A KINETIC STUDY ON THE EFFICIENT DECOLOURIZATION OF TEXTILE DYE USING STARCH AND STARCH BASED BIOPLASTIC

CONTENTS

ABBREVATIONS

ml	milli liter
L	litre
g	grams
Kg	kilograms
oC	degree centigrade
nm	nanometer
MB	methylene blue
Mg	milligram

ABSTRACT

In the present study, starch and starch based bioplastic were used for the adsorption of textile dye. The adsorption capacities were monitored using colorimetry. Starch based bioplastic were made using glycerine as plasticizer in our chemistry lab. Adsorption of dyes using the both adsorbents were done in two different concentrations for both congored and methylene blue. The colorimetric results were plotted as absorbance versus time graph using Microsoft excel software . Rate constants were calculated and the obtained data showed that both starch and starch bioplastic can be used as adsorbents for dye degradation. However starch bioplastic is better adsorbent than starch.

CHAPTER 1
INTRODUCTION

INTRODUCTION

1.1 A BRIEF INTRODUCTION TO STARCH

In green plants starch is the major energy reserve and is commonly found in seeds, for e.g., in cereal grain and pulses, tubers of potato, in roots for e.g., roots of cassava and sweet potato, fruits for e.g., banana and squash, stems of sago and leaves of tobacco. Starch is the main component of cereal grains, pulses, and tuber and root crops. Starch molecules are effectively organized in semicrystalline granules, which has a density of around 1.5 g/cm3. Since starch granules has greater density than water it helps in the easy isolation and purification of them using gravity separation. The semicrystalline structure of starch granules maintains the granular integrity and prevents the dispersion of the granules in water at ambient temperature. Starch on heating in presence of water gelatinizes and disperse native starch granules. Starches from different botanical origins display characteristic gelatinization properties, reflecting distinct structures of starch molecules, and the organization of double-helical crystalline structures inside starch granules. Starch in the absence of water or other plasticizer doesnot undergo gelatinization but will decompose beyond 250 oC. Starch is composed of two major polysaccharides: amylose and amylopectin. Amylose is a primarily linear polysaccharide of 1,4-linked D-glucopyranose with a few branches of 1,6 linkages. Amylopectin, is a highly branched polysaccharide with 1,4- linked linear chains of different lengths connected by approximately 5% 1,6 branch linkages. The two main components of starch have distinctly different properties. Amylose in aqueous medium

has greater tendency to recrystallize (known as retrogradation) which forms strong gels and films and develops a dark blue colour on complexing with iodine. In contrast, amylopectin retrogrades more slowly and forms weak gels and brittle films and develops purple to red color after complexing with iodine. Amylose content and branch chain length distribution of amylopectin directly determine many functional properties of starch, including gelatinization, pasting, gelling, and retrogradation/syneresis. Starch displays characteristic gelatinization temperatures, paste viscosity and clarity, gelling ability, and retrogradation rate (relating to syneresis) depending on their botanical orgin.

Light scattering and iodine reaction of starch:

The appearance is such that under polarized light starch has a birefringence appearance. Starch gives a characteristic purple –black color in the presence of iodine ions this is because the amylase chainis coiled in shape of a helix. The colour reaction in iodine dissolved in potassium iodide solution to form the lineartriiodide ion complex that enters the helical structure of the amylase moiety is an important identification test for starch. The purple-black colours formed when the iodine ions insert itself into the helical network of the amylose chain making it rigid. The change in colour of the starch either blue or purple will depend on thelength of the amylase molecule.

Chemical structure of starch:

It consists of two main naturally occurring high molecular weight polymers: amylose and amylopectin, which consists of a single carbohydrate repeating unit of D-glucose.

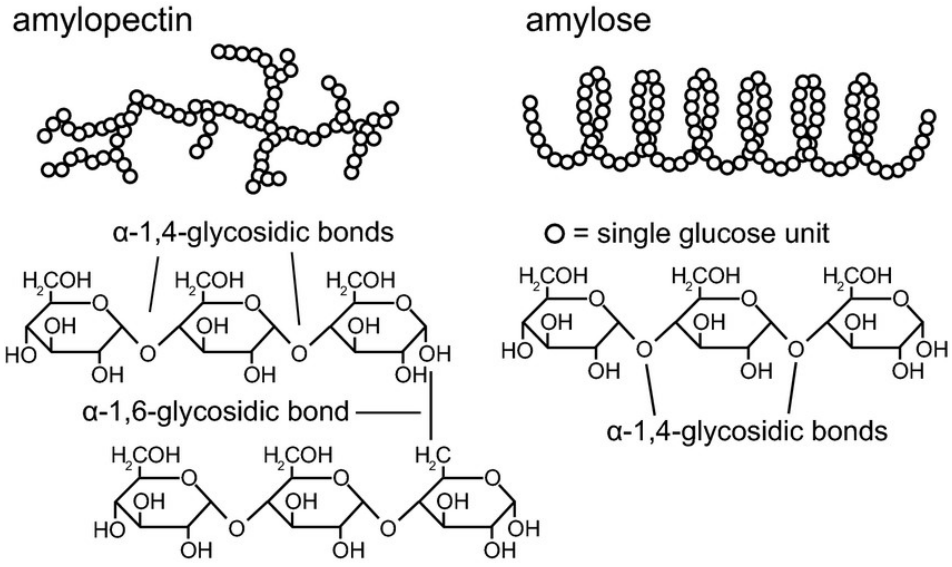


fig1: structure of starch

modification of starch:

Different structural and functional modifications are done 14 to employ the target application . Different methods used to modify starch characteristics include enzymatic, physical, or chemical modification. Starch can be either depolymerized or extended by using various enzymes. Enzymatic degradation by food-grade enzymes, such as amyloglucosidase, pullulanase, a-amylase, b-amylase, and isomerase, is used in the production of maltodextrin, modified starches, or glucose and fructose syrups. Physical methods of starch modification include hydrothermal treatments, pregelatinization, and nonthermal processes. Chemical modification is generally achieved through derivatization such as etherification, esterification, cross-linking, and grafting. The physicochemical properties of the modified starches can be quantified using differential scanning calorimetry (DSC), Rapid Viscosity Analyzer (RVA)/dynamic rheometer,microscopy,respectively.

COMMON TYPES OF CHEMICAL MODIFICATIONS:

The presence of a large number of hydroxyl groups on starch polymer provides active sites for chemical modification. The introduction of functional group such as carboxyl, acetyl, hydroxypropyl, amine, amide, or any other to the starch polymer is chemical modification of starch. The new functional groups give starches specific properties to improve its functional and nutritional characteristics that tailor starch to specific food application. Different chemical modification methods are achieved by decomposition such as acid hydrolysis and oxidation or by derivatization, such as, etherification, esterification, crosslinking, and dual modification.

Physical modification of starch:

Physical modifications of starches are starch property modifications done by physical treatments which do not cause any chemical modification of the starch other than limited glycosidic bond cleavages. Thermal treatments are those that produce 15 pregelatinized and granular cold-water-swelling starches, heat-moisture treatment, annealing, microwave and other heating of "dry" starch, and "osmotic pressure treatment. Sonication, milling, static ultrahigh (high hydrostatic) pressure treatments, use of highpressure homogenizers, pulsed electric field, freezing and thawing, and freeze-drying includes some nonthermal treatments

Enzymatic modification of starch: An alternative method for obtaining modified starch is by using various enzymes. These include enzymes occurring in plants, e.g. pullulanase and isoamylase groups. Pullulanase is a 1, 6- glucosidase, which statistically impacts the linear -glucan, a pullulan which releases malt triose oligomers. This enzyme also hydrolyses -1, 6 -

glycoside bonds in amylopectin and dextrines when their side-chains include at least two -1,4- glycoside bonds. Isoamylase is an enzyme which totally hydrolyses -1, 6-glycoside bonds in amylopectin, glycogen, and some branched maltodextrins and oligosaccharides, but is characterized by low activity in relation to pullulan.

Uses of Starch: In textile industry starch is used mainly as sizing agents. Starch can be hydrolysed into less complex sugars by acids, various proteins, or a mix of the two. The subsequent parts are known as dextrins. The fraction of the glycosidic bonds in starch that have been broken is generally the dextrose equivalent (DE) and can be used to regularly evaluate the degree of change. These starch sugars are by a long shot the most widely recognized starch-based nourishment fixing and are utilized as sugars in numerous beverages and food sources.

