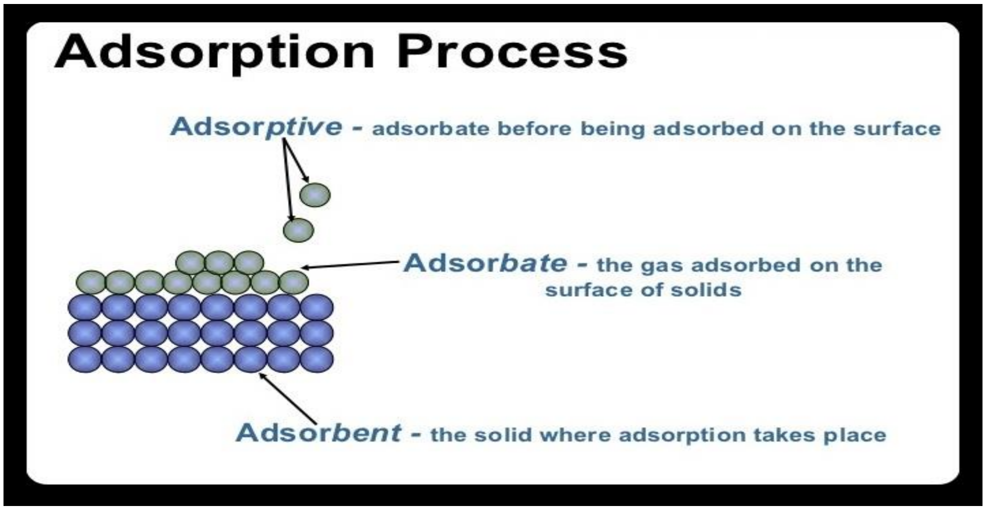
Bio sorption: Certain types of dead, inactive, microbial biomasses bind with heavy metals from every dilute aqueous solution. Particularly some algae, fungi's,yeast cell structures are responsible for this phenomenon and act as metal bio sorbents[9]. Advantages of this process are low cost, environment friendly, possibility of metal recovery, regeneration of bio-sorbent and minimization of chemical , biological sludge. But efficiency is comparatively low.

Hence now it is essential to remove the toxic elements and pathogens from wastewater in order to meet the necessities of various purposes like industrial ,irrigation and domestic use. Previously, for removing organic pollutants several traditional physical and biological treatment methods (coagulation, adsorption, ultrafiltration, etc.) have been used. These methods are either inefficient or costly for removal of harmful toxic pollutants from wastewaters. So the is a urgent requirement to develop novel techniques for transferring the toxic, hazardous pollutants chemically into inorganic, benign species. AOPs are more efficient, cheap, and eco-friendly in the nature and has the ability to degrade every category of toxic pollutants. Advance oxidation processes the ability to generate a strong oxidant(i.e. hydroxyl radical) , which completely degrade and mineralize every type of pollutants into products without causing any harm.

In this discussion we will compared the efficiency of the two processes-Adsorption and Heterogeneous photo catalytic degradation taking textile wastewater containing RG19 dye .Their corresponding advantages and disadvantages will also be discussed. Industrial slag has been taken as an adsorbent and catalyst TiO_2 for Heterogeneous Photo catalysis has been used.

1.6.ADSORPTION

Adsorption is described as the process of collecting of molecules by the liquids surface or the external surface (walls of capillaries or crevices) of solids. Solids that are used to adsorb gases or dissolved substances are called adsorbents and adsorbed molecules are referred as the adsorbate. Absorption refers to processes in which a substance penetrates into the actual interior of crystals, blocks of amorphous solids, liquids. Sorption indicates the process of taking up of a liquid or gas by a solid without specifying whether the process is adsorption or absorption. Thus sorption encompasses both the adsorption and absorption processes. Adsorption process is defined as a surface phenomenon. Like surface tension, adsorption takes place due to the presence of surface energy. In bulk materials, the necessity of bonding (be they, metallic or ionic covalent) of the material's constituent atoms are filled by other atoms of the material. But, atoms of the adsorbent's surface are not fiully surrounded by other adsorbent atoms and so it can attract adsorbate. Depending on the details of the species involved the exact nature of the bonding can be defined. There are two types of adsorption- chemisorptions and physiosorption. Physical adsorption depends on van der Waals force of attraction between the adsorbate molecules and solid adsorbent. There is no chemical specificity in this type of adsorption. Any gas tending to be adsorbed on any solid if the pressure of the gas sufficiently high or the temperature is sufficiently low. In chemical adsorption, gases get attached to a solid surface by chemical forces which are specific for every adsorbate and each gas. Chemical adsorption occurs usually at temperatures higher than the temperature at which physical adsorption. Adsorption is present in many natural, chemical, biological and physical systems, and is also used in industrial applications Adsorption, chromatography and ion exchange are sorption processes in which there is selective transfer of adsorbate from the fluid phase into the surface of insoluble, rigid particles packed in a column or suspended in a vessel [10].



FigIII: Schematic diagram of Adsorption process

1.6.1.APPLICATIONS OF ADSORPTION

I. Adsorption process is used for the separation of gases from a gas mixture, removal of toxic gases.
II. It is used for separating water vapours from air.Moreover it is applied for return of valuable solvent vapors from solvent-laden air and other gases.
III. Adsorption process is used for separation of solute from solution and removal of moisture dissolved in gasoline, decolonization of sugar solution, vegetables oils and petroleum products, removal of objectionable odor ,taste and separation of organic components from aqueous waste for water pollution control.
IV. Separation of ions from solutions and demineralization of water by ion exchange.
V. This process is used to remove odour from municipal illuminating-gas supplies.
VI. This process is used for clarification of beverages.

1.6.2.VARIOUS ADSORBENTS

Popular types of adsorbents are Activated Alumina, Zeolites, clay, silica gel, carbons, polymer and resins. Each adsorbent has its own characteristics such as pore structure, pore size and surface nature. Some of the adsorbents and their applications are given below:

Activated Alumina: It is used for drying of gases, organic solvents, transformer oils and removing HCl gas is removed from hydrogen. In alkylation process removing of fluorine is done using activated alumina.

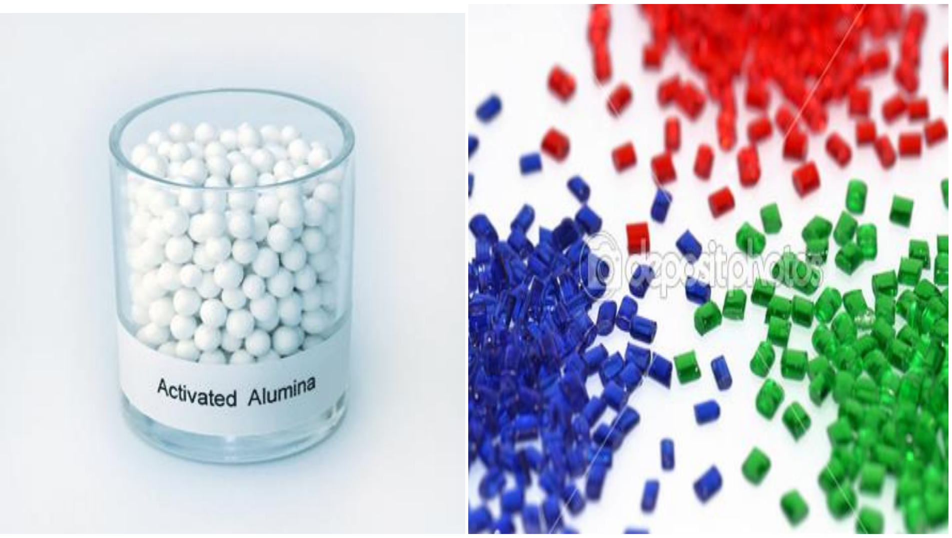
Silica Gel: Drying of gases, organic solvents, refrigerants, transformer oils, desiccant in packing, dew point control of natural gas and double glazing are some of the fields in which they are applied.

Activated Carbons: It is applied for removing hydrogen from syn gas, nitrogen from air, vinyl chloride monomer (VCM) from air ,ethane from methane and hydrogen, odours from gases, cleaning of nuclear off-gases.

Polymers & Resins: Separation of fatty acids from water and toluene,Removal of colors from syrups,Removal of organics from Hydrogen peroxide,Water purification,Recovery and purification of steroids, amino acids.

Zeolites: It is used for removing water from azeotropes, sweeting of sour gases and liquids, purification of hydrogen, recovery of carbon monoxide from methane and hydrogen, recovery of acetylene, propane and butane from air and separation of xylene and ethyl benzene

Silica Gel ***Activated Carbon***



Activated Alumina ***Polymer Resins***

Fig IV: Several popular Adsorbents

1.6.3.ADVANTAGES AND DRAWBACKS OF ADSORPTION PROCESS

Advantages:

- Products can be recovered.
- This systems can be fully automatic.
- The process parameters can easily be manipulated and controlled and the response obtained is excellent.

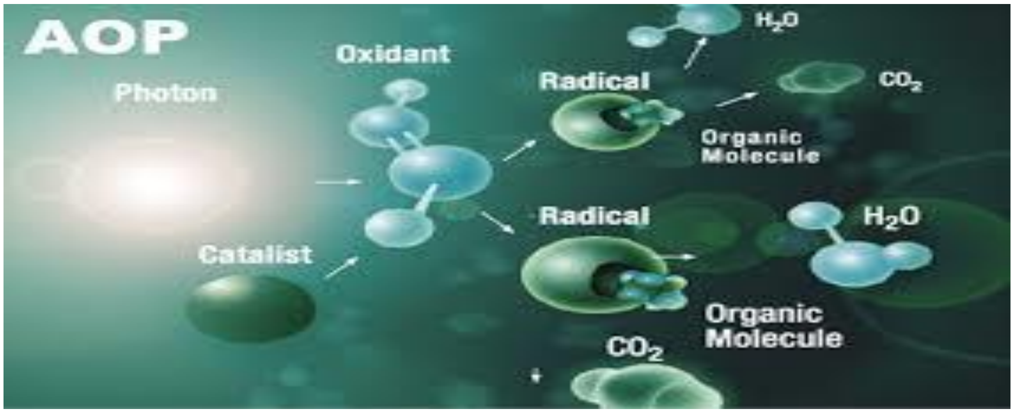
Disadvantages:

- Following a special, expensive distillation (or extraction) product can be recovered.
- Efficiency of adsorption process decreases due to the reduction of adsorbent capacity. In some cases product recovery involves high capital cost.
- Used adsorbent sometimes considered as hazardous secondary waste.

In order to overcome these disadvantages now a days more efficient alternative methods are followed one among them is Advance oxidation process.

1.7.ADVANCED OXIDATION PROCESSES (AOPs)

Advanced oxidation processes (AOPs) refer a set of oxidative wastewater treatment processes. It is used to treat toxic effluents of industries, hospitals and wastewater treatment plants. It is more efficient, cheap, and eco-friendly in the degradation of any kind of toxic pollutants because AOPs are successful to transform toxic organic compounds (e.g. drugs, pesticides, aromatics, volatile organic matter, petroleum chemical constituents, endocrine disruptors etc) into biodegradable substances. AOPs generate hydroxyl radical, a strong oxidant, which can completely degrade or mineralize the pollutants non-selectively into harmless products. It is mainly used for cleaning biologically toxic, non degradable materials such as volatile organic matters of industries, pesticides from agricultural waste etc. Contaminant materials through mineralization are converted into water, CO_2 and salts. A objective of using AOP is to reduce the concentration of hazardous chemical contaminants and their toxicity to such an extent that the waste water after treatment can be recycled or discharged into a sewage treatment plant so that it do not cause any harm.