Pharmaceutical applications: Starch granule has some important influence on the functional application of some native starches due to its extremely small size. Rice starch grain is among the smallest of the starch grains measuring 7–9mm. This has made it desirable for the production of both cosmetic and medicated powders for topical application. This smallness in granule size is the reason for its extraordinary soft-touch and large surface area. When applied to the skin, rice starch produces a soft, reduce oiliness of skin, which also helps minimize the appearance of fine lines, wrinkles, and blemishes. In dry shampoo rice starch is used as an 16 ingredient because it absorbs oil in the hair and also adds volume and is easily brushed out. Approximately 1.0 g of rice starch has a surface area of 1.6 m2 resulting in excellent adsorption and absorption characteristics. This is why starch is used as classical material for making powders for topical application. Sago starch which is an

unofficial starch obtained from the sago palms, used as body powder and lubricant in certain surgical and diagnostic materials due to its physiochemical properties has been investigated.

Advanced drug delivery: Starch has been investigated as a conventional excipient and special carrier for various molecules in novel drug delivery systems. Variants of native maize starch has been evaluated as an effective film coat for tablets and has also shown potential to retard dissolution and confer controlled release activity. Nanoparticles and matrix systems to deliver drugs to specific sites has also been fabricated with starch . Drug delivery to the lungs via the nasal pathway and other specific sites such as to cancer cells and colons has also been evaluated. The objective of using starch-based nanoparticles as a ligand to target cancer cells was aimed potentially to reduce the dose of the toxic anticancer molecules while maintaining its therapeutic effect. Starch nanoparticles have been fabricated by carboxylation and oxidation of the granules. Assam Bora rice starch has been evaluated as a drug carrier for bioadhesive and matrix system to controlled drug delivery to the colon.

Application of the modified starch as an adsorbent :

The application of modified starch as an adsorbent can be categorized into two groups.

Removal of heavy metals: Heavy metals are harmful unit for both human beings and aquatic life and cause diseases like cancer, hyperkeratosis, tremor and depression in human beings and cardiovascular hematologic reproductive metabolic and endocrine disturbances and necrosis hence their removal is very necessary. Amino starch was used to expel Cu2+ and Cr4+ from water. The 17 adsorption capacity was higher for Cu2+ than Cr4+. Succinylated corn starch and oxidized corn starch was also used for the adsorption of Cu2+,

Zn2+, Pb2+, and Cd2+. Succinylated starch was more powerful than oxidized starch. Kim et al. used carboxymethyl cross-linked starch to remove divalent toxic cations (Cu2+, Pb2+, Cd2+, and Hg2+) from wastewater. Xu et al. applied crosslinked amphoteric starch having quaternary ammonium and carboxymethyl groups for adsorption of Pb2+ from water. The greatest adsorption happened at pH 4–5. They likewise utilized such starch to expel Cr4+ from water. Sancey et al. used cross-linked carboxymethyl corn starch for the adsorption of heavy metals from industrial effluents. Cu2+ and Fe2+ were completely removed, while the concentration of Pb2+, Cd2+, and Ni2+ was greatly decreased and the concentration of Zn2+ was decreased to the legally permitted limit. Liu et al. used dialdehyde 5-aminophenanthroline starch (DASAPL) to expel Cd2+ from water. Zheng et al. utilized starchgraft- poly (acrylic corrosive)/sodium humate (St-g- PAA/SH) hydrogels for the adsorption of Cu2+. The adsorption phenomenon was exothermic and obeyed Freundlich and Langmuir isothermal model. The adsorption occurred by the ion exchange and chelation between carboxylic acid and Cu2+ ions and it was confirmed by pH and FTIR studies. When Li et al. used crosslinked amino starch (CAS) and DTCS to remove Cu2+ from water, they found that DTCS had higher adsorption ability than CAS for Cu2+.

Removal of dyes: Dyes being dumped into water is a big environmental issue. The various sources of dyes are human activities, plastics, textiles, papers and cosmetic industries. The dyes should be removed from the water because these resist degradations, cause allergies and are mutagenic. Dyes cause kidney disorder, defect reproductive system and damage the central nervous system, liver and brain in human beings. The most important and effective one for the removal of these dyes is by adsorption with low-cost biodegradable substances

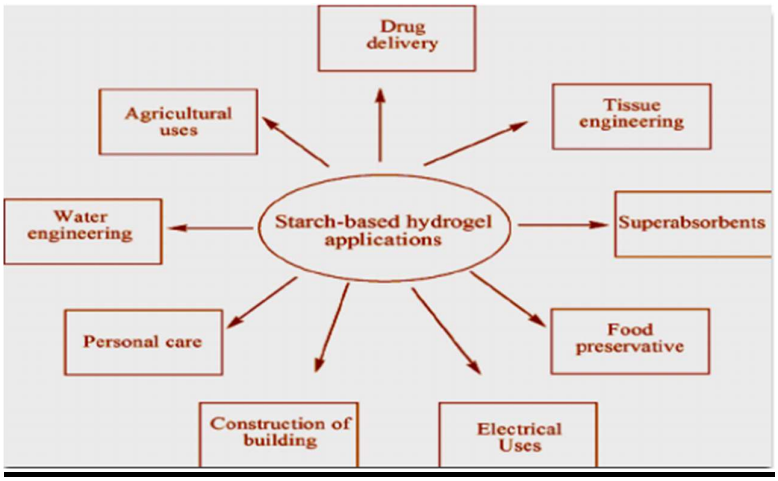
than the various biological and physio-chemical methods that have been used. Sekhavat et al. synthesized magnetic nanocomposite hydrogel (m-CVP) beads by cross-linking the mixture of carboxymethyl starchgraft-polyvinyl imidazole (CMS-g-PVI), poly(vinyl alcohol) (PVA) and Fe3O4with 18 glutaraldehyde (GA) in boric acid and used these beads for the removal of Congo red (CR) and crystal violet (CV) dyes along with some transition. metal ions like Cu2+, Pb2+ and Cd2+. Chemisorption occurred spontaneously and endothermically and fitted with Langmuir model. The important point related to the beads was their reusability. Another important thing was ease of separation of these beads by external magnet, which prevented secondary pollution in water. Xu et al. used cross-linked amphoteric starch having quaternary ammonium and carboxymethyl groups for the removal of acid dyes (acid light yellow 2G, acid red G) and basic dyes (methyl green, methyl violet).

Starch based hydrogels: Hydrophilic, three-dimensional polymer networks with corresponding absorption capacity up to 10 g/g is called hydrogels . Variety of fields such as agriculture , drug delivery , tissue engineering , water purification , contact lenses, sensors , etc made use of hydrogels. Wichterle and Lim in 1960 was the first to report the application of hydrgel. Hydrogels are water-swollen, three-dimensional polymeric structures involving covalent bonds created by the reaction of one or more comonomers, association bonds such as van der Waals interactions or hydrogen bonds between chains, physical crosslinks because of chain entanglements, and crystallites gathered together in two or more macromolecular chains. Based on different parameters such as the overall charge, the preparation method, and the mechanical and structural characteristics hydrogels can be divided into several categories. Hydrogels can be divided into homopolymer and copolymer hydrogel on the basis of the

preparation method. On the basis of overall charges of the building blocks they can be classified into neutral, cationic, or anionic hydrogel. Hydrogen-bonded, semicrystalline, amorphous, supramolecular, or hydrocolloidal structures are the classification based on physical structure. Crosslinker type and concentration, initiator type and concentration, monomer(s) type and concentration, type and amount of inorganic particles introduced (if any), polymerization method, reaction temperature, amount and type of the surfactant used, stirrer/ reactor geometry, and the rate of stirring are the most important factors which affect the property of hydrogel. . However, a set of factors having 19 most effects on the desired hydrogel product should be considered to achieve optimal value of the desired hydrogel product. Due to the safety, biocompatibility, hydrophilicity, and biodegradability preparation of hydrogels using natural polymers has been recently given more attention. Using alginate , gelatine, starch, chitosan, their derivatives and cellulose various hydrogels from natural polymers have been synthesized . Starch is the most abundant storage polysaccharide in plants, and exists as granules in the chloroplast of green leaves and the amyloplast of seeds, pulses, and tubers . Starch changes to the gelatine in a thermally three-step assisted, hydration-plasticization of the polymeric network. In the first step, adsorption of water in the hydrophilic starch granules results in swelling. In the second step, starch is dissolved by heating gelatinization occurs, resulting in leaching of the amylose component, irreversible physical changes, and the destruction of the granule structure. In the third step, the starch hydrogel network is created upon cooling and aging, resulting in partial recrystallization and reorganization of the polysaccharide structure and is called retrodegradation step. The two main process parameters affecting the gel formation are the amount of amylase and

gelatinization temperature. For non-food uses, starch can be modified to obtain products with suitable properties for various applications.

Starch-Based Hydrogel Applications:



1.2 A BRIEF INTRODUCTION TO STARCH BASED BIOPLASTIC

Plastic is a wonderful invention and it has changed the world. Plastic is used everywhere and every day across the globe. Its disposal has threatened the environment despite of its varied uses. Biodegradable plastics can meet these needs and at the same time they are environmental friendly. Not all bioplastic are biodegradable but biodegrade more readily than commodity fossil-fuel derived plastics. According to IUPAC definition, Biobased polymer derived from the biomass or issued from monomers derived from the biomass and which, at some stage in its processing into finished products can be shaped by flow. Due to its biodegradable properties, starch is a promising candidate for developing sustainable materials low cost and renewability. In order to conserve petrochemical resources and reduce environmental impact a lot of research has been done to develop

starch-based polymers. Long term stability, aging, and poor mechanical properties are some drawbacks of starch based materials. To improve shelf-life, elasticity, and limitations of the product a plasticizer such as glycerin has been added. In the presence of the plasticizer, space is developed between the starch polymer chains, which reduces the plastic crystallinity. For numerous applications they can be blended with various polymeric materials and is more versatile. To improve the characteristics of starch bioplastic various physical or chemical modifications like derivation, graft copolymerization, and blending have been investigated. Thermoplastic starch is the most widely used bioplastic, constituting about 50 percent of the bioplastics market. By gelatinizing and solution casting simple starch bioplastic film can be made at home. Pure starch is a suitable material for the production of drug capsules by the pharmaceutical sector since it can absorb humidity. However, they are brittle. Plasticizer such as glycerol, glycol, and sorbitol and can also be added so that the starch can also be processed thermoplastically. The characteristics of the resulting bioplastic (also called "thermoplastic starch") can be altered to specific needs by adjusting the amounts of these additives. Conventional polymer processing techniques, such as extrusion, injection molding, compression molding and solution casting can be used to process starch into bioplastic. The properties of starch bioplastic depends largely on the amylose/amylopectin ratio. Generally, high-amylose starch results in superior mechanical properties. Nevertheless, high-amylose starch has less processiblity because of its higher gelatinization 21 temperature and higher melt viscosity.

Due to its relative abundance, low-cost, and low energy inputs with minimal infrastructure requirements for adsorptive-based fractionation biopolymer adsorbent technology that utilize starch and cellulose has gained increasing attention. Structural variation of the polysaccharide (i.e. branching, molecular weight, and relative amylopectin/amylose content) cause sorption properties by modifying their surface chemistry and textural properties.

STRUCTURE OF STARCH BIOPLASTIC

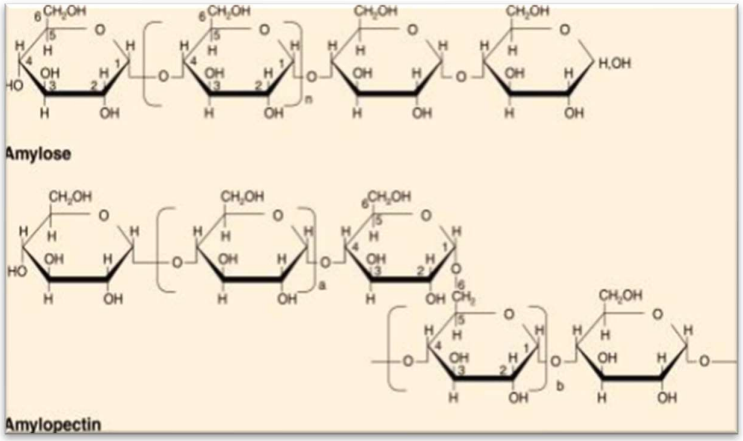


Fig 2: Structure of starch bioplastic

1.3 A Brief Introduction to Synthetic Dye degradation

Process in which the large dye molecules are broken down chemically into smaller molecule is Dye degradation. Water, carbon dioxide, and mineral byproducts that give the original dye its color are the resulting products. During the dyeing process, not all of the dye molecules are used. The water waste that the industry releases contains a percentage of these dye molecules. Many of them are not reactive towards light, acids, bases and oxygen and hence they persist in the environment . The color of the material becomes permanent

Photocatalysis

Heterogeneous photocatalysis is a widely accepted technique of choice for environmental purification. The standard experimental set up for dye degradation photocatalysis is by using a UV lamp to provide energy for the creation of oxidizing radicals. Photocatalysis is the addition of light to a semiconductor oxide/ sulphide that results in electrons moving from the valence band to the conduction band. The electron-hole pairs formed will react with oxygen and water molecules to create superoxide anions and hydroxide radicals that have increased oxidizing and reducing abilities to be used on numerous industrial dye compounds

Methods

CuS

3-D structures of copper sulfide (CuS) is favoured for methylene blue degradation because it is nontoxic, inexpensive, and stable under ambient conditions. It has efficient

catalytic ability because of its high surface area to volume ratio allowing for better contact between the reactants and CuS.

Graphite Carbon Nitride

Hierarchically porous graphite carbon nitride (hp-g-CN) had a 90% photodegradation of methyl orange, which is an improvement over other commercial photocatalysts. This is due to a higher surface area for an increased absorption capacity and porous features that allow for an increased diffusion of methyl orange.

Fenton Process

The Fenton process utilizes iron catalysts with H2O2 to create powerful, oxidizing hydroxides for the degradation of organic pollutants such as sewage and sludge as well as dyes. To enhance the catalytic abilities, a combination of Fe2+ cations, ultraviolet light, and hydrogen peroxide can be used and has shown greater removals of dye solutions.

Biomass

Biomass degradation refers to the utilization of microorganisms such as bacteria and fungi to produce enzymes that can interact with molecules of dyes. Laccases are proteins that are produced by Lentinus sp; its active site contains a group of polyphenol oxidases incorporated with four copper ions. These can form hydrogen bonds with synthetic dyes. The efficiency of this enzyme is proportional to the number of hydrogen bonds that form between the enzyme and dyes. Microorganisms are easy to manipulate, but the

efficiency is highly dependent on the pH, ionic strength, and temperature. This will be varied with different effluents. Effluents can be first processed by a strain of yeast Candida tropicalis JKS2 then post-treated by photocatalytic processes to degrade the aromatic rings so a costeffective outcome can be achieved. Immobilized fungal cells are more resistant to environmental stress and cells can be used repeatedly.

Hazards

Many dyes, specifically in the textile industry such as methylene blue or methyl red, are released into ecosystems through water waste. Many of these dyes can be carcinogenic and can come into contact with humans. As a result, newer treatments of the water waste are still in development.

1.4. BRIEF INTRODUCTION TO TEXTYL DYES

1.4.1 METHYLENE BLUE

Methylene blue, also called methylthioninium chloride, is a salt used as a medication and dye. It is mainly used to treat methemoglobinemia as a medication agent. It is a heterocyclic aromatic chemical formulae C16H18N3SCl. At room temperature it appears as a solid, odorless dark green powder, that yields a blue solution when dissolved in water. The hydrated form has 3 molecules of water per unit of 24 methylene blue. Methylene blue should not beconfused with methyl blue, anotherhistology stain, new methylene blue, nor with the methyl violets often used as pH of 3 in water(10G/l) at 25 degree Celsius.