Now a day's AOP is usually used for eliminating contaminants from polluted water coming out of many types of heavy industries like chemical industry, Petrochemical & Plastic Industry, pharmaceutical industry, Food processing industry, textile and dying industries. At present the main cause of generation of effluents in textile industries is the use of huge volume of water either in chemical processing or during re-processing in dyeing, preparatory, printing and finishing.

1.7.1.AOP MECHANISM

It takes place in the following sequential steps:

1. Formation of strong oxidants(i.e. hydroxyl radical)
2. Reaction of the oxidant with toxic non biodegradable toxic compounds in the water producing biodegradable intermediates.
3. Reaction of the biodegradable intermediates with oxidants is referred as mineralization.

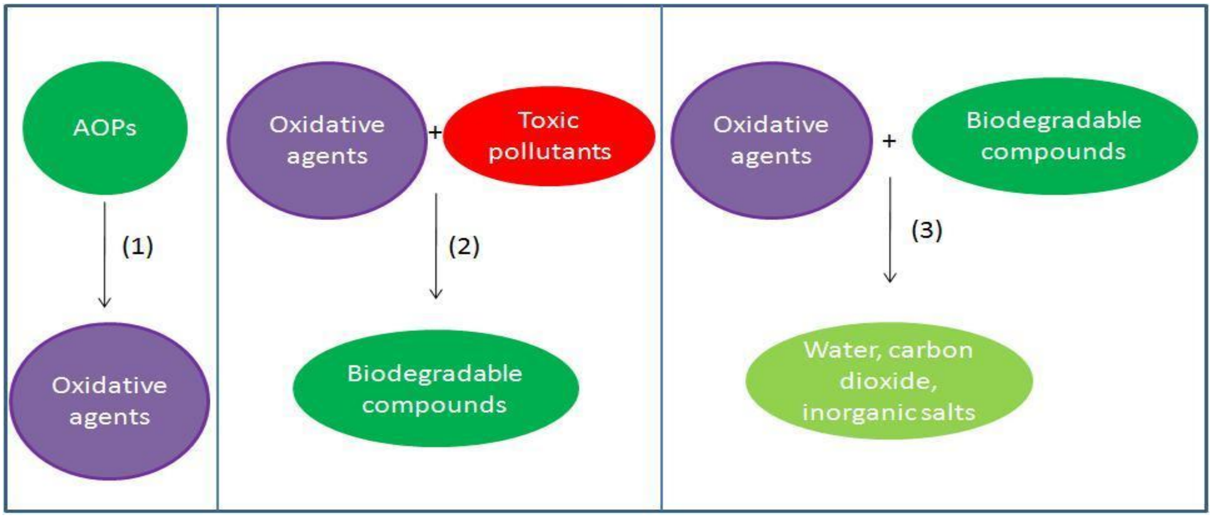


Fig V: Mechanism of AOPS

1.7.2.ADVANTAGES AND DRAWBACKS OF ADVANCE OXIDATION PROCESSES

Advantages of AOPs:

- Reaction rate is fast.
- Capability of complete mineralization and reduction of toxicity of organic wastes into stable inorganic compounds such as CO_2, water and salts. There is no necessity of any more treatment by different methods like membranes.
- Because of complete reduction by $^{\bullet}OH$ the final product is H_2O. Thus AOPs do not generate new hazardous substances.
- Does not create secondary products as produced by biological processes or physical chemical process.
- It could effectively degrade organic contaminants present in the aqueous phase, instead of collecting or transferring pollutants into another phase.

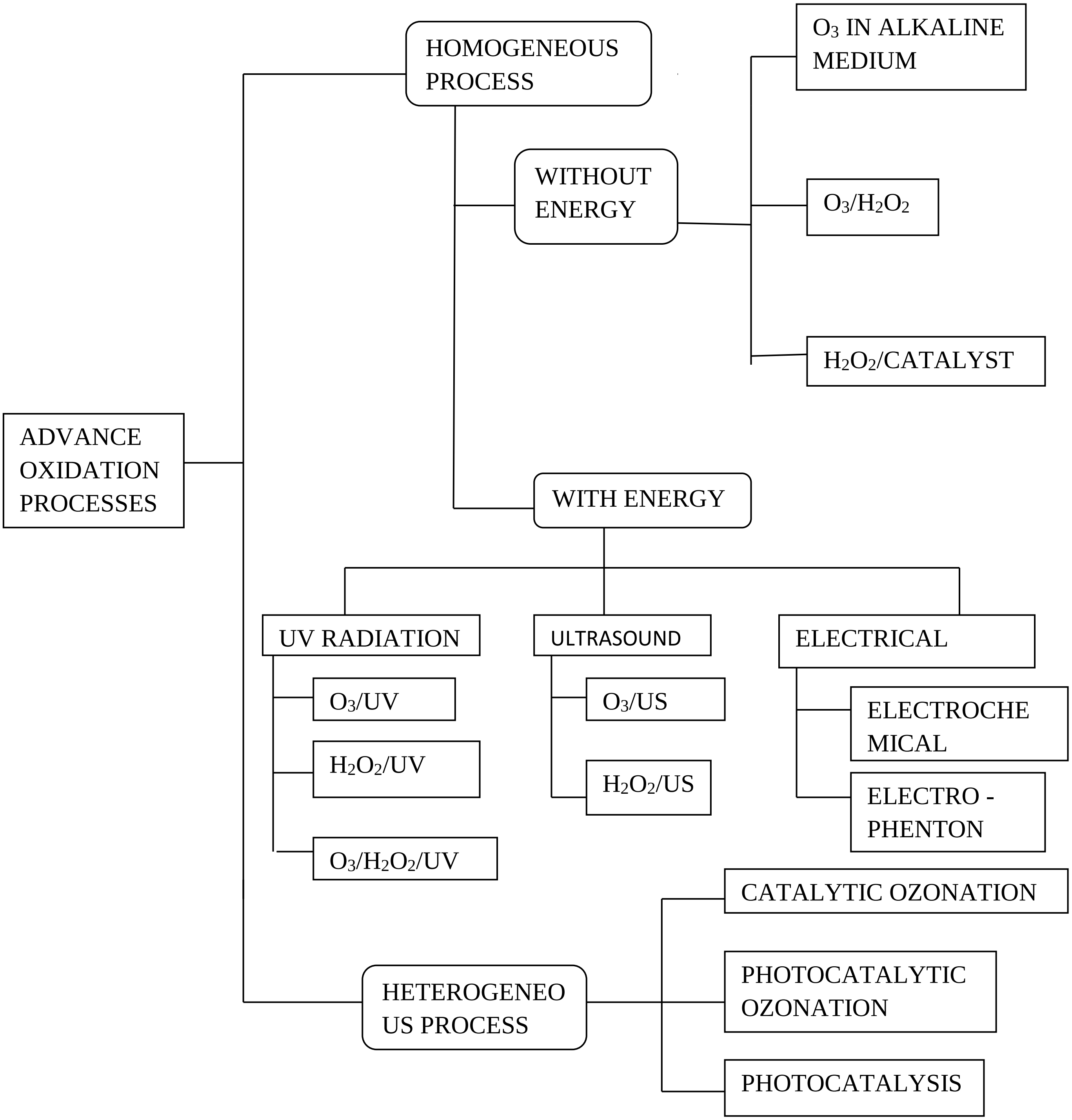
- Following AOPs several organic contaminants of the waste water get degraded at a same time due to the non selective nature of $^{\bullet}OH$ radical.
- By the formation of precipitates of $M(OH)_x$ certain heavy metals are removed.
- To solve water quality problems certain AOP design could also be used.
- Adaptable to small scales in developing countries.

Drawbacks:

- Relatively high cost of operation due to chemicals and/or energy input.
- Oxidative intermediates formed may be potentially toxic.
- Engineers are required for operation and design.
- Emerging technologies still require lot of researches.
- Requirement of complex chemistry to specific application.

1.7.3.TYPES OF AOPS

There are different categories of AOPS. They are as follows.:



Among these AOPs, for our analysis we have used Heterogeneous Photo catalysis by TiO_2 for degradation of RG19 dye.

1.7.4. <u>HETEROGENEOUS PHOTO CATALYSIS USING TiO_2</u>

This process of degradation can be defined broadly as an oxidation process occurring in aqueous phase. It is basically based on the attack of the hydroxyl radical, resulting in the destruction of toxic organic contaminated compound. A substance that gets activated by adsorbing photon and then become capable of accelerating the reaction without being consumed is defined as photo catalyst. These substances are invariably semiconductors. These have been increasingly focused in recent years due to their potentiality of environmental purification and ability of converting solar energy. Semiconductor heterogeneous photo catalysis has huge potential to convert organic contaminants into water and air. Among AOPs, heterogeneous photo catalysis has proven to be of interest because it being efficient in degrading recalcitrant organic compounds. This oxidation has been given considerable attention since 1970 and in the last two decades numerous studies have been carried out on the application of heterogeneous photo catalytic process with the aim of decomposing and mineralizing recalcitrant organic compounds. It involves in increasing the rate of photoreaction with semiconductor catalyst. Several semiconductors (TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as photo catalysts but TiO_2 has been most commonly studied due to its ability to degrade organic pollutants and even achieve complete mineralization. Hydrophilic and photo catalytic properties of TiO_2 makes it an ideal catalyst because of its high reactivity, chemical stability, reduced toxicity and lower costs.

<u>Mechanism:</u> Heterogeneous photo catalysis using UV/TiO_2 is a effective method for dye degradation. and day by day this process is becoming popular because this technique could degrade organic pollutants into water and CO_2 without generation of any harmful by products. This technique depends on adsorption of photons with energy greater than 3.2 eV (wavelengths lower than ~390 nm) on catalyst resulting in initiating excitation. This leads to charge separation event (gap band). Generation of excited high-energy states of hole and electron pairs happens when semiconductors are irradiated with energy higher than their band gap energy. It results in promoting an e^- in the conductive band (e_{CB}^-) and forming a positive hole in the

valence band (h_{VB}^+). The h_{VB}^+ (powerful oxidizing agent) and e_{CB}^- (reducing agent) plays important roles.Reaction of h_{VB}^+ with water result in formation of hydroxyl radical (•OH).Organic compounds react with these •OH radical, producing CO_2, mineral acids and H_2O as end products. Hydroxyl radical (•OH) produced by this process has the second highest oxidation potential (i.e. 2.80 V), which is only bit lower than the strongest oxidant – fluorine. Oxidation potential of other oxidizing agents such as singlet oxygen, ozone, permanganate and hydrogen peroxide, and with the oxidation potentials 2.42, 2.07, 1.68, and 1.78 V, respectively, which are less than that of •OH .Due to its electrophilic nature (electron preferring), the •OH has the ability to non-selectively oxidize almost all electron rich organic molecules, and finally convert them into CO_2 and water.

TiO_2 +hv(387 nm)→ e_{CB}^- + h_{VB}^+ ....(1)

H_2O + h_{VB}^+ →·OH + H^+ ....(2)

h_{VB}^+ +R → intermediates → CO_2+ H_2O ....(3)

·OH + R → intermediates →CO_2+ H_2O .... (4)

Dye+ h_{VB}^+ = oxidization products ……..(5)

Dye+ e_{CB}^- = reducing products ……..(6)

e_{CB}^- + O_2→ O_2· …….(7)

R is representing organic compounds

The conductive band when react with O_2 forms an anion radical superoxide as shown in Eq. 5. If reaction continues then it leads to the generation of hydrogen peroxide which further results to the formation of •OH.