Medicinal uses :

Methemoglobinemia

Methylene blue is used as a medication for the treatment of methemoglobinemia. It is injected intravenously as an antidote, is itself first reduced to leucomethylene blue, which then reduces the heme group from methemoglobin to hemoglobin. Methylene blue can reduce the half life of methemoglobin from hours to minutes. At high doses, though, methylene blue actually induces methemoglobinemia, reversing this pathway

Methylene blue is a component of frequently prescribed urinary analgesic/and-infective/andspasmodic known as “Prosed”, a combination of drugs is also contain phenyl salicylate, benzoic acid, hyoscyamine sulphate, and methenamine (aka hexamethylenetrtramine and not be confused with ‘methanamine’)

Dye or stain

Methylene blue is used in endoscopic polypectomy as an appendage to saline or epinephrine, and is used for injection into the submucosa around the polyp to be removed. It is also used as a dye in chromoendoscopy, and is sprayed onto the mucosa of the gastrointestinal tract in order to identify dysplasia, or pre-cancerous lesions. Intravenously injected methylene blue is gladly discharged into the urine and thus can be used to test the urinary tract for leaks or fistulas.Methylene blue can be used to visually trace the lymphatic drainage of tested tissues in surgeries such as sentinel lymph node dissections. Likewise, it is added to bone cement, in orthopedic operations to supply easy 25 discrimination between native bone and cement. Besides, methylene blue accelerates the hardening of bone cement, increasing the speed at which bone cement can be effectively applied. Methylene blue is used as an succor to visualisation/orientation in a number of medical devices, including a surgical sealant film, Tissue Patch. It is used to detect the tract for complete extirpation in fistulas and pilonidal sinuses. It can also be employed during gastrointestinal surgeries (such as bowel resection or gastric bypass) to test for leaks.

Methylene Blue In Biology

In biology methylene blue is used as a dye for a number of different staining procedures, such as Wright's stain and jenners stain. Since it is a temporary technique, Methylene blue can also be used to examine RNA or DNA under the microscope or in a gel as an example, a solution of methylene blue can be used to stain RNA on hybridisatin membranes in northern blotting to verify the amount of nuclic acid present. While

methylene blue is not as sensitive as ethidium bromide, it is less toxic and it does not intercalate in nuclic acid chains thus avoiding interference with nucleic acid acid retension on hybridization membranes or with hybridization process itself.

It can be also used as indicator to determine wheather eukaryotic cells such as yeast are alive or not. The methylene blue is reduced in viable cells leaving them unstained. However dead cells are unable to reduce the oxidized Methylene blue and the cells are stained blue. Methylene blue can interfere with the respiration of the yeast as it picks up hydrogen ions made during the process. In neuroscience, Methylene blue can also serve as anion-selective inhibitor of NO synthase

Aquaculture

Methylene blue is used in aquaculture and by tropical fish hobbyists as a cure for fungal infections. It can also be effectual in treating fish infected with ich although a combination of malachite green and formaldehyde is far more successful against the 26 parasitic protozoa Ichthyophthirius multifiliis. It is generally used to shield newly laid fish eggs from being infected by fungus or bacteria. This is helpful when the hobbyist wants to artificially hatch the fish eggs. Methylene Blue is also very fruitful when used as part of a "medicated fish bath" for treatment of ammonia, nitrite, and cyanide poisoning as well as for topical and internal treatment of injured or sick fish as a "first response".

History of methylene blue

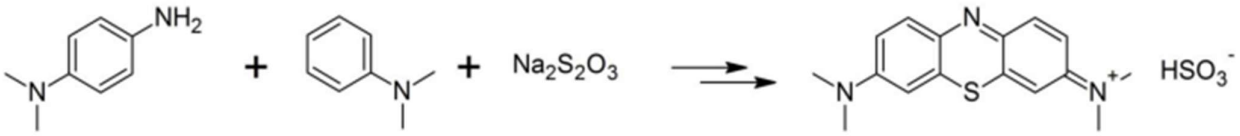
Methylene blue has been delinated as "the first fully synthetic drug used in medicine." It was first prepared in 1876 by German chemist Henrich Carlo. Its use in the treatment of malaria was first used by Paul Guttmann and Paul Ehrlich in 1891. During this period before the first World War, researchers like Ehrlich trusted that drugs and dyes worked in the same way, by advantageously staining pathogens and possibly harming them. Changing the cell membrane of pathogens is in fact how various drugs work, so the theory was partially correct notwithstanding the fact that it is far from complete . Methylene blue keep on with to be used in the second World War, where it was not well liked by soldiers, who perceived, "Even at the loo, we see, we pee, navy blue." Antimalarial use of the drug has recently been revived. It was discovered to be an antidote to carbon monoxide poisoning and cyanide poisoning in 1933 by Matilda books. The blue urine was used to monitor psychiatric patients' compliance with medication regimes. This led to interest - from the 1890s to the present day - in the drug's antidepressant and other psychotropic effects. It became the lead compound in research leading to the disclosure of chlorpromazine.

Structure of Methylene Blue

Methylene blue dye (MBD) is a heterocyclic aromatic chemical compound with the lecular formula of C16H18N3SCl and molecular weight of 319.85 g/mol.

Preparation of methylene blue

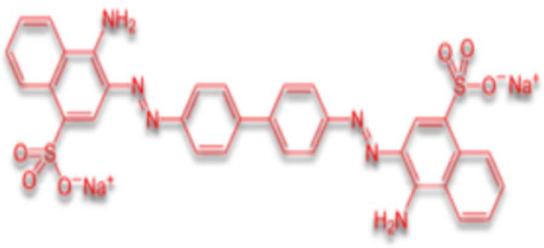
Methylene blue is a formal derivative of phenothiazine. It is a dark green powder that gives a blue solution in water. The hydrated form has 3 molecules of water per unit of methylene blue. Methylene blue has a pH of 6 in water (10g/L) at 25 °C. It is prepared by oxidation of dimethyl-4-phenylenediaminein the presence of sodium thiosulphate .



1.4.2 Congored Congored is an organic compound the sodium salt of 3, 3′-([1, 1′-biphenyl]-4, 4′-diyl) bis (4-aminonaphthalene-1-sulfonic acid). It is an azodye. Congo red is water-soluble, surrendering a red colloidal solution; its solubility is greater in organic solvents. But, the 28 use of Congo red has long been abandoned, primarily because of its carcinogenic properties.

Chemical formula: C32H22N6Na2O6S2

Molar mass: 696.665

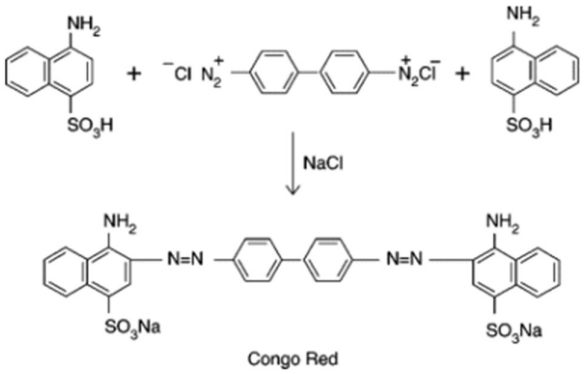


History of congored

It was first synthesized in 1883 by Paul Böttiger, who had been working at Friedrich Bayer Company in Elberfeld, Germany. He was in search for textile dyes that did not need a mordant step. He filed the patent under his own name and sold it to the AGFA company of Berlin because his company was not riveted in this bright red color. AGFA vended the dye under the name "Congo red", a appealing name in Germany at the time of the 1884 Berlin West African Conference, an important event in the colonisation. The dye was a vital commercial success for AGFA. In the subsequent years, for the same reason, other dyes were retailed using the "Congo" name: Congo rubine, Congo corinth, brilliant Congo, Congo orange, Congo brown, and Congo blue. Once of economic significance, Congo red has fallen into disertion as have all benzidine -derived dyes, due to their carcinogenic activity

Preparation of congored

It is synthesised by coupling bis-diazotised benzidine with two molecules of napthionic acid. The blue dye so acquired is transformed into its red disodium salt during its salting with sodium chloride.



Congo Red

.

Behavior in solution

Congored shows a color change from blue to red at pH 3.0 – 5.2, hence it can be used as a pH indicator. As this color change is an imprecise inverse of that of litmus, it can be used with litmus paper in a simple parlor trick: add a drop or two of Congo red to both an acid solution and a base solution. Soaking red litmus paper in the red solution will turn it blue, while dipping blue litmus paper in the blue solution will turn it red. This property gives Congo red a metachromatic property as a dye, both in strongly acidic solutions and with strongly acidophilic tissue.Congo red has a tendency to aggregate in aqueous and organic solutions. The suggested mechanisms offer hydrophobic interactions between the aromatic rings of the dye molecules, leading to a π–π stacking phenomenon. However, these aggregates are present under various sizes and shapes, the "ribbon-like micelles" of a few molecules seem to be the principal form (even if the "micelle" term is not an entirely appropriate name for it). This 30 aggregation phenomenon is more common in high Congo redconcentrations, at high salinity and/or low pH.