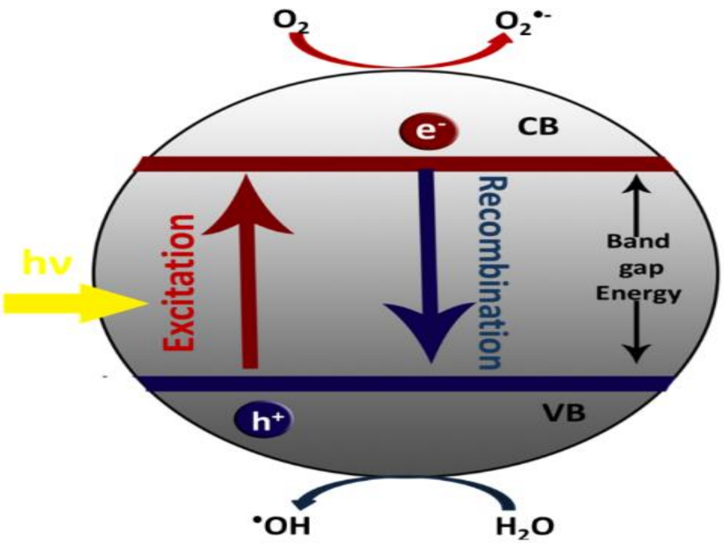


Fig VI: Mechanism of Heterogeneous Photocatalytic degradation

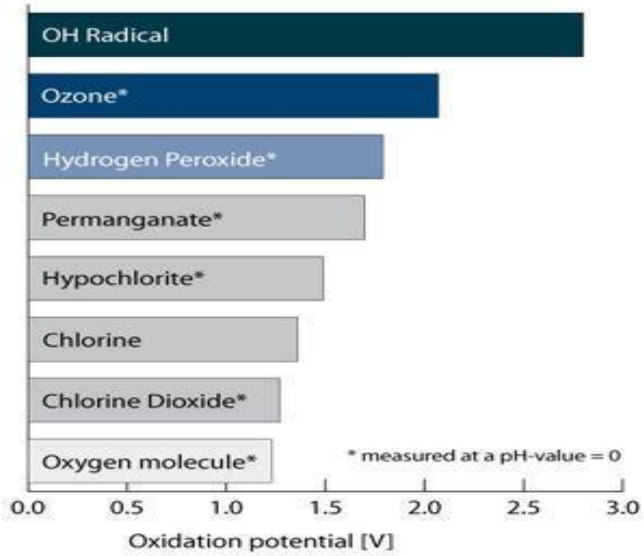


Fig VII: Oxidation potential of the elements in ascending order

Dissolved oxygen presence plays an vital role in photocatalytic degradation activity as it prevents the recombination process on TiO_2 (e_{CB}^- /h_{VB}^+) Thus it helps to maintain the electro neutrality of the TiO_2 particles[11].

1.7.5.FACTORS AFFECTING HETEROGENEOUS PHOTOCATALYSIS

From literature study we can come to a conclusion that there are several parameters that controls the rate of photocatalytic degradation process. They are nature and composition of the photo catalyst, intensity of light, Initial concentration of substrate, Catalyst Dose and mode of its application, pH of the reaction medium, type of oxidizing agents, temperature, types of solvents that are used, ionic compounds in water etc.

1.7.6.ADVANTAGES OF CATALYST-TiO_2

Several researches are performed to photo catalytically degrade toxic organic pollutants of waste water into CO_2, mineralize salts and H_2O. In this process TiO_2 is proved to be a very efficient catalyst because of the following reasons:

- The process will also give good result using sunlight. Thus the reaction can also take place under ambient conditions. It can be accelerated with the help of UV light.
- TiO_2 is easily available. It’s non-toxic nature, mechanically and chemically stability makes it highly acceptable in research field.
- TiO_2 can be coated in the form of thin films on desired suitable reactor substrates. So it is easy to use and highly efficient.
- Complete oxidation of the hazardous toxic chemicals into CO_2 is feasible.

Hence our study tries to create an overview for treatment of textile waste water by using adsorption process and Heterogeneous photo catalysis .

CHAPTER – 2

LITERATURE REVIEW

2.1.<u>ADSORPTION</u>

*Haizhen Li(2016)*used modified pomelo peel as a new non-conventional and low-costadsorbent for the removal of cationic dye (methylene orange) from aqueous solution. Batch adsorption experiments were carried out at 273 K, 293 K and 327 K. Equilibrium sorption isotherms and kinetics were investigated. The maximum adsorption capacity calculated from the Langmuir model was 680 mg/g (temperature= 323 K)[12].

Kheira Chinoune (2016) showed removal of anionic dyes i.e. Reactive blue 2 (PB) and Reactive blue 19 (RB) using brucite-coated bentonite .The maximum adsorption capacities for reactive dyes PB and RB were estimated at 298 K are 40.22 and 66.90 mg dye/g adsorbent, respectively. This adsorption process fits by the Langmuir model and thermodynamic studies showed that the adsorption of dyes is endothermic process[13].

Gabriela G. Sonai (2016) showed use of sludge generates from textile industries as adsorbents for the removal of Reactive Red 2 dye. Adsorption isotherm modeling and batch kinetic experiments were conducted under different temperature and pH conditions. This adsorption process was totally dependent on the pH of the medium but not on the temperature within the ranges studied. The maximum adsorption capacities were 159.3 mg g/1 for the biologically treated adsorbent and 213.9 mg g/1 for physical-chemically treated adsorbent at pH of 2 and 25 ^{0}C. The equilibrium data fits Langmuir model. Kinetic studies indicate that these process obeys pseudo-second-order model .[14].

Jian-Zhong Guo.et.al. (201*4)* used Chemically modified bamboo (CMB) as an adsorbent whose characterization study was done by using Fourier transform infrared (FTIR) spectra. Adsorbent was methylene blue (MB) in aqueous solution. Elemental analysis, help to conclude the introduction of carboxyl groups and diethylenetriamine into the adsorbate's surface. Effect of different parameters like pH, temperature, amount of Adsorbent etc was observed. It was found that this process fits Langmuir mode. Maximum adsorption capacity of CMB was 606 mg g^{-1} at 298 K, which is much more than the values obtained using other bio adsorbents previously.[15].

Emna Errais(2012) investigated the adsorption mechanism of anionic Reactive Red 120 dye using raw clay as an adsorbent. Surface properties of raw clay were studied. Natural untreated clay due to the presence of major amount of kaolinite is an effective material for adsorption of anionic dye at ambient temperature & initial pH(pH=4)[16] .

Mohamad Rasool Malekbala(2012) shows the use of sugar beet pulp as a low-cost adsorbent for the removal of dyes safranine and methylene blue from aqueous solutions. These dyes are cationic in nature.Several factors such as adsorbent mass, isotherm models, pH pzc, adsorption kinetic, pH of the solution and surface chemistry were investigated. Kinetic data fits pseudo second-order model for both the dyes[17].

Tayyebeh Madrakian.et.al. (2012) assessed adsorption of seven different organic dyes such as Congo red, neutral red, methylene blue , reactive blue 19, Janus green, crystal violet and thionine from aqueous solutions using magnetite nano particles loaded tea waste (MNLTW). MNLTW was prepared following a simple method . It's properties ware fully characterized by X-ray diffraction , scanning electron microscopy .[18].

V.K. Gupta (2009) showed the use of three different low cost adsorbents for dye removal. It was observed that some low cost adsorbents has fast and efficient adsorption capacities . Adverse effects and benefits of these adsorbents are mentioned. Optimum conditions in which the systems efficiency is favourable is obtained in this study. Adsorption capacities of these low-cost adsorbents available in this study were shown[19].

2.2.PHOTO CATALYTIC DEGRADATION

Elisabetta Petrucci(2015) illustrated modeling and optimization of Reactive Green 19 by Oxidation on a BDD thin-film electrode. Under galvanostatic conditions oxidation experiments were carried following a central composite design. Current density (100–500A/m^2), pH (3–11), chloride concentration (0–0.5) M and agitation rate (250–750) rpm are the investigated factors , while the efficiencies of color and TOC removal are shown by the response variables. Under optimal conditions, the efficiencies of color and TOC removal values reached nearly to 90% and 80%, respectively[20].

Said Alahiane (2014) assessed photo catalytic degradation of the dye(Reactive Yellow 145) in the presence of TiO_2-Coated Non-Woven Fibers. Effect of different operational parameters (initial concentration, pH, addition of H_2O_2, addition of ethanol) on the reaction rate had been investigated. Effect of some inorganic ion generally present in real effluents such as SO_4^{-2}, Cl^-, NO_3^-, CH_3COO^-,$HCO_3^-$and $HPO_4^{-2}$was also examined. Optimum pH for maximum dye removal was observed to be 3 and that of ethanol was 2ml. TiO_2-Coated Non-Woven Fibers eliminate tedious effluent filtration process[21].

M. Rastegar (2012) optimized photo catalytic degradation process RG 19 using ceramic-coated TiO_2 nano particles. RG19 is sulphonated diazo in nature.Reaction time 240 mins, flow rate 150mL/min, UV light intensity 47.2W/m^2 and initial dye concentration 10 mg/L were the optimum values for maximum decolonization using central composite design . Mineralization of RG19 was monitored through chemical oxygen demand (COD) decrease and changes in the UV–Vis spectrum[22].

Antonio Zuorro(2013) explained advanced oxidation process of RG 19 dye using TiO_2.Effect of UV radiation and hydrogen peroxide had been explained. Kinetic analysis explained that the process obeyed first ordered kinetics. Total organic carbon (TOC) measurement value showed that mineralization was slower than decolonization. More than 63% of TOC was removed in 90 min. Overall, the results obtained indicates that the UV/H_2O_2 treatment can be an effective, efficient method for the removal of dye RG19 from textile effluents[23].

D. H. Tseng.et.al (2012) assessed the effects of H_2O_2 and oxygen for degradation of monochlorobenzene (MCB) in the presence of UV and TiO_2 process. This study provided important information that the oxygen is a vital parameter for initiating this degradation process.[24].

S. Ahmed.et.al (2011) investigated the effect of several parameters i.e. temperature, pH, catalyst dose, initial dye concentration etc on the heterogeneous photo catalytic degradation. Pesticides and phenol were the contaminants present in the effluents[25].

M. N. Chong.et.al (2011) studied the modeling and optimization of photo oxidation processes for treatment of wastewater. They showed the technique of using multi-variables optimization in order to calculate the optimum values of operation parameters and to increase the efficiency of photo oxidation. The effects of different parameters are assessed in this study.[26].

A.H. Mahvi et al (2009) studied the photo catalytic oxidation of reactive orange-16(RO-16) in aqueous solution in presence of TiO_2 and UV radiation. Effects of several parameters and their optimum values such as pH, amount of TiO_2, initial dye concentration, presence of anion on dye degradation has been investigated. The mineralization result was obtained by measuring initial and final values of COD in the solution. Data fits a pseudo-first order equation[27].

CHAPTER – 3

AIMS AND OBJECTIVES

We have derived from several literature reviews that textile waste water containing dyes have several adverse effects on the environment. So many researches had been done on degradation, decolonization of textile dye present in waste water. We have assessed that waste water containing dye of concentration in the range of 30 – 40 ppm can be discharged in the environment safely. So several research work have been performed on adsorption& photo catalytic degradation Process (Heterogeneous AOP) had been performed to meet the requirement by degrading the dye to the mentioned safe range .

At first textile wastewater containing RG 19 was simulated. Then industrial slag was used as adsorbent. Industries are recently facing problem regarding disposal of slag. It is reused as adsorbent for adsorption process. Different runs in batches were taken by varying different parameters (i.e. Temperature, pH, RPM , Adsorbent Dosage, etc.).Characterization like SEM, kinetic studies and analysis of different adsorption isotherms (Langmuir, Freundlich etc.) were done.

Photo catalysis process was used for dye degradation.