Diagnostic use

Congo red is used for staining in amyloidosis, and for the cell walls of plants and fungi,and for the outer membrane of Gram - Negative bacteria in histology and microscopy. Apple-green double refraction of congo red stained preparations under polarized light is evocative of the presence of amyloid fibrils. Moreover, Congo red is used for the diagnostics of the shigella flexneri serotype 2a, where the dye binds the bacterium's distinctive lipopolysaccharide structure. Besides, Congo red may also be used to get expression of the type III secretion system of Shigella flexneri, bringing about the secretion of IpaB and IpaC, which form translocation pores inside host cell membrane, allowing effector proteins to pass through and alter the host cell's biochemistry. The dye can also be used in flow cytometry experiments for the identification of Acanthamoeba, Naegleria and other amoebal cysts.

A Brief Introduction to Purification of Water

Water purification is the process of removing unpleasant chemicals, biological contaminants, suspended solids, and gases from water. The goal is to produce water fit for specific purposes. Most water is purified and disinfected for human consumption, but water purification is also carried out for a variety of other purposes, including medical, pharmacological, chemical and industrial applications. Physical process such as slow and filters or biologically active carbon; chemical process such as flocculation and chlorination; and the use electromagnetic radiations such as ultraviolet light are some methods used . Color removal from waste water has been a matter of concern, both in the beauteousness and health point of view. Color removal from textile effluents on a

continuous industrial scale has been given much consideration in the last few years not only because of its potential toxicity but also mainly due to its visibility problems. There have been various auspicious techniques for the removal of dyes from waste water. The standards for drinking water quality are typically set by government or by international standards. These standards usually include minimum and maximum concentration of pollutants, depending on the deliberate use of the water. According to a 2007 World Health Organization (WHO) report, 1.1 billion people lack ingress to an improved drinking water supply; 88% of the 4 billion annual cases of diarrheal disease are credited to unsafe water and sanitation and hygiene, while 1.8 million people die from diarrheal disease each year. The WHO evaluates that 94% of these diarrheal disease cases are preventable through modifications to the environment, as well as access to safe water. Simple technique for treating water at home, such as chlorination, filters, and solar disinfection, and for storing it in secure containers could save a huge number of lives each year. Reducing deaths from waterborne disease is a important public health goal in developing countries.

1.5 AIM OF THE PROJECT

The overall objective of this study is to investigate the potential use of starch and starch bioplastic for the removal of dyes from industrial waste water, specifically from textile industries. We aim to study the feasibility of using starch and starch bioplastic for dye removal in a low cost method to treat waste water from textile industries. This study is to address the issue of water availability by increasing the water reuse in the textile industry.

CHAPTER 2

REVIEW OF LITERATURE

1)Ghada Adel Mahmoud, Samia.E.Abdul-Aal, Nabil A.El-kelesh, E.A.Al Shafei(polymer chemistry department, National Counter for Radiation Research and Technology(NCERT),EGYPT) published paper on effective removal of Hazardous dye from aqueous solution using starch based hydrogel and Gamma radiation.

2)Nada Mustafa H.AL-Nakibv(Biochemical Engineering Department, Al-Khwarismi college of Engineering, University of Baghdad, IRAQ) published paper "Reverse osmosis polyamide membrane for the removal of blue and yellow dye from waste water".

3)U.J.Etim, SA.Umoren, UM.Eeluobk (Department of chemistry, faculty of science, University of Uyo, P.M.B.1017, Uyo, Nigeria) published a paper on "Coconut dust as a low cost adsorbent for the removal of cabionic dye from aqueous solution."

4)Juzhen Yi, Yonggiu Li, Ligun Yang ad Li-Ming Zhang (School of Engineering, Sun Yat-Sem University, Guangzhou, 510275, China) of adsorption of cu2+ and methelene blue to starch hydrogels."

5) Shahnawas Ahmad Bhat, Fahmina Zafar, Azar Ullah Mizra, Nahib Nishat (Organic Material Research Labortary, Department of Chemistry), Jamia Milia Islamia, New Delhi, India) Qazi Mohd Rizwanul Haq, Aftab Hossain Mondal(Department of Bio Science, Jamia Millia Islamia, New Delhi, India) published a paper on "efficient removal of congo red dye from aqueous solution by adsorbent films of polyvinyl alcohol/melamine-formaldehyde composite and bactericidal effect."

CHAPTER 3

MATERIALS AND METHODS

Materials and Method

3.1 Materials

The absorption capacities of both starch and starch based bioplastic investigated, and conducted at varying concentrations of dyes. The materials used in this study were starch, white vinegar, glycerine and dyes such as methylene blue and Congo red. These materials are purchased from the market and are used without further purification. Many dyes and their breakdown products may be toxic for living organism. Therefore, removal of dye is an important aspect. Recently many studies have been carried out for the removal of dyes. In this study we compare the rate of absorption of starch and starch bioplastic at different temperature and at different time period. The instrument used for this study is colorimeter

3.2 Methodology

3.2.1 Preparation of Starch Bioplatic

Take 1.5g corn starch, 0.25g glycerine, 1ml white vinegar and 6ml distilled water in a beaker mixed and stirred continuously till the mixture became a milky white color and quite watery. The beaker was placed on the stove and heat was set. While heating, the mixture was stirred constantly and it became more translucent and began to thicken. The clear and thicken mixture was detached from the stove at the temperature of 85˚C for 3 min. Afterward the heated mixture was spread on the aluminium foil or on the tray. The sample was dried undisturbed at room temperature for three days.

Fig 3 starch bioplastic obtained

Fig 4 bioplastic after adsorption

3.2.2 Evaluation of absorption of methylene blue by starch and starch bioplastic

. At room temperature: About 10-5 and 10-6 concentrations of methylene blue solution is prepared and divided into two equal parts. Add about 1 g of starch and starch biofilm to each solutions. Kept it at room temperature for about 30 minutes and then centrifuged and absorbents of the solution is measured using colorimeter. The process of centrifugation and measurement of the absorbents is repeated in a regular interval of time (30 mins). These are recorded in a table and a graph is drawn.

3.2.3 Evaluation of absorption of congo red by starch and starch bioplastic

At room temperature: About 10-5 and 10-6 concentrations of congo red solution is prepared and divided into two equal parts. Add about 1 g of starch and starch biofilm to each solution. Kept it room temperature for about 30 min and then centrifuged and absorbance of the solution is measured using colorimeter. The process of centrifugation and measurement of the absorbents is repeated in a regular interval of time (30 min). These are recorded in a table and a graph is drawn.

From the above methods, we can calculate the rate constant (k) and half-life period (t1/2) for the removal of dyes.

Rate constant (k) = 2.303/t (log (a/a-x)) sec-1

Half life period = 0.693/k sec

Where k is rate constant.

'a' initial absorbance and 'a-x' absorbance after 't' time.

CHAPTER 4

RESULT AND DISCUSSION

RESULT AND DISCUSSION

4.1 ABSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION BY USING STARCHCOMPARATIVE STUDY

The absorption capacities of starch is investigated in this section. The experiments is conducted at various concentrations of dye to determine the optimum conditions and absorption kinetics for the removal of dye from aqueous solution.

4.1.1 Absorption of methylene blue of two different concentrations at room temperature

The experiment is conducted at two different concentrations of methylene blue. The amount of dye removed is monitored in real time using colorimeter. The data obtained is needed to determine the absorption kinetics

Time(min)	Absorbance (688nm)
0	0.09
30	0.07
60	0.05
90	0.04

120	0.03
150	0.02
180	0.01

Table1. Absorbance of MB (0.3439×10-6) at regular time intervals

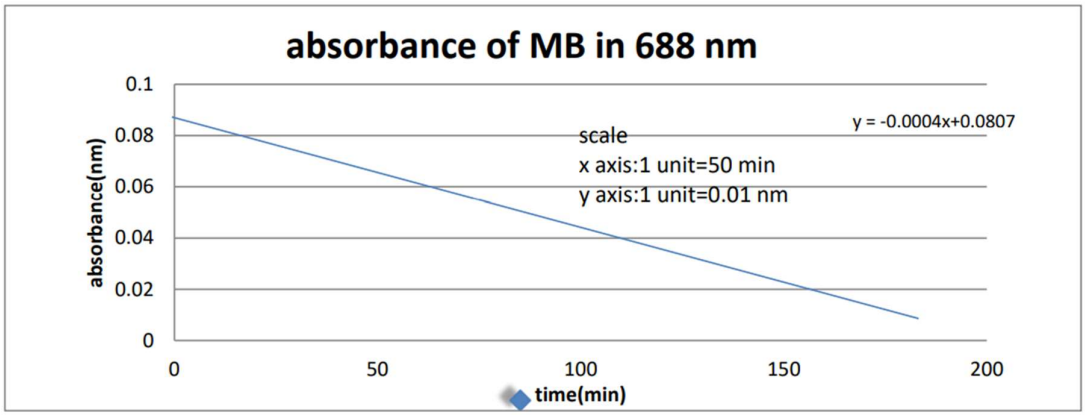


Figure 1. Absorbance of MB at 0.3439×10-6 concentration

Time (min)	absorbance of MB (10^{-5}) in 688nm
0	**0.54**
30	**0.53**
60	**0.51**
90	**0.48**
120	**0.43**
150	**0.41**
180	**0.39**

Table2 Absorbance of MB ($3.439x10^{-5}$ M) at regular time intervals

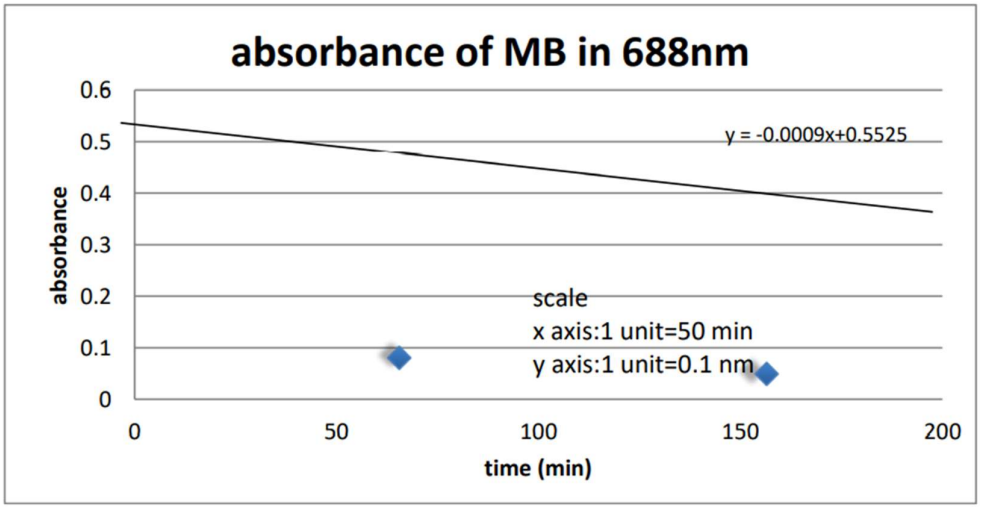


Figure2. Absorbance of MB at $3.439x10^{-5}$ concentration.

From figure1 and figure2 it is evident that the absorbance decreases linearly with increase in time. At lower concentration of dye (figure1), absorbance reaches to a minimum value.

The rate and half life period is calculated using the equations given below,

Rate constant (k) = 2.303/t (log (a/a-x)) sec-1

Half life period = 0.693/k sec

Sl no	Concentration of dye(M)	. Rate constant	Half-life period
1	$0.3439 x10^{-6}$	$0.76x 10^{-4}$	$91.18x 10^{2}$
2	$3.439x 10^{-5}$	$6.2x 10^{-4}$	$11.12x 10^{2}$

Table3.Rate constant and half-life period of different concentrations

From table3, it is evident that the rate of dye degradation increases with concentration of dye. This indicates that the degradation of MB with starch depend on dye concentration.

4.2 ABSORPTION OF CONGO RED DYE FROM AQUEOUS SOLUTION BY USING STARCH – COMPARATIVE STUDY

The absorption capacities of starch is investigated in this section. The experiments is conducted at different concentrations of dye to determine the optimum conditions and absorption kinetics for the removal of dye from aqueous solution.

4.2.1 Absorption of Congo red of two different concentrations at room temperature

The experiment is conducted at two different concentrations of methylene blue. The amount of dye removed is monitored in real time using colorimeter. The data obtained is needed to determine the absorption kinetics

5.02x 10^{-5}M		0.502x 10^{-6} M	
Time	**Absorbance**	**Time**	**Absorbance**
0	0.92	0	0.08
30	0.91	30	0.06
60	0.89	60	0.05
90	0.87	90	0.04
120	0.81	120	0.03
150	0.77	150	0.02
180	0.71	180	0.02

Table4. Absorption of Congo red of two different concentrations at room temperature

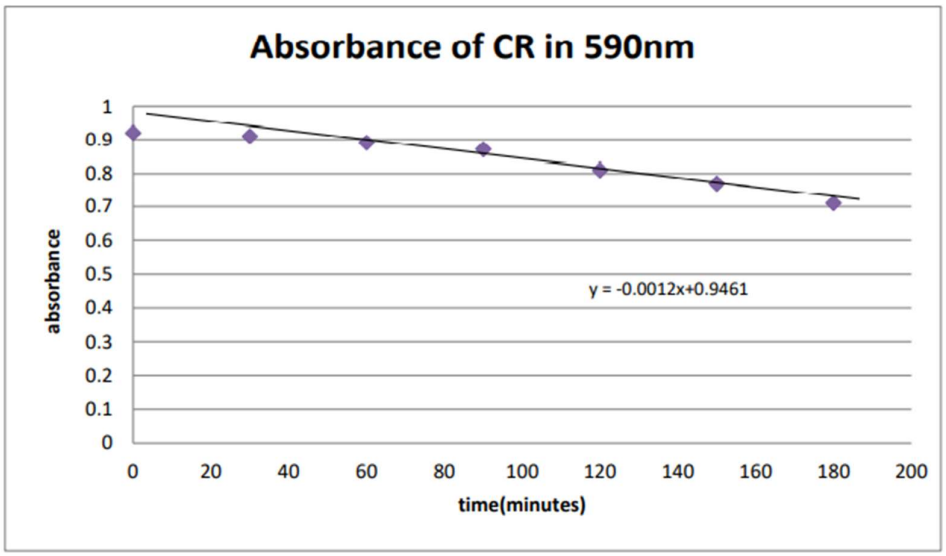


Figure3. Absorbance of CR at 5.02×10-5 M concentration

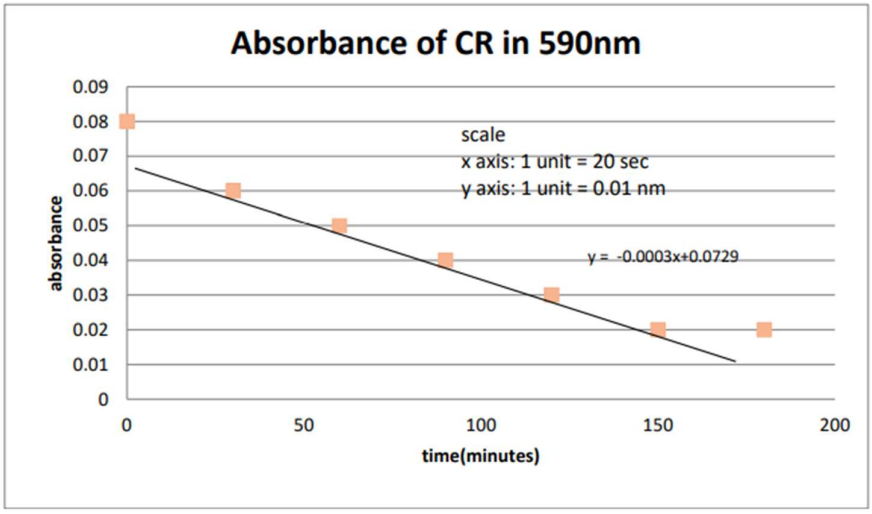


Figure4. Absorbance of CR at 0.502×10-6 concentration

From figure3 and figure4, it is evident that the absorbance decreases linearly with increase in time. At lower concentration of dye (figure7), absorbance reaches to a minimum value.