- Different runs in batches were taken at different parameters e.g. pH, TiO_2dosage,intensity etc. and optimizing them.
- Comparison between % removal between adsorption and photocatalysis was done.
- Kinetics studies based on those data was carried out.

FLOW SHEET

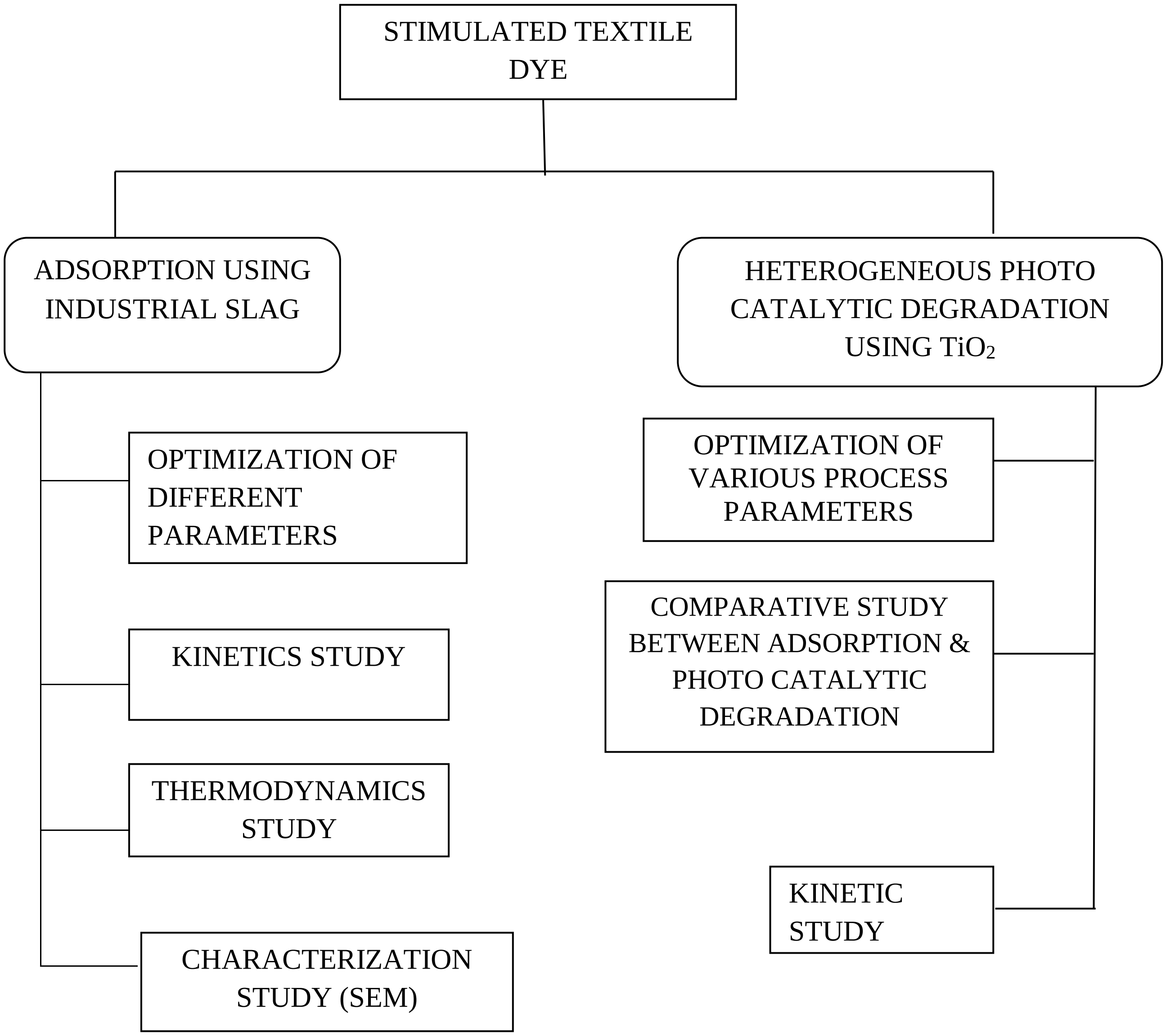


Fig VIII: Flow chart of the work to be done

CHAPTER – 4

ADSORPTION STUDY OF TEXTILE EFFULENT BY INDUSTRIAL WASTE

4.1 CHEMICALS

Reactive Green 19 of molecular formula $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$ (molecular weight 1418.94) was purchased from Sigma-Aldrich Chemicals and used without purification. A stock solution of 300 ppm of RG 19 solution was prepared by mixing the dye with double distilled water and diluted as per requirement.H_3PO_4 and NaOH were purchased from Mark India Ltd., Mumbai, India. Laboratory grade water was produced from Sartorious arium pro VF(Germany) pure water system. Industrial slag was collected from a local steel industry.

4.2. EQUIPMENTS

The batch experiments were conducted in aSartorius made rotating & time controlling shaker. The pH of the different samples was checked by pH meter(Hanna).The samples were centrifuged by a cold centrifuge (Superspin RV/ F m Plasto crafts).

4.3.INSTRUMENTS FOR ANALYSIS

The dye concentration was determined by finding out the absorbance at λ max= 630 nm by using UV-Vis spectrophotometer (Varian Cary Bio50).

4.4.EXPERIMENTAL METHOD

The batch experiments were performed in an Erlenmeyer flask by taking 30 ml of the dye solution of desired concentration. The solution pH was adjusted by 1(N) NaOH or 1% H_3PO_4. Then required amount of industrial slag was added to the dye solution and was placed in a rotary shaker for 130 mins. After that the samples were collected and centrifuged for 10 minutes in a cold centrifuge.After centrifugation the supernatant was analyzed with the help of a Spectrophotometer. The percentage removal of RG19 dye was calculated using the following equation

$$\text{Percentage Removal} = (C_0 - C_t)/C_t \times 100 \qquad \text{……… (1)}$$

Where, C_o = Initial dye concentration

C_t = Dye concentration at time t

4.4.1SOLUTION pH

In this present study, pH of the 30 ml of 100 ppm dye solution was varied with the help of acid or base. Then 0.09 gm of industrial slag was added to the simulated dye solution and kept in a thermostatic rotary shaker at a constant speed of 150 rpm for 130 mins at 30° C.

4.4.2. AMOUNT OF ADSORBENT

To study the effect of amount of adsorbent on removal of RG-19, different amounts of slag (0.01 – 0.17) g were taken and agitated with 30 ml of RG-19 solution of 100ppmfor 130 mins at 30° C without changing the pH. The experiments were performed in Erlenmeyer flasks..The flasks were kept in a thermostatic rotary shaker at a constant 150 rpm at 30° C. The dye concentrations were measured at equilibrium condition.

4.4.3. EQULIBRIUM STUDIES

Adsorption process studies were performed by adding a fixed amount ofadsorbent (0.3 g) into a number of stoppered glass Erlenmeyer flasks containing a specific volume of different initial concentrations (50–200 mg/L).The simulated dye solution pH and temperature of 30 ◦C kept constant. The flasks were kept in atime controlled rotary shaker and a fixed rotation speed was provided for 130 mins to make sure equilibrium was reached. The dye concentrations were measured using UV–vis spectrophotometer at 630 nm wavelength. The amount of dye adsorbed at equilibrium, q_e (mg/g), was evaluated by the equation given below:

$q_e = (C_0 - C_e) \times (V/W)$……………………………… (2)

Percentage dye removal = $[(C_0 - C_e)/C_0] \times 100$………………….. (3)

Where C_o and C_e (mg/L) are the liquid-phase dye concentrations at initial and equilibrium, condition. *V* (L) is the volume of the solution and *W* (g) is the weight of dry sorbent used. The dye removal percentage can be calculated as follows:

4.4.4. BATCH KINETIC STUDIES

Kinetic tests were performed in similar pattern to that of equilibrium experiments. The samples were collected at certain time intervals. Then the samples were centrifuged and the dye concentrations were measured. pH was not adjusted for these kinetic tests.

At time t the amount of sorption, q_t (mg/g), was calculated by:

$q_t = (C_0 – C_t) \times (V/W)$ ………………………………… (4)

whereC_t (mg/L) is the liquid-phase concentration of dye at any time.

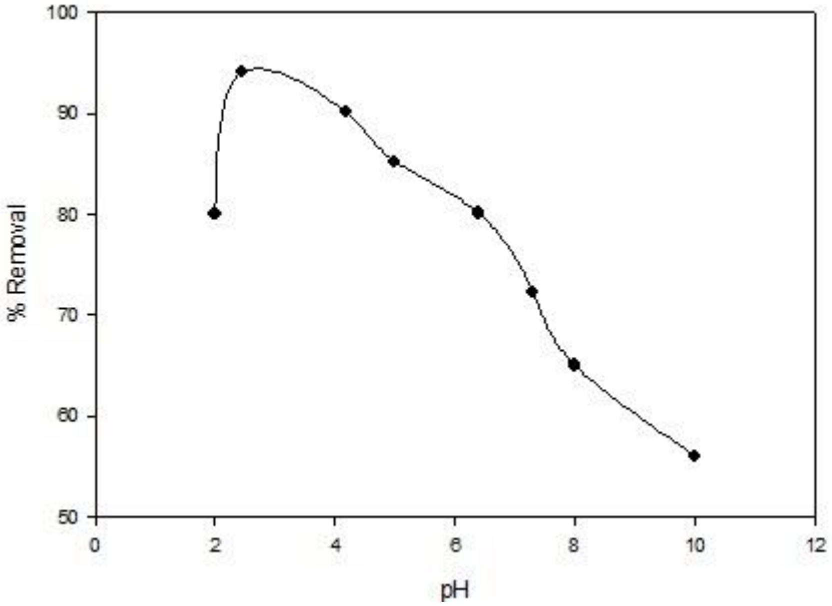
4.5. METHODSFOR ANALYSIS

First the dye samples containing slag were collected.Then they were centrifuged for 10 minutes. Using a double beam UV spectrophotometer the dye concentrations were measured at an absorbance of 630 nm.Using the standard RG solution of known concentrations.the calibration curve was derived before the measurements were taken.

4.6. RESULTS AND DISCUSSION

4.6.1.EFFECT OF SOLUTION pH

To study the effects of pH of the solution its value was varied from 2 to 10.0.The experimental results are illustrated in the Fig IX. It is clearly shown in the figure that percentage removal decreases from 80% to 56%as initial dye solution pH changes from acidic to basic region. pH influences the surface charge of adsorbent, the structure of the dye ,the degree of ionization of various pollutants, as well as the degree of dissociation of functional groups on the active sites of slag. At lower pH, the large quantity of hydrogen ions (H^+) in the solution made the slag surface positively charged and this leads to a higher adsorption performance for RG 19 due to the strong electrostatic attraction between positive charged surfaces and the anionic dye [12]. In contrast, in alkaline medium the negatively charged surface causes repulsion between OH^- ions of the surface and the dye molecules. But if the concentration of H^+ become excess (i.e. pH<2.5) % removal decreases because of hydrogen bonding, ion exchange. Hence we can conclude that at pH 2.45 amount of dye removal is maximum and it can be used for the optimum pH for this study.