The rate and half life is calculated using the below equations,

Rate constant (k) = 2.303/t (log (a/a-x)) sec-1

Half life period = 0.693/k sec

Sl .no	Concentration of dye(M)	Rate constant (s-1)	Half-life period (s)
1	5.02×10^{-5}	7.5×10^{-4}	9.24×10^{2}
2	0.502×10^{-6}	0.92×10^{-4}	75.32×10^{2}

Table5. Rate constant and half-life period at different concentrations

From table 5, it is evident that the rate of dye degradation increases with concentration of dye. This indicates that the degradation of CR with starch depend on dye concentration.

4.3 ABSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION BY USING STARCH BASED BIOPLASTICCOMPARATIVE STUDY

The absorption capacities of starch bioplastic is investigated in this section. The experiments is conducted at various concentrations of dye to determine the optimum conditions and absorption kinetics for the removal of dye from aqueous solution.

4.3.1 Absorption of methylene blue of two different concentrations at room temperature.

The experiment is conducted at two different concentrations of methylene blue. The amount of dye removed is monitored in real time using colorimeter. The data obtained is needed to determine the absorption kinetics.

Time (sec)	Absorbance (688nm)
0	0.08
30	0.06
60	0.04
90	0.02
120	0.01

Table6. Absorbance of MB ($0.3439^{x}10$-6) at regular time intervals

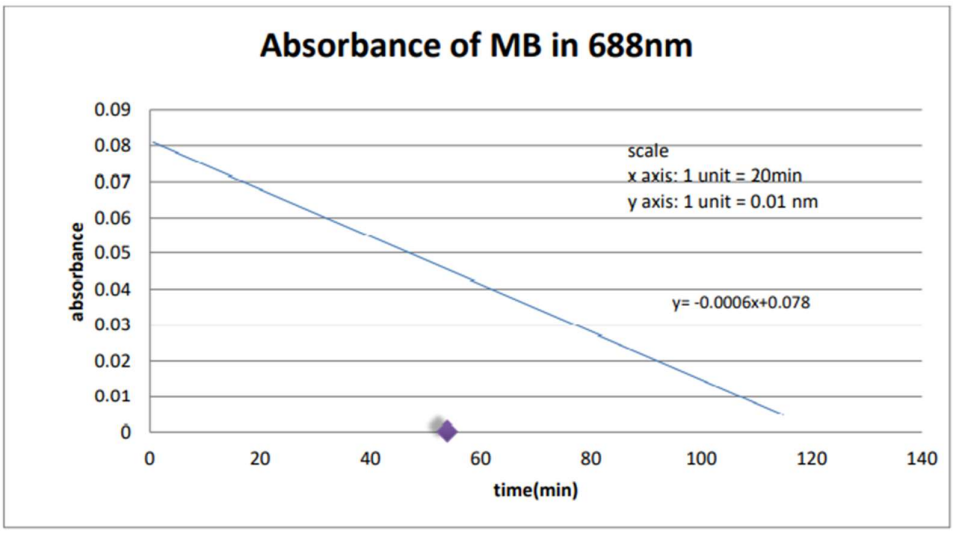


Figure5. Absorbance of MB at 0.3439x10-6 concentration

Time(sec)	Absorbance of MB in 688nm
0	0.54
30	0.52
60	0.48
90	0.45
120	0.43
150	0.42
180	0.41

Table7. Absorbance of MB (3.439x10-5) at regular time intervals

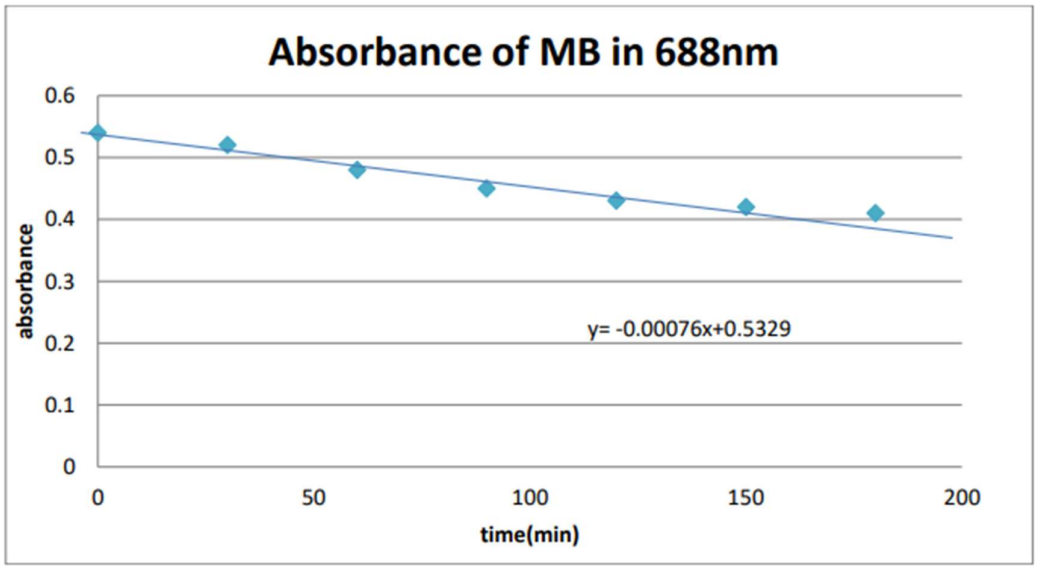


Figure6. Absorbance of MB at 3.439×10-5 concentration

From figure5 and figure6 it is evident that the absorbance decreases linearly with increase in time. At lower concentration of dye, absorbance reaches to a minimum value. , so observing the absorbance as a function of time is essentially the same as observing the concentration as a function of time. Rate = k [MB]

4.4. ABSORPTION OF CONGO RED DYE FROM AQUEOUS SOLUTION BY USING STARCH BASED BIOIPLASTIC– COMPARATIVE STUDY

The absorption capacities of starch is investigated in this section. The experiments is conducted at various temperatures and concentrations of dye to determine the optimum conditions and absorption kinetics for the removal of dye from aqueous solution.

4.4.1. Absorption of Congo red of two different concentrations at room temperature

The experiment is conducted at two different concentrations of methylene blue. The amount of dye removed is monitored in real time using colorimeter. The data obtained is needed to determine the absorption kinetics.

$5.02x10^{-5}M$		$0.502X10-^{6}$ M	
Time	**Absorbance**	**Time**	**Absorbance**
0	**0.92**	**0**	**0.08**
30	**0.90**	**30**	**0.06**
60	**0.86**	**60**	**0.04**
90	**0.84**	**90**	**0.03**
120	**0.82**	**120**	**0.02**
150	**0.81**	**150**	**0.01**
180	**0.80**	**180**	**0.01**

Table6. Absorption of Congo red of two different concentrations at room temperature