FigIX: Effect of pH for decoloration of RG19 on slag (Adsorbent dose = 0.09g/30mL; stirring rate=150 rpm; C_0 =100mg/L; temperature = 30^0C)

4.6.2. EFFECT OF ADSORBENT DOSAGE

The amount of adsorbent (g) was varied to determine the effect of adsorbent dose on % removal of dye. The initial concentration of dye was taken as 100 mg/L. Fig X shows the effect of various amount of industrial slag on the % reduction of RG 19 dye concentration. From the figure it can be derived that the removal percentage is proportional to the dose of adsorbent. But after the optimum value of adsorbent was obtained there was no significant change in the removal % of dye. When equilibrium is reached, the % removal increased from 72 % to 94.09 % with slag amount from 0.01 to 0.09 g. After that, further increase of adsorbent amount from 0.09 to 0.17g the % removal does not varies as such. Number of active adsorption sites and available sorption surface are the factors that helps in decolorization of the dye[17]. But after the equilibrium is reached (i.e. 0.09 g) the overlapping of the adsorbate's active sites kept the degradation rate constant. So, optimum slag amount was 0.09g of adsorbent per 30mL of dye solution.

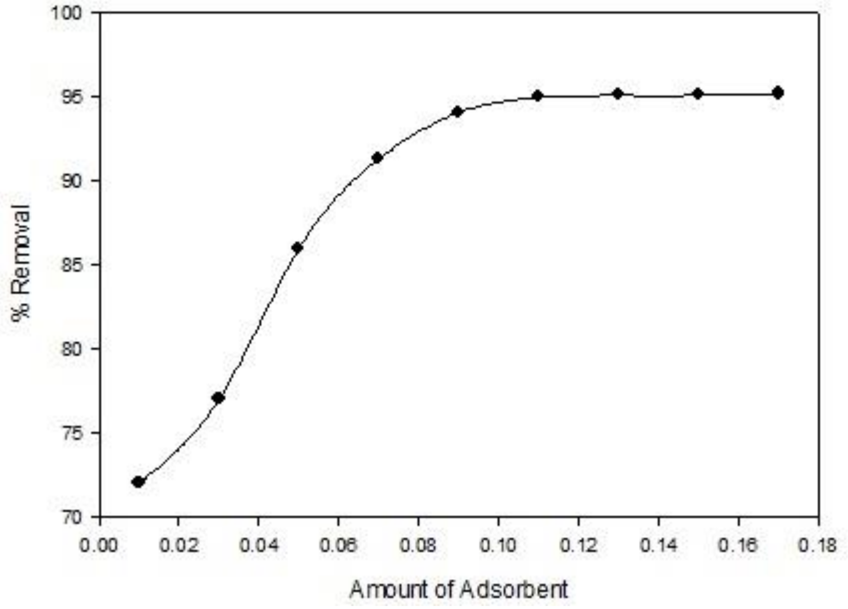


Fig X: Effect of adsorbent dose for decoloration of RG19 on slag (Adsorbent dose = 0.09g/30mL;stirring rate=150 rpm; C_0 =100mg/L; temperature = 30^0C)

4.6.3 EFFECT OF STIRRING SPEED

Different experiments were performed at different (100 – 200) rpm in order to assess how stirring speed effect decoloration of RG19.Slag was used as an adsorbent.It is seen in the fig XI that % removal increases from 83% to 94.09% with the increase of stirring speed from 100 rpm to 150 rpm. As the rpm increases more amount of RG19 will come in contact with the adsorbent.. But, when the stirring speed increases beyond 150, there will be a decrease in % removal to 80%. Hence the turbulence caused due to increase of agitation lowers the thickness of the adsorbent boundary layer .This results in decrease of the resistance for transfer of dye to the surface of slag. Thus the RG19 molecules will easily get adsorbed on the surface of the adsorbent and the efficiency of adsorption will increase. The optimum stirring speed is derive at a speed of 150rpm.

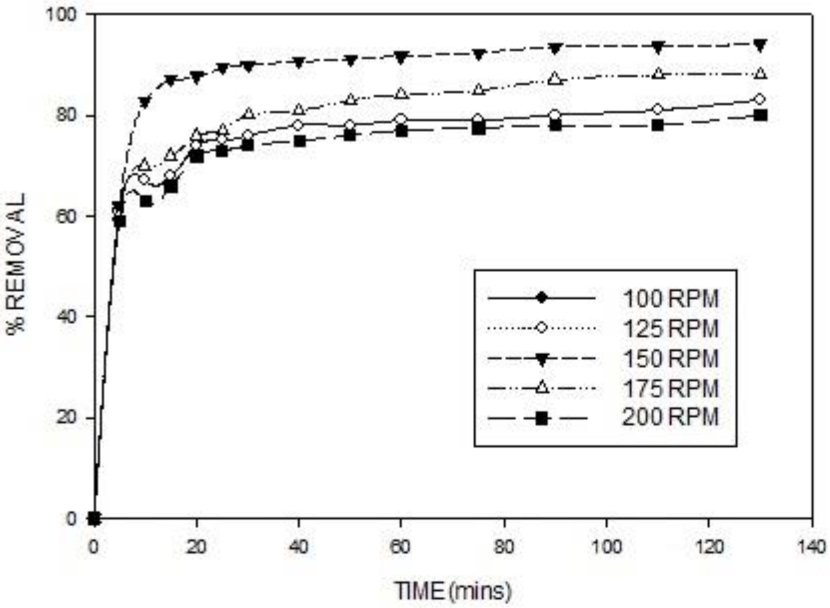


Fig XI: Effect of stirring rate on decolouration of RG19 on slag (Adsorbent dose = 0.09g/30mL;pH=2.5; C_0 =100mg/L; temperature = 30^0C)

4.6.4 EFFECT OF TEMPERATURE

Several runs in batches were taken at different temperatures (20°C, 25°C, 30°C, 35°C,40°C) maintaining other parameters at optimum values. From fig XII the effect of temperature can easily be investigated. It was concluded that the adsorption capacity decreases with the increase of temperature. Thus we can conclude this process as an exothermic process. % removal increases from 92 – 97.4. with the increase in temperature from 20^0C to 40^0C .But we had taken all the runs at room temperature (i.e.=30°C).

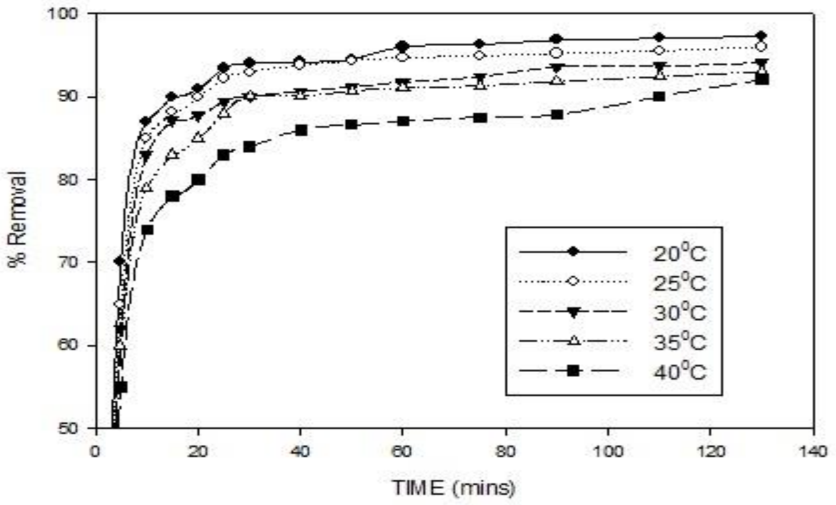


Fig XII: Effect of temperature on decoloration of RG19 on slag (AdsorbentDose =0.09g/30ml;pH=2.5; C_0 =100mg/L; stirring rate = 150rpm)

4.6.5 EFFECT OF INITIAL CONCENTRATION ON ADSORPTION OF DYE

We can derive from Fig XIII the effect of initial concentration and contact time. It is seen that the amount of dye(RG19) adsorbed per unit mass of adsorbent is directly proportional to initial concentration even if % removal is inversely proportional to initial concentration. When the initial dye concentration was increased from 50 to 200 mg/L the amount of dye adsorbed at equilibrium (q_e) also increased from 16 to 45.3 mg/g. Mass transfer resistances present between the aqueous and solid phases is overcome through the driving force provided by the initial concentration of dye. The RG 19 % removals decreased from 98.71% to 68.085% as the dye concentration increased from 50 to 200 mg/L even though higher initial dye concentration enhance the adsorption process. Hence we can conclude that for all initial concentrations, higher rate of adsorption of RG 19 took place for first 50 min and after that, the adsorption rate get reduced slowly until equilibrium value obtained.

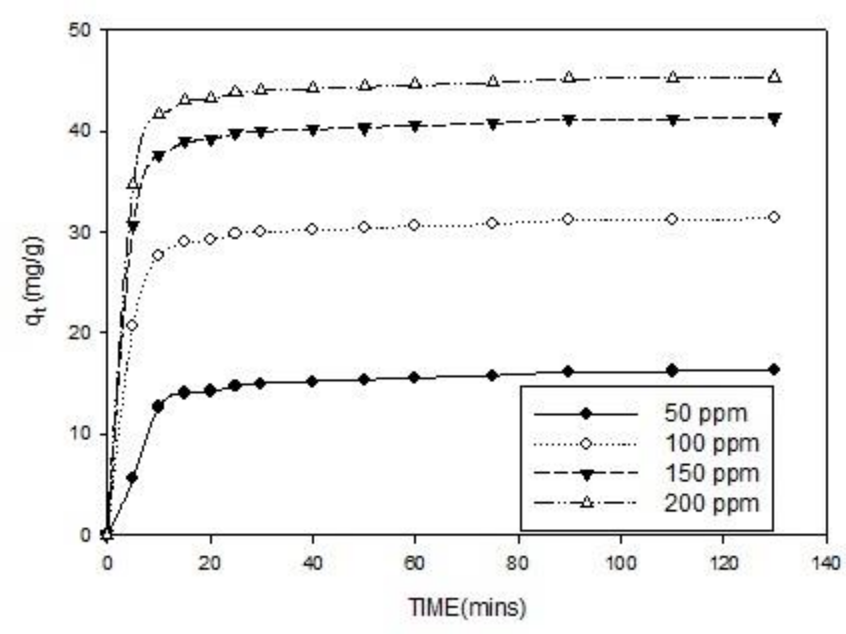


Fig XIII: Effect of contact time and initial concentration on the adsorption of RG19 on slag (pH= 2.5; Adsorbent dose = 0.09g/l; temperature = 30 °C; stirring rate = 150 rpm)

4.7. EQULIBRIUM STUDIES AND ISOTHERM ANALYSIS

In order to derive a relation between the equilibrium condition of RG 19 concentration on slag & that of solution different equilibrium isotherms were used. The equilibrium isotherms like Langmuir, Freundlich were studied at room temperature (i.e.30°C).

4.7.1. LANGMUIR ISOTHERM

The Langmuir isotherm model is based on the assumption that it is a monolayer adsorption process. Moreover, the adsorbent surface is assumed to be in homogeneous form.Thus it indicates that when one molecule get adsorbed on one active site, then these sites will be restricted for other molecules The Langmuir isotherm is represented by the following equation:

$Ce/qe= 1/q_m k_L+ Ce/q_m$…………………… (5)

Where. Langmuir isotherm constants are q_m in (mg/g), K_L in (L/mg). From the fig XIV we can conclude the equilibrium data satisfied Langmuir isotherm .The values of the constants and R^2 value are mentioned in Table 1.

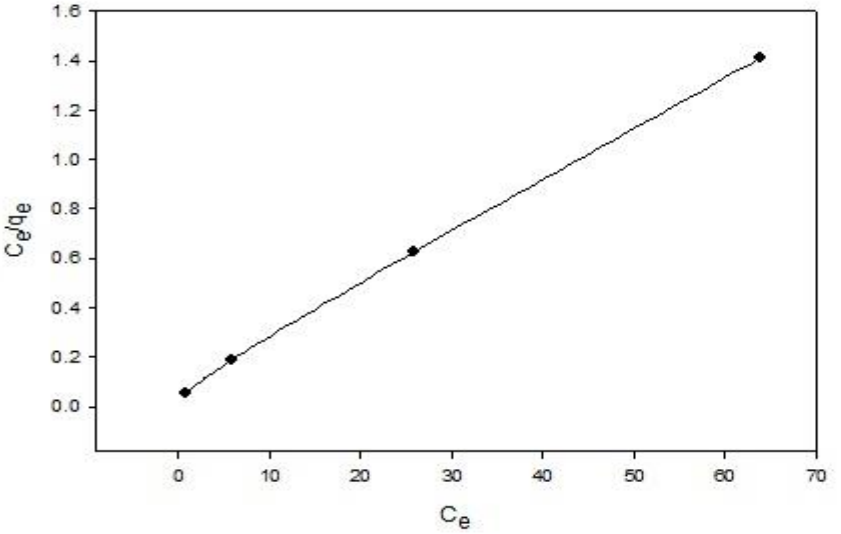


Fig XIV: Isotherm analysis for Langmuir model

4.7.2. FRENDLICH ISOTHERM

Assuming that adsorption process takes place on heterogeneous surfaces Freundlich isotherm is expressed in empirical equation form. Here the relation between adsorption capacity and concentration of RG 19 dye at equilibrium is expressed:

$\ln q_e= \ln k_f+ (\ln c_e)(1/n)$ …………………..…. (6)

Where, k_f (mg/g (L/mg) $^{1/n}$) =indicator of the adsorption capacity,

$1/n$ =adsorption intensity.

The value of the exponent, $1/n$, help us to decide whether the adsorption process is favourable or not. Value of $n>1$ will be favorable for adsorption. A graph between ln C_e and ln q_e is drawn. The values of n, k_f , and the linear regression (R^2) obtained from the graph for Freundlich model are mentioned in table 1.

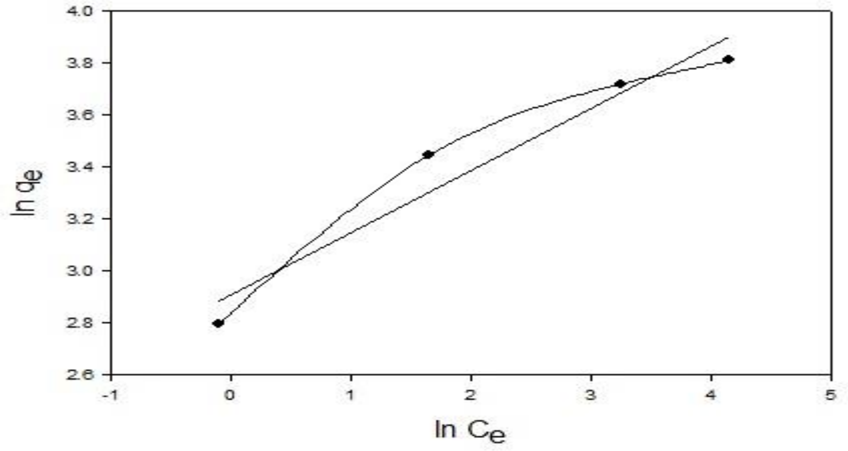


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Fig XV: Isotherm analysis for Frendlich model

Isothermal Parameters: (Table 1)

Langmuir	**Freundlich**
R^2=0.99	R^2=0.94
K_L=0.389	K_F=18.357
q_m=47.62	n=4.2

4.8. ADSORPTION KINETICS

Kinetics of adsorption of RG 19 on slag was modeled and investigated by two common models, Lagergren pseudo-first-order model & pseudo-second-order model.

The pseudo-first-order model was expressed as:

$\log(q_e - q_t) = \log q_e - (k_1 * t)/2.303$………….. (8)

where, q_e (mg/g) = amount of dye RG 19 adsorbed at equilibrium,

q_t (mg/g) =amount of dye RG19 adsorbed at time t ,

k_1 (1/min) =rate constant of pseudo-first-order adsorption.

A linear plot of log (q_e−q_t) verses time (t) help one to find out the rate constant values. The linearity of the graph with proper correlation coefficient, proves that pseudo-first-order Lagergren's equation is applicable for adsorption of RG 19 on slag.. In Table 2 the Lagergren's first-order rate constant (k_1) and q_e values along with their corresponding correlation coefficients obtained from the model are mentioned. Due to the non linearity nature of the graph (fig XVI) it can be concluded that the pseudo-first-order model do not fit well. Moreover, the calculated q_e values did not match with the experimental qe values mentioned in Table 2. Hence the adsorption of RG 19 do not satisfy first-order kinetics.

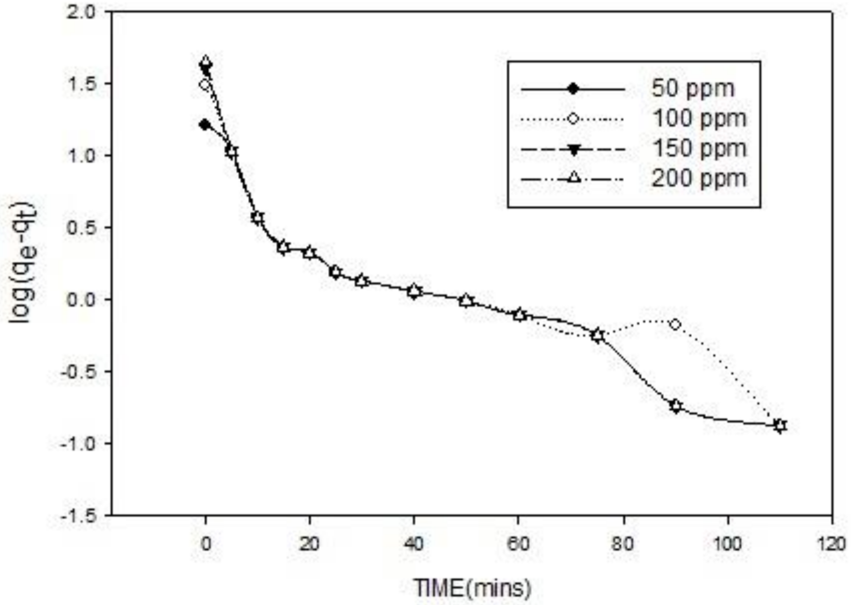

Fig XVI: Pseudo-first-order kinetics

The pseudo-second-order kinetics equation was described by Lagergren as:

$t/q_t=1/(k_2*q_e^2)+t/q_e$……………………………… (9)

Here Fig XVII. shows a plot of t/qt versus t .Now from the slope and intercept of the graph the equilibrium adsorption capacity (q_e) and the second order rate constant k_2(g/mg min) can be determined experimentally. The values of k_2 and q_e calculated from the model and the corresponding correlation coefficients are given in Table 2. Both the calculated and experimental q_e values are mentioned in Table 2. From here we can conclude that since the pseudo-second-order model represents the adsorption kinetics in a better fashion, this the adsorption process follows chemisorptions[28].

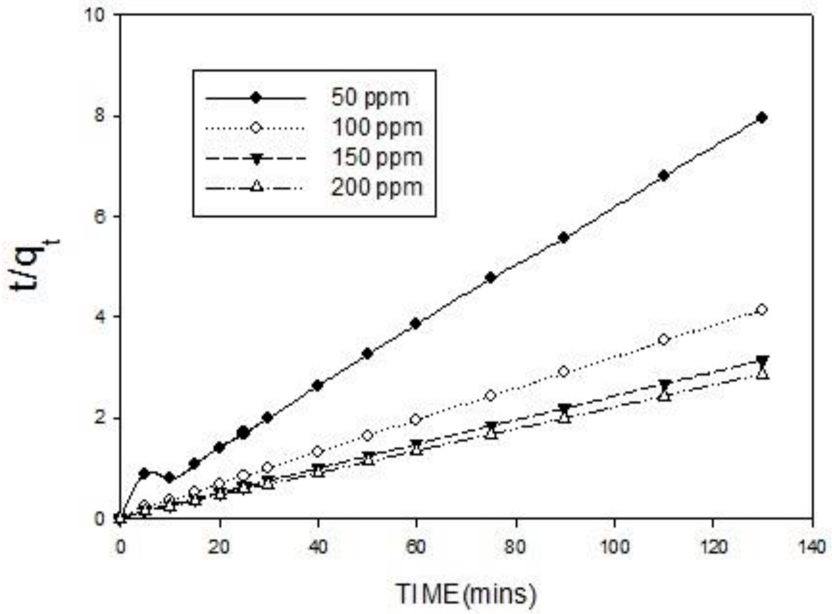

Fig XVII: Pseudo-second-order kinetic

Comparative study between pseudo-second-order and pseudo-first-order adsorption rate constants .Calculated q_e (q_e, cal) and experimental qe (qe, exp) values obtained at various initial RG 19 concentrations: (Table 2)

Initial dye concentration (mg/L)	**q_e, exp (mg/g)**	**Pseudo-first-order kinetic model**			**Pseudo-second-order kinetic model**		
		k_1 (1/min)	**q_e, cal (mg/g)**	**R^2**	**K_2 (1/min)**	**q_e, cal (mg/g)**	**R^2**
50	16.333	0.0368	6.486	0.890	0.0043	16.949	0.997
100	31.333	0.035	6.776	0.779	0.0196	32.26	0.999
150	41.333	0.039	7.78	0.825	0.0213	41.667	0.999
200	45.333	0.039	7.91	0.818	0.0200	47.62	0.999

4.9. THERMODYNAMICS STUDY

The temperature is an important parameter used to know kinetic process of dye adsorption. Therefore values of several thermodynamic parameters such as enthalpy $\Delta H°$(kJ/mol) entropy $\Delta S°$(kJ/mol K)and free energy $\Delta G°$(kJ/mol) were determined using the following equations.

$\ln K° = (\Delta S°/R) - ((\Delta H°)/RT)$ ………..(10)

$\Delta G° = \Delta H° - T\Delta S°$ ………..(11)

Where$K°$is thermodynamic equilibrium constant,T is the temperature in Kelvin, and R (8.314 $\mathrm{Jmol^{-1}K^{-1}}$) is the gas constant .In the equations, R is the gas constant (8.314 $\mathrm{Jmol^{-1}K^{-1}}$).Value of thermodynamic equilibrium is calculated from the data qe (amount of dye (RG19) adsorbed per unit mass of slag (mg/g)) and Ce (equilibrium concentration of dye in solution in (mg/L))

Experiments were performed at different temperatures (i.e. 20^0C,25^0C, 30^0C, 35^0C and 40^0C) The values of the parameters are given in table 3.The values of the enthalpy of adsorption $\Delta H°$and the entropy of adsorption $\Delta S°$ were determined from the slope and intercept of the linear plot of between ln K^0 and T .When the values of $\Delta H°$and$\Delta S°$were obtained, the value of $\Delta G°$was determined from Eq. 11.

The negative values of$\Delta H°$illustrates the process to be exothermic in nature. The values of $\Delta H°$for the physical adsorption lies within the range of 0 to −42 kJ/mol that of chemical adsorption is −42 to −125 kJ/mol[29]. Hence adsorption of RG 19 is found to be physical in nature. $\Delta G°$Data is found to be negative which indicates the spontaneity of the forward reaction. In addition, the positive value of $\Delta S°$ illustrates enhancement of randomness between the solid liquid interfaces[30] .