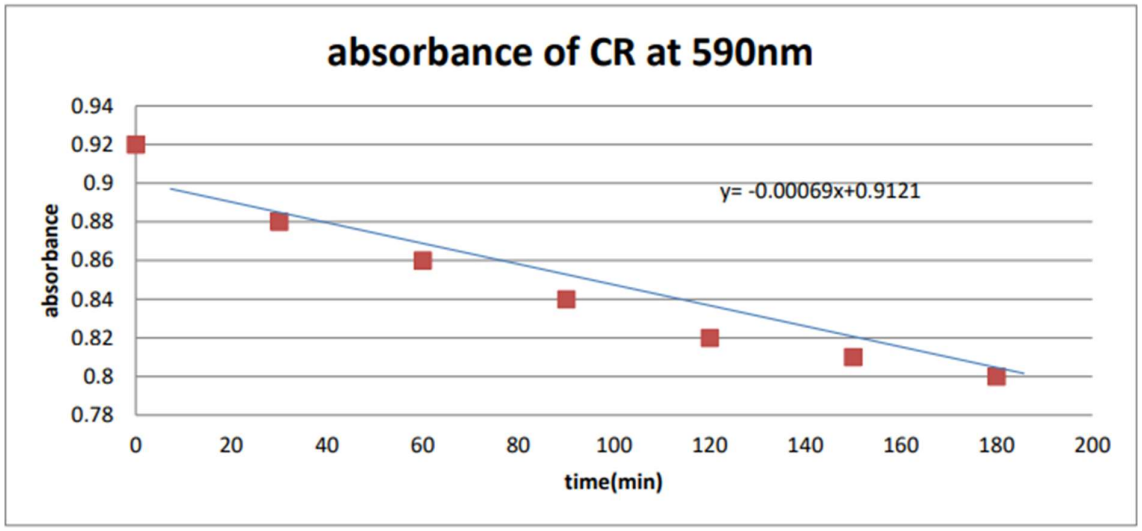


Fig 7 Absorbance of CR at 5.02*10-5 concentration

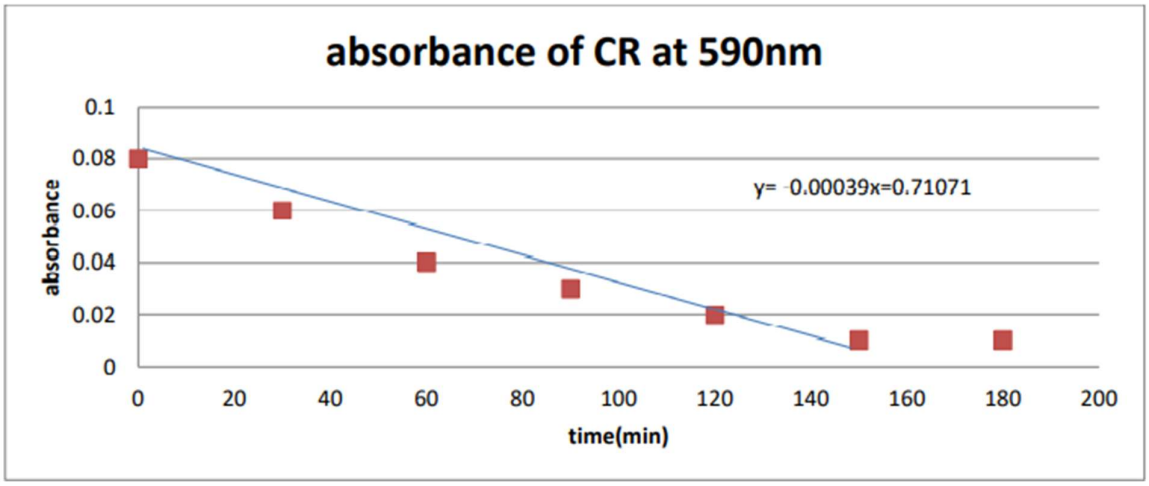


Fig8 Absorbance of CR at 5.02*10-6 concentration

From figure5 and figure6 it is evident that the absorbance decreases linearly with increase in time. At lower concentration of dye, absorbance reaches to a minimum value, so observing the absorbance as a function of time is essentially the same as observing the concentration as a function of time.

Rate = k [CR]

4.5. COMPARITIVE STUDY-STARCH AND STARCH BIOPLASTIC

4.5.1. Comparison of degradation of three dyes with starch

Among the 2 dyes, the higher concentration of 2 dyes gives higher rate

. 4.5.2. Comparison of degradation of these dyes with starch bioplastic

Here also higher concentration gives higher rate of degradation. Starch bioplastic is comparatively good adsorbent than starch.

CHAPTER 5

CONCLUSION

CONCLUSION

In this work the removal of different dyes from aqueous solution using starch and starch based bioplastic was investigated. This study monitored the ability of starch and starch biofilm for removing dyes from water. From the above experimental result it can be concluded that the absorbents of dyes from aqueous solution dependent on various factors such as concentration, time, adsorbents, etc. The parameters used to express the rate of dye degradation are rate constant, half-life period etc. From the above result it can be concluded that:

❖ Comparing the dye degradation using starch and starch bioplastic, it can be concluded that the dye degradation is higher with starch biofilm than starch.

❖ Higher concentration of both dyes gives higher rate than low concentration for both starch and starch bioplastic. Finally, the result of adsorption study, it is concluded that starch bioplastic can be used as an adsorbent for dyes from the textile waste water with better adsorption capacity than starch, because of its higher adsorptive capacity, availability and environment friendly behavior

REFERENCE

1. Harunsyah, Sariadi, Raudah, The effect of clay nanoparticles as reinforcement on mechanical properties of bioplastic base on cassava starch, J. Phys.: Conf. Ser. 953 (2018). Conference 1.

2. Delville, C. Joly, P. Dole, C. Bliard, Influence of photocrosslinking on the retrogradation of wheat starch-based films, Carbohydr. Polym. 53 (4) (2003).

3. [9] M. Avella, A. Buzarovska, M.E. Errico, Gennaro gentile and grozdanovaecochallenges of bio-based polymer composite.

4. Hanafi Ismail, Maryam Irani, Zulkifli Ahmad, Starch based hydrogels: present status and application, International Journal of polymeric materials and polymeric biomaterials, 2010.

5. H.M. Aamir, R.U. Khan, R Mujahid, S Tahir, A. Ijaz, removal of anionic dyes by modified cationic starch, Journal of Pakistan Institute of Chemical Engineers, 2014.

6. Sati Saha, M Yousuf Ali Mollah, Md. Abu Bin Hasan Susan and Md. Mominul Islam, Treatment of waste water containing organic dyes: Recovery of dye adsorb on starch based material through conversion of adsorbant in alcohol, Vol 63(2), Pg. 119-124,2015.

7. Rauf, M.A.; Ashraf S.S. Fundamental Principles and Application of Heterogeneous Photocatalytic Degradation of Dyes in Solution. Chemical Engineering Journal 2009, 151, 10- 18.

8. Lachheba, H.; Puzenata, E.; Houasb, A.; Ksibib, M.; Elalouib, E.; Guillarda, C.; Herrmanna, J. Photocatalytic degradation of various types of dyes (Alizarin S, Crocein

Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated Titania. Applied Catalysis B: Environmental 2002, 39 (1), 75-90.

9. Shu, Q.W.; Lan, J.; Gao, M.X.; Wangb, J.; Huang, C.Z. Controlled synthesis of CuS caved superstructures and their application to the catalysis of organic dye degradation in the absence of light. CrystEngComm 2015, 17, 1374-1380. 54

10. Gu, S.; Xieb, J.; Li, C.M. Hierarchically porous graphitic carbon nitride: large-scale facile synthesis and its application toward photocatalytic dye degradation. RSC Adv. 2014, 4, 59436- 59439.

11. Xu, X.; Li, H.; Wang, W.; Gu, J. Degradation of dyes in aqueous solutions by the Fenton process. Chemosphere 2004, 57, 595-600. .

12. Prachi, K.; Anushree, M. Fungal dye decolourization: recent advances and future potential. Environment International 2009, 35 (1), 127-41.

13. Builders, P. F., & Arhewoh, M. I. (2016). Pharmaceutical applications of native starch in conventional drug delivery. Starch - Stärke, 68(9-10), 864–873.

14. Woodhead Publishing Series in Food Science, Technology and Nutrition Starch in Food Structure, Function and Applications Second Edition.

15 Nada Mustafa H AL-Nakib; Reverse osmosis polyamide membrane for the removal of blue and yellow dye from waste water, Iraqi Journal of Chemical and Petroleum Engineering Vol 14(2), pg 49-55,2013

16 UJ. Etin, SA Umoren, UM E Cluok, Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution, Journal of Saudi Chemical society 20,S67-S76,2017

17 Yian Zheng, Shuibo Hua, Aiqin Wang, Adsorption behavior of cu2+ from aqueous solution onto starch hydrogels Journals Destination Vol(1-3), pg170, 2010.

18 R. Jumaidin, S. Sapuan, M. Jawaid, M.R. Ishak, J. Sahari, Curr. Anal. Chem. 14, 249–267 (2018).

19 J.F. Martucci, R.A. Ruseckaite, Food Hydrocolloids 64, 70–77 (2017)

20 M. Huang, H. Wang, J. Yu, Polym. Compos. 27, 309–314 (2006).

21 H. Almasi, B. Ghanbarzadeh, A.A. Entezami, Int. J. Biol. Macromol. 46, 1–5.

22 . A. Buléon, P. Colonna, V. Planchot, S. Ball, Int. J. Biol. Macromol. 23, 85–112 (1998).