Table 3

T(K)	**ln K^0**	$\Delta H°$(kJ/mol)	$\Delta S°$(kJ/mol K)	$\Delta G°$(kJ/mol)
293	2.49	-37.637	0.109	-69.574
298	2.078			-70.119
303	1.67			-70.664
308	1.487			-71.209
313	1.342			-71.754

4.10. CHARACTERIZATION

SEM image

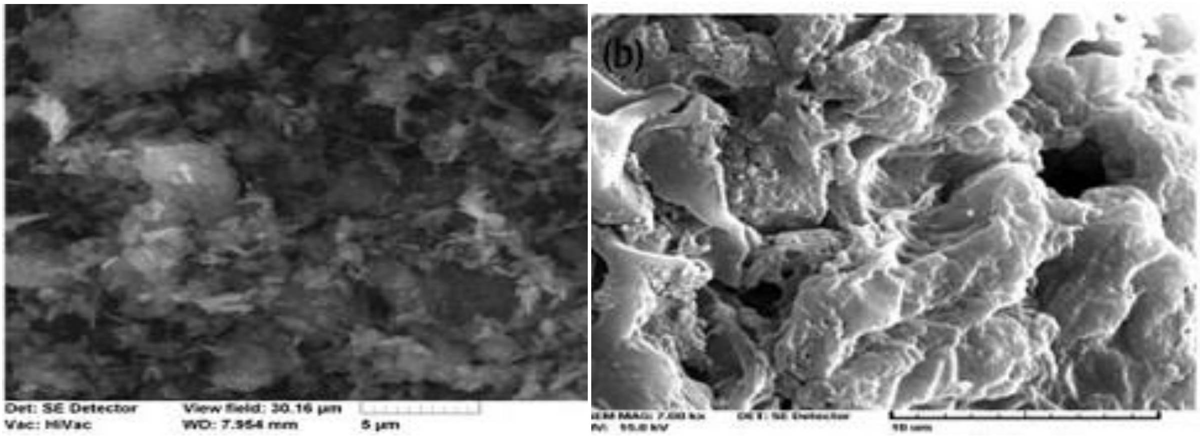

Fig XVIII: SEM image (a) Before adsorption (b) After adsorption

Fig XVIII showed the difference in the nature of the adsorbent surface before and after adsorptions. Highly porous nature of the adsorbent is observed which after adsorption were packed with RG19 dye molecules.

OUTCOME OFTHESTUDY

The results derived from several batch experiments, conformed that slag can be used as an effective adsorbent for removing RG 19. At optimum conditions (i.e. C_0=100 ppm, pH=2.5, stirring rate=150 ppm, temp=30^0C) percentage removal is 94.09%.Among different isotherm Langmuir isotherm model fits the experimental data . Pseudo-first-order and pseudo-second-order kinetic models were used for testing the kinetic data. The data fits satisfactorily in pseudo-second-order kinetic model. The advantages of this processes are its efficiency and the possibility of reusing slag for decoloration of dye. Apart from that production of secondary wastes is its drawback. Hence to bring a solution of this problem we will draw our attention towards a recently developed process namely Heterogeneous photo catalytic degradation using TiO_2 .

CHAPTER – 5

HETEROGENEOUS PHOTOCATALYTIC DEGRADATION USING TIO$_2$

5.1. CHEMICALS

Reactive Green 19 of molecular formula $C_{40}H_{23}C_{l2}N_{15}Na_6O_{19}S_6$ (molecular weight 1418.94) was purchased from Sigma-Aldrich Chemicals and used without purification. A stock solution of 300 ppm of RG 19 solution was prepared by mixing the dye with double distilled water and diluted as per requirement. TiO_2 (Degussa P25) waspurchased from Sigma-Aldrich Chemicals (USA). H_3PO_4 and NaOH were purchased from Mark India Ltd., Mumbai, India. Laboratory grade water was produced from Sartorious arium pro VF (Germany) pure water system.

5.2. EQUIPMENTS

Batch experiments were performed in a UV photo reactor for treatment of synthetic wastewater. The reactor comprises a square chamber (17 cm × 17 cm × 17 cm) with UVA lamp (10 W, Concept International, Kolkata, India) mounted at the top of the chamber .A magnetic stirrer was inserted within the chamber for proper mixing of the solution.

The pH of the samples was measured by using microprocessor based pH meter by Hanna Instruments. The samples were centrifuged by a cold centrifuge (Plasto crafts, Mumbai).

5.3 INSTRUMENTS FOR ANALYSIS

The dye concentration was determined by finding out the absorbance at λ max= 630 nm by using UV-Vis spectrophotometer (Varian Cary Bio50).

5.4. METHODS

The batch experiments were performed by taking the dye desired concentration dye solution in a slurry photo reactor (30 ml) pH of the solution was adjusted using NaOH or H_3PO_4as per requirement. Then requisite amount of TiO_2 after being added to the prepared solution it was placed on the magnetic stirrer for well mixing. Then it was kept in the UV photometer for 2 hrs. The UV light was kept switched on or off mode as per the requirement of the experimental purpose. At desired time interval samples was collected and centrifuged in a cold centrifuge & finally the supernatant was analyzed with the help of a UV Vis Spectrophotometer. The removal of dye was measured by the following equation:

%Removal= $(C_0 - C_t)/C_t \times 100$…………..……………………… (1)

Where, C_o = Initial dye concentration

C_t = Dye concentration at time t

5.4.1. SOLUTION pH

To study the effect of pH on the removal of RG-19, H_3PO_4 or NaOH were added to 50 ppm synthetic dye solution to adjust the solution pH (pH 3-12). Then the sample was placed in a UV photo reactor for 120 minutes without varying the TiO_2 amount and other parameters. Samples were collected at a definite time interval and analyzed.

5.4.2. TiO_2 DOSAGE

To study the effect of TiO_2 dosage on removal of RG-19 using photo catalytic degradation, different amounts of TiO_2 was added to 50 ppm synthetic dye solution at a constant pH.Then the sample was placed in a UV photo reactor for 120 minutes. Samples were collected at a definite time interval and analyzed.

5.4.3. UV LIGHT INTENSITY

To study the effect of intensity on removal of RG-19 using photo catalytic degradation, the experiments were performed at three different intensities 50µW/cm^2, 80 µW/cm^2 and 125 µW/cm^2.The TiO_2 dose, pH and concentration of RG 19 were kept fixed. The sample was placed in a UV photo reactor for 120 minutes. Samples at definite time intervals were collected and analyzed.

5.5. RESULTS AND DISCUSSIONS

5.5.1 EFFECT OF SOLUTION pH

The effect of solution pH was studied in the solution pH range of 3–10. Others parameters were kept constant, such as dye concentration, solution temperature, catalyst loading and UV-irradiation time and intensity. Fig XIX demonstrates the effect of solution pH. From the graph we can conclude that for 50 ppm and 16 mg TiO_2 at dye pH the % removal is 80%,whereas it reduces to 36% and 32% at alkaline(pH =10) medium and highly acidic(pH=3) medium respectively. The interpretation of pH effect on the efficiency of the photo degradation process plays a very significant role in TiO_2 activity, including the charge on the particles, the positions of the conductance and valence bands and the size of the aggregates it forms. Thus pH changes can influence the adsorption of dye molecules onto the TiO_2 surfaces, an important step for the photo catalytic oxidation to take place.

In acidic solution the pH is lower than pzc and hence the TiO_2 surface is positively charged.

$TiOH + H^+ \longleftrightarrow TiOH_2^+$

In the basic solution the surface is negatively charged as given in the following
Equation:

$TiOH + OH^- \longleftrightarrow TiO^- + H_2O$

The point of zero charge (pzc) of the TiO_2 (Degussa P25) is at pH 6.8. Thus, the TiO_2 catalyst surface is positively charged in the acidic media ($pH < 6.8$), whereas it is negatively charged under alkaline conditions ($pH>6.8$). Since the dye anionic in nature in alkaline medium the percentage removal is low as seen from the graph. Because of the Columbic repulsion between the negative charged surface of photo catalyst and the hydroxide anions. This fact prevents the production of •OH and thus decrease the photo oxidation[31].The acidic solution favors adsorption of dye onto the photo catalyst surface. Thus, decolorization efficiency increases with increase in H^+ concentration. But after a certain optimum pH (i.e. dye pH) value with excess H^+ concentration the removal efficiency decreases because the highly acidic medium brings the TiO_2 particles agglomerate and consequently reduces the adsorption capacity of the dye onto the TiO_2 surface due to the decrease in the number of active sites on the catalyst surface.

Moreover, excess H^+ ions interact with N=N bond by decreasing electron density .Hence it decreases electrophillic mechanism efficiency[32]. .

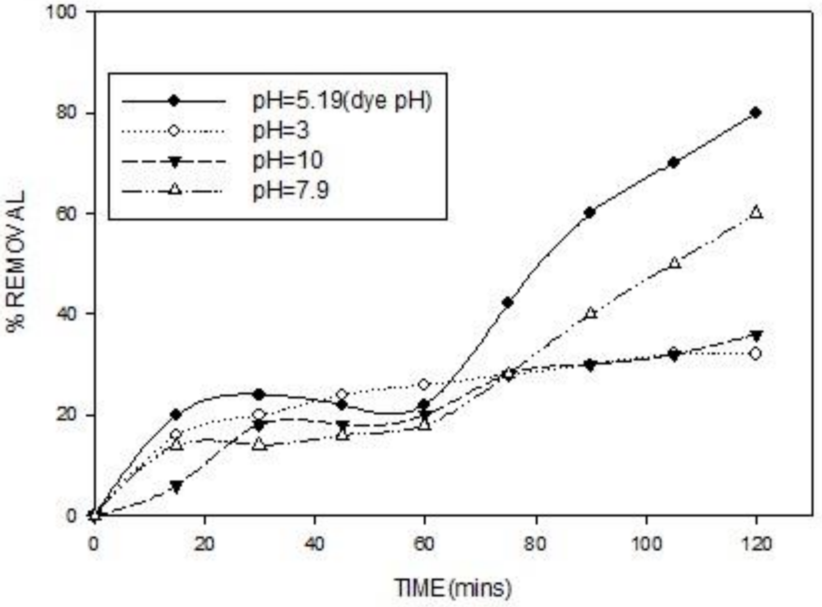

Fig XIX: Effect of solution pH on decoloration o for photo catalytic degradation (TiO_2 = 16mg/30ml; UV light intensity= 125µW/cm$^{2;}$ Co = 50ppm)

5.5.2 EFFECT OF TiO_2 DOSAGE

The catalyst dose is one of the important parameters for the study of photo degradation. The significance of TiO_2 dose for degradation is shown in the fig XX. Here the amount of the catalyst used is directly proportion to the % removal up to an optimum value (i.e. 14 mg).Beyond the optimum value % removal decreases. The dye degradation increases with the increase in catalyst loading, which is the characteristic of heterogeneous photo catalysis. This can be rationalized in terms of the availability of active sites on catalyst surface and penetration of photo activating light into the suspension. The increase in catalyst amount actually increases the number of active sites on the photo catalyst surface (i.e. TiO_2) thus causing an increase in the number of •OH radicals which can take part in actual discoloration of solution containing dye. Beyond a optimum dose of catalyst amount, the solution becomes turbid and thus blocks UV light that prevents the reaction to proceed and therefore percentage degradation starts decreasing. Agglomeration and sedimentation of excess TiO_2 particles may also occur[33].

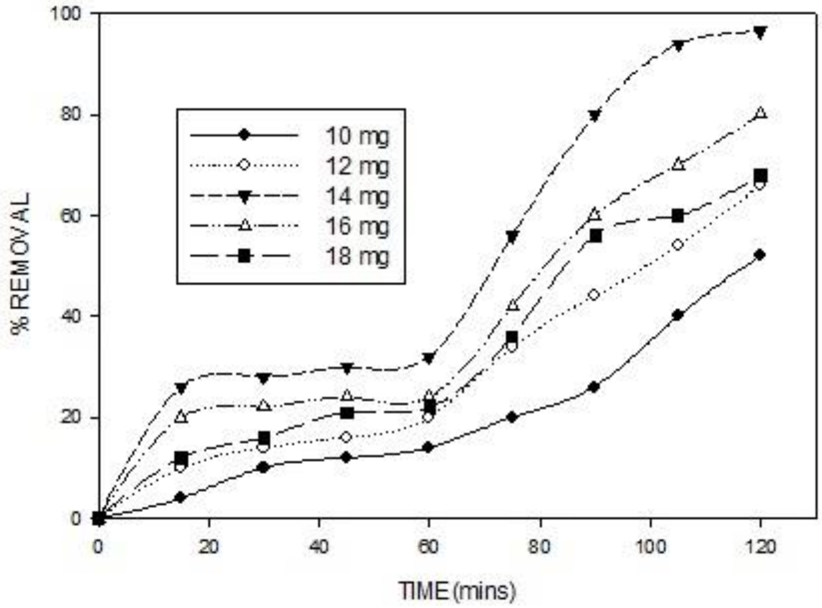

Fig XX: Effect of amount of TiO_2 on decoloration for photo catalyticdegradation (pH=5.19[Dye pH]), UV light intensity= 125µW/cm^2 ; Co = 50ppm)

5.5.3 EFFECT OF UV LIGHT INTENSITY

The effect of UV intensity is shown in the fig XXI. The UV lamp was varied from 50 µW/cm^2 to 125 µW/cm^2 for a constant concentration of dye solution.The % removal increases from 80% to 96.6%. At a given wavelength, UV intensity determines the extent of radiation to be absorbed by the TiO_2 catalyst. The rate of initiation of photo catalytic degradation is the electron−hole pair formation in the reaction which is strongly dependent on the UV intensity. The light intensity distribution inside the photoreactor also was reported to invariably determine the overall substrate conversion and degradation efficiency[34].

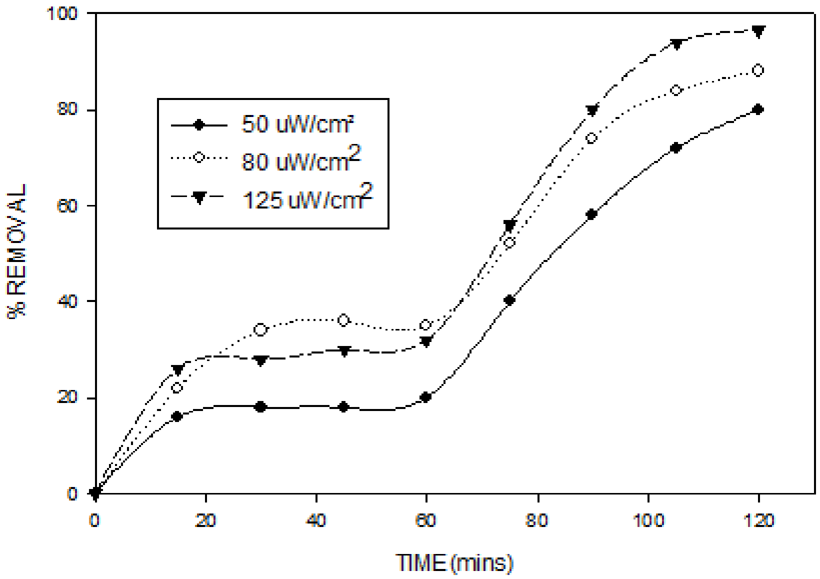

Fig XXI: Effect of UV intensity on decoloration for photocatalytic degradation (pH=5.19[Dye pH]),TiO_2=14 mg/30ml; Co = 50ppm)

5.6. COMPARITATIVE STUDY BETWEEN ADSORPTION AND PHOTO CATALYTIC DEGRADATION PROCESSES OF RG 19 USING TiO_2

It is clearly seen from figure XXI the % removal of the dye RG 19 via adsorption and adsorption followed by photo degradation at optimum pH, intensity and amount of TiO_2. In the absence of UV light after 2 hours the % removal is only 31% and 19 % for 50 ppm and 75 ppm respectively, whereas using UV light the % removal increases to 96.6% and 86 % respectively. In case of only adsorption comparatively less decrease in the concentration of dye is probably due to adsorption of the dye on the TiO_2 surface. The TiO_2 acts as adsorbent had achieved almost maximum uptake of the azo dye at the end of 1 h and beyond this adsorption was negligible for next 1 hour. But as TiO_2 is illuminated by UV irradiation, the photons excite the valence band electrons overcome the band gap and finally enters into the conduction band, leaving holes in the valence band which will then react with hydroxide ions or water molecules to generate OH radical. The azo bond which is rich of electrons in RG19 was mostly attacked by ·OH radicals and which results in the cleavage of azo bond and results in the decolorization of the dye solution.

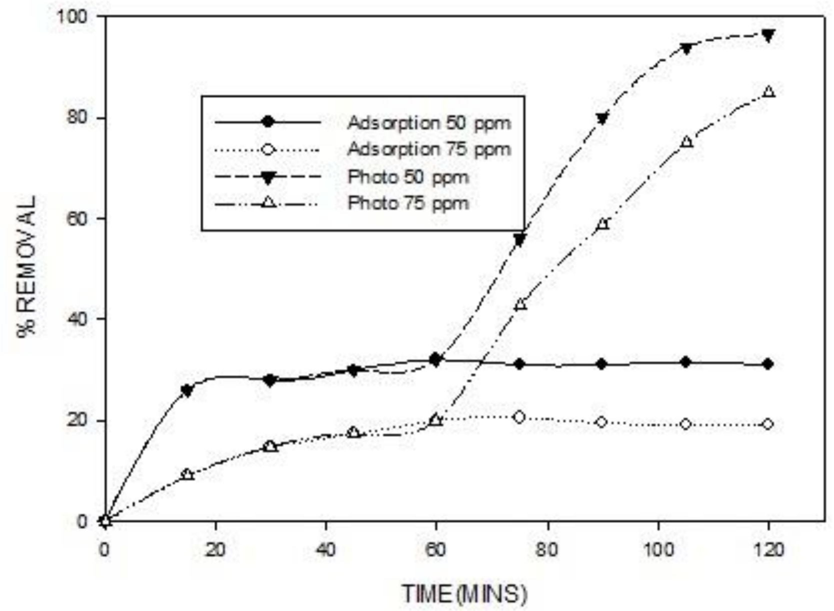

Fig XXII: Comparison between Photo catalytic degradation and adsorption process

5.7. KINETICS STUDY FOR PHOTO CATALYTIC DEGRADATION

The photo catalytic degradation of RG 19 dye containing TiO_2 was investigated by Langmuir–Hinshelwood kinetic model.

Rate = - (dC /dt)= $kK_C/(1+K_C)$

Where C represents the concentration of dye (milligrams per liter),t the time for irradiation, k the rate constant of the reaction(milligrams per liter per hour), and K the adsorption coefficient of RG19 onto the catalyst. For low concentrations of dyes ($K_C<<1$), neglect K_C in the denominator and integrate w.r.t time t. Equation can be simplified to the pseudo-first-order kinetic model equation.

$\ln (C_0/C) = k_{app}\, t$

A linear plot of ln (C_0/C) against time allows one to obtain the rate constant. The plots were found to be linear with good correlation coefficient. Hence it indicates that Langmuir–Hinshelwood kinetic equation is satisfying photo catalytic degradation process of RG19 on TiO_2 using UV radiation. So, the degradation process is a pseudo-first-order process. The pseudo-first-order rate constant for the azo dyes decreased as the initial concentration of dye increased. The value of R^2 and k_{app} are calculated and presented in the table 4.

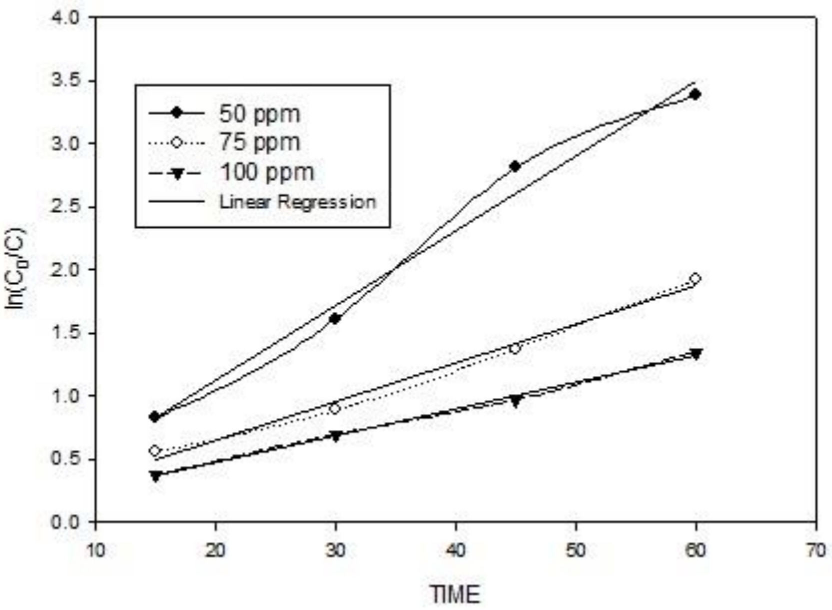

Fig XXIII: Pseudo-first-order kinetics for photocatalytic degradation

Table 4

Concentration(ppm)	**R^2**	**k_{app}**
50	0.983	0.059
75	0.988	0.030
100	0.996	0.021

OUTCOME OF THE STUDY

After performing the batch experiments, from the results we can conclude heterogeneous photo catalytic process using TiO_2 is very efficient in decolorizing of Reactive green 19 in aqueous solutions. The decoloration is obviously affected by pH, TiO_2 dose and UV intensity. The optimum conditions for decoloration are: TiO_2 = 14 mg; UV intensity= 125 $\mu W/cm^2$&pH = 5.19 and decoloration efficiency is 96.6% in 120 minutes. It obeys pseudo-first-order kinetics model. The comparision between photo catalytic degradation processes using TiO_2 and adsorption shows increase of % removal from 31% to 96.6% for 50 ppm and 19% to 85% for 75 ppm. Thus oxidation power is remarkably enhanced by UV irradiation. In this process the toxic organic compounds of liquid phase get reduced by •OH radicals and finally water and CO_2 are produced as byproducts. Hence we can conclude this process as a eco friendly, efficient process.

CHAPTER - 6

CONCLUSION

In this current study some advance techniques are used for the treatment of textile waste water containing dye Reactive Green 19.Initially experiments on adsorption were performed taking industrial slag, whose disposal creates many problem to the environment. From the results we can concludeit as a very effective adsorbent. At optimum conditions (i.e. C_0=100 ppm, pH=2.5, stirring rate=150 ppm, temp=30^0C) % removal is 94.09%.Among different isotherm Langmuir isotherm model perfectly fits the experimental data.Pseudo-first-order and pseudo-second-order kinetic models were used for testing the kinetic data. The data fits satisfactorily in pseudo-second-order kinetic model, thus concluding that the adsorption process is controlled by chemisorptions. Production of secondary wastes is its drawback. Hence to bring a solution of this problem we will draw our attention towards a recently developed process namely heterogeneous photo catalytic degradation using TiO_2.Advanced oxidation processes, is the process where •OH radicals plays the vital role for efficientand complete degradation of dye. So we have selected heterogeneous photo catalytic degradation process for dye removalusing TiO_2 as the catalyst. It is observed as a very effective process for the decoloration of Reactive green 19 in aqueous solution.Optimum values areTiO_2 = 14 mg; UV intensity= 125 μW/cm^2&pH = 5.19 and decoloration efficiency is 96.6% in 120 minutes.It obeys first order kinetics. Thus we can conclude this process as an efficient,eco friendly process without generating any hazardous secondary wastes.

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